

Special Issue Reprint

Catalytical Methods for the Production of Fine and Bulk Chemicals and Biomaterials from Biomass

Edited by
Indra Neel Pulidindi, Aharon Gedanken and Pankaj Sharma

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Guest Editors

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About the Editors

Indra Neel Pulidindi

Dr Indra Neel Pulidindi is currently working as an assistant professor at the Saveetha Medical College (SMC), Thandalam, India (from 2/5/2025 - till date). He received his PhD from the Indian Institute of Technology Madras under the supervision of Professor T K Varadarajan and Professor (Em) B Viswanathan. (2002-2010). He worked in the laboratory of Professor Aharon Gedanken Israel on biomass conversion of biofuels and biochemicals (2/9/2010-30/10/2016). He worked in the laboratory of Professor Tae Hyun Kim at the Konju National University and the Hanyang University in South Korea on the biomass composition analysis, pretreatment and conversion (1/11/2016-12/2017). Subsequently, he worked in the laboratory of Professor Xinling Wang Shanghai Jiao Tong University on Carbon fiber reinforced plastics. (14/4/2019-/4/2021). Dr Neel has 75 research papers, 3 Indian patents (granted), 4 US patent applications, 2 Indian patent applications 5 books, 1 e-book and 7 book chapters and 5 ebook chapters to his credit. Dr Neel has guided several Ph D, masters, undergraduate and freshmen in their academic research curriculum and helped them to earn their degrees. His research metrics, namely H index and the number of citations are 28 and 1949, respectively. His researcher interests include Medicinal chemistry, Artificial intelligence, Nanotechnology and Nanobiotechnology.

Aharon Gedanken

Professor Aharon Gedanken is an outstanding and legendary scientist with over 900 publications in peer reviewed journals of international repute and with high impact factors. He has 37 patent applications and 5 books and over 10 book chapters to his credit. Professor Gedanken made remarkable contributions to the fields of sonochemistry and microwave technology and their application to nanomaterials, biomaterials and biofuels. He served as a faculty in the department of Chemistry at Bar Ilan University for over 34 years (1975-2009), and has been an Emeritus professor in the same institute for over 14 years (2009-todate). Professor Gedanken's research metrics, namely, H-index and citations are 129 and 64632, respectively. His research interests include Solid State Chemistry, Catalysis, Energy, Materials Science, and Biochemistry.

Pankaj Raj Sharma

Pankaj Sharma (Varanasi, INDIA, 1976), presently working as an Assistant Professor in the Department of Applied Chemistry, Faculty of Technology and Engineering, The Maharaja Sayajirao University of Baroda, Vadodara, Gujarat, India. He earned his B.Sc. (Chemistry Hons.) and M. Sc. (Organic Chemistry) from Banaras Hindu University, Varanasi, India and Ph.D (Chemistry) from The Maharaja Sayajirao University of Baroda, Vadodara, Gujarat, India. He entered the academic profession by choice. The prime goal of his life is to encourage, inspire and motivate the young talents to prepare them to achieve their aim and contribute their best to society. He has been carrying out research in the field of Pharmaceutical chemistry, Nanotechnology, Energy storage materials, Bioplastic, Heterogeneous catalysis, Mesoporous materials, Task Specific Ionic Liquids (TSIL), Green chemistry and Carbon capture and sequestration (CCS). Until now, he has published 18 peer-reviewed papers among reputed journals out of them some are SCI and SCIE. In addition to this, he published one book chapter in Elsevier. He published two reprints by MDPI.

Preface

The salient features of the reprint are exemplified by the keywords, namely, catalysis, fine chemicals, bulk chemicals and biomaterials, thus present in the title of the reprint: “Catalytic methods for the production of fine and bulk chemicals and biomaterials and biomass”. With a growing population and a demand for comfortable and healthy lifestyles, the rapid production of fine and bulk chemicals and biomaterials is very much sought after through catalysis. Catalysis is a science that deals with materials that accelerate the rate of chemical reactions by themselves, remaining unchanged by the end of the reaction, and which can be recycled and reused. The science of catalysis is extensively used in fine chemical, bulk chemical, and materials industries. Conventionally fine chemicals are those that are produced in small quantities (< 1000 tons per year) and are expensive (> 10 USD per kg). Typical examples of fine chemicals, include the life-taxing neuroactive and psychoactive drugs like Opioids, morphine, codeine, thebaine, cocaine, heroin, amphetamines and others. Typical examples of bulk chemicals include refinery products, like the chemicals petrol and diesel. The current edition of the reprint only deals with the production of bulk chemicals, namely, levulinic acid, 2,5-furan dicarboxylic acid, pentanediol, dimethyl adipate, and renewable fuels like the hydrogen and biodiesel. The afore mentioned biobased bulk chemicals were produced using conventional catalytic reactions like hydrolysis, dehydration, hydration, isomerization, hydrogenolysis, carboxy methylation, retro-Dieckman condensation, oxidation, reduction, transesterification, controlled gasification and many more. The reprint comprises 10 chapters judiciously arranged in a sequential order based on the nature, application of the product and the readiness of the technology for industrial adaptation.

We do hope that the current edition of the reprint on “Catalytic methods for the production of fine and bulk chemicals and biomaterials from biomass” will serve the scientific community to advance further towards the goal of a breakthrough in the field.

The reprint is dedicated to “My LORD and my God Jesus Christ.”

My grace is sufficient for thee. In your weakness my strength is made perfect.

2 Corinthians 12:9

Indra Neel Pulidindi, Aharon Gedanken, and Pankaj Sharma

Guest Editors

Editorial

Catalytic Methods for Producing Fine and Bulk Chemicals and Biomaterials from Biomass

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Editorial: Prevention is better than a cure, and adopting green technologies can prevent many health complications. Following a paradigm shift in the raw inventories of the chemical industry (including the pharmaceutical, refinery, and manufacturing industries), catalysis chemists have begun a race to explore the feasibility of extending the use of the conventional and classical industrial catalysts (e.g., zeolites, modified alumina, polyoxometalates, noble- and non-noble-metal-based supported catalysts, and sulfuric, nitric, and hydrochloric acid) used to convert bio-based resources into biofuels, biochemicals, and biomass. Breakthroughs as vital as the two Nobel prize-winning epochal achievements of Haber Bosch, who activated elemental nitrogen and hydrogen on the surface of iron to induce ammonia synthesis, and Gerhard Ertl, who elucidated the reaction mechanism of the ammonia synthesis process, are anticipated in the realm of the catalytic conversion of biomass into fine and bulk chemicals and biomaterials like artificial rice, biodegradable plastics, and metal substitutes for the construction industry. The opportunities are as abundant as the challenges in this field, hence initiation of this Special Issue on “Catalytic Methods for Producing Fine and Bulk Chemicals and Biomaterials from biomass”. Since the launch of this Special Issue on 22 March 2022, this research topic has been attracting the attention of pioneering researchers worldwide—namely, the Israeli group headed by Professor Aharon Gedanken (AG), the Chinese group headed by Professor Yunlei Zhang, another renowned group from China headed by Professor Qiaoyun Liu and Professor Zhong Yi Liu, the Spanish group headed by Professor Irene Martinez-Salazar, the Japanese group headed by Professor Haruo Kawamoto, the Pakistani group headed by Professor Farrukh Jamil and Professor Murid Hussain, the Omani group headed by Professor Ala’a H Al-Muhtaseb, the Emirati group headed by Abrar Inayat, the Italian group headed by Cleofe Palocci and Professor Laura Chronopoulou, the Chinese group headed by Hongyun Hu, another Chinese group headed by Jifei Xu, and the Indonesian–American–Taiwanese group headed by Professor Venkatachalam—who have contributed ten state-of-the-art research articles or reviews that form the various chapters of this Special Issue. The salient features of this issue are exemplified by the keywords in the title: catalysis, fine chemicals, bulk chemicals, and biomaterials. With the growing population and demand for comfortable and healthy lifestyles, the rapid production of fine and bulk chemicals and biomaterials through catalysis is highly sought-after. Catalysis is a science that deals with substances that accelerate the rate of a reaction by themselves, remaining unchanged by the end of the reaction, and that can be recycled and reused. The science of catalysis is extensively used in

the fine chemical, bulk chemical, and materials industries. Conventionally, fine chemicals are produced in small quantities (<1000 tons per year) and expensive (>10 USD per kg). Typical examples of fine chemicals include life-taxing neuroactive and psychoactive drugs like opioids, morphine, codeine, thebaine, cocaine, heroin, amphetamines, and others. Typical examples of bulk chemicals include refinery products like petrol and diesel. This Special Issue only addresses the production of bulk chemicals, namely, levulinic acid; 2,5-furan dicarboxylic acid; pentanediol, dimethyl adipate; and renewable fuels like hydrogen and biodiesel. These biobased bulk chemicals are produced using conventional catalytic reactions like hydrolysis, dehydration, hydration, isomerization, hydrogenolysis, carboxy methylation, retro-Dieckman condensation, oxidation, reduction, transesterification, controlled gasification, and many more. State-of-the-art catalysts like polyoxometalates (also called heteropoly acids), Au-Pd bimetallic catalysts supported on nitrated carbon, Pt/MgO, CaO, lipases supported on iron oxide, and others were introduced as catalysts to bring about the catalytic conversion of biomass into bulk chemicals.

We are grateful to all of the research groups from each corner of the world for contributing their findings that constitute the ten chapters of this Special Issue. Special thanks are due to the untiring efforts of Ms. Cathy Yang, the managing editor of the MDPI journal *Catalysts*, for her bravery in approving the launch of the Special Issue that resulted in the publication of this reprint. Her consistent efforts in preparing the contact list of experts in the field resulted in the successful completion of this Special Issue. We are deeply indebted to Professor B Viswanathan (BV), NCCR, IIT Madras, for introducing Dr. Neel to the wonderful world of catalysis back when he was a research scholar under the supervision of Professor T K Varadarajan (TKV). More so than the science of catalysis, the dedication, hard work, and selflessly helpful attitude of Professor BV have always motivated Dr. Neel to advance his scientific research against unfavorable conditions and many difficult situations and persevere to acquire his rightful position in the academic circles. We are also grateful to Professor TKV for disseminating smart ways of attaining success. Coincidentally, it was Professor TKV who offered, for the first time, the CSIR-funded project on the development of heteropoly acid catalysis for the production of fine and bulk chemicals at IIT Madras on 3 July 2002—and the rest is history. Thanks are also due to Rev. Pastor Ernest Selvadurai and Pastoress Nilofer, Rev. Pastor Richard Ambrose Jebakumar and Pastoress Ms. Lily Ambrose, Mr. Usha Priyan (uncle), Ms. Harriot Usha Priyan (aunt), Ebinezer (brother), and the saints in the House of Prayer Adyar for their loving fellowship, prayers, and Holy communion, which have been the source of strength allowing Dr. Neel to complete this endeavor successfully. Special thanks are due to Miss Tabitha Victor Pulidindi, Dr. Neel's only daughter, for her selfless love.

We hope that the current edition of this Special Issue on “Catalytic Methods for Producing Fine and Bulk Chemicals and Biomaterials from Biomass” will help the scientific community to advance towards the goal of a breakthrough in the field, leading to sustainability for the alleviation of human suffering.

This reprint of the special issue is dedicated to the savior and the LORD Jesus Christ.

Conflicts of Interest: The authors declare no conflict of interest.

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Levulinic Acid Is a Key Strategic Chemical from Biomass [†]

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[†] Dedicated to the legendary Indian Chemist Professor C. N. R. Rao on his 88th birthday on 30 June 2022.

Abstract: Levulinic acid (LA) is one of the top twelve chemicals listed by the US Department of Energy that can be derived from biomass. It serves as a building block and platform chemical for producing a variety of chemicals, fuels and materials which are currently produced in fossil based refineries. LA is a key strategic chemical, as fuel grade chemicals and plastic substitutes can be produced by its catalytic conversion. LA derivatisation to various product streams, such as alkyl levulinates via esterification, γ -valerolactone via hydrogenation and N-substituted pyrrolidones via reductive amination and many other transformations of commercial utility are possible owing to the two oxygen functionalities, namely, carbonyl and carboxyl groups, present within the same substrate. Various biomass feedstock, such as agricultural wastes, marine macroalgae, and fresh water microalgae were successfully converted to LA in high yields. Finding a substitute to mineral acid catalysts for the conversion of biomass to LA is a challenge. The use of an ultrasound technique facilitated the production of promising nano-solid acid catalysts including Ga salt of molybophosphoric acid and Ga deposited mordenite zeolite, with optimum amounts of Lewis and Bronsted acidities needed for the conversion of glucose to LA in high yields, being 56 and 59.9 wt.% respectively. Microwave irradiation technology was successfully utilized for the accelerated production of LA (53 wt.%) from glucose in a short duration of 6 min, making use of the unique synergistic catalytic activity of ZnBr_2 and HCl.

Keywords: levulinic acid; biomass; solid acid catalysts; biochemicals; biofuels; biomaterials; heteropoly acids; zeolites; microwave irradiation; ultrasound

1. Introduction

Biomass is a renewable energy resource which is underutilized. Biofuels such as biodiesel and bioethanol, biochemicals such as glucose and levulinic acid (LA), and biomaterials such as biodegradable polymers can be produced from biomass [1]. On average, 32.8 papers/month were published on the subject with keywords, namely, LA and biomass, from the period 1 January 2022 to 30 June 2022, based on the Web of Science database [2–62]. Indeed, proliferation in this field of research is professed due to the strategic significance of LA. The unique feature of LA is that the molecule has two oxygen-containing functional groups, namely, carbonyl and carboxyl, which could be converted easily, making the derivatization of LA prolific. The intention of the authors in compiling this review is not to summarize the history of LA from biomass. On the contrary, the objective is to provide a possible solution to the war-torn and resource-depleted world.

The majority of the content of this review is devoted to the results from Professor Gedanken's laboratory [63–71]. In addition, for want of time, only the major developments during the period from 1 January 2022 to 30 June 2022 are outlined [2–62].

2. Possible Biomass Feedstock for Levulinic Acid (LA) Production

Literally all lignocellulosic biomass (terrestrial), as well as unconventional glucosic feedstock such as marine and fresh water algae, and bacterial sources like cyanobacteria can be used for LA production. The diverse agricultural wastes (lignocellulosic biomass), namely, cotton, sugar cane bagasse, *Cicer arietinum*, rice straw, corn stover, sweet sorghum bagasse and miscanthus, that form a potential source of LA are shown in Figure 1.

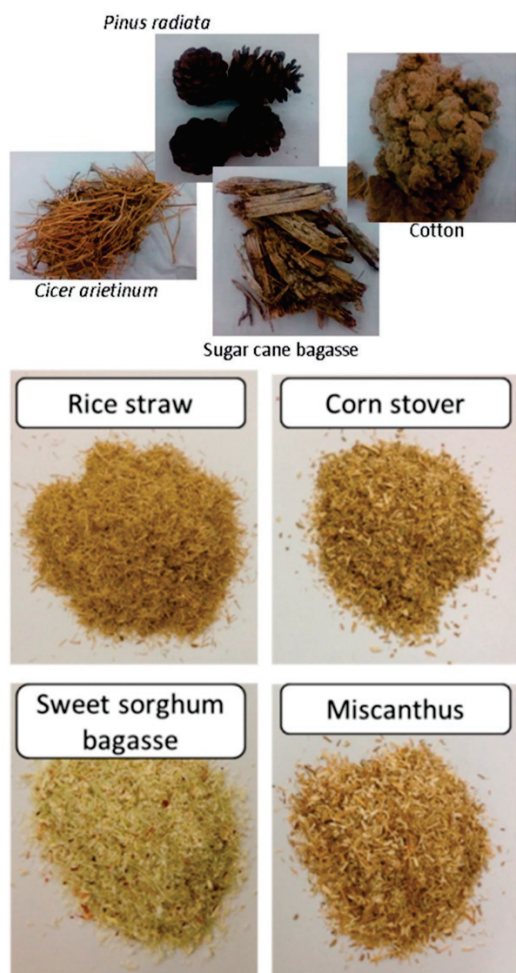


Figure 1. Diversity in cellulosic feedstock for levulinic acid production. Adapted with permission from ref. [63,70].

Fructose or fructose-containing feedstock, such as sugar cane juice, is an ideal feedstock [5,11,14,66] for LA production. This is because of the mechanistic steps involved in the direct conversion of cellulosic biomass to LA. The mechanistic steps involved in the conversion of cellulose to LA comprise the initial step of hydrolysis of cellulose to glucose catalysed by an acid; the glucose then isomerizes to fructose. By consecutive dehydration and rehydration steps, fructose is converted to hydroxy methyl furfural and LA, respectively. Each mole of fructose yields a mole of LA and formic acid, as shown in Figure 2. The difficult stages in the direct conversion of biomass to LA, namely hydrolysis of cellulose and isomerization of glucose, could be avoided if fructose/fructose-containing carbohydrates were used by industry as feedstock instead of cellulosic biomass, until the technology for the direct conversion of lignocellulosic biomass to LA is mature. This would hasten the appearance of LA based products in the market at the service of mankind, alleviating the problems of energy and environmental crises.

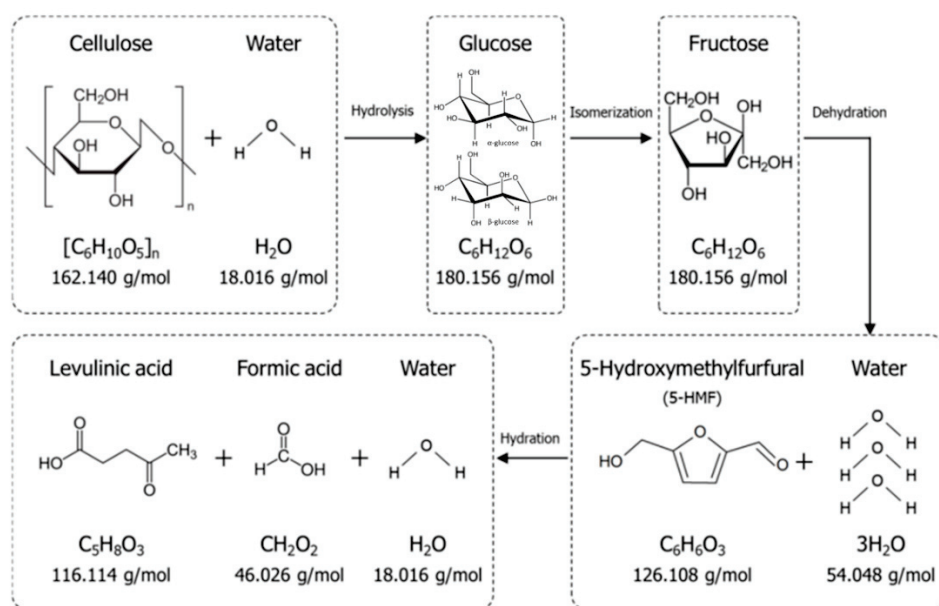


Figure 2. Consecutive reactions in the conversion of lignocellulosic biomass to levulinic acid. Adapted with permission from MDPI [63].

This is analogous to the use of sugar cane as a feedstock for the production of bioethanol in Brazil and the US, that has seen the light of the market as a gasoline substitute/additive. Until the technology for the direct conversion of cellulosic feedstock to fuels (bioethanol) and chemicals (LA) is ripe, facile carbohydrates (monomeric/dimeric) should be used as feedstock to meet the growing demand for fuel, as can be seen from the fuel and economic crises in Sri Lanka. A LA yield of 100 mol% and a conversion of 100% of fructose is achieved at 120 °C in 30 h using a commercial perfluorosulfonic acid resin in a pellet form as the catalyst (Aquavion[®]P98 PFSA) [5]. Such catalytic strategies need to be scaled up for the industrial production of LA. The diversification of LA to fuels, chemicals and materials requires a huge supply of this strategic chemical. The diversity in biomass (terrestrial, fresh water and marine) feedstock, and various catalysts innovatively used for the production of LA are shown in Table 1.

The use of an unconventional reaction medium such as γ -valerolactone (GVL), as a solvent, reduced the activation energy of the process of conversion of biomass to LA. The reaction kinetics of glucose conversion to LA was accelerated by the use of GVL as a solvent instead of water. The adsorption of glucose on the surface of the solid acid catalyst (CH_3 -SBA-15- SO_3H) was enhanced. Moreover, the rate determining step, namely, direct dehydration of glucose to 5-HMF was accelerated in the GVL medium as the intermittent step of isomerization of glucose to fructose was completely eliminated in this medium. The activation energy for the conversion of glucose to LA was reported to be 62.66 kJ/mol. The yield of LA was enhanced by five times when the reaction was carried out in GVL medium instead of water, with the reaction conditions being a temperature of 160 °C for 120 min [10]. Another new avenue in this field of research is the use of environmentally friendly organic solvents, namely, deep eutectic solvents (DESs), for the pretreatment of lignocellulosic biomass to reduce the recalcitrance of the biomass and to improve the accessibility of the reaction site by the acidic catalyst. The reaction site in question is the β -1,4 glycosidic bond, as shown in Figure 3.

Table 1. Diverse biomass feedstock and catalysts used for levulinic acid (LA) production.

Feedstock for LA Production	Catalyst	Yield of LA	Reference
Fructose	Aquivion®P98 PFSA, a commercial perfluorosulfonic acid resin in a pellet form	100 mol% at 120 °C for 30 h;	[5]
Glucose	LaMnO ₃	69.5 mol%;	[6]
Glucose	MOF (UIO-66-NH-R-SO ₃ H)	71.6 mol% at 170 °C;	[7]
Corn cob	Mo doped carbon microspheres; presence of Lewis acid sites, namely, Mo ₂ C and Mo ⁶⁺ promoted the isomerization of glucose to fructose	33.02 (% of theoretical maximum) yield of LA at 195 °C in 90 min;	[8]
Glucose	Para-toluene sulfonic acid (PTSA) functionalized activated carbon with CaCl ₂	61 mol% at 175 °C in 120 min with MIBK-H ₂ O solvent system;	[9]
Fructose	ZrO ₂ -SiO ₂ -SnO ₂ Solid super acid catalyst with H ₀ = −14.52	80 mol% at 180 °C in 3.5 h;	[14]
<i>Laminaria digitata</i> (wild brown seaweed)	4 wt.% H ₂ SO ₄	12.5 wt.% at 200 °C in 30 min;	[15]
<i>Spirulina platensis</i> residue	1 M H ₂ SO ₄	16.36 wt.% at 180 °C for 30 min;	[16]
Glucose	Cr-MCM-22	60 wt.% at 200 °C in 1 h;	[17]
Glucose and cellulose	Cu HZSM-5-HMS (hexagonal mesoporous silica) hybrid catalyst	45 and 30 mol% from glucose and cellulose, respectively. Ideal conditions for glucose conversion are: 200 °C; 10 bar N ₂ ; 5 h; Ideal conditions for cellulose conversion are: 230 °C; 5 h;	[18]
Newspaper wastes with crystalline cellulose	0.5 M H ₂ SO ₄	23–27 wt.% obtained from sanitary papers, tracing/parchment papers and paper food box; 180 °C; 5 min, 1:1 GVL/H ₂ O solvent;	[19]
Rice straw	1.5 wt.% HCl	52 mol% obtained from rice straw pretreated with choline chloride—oxalic acid deep eutectic solvent; Pretreatment: 100 °C for 2 h; Acid hydrolysis: 120 °C for 2 h;	[20]
Rice straw	Polyethyleneimine functionalized acidic ionic liquid (PolyE-IL) with HSO ₄ [−] counter cation	65.5 (% of theoretical maximum) from pretreated rice straw; Hydrolysis conditions: 210 °C for 120 min;	[21]
Safflower stalk with 45.2 wt.% cellulose content	0.3 M PTSA	30 (% of theoretical maximum) at 200 °C for 120 min;	[22]
Cellulosic residue from corn stover	Phosphoric acid activated lignin based activated carbon	67.9 mol% at 190 °C in 150 min in MIBK/H ₂ O-NaCl medium;	[23]

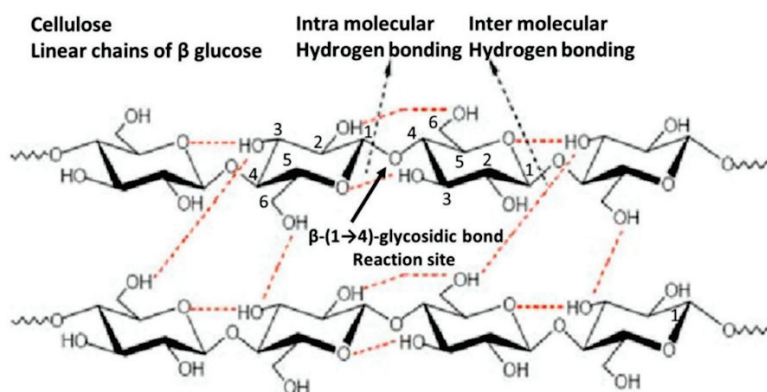
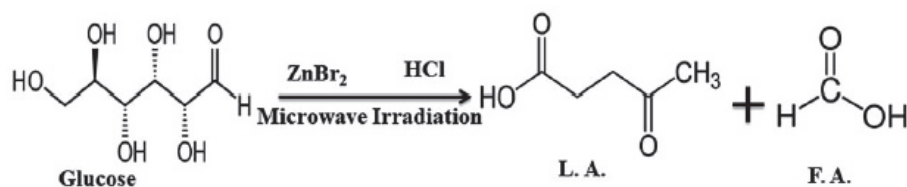


Figure 3. The reaction site β -1,4 glycosidic bond in cellulosic biomass surrounded by extensive hydrogen bonding network. Adapted with permission from Peertechz [71].

The use of DESs for pretreating the biomass improves the accessibility of the catalytic acid site (H^+) to the reaction site in the substrate by a two-fold action, namely, by dissolving the hemicellulose component as well as by weakening the inter and intramolecular hydrogen bonding that hinders the accessibility to the reaction site. Typical examples of such DESs include choline chloride-acetic acid, choline chloride-succinic acid, choline chloride-oxalic acid, choline chloride-malonic acid, and choline chloride-lactic acid [20,23]. Innovation in catalyst design includes heteroatom doping or heteroatom functionalization in activated carbon materials, making them environmentally benign catalysts for biomass conversion. Strategies for sulphur functionalization of biomass (*Ipomoea carnea*) derived activated carbon material using elemental sulphur/hydrazine solution under modest reaction conditions (400 °C) resulted in the sulphur loading of 0.34 wt.%, and the resulting material was used as an adsorbent for Hg for environmental applications [72]. Sulfonate/sulphate functionalized carbon nitride ($g-C_3N_4$) with a sulphur content of 9.2% catalysed the conversion of glucose to LA with a yield of 48 mol% and a selectivity of 57 mol% [12].

3. Possible Catalysts for Accelerated Levulinic Acid (LA) Production from Biomass

In addition to the catalysts summarized in Table 1, innovation is achieved in the design of heteropoly acid based solid acid catalysts with optimal amounts of Lewis and Bronsted acidity, a combination that is vital for the conversion of biomass to LA. Gedanken's group made a significant contribution to the use of microwave technology and the design of solid acid catalysts for the accelerated production of LA from biomass [63–71]. A total of 53 wt.% LA yield was obtained from glucose by the synergistic catalytic activity of HCl and $ZnBr_2$ under microwave irradiation for 6 min. The improved catalytic activity was attributed to the in situ generation of HBr (Scheme 1).



Scheme 1. Synergistic catalytic activity of HCl and $ZnBr_2$ under microwave irradiation leading to in situ generation of HBr for accelerated production of levulinic acid [67].

Pretreatment with a simulated green liquor (Na_2CO_3 - Na_2S , 20 wt.% total titratable alkali, TTA, and 40 wt.% sulfidity) at 200 °C for 15 min was an effective strategy to delignify (64.8–91.2 wt.%) various herbaceous biomasses, namely, rice straw (RS), corn stover (CS), sweet sorghum bagasse (SSB), and Miscanthus (MS). As a consequence, the cellulose content of the delignified biomasses increased from 33.0–44.3 to 61.1–68.4 wt.% depending

on the source of the biomass. However, under similar conditions of biomass conversion to LA, namely, 1 M HCl, 150 °C, 5 h, 20 g/L solid loading, the yield of LA from the original untreated and delignified biomasses was 60.2–78.5 and 50.4–56.0 wt.% (% of the theoretical maximum). The variation of the yield of LA as a function of reaction time in the untreated and pretreated biomass is shown in Figure 4. The concentration of LA in the products from the pretreated biomass increased by a factor of 1.5.

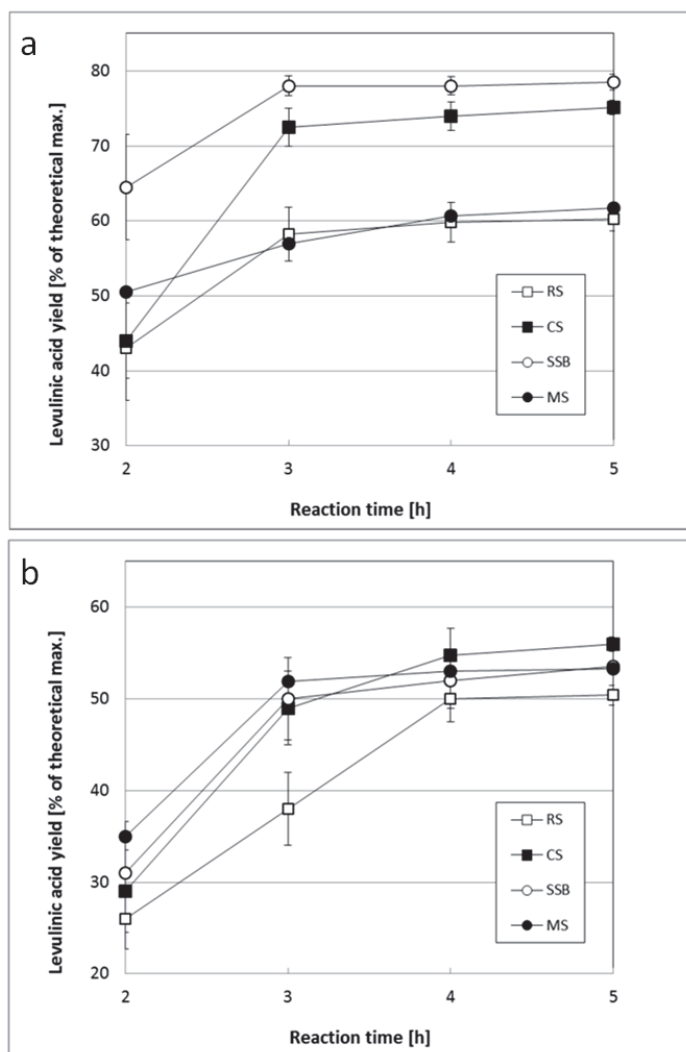


Figure 4. Variation of the yield of LA as a function of reaction time from (a) untreated and (b) green liquor pretreated biomass (rice straw, RS; corn stover (CS); sweet sorghum bagasse (SSB) and miscanthus (MS) [Reaction conditions: 1 M HCl, 150 °C, 50 g/L solid loading; biomass particle size > 2000 µm]. Adapted with permission from MDPI [63].

The lower yield of LA in RS and MS compared to either CS or SSB could be partially attributed to the higher lignin contents of 17.1 and 19.6 wt.% respectively. As expected, the biomass with the lowest lignin content (~13.3%) showed the highest LA yield (78.5 wt.%). However, the relationship between the lignin content of the biomass and the yield of LA is unclear and indirect as other factors, such as the relative binding strength of lignin to cellulose as well as the location of the lignin in the biomass and the ash content of the biomass also play a role in the conversion of biomass to LA. This is because the yield of LA from corn stover (75.1 wt.%) is higher than that of RS (60 wt.%), even though the lignin contents of both are ~17 wt.%. The distinguishing feature between CS and RS is their ash content, which is 1.5 and 8.2 wt.%, respectively. The higher ash content of the RS could have retarded the activity of the catalyst (HCl) leading to a lower yield of LA [63].

Among the various agricultural wastes, namely, *Cicer arietinum* (CA), cotton, *Pinus radiata* (PR) and sugar cane bagasse (SCB), cotton showed the best performance with the highest yield of LA (44.0 wt.%) under modest hydrothermal reaction conditions (423 K, 1 M HCl, 2 h) (Figure 5). This could be attributed to cotton containing the highest cellulose content (>99 wt.% from Milouban cotton linters pulp, MCP Ltd., Israel). Biomass with a high cellulose content is an ideal feedstock for obtaining high yields of LA [70].

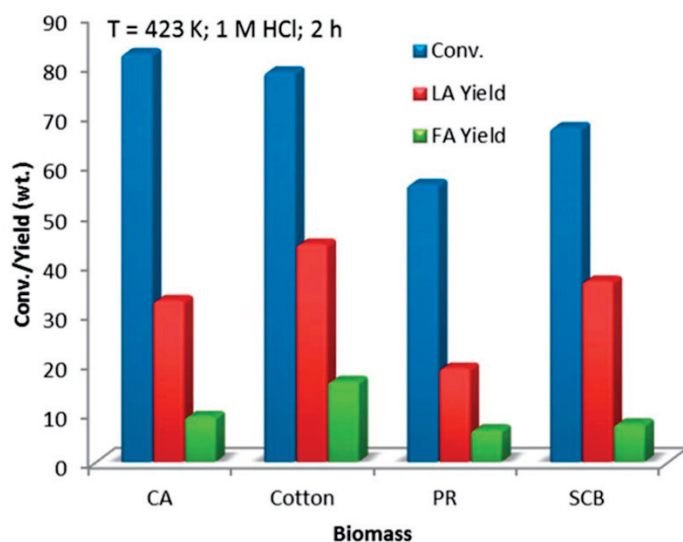


Figure 5. Hydrothermal conversion of agricultural wastes, namely, *Cicer arietinum* (CA), cotton, *Pinus radiata* cones (PR) and sugar cane bagasse, to levulinic acid. Adapted with permission from RSC [70].

Heteropoly acids are ideal solid Bronsted super acids with a potential to catalyse vital reactions, such as alkylation, esterification, hydration, dehydration, polymerization and many others that are involved in the conversion of biomass to biochemicals and biofuels [64,65,68,69,73–77]. Supporting heteropoly acids on activated carbon materials is an innovative strategy to exploit their unique selectivity for catalytic reactions involved in biomass conversion [68,69]. Silicotungstic acid supported on activated carbon showed high activity and selectivity (94 wt.% glucose) for the conversion of starch to glucose, a precursor to LA. The catalyst, prepared by wet impregnation, could be used for five reaction runs without appreciable loss of activity (Figure 6). By suitably tuning the reaction conditions, the catalyst, 20 wt.% $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ /activated carbon, could be exploited for high yield and selective production of LA from biomass, and efforts in this direction are awaited [68].

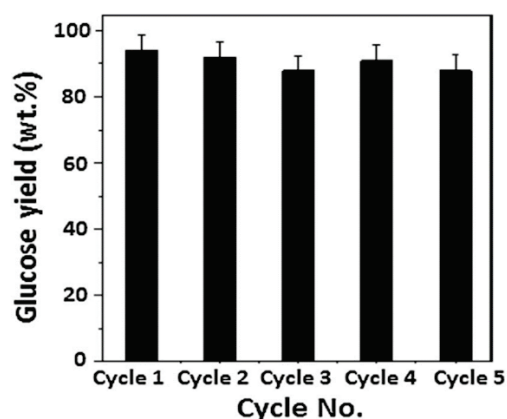


Figure 6. Reusability of the solid acid catalyst, 20 wt.% $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ nH_2O /activated carbon for the conversion of starch to glucose (reaction conditions: starch, 0.5 g; catalyst, 0.5 g; H_2O , 20 mL; 423 K; 4 h). Adapted with permission from Elsevier [68].

To obtain optimal amounts of Lewis and Bronsted acid sites, efforts were devoted for preparing Ga salt of molybdophosphoric acid (GaHPMo) [64] and Ga deposited on mordenite zeolite (Ga@mordenite) [65] using an ultrasound irradiation technique. SEM images of GaHPMo with elemental mapping and the EDS plot are shown in Figure 7. Likewise, the TEM images of Ga@mordenite with elemental mapping and the EDS plot are shown in Figure 8. Uniform distribution of the constituent elements throughout the surface of the catalyst are shown in the images showing elemental mapping (Figures 7 and 8). High yields of LA, 56 and 59.9 wt.% respectively, were obtained from glucose using GaHPMo and Ga@mordenite catalysts [64,65].

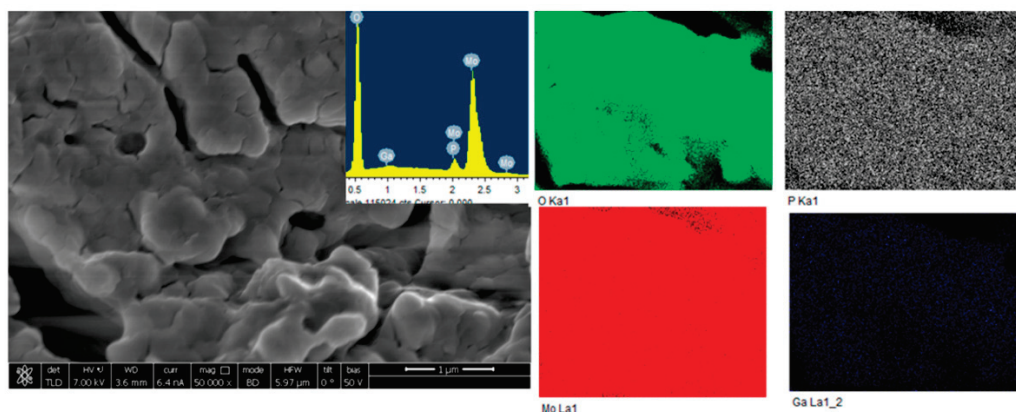


Figure 7. SEM image of Ga salt of molybdophosphoric acid (GaHPMo) with the EDS plot and elemental mapping. Adapted with permission from ACS [64].

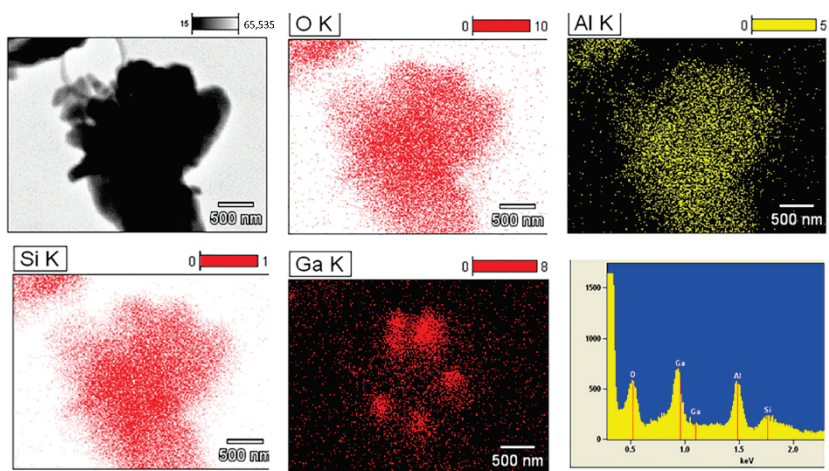


Figure 8. TEM image of Ga deposited on mordenite zeolite (Ga@mordenite) with elemental mapping (O, Al, Si, Ga) and EDS plot. Adapted with permission from Wiley-VCH [65].

Thus, heteropoly acids supported on activated carbon as well as Ga modified heteropoly acids and Ga modified zeolites are promising solid acid catalysts for LA production from glucose.

4. Possible Biochemicals from Levulinic Acid

4.1. Alkyl Levulinates from Levulinic Acid

Alkyl levulinates are potential fuel blends and additives [25,26,28,32,33,35,36,45,49]. Upgrading LA to levulinates via esterification using a variety of catalysts, namely, zeolites, mesoporous silica, carbon materials, metal organic frame works (MOFs), ion exchange resins and enzymes has received considerable attention globally, owing to their potential as fuel-blending chemicals used in biofuel production. Use of such blending agents reduce the emission of polluting gases and thereby global warming. Use of alkyl levulinates as

additives improve the physical, chemical and combustion properties of fuels. Moreover, the performance of the engine is also enhanced. Catalytic strategies for the production of alkyl levulinates, either linear (with varying chain length) or branched, are being developed. Alkyl levulinates are excellent additives to gasoline and diesel, resulting in an improvement in engine performance and a reduction in the emission of polluting gases. In addition to being used as fuel additives, alkyl levulinates find application in pharmaceutical, polymer, agriculture, cosmetic, resin and coating and solvent industries [2]. Currently, ~90% of industrial research and development is devoted to heterogeneous catalysis owing to the advantages of solid acid catalysts, such as zeolites, mesoporous silica, carbon materials, polyoxometalates, metal organic frame works, ion-exchange resins and biocatalysts. Tuning the porosity and acidity of zeolites has been an active area of research. Constraints with conventional mesoporous silica, namely, high reaction temperatures, reaction times and consumption of alcohol are being solved using hybrid mesoporous inorganic-organic silica as catalysts. As a result, improvements in green chemistry metrics, namely, E-factor, atom economy, recyclability and product yield were achieved. Though carbon materials are active and promising catalysts for the esterification of LA, the high cost of production and harsh production conditions (high temperature and the use of corrosive acids and alkalies) impose restrictions on large scale production. Moreover, strong affinity between the sulfonic acid functional groups on the carbon surface and the substrate, namely LA, causes problems of reduced activity and recyclability. Efforts in the direction of functionalization of carbon materials with solid acids, namely, zeolites or hetropoly acids, are being made to surmount these problems [64,65,68,69,71]. Moreover, efforts are dedicated to produce carbon materials from wasteland weeds (such as *Calotropis gigantea* and *Ipomoea carnea*) and agricultural wastes (such as *Borassus flabellifera* and *Limonia acidissima*) using environmentally friendly activating agents, such as alkali salts of organic acids (for example, sodium oxalate) under mild production conditions so as to reduce the cost of production and make the process more environmentally friendly [72]. Typical wasteland weeds and agricultural wastes exploited for the production of high surface area microporous activated carbon materials are shown in Figure 9 [72,78,79].



Figure 9. Wasteland weeds, (a) *Calotropis gigantea*, (b) *Ipomoea carnea*; and agricultural wastes, (c) spikes of *Borassus flabellifera* and (d) shells from *Limonia acidissima* used for the production of microporous high surface area activated carbon materials [72].

Recent developments in the esterification reaction of LA to alkyl levulinates are highlighted in Table 2.

Table 2. Biochemicals from levulinic acid (LA).

Biochemical from LA	Catalyst	Product Yield	Reference
GVL	Hf-FDCA (catalyst prepared from the hybrid of a metal precursor and 2,5 furan dicarboxylic acid)	88% yield of GVL at 180 °C in 24 h;	[24]
Hexyl levulinate	Sulfated silica prepared by the sulfonation of amorphous bamboo leaf ash	95.2% conversion of LA at 90 °C in 7 min with 98.0% selectivity to hexyl levulinate; catalyst reused six times;	[25]
GVL	2 wt.% Pt on ZrO ₂	97% GVL yield; formic acid used as hydrogen source; T = 140 °C; t = 180 min; triethyl amine used to facilitate formic acid decomposition; catalyst reused for four consecutive cycles;	[27]
Methyl levulinate	MOF containing Zr metal cluster with amino terephthalic acid (UiO-66-NH ₂) ligand	85.89% yield of methyl levulinate in an autoclave in 1 h; T = 130 °C; P = 30 bar N ₂ pressure; k = 3.57 × 10 ^{−3} min ^{−1} ; activation energy = 48.99 kJ/mol;	[28]
Chiral GVL	Nickel phosphine complex; Ni(OTf) ₂ ; (S, S) Ph-BPE/(R, R) Ph-BPE; TFE; 50 °C; 12 h; in a gram scale preparation	78.6% yield of (R)-GVL with 96% ee; 79.05% yield of (S)-GVL with 96% ee;	[29]
GVL	Ru nanoparticles anchored on hierarchical porous N-doped carbon nanospheres (3 wt.% Ru/HPNC)	GVL yield > 99% at 100 °C in 2 h under solvent-free conditions; 2.5 MPa H ₂ ; catalyst reused for six reaction cycles;	[30]
<i>n</i> -butyl levulinate (BL)	LiCl·3H ₂ O + AlCl ₃ (molten salt hydrates) with microwave irradiation	95.5% yield of <i>n</i> -butyl levulinate; T = 100 °C; t = 2.5 h; activation energy of <i>n</i> -butyl levulinate formation with LiCl·3H ₂ O and LiCl·3H ₂ O + AlCl ₃ were 70.9 kJ/mol and 31.8 kJ/mol respectively;	[35]
GVL	Zr-Al beta	85.5% yield of GVL; isopropyl alcohol used as hydrogen donor;	[36]
(R)-4-amino pentanoic acid	Glutamate dehydrogenase coupled with formate dehydrogenase	97% conversion of LA with a (R)-4-amino pentanoic acid stereoselectivity of >99% in 11 h;	[37]
GVL	Ru/PEG (ruthenium nanoparticles stabilized by water soluble polymer PED)	82 mol% conversion of LA with 99.2 mol% selectivity for GVL; T = 140 °C; t = 15 min;	[38]
GVL	Zr@PS-FA (successful coordination observed in the catalyst between Zr ⁴⁺ and OH and COOH groups of the partially hydrolysed <i>Pinnistum sinense</i> in formic acid)	95.6 mol% yield of GVL; T = 180 °C; t = 1.5 h; TOF = 9.76 h ^{−1}	[39]
2-methyl tetrahydrofuran	Ni-Cu-OMA (ordered mesoporous alumina)	73.0% selectivity towards 2-MTHF; two steps are involved in the production of 2-MTHF; Step 1: 190 °C; 30 bar H ₂ ; 4 h Step 2: 230 °C; 50 bar H ₂ ; 12 h	[41]
GVL	Ru@GOF (Ru nanoparticles confined in the gallery space of graphene oxide frameworks pillared with organic linkers)	93 mol% yield of GVL; T = 90 °C; t = 8 h; TOF = 7240 h ^{−1} ; catalyst reusable for at least five reaction runs	[42]

Table 2. Cont.

Biochemical from LA	Catalyst	Product Yield	Reference
GVL	5% Ru/Sn-SBA-15	LV conversion—99%; GVL selectivity—98%; T = 250 °C; t = 3 h; H ₂ flow = 25 mL/min;	[43]
GVL	10 wt.% Re supported on activated carbon	LA conversion—100% GVL selectivity—99% T = 120 °C; t = 4 h;	[44]
Ethyl levulinate	H ₃ PMo ₁₂ O ₄₀ /Activated carbon	Ethyl levulinate yield = 80%; T = 80 °C; t = 15 h;	[45]

4.2. Hydrogenation of LA to γ -Valerolactone

Apart from the esterification of LA to levulinates, hydrogenation of LA is a promising route for the production of the biochemical and biofuel precursor γ -valerolactone, using either H₂ or formic acid or alcohols as the hydrogen source, and this has been extensively studied [27,29,30,36–44,46,50]. Promising catalysts developed for the conversion of LA to γ -valerolactone are summarized in Table 2.

4.3. Reductive Amination of LA to N-Substituted Pyrrolidones and N-Substituted Pyrrolidinones

Production of biobased nitrogenous chemicals is of vital significance to food security and for the pharmaceutical industry. Studies on the conversion of LA to N-containing organic compounds, especially N-substituted pyrrolidones [31,34] and N-substituted pyrrolidinones [47] are highlighted in Table 3.

Table 3. Production of biobased nitrogenous chemicals.

Nitrogenous Chemical	Catalyst	Product Yield	Reference
N-substituted pyrrolidones	No catalyst; HBpin used as reducing agent	28–94% yield of N-substituted pyrrolidones;	[31]
5-methyl-2-pyrrolidone	20 molar percent of Zr in the Co, Zr bimetallic carbon-nitrogen doped catalyst (Co-Zr@chitosan-20)	92.5% yield of 5-methyl-2-pyrrolidone; ammonia as N source; T = 130 °C; P = 30 bar H ₂ ; 24 h;	[34]
N-butyl-5-methyl-2-pyrrolidinone	Cu ₁₀ /AlB ₃ O	N-butyl-5-methyl-2-pyrrolidinone yield = 94%; LA conversion = 99%; stable catalytic performance for 200 h; T = 200 °C; LHSV = 0.3 h ^{−1} ; 1,4-dioxane solvent; LA:n-butyl amine mole ratio = 1:1; H ₂ pressure, 3 MPa;	[47]

5. Possible Biofuels from Levulinic Acid (LA)

Hydrocarbons such as ethylene and propylene can be produced from LA via bio 1-butene through a series of reactions, namely, hydrolysis, hydrogenation, decarboxylation, metathesis and cracking [51]. Ethylene and propylene are produced from sugar cane bagasse by the hydrolysis of the cellulose component to glucose, followed by the isomerization of glucose to fructose and subsequent dehydration of the fructose to 5-HMF, followed by the dehydration of 5-HMF to LA. The LA thus generated is hydrogenated to GVL. GVL is decarboxylated to 1-butene using an SiO₂/Al₂O₃ catalyst at a WHSV of 0.18 h^{−1} at 375 °C and 36 bar N₂. Bio 1-butene thus obtained is converted (81.5%) to propylene (selectivity: 42.02 wt.%) and ethylene (selectivity: 19.36 wt.%) at 500 °C and 1 bar and at a WHSV of 6 h^{−1}. 2-MTHF is another promising biofuel derived from LA. MTHF is a more promising biofuel and gasoline additive than bioethanol owing to

its lower miscibility with water, high heating value, energy density, and higher stability, despite its lower octane number (87 vs. 108.6) [53]. Hydrodeoxygenation of LA over a bimetallic $\text{Ni}_5\text{Co}_{25}/\gamma\text{-Al}_2\text{O}_3$ catalyst gave high activity with 73.4% yield of 2-MTHF at 240 °C. Commercial production of 2-MTHF is based on corn cob derived furfural. Recently, advances have been made for the production of 2-MTHF from a cellulose base biochemical such as LA. The existence of metal as well as metal oxide species in the $\text{NiCo}/\gamma\text{-Al}_2\text{O}_3$ bimetallic system is necessary for the conversion of LA to 2-MTHF as the metal sites activate the H_2 , promoting the hydrogenation, while the metal oxides provide the necessary acid sites for the dehydration reaction. 2-propanal was found to be a promising reaction medium for the dehydration of 1,4-pentandiol to 2-MTHF [53]. Dimers (C_{10}) of LA, namely, tetrahydro-2-methyl-5, γ -dioxo-2-furanpentanoic acid (TMDFA), 3-(2-methyl-5-oxotetrahydrofuran-2-yl)-4-oxopentanoic acid (MOTOA) and 3-acetyl-2-methyl tetrahydro-5-oxo-2-furan propanoic acid (AMTOFA) are potential biojet fuel ($\text{C}_8\text{-C}_{16}$) precursors from the dimerization of LA using an H-Beta 19 catalyst at 148 °C for 24 h with a LA conversion of 79 mol% and a selectivity towards LA dimers of >98 mol% [53]. Valeric acid is a strategic platform chemical derived from the hydrogenation of LA that yields a new class of biofuels called valeric biofuels [61].

6. Possible Biomaterials from Levulinic Acid (LA)

Polyhydroxy-alkanoates (HPAs) are a viable alternative to non-biodegradable plastics derived from fossil resources [62]. Chiral GVL derived from the asymmetric hydrogenation of LA leads to the production of diverse natural products [29].

7. Conclusions

The use of microwave technology for the conversion of biomass to biochemicals, biofuels and biomaterials offers a solution to the resource depleted world. The use of concentrated solar energy combined with activated carbon supported heteropoly acids hold a promise for the energy efficient and selective conversion of biomass to levulinic acid (LA). The use of simulated green liquor pretreatment effectively delignified the herbaceous biomasses used in this study. However, it is not only the amount of lignin but also the relative location of the lignin and the strength of the bonding between the lignin, cellulose and ash content in the biomass that are crucial for obtaining high yields of LA from biomass. Biomass with a high cellulose content (>99%), such as cotton, is an ideal feedstock for LA production. Until the technology for the direct conversion of lignocellulosic biomass to LA using solid acid catalysts is mature, fructose could be used as the starting material and Ga@mordenite could be used as the solid acid catalyst for the large-scale production of LA. Though significant progress has been made in the diversification of LA to biofuels and biochemicals, progress is awaited in the production of plastic substitutes, natural products and chiral nitrogenous biomaterials from LA.

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Article

Mechanistic Studies into the Selective Production of 2,5-furandicarboxylic Acid from 2,5-bis(hydroxymethyl)furan Using Au-Pd Bimetallic Catalyst Supported on Nitrated Carbon Material

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Abstract: Aerobic oxidation of bio-sourced 2,5-bis(hydroxymethyl)furan (BHMF) to 2,5-furandicarboxylic acid (FDCA), a renewable and green alternative to petroleum-derived terephthalic acid (TPA), is of great significance in green chemicals production. Herein, hierarchical porous bowl-like nitrogen-rich (nitrated) carbon-supported bimetallic Au-Pd nanocatalysts ($\text{Au}_m\text{Pd}_n/\text{N-BN}_x\text{C}$) with different nitrogen content and bimetal nanoparticle sizes were developed and employed for the highly efficient aerobic oxidation of BHMF to FDCA in sodium carbonate aqueous solution. The reaction pathway for catalytic oxidation of BHMF went through the steps of $\text{BHMF} \rightarrow \text{HMF} \rightarrow \text{HMFCa} \rightarrow \text{FFCA} \rightarrow \text{FDCA}$. Kinetics studies showed that the activation energies of BHMF, HMF, HMFCa, and FFCA were $58.1 \text{ kJ}\cdot\text{mol}^{-1}$, $39.1 \text{ kJ}\cdot\text{mol}^{-1}$, $129.2 \text{ kJ}\cdot\text{mol}^{-1}$, and $56.3 \text{ kJ}\cdot\text{mol}^{-1}$, respectively, indicating that the oxidation of intermediate HMFCa to FFCA was the rate-determining step. ESR tests proved that the active species was a superoxide radical. Owing to the synergy between the nitrogen-rich carbon support and bimetallic Au-Pd nanoparticles, the $\text{Au}_1\text{Pd}_1/\text{N-BN}_2\text{C}$ nanocatalysts exhibited BHMF conversion of 100% and FDCA yield of 95.8% under optimal reaction conditions. Furthermore, the nanocatalysts showed good stability and reusability. This work provides a versatile strategy for the design of heterogeneous catalysts for the highly efficient production of FDCA from BHMF.

Keywords: 2,5-bis(hydroxymethyl)furan; 2,5-furandicarboxylic acid; aerobic oxidation; nitrogen-doped carbon; bimetallic Au-Pd nanoparticles

1. Introduction

Dwindling fossil stocks and increased environmental awareness have triggered a rush to find renewable resources [1]. Biomass, derived from plant photosynthesis, is a new source of cheap, available, and renewable energy and has been widely used to produce high value-added fuels and chemicals [2–4]. Biomass has been identified as an ideal candidate for the development of sustainable energy and value-added materials that can partially replace current petrochemicals [5]. Therefore, research and development of renewable biomass are of great significance and urgent need. 5-hydroxymethylfurfural (HMF) is a biomass-based platform compound containing active aldehyde, hydroxyl, and furan ring structures. Through further reaction, many downstream products can be derived from HMF, which is a crucial intermediate connecting biomass chemistry and petrochemistry. Among them, 2,5-furandicarboxylic acid (FDCA) was the sole aromatic molecule among the “twelve platform bio-based compounds” that the U.S. Department of Energy presented back in 2004 and was subsequently significantly used in the synthesis of polyester, polyamide, epoxy resin, and other polymers [6–8]. FDCA is considered as an ideal substitute for the petroleum derivative terephthalic acid (TPA) due to its similar physical and chemical

properties. In addition, compared to TPA-derived polyethylene terephthalate (PET), the bio-based polyester 2,5-furandicarboxylate (PEF) produced by FDCA has better gas insulation, thermal stability, and mechanical properties, and FDCA has broad application prospects and high market potential [9–12].

Due to the great potential of FDCA, a variety of catalysts for FDCA production from HMF have been developed in recent years [13–15]. In previous studies, homogeneous and heterogeneous catalysts were used for the catalytic production of FDCA. It is difficult to separate the homogeneous catalysts from the reaction medium, and their stability and recyclability are poor. The study of heterogeneous catalysts has greater commercial potential and practical application as well [16]. At present, most research on catalytic oxidation for FDCA preparation is focused on supporting precious metals (Pt [17], Au [18,19], Pd [20,21], and Ru [16,22]) on multiphase catalysts. Davis et al. found that Au-based catalysts have strong aldehyde oxidation activity in alkaline circumstances [23]. Lei et al. found that palladium is more favorable for the oxidation of alcohols [24]. Combining the advantages of Au and Pd, the preparation of a bimetallic catalyst for FDCA with high activity, high selectivity, and high stability through catalytic oxidation of HMF is of great significance [25,26]. Although significant progress has been made in this regard [27–30], HMF is thermally and chemically unstable, often leading to severe degradation that hinders its storage and industrialization. To solve this problem, an alternative pathway is used, in which the 2,5-bis(hydroxymethyl)furan (BHMF) is first converted to HMF and then oxidized to produce FDCA. Because of the better storage stability of BHMF, the BHMF-mediated pathway has a brighter future for FDCA mass production [1,17,29].

The carrier in the supported metal catalyst not only disperses and stabilizes the metal nanoparticles, but the synergistic interaction between the carrier and the metal particles also leads to interfacial charge transfer, metal structure change, molecular adsorption modulation, and other phenomena, thus affecting the activity, selectivity, and stability of the catalyst. Carbon materials are promising supports for metal nanoparticles, especially fuel cell catalysts and catalysts for reactions in aqueous medium, due to their high stability over a wide pH range and the ease of surface functionalization through the incorporation of other elements, such as oxygen and nitrogen [31–33]. In general, for faster reaction rates and better product solubility, selective BHMF oxidation must be carried out in more alkaline conditions. However, use of strong alkalis will make it hard to separate the finished product, which will cause the active phase to leak out of the reactor and will result in corrosion [34]. In our previous study, nitration improved the adsorption capacity of the substrate, allowing the reaction substrate to more easily come into contact with the active site on the catalyst surface and improving the desorption ability of the product (FDCA) [35]. Nitrogen-doped carbon materials show excellent performance in the field of catalysis, which is expected to become a forward-looking field of catalyst development and promote the progress of related industrial technology [7]. In this study, nitrogen-doped carbon material after nitrification, which can provide basic sites, was used as support to synthesize a highly efficient catalyst. Due to the introduction of nitrogen, nitrogen-doped carbon materials have a special structure and have more advantages than traditional catalysts [36]. The nitrogen doping process can introduce defect sites and nitrogen species, improve the physical and chemical properties of catalysts, and interact with active species to improve catalytic performance. The interaction between nitrogen species and active components, such as metal components or metal oxides, can effectively improve the dispersion and stability of active species and adjust their redox properties, thus realizing improvements in catalytic performance [37].

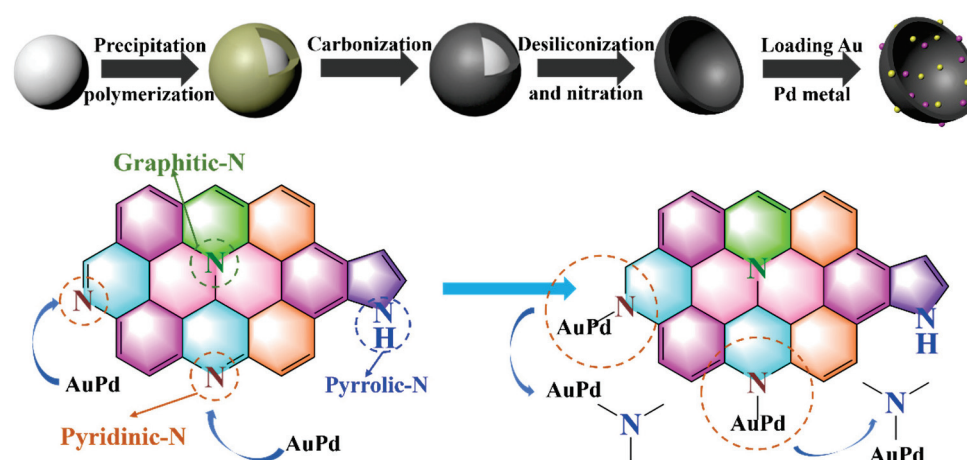
In this work, hierarchical porous bowl-like nitrogen-rich carbon-supported bimetallic Au-Pd nanocatalysts ($\text{Au}_m\text{Pd}_n/\text{N-BN}_x\text{C}$) were synthesized by precipitation polymerization employing uniform silica nanospheres as a template, which was followed by carbonization, removal of SiO_2 spheres, and loading of Au-Pd bimetallic procedures. $\text{Au}_m\text{Pd}_n/\text{N-BN}_x\text{C}$ catalysts were obtained by adjusting the polymerization ratio and Au-Pd ratio. The catalysts were characterized by TEM, XRD, TGA, SEM, Raman spectroscopy, FT-IR spectroscopy, N_2

adsorption/desorption isotherms, and XPS, and catalytic reactive species were determined by ESR spectroscopy. Through aerobic oxidation of BHMF to FDCA experiments, the influences of nitrogen content and metal ratio on the catalytic performance of catalysts were explored, and the influences of reaction factors such as time, temperature, and pressure were considered. The catalytic performance of the catalyst was elucidated. The possible reaction pathway and catalytic mechanism were proposed. Finally, the stability and reusability of the catalyst were evaluated through cyclic experiments. An alternative pathway was used to solve the problem regarding hydroxymethylfurfural being unstable in heat and chemistry, which often resulted in serious degradation. This is of great significance to the industrial production of FDCA.

2. Results and Discussion

2.1. Preparation and Characterization of the $Au_mPd_n/N-BN_xC$ Nanocatalysts

As shown in Scheme 1, employing SiO_2 nanospheres as a template, $Au_mPd_n/N-BN_xC$ nanocatalysts were prepared via precipitation polymerization, carbonization, SiO_2 sphere removal, nitrification, and the loading of Au-Pd bimetal nanoparticles. According to the SEM image of Figure 1a and Figure S1, compared to the smooth surface before polymerization, an uneven flower-like polymerization layer appeared on the surface after polymerization, showing that the precipitation polymerization effectively covered SiO_2 spheres. By altering the proportion of AM and MBA monomers (1:1, 2:1, 3:1), polymers with different nitrogen content were obtained. As shown in Figure 2(a1–a3), it was observed that the thickness of the polymerization layer changed obviously with the adjustment of the proportion of polymerization monomer. The polymer layer was then carbonized via calcination at 800 °C under the protection of nitrogen, and the SiO_2 nanospheres ($SiO_2@N_xC$) were wrapped by a thin and uniform nitrogen-doped carbon shell.



Scheme 1. Schematic illustration for preparing $Au_mPd_n/N-BN_xC$ nanocatalysts.

To obtain the porous structure, the SiO_2 template was removed with hydrofluoric acid. The porous structure can be clearly seen in the SEM (Figure 1b) and TEM (Figure 2(b1–b3)) images. The porous bowl structure had a very large contact area with the substrate, named BN_xC , which effectively improved the adsorption of the substrate. However, the contact angle test found that the carrier had superhydrophobicity at this time (Figure S2). On this basis, the carrier was treated with nitric acid to weaken its hydrophobicity, and $N-BN_xC$ was obtained (Figures 1c and 2(c1–c3)). Finally, the bimetal was loaded onto the carrier using the injection reduction method, and the final samples were named $Au_mPd_n/N-BN_xC$. TEM images showed that the metal particles had been successfully loaded [7]. The metal nanoparticles were well dispersed across the surface of the carrier, as shown in Figure 2(d1–d3), and the particle sizes of the metal particles with different polymerization thicknesses were also different. The average metal particle size of $Au_1Pd_1/N-BN_1C$, $Au_1Pd_1/N-BN_2C$, and $Au_1Pd_1/N-BN_3C$ was 11.26, 10.65, and 11.88 nm, respectively.

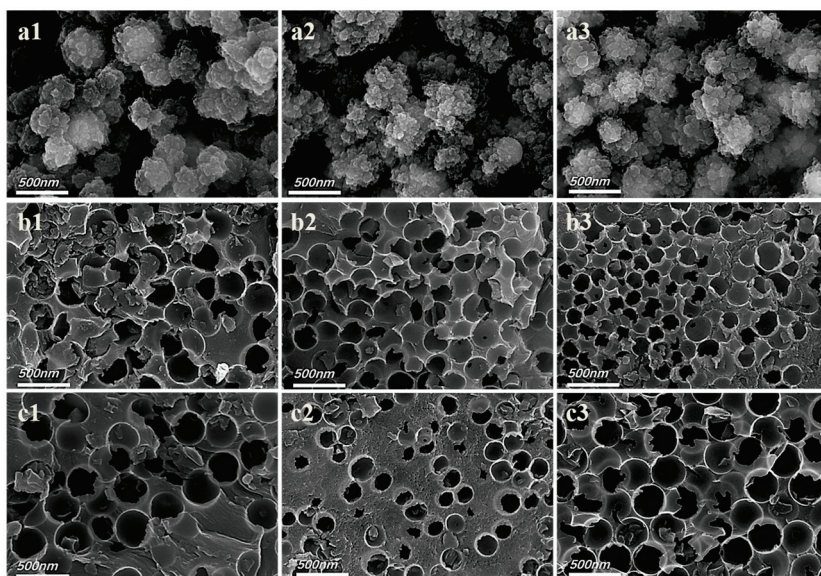


Figure 1. SEM images of $\text{SiO}_2@\text{N}_x\text{P}$ (a1–a3), BN_xC (b1–b3), and $\text{N-BN}_x\text{C}$ (c1–c3) ($x = 1, 2, 3$, corresponding to MBA:AM = 1:1, 1:2, 1:3, respectively).

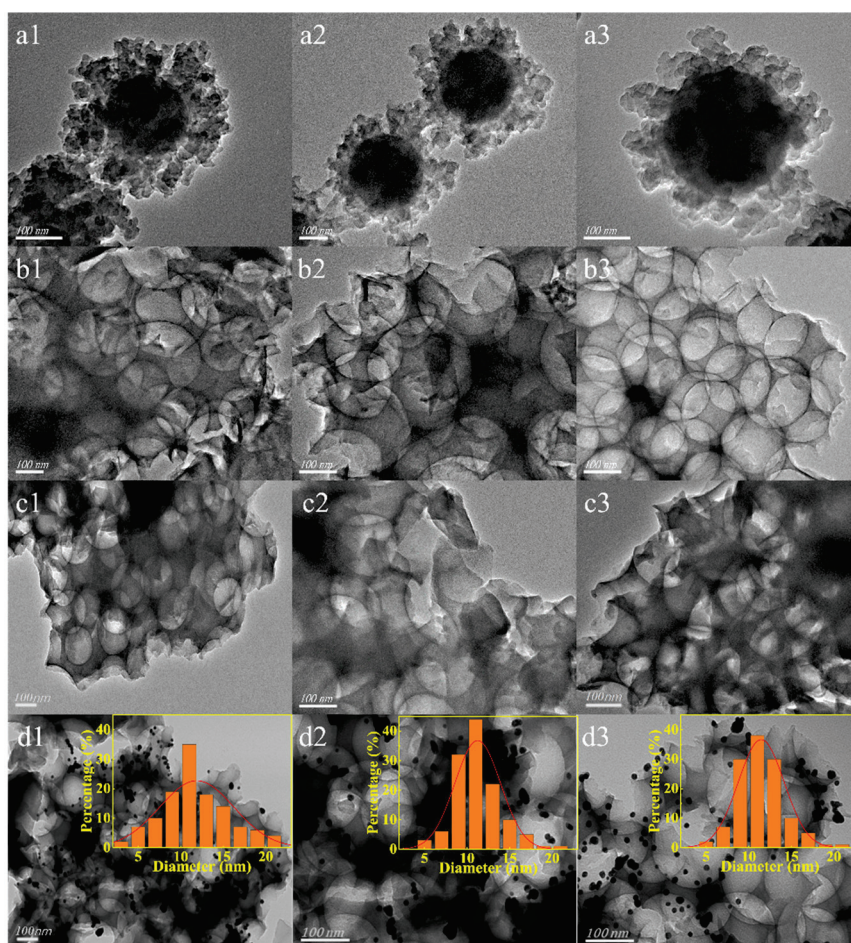


Figure 2. TEM images of $\text{SiO}_2@\text{Poly}_x$ (a1–a3), BN_xC (b1–b3), $\text{N-BN}_x\text{C}$ (c1–c3), and $\text{Au}_1\text{Pd}_1/\text{N-BN}_x\text{C}$ (d1–d3) nanocatalysts ($x = 1, 2, 3$, corresponding to MBA:AM = 1:1, 1:2, 1:3, respectively).

Furthermore, the components of the representative $\text{Au}_1\text{Pd}_1/\text{N-BN}_2\text{C}$ nanocatalyst were characterized by HR-TEM, SAED, and EDS. HR-TEM images (Figure 3a,b) of $\text{Au}_1\text{Pd}_1/\text{N-BN}_2\text{C}$ showed the crystal planes of Pd (111), Pd (200), and Au (311), which were 0.2219 nm,

0.2034 nm, and 0.1153 nm, respectively. In addition, selective electron diffraction (SAED) of the $\text{Au}_1\text{Pd}_1/\text{N-BN}_2\text{C}$ catalyst (Figure 3c) also showed the (111), (200), and (311) crystal faces of Au and Pd, respectively. The representative $\text{Au}_1\text{Pd}_1/\text{N-BN}_2\text{C}$ nanocatalyst was composed of C, N, O, Au, and Pd elements (Figure 3d). Moreover, the bimetallic nanoparticles were uniformly loaded on the support surface (Figure 3e–i).

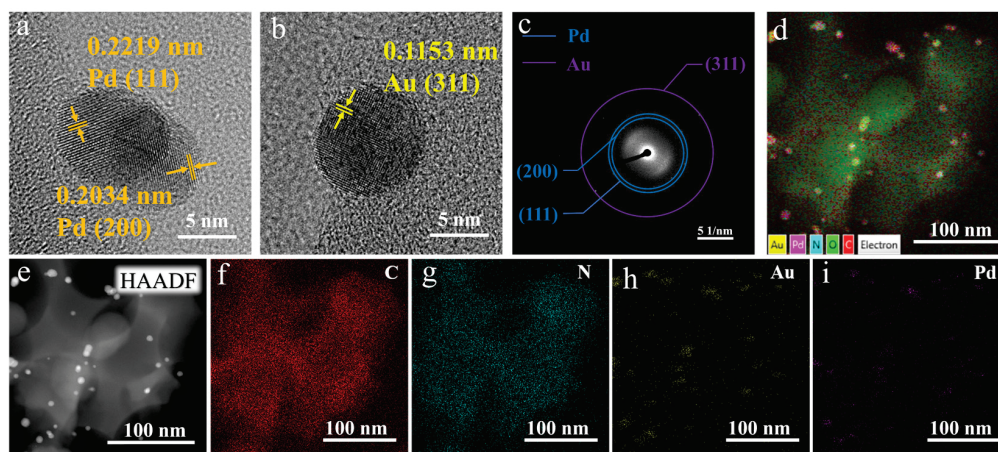


Figure 3. HR-TEM (a,b), SAED (c), EDS (d), HAADF (e) and element mapping images (f–i) of the representative $\text{Au}_1\text{Pd}_1/\text{N-BN}_2\text{C}$ nanocatalysts.

A nitrogen adsorption–desorption experiment was used to investigate the pore size distribution and BET specific surface area of materials. As shown in Figure 4, the H4 hysteresis loop could also be seen in the adsorption and desorption isotherms [38], indicating the existence of a cavity in BN_xC and $\text{N-BN}_x\text{C}$ carriers. Correspondingly, it could be clearly seen in the transmission diagram of Figure 2 that there were indeed many holes. According to the adsorption data, the pore size of the $\text{N-BN}_x\text{C}$ sample was similar, while the pore size of the BN_3C sample was slightly different from that of BN_1C and BN_2C . Table 1 shows the pore structure data of different catalysts. By comparing the data of different carriers, the specific surface area decreased from 53.9, 35.1, and 119 to 9.4, 13.2, and 11.4 m^2g^{-1} after nitric acid treatment. We speculate that nitrification alters the pore structure of carbon materials, resulting in a reduction in specific surface area and a change in pore size, but that the fundamental morphology of carbon materials remains largely unchanged. The porous structure improves the penetrability of the catalyst and the speed at which carriers transfer mass. According to the results of TEM, BET, and elemental analysis, it could be determined that porous nitrogen-doped carbon carriers were successfully prepared.

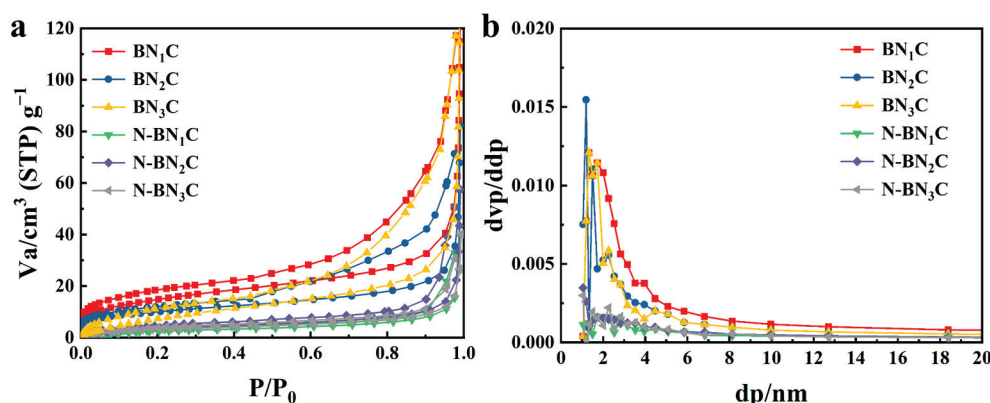


Figure 4. N_2 adsorption–desorption isotherms (a) and pore diameter distribution (b) of BN_xC and $\text{N-BN}_x\text{C}$ ($x = 1, 2, 3$, corresponding to MBA:AM = 1:1, 1:2, 1:3, respectively).

Table 1. Pore structure and nitrogen content of BN_xC and $\text{N-BN}_x\text{C}$.

Samples	Surface Area ^a (m^2g^{-1})	Average Pore ^a (nm)	Pore Volume ^a (cm^3g^{-1})	Nitrogen Content ^b (%)
BN_1C	53.9	14.5	0.20	4.0
BN_2C	35.1	13.6	0.12	7.2
BN_3C	119	5.3	0.16	9.0
$\text{N-BN}_1\text{C}$	9.4	24	0.06	9.7
$\text{N-BN}_2\text{C}$	13.2	24.3	0.08	10.1
$\text{N-BN}_3\text{C}$	11.4	16.6	0.05	11.6

^a Brunauer–Emmett–Teller (BET) surface area is determined by nitrogen adsorption and desorption isotherms.

^b Nitrogen content is calculated by elemental analysis.

To better understand the influence of the temperature of calcination on carbon morphology and whether nitrification also has an impact, Raman tests were conducted, as shown in Figure 5a. There were obvious peaks at 1350 cm^{-1} and 1590 cm^{-1} , which were the D and G bands of carbon [34]. The defect stretching vibration of the sp^3 carbon in support was visible in the D band, while the stretching vibration of the sp^2 carbon was visible in the G band [39]. The high I_D/I_G value indicated that the carbon frame structure had defects, which may be because of the structure breaking down due to the bowl structure formed by the removal of silica during the processing process. In addition, the defect concentration of the catalyst increased after nitrification, and the defect concentration of $\text{N-BN}_2\text{C}$ was 1.1.

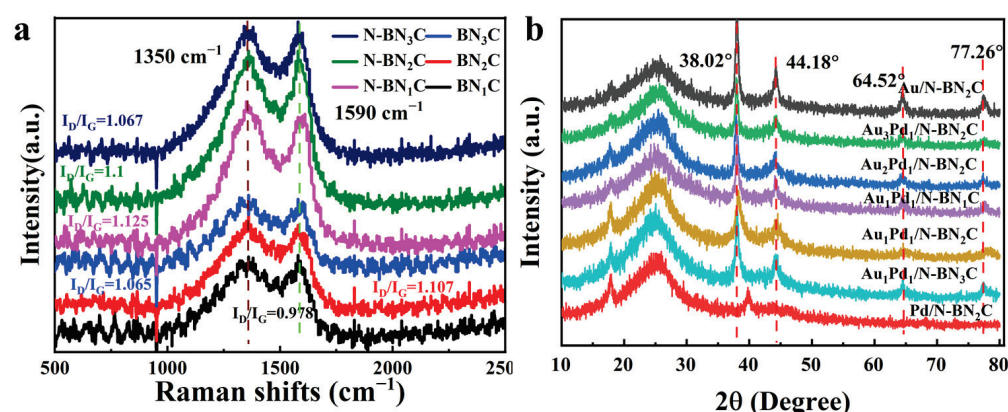


Figure 5. Raman spectra of BN_xC and $\text{N-BN}_x\text{C}$ (a) and XRD spectra of $\text{Au}_m\text{Pd}_n/\text{N-BN}_x\text{C}$ (b) ($x = 0, 1, 2, 3$).

As shown in Figure 5b, XRD was used to characterize nitrifying samples under different AM:MBA and different Au:Pd ratios. Due to the high-temperature treatment of the sample, the polymer gel was graphitized during calcination; thus, diffraction peaks appeared at 17° and 25° , which were the (111) and (002) crystal planes of the graphite structure. XRD peaks appear at 38° , 44° , 64° , and 77° in the $\text{Au/N-BN}_2\text{C}$ diagram, corresponding to the (111), (200), (220), and (311) crystal planes of Au. In the $\text{Pd/N-BN}_2\text{C}$ diagram, XRD peaks appeared at 39° and 46° , corresponding to the (111) and (200) crystal planes of Pd [39,40]. It was found that the diffraction peaks of gold at 38° and 44° weakened, and the diffraction peaks at 64° and 77° almost disappeared when the two precious metals were grafted simultaneously. The diffraction peak of Pd overlapped with the diffraction peak of Au, indicating that the Au-Pd alloy had been successfully loaded. The successful synthesis of the Au-Pd alloy on support was confirmed by XRD.

In order to identify different types of nitrogen functional groups in catalysts, these materials were characterized by FT-IR analysis, as shown in Figure S3. To examine the chemical state and composition of the samples, XPS analysis was then performed. The XPS spectra of N 1s, C 1s, Pd 3d, and Au 4f orbits are shown in Figure 6. It can be seen that the binding energy peaks of the C–O bond and C–N bond of $\text{SiO}_2/\text{N}_x\text{P}$ appeared at 288 eV and 285 eV, respectively. With carbonization, SiO_2 removal, and nitrification, their binding energies increased and their peak values decreased. For the C=C bond, the binding energy peak appeared at 284 eV, and there were no significant changes after subsequent treatment. However, the peak values of C–O and C–N bonds were increased when a single metal was loaded. In the N1s spectrum of $\text{SiO}_2/\text{N}_x\text{P}$, only the peak of quaternary-N (N-Q), with a binding energy of 400 eV, indicated that MBA and AM had been successfully introduced into the SiO_2 carrier. After calcination, SiO_2 removal, and nitrification, pyrrolic-N (N-5) and pyridinic-N (N-6) appeared, with binding energies of 404 eV and 398 eV, respectively [7]. The binding energies of quaternary-N were unchanged, and the peak value of pyridinic-N decreased slightly after nitrification. After loading the gold–palladium bimetal, the peak value of pyridinic-N decreased, but the peak value of quaternary-N and pyrrolic-N did not change obviously. The peak value of pyridine decreased while that of pyrrole-N increased with the loading of Au or Pd. The $4\text{F}_{5/2}$ and $4\text{F}_{7/2}$ binding energies of gold peaked at 87.85 eV and 84.15 eV, respectively. The binding energies for $3\text{d}_{5/2}$ and $3\text{d}_{3/2}$ in palladium peaked at 338 eV and 343 eV, respectively. The peaks of Au and Pd shifted to a higher energy level, and the N-5 and N-6 peaks changed to a lower level of energy. The results showed that there was an interaction between the metal and the support, which improved catalytic performance. The thermal stability of BN_xC and $\text{N-BN}_x\text{C}$ was tested using the TG-DSC method. As shown in Figure S4, all the catalysts had relatively good thermal stability.

2.2. Catalytic Performance of $\text{Au}_m\text{Pd}_n/\text{N-BN}_x\text{C}$ Nanocatalysts

The transformation of BHMf with $\text{Au}_1\text{Pd}_1/\text{N-BN}_2\text{C}$ was investigated regarding reaction time. As shown in Figure 7a, the yield of FDCA reached 95.8% after 24 h reaction. There were no significant changes in the FDCA yield when the reaction time was prolonged. Therefore, the reaction time was fixed at 24 h and other reaction conditions were discussed. Finally, it was discussed how the reaction pressure, temperature, and amount of catalyst affect the yield of FDCA (Figure S5). The catalytic activity of $\text{Au}_1\text{Pd}_1/\text{N-BN}_2\text{C}$ was investigated in a variety of temperatures. When the reaction was carried out at 80 °C, the yield of FDCA was 30.2%. When the temperature was increased to 90 °C, the yield increased to 57.4%. The yield of FDCA approached 95.8% when the reaction temperature was gradually increased to 100 °C. Therefore, 100 °C was chosen as the reaction temperature. Additionally, the effect of oxygen pressure on the catalytic activity of the catalyst was also studied. With increasing oxygen pressure, FDCA yield increased from 40.8% (1.0 MPa) to 58.6% (1.5 MPa). The yield of FDCA increased to 95.8% when oxygen pressure was increased to 2.0 MPa. When pressure was further increased to 2.5 MPa, the production of FDCA did not change. In addition, the influence of the dosage of the catalyst on the catalytic activity of the catalyst was studied. The yield of FDCA increased from 43.8% (30 mg) to 70.6% (40 mg) with an increase in catalyst dose. The yield of FDCA improved to 95.8% when the catalyst dose was increased to 50 mg. The yield of FDCA dropped when the catalyst dose was increased to 60 mg. Therefore, the optimal conditions were 24 h treatment, 100 °C reaction temperature, 2.0 MPa oxygen pressure, and 50 mg of catalyst.

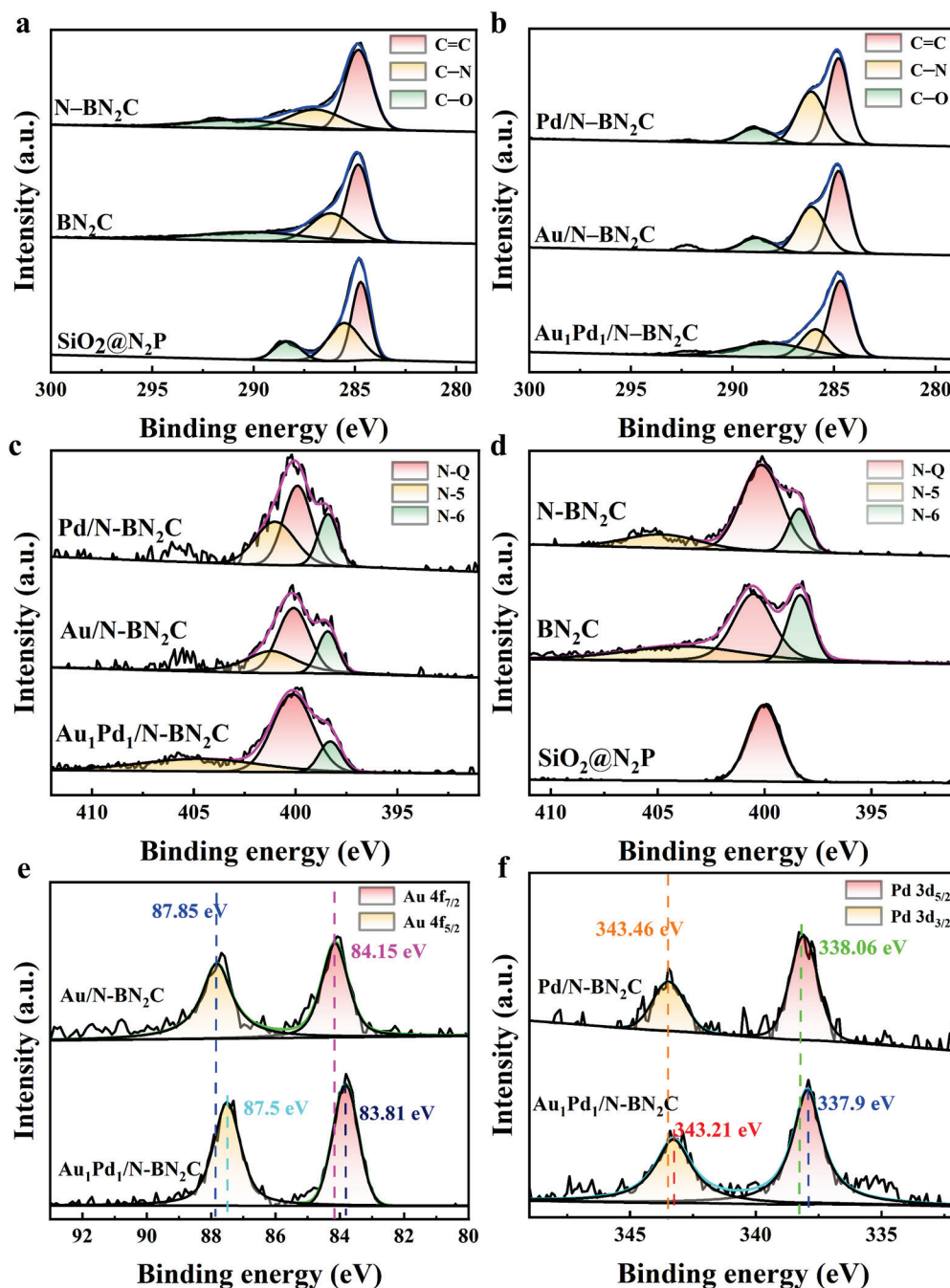


Figure 6. C 1s (a,b), and N 1s (c,d) XPS spectra of SiO₂@N₂P, BN₂C, N-BN₂C, Au/N-BN₂C, Pd/N-BN₂C, and Au₁Pd₁/N-BN₂C. Au 4f (e) and Pd 3d (f) XPS spectra of Au/N-BN₂C, Pd/N-BN₂C, and Au₁Pd₁/N-BN₂C.

The catalytic activity of Au_mPd_n/N-BN_xC nanocatalysts with different nitrogen content and gold–palladium ratios in the oxidation reaction from BHMF to FDCA was investigated, and Table 2 shows the results. The catalytic performance of the Au₁Pd₁/N-BN₂C nanocatalyst with moderate nitrogen content was the highest, and the Au₁Pd₁/N-BN₂C nanocatalyst could obtain the highest FDCA yield (95.8%). The thickness of the polymerization layer and the in situ doping of nitrogen could be adjusted using the polymerization method; thus, the thickness and nitrogen content of N-BN_xC could be adjusted. Nitrogen doping was able to interact with active species to enhance the adsorption of BHMF and improve catalytic performance. In our previous study, CO₂-TPD was used to detect basic sites on the surface of similar nanocatalysts, and the basic sites of materials increased with the increase in AM mole content [7]. Moreover, in the XPS analysis in Figure 6, the peak

of pyridine nitrogen can be observed. The catalyst had strong alkalinity due to its high pyridine nitrogen content. Thus, nitrogen doping also provided the bases that allowed the weak base to replace the strong base in the reaction. Nitrogen atoms also provide an anchor point for the metal particles, enhancing the interaction between the metal and the carrier. There was a significant interaction between Au and Pd in the bimetallic catalyst, which led to the achievement of 100% BHMF conversion and prominent FDCA yield under alkaline conditions. The recyclability of the catalyst was critical to this research and its performance was tested (Figure 7b). The catalytic performance of $\text{Au}_1\text{Pd}_1/\text{N-BN}_2\text{C}$ decreased slightly, and both were able to achieve 100% BHMF conversion after five cycles, showing good stability. The recycled $\text{Au}_1\text{Pd}_1/\text{N-BN}_2\text{C}$ was analyzed by TEM, XRD, Raman spectroscopy, and XPS, and the results are shown in Figures S6 and S7. It was also discovered that the support cracks and the metal particles decreased. We speculate that the loss of catalyst activity during the cycle may be due to metal shedding and support fragmentation.

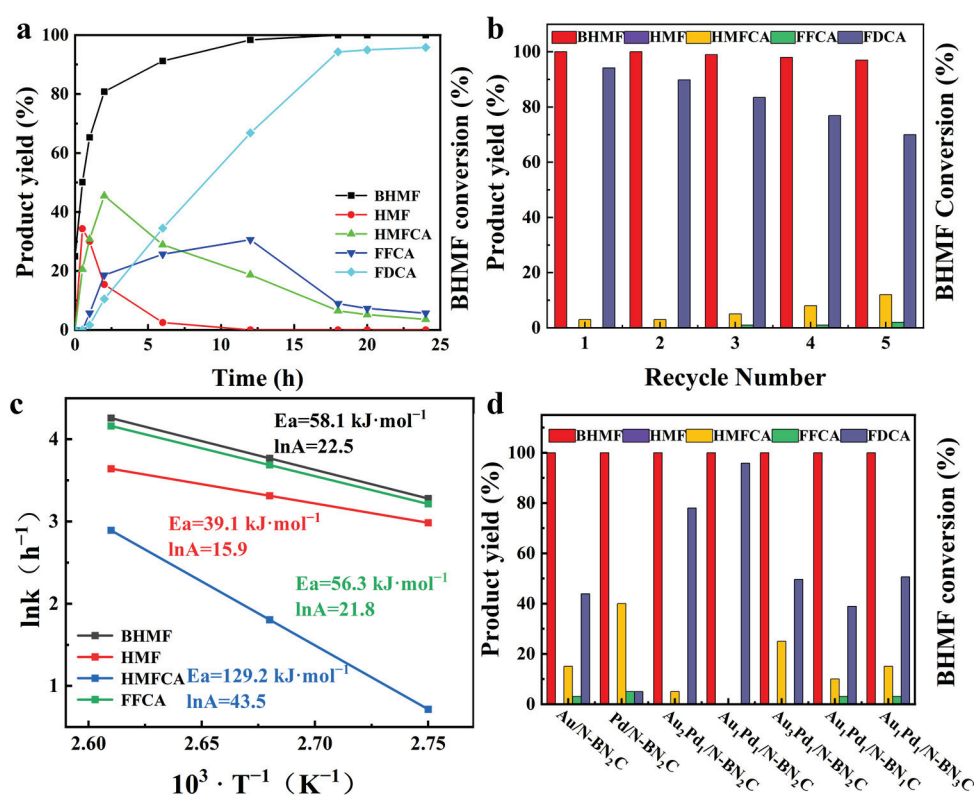


Figure 7. Effect of reaction time on the catalytic performance of the representative catalyst $\text{Au}_1\text{Pd}_1/\text{N-BN}_2\text{C}$ -800 (a) and a study on the circulation of the optimal $\text{Au}_1\text{Pd}_1/\text{N-BN}_2\text{C}$ nanocatalyst (b). Arrhenius plots of $\ln k$ based on different temperatures (c) and the catalytic oxidation performance of $\text{Au}_m\text{Pd}_n/\text{N-BN}_x\text{C}$ (d).

2.3. Kinetics and Catalytic Mechanism Studies

In the reaction process, we also detected that the intermediate substances were mainly HMF, 5-hydroxymethyl-2-furancarboxylic acid (HMFCFA), and 5-formyl-2-furancarboxylic acid (FFCA), but we did not find any DFF. It could be speculated that the predicted reaction path is shown in Figure 8a. A kinetic model of BHMF transformation was proposed based on the summary of the previous experimental results, in which K_i represents different rate constants [7]. The influence of the concentration of BHMF and reaction temperature on the reaction rate was studied using the power function form of the kinetic reaction equation. The concentration of sodium carbonate was kept at $0.04 \text{ mol} \cdot \text{L}^{-1}$; thus, the effect of sodium carbonate concentration on the reaction rate was ignored. Moreover, when the pressure of O_2 was higher than 3.0 MPa, the influence of O_2 pressure on the activity of the catalyst was almost zero; thus, its influence on the rate of reaction was ignored [7]. In the catalytic

reaction, a linear relationship between the BHMf conversion rate at 0.5 h and the amount of catalyst was discovered, and the kinetic reaction equation could be determined as:

$$r = \frac{dC_0}{dt} = kC_0^n \quad (1)$$

where k is the constant for the reaction rate; n is the order in which the various concentrations of the material react; r is the initial reaction rate of various materials, $\text{mol} \cdot \text{L}^{-1} \cdot \text{h}^{-1}$; and the initial concentration of various materials is C_0 , $\text{mol} \cdot \text{L}^{-1}$.

Table 2. Catalytic activity in the aerobic oxidation of BHMf by different $\text{Au}_m\text{Pd}_n/\text{N-BN}_x\text{C}$ nanocatalysts and the Au/Pd content of $\text{Au}_m\text{Pd}_n/\text{N-BN}_x\text{C}$.

Sample	BHMf Conversion (%)	HMF Yield (%)	HMfCA Yield (%)	FFCA Yield (%)	FDCA Yield (%)	Pd Content (wt%)	Au Content (wt%)
Au/N-BN ₂ C	100	0	15.9	3.6	43.9	0	1.58
Pd/N-BN ₂ C	100	0	40.6	5.8	8.7	1.67	0
Au ₂ Pd ₁ /N-BN ₂ C	100	0	5.5	0	78.9	0.38	1.16
Au ₁ Pd ₁ /N-BN ₂ C	100	0	0	0	95.8	0.63	0.76
Au ₃ Pd ₁ /N-BN ₂ C	100	0	25.7	0	49.6	0.26	1.35
Au ₁ Pd ₁ /N-BN ₁ C	100	0	10.5	3.8	38.9	0.58	0.81
Au ₁ Pd ₁ /N-BN ₃ C	100	0	15.6	4.3	50.6	0.55	0.72

Reaction condition: catalyst = 0.05 g; $n\text{BHMf} : n\text{Na}_2\text{CO}_3 = 1:4$; 100 °C; 24 h; 2.0 MPa O₂.

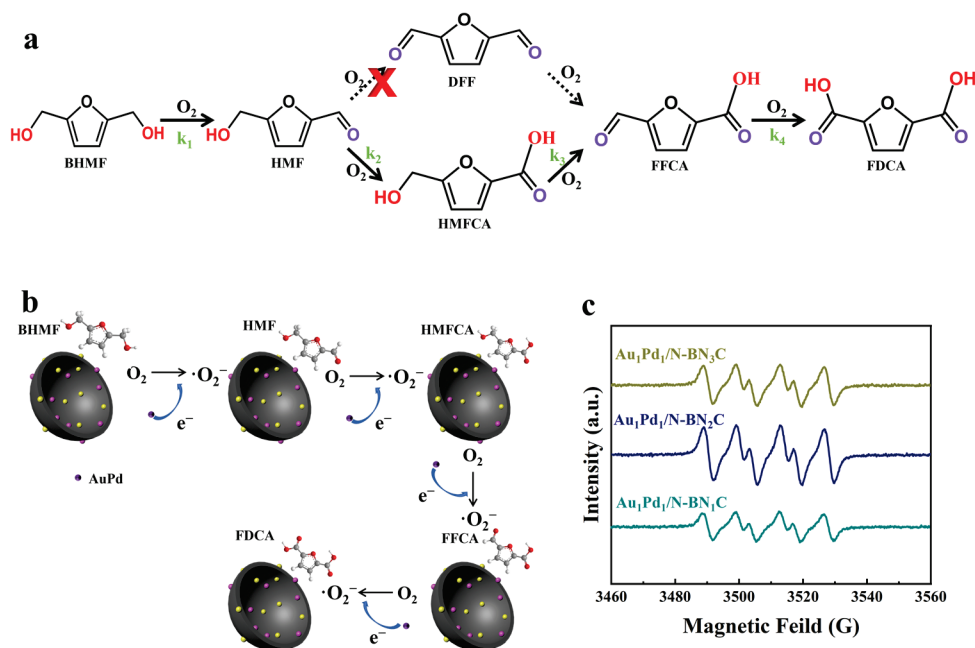


Figure 8. Reaction path of BHMf-catalyzed oxidation to FDCA (a), the mechanism of catalytic oxidation of BHMf to FDCA over $\text{Au}_m\text{Pd}_n/\text{N-BN}_x\text{C}$ nanocatalysts (b), and ESR spectra (superoxide radicals) of $\text{Au}_1\text{Pd}_1/\text{N-BN}_x\text{C}$ (c) ($x = 1, 2, 3$, corresponding to $\text{MBA}:\text{AM} = 1:1, 1:2, 1:3$, respectively).

In order to make the calculation more accurate, the determination and calculation were carried out before the rate of substrate conversion was lower than 20% [41]. The results of the experiment showed that the curve of $\ln C_0 - \ln r$ was drawn (Figure S8), and the first-order dynamics constant was obtained (Tables S1–S4). We find that all rate constants

increase with temperature, as we would expect. The Arrhenius equation could be used to determine the activation energy (E_a) and the pre-exponential factor (A):

$$\ln k = \ln A - \frac{E_a}{RT} \quad (2)$$

where k is the rate constant, A is the pre-exponential factor, r is the ideal gas constant, and E_a is the activation energy.

The activation energies of BHMF, HMF, HMFCA, and FFCA were $58.1 \text{ kJ}\cdot\text{mol}^{-1}$, $39.1 \text{ kJ}\cdot\text{mol}^{-1}$, $129.2 \text{ kJ}\cdot\text{mol}^{-1}$, and $56.3 \text{ kJ}\cdot\text{mol}^{-1}$, respectively. It was found that the activation energy required for HMFCA conversion to FFCA was the largest, which means that the conversion of HMFCA to FFCA was the rate-determining step of the whole experiment.

ESR spectroscopy with DMPO as the spin-trapping agent was used to further understand the active species involved in the oxidation process of the $\text{Au}_1\text{Pd}_1/\text{N-BN}_2\text{C}$ catalyst. As shown in Figure 8c, the characteristic peaks for $\text{DMPO}\cdot\text{O}_2^-$ were observed, and the signal intensity of $\text{Au}_1\text{Pd}_1/\text{N-BN}_2\text{C}$ was the highest, which had supreme catalytic performance. It is speculated that the formation of reactive oxygen species ($\cdot\text{O}_2^-$) further enhanced catalytic performance [15]. Combined with ESR spectroscopy and catalytic reaction, the selective oxidation mechanism of BHMF was speculated, as shown in Figure 8. The O_2 absorbed at the surface active center of the catalyst was transformed to $\cdot\text{O}_2^-$ by eliminating the electrons deposited on the Au nanoparticles. The interaction of superoxide radicals with water produces OH^- , which promotes the breakage of the C–H bond in the alcohol side chain of the BHMF to yield HMF. In an alkaline environment, OH^- will attack the aldehyde group of HMF, forming an alkoxide ion intermediate (geminal diol). The geminal diol intermediate was subsequently dehydrogenated to generate HMFCA, which was aided by the OH^- absorbed on the surface of Au nanoparticles. Subsequently, HMFCA was converted to FFCA through the same reaction pathway as BHMF, and FFCA was eventually converted to FDCA through the same reaction pathway as HMF.

3. Materials and Methods

3.1. Materials

All of the chemicals were analytical grade and could be utilized right away. Tetraethyl silicate (TEOS), acetonitrile, acrylamide (AM), 3-methacryloxy propyl trimethoxy silane (KH-570), methylene-bis-acrylamide (MBA), 2,2-azobisisobutyronitrile (AIBN), nitric acid (HNO_3), palladium chloride (PdCl_2 , 99.9%), and gold acid chloride trihydrate ($\text{HAuCl}_4\cdot 3\text{H}_2\text{O}$, 99.9%) were acquired from Aladdin Reagent Co., Ltd. (Shanghai, China). Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) provided the deionized water, ammonium hydroxide (NH_3OH , 25–28%), polyvinyl alcohol (PVA), sodium borohydride (NaBH_4 , 98%), ethanol, BHMF, HMF, HMFCA, FFCA, FDCA, and sodium carbonate (Na_2CO_3). Acetic acid, methanol, and acetonitrile were high-performance liquid chromatography (HPLC) grade.

3.2. Preparation of the $\text{Au}_m\text{Pd}_n/\text{N-BN}_x\text{C}$ Nanocatalysts

The specifics involved in preparing the catalysts are described in the Supplementary Materials.

3.3. Catalyst Characterizations

The morphology of samples was distinguished by transmission electron microscopy (TEM), scanning electron microscopy (SEM, Nova TM Nano SEM 230), and high-resolution TEM (HR-TEM). Fourier transform infrared (FT-IR) spectroscopy (Nicolet Nexus 470) was used to observe the changes that occurred in the functional groups of the samples. X-ray diffraction (XRD) was used to examine the samples. The scanning range was $10\text{--}80^\circ$ with a scan speed of $7^\circ\cdot\text{min}^{-1}$. Raman spectra were evaluated by Renishaw in a Via model Raman microscope with a CCD detector. Nitrogen adsorption–desorption isotherms were utilized in the process of determining Brunauer–Emmett–Teller (BET) surface area. On a Thermo ESCALAB 250 equipped with a monochromatic Al X-ray source, X-ray photoelectron

spectroscopy (XPS) measurements were carried out. Inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7700E) was used to measure the amounts of Au and Pd. Thermogravimetric analysis (TGA) treatment of the catalyst was carried out by heating the catalyst from an ambient temperature to 800 °C (heating rate 5 °C /min) with a Diamond TG/TGA instrument under nitrogen protection. The catalyst was tested via electron paramagnetic resonance (ESR) spectroscopy in deionized water with the same amount of catalyst and DMPO acting as a trapping agent. The resulting solution was sampled at 80 °C for 5 min in an oxygen environment for ESR detection to search the reaction system for reactive oxygen species.

3.4. BHMF Oxidation Reaction

The aerobic transformation of BHMF into FDCA was carried out in a batch-type teflon-lined stainless-steel autoclave (100 mL). The detailed reaction process was as follows: 50 mg BHMF, 50 mg catalyst, and 16.68 mg Na₂CO₃ were added to a high-pressure reactor containing 40 mL water. The reactor was pressurized to a predetermined pressure and cleaned with oxygen at least three times. After that, the reaction mixture was stirred at 600 rpm and heated to a predetermined temperature. After a fixed reaction time, a certain amount of solution was taken out for centrifugal filtration. On an Agilent 1260 series high-performance liquid chromatograph (HPLC) equipped with a UV detector (280 nm), the liquid product was analyzed with the Agilent TC-C18 column set to 30 °C. The mobile phase had a flow rate of 0.6 mL·min⁻¹ and was made up of acetic acid aqueous solution (0.1 wt%) and acetonitrile (V:V = 92:8).

The equation that follows was used to calculate the conversion rate of BHMF and the yield of the product.

$$\text{BHMF conversion (\%)} = \frac{\text{moles of reacted BHMF}}{\text{moles of initial BHMF}} \times 100 \quad (3)$$

$$\text{HMF, HMFCa, FFCA, or FDCA yield (\%)} = \frac{\text{moles of HMF, HMFCa, FFCA, or FDCA}}{\text{moles of initial BHMF}} \times 100 \quad (4)$$

In addition, the kinetics of the reaction were studied and calculated through catalytic experiments using BHMF, HMF, HMFCa, and FFCA as substrates.

3.5. Recyclability Test of Catalysts

The optimum reaction conditions were determined by optimizing reaction temperature, pressure, and time. Under ideal conditions, the recyclability of the catalyst for the aerobic oxidation of BHMF to FDCA was investigated. The reaction mixture was used to recover the catalyst through centrifugation and thorough cleaning with an ethanol/deionized water mixture before the catalyst was finally dried completely in a vacuum oven. After that, the recovered catalyst was used in the above method 5 times in a row, and the FDCA yield was recorded each time.

4. Conclusions

In summary, hierarchical porous bowl-like nitrogen-rich carbon-supported bimetallic Au-Pd nanocatalysts (Au_mPd_n/N-BN_xC) with different nitrogen content and bimetal nanoparticle sizes were successfully prepared and employed for the highly efficient aerobic oxidation of BHMF to FDCA. In the catalytic system, BHMF was oxidized to FDCA through three series steps of BHMF→HMF→HMFCa→FFCA→FDCA. Kinetic experiments showed that HMFCa→FFCA was the rate-determining step of this reaction. Oxygen transferred electrons from the nitrogen-doped carbon to the metal surface to form superoxide radicals, which were the active substance of the reaction. The nitrogen-doped carbon support facilitated the dispersity of Au-Pd bimetallic nanoparticles. In particular, the alloying effects in bimetallic Au-Pd nanoparticles favored the catalytic oxidation of the hydroxymethyl and the aldehyde groups, thus improving FDCA yield. Combined with the

synergistic effect of bimetal and metal size, the Au₁Pd₁/N-BN₂C nanocatalyst exhibited the highest catalytic activity, with BHMF conversion of 100% and FDCA yield of 95.8% in sodium carbonate aqueous solution. Moreover, the Au₁Pd₁/N-BN₂C nanocatalyst revealed good stability and could be reused at least five times without a significant loss in catalytic activity. Therefore, this work provides a versatile and promising strategy for the development of heterogeneous catalysts for effective catalytic oxidation of bio-sourced BHMF to FDCA in practical industrial applications.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal13020435/s1>.

Author Contributions: Y.L.: methodology, formal analysis, investigation, data curation, writing—original draft preparation, writing—review and editing, and visualization. Y.C. (Yao Chen): conceptualization, investigation, validation, data curation, writing—original draft, writing—review and editing, supervision, and project administration. W.G.: methodology, software, validation, resources, and writing—review and editing. Y.C. (Yu Cao): software and validation. F.W.: validation, resources, and data curation. Y.Z.: conceptualization, methodology, formal analysis, investigation, writing—review and editing, visualization, project administration, and funding acquisition. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The data presented in this study are available upon request from the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

BHMF (2,5-bis(hydroxymethyl)furan); HMF (5-hydroxymethylfurfural); HMFCFA (5-hydroxymethyl-2-furancarboxylic acid); FFCA (5-formyl-2-furancarboxylic acid); FDCA (2, 5-furandicarboxylic acid); TPA (terephthalic acid); PET (polyethylene terephthalate); PEF (2,5-furandicarboxylate). Au_mPd_n/N-BN_xC (hierarchical porous bowl-like nitrogen-rich nitrated carbon-supported bimetallic Au-Pd nanocatalysts); AM (acetonitrile, acrylamide); MBA (methylene-bis-acrylamide); TEOS (tetraethyl silicate); KH-570 (3-methacryloxy propyl trimethoxy silane); AIBN (2,2-azobisisobutyronitrile); PVA (polyvinyl alcohol); N-Q (quaternary-N); N-5 (pyrrolic-N); N-6 (pyridinic-N); k (reaction rate constant); n (reaction order); r (initial reaction rate); C₀ (initial concentration); k (rate constant); A (pre-exponential factor); R (ideal gas constant); E_a (activation energy).

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Article

Selective Hydrogenolysis of Furfuryl Alcohol to Pentanediol over Pt Supported on MgO

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Abstract: The catalytic conversion of naturally rich and renewable biomass into high-value chemicals is of great significance for pursuing a sustainable future and a green economy. The preparation of pentanediol from furfuryl alcohol is an important means of high-value conversion of biomass. The Pt-based catalyst supported on MgO was applied to the selective hydrogenation of biomass furfuryl alcohol to prepare pentanediol. By adjusting parameters such as catalyst loading, reduction temperature, reaction temperature, and pressure, a highly active catalyst was designed and the optimal catalytic hydrogenation conditions were determined. The hydrogenation experiment results showed that the selectivity of the 2Pt/MgO-200 catalyst for 1,2-pentanediol and 1,5-pentanediol reached 59.4% and 15.2%, respectively, under 160 °C and 1 MPa hydrogen pressure. The catalyst was characterized by X-ray powder diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectrometer (XPS), CO₂-temperature programmed desorption (CO₂-TPD), and other methods. The characterization results indicate that the reduction temperature has a significant impact on the metal Pt, and an appropriate reduction temperature is beneficial for the hydrogenation performance of the catalyst. In addition, the basic sites on the carrier are also another important factor affecting the activity of the catalyst. In addition, stability tests were conducted on the catalyst, and the reasons for catalyst deactivation were studied using methods such as thermogravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FT-IR). The results showed that the activity of the catalyst decreased after five cycles, and the deactivation was due to the hydrolysis of the carrier, the increase in metal particle size, and the surface adsorption of organic matter.

Keywords: selective hydrogenation; pentanediol; catalyst deactivation; basic site

1. Introduction

With the decrease in oil resources together with the increase in demand for energy and political and environmental concerns about fossil fuels, research on the exploration of renewable resources for sustainable supply has been conducted [1,2]. Biomass, as the only renewable carbon source at present [3], can be effectively and cleanly converted into fuel and chemical products through chemical reactions and biological conversion [4].

The catalytic conversion of biomass and biomass-derived platform molecules into fuels and value-added chemicals has attracted widespread attention to the development of the sustainable chemical industry [5–7]. Furfuryl alcohol (FFA), as an important biomass derivative, has irreplaceable advantages in the green manufacturing of high value-added chemicals. Among them, pentanediol is one of the most valuable products derived from FFA hydrogenolysis, and it is widely used in industries such as the food, chemical, and pharmaceutical industries. 1,2-pentanediol (1,2-PeD) is a key raw material for synthesizing the fungicide propiconazole and is widely used as a pharmaceutical intermediate for synthesis. 1,5-pentanediol (1,5-PeD) is an important monomer for synthesizing polyester and polyurethane. In addition, it can also be used as antifreeze and green solvent for chemical synthesis [8].

In previous reports on the selective hydrogenation of furfural and its derivatives, Pt-based [9–11], Ru-based [12–14], Rh-based [15], Ni-based [16,17], Cu-based [18–20], and Pd-based [21,22] catalysts exhibited high activity. Götz et al. [23] prepared Ru/Al₂O₃ catalysts for waterborne hydrogenation of FFA. Under the conditions of 200 °C and 10 MPa H₂ for 1 h, the yield of 1,2-PeD is 32%. Wang's team [10] pointed out that the Pt/CeO₂ catalyst can effectively catalyze the hydrogenation of FFA to 1,2-PeD. Extensive characterization indicates that the chemical state of Pt plays a crucial role in improving the catalytic activity and selectivity of 1,2-PeD, which is controlled by the surface oxygen vacancies of CeO₂ through metal carrier interactions. Zhu et al. [24] found that on the coordination unsaturated 3D Pt-Pt site, the hydrogenolysis of the furan ring occurs through the weakening and adsorption of furan C-O, resulting in 1,2-PeD as the main product. The dual functional Cu/MFI catalyst designed by Dai et al. [20] achieved selectivity of 1,5-PeD (69.2%) and 1,2-PeD (16.0%) at 160 °C and 2.5 MPa hydrogen pressure. Rizky Gilang Kurniawan et al. [25] designed a three-metal Ni-CoO_x-Al₂O₃ mixed metal-metal oxide catalyst to efficiently convert FFA into 1,5-PeD in one pot with a high yield of 47.5% at 160 °C and an initial H₂ pressure of 3 MPa. In the past, some catalysts had many drawbacks, such as low activity and insufficient stability. Pt-based catalysts had advantages such as high activity for the hydrogenolysis of FFA. However, a satisfactory yield of pentanediol has not yet been obtained under mild conditions.

In this work, we prepared a series of catalysts through the equal volume impregnation method and screened the performance of Pt/MgO on the selective hydrogenolysis of FFA. On this basis, further comparative experiments were conducted to optimize the optimal reaction conditions and catalyst preparation method. After a series of characterizations, the effects of different preparation conditions on catalyst activity and the relationship between catalyst carrier alkalinity and catalytic performance were studied. In addition, the cyclic stability of the catalyst was further investigated and the reason for catalyst deactivation was explained through characterization methods such as thermogravimetry and inductively coupled plasma.

2. Results and Discussion

2.1. Discussion on FFA Hydrogenation Results

Figure 1 is a schematic diagram of some FFA hydrogenation product routes. FFA can be hydrogenated to form cyclopentanone, cyclopentanol, and THFA on the C=C double bond. The production of target products 1,2-PeD and 1,5-PeD involves the cleavage and hydrogenation of C-O bonds in the furan ring. It is reported that the hydrogenation of FFA to 1,2-PeD requires ring opening hydrogenation to produce the intermediate product 1-hydroxy 2-Pentanone [24], and then further hydrogenation of C=O double bond to obtain the target product. Therefore, it is necessary to design a catalyst that can efficiently open the ring and hydrogenation.

2.1.1. Catalyst Screening

Compared with other active metal catalysts such as Pd and Ru (Table 1), Pt-based catalysts show higher activity in the catalytic hydrogenation of FFA. Among them, the catalyst supported by MgO showed high selectivity in the hydrogenation of furfuryl alcohol to pentanediol in the aqueous phase. Therefore, Pt/MgO was selected for further exploration.

Pt/MgO was selected as the catalyst for the hydrogenation of furfuryl alcohol to pentanediol for further investigation. Further exploration of the effects of platinum loading and catalyst reduction temperature on hydrogenation performance was conducted. As shown in Figure 2a, under low loading (<1.5 wt%), the low amount of active metal leads to a lower conversion rate of furfuryl alcohol. When the loading amount increases to 2 wt%, the conversion rate of FFA and the selectivity of pentanediol was highest. Further increasing the loading of metal Pt resulted in a decrease in the selectivity of pentanediol with increased selectivity for THFA. This indicates that too high an amount of metal

would facilitate the hydrogenation of the C=C bond. Therefore, 2 wt% Pt/MgO is a more reasonable choice. Further investigation was conducted on the effect of reduction temperature on the hydrogenation performance of the catalyst. Figure 2b shows the hydrogenation performance of the catalyst at different reduction temperatures. Comparing the catalytic performance at reduction temperatures of 150, 200, 300, and 400 °C, it can be observed that the conversion rate of FFA increases first and then decreases with increasing temperature. When the reduction temperature is 200 °C, the catalyst activity is optimal. After 6 h of reaction, the conversion rate of FFA reached 63.9%, and the selectivity of 1,2-PeD and 1,5-PeD were 58.2% and 12.7%, respectively. Therefore, 2 wt% Pt/MgO-200 was chosen as the catalyst for FFA hydrogenation and further exploration was conducted.

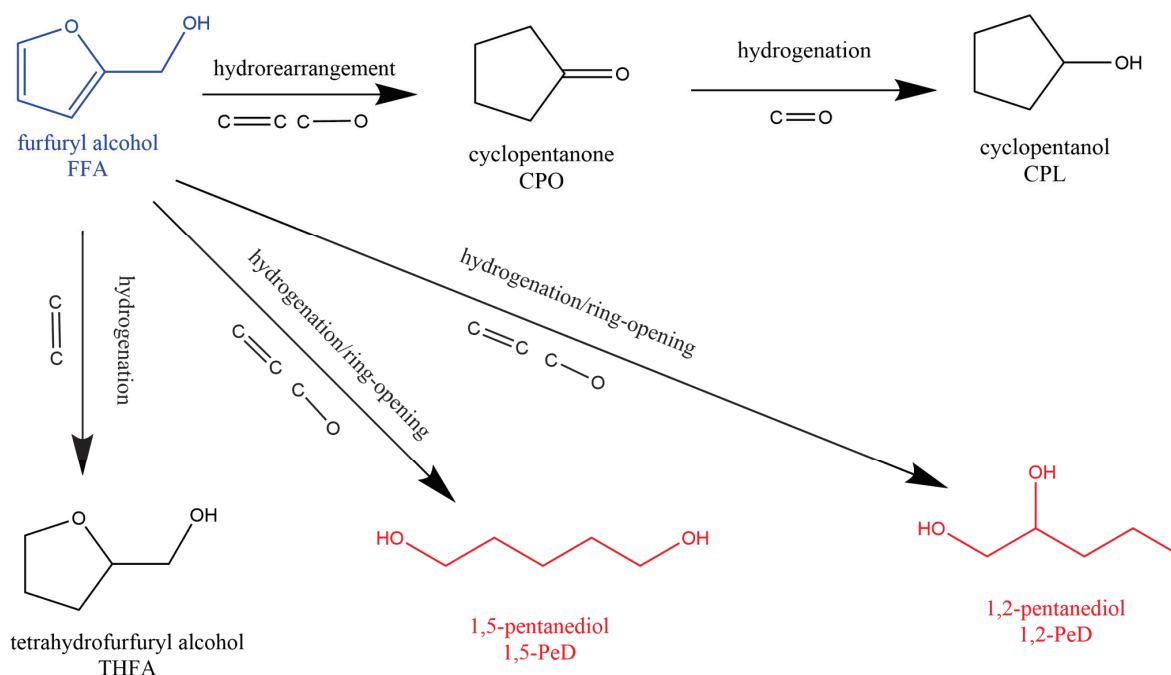


Figure 1. The reaction network of furfuryl alcohol hydrogenation and reaction path.

Table 1. Catalytic performance of different catalysts on the hydrogenolysis of FFA.

Entry	Catalysts	Conversion (%)	Selectivity (%)						
			1,2-PeD	1,5-PeD	1-Pentanol	CPO	CPL	THFA	Others
1	Pt/CeO ₂	99.9	18.5	5.1	1.4	26.3	39.1	9.5	0.1
2	Pt/Fe ₂ O ₃	99.9	1.5	/	/	53.3	45.2	/	/
3	Pt/TiO ₂	99.9	34.8	3.6	7.9	47.7	1.5	3.3	1.2
4	Pt/ZrO ₂	99.9	1.1	/	/	84.4	7.5	1.3	5.7
5	Pt/ α -Al ₂ O ₃	92.3	41.1	11.1	4.4	23.6	3.5	16.3	/
6	Pt/ γ -Al ₂ O ₃	87.3	37.7	15.1	2.6	10.8	/	31.6	2.2
7	Pt/MgO	96.8	58.4	12.8	1.7	1.3	0.5	17.9	7.4
8	Pd/MgO	93.5	3.7	1.1	/	2	/	89.8	3.4
9	Ru/MgO	15.8	13.2	/	/	17.7	/	47.5	21.6
10	Cu/MgO	16.8	33.9	8.9	/	35.1	/	21.4	0.7
11	Fe/MgO	7.5	17.3	/	/	34.7	/	20	28
12	Ni/MgO	6.3	/	/	/	38.1	/	23.8	38.1

Reaction conditions: 1.1 g FFA, 28.9 g H₂O, 0.2 g catalyst, 160 °C, 1 MPa H₂, 8 h. The metal loading mass in the catalyst is 2%.

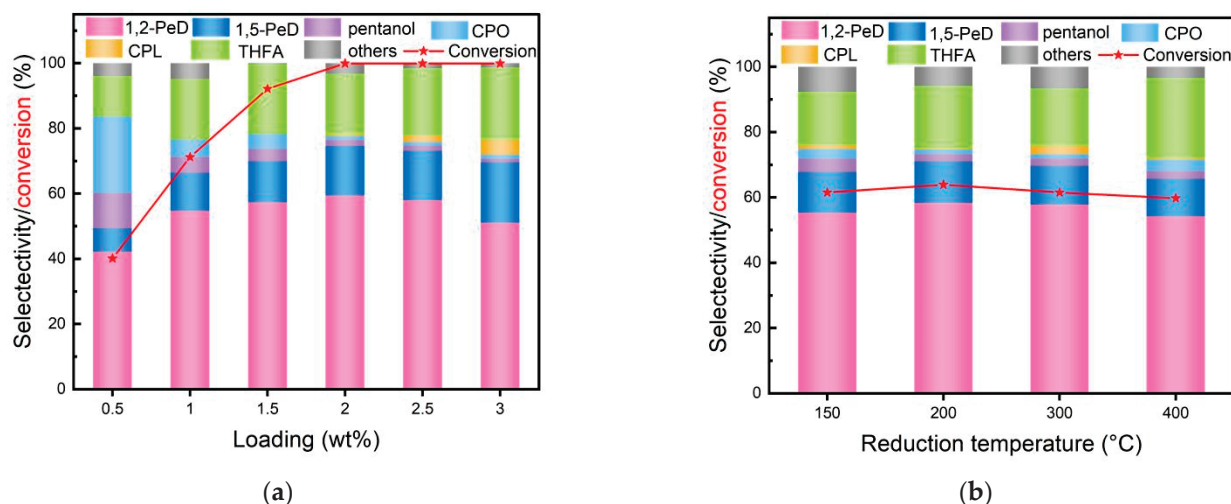


Figure 2. Catalytic conversion of FFA over Pt/MgO at (a) different metal loading and (b) different reduction temperatures. Reaction conditions: 1.1 g FFA, 28.9 g H₂O, 0.2 g catalyst, 160 °C, 1 MPa H₂, (a) 10 h and (b) 6 h.

To investigate the effect of reduction time on catalyst activity, the reduction temperature was controlled at 200 °C, and performance analysis was conducted on catalysts with different reduction times. As shown in Figure 3, when the reduction time is 0.5 h, the conversion rate of furfuryl alcohol is 75.8%, and the selectivity of the main byproduct tetrahydrofurfuryl alcohol reaches 37.2%, while the selectivity of the target product 1,2-PeD is only 45.7%. Extending the reduction time to 1 h, the conversion rate of furfuryl alcohol exceeded 99%, and the selectivity of 1,2-PeD reached 59.4%. Subsequently, by further prolonging the reaction time, there was no significant change in the catalyst activity. Therefore, it is believed that a time of 1 h is sufficient for the reduction of the catalyst.

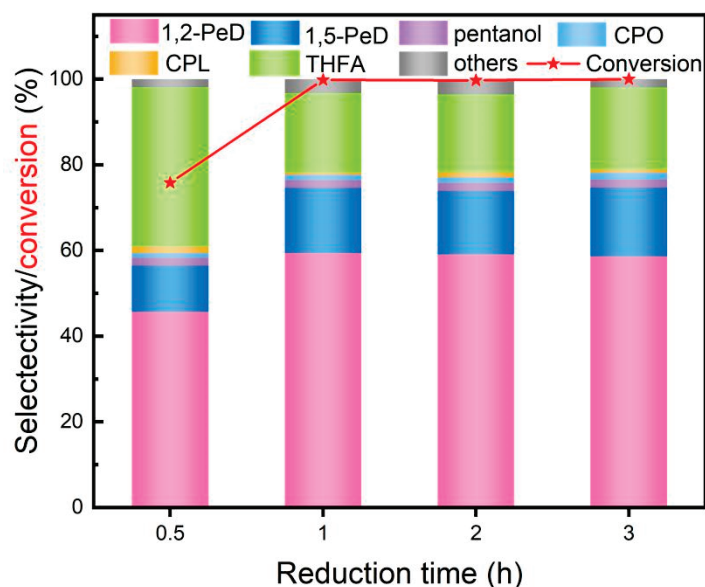


Figure 3. Catalytic conversion of FFA on Pt/MgO under reduction time. Reaction conditions: 1.1 g FFA, 28.9 g H₂O, 0.2 g catalyst, 160 °C, 1 Mpa H₂, 10 h.

2.1.2. Optimization of Catalytic Conditions

Reaction temperature is one of the key factors in chemical reactions, affecting the reaction rate and product selectivity. In order to explore the effect of reaction temperature on FFA hydrogenation, research was carried out within the range of 120 °C~200 °C. As

shown in Figure 4a, when the reaction temperature is controlled at 120 °C, the conversion rate of FFA after 6 h of reaction is about 40%. By further increasing the reaction temperature, the FFA conversion rate gradually increases. Meanwhile, it is found that in the temperature range of 120~200 °C, low temperature (<140 °C) is favorable for hydrogenation to THFA, while high temperature (>180 °C) conditions are more prone to rearrangement reactions to generate CPO, etc. At 160 °C, the comprehensive selectivity of pentanediol reaches its highest, with the selectivity of 58.3% and 12.7% for 1,2-PeD and 1,5-PeD, respectively.

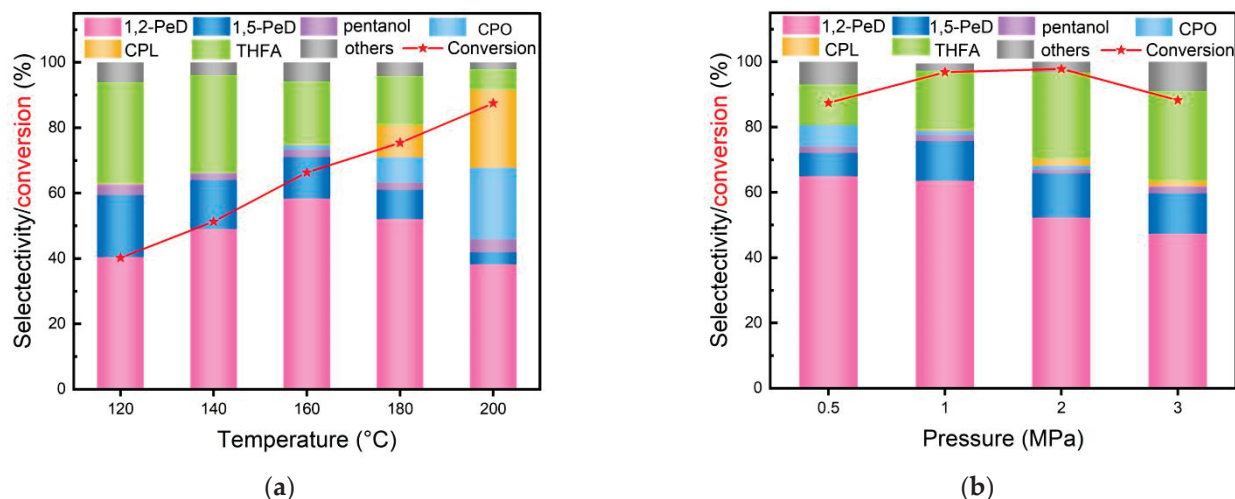


Figure 4. Catalytic conversion of FFA over 2Pt/MgO-200 at different (a) temperatures and (b) pressures. Reaction conditions: 1.1 g FFA, 28.9 g H₂O, 0.2 g catalyst. (a) 1 MPa H₂, 6 h; (b) 160 °C, 8 h.

Then, the temperature of the hydrogenation reaction was controlled at 160 °C and different hydrogen pressures were adjusted to explore the effect of reaction pressure on FFA hydrogenation. During this process, we appropriately shortened the reaction time to 8 h to demonstrate the effect of pressure on the selectivity of the target product. Figure 4b shows the hydrogenation results of hydrogen pressure within the range of 0.5~3 Mpa. It was found that at low hydrogen pressure, the reaction rate is slow and the conversion of furfuryl alcohol is not high. After increasing the pressure, the conversion rate significantly increases. However, a decrease in the selectivity of pentanediol was observed when the pressure increased. Therefore, 1 Mpa was chosen as the appropriate hydrogen reaction pressure.

In industrial production, controlling the amount of catalyst is crucial for reducing production costs. We investigated the effect of different 2Pt/MgO-200 catalyst dosages on the hydrogenation reaction and found that within a certain range (Figure 5), the conversion rate of furfural alcohol showed an upward trend with the increase in catalyst dosages. When the catalyst dosages increased to 0.2 g, the conversion rate of FFA reached the highest, and at this time, the comprehensive selectivity of pentanediol also reached its peak. When continuing to increase the catalyst input, the conversion rate of FFA and the selectivity of pentanediol did not increase. The concentration of the substrate also affects the yield of the product. Examining the hydrogenation reaction of FFA at different concentrations, it was found that at a higher concentration, the conversion rate of FFA significantly decreased, and the selectivity of 1,2-PeD also decreased to some extent (Figure 5b). Therefore, 0.2 g catalyst was selected to be added at a substrate concentration of 0.35 mol/L for further exploration.

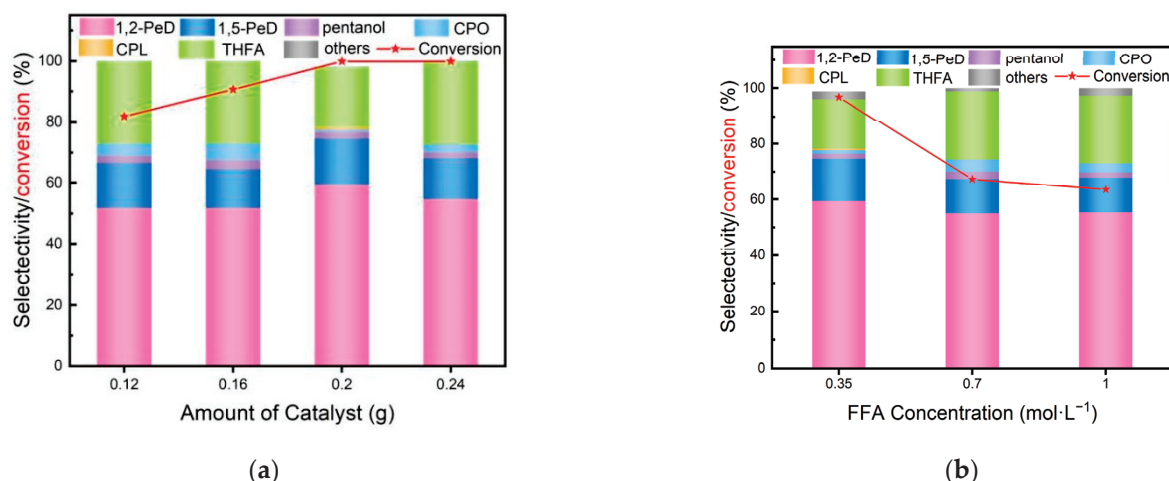


Figure 5. The influence of (a) catalyst amount and (b) substrate concentration on hydrogenation results. Reaction conditions: (a) 1.1 g FFA, 28.9 g H₂O; (b) 0.2 g catalyst, 160 °C, 1 MPa H₂, 10 h.

In order to elucidate the changes of product distribution during the hydrogenation reaction process, a curve was drawn for the relationship between yield and time. Figure 6a shows the changes of various substances in the system at different times. It can be seen that during the hydrogenation of furfuryl alcohol, the yield of 1,2-PeD increases the fastest, followed by 1,5-PeD and THFA. In addition, due to the influence of the substrate concentration, the conversion rate of the reaction in the first eight hours is significantly higher than that in the next two hours. In addition, the hydrogenation performance of Pt-based catalysts for furfuryl alcohol under different solvents was investigated. Previous literature has shown that in the hydrogenation of furfuryl alcohol catalyzed by active metal Pt, water plays a decisive role in the ring opening process of furfuryl alcohol and can improve the selectivity of 1,2-PeD [26]. As shown in Figure 6b, the yield of 1,2-PeD in the hydrogenation of furfuryl alcohol in organic solvents ethanol and isopropanol is much lower than in water, which is consistent with previous conclusions.

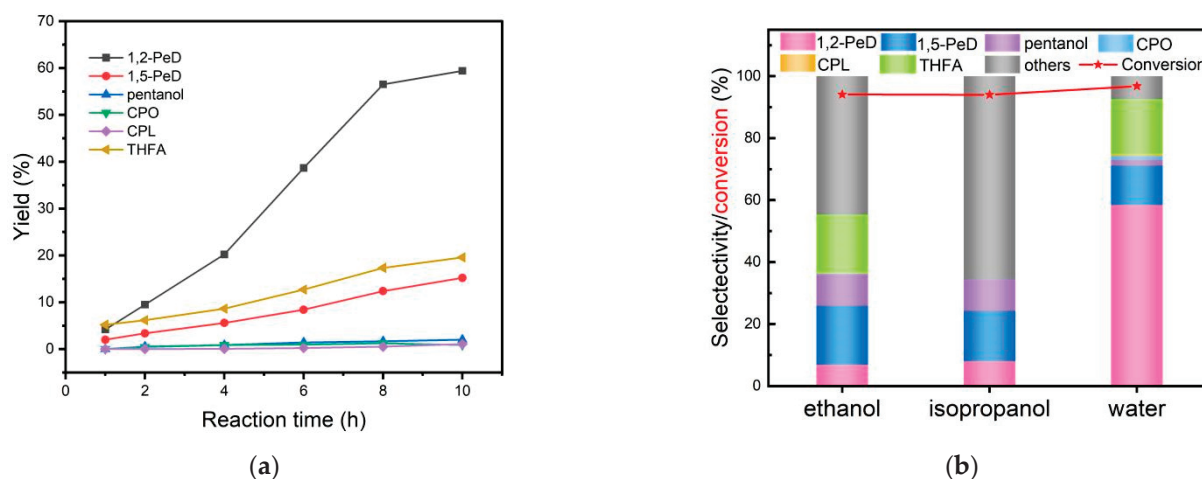


Figure 6. FFA conversion and product selectivity over 2Pt/MgO-200. Reaction conditions: (a) 1.1 g FFA, 28.9 g H₂O, 0.2 g catalyst, 160 °C, 1 MPa H₂; (b) 1.1 g FFA, 28.9 g H₂O, 0.2 g catalyst, 160 °C, 1 MPa H₂, 8 h.

2.2. Characterization Results

2.2.1. XRD Result Analysis

The formation of crystalline species in different catalysts was studied using wide-angle XRD technology, as shown in Figure 7. The results show that all peaks are related

to the carrier [27] ($2\theta = 37, 43, 62, 75, 78^\circ$), and no diffraction peaks of metal Pt were observed during reduction within the temperature range of 150–400 °C. This indicates the low loading of metal or the generation of small-sized and highly dispersed metal nanoparticles during the reduction process.

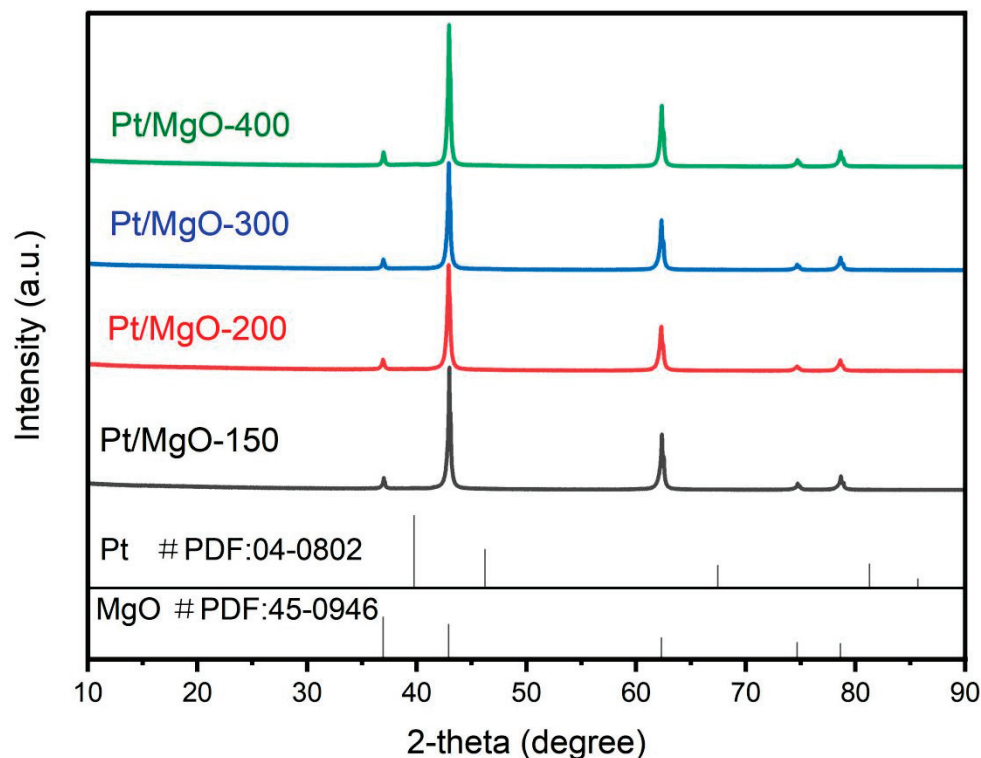


Figure 7. XRD patterns of 2Pt/MgO at different reduction temperatures.

2.2.2. TEM

From the hydrogenation performance Figure 2b, it can be observed that the reduction temperature has a significant impact on the activity of the catalyst. According to Figure 8, when the catalyst reduction temperature is not higher than 200 °C, the average particle size of metal Pt is about 1.62 nm. Further increasing the reduction temperature to 300 °C and 400 °C, the average particle size of Pt metal is 2.38 nm and 2.40 nm, respectively. Overall, higher temperatures lead to larger active metal particles in the catalyst, which is not favorable for the cleavage of the C–O bond, and it is more prone to the hydrogenation of the C=C bond, thus leading to the decreased selectivity of pentanediol.

2.2.3. H₂-TPR

In order to further explore the interaction between active metals and carriers, the catalyst samples were characterized by temperature programmed reduction. Figure 9 shows the H₂-TPR curve of Pt-based catalysts. It can be clearly observed that the Pt/MgO catalyst has a sharp main peak at 160 °C and a small peak near 350 °C, respectively. The small peak at 350 °C might be caused by the aggregation of metal nanoparticles. From H₂-TPR, Pt nanoparticles can be mostly reduced before 250 °C.

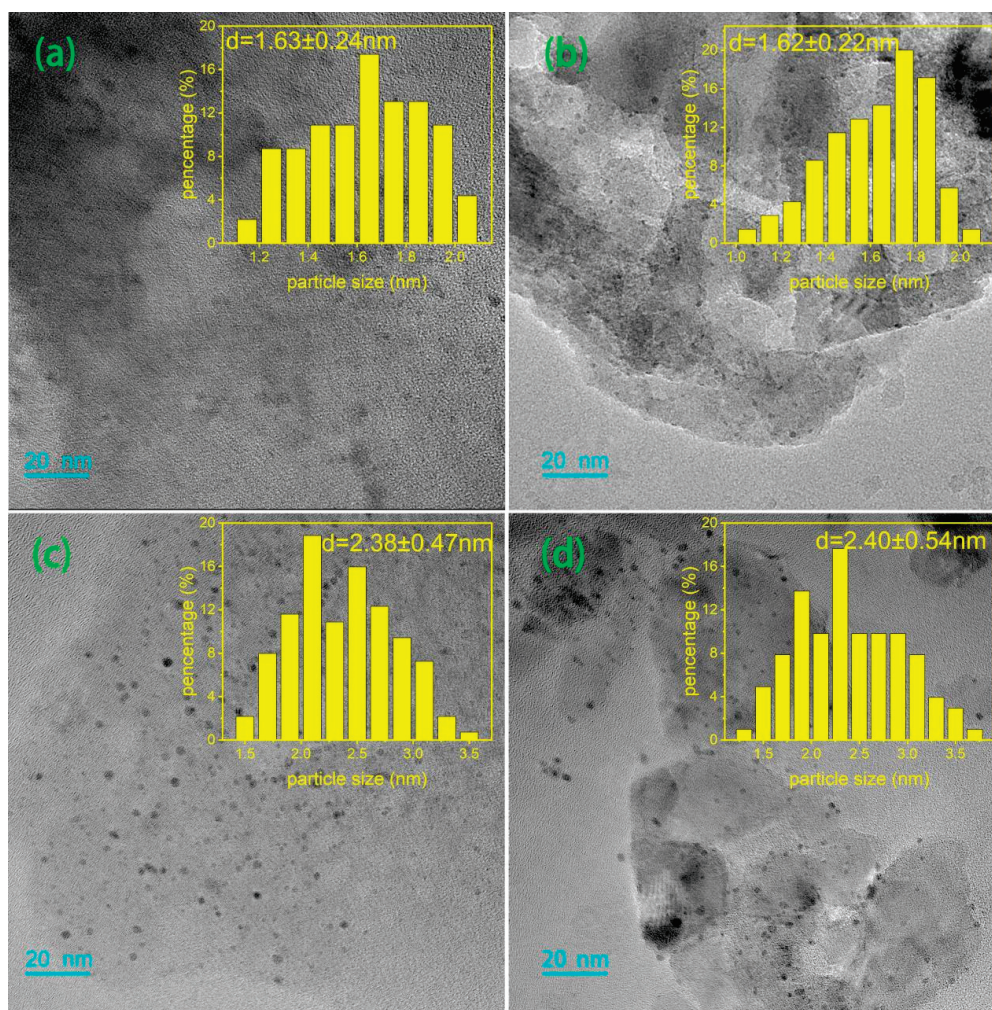


Figure 8. HRTEM images and particle size distribution of (a) Pt/MgO-150, (b) Pt/MgO-200, (c) Pt/MgO-300, (d) Pt/MgO-400.

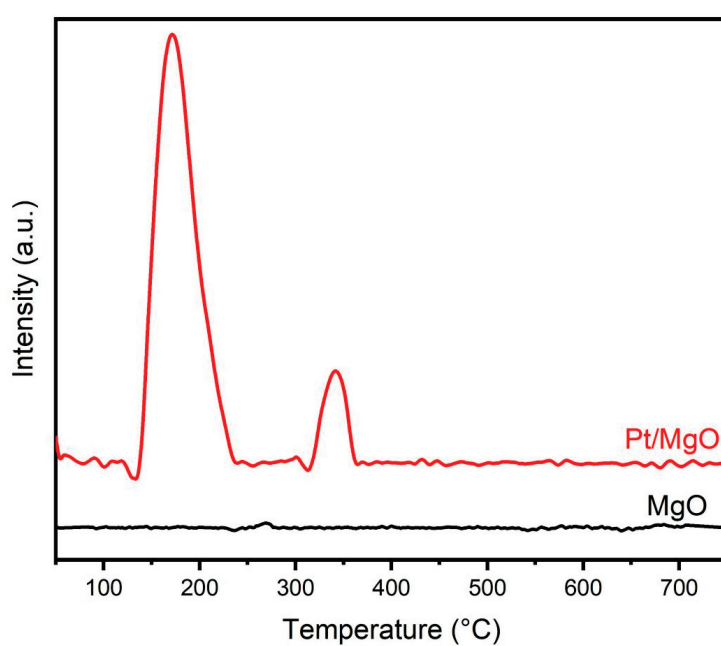


Figure 9. H_2 -TPR spectra of Pt/MgO and MgO.

2.2.4. XPS Analysis

In the XPS spectrum, as shown in Figure 10, the Pt 4f spectrum of the Pt/MgO catalyst can be deconvoluted into three Pt species, with Pt 4f 7/2 Bes at 71.0 (Pt⁰), 72.4 (Pt²⁺), and 74.9 eV (Pt⁴⁺) [28], respectively. It can be observed from the table that the relative ratios for 2Pt/MgO-200 of Pt⁰, Pt²⁺, and Pt⁴⁺ species are 34%, 37%, and 28%, respectively. Comparing the XPS spectra (Figure 10a) and elemental valence analysis (Table 2) under different temperature reduction conditions, it was found that the proportion of Pt⁰ in the catalyst after low-temperature reduction (150 °C) was only 26%, and the main forms of metal Pt in the catalyst were Pt²⁺ and Pt⁴⁺. After further increasing the reduction temperature, it was found that more active metal Pt was reduced in the catalyst. After reduction at 400 °C, the proportion of Pt⁰ reached 50%, which is consistent with the results of H₂-TPR.

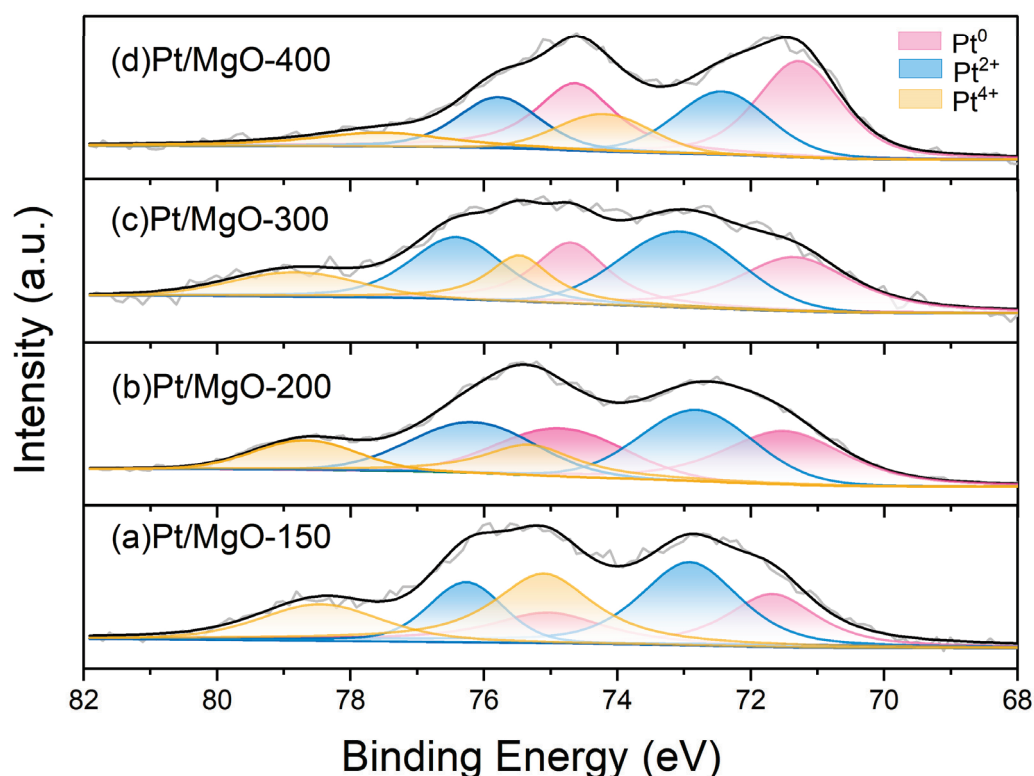


Figure 10. XPS spectra of Pt/MgO at different reduction temperatures.

Table 2. XPS analysis of Pt/MgO at different reduction temperatures.

Catalysts	Pt ⁰ _{7/2}		Pt ²⁺ _{7/2}		Pt ⁴⁺ _{7/2}	
	B.E. (eV)	Ratio (%)	B.E. (eV)	Ratio (%)	B.E. (eV)	Ratio (%)
Pt/MgO-150	71.6	26	72.9	39	75.1	35
Pt/MgO-200	71.5	34	72.8	37	75.3	28
Pt/MgO-300	71.2	38	73.0	42	75.4	19
Pt/MgO-400	71.3	50	72.4	32	74.2	18

Based on the results of hydrogenation (Figure 2b), TEM and XPS analysis indicate that metal Pt cannot be fully reduced at lower reduction temperatures. Raising the reduction temperature promotes the reduction of metal Pt, but at high temperatures, the particle size of Pt nanoparticles significantly increases, the metal dispersion decreases, and the catalytic activity decreases. Therefore, comprehensive consideration suggests that reduction at 200 °C is the optimal reduction temperature.

2.2.5. CO₂-TPD

According to previous reports [29,30], the basic sites on the catalyst play an important role in the ring-opening of furan rings in furfuryl alcohol. Through the CO₂-TPD spectrum (Figure 11), we found that the carrier MgO exhibited moderate intensity of basic sites at 300–350 °C, and the basic sites were not destroyed during the preparation process of 2Pt/MgO-200. As a comparison, almost no basic sites were observed in the CO₂-TPD spectrum of Pt/TiO₂, indicating that its alkalinity is much lower than that of 2Pt/MgO-200. And the total selectivity of Pt/TiO₂ for pentanediol in furfuryl alcohol hydrogenation is only 38.4%, with higher selectivity for CPO, which indicates that the rearrangement of the furan ring would compete with the hydrogenolysis of the C-O bond under the reaction conditions (Table 1, entry 3). This indicates that the selective hydrogenolysis of FFA is favorable under the basic sites.

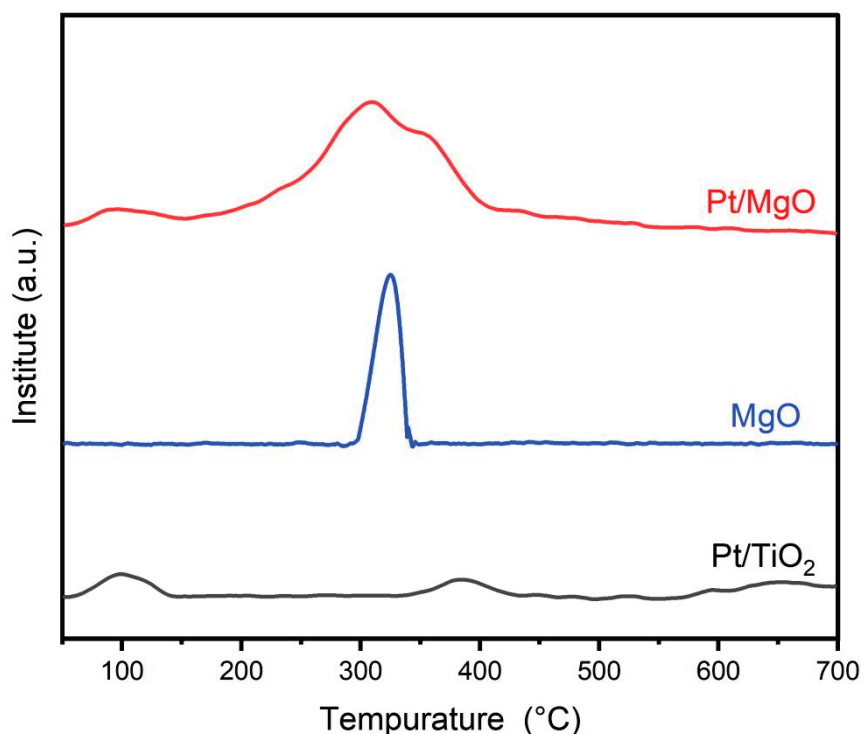


Figure 11. CO₂-TPD spectra of 2Pt/MgO-200 and 2Pt/TiO₂-200.

2.3. Exploring the Stability and Deactivation Causes of Catalysts

2.3.1. Catalyst Cycle Stability

In order to verify the cyclic stability of the catalyst, the cyclic performance of 2Pt/MgO-200 was tested under optimized reaction conditions. The experimental results are shown in Figure 12, and the performance of the 2Pt/MgO-200 catalyst maintained high activity in the first four cycles. In the fifth cycle, the conversion and selectivity for pentanediol decreased to 93.8% and 65.3%, respectively.

2.3.2. Exploring the Causes of Catalyst Deactivation

It is generally believed that in the process of heterogeneous catalysis, the causes of catalyst deactivation include toxic adsorption, the loss of active metals, and the enlargement of metal nanoparticles [31,32]. To investigate the reasons for catalyst deactivation during the hydrogenation of FFA, 2Pt/MgO-200 catalysts before and after cyclic testing were characterized by thermogravimetry and electron microscopy.

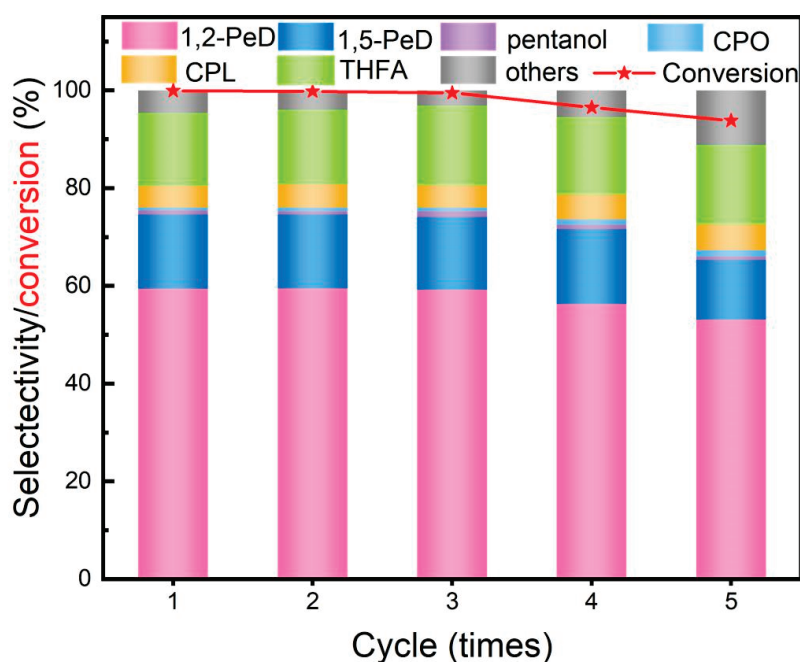


Figure 12. Cycling tests of FFA over the 2Pt/MgO-200 catalyst. Reaction conditions: 1.1 g FFA, 28.9 g H₂O, 0.2 g catalyst, 160 °C, 1 MPa H₂, 10 h. Catalysts were reused after centrifugation and drying.

Considering the instability of MgO carrier in water, XRD characterization was performed on the catalyst before and after cycling. As shown in Figure 13, it can be observed on the XRD spectrum of the catalyst after cycling. The diffraction peaks at 18.5, 32.8, 37.9, 50.8, 58.6, 62.1, 68.2, 72.1, and 81.3° correspond to the crystal planes of Mg(OH)₂ at 001, 100, 101, 102, 110, 111, 103, 201, and 202, respectively. The diffraction peak at 42.9° belongs to the 200 crystal plane of MgO. This indicates that the catalyst carrier MgO after the reaction is hydrolyzed into Mg(OH)₂, and during the catalytic process, the carrier may exist in the form of a complex of oxides and hydroxides. In addition, the diffraction peaks at the diffraction angles of 39.7° and 46.2° belong to the 111 and 200 crystal planes of the metal Pt. This indicates that there may be aggregation of active metal Pt on the catalyst after cycling.

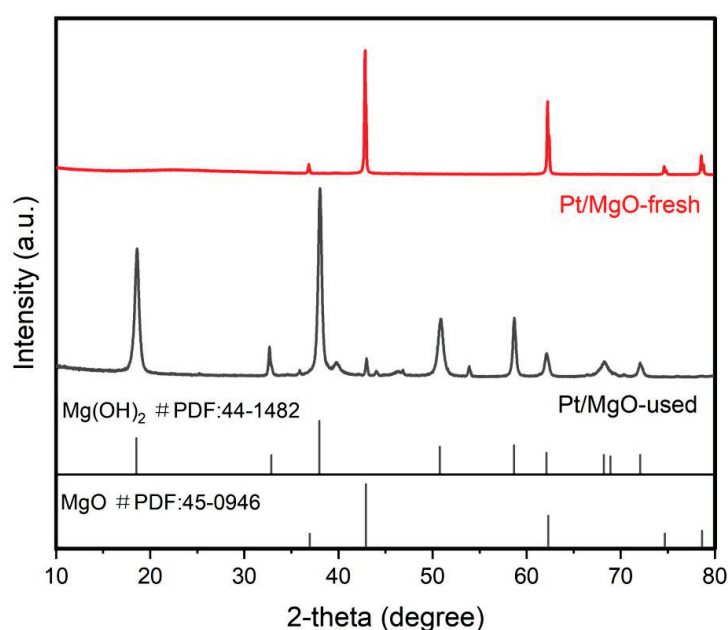


Figure 13. XRD patterns of 2Pt/MgO-200 before and after cycling.

Figure 14 shows the thermogravimetric curves of fresh and used 2Pt/MgO-200. It can be seen that at the high temperature of 800 °C, the mass of the unused catalyst only decreased to 96% even though treated until 800 °C, which might be caused by the adsorbed water in the catalyst. However, for the used 2Pt/MgO-200 after five cycling tests, the mass decreased obviously at 300 °C and further decreased to 65% after 550 °C. The mass decrease of the 2Pt/MgO-200 used might be ascribed to the organic matter adsorbed on the catalyst surface.

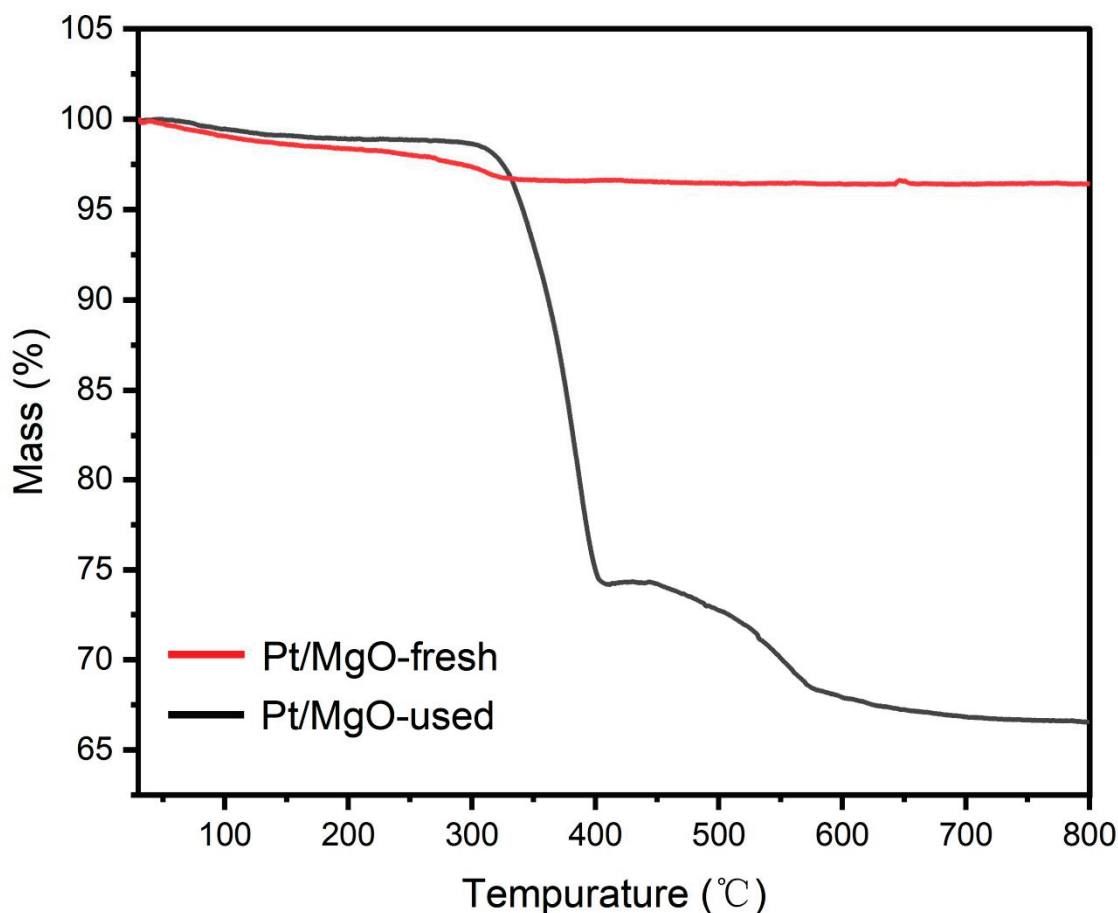


Figure 14. Thermogravimetric spectra of fresh and used 2Pt/MgO-200.

To further illustrate the adsorption of organic compounds on the catalyst, infrared spectroscopy characterization was performed on the catalyst before and after use. As shown in Figure 15, the absorption peaks at 2967 cm^{-1} and 2877 cm^{-1} are attributed to the stretching vibration of the methyl group. The absorption peaks at 1594 cm^{-1} and 1504 cm^{-1} are attributed to the stretching vibration of C=C on the furan ring. The absorption peaks at 1221 cm^{-1} , 1149 cm^{-1} , and 1074 cm^{-1} correspond to the stretching vibrations of C-C, C-O-C, and C-O on the furan ring, respectively [24]. As a comparison, no infrared absorption peak was observed on the fresh catalyst. Based on this, it is believed that there is adsorption of organic compounds such as furfuryl alcohol on the catalyst after cycling.

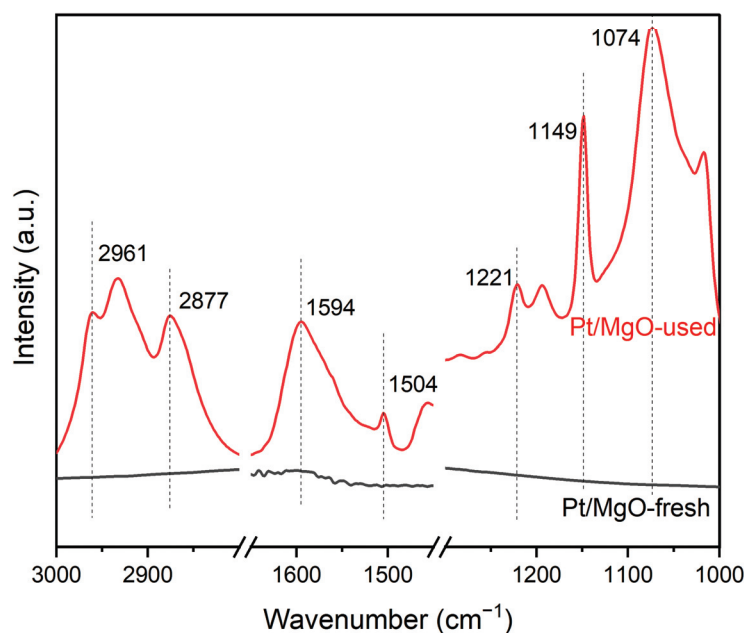


Figure 15. FT-IR spectra of Pt/MgO before and after cycling.

Figure 16 shows the particle size analysis of the catalyst before and after the 2Pt/MgO-200 cycles. The size of metal Pt particles in the catalyst increased from 1.62 nm to 2.59 nm after five cycles of testing. The increase in particle size will lead to a decrease in metal dispersion, which is another important reason for the decrease in catalyst activity.

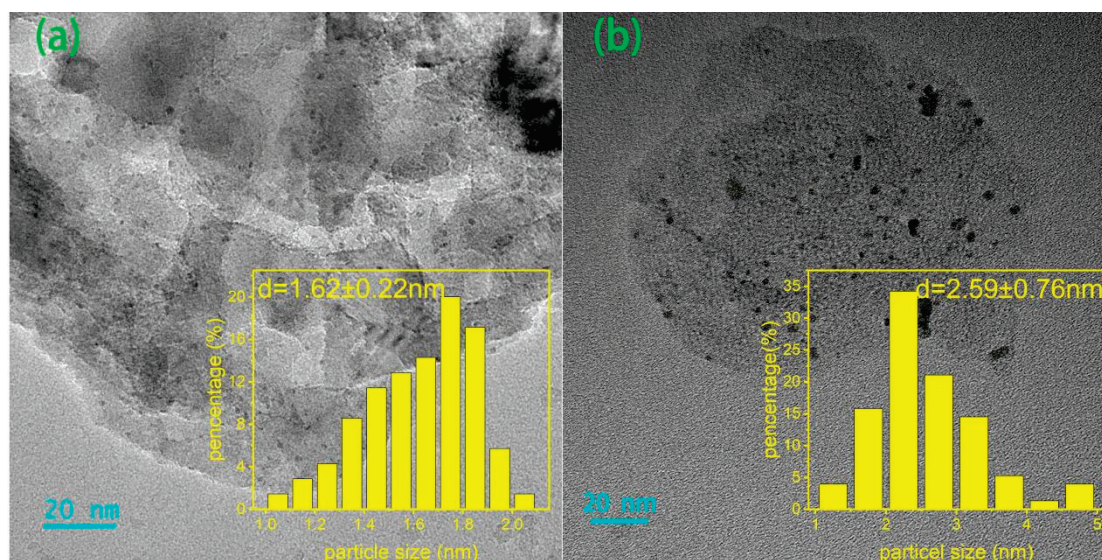


Figure 16. TEM images and particle size distribution of 2Pt/MgO-200 (a) fresh and (b) recycled.

In summary, the deactivation of the catalyst is due to the hydrolysis of the carrier, the adsorption of organic matter, and the growth of the active metal particle size.

3. Experimental Section

3.1. Catalyst Preparation

Materials: $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (Aladdin, Vienna, Virginia, USA), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{NiC}_4\text{H}_6\text{O}_4 \cdot 4\text{H}_2\text{O}$ (99.9%), $(\text{CH}_3\text{COO})_2\text{Mn}$ (Aladdin, 99%), $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (92%), MgO (Aladdin, AR), CeO_2 (Aladdin, 99%), RuCl_3 (97%), PdCl_2 (Aladdin, 99%), Active carbon (Aladdin, AR), TiO_2 (Aladdin, 99%), and Al_2O_3 (Aladdin, 99%).

The catalyst was prepared using an equal volume impregnation method. In a typical preparation, a certain amount of chloroplatinic acid aqueous solution was accurately added to a certain mass of MgO powder and stirred for 20 min. Then the mixture was kept stewing at room temperature for 6–8 h and then dried overnight at 60 °C. Next, the powder was calcinated under air at 350 °C for 3 h. Finally, the catalyst was reduced under H₂ atmosphere at different temperatures for 1 h. The final catalyst is expressed as xPt/MgO-T, where x represents the mass loading of Pt and T represents the reduction temperature.

3.2. Catalyst Characterization

X-ray diffraction (XRD) measurements were performed on an X'Pert PRO diffractometer using Cu K α radiation ($\lambda = 0.154$ nm) operated at 40 kV and 45 mA. The patterns were recorded from 10 to 90° in 2 θ with a scan speed of 10° min^{−1}.

The transmission electron microscopy (TEM) tests were carried out on JEM 2800 instruments of JEOL Company in Japan (Tokyo, Japan) with a working voltage of 200 KV.

The X-ray photoelectron spectroscopy was obtained using the PHI Quantera SXM spectrometer, and the laboratory used Al targets with K $\alpha = 1486.6$ eV as the radiation source. When estimating the binding energy (BE) values of various elements, the peak corresponding to C 1s (284.8 eV) was taken as a reference.

Infrared testing was performed on a Nicolet 6700 Fourier transform infrared spectrometer equipped with an MCT detector. Approximately 150 mg of catalyst sample was weighed and pressed into KBr tablets, then placed in a sample cell for testing.

The chemical adsorption was tested on Micromeritics Auto Chem 2910. Hydrogen Temperature Programmed Reduction (H₂-TPR) was used to determine the reduction properties of metal sites in the analytical catalysts. A total of 0.15 g unreduced catalyst was placed in a quartz tube and treated with Ar (99.999%, 30 mL/min) at 200 °C for 1 h to remove adsorbed water and other impurities. Then, a gas mixture of H₂ (10%)-Ar (90%) was passed through the U-shaped tube at 50 °C, and the temperature was raised to 800 °C at a heating rate of 10 °C/min. The rate of H₂ consumption was monitored by a thermal conductivity detector (TCD). Carbon Dioxide Temperature Programmed Desorption (CO₂-TPD) was used to test the basic sites. In a typical experiment, 0.15 g of catalyst sample was placed in a U-shaped flow through a quartz sample tube. Before measurement, the reduced catalyst was pretreated in Ar (99.999%, 30 mL/min) at 200 °C for 1 h. A mixture of CO₂ was injected in Ar (10%) at 30 °C (30 mL/min) for 30 min. Then, the sample was treated with Ar (30 mL/min) at 30 °C for 1 h. Finally, the temperature was increased from room temperature to 700 °C in an Ar atmosphere and the TCD signals were continuously collected.

3.3. Catalytic Performance Evaluation

Selective hydrogenolysis of FFA was carried out at a speed of 600 r/min in a 100 mL high-pressure reactor. All calcined samples were used in powder form. In a typical operation, 30 g of 4 wt% FFA aqueous solution and a certain amount of the reduced catalyst were introduced into the reactor. After blowing with H₂ at least three times, the reactor was pressurized to 1 MPa and heated to 160 °C to begin the reaction.

After the reaction, the products were centrifuged and the supernatant was identified using Agilent GC-7800A gas chromatography (Santa Clara, California, United States) and Pfeiffer Omnistar GSD 320 mass spectrometer (GC-MS). The conversion rate and product selectivity were determined using the external standard method, and the calculation formula is as follows:

$$\text{FFA Conversion (\%)} = [(\text{FFA}_{\text{before}} - \text{FFA}_{\text{after}}) / \text{FFA}_{\text{before}}] \times 100\%$$

$$\text{Product Selectivity (\%)} = [\text{Product}_{\text{after}} / (\text{FFA}_{\text{before}} - \text{FFA}_{\text{after}})] \times 100\%$$

3.4. Cycling Test

The cycling experiment involves recycling the catalyst after reactions. After each reaction, all products in the reactor were centrifuged and the catalyst powder was collected. The collected catalyst was washed with deionized water and then centrifuged. Finally, it was dried in a vacuum oven, ground, and subjected to the next hydrogenation reaction.

4. Conclusions

In the experiment of the catalytic hydrogenation of furfuryl alcohol to pentanediol, Pt/MgO showed good catalytic activity. Two percent Pt/MgO reduced at 200 °C showed the optimal catalytic performance. At 160 °C and 1 MPa H₂ pressure, when the concentration of furfuryl alcohol was 0.35 mol/L and 0.2 g of catalyst was added, the FFA conversion rate reached 100% within 10 h. The selectivity of 1,2-PeD and 1,5-PeD was 59.4% and 15.2%, respectively, with the total yield of pentanediol reaching 74.6%. Detailed characterization indicates that the reduction temperature has a significant impact on the chemical state of Pt and the particle size distribution. A low reduction temperature led to the insufficient reduction of metal Pt, which is unfavorable for the cleavage of the C-O bond. And a high reduction temperature would cause the aggregation of Pt nanoparticles, which would lead to low metal utilization and the hydrogenation of the C=C bond, thus decreasing the conversion and selectivity for pentanediol. In summary, the highly dispersed metallic Pt nanoparticles facilitate the selective hydrogenolysis of FFA to pentanediol. In addition, the basic sites on the MgO carrier are also the key to the ring-opening hydrogenation of FFA. The deactivation of catalysts during hydrogenation is caused by the hydrolysis of the support, adsorption of organic chemicals, and growth in the size of loaded metal particles. This work provides a meaningful reference for the hydrogenation of FFA to prepare pentanediol.

Author Contributions: Conceptualization, Q.L. and Y.Y.; methodology, Q.L.; validation, Y.Y.; formal analysis, Y.Y.; investigation, Y.Y.; resources, Z.L.; data curation, Q.L.; writing—original draft preparation, Y.Y.; writing—review and editing, Q.L.; visualization, Y.Y.; supervision, Q.L.; project administration, Z.L.; funding acquisition, Z.L. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The data that support the findings of this study are available from the corresponding authors upon reasonable request.

Conflicts of Interest: The authors declare no conflicts of interest.

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Article

Catalytic Conversion of Cyclopentanone into Dimethyl Adipate over Solid Basic Catalysts with Dimethyl Carbonate

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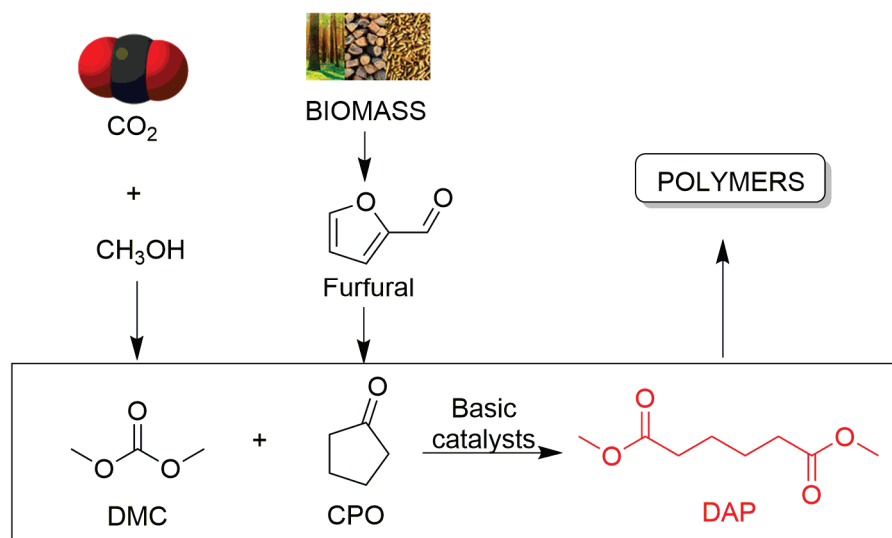
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Abstract: The synthesis of dimethyl adipate (DAP), a stable configuration of adipic acid, from biomass-derived cyclopentanone (CPO) and dimethyl carbonate (DMC) constitutes an attractive greener route than petroleum-based industrial processes. Solid basic catalysts such as MgO, $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$, KOCH₃ and Ca(OCH₃)₂ have been used achieving a DAP yield up to 30% at 533 K. In addition to the type of catalyst, other operating conditions such as the substrate, reaction time, temperature and CPO concentration have been studied. The methylation of DAP and CPO and the self-aldol condensation of CPO to form dimers and oligomers are reactions that occur in parallel with the production of DAP. It has been established that the main challenge is the self-aldol condensation of CPO. It has been identified that at short reaction times, to prevent methylation, and at dilute concentrations, to avoid CPO self-condensation, the DAP formation rate is much higher than these other competitive reactions. Finally, it should be noted that a DAP productivity up to $3.45 \text{ g} \cdot \text{gcat}^{-1} \cdot \text{h}^{-1}$ has been achieved under mild conditions.

Keywords: cyclopentanone; dimethyl carbonate; dimethyl adipate; solid basic catalysts

1. Introduction

Adipic acid (AdA) is an essential building block used to manufacture nylon 6-6, adipic esters and polyurethanes. Among its many applications, its uses in the pharmaceutical, cosmetic and food industries stand out [1,2]. Currently, adipic acid is mainly produced from petroleum-based feedstock. Benzene is hydrogenated to cyclohexane and further treated to synthesize ketone/alcohol oil (KA-oil), a mixture of cyclohexanone and cyclohexanol, which is oxidized with nitric acid to obtain AdA [3]. Given that this process is not sustainable due to its several steps and the nitrous emissions produced [4], a number of greener routes have been proposed over the last decade [5,6]. Lignocellulose biomass, made up of cellulose, hemicellulose and lignin, presents itself as a renewable carbon source, from which the conversion to valuable chemical products has attracted interest over the last years [7–9]. Among the processes to obtain AdA from biomass, an attractive process is the synthesis of dimethyl adipate (DAP) from cyclopentanone (CPO) and dimethyl carbonate (DMC). CPO is an interesting compound used in the synthesis of fungicides, pharmaceuticals, flavors, fragrances and rubber chemicals. Currently, it is obtained through petrochemical routes [10,11]; however, recently, its synthesis from biomass has been thoroughly studied via the hydrogenation of furfural [12–15]. DMC is an attractive solvent and reactant due to its chemical properties and low toxicity. It is used in methylation and carboxymethylation reactions as an eco-friendly substitute to phosgene, dimethylsulfate and metal halides [16,17]. Furthermore, its origin is also green, since it can be obtained from the reaction between CO₂ and CH₃OH [18]. Given that CO₂ is one of the compounds responsible for the greenhouse effect, its capture and use in the synthesis of carbonates is highly interesting. By choosing the DAP synthesis from CPO and DMC, we combine biomass and CO₂ to synthesize biopolymers (Scheme 1).

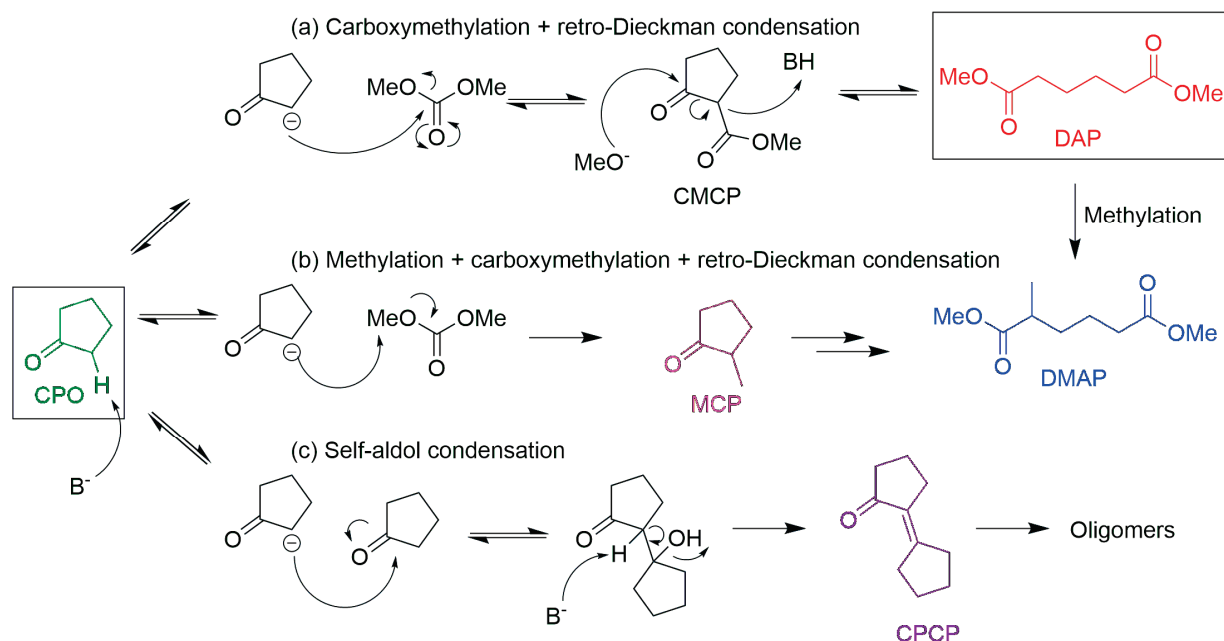


Scheme 1. Combination of CO₂ and biomass to synthesize polymers.

DAP has been obtained from CPO with PdCl₂, methanol and CO instead of DMC [19,20]. However, the use of DMC as a solvent and reactant makes the reaction greener. To carry out the desired synthesis, temperatures between 473 and 533 K and basic catalysts are required. The use of solid catalysts instead of homogeneous ones has several advantages. The ease with which the catalyst can be separated from the reaction mixture and later reused, the reduction in the waste produced during the reaction as a result of the elimination of the catalyst neutralization step, the capacity to run continuous processes and the ability to work at higher temperatures are just a few of them [21]. DAP has been obtained using organic carbonates as catalysts [22,23]. Its synthesis was also reported using a nanostructured CeO₂, giving an 84% DAP yield; however, a large amount of catalyst (catalyst/CPO wt% = 42) and highly diluted solutions (CPO/DMC wt% = 2.2) were used [24]. These authors have also tested MgO as a catalyst, giving a 47% yield of DAP. This catalyst was also studied by Wu et al. [25] under milder conditions (CPO/DMC wt% = 14.0 and catalyst/CPO wt% = 14.0), obtaining a 44% yield of DAP. Other cyclic ketones have been reported to react with DMC in a similar reaction using MgO and NaOCH₃ as catalysts, giving moderate yields [26].

Regarding the reaction mechanism, DMC facilitates both methylation and carboxymethylation reactions, as mentioned above. Therefore, the methylation of reagents, intermediates and products can represent a competitive route of the selective pathway towards DAP. Scheme 2 shows a plausible mechanism. The basic catalyst abstracts a proton from the CPO, forming an enolate that attacks the carbonyl group of DMC, possibly obtaining the intermediate 2-carbomethoxy-cyclopentanone (CMCP). Later, the previously leaving methoxide anion attacks CMCP, giving DAP (route a). The desired product can be further methylated in the reaction media to synthesize dimethyl 2-methyladipate (DMAP). This compound can also come from the carboxymethylation of 2-methyl cyclopentanone (MCP), which is obtained by CPO methylation (route b). Furthermore, the self-aldol condensation of CPO can occur, giving 2-cyclopentylidene-cyclopentanone (CPCP) (route c).

This study aims to analyze the different routes proposed in the mechanism to understand the selectivity of each of the products. It has been confirmed that the main challenge is to achieve a high selectivity towards DAP, since the methylation of the reactants and products and the self-aldol condensation of CPO to form dimers occurs at the same time. A study of the operation conditions has been conducted to understand the different reaction pathways' relevance.



Scheme 2. Reaction pathways for the catalytic conversion of cyclopentanone and dimethyl carbonate (adapted from [25]).

2. Results and Discussion

Initially, a study on the performance of different basic solid catalysts was conducted to determine the most promising catalyst to synthesize DAP (see Table S1 in the Supporting Information). It has been mentioned in the Introduction section that basic catalysts based on Ce have shown good behavior [24]. However, the tested cerium catalysts did not achieve a CPO conversion higher than 10% under our operation conditions, even after 2 and 4 h at 533 K (entries 1 to 3 in Table S1). CaO and Ca(OH)₂ gave higher CPO conversions; however, the selectivity for DAP did not reach satisfactory values (entries 6 and 7 in Table S1). Carbonates such as CaCO₃, (NH₄)₂CO₃ and Na₂CO₃ went up to a 30% conversion of CPO (entries 8 to 10 Table S1), but also, the selectivity for DAP was considerably low and even negligible. The catalysts that showed a higher CPO conversion, over 80%, were KOCH₃, Ca(OCH₃)₂, MgCO₃ (HC), Mg(NO₃)₂·6H₂O and MgO (entries 4, 5, 11, 14 and 15 in Table S1), with the magnesium catalysts being the ones showing the highest DAP yields. Mg(NO₃)₂·6H₂O did not prove to be a heterogeneous catalyst, since it melted at the high temperatures employed in the reaction; therefore, it was ruled out. Finally, Ca(OCH₃)₂ showed a high DMAP yield, compared to the other catalysts, which could be due to the methylation of DAP in the reaction media, suggesting that shorter reaction times would be more appropriate. The KOCH₃ catalyst did not show a high DAP or DMAP yield in the tested conditions; however, a new compound was found, which will be discussed later on. An interesting fact is that in some of the entries, we observe high conversions of CPO and relatively low yields of identified products. This study aims to explain the low carbon balance of this reaction.

2.1. A Kinetic Study of the Reaction Using MgO and MgCO₃ (HC)

Based on the DAP yield data, the chosen basic catalysts for this kinetic study were MgO and MgCO₃ (HC). Accordingly, the selectivity has been displayed versus the conversion of CPO for both basic solid catalysts (Figure 1 and Figure S1 in the Supporting Information). Although there are some quantitative differences between both basic catalysts, their behaviors are similar from a qualitative point of view. The products identified are the same, and their evolution over the conversion of CPO is similar. The CPCP dimer selectivity is the highest (over 40%) at a lower conversion of CPO. Since the self-aldol condensation reaction is not reversible, the decrease in the selectivity observed at a higher

conversion means that this compound is transformed into other side products, likely via the successive aldol condensation of CPCP into heavier oligomers. The DAP selectivity reaches a maximum at higher conversions (between 2 and 3 h of reaction) and then drops. Another product is DMAP, for which the yield increases with the conversion, suggesting the methylation of DAP occurs in the presence of DMC. It would explain, at least partially, the drop in the DAP selectivity at a higher conversion of CPO, indicating that DAP, once formed, further reacts in the reaction medium. Traces of MCP are also identified as a reaction product without a clear trend.

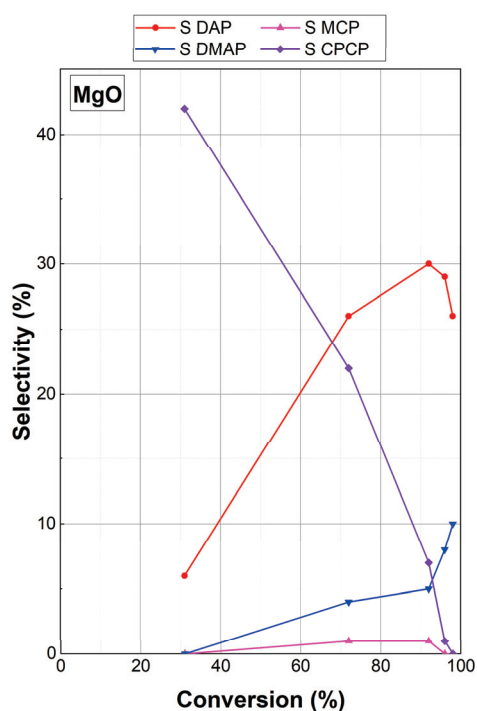


Figure 1. Product selectivity versus conversion using MgO as the catalyst. Reaction conditions: 0.5 g CPO, 5.4 g DMC, 0.05 g catalyst and 533 K.

Here, it should be noted that all the products identified after the reaction can be explained considering the reaction pathways shown in Scheme 2. It suggests that under our operation conditions, in the presence of basic solid catalysts, the reaction of CPO with DMC follows the three proposed pathways. Moreover, a further transformation of DAP in the reaction medium with DMC can also occur. Therefore, to increase the selectivity and consequently, the yield of DAP, route (a) in Scheme 2 should be promoted, whereas the other nonselective routes (b and c) must be inhibited. The main challenge here is the self-aldol condensation reaction of CPO to form the CPCP dimer and other oligomers, since its maximum selectivity is higher than the DAP selectivity. In an attempt to inhibit the undesired side products, the three routes mentioned above will be studied more in detail.

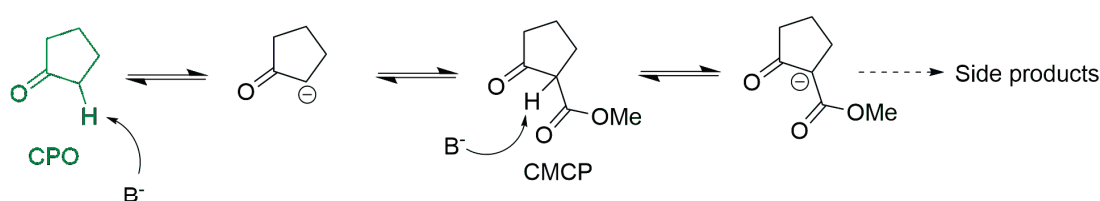
2.2. Study of the Selective Pathway (Route a) Using MgO and MgCO₃ (HC) Catalysts

The DAP yield using these two catalysts is approximately 30% at high conversions (Table S1). It has already been proven that route (c) in Scheme 2 is responsible for most of the selectivity loss. Nonetheless, there are other factors to take into account when route (a) in Scheme 2 is followed. Other side products could be formed before the synthesis of DAP, and additionally, DAP could further react in the reaction media to give other products, such as DMAP (Scheme 2). These two possibilities have been studied in more detail.

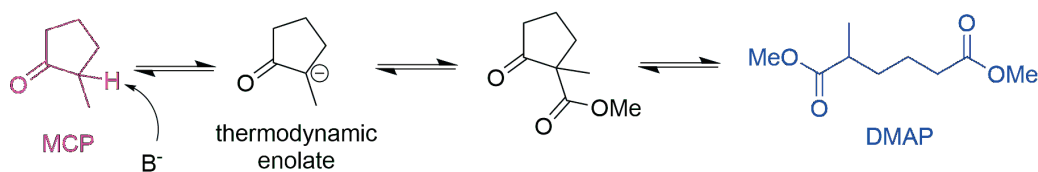
The selective pathway describes the synthesis of our target monomer DAP, where CMCP (Scheme 2) is possibly the intermediate compound in this route. This intermediate is highly reactive because of its acid proton located between the two carbonyl groups

(Scheme 3a). It is possible that, instead of following the selective route, the base catalyst abstracts this proton, synthesizing a different active intermediate that could end up giving other unidentified products at the expense of the DAP yield (Scheme 3a). To evaluate this hypothesis, a reaction using MCP as the substrate instead of CPO and MgCO_3 (HC) as the catalyst was conducted. In this case, due to the methyl group of the substrate, two possible enolates can be formed once the MCP is deprotonated: the kinetic and thermodynamic enolate. Given the use of high temperatures and low amounts of catalyst, the thermodynamic enolate is favored (Scheme 3b) [27–29]. This means that the produced intermediate lacks that acid proton found in CMCP. Since this proton is absent, this intermediate can only synthesize DMAP through a ring-opening reaction (Scheme 3b). If the acid proton in CMCP was responsible for the low DAP yields, in this second reaction (Scheme 3b), the DMAP yield would be higher. However, the DMAP yield was 30%, comparable with the 29% of DAP obtained using CPO as the substrate (Table 1, entries 1 and 2). Consequently, the consumption of the intermediate CMCP to form new compounds other than DAP can be ruled out as a source of DAP selectivity loss.

(a) Possible side reaction



(b) Testing of hypothesis



Scheme 3. Mechanism for the synthesis of DMAP from MCP via thermodynamic enolate.

Table 1. Product distributions for MgCO_3 (HC) and MgO catalysts using different substrates.

#	Catalyst	Substrate	Catalytic Results (%)				
			X_{Subs}	Y_{DAP} Route a	Y_{MCP} Route b	Y_{DMAP} Route b/Further a	Y_{CPCP} Route c
1	MgCO_3 (HC)	CPO ^a	85	29	0	3	10
2	MgCO_3 (HC)	MCP ^a	80	0	-	30	0
3	MgCO_3 (HC)	DAP ^b	32	-	-	5	-
4	MgO	DAP ^b	32	-	-	5	-

^a Reaction conditions: 0.5 g of substrate, 5.4 g DMC and 0.05 g catalyst at 533 K during 2 h of reaction; ^b 1 g of substrate.

Another challenge to this route is the transformation of the formed DAP into DMAP and other side products. To evaluate this possibility, DAP was exposed to each catalyst under the same reaction conditions (Table 1, entries 3 and 4). In both cases, quite similar results were obtained: a DAP conversion of 32% and a DMAP yield of 5%. Along with DMAP formation, DAP transforms into another four unknown products detected using GC (see chromatograms in Figures S2 and S3 of the Supporting Information). Therefore, it can be concluded that, at least partially, the observed DMAP is formed by the methylation of DAP and that part of the lack of carbon balance in the CPO transformation to DAP is due to the transformation of DAP to compounds that cannot be quantified using GC.

Consequently, the reaction time is an important variable, since the longer the reaction time, the higher the yield of DAP, but the further transformation to DMAP and other products is also favored; thus, a balance is required.

2.3. Cyclopentanone Methylation (Route b) Using KOCH_3 Catalyst

We have also studied the methylation of CPO to form MCP and its further conversion to DMAP (route b in Scheme 2). Since we found out that the potassium methoxide (KOCH_3) catalyst showed preference to the methylated products compared to other catalysts, we have considered it more appropriate to use this basic catalyst in the study of this nonselective route.

Figure 2 shows the conversion and yields at different temperatures using KOCH_3 as the catalyst. The yields of DMAP at all temperatures are higher than those of DAP. This could mean that the transformation of DAP to DMAP occurs faster using this catalyst. However, when the reaction was conducted at 473 K, the conversion of CPO is considerably low, whereas the DMAP yield is almost double to that of DAP, indicating clearly that the KOCH_3 catalyst is more selective to route b. Furthermore, a new compound was observed when the reaction was conducted at higher temperatures (503 and 533 K). Using GC–MS, this product was identified as dimethyl 2,5-dimethyl adipate, a DAP with two methyl groups labeled as DMMAP, a compound that comes from the further methylation of DMAP with DMC under the operating conditions.

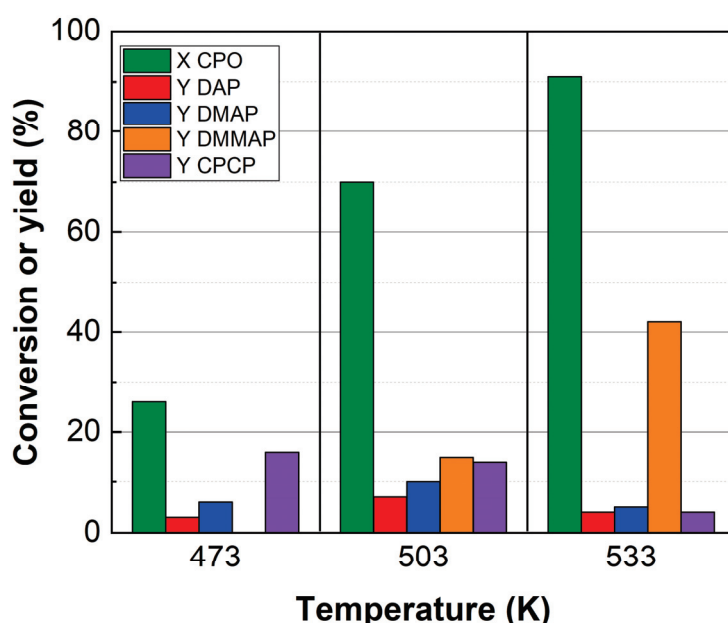


Figure 2. CPO conversion and product yields at different temperatures using KOCH_3 as the catalyst. Reaction conditions: 0.5 g CPO, 5.4 g DMC and 0.05 g catalyst for 2 h.

2.4. The Self-Aldol Condensation of CPO (Route c) Using MgCO_3 (HC), MgO and $\text{Ca}(\text{OCH}_3)_2$ Catalysts

The other nonselective and therefore competitive reaction for the synthesis of DAP is the self-aldol condensation of CPO (route c in Scheme 2). The relevance of this route can be previously observed in Figure 2, where a high CPCP yield at 473 K is reached, comparable to the other product yields. However, this value decreases with the increase in temperature. It suggests that temperature is an important variable in the selectivity towards the different routes. In this case, and since route c required to be compared to the selective synthesis of DAP (route a), the chosen basic catalysts were MgO and $\text{Ca}(\text{OCH}_3)_2$.

Figure 3 shows the use of MgO as the catalyst at 503 K and 533 K. In both cases, the CPCP yield at a shorter reaction time is higher than the DAP yield. While the CPCP yield goes up to 24% at 503 K before further reacting, with the increase in temperature

(533 K), this maximum yield is only 16%. Regarding the behavior of $\text{Ca}(\text{OCH}_3)_2$ catalysts, the difference between the CPCP yield is not so easily appreciated. While the maximum at 503 K is 16%, at 533 K, it is 12% (see Figure 3). This finding shows a lower selectivity for route c at higher temperatures. Nonetheless, the maximum DAP yield in all cases is approximately 30%, which could be due to the competitive nature of the aldol condensation reaction. The self-aldol condensation of CPO has proven to be one of the main challenges of this reaction regardless of the temperature. While the selectivity for CPCP is higher than that for DAP at shorter reaction times, a decrease in the yield of CPCP has been observed as the reaction time increases, possibly due to its ability to continue to react with more CPO to form oligomers [30].

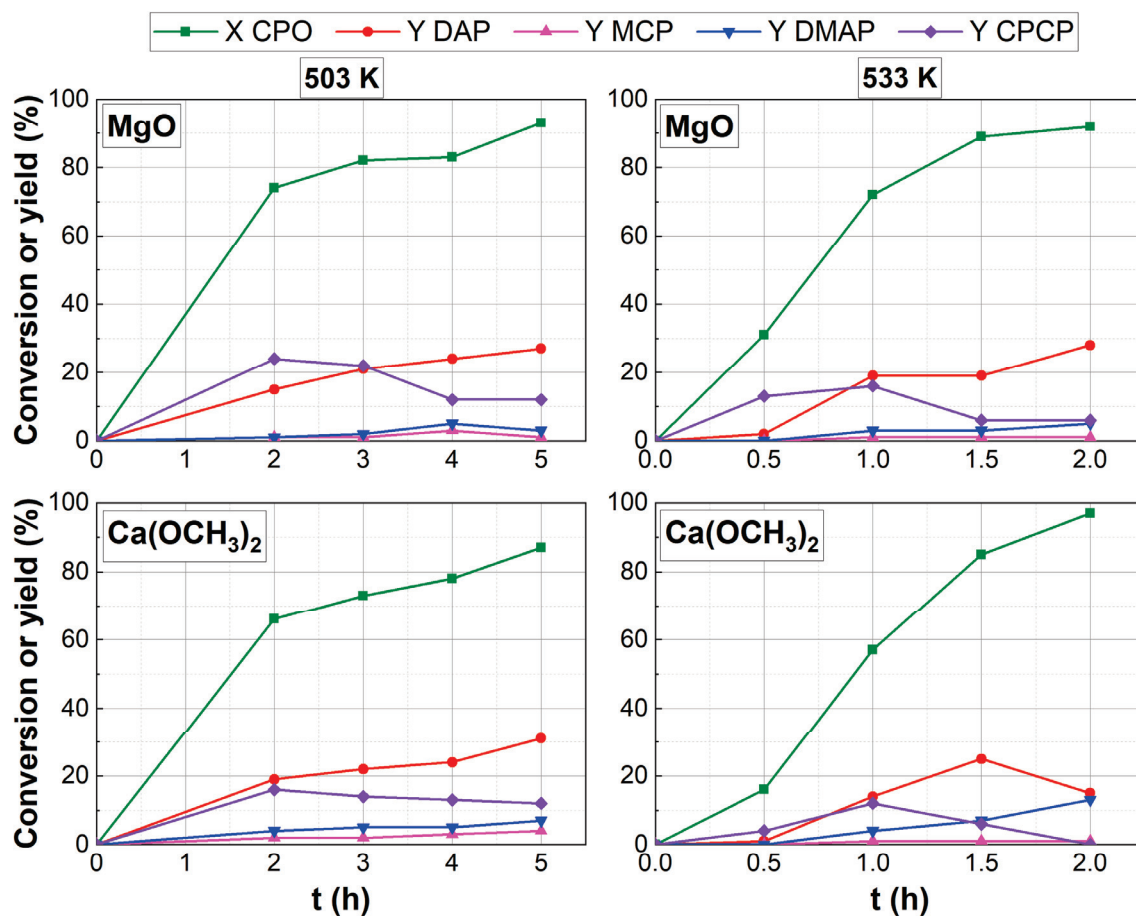


Figure 3. Kinetic experiments using MgO and $\text{Ca}(\text{OCH}_3)_2$ as catalysts at 503 K and 533 K temperatures. Reaction conditions: 0.5 g CPO, 5.4 g DMC and 0.05 g catalyst.

An approach to obtain a higher selectivity for DAP by eliminating the self-aldol condensation reaction is to use lower concentrations of CPO. Therefore, the CPO concentration was decreased, while the amount of catalyst, MgCO_3 (HC), was kept unchanged. In this case, the most appropriate way is to represent the formation rate of the main products, such as DAP and CPCP, against the concentration of CPO, which is shown in Figure 4 for 1 h of reaction.

At 1 h of reaction, the formation rate of DAP raises from 21.6 to 212.4 $\text{mmol h}^{-1} \cdot \text{g}^{-1}$, while the CPO concentration decreases from 9.3 to 2.3 wt%, since both the CPO conversion and DAP selectivity increase (Figure S4). On the other hand, the formation rate of CPCP is low (ca. 65 $\text{mmol h}^{-1} \cdot \text{g}^{-1}$) and remains practically constant regarding the concentration of the starting solution. These values result from the fact that the conversion of CPO and the CPCP selectivity decrease (Figure S4).

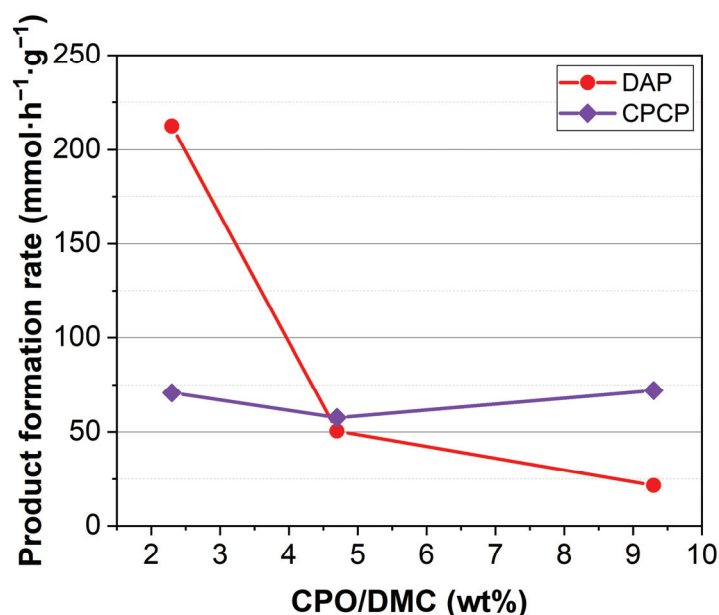


Figure 4. Product formation rate versus the CPO concentration at 1 h of reaction for MgCO_3 (HC) catalyst. Reaction conditions: 5.4 g of DMC and 0.05 g catalyst at 533 K.

The self-aldol condensation of CPO is the most relevant competitive reaction in the synthesis of DAP, and more research will be required to fully understand how to suppress this side reaction and obtain high DAP yields. At short reaction times (1 h), it has been observed that the CPO concentration is key to slowing down the advance of this unwanted reaction.

2.5. DAP Productivity for Different Basic Solid Catalysts

The productivity of the desired product (DAP) was calculated and compared with the results from other authors and collected in Table 2. MgCO_3 (HC) and MgO obtained yields up to 30% at 533 K after 2 h (Table S1, entries 11 and 15), giving productivities of 3.00 and 2.90 $\text{g} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$, respectively (Table 2, entries 2 and 3). On the other hand, the reaction using $\text{Ca}(\text{OCH}_3)_2$ at 533 K proved to be faster, with a 25% yield after 1.5 h, and therefore, a productivity of 3.45 $\text{g} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$ (Table 2, entry 1). These values are higher than those previously reported on basic catalysts, where the productivities are below 1.5 $\text{g} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$ (Table 2, entries 4–6). The use of less catalyst and shorter reaction times allowed us to achieve a higher productivity, being relevant parameters to implement this process at the industrial scale [31].

Table 2. Productivities of the best catalysts in optimized conditions.

#	Catalyst	CPO/DMC (wt%)	Cat/CPO (wt%)	T (K)	t (h)	Prod _{DAP} ($\text{g}/\text{g}_{\text{cat}} \cdot \text{h}$)	Ref
1	$\text{Ca}(\text{OCH}_3)_2$	9.3	10	533	1.5	3.45	This work
2	MgCO_3 (HC)	9.3	10	533	2	3.00	This work
3	MgO	9.3	10	533	2	2.90	This work
4	MgO	14.0	14.0	533	5	1.09	[25]
5	MgO	2.2	42.0	533	3	0.65	[24]
6	CeO_2 -nanorod	2.2	42.0	533	5	0.69	[24]

The data presented in this work confirm that the synthesis of DAP (selective pathway) is a challenge. The most relevant nonselective competitive pathways that we have demonstrated to occur are as follows: (i) the methylation with DMC towards DMAP, either by the reaction of MCP with DMC or the methylation of the product of interest (DAP) in the reaction medium and (ii) the self-aldol condensation of the CPO to its dimer CPCP. The

successive condensation to higher MW oligomers cannot be ruled out at a high temperature and long reaction times. The relevance of each one will depend on the catalyst used and the operating conditions. Nonetheless, the CPO self-aldol condensation route is the main barrier to reaching a high DAP selectivity. Unfortunately, the strategies followed by decreasing both the methylation and CPO self-aldol condensation in favor of the selective route have not been satisfactory at high CPO conversions, and more work needs to be performed in this direction.

In addition to looking for new compositions of basic catalysts that are more selective for the synthesis of DAP, another interesting approach would be to carry out this reaction in a continuous flow to study the DAP selectivity with the space velocity and catalyst deactivation. Lastly, the nature and strength of the basic sites of the catalyst could be interesting topics in future studies, since they could be important factors to control the reaction selectivity.

3. Materials and Methods

3.1. Reagents and Catalysts

The materials used as catalysts in the reactions were purchased from the following: (i) Alfa Aesar (Haverhill, Massachusetts, USA), $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ [labeled as MgCO_3 (HC)] and $\text{Ca}(\text{OH})_2$, purity 95%; (ii) Panreac (Madrid, Spain), $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$; and (iii) Sigma Aldrich (St. Louis, MO, USA), MgO nanopowder, KOCH_3 95%, $\text{Ca}(\text{OCH}_3)_2$ 97%, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O} \geq 99.0\%$, $(\text{NH}_4)_2\text{CO}_3 \geq 30.0\%$ NH_3 basis, CaCO_3 99.95–100.05% dry basis, CaO 99.9% trace metal basis, MgSO_4 anhydrous $\geq 99.5\%$, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} \geq 98\%$, $\text{Ce}(\text{OH})_4$, $\text{CeO}_2/\text{ZrO}_2$ nanopowder 99.0% and CeO_2 nanopowder.

The liquids used as solvents, reactants and products such as dimethyl carbonate 99%, cyclopentanone 99%, dimethyl adipate $\geq 99\%$ and dimethyl 2-methyl adipate were supplied by Sigma Aldrich, and 2-methylcyclopentanone 99% by Acros Organics (Thermo Fisher Scientific: Waltham, Massachusetts, USA). Finally, decane $\geq 99\%$ was used as the internal standard, and it was purchased from Sigma Aldrich. Mixtures at different concentrations of these products have been used for the chromatographic calibration.

3.2. Catalytic Activity Measurements

The reaction was carried out in a batch stainless steel reactor (20 mL volume) with an inner Teflon liner. The catalyst (0.05 g) was added first, followed by the CPO (0.5 g or 6 mmol) and the solvent, DMC (5.4 g or 60 mmol). The reactor was inserted in an aluminum block to maintain the temperature, and a thermocouple inserted in the block was used to control the reaction temperature. The mixture was heated at a temperature range between 473 and 533 K and stirred at 1200 rpm. The autogenous initial pressure was between 20 and 25 bars. After the reaction, the reactor was placed in an ice bath to stop the reaction. Afterward, an aliquot of the reaction (ca. 1.0 g) was taken from the mixture and decane (0.05 g) was added as the internal standard. The solution was analyzed using a gas chromatograph (6890N Agilent Technologies, Madrid, Spain) equipped with a flame ionization detector and an HP-5 column. The CPO conversion, the product yields and the productivities of the catalysts were calculated according to the following expressions:

$$\text{CPO conversion (mol\%)} = \frac{n_{\text{CPO}}^0 - n_{\text{CPO}}}{n_{\text{CPO}}^0} \times 100 \quad (1)$$

$$\text{Product yield (mol\%)} = \frac{n_{\text{prod}}}{n_{\text{CPO}}^0} \times 100 \quad (2)$$

$$\text{Productivity (g} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}) = \frac{Y_{\text{DAP}} \cdot \text{MW}_{\text{DAP}} / \text{MW}_{\text{CPO}}}{C / S \cdot t} \quad (3)$$

with n_{CPO}^0 being the initial mole quantities introduced in the reactor, n_{CPO} and n_{prod} being the mole quantities of CPO and the product after the reaction, Y_{DAP} being the DAP yield in

%, MW_{DAP} and MW_{CPO} being the molecular weights of DAP and CPO, respectively, C/S being the catalyst to substrate weight ratio in % and t being the time in hours. For the yield calculation, the stoichiometric relationship was taken into account.

4. Conclusions

The main challenge in the synthesis of dimethyl adipate from cyclopentanone and dimethyl carbonate using basic solid catalysts is the inhibition of the self-aldol condensation of cyclopentanone. This reaction can further evolve by synthesizing heavy oligomers, consuming the cyclopentanone starting material, and therefore, limiting the yield of dimethyl adipate. Other undesirable reactions such as the methylation of dimethyl adipate and cyclopentanone occur under the reaction conditions. The extent of these competitive reactions will depend on the catalyst and operating conditions used such as the temperature, reaction time, and concentration of cyclopentanone. The methylation of the dimethyl adipate formed is favored with the reaction time, and the self-aldol condensation of cyclopentanone with its concentration. Despite this, it can be remarked that we have achieved a dimethyl adipate productivity up to $3.45 \text{ g} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$ under moderate reaction conditions.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal14010086/s1>, Figure S1: Product selectivity versus conversion using MgCO_3 (HC) as the catalyst. Reaction conditions: 0.5 g CPO, 5.4 g DMC, 0.05 g catalyst and 533 K. Figure S2: Chromatogram of DAP decomposition with MgCO_3 (HC) as the catalyst. Retention times (product assignation): 1.0 (DMC); 1.7 (CP); 3.99 (Decane, internal standard); 8.0 (DAP); 8.5 (DMAP); 1.2 (side product of DMC); *6.4, 8.3, 13.0 and 18.5 (side products of DAP). Figure S3: Chromatogram of DAP decomposition with MgO as the catalyst. Retention times and (product assignation) equal to Figure S2; Figure S4: Conversion and product selectivity with different amounts of CPO at 1 h (left) and 2 h (right). Reaction conditions: 5.4 g of DMC and 0.05 g catalyst MgCO_3 (HC) at 533 K; Table S1: Study of basic catalysts in the synthesis of DAP from CPO and DMC.

Author Contributions: Conceptualization, I.M.-S. and R.M.; methodology, I.M.-S. and R.M.; formal analysis, R.M.; investigation, I.M.-S. and A.O.-S.; data curation, I.M.-S.; writing—original draft preparation, I.M.-S. and R.M.; writing—review and editing, I.M.-S., A.O.-S., M.L.G. and R.M.; visualization, I.M.-S. and R.M.; supervision, M.L.G. and R.M.; project administration, R.M. and M.L.G.; funding acquisition, M.L.G. and R.M. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The data presented in this study are available on request from the corresponding author.

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Conflicts of Interest: The authors declare no conflicts of interest.

List of Acronyms

2-Carbomethoxy-cyclopentanone	CMCP
2-Cyclopentylidene-cyclopentanone	CPCP
2-Methyl cyclopentanone	MCP
Adipic acid	AdA
Cyclopentanone	CPO
Dimethyl 2-methyladipate	DMAP
Dimethyl adipate	DAP
Dimethyl carbonate	DMC

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Article

Reaction Mechanisms and Production of Hydrogen and Acetic Acid from Aqueous Ethanol Using a Ru-Sn/TiO₂ Catalyst in a Continuous Flow Reactor

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Abstract: The catalytic reforming of bioethanol can produce green hydrogen (H₂) and acetic acid (AcOH). In the present study, the conversion of aqueous ethanol (EtOH) over 4 wt% Ru-4 wt% Sn/TiO₂ in a flow reactor was investigated at different temperatures at 0.1 MPa or at various pressures at 260 °C. The ethanol conversion was rather slow in liquid water, while the reactivity increased significantly when water was evaporated. Under gas-phase conditions at 0.1 MPa, the conversion rate increased with increasing reaction temperature, but the AcOH yield and H₂ purity decreased due to by-production of CH₄, CO, and CO₂. The CH₄ and CO generated by fragmentation of acetaldehyde (AA), an intermediate, were suppressed by increasing reaction pressure, although the formation of CH₄ and CO₂ generated from AcOH was pressure independent. Thus, the highest-pressure conditions in steam at a given reaction temperature are preferred for the production of pure H₂. The initial step, EtOH → AA, was the rate-determining reaction, and the model experiments using AA as a substrate showed that the Cannizzaro reaction of two AA molecules to form EtOH and AcOH occurred preferentially. This oxidation system was confirmed to be effective at EtOH concentrations of up to 500 g/L in water.

Keywords: ethanol; green hydrogen; acetic acid; Ru-Sn/TiO₂ catalyst; biomass; reaction mechanism

1. Introduction

The efficient use of biomass as an alternative to fossil resources is attracting attention as a means of mitigating climate change caused by increasing emissions of greenhouse gases. Specifically, bioethanol produced by the fermentation of sugars derived from biomass can be used as a substitute for gasoline. However, the demand for bioethanol as a fuel is expected to decline as electric and fuel cell vehicles become more widespread in the future. Therefore, it is important to develop alternative utilization technologies for bioethanol.

Because bioethanol produced by fermentation contains a large amount of water, it would be preferable to develop techniques that allow the utilization of aqueous ethanol (EtOH) solutions without removing this water. The reforming of EtOH with water is a potential method of converting aqueous EtOH to hydrogen (H₂) and acetic acid (AcOH) via the reaction shown in Equation (1).



Hydrogen is a clean energy carrier, producing only water as a by-product during combustion, but the extent to which this fuel is carbon neutral depends on the manner in which it is produced. Carbon dioxide is emitted in the process of producing H₂ from fossil resources, whereas green H₂ production without CO₂ emissions would be highly desirable. The reforming of bioethanol to generate H₂ is therefore a promising means of reducing CO₂ emissions and the H₂ produced in this manner also has numerous applications such

as a clean fuel and in the synthesis of various chemicals. AcOH is an important industrial chemical feedstock with a global demand of 16.1 million tons in 2022 [1] and can be used as a raw material for the generation of vinyl acetate, cellulose acetate, and other compounds, the majority of which are currently produced from petroleum-based AcOH.

Various organometallic complexes [2,3] and metal catalysts [4–8] have been investigated for the reforming of EtOH with water. Iridium complexes with bipyridonate ligands bearing *N,N*-dimethylamino substituents have been reported to convert aqueous EtOH to H₂ and AcOH with high yields and good selectivity [3]. In this catalytic system, the oxidation is able to proceed under mildly basic conditions, providing a 99% sodium acetate yield (based on the amount of EtOH used) and a 95% theoretical H₂ yield under reflux conditions. Even so, the required reaction time is very long (over 18 h) and the resulting sodium acetate must be protonated to generate pure AcOH. In addition, the spent catalyst must be dried under reduced pressure and then extracted with dichloromethane in preparation for reuse.

Due to their great advantages in industrial applications, many attempts have been made to use supported metal catalysts [4–8]. Cu/ZnO-ZrO₂-Al₂O₃ has been found to catalyze the conversion of aqueous EtOH to AcOH and H₂ with a maximum AcOH yield of 73.3% [4]. However, the selectivity of this process for AcOH decreases with increases in the EtOH concentration as by-products such as ethyl acetate, acetaldehyde (AA), methyl ethyl ketone, and butanol are produced. This previous work also did not report the purity of the H₂ obtained. CuCr can provide almost complete EtOH conversion but gives a reported AcOH yield of only 48.6% based on the formation of a high proportion of AA (approximately 50%) as an oxidation intermediate [5]. The temperature range used for these metal catalysts is also generally high (250–300 °C for Cu/ZnO-ZrO₂-Al₂O₃ and 350 °C for CuCr).

Supported precious metal catalysts have been used to lower the reaction temperature. Nozawa et al. [6] used Ru/TiO₂ for aqueous-phase reforming of EtOH at 200 °C, but the main products were CH₄ and CO₂ rather than AcOH, resulting in the lower H₂ purity. Such high selectivity of gaseous products in aqueous-phase reforming of EtOH has also been reported for carbon black- and carbon nanotube-supported Pd and PdZn catalysts at 250 °C [7]. The addition of rhenium to the TiO₂ supported Ru, Rh, Ir, and Pt catalysts was reported to improve the selectivity of AcOH and H₂, but the conversion of EtOH was only less than 37% even after 10 h at 200 °C in a batch reactor [8].

For all these reasons, the catalytic reforming of aqueous EtOH to H₂ and AcOH is not yet sufficiently mature to allow for practical applications as an approach to green H₂ production. On this basis, the present study assessed the performance of Ru-Sn/TiO₂ as an efficient and selective catalyst for the production of H₂ and AcOH in a flow reactor and discusses the reaction mechanisms involved in this conversion. In previous studies by the authors on the hydrogenation of AcOH to EtOH while investigating bioethanol production via AcOH fermentation, Ru-Sn/TiO₂ was developed as an effective catalyst capable of functioning in aqueous media [9,10]. The formation of the gaseous products was effectively suppressed by the addition of Sn to Ru/TiO₂ [9], and the hydrogenolysis efficiency of AcOH to EtOH was significantly improved by using a continuous flow reactor [10]. The 4 wt%Ru-4 wt%Sn/TiO₂ (based on the weight of TiO₂) was selected in accordance with the previous investigation to optimize the Ru and Sn contents and to minimize the production of gaseous by-products from the hydrogenolysis of aqueous AcOH [9].

2. Results and Discussion

2.1. Effect of Temperature at 0.1 MPa

The oxidation of a 10 g/L aqueous EtOH solution over 4 wt%Ru-4 wt%Sn/TiO₂ was performed over the temperature range of 190–260 °C at atmospheric pressure (0.1 MPa) in a flow-type reactor. The yields of liquid-phase products, of gaseous products other than H₂, and of H₂, together with the H₂ purity, are summarized in Figure 1A–C, respectively. Under all conditions, water vapor was present in the gas phase. The data show that two

moles of H_2 were obtained from each mole of EtOH (as expected according to Equation (1)) and so the H_2 yields are reported herein relative to the expected theoretical yields. That is, a theoretical yield of 100% H_2 would be equivalent to a yield of 200 mol% based on the initial amount of EtOH. Yields of other products are given as mol% based on the actual amount of EtOH used in the trial.

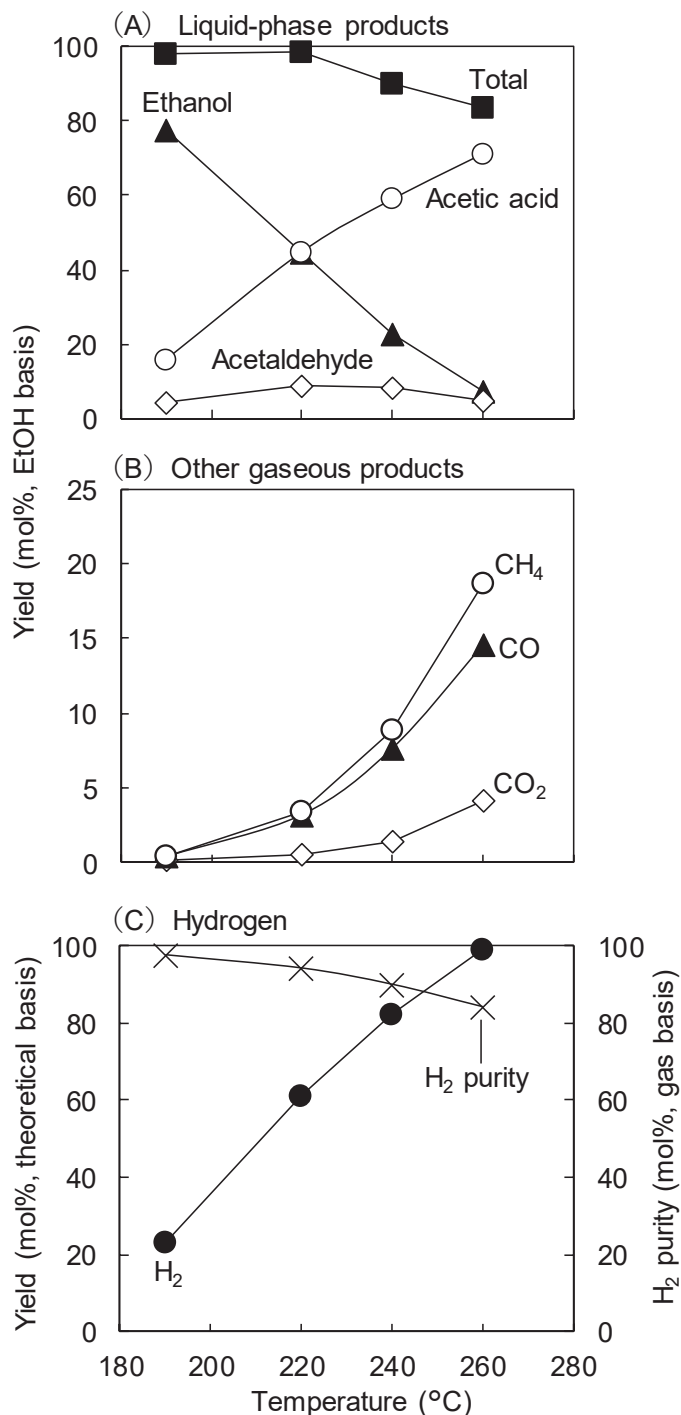


Figure 1. The effects of reaction temperature on the conversion of aqueous EtOH (10 g/L) to AcOH and H_2 , based on the outputs of (A) liquid-phase products, (B) gaseous products other than H_2 and (C) H_2 . The graph in (C) also plots H_2 purity in the gaseous products as a function of temperature. Data were acquired with a reactor column having a 3.9 mm diameter and 100 mm length with a pump flow rate of 0.3 mL/min at a pressure of 0.1 MPa.

The EtOH conversion efficiency increased from 22.4% to 92.8% as the reaction temperature was increased from 190 to 260 °C. The yields of H₂ and AcOH also increased, from 23.2% to 99.4% (on a theoretical basis) and from 16.0 mol% to 71.2 mol% (on an EtOH basis), respectively. The yield of AA, the intermediate in EtOH oxidation, remained low (from 4.6–8.7 mol% based on EtOH) regardless of the reaction temperature, indicating that the second step in this process (AA → AcOH) occurred more efficiently in the sequential oxidation scheme (EtOH → AA → AcOH).



The yields of all gaseous products, including H₂, increased with increases in the reaction temperature. However, the CH₄, CO, and CO₂ formation rates all increased exponentially, whereas that of H₂ exhibited a linear increase (Figure 1B,C). Consequently, the purity of H₂ decreased from 97.9 mol% at 190 °C to 84.1 mol% at 260 °C at 0.1 MPa. The total combined yield of CH₄, CO, and CO₂ reached 37.4 mol% (EtOH basis) at 260 °C, while the total combined yield of the liquid products (EtOH, AcOH and AA, Figure 1A) decreased from 98.1 mol% at 190 °C to 83.5 mol% at 260 °C. Although the EtOH conversion was low at the lower temperatures, the selectivities for H₂ and AcOH were relatively high, giving almost pure products. At higher temperatures, the conversion of EtOH was increased but the selectivity decreased as a result of the increased fragmentation of AA and AcOH.

2.2. Effect of Pressure at 260 °C

Additional reactions of 10 g/L aqueous EtOH were performed over the pressure range of 0.1 to 6.0 MPa at a fixed temperature of 260 °C (Figure 2). The aqueous phase transitioned from steam to liquid water upon increasing the reaction pressure to the saturated vapor pressure of water, which was estimated to be 4.7 MPa at 260 °C using the Soave–Redlich–Kwong model with the ProII 2022 process simulator. The residence time as shown in this figure was also increased up to 3.1 s at 4.0 MPa by compressing the steam, based on increasing the reaction pressure. The residence time was significantly longer in the liquid aqueous phase (93 s at 6.0 MPa). The amount of unreacted EtOH increased with increases in the reaction pressure, and this trend became more pronounced at 6.0 MPa, at which the water vapor was converted to liquid water even though the residence time increased with increasing pressure. Thus, the oxidation of EtOH was more efficient in the gas phase and a lower pressure improved the conversion of EtOH in the steam. The H₂ yields showed a similar trend to the EtOH conversion throughout the pressure range used in this study.

In contrast, the AcOH yield was almost constant at approximately 70 mol% over the pressure range of 0.1–4.0 MPa based on gas-phase reactions, while the H₂ purity gradually increased from 84.1 mol% at 0.1 MPa to 93.2 mol% at 4.0 MPa. The latter effect is ascribed to decreases in the yields of CO and CH₄ derived from the fragmentation of AA (Equation (3)). The yield of CO became almost zero at pressures of 3 to 4 MPa, indicating that the fragmentation of AA was completely suppressed under such conditions. Conversely, the CO₂ yield was constant over the pressure range of 0.1–4.0 MPa, whereas the CH₄ yield plateaued, suggesting that the fragmentation of AcOH (Equation (2)) also occurred but the progress of the reaction was independent of pressure. Therefore, a reaction pressure slightly lower than the saturated vapor pressure of water at a given reaction temperature was evidently optimal with regard to obtaining high-purity H₂.

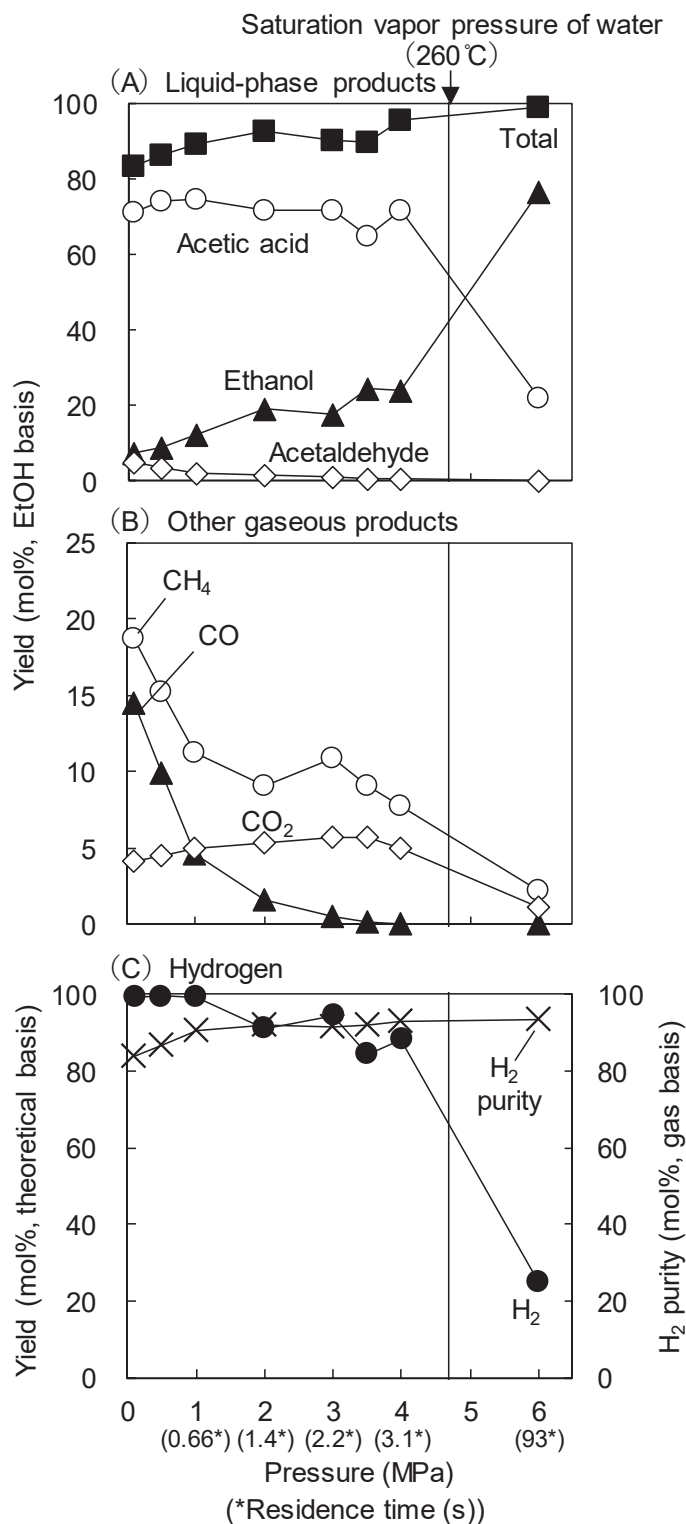


Figure 2. The effects of reaction pressure on the conversion of aqueous EtOH (10 g/L) to AcOH and H₂, based on the outputs of (A) liquid-phase products, (B) gaseous products other than H₂ and (C) H₂. The graph in (C) also plots H₂ purity in the gaseous products as a function of pressure. Data were acquired with a column having a 3.9 mm diameter and 100 mm length with a pump flow rate of 0.3 mL/min at a temperature of 260 °C.

The yield of AA was consistently low, as can be seen from Figure 1, but tended to decrease with increases in reaction pressure. From this outcome, it appears that the conversion of AA to AcOH was more efficient at higher pressures. The opposite trend

was observed for the fragmentation of AA to CH₄ and CO. The effects of reaction pressure on the various steps involved in the conversion of EtOH in the vapor phase at 260 °C are summarized in Table 1.

Table 1. Summary of the effects of reaction pressure on the steps involved in the conversion of aqueous EtOH in steam over 4 wt%Ru-4 wt%Sn /TiO₂ at 260 °C.

Step	Preferred Condition
EtOH → AA (rate-determining)	Lower pressure (0.1–2 MPa)
AA → AcOH	Higher pressure (2–4 MPa)
AA → CH ₄ + CO	Lower pressure (0.1–2 MPa)
AcOH → CH ₄ + CO ₂	No effect

2.3. Cannizzaro Reaction

To better understand the reactivity of the AA intermediate, a 10 g/L aqueous solution of AA was reacted over 4 wt%Ru-4 wt%Sn/TiO₂ at pressures between 0.1 and 4.0 MPa at 260 °C. The results are shown in Figure 3. At all pressures, the AA was almost completely reacted (with recoveries of 0.0–1.0%) and AcOH and H₂ were formed. The H₂ yields were high (82.2–93.2% on a theoretical basis), indicating that the conversion of AA to AcOH and H₂ was highly selective. Note that, in these trials, a 100% theoretical yield of H₂ was equivalent to 100 mol% based on the amount of AA used. Unexpectedly, EtOH was found to have been produced from the AA, although the yields were less than 10.2 mol%. Evidently, the Cannizzaro reaction occurred. In this reaction, two molecules of a non-enolizable aldehyde give a primary alcohol and a carboxylic acid (Equation (4)) [11,12].



The EtOH produced by the Cannizzaro reaction in these trials was subsequently converted to AA (Figure 4).

In addition to the Cannizzaro reaction, the direct oxidation of AA (Equation (5)) was also expected to take place during the conversion of EtOH to AcOH (Figure 4). To evaluate this phenomenon, the amount of EtOH produced by the Cannizzaro reaction, EtOH (Cannizzaro), was estimated based on Equation (6), assuming that the EtOH obtained from the original AA (Figure 3) had a reactivity similar to that of EtOH during the trials used to generate the data in Figure 2.

$$\text{EtOH (Cannizzaro)} \times \text{Recovery rate (EtOH ex)} = \text{EtOH (O)} \quad (6)$$

In this equation, Recovery rate (EtOH ex) is the percentage of the original EtOH recovered following the EtOH oxidation reaction used to generate the data in Figure 2. EtOH (O) is the amount of EtOH observed in the experiment of AA as a substrate (Figure 3). The estimated EtOH (Cannizzaro) yield values are plotted in Figure 5. Because the theoretical EtOH (Cannizzaro) yield had a maximum of 50 mol% based on the original amount of AA, the approximately 50 mol% values estimated for the trials at 0.1, 0.5, and 1.0 MPa indicate that the conversion of AA occurred primarily via the Cannizzaro reaction rather than the direct oxidation pathway. In contrast, the estimated EtOH (Cannizzaro) yields were lower (30–40 mol%) in the pressure range of 2.0–4.0 MPa, demonstrating that the direct oxidation of AA became competitive with the Cannizzaro reaction at these pressures, although the Cannizzaro reaction was still preferred even under these conditions.

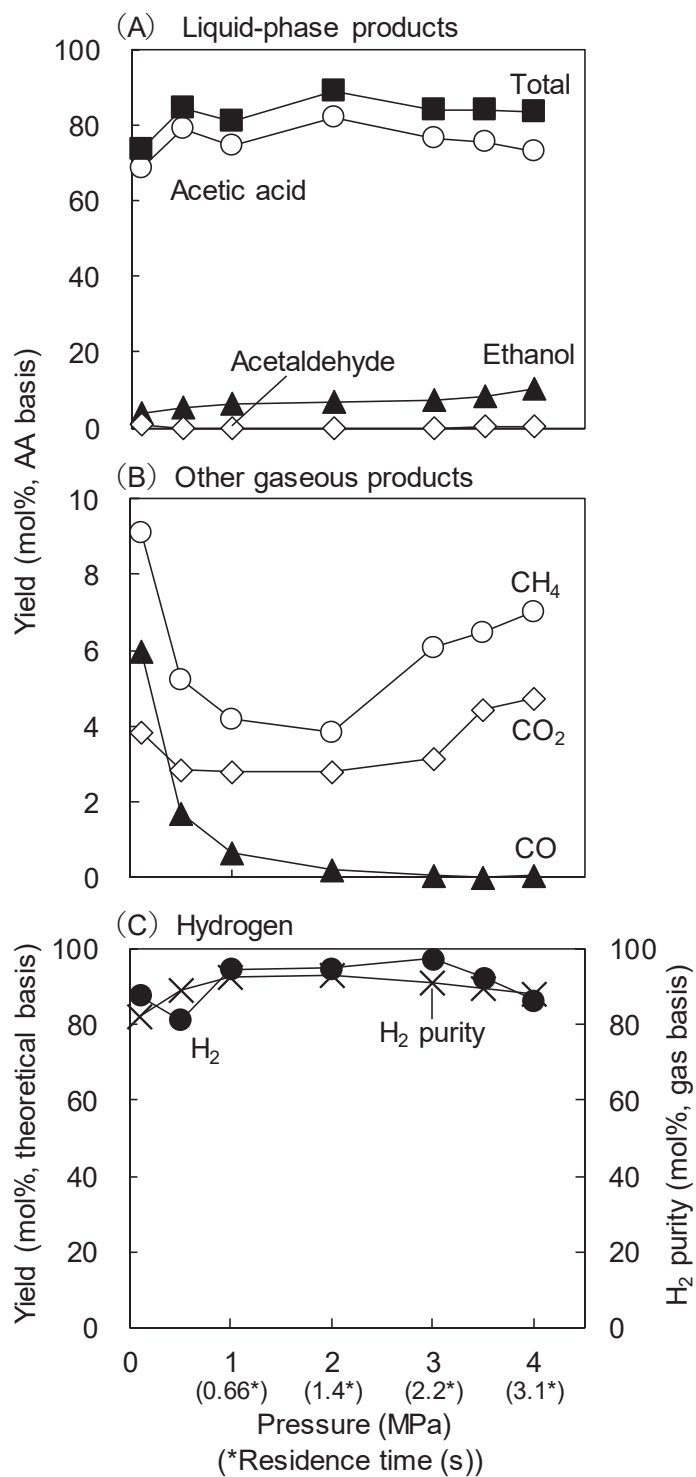


Figure 3. The effects of reaction pressure on the conversion of aqueous AA (10 g/L) to AcOH and H₂, based on the outputs of (A) liquid-phase products, (B) gaseous products other than H₂ and (C) H₂. The graph in (C) also plots H₂ purity in the gaseous products as a function of pressure. Data were acquired using a reactor column with dimensions of 3.9 mm diameter and 100 mm length with a pump flow rate of 0.3 mL/min at 260 °C.

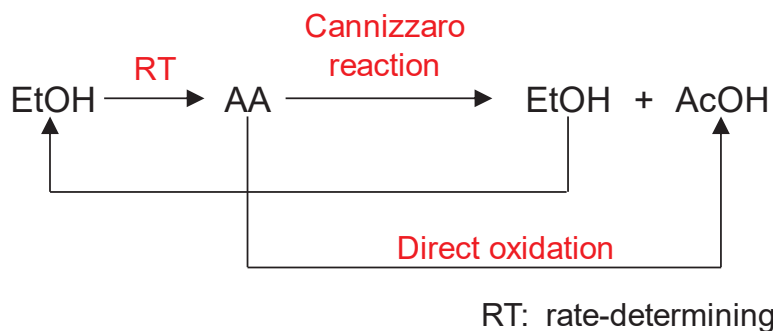


Figure 4. A diagram showing the Cannizzaro reaction and direct oxidation of AA, which represent competing pathways during the oxidation of EtOH.

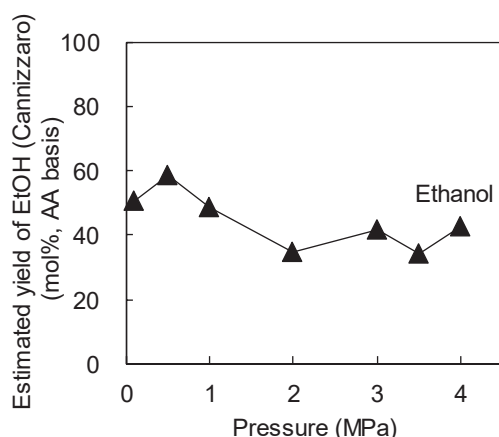


Figure 5. The effects of reaction pressure on the yield of EtOH produced by the Cannizzaro reaction during the reaction of AA. EtOH (Cannizzaro) refers to EtOH produced from AA by the Cannizzaro reaction. Data were acquired using a reaction column having dimensions of 3.9 mm diameter and 100 mm length with a pump flow rate of 0.3 mL/min at a temperature of 260 °C.

The composition of the gaseous by-product mixture provided insights into the fragmentation reactions of AA and AcOH. Similar to the trials using EtOH (as shown in Figure 2), the yields of CO and CH₄ resulting from the fragmentation of AA decreased with increases in reaction pressure (Figure 3B). Interestingly, the yields of CO and CH₄ obtained from the AA experiments were approximately half those obtained from trials using EtOH solutions (CO: 14.5 → 6.0 mol%, CH₄: 18.7 → 9.1 mol%). This change can be explained by considering that the fragmentation reaction of AA occurred only during the conversion of EtOH to AA on the surface of the 4 wt%Ru-4 wt%Sn/TiO₂, as shown in Figure 6. In the trials using the AA solutions, the amount of EtOH involved in the conversion process was approximately half the amount of AA because the Cannizzaro reaction converted AA according to the relationship 2AA → EtOH + AcOH. It is not presently clear why the fragmentation of AA did not occur in conjunction with the Cannizzaro reaction catalyzed by 4 wt%Ru-4 wt%Sn /TiO₂.

In contrast, the CO₂ yields obtained from the fragmentation of AcOH to give CO₂ and CH₄ were approximately 5 mol% when using either AA or EtOH. This outcome suggests that the yields of these compounds were dependent on the amount of AcOH that was produced. The yields of CO₂ and CH₄ during the AA trials (Figure 3B) tended to increase along with pressure on going from 2 to 4 MPa, showing that the fragmentation of AA was more efficient at higher pressures. However, this effect was not as evident during the experiments using the EtOH solution (Figure 2B).

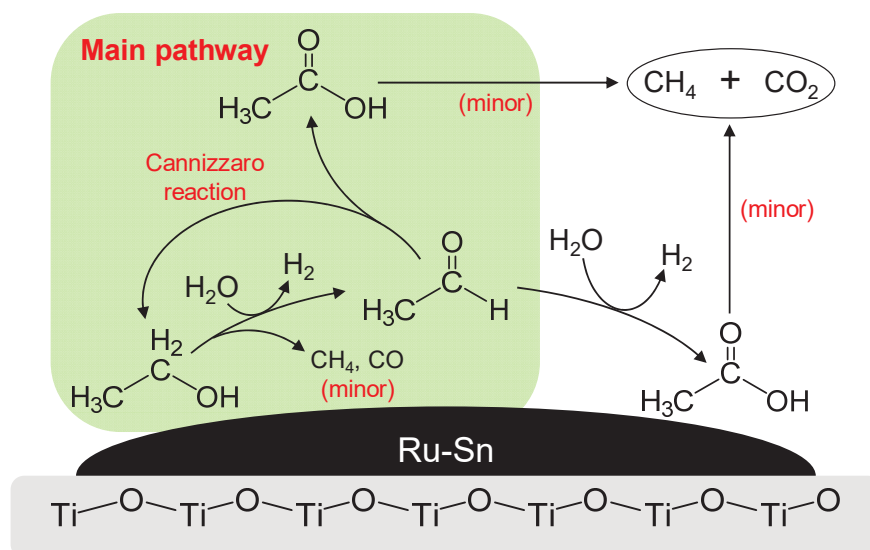


Figure 6. A proposed mechanism for the conversion of aqueous EtOH to AcOH and H₂ with the formation of gaseous by-products over a 4 wt%Ru-4 wt%Sn/TiO₂ catalyst.

Because the Cannizzaro reaction did not produce H₂ and the contribution of the direct oxidation of AA to AcOH was minimal, the majority of the H₂ would have been generated during the oxidation of EtOH to AA on the catalyst (Figure 6).

2.4. Oxidation of High-Concentration Aqueous EtOH Solutions

The oxidation of more highly concentrated aqueous EtOH solutions (100 and 500 g/L) was also attempted at 260 °C and 4 MPa or 320 °C and 10 MPa, with the results presented in Table 2. The latter conditions were the most extreme that could be obtained with the flow-type reactor system used in this study. The conversions obtained using the 100 g/L EtOH were 26.7% and 62.8% at 260 °C (4 MPa) and 320 °C (10 MPa), respectively. The corresponding yields of AcOH/H₂ were 21.4 mol%/30.1% and 50.7 mol%/72.3%, along with H₂ purities of 98.2% and 86.1%, respectively. Although the reactivity was not as high (with an EtOH conversion of just 13.1%) in trials with the 500 g/L EtOH at 320 °C and 10 MPa, the reacted EtOH was selectively converted to both AcOH and H₂ (10.4 mol% AcOH with a H₂ purity of 90.9%). These results suggest that this catalytic system could represent a viable approach to producing green H₂ and AcOH, although further development is needed to produce a larger-scale system capable of processing highly concentrated aqueous EtOH.

Table 2. Conversions of high-concentration aqueous EtOH solutions (10, 100 or 500 g/L) to AcOH and H₂ using a column with dimensions of 3.9 mm diameter and 100 mm length with a pump flow rate of 0.3 mL/min at various temperatures and pressures.

Temp. (°C)	Press. (MPa)	Conc. (g/L)	EtOH Conversion (%)	Yield (mol%) *						H ₂ Purity (%)
				AcOH	AA	CH ₄	CO	CO ₂	H ₂	
260	4	10	76.2	71.9	0.4	7.75	0.06	4.99	88.4	93.2
		100	26.7	21.4	1.0	0.66	0.07	0.38	30.1	98.2
320	10	100	62.8	50.7	2.4	10.89	1.18	7.23	72.3	88.1
		500	13.1	10.4	1.5	2.81	1.39	1.36	29.7	90.9

* The yields of AcOH, AA, CH₄, CO and CO₂ are on an EtOH basis, and the yields of H₂ are on a theoretical basis.

3. Materials and Methods

3.1. Materials and Catalyst Preparation

Titanium isopropoxide (>95%), tin (II) chloride dihydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, >97%), ruthenium (III) chloride (RuCl_3), sodium hydroxide (NaOH , >97%), 2-propanol (>99%), and hydrochloric acid (HCl , 6 mol/L) were used for catalyst preparation. EtOH (>99.5%), AcOH (>99%), and AA (>99%) were employed for the catalytic conversion trials. The RuCl_3 was purchased from the Tokyo Chemical Industry Co., Ltd., Tokyo, Japan, while all other reagents were obtained from Nacalai Tesque, Inc., Kyoto, Japan. Hydrogen (>99.9%) was purchased from the Imamura Sanso Co., Ltd., Shiga, Japan.

The 4 wt%Ru-4 wt%Sn/ TiO_2 catalyst was prepared by a sol-gel precipitation technique [10]. In this process, RuCl_3 (0.82 g, corresponding to 4 wt% Ru based on 10 g TiO_2) and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (0.76 g, corresponding to 4 wt% Sn based on 10 g TiO_2) were added to hot water (100 mL, 60 °C). Following this, a mixture of 2-propanol (20 mL) and titanium isopropoxide (37.2 mL) was added dropwise with stirring. After waiting 30 min for TiO_2 to precipitate, an aqueous NaOH solution (100 mL, having a concentration sufficient to neutralize the metal chlorides) was added and the mixture was stirred for 30 min. The mixture was subsequently allowed to stand for 12 h and the resulting precipitate was filtrated and then washed five times with water, oven-dried in air at 105 °C for 12 h, calcined at 450 °C for 1 h, and then reduced under a H_2 flow (100 mL/min) at 400 °C for 5 h. Following this, the material was ground to a powder having an average particle size in the range of approximately 50–70 μm and then packed into a stainless-steel column (internal diameter, 3.9 mm; length, 100 mm).

According to a previous study [9], the crystal structure of the TiO_2 is mostly anatase type, and the BET surface area and crystallite diameter of TiO_2 of the 4 wt%Ru-4 wt%Sn/ TiO_2 catalyst were reported to be 84.5 m^2/g and 7.7 nm, respectively. Regarding the stability of the catalyst, no difference in catalytic activity was observed even after the continuous use in the temperature range of 140–320 °C for 60 h in the hydrogenolysis of aqueous AcOH [10].

3.2. Catalytic Conversion and Product Analysis

A flow-type reactor (H-cube ProTM, ThalesNano Inc., Budapest, Hungary) equipped with an electric furnace (Phoenix, ThalesNano Inc.), as shown in Figure 7, was used for these trials. In each experiment, an aqueous solution of EtOH, AcOH, or AA (10 g/L in each case) was fed into the catalyst column at a flow rate of 0.3 mL/min at a temperature in the range of 190–260 °C and a pressure in the range of 0.1–6.0 MPa. The resulting mixture was fractionated into aqueous and gaseous phases.

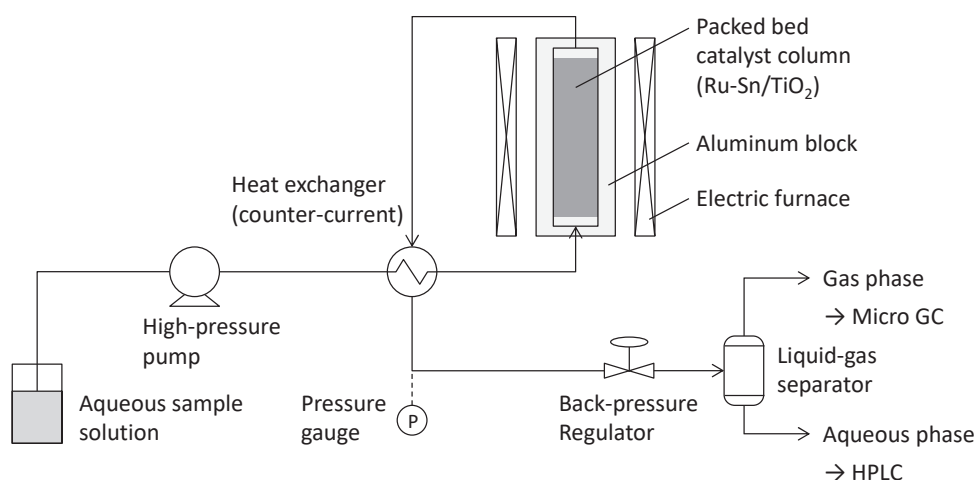


Figure 7. The flow-type reactor used for catalytic conversion trials.

The aqueous phase was analyzed by high-performance liquid chromatography (LC-20 system, Shimadzu Corp., Kyoto, Japan) using an Aminex HPX-87H column (300 mm × 7.8 mm, Bio-Rad Laboratories, Inc., Hercules, CA, USA) with 5 mM sulfuric acid in water as the mobile phase at a flow rate of 0.6 mL/min and a column temperature of 60 °C, employing a refractive index detector (RID-20A, Shimadzu Corp.). The total yield of gaseous products was quantified by the water displacement method using a graduated cylinder. The composition of these products was determined by micro gas chromatography (CP-4900, Varian Medical Systems, Palo Alto, CA, USA). These analyses used a 10 m MS5A column with argon as the carrier gas and a column temperature of 100 °C and inlet pressure of 170 kPa along with a thermal conductivity detector or a 10 m PoraPLOT Q column with helium as the carrier gas and a column temperature of 80 °C and inlet pressure of 190 kPa with a thermal conductivity detector.

4. Conclusions

The oxidation of aqueous EtOH (10 g/L) over 4 wt%Ru-4 wt%Sn/TiO₂ was investigated at various temperatures at a pressure of 0.1 MPa and at various pressures at a temperature of 260 °C. The following conclusions were obtained.

1. The conversion of aqueous EtOH to AcOH and H₂ over 4 wt%Ru-4 wt%Sn/TiO₂ was more efficient in the gas phase than in the liquid aqueous phase.
2. The selectivities for AcOH and H₂ were generally high.
3. Methane, CO, and CO₂ were produced as gaseous by-products via the fragmentation of AA to give CO and CH₄ and of AcOH to give CO₂ and CH₄, thus reducing the H₂ purity.
4. At a fixed reaction temperature of 260 °C in the gas phase, the EtOH conversion decreased with increasing pressure, whereas the H₂ purity increased because of the less-efficient reaction of AA to generate CO and CH₄ at the higher pressure.
5. The fragmentation of AcOH to CO₂ and CH₄ was independent of the reaction pressure.
6. The first reaction, EtOH → AA, was the rate-determining step in this process and AA was converted to AcOH and EtOH by the Cannizzaro reaction rather than undergoing direct oxidation to AcOH.
7. The fragmentation of AA occurred during the conversion of EtOH on the surface of the 4 wt%Ru-4 wt%Sn/TiO₂ catalyst prior to the removal from the surface.
8. Highly concentrated aqueous EtOH solutions (100 and 500 g/L) could also be employed with this process to selectively produce H₂ and AcOH.
9. The reaction pressure should be slightly less than the saturation vapor pressure of water to selectively obtain AcOH and H₂.
10. The use of the 4 wt%Ru-4 wt%Sn/TiO₂ catalyst in a flow reactor was found to be an effective method for the aqueous-phase reforming of EtOH to AcOH and H₂ with high purity. This provides insight into the industrial production of green hydrogen and AcOH.

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Article

Enhancing the Catalytic Activity of Eggshell-Derived CaO Catalyst and Its Application in Biodiesel Production from Waste Chicken Fat

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Abstract: The comparatively greater cost of producing biodiesel in comparison to petroleum diesel is one of the key drawbacks. Eggshells and leftover chicken fat are examples of poultry wastes that can be used to produce biodiesel at a low cost as catalysts and oil, respectively. In this study, eggshell-derived CaO and its doping with sodium methoxide catalyst for enhancing catalytic activity was synthesized for the transesterification of waste chicken fat and characterized by FT-IR and XRD analyses. XRD studies confirmed the crystalline structure of the developed catalyst and doping of sodium with eggshell-derived CaO. The transesterification reaction was performed at different reaction parameters such as the catalyst loading, the methanol to oil ratio, the reaction temperature, and the reaction time. The biodiesel produced at the maximum yield was evaluated by gas chromatography mass spectrometry analysis. A maximum yield of 96% biodiesel was obtained with catalyst loading of 2 wt% of oil, as well as a methanol to oil ratio of 13:1 at 60 °C in 1 h. The output demonstrates that eggshell waste is a potentially accessible source of biomass-derived nano catalyst for the synthesis of biodiesel using chicken fat as a feedstock.

Keywords: eggshells; catalysts; biofuel; renewable; sustainable

1. Introduction

From the last decade, there has been a continuous growing trend in producing and consuming biofuels in transportation and energy sectors [1–3]. Because of the problems and limitations associated with the use of fossil fuels, there will be a significant rise in the demand for biofuels in near future [4–6]. Biodiesel is one of the important biofuels and an alternative energy source because it possesses similar properties, such as a high flash point, a high cetane number, good lubricity, non-toxicity, low sulfur contamination, etc., compared to conventional fossil fuels [7,8]. Biodiesel is a mono alkyl ester of long-chain fatty acids produced from a range of feedstocks, e.g., edible and non-edible oils. Moreover, non-edible oils are in forefront of this field as these overcome the food vs. fuel debate caused by edible oils [9,10]. In the last few years, biodiesel has been produced and is being consumed as an alternative to fossil fuel on a commercial scale, and it is available in fuel markets [11,12]. The type of feedstock used is the main economic contributor, which can have a remarkable effect on biodiesel production costs [13,14]. Therefore, using non-edible

oils can reduce biodiesel production costs and biomass-derived feedstock costs. Hence, the choice of feedstock is very important in biodiesel production [15,16].

Animal fat wastes (AFWs) are easily available in slaughterhouses, farms, and restaurants in almost every region of the world. AFWs are not consumed by human beings directly and are disposed of in an open environment, which causes several health and environmental problems [17]. That is why the valorization of such wastes to derive different valuable products is more desirable to address these concerns. Numerous reports in the literature indicate that AFWs are composed of free fatty acids and triglycerides as major constituents [18]. Hence, AFWs such as tallow, lard, and chicken fats are considered as more promising candidates for producing biodiesel [19]. The biodiesel produced from using AFWs has number of advantages such as lower emissions and a higher cetane number due to the high ratio of free fatty acids in AFWs. Moreover, the biodiesel obtained from AFWs exhibits oxidative stable characteristics [20]. The transesterification of the oil extracted from AFWs is an obvious and affordable way to produce biodiesel from AFWs feedstock [21,22]. Transesterification is the reaction of triglycerides with methanol in presence of suitable catalyst and operating conditions. The reaction rate of transesterification can be faster when using different catalysts [23,24]. Different homogeneous and heterogeneous catalysts have been developed for optimum biodiesel production. Among these, heterogeneous catalysts are superior due to their ease of separation from the final products [25]. However, the synthesis of chemical and biological heterogeneous catalysts is a challenging task from an industrial point of view [26]. To cope with this problem, biomass-derived nano catalysts are intriguing due to their cost effective synthesis [27].

Waste eggshells are easily accessible as chicken eggs are commonly consumed on a regular basis by humans. Waste eggshells are recognized as one of the suitable precursors of CaO, an active catalyst in biodiesel production [28]. However, the lone CaO is not stable and active as it requires a long period of time to achieve equilibrium conversion [29]. Therefore, it has been attempted here to develop a CaO-based catalyst to overcome the mentioned problem. Various reports are available in the literature, which focus on enhancing the properties of CaO by using different chemical and physical ways [30–33]. It can also be concluded that the activity and stability of CaO can be improved by doping with a suitable dopant [34–36]. It has been reported that the employment of CaO as a catalyst resulted in an 80% increase in the amount of biodiesel produced. The yield with tungsten- and molybdenum-doped CaO, on the other hand, was roughly 96% [37,38]. The generation of biodiesel from Nahor oil (*Mesua ferrea* Linn) with lithium-doped CaO achieves an efficiency of approximately 94% [39]. In the process of producing methyl esters, the methoxide ions function as an active catalyst. This chemical unit is responsible for attacking the triglyceride molecules and resulting in the production of methyl esters. It is regenerated at the end of each reaction step when a hydrogen ion is stripped from a nearby methanol molecule. To the best of the authors' knowledge, there has been no report in the literature indicating a CaO-based catalyst with sodium methoxide as an active species. Hence, herein, a CaO-based catalyst with enhanced activity due to incorporation with sodium methoxide (CH_3NaO) as an active species is reported. Further, the designed catalyst $\text{CaO-CH}_3\text{NaO}$ was used in the transesterification reaction of oil obtained from chicken fat. Additionally, this work also emphasizes the optimization of catalyst loading and reacting conditions for transesterification to produce biodiesel from chicken fat oil.

2. Result and Discussions

2.1. FTIR Analysis

Figure 1 shows the FTIR analysis $\text{CaO-CH}_3\text{NaO}$ catalysts with different loadings and the uncalcined $\text{CaO-CH}_3\text{NaO}$ catalyst. The band of CaO appeared at around 649 cm^{-1} , which indicates the presence of Ca-O vibration [40]. The area looked different in uncalcined and calcined CaO at 649 cm^{-1} . The single bond region includes $1500\text{--}500\text{ cm}^{-1}$, and CaO peaks observed at 649 cm^{-1} , which are a strong indication of its presence. NaO stretching was observed at 719 cm^{-1} in calcined and un-calcined groups. As concentration increases,

the broader and strong peak observed shows stretching and an absorbance band of NaO. At 1090 cm^{-1} , the C-OH stretching is observed in that region. At 1390 cm^{-1} , the broader peak is shown due to the presence of CH_3 . As concentration increases and after calcination at 700°C , the CH_3 has a strong broader peak, indicating its confirmation. The presence of a peak for the produced catalyst at 3680 cm^{-1} is due to the formation of OH in $\text{Ca}(\text{OH})_2$ during H_2O adsorption by calcium oxide [40].

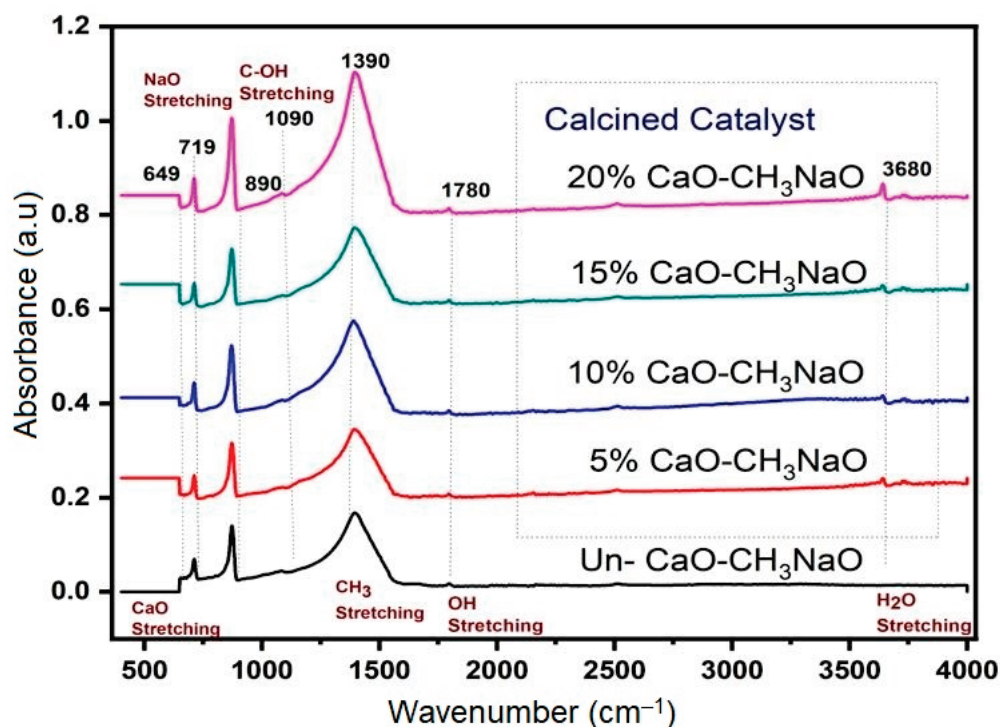


Figure 1. FTIR analysis of uncalcined and calcined CH_3NaO -doped CaO catalyst with different doping ratios.

2.2. XRD Characterization

XRD studies confirmed the crystalline structure of CH_3NaO -doped CaO catalyst using different doping ratios of dopant, as is shown in Figure 2. For the 5% $\text{CaO-CH}_3\text{NaO}$ catalyst, the peaks at 31.66° , 36.72° , and 52.92° correspond to CaO (COD entry no. 96-900-6706) [41], while the peaks at 29.84° , 42.70° , and 52.96° were found regarding sodium (COD entry no. 96-901-1003) [42]. The peaks at 31.78° , 36.86° , and 53.12° are CaO peaks (COD entry no. 96-900-6703) [41], and the peaks at 29.84° , 42.70° , and 52.96° are sodium peaks (COD entry no. 96-901-1003) [42] in 10% $\text{CaO-CH}_3\text{NaO}$ catalyst. As far 15% $\text{CaO-CH}_3\text{NaO}$ catalyst is concerned, the angles 32.24° , 37.38° , and 53.90° correspond to CaO (COD entry no. 96-720-0687) [43], and 29.90° , 42.80° , and 53.08° correspond to sodium (COD entry no. 96-900-8545) [44]. In 20% $\text{CaO-CH}_3\text{NaO}$ catalyst, CaO peaks (COD entry no. 96-900-6746) were found at 30.82° , 35.74° , and 51.44° [41], while sodium peaks were found at 29.84° , 42.70° , and 52.96° (COD entry no. 96-901-1003) [42]. In summary, it is clear from XRD studies that the calcined CaO XRD spectra of calcined CaO without sodium doping contain peaks corresponding to CaO only. No peaks relevant to sodium were found. Meanwhile, the XRD spectra of calcined CaO doped with sodium clearly showed additional peaks, indicating the successful doping of sodium responsible for enhancing the catalytic activity of calcined CaO .

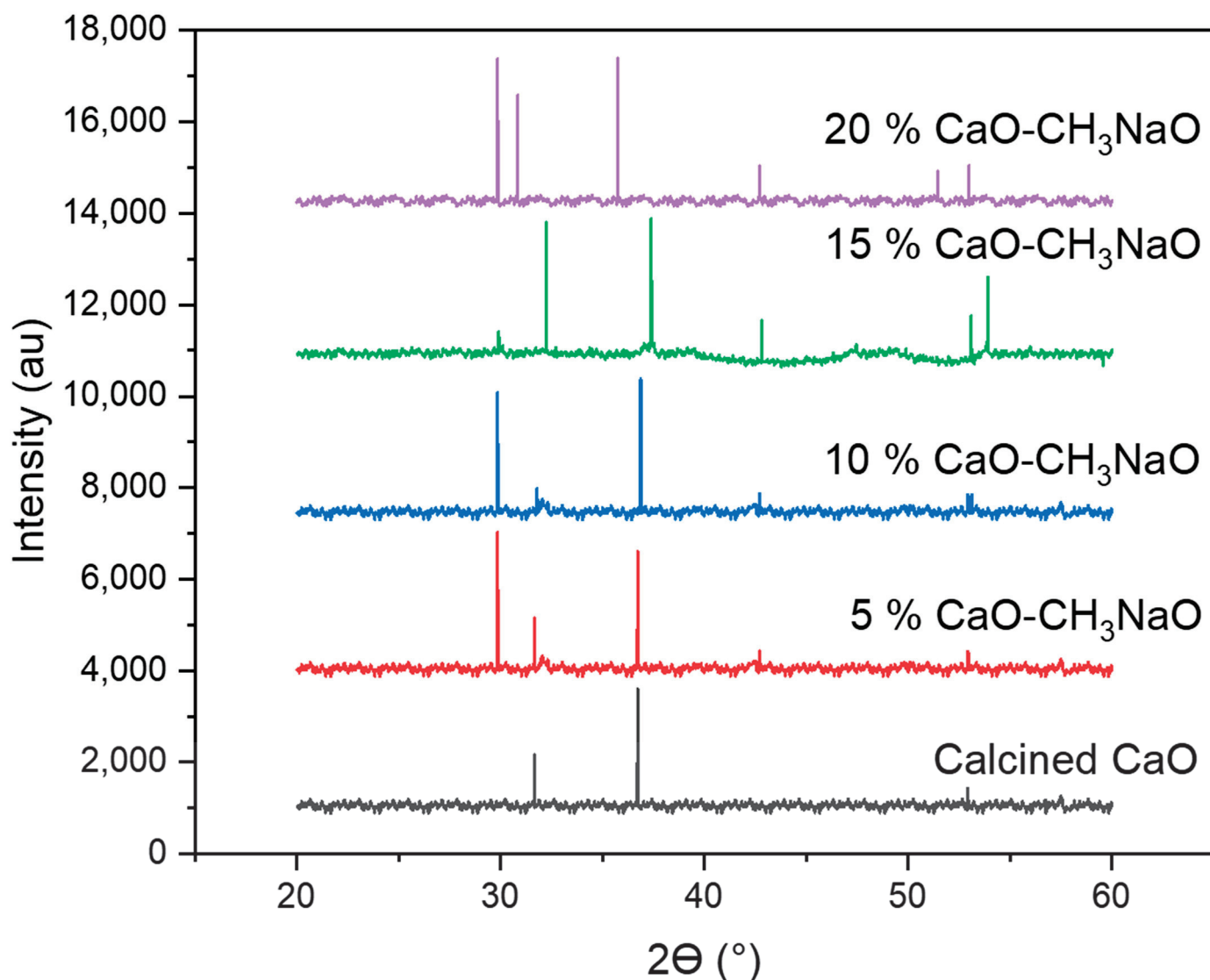


Figure 2. XRD studies of calcined CaO and CH₃NaO-doped CaO catalyst with different doping ratios.

2.3. GC-MS Analysis

The GC-MS analysis was performed to determine the composition of biodiesel obtained from chicken fat oil. Figure 3 shows the chromatogram of biodiesel obtained using 5% catalyst loading (sample B1), while Figures 4 and 5 show the chromatograms of biodiesel generated using 10% (sample B2) and 15% (sample B3) catalyst loading, respectively. Moreover, the detailed summary of the GC-MS analysis of biodiesel obtained by using CaO catalysts with 5, 10, and 15% loadings of sodium methoxide is presented in Table 1. The biodiesel produced using 5% CaO-CH₃NaO was composed of methyl esters at retention peaks of 18.46, 19.76, 33.49, and 35.57, with octenyl ester at 44.52. Similarly, the biodiesel produced using 10% CaO-CH₃NaO contained butyl esters at peaks of 8.24 and 11.41 and methyl esters at peaks of 14.71, 17.01, 20.12, 26.62, and 36.85. Meanwhile, the biodiesel produced using 15% CaO-CH₃NaO comprised methyl esters at peaks of 8.22, 29.86, 33.64, 37.04, 40.35, and 44.5.

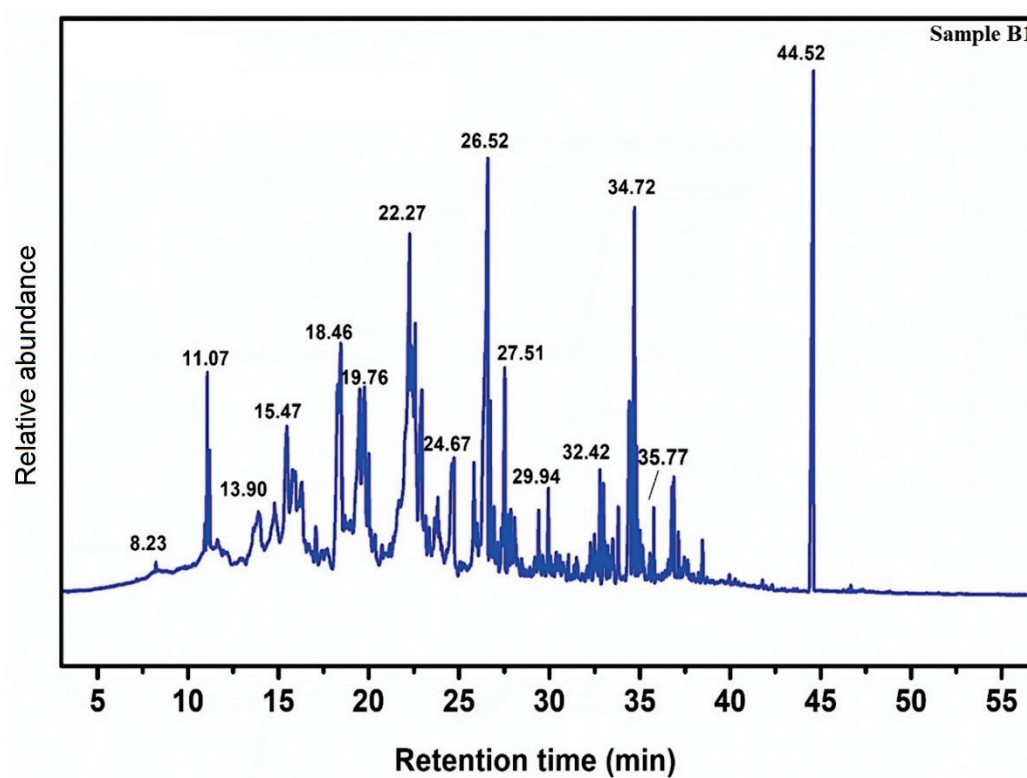


Figure 3. GC-MS analysis of sample B1.

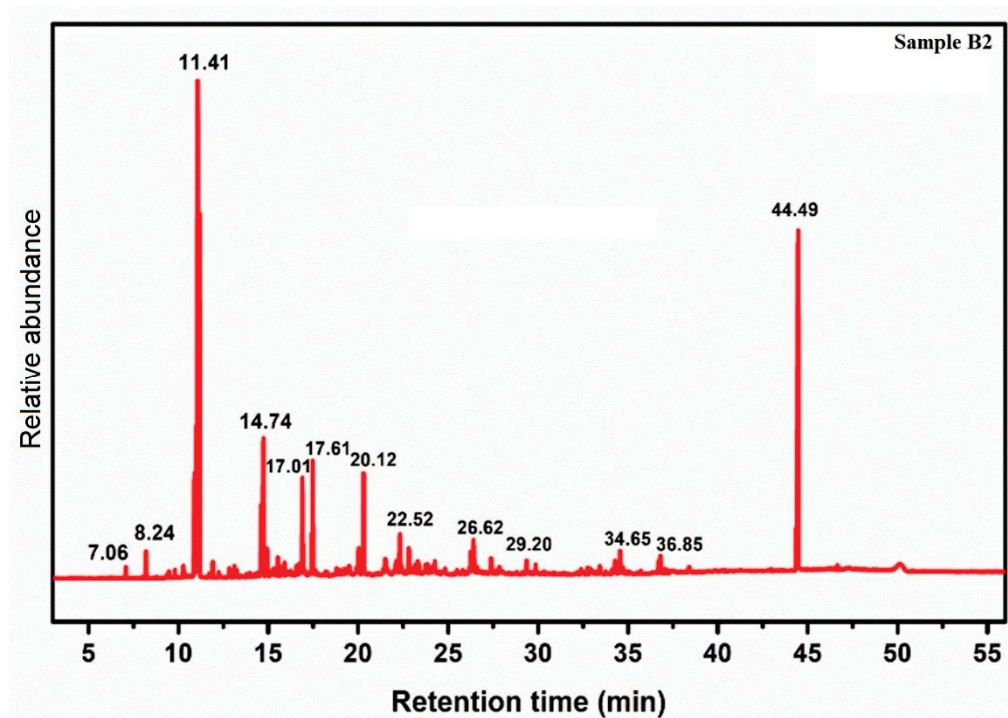


Figure 4. GC-MS analysis of sample B2.

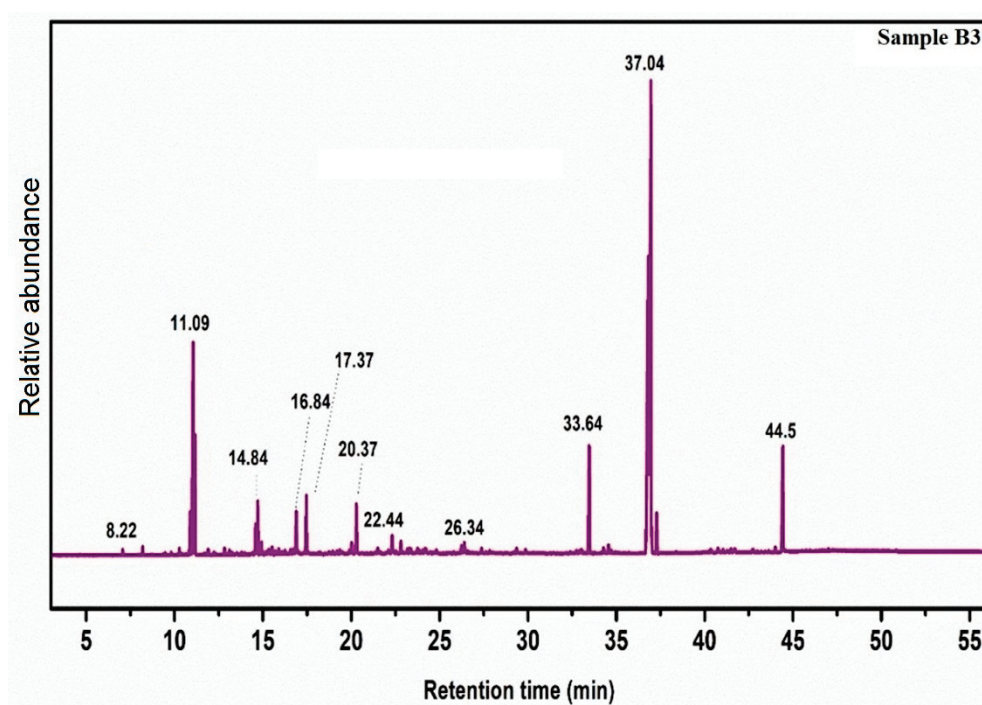


Figure 5. GC-MS analysis of sample B3.

Table 1. Summary of GC-MS analysis of biodiesel produced using CaO-CH₃NaO catalysts with different doping ratios.

5% CaO-CH ₃ NaO			10% CaO-CH ₃ NaO			15% CaO-CH ₃ NaO		
Ret. Time	Composition	M _w	Ret. Time	Composition	M _w	Ret. Time	Composition	M _w
8.23	Cyclohexene,1-methyl-5	270	8.23	Cyclohexene,1-methyl-5	128	8.22	Methyl ethyl ester	186
13.90	5-dimethyl-benzene methanol	398	8.24	Isobutyl ester	128	11.09	Encalyptol	284
18.46	6-heptanoic acid, methyl ester	438	11.41	3-methyl butyl ester	284	14.84	Cyclo hexene	296
19.76	2,4-hexadenoic acid, methyl ester	264	14.71	2-propenoic acid, methyl ester	296	16.84	Citronellol	208
22.27	3-hexadiene-1-ol	100	17.01	7-methylene-2,4,4-timethyl, methyl ester	320	22.24	2-cyclo hexe-1one	296
32.42	6- Octenoic acid	214	17.61	Mono-(2,2-dimethyl cyclo hexyl acid) ester	250	26.34	Napthalene	156
33.49	Hexadecanoic acid, methyl ester	438	20.12	Hexa decanoic acid, methyl ester	138	29.86	Docosaptenoic acid, methyl ester	214
35.577	Pentadecanoic acid, methyl ester	466	26.62	6-octenoic acid, methyl ester	284	33.64	Hexa decenoic acid, methyl ester	310
44.52	7-dimethyl-6-octenyl ester	389	34.65	Tetra methyl thioctic acid	160	37.04	Hepta deconic acid, methyl ester	348
			36.85	9-octenoic acid, methyl ester	203	40.35	11-eicosenoic acid, methyl ester	408
			44.49	Mono ethyl hexyl ester	307	44.5	Docasenoic acid, methyl ester	450

2.4. Effect of Reaction Parameters

2.4.1. Effect of Oil to Methanol Ratio

Methanol to oil molar ratio is one of the most important elements affecting biodiesel formation. Even though the transesterification reaction requires a 3:1 M ratio to produce

three moles of ester and one mole of glycerol, most experiments revealed that more alcohol was needed to complete the reaction [45]. The methanol to oil ratio ranged from 6:1 to 14:1 at 55–70 °C in the investigation. The biodiesel yield was increased when the methanol to oil ratio was increased, as illustrated in Figure 6. When the molar ratio is greater than 13:1, the biodiesel output decreases. The yield of biodiesel decreases if the molar ratio is increased over 13:1 because too much methanol and glycerol dissolve in methanol, which stops the reaction. Additionally, the reaction inhibition would cause a reaction direction to reverse and reduce the yield. On the other hand, the reactions would not continue, and no fatty acid methyl ester (FAME) would be produced if the molar ratio were too low.

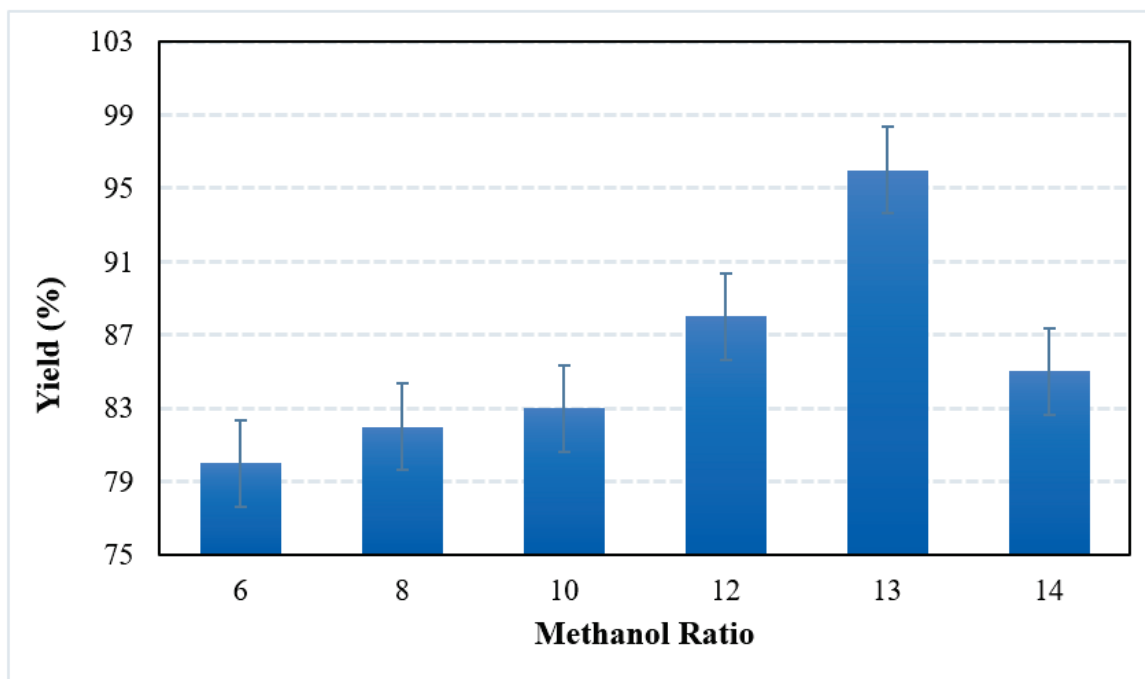


Figure 6. Effect of methanol to oil ratio on biodiesel production.

2.4.2. Effect of Catalyst Loading

The choice of the catalyst and its concentration are crucial in the transesterification reaction since they both influence how well methanol and oil combine. The catalyst's loadings wt.% of oil varied from 1 to 5 wt.% to examine the biodiesel yield (Figure 7). The yield increases with time with an oil catalyst loading of 2wt.% and subsequently falls after reaching the maximum point that kept the others factor constant, as given in Figure 8. The reason was that as more catalyst was added, the viscosity of the reaction mixture was changed as a result of soap formation and the difficulties in separating biodiesel from glycerol and catalyst. Therefore, a catalyst concentration that is either too low or too high would reduce the output of biodiesel.

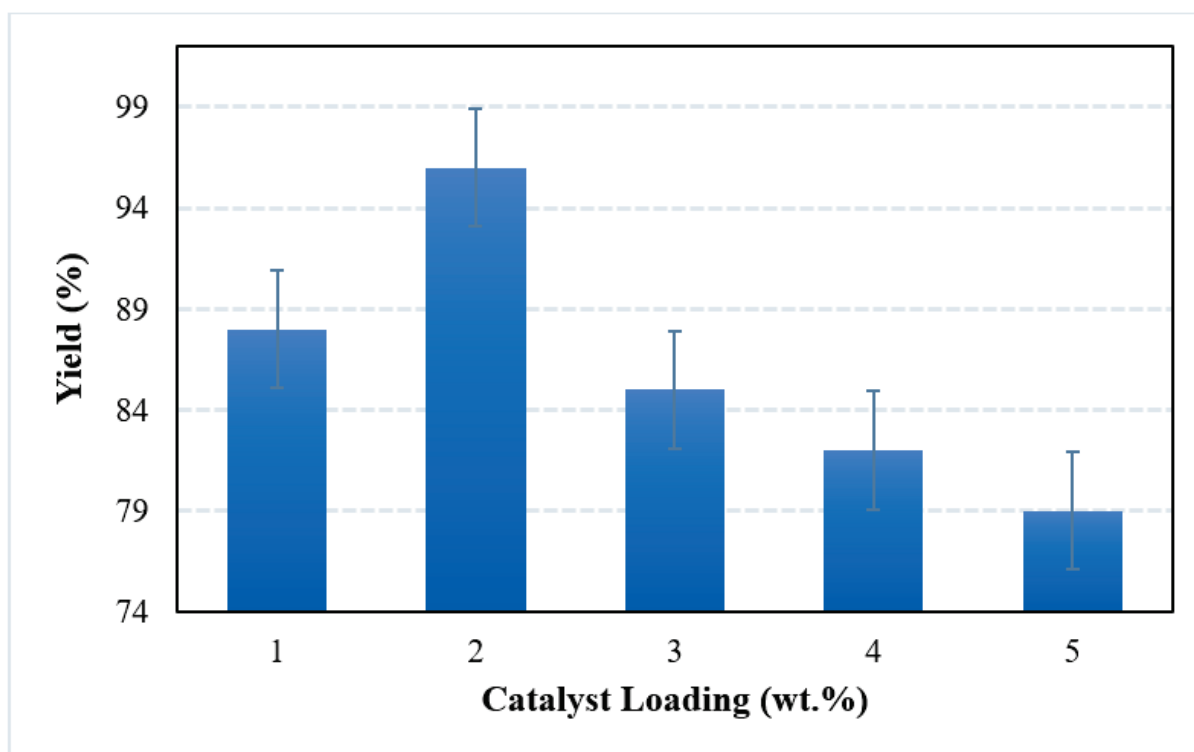


Figure 7. Effect of catalyst loadings on biodiesel production.

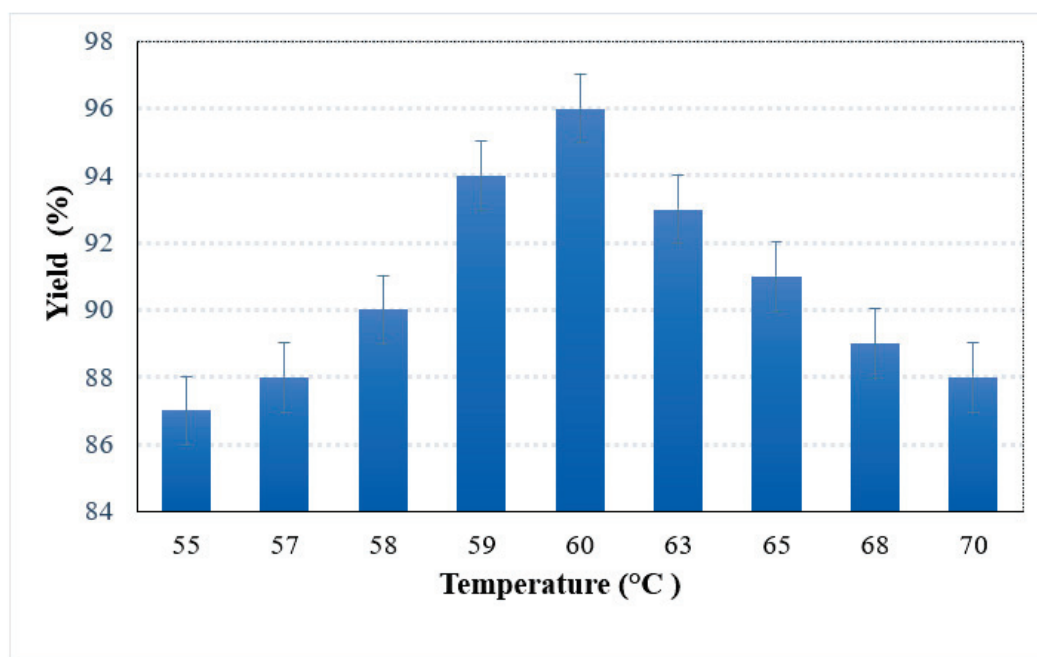


Figure 8. Effect of reaction temperature on biodiesel production.

2.4.3. Effect of Temperature

Figure 8 shows the effect of the reaction temperature on biodiesel production from catalyzed transesterification. The biodiesel yield was improved when the temperature was increased. When the temperature is increased from 45 to 60 °C, the biodiesel yield increased. This was due to the fact that as the temperature rises, so does the miscibility of alcohol in the waste chicken fat oil, as does the average speed (kinetic energy) of the molecules, resulting in more successful collisions and higher reaction rates. The viscosity

of the reaction mixture was reduced as the reaction temperature was increased, lowering the diffusion barrier between the distinct phases (oil, methanol, and catalyst). As the temperature rises to 65 °C, methanol evaporation causes the cavitation bubble to become supersaturated with methanol vapor, cushioning the collapse. Bubbles collapse with less force as a result, reducing mass transfer and yield. The effect of temperature on biodiesel yield was investigated in this study at temperatures ranging from 55 to 70 °C. By keeping the remaining parameters constant, the reaction at 65 °C yielded the highest yield. At 55 °C, the reaction was partial, resulting in reduced conversion. Further increasing the temperature to 65 °C yielded the best results; however, as the temperature was increased, the yield dropped due to the evaporation of alcohol, resulting in a loss in mass transfer.

2.4.4. Effect of Reaction Time

At reaction temperature of 60 °C and 1 h reaction time, the highest biodiesel yield of 96% was produced, as is shown in Figure 9. The yield was found to be lower during the shortest reaction time due to incorrect diffusion between the three phases of the reaction mixture. Increasing the reaction time beyond 1 h, on the other hand, resulted in a reduced yield. The longer reaction time leads to a reduction in biodiesel yield due to the reversible reaction of transesterification resulting in the loss of esters, as well as soap formation.

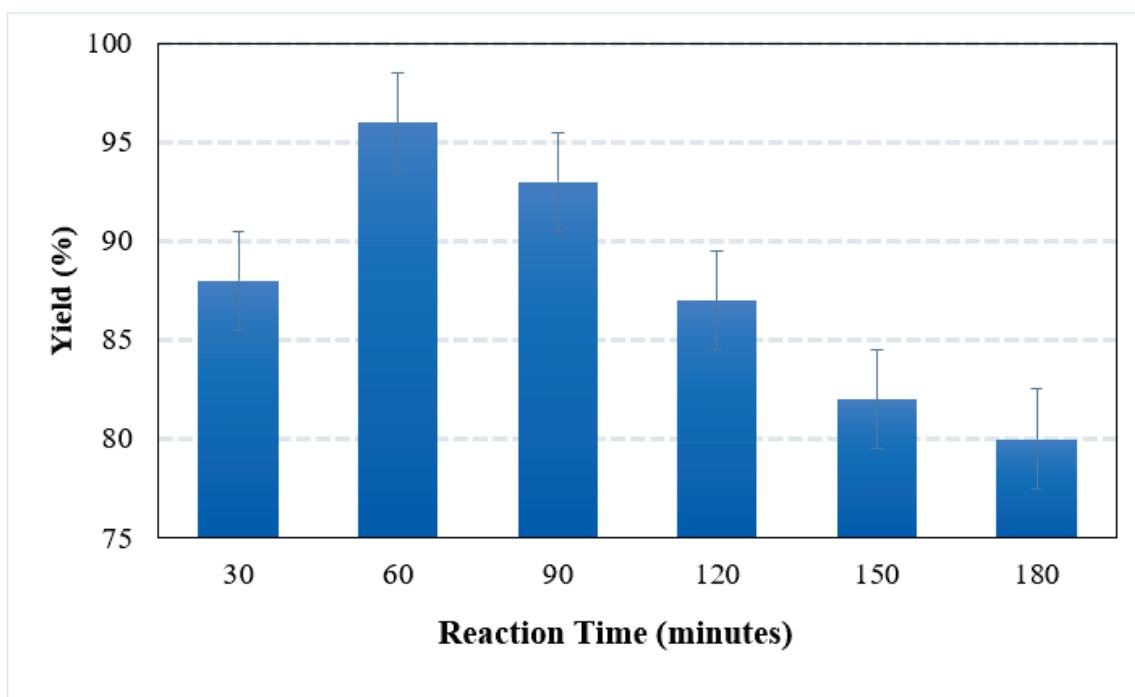


Figure 9. Effect of reaction time on biodiesel production.

2.4.5. Comparative Study of Biodiesel Yield from Waste Chicken Fat

Table 2 shows the comparative study of biodiesel yield from waste chicken fat as feedstock using CaO and different catalysts. The catalysts used for biodiesel production from waste chicken fat other than CaO showed lower yields of biodiesel, as shown in Table 2. However, using the CaO catalyst, the biodiesel yield was obtained to 90.2%. Similarly, a biodiesel yield up to 94.5% was observed using CaO/CuFe₂O₄ but with catalyst loading higher than 2 wt%. In this study, the developed catalyst produced biodiesel up to a maximum of 96% with 2 wt% catalyst loading due to enhanced activity.

Table 2. Comparative study of biodiesel from waste chicken fat using different catalysts.

Sr. No	Catalysts	Catalyst Loading, wt%	Biodiesel Yield, %	Reference
1.	KOH	0.5	67	[46]
2.	NaOH	1	71.3	[47]
3.	KOMe	0.5	88.5	[47]
4.	KOH	0.8	76.8	[46]
5.	CaO	2	90.2	[48]
6.	CaO/CuFe ₂ O ₄	3	94.5	[49]
7.	CaO-CH ₃ NaO	2	96	This study

3. Materials and Methods

3.1. Materials

Chicken fat and waste eggshells were collected from the nearby slaughterhouse and bakery shop, respectively, and washed with distilled water several times to eliminate impurities such as dust particles and other odorous wastes.

3.2. Methods

3.2.1. Oil-Extraction Method

This step involved oil extraction from chicken fat, which was achieved by placing chicken fat in microwave oven until the oil was produced. To remove the water content, the collected oil was heated over 100 °C before being purified. The waste chicken fat oil was filtered for further purification and stored.

3.2.2. Determination of Acid Value

High free fatty acids (FFA) reduce biodiesel yield by generating soap during the transesterification cycle. The acid value was determined using the following equation:

$$\text{Acid value (AV)} = V \times C \times 56.11/m$$

where 'V' represents the volume of the KOH solution (mL), 'C' represents the KOH concentration (mol L⁻¹), and 'm' represents the mass of oil extracted (gram).

The acid value (AV) was 0.86 mg KOH/g of oil, which equates to 0.43% free fatty acids (FFA).

3.2.3. Catalyst Synthesis and Characterization

The sodium-methoxide-doped CaO was prepared by the simple impregnation method [34]. The complete synthesis procedure is as follows. The washed waste eggshells were crushed into tiny pieces and heated to 105 °C for 24 h in a hot air oven to eliminate the moisture. The dried shells were then ground with a pestle and mortar followed by calcination at 700 °C for 5 h in a muffle furnace. The obtained powder was labeled as an active CaO catalyst and was stored in tightly closed vial for further use. Further, the aqueous solution of sodium methoxide with a suitable concentration was prepared and then drop-wise added to CaO powder carefully. The resulting mixture was placed in an oven for drying for 10 h at 110 °C. After drying, the resulting solid was named the CaO-CH₃NaO catalyst and was used for the transesterification process and characterized. The X-ray diffraction (XRD) patterns were acquired by using the PRO analytical X-ray diffractometer. Fourier transform infrared spectroscopy (FTIR) spectra were recorded by infrared spectroscopy with KBr pellets in the range 400–4000 cm⁻¹. The signal resolution of 4 cm⁻¹ with 40 scans was applied. The same procedure was followed to develop different catalysts with varying loadings of dopant. Figure 10 shows the complete synthetic procedure of the CaO-CH₃NaO catalyst.

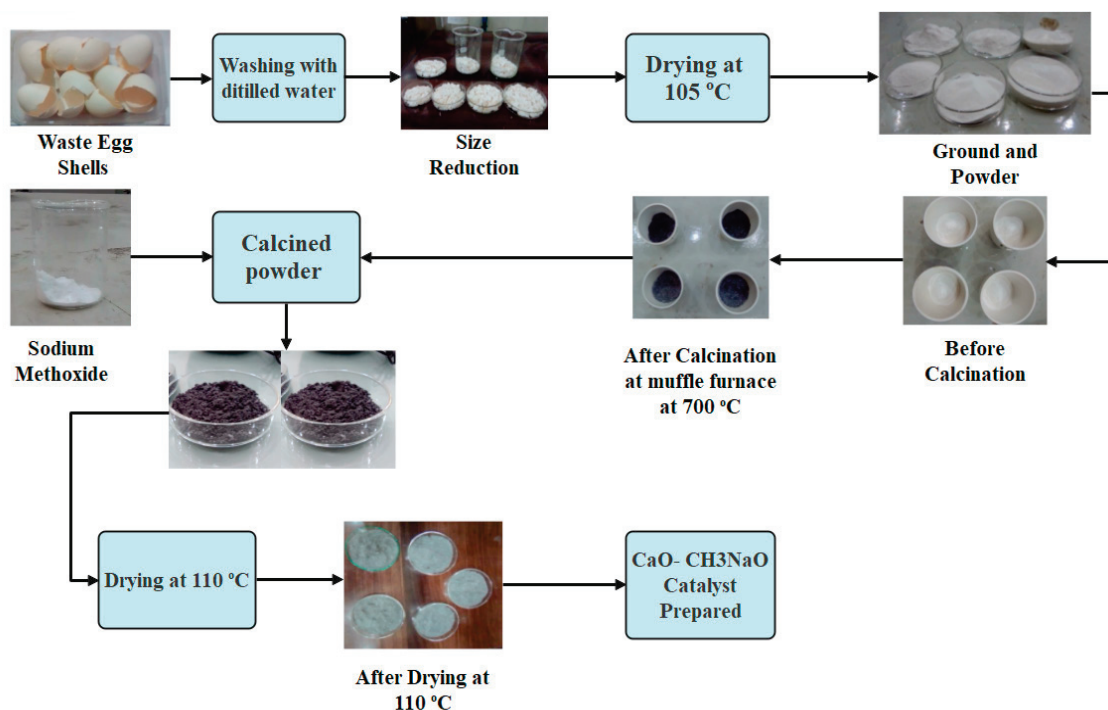


Figure 10. Steps involved in complete synthesis of CH_3NaO -doped CaO catalyst.

3.2.4. Transesterification of Chicken Fat Oil

The transesterification reaction was carried in a two-neck round-bottom flask (250 mL) connected with a refluxing condenser on a magnetic stirrer. An appropriate volume of oil and methanol was poured into a flask followed by the addition of the synthesized catalyst. The reaction was conducted under continuous stirring with different catalyst loadings and a methanol to oil ratio at suitable temperatures. The catalyst was removed by centrifugation after the reaction was completed. The resulting mixture after centrifugation was transferred into a separating funnel. The biodiesel and glycerol layers were separated in a separating funnel after 34 h. The biodiesel layer was carefully collected and heated up to 100 °C to remove any unreacted methanol. The biodiesel sample was sent for GC-MS analysis. The FAME of biodiesel was characterized by a Perkin Elmer (Waltham, MA, USA) Clarus 600 gas chromatograph mass spectrometry (GC-MS) using a DB-Wax column. Helium was used as a carrier gas with constant flow of 1.0 mL/min, with a 1 μL sample injected with a mass spectrometer set to scan a frequency range of 40–550 amu. The initial oven temperature was set to 80 °C and held for 5 min before being increased to 240 °C at a heating rate of 4 °C/min. Finally, the biodiesel yield was calculated as given below. In addition, multiple reactions were performed to study the effect of different parameters such as the catalyst loading (1–5 wt%), the methanol to oil ratio (6–14), the temperature (55–70 °C), and the reaction time on biodiesel yield (30–180 min).

$$\text{Yield} = \frac{\text{Mass of biodiesel in grams}}{\text{Mass of oil taken in grams}} \times 100$$

4. Conclusions

Waste chicken fat and eggshell are examples of poultry wastes that could serve as inexpensive sources of raw materials for the production of biodiesel. In this work, used chicken eggshells were calcined at 700 °C and effectively turned into CaO and doped with sodium methoxide for an effective catalyst for biodiesel production. The waste chicken fat that was recovered using a straightforward non-solvent approach was trans-esterified (valorized) using a heterogenous catalyst made from chicken eggshell. The maximum yield of 96% biodiesel was obtained with catalyst loading of 2 wt% of oil, and a methanol to

oil ratio of 13:1 at 60 °C in 1 h. The analysis of the resulting biodiesel provides additional evidence for the viability of the raw materials for the synthesis of biodiesel. This research has established the transesterification of oil from chicken slaughter waste using a low-cost, non-solvent extraction method and a low-cost catalyst source. A future study for a suitable and feasible commercialization of the process is proposed, including optimization studies, eggshell catalyst treatment with metal oxide reagents, and pilot-scale investigations of the procedure.

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Review

Magnetic Iron Oxide Nanomaterials for Lipase Immobilization: Promising Industrial Catalysts for Biodiesel Production

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Abstract: Biodiesel is a mixture of fatty acid alkyl esters (FAAEs) mainly produced via transesterification reactions among triglycerides and short-chain alcohols catalyzed by chemical catalysts (e.g., KOH, NaOH). Lipase-assisted enzymatic transesterification has been proposed to overcome the drawbacks of chemical synthesis, such as high energy consumption, expensive separation of the catalyst from the reaction mixture and production of large amounts of wastewater during product separation and purification. However, one of the main drawbacks of this process is the enzyme cost. In recent years, nano-immobilized lipases have received extensive attention in the design of robust industrial biocatalysts for biodiesel production. To improve lipase catalytic efficiency, magnetic nanoparticles (MNPs) have attracted growing interest as versatile lipase carriers, owing to their unique properties, such as high surface-to-volume ratio and high enzyme loading capacity, low cost and inertness against chemical and microbial degradation, biocompatibility and eco-friendliness, standard synthetic methods for large-scale production and, most importantly, magnetic properties, which provide the possibility for the immobilized lipase to be easily separated at the end of the process by applying an external magnetic field. For the preparation of such effective magnetic nano-supports, various surface functionalization approaches have been developed to immobilize a broad range of industrially important lipases. Immobilization generally improves lipase chemical-thermal stability in a wide pH and temperature range and may also modify its catalytic performance. Additionally, different lipases can be co-immobilized onto the same nano-carrier, which is a highly effective strategy to enhance biodiesel yield, specifically for those feedstocks containing heterogeneous free fatty acids (FFAs). This review will present an update on the use of magnetic iron oxide nanostructures (MNPs) for lipase immobilization to catalyze transesterification reactions for biodiesel production. The following aspects will be covered: (1) common organic modifiers for magnetic nanoparticle support and (2) recent studies on modified MNPs-lipase catalysts for biodiesel production. Aspects concerning immobilization procedures and surface functionalization of the nano-supports will be highlighted. Additionally, the main features that characterize these nano-biocatalysts, such as enzymatic activity, reusability, resistance to heat and pH, will be discussed. Perspectives and key considerations for optimizing biodiesel production in terms of sustainability are also provided for future studies.

Keywords: biodiesel; renewable fuels; lipase; nano-biocatalysts; Fe₃O₄ nanoparticles; magnetic nanoparticles; surface functionalization; waste oil; edible oil; non-edible oil

1. Introduction

The rapid growth of industrialization and modernization has progressively increased the consumption of fossil fuels (e.g., coal, oil, gas), causing tremendous environmental, economic and ecological impacts [1,2]. Currently, non-renewable energy resources account for 70–80% of the total energy demand, and their use has generated uncontrolled greenhouse

gas emissions that are considered the main cause of the warming up of our planet [3]. Even if some countries, including European countries, Japan and the USA, are reducing their oil consumption (Table 1), it is projected that the worldwide need for petroleum liquid fuels will experience a 38% increase by 2040, reaching 119 million barrels/day. Such growth in fuel demand is already occurring mainly in developing countries, such as Middle Eastern nations, India, and China [4,5].

Table 1. Oil consumption share and annual growth rate of major countries. Reprinted from Ref. [4], copyright (2024), with permission from Elsevier.

Country	2022 Share	2012–2022 Annual Growth Rate
USA	19.7%	0.9%
China	14.7%	3.6%
European Union	11.1%	−0.4%
India	5.3%	3.5%
Saudi Arabia	4.0%	1.1%
Russia	3.7%	1.2%
Japan	3.4%	−3.3%
South Korea	2.9%	1.5%
Brazil	2.6%	−0.3%
Canada	2.4%	−0.6%
Turkey	1.1%	−0.6%
Mexico	2.2%	−0.6%
New Zealand	0.2%	−0.1%
Luxembourg	0.1%	−1.6%
Estonia	Less than 0.05%	−2.5%
OECD * countries	46.4%	Less than 0.05%
Non-OECD countries	53.6%	1.8%
Global Total	100%	0.9%

* OECD: Organization for Economic Cooperation and Development.

As an alternative to limited fossil resources, renewable energy sources are attracting growing attention, as they may offer environmental and energy sustainability benefits [6]. Vegetable oils and animal fats are widely available feedstocks that are rich in long-chain triglycerides, which can be converted into biodiesel (fatty acid alkyl esters), a biodegradable and eco-friendly fuel. Compared to conventional fossil fuels, biodiesel provides higher combustion efficiency and lower sulfur and aromatic content, with a significant decrease in the emission of toxic compounds and greenhouse gases [7]. Another benefit of biodiesel is that it can be easily blended with petroleum diesel (e.g., B20 and B5, indicating the percentage of biodiesel). Such blends have high flash points and cetane numbers, and they may be used without any modifications to current engines [8]. From another point of view, biodiesel can be obtained from locally available natural resources, which improves the economy of local communities [9].

Chemical production of biodiesel includes the transesterification of triglycerides (from the feedstocks) with short-chain alcohols (e.g., methanol, ethanol, propanol), in which methanol is the most preferred due to its low cost [10]. There are many types of feedstocks for biodiesel production, and among them, edible vegetable oils and discarded oils are commonly employed because of their potential economic feasibility [11]. Of course, every country has its own suitable oil feedstock because of the unique regional ecosystems. The global manufacturing of biodiesel is steadily increasing to reach, as projected, about 41.4 billion litres in 2025 [12]. Considering the main biodiesel producers, the USA is ranked first (18%), followed by Indonesia (17%), Brazil (13%), Germany (8%) and Thailand (4%). In the USA and Brazil, the main feedstock for biodiesel production is soybean biomass, while in Europe, Indonesia, and Thailand, biodiesel production mostly depends on rapeseed, palm and coconut oils, respectively [13]. Compared to these pure oils, waste oils (e.g., waste cooking oils) are cost-effective alternatives for biodiesel production [14].

Currently, different countries are focusing on finding more effective catalysts to enhance reaction efficiencies, maximize profits and minimize waste production [15,16]. In fact, commonly used basic catalysts (e.g., KOH and NaOH) have some disadvantages, including high environmental pollution, difficult catalyst recovery and high reaction temperature, which promotes the undesirable hydrolysis of triglycerides, producing large amounts of free fatty acids (FFAs) [17], decreasing the reaction efficiency. To address such issues connected with the use of chemical catalysts, lipases (triacylglycerol hydrolases, EC 3.1.1.3-IUPAC) have been introduced as highly effective biocatalysts for the enzymatic transesterification of triglycerides for biodiesel production, as shown in Figure 1 [18].

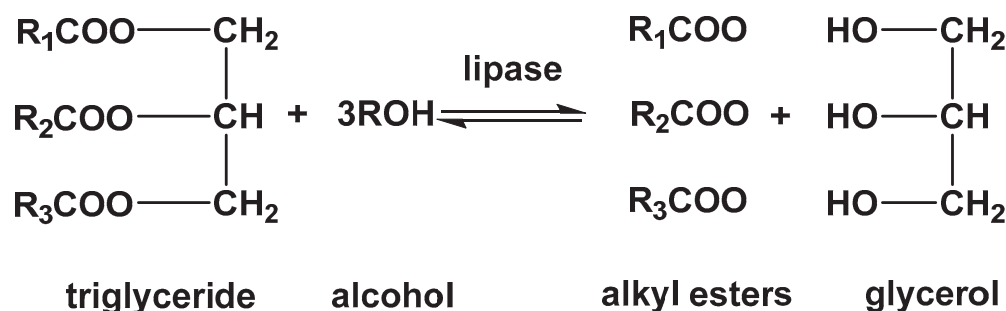


Figure 1. Enzyme-based transesterification reaction. Reprinted from Ref. [18], copyright (2020), with permission from Elsevier.

Compared with alkaline catalysis, the use of lipolytic enzymes displays several advantages, including easy glycerol recovery and product separation, minimal by-product formation and mild reaction conditions [19,20]. Unlike alkaline catalysts, lipases can efficiently catalyze biodiesel production from feedstocks containing high amounts of FFAs mixed with triglycerides in mild reaction conditions [21,22]. However, for scaling up lipase-catalyzed approaches, three main challenges should be addressed: (1) high enzyme cost, (2) non-separability of enzymes due to their water solubility, and (3) low biodiesel production yield. All these factors increase the costs of the final biodiesel product [23,24]. Cheap alcohols, e.g., ethanol and methanol, are used to optimize production costs. As shown in Figure 2, a 3:1 methanol/triglyceride ratio allows the use of the methanol excess, increasing the transesterification yield. However, such alcohol excess can also inhibit the enzyme, particularly for those alcohols which are insoluble in the reaction mixture [25,26]. Therefore, the alcohol:triglyceride molar ratio must be optimized for each alcohol-fat-lipase system. To minimize this inhibition effect, stepwise alcohol addition was successfully introduced [27,28]. However, maintaining low alcohol concentrations is not an appropriate approach for large-scale biodiesel production. So, alternative strategies have been developed to overcome the methanol deactivation of lipases, including (1) using organic solvents to improve methanol solubility, (2) replacing methanol with methyl acetate, and (3) applying salt-saturated solutions and silica-gel based controlled release systems for methanol. However, organic solvents (e.g., hexane) decrease the methanolysis compared with aqueous-based mediums. Although a significant increase in reaction rate using tert-butanol has been reported, a large molar excess of methanol (6:1 methanol to oil ratio) is required to obtain higher biodiesel yields. Replacing methanol with methyl acetate produces the by-product triacylglycerol, which complicates product purification. Furthermore, methyl acetate increases the costs of the process. Finally, salt-saturated solutions and silica-gel methods cause difficulties in downstream separation.

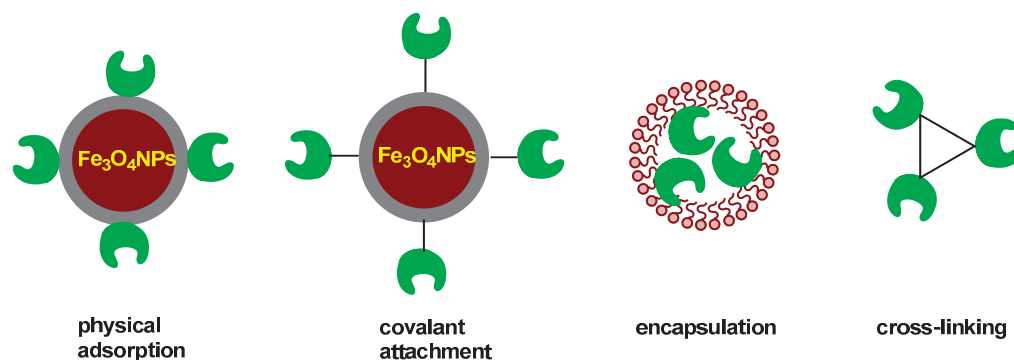


Figure 2. Main types of enzyme immobilization strategies. Adapted from Ref. [29], copyright 2022, with permission from Elsevier.

In order to maximize lipase efficiency while minimizing operational costs, enzymes can be immobilized on different micro- or nano-materials to provide lipase stability, higher efficiency and easy purification. Moreover, enzyme immobilization strategies enhance enzyme dispersity in low-water content media, resulting in higher catalytic activity compared to reactions catalyzed by free lipases [30]. Regarding the supporting materials, nano-based immobilization is particularly promising because of the unique surface properties of nano-materials, which provide large specific surface areas, low mass transfer resistance and superior loading capacity [31].

For lipase immobilization, an ideal nano-carrier should possess mechanical and chemical stability, be resistant to microbial attack, and have a low cost for industrial purposes and development [32,33]. Currently, several organic and inorganic nanostructures are used for lipase immobilization [34], such as: carbon nanotubes [35,36], nanofibers [37,38], graphene oxide nanostructures [39,40], chitosan [41,42], niobium oxide [43], magnetic nanoparticles [44], silica [45], agarose [46], metallic nanoparticles (Ag- [47] and AuNPs [48]) and TiO₂ nanoparticles [49]. Among them, magnetic iron oxide nanoparticles have stood out as superior enzyme immobilization matrices due to their unique superparamagnetic properties, which allow easy lipase recovery at the end of the process and controlled stabilization in packed and fluidized bed reactors using an external magnetic field [50,51]. Magnetite (Fe₃O₄) and maghemite (γ-Fe₂O₃) nanostructures are the most common magnetic nano-carriers due to their high magnetizations, well-known chemistry and ease of synthesis [52,53]. Surface modification of these magnetic nanostructures is an effective strategy to increase the stability of the magnetic core against oxidation and agglomeration, as well as its flexibility for the effective interaction with enzymes in order to achieve high loading and enhancement of lipase effectiveness [54].

This review presents an update on biodiesel biotechnological production using magnetic-based immobilization of lipolytic enzymes. Currently used nanostructures include both magnetite (Fe₃O₄) and maghemite (γ-Fe₂O₃), used in different nanocomposites containing other organic and inorganic components. First, a brief discussion of influencing factors on biodiesel production using immobilized lipases will be presented, followed by the review and critical analysis of the magnetic nanomaterials used for lipase immobilization based on recent publications.

2. Main Factors Influencing Biodiesel Bio-Production Using Immobilized Lipases

2.1. Feedstocks

The main feedstocks suitable for biodiesel production are vegetable oils, animal fats, and microbial and algae oils. Regarding the production price of biodiesel, the cost of the raw materials is the most important parameter [55]. Based on their availability and source, feedstocks are classified into three main groups: edible, non-edible, and waste oils [56,57]. Edible vegetable oils, e.g., palm and soybean oils, are the most commonly used feedstocks for biodiesel production [58,59]; however, the supply of this type of raw

materials strongly depends on the food market, which is not completely predictable [60]. Conversely, non-edible oils are cheaper and not influenced by the food industry; hence, they are better candidates as biodiesel feedstocks [61]. Among them, *Jatropha* plants are particularly interesting since they can grow on wasteland with little demand for water and fertilizers, producing seeds with high oil content (30–50% of plant weight) [62]. *Jatropha* food applications are restricted by the presence of toxic compounds, e.g., phorbol esters, but present no limitation for biodiesel production. The general disadvantages of non-edible oils are their high FFAs and water content, which limit their use in alkaline-catalyzed transesterification processes. It is worth mentioning that both edible and some non-edible oils are agricultural feedstocks, requiring large amounts of land and other resources (water, fertilizers, etc.) for their production, which still compete with the food market [63] and cause environmental problems (i.e., deforestation) that are not compatible with current sustainable development goals. For these reasons, non-edible microalgae oil, not requiring land for its production, is a promising alternative source for biodiesel [64]; however, current technologies for algae farming, oil recovery and separation are still expensive; therefore, further research is required for large-scale biodiesel production from algal oil.

Another important feedstock is waste oil that includes frying oil, waste cooking oil and other waste products, including waste animal fat (major wastes of the leather industry, the meat industry and fish processing), tall oil (a by-product of the paper industry) and tobacco seed oil (a by-product of tobacco leaf manufacturing) [29]. Every day, a large amount of waste cooking and frying oils are ubiquitously produced by the cooking and food industries and require to be properly disposed of. Obviously, the use of these waste oils as a feedstock brings environmental and economic benefits and is perfectly in line with the principles of circular economy. Compared to non-edible and edible oils, the acquisition of waste oil is much cheaper because it does not require additional land use or other resources, and, more importantly, it can reduce the environmental pollution caused by their disposal in nature [65]. Waste animal fats contain more FFAs and saturated fatty acids. The traditional alkaline-catalytic biodiesel process promotes the hydrolysis of triglycerides, which increases the FFA content when waste frying oils or cooking oils are used as raw materials [10]. Moreover, these waste frying oils have high water content and include other animal or vegetable oils, depending on what food was cooked with them. However, high FFAs and water contents are not compatible with the traditional alkaline-based transesterification technology in which the FFAs form soap in the presence of water (catalyzed by the basic catalyst), which decreases catalyst efficiency, leading to a difficult downstream separation of glycerol [66]. Therefore, waste oils are not suitable for alkaline-catalyzed biodiesel production. Conversely, lipase-catalyzed transesterification is compatible with the high FFAs and water contents of waste oil feedstocks [67].

2.2. Immobilization Methods

There are four general strategies for lipase immobilization, including (1) physical surface adsorption, (2) chemical surface attachment, (3) encapsulation and (4) cross-linking (Figure 2). Via physical adsorption, the enzyme is immobilized on the surface of the carrier material through non-covalent interactions such as hydrogen bonding, electrostatic attraction, van der Waals forces and hydrophobic interactions. Despite the simplicity and popularity of this method, the weak interactions between lipase and carrier usually result in enzyme leakage issues, especially in complex media having high ionic strengths. This kind of immobilization is commonly used for porous supports [68], which can efficiently trap lipase molecules inside their pores and protect them from external denaturing conditions and subsequent leakage. Lipases have a natural affinity for hydrophobic supports, so physical adsorption occurs fast by hydrophobic interactions [69,70] to form a shell of immobilized enzyme molecules on the carrier surface, in which the lipase assumes a monomeric, open and catalytically active conformation. The so-called “open” conformation of the lipase can be maintained by the support and protected from other external interfaces [71,72].

In this scenario, hydrophobic triacylglycerols and fatty acid esters (precursors) strongly interact with the hydrophobic support, but the hydrophilic glycerol (product) shows no affinity for it. Both factors favour reaction efficiency [73].

In covalent immobilization, the lipase is chemically attached to the functional groups of the support to guarantee strong enzyme adhesion with negligible leakage during the catalytic process. Both lipase and support usually require a pre-activation of their functional groups before covalent attachment. Bifunctional organic molecules having suitable functional groups (e.g., glutaraldehyde), are commonly used for the covalent conjugation of lipases onto support surfaces. For instance, the aldehyde moiety of glutaraldehyde can be easily condensed with the amine groups of both lipase and support under mild conditions [74,75], which also enhances the hydrophobicity of the surface [76]. There are also other conjugating reagents, such as EDC (*N*-ethylcarbodiimide hydrochloride) and NHS (*N*-hydroxysuccinimide), that drive the formation of amide bonds between lipase amine groups and carboxyl groups of the support or vice versa [77,78]. There are also epoxy functional groups for activating the supports, which are suitable for covalent immobilization by direct mixing of these activated supports with lipases [79]. In some supports, multi-point covalent binding may occur due to the surface properties of the support and lipase molecular structure, which provides enhanced stability to the immobilized enzyme [80]. This multiple covalent attachment fixes the native lipase structure on the surface of the support, which protects it against external denaturing conditions such as high ionic strength, heat and organic solvents. However, covalent conjugation should be designed accurately in order to preserve the catalytically active conformation of lipase molecules [81].

In the third method, lipases are encapsulated into porous supports by a simultaneous co-precipitation method, which rarely has leakage problems. The other advantages of this method are the high compatibility with the enzymes and a fast immobilization process [82]; however, high mass transfer resistance limits this type of immobilization.

Regarding the fourth immobilization strategy, cross-linking, lipases are interconnected by crosslinking agents, e.g., glutaraldehyde, to form multiple covalent bonds within or among enzyme molecules. These multi-point attachments enhance the rigidity of the lipase and protect the immobilized enzyme against external agents (heat, organic solvents, etc.). Additionally, there can be a combination of these four immobilization methods to enhance enzyme loading and stability [83], which eventually results in improving catalytic performance. Finally, it is worth mentioning that for all these immobilization methods, the reaction conditions should be optimized in terms of pH, immobilization time, temperature, lipase concentration and enzyme/support ratio.

2.3. Lipase Specificity

In transesterification reactions, lipases follow a two-step mechanism for the synthesis of fatty acid methyl esters, usually through the Ping-Pong Bi Bi mechanism [84]. Most lipases are regiospecific due to their specificity to only hydrolyze primary ester bonds at the sn-1 and sn-3 sites, external positions within the triacylglycerol, generating either one free fatty acid and diacylglycerol or two free fatty acids and 2-monoacylglycerol (Figure 3) [85].

Monoacylglycerol lipases (EC 3.1.1.23) catalyze the hydrolysis at the specific sn-2 position of 2-monoacylglycerol into free fatty acid and glycerol. Such lipases may be present in the enzyme extract and masked when measuring activity with standard methods. Monoacylglycerol lipases have been the object of only a few studies [86], although they might be present in microbial enzyme preparations [87]. Other lipases are nonspecific and can act on any of the ester bonds of the triacylglycerol and, therefore, break down the triacylglycerol to release free fatty acids and glycerol as the final products. This is the case of lipases from *Staphylococcus aureus* and *hyicus* [88], *Geotrichum candidum*, *Corynebacterium acnes*, *Penicillium cyclopium* [24] and *Chromobacterium viscosum* [89]. Another alternative for the hydrolysis of monoacylglycerols is the acyl migration in the glycerol backbone from the sn-2 position to the sn-1 or sn-3 positions [90].

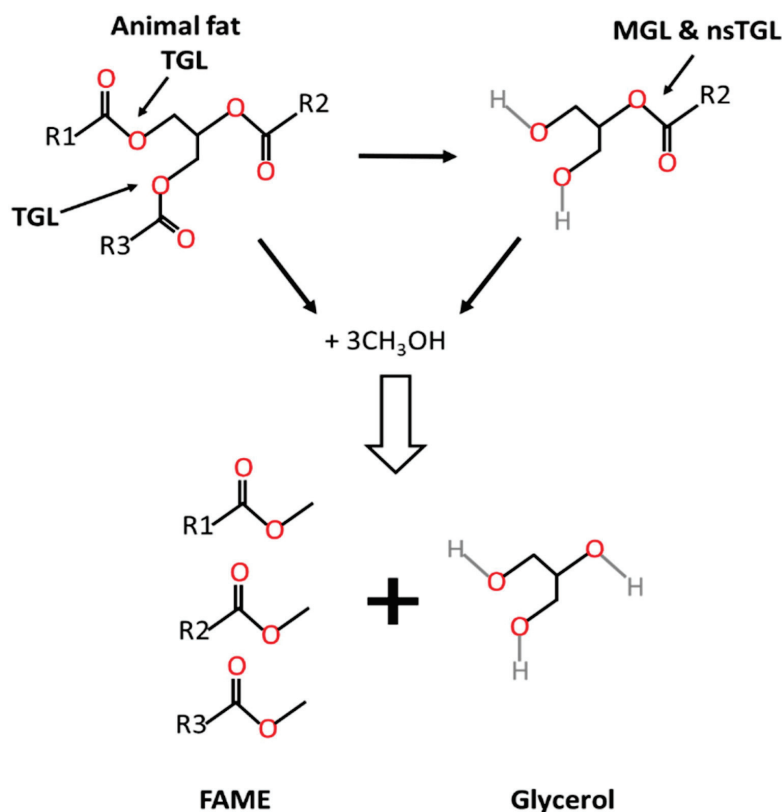


Figure 3. Transesterification of animal fat to biodiesel. TGL: triacylglycerol lipase; nsTGL: non specific triacylglycerol lipase; MGL: monoacylglycerol lipase. Reprinted from Ref. [85], MDPI, 2020.

Lipase specificity depends on the length of fatty acids, the presence of double bonds and branched groups. Consequently, reaction rates may have important variations depending on the triacylglycerol composition of the fat waste. Lipases are especially active on medium to long-chain fatty acids, which are more commonly present in animal fat waste [91].

2.4. Lipase Source

As triacylglycerol hydrolases, lipases are commonly used for the biocatalytic hydrolysis of long-chain insoluble glycerides in aqueous media. Lipases belong to the serine hydrolase class and have a catalytic centre composed of three amino acids: a histidine, a nucleophilic serine and an aspartic acid or glutamic acid [92,93]. As mentioned above, lipases can also catalyze the multi-step transesterification of triglycerides with short-chain alcohols with high selectivity [94], which makes them promising biocatalysts in different industries, e.g., food, cosmetics, textile, pharmaceutical, as well as biodiesel technology [95]. Lipases are enzymes working at water/lipid interfaces [96]. In more detail, lipases possess amphiphilic polypeptide chains that are able to form an interface between water and the substrate. In this way, the hydrophobic substrate can selectively interact with the active centre of the lipase due to the amphiphilic nature of the lipase and its unique stereo-specificity. Lipases obtained from different sources have different molecular structures and, therefore, show different substrate selectivity. In fact, the reaction rate strongly depends on the type of lipase as well as on the molecular structure of the substrate [97,98]. For biodiesel production, the transesterification ability of lipases can convert long-chain triglycerides into FFAEs and simultaneously catalyze the esterification of alcohol with FFAs, which is valuable when using feedstocks with high FFA content. Biodiesel production does not require the use of stereo-specific lipases, so all tri-, di-, monoglycerides and FFAs with different molecular weights can be converted into FFAE [99]. The feedstocks generally contain heterogeneous mixtures of triglycerides and FFAs; hence, using a mixture of different lipases (includ-

ing selective and nonselective enzymes) can be useful to enhance catalytic activity [100]. In order to reduce lipase specificity and improve reaction efficiency, the stereo-chemical structure of lipases can also be modified by immobilization [101,102]. Lipases may be obtained from different natural sources, including microorganisms, plants and animals. Hence, different lipases show different catalytic performance and physicochemical properties due to their diverse origin, resulting in differences in production processes and immobilization methods. Similarly to other catalysts, lipases should have high diversity, low price and long-term chemical stability. In this regard, microbial-derived lipases (e.g., from fungi, yeast and bacteria) fulfil all requirements. For industrial production, lipase-producing microorganisms should have high specificity and be amenable to genetic modification [103]. There are several suitable microorganisms, e.g., *Rhizopus oryzae* [104], *Pseudomonas cepacia* [105], *Aspergillus niger* [106], *Candida antarctica* [107], *Pseudomonas fluorescens* [108], *Burkholderia cepacia* [109], *Candida rugosa* [110], *Rhizomucor miehei* [111], and *Thermomyces lanuginosus* [112]. Regarding animal-derived lipases, porcine pancreatic lipase (PPL) can be manufactured by transgenic recombinant bacteria with high yield [113] and has received much attention also for applications in biodiesel manufacturing.

2.5. Operation Mode

The operational process of biodiesel manufacturing has a significant impact on the versatility, feasibility and final cost of the product. Lipase-based catalysis can make the process more simple, environmentally valuable and cost-effective. Figure 4 presents the schemes of alkaline-catalyzed and lipase-catalyzed biodiesel production. However, chemical catalysis still requires additional subsequent steps, which are not shown in the figure. For instance, the produced glycerol needs to be separated from biodiesel by, for example, methanol evaporation and removal of saponification products, and, more importantly, the alkaline process produces large amounts of toxic wastewater. As shown in Figure 1, the transesterification reaction employed for biodiesel production is reversible, and in the alkaline process, methanol is usually used in excess to push the reaction forward, based on Le Chatelier's principle [114]. In contrast, this excess addition of methanol is not compatible with enzyme-catalyzed reactions because of its inactivating effect on lipases; hence, a lower methanol-to-oil ratio is used, and therefore longer reaction times are needed. Additionally, in lipase-based processes, there are no saponification by-products or large amounts of wastewater, which is another benefit of this method since, after the separation of the immobilized enzyme, highly pure biodiesel (and glycerol) is obtained [115].

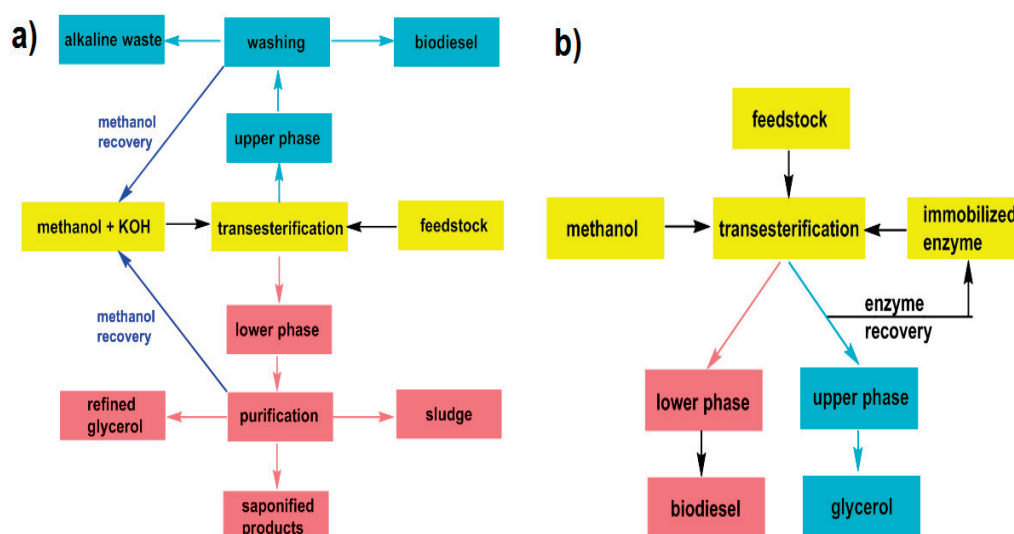


Figure 4. Biodiesel production using: (a) alkali-catalyzed and (b) enzyme-catalyzed transesterification processes. Adapted from Ref. [18], copyright (2020), with permission from Elsevier.

For the scale-up of lipase-based methods, reactors are another important factor to take into consideration. In this regard, there are two general types of production processes: batch reactions and continuous reactions. As shown in Figure 5, different reactors have been used with immobilized lipases for biodiesel production, including fluidized-bed reactors (FBRs), stirred-tank reactors (STRs) and packed-bed reactors (PBRs) [116]. Table 2 summarizes some studies on reactor-scale biodiesel production employing nano-based lipase processes. In 2019, Tabatabaei et al. published a comprehensive review on reactor technologies for biodiesel production and processing, so we will not discuss this topic further in this context [117]. The commonly used batch reactions are usually carried out in STRs, which show simplicity of operation and are suitable for laboratory-scale research.

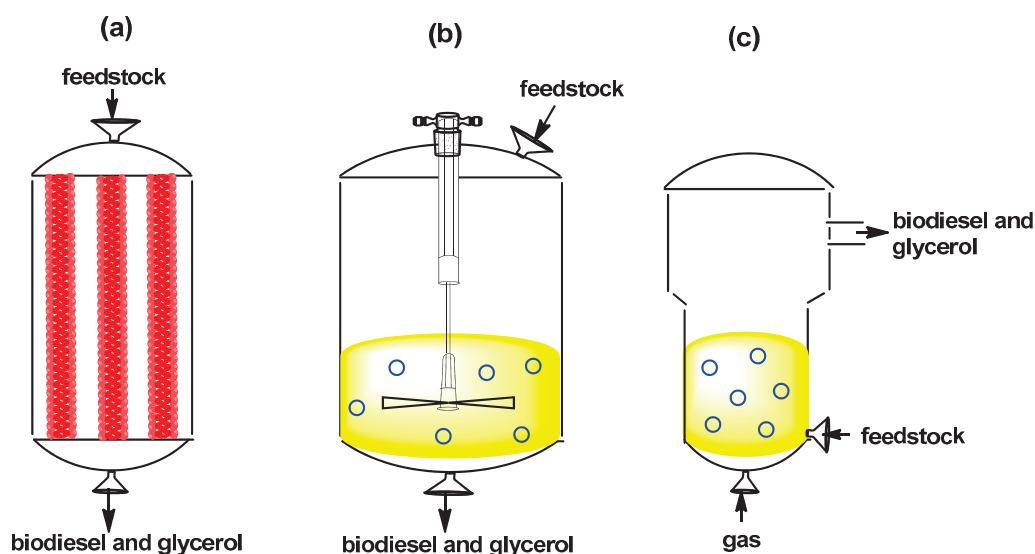


Figure 5. Bioreactors developed for enzymatic biodiesel production: stirred tank reactor (a), packed-bed reactor (b) and fluidized-bed reactor (c). Reprinted from Ref. [18], copyright 2020, with permission from Elsevier.

Other benefits of batch reactions are the simple equipment required, easy process control and high mixing of the substrate. However, the separation of nano-based immobilized lipases in these kinds of reactors requires additional purification steps such as nano-filtration and ultracentrifugation, which are expensive and may lead to lipase inactivation, so these simple reactors are not beneficial for large-scale biodiesel production. This disadvantage can be handled by using magnetic nanomaterials as lipase carriers that can be easily separated from the reaction products, reducing both the cost of recovery and the loss of enzyme activity. Batch processing usually suffers from long reaction times, which require high volume-reactors for industrial production. High-capacity reactors increase the time and operational costs of unloading, cleaning and reloading of products and raw materials [118]. Another challenging factor is the high shear force of the stirrer, which might impact the activity of the immobilized lipase [119]. From these points of view, continuous flow reactions have higher efficiencies than batch reactions for large-scale production [120]. Continuous reactors are superior to batch reactors in terms of long-term stability of processing maintaining lipase productivity and activity. There are many kinds of continuous flow reactors and among them, PBRs are the most popular ones, in which the immobilized lipase is loaded into the column, followed by continuous pumping of the feedstock into the column. To control the pressure, the size of the immobilized biocatalyst should not be too small [121], so large nanofibers are more effective and practical for PBRs.

Table 2. Reactor-scale biodiesel production with nano-immobilized lipase. Reprinted from Ref. [18], copyright (2020), with permission from Elsevier.

Nano-Support	Reactor	Process	Ref.
magnetic nanoparticles	STR	batch	[122]
snowman-like Fe ₃ O ₄ /Au nanoparticles	STR	batch	[123]
Fe ₃ O ₄ coated with poly(styrene-methacrylic acid)	STR	batch	[124]
electrospun poly(acrylonitrile)	PBR	continuous	[125]
nano silicon	FBR	batch	[126]
nano silicon	reverse fluidized-bed reactor	continuous	[127]
nano silicon	PBR	continuous	[128]
Fe ₃ O ₄ nanoparticles	PBR	continuous	[129]
Fe ₃ O ₄ nanoparticles coated with glutaraldehyde	PBR	continuous	[130]

The FBR system is a hybrid of both STR and PBR, in which catalysts with smaller particles than PBRs can be used because there is no need to control the pressure. However, traditional FBRs still have problems, such as catalyst settling, because nano-carriers are easily carried away in the reaction mixture, even at very low flow rates. This problem can be solved by applying circulating fluidized-bed bioreactors, as previously reported [131]. However, separation devices in FBRs are still necessary to recover the nano-catalysts, and the cost of nano-filtration remains high. Again, an alternative strategy could be the use of magnetic nanoparticles for lipase immobilization, but it has not been reported yet in large-scale biodiesel production processes [132].

In general, the scale-up of biodiesel production using nano-based biocatalysts requires optimizing the reactor/process, and in this field, there has been much research for STRs, PBRs and FBRs using nano-biocatalysts, which proves their feasibility; however, the high cost of nano-biocatalyst separation and enzyme deactivation should be taken into account. For industrial biodiesel production, more reactor-scale studies are still required to gather the advantages of batch and continuous processing in a single platform, reducing overall costs and improving the feasibility and versatility of the process.

Regarding the current reactor technology, other types of transesterification reactors were comprehensively reviewed by Tabatabaei et al. [117]. The authors discussed in detail the effects of the main parameters on the transesterification reaction in order to better understand the mechanisms behind each reactor technology. Different transesterification reactors, including rotating, tubular/plug-flow, cavitation, simultaneous reaction-separation and microwave reactors, were then described from scientific and practical viewpoints. The merits and drawbacks of each reactor technology for biodiesel production were highlighted to guide future R&D in this field.

2.6. Glycerol

Glycerol is the major by-product of biodiesel production, and it is a valuable material for other industries. Glycerol accumulates on the surface of catalysts and changes the reaction direction, reducing the yield. More importantly, the surface accumulation of glycerol leads to the formation of a hydrophilic environment around the catalyst, which hinders its catalytic performance [133,134]. To solve this inhibition effect, hydrophobic carriers are used for catalyst immobilization, while the use of organic solvents (hexane, petroleum ether, *n*-heptane and *tert*-butanol) is another option to decrease the reaction medium viscosity and increase the solubility of the organic phase, avoiding phase separation and improving mass transfer efficiency [135,136]. Among suitable organic solvents, *tert*-butanol has the advantage of providing steric hindrance through its *tert*-butyl group, which inhibits its participation in the transesterification reaction. However, the environmental concerns, toxicity and flammability of organic solvents limit the large-scale application of this strategy due to

safety and economic aspects. Therefore, solvent-free systems and green solvents such as supercritical carbon dioxide and ionic liquids have been studied as alternatives to organic solvents [137,138].

3. Inorganic Nanocarriers Used to Develop Lipase-Based Nano-Biocatalysts

To date, some noteworthy nanocatalysts have been developed for biodiesel production, as comprehensively reviewed by Pandit et al. in 2023 [139]. In the case of inorganic nanocatalysts, CaO, ZnO, zeolites, and hydrotalcites have attracted significant research interest [140], however magnetic nanostructures are a unique class of nanomaterials that are able to allow the easy recovery and recycling of the catalyst.

3.1. Magnetic Iron Oxide Nanoparticles

After catalyzing biodiesel synthesis, the biocatalyst should be separated from the mixture and reused again for the next catalytic cycles [141]. As mentioned above, this recovery process is considered one of the main challenges in the biodiesel industry, so recyclable catalysts are urgently required to replace non-recyclable ones. A promising alternative is the immobilization of lipases onto magnetic nanoparticles (MNPs), which allows the separation of the biocatalyst by simply applying an external magnetic field. Magnetic nanostructures have been extensively applied as nanocarriers for different pharmaceutical and biological species to improve the effectiveness of the immobilized molecules and, more importantly, to provide magnetic properties to the resultant nanosystem. In fact, magnetic nanostructures benefit from both their nano- and magnetic aspects and have several advantages for industrial applications, such as ease of synthesis, low cost, biocompatibility, superparamagnetism and magnetic separability, high loading capacity for the loading of different molecules and standardized methods for their large-scale production [142,143]. For biodiesel technology, considerable efforts have been devoted to developing efficient magnetic supports for lipase immobilization, simplifying the post-treatment process and catalyst recovery, and decreasing operation costs [144,145]. Among MNPs, Fe_3O_4 (magnetite) nanoparticles are the most widely used systems for different technologies [146,147]. In this section, the most recent publications on the application of this type of nano-support for lipase immobilization will be discussed in detail.

3.2. Importance of Surface Modification of Magnetic Nanoparticles

The main methods to fabricate Fe_3O_4 nanoparticles (Table 3) [148] include chemical co-precipitation, micro-emulsion, thermal decomposition and solvothermal methods [149]. For large-scale applications, MNPs should first be modified/functionalized to prevent their aggregation, oxidation of the magnetic core, loss of magnetism and dispersibility. Further, surface modification facilitates lipase loading by providing suitable functional groups on the surface of MNPs [150,151].

The functionalizing molecules can attach to Fe_3O_4 NP surfaces by either physical or chemical interactions. Chemical functionalization is much more favourable than physical functionalization, especially when the long-term stability of the modified Fe_3O_4 NPs is required. In the following sections, recent publications on biodiesel production will be divided into two groups: (1) those performed using silane-functionalized MNPs and (2) nanocarriers functionalized with non-silane organic molecules. In the structure of silane molecules, there are active functional groups (e.g., hydrolysable alkoxys) which are suitable for the condensation with $-\text{OH}$ surface groups of MNPs. Conversely, physical modification occurs via electrostatic, hydrogen bonds, van der Waals, and hydrophobic interactions [152].

Table 3. Methods for the synthesis of MNPs, their advantages and disadvantages. Reprinted with permission from an open-access article distributed under the terms and conditions of the Creative Commons Attribution license, MDPI [150].

Method	Advantage	Disadvantage
physical methods (gas-phase deposition)	easy to perform	difficult to control particle size
electron beam lithography	well controlled inter-particle spacing	requirement of expensive and highly complex machines
wet chemical methods (sol-gel synthesis)	precisely controlled in size, aspect ratio, and internal structure	weak bonding, low wear-resistance, high permeability
oxidation method	uniform size and narrow size distribution	small-sized ferrite colloids
chemical co-precipitation	simple and efficient	not suitable for the preparation of highly pure, accurate stoichiometric phase
hydrothermal reactions	easy to control particle size and shape	high reaction temperature, high pressure
flow injection synthesis	good reproducibility and high mixing homogeneity together with a precise control of the process	segmented mixing of reagents under a laminar the flow regime in a capillary reactor
electrochemical method	easy to control particle size	reproducibility
aerosol/vapour phase method	high yields	extremely high temperatures
sonochemical decomposition reactions	narrow particle size distribution	mechanism not yet understood
supercritical fluid method	efficient control of the particle size, no organic solvents involved	critical pressure and temperature
synthesis using nanoreactors	possibility to precisely control NP size	complex conditions
microbial methods (microbial incubation)	high yield, good reproducibility, good scalability, low cost	time-consuming

3.3. Silane-Functionalized Magnetic Nanocarriers

3.3.1. Silane Functionalization Providing $-NH_2$ Groups

In a recent research, João Brandão Júnior et al. studied biodiesel production from vegetable oils obtained from two common Brazilian trees: tucuman and babassu, whose composition is dominated by petroleum acid [153,154]. The authors first synthesized Fe_3O_4 NPs by the co-precipitation method and then functionalized them with APTES ((3-aminopropyl)triethoxysilane) to introduce $-NH_2$ groups on the magnetic core. Afterwards, Fe_3O_4 NPs-APTES were activated with glutaraldehyde to convert their amine groups into $-CHO$ groups in mild conditions and at 20 °C. Lipase immobilization was then performed in the last step by introducing a low-cost commercial lipase (Eversa[®] Transform 2.0 (Novozymes, Bagsvaerd, Denmark), derived from genetically modified *Aspergillus oryzae*) into the Fe_3O_4 NPs-CHO NPs to chemically link the lipase to the magnetic nanocarrier [155]. Biodiesel production from two vegetable oils was studied using both free and immobilized lipase (enzymatic load: 80 UpNPB g^{-1}) through esterification of the FFAs with both ethanol (E) and methanol (M). Upon the selected reaction conditions (1:1 oil:alcohol molar ratio; temperature: 37 °C; reaction time: 2–8 h for free enzyme and 8 h for the immobilized biocatalyst), the free Eversa[®] Transform 2.0 lipase showed higher conversion efficiency for the babassu oil (96.7% (M) and 93.4% (E)) than tucuman (52.6% (M) and 57.5% (E)). The free lipase worked very well on babassu oil with both methanol and ethanol. However, for the heterogeneous esterification reactions using the immobilized enzyme, the best results were obtained with ethanol for both tucuman and babassu oils, with 86.0% and 82.2% yields, respectively. Furthermore, the immobilization resulted in a dramatic enhancement of the conversion efficiency in methanol for tucuman, from 52.6% (free lipase)

to 68.7% for immobilized lipase. After each catalytic cycle, the immobilized biocatalyst was magnetically separated, washed with hexane and reused for three cycles. The results indicated a subtle decrease in catalytic activity after the third cycle, which might be due to the residual hexane (not evaporated) in the enzymatic fraction, interfering with the enzyme's behaviour by changing its 3D structure and, consequently, its catalytic activity.

In 2022, Parandi et al. studied biodiesel production from waste cooking oil (WCO) catalyzed by immobilized *Candida antarctica* Lipase B (CALB) [156]. To this aim, the authors synthesized Fe_3O_4 NPs (by the co-precipitation method) and then functionalized them using two silane reagents, tetraethyl orthosilicate (TEOS) and *N*-[3-(trimethoxysilyl)propyl] ethylenediamine (TSD), to improve their colloidal stability and provide $-\text{NH}_2$ groups onto the surface of functionalized Fe_3O_4 NPs to facilitate and enhance lipase immobilization (Figure 6). After optimizing lipase immobilization (2.5 mg mL^{-1} , 5 h, 35°C , pH 7), they studied operating parameters such as temperature ($30\text{--}70^\circ\text{C}$), methanol:oil molar ratio (1:1 to 5:1), contact time (12–36 h) and catalyst dosage (0.2–1 g) to maximize biodiesel production yield. The highest yield (96%) was obtained using 1 g catalyst and 4:1 methanol:oil molar ratio at 40°C for 30 h. The reusability of this nano-biocatalyst was performed by magnetic separation, washing with hexane-acetone (1:1), and the results showed the maintaining of the catalytic activity until the 6th cycle ($>70\%$), then it dropped to $<50\%$ which can be due to the detachment of lipase from the nano-support (due to weak physical interactions among lipase molecules and MNPs) and lipase denaturation due to sequential washing steps with organic solvents.

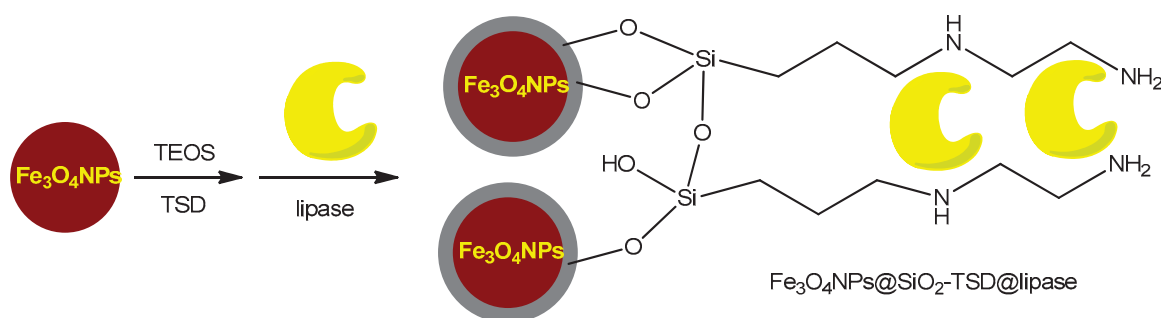


Figure 6. Schematic routes for the preparation of $\text{Fe}_3\text{O}_4\text{NPs@TEOS-TSD}$ nanocomposite and immobilization of CALB onto the magnetic support. Adapted from Ref. [156], copyright (2021), with permission from Elsevier.

For the long-term sustainable development of lipase-based biodiesel technology, the organic solvents commonly used in the production process should be changed with green solvents that are easy to recycle and recover. Ionic liquids (ILs) [157], supercritical carbon dioxide (scCO_2) [158] and deep eutectic solvent (DES) [159] have been proposed as eco-friendly candidates for biodiesel manufacturing. ILs can act as non-aqueous reaction media due to their unique characteristics, such as low toxicity, low volatility, low flammability and high solubility in both inorganic and organic materials [160,161]. Furthermore, ILs exhibit a stabilizing effect on enzymes and have negligible vapour pressures [162]. For instance, Patel et al. used $[\text{Hmim}][\text{PF}_6]$ as the reaction medium to use *Candida rugosa* lipase (CRL) for biodiesel production from Chinese tallow kernel oil [163]. In this sense, the application of MNPs for this type of solvent-free enzymatic biodiesel production is rare. In a recent study in 2022, Xing's group [164] immobilized *Rhizomucor miehei* lipase (RML) onto $\text{Fe}_3\text{O}_4\text{NPs-APTES}$ using glutaraldehyde and studied Jatropha oil transesterification for biodiesel production in ILs (Figures 7 and 8). Fifteen kinds of ILs were assessed as the reaction medium, and several reaction parameters were also optimized in this study, e.g., IL:substrate weight ratio, methanol:oil molar ratio, amount of catalyst, oil feedstock, reaction temperature and time.

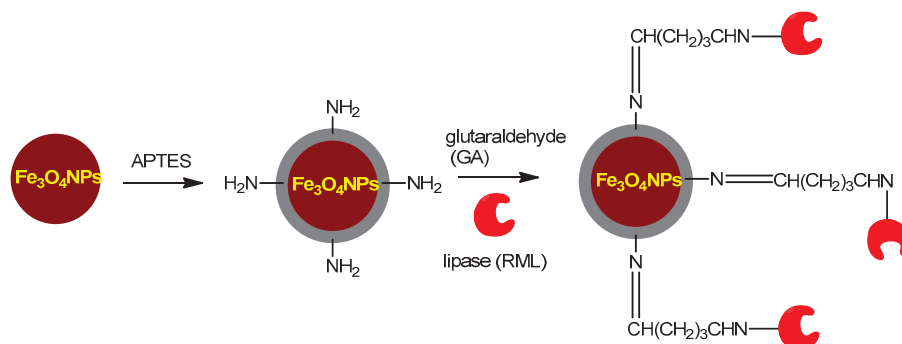


Figure 7. Preparation of magnetic $\text{Fe}_3\text{O}_4\text{NPs}$ -APTES-GA-RML. Redrawn from Ref. [164], copyright 2022, with permission from Springer.

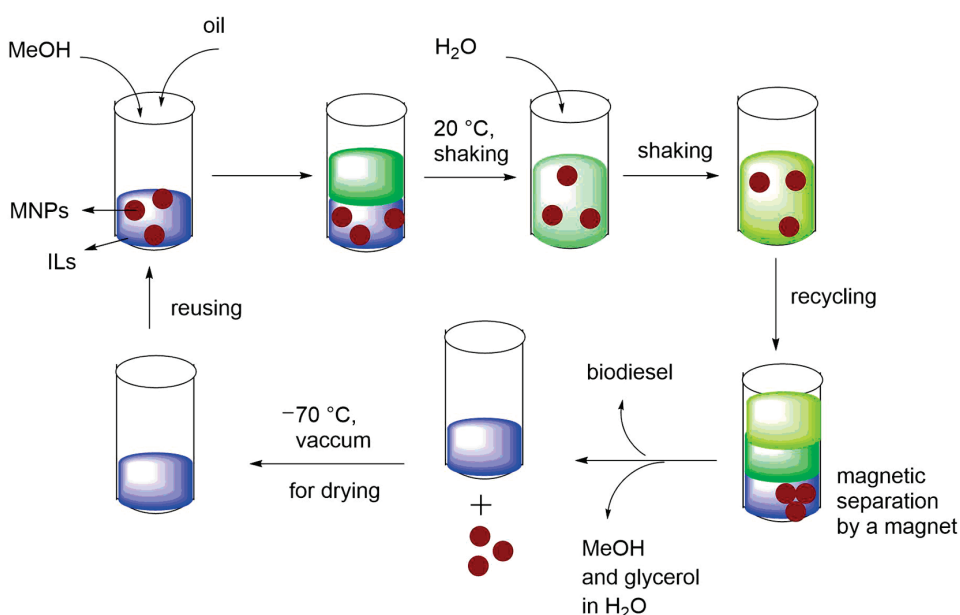


Figure 8. Schematic representation of the cyclic process for the biocatalytic synthesis of biodiesel in ILs. Adapted from Ref. [164], copyright (2022), with permission from Springer.

[BMIM][PF₆] demonstrated to be the best medium for immobilized RML, showing five times higher catalytic activity than the free enzyme and maintaining 60% of its initial performance after five cycles in a 48 h reaction. Moreover, the immobilized RML showed high storage stability, maintaining its catalytic activity after a 98-day storage at $-20\text{ }^{\circ}\text{C}$.

As mentioned in Section 2.4, there are two general types of production processes for scaling up lipase-based methods: continuous and batch operations. In this regard, continuous reactions are more economical when compared to batch systems [165]. In lab-scale studies, continuous systems can be made by glass columns with a packed-bed structure in which there is an upward or downward flow of starting materials and feedstock, and the products are gathered from the outlet of the column. Despite the low flow rates of packed-bed reactors (PBR), they show increased contact time between the oil feedstock and biocatalyst, leading to high conversion rates [166], so the application of continuous-type compacted-bed reactors for immobilized lipases is increasing [167]. In this regard, Bento et al. immobilized a commercial *Burkholderia cepacia* lipase onto MNPs-APTES ($\text{Fe}_3\text{O}_4/\gamma\text{-Fe}_2\text{O}_3$) using glutaraldehyde as a coupling agent [168]. The immobilized biocatalyst was used for producing biodiesel from kernel oil in a continuous-operating fixed-bed reactor operating in a flow with ethanol at an oil:ethanol molar ratio of 1:12, $50\text{ }^{\circ}\text{C}$ and 16 h reaction time. The enhanced stability of the immobilized lipase allowed operating up to 47 days with high productivity of $38.7 \pm 0.7\text{ mg g}^{-1}\text{ h}^{-1}$, ester content of $>96.5\%$ and kinematic viscosity value of $5.32 \pm 0.4\text{ mm}^2\text{ s}^{-1}$ at $40\text{ }^{\circ}\text{C}$, meeting the requirements of the ASTM (D6751) and ANP

standards for biodiesel fuel. These results indicate that this magnetic biocatalyst can be further studied for the continuous development of different industrial sectors.

Lipase-producing microorganisms are important biotools for preparing lipases due to their unique features such as rapid reproduction, large variety, short production cycle, adaptability and easy scale production. Biodiesel production from microbial oils and plants requires two steps: (1) oil extraction and (2) transesterification; however, during oil extraction, some unsaturated fatty acids are lost due to their oxidation, decreasing biodiesel yield. Hence, the one-step synthesis of microorganism-derived biodiesel has attracted growing interest in recent years. For instance, Cao et al. used a lipase-producing *Burkholderia pyrrolica* WZ10-3, isolated from the soil of Mt. Emei in China, possessing high lipase activity (up to 280.0 U/mL) and good tolerance to pH and temperature (with maximum transesterification rate of 97%) [169]. To enhance lipase efficiency, the authors developed a one-step transesterification method of wet yeast using the immobilized lipase, the oleaginous yeast *Saitozyma podzolica* ZwY-2-3 and the lipase-producing *Burkholderia pyrrolica* WZ10-3. To achieve this, Fe₃O₄NPs were first functionalized with APTES, followed by glutaraldehyde activation and condensation with the primary amine of WZ10-3 lipase to realize the covalent immobilization of the enzyme. The APTES-glutaraldehyde modification can change the surface property from hydrophilic to hydrophobic, and during this immobilization process, the hydrophobic interface activated the lipase conformation and its “open” form on the Fe₃O₄NPs, improving its dispersion stability, surface hydrophobicity and biocompatibility. Furthermore, compared with direct immobilization, the use of APTES-glutaraldehyde extends the spacer arm, which results in lower steric hindrance and higher activity of the immobilized enzyme. In the optimized lipase immobilization conditions (enzyme dosage: 30.22 mL, glutaraldehyde concentration: 2.0%, T: 40 °C and time: 4 h), the immobilized lipase showed a 50% enhanced temperature tolerance. Additionally, immobilization dramatically improved lipase stability for up to 48 days when stored at 4 °C. Besides enhancing the transesterification rates, the immobilized enzyme still showed 90% catalytic activity after ten cycles.

Carbon-based stabilizing agents have been extensively used for Fe₃O₄NP functionalization because of their biodegradable nature and thermo-chemical stability, which makes them suitable for the physical adsorption and covalent binding of the enzyme to the support. Graphene oxide (GO) has been used in many enzyme immobilization studies because of its thermal stability, large surface area with suitable functional groups for high enzyme loading and easy modification [170,171]. In 2020, Nematian et al. studied the immobilization of *Rhizopus oryzae* lipase (ROL) on GO-functionalized MNPs (MGO) and used it for producing biodiesel from *Chlorella vulgaris* microalgae oil [172]. Additionally, the authors studied the immobilization of MGO-APTES and MGO-APTES-GA (where both APTES and glutaraldehyde were used). *Rhizopus oryzae* lipase was immobilized on MGO and MGO-APTES through electrostatic interactions, while the MGO-APTES-GA support immobilized lipase through covalent bonding. The maximum loading of ROL (70.2%) and the highest biodiesel conversion (71.19%) was achieved by MGO-APTES-GA-ROL, which maintained 58.77% of its initial catalytic performance after five cycles of biodiesel production and showed the best catalyst reusability. The authors reported an enhanced loading capacity and thermal and storage stability due to the covalent linkage of the enzyme.

In 2020, Nematian et al. compared the physical and chemical loading of *Rhizopus oryzae* lipase (ROL) on MNPs for producing biodiesel to study the effect of enzyme covalent bonding on catalytic performance [173]. For non-covalent immobilization, ROL was loaded onto bare MNPs and APTES-functionalized MNPs, while for covalent attachment, glutaraldehyde (GA) was used to chemically link ROL to MNPs-APTES (Figure 9). The authors compared these three nano-biocatalysts for their esterification productivity, hydrolytic activity, kinetic parameters and reusability. For all the immobilized nanosystems, rapid magnetic separation was achieved and successfully repeated for five cycles. The results showed an increased conversion in the presence of MNPs-APTES-ROL, compared to MNPs-ROL, which can be due to a larger polar area around the support surface provided by

APTES amine groups. It results in dipolar interactions between ROL and the support surface, providing less steric hindrance compared with MNPs-ROL. The results showed that the covalent attachment enhanced lipase loading from 36.35% (in MNPs-ROL) to 51.75 wt% (in MNPs-APTES-GA-ROL). The covalent bonding of this lipase resulted in an improved transesterification reaction with the highest conversion (69.8%) among the immobilized biocatalysts, minimized catalyst wasting and maximum recyclability. The formation of covalent bonds promotes lipase rigidity, protects it from leakage, and maintains its activity for longer periods.

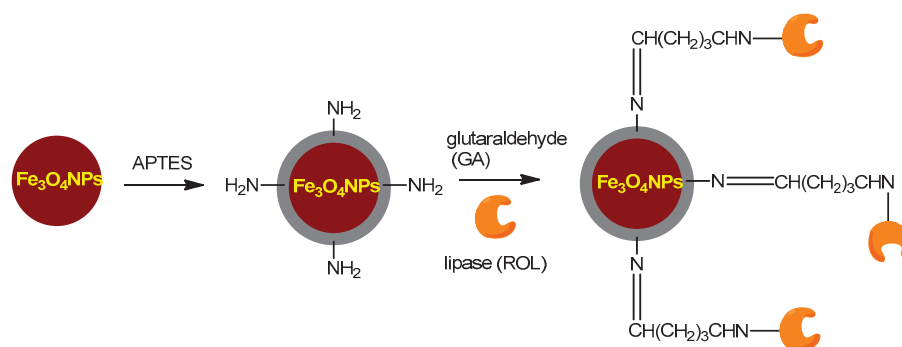


Figure 9. Schematic routes for the preparation of biocatalysts to produce biodiesel. Redrawn from Ref. [173], copyright 2020, with permission from Elsevier.

Palm fatty acid distillate (PFAD) is a by-product of palm oil refining, which can be a promising feedstock for biodiesel production, reducing by 60–70% biofuel cost [174]. PFAD is considered a low-grade feedstock and can be used instead of coconut oil as a food ingredient, solving disposal-related problems. Cho et al. studied the non-catalytic esterification process of PFAD and obtained >85% conversion efficiency [175]. The produced biodiesel was in accordance with European standards, but the whole process required long times and high temperatures, increasing the production cost. Hidayat et al. studied biodiesel production from PFAD from coconut shells using activated carbon catalysts at 60 °C with a conversion efficiency of 91% [176].

For this type of oil feedstock, biocompatible composites such as carbon-based materials (e.g., activated carbon, graphene oxide and chitosan) can increase the catalytic activity of the lipase.

Buchori et al. reported PFAD-derived biodiesel production using MNPs-APTES-GA-lipase impregnated with activated carbon oxide [177]. The transesterification reaction was carried out at 56 °C for 6 h, with a 16:1 methanol to PFAD molar ratio. A 94.915% yield for biodiesel production was obtained in such conditions. Biodiesel yield decreased with repeated use of the catalyst after three cycles due to lipase morphological changes.

3.3.2. Silane Functionalization Providing Epoxy Groups

In 2023, Wang et al. studied biodiesel production from waste oil using the co-immobilization of two different lipases, non-specific *Burkholderia cepacia* lipase (BCL) and 1,3-specific *Thermomyces lanuginosus* lipase (TLL), on Fe₃O₄ MNPs functionalized with 3-glycidyloxypropyltrimethoxysilane (3-GPTMS) (co-BCL-TLL@Fe₃O₄NPs) [178]. The 3-GPTMS silane acts as both a stabilizer and coupling agent, linking the magnetic core to the lipases. Fe₃O₄ NPs were synthesized using the well-known co-precipitation method, which is suitable for large-scale production. In the next step, they were functionalized with 3-GPTMS silane in a typical sol-gel reaction. In detail, –OCH₃ groups of the silane were hydrolyzed and condensed with the surface –OH groups of bare MNPs to form a silica network around the magnetic core. More importantly, this silane provided epoxy groups on the surface of functionalized Fe₃O₄ NPs for the next step, lipase immobilization, which was achieved by a multicomponent reaction between epoxy group, cyclohexyl isocyanate and carboxy residues of lipase, accelerated by nucleophilic attack of isocyanate to

epoxy functional groups of modified Fe_3O_4 NPs. The co-immobilization process was optimized by tuning the main factors affecting the catalytic activity of co-BCL-TLL@ Fe_3O_4 NPs in biodiesel production: e.g., amount of carrier (functionalized Fe_3O_4 NPs), TLL:BCL immobilization ratio and cyclohexyl isocyanate dosage for the coupling reaction. The co-immobilized lipases exhibited an enhanced catalytic activity (92.9% yield) after 6 h, compared with individually immobilized-TLL (63.3% yield), -BCL (74.2% yield) and their combined-use of free forms (70.6%). Under optimal reaction conditions, six various feed-stocks were used for biodiesel production, catalyzed by co-BCL-TLL@ Fe_3O_4 NPs, including waste oil (waste cooking oil and rancid oil), edible vegetable oil (soybean oil), animal oil (chicken oil) and non-edible vegetable oil (cottonseed oil and jatropha oil).

co-BCL-TLL@ Fe_3O_4 NPs showed superior catalytic activity (above 90%) for all tested oils after 12 h, compared to the mono-lipase immobilization and combined use of free lipases. Both free lipases showed an oil-dependent catalytic activity, indicating that they possessed different typoselectivity and regioselectivity for the transesterification with triacylglycerols. Furthermore, the recycling operation of co-BCL-TLL@ Fe_3O_4 NPs was tested by rapid magnetic separation, and results showed that this nano-enzyme could maintain 77% of its initial activity after nine cycles. The reusability, high catalytic efficiency and wide substrate adaptability of this co-BCL-TLL@ Fe_3O_4 NPs catalyst introduce it as an economical biocatalyst for further studies on biodiesel production.

In another study, two lipases from *Rhizomucor miehei* (RML) and *Thermomyces lanuginosa* (TLL) were immobilized on silica-modified magnetic nanoparticles (Fe_3O_4 NPs@ SiO_2) [179]. Tetraethoxysilane (TEOS) was used as the silane coupling agent, followed by the introduction of epoxy groups on their surface by using a second silane, 3-glycidyloxypropyl trimethoxysilane. As the third step, the epoxy groups were oxidized to activate the surface and provide aldehyde functionalities, which can react with different nucleophilic amine groups of the lipase surface, leading to its covalent binding and high stability against conformational changes by external stimuli (e.g., pH, heat, organic solvents) (Figure 10). These sequential functionalizations also benefit high loading capacity for the RML (81 mg) and TLL (97 mg) with enhanced thermal stability (54 and 97% initial activity retention at 65 °C for RML and TLL, respectively). The immobilized lipases were used for biodiesel production from waste cooking oil with yields of 93.1% (immobilized TLL) and 57.5% (immobilized RML) under optimal conditions. The results showed good reusability of both nano-catalysts at 50 °C with the retention of 80% (for immobilized RML) and 95% (for immobilized TLL) of the initial catalytic activities after five cycles. This can be a good indication of the covalent binding of lipases onto the support, which prevents enzyme leakage under mechanical stirring during FAME production.

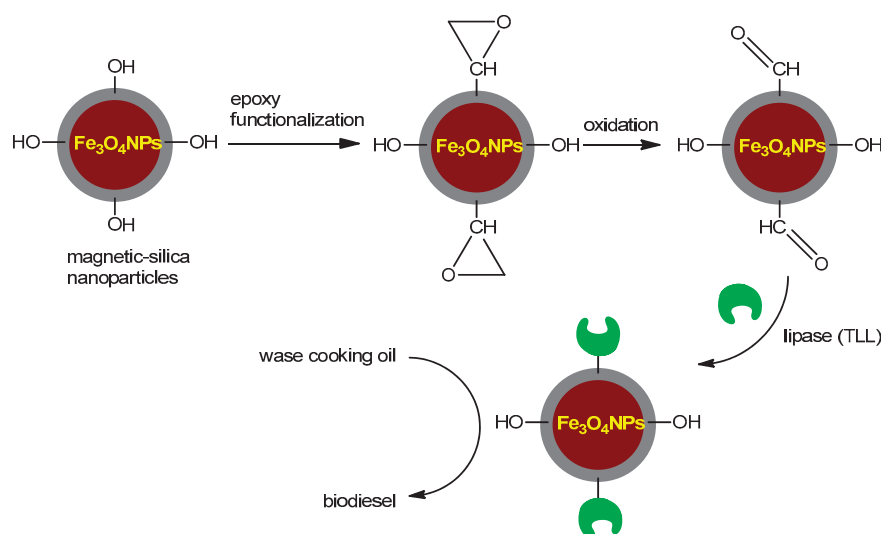


Figure 10. Schematic routes for the preparation of biocatalysts to produce biodiesel. Adapted from Ref. [179], copyright (2020), with permission from Elsevier.

3.4. Magnetic Nanocarriers Functionalized with Non-Silane Linkers

3.4.1. Magnetic Nanocarriers Functionalized with Small Molecules and Other Functionalizing Agents

In 2023, Parandi et al. studied the non-covalent immobilization of *Candida antarctica* Lipase B (CALB) on the surface of a magnetic nanocomposite containing a $\text{Fe}_3\text{O}_4\text{NPs}$ core coated with TiO_2 and a secondary layer of graphene oxide (GO) to form $\text{Fe}_3\text{O}_4\text{NPs-Ti-GO}$ (Figure 11) [180]. The presence of TiO_2 and GO layers enhanced the stability of the magnetic core against oxidation and aggregation. Furthermore, GO contains some hydrophilic functional groups which facilitate the accessibility of oil to alcohol to convert FFA into esters. The GO layer also improved the charge transfer via the interface, providing a synergistic catalytic activity [181,182]. The hydrophobic TiO_2 layer, on the other side, enhanced the immobilization rate of the lipase via hydrophobic interactions [183]. $\text{Fe}_3\text{O}_4\text{NPs-Ti-GO}$ improved lipase stability, lifetime and catalyst recovery. The authors studied the effect of different parameters on the immobilization efficiency and immobilized lipase activity, including lipase concentration, pH, temperature and time. For lipase immobilization, the optimum condition was found to be: 2 mg/mL of lipase, 4 h immobilization time at pH 7 and 35 °C. Beyond each of these parameters, there is a diminishing trend for both immobilization efficiency and catalytic activity due to the blocking of lipase active sites (increasing lipase concentration) or lipase denaturation (pH and temperature parameters). The authors also evaluated the thermal stability of both free and immobilized lipase in the range of 30–80 °C. The complete inactivation of free lipase was observed at 80 °C; however, the immobilized lipase maintained 64% of its initial activity at the same temperature, attributed to the rigidity of the immobilized lipase skeleton as a result of the binding to the magnetic support. The results also showed an enhanced stability of immobilized lipase in methanolic solutions. The highest biodiesel yield of 92% was observed with 4 wt% of catalyst, the methanol:oil ratio of 5:1, at 45 °C and for 40 h. The reusability of the magnetic nanocatalyst was tested by separation of $\text{Fe}_3\text{O}_4\text{NPs-Ti-GO-CALB}$ using a magnet, followed by washing with hexane. Biocatalyst activity was maintained until the 5th cycle and then reduced due to lipase denaturation owing to continuous washing and recycling.

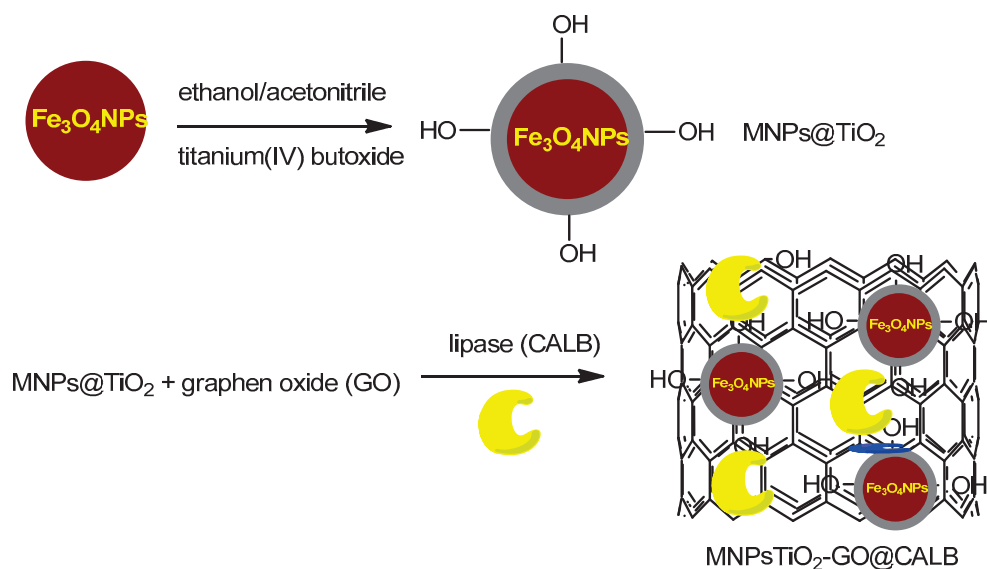


Figure 11. Schematic illustration of the preparation process of magnetic $\text{Fe}_3\text{O}_4\text{NPs-Ti-GO-CALB}$ biocatalyst. Redrawn from Ref. [180], copyright 2023, with permission from Elsevier.

Zhong et al. synthesized a hybrid nanoflower through the self-assembly of $\text{Cu}_3(\text{PO}_4)_2$ and loaded it with enzyme molecules, obtaining low diffusion limits and high enzyme loading (Figure 12) [184]. In the enzyme-hybrid nanoflowers, the favourable interactions among enzymes and metal ions afford high enzyme activity and stability. The hybrid

nanoflowers can be synthesized in mild conditions and are suitable for preparing hybrid nanocatalysts for biodiesel production. Additionally, the combination of specific surfactants can activate lipases that maintain a higher activity even after immobilization. Despite the unique features of hybrid nanoflowers, they have low mechanical properties and reusability due to their fragile nanostructures, which can be improved by their combination with MNPs to achieve magnetic recoverability of the catalyst. To this aim, the authors integrated two types of $\text{Fe}_3\text{O}_4\text{NPs}$ into the surfactant-activated lipase hybrid nanoflowers by co-precipitation ($\text{Fe}_3\text{O}_4\text{NPs}$ embedded-MhNF) and covalent cross-linking ($\text{Fe}_3\text{O}_4\text{NPs}$ -APTES-GA cross-linked-MhNF) to obtain recyclable and magnetic activated lipase-inorganic hybrid nanoflowers (MhNF). In biodiesel production from soybean oil, a dramatic enhancement of activity recovery was observed for both MhNF (190%) and cross-linked-MhNF (174%), compared to low activity recovery of non-magnetic lipase hybrid nanoflowers (77%). Compared with activated free lipase, the MhNF showed high resistance against methanol and longer storage stability; they could be easily recovered by applying a magnet and reused with no significant activity loss even after ten cycles (84% of initial activity), unlike the activated hNF which retained only 26% of their initial activity. In repeated batch biodiesel production, the yield obtained with MhNF catalysis reached 88%, while the free enzyme afforded only 69%. More importantly, the yield of the MhNF-catalyzed process was maintained at 76% even after six cycles.

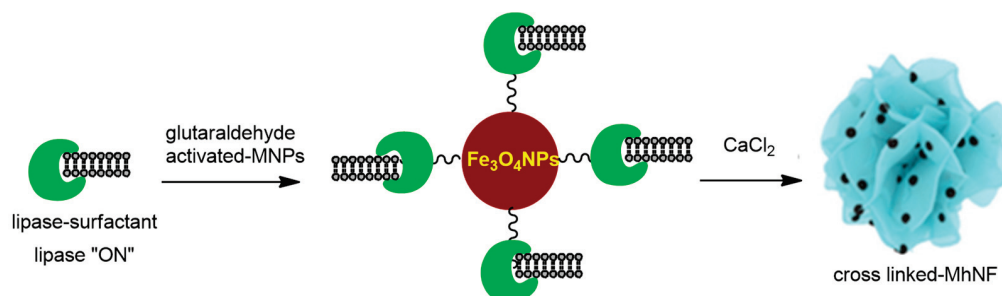


Figure 12. Schematic illustration of the preparation process for magnetic activated lipase-inorganic hybrid nanoflowers (MhNF). Adapted from Ref. [184], copyright 2021, with permission from Elsevier.

As mentioned previously, agricultural wastes are available worldwide, and their exploitation may provide significant economic, social and environmental benefits. Approximately 38–52% of solid wastes in wine industries are grape seeds, which account for 2–5% of the grape weight. Grape seeds generally contain about 10% proteins, 10–20% lipids, 40% fibres, sugars, minerals, complex phenolics and indigestible components (mainly pectins and cellulose). Particularly, grape seed oil comprises high amounts of unsaturated fatty acids, e.g., linoleic acid (72–76% *w/w*), so this agricultural waste may be considered as a new potential feedstock for large-scale biofuel production. In a first study aimed at exploring the potential of such feedstock, Sarno et al. synthesized $\text{Fe}_3\text{O}_4\text{NP}_5/\text{AgNPs}$ made of 9 nm- $\text{Fe}_3\text{O}_4\text{NPs}$ supporting AgNPs (~6 nm), coated with tartaric acid and used for the electrostatic immobilization of *Thermomyces lanuginosus* (TLL) lipase [185]. The activity recovery and immobilization efficiency of this $\text{Fe}_3\text{O}_4\text{NPs}/\text{AgNPs}$ support have an indirect relationship with the initial enzyme concentration due to the saturation of binding sites of support and diffusion restrictions. With a lipase concentration of 0.1 mg/mL, activity recovery and immobilized efficiency of 92% and ~90% were obtained, respectively, after 3 h. Regarding the AgNPs' function, they facilitate the transfer of electrons (acting as conduction centres), inducing enzymes to adopt an advantageous alignment, leading to high conversion yields (94%). The analysis of the biodiesel showed that linoleic acid methyl ester and oleic acid methyl ester account for ~89% of the total biodiesel, consistent with the oil composition. Using an oil:methanol ratio of 1:6, lipase concentration of 10%, and 45 °C for 24 h, a total FAME of $96.54 \pm 0.26\%$ was obtained, in accordance with the requirements reported in European EN14124 standard for biodiesel [186].

Sarno et al. reported the synthesis of MNPs-tartaric acid (TA) through a solvothermal method and subsequently used for direct physical immobilization of *Thermomyces lanuginosus* (TLL) lipase (via interaction between support functional groups and the enzyme) [187]. MNPs-tartaric acid-TLL was used for biodiesel production from DWSO in a solvent-free system. With an alcohol/oil molar ratio of 6:1, the immobilized lipase afforded a 90% yield (with excellent reusability), higher than the yield of free lipase (76% with a molar ratio of 3:1). DWSO-derived biodiesel presented a total FAMES content of about $96.6 \pm 0.02\%$ with a linolenic methyl ester content of $0.62 \pm 0.07\%$, in agreement with the EN14214 standard, indicating the feasibility of DWSO as feedstock for biodiesel production.

In 2020, Sarno et al. studied biodiesel production from WCO using *Thermomyces lanuginosus* (TL) lipase (E.C.3.1.1.3) directly immobilized on citric acid/oleic acid modified $\text{Fe}_3\text{O}_4/\text{Au}$ nanocomposite, without requiring complex procedures and reagents, through physical interactions [188]. The snowman-like $\text{Fe}_3\text{O}_4/\text{Au}$ nanocomposite was synthesized by a hydrothermal reaction of $\text{Fe}(\text{acac})_3$, HauCl_4 and oleic acid precursors at high temperatures ($>200\text{ }^\circ\text{C}$) for 2 h, followed by a ligand exchange of oleic acid with citric acid at room temperature, to obtain hydrophilic $\text{Fe}_3\text{O}_4/\text{Au}$ nanocomposite. This immobilized lipase afforded a remarkable biodiesel yield of $\sim 90\%$ without any pre-treatment under the selected conditions (lipase concentration of 20%, $45\text{ }^\circ\text{C}$, 24 h, 1:6 oil/methanol molar ratio), maintaining its catalytic performance above 74% after the first three cycles of use. The produced biodiesel was analyzed according to the European biodiesel specification, and the results obtained (ester content of $97.8 \pm 0.21\%$ and a linolenic methyl ester content of $0.53 \pm 0.03\%$) were in agreement with the EN14214 requirements, demonstrating the feasibility of WCOs-derived biodiesel as a fuel. Regarding the role of $\text{Fe}_3\text{O}_4/\text{Au}$ nanocomposite, they reported that the citric acid and the presence of residual oleic acid help the lipase to expose its polar tail to the medium. This not only favours interfacial activation but also good activity in the presence of water. The comparison between different AuNP sizes containing $\text{Fe}_3\text{O}_4/\text{Au}$ highlights that AuNPs help favourable lipase orientation and thus increase enzyme loading and activity.

In 2020, Li et al. selected *Thermomyces lanuginosus* lipase (TLL) due to its relatively low cost and covalently immobilized it onto Fe_3O_4 NPs, obtaining a magnetic responsive biocatalyst [189]. Aqueous monodisperse Fe_3O_4 NPs with surface carboxyl group were synthesized by thermal decomposition of iron carboxylate salts. These carboxylate functional groups were activated using EDC/NHS coupling agents. Then, TLL amine groups were covalently linked with MNPs-activated groups to form amide bonds. The effects of pH and temperature on the enzymatic activity of both Fe_3O_4 NPs-TLL and free TLL were studied. The same optimal pH (8.5) and temperature ($40\text{ }^\circ\text{C}$) values were obtained for both free and immobilized TLL, but the latter showed a higher tolerance to both pH and temperature variations [190,191]. The improved tolerance of immobilized lipase might be due to a stabilization of the covalent immobilization. The optimized parameters for biodiesel synthesis were the following: methanol:oil molar ratio = 4.0, water content = 1.5% of oil weight, immobilized lipase to oil = 9.0% (w/w) at $41\text{ }^\circ\text{C}$ for 28 h, which resulted in an 82.20% yield. The immobilized biocatalyst could be recycled and reused up to 10 cycles with a 10.97% yield decrease.

3.4.2. Magnetic Nanocarriers Functionalized with Polymers

Chitosan (CS) is another biocompatible and cost-effective functionalizing molecule for MNPs to enhance lipase loading and prevent the surface oxidation of the magnetic core [192,193]. The polycationic CS can form microaggregates in the presence of multivalent anions, such as phosphate or citrate, to mediate the self-assembly of anionic MNPs and form a surrounding shell. Then, this template can be disassembled, leaving a microcapsule structure suitable for the encapsulation of different negatively charged lipases by electrostatic interaction with the polycationic chains of CS [194,195]. The microcapsule structure protects the confined lipases against the external environment, simultaneously allowing the transport of substrates and products across the shell [196]. For instance, Wei et al. developed

a one-pot, cost-effective and fast co-immobilization of *Aspergillus oryzae* (AOL) and *Rhizomucor miehei* (RML) lipases in magnetic chitosan microcapsules to obtain highly efficient biocatalysts for WCO (waste cooking oil)-derived biodiesel production (Figure 13) [197]. For heterogeneous oils such as WCO, the combination or co-immobilization of different lipases with various selectivities is considered an efficient strategy for increasing biodiesel yield. In previous studies, AOL exhibited high resistance to FFA and methanol, while RML showed improved acyl migration efficiency and prominent tolerance under anhydrous conditions, showing selectivity for oleic/elainic acids-containing substrates, which are present in WCOs.

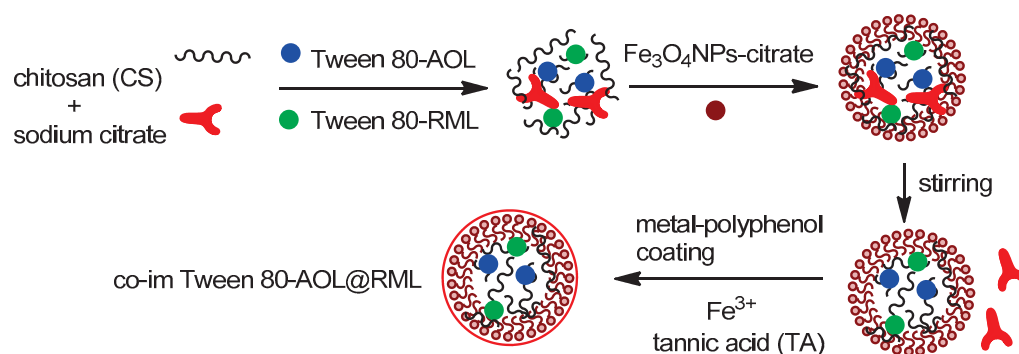


Figure 13. Schematic diagram of the preparation of co-immobilized Tween 80-AOL@RML. (Key: AOL: free *Aspergillus oryzae* lipase; RML: free *Rhizomucor miehei* lipase; Tween-AOL: *Aspergillus oryzae* lipase bio-imprinted using Tween 80; Tween-RML: *Rhizomucor miehei* lipase bio-imprinted using Tween 80; co-im Tween-AOL@RML: co-immobilized Tween-AOL and Tween-RML). Adapted from Ref. [197], copyright 2022, with permission from Elsevier.

Lipase encapsulation was performed by self-assembly of negatively-charged Fe₃O₄NPs-citrate onto cationic cross-linked chitosan-citrate aggregates containing lipases. The co-immobilization of AOL@RML achieved a dramatic increase in biodiesel yield under optimum conditions (up to 98.5%). The presence of thermally stable RML and methanol-tolerant AOL in a single nanoplatform provided a synergic catalytic performance under excess methanol and variable temperatures, which was superior to the individual lipase counterparts. The co-immobilized AOL@RML maintained 96% of its initial activity after three cycles without inactivation. This research was introduced as the first study of the synergic effect between co-immobilized RML and AOL for WCO-derived biodiesel production, and this easy and cost-effective biocatalyst preparation suggests a promising pathway for the preparation of highly efficient industrial co-immobilized lipases.

Both natural and synthetic polymers have been used as coatings for MNPs, providing active surface functionalities, such as epoxy and amine groups, suitable for lipase immobilization through interaction with amine groups. Despite the popularity of this type of surface modification, it still requires the activation of amine groups using aldehydes (e.g., glutaraldehyde), which adds operational costs and time to the whole process, prompting the search for alternative strategies.

As a versatile coating for MNPs, polydopamine contains both amine and catechol groups, which efficiently modify the surface of NPs and enhance the colloidal stability [198,199]. For one-step surface modification of MNPs with polydopamine, a common method is alkaline self-polymerization of dopamine in the presence of MNPs, in which the catechol group of dopamine converts into the indo-5, 6-quinone, followed by a series of inter/intra molecular reactions to form a polydopamine layer on MNPs surface. After polymerization, there will be residual catechol and quinone surface groups, which can react with nucleophiles such as amine and thiol groups through Schiff base formation and Michael addition reaction.

Touqeer et al. synthesized Fe₃O₄NPs by solvothermal method and functionalized them with polydopamine through the self-polymerization of dopamine in alkaline conditions in

the presence of MNPs [200]. The thiol and amine nucleophilic groups of *Aspergillus terreus* AH-F2 lipase reacted with the surface quinone and catechol groups of $\text{Fe}_3\text{O}_4\text{NPs}$ -PDA by Michael addition and Schiff base mechanisms without the need for any activating or coupling agents (Figure 14). The synthesized ($\text{Fe}_3\text{O}_4\text{NPs}$ -PDA-Lipase) biocatalyst was used for biodiesel preparation from WCO, achieving a maximum activity of 17.82 U/mg/min (equal to 97.27% of free lipase activity). Moreover, the immobilized biocatalyst revealed better tolerance to higher temperatures/pHs compared with the free lipase. Under optimum conditions (10% biocatalyst percentage concentration, 6:1 CH_3OH :oil ratio and 0.6% water content, at 37 °C and 30 h), the highest yield of 92% was achieved and maintained for the first four cycles, then dropping to 25.79% after seven cycles. The properties of the produced biofuel were in agreement with the ASTM D standard, qualifying this system as a cost-effective and sustainable biocatalyst for biodiesel production.

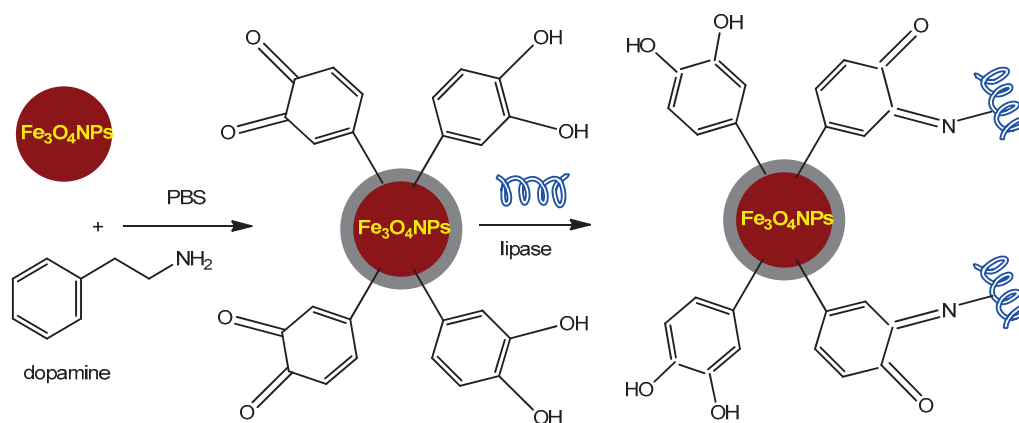


Figure 14. Schematic representation of lipase immobilization on dopamine-coated MNPs. Redrawn from Ref. [200] under the terms and conditions of the Creative Commons Attribution (CC BY) license, MDPI.

Waste chicken fat is another alternative feedstock for biodiesel production due to its high-fat content (about 10% *w/w*) and low cost. Commercial broiler chicken meat has a relatively higher polyunsaturated lipid content than organic chicken, and it is known that chicken fat comprises about 40–75% unsaturated- and 25–35% saturated fatty acids [200]. Oleic acid, stearic acid, palmitic acid and linoleic acid are the main fatty acids in chicken fat [201]. Regarding the biocatalytic transesterification of chicken fat oil, there are few reports; for instance, Shafiq et al. used waste chicken fat oil for biodiesel production through both enzymatic and chemical (using KOH and sodium methoxide) approaches [202]. The process of enzymatic transesterification was performed by using free and immobilized forms of *Aspergillus terreus* lipase on $\text{Fe}_3\text{O}_4\text{NPs}$ -PDA-Lipase. Under the reaction conditions of methanol:oil ratio of 6:1, 42 °C for 36 h, the maximum biodiesel yield (90.6%) was achieved from waste chicken fat oil by 6% *w/w* $\text{Fe}_3\text{O}_4\text{NPs}$ -PDA-Lipase nano-biocatalyst. The measured fuel properties (kinematic viscosity, flash point, pour point, cloud point, fire point) met ASTM standard biodiesel specifications, suggesting the compatibility of waste chicken fat with biodiesel production.

Regarding the non-silane-based approach for the chemical attachment of lipase on MNPs, Xie et al. coated $\text{Fe}_3\text{O}_4\text{NPs}$ with a synthetic poly(glycidyl methacrylate-co-methacrylic acid) in an in situ reaction, providing reactive epoxy and carbonyl groups on the surface of NPs [203]. Then, *Candida rugosa* lipase was immobilized onto the magnetic core through coupling reactions between the functional groups of the modified MNPs and lipase amine groups via EDC/NHS chemistry (1-ethyl-3-(3-dimethylaminopropyl)carbodiimide/hydroxysulfosuccinimide) (Figure 15). This covalent attachment led to increased stability of the immobilized lipase by preventing its leakage and reducing its conformational changes [204,205]. As mentioned in Section 2.1, unmodified MNPs aggregate easily due to their high surface energy and their attractive magneto-dipole forces, so the authors

encapsulated MNPs into a synthetic copolymer as a reliable strategy to improve their long-term colloidal stability. They selected glycidyl methacrylate (GMA) and methacrylic acid (MAA) monomers for their in situ co-polymerization onto MNPs because they provide both epoxy and carboxylate groups on the surface of modified MNPs, resulting in multipoint covalent attachments between the lipase and the nano-carrier [206]. Before the co-polymerization step, the authors synthesized MNPs through a solvothermal method, using sodium polyacrylate (PAAS), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, urea and sodium citrate precursors in a two-step reaction. The use of urea and citrate in the synthesis of $\text{Fe}_3\text{O}_4\text{NPs}$ provided surface hydroxyl and carboxyl groups, which can form hydrogen bonds with the functional groups of the co-polymer to encapsulate the magnetic core into the polymeric layer. *Candida rugosa* lipase can form covalent bonds with such groups, including (1) the carboxylic groups of the modified- $\text{Fe}_3\text{O}_4\text{NPs}$, activated by EDC/NHS reagents to convert the surface carboxylic groups to active NHS esters, which can react with the primary amine of lipase forming amide bonds, as shown in Figure 15, (2) the epoxy groups also can take part in nucleophilic substitution reactions with the N-terminal amino groups of the lipase. This dual modality of covalent attachment guarantees the stability of the immobilized lipase, preventing its leakage. The authors also tested the magnetic support (without immobilized lipase), as well as $\text{Fe}_3\text{O}_4\text{NPs}$ -immobilized lipase in biodiesel production from soybean oil. The Fe_3O_4 -poly(GMA-co-MAA) displayed no catalytic activity, whereas the free lipase afforded a biodiesel yield of 91.8%, obtained by the three-step addition of methanol at 40 °C. On the other hand, the use of Fe_3O_4 -poly(GMA-co-MAA)-lipase not only maintained enzymatic activity in the transesterification reaction (yield of 92.8%) but also showed good long-term stability. Thanks to the magnetic carrier, the immobilized lipase was recovered and reused for five cycles, still retaining 79.4% of biodiesel yield.

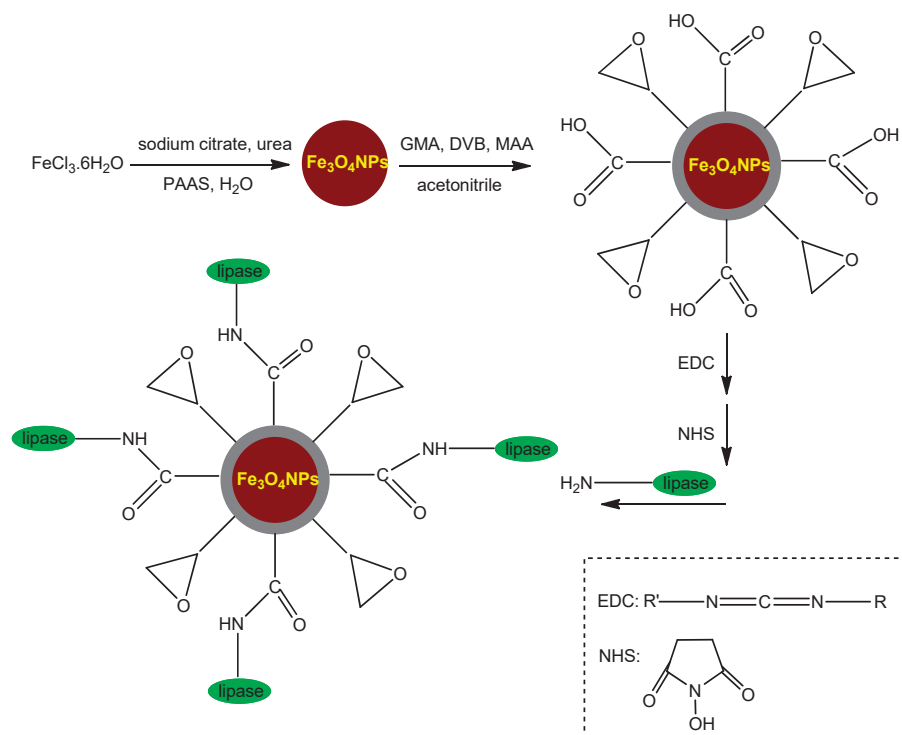


Figure 15. Preparation of Fe_3O_4 -poly(GMA-co-MAA) composite and subsequent immobilization of lipase onto the magnetic support. Abbreviations: NHS = N-hydroxysulfosuccinimide; EDC = 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide; GMA = glycidyl methacrylate; DVB = divinylbenzene; PAAS = sodium polyacrylate; MAA, methacrylic acid. Adapted from Ref. [203], copyright 2020, with permission from Elsevier.

Table 4 shows other magnetic nano-supports for lipase immobilization used in biodiesel production.

Table 4. Other magnetic nano-supports for lipase immobilization used in biodiesel production.

Lipase Source	Nano-Support	Immobilization Methodology	Feedstock	Solvent	Biodiesel Yield (%)	Ref.
<i>Thermomyces lanuginosa</i>	APTES-modified Fe ₃ O ₄	covalent attachment	soybean oil	solvent-free	92.8	[207]
<i>Candida antarctica</i>	APC-modified Fe ₃ O ₄ (APC: (3,4-dihydroxyaldehyde or protocatechuic aldehyde)	covalent attachment	soybean oil	anhydrous methanol	4.6	[208]
<i>Rhizopus oryzae</i>	ROL-MNPs@MS-AP-GA	covalent attachment and physical adsorption	olive oil	anhydrous methanol	88	[209]
<i>Rhizomucor miehei</i>	CRL/MNP@ZIF-8	encapsulation	soybean oil	-	84	[210]
<i>Thermomyces lanuginosus</i> <i>Rhizomucor miehei</i>	3-glycidyloxypropyl trimethoxysilane modified mesoporous silicon	covalent attachment	canola oil	solvent-free	98	[211]
<i>Candida antarctica</i>	APTES modified Fe ₃ O ₄	covalent attachment	rapeseed oil	solvent-free	89	[212]
<i>Aspergillus niger</i>	Fe ₃ O ₄ coated with APTES/MPTMS modified mesoporous silicon	covalent attachment	soybean oil	solvent-free	>90	[213]
<i>Candida rugosa</i>	hollow Fe ₃ O ₄ coated with mesoporous dopamine	physical adsorption	oleic acid	solvent-free	87	[214]
	APTES modified Fe ₃ O ₄	cross-link and covalent attachment	waste cooking oil	solvent-free	71	[215]
<i>Candida antarctica</i>	APTES modified Fe ₃ O ₄	cross-link and covalent attachment	waste frying oils Unrefined soybean oil	solvent-free	80–92	[216]
<i>Candida antarctica</i>	tannic acid-modified Fe ₃ O ₄	cross-link and physical adsorption	sunflower oil	solvent-free	67	[217]
<i>Enterobacter</i> MG10	graphene oxide with APTES-modified Fe ₃ O ₄	cross-link and covalent attachment	<i>Ricinus communis</i> oil	solvent-free	78	[218]

A few real-world applications of lipases immobilized on magnetic nanosupports for biodiesel production have been reported [219]. These feature enzyme immobilization via glutaraldehyde crosslinking and provide high yields as well as excellent reusability, paving the way for further future industrial applications.

4. Conclusions: Current Challenges and Future Trends

Nano-biocatalysts have attracted a growing interest in the field of biodiesel production due to the rapid development of both lipase- and nano-technologies. Such interest will undoubtedly continue to grow; however, these technologies still require improvements in the preparation of robust nano-biocatalysts to ensure higher enzyme activity and stability on the nano-surface. Enzyme immobilization via physical methods (i.e., physical adsorption) benefits from maintaining lipase conformation but is prone to lipase desorption, affected by external stimuli such as pH, temperature, light and mechanical forces. Conversely, with chemical attachment, the enzyme is irreversibly linked to the support, although the altered enzymatic structure may affect catalytic properties. So, it is vitally required to find a good balance among the different structural and biological properties of nano-based immobilization systems while having the highest economic efficiency. To date, most research on biocatalyzed biodiesel preparation has been performed on a bench scale with outstanding results; however, there are few reports on the scale-up of biocatalyzed biodiesel production. Thus, the transfer of knowledge from lab to industry is considered another important challenge in this field. The development of engineered reactors is expected to provide promising advancements in large-scale biodiesel production. Optimizing the structure-function interactions of nano-immobilized lipases and lowering the operational

costs of their manufacturing is of profound relevance to achieving long-term sustainability and development.

Feedstocks are another important factor for the advancement of biodiesel technology. As the major feedstock of biodiesel (95%), vegetable oils need agricultural resources (e.g., water, land, fertilizers) and indirectly increase biodiesel carbon emissions due to their life cycle. Furthermore, vegetable oil accounts for 75–80% of biodiesel production costs. Research should, therefore, be oriented towards the use of cost-effective and regionally available feedstocks in order to address energy security and economic viability challenges. Waste cooking oils (WCO) are easily accessible raw materials with an increasing production trend due to the global development of the catering trade. Furthermore, using WCO for biodiesel production prevents relevant environmental pollution caused by their disposal. Due to their local availability, WCO may replace part of the current feedstocks based on vegetable oils. Further, other waste oils, such as dairy waste scum and waste chicken fat oil, can also be considered a potential feedstock for biodiesel production, in perfect agreement with the principles of a circular economy.

The interference of alcohol with lipase activity can be solved by using solvent-free systems (e.g., ionic liquids) that also allow the avoidance of large amounts of organic solvents. Like any other technology, lab-scale research in this field is developing faster than large-scale manufacturing, and, with an organized and multidisciplinary collaboration between industry and academy, the bench-scale knowledge can be transferred to industry, for example by developing engineered reactors providing high operational speed and efficiency to maximize the production yield and minimize the cost of the process.

Although there have been admirable efforts to develop efficient and robust nanobiocatalysts, the involvement of conformational changes in the immobilization process, nanoparticles-enzyme binding sites, and structure-function relationships still require to be fully addressed. From a perspective point of view, magnetic immobilization can be a successful strategy for the industrial development of biodiesel technology. However, there are still some issues that need to be overcome. Although the reusability allowed by these materials is one of their most appealing advantages, the complexity of the synthesis and subsequent lipase immobilization process still requires research and optimization. To date, several reactors have been developed to enhance the possibility of using magnetic biocatalysts in large-scale applications. Companies working in the field have shown a growing interest in these smart materials, with an increasing number of new patents year by year. Future perspectives related to magnetic biocatalysts are connected to developing immobilization technologies to guarantee the stability and catalytic activity of the enzyme while resulting in low production costs. The evolving regulations on the use of fossil fuels will most probably influence the market, making biodiesel more sought after. However, in order to become more advantageous than chemical catalysis, enzymatic catalysis for biodiesel production will necessarily require further research and technological evolutions.

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Article

Effects of Ca-Compounds on the Gases Formation Behavior during Molten Salts Thermal Treatment of Bio-Waste

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Abstract: Bio-waste utilization is essential, and pyrolysis is a prominent way for its effective utilization. However, the gradual accumulation of ash compounds in the intermediate products probably affects the thermal conversion characteristics of bio-waste. In the present study, beech wood and disposable chopsticks were selected as bio-waste samples. The effects of typical ash components (Ca-compounds) on volatile formation behavior were investigated during the molten salts thermal treatment of bio-waste. Results demonstrated that about 80% mass of initial bio-waste was gasified into the volatiles at 300 °C. The introduction of Ca-compounds in the molten salts slightly decreased the total yield of gaseous products. More specifically, Ca^{2+} could improve the generation of CO_2 and suppress the generation of other gases (CO , H_2 , and CH_4), and this is accompanied by a reduction in the low heating value (LHV) of the gases. The possible reason is that Ca^{2+} might act on the -OH bonds, phenyl C-C bond, methoxy bond and carboxylic acid -COOH bonds of the bio-waste to promote CO_2 release. In contrast, the introduction of CO_3^{2-} and OH- tended to relieve the inhibition effect of Ca^{2+} on the generation of H-containing gases. Meanwhile, the introduction of Ca^{2+} can promote the conversion of bio-waste into liquid products as well as increase the saturation level of liquid products. Moreover, as a vital form of carbon storage, CO_2 was found to be abundant in the pyrolysis gases from molten salts thermal treatment of bio-waste, and the concentration of CO_2 was much higher than that of direct-combustion or co-combustion with coal. It's a promising way for bio-waste energy conversion as well as synchronized CO_2 capture by using molten salts thermal treatment, while the introduction of small amounts of Ca-compounds was found to have no significant effect on the change of CO_2 concentration.

Keywords: bio-waste; molten salts thermal treatment; gases formation; Ca-compounds; CO_2 capture

1. Introduction

Energy utilization of bio-waste is one of the prominent ways to mitigate carbon dioxide emissions [1]. However, low energy density and high cost in energy conversion process both restrict the development and application of bio-waste energy technology. Accordingly, many efforts have been made to convert bio-waste into high-valued energy products such as syngas and pyrolysis carbon [2,3]. On the other hand, researchers are committed to reducing the energy consumption cost, to improve the economy of the utilization [4]. During this process, many scholars have attempted to apply solar energy to the bio-waste thermal conversion, aiming at producing economical, high-value gases [5]. Furthermore, in order to solve the stability problems caused by the fluctuation of solar energy [6], molten salts have been used as the reaction medium for heat storage to realize the stable utilization of bio-waste [7]. It is noteworthy that bio-waste contains a certain amount of ash, which has been proved to change the physicochemical properties of molten salts. The accumulation of biomass ash in molten salts will lead to a decrease in the thermal diffusivity and thermal

conductivity as well as an increase in the specific heat capacity of the eutectic system [8]. Therefore, it is necessary to study the influence of ash on bio-waste reaction characteristics during molten salts thermal treatment.

Calcium is one of the most common elements in bio-waste ash, which is absorbed by bio-waste from the natural environment during the growth process [9]. Ca-compounds are the vital components of bio-waste ash, and the content can reach 68.2% in beech bark [10,11]. At the same time, Ca-compounds in the biomass have been confirmed to be involved in the thermal conversion of organic components in bio-waste [12]. In addition, researchers have pointed out that the added Ca-compounds could improve the pyrolysis performance of three-components (cellulose, hemicellulose and lignin), during which the bio-waste pyrolysis could be affected through converting epoxy into aromatic compounds or through cracking into aliphatic derivatives [13,14]. Meanwhile, the presence of Ca also has a certain catalytic effect on the decomposition of pyrolytic oil. Feng et al. explored the effect of Ca on the pyrolysis behavior of rice husk and found that Ca can promote the formation of aldehydes, ketones and acids produced by aromatic ring opening and cracking reactions [15]. Furthermore, Maxim et al. [16] found that Ca played an important role in the reforming of pyrolysis gases. Compared to the conventional pyrolysis process, molten salts thermal treatment could improve the catalytic activity of the reaction and enhance the heat transfer [17]. It is noteworthy that the generation of three-phase (gas-liquid-solid) products would be more intense during molten salts thermal treatment. However, little research has focused on the effects of the bio-waste ash (especially Ca) introduction on the pyrolysis behavior during molten salts thermal treatment.

Many studies have indicated that different Ca-compounds undergo complex thermo-chemical reactions such as decomposition, carbonation, sulfation, and even electrochemical reaction during bio-waste pyrolysis [18–20]. Therefore, it is worth noting that the role of calcium in the bio-waste thermal treatment process is also related to its species. Yuan et al. evaluated the pyrolysis of bio-waste in the presence of CaCO_3 , and the results showed that CaCO_3 can improve the pyrolysis of rice husk [21]. Chen et al. [22] pointed out that the existence of Ca(OH)_2 increased the biochar yield, and generated larger amounts of phenols and aromatics. In the research of Raymundo et al., Ca(OH)_2 , CaO and Ca(COOH)_2 were further confirmed to promote deoxygenation of bio-oils, and the promotion effect is in the order: Ca(OH)_2 , CaO , and Ca(COOH)_2 [23]. In general, CaO is an important component of bio-waste ash [10,24,25]. CaCO_3 and Ca(OH)_2 would be formed by the reaction between CaO and a small molecule (CO_2 and H_2O) [26]. From the related studies for fuel cells, it was found that the reaction of solid fuel is affected by both cations and anions in molten salts [27–30]. Zeng et al. investigated the pyrolysis of bio-waste using the Li_2CO_3 - Na_2CO_3 - K_2CO_3 ternary molten salts. Results indicated that alkali metal carbonates were participating in the bio-waste thermal conversion [31]. Various Ca-compounds (like CaCO_3 and Ca(OH)_2) introduced into the molten salts probably changed the distribution characteristics of anions in the reaction system, which might affect the properties of pyrolysis products in molten salts.

To improve the utilization efficiency of solar energy over a longer period of time, molten nitrates were selected as medium for the storage of solar energy as well as the conversion of bio-waste into high-value gases [32]. In the present study, two typical bio-wastes (beech wood and disposable chopsticks) were selected to comparatively analyze the effects of Ca-compounds on the gas formation behavior during molten salts (NaNO_3 - NaNO_2) thermal treatment. Firstly, considering the dissolution and dispersion characteristics of calcium in the molten salts, the $\text{Ca(NO}_3)_2$ (only added with Ca^{2+}) was chosen to study the effect of Ca^{2+} on the bio-waste pyrolysis characteristics. Subsequently, in order to explore the effect of different Ca-compounds on the pyrolysis characteristics of the two bio-wastes, $\text{Ca(NO}_3)_2$, CaCO_3 , and Ca(OH)_2 were added in the molten salts system, respectively. In detail, the gaseous and liquid products were detected using GC and GC-MS to further understand the thermal conversion behavior of the two bio-wastes.

2. Results and Discussion

2.1. Releasing Characteristics of Gases with the Addition of Different Ca-Compounds

The distribution characteristics of the pyrolysis (including conventional pyrolysis and molten salts thermal treatment) products from beech wood and disposable chopsticks is compared in Figure 1. It's obviously that more bio-waste was converted into pyrolysis gases and liquid products in the case of molten salts thermal treatment, which is consistent with previous studies [8,17]. The mass ratios of volatiles from the two bio-wastes ranged from 79.4% to 89.3% during the molten salts thermal treatment, while the volatile yield was 18.3% to 20.5% in conventional pyrolysis. It suggests that molten salts probably had a catalytic effect on the release of volatiles during bio-waste pyrolysis, regardless of the type of the bio-waste. After the addition of various Ca-compounds, the distribution characteristics of the volatiles (including gaseous and liquid products) were changed, to a certain extent, ranging from 79.8% to 85.6% for beech wood and from 79.4% to 87.5% for disposable chopsticks. Moreover, the gas yield ranged from 54.6% to 62.3% for beech wood and from 55.4% to 63.3% for disposable chopsticks.

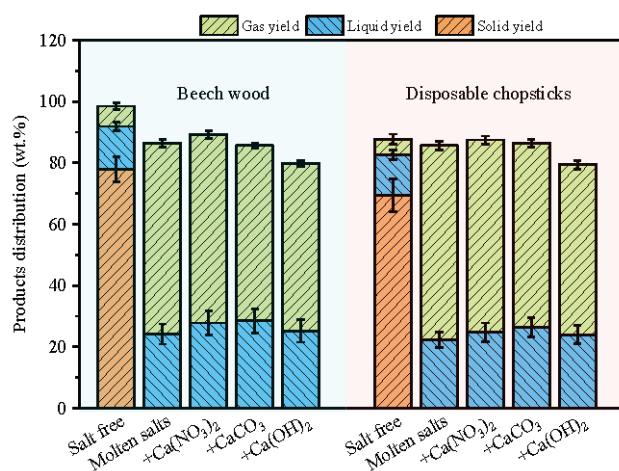


Figure 1. Products distribution in salt free/molten salts pyrolysis of the two bio-wastes.

In order to further explore the effect of Ca^{2+} on bio-waste pyrolysis characteristics, different contents of $\text{Ca}(\text{NO}_3)_2$ were selected to study the gas generation characteristics during molten salts thermal treatment. As shown in Figure 2, compared with the conventional pyrolysis (salt-free), more gaseous products were generated from the selected bio-waste in the molten salts pyrolysis. It is supposed that the catalysis of ions in molten salts greatly reduced the reaction activation energy during bio-waste pyrolysis [17]. In addition, the gas yield was reduced with the addition of $\text{Ca}(\text{NO}_3)_2$, and the inhibition effect was more obvious with an increase in $\text{Ca}(\text{NO}_3)_2$ content. On the one hand, the introduction of Ca^{2+} may change the physicochemical properties of molten salts [28]. On other hand, Ca^{2+} could promote the synthesis of small molecules, which then decreased the pyrolysis gas yield. In conventional pyrolysis (salt-free) process, the gaseous product is only CO_2 at 300 °C, which is mostly produced from the decomposition of low- thermal-stability components in the bio-waste [33]. From Figure 3, adding 10 g $\text{Ca}(\text{NO}_3)_2$ could promote the CO_2 yield, while excess $\text{Ca}(\text{NO}_3)_2$ might suppress the formation of CO_2 . It is suggested that Ca^{2+} promotes the release of CO_2 by breaking the-OH bond, phenyl C-C, and methoxy and carboxylic acid-COOH bonds, which attach to the end of the bio-waste molecular structure [34]. However, excess Ca^{2+} may inhibit the transfer of NO_3^- to NO_2^- , which has been proved to play an important role for the bio-waste pyrolysis [32]. Thus, the excess $\text{Ca}(\text{NO}_3)_2$ further reduces the gases yield, and will decrease the CO_2 concentration in pyrolysis gases.

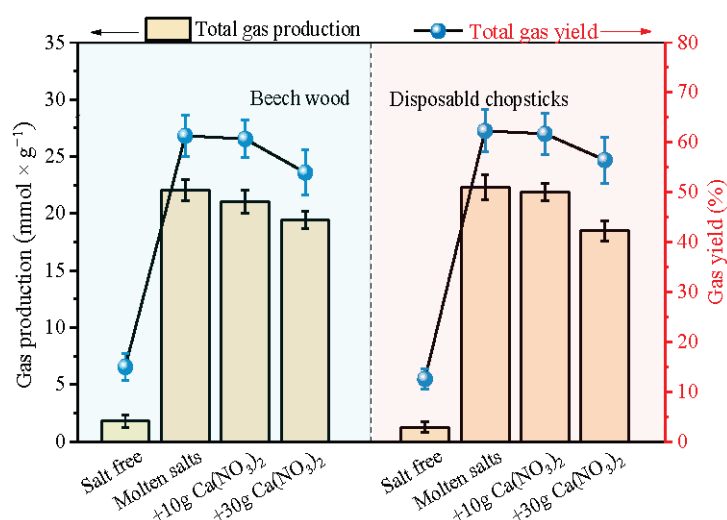


Figure 2. The generation properties of pyrolysis gases under different conditions.

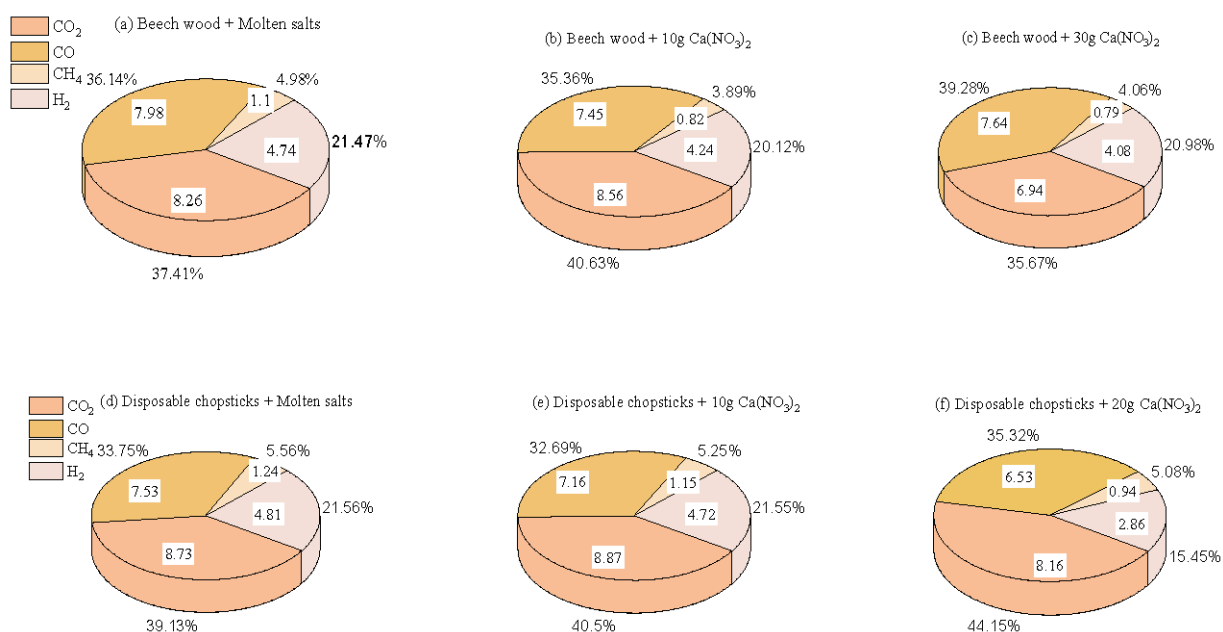


Figure 3. Gas distribution characteristics of the bio-wastes during NaNO₃-NaNO₂ adding Ca(NO₃)₂ (a–c) Beech wood (d–f) Disposable chopsticks.

The gas yield of the examined two bio-wastes with the addition of different Ca-compounds are shown in Figure 4a. The gas yield all decreased after the addition of Ca-compounds (Ca(NO₃)₂, CaCO₃, and Ca(OH)₂), which was consistent with previous work [23,35]. Among those Ca-compounds, Ca(OH)₂ seems to have had the strongest inhibitory effect on the pyrolysis gases generation, which decreased by 12.33% for beech wood and 12.37% for disposable chopsticks. It has been pointed out that OH[−] could inhibit decarbonylation (C–O) and decarboxylation (C–O–C) in hemicellulose [36]. Another reason is that CO₂ can be easily captured by Ca(OH)₂ to form CaCO₃(s). Moreover, the distribution of different gaseous products are presented in Figure 4b. Compared with the NaNO₃-NaNO₂ system, the addition of Ca-compounds hardly changed the types of gaseous products during the pyrolysis process, while it did affect the yield of each gas.

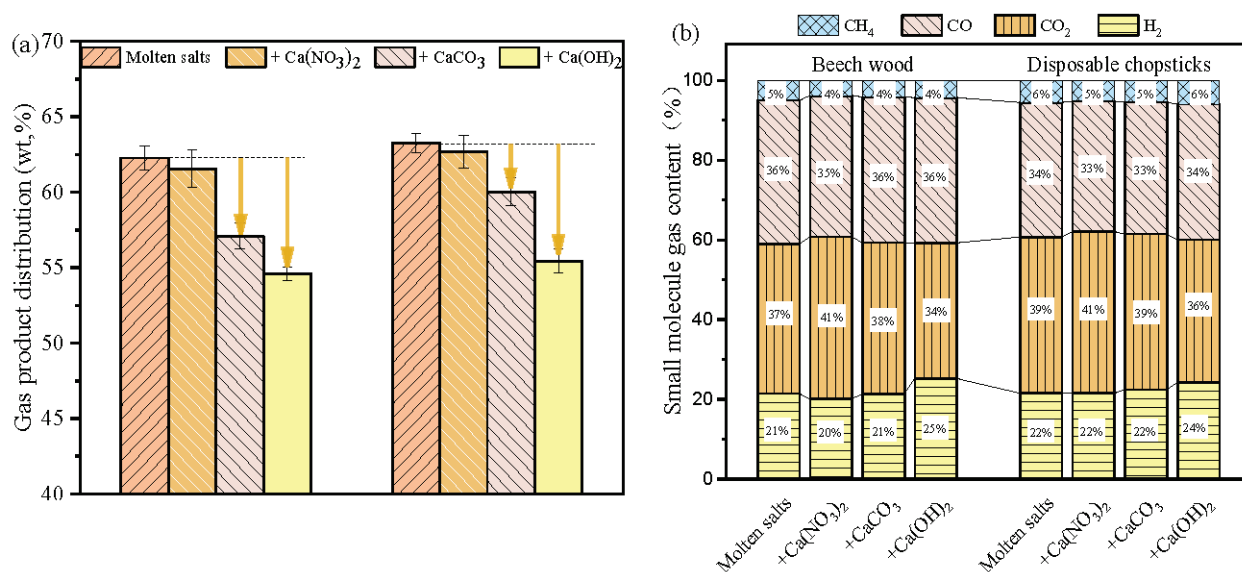


Figure 4. The distribution characteristics of gaseous products in molten salts pyrolysis. (a) Gas yield, (b) distributions of small molecules.

2.2. Effects of Ca-Compounds on Combustible Gases Release in Molten Salts

The change ratios of different small molecule gases (H₂, CO₂, CO, and CH₄) produced during the thermal conversion of beech wood and disposable chopsticks are shown in Figure 5. Compared with NaNO₃-NaNO₂ salt, the conversion ratios of combustible gases (H₂, CO, and CH₄) decreased with the addition of Ca(NO₃)₂. It should be pointed out that the only distinction between the two molten salts is the existence of Ca²⁺, which could inhibit the decomposition of components, resulting in the yield decrease of gaseous products during the pyrolysis process [37]. Notice that CO₂ increased by 3.63% and 1.60%, respectively, after adding Ca(NO₃)₂ in the thermal conversion process of beech wood and disposable chopsticks. Ca²⁺ will attach to the pyran ring of the bio-waste, and the ion effect will make it prone to ring-opening decarbonylation (C=O) at C1~C2, C1~O5, C3~C4, and C5~O5. Thus, more CO₂ could be formed through the decarbonylation (C=O) reaction [38,39]. It indicates that the introduction of carbon dioxide could dilute the calorific value of combustible gas in the mixture.

Compared to molten salts with Ca(NO₃)₂, the introduction of CaCO₃ and Ca(OH)₂ provide OH[−] and CO₃^{2−}. From Figure 5, taking the NaNO₃-NaNO₂ as the control, the ratios of total H-containing gases (H₂ and CH₄) were changed by −15.27%, −13.98% and 0.86% in those three molten salts systems for beech wood, and −3.70%, −2.33% and 1.78% for disposable chopsticks. It was concluded that OH[−] and CO₃^{2−} can relieve the negative effect of Ca²⁺ on the generation of H-containing gases. The reason is that Ca(OH)₂ can provide more dissociative OH[−], which can reduce the energy of C-H bond-breaking in cellulose and promote H-containing gas production [40,41]. Moreover, CO₃^{2−} can significantly promote the cracking and deformation of C=C and C-H groups, and thus increase the formation of H-containing gases [42].

As shown in Figure 6, compared with conventional pyrolysis, more bio-waste is converted into the liquid volatile at 300 °C. The main reason is that NO₂[−] in molten salts could play a prominent catalytic role, and the presence of Na⁺ can lower the pyrolysis temperature. Meanwhile, NO₂[−] can participate in the reaction to form more volatiles, leading to a higher liquid yield [32]. Moreover, the addition of Ca-compounds promotes the yield of liquid products, which is in agreement with the previous work [13]. The reason is that Ca-compounds may enhance the process of dehydroxyl, which is beneficial at forming liquid volatiles during the pyrolysis process. Furthermore, the promotion degree of different Ca-compound is in the order: CaCO₃ > Ca(NO₃)₂ > Ca(OH)₂. Therefore,

the introduction of Ca-compounds can promote the formation of macromolecular liquid volatiles from bio-waste and reduce the yield of gas products.

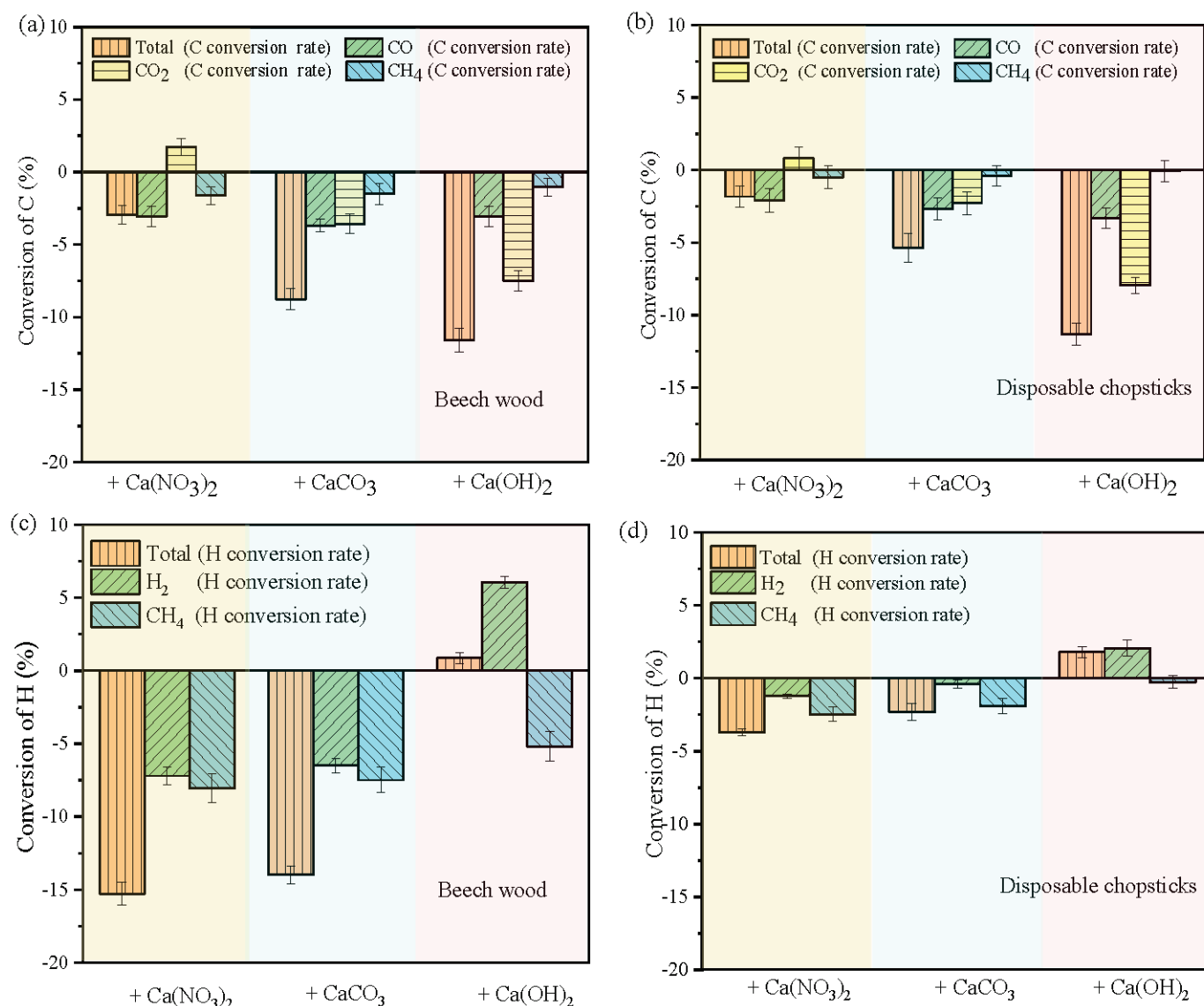


Figure 5. Effects of Ca(NO₃)₂/CaCO₃/Ca(OH)₂ on the conversion of C or H of the small molecule gas. (a) C conversion rate of beech wood, (b) C conversion rate of disposable chopsticks, (c) H conversion rate of beech wood, (d) H conversion rate of disposable chopsticks.

In order to clearly explain the release characteristics of small molecule gas, the major organic composition of liquid products from the two bio-wastes were analyzed, as presented in Figure 7. CG-MS was used to test the composition and relative content of liquid products, and the major organic composition matter by functional group classification statistics. In this experiment, the liquid products were mainly divided into furan, aldehyde ketone, phenol, aromatic hydrocarbon and nitrogen-containing compounds. For the beech wood and disposable chopsticks, the introduction of Ca(NO₃)₂, CaCO₃, and Ca(OH)₂ inhibited the formation of furan and phenols, while it enhanced the formation of ketones/aldehydes. Ca-compounds will reduce the formation of oxygen-containing compounds (like phenols), because Ca-compounds can enhance the deoxygenation reaction of bio-waste pyrolysis [43,44]. The catalytic action of Ca can promote the formation of ketones/aldehydes by ring opening and cracking of aromatic rings [45,46].

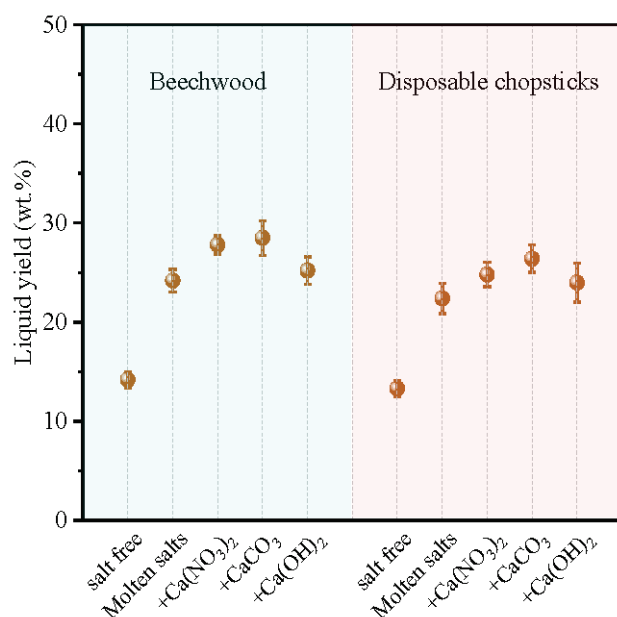


Figure 6. Liquid yield of thermal conversion in molten salts with different Ca-compounds.

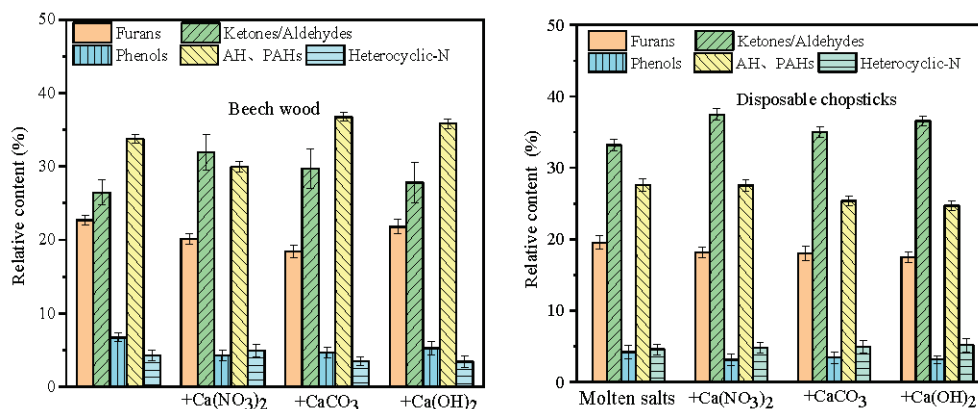


Figure 7. Liquid products of thermal conversion in molten salts.

Moreover, in order to explore the effect of Ca-compounds on the saturation level of liquid products, the ratios of C/H in liquid products in different molten salts systems were calculated, as shown in Figure 8. The curves of the C/H ratios in liquid products were calculated after removing the O atom for those molten salts systems. O atoms in liquid products could be removed according to the following routes. First, The -OH was removed due to the internal dehydration reaction. Secondly, CO₂ was produced by the cleavage/reforming of carboxyl (O=C=O) and carbonyl (C=O) groups. Thirdly, CO was mainly generated by cleavage of lignin units and diaryl ether bonds and ether bridges [47,48]. In general, the saturation level of the liquid phase product was inversely proportional to the C/H ratio in liquid products, and the change of C/H ratio in liquid products was used to characterize the changing trend of the saturation level of the liquid product. A higher C/H ratio in liquid products corresponds to a lower saturation level. From Figure 8, it could be seen that the C/H ratio in liquid products corresponding to the highest content decreased with the addition of Ca-compounds, which indicates that Ca²⁺ can promote the saturation level of liquid products. As mentioned above, compared to NaNO₃-NaNO₂ system, the addition of Ca-compounds will decrease the yield of H-containing gases, and in turn promote the saturation level of liquid products. In addition, the degree of decrease for the C/H ratio in liquid products is as follows: Ca(NO₃)₂ > CaCO₃ > Ca(OH)₂. Compared with Ca(NO₃)₂, CO₃²⁻ and OH⁻ were introduced in NaNO₃-NaNO₂ salt for CaCO₃ and Ca(OH)₂, which

suggested that anions may relieve the inhibition effect of Ca^{2+} on the saturation level of bio-waste pyrolysis products.

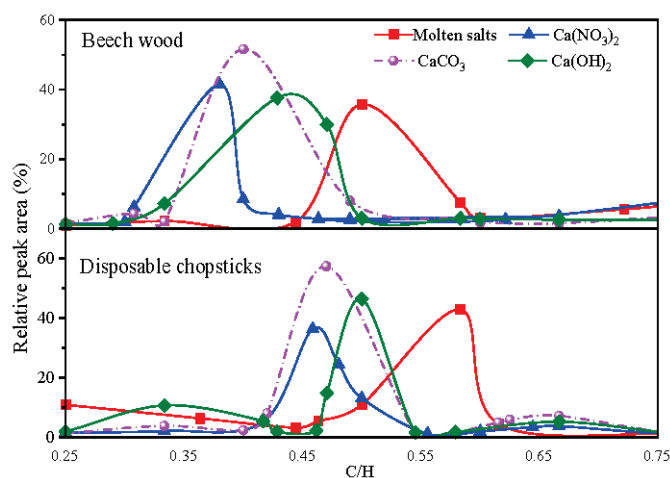


Figure 8. Effects of $\text{Ca}(\text{NO}_3)_2/\text{CaCO}_3/\text{Ca}(\text{OH})_2$ on the saturation level of the liquid products.

2.3. Application and Discussion

The combustible gases can be used in many ways, such as power generation, heating systems, and so on. In addition, the high concentration of CO_2 is a benefit for its recycling, which is an effective way to reduce carbon emissions. The LHVs of bio-waste pyrolysis gases were calculated according to their yield and composition, and the results are listed in Figure 9. The LHVs of pyrolysis gases are marked with black dots, and red dots represent the LHVs without CO_2 . From Figure 9, the LHVs obviously varied with the addition of different calcium mixtures, while the LHVs of pyrolysis gases without CO_2 changed little. The reason is that the Ca-compounds have the greatest impact on CO_2 generation compared with other pyrolysis gases. In addition, for the pyrolysis gases of beech wood and disposable chopsticks, the LHVs ($13.83 \text{ MJ}/\text{Nm}^3$ and $14.08 \text{ MJ}/\text{Nm}^3$) without CO_2 were significantly higher than that ($8.66 \text{ MJ}/\text{Nm}^3$ and $8.57 \text{ MJ}/\text{Nm}^3$) with CO_2 .

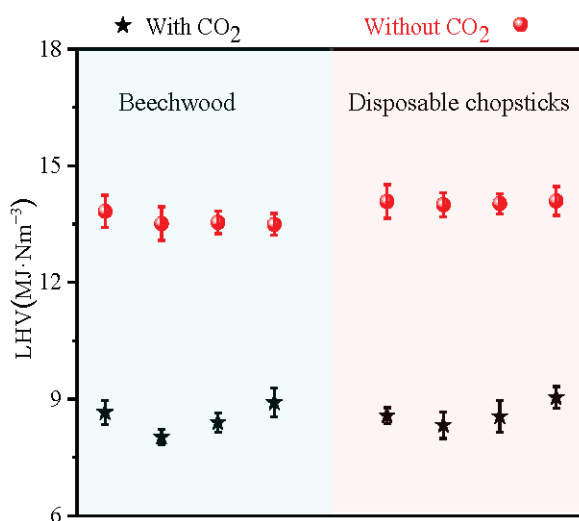


Figure 9. Effects of $\text{Ca}(\text{NO}_3)_2/\text{CaCO}_3/\text{Ca}(\text{OH})_2$ on LHVs of small molecule gas: with/without CO_2 .

Combined with Figures 4b and 9, the LHVs of pyrolysis gases with the addition of $\text{Ca}(\text{NO}_3)_2$ and CaCO_3 were lower than that in $\text{NaNO}_3\text{-NaNO}_2$ salt. The main reason is that the addition of the two Ca compounds would increase the proportion of CO_2 in the pyrolysis gases. In addition, it was found that the LHVs of pyrolysis gases with the

addition of $\text{Ca}(\text{OH})_2$ were the highest for those two bio-wastes in Figure 9. As mentioned in Section 2.2, although the total gas yield reduced in the presence of OH^- , the proportion of the combustible gas increased in this circumstance.

The capture and utilization of CO_2 can not only effectively reduce the pressure of greenhouse gas emissions, but also produce huge economic benefits [49]. In Figure 10, the five-pointed stars and dots represent the CO_2 concentration after pyrolysis gas (including and excluding CO_2) combustion. As to the pyrolysis gases in different molten salts systems, the CO_2 concentrations were 23.6%, 25.2%, 24.1% and 22.6% for beech wood, respectively, and 24.1%, 24.5%, 23.8% and 22.5% for disposable chopsticks, respectively. From the results, the CO_2 concentration after pyrolysis gas combustion was much higher than that for bio-waste direct-combustion and for coal-fired power plants. As for the bio-wastes studied in the paper, the introduction of Ca-compounds can increase the CO_2 concentration after pyrolysis gas combustion, which is a benefit for the CO_2 separation and capture [50].

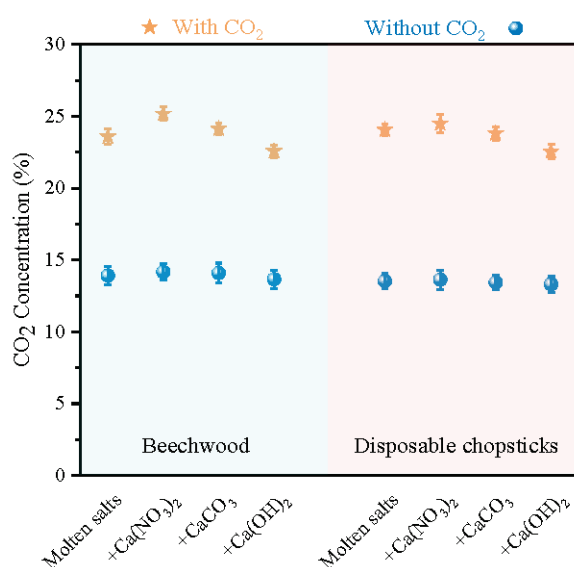


Figure 10. CO_2 concentration after combustion: with/without CO_2 before combustion.

Figure 11 shows that the main negative carbon reactions during molten salt pyrolysis, and CO_2 cycling would be accompanied by energy conversion during this process. In detail, for the energy conversion, solar energy is used for photosynthesis of plants and for heating low-temperature molten salts in this work. A large amount of combustible gas would be generated from waste bio-waste after molten salts thermal conversion. In addition, for CO_2 cycling, the combustible gas will generate CO_2 again, and then the CO_2 could be absorbed and stored by a capture system.

In particular, ash matter would remain and change the physicochemical properties of molten salts during the thermal treatment process. In this paper, $\text{Ca}(\text{NO}_3)_2/\text{CaCO}_3/\text{Ca}(\text{OH})_2$ were simulated as the main impurities to explore their effect on the pyrolysis characteristics of bio-waste in molten salts. Summarily, Ca^{2+} can promote the CO_2 concentration of pyrolysis gases, while the accompanying anions (CO_3^{2-} , OH^-) weaken this promotional effect by increasing the concentration of H-containing gases. Overall, bio-waste thermal conversion could be a potential carbon capture method.

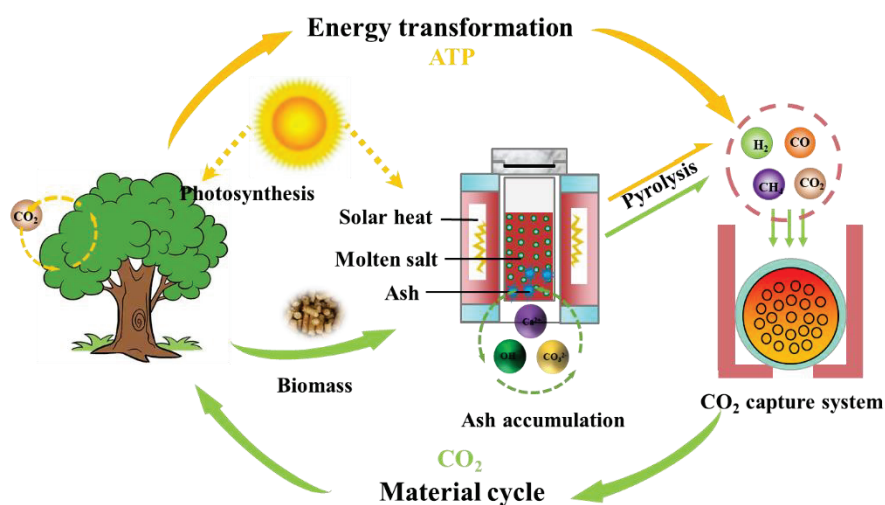


Figure 11. Main negative carbon reaction pathways of bio-waste pyrolysis in molten salts.

3. Materials and Methods

3.1. Materials

Two typical kinds of bio-waste, beech wood and disposable chopsticks were used in the present study. Beech wood is a common furniture material, which has the characteristics of stable wood property; hard material, impact resistance, and difficulty to deform. In addition, disposable chopsticks were selected to conduct pyrolysis experiments due to its huge abundance in China. Strips or tablets (1–2 cm) of feedstocks were dried at 105 °C for 24 h in an oven before the experiments. Analytical grade reactants, NaNO_3 - NaNO_2 (SCR Co., Ltd., Shanghai, China) molten salts was physically mixed with a weight ratio of 56.3–43.7%. The three Ca-compounds, $\text{Ca}(\text{NO}_3)_2$ - CaCO_3 - $\text{Ca}(\text{OH})_2$ (SCR Co., Ltd., Shanghai, China), were obtained with an analytical grade. It should be noted that $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ was used to substitute for $\text{Ca}(\text{NO}_3)_2$.

The proximate/ultimate analysis results and three-components of beech wood and disposable chopsticks are listed in Table 1.

Table 1. Proximate and ultimate analysis on dry basis and three-components of the samples.

Samples	Proximate Analysis (wt%)				Ultimate Analysis (wt%)					Cellulose	Hemicellulose	Lignin
	V _d	FC _d	A _d	C	H	O ^a	N	S				
Beech wood	85.4	13.2	1.4	45.2	5.7	49.1	- ^b	-		47.3	15.2	28.4
Disposable chopsticks	80.0	18.7	1.3	45.3	5.6	48.7	0.3	0.1		32.9	29.4	19.2

^a Calculated by difference. ^b Not detected.

3.2. Experimental Methods

In this experiment, 300 g of the mixed salt was added to the reactor (shown in Figure 12) and heated to 300 °C, and then the temperature was kept for at least 3 h to form a homogeneous liquid phase before experiments. In order to study the effect of Ca^{2+} , 10 g or 30 g of $\text{Ca}(\text{NO}_3)_2$ were added to the molten salts system. In addition, to explore the effect of different Ca-compounds on the pyrolysis behavior of the bio-wastes, 10 g of $\text{Ca}(\text{NO}_3)_2$, CaCO_3 , and $\text{Ca}(\text{OH})_2$ were introduced into the molten salts, respectively. Considering the consumption of molten salts and the accumulation of impurities during the experiment, the number of experiments in each reactor was less than 12 groups. This ensures that the experimental results cannot be affected by the attenuation of the molten salts performance. In the experiments, about 1 g of the sample was added to the metal pocket placed above the molten salts, and nitrogen gas was constantly input to the reactor at 700 mL/min. Then, the nitrogen gas flowed for 3 min to evacuate the air in the reactor and pipeline. After that, the sample was put into the molten salts for 10 min thermal treatment. The U-shaped tubes

were bathed in the liquid nitrogen to collect the liquid products. Meanwhile, the gaseous products were collected in a gasbag for subsequent experimental tests. After the pyrolysis process, the metal mesh pocket was lifted by connected rods from the molten salts to the upper part of the reactor, then cooled by nitrogen, and taken out at last.

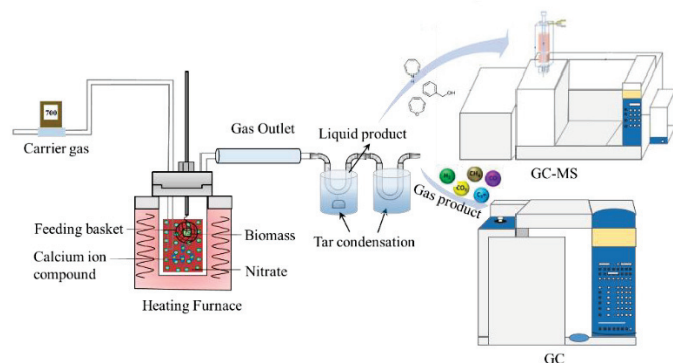


Figure 12. Schematic diagram of the molten salts pyrolysis reactor.

3.3. Analytical Methods

An element analyzer (Vario Micro cube, Elementar, Langenselbold, Germany) was employed to determine the carbon, hydrogen nitrogen and sulfur content. The proximate analysis was measured according to GB/T28731-2012. The LHV of gaseous products was calculated through Equation (1):

$$\text{LHV (MJ/Nm}^3\text{)} = 12.6 \times y_{\text{CO}} + 10.8 \times y_{\text{H}_2} + 35.8 \times y_{\text{CH}_4} \quad (1)$$

where, y_{CO} , y_{H_2} and y_{CH_4} are the volume fractions (vol%) of carbon monoxide, hydrogen and hydrocarbons in the gaseous products respectively [51].

The water content of liquid products was examined with a Volumetric KF Titrator (V10S, Mettler Toledo, Greifensee, Switzerland). The chemical composition of tar was determined with using GC-MS (Agilent, 7890A/5975C, Santa Clara, CA, USA) with a capillary column (Agilent: HP-5MD, 19091s-433; 30 m $\times$ 0.25 mm i.d. $\times$ 0.25 μm d.f.). The injection volume of each sample was 1 μL , and the split ratio was 1:1. The gaseous products were analyzed with a GC (Agilent 7890B, USA). The compounds were identified using a National Institute of Standards and Technology library (NIST14.L).

4. Conclusions

In the present work, two bio-wastes (beech wood-disposable chopsticks) were selected to reveal the effects of Ca-compounds ($\text{Ca}(\text{NO}_3)_2$, CaCO_3 , $\text{Ca}(\text{OH})_2$) on the gas formation characteristics in a nitrates (NaNO_3 - NaNO_2) system. The main conclusions of this study are as following: the mass ratios of the volatiles from the two bio-wastes were much higher (86.4% and 85.6%) during molten salts thermal treatment than that in conventional pyrolysis (20.5% and 18.3%) at 300 $^\circ\text{C}$. The main reason is that the ions in molten salts greatly reduced the reaction activation energy during the bio-waste pyrolysis process. As for the gaseous products, the addition of Ca-compounds in molten salts would slightly reduce the gas yield. Moreover, $\text{Ca}(\text{OH})_2$ seems to have the strongest inhibitory effect on the pyrolysis gas generation, decreasing the gas production by 12.33% for beech wood and 12.37% for disposable chopsticks. From the perspective of ions, Ca^{2+} can promote the production of CO_2 , while the release of other gases (CO , H_2 and CH_4) will be inhibited. At the same time, the OH^- and CO_3^{2-} could relieve the effect of Ca^{2+} on gas formation. For the liquid products, the introduction of Ca^{2+} increases the saturation level of liquid products as well as increases the liquid yield. In particular, the addition of CaCO_3 contributed to an increase in liquid yield from 24.2% to 28.5% for beech wood and from 22.4% to 26.7% for disposable chopsticks. The addition of Ca-compounds in molten salts could increase the CO_2 concentration after the combustion of pyrolytic gases, which would benefit CO_2

separation and capture. Meanwhile, it is suggested that molten salts thermal treatment is a promising carbon negative technology to achieve carbon neutrality.

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Article

Multivariable Analysis Reveals the Key Variables Related to Lignocellulosic Biomass Type and Pretreatment before Enzymolysis

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Abstract: In this study, partial least square (PLS), a multivariable analysis, was used to simultaneously quantitatively evaluate the effects of variables related to three pretreatments (alkaline, hot water and acid) and the biomass properties of poplar, salix and corncob. The results showed that biomass type was the most important variable influencing enzymolysis reducing sugar yield (ERSY). The biomass compositions affected the ERSY more than the pretreatment conditions, among which hemicellulose and lignin played vital roles. The alkaline pretreatment had a more positive effect on the ERSY than the acid and hot water pretreatments, in which alkaline content had more influence than temperature. This work provides a deeper understanding of the material properties and the pretreatment conditions in different complex systems before enzymolysis, which might be a guidance to future study.

Keywords: lignocellulosic biomass; pretreatment; enzymolysis reducing sugar; partial least squares (PLS); quantitative evaluation

1. Introduction

Lignocellulosic biomass, an abundant and renewable resource, has attracted much attention for its great potential to mitigate the fossil energy crisis [1,2]. However, the natural composition and structure of lignocellulosic biomass impede its effective utilization and commercialization [3]. In this regard, the pretreatments of raw materials that aim to conquer those difficulties are particularly necessary and needed to transform the lignocellulosic biomass to the readily enzymatic substrates [4]. Nowadays, kinds of physical, chemical, biological and co-pretreatment are promising approaches [5,6], among which acid, alkaline and liquid hot water pretreatments are the typical methods [5,7–9].

Pretreatment conditions might be the influential factors to the enzymolysis efficiency of lignocellulosic biomass [10,11]. However, most efforts were taken to analyze the responses and behavior of these factors without evaluating their interactions, making it hard to adopt problem-oriented strategies. Partial least square (PLS), a multivariable analysis method, is not only suitable to dig information on the contribution of a single variable to the whole enzymatic saccharification process quantitatively, but it could also gather valuable information from the whole process and identify the most important variable to the complex multivariate systems [12–14]. Li et al. [15] and Xu et al. [16] revealed that the main factors that influenced the enzymatic hydrolysis were the alkaline dosage and the lignin removal rate in the pretreatment process by PLS. Additionally, Xu et al. [2] reported that the acid steam explosion pretreatment was a key factor that enhanced the total saccharification efficiency of corn stover according to PLS. The characters of raw

materials that are mainly different in cellulose, hemicellulose and lignin content were also important influential factors to enzymolysis efficiency [17]. But to our knowledge, few analyses simultaneously evaluate the materials and pretreatment variables in multivariate systems, which might lead to a mismatch material to pretreatment.

In order to evaluate the effects of different materials and pretreatments variables on the enzymolysis reducing sugar yield (ERSY), experiments based on three raw materials (poplar, salix and corncob) subjected to the acid, alkaline and hot water pretreatments were set up, respectively. The key influential factor to the ERSY was identified by PLS. This study provides new insights in the optimization of lignocellulosic biomass and pretreatments to enhance the enzymolysis effects.

2. Results and Discussion

2.1. Effects of Three Pretreatments on the Sugar Yield in the Enzymolysis

After being pretreated, some components are hydrolyzed into a liquid part, and the filtered solid is seen as pretreated residues. The liquid part contained reducing sugar, which is readily utilized by the microorganism to ferment [18]. Since the focus of this study was reducing sugar from raw material in the enzymolysis process, the ERSY was seen as the evaluation index for the potential of sugar production of raw material in the enzymolysis.

The changes of the ERSY of the three biomasses under the different pretreatments are visualized in Figure 1 and the experiment data are summarized in Supplementary Material (Table S1). The untreated poplar, salix and corncob produced 156.45 mg/g, 184.87 mg/g and 342.23 mg/g of the ERSY, respectively. After the alkaline pretreatment, the ERSY of poplar and corncob significantly increased by 3.45~49.38% and 15.80~98.51% ($p < 0.01$). Moreover, the increasing temperature had little influence on the ERSY of corncob. When the alkaline content was 1% at 30 °C, 80 °C and 121 °C, the similar ERSY of corncob were 643.64 mg/g, 635.82 mg/g and 610.04 mg/g, respectively. Under the hot water pretreatment, the ERSY of poplar and salix significantly increased by 1.14~23.78% and 23.15~41.06% ($p < 0.01$), but the ERSY of corncob significantly decreased ($p < 0.05$). One plausible explanation was that the hot water pretreatment usually increases the crystallinity index of some lignocellulosic biomass [19,20], and the other might be that the microsphere formation of some condensed lignin during the hot water pretreatment process may also inhibit the enzymolysis of corn stover [21,22]. Despite all those above, the hot water pretreatment enhanced the enzymolysis of poplar and salix probably due to their different compositions and structures from the corncob. For the acid pretreatment, the ERSY of poplar, salix and corncob significantly decreased ($p < 0.01$) compared with those in the untreated samples. Moreover, the ERSY decreased with the increasing temperature and acid content. Dilute acid destroyed the structure of the hemicellulose fraction, and more polysaccharides hydrolyzed to monosaccharides or disaccharides at elevated temperature [23,24], affecting strongly on the mass balance of the materials.

Generally, the alkaline pretreatment improved the ERSY of the lignocellulosic biomass while the acid pretreatment did not. The hot water pretreatment improved the potential of saccharification for salix and poplar. Regardless of the pretreatment methods and conditions, corncob had the highest ERSY, followed by salix and poplar.

2.2. Influence and Estimation of Factors on Enzymolysis

2.2.1. Establishment of PLS Models for the Analysis of Enzymolysis

The sugar yield in the enzymolysis depends on multiple factors, such as types of lignocellulosic biomass and pretreatments [3,25], which could be explored by the PLS models. Herein, the PLS models were applied to identify the key variables influencing the ERSY. The biomass types (poplar, salix and corncob), pretreatment methods (acid, alkaline, hot water), pretreated residues and pretreatment reducing sugar yield (PRSY) were set as independent variables (X variables), and the result of the ERSY was set as a dependent variable (Y variable). R^2 (cum) and Q^2 (cum) suggests the fitness degree and the predictive ability for the dataset [2]. The values of R^2 and Q^2 that exceed 0.5 indicate good data

fitting and predictive ability for the model. Biplot served to co-chart score vectors plot and loading scatter plot together to simultaneous display samples and interpretation of variables. The closer the X variable is to the Y variable, the closer relationships they have. By contrast, the variables that are close to the plot origin were poorly described by the model. The coefficient plot and the variable importance degrees (VIP) plot indicate the quantitative contribution and importance degree of the variables on the ERSY [26].

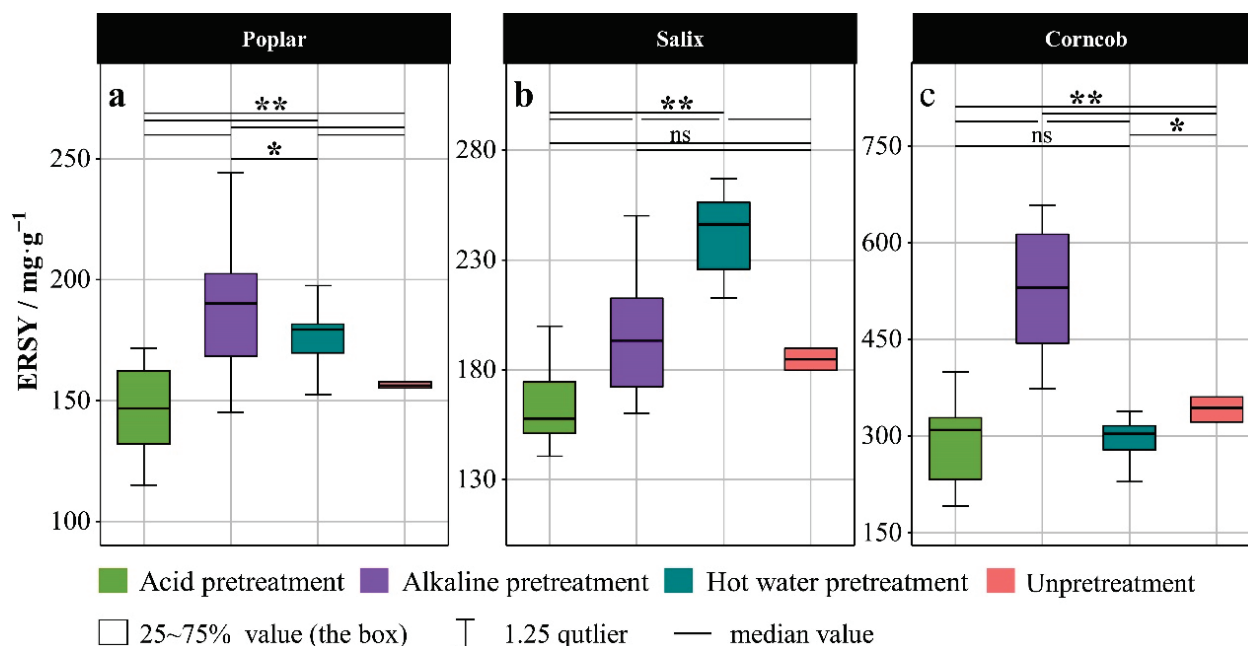


Figure 1. Distribution of enzymatic reducing sugar yield (ERSY) under different pretreatment methods. (a). Poplar. (b). Salix. (c). Corncob. All boxplot distributions are tested using Independent-Samples t-test at the 95% level compared with each other; *, $p < 0.05$; **, $p < 0.01$. Note: Each box represents a distribution of one pretreatment method containing a nine-condition dataset.

2.2.2. Comparison of Different Lignocellulosic Biomass and Pretreatment Methods on ERSY

The effects of different biomass types and pretreatment methods on the ERSY were analyzed by PLS model 1 (Figure 2). The R^2X (cum) was 0.530, and the R^2Y (cum) was 0.766. The Q^2 (cum) was 0.724. It showed that this model explained the 76.6% information of the ERSY and had 72.9% predictive ability of variables. As is shown in Figure 2a, the corncob and alkaline pretreatments were close to the ERSY, indicating that corncob pretreated by alkaline was more capable of producing the ERSY than others. Moreover, corncob had a closer distance to the alkaline pretreatment, while poplar and salix had a closer distance to the hot water pretreatment, suggesting the suitable pretreatment methods for the different types of biomasses.

Figure 2b showed the contributions of the different independent variables. The corncob (0.58) and alkaline pretreatments (0.13) had positive contributions to the ERSY. The other X variables had negative coefficients, which indicated they were negatively related to the ERSY. The negative coefficients of poplar (−0.35) and salix (−0.23) are in line with their lower performance in the ERSY. The acid pretreatment of those three materials had negative contributions and a lower ERSY than the unpretreated samples, which was consistent with that in Figure 1. As shown in Figure 2c, the importance values of the corncob (2.00) and poplar (1.23) were higher than other variables. The pretreated residues (0.83) also played a greater role in the ERSY. The VIP of alkaline pretreatment (0.91) and acid pretreatment (0.88) were higher than the hot water pretreatment (0.27) and the unpretreatment (0.13). In summary, for the different lignocellulosic biomass and pretreatment methods, the biomass type was the most important variable for the enzymolysis. Corn cob was a better biomass

for enzymolysis, and the alkaline pretreatment was suitable for the three materials to increase the ERSY.

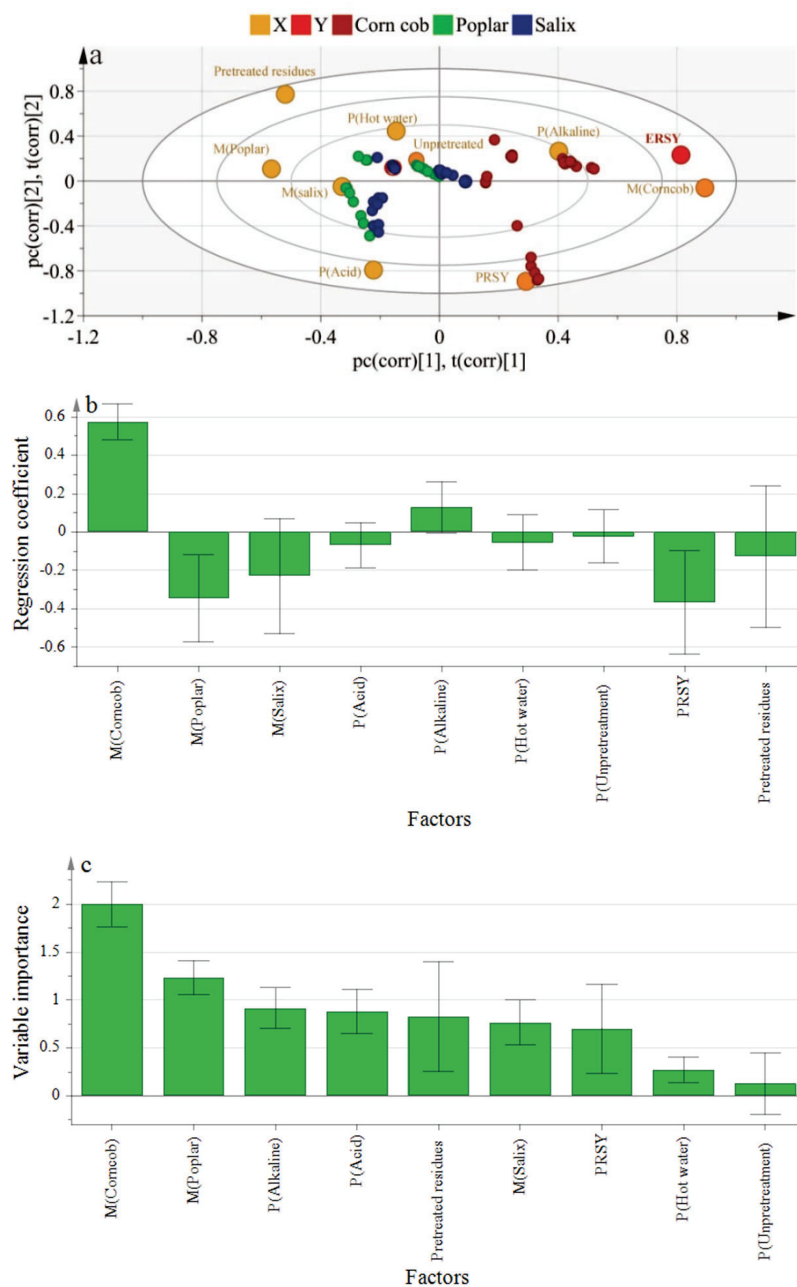


Figure 2. PLS model 1 analysis for the effects of biomass type and pretreatments on the ERSY. (a) Biplot. (b) Regression coefficients of X variables on the Y variable. (c) Importance of X variables on the Y variables for the projection. Note: (a) The poplar, salix and corn cob were the pretreated samples under different experimental conditions. The scores $t[1]$ and $t[2]$ summarize the X variables, which are orthogonal and completely independent of each other. The score $t[1]$ (first component) explains the largest variation of the X space, followed by $t[2]$. The regular loading values p correspond to the covariances between the X variables and the score vectors (t) in question, which mean that the magnitude (numerical range) of each X variable is reflected in the loading value. The weights of the variables were indicated by $pc[1]$ (for the first component) and $pc[2]$ (for the second component). The error bars mean the confidence intervals of the coefficients, which indicate the influence degree of each variable, and the influence is significant when the confidence intervals do not include zero.

2.3. PLS Analysis for the Effects of the Biomass Compositions and Conditions on the ERSY under Three Pretreatments

To better understand the effects of the biomass properties on the enzymolysis under the three pretreatments, three PLS models were established based on alkaline, hot water and acid pretreatment conditions and biomass properties, respectively. Each pretreatment had nine pretreatment conditions to pretreat the three biomasses. Thus, each PLS model had 27 samples and 8 X variables.

PLS model 2 was developed to study the effects of the biomass compositions and the alkaline pretreatment conditions on the enzymolysis reducing sugar. Five compositions, including neutral detergent fiber (NDF), hemicellulose, cellulose, lignin, ash, alkaline content, temperature and PRSY were set as X variables and the ERSY of the alkaline pretreatment was set as Y variable. The R^2X (cum) was 0.740. The R^2Y (cum) was 0.942. The Q^2 (cum) was 0.912. Results showed that this model perfectly explained the information (94.2%) of the whole process and had good predictive capability (91.2%). As is shown in Figure 3a, the samples were divided into three groups, and the distances between X variables and the ERSY indicated that the biomass compositions had stronger inter-related connections with the ERSY than the alkaline pretreatment conditions. The coefficient values in Figure 3b showed that hemicellulose (0.25) and alkaline content (0.25) had positive contributions to the ERSY, while the lignin (−0.20) and cellulose (−0.20) had negative contributions. The lowest coefficient value of temperature at the 95% level contained “0”, suggesting it had little contribution to the ERSY. Figure 3c sorted the variable importance from high to low. Hemicellulose (1.27) and lignin (1.22) were more important variables for the ERSY than others. The alkaline content (0.71) had a greater impact than temperature (0.13). When the alkaline contents were 0.25%, 0.50% and 1.00% at 30 °C, the ERSY of corncob were 375.45 mg/g, 464.26 mg/g and 643.64 mg/g, respectively, which were similar to those under the same alkaline contents at 121 °C. The alkaline pretreatment had advantages over the improvement of lignocellulose, which removed the lignin and preserved the carbohydrates at room temperature or moderate temperature [27]. High alkaline content also improved the hydrolysis of lignin to enhance the subsequent enzymolysis [28].

In Figure 4, the effects of the biomass properties and the hot water pretreatment on the ERSY are described by PLS model 3. Five compositions, ratio of solid to liquid (S/L), temperature and PRSY were set as the X variables and the ERSY of the hot water pretreatment was set as the Y variable. The R^2X (cum) was 0.750. The R^2Y (cum) was 0.949. The Q^2 (cum) was 0.908. According to Figure 4a, NDF was the closest variable related to the ERSY. Temperature had little influence on the ERSY, since it had a close distance to the plot origin. According to Figure 4b,c, compositions had a greater effect on the ERSY than the hot water pretreatment conditions. The coefficients of NDF (0.38) and cellulose (−0.23) illustrated that the two compositions were the main variables affecting the ERSY. Additionally, the importance degrees of temperature (0.40) and S/L (0.044) were lower than 0.5 and the confidence intervals for the VIP values at the 95% level contained “0”, indicating that they were insignificant X variables. Variations of the hot water pretreatment conditions hardly contributed to the significant differences of the ERSY, probably due to the limitation of the temperature gradients. The hot water pretreatment usually treated materials at elevated temperatures (160–240 °C) and this process could remove hemicellulose and lignin to enhance the enzymatic hydrolysis [29].

As shown in Figure 5, PLS model 4 described the effects of the acid pretreatment conditions and the biomass properties on the ERSY. Five compositions, acid content, temperature and PRSY were set as the X variables and the ERSY of the acid pretreatment was set as the Y variable. The R^2X (cum) was 0.758. The R^2Y (cum) was 0.883, and the Q^2 (cum) was 0.851. In Figure 5a, all the X variables were far away from the plot origin, indicating their great influences on the ERSY. Comparing the distances between the Y variable of the ERSY and the X variables, hemicellulose and NDF had closer relationships with the ERSY than other variables. The coefficients in Figure 5b showed that lignin, acid content, temperature and PRSY had negative contributions to the ERSY, and the

hemicellulose and NDF had positive contributions. The VIP of the X variables are shown in Figure 5c. Among all the variables, hemicellulose (1.25) and lignin (1.24) were the most important variables. The temperature (0.69) had a greater effect than the acid content (0.52) on the the ERSY. Combining the results from Figure 5b showed that a higher temperature in the acid pretreatment would lead to a lower ERSY. Jung et al. [30] found that the increasing temperature promoted the degradation of hemicellulose and cellulose in the acid pretreatment and decreased the recovery of the pretreated solid residues, which is in line with our study.

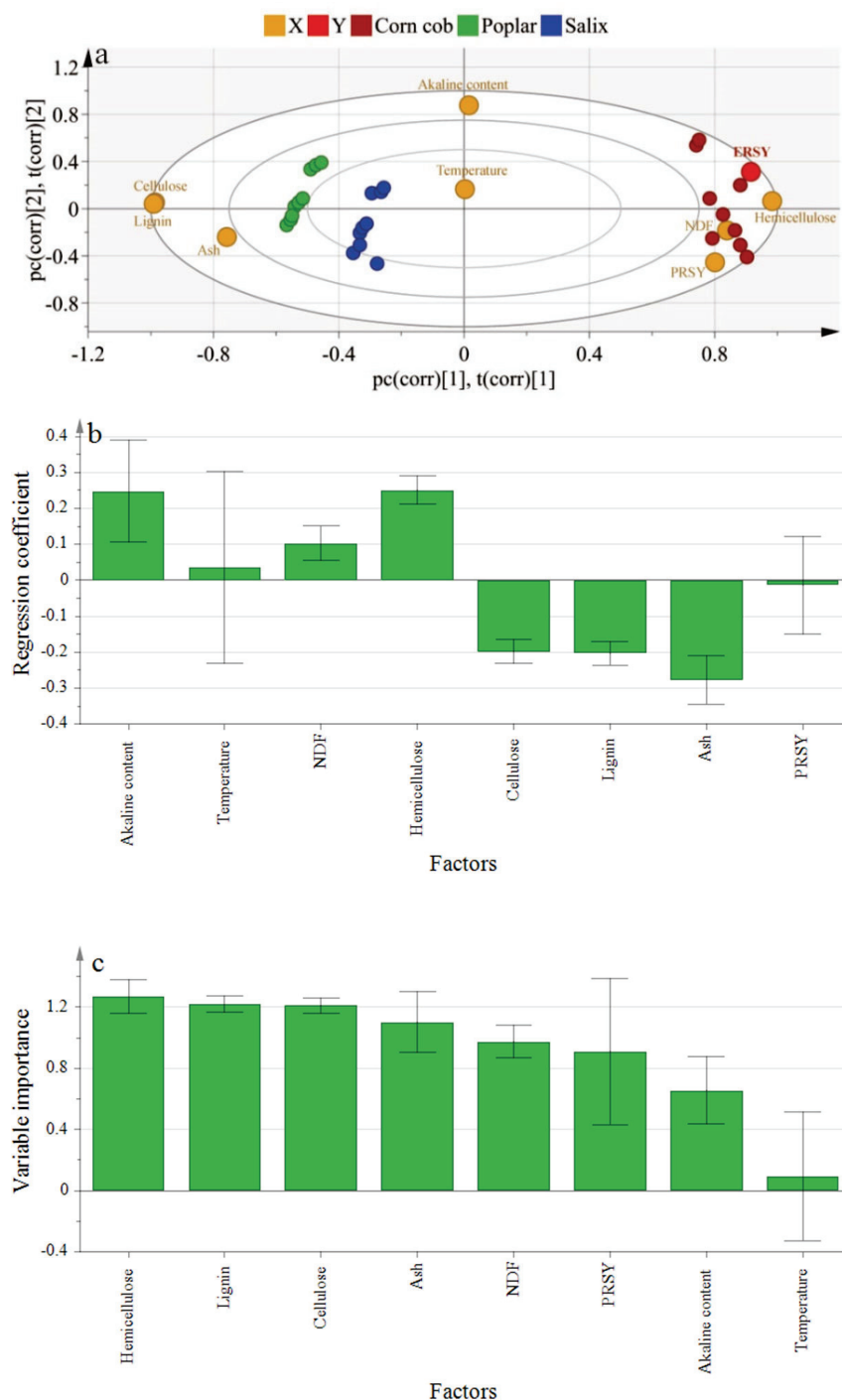


Figure 3. PLS model 2 analysis for the alkaline pretreatment followed by enzymolysis. (a) Biplot. (b) Regression coefficients of X variables on the Y variable. (c) Importance of X variables on the Y variables for the projection.

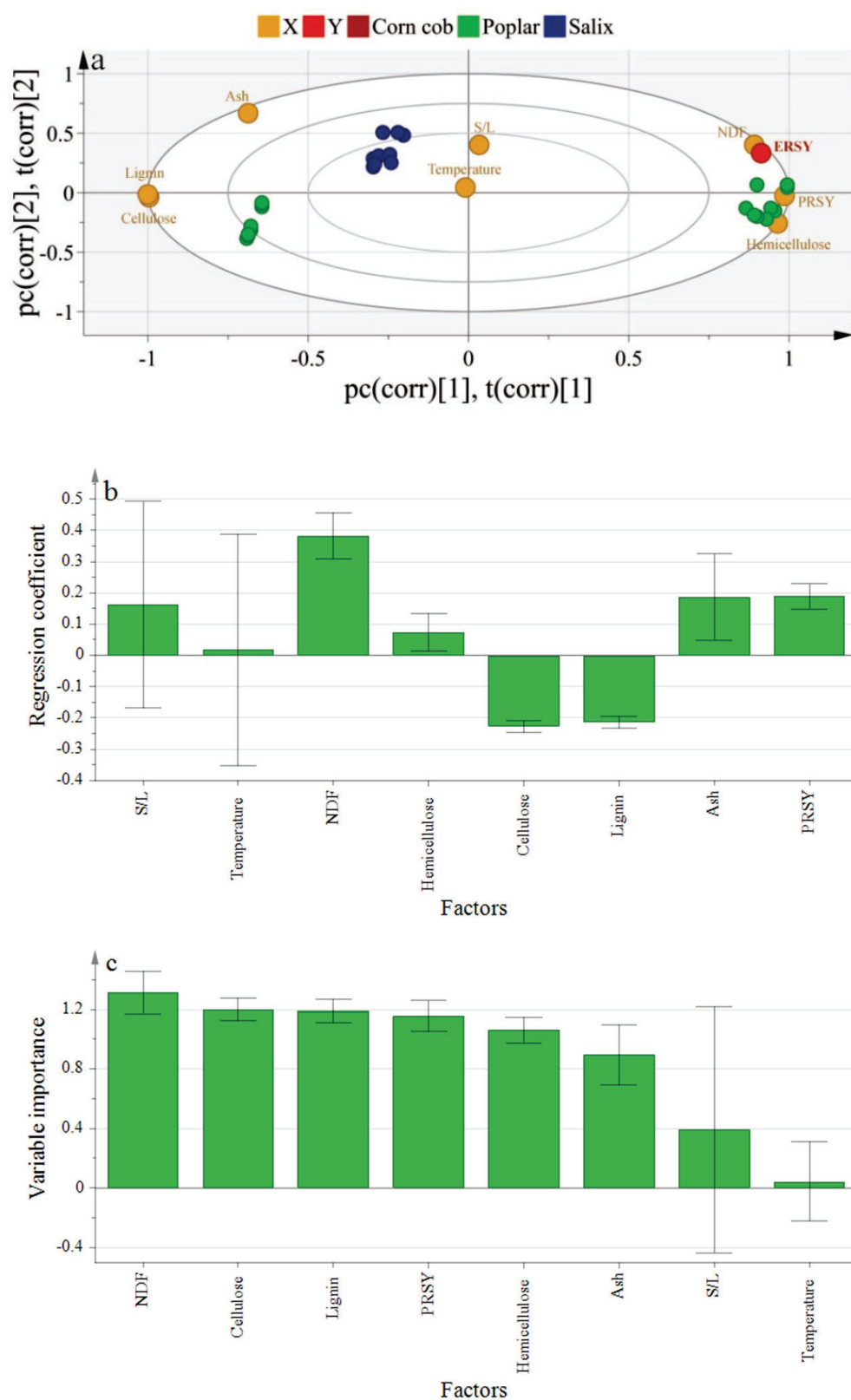


Figure 4. PLS model 3 analysis for the hot water pretreatment followed by enzymolysis. (a) Biplot. (b) Regression coefficients of X variables on the Y variable. (c) Importance of X variables on the Y variables for the projection.

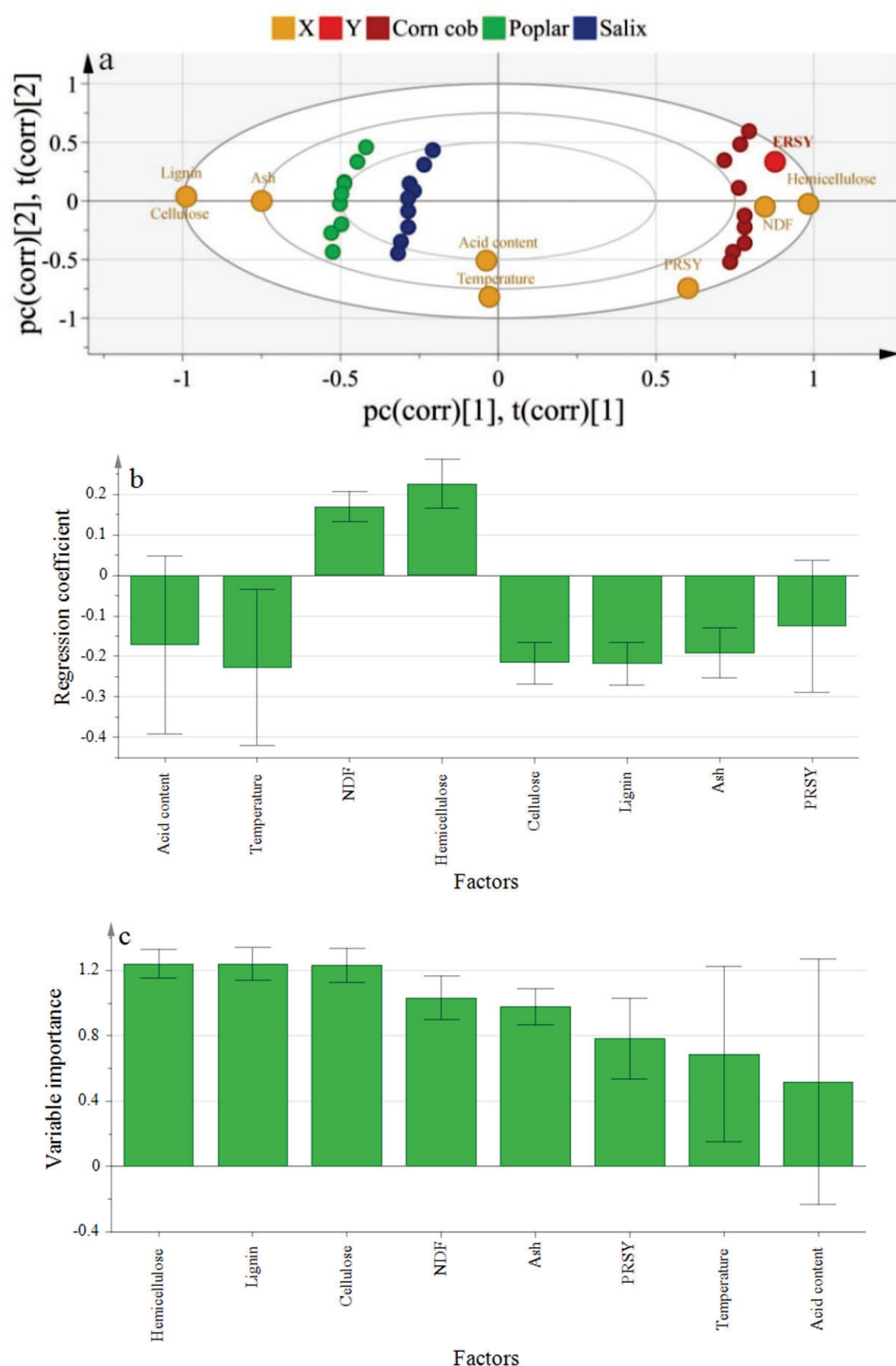


Figure 5. PLS model 4 analysis for the acid pretreatment followed by enzymolysis. (a) Biplot. (b) Regression coefficients of X variables on the Y variable. (c) Importance of X variables on the Y variables for the projection.

Overall, the PLS models showed the biomass compositions had greater influence on the ERSY than the variables of the pretreatments. They also suggested that the type of lignocellulosic biomass was the most important factor influencing the enzymolysis, which was consistent with the previous studies [31]. The common types of lignocellulosic biomass are usually woody plants and herbaceous plants, and the herbaceous species are more readily hydrolyzed by enzymes than the woody species [32]. The corncob is a suitable herbaceous biomass for enzymolysis, due to its low lignin content (7.29%) and

high potential for saccharification. Meanwhile, hemicellulose can be easily hydrolyzed in the acid or alkaline environment, which could increase the accessibility of cellulase [33]. Therefore, the corncob after the pretreatments produced more ERSY than poplar and salix. The high lignin content in poplar and salix may lead to the dense combination that is resistant to degrading, causing a negative effect on the enzymatic saccharification. Though high cellulose content was found in poplar and salix, the ERSY of these two materials were lower than the corncob. Cellulose usually presents as a crystalline form or an amorphous form [3]. The crystalline form is more difficult to hydrolyze, and it was probably the main form of cellulose that existed in poplar and salix. Moreover, the effective pretreatment could further attain a better goal of the sugar yield. The alkaline pretreatment was the best method to pretreat the lignocellulosic biomass, and high alkaline content at room temperature can be used to further improve the ERSY.

3. Materials and Methods

3.1. Materials and Preparation

Corn cob is produced by herbaceous corn (*Zea mays.*), with the high energy density for enzymatic hydrolysis [34]. Poplar (*Populus euphratica.*) is a tree species and salix (*Salix psammophila.*) is a shrub species, which commonly grows in Western China.

The poplar, salix and corncob were collected locally in Hohhot, China (the poplar and salix picked the branches without leaves). Three biomass types were milled and screened using a 60-mesh sieve, and then dried in the oven at 60 °C to a constant weight. The composition analysis of NDF, hemicellulose, cellulose, lignin and ash were measured (Table 1) based on Van Soest. All reagents and chemicals are analytical grade.

Table 1. Compositions of lignocellulosic biomass.

Lignocellulose Biomass	NDF (%)	Hemicellulose (%)	Cellulose (%)	Lignin (%)	Ash (%)
Poplar	22.45 ± 0.62	25.72 ± 0.93	34.89 ± 0.32	16.59 ± 0.09	0.34 ± 0.02
Salix	28.43 ± 1.13	25.43 ± 0.17	31.54 ± 0.47	13.94 ± 1.25	0.65 ± 0.06
Corn cob	31.32 ± 0.71	37.23 ± 0.54	24.09 ± 0.12	7.29 ± 0.26	0.07 ± 0.01

3.2. Pretreatment

The poplar, salix and corncob were pretreated by acid, alkaline, and hot water. The specific operation methods were as follows. Each condition was performed in triplicate.

Acid pretreatment: The milled materials (5.0 g) and 50 mL of H₂SO₄ (0.25%, 1.00% and 2.13% *v/v*, respectively) were put into the micro-polymerization reactors (250 mL). Then the samples were performed at 30 °C, 105 °C and 121 °C for 30 min.

Alkaline pretreatment: The milled materials (5.0 g) and 50 mL of NaOH (0.25%, 0.50 and 1.00% *w/v*, respectively) were put into the micro-polymerization reactors (250 mL). Then the samples were performed at 30 °C, 105 °C and 121 °C for 30 min.

Hot water pretreatment: The milled materials (5.0 g) and the deionized water (the ratio of solid to liquid (S/L) set 1:10, 1:20 and 1:30 (*w/v*), respectively) were put into the micro-polymerization reactors (250 mL). Then the samples were performed at 30 °C, 105 °C and 121 °C for 30 min.

After being treated, the mixtures were filtered through a piece of gauze (500 mesh) to separate the solid residues and liquid fractions. The solid residues were washed to neutral pH and dried at 80 °C to a constant weight for subsequent enzymolysis. The liquid stored at −20 °C to determine the reducing sugar concentration.

3.3. Enzymolysis

The dryly pretreated residues that were obtained from the above pretreatment processes and unpretreated samples (raw materials) were applied for enzymolysis. The digestion system contained 2.0 g samples, 200 mL of acetate buffer solution (pH 4.8) and 0.5 g cellulase which equaled to 100 U/mL (Zhaodong Sun Shine Enzyme Co., Ltd., Hei-

longjiang, China), and it was performed at 50 °C in an orbital shaker at 135 rpm. To prevent the interference of microorganisms, 100 mg/L of ampicillin and 100 mg/L of kanamycin were added in the system. The enzymolysis processes lasted seven days. The samples of enzymatic mixtures were collected and put in the boiling water bath for 5 min, and then stored at −20 °C.

3.4. The Reducing Sugar Analysis and Calculation

The pretreated liquid and enzymatic liquid were centrifuged at 12,000 rpm for 5 min. Then the supernatant samples of 1 mL were used to test the reducing sugar concentration using the 3,5-dinitrosalicylic acid (DNS) method [35].

The reducing sugar obtained from the pretreatment and enzymolysis was divided into two parts. The PRSY was calculated by the reducing sugar produced in the pretreatment processes. The ERSY was evaluated by the enzymatic saccharification efficiency multiplied by the ratio of pretreated residues to raw materials used. The specific formulas are as follows:

$$\text{PRSY (mg/g)} = \frac{\text{Reducing sugar concentration (mg/L)} \times \text{Pretreatment reaction volume (L)}}{\text{unpretreated samples (g)}} \quad (1)$$

$$\text{ERSY (mg/g)} = \frac{\text{Reducing sugar concentration (mg/L)} \times \text{Reaction volume (L)}}{\text{Enzymatic sample weight (mg)}} \times \frac{\text{Pretreated residues (mg)}}{\text{unpretreated samples (g)}} \quad (2)$$

3.5. Multivariate Data Analysis and Statistical Analysis

The PLS models were developed by SIMCA-P (Umetrics, version 14). The datasets were normalized by the unit variance scaling (UV) and screened differences of variables by the coefficient plot and variable importance for the projection (VIP) plot. The amount of the ERSY for each pretreated sample was determined via the Independent-Samples t-test, compared with unpretreated materials to test the significant difference at the 95% level by SPSS (USA, version 24).

4. Conclusions

The ERSY produced from corncob was greatly improved after the alkaline pretreatment with a maximum of 98.51%, and the alkaline pretreatment was more advantageous over the hot water and acid pretreatments. PLS analyses indicated that the biomass types and compositions had greater impacts on the production of the ERSY than the pretreatments. To be specific, hemicellulose and lignin were the key variables for the alkaline and acid pretreatments. NDF was too critical to produce the ERSY under the hot water pretreatment. PLS analysis has great applicability in the analysis of the process variables for the effective pretreatment of the various lignocellulosic biomasses.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal12101142/s1>. Table S1: The datasets during the different pretreatment processes and enzymolysis processes.

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Review

An Overview of Solid Acid Catalysts in Lignocellulose Biorefineries

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Abstract: The continuous depletion of fossil fuels demands their replacement with renewable energy sources for the production of fuels, chemicals, and materials. Lignocellulosic biomass can serve as a sustainable raw material for the manufacturing of various industrial products, such as fine chemicals, biofuels, polysaccharides, and biofuel precursors. Though numerous homogeneous catalysts are available for converting lignocellulosic biomass into fermentable sugars and biofuels, they require harsh environmental conditions, and their recovery is often difficult. Heterogeneous solid acid catalysts are efficient for biomass conversion, are environmentally benign, and can replace homogeneous catalysts in biorefineries to make them green. Zeolites, metal oxides, heteropoly acids, mesoporous silica nanoparticles, and carbon solid acid catalysts are some of the heterogeneous catalysts employed in lignocellulose biorefineries. This comprehensive review covers the different solid acids that can be used in biomass refineries, the factors influencing their catalytic activity, and the progress made towards their application in lignin depolymerization and the production of fermentable sugars, biofuels, and platform chemicals.

Keywords: biofuel; biorefinery; cellulose; lignocellulose; solid acid

1. Introduction

Lignocellulose, composed of lignin, hemicellulose, and cellulose, is the most abundant renewable organic material on Earth. Worldwide annual biomass production is estimated at around 200 billion metric tons ³ [1]. This includes agricultural residues (e.g., straw, husk), forestry residues (e.g., sawdust, wood chips), and dedicated energy crops (e.g., miscanthus, switchgrass). Biorefineries aim to convert the lignocellulosic biomass into fuels, chemicals, and materials that can substitute traditional petroleum-based products. Integrated biorefineries help to minimize landfilling and the open burning of agricultural and forestry wastes. This, in turn, helps to reduce environmental pollution and greenhouse gas emissions. Cultivating dedicated energy crops for lignocellulosic feedstock enhances carbon sequestration in soils, contributing to climate change mitigation. Thus, biorefineries can significantly contribute to achieving the Sustainable Development Goal (SDG) 7 (Affordable and clean energy), SDG 12 (Responsible consumption and production), SDG 13 (Climate action), and SDG 15 (Life on land).

However, the complex structural composition of lignocellulose necessitates effective pretreatment and conversion strategies to achieve efficient biomass conversion and utilization. Various catalytic processes are required to break down the complex lignocellulose and transform the resulting intermediates into value-added products. Typically, in a biorefinery, processes such as lignocellulose pretreatment, the depolymerization of lignin, the pyrolysis and gasification of biomass, the hydrolysis of carbohydrates, hydration, dehydration, esterification, transesterification, and the upgradation of bio-oil rely heavily on the use of catalysts. Enzymatic catalysts (e.g., cellulases, hemicellulases), homogeneous catalysts (e.g., H_2SO_4 , H_3PO_4 , NaOH) and heterogeneous catalysts (e.g., solid acid, solid base, redox, metallic, bifunctional) are used in the above mentioned processes. Among these, solid acid catalysts are well suited to handle the complex and diverse chemical composition of the biomass sources and play a crucial role in the lignocellulose conversion process, offering distinct advantages, such as recyclability, ease of separation, and reduced environmental footprint, compared to traditional liquid acids. Furthermore, solid acid catalysts offer higher product yield and fewer byproducts. Solid acid catalysts enable efficient conversion, minimize waste generation during processing, and reduce the need for harsh chemicals, aligning with green chemistry principles. Moreover, using solid acid catalysts helps to reduce the carbon footprint of biorefinery operations through energy-efficient processing and offers a longer catalyst lifetime compared to conventional acids. For these reasons, solid acid catalysts are considered to be more sustainable. This review discusses the different solid acid catalysts used in biorefineries and their role in lignocellulose pretreatment, lignin depolymerization, carbohydrate hydrolysis, hydration, dehydration, esterification, and transesterification.

2. Solid Acid Catalysts

Solid acid catalysts (SACs) are heterogeneous catalysts that exhibit acidic properties through Brønsted acid sites (donate protons) and/or Lewis acid sites (accept electron pairs). These solid acids catalyze the reactions for the conversion of lignocellulosic biomass into second-generation biofuels, such as bioethanol, biodiesel, and bio-oil. SACs improve the efficiency in cellulose and hemicellulose hydrolysis, as well as the subsequent dehydration and isomerization steps. They are found to be effective in the production of platform chemicals, such as levulinic acid, furfural, and 5-hydroxymethylfurfural (HMF), which serve as building blocks for bioplastics, solvents, and a range of value-added products. SACs are advantageous because they can be easily recovered from the reaction mixture and recycled efficiently. The efficiency of the catalysts depends on various factors, including the reaction conditions (such as the reaction temperature, pressure, and reaction time) and the properties of the catalysts (such as the acid site density, strength, and type of functional groups), affecting the selectivity and yield. A variety of SACs are employed for this catalytic conversion, and some of them are classified in Figure 1 below.

2.1. Zeolite

Zeolites are crystalline microporous aluminosilicates and exhibit diverse crystal structures with large open pores. The International Zeolite Association has recognized 267 types of zeolites with differences in terms of shape, size, pore size, and rings, including 40 naturally occurring zeolites [2]. They have high thermal and chemical stability, making them suitable for reactions under harsh conditions. Shape selectivity, tunable acidity, and highly porous structures are the major advantages of zeolites [3]. The acidity and reactive properties of zeolites are strongly influenced by their crystalline structure, pore structure, and Si/Al ratio [4]. The Si/Al ratio directly impacts the Brønsted acidity of the zeolites and their physical and chemical properties. A higher Si/Al ratio increases their hydrophobicity

and thermal stability. Y-zeolites typically have an Si/Al ratio of ~1 to 5 and exhibit strong acidity due to their greater number of Brønsted acid sites. Zeolites, such as HZSM-5, typically have intermediate Si/Al ratios in the range of 10 to 50. They combine strong acidity with higher thermal and hydrothermal stability. Meanwhile, in zeolites with a high Si/Al ratio (>100), the number of acid sites decreases, lowering overall acidity. These zeolites are more hydrophobic and resistant to deactivation in water-rich environments, making them suitable for biomass conversion reactions. The acidity is enhanced when Al^{3+} is substituted for Si^{3+} in a silanol structure. Therefore, adjusting this ratio allows for the fine-tuning of catalytic activity in acid-catalyzed conversions commonly used in biorefineries.

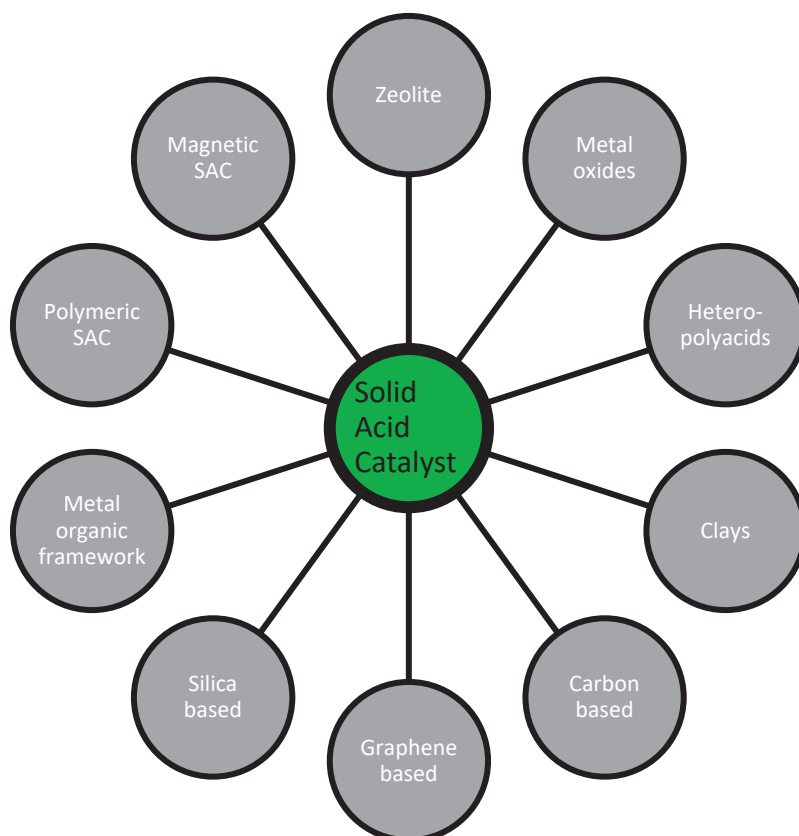


Figure 1. Classification of solid acid catalysts.

Figure 2 shows a representative mechanism for polysaccharide hydrolysis using zeolites. Initially, the water molecules adsorb on the acid sites in the zeolite through hydrogen bonding. The water-soluble oligomeric substrate enters the internal pores of the zeolite. After hydrolysis, the products diffuse out through the pores.

2.2. Metal Oxides

Metal oxides have emerged as one of the highly effective SACs in a wide range of acid catalytic processes in biorefineries due to their tunable Brønsted and Lewis acidity, thermal stability, and structural versatility. Metal oxides exhibit Lewis and Brønsted acidity depending on their surface structure and chemical composition. The strength of acidity is influenced by electronegativity, the oxidation state, the surface structure, and defect chemistry [5–7]. Lewis acid sites originate from coordinatively unsaturated metal cations, such as Al^{3+} in Al_2O_3 , which accept electron pairs from bases like NH_3 or pyridine, forming coordinate bonds. The strength of these sites increases with lower coordination numbers, commonly found at edges or defect sites. Mixed oxides, such as $\text{SiO}_2\text{--Al}_2\text{O}_3$, enhance Lewis acidity due to the inductive effects of the silica network, further

polarizing Al^{3+} . Transition metal oxides, including TiO_2 , ZrO_2 , and SnO_2 , exhibit Lewis acidity via their exposed Ti^{4+} , Zr^{4+} , and Sn^{4+} cations, respectively, with their acid strength tunable through synthesis and calcination [8]. Brønsted acidity, on the other hand, arises from surface hydroxyl groups ($\text{M}-\text{OH}$), especially prominent in hydrated metal oxides, where moisture leads to protonated surface oxygen atoms. Brønsted acidity in metal oxides is fundamentally associated with the presence of surface hydroxyl groups ($\text{M}-\text{OH}$). These surface-bound hydroxyl groups possess a proton (H^+) that can be donated to an adsorbed molecule. Strong Brønsted sites are observed in supported metal oxides, such as $\text{WO}_3/\text{Al}_2\text{O}_3$ [9] and $\text{MoO}_3/\text{Al}_2\text{O}_3$ [10], where interaction with the support enhances the proton-donating ability. In WO_3 , the protonation of terminal $\text{W}=\text{O}$ groups forms active Brønsted sites. Crystalline aluminosilicates, such as zeolites, display robust Brønsted acidity through bridging hydroxyls ($\text{Si}-\text{OH}-\text{Al}$), with strength modulated by the Si/Al ratio and framework structure. Comparative trends show that CrO_3 (Cr^{6+}) is more acidic than Cr_2O_3 (Cr^{3+}) due to a higher oxidation state. Smaller ionic radii and higher charge densities (e.g., $\text{Ti}^{4+} > \text{Ti}^{3+}$) correlate with stronger Lewis acidity. Furthermore, modification strategies, such as the sulfation of ZrO_2 , introduce SO_4^{2-} groups, generating superacid sites by strongly polarizing Zr^{4+} , and thus dramatically enhancing both the Lewis and Brønsted acid strength.

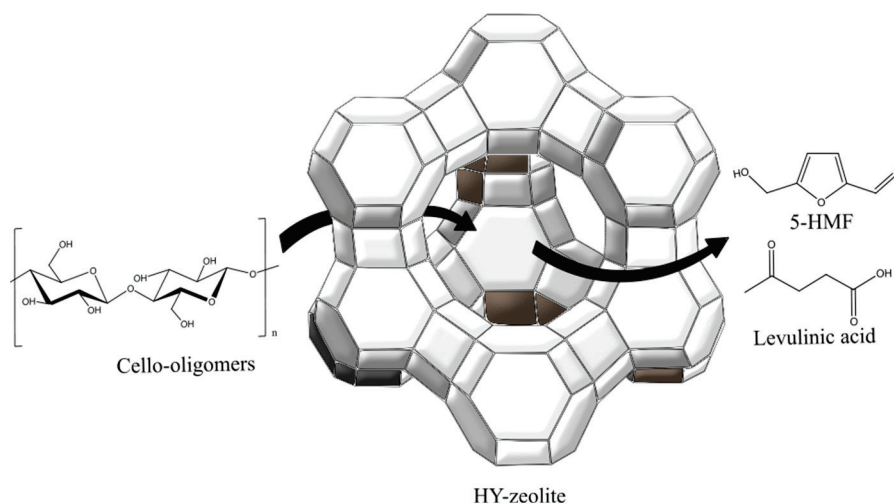


Figure 2. Schematic illustration of the microporous structure of HY zeolite, highlighting its interconnected supercages and 12-membered oxygen ring channels. The pore size ($\sim 0.74 \times 0.74$ nm) facilitates molecular diffusion and adsorption in the LA production from cello-oligomers.

Various metal oxides have been studied for sugar conversions, such as layered transitional metal oxides, nanosheet aggregates, and mesoporous and amorphous metal oxides, as well as sulfated metal oxides and mixed metal oxides [11]. The thermal stability and structural integrity of metal oxides, such as zirconia (ZrO_2) [12], alumina (Al_2O_3), and tungsten trioxide (WO_3) [13] make them suitable for biomass conversion processes. To enhance the acidity and catalytic performance of metal oxides, they can be modified or functionalized (e.g., by adding sulfate or phosphate groups) and transformed into superacid catalysts [14]. Synthesis and structure are key to tailoring acidity, porosity, and thermal stability for specific applications in biorefineries. Metal oxides, such as ZrO_2 , WO_3 , and Al_2O_3 possess distinct crystal structures, typically based on octahedral or tetrahedral coordination of metal cations with oxygen atoms. These crystalline frameworks can exhibit polymorphism, where different crystalline phases (e.g., $\gamma\text{-Al}_2\text{O}_3$ vs. $\alpha\text{-Al}_2\text{O}_3$) possess different acidic properties. The well-defined mesoporous pore structure of the catalysts enhances the reactants' access to acid sites and improves catalytic activity.

The synthesis of metal oxides is a key step in determining their structural properties, acid site distribution, and catalytic performance. Common synthesis routes employed to tailor these properties include precipitation and co-precipitation, sol-gel, and hydrothermal and solvothermal methods. Similarly, the post-synthesis steps, such as surface functionalization and calcination, also play a critical role in fine-tuning the properties of metal oxide catalysts.

2.3. Heteropolyacids (HPAs)

Heteropolyacids (HPAs) are made of hydrogen, oxygen, Group IV transition metals (primarily molybdenum and tungsten), and a p-block element (typically phosphorus, silicon, or arsenic) [15]. They are used in liquid form for various organic reactions, such as hydration, oxidation, polymerization, and transesterification. They are used in heterogeneous conditions for etherification and esterification reactions. High stability, high proton mobility, strong Brønsted acidity (near the superacid region), additional Lewis acid sites, and fewer side reactions make them environmentally benign catalysts. HPAs can contain Brønsted and/or Lewis acid sites. Their type and number affect polysaccharide conversion [15].

HPAs are becoming very important in the field of biomass conversion. HPAs have flexible molecular structures that can be adjusted for different reactions, and they work well in eco-friendly and efficient processes. HPAs can perform both acid-based and redox (electron transfer) reactions, making them useful for many steps in converting biomass into valuable chemicals. New techniques, such as chemical looping and the use of green solvents, widen the application of HPAs and make HPAs strong candidates for sustainable biorefinery systems. HPAs, particularly vanadium-substituted Keggin-type polyoxometalates (POMs), have drawn significant attention as multifunctional solid acid catalysts in biomass valorization owing to their dual Brønsted acidity and redox capabilities. Recent studies have emphasized their efficiency and versatility in selective oxidation and hydrolysis reactions under mild conditions [16]. Keggin-type polyoxymetalate, $H_5PV_2Mo_{10}O_{40}$ (HPA-2), exhibited isomer-specific activity and additive effects in the aerobic oxidation of sugar-derived intermediates to formic acid. The addition of alcohols such as methanol suppresses CO and CO₂ formation while preserving high formic acid yields under relatively low temperatures (80 °C) and pressure (5 bar O₂) [17]. Complementing this, He et al. [18] developed a chemical looping strategy using $H_8PV_5Mo_7O_{40}$ (HPA-5) as both the catalyst and oxygen carrier, which significantly enhanced formic acid selectivity (up to 95.4%) by temporally separating substrate oxidation and catalyst regeneration steps. This method demonstrated applicability beyond glucose, extending to xylan, cellulose, and raw biomass, highlighting its potential for scalable biorefinery integration [18]. Raabe et al. [17] provided a comprehensive review of HPA-5's structural and catalytic versatility, emphasizing its role in green chemical transformations, such as the esterification, oxidative delignification, dehydration, and fractionation of lignocellulosic biomass. Incorporating vanadium into the Keggin structure enhances redox activity while preserving the catalyst's structural integrity, allowing HPA-5 to outperform many conventional catalysts [17]. Rafiee and Eavani [19] provided insights into the heterogenization of HPAs and reviewed in detail the use of HPAs in organic synthesis, i.e., oxidation, reduction, and multicomponent reactions. The conversion of HPAs to heterogeneous catalysts will help to utilize them as efficiently as possible in biorefinery processes with easy catalyst recovery and reuse, which is critical for economic viability in industrial applications [19].

2.4. Clays

Clays are naturally occurring layered silicate materials with a unique structure, a high surface area, and tunable acidity. They are composed of alternating layers of tetrahedral silicon-oxygen sheets and octahedral aluminum-oxygen sheets. Due to their natural abundance and desirable physicochemical properties, such as their ion-exchange capacity and thermal stability, they are considered attractive candidates for biomass conversion processes. Both natural clays (e.g., kaolinite, montmorillonite, and bentonite) and their modified forms (e.g., acid-activated clays and pillared clays) are recognized for their superior performance in biomass conversion processes.

2.5. Carbon-Based SAC

Carbon-based SACs have recently gained attention in biorefineries. Like other SACs, carbon-based SACs are sustainable and exhibit high thermal stability and tunable surface properties. Due to their low cost, chemical and mechanical stability, and high efficiency, carbon-based SACs are suitable for cellulose/lignocellulose conversion.

Surface groups on the carbon catalysts play a significant role in their function. Functional groups like -COOH and phenolic -OH enhance the substrate affinity of carbon solid acids [20]. The synthesis of functionalized carbon solid acids is illustrated in Figure 3. The synthesis of solid carbon acids with strong acid sites usually involves a two-step process where the carbon sources, e.g., glucose, cellulose, and lignin, are partially carbonized and subsequently sulfonated with acid at lower temperatures. Alternatively, it can be synthesized directly by a single-pot method using a suitable carbon precursor [21]. Carbon solid acid catalysts with higher adsorption capacity have demonstrated better catalytic activity [22].

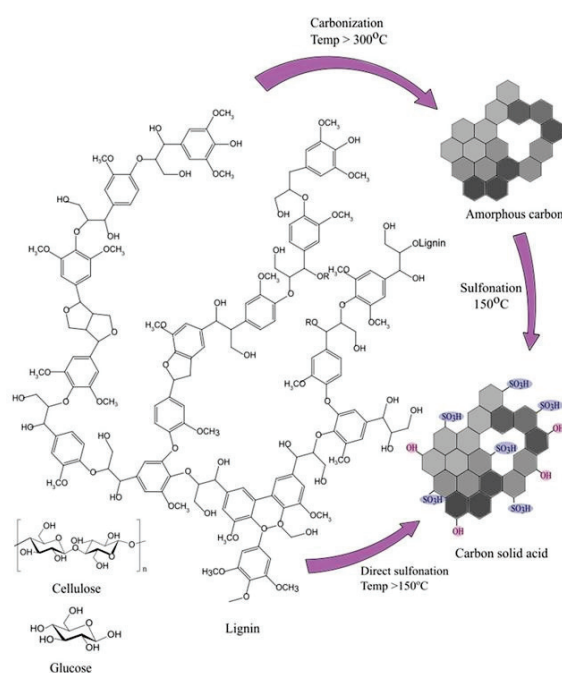


Figure 3. Schematic representation of the synthesis pathways for carbon solid acid catalysts from biomass-derived precursors (glucose, cellulose, and lignin). In the two-step method, biomass is first carbonized at temperatures above 300 °C to form amorphous carbon, followed by sulfonation at approximately 150 °C to introduce $\text{-SO}_3\text{H}$ functional groups. Alternatively, a direct one-step route involves simultaneous carbonization and sulfonation of the biomass at temperatures above 150 °C, producing sulfonated carbonaceous solid acid materials.

2.6. Graphene/Graphene Oxide

Graphite oxidized by potent oxidizing agents like sulfuric acid shows numerous oxygen functionalities, such as $-OH$, $-COOH$, and epoxide, in their structure. These functionalities convert graphite into hydrophilic graphene oxide (GO), enhancing the interaction with cellulose. GO can be reduced to graphene by numerous thermal, chemical, and electrochemical reduction methods. This reduced graphene oxide has residual $-OH$ and $-COOH$ functionalities. Graphene oxide has been used as a structure-directing agent while preparing carbon-based solid acid using cellulose [23]. The addition of GO led to the formation of a lamellar structure and the increased hydrophilicity of the catalyst. It caused better catalyst dispersion in the aqueous system and improved interaction with the substrate, resulting in nearly 94% glucose selectivity [23].

2.7. Mesoporous Silica Nanoparticles (MSNs)

Mesoporous silica nanoparticles (MSNs) are porous, honeycomb-like structures with a high surface area and tunable pores. Particles of smaller size can pass through the channels and interact with the functional groups attached to the channels. MSNs exhibit a high surface area and tunable pore sizes. Silanol groups on pure SiO_2 facilitate functionalization with versatile moieties to tailor the surface properties of SiO_2 [24]. Functionalization with sulfonic acid or phosphoric acid groups enhances the hydrophilicity and polarity of these materials [25–27]. Thus, MSNs and functionalized MSNs can catalyze hydrolysis, esterification, deoxygenation, and dehydration reactions in biorefineries. The introduction of sulfonic groups can be achieved through post-synthetic grafting methods. The thiol groups are first attached to the silica surface and subsequently oxidized to sulfonic groups using oxidizing agents like hydrogen peroxide.

Much research has been done using mesoporous functionalized silica in the hydrolysis. Pure silica has hydrophobic characteristics, but Brønsted and Lewis acid sites like Al make them hydrophilic [28]. Unlike liquid mineral acids, MSNs are easily separable and can be reused several times, and they are thermally stable to withstand harsh reaction conditions required for biomass conversion reactions.

The most common types of MSNs are Santa Barbara Amorphous-15 (SBA-15) and Mobil Composition of Matter No-4y81 (MCM-41). MCM-41 is made by using the surfactant cetyl trimethyl ammonium bromide (CTAB) and dissolved silica precursor, while SBA-15 is prepared using an amphiphilic block copolymer (Pluronic 123) and silica source, such as tetraethylorthosilicate (TEOS). The silica precursor reacts with the micellar rod template formed by the surfactant, resulting in MSN particles. The template is washed off, resulting in a highly stable/ordered structure with mesopores (Figure 4) [29]. Though MSN displays a high surface area, it requires surface functionalization to improve its catalytic activity. Cellulase-immobilized MSNs are also used for glucose conversion from cellulose hydrolysis.

2.8. Metal-Organic Frameworks (MOFs)

MOFs are made of metal clusters and ligands that can serve as active sites. They have a highly nanoporous structure, a large pore volume, tunable cavities, a high specific surface area, and mainly copious Brønsted and Lewis acid sites. Also known as porous coordination polymers, they can form porous structures made of inorganic metal ions (joints) with organic ligands (linkers). Nodes from metal ions bind with arms of linkers, resulting in a one-, two-, or three-dimensional cage-like structure. Joints consist of transition and post-transition metals and lanthanides, while linkers are made of anions (e.g., heterocyclic compounds, sulfonates, or carboxylates) [30]. The presence of organic ligands makes MOFs heat sensitive, and, therefore, their application is limited to low-temperature applications.

MOFs can be combined with graphene, porous carbon, enzymes [31], or metal oxides [32] and used in various applications. Carbon/metal oxide MOF has good stability under high temperatures [33]. MOFs can be tailored to applications like catalysis and separation by carefully selecting metal ions and ligands.

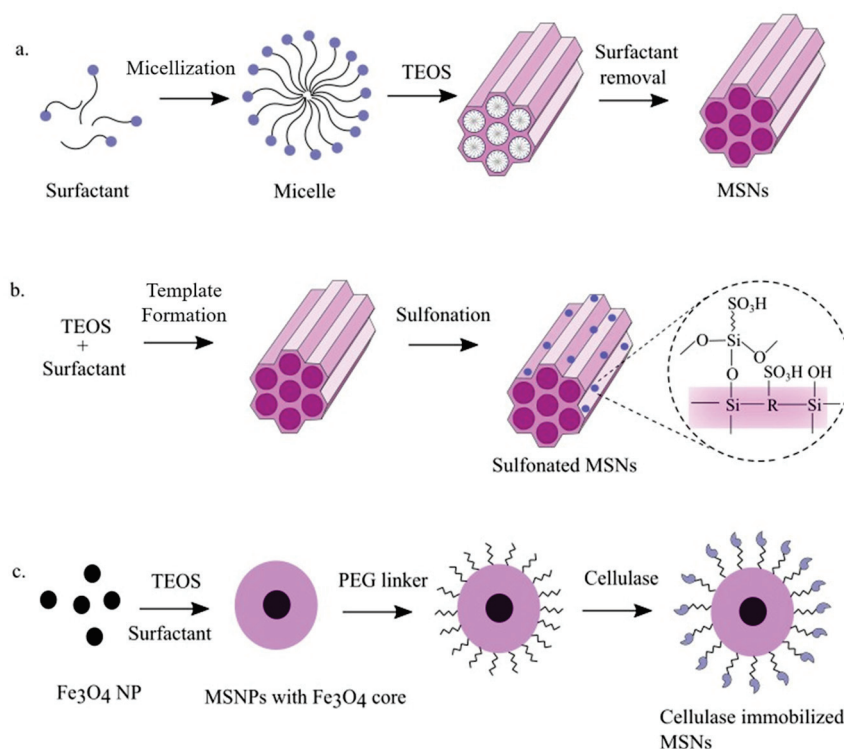


Figure 4. Schematic illustration of the synthesis routes for mesoporous silica nanoparticles (MSNs) and their functionalization. (a) Formation of MSNs via micellization of surfactants, silica condensation using TEOS, and subsequent surfactant removal by calcination. (b) Sulfonation of MSNs to introduce sulfonic acid ($\text{-SO}_3\text{H}$) functional groups for catalytic applications. (c) Fabrication of core-shell structured MSNs with Fe_3O_4 nanoparticles as core, functionalized with PEG linkers, followed by cellulase immobilization for biocatalytic processes.

2.9. Polymeric Catalysts

Polymeric catalysts are ion-exchange resins in which the polymeric chains contain the sulfonic acid groups. For example, Amberlyst-15 is a polystyrene-based sulfonic acid resin, and Nafion[®] is a perfluorinated sulfonic acid resin. Polymeric catalysts are hydrophobic, attracting fatty acid or alcohol tails that enhance catalytic activity for esterification reactions. The length of polymer chains influences their hydrophobicity, and such catalysts are generally used for non-aqueous reactions. For cellulose hydrolysis, the catalysts must be hydrophilic to interact with the substrate (cellulose, β -1, 4 glucan). The catalytic activity is determined by the nature of the reaction medium, owing to which polymeric catalysts exhibit good activity in a non-aqueous medium. Generally, such catalysts are not soluble in water; therefore, they are either used in combination with organic solvents or in modified form for aqueous reactions. For example, Villandiera and Corma [34] employed Amberlyst 15 DRY in ionic liquid media for cellulose hydrolysis and the glycosidation of the monomers obtained in a single pot reaction. Jin et al. [35] modified commercial Amberlyst 15 by chloromethylation and reported the enhanced hydrolysis of cellulose in aqueous medium. The improved performance (67.2% glucose yield) of the catalyst was attributed to the synergistic effect between the sulfonic group and the chlorine in the synthesized catalyst.

2.10. Magnetic Solid Acid Catalyst

Extensive research has been carried out for synthesizing magnetic silica-coated nanoparticle solid acids. Most of the works used thiol group formation for SO_3H functionalization rather than sulfonation using sulfuric/sulfonic acids. Takagaki et al. [36] prepared CoFe_2O_4 -embedded silica nanoparticles. Lai et al. [37] claimed to have synthesized the first ordered mesoporous magnetic solid acid by combining magnetic nanoparticles (MNP) and mesoporous SBA-15. They fabricated magnetic SO_3H functionalized SBA-15 by co-condensing tetraethoxysilane and mercaptopropyl trimethoxysilane. Mercapto groups were oxidized by 30% H_2O_2 with Fe_3O_4 particles and triblock copolymers to give Fe_3O_4 -SBA- SO_3H . Good catalytic activity with 96, 50, and 26% total reducing sugar (TRS) yield for cellobiose, amorphous cellulose, and microcrystalline cellulose, respectively, was reported. They also extended the catalyst for lignocellulose, such as corncob, and obtained a 45% TRS yield [37]. Xiong et al. [38] prepared MNPs by immobilizing sulfonic acid groups on $\text{Fe}_3\text{O}_4@/\text{SiO}_2$. They added chlorosulfonic acid to $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ and mixed it at room temperature for 30 min (Figure 5). The nanoparticles were sulfonated by reacting OH groups of $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ and sulfonic acid chlorides. The resulting MNPs were used for cellulose hydrolysis in $[\text{BMIM}]\text{Cl}$ at 130°C for 3 h with a TRS yield of 73.2%. The magnetic property of the catalyst was retained and achieved nearly 69.4% TRS yield even in the 6th cycle.

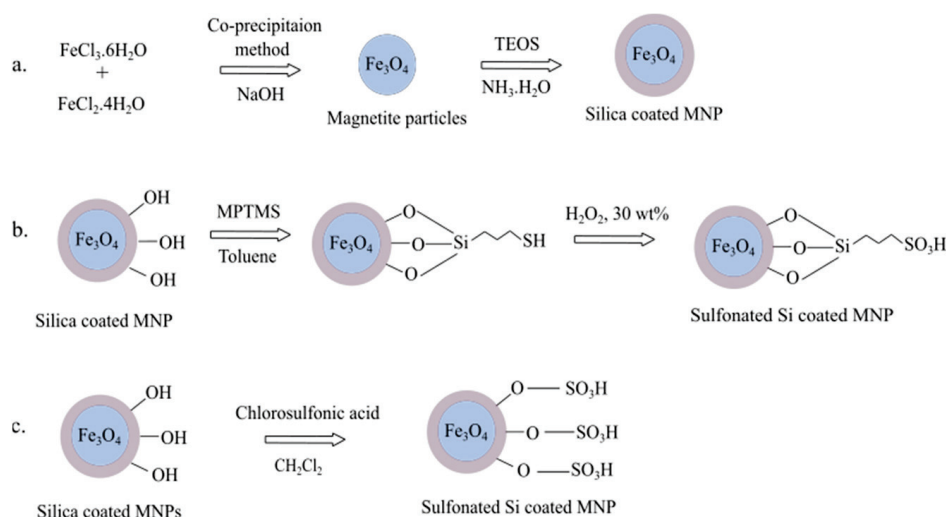


Figure 5. Synthesis of (a) Si-coated magnetic nanoparticle (MNP), (b) sulfonated Si-coated MNP using (3-mercaptopropyl) trimethoxysilane (MPTMS), and (c) sulfonated Si-coated MNP using chlorosulfonic acid.

Carbon-encapsulated magnetic catalysts have been prepared by various methods, such as spraying, catalytic chemical vapor deposition, ion beam co-sputtering, magnetron, high-temperature annealing of carbon-based materials and metal precursor mixtures, organometallic compound pyrolysis, and methane catalytic decomposition. However, these methods typically require sophisticated hardware and are energy-intensive. Xuan et al. [39] followed a simple one-step process to synthesize carbon-coated Fe_3O_4 particles. They used glucose for FeCl_3 reduction and adsorption on Fe_3O_4 nuclei to reduce interfacial tension and as a carbon shell precursor. As a result, 100 to 200 nm nanoparticles with an average carbon shell thickness of 10 nm were synthesized. Increasing glucose content produced impure and irregular Fe_3O_4 carbon particles. Therefore, the synthesis of thick shell-coated Fe_3O_4 remains a challenge.

Zhang et al. [40] followed the same procedure and sulfonated carbon-coated Fe_3O_4 for synthesizing $\text{Fe}_3\text{O}_4@\text{C-SO}_3\text{H}$ nanoparticles. They used the catalyst for hydrolyzing

ball-milled cellulose and obtained 48.6% cellulose conversion. They also exhibited good stability both in terms of catalytic and magnetic properties. Therefore, such an environmentally friendly process can be studied further for biomass conversions. Hu et al. [41] used electronegative $-Cl$ groups to enhance the catalytic surface property for binding with cellulose. The enzyme-hydrolyzed corn stover lignin and chloromethyl polystyrene were used for synthesizing Cl -doped $Fe_3O_4@C-SO_3H$. This catalyst was applied for the hydrolysis of microcrystalline cellulose and rice-straw-derived cellulose in $[BMIM]Cl$, achieving a reducing sugar yield of 78.5% and 73.2%, respectively. Though they displayed good stability, many steps were involved, including $FeCl_3$ impregnation and evaporation, co-carbonization with chloromethyl polystyrene, and sulfonation with H_2SO_4 . Therefore, alternate methods with minimal process steps should be investigated.

3. Characteristics of Solid Acids

The catalytic performance of solid acid catalysts depends on several characteristics, including the surface area, pore size distribution, density and strength of acid sites, thermal and mechanical stability, etc. Acid sites are a major governing factor for the catalytic activity of solid acids. Both the type of acid sites and their strength affect the conversion process. Weak acid sites do not undergo leaching through ion exchange and exhibit hydrothermal stability [42]. On the other hand, degradation side reactions are prompted by the leaching of strong acid sites. Thus, weak acid sites are preferred, owing to their superior stability. The leaching of strong acid sites from sulfonated resins (Amberlyst 70/30) has been reported in reactions at high temperatures. One of the most powerful methods for the estimation of Brønsted acid densities is temperature-programmed desorption (TPD) [43,44]. The acidic strength is directly proportional to the temperature the probe gas molecules require to get released [45]. Ammonia is the most commonly used probe gas in TPD to estimate the acidic strength. However, for the determination of acidic strength, NH_3 has several limitations, and the most important limitation is that ammonia is not specific to the Brønsted acid sites [43]. To overcome this limitation, TPD with alkyl amines, such as isopropylamine, is preferred, since alkyl amines exclusively bind to Brønsted acid sites, providing more accurate measurements. The interaction of amines is stronger compared to ammonia, as they form a stable bond with Brønsted acid sites. Alcohols, such as isopropyl alcohol (IPA), can also be used as probe molecules in TPD. Alcohol adsorbs on the surface and undergoes desorption or surface reactions, such as dehydration or dehydrogenation, upon heating, providing mechanistic insights into surface interactions. Each probe molecule interacts differently with the materials' acid sites, offering unique perspectives on acidity [43,46]. In addition to TPD techniques, infrared (IR) spectroscopy with pyridine adsorption serves as a complementary method. Pyridine forms pyridinium ions, specifically with Brønsted acid sites. On the other hand, when pyridine binds with Lewis acid sites, it forms coordination complexes. The interaction of pyridine with Brønsted and Lewis acid sites can be studied using Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectroscopy to reveal specific absorption peaks for each type of site [47]. This method provides both qualitative and quantitative data on acid site characteristics. Together, these techniques enable comprehensive characterization of the acid sites in SAC materials [47]. Hydrogen-deuterium exchange (HDX) is another effective method for estimating acid sites in solid acid catalyst (SAC) materials. This approach involves the replacement of hydrogen atoms within the catalysts' acid sites with deuterium atoms, resulting in the formation of deuterated materials. The exchange process is monitored using techniques such as mass spectrometry, which detects the presence of deuterium within the material. By analyzing the rate and extent of H-D exchange, it is possible to determine the quantity and strength of the acid sites with precision [48]. Reactive gas chromatography using tert-butylamine has been found to be

highly sensitive to low acid site concentration and has been found to quantify Brønsted acid site densities more accurately than traditional NH_3 -TPD and FT-IR techniques [49]. Accordingly, acidic strength has been graded as weak (100–200 °C), medium (200–300 °C), strong (300–400 °C), and very strong (400–500 °C) depending on the release temperature. Sulfonated silica exhibits weak activity but more stability, whereas zeolites are active and stable [50]. Therefore, along with the strength of the acid site, the hydrothermal stability of the acid site is also a critical factor in determining the efficiency of the catalyst. For weak acid sites, carbon has been preferred due to hydrophilic groups such as phenolic OH and $-\text{COOH}$. These groups are active in carbohydrate hydrolysis. Even silica and alumina, having weakly acidic hydroxyl groups, can induce reactions by forced interaction with glycosidic oxygen groups. Gazit et al. [51] studied silica with weakly acidic surface silanols and grafted β -glu strands. The β -glu strands were hydrolyzed by the surface silanols at a pH of 4. The silica surface creates a robust hydrogen bonding environment for β -glu strands. They reported that the role of silanols is analogous to the precisely positioned carboxylic groups used by Capon [52] to give a similar effect on glycoside hydrolysis. The Lewis acidic properties of silica can be altered by careful Al incorporation to yield silica with different Si/Al ratios, providing varied acidic properties. Similarly, Brønsted acidity can be modified by $-\text{SO}_3\text{H}$ group addition. Though a strong acid site is a principal factor for determining the efficiency of solid acid catalysts, excess acid sites will cause the formation of unwanted products like furfural and humins. Shen et al. [53] observed an increase in humin formation when the catalyst-to-substrate ratio was increased above 5. The $-\text{SO}_3$ sites promoted the transformation of 5-HMF to both levulinic acid and humin. Vu et al. [54] used 50% γ -valerolactone with ionic liquid for curbing humin formation during cellulose hydrolysis and obtained a high total reducing sugar yield of 94.5%. Despite these drawbacks, researchers have preferred strong acid sites for efficient hydrolysis in many works. Tan and Lee [55] used the strong acid sites of DowexTM DR-G8 to treat macroalgae cellulosic residue and subsequent enzymatic conversion to yield glucose. Glucose yield reached 80.6% after enzymatic hydrolysis for solid acid-pretreated macroalgae, while conventional acid and alkali pretreatment yielded 80% and 64.9%, respectively.

Pore size distribution is another important characteristic that determines catalytic activity. Most strong acid sites are typically found in the internal pores of the catalysts rather than on their external surface [56]. For example, zeolites have strong acid sites in their internal pores. However, these internal active acid sites are not accessible to cellulose due to pore diffusional resistance. Particularly, when water is used as a green solvent for hydrolysis, cellulose hydrolysis takes place only on the interface of the catalyst and substrate, as the insoluble cellulose does not diffuse into pores where the active sites are located. Therefore, a larger pore diameter and external area are favored for the hydrolysis of biomass [57]. For example, in ZSM-5, only 62.6% of the Brønsted acid sites are easily accessible, as its pore size is a mere 5.6 Å [58]. Thus, the overall catalytic activity of zeolites depends on their pore size. They can only effectively bind to the substrates that fit into their pores [59]. Jow et al. [60] obtained a 56% levulinic acid yield from fructose using LZY zeolite for 15 h at 140 °C. They explained the high yield based on the molecular tailoring of LZY zeolite. Fructose enters through the 0.75 nm pores of LZY and gets converted to HMF by acidic sites in pores. HMF, having a molecular size of 0.82 nm, gets trapped inside the pores unless it gets converted into levulinic acid, resulting in the high yield and selectivity of levulinic acid. These zeolites are unsuitable for treating cellulose as they have 2–20 nm diameters. Ishida et al. [61] studied the effect of four different zeolites, mordenite, faujasite, ZSM-5 type (Si/Al = 50), and ZSM-5 type (Si/Al = 150), for cellulose hydrolysis in both water and ionic liquid, [BMIM]Cl. Mordenite and faujasite, with pore sizes of around 0.7 to 0.8 nm, were superior to the other two, with pore sizes of 0.5 nm.

Cai et al. [62] employed zeolites of different pore sizes and the same acidity to understand the influence of pore size on cellulose hydrolytic activity in [BMIM]Cl. They found that the cellulose hydrolyzing efficiency increased with an increased catalyst pore size. The pore diameter varied as follows: HY- 0.74×0.74 nm > HBeta, HZSM-5- 0.66×0.67 nm, 0.53×0.56 nm > and SAPO-34- 0.38×0.38 nm. HY, having the largest pore size, had the highest conversion (84.3%); HBeta and HZSM-5, with medium-sized pores, had moderate conversion (77 and 80.9%); and the lowest pore size catalyst, SAPO-34, had the poorest conversion (2.90%). In systems with water as the solvent, the reason for their dependence on pore size was the restriction posed by the pores for interaction with acid sites. In ionic liquid, cellulose is in the solution in a dissolved state and experiences relatively lower diffusional resistance. However, Cai et al. [62] explained the effect of pore size based on the release of H⁺ from the reaction of ionic liquid cation with the Brønsted acid sites of HY. Y zeolite is commonly used in petroleum refineries as a cracking catalyst. Ultra-stable Y zeolite (USY zeolite) is obtained by processing Y zeolite through steaming and yields a hydrothermally stable catalyst. The Al extraction from the framework (dealumination) decreases the acidic sites of the catalyst. Zeolites with at least two different porosity levels with meso/micro or macro pores are called hierarchical zeolites. These additional larger pores can overcome the mass transfer limitations arising from smaller pores. Zhou et al. [57] prepared H-USY-meso zeolite using oxalic acid dealumination of H-USY zeolite and studied the effect on cellulose conversion. Even though H-USY-meso zeolite has many fewer lower acid sites than the parent H-USY zeolite, it had a better external surface area and higher conversion. Parent zeolite and H-USY-meso zeolite achieved a 5.8% and 55.7% TRS yield for hemicellulose hydrolysis, respectively. It was attributed to the macro- and mesopore formation in USY zeolite, which increased the internal acid site accessibility and reactant/product mass transfer, avoiding byproduct formation. The low number of acidic sites in these H-USY-meso zeolites will not allow cellulose hydrolysis. Zhou et al. [57] sulfonated H-USY-meso zeolite (H-USY-meso-SO₃H) for its application to hemicellulose and cellulose hydrolysis. TRS yield reached 78 and 43.7% for hemicellulose and microcrystalline cellulose, respectively. For hemicellulose, TRS yield increased from an initial 5.8% for USY zeolite to 55.7% for H-USY-meso and, finally, 78% for H-USY-meso-SO₃H. It signifies the equal importance of the catalyst pore size and acidic sites in catalytic activity. Therefore, cellulose must be either dissolved in a suitable solvent or the zeolite pore size must be carefully selected to ensure proper contact between the acid sites and cellulose. Nevertheless, the product of cellulose hydrolysis, glucose monomers, can effectively pass through the pores, diffuse through the inner channels, and be converted into 5-HMF or levulinic acid in suitable conditions [63].

Silica nanoparticles (MSNs), such as SBA-15, MCM-48, MCM-50, and FSM-16, are widely studied due to their high surface area (typically > 600 m²/g) and tunable mesopore diameters, ranging from 2 to 50 nm. Under conventional synthesis conditions, MCM-41 and MCM-48 typically exhibit pore sizes between 2 and 4 nm, while SBA-15 has pore diameters ranging from 5 to 10 nm. Degirmenci et al. [64] used zirconia-modified sulfonated SBA-15 for efficiently converting cellobiose to glucose. The sulfation of zirconia patches results in strong acidity on the surface of the SBA-15. IR spectroscopy revealed that, in the sulfated zirconia-modified SBA-15, the Brønsted acidity arises from interactions between sulfate groups attached to zirconia and the silanol groups [64]. The reaction temperature also influences the pore structure of nanoparticles, with damage observed at 130 °C and an ordered structure at 150 °C. To prevent aggregation during synthesis, diluted surfactant concentrations or additives, such as triethanolamine, pluronic polymer, PEG, and L-lysine, are commonly used. Pore size can be tailored through the surfactant chain length. Longer chains yield larger pores, and shorter chains yield smaller pores. Swelling agents, such as DMHA and TMB, can also create pore-expanded MSNs [65]. Lanza fame

et al. [66] developed a bifunctional catalyst (possessing both Brønsted and Lewis acidic sites) by modifying SBA-15 with sulfated zirconia for cellulose hydrolysis. They achieved an enhanced surface area and acid functionality without compromising the mesoporous structure. After cellulose depolymerization, interaction within the internal pores leads to glucose formation and its subsequent dehydration to 5-HMF. It was stated that even though catalytic activity was not affected notably by internal pores, they play an essential role in product selectivity. Glucose can penetrate the inner channels, preventing secondary polymerization and exhibiting a shape-selective effect. MSNs have tunable mesopores (2–50 nm), offering high accessibility and broader applications, whereas zeolites, with micropores (<2 nm), specialize in catalysis. A study explored the tunability of MSNs in the sub-micrometer range using NaOH as a base catalyst. Two synthetic approaches were compared: one using a homogenous aqueous/ethanol solution and another using a two-phase system where ethanol was replaced with ethyl acetate. The two-phase system produced a broader pore width distribution, mainly in the 2–5 nm range, which was highly dependent on the reaction temperature [67]. Conventionally prepared MSN using CTAB as a surfactant has a small pore size of 2 nm, which restricts large substrates like cellulose. Therefore, even though MSN has a high internal surface area, the small pore size did not allow the substrate to diffuse into the mesopores. Large-pore-sized MSN can be obtained through two methods: (1) surfactants with a high molecular weight as templates or (2) hydrophobic swelling agents as additives. PEO-*b*-PMMA, a high-molecular-weight surfactant, was used by Fan et al. [68] to synthesize MSN with an ultra-large pore size of ~37 nm. A pore size of ~25 nm was achieved using swelling agent 1,3,5 trimethylbenzene (TMB) for MSN synthesis [69]. For small-pore-sized catalysts, cellulose should be dissolved in suitable solvents and simultaneously treated by catalysts. Peng et al. [70] first dissolved cellulose in ionic liquid, followed by hydrolysis, isomerization, and dehydration using bi-functionalized MSN. They used acid (SO_3H) and base (NH_2)-bi-functionalized MSN for cellulose conversion to HMF. Moreover, wormhole mesoporous silica nanoparticles (WMSNs), with disordered pore channels, serve as an alternative to traditional honeycomb-structured MSNs. They are synthesized using triethanolamine as a cosolvent, resulting in narrower pore size distributions. In contrast, NaOH-based MSN synthesis results in honeycomb-like pore structures [71]. This can also be achieved by double-chained or specific swelling agents [72].

The synthesis of mesoporous silica nanoparticles (MSNs) has recently gone beyond template-directed synthesis and swelling agents. Atomic layer deposition (ALD) allows for the precise control of pore architecture and surface functionality. ALD enables the conformal coating of internal pore walls with metal oxides, such as TiO_2 , WO_3 , or Nb_2O_5 , at an atomic level. Thus, fine control over acid site density and pore size without collapsing the mesostructure is achieved. Ke et al. [73] demonstrated that TiO_2 films could be deposited on SBA-15 at the submonolayer level using ALD. The synthesized catalysts retained mesoporosity while gradually reducing the pore size from ~8 nm to ~6–7 nm as film thickness increased. The uniformity of these coatings ensured that diffusion pathways remained open, and hence the resulting catalysts were suitable for size-sensitive reactions [73]. In another work using ALD, niobia was deposited on SBA-15, yielding highly ordered and hydrothermally stable solid acids. Although the pore diameter decreased with increasing ALD cycles, the mesoporous framework was preserved. These catalysts exhibited enhanced activity in reactions such as alcohol dehydration due to increased acid site dispersion and accessibility [74]. Majumder et al. [75] investigated polymer–nanoparticle interfaces by coating silica nanoparticles with metal oxides, such as TiO_2 and CaCO_3 . Their findings showed that surface chemistry directly influenced polymer infiltration, suggesting ALD's broader relevance for modulating interfacial interactions in catalytic and materials applications [75].

Unlike cellulose, hemicellulose is more vulnerable to hydrolysis. Xylan is extracted from lignocellulose by either hot water or NaOH treatment, and the precipitated xylan is dissolved in an aqueous medium to react with a solid acid. Charmot et al. [76] used a confining pore radius (3.2 nm diameter) and the high curvature of the mesoporous carbon nanoparticle (MCN) for the conversion of glucan to glucose in buffered solution using weak acidic sites of modified MCN [76]. Cellulose, being resistant to hydrolysis, was converted to β -glucan by mixing crystalline cellulose and a concentrated acid solution. The ensuing β -glucans of different molecular weights were adsorbed on MCN and separated for further hydrolysis in buffer ($\text{pH} \geq 2$). Nafion[®] and Amberlysts are polymer-based catalysts with large pore sizes and strong sulfonic groups. The acidic sites provided by these sulfonic groups are higher than the hydroxyl groups of zeolites [59]. The normal temperature range for hydrolysis reaction is between 120 and 180 °C for solid acid. Brønsted acid sites of Amberlyst 15 get removed, and the catalyst becomes discolored and deactivated at higher temperatures [77]. Among metal-organic frameworks (MOFs), MIL-101 is more frequently used due to its highly porous MOF structure. Their large (3.4 nm) mesoporous cavities allow proper mass transfer through the MOF. Zeolites and MSNs have internal pore structures with acid sites, and therefore, the substrate must be effectively depolymerized or the pore size must be tailored correspondingly. But solid carbon acid catalysts are not open-pore-structured like zeolite. The number of acid sites and external surface areas affects the catalyst efficiency more than the pore size. Generally, carbon-based solid acids are mesoporous/macroporous. Therefore, substrate conversion will not be significantly affected by pore size.

4. Application of Solid Acids in Biorefinery Processes

Renewable energy sources must be explored due to growing demands on fossil fuels. In biorefineries, lignocellulosic biomass is transformed into a range of products such as biofuels, biochemicals, fine chemicals, and energy through various biological, chemical, and thermochemical processes. The wide variety of lignocellulose falls under two major types, namely cellulose-rich and hemicellulose-rich lignocelluloses. Hemicellulose conversion is generally easier than cellulose conversion because of cellulose's inter- and intra-hydrogen bonding. Hemicellulose contains both C₅ and C₆ sugars, while cellulose is made of repeating units of D-glucose. Most agricultural plants and hardwood hemicelluloses contain xylan, while softwood contains glucomannan. Both hemicellulose and cellulose can be converted to platform chemicals. The U.S. Department of Energy has recognized many potential biobased products as valuable platform chemicals, e.g., levulinic acid, furfural, 5-HMF, ethanol, isoprene, lactic acid, fumaric acid, xylitol, arabinitol, etc. [78]. Platform chemicals can be used as substrates to produce higher value-added products. Other wastes like oilseed cake, algae, and vegetable oil have been used as a substrate for biodiesel production [79]. As mentioned earlier, solid acids can play an influential role in processes such as (i) lignin depolymerization, (ii) carbohydrate hydrolysis, (iii) the conversion (fermentation, hydration, and dehydration) of sugars, (iv) the esterification and transesterification of vegetable oils, etc.

4.1. Lignin Depolymerization

Lignin is an amorphous aromatic polymer found in plant cell walls, making up 18–35% of wood. It is a complex, highly cross-linked macromolecule composed of three main types of phenylpropanoid units: p-coumaryl alcohol (p-hydroxyphenyl unit or H-unit), coniferyl alcohol (guaiacyl unit or G-unit), and sinapyl alcohol (syringyl unit or S-unit). These aromatic alcohols, also called monolignols, are linked together through ether (C–O) and carbon-carbon (C–C) linkages. It is a valuable byproduct of the pulp and paper indus-

try, which produces over 50 million tons annually. However, most lignin is burned as a low-cost fuel in mills for heat generation. Valorizing lignin is important for its industrial, environmental, and economic benefits. Consisting of repeating three phenylpropane monomers, lignin can replace petroleum-derived phenol in phenolic resins. Currently, lignin is primarily used as a low-grade fuel in the pulp and paper industry. Only a small fraction is utilized in binders, dispersants, emulsifiers, carbon fiber, phenolic resins, and biofuels. Recent chemical and thermochemical methods, including hydrolysis, hydrogenolysis, pyrolysis, solvolysis, and oxidation, have been explored for converting lignin into low-molecular-weight phenolic compounds using various catalysts, such as solid acids, metal oxides, and heteropoly acids. Solid acid catalysts have been shown to depolymerize different types of lignin effectively [80,81]. Deepa and Dhepe [81] demonstrated solid acid catalysts could efficiently depolymerize various lignin substrates, offering up to 60% yield at relatively low temperatures (<250 °C) to produce aromatic monomers. The authors evaluated various solid acid catalysts, including zeolites (H-USY, H-MOR, H-BEA, H-ZSM-5), clay, and metal oxides for lignin depolymerization and found that among all the catalysts studied, H-USY zeolites (Si/Al ratio 15) offered a maximum of about 60% monomer recovery. Solid acids such as zeolite are also effective in accelerating lignin depolymerization during thermochemical processes like pyrolysis [82]. Asawaworarit et al. [83] examined lignin depolymerization from bagasse using carbonaceous solid acids (CSA) from glucose, cellulose, and lignin. CSA lignin had the highest phenolic monomer yield and stability over five cycles. The optimal condition achieved a 32.8% phenolic yield, mainly 4-ethylphenol and guaiacol. The findings suggest that CSAs, particularly CSA lignin, are effective for high-value chemical production from lignin, with the catalyst dosage, solvent, reaction temperature, and time being crucial factors. Li et al. [84] reported a new strategy that efficiently cleaves $C_{ar}-C_{\alpha}$ and $C_{\beta}-O$ bonds in pine lignin using a 2D hybrid solid superacid named $n\text{ PP@M-[PS][TFMS-]}$, producing guaiacol. The guaiacol yield was 18.2 wt% in aqueous methanol solution, and it was 5.6 wt% higher than that in pure methanol. Adding water promotes methanol decomposition, enhancing the cleavage process. The solid acid-catalyzed phenolation process has been shown to reduce molecular weight and thereby increase phenolic hydroxyl groups in alkali lignin (AL) [85,86]. High-lignin-based phenolic foam (LPF), made by substituting up to 40% phenol with AL or phenolated AL (PAL), exhibited lower water absorption and slag rate and better thermal stability and compressive strength, proving AL's potential in high-performance phenolic foam production [85].

4.2. Carbohydrate Hydrolysis

Generally, cellulose hydrolysis is carried out at high temperatures where it will be slightly depolymerized and hydrolyzed effectively by solid acid. Therefore, solid acids used in this process must be hydrothermally stable. Furthermore, other features like surface groups, hydrophilicity, pore volume, and surface area play an influential role in hydrolysis. Zeolites, metal oxides, heteropolyacids, graphene oxide, polymeric catalysts, and carbon-based solid acids are most commonly used in cellulose hydrolysis. Lignocellulose contains crystalline cellulose made of reducing sugars that can be converted into various value-added bio-based products. Cellulose, being highly crystalline due to intra- and intermolecular hydrogen bonding, requires additional pretreatment techniques before conversion to reducing sugars. For this purpose, biorefinery generally uses chemicals like acids or bases that are not environmentally benign. Solid acid catalysts can be easily recovered and reused after cellulose treatment and present a viable alternative to conventional catalysts used in biorefineries. Various first-generation feedstocks, such as starch and molasses, have been exploited to produce reducing sugars. However, due to their competition for utilization as food, these feedstocks are not preferred. Second-generation

feedstocks made of lignocelluloses have been studied in reducing sugar production using environmentally friendly solid acid catalysts. Dongshen's group prepared a catalyst composite using $\text{SO}_4^{2-}\text{-ZrO}_2$ and cationic montmorillonite (Mt) [87]. Clay structures possess numerous unique stacked nano-sheets with a high surface area and good thermal and hydrothermal stability. Though the catalyst had mesoporous structures, only 30% TRS yield was obtained, which can be explained by the low number of $-\text{SO}_3\text{H}$ functional groups (0.03 mmol/g). Carbon-based catalysts have many advantages over zeolites, including water and thermal stability, good catalytic activity, and reusability. Another vital feature of carbon-based catalysts is their ability to effectively adsorb β -1,4 glycosidic bonds, resulting in hydrolysis to sugars. This adsorption ability is attributed to $-\text{COOH}$, $-\text{OH}$, and $-\text{SO}_3\text{H}$ groups in the partially carbonized catalyst [88]. Cornstarch hydrolysis using a carbon-based catalyst with a TRS yield of 99.87% has been reported [89]. The catalyst was prepared using one-pot hydrothermal conversion using a glucose-acrylic acid solution and hydroxyethylsulfonic acid. They claimed that acrylic acid addition as a co-monomer resulted in increased carboxylic group content in the carbonaceous catalyst, which enhanced the hydrophilic nature of the catalyst. To improve the reaction of water-insoluble cellulose and solid acid, cellulose can be dissolved in an ionic liquid, and the resulting oligomers can be hydrolyzed by solid acid. Rinaldi and Schüth [90] first reported the hydrolysis of cellulose by Amberlyst-15DRY in ionic liquid. Zeolites exhibited lower activity than Amberlyst-15 in water but higher activity in [BMIM]Cl [61]. A combination of ionic liquid and solid acid catalysts for simultaneous cellulose dissolution and hydrolysis was also reported. Geboers et al. [91] depolymerized cellulose using the hydrolyzing action of water with a trace amount of acids at high temperatures. The resulting soluble glucan was converted to glucose using zeolite and simultaneously hydrogenated by having ruthenium (Ru) present in the bifunctional Ru-zeolite catalyst. Therefore, it can be concluded that zeolites are more suited for soluble glucan and glucose conversion rather than cellulose hydrolysis. A carbon-based catalyst from black liquor obtained by the KOH treatment of rice straw was synthesized and used for the hydrolysis of rice straw [92]. KOH played a dual role as an activation agent for carbon catalyst synthesis and as a lignin-extracting agent for rice straw pretreatment, resulting in a 63.4% TRS yield. Similarly, Vu et al. [54] synthesized catalysts with dual polymeric chains made of acidic polystyrene sulfonic acid for hydrolysis and polyvinyl imidazolium chloride for cellulose solubilization. Alkali-treated cellulose was hydrolyzed to 74% TRS yield using this polymeric catalyst, and no significant loss of activity was observed over repeated runs. Chang et al. [93] explored the synergistic effect of surfactants with ionic liquids for lignocellulose hydrolysis. Si et al. [94] hydrolyzed bamboo biomass using a solid acid catalyst made from crosslinked sulfonated chitosan and obtained a 68% TRS yield. Hydrolysis of crosslinked chitosan using hydrochloric acid was carried out in ionic liquid in the presence of surfactants. Among the various surfactants studied, Tween 80 displayed increased TRS yield from 51 to 68% in ionic liquid while using the solid catalyst. It was reported that the use of surfactants improved the removal of lignin and enhanced cellulose hydrolysis in the ionic liquid. Even third-generation feedstocks like macroalgae have been utilized for reducing sugar production [95]. Jeong et al. [96] reported 51.9% TRS yield from macroalgae using Amberlyst 15 at 140 °C for 120 min. Although good TRS yield was achieved, catalyst recyclability was not studied. Nearly 45.6% TRS yield has been achieved using Purolite CT269DR, a polymeric cation exchange resin, from the hydrolysis of *Chlorella* sp. microalgae [96].

TRS produced from hydrolysis can be used as a substrate in microbial fermentation. Some main factors to be considered during TRS production are the nature of the catalyst, the reaction temperature, and time. These factors influence the formation of byproducts like phenolic and furan compounds, which inhibit the growth of microorganisms. Recently,

a magnetically separable catalyst made using magnetic mesocarbon and chlorosulfonic acid was used for cellulose conversion [97]. Magnetic mesocarbon was prepared through coal tar and ferroferric oxide co-calcination and was treated with aluminum chloride to introduce cellulose binding sites ($-Cl$). Upon subsequent sulfonation with chlorosulfonic acid, the catalyst yielded 68.6% TRS and showed good activity even after six runs (61% TRS yield). Polycyclic aromatic rings in coal tar carbon enhanced $-SO_3H$ and $-Cl$ functionalization. Similarly, the magnetic catalyst, made from Fe_3O_4 and glucose, used for the hydrolysis of alkali-free-treated sugarcane bagasse resulted in a 73% TRS yield [98]. Thus, various solid acid catalysts have been successfully utilized for high TRS yield from lignocelluloses. Li et al. [99] developed a carbon-based catalyst from sodium lignosulfonate, which was treated with 98% H_2SO_4 , followed by H_2O_2 treatment. The catalyst was found to have 0.68 mmol/g SO_3H and 4.78 mmol/g total acid content. When corncob was hydrolyzed with this catalyst at 130 °C for 12 h, it demonstrated high selectivity, yielding up to 84.2% xylose (w/w) with minimal byproducts. Under these conditions, the cellulose retention rate was 82.5%, and the selectivity reached 86.75%. A nanoscale solid acid SO_4^{2-}/Fe_2O_3 was used to hydrolyze wheat straw. With both Lewis and Brønsted acidity, the catalysts selectively hydrolyzed hemicellulose from wheat straw, maintaining cellulose and lignin stability. Under optimal conditions (4.10 h, 141.97 °C, and a 1.95:1 ratio), a 63.5% hemicellulose yield was attained [100].

4.3. Esterification and Transesterification

Biodiesel can be obtained either by the transesterification of triglycerides in vegetable oil or by the esterification of free fatty acids (FFA) [101]. The transesterification of animal fat or vegetable oil in the presence of a catalyst with low-molecular-weight alcohol, like methanol, yields fatty acid methyl esters (FAME) and glycerol as byproducts [102]. Esterification involves the reaction of free fatty acids and alcohol in the presence of a catalyst to yield biodiesel and water as byproducts. They are renewable, non-toxic, and fully degradable in water within a few weeks. The normal manufacturing of biodiesel utilizes NaOH or KOH as a base catalyst for the transesterification of triglycerides with methanol [103]. Though alkali-catalyzed transesterification is capable of high yields, it is expensive as it requires pure oil feed, as the process is FAA- and water-intolerant. Owing to the soapy byproduct formation and non-recyclable corrosive nature of NaOH, alternate catalysts for esterification are in great demand. Homogeneous acid can utilize low-quality oil for transesterification but is extremely slow. Using sulfuric acid in the esterification of fatty acid leads to difficulties in water removal and the purification of ester. Another method for biodiesel production is supercritical alcohol [104]. Though this process does not require additional catalysts, it is set back by using expensive materials to design equipment to withstand high pressure. Therefore, inexpensive solid acid catalysts with good product selectivity, water tolerance, and thermal stability are required for industrial biodiesel production. Solid acids like zeolites, metal oxide catalysts, carbon-based polysulfonic acid, and ion exchange resins were used in the esterification of dodecanoic acid with different alcohols [105]. Among these solid catalysts, sulfonated zirconia (metal oxide) was suitable for biodiesel production. Unlike hydrolytic reactions for esterification, which involve organic reactions in water, hydrophobic catalysts are preferred. Water covers the catalyst surface, preventing organic molecule adsorption onto the catalyst. Esterification by zeolites was limited as the bulky reactants could not diffuse into the zeolite pores [106]. A higher SiO_2/Al_2O_3 ratio can increase the hydrophobicity of zeolite but will decrease the acidic strength. Therefore, the optimum ratio must be chosen for the esterification reaction using zeolites [107]. Ion exchange resins like Amberlyst and Nafion-NR50 showed good activity initially but were deactivated after a few hours. A catalyst that can catalyze

both esterification and transesterification simultaneously was synthesized by Kulkarni et al. [108] for biodiesel production from waste canola oil. HPA 12-tungstophosphoric acid (TPA), a highly acidic acid, was supported on hydrous zirconia, Si, Al, and activated carbon (AC). Canola oil, with 10% free fatty acid, resulted in the highest ester yield of 77% upon treatment with zirconia-supported TPA. This higher activity compared with other catalysts was explained by the Lewis acidity formed from the interaction of the zirconia -OH group and TPA. For silica-supported TPA, weaker TPA and Si surface interaction gave rise to weaker Lewis acid sites. The lower yield of AC-supported TPA was explained by the catalyst's smaller pore size, which restricts the bulky reactants. In addition to a strong acidic site, good accessibility is also required for the esterification reaction. Andrijanto [109] used sulfonated hyper-crosslinked polystyrene for biodiesel production from oleic acid using methanol. Compared with Amberlyst 15 and 35, the catalyst had fewer acidic sites but exhibited better catalytic activity, as esterification does not require very high acid strength. Degirmenci et al. [64] studied the effect of a carbon catalyst (biochar from wood pyrolysis) sulfonated by concentrated sulfuric acid and fuming sulfuric acid for both the esterification and transesterification of canola oil. Fuming sulfuric acid, being a stronger sulfonating agent, had higher transesterification efficiency. They also studied the importance of surface area on transesterification by activating the biochar with KOH. The importance of the surface area for transesterification was noted when the catalysts with the highest surface area among equally acidic counterparts exhibited the highest efficiency. Carbon-based solid acids prepared from glucose, a glucose and starch mixture, starch, and sucrose have also been applied in esterification reactions [110]. Acidified biochar from sugarcane bagasse was used for algal oil transesterification with a FAME yield of 94.91% [111]. Carbon solid acids prepared by Hara et al. [112] showed better activity than conventional Brønsted acids, such as cation exchange resins and niobic acid, and they were nearly 60% as active as H_2SO_4 for the esterification reaction. The catalyst was used for free fatty acid conversion from low-cost oil feedstock and was recycled without significant activity loss for nearly ten cycles. Similar results were reported by Zong et al. [113], where the sulfonated sugar catalysts used for esterification exhibited better catalytic efficiency than niobic acid and Amberlyst-15. The catalyst showed good stability, yielding ca. 93% of its original activity even after 50 recycles. A carbon catalyst displaying even higher activity than sulfuric acid was synthesized from *Jatropha curcas* oilcake and concentrated sulfuric acid by Mardhiah et al. [114] for the esterification of *Jatropha curcas* oil. However, after recycling for four cycles, catalyst efficiency decreased from 99.13 to 81%.

Ordered mesoporous carbon (OMC) made using a rigid template like SBA-15 and a carbon source followed by sulfonation has also been utilized for esterification. Liu and co-workers synthesized OMC using a nano-casting technique using MCM-48 and SBA-15 templates [115]. The sulfonation of OMC using H_3PO_2 resulted in a 73.59% conversion of oleic acid [115]. As OMCs are hydrophobic and challenging to sulfonate, Dong's group pre-treated OMCs with H_2O_2 to introduce hydrophilic moieties, making sulfonation easy [116]. The presence of hydrophilic -OH, - SO_3H , and -COOH groups and a hydrophobic polycyclic aromatic carbon framework resulted in improved biodiesel production owing to the better adsorption of both methanol and aliphatic acid simultaneously. Sulfonated OMC achieved an oleic acid conversion of 88%, and the catalyst exhibited no activity loss even after five recycles. Lee et al. [117] developed a new method for converting VFAs to FAMEs using OMC prepared using various mesoporous carbon materials. CMK-5 exhibited the highest FAME yield of ~98% due to its hollow rod-like structures [117]. A magnetically separable metal oxide nano-solid acid catalyst [$\text{SO}_4/\text{Fe-Al-TiO}_2$] resulted in a 95.6% FAME yield using waste cooking oil and displayed good stability over ten cycles [118]. There-

fore, new materials with increased porous structure and stability are continuously being explored for biodiesel production.

4.4. Platform Chemicals

Lignocellulosic wastes represent a renewable source for platform chemical production due to their high cellulose and hemicellulose content. Solid acid catalysts can play a significant role in these conversions. While using lignocellulose as a substrate, pentoses (xylan/arabinose) will be released from the hemicellulose fraction. Degradation of these pentoses produces furfural, which can undergo hydrogenation to form furfuryl alcohol. The furfuryl alcohol can be converted to levulinic acid (LA) through acid-catalyzed hydrolysis [119]. The C-6 sugars from cellulose and hemicellulose can also be converted to HMF using a variety of solid acid catalysts.

4.4.1. HMF

A novel bifunctional carbon solid acid catalyst developed from biochar was employed for glucose-to-HMF conversion. The catalyst with sulfonation and Al-Ti metal loading, under optimal reaction conditions, resulted in a 96.1% conversion of glucose with a 74.6% HMF yield. The presence of both Lewis acid sites and Brønsted acid sites resulted in a synergetic effect favoring the two-step (glucose isomerization followed by fructose dehydration) conversion of glucose to HMF. The addition of Ti enhances the stability of the Al [120]. Iron-sulfonated magnetic biochar was developed and employed to produce 5-HMF from white wine industry waste. Under optimal conditions, a 40.9 ± 1.1 mol% 5-HMF yield with a selectivity of 59.8 ± 2.6 mol% was achieved. The biochar itself was obtained through the pyrolysis of pomace and grape stalk wastes from the white wine industry. The magnetic catalysts were recovered and reused for five cycles without significant change in the activity [121]. A list of solid acid catalysts used in HMF conversions is given in Table 1.

Table 1. HMF production using various solid acid catalysts.

Catalyst	Catalyst Preparation	Substrate	Substrate:Catalyst Ratio	Solvent	Temp (°C)	Time, min	HMF Yield%	Ref.
Carbon-based Al-Ti-loaded bifunctional catalyst	Bio-tar-derived porous carbon from pyrolysis was activated using H ₂ O ₂ and acetic acid; bifunctionalization using Al-Ti metal loading followed by sulfonation and calcination.	Glucose	1:1	20 wt% NaCl in DMSO: Water (4:1)	140	240	74.6	[120]
Iron-sulfonated magnetic biochar	Biochar obtained from pyrolysis was subjected to sulfonation at 150 °C, and then iron was deposited using the wet impregnation method.	Fructose	0.36:1	GVL: Water (2:1)	130	360	40.9	[121]
Nb ₂ O ₅ ·nH ₂ O	Mixing niobic acid with H ₃ PO ₄ , stirring for 52 h, aging for 12 h, washing, drying at 333 K and 383 K, and calcining at 573 K for 3 h.	Fructose	1.2:0.1	Water and 2-butanol	160	50	89	[122]
Silicoalumino-phosphates (SAPO)	Mixing aging gels (pseudoboehmite and phosphoric acid) and cyclohexylamine and silica, followed by stirring, aging, filtration, washing, drying, and calcining at 550 °C.	Fructose	1:0.286	Water and methyl iso-butyl ketone (1:5 v/v)	175	60	78	[123]
Sulfonated polymer polytriphenylamine (SPTPA-1)	Triphenylamine was polymerized using FeCl ₃ in dichloroethane to create PTPA-1; sulfonation of PTPA-1 with chlorosulfonic acid yielded SPPTPA-1.	Fructose	1:0.2	DMSO	140	20	94.6	[124]
SBA15-PrSO ₃ H	SBA15PrSO ₃ H (2a) is synthesized by combining TEOS, MPTMS, PTES, and CSPTMS.	Fructose	1:0.02	Water/nitromethane	140	30	69.8	[125]
HCSS	Treating corn stalks with water under pressure at 250 °C, centrifuging, and then drying the solid. Then, it is heated with concentrated sulfuric acid at 200 °C, cooled, washed, and dried.	Corn stalks	1:1	[BMIM][Cl]	150	30	44.1	[126]

Table 1. Cont.

Catalyst	Catalyst Preparation	Substrate	Substrate:Catalyst Ratio	Solvent	Temp (°C)	Time, min	HMF Yield%	Ref.
PorPOPS	Terephthalaldehyde, pyrrole, and FeCl ₃ are stirred with colloidal silica and then heated in a Teflon autoclave at 180 °C for 48 h. The precipitate is filtered, washed, and dried to get PorPOP. PorPOP is treated with chlorosulfonic acid, washed, and dried.	Fructose	1:0.5	Water	160	120	85	[127]
Phosphoric carbons (PC)	1 g glucose in 56% phosphoric acid is heated at 180 °C for 12 h and then cooled. The water is evaporated and the mixture is calcined at 300 °C for 4 h in nitrogen.	Fructose	1:0.2	DMSO	160	180	93.7	[128]
HTC 24-140	Hydrothermal carbonization of freeze-dried softwood pulp at 200–240 °C, followed by filtration, washing, and drying. The material is then sulfonated with concentrated H ₂ SO ₄ at 140 °C, filtered, washed until neutral pH, and dried.	Fructose	1:0.05	[BMIM][Cl] and methyl iso-butyl ketone	112	24	98.6	[129]
LDMCS-700	Alkali lignin and KCl are mixed and carbonized in a tube furnace at 700 °C. The carbonized product is washed, dried, and sulfonated with sulfuric acid at 180 °C. The resulting sulfonated product is washed to neutral pH and dried.	Glucose	1:1	Aq. NaCl-THF	160	150	57.8	[130]
Nafion [®] 50 resin (NR50)	Commercially purchased.	Chitosan	1:0.55	Methyl isobutyl ketone and DI water	180	120	32.6	[131]
Cellulose sulfuric acid	Cellulose (5 g) is mixed with CHCl ₃ and chlorosulfonic acid and stirred at 0 °C for 2 h. The mixture is stirred, filtered, washed with CHCl ₃ , and vacuum-dried at room temperature for 6 h.	Fructose	1:0.28	DMSO	100	45	93.6	[132]

For HMF production, mostly fructose, glucose, and various other substrates have been employed with different catalysts to investigate the catalyst potential. Acid catalysts like $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ and cellulose sulfuric acid have acidic sites in the pores that enable the dehydration of fructose into HMF. The strong Lewis acid and Brønsted sites on these catalysts boost the reaction rate and selectivity towards the production of HMF, with high yields of 89% and 93.6%, respectively, from fructose [122,132]. Zeolite-based catalysts like silicoaluminophosphates (SAPO) have a microporous structure that provides a high surface area and myriad acidic sites that help to catalyze the conversion of sugars to HMF. The unique property of zeolites allows for the effective adsorption and reaction of fructose molecules, yielding up to 78% HMF [123]. Polymer-based catalysts like sulfonated polymer polytriphenylamine (SPPTPA-1) and SBA15- PrSO_3H are sulfonic acid groups functionalized in the polymer, which provide strong acidic sites for catalysis. The polymer backbone offers a flexible and tuneable structure, improving the catalytic performance in organic and aqueous solvents, yielding up to 94.6% and 69.8% of HMF from fructose, respectively [124,125]. Biomass-derived catalysts like HCSS (hydrothermal carbonized sulfuric acid) and HTC 24-140 are derived from lignocellulose biomass materials. These catalysts are synthesized by hydrothermal sulfonation and carbonization, generating a high density of acidic sites. The origin of the biomass makes these catalysts environmentally friendly and sustainable options for HMF production from sugars [126,129]. Heterogeneous catalysts like PorPOPS (porous polymer organic frameworks) and phosphoric carbons (PC) have a porous structure that offers a large surface area and enables mass transfer. The acidic sites in the pores catalyze the conversion of fructose to HMF efficiently with 85% and 93.7% yield, respectively [127,128]. Commercial catalysts like Nafion[®] 50 Resin (NR50) are also used in HMF conversion [131]. In HMF production, its stability and strong acidic sites under various reaction conditions make it an effective catalyst, though its use may be limited by cost and availability.

The primary role of these catalysts in HMF production is to facilitate the dehydration of sugars such as glucose and fructose. Catalysts activate sugar molecules, causing them to be more reactive towards dehydration. Acidic sites in the catalysts enable the removal of water molecules from sugars, leading to the formation of HMF. Catalysts improve the selectivity towards HMF, diminishing the formation of byproducts and enhancing the overall yield. Effective catalysts sustain their structure and activity over numerous reaction cycles, offering practical and economic benefits for industrial applications. Heterogeneous and biomass-derived catalysts are more environmentally friendly and sustainable, positioning them with green chemistry principles. The choice of catalyst in HMF production from sugars significantly influences the sustainability of the process, efficiency, and yield. Acid catalysts, polymer-based catalysts, zeolite-based catalysts, heterogeneous catalysts, biomass-derived catalysts, and commercial catalysts each have specific advantages that make them appropriate for industrial applications and specific reaction conditions. By optimizing these catalysts and their preparation, researchers can improve the production of HMF from renewable lignocellulosic biomass sources, contributing to the eco-friendly chemical and development of sustainable processes. These findings highlight the importance of catalyst optimization and selection in the field of chemical synthesis, specifically for biomass conversion and other environmentally friendly processes. The future of catalytic processes lies in developing more efficient, sustainable, and cost-effective catalysts to meet the rising demands for renewable resources and green chemistry.

4.4.2. Furfural

Solid acid catalysts are also used for the production of furfural from xylose- and biomass-derived sugars. Table 2 below tabulates a list of solid acid catalysts used in furfural production from sugar/biomass. Carbon solid acids derived from cotton [133], lignin and polyvinyl chloride [134], and rice straw [135] were effective in the conversion of xylose to furfural. Sulfonated carbon solid acid was synthesized by a one-pot method using cotton as a precursor. When used for the conversion of xylose, under optimal reaction conditions, an 87.3% furfural yield was obtained. Meanwhile, the catalyst resulted in a 63.2% furfural yield from corn cob. Though the catalyst activity is reduced upon use, it could be regenerated to restore its activity [133]. In a similar study, a sulfonated carbon catalyst synthesized from lignin and polyvinyl chloride resulted in 84.3%, 76.4%, and 66.3% furfural yields from xylose, corn cob, and rice husk, respectively [134]. Similar furfural yields of 88.2%, 95.0%, and 77.4%, respectively, from xylose, corn cob, and rice husk were reported by Gao et al. [136] while using a nitrogen-doped sulfonated carbon acid catalyst synthesized from polyaniline.

Li et al. [137] developed a solid acid catalyst ($\text{SO}_2^-/\text{TiO}_2^-/\text{ZrO}_2/\text{La}^{3+}$) using the co-precipitation and impregnation method. This catalyst demonstrated high thermal stability, and its strong acid sites facilitated the hydrolysis of polysaccharides and the dehydration of monosaccharides. The maximum furfural yield (6.18 g/100 g) was achieved at 180 °C for 120 min at a corncob/water ratio of 10:100.

Table 2. Furfural production using various solid acid catalyst.

Catalyst	Catalyst Preparation	Substrate	Substrate:Catalyst Ratio	Solvent	Temp (°C)	Time, min	Furfural Yield%	Ref.
Polyaniline carbon-based solid acid catalyst (PAC-S)	Prepared polyaniline precursor was carbonized at 800 °C in nitrogen atmosphere for 2 h and sulfonated using conc. H ₂ SO ₄ at 180 °C for 3 h to obtain PAC-S.	Xylose	4:1	GVL	170	45	88.2 *	[136]
Polyaniline carbon-based solid acid catalyst (PAC-S)	Prepared polyaniline precursor was carbonized at 800 °C in nitrogen atmosphere for 2 h and sulfonated using conc. H ₂ SO ₄ at 180 °C for 3 h to obtain PAC-S.	Corn cob, rice husk, corn stalk, rice straw, wheat straw	1:1	GVL:Water (4:1)	180	30	95, 77.4, >40, <20, ~20 *	[136]
Sulfonated carbon derived from lignin, polyvinyl chloride	Synthesized using the calcination-sulfonation method using lignin, KOH, polyvinyl chloride-in mass-ratio of 1:1:1 calcined at 750 °C in N ₂ atmosphere for 4 h, and sulfonated using p-aminobenzenesulfonic acid.	Xylose	2:1	GVL	160	60	84.3 *	[134]
Sulfonated carbon derived from lignin, polyvinyl chloride	Synthesized using the calcination-sulfonation method using lignin, KOH, polyvinyl chloride-in mass-ratio of 1:1:1 calcined at 750 °C in N ₂ atmosphere for 4 h, and sulfonated using p-aminobenzenesulfonic acid.	Corn cob, rice husk, corn stalk, rice straw, wheat straw	2:1	GVL:Water (4:1)	160	60	76.4, 66.3, 16.1, 13.5, 5.3 *	[134]
Sulfonated carbon derived from cotton	Using the one-step carbonization-sulfonation method, cotton in sulfuric acid is stirred at different mass ratios and carbonized subsequently at various temperatures.	Xylose	2:1	GVL:Water (5.67:1)	180	90	87.3 *	[133]
Sulfonated carbon derived from cotton	Using the one-step carbonization-sulfonation method, cotton in sulfuric acid is stirred at different mass ratios and carbonized subsequently at various temperatures.	Corn cob	1:1	GVL:Water (4:1)	190	90	63.2 *	[133]
SO ₄ ^{2−} /TiO ₂ −ZrO ₂ /La ³⁺ Solid acid catalyst	Using the coprecipitation and impregnation method. Ti, La, and Zr salts are used to form TiO ₂ −ZrO ₂ /La ³⁺ , impregnated in 1M H ₂ SO ₄ , dried, and calcined at 550 °C for 4 h.	Corn cob	10:1	Water	180	120	6.18 **	[137]
Rice-straw-derived sulfonated SAC	Two-step procedure consists of rice straw carbonization at 300 °C for 2 h in N ₂ atmosphere, followed by sulfonation using conc. H ₂ SO ₄ , ultrasonication at 150 °C.	Rice straw	10:1	Water	160	300	6.83 **	[135]

* mol of furfural/ mol of xylose (or xylan) unit in biomass × 100, ** g of furfural/ g of dry biomass × 100.

4.4.3. Levulinic Acid

Levulinic acid produced by cellulose conversion is an important, versatile intermediary for the production of various chemicals, e.g., γ -valerolactone, δ -aminolevulinic acid, levulinate esters, methyltetrahydrofuran, and diphenolic acid [138,139]. The U.S. Department of Energy recognized LA as one of the top 12 bio-based platform chemicals. LA has found increasing applications in the pharmaceutical and cosmetic industries as a solvent and in pesticide manufacturing. Its applications include fertilizer, plasticizer, fungicide, antifreeze, food, and feed additive. Aminolevulinic acid produced from LA is an effective biodegradable herbicide. Ethyl levulinate production from LA makes it a potential biofuel precursor. Since LA has an LD50 value of 1850 mg/kg, it is also relatively non-toxic [140]. The worldwide reports published on levulinic acid production are illustrated in Figure 6a. The graph (Figure 6b) displays a steady increase in the number of publications related to levulinic acid production. Focus on sustainable growth through the production of bio-based products has led to a rise in LA demand. Global demand for LA elevated from 2606 tons in 2013 to 3820 tons by 2020. By 2020, nearly 84 articles reported the use of lignocellulose for LA production (Figure 6c).

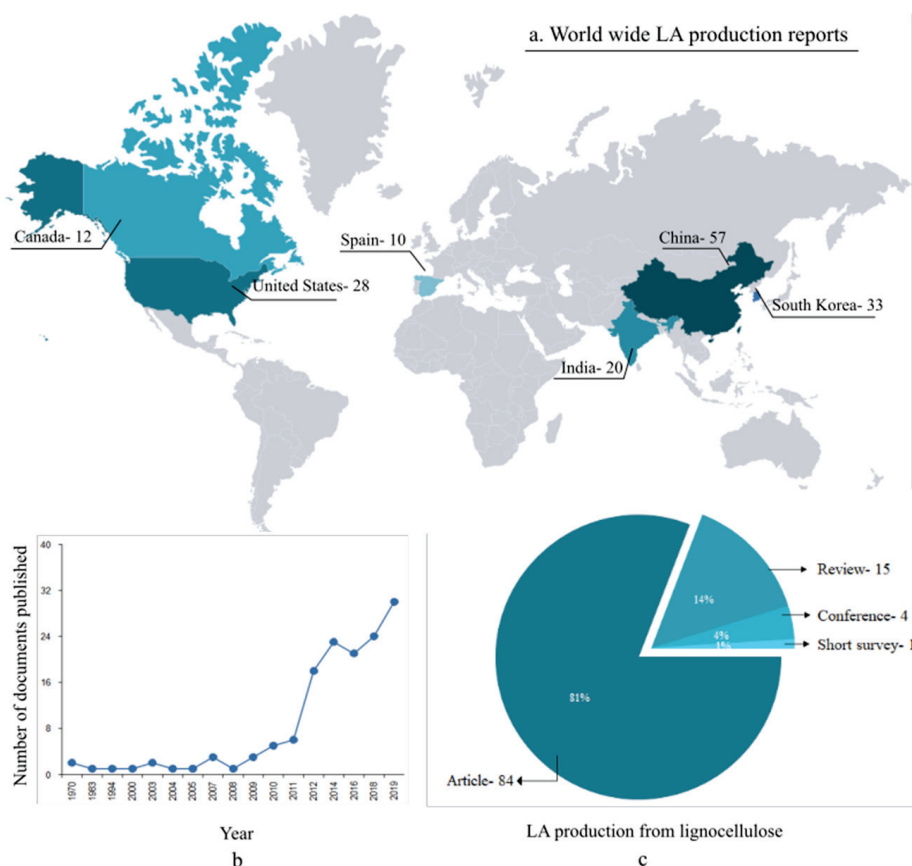


Figure 6. (a) Illustration of the worldwide reports published on levulinic acid production, (b) year-wise trend of the number of documents published on levulinic acid production, and (c) number of articles published on levulinic acid by 2020.

A variety of biomasses, including rice husk [141], paper towel waste [142], food waste [143], waste paper [144,145], and paddy straw [146], have been utilized for LA production. The market growth for levulinic acid is mainly influenced by the demand for LA in the agricultural sector. By 2027, the global market for LA is expected to reach USD 61.2 million. LA is mainly produced from hexose, carbohydrates, and cellulose by the degradation of sugars to 5-HMF followed by rehydration to LA and formic acid

(FA) [92]. The reaction proceeds via several steps, i.e., the production of glucose from cellulose hydrolysis, 5-HMF and acetic acid formation through glucose degradation, and the equimolar synthesis of LA and FA through rehydration of 5-HMF. Initial studies for LA synthesis from hexoses involved the conversion of glucose/cellulose/lignocellulose using homogenous acid catalysts like H_2SO_4 , HCl , and H_3PO_4 [147–149].

Lewis and Bronsted acids greatly influenced the LA yield when the starting material was fructose and glucose, respectively [150]. Beh et al. [150] synthesized solid acid based on amorphous Si alumina and amorphous Si alumina phosphate through flame spray pyrolysis for glucose conversion. Si-alumina solid acid with an Al/(Al + Si) ratio of 0.4 and Si-alumina phosphate with a Si/(P + Si) ratio of 0.25 exhibited the highest LA yield. Kumar et al. [151] entrapped heteropolyacid (polyoxometallate) in gallium micro/nanoparticles to convert glucose to LA. They also applied the catalyst for LA production from rice straw. Acharjee and Lee [152] studied the isomerization of glucose to fructose using various Lewis acid catalysts. Sn-Beta, a zeolite with large pores embedded with tin, displayed the highest activity for glucose isomerization. Dual acid catalysts with Sn-Beta and Amberlyst-15 had the highest LA yield of 45% from glucose. Co-solvent GVL improves cellulose depolymerization and LA production. The polar aprotic property of GVL improves proton reactivity by stabilizing the solvated protons [142]. A proposed reaction pathway for the synthesis of levulinic acid is given in Figure 7.

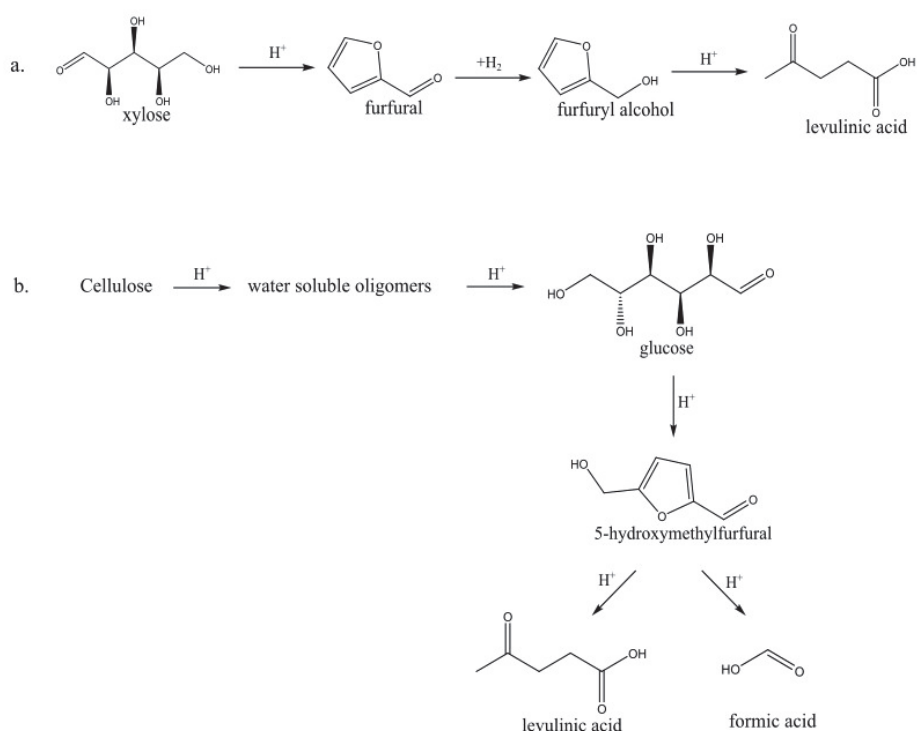


Figure 7. Acid-catalyzed reaction pathways for LA synthesis from hemicellulose and cellulose. (a) Conversion of xylose (from hemicellulose) to furfural, followed by formation of furfuryl alcohol and levulinic acid via hydrolysis. (b) Conversion of cellulose to glucose, followed by 5-hydroxymethylfurfural (HMF), and then levulinic acid and formic acid by hydrolysis.

For cellulose hydrolysis using Amberlyst 70, using 90 wt% GVL as solvent resulted in a high LA yield of 69%, while water resulted in only 20%. GVL solubilizes cellulose and results in oligomers that have better accessibility to solid acid sites. Furthermore, GVL swells Amberlyst 70, leading to better diffusion through pores, resulting in higher catalytic activity. Cellulose remained solid when water alone was used as the solvent, even after 16 h. When GVL replaced 50 wt% solvents, cellulose was completely solubilized. Low glucose

and 5-HMF indicated that cellulose hydrolysis to glucose is the rate-limiting step [153]. Zuo et al. [154] synthesized chloromethyl polystyrene resin, containing acid sites ($-\text{SO}_3\text{H}$) and binding sites ($-\text{Cl}$) for cellulose conversion. The improved activity of the catalyst was ascribed to the excellent affinity to the substrate rendered by the $-\text{Cl}$ sites [154]. Around 60% of the polymer was adsorbed to the cellulose, which indicated the high affinity of the catalyst for cellulose. The water-soluble polymeric catalyst can be recovered by the ultrafiltration of the reaction mixture after reaction completion [155]. Solid acid prepared through the carbonization of lignin (200 °C) and subsequent mixing with ferrous sulfide at 105 °C resulted in a 35.64% LA yield from cellulose [156]. Ding et al. [157] prepared aluminum-modified mesoporous niobium phosphate with an enhanced strong Lewis acid site, resulting in improved LA yield. Simultaneous conversion of the produced LA to GVL was achieved using an Ru/C catalyst after replacing N_2 with H_2 in the reaction medium. The presence of strong Lewis acid sites was enhanced by increasing the aluminum content in the catalyst [157]. Wei et al. [158] synthesized chromium-modified niobium phosphate for LA production from cellulose, since chromium(III) exhibits better glucose-to-fructose isomerization efficiency than Fe. A novel carbon foam-supported aluminotungstic acid (HAIW/CF) catalyst with Brønsted and Lewis acid sites was synthesized and employed for the conversion of cellulose to LA. The synergistic effect between the dual acid sites resulted in an improved cellulose conversion of 89.4%, and the corresponding LA yield was 60.9% [159]. Ya'aini et al. [160] explored the use of hybrid catalysts made from chromium chloride (CrCl_3) and HY zeolite for LA production from empty fruit bunches. HY zeolite (a Brønsted acid) has high catalytic activity and shape selectivity, while CrCl_3 can facilitate the mutarotation and isomerization of glucose to fructose and simultaneous dehydration to 5-HMF. When HY zeolite and CrCl_3 were used separately, only 15% and 20% LA were obtained. HY zeolite, having a 0.75 nm pore size, can trap the substrate and facilitate its rehydration to LA and FA through the strong acid sites, resulting in increased LA yield. In rice straw conversion, Chen et al. [161] used a superacid, $\text{SO}_4^{2-}/\text{ZrO}_2\text{--SiO}_2\text{--Sm}_2\text{O}_3$. They enhanced the LA yield through the steam explosion and superfine grinding of the substrate (15 μm) using a fluidized-bed-opposed jet mill. Superfine grinding decreased the cellulose crystallinity and increased the accessibility of acid sites. Wang et al. [162] impregnated montmorillonite (MMT) with SnCl_4 and subsequently sulfonated using sulfuric acid to yield $\text{Sn-MMT}/\text{SO}_3^-$. This catalyst was used to produce furfural and LA from bagasse through a two-step process. The first step involved the conversion of hemicellulose to furfural, followed by a second step where cellulose was converted to LA at elevated temperatures. This process resulted in an 88% furfural yield and a 62% LA yield in the first and second steps, respectively. Li et al. [99] used biomass-based magnetic ferric oxide solid acid for corn straw conversion to LA. The magnetic particles in the catalyst core aid in the easy separation of the catalyst for reuse. Microbial fuel cell waste obtained after soil remediation contaminated with Cr(VI) was utilized for conversion to LA using Amberlyst 36 at 180 °C [13]. The various solid acid catalysts reported for LA production from cellulose and lignocellulose wastes are indicated in Table 3.

Table 3. Levulinic acid production from lignocellulosic biomass using solid acid catalysts.

Catalyst	Catalyst Preparation	Substrate and Solvent	Substrate: Catalyst Ratio	Solvent	Temp, °C	Time, min	Levulinic Acid Yield	Ref.
Amberlyst 70	Commercial catalyst.	Corn stover	0.18:0.2	Water	160	120	54 wt%	[153]
Hybrid catalyst chromium chloride (CrCl ₃) and HY zeolite	The hybrid catalyst was synthesized using the wet impregnation method. Commercial HY zeolite and aqueous CrCl ₃ (10 wt/v%) were mixed and dried at 120 °C followed by calcination at 400 °C.	Empty fruit bunch (41.1% cellulose) Kenaf (32% cellulose)	1:12 1:12	Water Water	145.2 145.2	146 146	15.5 wt% 15 wt%	[161]
S ₂ O ₈ ^{2−} /ZrO ₂ –SiO ₂ –Sn ₂ O ₃ (solid super acid)	The catalyst was synthesized using the precipitation method with ammonia persulfate as the promoter instead of H ₂ SO ₄ . Two wt% montmorillonite (MMT) was mixed in distilled water, followed by the slow addition of SnCl ₄ . The solution was heated at 85 °C for 2 h through microwave irradiation. The resulting Sn-MMT 5 wt% was mixed with 1 mol/L H ₂ SO ₄ at 30 °C for 6 h to obtain Sn-MMT/SO ₄ ^{2−} . Corn straw was carbonized at 549 °C for 13 h, and the resulting carbon was sulfonated with H ₂ SO ₄ at 121 °C for 6 h to obtain the biomass-based precursor. Magnetic iron oxide particles were mixed with the precursor (1:2 ratio) in 1 mol/L H ₂ SO ₄ for 24 h. They were calcined at 500 °C for 3 h to obtain magnetic ferric oxide/SO ₄ ^{2−} .	Steam-exploded rice straw (superfine grinded)	1:2	Water	200	10	22.8 wt%	[163]
Sn-MMT/SO ₄ ^{2−}		Sugarcane bagasse	0.2:0.15	DCM-water	170	144	62 mol%	[162]
Biomass-based magnetic ferric oxide/SO ₄ ^{2−}		Corn straw	2:1	Water	250	67	23.17 wt%	[164]
Amberlyst 36	Commercial catalyst.	Paper towel	1:1	Water	150	60	40 mol%	[145]
Amberlyst 36	Commercial catalyst.	<i>Pennisetum alopecuroides</i>	1:1	30:70 (wt%) GVL:water	180	60	20 mol%	[13]
Gallium salt of molybdophosphoric (Ga@HPMo)	Gallium (Ga) metal was dissolved in molybdophosphoric acid ethanol solution at 50 °C and sonicated for 12 min. The precipitated Ga@HPMo was separated and dried under an N ₂ atmosphere.	Glucose	1:5	Water	150	600	56 wt%	[151]
Dual acid catalyst (Amberlyst 15 and Sn-Beta)	Zeolite beta 5 wt% was mixed with 13 M HNO ₃ at 90 °C for 20 h (dealumination). The recovered zeolite was ground with tin(II) acetate for 15 min, followed by calcination at 550 °C for 6 h. The catalyst was mixed with Amberlyst 15 at a 1:10 ratio.	glucose	1:2.2	Water	140	120	45 mol%	[152]
Amberlyst 70	Commercial catalyst.	Cellulose	0.3:1	90:10 (wt%) GVL:water	160	120	69 wt% (based on theoretical LA yield)	[153]

Table 3. Cont.

Catalyst	Catalyst Preparation	Substrate and Solvent	Substrate: Catalyst Ratio	Solvent	Temp, °C	Time, min	Levulinic Acid Yield	Ref.
Chloromethyl polystyrene resin	Chloromethyl polystyrene (CP) resin with a -Cl group was partially substituted with a -SO ₃ H group using thiourea as sulfonic acid as a precursor. Thiourea-substituted resin was added to 1N NaOH resin, followed by washing with water and protonation by 2N H ₂ SO ₄ .	Cellulose	1:3	90:10 (wt%) GVL:water	170	600	65 wt%	[154]
Sulfonated hyperbranched poly(arylene oxindole)	A ₂ monomer isatin and B ₃ monomer (0.11:0.5) were used for hyperbranched polymer synthesis through polycondensation. The monomers were mixed with methanesulfonic acid (0.05M), and the polymerization was carried out at 35 °C for 48 h. The precipitated powder was dissolved in DCM and reprecipitated to remove impurities, resulting in sulfonated hyperbranched poly(arylene oxindole).	Ball-milled cellulose	1:1	Water	170	180	25 wt%	[155]
Zirconium di oxide	Commercial catalyst.	Cellulose	1:1	Water	180	180	53.9 mol%	[165]
Lignin-based solid acid	Alkali lignin was carbonized at 200 °C for 5 h. The resulting 1 g of carbon was mixed with ferrous sulfide solution (25 g/L) and heated to 105 °C for 10 h. The recovered solid acid was washed with diethyl ether and dried.	Microcrystalline cellulose	1:1	10:1 (wt%) GVL:water	185	120	35.64 wt%	[156]
Aluminum-modified mesoporous niobium phosphate	(NH ₄) ₂ HPO ₄ 0.01 M was mixed in 20 mL of water with pH adjusted to 2 with H ₃ PO ₄ . Al precursor, prepared by dissolving Al(OH ₃) in 1.5 M oxalic acid solution, was added. Niobium tartrate, 20 mL, was added to the mixture and poured into CTAB (1 g in 13 mL water). The precipitated niobium phosphorous was aged at 160 °C for 24 h. After drying, the catalyst was calcined at 500 °C for 5 h.	Cellulose	0.5:0.4	Water	180	720	52.9 wt%	[157]
Chromium-modified niobium phosphate (Cr/NbP)	Niobium tartrate solution, 0.5 mol/L, was added to 3.3 g (NH ₄) ₂ HPO ₄ and chromium precursor (CrCl ₃). The mixture was added to CTAB solution with pH adjusted to 2 using H ₃ PO ₄ . The mixture was aged at 60 °C for 24 h followed by calcination at 500 °C for 5 h.	Cellulose	1:0.3	Water	180	180	62.4 mol%	[158]

4.4.4. γ -Valerolactone (GVL)

Liu et al. [166] reported 99% conversion of furfural with a GVL selectivity of 93.3% in a single-pot conversion using the Zr-SBA-15 25 catalyst. Liu et al. [167] used a mesoporous silica-based catalyst with the mass ratio of phosphotungstic acid (HPW): $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$: SBA-15 as 2:4:15 and attained an 83% GVL conversion from furfural. This work highlighted the balance of Lewis acid sites and Brønsted acid sites using Zr^{4+} and HPW in the catalyst preparation. Jinhua Lai et al. [168] achieved a 58.6% GVL yield with ethyl levulinate, indicating graphene oxide supported zirconia (GO/ZrO_2) potential as a catalyst for GVL production, although its activity was comparatively lower than that of the zeolite-based catalysts. Jian He et al. [169] employed Al-Zr-mixed oxide, synthesized using the co-precipitation method, and yielded 83.2% GVL from ethyl levulinate at a higher temperature of 220 °C. Recently, Malu Thayil Jayakumari et al. [170] achieved a 94% GVL yield from levulinic acid at 175 °C using tuned Al sites in Y zeolite, highlighting the importance of active site modification for catalytic performance.

Xiao Yu et al. [171] reported a 67.5% GVL yield from ethyl levulinate, demonstrating the potential of mixed Mn/Cu oxides in GVL production in 2-propanol. Tingting Yang et al. [172] adopted the sol-gel method for the preparation of Ti/Zr porous oxide and reached a 90.1% GVL yield from ethyl levulinate at 180 °C and investigated the effectiveness of porous oxides in this conversion. Chuntao Zhang et al. [173] prepared a ternary catalyst, $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$, using the co-precipitation method, exhibited an impressive 99% GVL yield from ethyl levulinate at a lower temperature of 140 °C, showcasing the potential of ternary metal oxides for highly efficient GVL production. Tommaso Tabanelli et al. [174] achieved a 64% GVL yield from ethyl levulinate at a higher temperature of 250 °C, demonstrating the catalytic activity of zirconia in this conversion. Shaodan Xu et al. [175] synthesized an Sn-modified silica catalyst and reported an 81% GVL yield from levulinic acid at a lower temperature of 110 °C, indicating the potential of modified silica catalysts for GVL production. The list of solid acid catalysts employed for GVL production is shown in Table 4.

Table 4. GVL production employing solid acid catalysts.

Catalyst	Catalyst Preparation	Substrate	Substrate:Catalyst Ratio	Solvent	Temp (°C)	Time, min	Valerolactone Yield%	Ref.
Zr-SBA-15_x (x-molar ratio of Si/Zr)	In situ synthesized zirconia-incorporated SBA-15 was calcined at 550 °C for 3 h with different molar ratios of Si/Zr.	Furfural	1.92:1	2-propanol	190	1440	93.3	[166]
Phosphotungstic-acid-supported Zr-SBA-15	Prepared by an impregnation method using SBA-15, ZrOCl ₂ ·8H ₂ O, calcined at 300 °C for 3 h, and obtained HPW/Zr-SBA-15 (x:y:z). [x:y:z-mass ratio of HPW: ZrOCl ₂ ·8H ₂ O: SBA-15]	Furfural	1.92:1	2-propanol	190	1440	83	[167]
Graphene-oxide-supported Zirconia catalyst (GO/ZrO ₂)	GO prepared using the modified Hummer's method. Further, preparation of ZrO ₂ /GO was carried out using the hydrothermal method using ZrOCl ₂ ·8H ₂ O at 160 °C for 12 h.	Ethyl levulinate	7.2:1	2-propanol	180	180	58.6	[168]
Al-Zr-mixed oxide	ZrOCl ₂ ·8H ₂ O (18 mmol) and Al(NO ₃) ₃ ·9H ₂ O (42 mmol) employed using co-precipitation method to obtain Al-Zr-mixed oxides at different calcination temperatures.	Ethyl levulinate	2:1	2-propanol	220	240	83.2	[169]
Al sites tuned Y zeolite	Y zeolite-treated samples treated at different temperatures either in water vapor saturated air or in air atmosphere.	Levulinic acid	1:1	2-propanol	175	720	94	[170]
Mn Cu-mixed oxide	Simple co-precipitation method employed utilizing Cu(NO ₃) ₂ ·3H ₂ O and Mn(NO ₃) ₂ ·6H ₂ O calcined at 400 °C in air for 8 h.	Ethyl levulinate	8.64:1	2-propanol	200	180	67.5	[171]
Ti/Zr porous oxides	By using the sol-gel method, titanium isopropoxide and zirconium propoxide as precursors at different molar ratios, and calcined at 500 °C for 2 h.	Ethyl levulinate	2:1	2-propanol	180	360	90.1	[172]
Cu/ZnO/Al ₂ O ₃	Cu/Zn/Al molar ratio of 6/3/1 utilized to prepare ternary catalyst using the co-precipitation method and calcined at 300 °C for 3 h in 5% H ₂ /Ar mixture.	Ethyl levulinate	0.96:1	2-propanol	140	120	99	[173]
ZrO ₂	ZrO ₂ prepared using zirconium(IV)nitrate dihydrate calcined at 500 °C for 12 h.	Ethyl levulinate	-	2-propanol	250	1440	64	[174]
SnO ₂ /SBA-15 (Sn-modified silica catalyst)	Using dimethyldichlorostannane as Sn precursor and SBA-15, a bifunctional catalyst was prepared, calcined at 600 °C for 2 h.	Levulinic acid	2.49:1	2-propanol	110	480	81	[175]

4.4.5. Lignin Monomers

A complex and irregular aromatic polymer that is widely present in lignocellulosic biomass, lignin, has a lot of potential as a renewable feedstock for the production of chemicals, fuels, and aromatic compounds with added value (Table 5). However, catalytic depolymerization is severely hampered by its extremely cross-linked and complex structure. Solid acid catalysts have become one of the most promising methods for lignin valorization because of their excellent thermal stability, reusability, environmental friendliness, and capacity to precisely control surface acidity and porosity to target particular bond cleavages in lignin. For effective lignin breakdown, a range of solid acid catalysts with various structures and functions has been studied. The sulfonated polypyrrole-based catalyst, PP@M-[PS][TFMS-], combines sulfonic acid groups and a trifluoro-methanesulfonic anion and is among the most efficient. This catalyst demonstrated exceptional selectivity and catalytic efficacy by achieving a 96.6% guaiacol yield from lignin model compounds with β -O-4 and Car-C α links in methanol at 250 °C under 10 bar N₂ [84]. Zeolites are common commercial solid acid catalysts, including HUSY, employed for this application. In a water-methanol (1:5 *v/v*) solvent at 250 °C, their inherent Brønsted acidity and microporous structure enable lignin conversion, producing 60% lignin oil from dealkaline lignin. However, the narrow pore size might make it difficult to reach large lignin fragments, which would reduce the conversion efficiency overall [80]. A more environmentally friendly option is carbonaceous solid acids, which are made by hydrothermally carbonizing and then sulfonating precursors sourced from biomass. These catalysts generated 32.8% lignin oil in methyl isobutyl ketone at 300 °C and 20 bar N₂ when used to organosolv lignin from bagasse. These materials may be less active and durable than metal-doped systems, despite being environmentally friendly and simple to prepare [83]. Ni/Al-SBA-15 and other mesoporous metal-supported catalysts have been used to improve performance. By hydrolyzing lignin in ethanol at 300 °C under H₂ for 240 min, this catalyst produced 17.83% lignin oil, illustrating the complementary roles of mesoporous channels for lignin accessibility and metal sites for hydrogenation [176]. Bimetallic catalysts, such as Ni-Cu/H-Beta and Ru-Cu/HY, enhance catalytic efficacy by facilitating hydrodeoxygenation and extensive hydrogenation processes. Ni-Cu/H-Beta transformed Kraft lignin into 40.39% cycloalkanes at 350 °C in isopropanol under a nitrogen atmosphere [177]. Ru-Cu/HY effectively converted model lignin compounds and softwood lignin into cyclohexane, octahydrobenzofuran, and hydrocarbons, achieving yields of up to 85.1%, utilizing water as a solvent under 40 bar H₂ at 250 °C [178]. Ultimately, Cu/Mo-ZSM-5, a zeolite doped with molybdenum and copper, yielded 20.6% alkyl phenols from Kraft lignin under inert circumstances, underscoring the significance of molybdenum in selective C–O bond cleavage and phenol stabilization [179]. Solid acid catalysts provide a flexible framework for lignin depolymerization, where the catalyst structure, acidity, metal composition, and reaction conditions markedly affect product yield and selectivity. Future developments focus on creating multifunctional and hierarchical catalysts to enhance lignin valorization for sustainable industrial uses.

Table 5. Lignin monomer production using various solid acid catalysts.

Catalyst	Catalyst Preparation	Substrate	Substrate:Catalyst Ratio	Solvent	Pressure Bar	Atmosphere	Temp (°C)	Time, min	Product	Yield %	Ref.
PP@M-[PS]/[TFMS-]	The sulfonated polypyrrole (PP)@M complex was sulfonated by 1,3-propanesultone (PS), Tri-fluoromethanesulphonic anion (TFMS-) was attached to the sulfonated PP to generate LASs.	Lignin model (C β -O and C α -C bonds)	1:0.1	Methanol	10	N ₂	250	60	Guaiacol	96.6	[84]
Zeolites (HUSY)	Commercial.	Dealkaline lignin	1:1	Water-methanol (1:5 v/v)	7	N ₂	250	30	Lignin oil	60	[80]
Carbonaceous solid acids	Prepared by hydrothermally carbonizing carbon precursor in water at 220 °C for 3 h. Then, filtered, washed to neutral pH, dried, then treated with concentrated H ₂ SO ₄ at 150 °C for 15 h.	Organosolv lignin from bagasse	1:0.1	Methyl isobutyl ketone	20	N ₂	300	60	Lignin oil	32.8	[83]
Ni/Al-SBA-15 (20)	Synthesized using P123, hydrothermally aged at 110 °C, dried, and calcined at 550 °C. Nickel nitrate solution (20 wt.% Ni) was impregnated on Al-SBA-15, dried at 100 °C, and calcined at 550 °C.	Hydrolyzed lignin	1:0.4	Ethanol	10	H ₂	300	240	Lignin oil	17.83	[176]
Ni-Cu/H-Beta	Ni and Cu precursor solutions were mixed, supports added, and urea introduced. The mixture was stirred, filtered, washed, dried, calcined at 400 °C, and reduced at 550 °C in H ₂ /N ₂ flow for final activation.	Kraft lignin	1:0.4	Isopropanol	-	N ₂	350	300	Cycloalkanes	40.39	[177]
Ru-Cu/HY	Prepared by incipient wetness impregnation with metal salt solutions, stirred, dried, calcined at 550 °C, and reduced at 250 °C under hydrogen pressure before use.	Diphenyl ether Benzyloxy benzene Benzofuran	1:1	Water	40	H ₂	250	120	Cyclohexane Cyclohexane octahydrobenzofuran	81.6 56.1 85.1	[178]
Cu/Mo-ZSM-5	Prepared by dissolving ammonium heptamolybdate and copper sulfate in water, mixing with HZSM-5, and adding NaBH ₄ . The mixture was centrifuged, washed, dried, and calcined at 500 °C.	Kraft lignin	1:0.25	Water-methanol (1:1 v/v)	-	Ar	220	420	Alkyl phenols	20.6	[179]

5. Summary and Outlook

In this comprehensive review, various classes of solid acid catalysts (SACs) and their roles in the catalytic conversion of lignocellulosic biomass into value-added fuels and chemicals were discussed. The catalytic systems examined include zeolites, mesoporous silica nanoparticles (MSNs), metal oxides, carbon-based materials, polymeric catalysts, heteropolyacids (HPAs), metal-organic frameworks (MOFs), and magnetic solid acids. Among these, zeolites stand out due to their crystalline framework, strong Brønsted acidity, selectivity, and exceptional thermal stability [180]. However, their microporous structure limits their accessibility for bulky biomass molecules, reducing their efficiency in raw lignocellulose processing [181]. Strategies such as adjusting the Si/Al ratio or developing hierarchical zeolites can mitigate these limitations by enhancing both acidity and pore accessibility. MSNs, such as SBA-15 and MCM-41, provide improved substrate diffusion through larger pore structures. When functionalized with sulfonic or phosphoric acid groups, MSNs can achieve considerable acidity, making them effective in esterification and hydrolysis reactions [167,182–184]. Nonetheless, their thermal and hydrothermal stability requires further enhancement for long-term use in industrial settings. Metal oxides (e.g., ZrO_2 , WO_3) offer a versatile platform with both Brønsted and Lewis acid sites. These materials are highly robust and can be modified with sulfate or phosphate groups to increase acidity. However, control over the surface area and dispersion of active sites remains critical for optimizing their performance. Catalyst poisoning, the high cost of noble metals, and intense energy demands are some of the known limitations of metal oxides [185].

Carbon-based SACs derived from biomass offer several advantages, including low cost, tunability, reusability, and environmental friendliness. Carbon-based SACs can be synthesized from underutilized biomasses [186]. These materials exhibit a combination of acidic functional groups and porous structures, allowing the effective hydrolysis and dehydration of sugars. While their reusability and catalytic activity are promising, variability in acid site density and distribution still poses a challenge for standardization and scale-up.

HPAs, although possessing strong Brønsted acidity, are structurally unstable in aqueous systems and tend to leach, which hinders their reuse and applicability in continuous processes. Immobilization techniques on solid supports are promising but add complexity to the synthesis [187,188]. Polymeric catalysts such as Amberlyst and Nafion are attractive for their tunable surface properties and recyclability. However, their low stability under aqueous and high-temperature conditions limits their application in biomass hydrolysis unless chemically modified or used in composite forms. MOFs, with their high surface area and ordered pore structure, present a unique opportunity for selective biomass conversion. Still, they suffer due to poor hydrothermal stability, thermal stability, reproducibility, and scalability, which hinder their industrial viability [189–191]. Recent efforts have aimed to hybridize MOFs with more stable materials or use them in tandem with other SACs. Magnetic solid acids combine catalytic function with the ease of recovery via magnetic separation, making them suitable for integration into continuous processes. Nevertheless, their synthetic complexity and less-established long-term durability require further investigation [192–194]. In terms of industrial applicability, zeolites and metal oxides are more established due to their availability and proven stability. Carbon-based and mesoporous silica catalysts, while sustainable and efficient, demand advances in reproducibility and resistance to deactivation [195]. Polymeric and magnetic catalysts offer functional advantages, but need tailored modifications for demanding biorefinery environments. While a lot of progress has been made in designing and comparing different solid acid catalysts, future improvements will depend on solving practical problems. These include how to better apply catalysts to real biomass, deal with complex feedstocks, and make the overall

process more efficient. Some of these key challenges and promising directions in using solid acid catalysts for converting cellulose and other plant materials are to be addressed to achieve sustainable development goals.

In the last decade, heterogeneous catalysts used in cellulose processing have rapidly expanded from aluminosilicate minerals to magnetic carbon-based solid acids. Several groups have explored the synthesis of biofuels and other value-added chemicals from cellulose using heterogeneous catalysts. Still, deeper insights into the mechanism of action are needed to prevent humin formation upon using different substrates. For enabling biorefinery, lignocellulosic substrates can be initially treated to recover lignin, followed by hydrolysis of the structural carbohydrates. The most important challenges in applying solid acids for cellulose hydrolysis are the chemical and thermal stability of the catalyst, limiting the use of catalysts at high temperatures to produce chemicals like 5-HMF, levulinic acid, and GVL. Though several groups have obtained interesting results with glucose as the main product, more work on direct cellulose conversion to other fine chemicals is needed. Carbon-based solid acids present a viable solution for economic and stable solid acids for cellulose conversion. Heterogeneous catalysts with different properties have been applied for biodiesel and cellulose conversion. Carbon-based catalysts offer good thermal and chemical stability and can be obtained from low-cost lignocellulosic/carbohydrate materials. Also, carbon catalysts with enhanced affinity for hydrophilic substrates have been reported for cellulose hydrolysis. Though many studies have reported disaccharides and glucose conversion to platform chemicals, biomass conversion over heterogeneous catalysts still requires more research. Some groups have synthesized magnetic solid acid catalysts, which can be recovered using an external magnetic field. The appropriate pretreatment of lignocellulose before hydrolysis is preferable to improve catalytic activity and recovery. Recently, applying green solvents like a deep eutectic solvent for lignocellulose treatment has gained momentum. These solvents selectively remove lignin and hemicellulose by disrupting the LCC linkages. The remaining cellulose-enriched substrate can then be converted into a broad range of platform chemicals, 5-HMF, and levulinic and formic acid.

6. Conclusions

This review summarizes the improvements in cellulose processing using heterogeneous catalysts. Over the last decade, various heterogeneous catalysts with different structural and chemical properties have been employed for cellulose treatment. The commercial production of platform chemicals from lignocellulose is still challenged by the efficiency and cost of the catalyst, competing with petroleum-based fuels and products. Though improvements in the separation and recycling of solid acids have been achieved using magnetic solid acids, the minimization of process steps involved in the synthesis is essential for application in biorefinery. Therefore, more focus must be given to economically and environmentally favorable solid acid catalysts, which can be utilized for lignocellulose processing, coupled with other pretreatment technologies.

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List of Abbreviations

AL	Alkali lignin
CP	Chloromethyl polystyrene
CTAB	Cetyl trimethyl ammonium bromide
FAME	Fatty acid methyl ester
FFA	Free fatty acids
GO	Graphene oxide
GVL	γ -valerolactone
HCSS	Hydrothermal carbonized sulfuric acid
HMF	5-hydroxy methyl furfural
HPA(s)	Heteropoly acid(s)
LA	Levulinic acid
LPF	Lignin based phenolic foam
MCM	Mobil Composition of Matter
MNP	Magnetic nanoparticle
MOF(s)	Metal organic framework(s)
MPTMS	3-(mercaptopropyl) trimethyl silane
MSN(s)	Mesoporous silica nanoparticle(s)
OMC	Ordered mesoporous carbon
PAL	Phenolated alkali lignin
PC	Phosphoric carbons
POM	Polyoxometalates
POPS	Porous polymer organic frameworks
SAC(s)	Solid acid catalyst(s)
SAPO	Silico aluminophosphates
SBA	Santa Barbara Amorphous
SDG	Sustainable development goal
TEOS	Tetraethylorthosilicate
TPA	Tungstophosphoric acid
TPD	Temperature programmed desorption
TRS	Total reducing sugar
USY zeolite	Ultra stable Y zeolite

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