

Review

Continuous Valorization of Glycerol into Solketal: Recent Advances on Catalysts, Processes, and Industrial Perspectives

Isabella Corrêa , Rui P. V. Faria *  and Alírio E. Rodrigues 

Laboratory of Separation and Reaction Engineering–Laboratory of Catalysis and Materials (LSRE-LCM), Department of Chemical Engineering, Faculty of Engineering, University of Porto, 4200-465 Porto, Portugal; up201902799@fe.up.pt (I.C.); arodrig@fe.up.pt (A.E.R.)

* Correspondence: ruifaria@fe.up.pt

Abstract: With the global biodiesel production growing as never seen before, encouraged by government policies, fiscal incentives, and emissions laws to control air pollution, there has been the collateral effect of generating massive amounts of crude glycerol, a by-product from the biodiesel industry. The positive effect of minimizing CO₂ emissions using biofuels is jeopardized by the fact that the waste generated by this industry represents an enormous environmental disadvantage. The strategy of viewing “waste as a resource” led the scientific community to propose numerous processes that use glycerol as raw material. Solketal, the product of the reaction of glycerol and acetone, stands out as a promising fuel additive capable of enhancing fuel octane number and oxidation stability, diminishing particle emissions and gum formation, and enhancing properties at low temperatures. The production of this chemical can rely on several of the Green Chemistry principles, besides fitting the Circular Economy Model, once it can be reinserted in the biofuel production chain. This paper reviews the recent advances in solketal production, focusing on continuous production processes and on Process Intensification strategies. The performance of different catalysts under various operational conditions is summarized and the proposed industrial solketal production processes are compared.

Keywords: glycerol valorization; solketal; continuous process; heterogeneous catalyst; Green Chemistry; process intensification strategies



Citation: Corrêa, I.; Faria, R.P.V.; Rodrigues, A.E. Continuous Valorization of Glycerol into Solketal: Recent Advances on Catalysts, Processes, and Industrial Perspectives. *Sustain. Chem.* **2021**, *2*, 286–324. <https://doi.org/10.3390/suschem2020017>

Academic Editor: Matthew Jones

Received: 12 March 2021

Accepted: 12 April 2021

Published: 21 April 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

The growing interest in processes that can combine economical savings and environmental preservation has driven not only research groups but also industry to find alternative technologies and methods that conform to Green Chemistry principles [1]. It was not a tough challenge to combine the interests of society, industry, and scientific groups when it has become clear that applying these principles is economically profitable [2]. The first concepts regarding Green Chemistry arose in 1990 and, since its creation, it has been based on improving design to reduce consumption of raw materials rather than treating waste [2,3]. Anastas and Warner introduced, in 1998, the guidelines necessary to redesign processes and products systematically, more known as The Twelve Principles of Green Chemistry [3].

Even before the introduction of the concepts of Green Chemistry, stimulated by the international petroleum crisis from the 1970s, the search for renewable energy sources led to the discovery of biofuel as the most promising alternative to the use of fossil fuels, since it is appropriate for the transportation sector, responsible for 57% of the global oil demand and for 24% of direct CO₂ emissions [4–6]. Considering the significant share of the transportation sector on the Greenhouse Gases emissions and on the air quality of cities, replacing fossil fuel with biofuel arises as a promising alternative to diminish emissions, specially where the renewable alternative does not seem to be extensively applied, for instance, in jet and maritime fuel.

Biodiesel manufacture is a well-established process with billions of gallons being produced yearly; however, it still has room for improvements to maximize the economic value and minimize the environmental impact, especially in what concerns diminishing waste production [7,8]. Avoiding the generation of waste is so relevant that it has been highlighted as one of the main issues since the first discussions about environmental preservation. In 1980, Roger Sheldon proposed a metric to measure the production efficiency taking into account the amount of waste generated, the E-factor [9]. The first principle of Green Chemistry, indeed, is waste preservation [3].

The main production process of biodiesel is the catalyzed transesterification of triglycerides with an alcohol (mainly methanol and ethanol), generating an ester (biodiesel) and glycerol (by-product) (Figure 1) [10].

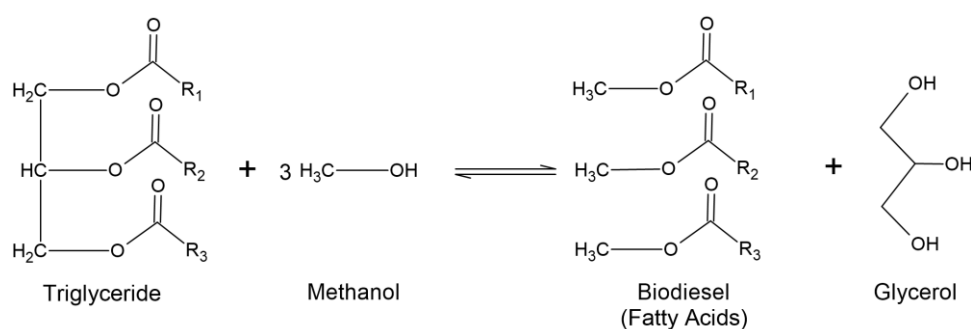


Figure 1. Biodiesel production with glycerol as by-product.

The main environmental disadvantage of the biodiesel industry is the massive amount of glycerol generated as by-product, at a rate of 10–12% and a purity of about 50–55% [11]. Since 68% of the glycerol supply comes from the biodiesel industry, the expected growth in the supply of this commodity follows the tendency of the biofuel industry, with a growth rate of 5.2% until 2027 [12,13]. In fact, the side production of glycerol, viewed as a problem in the past, helped to alleviate the economic pressure over biodiesel plants as a consequence of the demand reduction by the COVID-19 pandemic, because as less biodiesel was produced, the market felt glycerol supply pressure, and its prices rose to levels not seen in years. However, it is relevant to note that this effect was not due to a lack of glycerol on the market, but due to logistics problems caused by the mobility restrictions. Glycerol is viewed as a safe chemical in terms of supply [12,14].

Despite that temporary shortcut, glycerol supply continues to expand at a much faster pace than the new applications to absorb it. Many alternatives have been studied to avoid treating this chemical as waste [15]. The alternatives are particularly interesting if the use of crude glycerol is enabled, without the need of purifying it [16]. Refined glycerol has found numerous applications in cosmetics, pharmaceuticals, and food industries for a long time and, by 2019, this segment accounted for 65.1% of the glycerol market [17,18]. However, traditional markets are not able to absorb crude glycerol from biodiesel plants, both because of its low purity and the amount generated [16].

One of the most promising chemicals derived from glycerol is solketal (2,2-Dimethyl-4-hydroxymethyl-1,3-dioxolane), an oxygenated cyclic ketal with two methyl groups. It is produced by the ketalization of glycerol with acetone in the presence of an acidic catalyst, with water as the by-product (Figure 2). It is an emerging fuel additive by reason of improving the fuel octane number, enhancing liquid properties at low temperatures, reducing gum formation, thus aiding maintenance and cleanliness of engines, and reducing particle emission, which diminishes atmospheric pollution [10,19,20]. Its potential as a fuel additive for the aviation industry, responsible for 2% of the global CO₂ emissions, is noteworthy because of its icing inhibition and de-icing properties, improving the storage stability of aviation fuels [21–23].

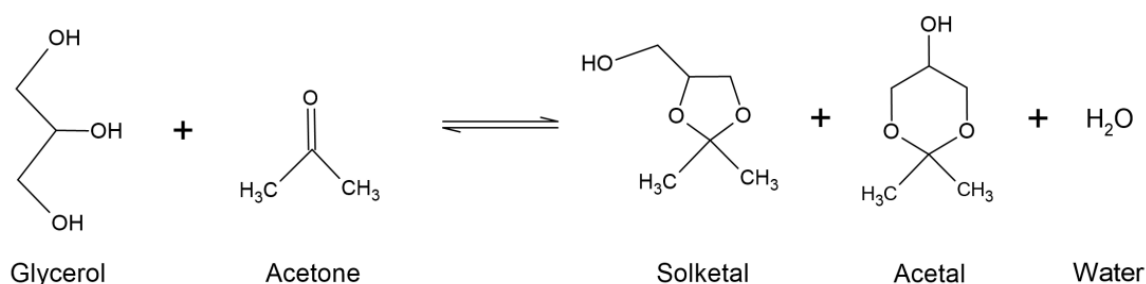


Figure 2. Glycerol ketalization with acetone to produce solketal and water.

Glycerol valorization into solketal is attractive from the environmental and economical perspectives [24]. The reaction conforms to several of the Green Chemistry principles; as all the reactants are from renewable sources, the reaction can be catalyzed by a heterogeneous catalyst and performed under mild conditions, the chemicals involved present relatively low toxicity and the by-product of the reaction is water. Furthermore, by using it as fuel additive, this chemical is reinserted in the biofuel production chain, constituting a mass and energy closed flow that complies with the Circular Economy Model and improves the carbon footprint and life cycle parameters. Economically, the by-product is valorized and capitalized on, once the selling price of crude glycerol is US\$210–390/ton (pre-pandemic scenario) and of solketal is around US\$3000/ton, clearly enhancing the industry profitability [14,24,25].

Over the years, especially from 2015 on, numerous technologies have been proposed for the synthesis of solketal, notably concerning the use of heterogeneous catalysts and continuous processes. This review aims to summarize these new catalysts and the Process Intensification strategies that have been investigated for solketal production. Moreover, it is aimed to deeply explore the kinetic models usually proposed and explain the reasons why different models better describe the reaction behavior for each type of catalyst. Furthermore, the works and the patents with proposed industrial plants for the production of this chemical are exposed, discussed, and compared to appoint solutions for the implementation of large-scale processes, a literature examination never reported before, to the authors' knowledge. This work also briefly discusses the biofuel and glycerol markets and the influence that the COVID-19 pandemic had and will have over it.

2. Biodiesel Production and Glycerol Market

The International Energy Agency (IEA) foresees a global energy demand growth of 9% annually between 2019 and 2030 if the policies in the field are kept unchanged, slightly slower than in the pre-pandemics scenario when the expected growth rate was 12% [26]. Nevertheless, it is imperative to invest in the use of renewable feedstocks, one of the most disseminated principles of Green Chemistry, to control global warming [3].

Considering the significant share on the oil demand of the transportation sector (almost 60%, as previously stated), COVID-19 mobility restrictions deeply affected the petroleum market, returning the oil consumption to the levels of 2012 [4]. The expected demand drop for gasoline, diesel, and jet fuel is 9%, 6%, and 26%, respectively, and numerous predictions foresee a smaller growth in the oil demand than expected prior to the COVID-19 crisis and an anticipation to reach the oil demand plateau, as can be seen in Figure 3 [4,26–28].

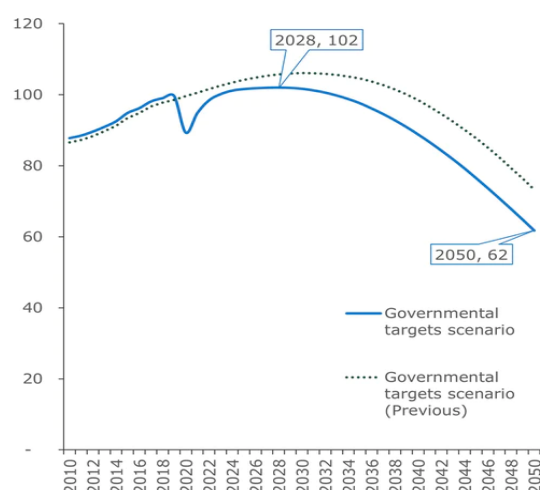


Figure 3. Global oil demand forecast (adapted; Source: Rystad Energy research and analysis) [29].

The new scenario also impacts biofuel consumption once they are blended with fossil fuels. Thus, a production contraction of 13% is expected, returning to the 2017 levels [27,30]. The pressure on the biofuel industry is not expected to diminish in the following years because of the lower oil prices caused by the demand reduction and the delay in the adoption of blending mandates to enable the fossil fuel industry to recover [4]. Nevertheless, the predictions for the biofuel industry are still optimistic, as the demand for biofuel is estimated to grow at a rate of 6.4% from 2020 to 2024, mainly explained by the increasing awareness of the environmental concerns and by the desire to avoid relying on the petroleum industry [31].

The environmental benefits of using biodiesel over traditional fossil fuels are noteworthy: it is renewable, biodegradable, and non-toxic; it reduces CO, hydrocarbon (HC), and nongaseous emissions; it produces no sulfur and no net CO₂ (on a life cycle basis); and usually, they have a higher cetane number and better lubricant properties, which is beneficial for the maintenance of the engine [11,32]. Furthermore, biodiesel plants are often local, which reduces transport costs, create jobs, and aid local economies [32]. Nonetheless, biodiesel also presents some disadvantages: it emits higher levels of nitrogen oxides; engines may perform worse in severe winter temperatures when compared to petrodiesel and require adaptations for the use of biodiesel; the energy content is lower than petrodiesel; and biodiesel can present considerable variations depending on which raw material is used to manufacture it. Part of these disadvantages, however, such as performance in cold weather and less energy content, is dampened with the use of fuel additives, such as solketal [32].

The decline in the CO₂ emissions caused by the slowdown of the economy and by the mobility restrictions is estimated to reach between 4.2 and 7.5%, a level that would enable us to stay below the 1.5 °C warming limit defined in the Paris Agreement [33]. Nearly half of the decrease in emissions is accounted for surface transportation. This new scenario is, at the same time, challenging, because it reveals the magnitude of the changes that would have to be established to control the emissions, and appealing, as it disclosed part of the path that governments, companies, and citizens would have to follow to control global warming [33].

The biofuel industry is divided into two main products: ethanol and biodiesel. The primary use of ethanol is as a blending agent, as it has the capacity of increasing fuel oxygen content, which enhances the combustion process and releases less CO and HC into the atmosphere [34]. Since ethanol is mainly employed as a blending agent for gasoline, mostly used in passengers' cars, its market has felt more the effects of the pandemic, with a demand reduction of 15% [30]. As for biodiesel, it is primarily used for rail transport of goods, a less-affected sector when compared to personal mobility, with an estimated contraction of 6%, less than half of the predicted contraction for ethanol [30]. The aviation

and marine sectors are the less developed in terms of using renewable sources of energy, responsible for less than 0.01% in 2018 [35]. The US production predictions for all types of biofuels is exhibited in Figure 4, in which the “other biofuels” category refers to the fuels of the aviation and marine sectors.

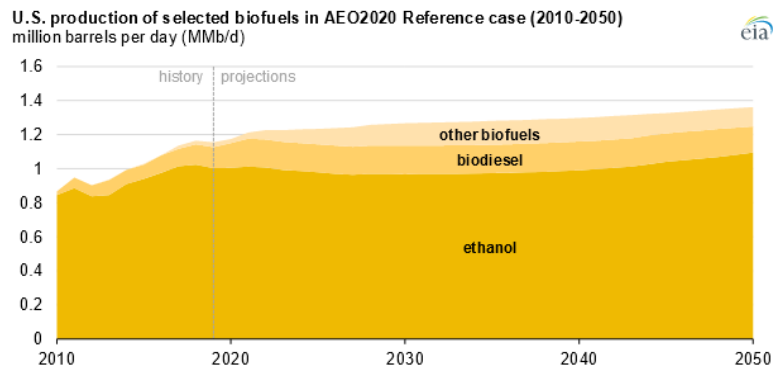


Figure 4. Predictions for the US production market of biofuels (Source: U.S. Energy Information Administration, Annual Energy Outlook 2020) [36].

The global glycerol supply is secure, as this chemical has been, for years, more produced than demanded. The reason why the market felt the effects of the COVID-19 crisis was not because there was a global lack of glycerol, but because of the logistics involved in delivering it to the countries where it was required, especially with the closure of the borders [14]. The main segments that exploit glycerol are personal care and chemical intermediates, the difference between them is that the first requires refined glycerol, and in many applications of the second, less purified glycerol can be used [13]. Due to its physicochemical properties (colorless, odorless, viscous, biodegradable, and non-toxic liquid) and three hydroxyl groups that can be easily replaced by other groups, glycerol is a reactive molecule frequently used as a platform chemical [15,37]. Some of the products derived from glycerol and their respective synthesis routes are exhibited in Figure 5.

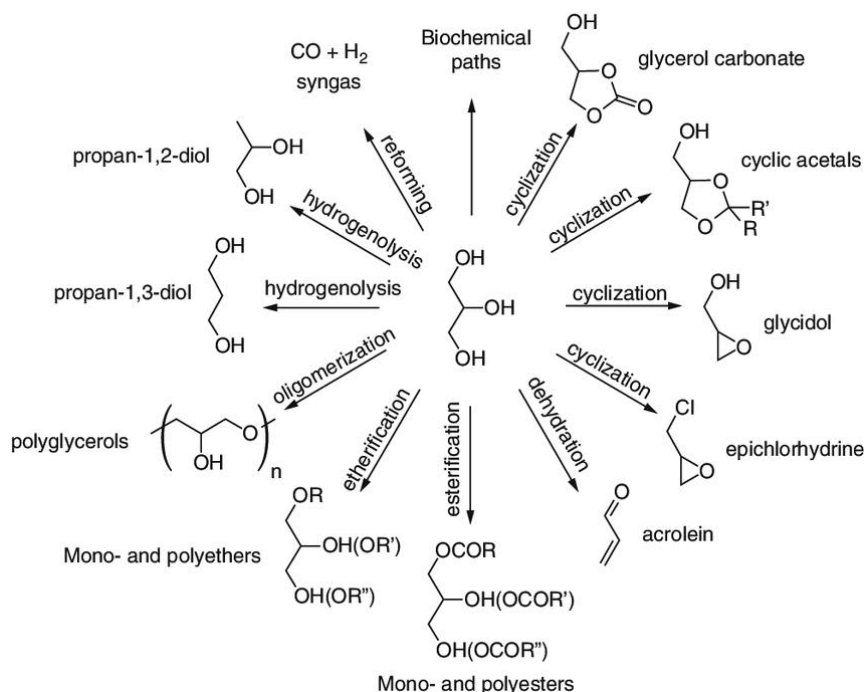


Figure 5. Glycerol valorization reactions (reprinted from Springer Nature, Juan A. Cecilia, Cristina García-Sancho, Pedro J. Maireles-Torres et al., Industrial Food Waste Valorization: A General Overview, 253–277, Copyright 2021, with permission from Elsevier) [38].

An intensive search has been occurring for glycerol valorization routes. The use of refined and crude glycerol has been reported for the production of biofuels, such as hydrogen, ethanol, and methanol [16,37,39]; fuel additives, such as glycerol ethers, esters, and formal (mix of solketal and acetal) [16,19,40]; and as a precursor for several other chemicals that can compete with petroleum products [15,18,37,39].

A noteworthy alternative for the valorization of glycerol is its conversion through biotechnological processes, such as fermentation and anaerobic digestion, because of their capacity to absorb crude glycerol. The literature is substantial in fermentation processes with different types of microorganisms that can generate hydrogen, methane, ethanol, and numerous other chemicals [16,20,39].

3. Solketal

3.1. Solketal Properties

Solketal (CAS 100–79–8) has low viscosity at room temperature (~11 cP) and freezing, boiling, and flash points of about $-26\text{ }^{\circ}\text{C}$, $190\text{ }^{\circ}\text{C}$, and $80\text{ }^{\circ}\text{C}$, respectively. The density is 1.06 g/cm^3 and the vapor pressure is 107.32 mmHg. It has low toxicity, slight odor, and it is non-irritant for humans; due to these characteristics and to the renewable origin, it is considered an environmentally friendly substance. It is completely miscible in water and in most organic compounds, which endows its solvent capacity [41,42].

3.2. Solketal Uses

Owing to the high compatibility and miscibility of solketal, the major application is as a solvent in resins, paints coatings, and cleaning agents, also because it can influence film-formation and drying time [41]. Its low toxicity and solubility in body fluids enable it to be used also as a solvent in medicaments (i.e., driving agent), and as a precursor of other chemicals of medical interest [43].

Nevertheless, the most-studied solketal application is as fuel additive. Malero et al. studied the benefits of adding oxygenated compounds in biodiesel and if the blends would be under the EN 14214 standard. Solketal has the positive effect of diminishing biodiesel viscosity and the negative effect of increasing fuel density, fundamental properties for the correct operation of the engine. Because of the amount of saturated fat in biodiesel, it presents poor cold properties, a problem proved to be aided by the addition of solketal in the fuel [44]. Giraldo et al. also attested the positive effect of using this ketal on diminishing the cloud point (the temperature at which wax crystals begin to form) and pour point (the temperature at which the fuel no longer flows) [32].

Another parameter analyzed was the flash point (“the lowest temperature at which a volatile substance evaporates to form an ignitable mixture with air in the presence of an igneous source,” according to Isac-García et al.), in which the addition of solketal decreased the properties’ value [44,45]. Conversely, Alptekin registered higher flash point of the biodiesel blend and higher brake specific fuel consumption (measure of the fuel efficiency—rate of fuel consumption divided by the power produced) due to the low energetic efficiency of solketal. Despite that, CO_2 , CO, and THC (total hydrocarbon) emissions were lower [46]. Mota et al. tested the addition of solketal in gasoline and concluded that it improved octane number and reduced gum formation, results confirmed by Ilgen et al. [19,47].

4. Solketal Synthesis

The ketalization reaction between acetone and glycerol is a process that adheres to the Green Chemistry principles because it is a condensation reaction, an example of atom economy, and it is a catalytic conversion [2,48]. According to Anastas and Warner, catalysis can improve energy efficiency, avoid the use of reactants in great excess, and enhance product selectivity [2]. The reaction produces two ketal species, one five-membered ring (solketal) and one six-membered ring (5-hydroxy-2,2-dimethyl-1,3-dioxane), with much higher selectivity for the first compound (99:1 molar ratio in recent studies), further explained by the mechanism of the reaction described in Section 4.2.2 [10,48]. The reaction

has a low equilibrium constant; therefore, it is thermodynamically limited. To obtain high conversion yields, it is necessary to shift the reaction in favor of product formation by either removing water or by adding acetone in excess [48].

4.1. History

The first solketal synthesis dates back to 1895 when it was obtained by the reaction of glycerol with acetone under acidic conditions (hydrogen chloride catalyst) in a batch reactor [49]. Years after that, the process was repeated varying the reaction medium (addition of anhydrous sodium sulphate) and the operating conditions, using different equipment, solvents (petroleum ether), and catalysts (p-toluenesulfonic acid-pTSA) [48,50]. At that time, the reaction with pTSA resulted in high conversion (87–90%); however, acetone was used in great excess and a long reaction time was necessary, which made the production in large scale unviable. New routes for solketal synthesis were deeply investigated only when the massive glycerol generated by the biofuel industry became a problem and society turned its attention to the Green Chemistry concepts [48].

In the following years, new approaches were proposed to obtain higher productivity in less time. Initially, the reaction was mainly made with homogeneous catalysts, as the pTSA was also used by Newman and Renoll back in 1945, and strong acids such as sulfuric, hydrochloric, hydrofluoric, and phosphoric acids [51]. Some authors registered good solketal yields (88 and 90% with pTSA as the catalyst). Despite that, the long reaction times were still a problem that rendered the process discouraging; moreover, acetone in excess was still required, and often a strategy to remove water from the reaction medium was applied, as the use of desiccants, entrainers, or molecular sieves [21,50,52]. Furthermore, the problems related to the use of homogenous catalysts are well known: difficult separation from the products, equipment corrosion, and serious concerns about effluent disposal [8,53]. The use of heterogeneous catalysts, as was later proposed, conforms to some of the Green Chemistry principles: less hazardous chemical synthesis, safer solvents, and auxiliary, inherently safer chemistry to accident prevention [2].

There has been an extensive study of alternative heterogeneous catalysts, with emphasis on zeolites, acidic resins, and montmorillonite [8,10,48,54]. The performance of several zeolites under different conditions revealed that beta zeolites can achieve the highest conversion rates [10,55–58]. The resins tested, mainly Amberlyst–15, 35, and 36, showed satisfactory activity as a catalyst in the conversion of glycerol to solketal. Moreover, they can be used as adsorbent, which may help to overcome the thermodynamic limitation of glycerol conversion when used in multifunctional reactors [10,55,58,59]. Since the hybrid solid must perform two tasks, catalysis and adsorption, besides considering the catalytic activity in the ketalization of glycerol with acetone, the adsorbent must have a strong affinity to water. Interesting results about the use of ion exchange resins in the synthesis of oxygenated compounds have been reported in several studies, especially because of their affinity with water [60].

Da Silva et al. compared the performance of the three types of heterogeneous catalysts mentioned above. The study was conducted in a batch reactor at 373 K and the authors stated that Amberlyst–15 achieved the highest conversion (95%) in only 15 min of reaction. Zeolite beta and Montmorillonite K–10 achieved conversions up to 90%, but only after 40 min. Other zeolites tested, namely ZSM5 and USY, presented poor catalytic activity due to the small pore diameter of the first that impair the reaction from occurring inside the pores and to the hydrophilic character of the second, responsible for retaining the water formed as by-product inside the pores and deactivating the acid sites [58]. From the three types of catalysts, despite the low cost of Montmorillonite K–10, zeolites and ion exchange resins have been preferred due to the higher conversion rates with the same catalyst load [58,59,61].

Nanda et al. stated that the catalyst acidity and acetone to glycerol molar ratio have a great influence on the reaction (kinetics and conversion), but the physical characteristics of the resin, such as pore volume and particle size, have a negligible effect on catalysts

activity [48]. Nonetheless, Faria et al. studied the effect of the particle size of Amberlyst-15 for a similar reactive system and concluded that the reaction occurs under diffusion-controlled regime; therefore, the internal mass transfer resistances effectively influence the catalytic activity, which makes particle size a relevant parameter [62].

The limited miscibility between acetone and glycerol is one of the obstacles of this reactive system [48]. To overcome this challenge, the most common solutions are using acetone in great excess and applying auxiliary solvents that enhance the miscibility of the system. For the solvent selection, Faria et al. developed a methodology to determine the most appropriate solvent for reactive-adsorptive processes considering properties that directly affect the system as miscibility, reactivity, adsorption, and kinetics. The method also evaluates environmental aspects as lethal dose (LD50), NFPA health hazard classification, octanol–water partition coefficient, and persistence time [63]. According to this methodology, solvents that are reactive to any of the reagents at the reaction operating conditions cannot be used and the interaction of the solvent with the catalyst is a key factor [10].

Different production processes were proposed for the synthesis of solketal in batch and continuous modes of operation (most of the studies about batch processes), especially in what concerns surpassing the thermodynamic limitation. This can be done by either removing one of the products from the reaction medium, typically water, or by adding acetone in excess. In batch processes, a major issue is reaction rate drop when the equilibrium is nearly reached, being necessary to stop the synthesis to collect and purify the products, then clean and refill the reactor to restart the process. Depending on the catalyst, some sort of regeneration may be required after each run [48].

When operating in batch, water removal can be accomplished by the use of entrainers, as previously mentioned [50]. The open literature reports the use of substances, such as benzene, petroleum ethers, and chloroform; however, the problem faced in this operation is the relatively low boiling point of acetone, which often was removed from the reaction medium even before the entrainers [48,64]. Another alternative explored was the use of desiccants with a role in catalysis as well (sodium sulphate and phosphorus pentoxide). Experiments confirmed the economic unfeasibility of this option due to the high solid consumption, together with some environmental concerns, due to the waste generation [48,64]. Furthermore, technologies as membrane sieves, membrane batch reactors, and modified batch operations were experimented and achieved good conversion yields, but in all cases, acetone in great excess was necessary [48]. Because of the already mentioned miscibility issues, Royon et al. tested the use of supercritical acetone to improve the contact of the reagents, yet the low conversion yields reached were discouraging [48,65].

The results reported for the continuous processes are encouraging, showing much higher efficiency, with solketal being produced in less time [48]. Among the numerous advantages of studying continuous processes, the one that needs to be highlighted is the possibility of scaling up the process to the industrial level [60]. The most explored technology for the large-scale production of basic chemicals and intermediates is the catalytic fixed-bed reactor; thus, this operation is the most applied in studies concerning the continuous ketalization of glycerol [66]. Most of the research on the field is recent and more details are provided in Section 4.3.

One of the first continuous operations proposed for the solketal synthesis was actually a semi-continuous counter-current distillation reaction, investigated by Clarkson et al., where glycerol was fed in batch and acetone in continuous, and the reaction was catalyzed by Amberlyst-DPT. Using acetone to glycerol molar ratio of 2, the authors registered a conversion value of 98%, but the temperature of the process had to be carefully monitored since providing much heat removes acetone from the reaction medium and low temperatures affect the conversion due to glycerol's miscibility [67]. The studies on continuous operations also considered the use of homogeneous catalysts, such as the synthesis in a Continuous Microwave Reactor proposed by Cablewski et al. with pTSA as catalyst (84% conversion yield) [68] and in a module of several continuous glass flow reactors connected in series with sulfuric acid as

catalyst (98–99% conversion with acetone to glycerol molar ratio between 8 and 14 and 69% with acetone: glycerol molar ratio of 4) [40]. The main disadvantages, however, are related to the use of the homogenous catalysts, as already mentioned.

4.2. Catalyst Study

4.2.1. Recent Advances on Catalysts

Most of the recent studies on solketal synthesis comprise the development of heterogeneous catalysts or homogeneous catalysts that can be recovered, as seen in Table 1, where the most recent studies on catalysts performance are summarized. Despite being a relatively simple reaction, the ketalization of glycerol with acetone faces the previously mentioned challenges: thermodynamic limitation and mass transfer resistance.

From the catalyst development point of view, to overcome the mass transfer resistance, it is preferable to avoid microporous catalysts [69]. As for the thermodynamic limitation, by exploiting the differences in affinity with the solid phase, water separation may be promoted, and the direct reaction can be fostered. This can be accomplished by using hybrid solids with higher affinity to water than to solketal, such as ion exchange resins; therefore, the by-product is adsorbed and the direct reaction is favored [11,70,71]. Furthermore, the catalyst must be water tolerant to preserve the active sites along the reaction and it must remain active after more than one cycle, ideally with large production capacity [58,72].

Table 1. Summary of the recent investigations (from 2015 on) on catalysts for the synthesis of solketal.

Author	Catalyst	Acidity (mmol/g _{cat})	Reaction Conditions	Results (%)	Reusability	Ref.
Homogeneous Catalysts						
Esposito, 2019	Iron (III) Complex FeCl ₃ (1–NO ₂) 0.05 mol% (glycerol)	N.A. ¹	G:A = 1:4 T = – t = 90 min	X _{gly} > 99% Sel ≥ 98.5%	N.A. ¹	[73]
Da Silva, 2020	Fe (NO ₃) ₃ · 9·H ₂ O 0.30 mol% ²	N.A. ¹	G:A = 1:20 T = 298 K t = 60 min	X _{gly} = 98% Sel = 97%	Four cycles without significant activity loss.	[74]
Zeolites						
Manjunathan, 2015	H–Beta 5 wt% (glycerol)	1.51	G:A = 1:2 T = 301 K t = 60 min	X _{gly} = 86% Sel = 98.5%	One cycle without significant activity loss.	[75]
Rossa, 2017	H–Beta 5 wt% (glycerol)	0.094	G:A = 1:4 T = 333 K t = 60 min	X _{gly} = 72.62% Sel = 98.3%	A 22% decrease on the activity after the first use. Activity remained until the fourth cycle.	[76]
Kowalska–Kus, 2017	MFI Beta MOR 1 wt% (glycerol)	0.369 0.388 0.55	G:A = 1:1 T = 343 K t = –	X _{gly} = 85, 85, 80% Sel < 99% Y _{solk} ≈ 80%	N.A. ¹	[69]
Talebian–Kiakalaieh, 2019	HR/Y–W ₂₀ 10 wt% (glycerol)	1.806	G:A = 1:10 T = 313 K t = 90 min	X _{gly} = 100% Sel = 97.9% Y _{solk} = 97.9%	Four cycles without significant activity loss.	[77]
Ion Exchange Resins						
Esteban, 2015	Lewatit GF101 0.5 wt% ²	5.11	G:A = 1:12 T = 313 K T = 240 min	X _{gly} = 96% Y _{solk} ≈ 80%	N.A. ¹	[70]
Cornejo, 2019	Purolite CT275 5 wt% (glycerol)	5.2	G:A = 1:12 T = 323 K T = 300 min	X _{gly} = 93%	N.A. ¹	[71]

Table 1. Cont.

Author	Catalyst	Acidity (mmol/g _{cat})	Reaction Conditions	Results (%)	Reusability	Ref.
Moreira, 2019	Amberlyst-35 0.5 wt% (reactants)	5.08	G:A = 1:2 T = 303 K T = 480 min Solv. = Ethanol	X _{gly} = 70%	N.A. ¹	[10]
Sulistyo, 2020	Indion 225 Na 5 wt% ²	N.A. ¹	G:A = 1:5 T = 328 K T = 180 min	X _{gly} = 31.9%	N.A. ¹	[78]
Clays						
Timofeeva, 2017	HNO ₃ Modified montmorillonite clay 5 wt% (glycerol)	0.015 ³	G:A = 1:2.5 T = 298 K T = 15 min Solv. = acetonitrile	X _{gly} = 94% Sel = 95.4%	Three cycles without significant activity loss.	[79]
Amri, 2019	HCl activated clay 5 w/v% (reactants)	0.0065 ³	G:A = 1:6 T = 298 K T = 60 min Solv. = Isopropanol	Y _{solk} = 69.3%	Significant activity loss in the second cycle.	[80]
Metal Oxides						
Zhang, 2015	M-NiAlPO ₄ 4 wt% (glycerol)	0.12	G:A = 1:8 T = 353 K T = 60 min	Sel = 75.1% Y _{solk} = 75.4%	Three cycles without significant activity loss. Activity decreased from the fourth cycle on.	[81]
Gadamsetti, 2015	MoPO/SBA-15 2.7 wt% (reactants)	≈ 1	G:A = 1:2 T = 301 K T = 60 min	X _{gly} = 100% Sel = 98%	A 30% activity loss after the first cycle. Activity remained until de fourth cycle (X _{gly} = 100, 70, 68, and 62%).	[82]
Rodrigues, 2016	1Nb:0.05Al 2.7 wt% (glycerol)	0.094	G:A = 1:4 T = 323 K T = 360 min	X _{gly} = 84% Sel = 98%	Four cycles without significant activity loss.	[83]

Table 1. Cont.

Author	Catalyst	Acidity (mmol/g _{cat})	Reaction Conditions	Results (%)	Reusability	Ref.
Ionic Liquid						
Gui, 2016	1-(4-sulfonylbutyl)triphenylphosphonium methanesulfonate 2.7 mol% (glycerol)	N.A. ¹	G:A = 1:15 T = 298 K T = 30 min	X _{gly} = 96% Sel = 98.5%	Four cycles without significant activity loss.	[84]
Ji, 2020	[P (C ₄ H ₉) ₃ C ₁₄ H ₂₉] [TsO] 5 wt% (glycerol)	N.A. ¹	G:A = 1:6 T = 303 K t = 30 min	Y _{solk} = 86%	Ten cycles without significant activity loss.	[85]
Sulfonated Carbon based						
Gonçalves, 2016	GC-1:2 3 wt% (glycerol)	3.8	G:A = 1:4 T = 298 K t = 240 min	X _{gly} = 82% Sel = 95%	A 10% activity loss after five cycles.	[86]
Fernández, 2019	Cel-215-2 M-20 h-S		G:A = 1:7		Stable for 60 h of operation. No information on the recycle.	[87]
	Glu-195-20 h-S 1 wt% (glycerol)	5.43 3.42	T = 298 K t = 120-240 min	Y _{solk} = 80 – 86% Y _{solk} = 80 – 86%		
Ballotin, 2020	BS _{9,2} 0.6 wt% ²	0.3	G:A = 1:10 T = 298 K t = 120 min	X _{gly} = 93% Sel = 98%	A 4% activity loss after four cycles.	[88]
Others						
Sandesh, 2015	Heteropoly acids (C ₃ H ₇) ₄ N ⁺ /PWA 3 wt% (reactants)	0.6	G:A = 1:6 T = 303 K t = 120 min	X _{gly} = 94% Sel = 98% Y _{solk} = 93%	A 5% activity loss after three cycles.	[89]
Li, 2019	Layered crystalline α-zirconium phosphate 5 wt% (glycerol)	1.3	G:A = 1:10 T = 323 K t = 180 min	X _{gly} = 85.7% Sel = 98.3%	Four cycles without significant activity loss. Activity decreased until the fifth cycle.	[90]

Table 1. Cont.

Author	Catalyst	Acidity (mmol/g _{cat})	Reaction Conditions	Results (%)	Reusability	Ref.
Vannucci, 2020	Sulfated zirconium oxide 0.3 wt% (glycerol)	0.09	G:A = 1:8 T = 313 K t = 280 min	X _{gly} ≈ 80%	A 16% activity loss after four cycles.	[91]
Sulistiyio, 2020	Basolite F300 1 wt% (glycerol)	N.A. ¹	G:A = 1:4 T = 323 K t = 60 min	X _{gly} ≈ 84.3%	N.A. ²	[92]
Da Silva, 2020	Tin (II) silicotungstate acid salt 0.01 mol% ²	1.3	G:A = 1:4 T = 298 K t = 120 min	X _{gly} ≈ 74% Sel > 98% Y _{solk} = 73%	“No decrease in the catalytic activity was found.”	[93]
Podolean, 2020	Germanosilicate zeolite 5 wt% (glycerol)	N.A. ¹	G:A = 1:5 T = 298 K t = 180 min	X _{gly} = 56% Sel = 98%	Six cycles without significant activity loss. Stable up to 12 h on stream.	[94]
Li, 2020	Zirconium organophosphonate 5 wt% ²	1.12	G:A = 1:10 T = 313 K t = 360 min	X _{gly} = 90.2% Sel = 98.5%	A 2.7% activity loss after five cycles. Stable up to 10 h on stream.	[95]
Hussein, 2020	Gallosilicate 10 mg	0.39	G:A = 1:4 T = 353 K t = 180 min	X _{gly} = 34% Sel > 95%	Seven cycles without significant activity loss. Stable up to 6 h on stream.	[96]
Vivian, 2021	Gallosilicate 3.2 wt% (glycerol)	N.A. ¹	G:A = 1:4 T = 323 K t = 60 min	X _{gly} = 43% Sel = 93%	Four cycles without significant activity loss.	[97]

¹ Not available. ² Not stated whether in relation to glycerol or to total reactants. ³ Bronsted Acidity.

Iron (III) complexes homogeneous catalysts were investigated recently due to their potential to be recovered and their low cost, desirable characteristics when considered on the industrial scale. Esposito et al. tested several types of iron (III) catalysts in an apparatus where water was removed by molecular sieves to shift the reaction equilibrium towards product formation and concluded that $\text{FeCl}_3(1\text{-NO}_2)$ had the better performance, achieving almost total glycerol conversion and 100% selectivity to solketal [73,98]. Da Silva et al. compared different transition metal salts and found the best result for $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, also converting almost all of the glycerol and achieving selectivity of 95%. Then, the authors compared the conversions of Brønsted acid catalysts (pTSA and H_2SO_4) and confirmed that the iron (III) salt is more efficient probably because besides polarizing acetone's carbonyl group, it releases H^+ ions in the reaction medium, therefore acting like Lewis and Brønsted acid simultaneously [74]. Another common conclusion of the articles is the high catalyst efficiency, once a small catalyst load leads to great conversion values [73,74].

Ionic Liquids (ILs), as iron (III) catalysts, combine the advantages of homo- and heterogeneous catalysts, although its major drawback is usually the high cost. Ji et al. avoided this problem by exploring the tributyl (tetradecyl)phosphonium p-toluenesulfonate (TPPT), an inexpensive IL. The researcher obtained high solketal yield (85.9%), also with a high reaction rate, because the reaction was not impaired by internal mass transfer resistance; however, he had to use excessive acetone, probably to diminish external mass transfer resistance. The results are in line with the ones obtained previously by Gui et al. ($X_{\text{gly}} = 96\%$) with 1-(4-sulfonylbutyl) triphenylphosphonium methanesulfonate. The second study used almost half of the catalyst load, but more than double the acetone to glycerol ratio. The ILs of both studies were recovered and used in several cycles without losing the catalytic activity, an important characteristic for the industrial application [84,85].

One of the main reasons that make zeolites so deeply studied is their versatility, once the acidity, pore size distribution, and crystallite size can be relatively easily manipulated under adequate treatment [99]. Nowadays, many researchers compare the performance of the modified zeolites (usually called Hierarchical—H—due to the presence of more than one type of pore) with their respective Parent (P) zeolites to assess the effect of the changes on the catalytic activity. Manjunathan et al. studied the effects of dealuminating, increasing crystallite size, and preparing copper ion exchange zeolites and concluded that the highest conversion (86%) was attained by H-Beta zeolite with enlarged pores, small crystallite size (low diffusion path length), and higher amount of strong acidic sites. The dealumination led to a decrease in strong acidic sites that reduced glycerol conversion [75]. The findings of Rossa et al., also with H-Beta, agree with this previous study. Furthermore, Rossa et al. attributed the activity reduction along with the number of recycles to the blockage of the acidic sites by the water molecules formed inside the pores, but not to the deactivation of the surface acidic sites, once the hydrophobicity of the zeolite impaired water to approach to the surface of the catalyst [76]. This statement is contrary to what Silva et al. reported in a similar study with the same catalyst, where it was affirmed that the hydrophobic zeolite environment expels off from the pores the water formed, preserving the acid sites, besides preventing water diffusion from the medium to the interior of the pores [99]. The hydrophobicity is related to the silicon to aluminum ratio, which is also related to the porosity and to the acidity of the catalyst, thus selecting the parent zeolites and the adequate treatment is a convoluted process [58,69]. Nonetheless, the good conversion achieved with modified zeolites, with reactions performed under mild conditions and with reasonable amounts of acetone makes the use of zeolites favorable for industrial application [69,75,76].

Talebian-Kiakalaieh et al. synthesized a NaY zeolite supported over heteropoly acid to enhance its acid strength and active sites. The zeolite went over a dealumination process to enlarge its pores and create the mesoporous structure, the downside is the consequent reduction in the total acidity. Nonetheless, 98% glycerol conversion and 96.6% selectivity were achieved, and the authors affirmed that the mesoporosity and the acidity are the main parameters that affect the catalytic activity and stability [77]. Sandesh et al. also explored the potential of heteropoly acids and reported the use of $(\text{C}_3\text{H}_7)_4\text{N}^+/\text{PWA}$ to achieved

94% glycerol conversion and 98% selectivity for solketal. These results are attributed to its acidity and to its pseudo liquid behavior: the polar reactants absorb into the polyanion space of the catalyst, contact the active sites, react, and then the products desorb [89].

Recently, studies comprise a variety of ion exchange resins, as this type of catalyst is particularly interesting for glycerol ketalization because of its affinity with water. From Table 1, one can conclude that the mass transfer hinders the use of this type of hybrid solid, once acetone in large excess is necessary to attain conversions as high as 90% when selected a solvent-free environment [70,71]. To overcome this issue, Moreira et al. opted for using a solvent to enhance the reactants miscibility and the result was promising, achieving conversions almost 20% higher than the industrial process used nowadays (i.e., 52.55% with pTSA), accordingly to Rossa et al. [10,76].

One of the main advantages that renders clays a relevant alternative for industrial application is their low cost. The latest studies focus on modifying its textural and acid properties to enhance its conversion and selectivity. Timofeeva et al. studied the modification of montmorillonite with nitric acid (HNO_3) and Amri et al. the modification of a natural clay with hydrochloric acid (HCl). Both systems used solvents (acetonitrile and isopropanol, respectively) in the reaction medium and mild conditions (273 K and ambient pressure). The first study presents better conversion values, 94%, with a lower catalyst loading, probably due to its higher density of strong acidic sites, together with the fact that it was more stable in terms of catalyst deactivation [79,80]. The mild conditions used, the results attained, and the catalyst cost makes the research on modified clays promising; however, further studies on the reaction kinetics must be performed.

The metal oxides' catalysis is similar to the zeolite's; therefore, the surface area, the size of the pores, and the strength of the acidic sites play major roles in the conversion and selectivity to solketal [83]. Zhang et al. investigated the effect of introducing a heteroatom in the structure of a metal oxide and concluded that Ni promoted the highest solketal yield (75.44%), a fact that he attributed to the larger surface area of M-NiAlPO₄, which increased the number of surface-exposed Ni atoms responsible for the stronger acidity of the catalyst [81]. Gadamssetti et al. and Rodrigues et al. found that molybdenum and niobium have high activity to glycerol conversion to solketal in similar systems, but the first presented better results because, besides the total conversion of glycerol, the reaction was performed under milder conditions [82,83]. There are numerous similar studies in the literature, many of them with low selectivity to solketal which were not included as inputs to Table 1 [100,101].

A noteworthy new green catalyst was proposed by Gonçalves et al., a carbon-based solid prevented from biodiesel waste acidified by sulfuric acid (H_2SO_4). The catalysts were prepared with different amounts of sulfuric acid and the one that performed better ($X_{\text{gly}} = 82\%$) was the GC-1:2 (i.e., 1:2 mol carbon-based material:acid), besides being more stable at higher temperatures (373 K). Doping the catalyst with higher sulfur concentrations does not make difference in its structural properties [86]. Similarly, Ballotin et al. produced a sulfonated catalyst based on bio-oil with amphiphilic characteristics: hydrophobic carbon matrix with hydrophilic oxygen and sulfonic surface groups. The system was kept under mild conditions, without solvent, and the catalyst was in emulsion. The conversion was up to 98% with a large excess of acetone [88]. The sulfonation strategy was also used by Vannucci et al.; however, the matrix was zirconium oxide. Despite achieving good conversion yields of 80%, the previous materials are more appealing environmentally because they are obtained from renewable sources and are more resistant to recycle [91].

The growing number of studies investigating alternative catalysts evidence the potential and the relevance of solketal on the market, but it also reveals how far the industrial process applied nowadays is from the optimum. Many research works disclose promising catalysts that attain high glycerol conversions and that can be recycled; however, almost none assess the viability of using them on larger than laboratory scale. Furthermore, only a few assess the impacts of the impurities of crude glycerol over the catalysts or suggest pre-treatments for this reactant. There is also a lack of thermodynamic and kinetic study

for several of the mentioned catalysts, fundamental data to deliberate whether the catalyst is appropriate for industrial application. Therefore, the development of new catalysts must be supported by data that disclose their capacity to be used on a large scale.

4.2.2. Kinetics and Mechanisms of Reaction

Solketal synthesis is a relatively simple reaction, with controlled potential hazards; therefore, it could be carried in less carefully designed reactors when compared to inflammable or explosive reactions. However, since it is also a limited reaction, to make it industrially viable, it is necessary to rely on kinetic and thermodynamic data to design efficient equipment. The most-cited kinetic models in the open literature are the Pseudo-homogeneous (PH), Langmuir-Hinshelwood-Hougen-Watson (LHHW), and Eley-Rideal (ER) models.

The simplest approach is the Pseudo-homogeneous (PH) model, based on Potential Laws and often referred to with this term. It considers a reversible reaction of the first order in each species with virtually no adsorption of the species on the catalyst; therefore, the reaction would occur exclusively in the fluid phase [10,70]. It is usually represented by the following expression:

$$\mathfrak{R} = k \left(C_{gly} C_{acetone} - \frac{C_{solketal} C_{water}}{K_{eq}} \right) \quad (1)$$

where C represents the concentration of each species, k the reaction kinetic constant, and K_{eq} the thermodynamic equilibrium constant.

In the Langmuir-Hinshelwood-Hougen-Watson (LHHW), the mechanism comprises three steps: in the first, there is the adsorption of acetone and glycerol on the catalyst surface; in the second, a bimolecular reaction of adjacent molecules occurs to form a short-lived hemiketal (rate-controlling step), followed by two reactions that originate solketal and water; finally, in the third step, both products desorb from the surface of the catalyst [10,70]. The usual equation is:

$$\mathfrak{R} = k \frac{C_{glycerol} C_{acetone} - \frac{C_{solketal} C_{water}}{K_{eq}}}{(1 + K_{water} C_{water})^2} \quad (2)$$

where K_{water} is the adsorption equilibrium constant for water. Equation (2) is a simplification of the actual rate law, as the adsorption of water is usually much stronger than the other compounds; therefore, these terms are neglected in the denominator [10,70].

The Eley-Rideal (ER) model considers that only one of the molecules adsorb into the catalyst surface, while the other reacts directly from the fluid phase. It is expressed as follows:

$$\mathfrak{R} = k \frac{C_{glycerol} C_{acetone} - \frac{C_{solketal} C_{water}}{K_{eq}}}{1 + K_{water} C_{water}} \quad (3)$$

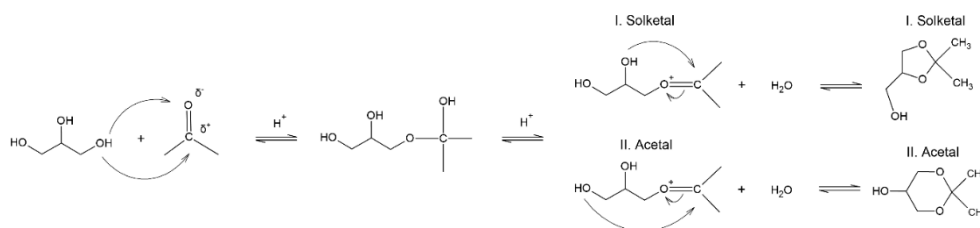
All the studies reviewed report the use of one of these three models. Table 2 summarizes the recent literature (from 2015 on) on kinetic studies for solketal synthesis over a range of catalysts.

Being mindful that the PH model does not consider the adsorption of molecules onto the catalyst surface, it is intuitive to think that reactions with homogeneous catalysts are well described by this model. Dmitriev et al. proposed a mechanism (Figure 6) for the reaction with sulfuric acid (strong Brønsted acid) as a catalyst comprising a nucleophilic addition of glycerol to the carbonyl group of acetone, forming a semiketal. Then, the ring closure takes place, forming a carbenium ion (limiting step). Finally, the H^+ ion is released and solketal is formed [102].

Table 2. Summary of the recent investigations on the kinetic study of solketal synthesis.

Author	Catalyst	E_A (kJ·mol ⁻¹)	Other Parameters ^{1,2,3,4,5}	Ref.
Pseudo-homogeneous (PH)				
Rossa, 2017	Zeolite H-Beta	44.77 ± 1.2	$E_{A-1} = 41.40 \pm 1.8$ kJ·mol ⁻¹ $K_{eq} = 0.5159$ (313 K)	[76]
Dmitriev, 2018	Sulfuric acid	87.1	$E_{A-1} = 101.67$ kJ·mol ⁻¹ $K_{eq} = 0.77$ (303 K)	[102]
Cornejo, 2019	Purolite® CT275	39.78 ± 0.34	$k = (4.800 \pm 0.030) \cdot 10^{-3}$ L ² mol ⁻¹ ·g _{cat} ⁻¹ ·min ⁻¹ (298 K) $\Delta H = -6.605 \pm 0.168$ kJ·mol ⁻¹	[71]
Amri, 2019	HCl activated clay	65.4	$E_{A-1} = 70.65$ kJ·mol ⁻¹ $K_{eq} = 0.3931$ (313 K)	[80]
Ji, 2020	Ionic Liquid [P(C ₄ H ₉) 3C ₁₄ H ₂₉][TsO]	28.2	$K_{eq} = 0.4703$ (298 K)	[85]
Vannucci, 2020	Sulfated zirconium oxide	88.1 ± 8.9	$k = 0.11516 \pm 0.0093$ mol·g _{cat} ⁻¹ ·min ⁻¹ $\Delta H = -11.6 \pm 1.1$ kJ·mol ⁻¹ $\Delta G = 4.0 \pm 0.1$ kJ·mol ⁻¹	[91]
Taddeo, 2021	Iron(III) Complex FeCl ₃ (1-NO ₂)	13	$E_{A-1} = 64$	[103]
Langmuir-Hinshelwood–Hougen–Watson (LHHW)				
Moreira, 2019	Sulphonic Ion Exchange Resin Amberlyst-35	69.0 ± 6.6	$k = 0.492 \pm 0.093$ mol·g _{cat} ⁻¹ ·s ⁻¹ $K_{water} = 14.4 \pm 3.1$ $\Delta H = -20.1 \pm 1.1$ kJ·mol ⁻¹ $\Delta G = 1.4 \pm 0.3$ kJ·mol ⁻¹	[10]
Sulistyo, 2020	Metal Organic Framework Basolite F300	15.7	$K_{eq} = 6.345$ (at 303 K) $K_{water} = 1.029$ $\Delta H = -29.7176$ kJ·mol ⁻¹ $\Delta G = -4.8675$ kJ·mol ⁻¹	[92]
Li, 2020	Cation Exchange Resin NKC-9	44.3	$E_{A-1} = 47.23$ kJ·mol ⁻¹ $K_{eq} = 0.9690$ (323 K) $K_{water} = 0.7511$	[104]
Eley–Rideal (ER)				
Esteban, 2015	Ion Exchange Resin Lewatit GF101	124.0 ± 12.9	$E_{A-1} = 127.3 \pm 12.6$ kJ·mol ⁻¹ $K_{eq} = 0.367879441$ $K_{water} = 128.0 \pm 21.4$	[70]
Sulistyo, 2020	Ion Exchange Resin Indion 225 Na	21.2	$K_{acetone} = 0.62$ $K_{solketal} = 0.03$	[78]

¹ E_{A-1} : reverse reaction activation energy. ² K_{eq} : equilibrium constant. ³ ΔH : enthalpy ⁴ ΔG : reaction Gibbs free energy. ⁵ K_i : adsorption equilibrium constant of species i .

**Figure 6.** Plausible mechanism of reaction catalyzed by sulfuric acid (based on [102]).

It is important to notice, however, that the mechanism proposed by Dmitriev et al. is unlikely to occur since the protonation of the oxygen from the carbonyl group, promoted by the ions of the acidic medium, is what impels the nucleophilic attack, similar to what is proposed by Nanda et al., described in Figure 7 [48].

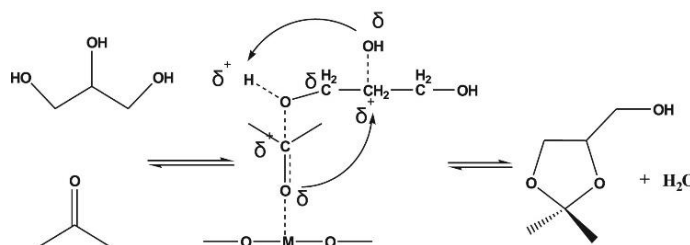


Figure 7. Mechanism of reaction of Lewis acid catalysts (reprinted from Renewable and Sustainable Energy Reviews, 56, Nanda, M.R.; Zhang, Y.; Yuan, Z.; Qin, W.; Ghaziaskar, H.S.; Xu, C., Catalytic conversion of glycerol for sustainable production of solketal as a fuel additive: A review, 1022–1031, Copyright 2021, with permission from Elsevier) [48].

With ionic liquid as the catalyst, Ji et al. obtained activation energy of $28.2 \text{ kJ}\cdot\text{mol}^{-1}$. The authors highlighted the high activity of this catalyst, tested for the first time in the study [85]. Taddeo et al. proposed a mechanism with two steps to describe the formation of solketal: first, the coordination of the carbonyl oxygen of acetone with the metal center, then the nucleophilic attack of a glycerol oxygen molecule to the carbonylic carbon of the coordinated acetone, followed by ring closure, forming solketal, and releasing of a molecule of water. This mechanism is generally accepted for solketal formation with Lewis acid catalysts (Figure 7). The authors reported the lowest activation energy of $13 \text{ kJ}\cdot\text{mol}^{-1}$ (Table 2), a result that may be supported by da Silva et al. in a study where they affirm that Lewis acid catalysts are more effective than Brønsted acid catalysts for this ketalization [74,103]. Nevertheless, it is notable that this value is very low for the ketalization reaction.

Despite using a sulphonic ion exchange resin Purolite® CT275, contrary to other authors, Cornejo et al. opted for using the PH model, which they named Low Range Adsorption in their study. After testing ER and LHHW, the authors affirmed the adsorption term was zero in the modelling studies, which justifies the choice for the model that does not consider adsorption of water. They reported smaller activation energy than other authors usually found for this type of catalyst, $39.78 \pm 0.34 \text{ kJ}\cdot\text{mol}^{-1}$ [71].

Vannucci et al. explained their choice for the PH model instead of the LHHW model: water does not affect the number of active sites of the sulfated zirconium oxide, because, in the presence of water, the Lewis acid sites (Zr (IV) species) are converted to Brønsted acid sites. Therefore, the LHHW equation can be simplified to the PH equation [91].

The comparison of the studies that used the LHHW model reveals that the reaction conducted by Sulistyó et al. with MOF Basolite F300 would be the easiest to carry, analyzing solely the activation energy estimated by the authors [92]. Basolite F300 is a highly active Lewis acid catalyst; therefore, the explanation for this low activation energy value (i.e., $15.7 \text{ kJ}\cdot\text{mol}^{-1}$) may also be explained by da Silva et al., who showed a higher activity of Lewis acid catalysts when compared to Brønsted acid catalysts [74]. Moreira et al. and Li et al. reached approximate values using different ion exchange resins as catalyst, 69.0 and $44.3 \text{ kJ}\cdot\text{mol}^{-1}$, and the latter found that the reverse reaction is less favorable than the forward reaction. As for K_{water} , it is notable that Amberlyst-35 has much more affinity to this compound [10,104].

Esteban et al. compared the PH, LHHW, and ER models and concluded that the latter provided the best fit, considering that the rate law is zero order for the reactants. However, the activation energy was high (over $120 \text{ kJ}\cdot\text{mol}^{-1}$) compared to the remainder estimations in Table 2 [70]. Conversely, using the same model but with a rate law of the first order for the reactants, Sulistyó et al. found a slightly lower value with Indion 225 Na [78]. As previously stated, this is probably due to the different characteristics of the catalysts.

The generally accepted mechanism for the solketal synthesis using Brønsted acid catalysts is shown in Figure 8.

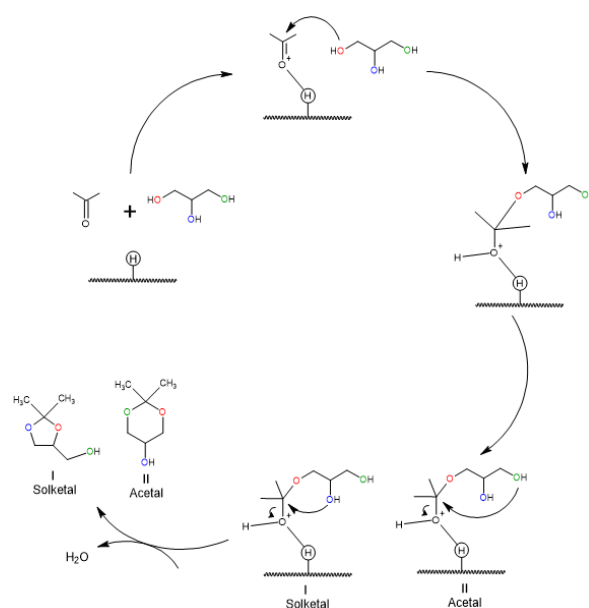


Figure 8. Mechanism of reaction of Brønsted acid catalysts.

The difference between the ketalization catalyzed by Brønsted and Lewis acids is that for the first, a short-lived hemiketal is formed and suffers a nucleophilic attack from one of the hydroxyl groups of glycerol to its central carbon, leading to the formation of solketal or the six-membered ring ketal (2,2-dimethyl-1,3-dioxan-5-ol). For Lewis catalysts, the metal site coordinates and activates the carbonyl group of acetone, followed by an attack from the glycerol alcoholic group to this carbonyl and a consequent bond forming between the carbonyl oxygen atom and the secondary carbon atom of glycerol. Finally, dehydration occurs to form the five-membered ring [48,91].

The products of the reaction are a five-membered ring (solketal) and a six-membered ring (5-hydroxy-2,2-dimethyl-1,3-dioxane), with much higher selectivity for the first compound [10,48]. This is probably due to the more likely acetone attack on the end-chain hydroxyl group than on the middle-chain hydroxyl group [10]. Additionally, the most energetically favorable product is the five-membered ring, because one of the methyl groups of the six-membered ring is in the axial position of the chair conformation, an unstable position due to the steric repulsion between the methyl group and the hydrogens bonded to the carbons of the ring [55].

4.3. Recent Advances on the Continuous Process

Among the continuous process strategies studied, the fixed-bed reactor stands-out owing to its relatively simple operation with mild conditions, the use of heterogeneous catalysts, and the possibility of coupling other processes (as downstream distillation separation), or unit operations (as adsorption or membrane permeation). Most of the recent studies still relied on ion exchange resins and hierarchical zeolites. The latest developments and tests on conventional continuous processes are summarized in Table 3.

Table 3. Summary of the recent investigations on the continuous synthesis of solketal.

Author	Catalyst	Catalyst Loading	Reaction Conditions	Results	Ref
Fixed Bed					
Dmitriev, 2016	KU-2-8 Cation-Exchange Resin	205 g	G:A = 1:5 T = 308 K P = N.A. Solv. = Ethanol Space time = 1.45 h	X _{gly} = 65%	[105]
Oliveira, 2016	Amberlyst-15	7 g	G:A = 1:20 T = 323 K P = 1 bar Solv. = DMF Space time = 0.2 h	X _{gly} = 96% Sel = 94%	[106]
Guidi, 2016	Amberlyst-36	0.09 g _{cat} /g _{gly}	G:A = 1:4 T = 298 K; 373 K P = 10 bar Solv. = Methanol WHSV ¹ = 2 h ⁻¹	X _{gly} = 95% Sel > 99%	[107]
	AlF ₃ ·3H ₂ O	0.067 g _{cat} /g _{gly}		X _{gly} = 80% Sel > 99%	
Konwar, 2018	Lignosulfonate-based macro/mesoporous solid protonic acids	0.5 g	G:A = 1:8 T = 313 K P = 1 bar Solv. = Ethanol Space time = 0.25 h	X _{gly} = 92% Sel = 99.5%	[108]
Cornejo, 2019	Purolite CT275	N.A. ²	G:A = -- T = 323 K P = High pressure ² Solvent Free Space time = --	X _{gly} = 91% Sel > 99.5%	[71]
Domínguez-Barroso, 2019	Monolithic structured carbon-based functionalized with sulfonic acid	0.345 g _{cat} /g _{gly}	G:A = 1:8 T = 330 K P = N.A. Solvent Free WHSV ¹ = 2.9 h ⁻¹	X _{gly} = 99% Sel > 99%	[109]
Kowalska-Kus, 2019	ZSM5(P)	0.083 g _{cat} /g _{gly}	G:A = 1:3 T = 323 K P = 1 bar Solv. = Methanol WHSV ¹ = 3.4 h ⁻¹	X _{gly} = 35%	[110]
	ZSM5(H)			X _{gly} = 90%	
	Beta(P)			X _{gly} = 90% Sel > 97%	
	Beta(H)			X _{gly} = 90% Sel > 97%	
	Mordenite(P)			X _{gly} = 86% Sel = 97%	
Mordenite(H)	X _{gly} = 86% Sel = 97%				
Fernández, 2019	Sulfonated hydrothermal carbons (SHTC)	0.00085 g _{cat} /g _{gly}	G:A = 1:9 T = 298 K P = 1 bar Solv. = Ethanol Space time = 1 min	Prod = 2048 mmol _{solketal} g _{catalyst} ⁻¹ h ⁻¹ ³	[87]
Moreira, 2019	Amberlyst-35	25 g	G:A = 1:2 T = 313 K P = N.A. Solv. = Ethanol Space time = 0.25 h	X _{gly} = 81%	[11]

Table 3. Cont.

Author	Catalyst	Catalyst Loading	Reaction Conditions	Results	Ref
Kowalska-Kus, 2020	ZSM5 (H)	0.083 g _{cat} /g _{gly}	G:A = 1:3 T = 323 K	X _{gly} = 85% Sel > 95%	[111]
	Beta(P)		P = 1 bar	X _{gly} = 69% Sel > 95%	
	USY(P)		Solv. = Methanol Space time = 5 min	X _{gly} = 85% Sel > 95%	
Capillary Microreactor					
Huang, 2020	ZSM5 Film	0.050 g _{cat} /g _{gly}	G:A = 1:2 T = 323 K P = N.A. Solvent Free Space time = 2.86 min	Y _{solk} = 30%	[112]
Zhang, 2020	ZSM5 Film	4.7 μm film thickness	G:A = 1:8 T = 323 K P = N.A. Solvent Free Space time = 2.86 min	X _{gly} = 62%	[113]
Continuously Stirred Tank Reactor					
Dmitriev, 2018	Sulfuric Acid	0.00066 g _{cat} /g _{gly}	G:A = 1:5 T = 308 K P = N.A. Solvent Free Space time = 1.73 h	X _{gly} = 68.4%	[102]

¹ Weight hourly space velocity. ² Not available. ³ Only result provided.

Nanda et al. and Moreira et al. proposed a similar system for the solketal synthesis in a fixed-bed reactor, both at 313 K, and an acetone to glycerol molar ratio of 2; the first, with the ion-exchange resin Amberlyst-36, achieved a conversion of 74%, and the latter, with Amberlyst-35, achieved a conversion of 81%. It is important to emphasize that these conversion values were obtained under transient operation [11,51]. Additionally, Nanda et al. achieved a conversion of 94% using optimized conditions and an acetone to glycerol molar ratio of 4, like Guidi et al., who used the same resin under similar reaction conditions [51,107]. Oliveira et al. also proposed an analogous system, but with the use of Amberlyst-15, and achieved excellent conversion, but the excessive acetone was a problem that could not be overcome [106].

Kowalska-Kuś et al. compared the catalytic performance of three zeolites (H-Beta, H-Mordenite, and H-ZSM5), also in a fixed-bed reactor, with methanol as the solvent in mild conditions, and found conversion about 88%, with an acetone to glycerol molar ratio of 3. The H-ZSM5 needed a desilication and acid pre-treatment to enlarge the pores and achieve an acceptable conversion. Moreover, the zeolites presented a loss in their activities over time [110]. The same researcher investigated the performance of zeolites with crude glycerol and achieved good conversion rates after just 1 h of reaction, but there was a fast deactivation of the catalysts and there was almost no conversion after 6 h [111].

Still on a fixed-bed reactor, but with a different type of packing, Domínguez-Barroso et al. built a carbon-based monolithic structure from spiral-wound laminated cellulose, constituting a structured packed reactor. The structure was impregnated with methanesulfonic acid solution with SO₃H to provide the catalyst acidic sites. The authors reported a complete glycerol conversion at WHSV = 2.9 h⁻¹ and no catalytic activity loss, which they attributed to the possible hydrophobic character of the monolithic structure [109].

Solketal synthesis was also tested in capillary microreactors with zeolite ZSM5 film, as proposed by Huang et al. and Zhang et al.; however, the results are not encouraging when considering scaling-up the process [112,113].

Most of the studies on the continuous production of solketal are still done on a very small scale, which inhibits its industrial application, required to solve the problem of the gut of glycerol. Furthermore, many continuous technologies still focus on catalyst performance rather than on intensifying the overall operation by handling the limitations inherent to this reaction.

Process Intensification

Process Intensification (PI) is one of the most promising approaches to attain environmental sustainability at the industrial level. According to Stankiewicz and Moulijn, by definition, PI is an engineering strategy for the development of new equipment and techniques expected to spawn in “substantially smaller, cleaner, safer and more energy-efficient technologies” [114,115]. It is divided into two main areas: process-intensifying equipment (new reactors, intensive heat, and mass transfer devices) and process-intensifying methods (integration of reaction and separation, heat exchange, or phase transition—multifunctional reactors—hybrid separations, and techniques using alternative energy sources—solar energy, ultrasound—and new process-control methods—intentional unsteady-state operation) [114].

For the solketal synthesis, there are a few registries in the literature about the use of such strategies to minimize the mass transfer and thermodynamic limitations, or even to couple biodiesel and ketal production, as listed in Table 4.

Table 4. Process intensification strategies for the synthesis of solketal.

Author	Catalyst	Catalyst Loading	Reaction Conditions	Results	Observations	Ref
Microwave Reactor						
Cablewski, 1994	pTSA	0.05 g_{cat}/g_{gly}	G:A = 1:13.5 T = 405 K P = 1 bar Space time = 1.2 h	$Y_{solk} = 84\%$	Continuous process.	[68]
Priya, 2017	Copper metal supported on Mordenite	0.43 g_{cat}/g_{gly}	G:A = 1:3 T = 373 K P = 1 bar Space time = 0.25 h	$X_{gly} = 95\%$ Sel > 98%	Three cycles without significant activity loss. Activity decreased slightly from the fourth cycle on.	[116]
Reactive Distillation						
Clarkson, 2001	Amberlyst DPT-1	0.05 g_{cat}/g_{gly}	G:A = 1:23.6 T = 343 K Reactive Stages = 10 Space time = 0.5 h/stage	$X_{gly} = 70\%$ Sel > 99%	“Only a slight loss of catalytic activity was observed.”	[67]
Li, 2020	Seepage packing internals filled with cation Exchange ResinNKC-9	NA	G:A = 1:3 T = 323 K P \approx 1 bar Reactive Stages = 20 ¹ Space time = 20 s Reflux ratio = 2.5	$X_{gly} = 85.9\%$		[104]
Membrane Reactor						
Roldán, 2009	K10 montmorillonite	0.1 g_{cat}/g_{gly}	G:A = 1:2 T = 333 K P = 1 bar Vaccum = 2 mbar	$X_{gly} > 90\%$	Vapor permeation.	[54]
Adsorptive Reactor						
Moreira, 2020	Amberlyst-35	25 g	G:A = 1:2 T = 313 K P = N.A. Solv. = Ethanol Space time = 0.25 h	$X_{gly} = 81\%$		[11]

Table 4. Cont.

Author	Catalyst	Catalyst Loading	Reaction Conditions	Results	Observations	Ref
Reactive coupling						
Eze, 2018	Amberlyst 70-SO ₃ H Amberlyst 70-SO ₃ H Amberlyst A26-OH	9 g	1 glycerol:4 acetone ² ; 30 methanol:1 triacetin:4 acetone ³ ; 6 methanol:1 triacetin:4 acetone ⁴ T = 323 K P = N.A. Sol = Methanol Space time = 0.5 h	X _{gly} = 80.6% ² X _{gly} = 48.5% ³ X _{gly} = 80.6% ⁴	Mesoscale oscillatory baffled reactors (meso-OBRs).	[117]
Al-Saadi, 2019	DBSA (<i>p</i> -Dodecylbenzene sulfonic acid)	0.5 mol	10 methanol: 1 triacetin: 7 acetone T = 323 K P = N.A. Space time = 8 h	Y _{solk} = 82%	Silica gel added as dehydrating agent to overcome the thermodynamic equilibrium limitation.	[118]

¹ Number of theoretical stages. ² Synthesis of only solketal. ³ Synthesis of biodiesel and solketal in one reactor. ⁴ Synthesis of biodiesel and solketal in two reactors.

Microwave irradiation has been explored as a heating intensification strategy in continuous and batch processes. According to the authors, heat transfer is more efficient because the microwave energy is transferred directly to the reaction molecules; moreover, since there is a faster response in comparison to conventional heating, the process is safer. Cablewski et al. produced solketal with pTSA and high excess of acetone in an apparatus that comprises a reaction coil inside a microwave cavity. The reactants were preheated and fed together with the catalyst continuously. Years later, Priya et al. tested a more environmentally friendly process in batch with several transition metals supported over Mordenite and stated that Cu-Mor performed better, which they attributed to the greater acidity of this catalyst [68,116].

Reactive distillation is an appealing PI strategy because it tackles the thermodynamic limitation by removing water from the reaction medium at the same time it integrates reaction and separation by distillation, eliminating the need for post-treatment processes.

Clarkson et al. proposed to carry the reaction on a multitray reactive distillation column with deep stages containing Amberlyst-DPT in suspension. They proposed a 15 stages column, with 10 reactive stages. Pre-heated glycerol would be fed at the top of the column so it could flow down through all the stages and acetone would be fed at the bottom so it could pass up the column agitating the resin and stripping out the water generated. Solketal would be purified in the bottom three stages and collected with a purity of more than 99% [67].

A similar system was proposed by Li et al., followed by optimization in Aspen Plus software and comparison with a novel equipment, the reactive dividing-wall column (RDWC). The experimental parameters and results are shown in Table 4. As for the optimization results considering the energy consumption (reboiler duty), it was found that the ideal scenario is nine theoretical reaction stages, five theoretical rectifying stages, and six stages in the stripping section (solketal purification), with a G:A molar feed ratio of 1:2–3 and a reflux ratio of 2.4. The comparison of the optimized traditional process with the RDWC resulted in a reduction in energy consumption by 13.6%; therefore, the authors address the RDWC as a PI strategy. This column promotes a more efficient purification of the solketal because it simulates a distillation column (II) alongside the reactive distillation column (I) inside the same unit, as seen in Figure 9 [104].

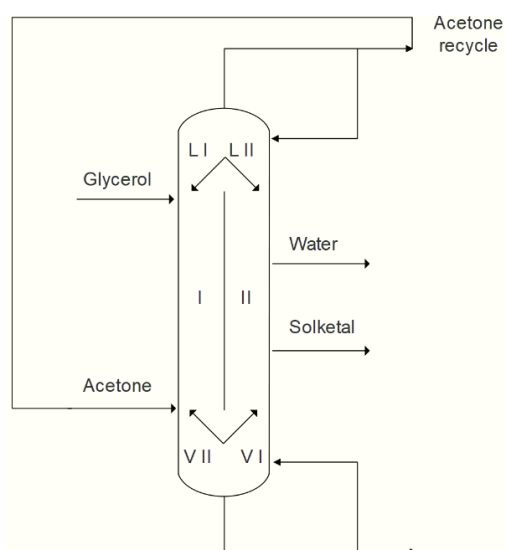


Figure 9. Diagram of the reactive dividing-wall column (based on [104]).

Membrane reactors also approach PI by diminishing the thermodynamic limitations, i.e., removing water from the reaction medium. Pervaporation and vapor permeation are already industrially well-established processes for water removal; the challenges faced with the use of these technologies for solketal synthesis are the catalyst activity and the mass transfer limitation. Roldán et al. avoided these problems by using K10 montmorillonite as catalyst dispersed in the reaction medium, thus handling catalysis and water removal separately, and preventing membrane contact with the liquid phase by promoting vapor permeation [54,119]. Qing et al., on the other hand, used a catalytically active membrane to react glycerol with cyclohexanone in a very similar system to solketal synthesis. The catalyst is constituted of three layers: the top being a catalytic layer, the middle a dense selective layer, and the bottom a porous support layer. The results were promising, and the behavior may be the same for the reaction of glycerol with acetone [119].

Moreira et al. also explored water removal as a strategy to conform to the PI guidelines. In a simple system already explained in Section 4.3., the authors exploit Amberlyst-35 affinity to water to shift the equilibrium toward the formation of solketal, transforming a simple fixed-bed reactor in an adsorptive reactor [11]. This was a remarkable study in comparison to other studies described Section 4.3 because many of the authors that employed fixed-bed columns mentioned the use of acetone as a stripping agent rather than the use of a separation strategy to favor glycerol conversion.

Eze et al. proposed an interesting system where the biodiesel preparation and glycerol conversion would be carried at the same time (reaction coupling) so that the valorization of glycerol would occur in situ. To do so, the reactions would occur in two oscillatory baffled reactors in series packed with Amberlyst-70. Methanol and triacetin would be fed to the first reactor and the products would follow to the second, where acetone would be fed. A glycerol conversion of 80.6% was achieved [117].

Similarly, Al-Saadi et al. proposed a reaction coupling in batch catalyzed by *p*-Dodecylbenzenesulfonic acid (DBSA). This catalyst is a homogeneous strong Brønsted acid chosen because of the surfactant-like nature of the catalyst, the high rate of reaction, and the low corrosivity compared to mineral acid catalysts, according to the authors. The authors compared the effect of feeding acetone at the beginning of the process with feeding when almost complete triacetin conversion would be reached and found that the second strategy is much more efficient, achieving 82% glycerol conversion against 39.5% achieved by the first strategy [118].

5. Solketal Production

The number of studies on solketal synthesis available in the open literature is substantial, with many new catalysts being explored. However, the number of studies on solketal production at an industrial scale grows at a much slower pace and the literature on large-scale methods for the production of solketal is rather scarce.

Solketal production plants are normally divided into Reaction Section and Separation Section. On a usual flowsheet, there is necessarily a reactor, the type depending on the catalyst and on the process, and a separation unit, usually a sequence of distillation columns. There can also be one or more mixers to homogenize the reactants and a heat exchanger to heat the compounds to the reaction temperature. Usually, a vessel is used to collect the products before they enter the separation section. The distillation columns are responsible for solketal purification and for the recovery of the eluent and unreacted reactants that can be recycled back to the column.

The proposed flowsheets found after an extensive bibliographic search are described with more details in Section 5.1. Then, the patented processes that could be industrially implemented are described in Section 5.2.

5.1. Processes

Zaharia et al. proposed an industrial flowsheet divided into two sections: in the reaction section, solketal production would be carried in a Continuously Stirred Tank Reactor (CSTR) and in the separation section, three distillation columns would purify the products and recycle the unconverted reactants. The proposed flowsheet is exhibited in Figure 10. The authors used the kinetic and thermodynamic data from Nanda et al. to estimate the mass and energy balances necessary to process a glycerol stream resultant from a biodiesel plant, aiming to reach a glycerol conversion of 76.5% with Amberlyst-35 as a catalyst [53]. The stream is considered pure glycerol and there is no information about its pre-treatment. The flowsheet was designed in Aspen Plus software. The reaction section comprises two mixers, one for each reactant, followed by a heat exchanger to assure the reactor's inlet stream is at 308 K and then the CSTR. The authors proposed that the catalyst could be retained inside the reactor by placing it in a basket or it could be later separated in a cyclone or in a decanting unit. The separation section consists of three distillation columns; in the first, acetone would be separated and recycled, in the second, water would be removed as distillate with 99.9% of purity, and in the third, solketal would be recovered as distillate also with high purity (99.8%) and the unreacted glycerol would be recycled [120].

In this study, an economic evaluation of the industrial plant is presented; however, the authors have not accounted for the reactants and catalyst costs. Moreover, they have not provided information about glycerol purification costs, which is a necessary step once Amberlyst-35 is deactivated when salts are present in crude glycerol. Thus, considering a payback period of five years, the cost to produce 3720 t of solketal/year was estimated at US\$128.50/ton, a much lower value than what was estimated in other studies and which can be considered unrealistic [10,25,120].

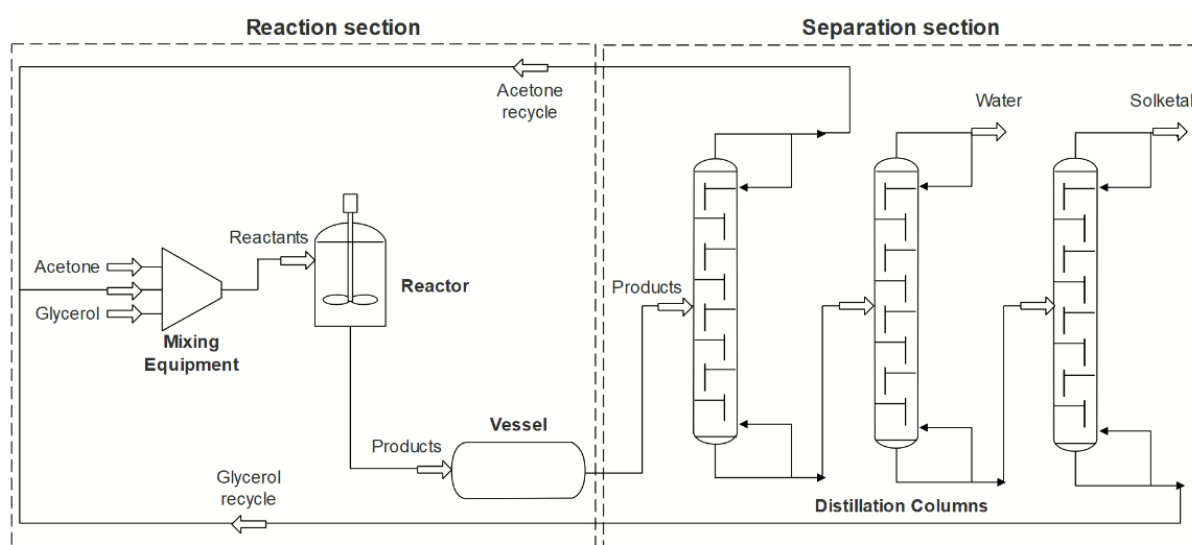


Figure 10. Flowsheet of the industrial solketal production plants proposed by Zaharia et al. (without vessel) and Dmitriev et al. (without mixing equipment) [120,121].

Dmitriev et al., one of the few authors that endorsed the use of traditional homogeneous catalysts, performed experiments with H_2SO_4 and a series of heterogeneous catalysts and concluded that H_2SO_4 was the most economically appealing for the industrial production of solketal. The authors proposed a similar flowsheet to Zaharia et al. comprising a CSTR, where the reactants and the catalyst would be directly fed, followed by a vessel to collect the reaction products and then three Rectification Columns with the same separation procedure suggested by Zaharia et al. The neutralization of H_2SO_4 would be carried by adding NaOH in the stream between the vessel and the first column. The authors highlighted that the most energetically demanding step would be acetone recovery because a large reflux ratio is necessary to assure the water content in the unconverted acetone is low [121].

After stating the many benefits of using heterogeneous catalysts, as higher productivity, no need to purify the products by neutralization, the consequent absence of wastewater due to not needing this step and the prevented corrosion of the apparatus, the authors counteracted the mentioned benefits. They stated that the low miscibility between acetone and glycerol impairs the reaction; thus, low conversion is attained and there is the need of adding a solvent in the reaction mixture. By using H_2SO_4 , there would be no need to use a solvent to enhance the reactants miscibility, which would diminish the equipment costs (no need for a pre-mixer before the reactor) and operational costs (no need to separate ethanol from the products). Additionally, the glycerol recycled back to the reactor has high impurity content, which would quickly deactivate the heterogeneous catalyst and greatly increase the operational costs. The study affirms the proposed flowsheet is simple, reliable, economically efficient and would reach a solketal yield near 100%. No economic evaluation data were provided [121].

Da Silva et al. proposed a similar flowsheet (Figure 11) but performed a more meticulous economic analysis. The flowsheet comprises two mixers, one for uniting fresh and recycled glycerol, followed by the second mixer where acetone, glycerol from the first mixer, and the Lewis catalyst (solid-supported SnF_2) are added. The second mixer's outlet stream is the inlet of the reactor (generic conversion reaction vessel operating at 298 K and 1 bar), which is expected to reach a glycerol conversion of 80%. The condensate stream with the products, unconverted reactants and catalyst follows to a filter to remove the catalyst. The filter's outlet stream is inserted in the first distillation column to separate the remainder of acetone and water, which is the most energetically demanding step. The bottom stream follows to the second distillation column to obtain high purity solketal (99.6%) and the unreacted glycerol that will be recycled back to the system. Acetone is not recycled [122].

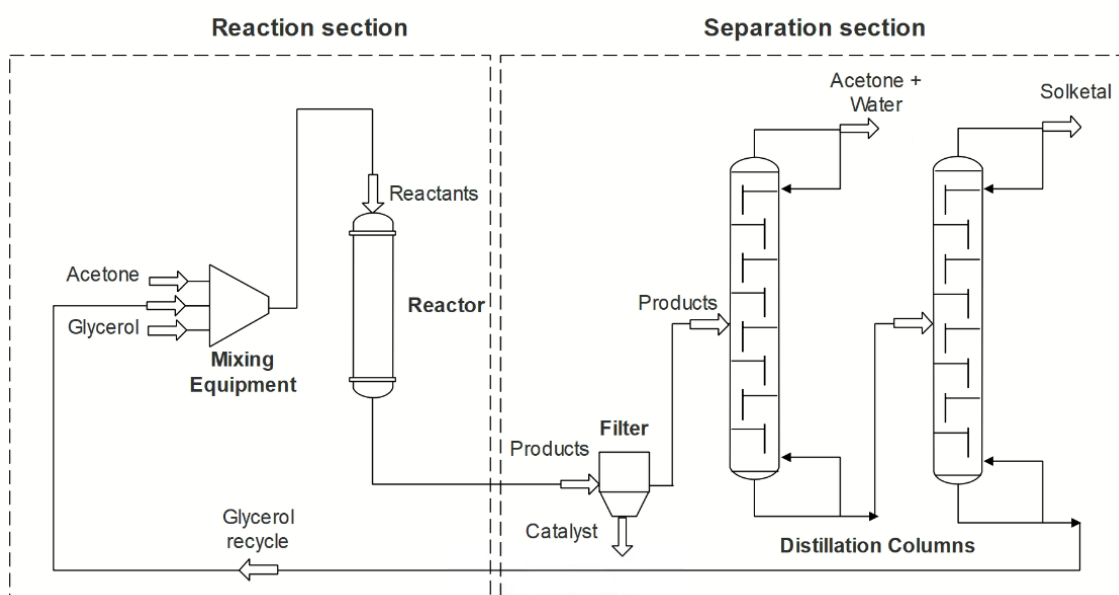


Figure 11. Flowsheet of the industrial solketal production plant proposed by da Silva et al. [122].

One of the most significant economic concerns of an industrial plant is the catalyst cost. SnF_2 is highly recoverable and recyclable; therefore, it was assumed to be replaced twice a year, accounting for only 0.005% of the annual operating costs. The other consumables account for nearly 17.50% of the operating costs. The total cost of producing solketal was US\$1229/ton; thus, when compared to the selling price stated by Al-Saadi et al. of US\$3000/ton, one can assume implementing a solketal production plant would be highly profitable [122,123].

Al-Saadi et al. simulated and compared the performance of three industrial flowsheets: (I) a one-stage solketal process plant operated at 8.5 wt% Sulphonic Acid-Functionalized Copolymer catalyst (ST-DVB- SO_3H), 323 K, and a glycerol to acetone molar ratio equal 1:6, obtaining 87% solketal yield; (II) a similar plant with a glycerol to acetone molar ratio equal to 1:12, obtaining 98% solketal yield; (III) and a two-stage plant with the first step operating at 8.5 wt% ST-DVB- SO_3H , 323 K, and a glycerol to acetone molar ratio equal to 1:10, obtaining 84% solketal yield in the first step, followed by removal of formed water, and another reaction under the same conditions to achieve 98% solketal yield. The two-stage plant (Figure 12) was found to be the most economically appealing, because the separation costs were lower than the one-stage processes, resulting, according to the authors, in a Net Present Value (NPV) 45.7% higher when compared with (I) and 0.57% higher when compared with (II); therefore, (III) will be described further [25].

The flowsheet comprises two mixers, the first to unite recycled and fresh acetone, followed by the second where glycerol is inserted. Then, the stream is heated in a heat exchanger up to the reaction temperature, which occurs in a plug-flow reactor packed with the catalyst. The first reaction's product stream is separated in a distillation column, the acetone recovered as distillate is reinserted in the second reactor and the bottom stream containing glycerol, water, and solketal is fed to a separation unit (not specified), where water is removed. The products stream is cooled in a heat exchanger prior to being fed to the second reactor, where almost all the remainder glycerol is converted. What follows is the second distillation column, where acetone is collected and recycled back to the system and solketal is the bottom product with a content of 98% solketal and 2% glycerol. According to the authors, the separation cost is lower because, in the second reaction, only 0.16% of the products' stream is water. The cost of producing solketal in the described plant, considering a capacity of 100,000 t/years and a 20-year lifetime, was estimated at \$2058/ton, well below the selling value reported by the authors US\$3000/ton [25].

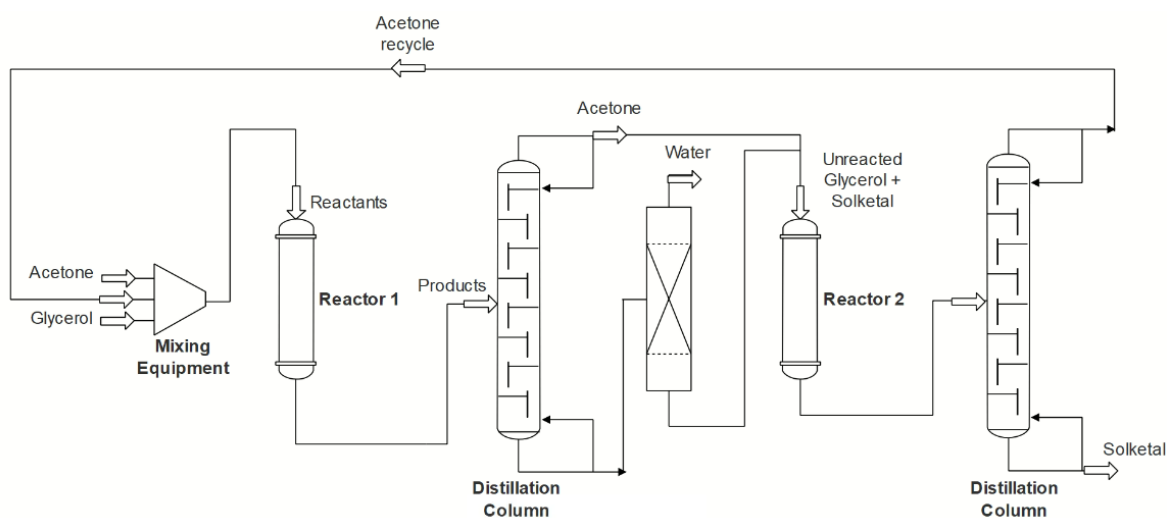


Figure 12. Flowsheet of the industrial solketal production plant proposed by Al-Saadi et al. [25].

An even deeper analysis was proposed by Chol et al. in a study that compared three scenarios comprising the treatment of crude glycerol and its valorization into solketal and glycerol carbonate. The authors concluded that the most economically advantageous flowsheet performs the valorization into both products, with glycerol equally divided for both routes [124].

The flowsheet (Figure 13) will be briefly described, with more focus on the solketal production steps. Initially, crude glycerol and methanol were fed into a mixer to lower glycerol viscosity so the mixture can undergo a saponification reaction using KOH in the first reactor. The resultant stream was fed to a second reactor to be acidified using HCl before being transferred to a gravity separator for sedimentation, where glycerol (bottom layer) was separated from free fatty acids (light liquids) and vapors. The resultant glycerol was cooled in a heat exchanger prior to solvent extraction using petroleum ether in a liquid-liquid extraction vessel. Petroleum ether was then recovered in a flash separator for reuse and glycerol was neutralized with KOH in another reactor. Then, the resultant glycerol was fed into a membrane separator, where impurities were separated from the glycerol, methanol, and water solution, and in turn, vaporized in a flash separator. Glycerol was cooled and split into two streams. Half of the glycerol was converted into glycerol carbonate by feeding it to a mixer, where it was combined with recovered methanol, then heated and inserted in the reactor with dibutyltin oxide (catalyst) and excess CO₂. The other half of glycerol, i.e., the stream leading to solketal production, was pressurized (12,000 kPa) before being fed into a conversion reactor with acetone and heterogeneous catalyst Amberlyst-15. The reaction was carried at 343 K for 1.5 h. The separation was promoted by a flash separator, where acetone with trace water was vaporized and recovered and the solketal stream was split into pure solketal and a recycle stream that was sent back to the reactor to improve conversion, since glycerol conversion is only 35% but can be enhanced with product recycle, according to the authors [124].

The economic analysis of implementing this industrial flowsheet is also promising, the cost of treating one ton of crude glycerol would be US\$5045, while the revenue cost would be US \$8036, resulting in a profit of almost US \$3000/ton of glycerol. The total investment cost was expected to be recovered within three years of operation; considering that the first three years would be dedicated to building the facility, complete recovery is made within six years. According to the authors, these margins are decent for a biodiesel plant and the increased profit indicate that it would be worth it investing in crude glycerol purification and valorization plant [124].

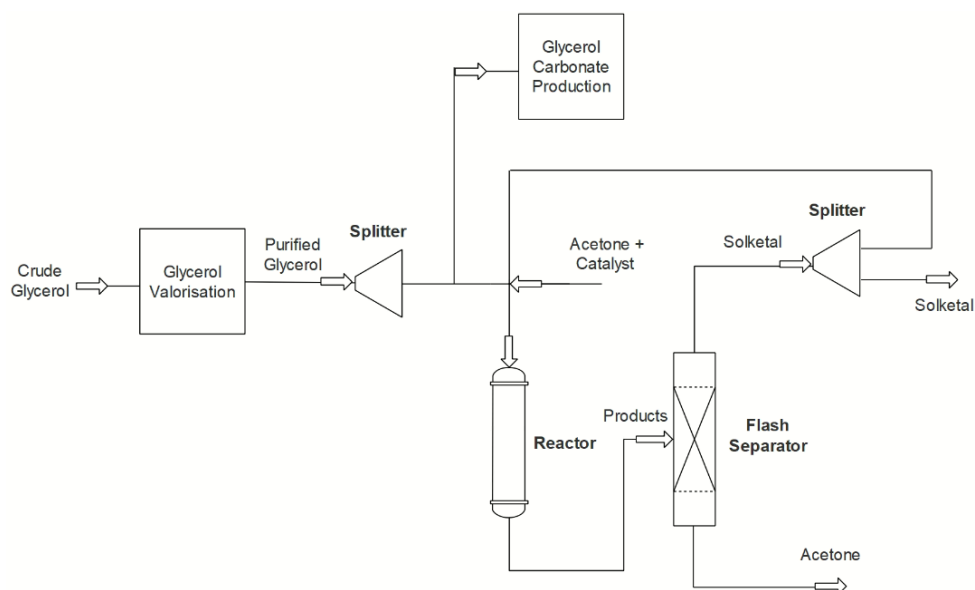


Figure 13. Flowsheet of the industrial solketal production plant with glycerol purification proposed by Chol et al. [124].

Another project proposed by Al-Saadi et al. is a plant where solketal would be valorized in situ simultaneously to biodiesel production. The authors studied an industrial facility operating at a molar ratio of 7:1:10 acetone:triolein:methanol, 323 K, 1 h of reaction, and 0.5 mol of DBSA (*p*-Dodecylbenzenesulfonic acid) catalyst to oil. The objective was to attain triolein conversion of 98% and glycerol conversion of 82% [118,123].

The flowsheet (Figure 14) comprises one mixer where the catalyst (DBSA) and the oil are fed, parallel to a mixer where fresh acetone, fresh methanol and the recycled streams are inserted. The reactants are preheated and delivered to the reactor (generic conversion reaction vessel). The outlet of the reactor flows to a separator to be divided in a light organic fraction (the 'biodiesel-rich phase') and the heavy more polar fraction (glycerol, catalyst, solketal, unreacted methanol, and water). Then, the light fraction follows to a distillation column to separate acetone in the top and biodiesel in the bottom. The heavy fraction is separated in methanol in the top and low purity solketal in the bottom, and this is the most energetically demanding step. No information is given about the water produced as by-product or the recovery of the catalyst; however, it is stated that methanol and acetone are recycled [123]. Therefore, one can conclude that the flowsheet is not a complete industrial plant, as there are some missing purification steps necessary to attest the process is techno-economically feasible.

Nonetheless, the economic analysis was performed considering an oil feed of 100,000 t/year and a plant lifetime of 20 years. Compared to an industrial process producing biodiesel alone, which would cost approximately US\$927.9/ton of biodiesel, coupling the production with solketal makes the industry more profitable and the cost of producing biodiesel is reduced to US\$824.8/ton [123].

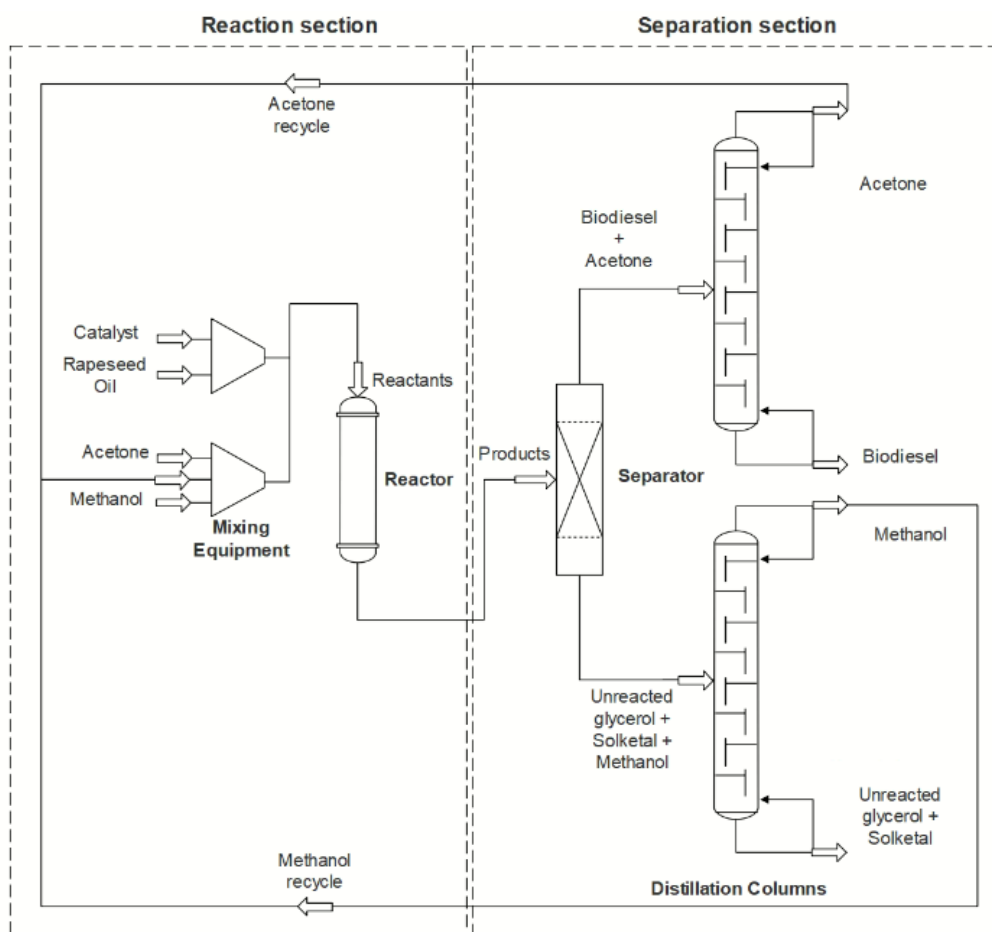


Figure 14. Flowsheet of the industrial solketal production plant with glycerol valorization in situ proposed by Al-Saadi et al. [123].

5.2. Patents

A meaningful indication of the industrial relevance of a process or new compound is the number and technological value of the patents developed by major market players. Patent research reveals the most recent advances in a specific field, the development of new technologies, and the relevant course of events concerning the subject searched. Additionally, it reveals the gaps in the literature that can be seen as an opportunity to develop and propose new processes. A good patent is comprehensive; therefore, the claims must be concise but not specific, which explains why most of the patents of solketal production generically mention the production of acetals and ketals [125].

Usually, when a technologically valuable innovative process or product is developed and patented, it is followed by several related patents with lower value when analyzed singly [126]. Concerning the use of solketal, it was initially deeply explored as solvent and plastifying agent in paints, films, and cleaning products; therefore, several products with different solketal contents were created and patented. Then, it was discovered to be useful as an antifreezing compound, which drove the research to its use as an additive for aviation fuel. Closely related, solketal use as fuel additive for surface transport was investigated due to the enhancement of fuel properties. Nowadays, the current trend of solketal application is its use as a biocompatible solvent in medicaments, since it is non-toxic for humans and it is soluble in body fluids. It is important to highlight that these research fields overlap each other; therefore, the described timeline is a draft of the trend of the new uses of this ketal based on the patents published.

Concerning solketal production, the initial innovation was to carry the process in batch reactors with homogeneous catalyst, which was followed by the study of the performance of different homogeneous catalysts. Then, heterogeneous catalysts were proposed, still in batch, soon upgraded by the use of fixed-bed reactors, which nowadays have been extensively studied. Few patents were published proposing alternative production processes.

A common conclusion to many of the authors that proposed and simulated industrial flowsheets for producing solketal is that the costliest step is the separation in distillation columns to remove the excess of acetone [25,121,122]. In view of that, the focus of several patents is intensifying the process to obtain purer products already in the outlet stream of the reactor or to use different separation technologies. The alternative technologies and the most promising patents (based on the possibility of scaling-up the process to the industrial level) proposed by some of the major players on the market are summarized in Table 5.

Table 5. Summary of the patents for solketal production.

First Inventor, Publication Date	Patent	Assignee	Catalyst	Reaction	Separation	Ref
Process Intensification Strategies/Non-conventional operation						
Bruchmann, 1999	US5917059A	BASF SE	Homo- or heterogeneous	Reaction vessel with continuous distillation	Not necessary	[64]
Boesch, 2003	US6528025B1	Roche Vitamins Inc.	Heterogeneous	Not specified	Pervaporation unit	[127]
Winkler, 2004	US20040024260A1	Evonik Degussa GmbH	Homo- or heterogeneous	Not specified	At least two-stage pervaporation or vapor permeation	[128]
Dubois, 2008	FR2906246A1	Arkema France SA	Heterogeneous catalyst	Simulated Moving Bed Reactor	Not specified	[129]
Dubois, 2008	FR2906807A1	Arkema France SA	Homo- or heterogeneous	Reactive extraction	Vacuum evaporation	[130]
Haiyu, 2018	CN107698552A	Guangzhou Yintian New Material Co., LTD	Heterogeneous catalyst	Membrane reactor	Not specified	[131]
Haiyu, 2018	CN107652263A	Guangzhou Yintian New Material Co., LTD	Heterogeneous catalyst	Reactive distillation on a shell and tube or column plate device	Not specified	[132]
Yujia, 2020	CN111253359A	China Petroleum & Chemical Corporation	Heterogeneous catalyst	Tank, fixed bed, moving bed, suspended bed, or slurry bed reactor with tin-titanium-silicon molecular sieve as catalyst	Not specified	[133]

Table 5. Cont.

First Inventor, Publication Date	Patent	Assignee	Catalyst	Reaction	Separation	Ref
Yujia, 2020	CN111253363A	China Petroleum & Chemical Corporation	Heterogeneous catalyst	Tank, fixed bed, moving bed, suspended bed, or slurry bed reactor with a mixture of a titanium silicalite and a tin silicalite molecular sieves	Not specified	[134]
Yujia, 2020	CN111253362A CN111253364A	China Petroleum & Chemical Corporation	Heterogeneous catalyst	Tank, fixed bed, moving bed, suspended bed, or slurry bed reactor with tin-silicon molecular sieve	Not specified	[135, 136]
Traditonal production methods						
Abe, 2004	JP2006273750A	Nippon Oil & Fat Co. Ltd.	Homogeneous catalyst	Reactor with stirring equipment	Distillation column(s)	[137]
Wimmer, 2011	EP2183238A1	Christof International Management GmbH	Heterogeneous catalyst	Plug-flow reactor	Distillation column(s)	[138]
Terrill, 2012	US20120330033A1	Eastman Chemical Co	Homogeneous catalyst	Reaction vessel	Distillation column(s)	[139]
Mastroianni, 2013	US20130178638A1	Rhodia Operations SAS	Homo- or heterogeneous	Reaction vessel or fixed-bed reactor	Distillation column(s)	[140]
Rodrigues, 2013	WO2013045967A1	Rhodia Poliamida e Especialidades Ltd.a	Homogeneous catalyst	Reaction vessel	Decantation, filtration, or centrifugation, followed by liquid-liquid extraction and distillation(s)	[141]
Rodrigues, 2014	US20140235878A1	Rhodia Poliamida e Especialidades Ltd.a	Homogeneous catalyst	Reaction vessel	Distillation column(s)	[142]
Terrill, 2014	US8829206B2	Eastman Chemical Co	Heterogeneous catalyst	Fixed-bed reactor	Distillation column(s)	[143]
Terrill, 2016	US9440944B2	Eastman Chemical Co	Heterogeneous catalyst	Fixed-bed reactor	Distillation column(s)	[144]
Varfolomeev, 2018	RU2625318C2	Institute of Biochemical Physics, Russian Academy of Sciences, in association with Company Tatneft	Homogeneous catalyst	Reaction vessel	Distillation column(s)	[145]

Evidencing the industrial applicability of reactive distillation as a PI strategy, BASF SA and Guangzhou Yintian New Material Co. proposed new methods for producing

acetals and ketals. BASF SA patented a process of reaction preferentially in batch with continuous distillation of the azeotrope acetone-water, ideally after the equilibrium was reached, and continuous addition of fresh acetone. The azeotrope would have to be treated by distillation or absorption with desiccants, but the products would be obtained with purities of 95 to 99.5%, high enough for many applications, according to the authors, so further downstream would be unnecessary [64]. Guangzhou Yintian New Material Co. proposed a similar process to the proposed by Clarkson et al. [67,132].

Aiming to replace the traditional and energy-intensive distillation, Roche Vitamins Inc. and Evonik Degussa presented pervaporation or vapor permeation for downstream separation. The basic flowsheet of the first comprises at least three modules of a reactor with acidic ion exchange resin, followed by a vessel with basic ion exchange resin and then the pervaporation unit. The vessel with the basic ion exchange resin is required for the formation of other acetals and ketals that have acidic compounds as by-product, but not for glycerol ketalization. As for the second, at least two modules of a reactor followed by the pervaporation unit, with more acetone fed between the first membrane module and the second reactor and, in the end, another module to remove unreacted acetone. The inventors have not specified the type of reactor in which the reaction would be carried; however, both stated the importance of installing a heat exchanger between the reaction and separation sections [127,128].

Arkema France SA proposed a promising PI strategy based on the separation of water by adsorption in a Simulated Moving Bed Reactor (SMBR). The equipment comprises a series of columns packed with a hybrid acid solid that perform catalysis and selective adsorption of one of the reaction products. There are two inlet streams where the reactants and the eluent are fed and two outlet streams, where the products are withdrawn. Since the thermodynamic equilibrium is surpassed, as water is continuously separated, high conversions are achieved. Nonetheless, a later treatment step is required to remove the eluent from the products, but much less energy-demanding than the traditional separation of unreacted acetone and water [129].

Arkema France SA also invented a reactive liquid-liquid extraction methodology to allow the continuous process and to enhance conversion. During the reaction, part of the fraction containing the cyclic acetal products would be continuously removed from the continuous phase, driving the reaction towards product formation [130].

Relying on another PI strategy, Guangzhou Yintian New Material Co. patented a process in which the reaction occurs in a membrane reactor. The reactants would be continuously fed in a shell and tube membrane reactor with a heterogeneous catalytic layer and the water formed as by-product would permeate in the membrane and be removed from the medium. The benefits of the process are high conversion due to overcoming the thermodynamic limitation, diminished or no need for products downstream separation, that the catalyst is easily recovered, and that wastewater production is avoided [131].

China Petroleum & Chemical Corporation approached the thermodynamic limitation problem by using tin or titanium (or both) silicalite molecular sieves in form of powder mixed with the heterogeneous catalyst. The invention stated that the preferred types of reactor used would be tank, fixed bed, moving bed, suspended bed, or slurry bed, but it was not specified whether a downstream separation would be required [133–136].

The other patents exhibited in Table 5 are more well-known processes of reaction in tank or fixed-bed reactors with homogeneous or heterogeneous catalyst and separation in distillation columns, with small particularities among them. These inventions are relevant to the industry once they are the most industrially accepted and supported by years of extensive know-how on the operation.

6. Conclusions and Future Prospects

Like almost all other sectors, the glycerol market was affected by the COVID-19 crisis mainly because many biodiesel plants have diminished production. Despite that, it was attested by the Independent Commodity Intelligence Services that glycerol supply is

safe, and the shortcut was caused by logistic problems. Considering that relying on such chemical as raw material is advantageous due to its low cost, favorable physicochemical properties, and the environmental benefits of valorizing it. The main issue of the glycerol side-stream produced by the biodiesel industry is its inability to be absorbed by the traditional markets for pharmaceuticals and cosmetic applications. Thankfully, new uses for glycerol were discovered and, along with that, new treatment methods and even processes capable of using crude glycerol. Among the many subproducts of glycerol, solketal stands out due to its versatility and promising improvements in fuels when used as additive. Moreover, solketal does not require high-purity reactant, depending on how it is proposed to be produced.

New alternative catalysts have been studied to allow the use of crude or less treated glycerol and to diminish the cost of producing solketal. Additionally, new processes have been proposed to overcome the thermodynamic limitation inherent to this ketalization reaction. Nevertheless, the literature on the use of crude glycerol is still scarce, as well as on alternative technologies that can be applied at large scale to keep up with the glycerol production rate. The Process Intensification strategies proposed in the open literature for the production of solketal present great potential to be applied at industrial scale and an immensurable prospective environmental benefit. Besides enabling the reaction to achieve higher conversion, these strategies can diminish or even eliminate the need for downstream treatment, appointed by some authors as the most energy demanding step (consequently the costliest) [25,121,122]. Therefore, the most promising strategies are the continuous processes that result in purer product streams, as the Simulated Moving Bed Reactor, thoroughly investigated for the production of other chemicals [146–151], Membrane Reactors [152–155], and other hybrid reaction–separation technologies.

Unfortunately, these Process Intensification strategies are developed at a slow pace, and only few patents propose these strategies at an industrial scale. Additionally, there is a gap in the literature on studies that evaluate the environmental impacts of producing solketal, a common point for all the process mentioned in the present review. Considering that this indicator has been gaining strength, it is relevant that the studies perform a Life Cycle Analysis and provide these type of data to evidence if the proposed technologies are competitive from both economic and environmental aspects. This proves the research on solketal still has plenty of room for investigation.

Funding: This work was financially supported by: Base Funding—UIDB/50020/2020 of the Associate Laboratory LSRE-LCM—funded by national funds through FCT/MCTES (PIDDAC); Project PTDC/QEQ-ERQ/2698/2014—POCI-01-0145-FEDER-016866—funded by FEDER funds through COMPETE2020—Programa Operacional Competitividade e Internacionalização (POCI); Isabella Corrêa gratefully thanks the FCT—Fundação para a Ciência e a Tecnologia for the Doctoral Grant (2020.07258.BD) through NORTE2020—Programa Operacional Regional do Norte from the FSE—Fundo Social Europeu of the UE.

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

References

1. Anastas, P.T.; Beach, E.S. Changing the course of chemistry. In *Green Chemistry Education*; American Chemical Society: Washington, DC, USA, 2009; Volume 1011, pp. 1–18. ISBN 9780841274471.
2. Anastas, P.; Eghbali, N. Green chemistry: Principles and practice. *Chem. Soc. Rev.* **2010**, *39*, 301–312. [CrossRef]
3. Anastas, P.T.; Warner, J.C. *Green Chemistry: Theory and Practice*; Oxford University Press: Oxford, UK; New York, NY, USA, 1998; ISBN 9780198506980.
4. *Global Energy Review 2020*; International Energy Agency: Paris, France, 2020.
5. *Tracking Transport 2020*; International Energy Agency: Paris, France, 2020.
6. Pousa, G.P.A.G.; Santos, A.L.F.; Suarez, P.A.Z. History and policy of biodiesel in Brazil. *Energy Policy* **2007**, *35*, 5393–5398. [CrossRef]
7. Rouhany, M.; Montgomery, H. Global biodiesel production: The state of the art and impact on climate change. In *Biodiesel: From Production to Combustion*; Tabatabaei, M., Aghbashlo, M., Eds.; Springer International Publishing: Cham, Switzerland, 2019; pp. 1–14. ISBN 978-3-030-00985-4.

8. Trifoi, A.R.; Agachi, P.Ş.; Pap, T. Glycerol acetals and ketals as possible diesel additives. A review of their synthesis protocols. *Renew. Sustain. Energy Rev.* **2016**, *62*, 804–814. [CrossRef]
9. Sheldon, R.A. The E factor 25 years on: The rise of green chemistry and sustainability. *Green Chem.* **2017**, *19*, 18–43. [CrossRef]
10. Moreira, M.N.; Faria, R.P.V.; Ribeiro, A.M.; Rodrigues, A.E. Solketal production from glycerol ketalization with acetone: Catalyst selection and thermodynamic and kinetic reaction study. *Ind. Eng. Chem. Res.* **2019**, *58*, 17746–17759. [CrossRef]
11. Moreira, M.N.; Corrêa, I.; Ribeiro, A.M.; Rodrigues, A.E.; Faria, R.P.V. Solketal production in a fixed bed adsorptive reactor through the ketalization of glycerol. *Ind. Eng. Chem. Res.* **2020**, *59*, 2805–2816. [CrossRef]
12. *Analysis and Forecasts of the Glycerine Market*; LMC: Oxford, UK, 2020.
13. *Glycerine Market Size, Share & COVID-19 Impact Analysis, By Grade (USP Grade, and Technical Grade), by Application (Personal Care, Food & Beverages, Pharmaceuticals, Polyether Polyols, Chemical Intermediate, Tobacco, and Others), and Regional Forecast 2020–2027*; Fortune Business Insights: Pune, Maharashtra, India, 2020.
14. *INSIGHT: Spot Glycerine Soars on Biodiesel Cut Fears*; Independent Commodity Intelligence Services: London, UK, 2020.
15. Pagliaro, M. Chapter 1—Properties, applications, history, and market. In *Glycerol*; Pagliaro, M., Ed.; Elsevier: Amsterdam, The Netherlands, 2017; pp. 1–21. ISBN 978-0-12-812205-1.
16. Nda-Umar, U.I.; Ramli, I.; Taufiq-Yap, Y.H.; Muhamad, E.N. An overview of recent research in the conversion of glycerol into biofuels, fuel additives and other bio-based chemicals. *Catalysts* **2018**, *9*, 15. [CrossRef]
17. *Glycerol Market Size, Share & Trends Analysis Report By Source (Biodiesel, Fatty Acids, Fatty Alcohols, Soap), by Type (Crude, Refined) By End Use (Food & Beverage, Pharmaceutical), By Region, And Segment Forecasts, 2020–2027*; Grand View Research: San Francisco, CA, USA, 2020.
18. Ciriminna, R.; Pina, C.D.; Rossi, M.; Pagliaro, M. Understanding the glycerol market. *Eur. J. Lipid Sci. Technol.* **2014**, *116*, 1432–1439. [CrossRef]
19. Mota, C.J.A.; da Silva, C.X.A.; Rosenbach, N.; Costa, J.; da Silva, F. Glycerin derivatives as fuel additives: The addition of glycerol/acetone ketal (solketal) in gasolines. *Energy Fuels* **2010**, *24*, 2733–2736. [CrossRef]
20. Anitha, M.; Kamarudin, S.K.; Kofli, N.T. The potential of glycerol as a value-added commodity. *Chem. Eng. J.* **2016**, *295*, 119–130. [CrossRef]
21. Mushrush, G.W.; Stalick, W.M.; Beal, E.J.; Basu, S.C.; Slone, J.E.; Cummings, J. The synthesis of acetals and ketals of the reduced sugar mannose as fuel system icing inhibitors. *Pet. Sci. Technol.* **1997**, *15*, 237–244. [CrossRef]
22. *Aviation: Benefits Beyond Borders*; Air Transport Action Group: Geneva, Switzerland, 2018.
23. Mushrush, G. Fuel System Icing Inhibitor and Deicing Composition. U.S. Patent No. US5705087, 6 January 1998.
24. Cornejo, A.; Barrio, I.; Campoy, M.; Lázaro, J.; Navarrete, B. Oxygenated fuel additives from glycerol valorization. Main production pathways and effects on fuel properties and engine performance: A critical review. *Renew. Sustain. Energy Rev.* **2017**, *79*, 1400–1413. [CrossRef]
25. Al-Saadi, L.S.; Eze, V.C.; Harvey, A.P. Techno-economic analysis of glycerol valorization via catalytic applications of sulphonic acid-functionalized copolymer beads. *Front. Chem.* **2020**, *7*. [CrossRef]
26. *World Energy Outlook 2020*; International Energy Agency: Paris, France, 2020.
27. *The Covid-19 Crisis and Clean Energy Progress*; International Energy Agency: Paris, France, 2020.
28. Browning, N. Factbox: Pandemic Brings Forward Predictions for Peak Oil Demand. Available online: <https://www.reuters.com/article/oil-demand/factbox-pandemic-brings-forward-predictions-for-peak-oil-demand-idUSL8N2IB5EG> (accessed on 15 January 2020).
29. Offshore. Analyst Revises Long-Term Oil Demand Forecast. Available online: <https://www.offshore-mag.com/production/article/14186589/analyst-revises-longterm-oil-demand-forecast> (accessed on 20 January 2021).
30. International Energy Agency. *Renewable Energy Market Update*; International Energy Agency: Paris, France, 2020.
31. *Liquid Biofuels Market Size, Share & Trends Analysis Report by Product (Biodiesel, Bioethanol), By Application (Transportation Fuel, Power Generation, Thermal Heating), and Segment Forecasts, 2020–2027*; Grand View Research: San Francisco, CA, USA, 2020.
32. Giraldo, S.Y.; Rios, L.A.; Suárez, N. Comparison of glycerol ketals, glycerol acetates and branched alcohol-derived fatty esters as cold-flow improvers for palm biodiesel. *Fuel* **2013**, *108*, 709–714. [CrossRef]
33. Le Quéré, C.; Jackson, R.B.; Jones, M.W.; Smith, A.J.P.; Abernethy, S.; Andrew, R.M.; De-Gol, A.J.; Willis, D.R.; Shan, Y.; Canadell, J.G.; et al. Temporary reduction in daily global CO₂ emissions during the COVID-19 forced confinement. *Nat. Clim. Chang.* **2020**, *10*, 647–653. [CrossRef]
34. Iodice, P.; Senatore, A.; Langella, G.; Amoresano, A. Advantages of ethanol–gasoline blends as fuel substitute for last generation Si engines. *Environ. Prog. Sustain. Energy* **2017**, *36*, 1173–1179. [CrossRef]
35. *Transport Biofuels*; International Energy Agency: Paris, France, 2020.
36. Shi, E.; Hanson, S.; EIA Projects U.S. Biofuel Production to Slowly Increase Through 2050. Available online: <https://www.eia.gov/todayinenergy/detail.php?id=43096> (accessed on 15 January 2020).
37. Tan, H.W.; Abdul Aziz, A.R.; Aroua, M.K. Glycerol production and its applications as a raw material: A review. *Renew. Sustain. Energy Rev.* **2013**, *27*, 118–127. [CrossRef]
38. Cecilia, J.A.; García Sancho, C.; Maireles-Torres, P.; Luque, R. Industrial food waste valorization: A general overview. In *Biorefinery*; Springer: Cham, Switzerland, 2019; pp. 253–277. ISBN 978-3-030-10960-8.
39. Garlapati, V.K.; Shankar, U.; Budhiraja, A. Bioconversion technologies of crude glycerol to value added industrial products. *Biotechnol. Rep.* **2016**, *9*, 9–14. [CrossRef] [PubMed]

40. Monbaliu, J.-C.M.; Winter, M.; Chevalier, B.; Schmidt, F.; Jiang, Y.; Hoogendoorn, R.; Kousemaker, M.A.; Stevens, C.V. Effective production of the biodiesel additive STBE by a continuous flow process. *Bioresour. Technol.* **2011**, *102*, 9304–9307. [CrossRef]
41. *Solketal: An EHS Friendly and Sustainable Solvent*; IMPAG Switzerland: Zürich, Switzerland, 2017.
42. National Center for Biotechnology Information. PubChem Compound Summary for CID 7528, Solketal. Available online: <https://pubchem.ncbi.nlm.nih.gov/compound/Solketal> (accessed on 13 December 2020).
43. Esteban, J.; García-Ochoa, F.; Ladero, M. Solventless synthesis of solketal with commercially available sulfonic acid based ion exchange resins and their catalytic performance. *Green Process. Synth.* **2017**, *6*, 79–89. [CrossRef]
44. Melero, J.A.; Vicente, G.; Morales, G.; Paniagua, M.; Bustamante, J. Oxygenated compounds derived from glycerol for biodiesel formulation: Influence on EN 14214 quality parameters. *Fuel* **2010**, *89*, 2011–2018. [CrossRef]
45. Isac-García, J.; Dobado, J.A.; Calvo-Flores, F.G.; Martínez-García, H. Chapter 5—Determining physical and spectroscopic properties. In *Experimental Organic Chemistry*; Isac-García, J., Dobado, J.A., Calvo-Flores, F.G., Martínez-García, H., Eds.; Academic Press: Cambridge, MA, USA, 2016; pp. 145–175. ISBN 978-0-12-803893-2.
46. Alptekin, E. Emission, injection and combustion characteristics of biodiesel and oxygenated fuel blends in a common rail diesel engine. *Energy* **2017**, *119*, 44–52. [CrossRef]
47. Ilgen, O.; Yerlikaya, S.; Akyurek, F.O. Synthesis of solketal from glycerol and acetone over amberlyst-46 to produce an oxygenated fuel additive. *Period. Polytech. Chem. Eng.* **2016**. [CrossRef]
48. Nanda, M.R.; Zhang, Y.; Yuan, Z.; Qin, W.; Ghaziaskar, H.S.; Xu, C. Catalytic conversion of glycerol for sustainable production of solketal as a fuel additive: A review. *Renew. Sustain. Energy Rev.* **2016**, *56*, 1022–1031. [CrossRef]
49. Fischer, E. Ueber die Verbindungen der Zucker mit den Alkoholen und Ketonen. *Ber. Dtsch. Chem. Ges.* **1895**, *28*, 1145–1167. [CrossRef]
50. Newman, M.S.; Renoll, M. Improved preparation of isopropylidene glycerol. *J. Am. Chem. Soc.* **1945**, *67*, 1621. [CrossRef]
51. Nanda, M.R.; Yuan, Z.; Qin, W.; Ghaziaskar, H.S.; Poirier, M.-A.; Xu, C. Catalytic conversion of glycerol to oxygenated fuel additive in a continuous flow reactor: Process optimization. *Fuel* **2014**, *128*, 113–119. [CrossRef]
52. García, E.; Laca, M.; Pérez, E.; Garrido, A.; Peinado, J. New class of acetal derived from glycerin as a biodiesel fuel component. *Energy Fuels* **2008**, *22*, 4274–4280. [CrossRef]
53. Nanda, M.R.; Yuan, Z.; Qin, W.; Ghaziaskar, H.S.; Poirier, M.-A.; Xu, C.C. Thermodynamic and kinetic studies of a catalytic process to convert glycerol into solketal as an oxygenated fuel additive. *Fuel* **2014**, *117*, 470–477. [CrossRef]
54. Roldán, L.; Mallada, R.; Fraile, J.M.; Mayoral, J.A.; Menéndez, M. Glycerol upgrading by ketalization in a zeolite membrane reactor. *Asia-Pac. J. Chem. Eng.* **2009**, *4*, 279–284. [CrossRef]
55. Maksimov, A.L.; Nekhaev, A.I.; Ramazanov, D.N.; Arinicheva, Y.A.; Dzyubenko, A.A.; Khadzhev, S.N. Preparation of high-octane oxygenate fuel components from plant-derived polyols. *Pet. Chem.* **2011**, *51*, 61–69. [CrossRef]
56. Serafim, H.; Fonseca, I.M.; Ramos, A.M.; Vital, J.; Castanheiro, J.E. Valorization of glycerol into fuel additives over zeolites as catalysts. *Chem. Eng. J.* **2011**, *178*, 291–296. [CrossRef]
57. Ruiz, V.R.; Velty, A.; Santos, L.L.; Leyva-Pérez, A.; Sabater, M.J.; Iborra, S.; Corma, A. Gold catalysts and solid catalysts for biomass transformations: Valorization of glycerol and glycerol–water mixtures through formation of cyclic acetals. *J. Catal.* **2010**, *271*, 351–357. [CrossRef]
58. Da Silva, C.X.A.; Gonçalves, V.L.C.; Mota, C.J.A. Water-tolerant zeolite catalyst for the acetalisation of glycerol. *Green Chem.* **2009**, *11*, 38–41. [CrossRef]
59. Deutsch, J.; Martin, A.; Lieske, H. Investigations on heterogeneously catalysed condensations of glycerol to cyclic acetals. *J. Catal.* **2007**, *245*, 428–435. [CrossRef]
60. Rodrigues, A.E.; Madeira, L.M.; Wu, Y.-J.; Faria, R. *Sorption Enhanced Reaction Processes*; World Scientific Publishing Co Pte Ltd.: Singapore, 2017; ISBN 978-1-78634-356-7.
61. De Torres, M.; Jiménez-osés, G.; Mayoral, J.A.; Pires, E.; de los Santos, M. Glycerol ketals: Synthesis and profits in biodiesel blends. *Fuel* **2012**, *94*, 614–616. [CrossRef]
62. Faria, R.P.V.; Pereira, C.S.M.; Silva, V.M.T.M.; Loureiro, J.M.; Rodrigues, A.E. Glycerol valorization as biofuel: Thermodynamic and kinetic study of the acetalization of glycerol with acetaldehyde. *Ind. Eng. Chem. Res.* **2013**, *52*, 1538–1547. [CrossRef]
63. Faria, R.P.V.; Pereira, C.S.M.; Silva, V.M.T.M.; Loureiro, J.M.; Rodrigues, A.E. Glycerol valorisation as biofuels: Selection of a suitable solvent for an innovative process for the synthesis of GEA. *Chem. Eng. J.* **2013**, *233*, 159–167. [CrossRef]
64. Bruchmann, B.; Haberle, K.; Gruner, H.; Hirn, M. Preparation of Cyclic Acetals or Ketals. U.S. Patent No. US5917059A, 29 June 1999.
65. Royon, D.; Locatelli, S.; Gonzo, E.E. Ketalization of glycerol to solketal in supercritical acetone. *J. Supercrit. Fluids* **2011**, *58*, 88–92. [CrossRef]
66. Eigenberger, G.; Ruppel, W. Catalytic fixed-Bed reactors. In *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-Vch: Weinheim, Germany, 2012; ISBN 9783527303854.
67. Clarkson, J.S.; Walker, A.J.; Wood, M.A. Continuous reactor technology for ketal formation: An improved synthesis of solketal. *Org. Process Res. Dev.* **2001**, *5*, 630–635. [CrossRef]
68. Cablewski, T.; Faux, A.F.; Strauss, C.R. Development and application of a continuous microwave reactor for organic synthesis. *J. Org. Chem.* **1994**, *59*, 3408–3412. [CrossRef]
69. Kowalska-Kus, J.; Held, A.; Frankowski, M.; Nowinska, K. Solketal formation from glycerol and acetone over hierarchical zeolites of different structure as catalysts. *J. Mol. Catal. A Chem.* **2017**, *426*, 205–212. [CrossRef]

70. Esteban, J.; Ladero, M.; García-Ochoa, F. Kinetic modelling of the solventless synthesis of solketal with a sulphonic ion exchange resin. *Chem. Eng. J.* **2015**, *269*, 194–202. [[CrossRef](#)]
71. Cornejo, A.; Campoy, M.; Barrio, I.; Navarrete, B.; Lázaro, J. Solketal production in a solvent-free continuous flow process: Scaling from laboratory to bench size. *React. Chem. Eng.* **2019**, *4*, 1803–1813. [[CrossRef](#)]
72. Zahid, I.; Ayoub, M.; Abdullah, B.B.; Nazir, M.H.; Ameen, M.; Zulqarnain; Mohd Yusoff, M.H.; Inayat, A.; Danish, M. Production of fuel additive solketal via catalytic conversion of biodiesel-derived glycerol. *Ind. Eng. Chem. Res.* **2020**, *59*, 20961–20978. [[CrossRef](#)]
73. Esposito, R.; Cucciolo, M.E.; D'Amora, A.; Di Guida, R.; Montagnaro, F.; Ruffo, F. Highly efficient iron(III) molecular catalysts for solketal production. *Fuel Process. Technol.* **2017**, *167*, 670–673. [[CrossRef](#)]
74. Da Silva, M.J.; Rodrigues, A.A.; Pinheiro, P.F. Solketal synthesis from glycerol and acetone in the presence of metal salts: A Lewis or Brønsted acid catalyzed reaction? *Fuel* **2020**, *276*, 118164. [[CrossRef](#)]
75. Manjunathan, P.; Maradur, S.P.; Halgeri, A.B.; Shanbhag, G.V. Room temperature synthesis of solketal from acetalization of glycerol with acetone: Effect of crystallite size and the role of acidity of beta zeolite. *J. Mol. Catal. A Chem.* **2015**, *396*, 47–54. [[CrossRef](#)]
76. Rossa, V.; Pessanha, Y.d.S.P.; Díaz, G.C.; Câmara, L.D.T.; Pergher, S.B.C.; Aranda, D.A.G. Reaction kinetic study of solketal production from glycerol ketalization with acetone. *Ind. Eng. Chem. Res.* **2017**, *56*, 479–488. [[CrossRef](#)]
77. Talebian-Kiakalaieh, A.; Tarighi, S. Hierarchical faujasite zeolite-supported heteropoly acid catalyst for acetalization of crude-glycerol to fuel additives. *J. Ind. Eng. Chem.* **2019**, *79*, 452–464. [[CrossRef](#)]
78. Sulisty, H.; Priadana, D.P.; Fitriandini, Y.W.; Ariyanto, T.; Azis, M.M. Utilization of glycerol by ketalization reactions with acetone to produce solketal using indion 225 Na as catalyst. *Int. J. Technol.* **2020**, *11*. [[CrossRef](#)]
79. Timofeeva, M.N.; Panchenko, V.N.; Krupskaya, V.V.; Gil, A.; Vicente, M.A. Effect of nitric acid modification of montmorillonite clay on synthesis of solketal from glycerol and acetone. *Catal. Commun.* **2017**, *90*, 65–69. [[CrossRef](#)]
80. Amri, S.; Gómez, J.; Balea, A.; Merayo, N.; Srasra, E.; Besbes, N.; Ladero, M. Green production of glycerol ketals with a clay-based heterogeneous acid catalyst. *Appl. Sci.* **2019**, *9*, 4488. [[CrossRef](#)]
81. Zhang, S.; Zhao, Z.; Ao, Y. Design of highly efficient Zn-, Cu-, Ni- and Co-promoted M-AlPO₄ solid acids: The acetalization of glycerol with acetone. *Appl. Catal. A* **2015**, *496*, 32–39. [[CrossRef](#)]
82. Gadamsetti, S.; Rajan, N.P.; Rao, G.S.; Chary, K.V. Acetalization of glycerol with acetone to bio fuel additives over supported molybdenum phosphate catalysts. *J. Mol. Catal. A Chem.* **2015**, *410*, 49–57. [[CrossRef](#)]
83. Rodrigues, R.; Mandelli, D.; Gonçalves, N.S.; Pescarmona, P.P.; Carvalho, W.A. Acetalization of acetone with glycerol catalyzed by niobium-aluminum mixed oxides synthesized by a sol-gel process. *J. Mol. Catal. A Chem.* **2016**, *422*, 122–130. [[CrossRef](#)]
84. Gui, Z.; Zahrtmann, N.; Saravanamurugan, S.; Reyer, I.; Qi, Z.; Bañares, M.A.; Riisager, A.; Garcia-Suarez, E.J. Brønsted Acid Ionic Liquids (BAILs) as efficient and recyclable catalysts in the conversion of glycerol to solketal at room temperature. *ChemistrySelect* **2016**, *1*, 5869–5873. [[CrossRef](#)]
85. Ji, Y.; Zhang, T.; Gui, X.; Shi, H.; Yun, Z. Solventless ketalization of glycerol to solketal with acetone over the ionic liquid [P(C₄H₉)₃C₁₄H₂₉][TsO]. *Chin. J. Chem. Eng.* **2020**, *28*, 158–164. [[CrossRef](#)]
86. Gonçalves, M.; Rodrigues, R.; Galhardo, T.S.; Carvalho, W.A. Highly selective acetalization of glycerol with acetone to solketal over acidic carbon-based catalysts from biodiesel waste. *Fuel* **2016**, *181*, 46–54. [[CrossRef](#)]
87. Fernández, P.; Fraile, J.M.; García-Bordejé, E.; Pires, E. Sulfonated hydrothermal carbons from cellulose and glucose as catalysts for glycerol ketalization. *Catalysts* **2019**, *9*, 804. [[CrossRef](#)]
88. Carvalho Ballotin, F.; da Silva, M.J.; Paula de Carvalho Teixeira, A.; Montero Lago, R. Amphiphilic acid carbon catalysts produced by bio-oil sulfonation for solvent-free glycerol ketalization. *Fuel* **2020**, *274*, 117799. [[CrossRef](#)]
89. Sandesh, S.; Halgeri, A.B.; Shanbhag, G.V. Utilization of renewable resources: Condensation of glycerol with acetone at room temperature catalyzed by organic-inorganic hybrid catalyst. *J. Mol. Catal. A Chem.* **2015**, *401*, 73–80. [[CrossRef](#)]
90. Li, X.; Jiang, Y.; Zhou, R.; Hou, Z. Layered α -zirconium phosphate: An efficient catalyst for the synthesis of solketal from glycerol. *Appl. Clay Sci.* **2019**, *174*, 120–126. [[CrossRef](#)]
91. Vannucci, J.A.; Nichio, N.N.; Pompeo, F. Solketal synthesis from ketalization of glycerol with acetone: A kinetic study over a sulfated zirconia catalyst. *Catal. Today* **2020**. [[CrossRef](#)]
92. Sulisty, H.; Perdana, I.; Pratiwi, F.T.; Hartati, I. Kinetics and thermodynamics studies of ketalization of glycerol and acetone in the presence of Basolite F300 as catalyst. *IOP Conf. Ser. Mater. Sci. Eng.* **2020**, *742*, 012007. [[CrossRef](#)]
93. Da Silva, M.J.; Teixeira, M.G.; Chaves, D.M.; Siqueira, L. An efficient process to synthesize solketal from glycerol over tin (II) silicotungstate catalyst. *Fuel* **2020**, *281*, 118724. [[CrossRef](#)]
94. Podolean, I.; Zhang, J.; Shamzhy, M.; Părvulescu, V.I.; Čejka, J. Solvent-free ketalization of polyols over germanosilicate zeolites: The role of the nature and strength of acid sites. *Catal. Sci. Technol.* **2020**, *10*, 8254–8264. [[CrossRef](#)]
95. Li, X.; Jiang, Y.; Zhou, R.; Hou, Z. Acetalization of glycerol with acetone over appropriately-hydrophobic zirconium organophosphonates. *Appl. Clay Sci.* **2020**, *189*, 105555. [[CrossRef](#)]
96. Hussein, H.; Vivian, A.; Fusaro, L.; Devillers, M.; Aprile, C. Synthesis of highly accessible gallosilicates via impregnation procedure: Enhanced catalytic performances in the conversion of glycerol into solketal. *ChemCatChem* **2020**, *12*, 5966–5976. [[CrossRef](#)]

97. Vivian, A.; Soumoy, L.; Fusaro, L.; Fiorilli, S.; Debecker, D.P.; Aprile, C. Surface-functionalized mesoporous gallosilicate catalysts for the efficient and sustainable upgrading of glycerol to solketal. *Green Chem.* **2021**, *23*, 354–366. [[CrossRef](#)]
98. Esposito, R.; Raucci, U.; Cucciolo, M.E.; Di Guida, R.; Scamardella, C.; Rega, N.; Ruffo, F. Iron(III) complexes for highly efficient and sustainable ketalization of glycerol: A combined experimental and theoretical study. *ACS Omega* **2019**, *4*, 688–698. [[CrossRef](#)]
99. Lee, D.-W.; Park, Y.-M.; Lee, K.-Y. Heterogeneous base catalysts for transesterification in biodiesel synthesis. *Catal. Surv. Asia* **2009**, *13*, 63–77. [[CrossRef](#)]
100. Gomes, I.S.; de Carvalho, D.C.; Oliveira, A.C.; Rodríguez-Castellón, E.; Tehuacanero-Cuapa, S.; Freire, P.T.C.; Filho, J.M.; Saraiva, G.D.; de Sousa, F.F.; Lang, R. On the reasons for deactivation of titanate nanotubes with metals catalysts in the acetalization of glycerol with acetone. *Chem. Eng. J.* **2018**, *334*, 1927–1942. [[CrossRef](#)]
101. Pinheiro, A.L.G.; do Carmo, J.V.C.; Carvalho, D.C.; Oliveira, A.C.; Rodríguez-Castellón, E.; Tehuacanero-Cuapa, S.; Otubo, L.; Lang, R. Bio-additive fuels from glycerol acetalization over metals-containing vanadium oxide nanotubes (MeVO_x-NT in which, Me = Ni, Co, or Pt). *Fuel Process. Technol.* **2019**, *184*, 45–56. [[CrossRef](#)]
102. Dmitriev, G.S.; Terekhov, A.V.; Zhanaveskin, L.N.; Maksimov, A.L.; Khadzhiev, S.N. Kinetics of the formation of solketal in the presence of sulfuric acid. *Kinet. Catal.* **2018**, *59*, 504–508. [[CrossRef](#)]
103. Taddeo, F.; Esposito, R.; Russo, V.; Di Serio, M. Kinetic modeling of solketal synthesis from glycerol and acetone catalyzed by an iron(III) complex. *Catalysts* **2021**, *11*, 83. [[CrossRef](#)]
104. Li, X.; Lai, J.; Cong, H.; Shu, C.; Zhao, R.; Wang, Y.; Li, H.; Gao, X. Toward sustainable and eco-efficient novel catalytic distillation process for production of solketal using seepage catalytic packing internal. *Catal. Today* **2020**. [[CrossRef](#)]
105. Dmitriev, G.S.; Terekhov, A.V.; Khadzhiev, S.N.; Zhanaveskin, L.N. Specific features of solketal synthesis on KU-2-8 cation-exchange resin. *Russ. J. Appl. Chem.* **2016**, *89*, 45–50. [[CrossRef](#)]
106. Oliveira, P.A.; Souza, R.O.M.A.; Mota, C.J.A. Atmospheric pressure continuous production of solketal from the acid-catalyzed reaction of glycerol with acetone. *J. Braz. Chem. Soc.* **2016**, *27*, 1832–1837. [[CrossRef](#)]
107. Guidi, S.; Noè, M.; Riello, P.; Perosa, A.; Selva, M. Towards a rational design of a continuous-flow method for the acetalization of crude glycerol: Scope and limitations of commercial amberlyst 36 and AlF₃·3H₂O as model catalysts. *Molecules* **2016**, *21*, 657. [[CrossRef](#)]
108. Konwar, L.J.; Samikannu, A.; Mäki-Arvela, P.; Boström, D.; Mikkola, J.-P. Lignosulfonate-based macro/mesoporous solid protonic acids for acetalization of glycerol to bio-additives. *Appl. Catal. B* **2018**, *220*, 314–323. [[CrossRef](#)]
109. Domínguez-Barroso, V.; Herrera, C.; Larrubia, M.Á.; González-Gil, R.; Cortés-Reyes, M.; Alemany, L.J. Continuous-flow process for glycerol conversion to solketal using a brønsted acid functionalized carbon-based catalyst. *Catalysts* **2019**, *9*, 609. [[CrossRef](#)]
110. Kowalska-Kuś, J.; Held, A.; Nowińska, K. Solketal formation in a continuous flow process over hierarchical zeolites. *ChemCatChem* **2020**, *12*, 510–519. [[CrossRef](#)]
111. Kowalska-Kuś, J.; Held, A.; Nowińska, K. A continuous-flow process for the acetalization of crude glycerol with acetone on zeolite catalysts. *Chem. Eng. J.* **2020**, *401*, 126143. [[CrossRef](#)]
112. Huang, X.; Zhang, G.; Zhang, L.; Zhang, Q. Continuous flow synthesis of a ZSM-5 film in capillary microchannel for efficient production of solketal. *ACS Omega* **2020**, *5*, 20784–20791. [[CrossRef](#)]
113. Zhang, G.; Zhang, L.; Wang, X.; Chen, A.; Zhang, Q. Microfluidic processing of HZSM-5 films in a capillary microreactor for the continuous acetalisation reaction of glycerol with acetone. *React. Chem. Eng.* **2020**, *5*, 539–546. [[CrossRef](#)]
114. Stankiewicz, A.; Moulijn, J.A. Process intensification: Transforming chemical engineering. *Chem. Eng. Prog.* **2000**, *96*, 22–33.
115. Stankiewicz, A.; Moulijn, J.A. Chapter 2—Process intensification—An overview. In *Process Intensification*, 2nd ed.; Reay, D., Ramshaw, C., Harvey, A., Eds.; Butterworth-Heinemann: Oxford, UK, 2008; pp. 21–45. ISBN 978-0-7506-8941-0.
116. Priya, S.S.; Selvakannan, P.R.; Chary, K.V.R.; Kantam, M.L.; Bhargava, S.K. Solvent-free microwave-assisted synthesis of solketal from glycerol using transition metal ions promoted mordenite solid acid catalysts. *Mol. Catal.* **2017**, *434*, 184–193. [[CrossRef](#)]
117. Eze, V.C.; Harvey, A.P. Continuous reactive coupling of glycerol and acetone—A strategy for triglyceride transesterification and in-situ valorisation of glycerol by-product. *Chem. Eng. J.* **2018**, *347*, 41–51. [[CrossRef](#)]
118. Al-Saadi, L.S.; Eze, V.C.; Harvey, A.P. A reactive coupling process for co-production of solketal and biodiesel. *Green Process. Synth.* **2019**, *8*, 516–524. [[CrossRef](#)]
119. Qing, W.; Chen, J.; Shi, X.; Wu, J.; Hu, J.; Zhang, W. Conversion enhancement for acetalization using a catalytically active membrane in a pervaporation membrane reactor. *Chem. Eng. J.* **2017**, *313*, 1396–1405. [[CrossRef](#)]
120. Zaharia, E.; Bildea, C.; Muntean, O. Design, economic evaluation and plantwide control of glycerol ketalization plant. *UPB Sci. Bull. Ser. B Chem. Mater. Sci.* **2015**, *77*, 41–52.
121. Dmitriev, G.S.; Terekhov, A.V.; Zhanaveskin, L.N.; Khadzhiev, S.N.; Zhanaveskin, K.L.; Maksimov, A.L. Choice of a catalyst and technological scheme for synthesis of solketal. *Russ. J. Appl. Chem.* **2017**, *89*, 1619–1624. [[CrossRef](#)]
122. Da Silva, M.J.; de Ávila Rodrigues, F.; Júlio, A.A. SnF₂-catalyzed glycerol ketalization: A friendly environmentally process to synthesize solketal at room temperature over on solid and reusable Lewis acid. *Chem. Eng. J.* **2017**, *307*, 828–835. [[CrossRef](#)]
123. Al-Saadi, L.S.; Eze, V.C.; Harvey, A.P. Techno-economic analysis of processes for biodiesel production with integrated co-production of higher added value products from glycerol. *Biofuels* **2020**, 1–8. [[CrossRef](#)]
124. Chol, C.G.; Dhabhai, R.; Dalai, A.K.; Reaney, M. Purification of crude glycerol derived from biodiesel production process: Experimental studies and techno-economic analyses. *Fuel Process. Technol.* **2018**, *178*, 78–87. [[CrossRef](#)]
125. Clarke, N.S. The basics of patent searching. *World Pat. Inf.* **2018**, *54*, S4–S10. [[CrossRef](#)]

126. Frietsch, R.; Schmoch, U.; Van Looy, B.; Walsh, J.P.; Devroede, R.; Du Plessis, M.; Jung, T.; Meng, Y.; Neuhäusler, P.; Peeters, B. *The Value and Indicator Function of Patents*; Studien zum Deutschen Innovations System: Berlin, Germany, 2010.
127. Boesch, V.; Herguiguera, J.R. Process of Manufacturing Equipment for Preparing Acetals and Ketals. U.S. Patent No. US 6528025 B1, 4 March 2003.
128. Winkler, H.; Poll, H.-G.; Neumann, M.; Koehler, G.; Bauer, F. Process for Preparing Acetals and Ketals with the Aid of Multistage Pervaporation or Vapor Permeation. U.S. Patent No. US20040024260A1, 5 February 2004.
129. Dubois, J.L. Synthesis of Cyclic Acetals by Reaction of Aldehyde and/or Ketone with a Polyol, in a Simulated Mobile bed Reactor Having Garnished Columns of Acidic Solid Bed Able to Selectively Adsorb the Reaction Products. French Patent No. FR2906246A1, 6 September 2008.
130. Dubois, J.L.; Iborra, C.S.; Corma, C.A.; Velty, A. Process for the Synthesis of Cyclic Acetals by Reactive Extraction of a Polyol in a Concentrated Solution. French Patent No. FR2906807A1, 2008. Available online: <https://patents.google.com/patent/US20100099894A1/en> (accessed on 11 March 2021).
131. Haiyu, Y.; Chunlong, H.; Peng, J.; Qingyan, C.; Liqing, X. A Kind of Method That Molecular Film Reactor Prepares Solketal. Chinese Patent No. CN107698552A, 16 February 2018.
132. Haiyu, Y.; Chunlong, H.; Peng, J.; Qingyan, C.; Liqing, X. Industrial Continuous Method for Preparing Solketal by Catalyst Distillation Device. Chinese Patent No. CN107652263A, 2 February 2018.
133. Yujia, L.; Changjiu, X.; Yamin, W.; Yongjia, Y.; Bin, Z.; Xinxin, P.; Min, L.; Yibin, L.; Xingtian, S. Method for Preparing Ketal Glycerine and/or Acetal Glycerine. Chinese Patent No. CN111253359A, 9 June 2020.
134. Yujia, L.; Yamin, W.; Changjiu, X.; Bin, Z.; Min, L.; Yibin, L.; Xingtian, S. Method for Preparing Ketal Glycerine and/or Acetal Glycerine. Chinese Patent No. CN111253363A, 9 June 2020.
135. Yujia, L.; Changjiu, X.; Xinxin, P.; Bin, Z.; Min, L.; Yibin, L.; Xingtian, S. Method for Preparing Ketal Glycerine and/or Acetal Glycerine. Chinese Patent No. CN111253362A, 9 June 2020.
136. Yujia, L.; Changjiu, X.; Yongjia, Y.; Bin, Z.; Xinxin, P.; Min, L.; Yibin, L.; Xingtian, S. Method for Preparing Ketal Glycerine and/or Acetal Glycerine by Catalyzing Glycerine. Chinese Patent No. CN111253364A, 9 June 2020.
137. Abe, T.; Kawakami, N. Method for Producing Dioxolane Compound. Japanese Patent No. JP2004059435A, 26 February 2004.
138. Wimmer, T.; Ertl, C.; Kalb, R. Process for Preparing Cyclic Glycerol Acetals or Cyclic Glycerol Ketals or Mixtures Thereof. European Patent No. EP2183238B1, 2 March 2011.
139. Terrill, D.L.; McMurray, B.D.; Billodeaux, D.R.; Little, J.L.; Howard, A.S. Production of Cyclic Acetals or Ketals Using Liquid-Phase Acid Catalysts. U.S. Patent No. US20120330033A1, 3 March 2012.
140. Mastroianni, S. Process for Producing Dioxolane. U.S. Patent No. US20130178638A, 13 July 2013.
141. Rodrigues, E.; Malheiro, A. Process for the Production of a Dioxolane Compound from Crude Glycerol Including a Liquid-Liquid Extraction Step. World Patent No. WO2013045967A1, 11 July 2013.
142. Rodrigues, E.; Malheiro, A. Process for the Production of a Dioxolane Compound from Crude Glycerol. U.S. Patent No. US20140235878A1, 8 September 2014.
143. Terrill, D.L.; McMurray, B.D.; Billodeaux, D.R.; Little, J.L.; Howard, A.S. Production of Cyclic Acetals or Ketals Using Solid Acid Catalysts. U.S. Patent No. US8829206B2, 9 September 2014.
144. Terrill, D.L.; McMurray, B.D.; Billodeaux, D.R.; Little, J.L.; Howard, A.S. Production of Cyclic Acetals or Ketals Using Solid Acid Catalysts. U.S. Patent No. US9440944B2, 13 September 2016.
145. Varfolomeev, S.D.; Makarov, G.G.; Volyeva, V.B.; Komissarova, N.L.; Malkova, A.V.; Ovsyannikova, M.N.; Koverzanova, E.V.; Usachev, S.V.; Aynullov, T.S.; Shamsullin, A.I.; et al. Method of Producing Solketal. Russian Patent No. RU2668987C1, 5 October 2018.
146. Constantino, D.S.M.; Faria, R.P.V.; Pereira, C.S.M.; Loureiro, J.M.; Rodrigues, A.E. Enhanced simulated moving bed reactor process for butyl acrylate synthesis: Process analysis and optimization. *Ind. Eng. Chem. Res.* **2016**, *55*, 10735–10743. [[CrossRef](#)]
147. Faria, R.P.V.; Pereira, C.S.M.; Silva, V.M.T.M.; Loureiro, J.M.; Rodrigues, A.E. Sorption enhanced reactive process for the synthesis of glycerol ethyl acetal. *Chem. Eng. J.* **2014**, *258*, 229–239. [[CrossRef](#)]
148. Pereira, C.S.M.; Gomes, P.S.; Gandi, G.K.; Silva, V.M.T.M.; Rodrigues, A.E. Multifunctional reactor for the synthesis of dimethylacetal. *Ind. Eng. Chem. Res.* **2008**, *47*, 3515–3524. [[CrossRef](#)]
149. Minceva, M.; Gomes, P.S.; Meshko, V.; Rodrigues, A.E. Simulated moving bed reactor for isomerization and separation of p-xylene. *Chem. Eng. J.* **2008**, *140*, 305–323. [[CrossRef](#)]
150. Ströhlein, G.; Mazzotti, M.; Morbidelli, M. Optimal operation of simulated-moving-bed reactors for nonlinear adsorption isotherms and equilibrium reactions. *Chem. Eng. Sci.* **2005**, *60*, 1525–1533. [[CrossRef](#)]
151. Kawase, M.; Suzuki, T.B.; Inoue, K.; Yoshimoto, K.; Hashimoto, K. Increased esterification conversion by application of the simulated moving-bed reactor. *Chem. Eng. Sci.* **1996**, *51*, 2971–2976. [[CrossRef](#)]
152. Dubé, M.A.; Tremblay, A.Y.; Liu, J. Biodiesel production using a membrane reactor. *Bioresour. Technol.* **2007**, *98*, 639–647. [[CrossRef](#)]
153. Itoh, N. A membrane reactor using palladium. *AIChE J.* **1987**, *33*, 1576–1578. [[CrossRef](#)]
154. De Falco, M.; Capocelli, M.; Giannattasio, A. Membrane reactor for one-step DME synthesis process: Industrial plant simulation and optimization. *J. CO₂ Util.* **2017**, *22*, 33–43. [[CrossRef](#)]
155. Deshayes, A.L.; Miró, E.E.; Horowitz, G.I. Xylene isomerization in a membrane reactor: Part II. Simulation of an industrial reactor. *Chem. Eng. J.* **2006**, *122*, 149–157. [[CrossRef](#)]