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# Thermochemical Conversion of Untreated and Pretreated Biomass for Efficient Production of Levoglucosenone and 5-Chloromethylfurfural in the Presence of an Acid Catalyst

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**Abstract:** Levoglucosenone (LGO) and 5-chloromethyl furfural (5-CMF) are two bio-based platform chemicals with applications in medicines, green solvents, fuels, and the polymer industry. This study demonstrates the one-step thermochemical conversion of raw and pretreated (delignified) biomass to highly-valuable two platform chemicals in a fluidized bed reactor. Hydrochloric acid gas is utilized to convert biomass thermochemically. The addition of hydrochloric acid gas facilitates the formation of LGO and CMF. Acid gas reacts with biomass to form 5-CMF, which acts as a catalyst to increase the concentration of LGO in the resulting bio-oil. The presence of higher cellulose content in delignified biomass significantly boosts the synthesis of both platform chemicals (LGO and CMF). GC-MS analysis was used to determine the chemical composition of bio-oil produced from thermal and thermochemical conversion of biomass. At 350 °C, the maximum concentration of LGO (27.70 mg/mL of bio-oil) was achieved, whereas at 400 °C, the highest concentration of CMF (19.24 mg/mL of bio-oil) was obtained from hardwood-delignified biomass. The findings suggest that 350 °C is the optimal temperature for producing LGO and 400 °C is optimal for producing CMF from delignified biomass. The secondary cracking process is accelerated by temperatures over 400 °C, resulting in a low concentration of the target platform chemicals. This work reveals the simultaneous generation of LGO and CMF, two high-value commercially relevant biobased compounds.

**Keywords:** biomass; levoglucosenone; furfural; 5-chloromethylfurfural; thermochemical conversion

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## 1. Introduction

Thermochemical conversion is a well-established technique that has the potential to develop biomass-derived high-value platform chemicals. The main building blocks of biomass—cellulose, hemicellulose, and lignin—affect the target platform chemicals and make a considerable difference in their properties individually [1]. Thermochemical conversion of biomass results in bio-oil, char, and gas. Bio-oil is a complex combination of oxygen and organic molecules such as esters, organic acids, ketones, furans, and anhydrosugars [2]. Significant advancements in the fractionation and analysis of bio-oil have been accomplished. However, due to the lack of selective biomass conversion and several chemical species in the complex bio-oil composition, the majority of research has prioritized qualitative analysis rather than focused quantitative analysis [3].

Because of this complexity of bio-oil composition, pretreatment can be an option to open up the biomass structure and select the sugar-based building block, for example, cellulose of biomass, to produce the platform chemicals [4]. Among biomass pretreatment, peracetic acid is a low-cost organic acid with its acidity and oxidation properties proving more successful for biomass delignification than other alkali pretreatments such as using NaOH. Oxidizing chemicals dissolve lignin, but hemicellulose and cellulose are only partially dissolved [1]. Peracetic acid pretreatment can remove 70–90% of lignin from biomass depending on the process condition. Combined pretreatment with peracetic acid and

NaOH enhanced cellulose digestibility by 98%. However, this research has concentrated on enzymatic digestibility to produce fermentable sugars [5,6]. The influence of reaction temperature on the generation of LGO and 5-CMF through thermochemical conversion of biomass in a fluidized bed reactor was examined in this work. Fluidized beds are often employed because they facilitate interaction between solid particles and fluid materials at the top of the bed [7]. Much research has been conducted to determine the feasibility of producing platform chemicals from cellulose, untreated, and pretreated biomass (e.g., LGO, furfural, levulinic acid, etc.) [8–11]. The literature discusses the pretreatment of biomass to remove lignin and hemicellulose prior to thermal conversion, which increases LGO production [11,12]. However, none of the literature examined the generation of platform chemicals in a fluidized bed reactor using peracetic acid (PAA)-treated delignified biomass. The literature discusses the pretreatment of biomass to remove lignin and hemicellulose before thermal conversion, which results in an increase in LGO production [9].

Additionally, the presence of lignin in biomass greatly decreases the output of target platform chemicals and produces certain undesirable compounds [13,14]. There is a significant information gap regarding the influence of delignification on the thermochemical conversion of biomass to specific platform chemicals such as LGO and CMF in the presence or absence of an acidic environment. LGO can be produced by dehydrating the oxygen-containing molecule levoglucosan (LGA), which is an anhydrosugar. Moreover, both LGA and LGO chemicals can be generated by biomass pyrolysis. However, these approaches result in limited yields of LGO when combined with other compounds. Due to the fact that LGO is a highly active chiral molecule at elevated temperatures, the undesirable byproducts reduce the selectivity of LGO formation during biomass conversion [15]. 5-(hydroxymethyl)furfural (HMF) and its derivatives have recently been promoted as promising platform molecules for acquiring access to various renewable chemical and materials applications. Unfortunately, HMF has only been made at pilot stages from fructose, and no scalable method for producing it from raw biomass has been documented yet [16]. The HMF analog CMF has recently been proposed as a potentially disruptive invention in the renewable chemical field [17,18]. Mascal group described a process for producing CMF from carbohydrates (such as glucose, sucrose, or cellulose) [19]. Szmant and Chundury investigated the effects of solvent type, HCl/substrate ratio, reaction temperature, reaction duration, surfactant type, and substrate on CMF yields in a thorough research [20]. Another study looked at converting soluble sugars (corn syrup) to CMF utilizing a continuous flow technique that can be pumped [21]. CMF is employed in pharmaceutical industries as an intermediate chemical building component in the manufacture of medicines [22]. CMF is also used to produce a popular synthetic insecticide which is known as phrothrin [23]. However, these two target chemicals (LGO and CMF) are currently produced from fossil-fuel-based petrochemicals through several catalytic oxidation and cyclization reactions.

This research aims to determine an efficient method for increasing the production of platform chemicals from delignified biomass. GC-MS analysis was used to determine the chemical composition of bio-oil produced from thermal and thermocatalytic conversion of delignified biomass. Calibration using a standard sample and the NIST library was used to determine the quantity and identity of the product. The temperature at which the platform chemicals reached their greatest concentration was deemed to be the optimal temperature. The discovered findings laid the groundwork for the large-scale operation of a continuous fluidized bed metallic reactor.

## 2. Materials and Methods

### 2.1. Furnace Calibration

The furnace was calibrated before the experiment to verify temperature consistency until 900 °C. From this calibration, the operating temperature was adjusted. This calibration demonstrates the precision of the furnace temperature across a broader range. Supplementary Figure S1 and Supplementary Table S1 show the temperature difference among the three external thermocouples and furnace built-in thermocouples.

### 2.2. Reactor, Flows, and Fluidization

This experiment used a vertical reactor made of quartz glass with 22 mm internal diameter and 820 mm height. A porous quartz plate (frit) was placed into the reactor from the bottom at a distance of 370 mm to support the bed material. Quartz is the popular choice of material since it is inert and can resist temperature up to at least 1100 °C. Figure 1 provides the schematic of the reactor along with its accessories. For better mixing in a fluidized bed reactor, the inert gas flow must be higher than the minimum fluidization velocity ($U_{mf}$) [7]. $N_2$ gas from the cylinder was passed through a rotameter and then to the glass column through a one-way valve. The reactor was observed visually to check the movement of the bed. The sand was used as the bed material because of its excellent heat distribution properties. The main working principle of a fluidized bed reactor is flowing an inert gas for moving the bed materials at a suitable velocity [24]. Cold flow studies were conducted to determine the lowest fluidization velocity with additional verification using the Wen and Yu correlation [7].

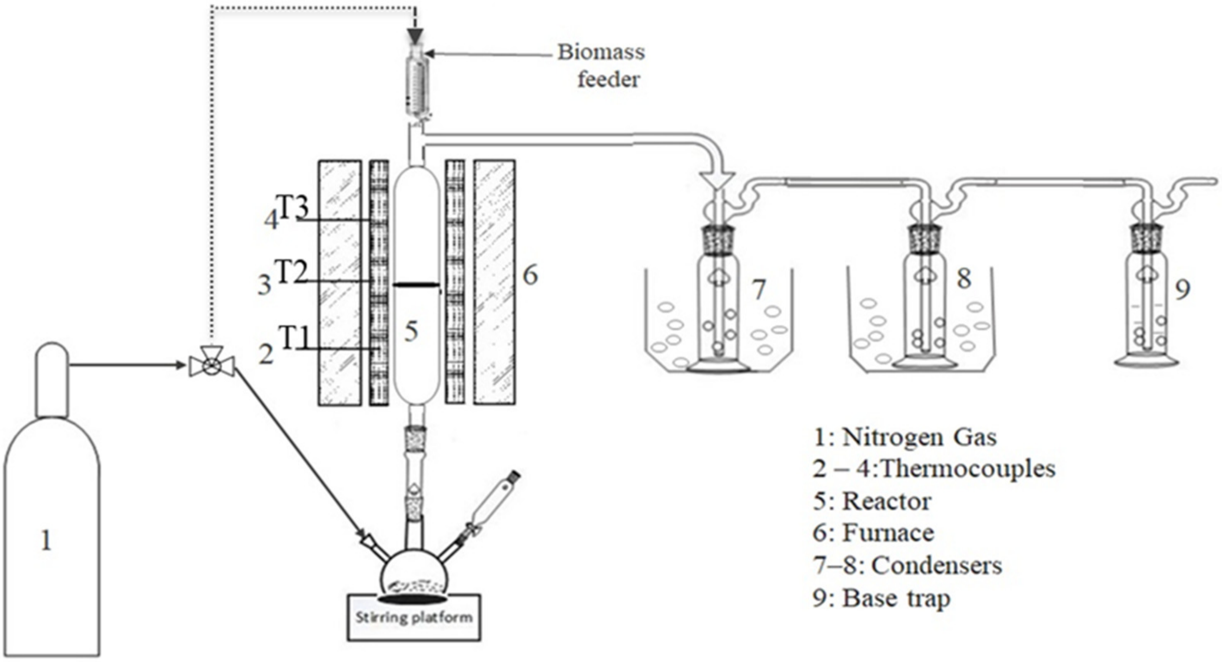

**Figure 1.** Schematic of the reaction system (dotted line used for the initial $N_2$ purging).

### 2.3. Biomass Pretreatment and Acid Feeding System

Peracetic acid was used for the pretreatment of biomass. Peracetic acid (PAA) was produced by reacting hydrogen peroxide with acetic acid in a one-to-one volumetric ratio in the presence of a 1% sulfuric acid catalyst. The PAA was diluted with Milli Q water (Q-POD-Merck, Massachusetts, USA) at a 3:7 (*v/v*) ratio. In detail, wood samples were combined with the PAA mixture in a round-bottom flask positioned on a heating mantle (Wise Therm heating mantle, Thermoline Scientific, New South Wales, Australia). Ten g (dry weight basis) and 200 mL of peracetic acid solution were used in each standard pretreatment run. The pretreatment temperature was set to 90 °C, the stirring speed to 150 rpm, and the reaction time to 5 h, skipping the needed 20 min to reach the target temperature. Our prior published paper discusses the pretreatment techniques and their influence [25]. The chemical compositions of raw hardwood biomass were glucan 40.51 ± 3.15%, xylan 22.12 ± 1.62%, Arabinan 1.06 ± 0.05%, and lignin 32.24 ± 1.64%. Besides, the chemical compositions of delignified hardwood used in this study were glucan 73.78 ± 1.30%, xylan 11.40 ± 0.37%, Arabinan 1.39 ± 0.07%, and lignin 5.85 ± 0.54%. The chemical composition of raw softwood were glucan 39.62 ± 0.49%, mannan 21.77 ± 1.13%, Arabinan 1.31 ± 0.01%, galactan 0.36 ± 0.03% and lignin 36.70 ± 0.35%; whereas the chemical composition of delignified softwood were glucan 70.83 ± 0.56%, mannan 11.78 ± 0.05%, Arabinan 0.40 ± 0.03%, galactan 0.21 ± 0.03% and lignin 10.64 ± 1.64%. According to compositional analysis, the acid-insoluble lignin recovery from hardwood resulted in a 92.13% delignification after five hours of pretreatment. Similarly, a five-hour pretreatment of softwood resulted in 86.88% delignification [25]. The experimental setup of biomass conversion in a fluidized bed reactor is schematically shown in Figure 1. A long borosilicate column with a pressure equalizing arm and a Teflon tap at the bottom was fabricated to pour acid into the three-necked round-bottom flask. The other side neck of the round bottom flask was designed for gas inlet cone. Furthermore, the central neck was intended to secure the reactor in place with a small glass reducer. In all situations, the compatibility of ground glass joints was assured. The transfer line connects the reactor with the quenching system. It was determined to keep the transfer line as short to allow the volatiles to flow through the quenching system with little loss. The quenching mechanism comprises a standard borosilicate glass cold trap. Dry ice was used for the purpose of quenching. The base trap is a standard dreschel bottle filled with 1 N NaOH to neutralize the acid gas.

A setup of a three-neck flat bottom flask with a pressure-equalizing funnel placed on a heating mantle (Wise Therm heating mantle, Themoline Scientific, New South Wales, Australia) to generate HCl gas. A calibrated thermocouple was placed at the bottom of the flask to monitor and record the temperature. Thirty-six wt% of aqueous HCl (RP1106-G 2.5 L RCI Labscan, Bangkok, Thailand) and anhydrous calcium chloride (Sigma-Aldrich, St Louis, MO, USA) are used to generate hydrogen chloride (HCl) gas. The flow rate of generated HCl gas was adjusted with the flow rate of $N_2$ gas used during the thermal and thermochemical conversion of biomass. For this experiment, 25 mL of 25 wt% prepared HCl solution was mixed with 25 g of calcium chloride to generate HCl gas at 70 °C [26]. The gas was dissolved immediately in 100 mL of 1 N NaOH solution. The reaction took ten minutes to complete. This solution was diluted to determine the chlorine ion concentration by using an ion selective electrode (Metler Tolledo, Greifensee, Switzerland). In addition, Kitagawa Hydrogen chloride tubes (Komyo Rikagaku Kogyo K.K., Kawasaki, Kanagawa, Japan) were used to confirm the presence of HCl gas instantly. The amount of HCl in 25 mL of 25 wt% aqueous HCl is 7 g (density 1.12 g/mL). The concentration of $Cl^-$ measured using Ion-Selective electrode was at 23.428 ± 1.37 g/L and it was callculated using the Equation (1) below.

The Concentration of pure HCl in the introduced gas:

$$= \frac{\text{Volume of solution } \times \text{ Concentration of Cl ion in the solution}}{\text{Amount of HCl in the aquous HCl}} \times 100 = 33.46\% \quad (1)$$

### 2.4. *Thermal and Thermochemical Conversion in a Batch-Feeding Fluidized Bed Quartz Reactor*

Two forms of biomass were employed in this study: softwood (*Pinus radiata*) and hardwood (*Victorian ash*), originating from two species—*Eucalyptus regnans* and *Eucalyptus delegatensis* (both of which were supplied from Victoria, Australia). The biomass was pretreated in Peracetic acid (PAA) following the optimal delignification condition previously determined [25]. The materials were milled and sieved to particle size ranging from 250 µm to 500 µm. All of these samples will be referred to as delignified hardwood or softwood from now on. The reaction temperature was varied between 300 and 500 °C. Thermochemical conversion of raw biomass and delignified biomass was carried out in a fluidized bed reactor. The reactor was electrically heated within a furnace, and reactions were carried out in an $N_2$ atmosphere using a three-necked flask and a hot stirrer plate. The space between the reactor and furnace at either end was filled with insulating glass wool to limit heat loss. An external calibrated thermocouple was used to measure the bed temperature of the reactor, hereafter referred to as reaction temperature. Additionally, thermocouples were installed at three points across the furnace (top, middle, and bottom) to determine the actual temperature gradient (Supplementary Table S1). There was no discernible temperature difference between the furnace's built-in middle point thermocouple and the actual thermocouple used for calibration. The biomass conversion temperatures for the reaction operation were determined using the middle-point furnace temperature as the reactor's bed temperature. This is a reactor that feeds from the top. However, after the biomass loading and before the thermochemical conversion, $N_2$ gas was supplied for a minute to ensure the biomass feeder and the reator was air-free, as illustrated by the dotted line. Once the bed of the reactor temperature reached the target reaction temperature, a weighed amount of biomass was added to the reactor. Each batch included 5g of oven-dried (at 50 °C, overnight) biomass, and each biomass feeding took 30 s, followed by a two-minutes reaction period to collect the condensable volatiles. In order to collect the condensable gases during the reaction, two condensers were placed in a dry-ice bath and connected to the outlet of the reactor. The solid char was collected after cooling down the furnace to room temperature and stored. The quencher was used to condense the volatiles from biomass conversion. GC-MS analysis of the condensed volatiles identified the required compounds, namely, LGO and 5-HMF or 5-CMF. Following calibration using standards, the concentration of the product was measured.

### 2.5. Gas Chromatography and Mass Spectrometry (GC-MS) Analysis

The chemical composition of the bio-oils were determined using a GC-MS (Clarus 600 TurboMass MS, Perkin Elmer, Waltham, MA, USA) equipped with a quadruple detector. The sample analysis was performed using a capillary column (HP-5MS, 30 mm × 0.25 mm inner diameter × 0.25 µm thickness, Perkin Elmer, Waltham, MA, USA). A carrier gas of high quality helium was employed at a constant flow rate of 1 mL/min. The injector was kept at a temperature of 300 °C. A starting temperature of 40 °C was used, followed by a 10 °C/min ramp to a final temperature of 280 °C. The MS was equipped with an electron impact ion source capable of scanning between 25–350 amu (atomic mass unit). By comparing the products to the National Institute of Standards and Technology (NIST) library database, the products were identified. To determine the concentration, an internal standard of LGO, HMF, and CMF was acquired from Toronto research chemicals (TRC, North York, Ontario, Canada). The calibration curve was created using the internal standard. The retention time of the standard samples was compared to the retention time of the bio-oil samples in order to confirm the presence of the specific chemicals (LGO, HMF, and CMF). Additionally, mass spectra from the reference sample were utilized to validate the existence of chemicals.

## 3. Results and Discussion

### 3.1. Feasibility Test of the Small-Scale Fluidized Bed Reactor

The reactor bed temperature was maintained at 350 °C throughout the commissioning run to determine the viability of biomass thermal conversion in a laboratory-scale fluidized bed reactor. The condensable volatiles were converted to bio-oil, which was evaluated using gas chromatography-mass spectrometry. Furans, aldehydes, organic acids, ketones, and anhydrosugars are produced during the thermal conversion of biomass. These are the typical compounds generated during cellulose or biomass conversion. In addition, some phenolic compounds are generated during the thermal conversion of lignin [27]. The list of compounds derived from the thermochemical conversion of HW-raw biomass at 350 °C is shown in Table 1 and Supplementary Figure S2. As can be observed, LGO is a minor byproduct of biomass pyrolysis (retention time 11.08 min), with anhydrosugars being the primary result. This conclusion is compatible with the Py-GCMS experiment [28].

**Table 1.** GC-MS analysis of bio-oil obtained from the thermochemical conversion of HW-raw biomass at 350 °C.

| Retention Time (min) | Chemical Name | Retention Time (min) | Chemical Name |
|---|---|---|---|
| 2.59 | Acetic acid | 12.72 | 5-hydroxymethyl furfural |
| 2.95 | 2-Propanone, 1-hydroxy | 13.09 | 2,5 hexanedione |
| 5.27 | 2(5H)-Furanose | 13.76 | Isosorbide |
| 5.92 | Furfural | 13.97 | 2-Butene-1,4 diol |
| 9.07 | Trimethylene oxide | 14.35 | 3-methyl-2-Hexanone |
| 11.08 | Levoglucosenone | 18.08 | 1,6-anhydro β-D-Glucopyranose |
| 12.16 | 2-pentanol, 5-(2-Propynyloxy) | 18.85 | D-allose |
| 12.65 | 1,4:3,6-Dianhydro-α-D-glucopyranose | 19.65 | 1,6-anhydro α-D-Galactofuranose |

### 3.2. Conversion of Raw and Delignified Biomass in a Small-Scale Reactor

Temperature plays a vital role on product distribution in the pyrolysis process. The temperature effect on the composition of LGO concentration in bio-oil obtained from the thermal conversion of biomass was investigated between the temperature range 300 to 500 °C [29]. Maximum bio-oil yields are obtained at temperatures between 500 and 600 °C. However, it is stated that the majority of chemical conversions and modifications occur within the specified temperature range [30]. Figure 2 summarizes the LGO concentrations obtained for both hardwood and softwood biomass. The mass spectrum of the product (*m/z* 39, 53, 68, 96, and 98) from the NIST library validated its identity as LGO (Supplementary Figure S2a). In comparison to raw biomass, delignified biomass pyrolyzed at 300–350 °C significantly boosted the LGO content. A temperature of 350 °C was suitablefor biomass conversion to LGO in both raw and delignified biomass, despite the fact that the concentration of LGO was much higher in delignified biomass. At 350 °C, HW and SW delignified biomass generated approximately 20 and 16 mg/mL of LGO, demonstrating that pretreatment significantly affected pyrolysis temperature (Figure 2). A high concentration of LGO at the same temperature indicated that the stiff structure of the biomass was disrupted during the delignification process. In this temperature range, a similar trend in LGO generation was seen in a fixed bed reactor [27]. This signifies that delignification and the loss of hemicellulose facilitate the conversion of the biomass residual cellulose. The results indicate that delignification using PAA is a viable strategy for producing LGO via biomass pyrolysis.

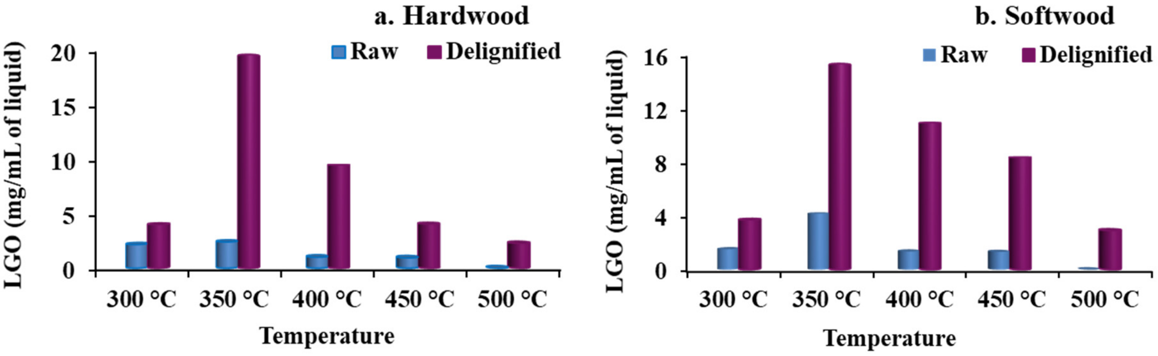

**Figure 2.** LGO concentration during the thermal conversion of raw and delignified biomass of hardwood (**a**) and softwood (**b**) in different reaction temperatures.

The increased temperature had a detrimental effect on LGO generation for both types of delignified biomass. Secondary cracking of the volatiles was occurring as a result of the high temperature, which may be related to the low LGO generation [31]. Reaction temperature plays a key role on the formation of platform chemicals and overall concentration [32]. At elevated temperatures, the formation of LGO is prevented by the radical scavenging process, which prevents dehydration. However, the trend toward decreasing LGO concentrations was more pronounced in SW-delignified biomass (Figure 2b). This was because the residual lignin concentration is more than that of the HW-delignified biomass [25].

Another interesting observation is that the formation of anhydrosugars was higher at 350 °C for raw and delignified biomass (Figure 3). However, delignified biomass removed sugars more effectively than raw biomass. At 350 °C, both the generation and conversion of anhydrosugars occur. As a result, this reaction temperature is conducive to dehydration, and anhydrosugars are a precursor to LGO formation. On the other hand, temperatures over 400 °C demonstrated a declining tendency in anhydrosugar. The anhydrosugar consists primarily 1,6-anhydro-β-D-Glucopyranose (LGA), 2,3-Anhydro-D-Mannose, and 1,4:3,6-Dianhydro-α-D-glucopyranose, and higher reaction temperature accelerates the secondary reactions during biomass conversion [32]. LGA is a primary product of lignocellulosic biomass pyrolysis and represents the cracking of carbohydrates from biomass [33]. A higher reaction temperature is not preferable for this particular experiment to produce LGO. Thus, the LGO concentration and anhydrosugar peak area suggested that the optimal reaction temperature for this fluidized bed reactor is 350 °C for pyrolysis.

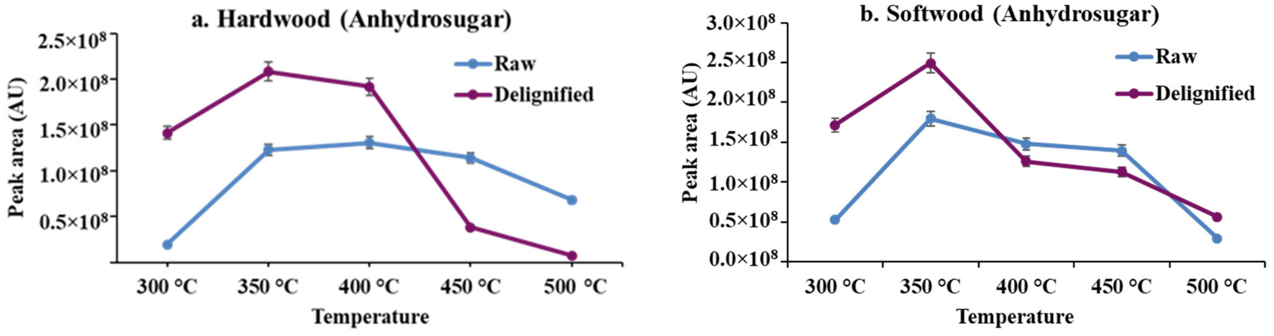

**Figure 3.** Anhydrosugars peak area during the thermal conversion of raw and delignified biomass of hardwood (**a**) and softwood (**b**) in different reaction temperatures.

Furfural and HMF were co-products of the bio-oil, along with anhydrosugar, LGO, and other compounds. LGO, as well as furfural, HMF, LGA, and other undesirable compounds, were produced by phosphoric acid impregnation followed by hydrothermal processing [9]. Furanic platform chemicals such as furfural and HMF are seen as more environmentally friendly alternatives to petrochemicals. These compounds are synthesized in industry by the dehydration of carbohydrates. 2,5-dimethylfuran, 2,5-diformylfuran, and 2,5 furandicarboxylic acid are all useful building block intermediates of HMF [34]. The concentration of 5-HMF generated from biomass at temperatures ranging from 300 to 500 °C is shown in Figure 4. The mass spectrum of the product (*m/z* 39, 41, 69, 97, and 126) from the NIST library validated its identity as LGO (Supplementary Figure S3b). When the pyrolysis temperature was increased from 300 °C to 400 °C, the HMF content increased for both hardwood and softwood biomass. At 300 °C, HW-raw and HW-delignified produced 4.99 ± 0.04 and 5.72 ± 0.06 mg/mL of HMF in the bio-oil, respectively. At 400 °C, the HMF concentration of HW-raw presented 8.46 ± 0.09 mg/mL of bio-oil, and HW-delignified showed 15.80 ± 0.08 mg/mL of bio-oil. Softwood biomass also followed the same trend as hardwood biomass (Figure 4). However, as compared to hardwood biomass, softwood biomass yielded less HMF. Thus, the chemical content and structure of biomass are critical factors in biomass conversion. 5-HMF is synthesized from the six-carbon sugars found in biomass components, mostly cellulose, by dehydration and side-chain reaction [34]. The increased content of HMF in the bio-oil produced during biomass thermal conversion was due to cellulose. Hardwood biomass has a higher proportion of cellulosic material than softwood biomass [25]. After 400 °C, the concentration of HMF significantly dropped owing to side reactions and more cracking.

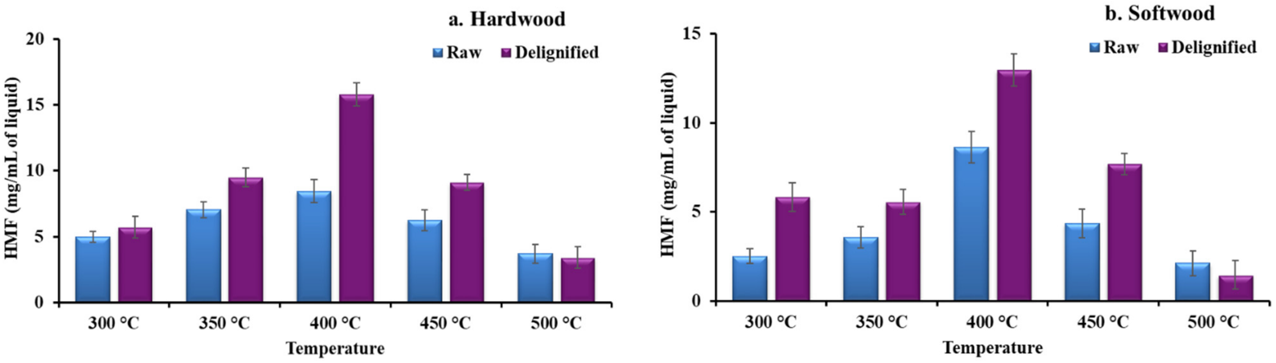

**Figure 4.** HMF concentration during the thermal conversion of raw and delignified biomass of hardwood (**a**) and softwood (**b**) in different reaction temperatures.

Furfural is also an important chemical, and it has gained increased attention for its production from sustainable biomass resources. Furfural is utilized generally as a solvent in the refining of lubricating oils and diesel fuels, as well as a chemical intermediary in the synthesis of solvents such as tetrahydrofuran and methyl tetrahydrofuran [35]. However, the primary purpose of this investigation is not to produce furfural. Furfural is formed as a byproduct of biomass thermal conversion. The formation of furfural during thermal conversion of biomass was explored between 300 and 500 °C since the majority of chemical reactions occur within this range. The relative quantities of furfural generated from biomass at various reaction temperatures are shown in Figure 5. It was evident from the concentration that less furfural was produced from delignified biomass than from raw biomass. As seen in Figure 5, low-temperature pyrolysis is effective for the production of furfural from both hardwood and softwood biomass. Furfural is synthesized from sugars with five carbons, mostly hemicellulose units. The conversion of biomass sugar to furfural involves a series of processes, including isomerization of sugars followed by dehydration to furfural [34].

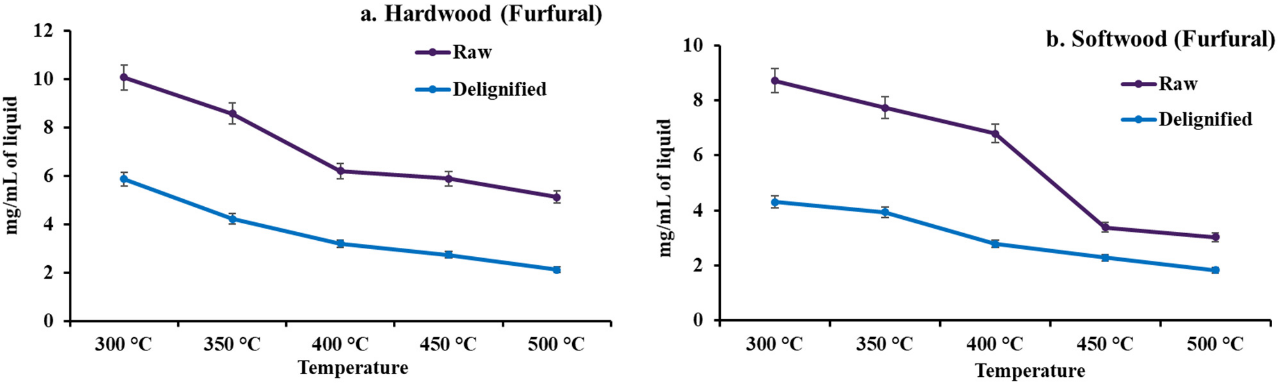

**Figure 5.** Furfural concentration during the thermal conversion of raw and delignified biomass of hardwood (**a**) and softwood (**b**) in different reaction temperature.

Supplementary Figure S4 shows the HW-delignified biomass thermally converted at 350 °C. This figure depicts that delignified biomass generated fewer peaks or undesired chemicals by comparing HW-raw biomass (Supplementary Figure S1) mostly due to the absence of lignin. The next part of this section will focus on the thermochemical conversion of delignified biomass in a small-scale fluidized bed reactor. This process includes one-step thermochemical conversion of biomass in the presence of a low concentration of acid. The generated HCl gas reacts with biomass-derived HMF and finally produces 5-CMF (Supplementary Figure S3c). CMF is classified as a chemical intermediate rather than a biofuel, owing to the presence of a halogen atom [36].

### 3.3. Thermochemical Conversion of Delignified Biomass in the Presence of HCl Gas

The catalytic impact of HCl gas promotes the formation of LGO in the thermochemically converted bio-oil. $H_2SO_4$ and ionic liquid have both been discovered to be capable of producing LGO. However, several issues will arise with the use of these catalysts, and they are thermally unstable [37,38]. The concentrations of LGO and CMF following thermochemical conversion of HW-Delignified biomass are shown in Figure 6. As seen in Figure 6 and Supplementary Figure S5, HCl gas has three benefits. To begin with, it acts as a reactant, converting HMF to CMF. Second, it may boost the concentration of LGO in the bio-oil. Finally, the presence of HCl gas during the reaction improves the process's product selectivity. A temperature of 350 °C is optimal for the generation of LGO, which was 27.70 mg/mL of bio-oil from HW-delignified biomass (Figure 6a). The presence of HCl gas during the conversion boosts the LGO concentration by 7 mg/mL of bio-oil compared to the conversion at 350 °C (Figure 2a) in the absence of HCl. At 400 °C, however, the concentration of LGO decreased considerably, but CMF concentration rose proportionately (Supplementary Figure S5). After 350 °C and 400 °C, respectively, the LGO and CMF concentrations rapidly decreased. A similar trend was seen with SW-delignified biomass, and it is worth noting that the reaction at 500 °C did not result in the formation of any LGO (Figure 6b). The breakdown of the primary components of biomass, hemicellulose, and cellulose, occurs in these temperature zones [39]. Kohl et al. showed that CMF can be synthesized directly from sucrose or glucose liquid in very short reaction times when using concentrated HCl at 100 °C [21]. In this study, using HCl gas produced fewer chemicals, increasing the concentration of LGO and CMF; while the thermal conversion of biomass produced some undesired chemicals even after using delignified biomass. As shown by the study, a relatively high concentration of chemicals would facilitate industrial-scale distillation and purification of these two target molecules, LGO and CMF. For LGO generation, a reaction temperature of between 300 °C and 400 °C, particularly 350 °C, is acceptable from biomass thermochemical conversion. Thus, delignified biomass showed superior performance for the target chemical synthesis based on these results. This result endorses up the idea that pretreatment of biomass before thermochemical processing for CMF generation can help to reduce the formation of co-products in bio-oil [40].

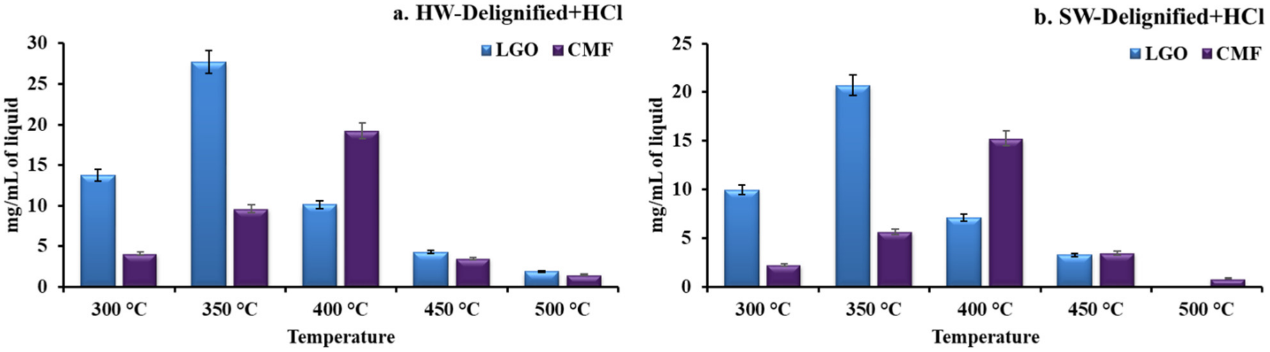

**Figure 6.** LGO and CMF concentration after the thermochemical conversion in small-scale fluidized bed reactor of hardwood (**a**) and softwood (**b**)delignified biomass in different reaction temperatures.

### 3.4. Reaction Pathways and Process Flow of the Biomass to LGO Conversion

The reaction pathways for thermochemical conversion of biomass are shown in Figure 7. Levoglucosan (LGA), 1,6-anhydro-β-D-glucopyranose, is an anhydrosugar that is produced during the pyrolysis of cellulosic biomass [33]. In proper circumstances, LGA is generated by dehydrating the glucopyranose unit of active biomass-cellulose. Secondary dehydration removes two water molecules from LGA in a favorable environment, resulting in the extremely important platform chemical LGO, which may be further modified at high temperatures by cracking, condensation, dehydration, decarboxylation, or decarbonylation. Lu et al. computed probable chemical routes from β-D-glucopyranose and cellobiose to

LGO using density functional theory (DFT) and determined that LGA was unlikely to be a critical intermediary for LGO [41]. Water is formed during the dehydration process, along with a variety of other furan products, including HMF [42,43]. HMF is transformed to CMF by treating it with hydrogen halide, which replaced the hydroxyl group in HMF with a halogen atom [44]. Cellulose is initially broken down into glucose. Later, it may undergo ring-opening, isomerization, and ring-closing (fructofuranose) reactions to yield HMF [21]. When utilizing HCl to create an acidic environment, CMF is preferred. As seen in the reaction pathway (Figure 7), given the reaction circumstances utilized in this work, a distinct competing reaction might occur. However, in-situ investigations are essential to know the changes in biomass structure, including functional group modifications, to grasp the fundamental mechanism of reaction pathways. Unfortunately, this is outside the scope of this research.

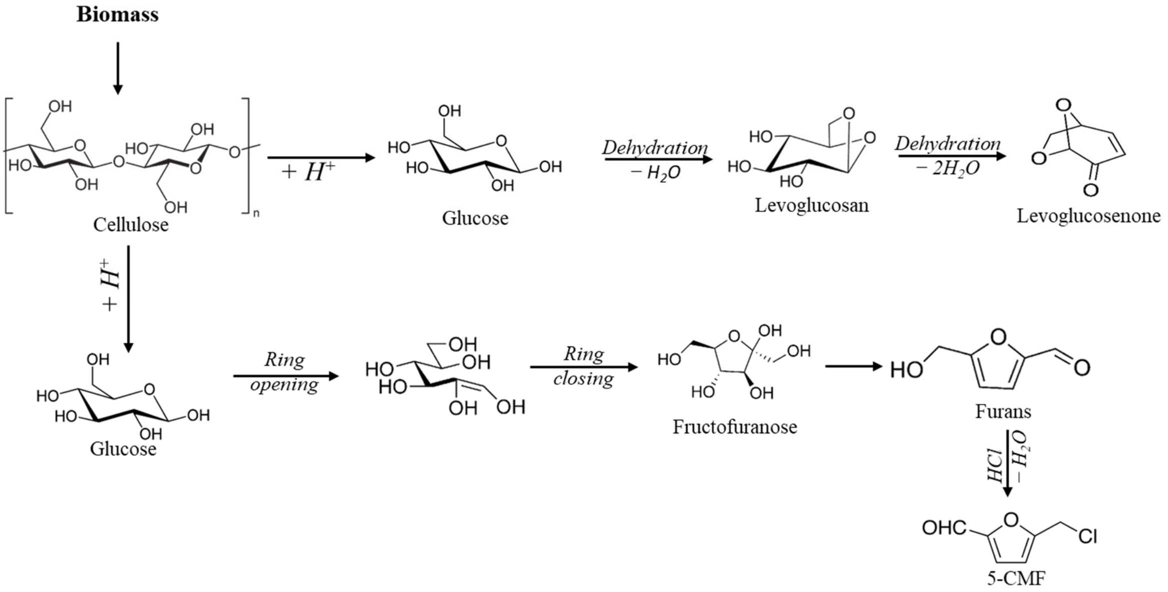

**Figure 7.** Possible reaction pathways to produce LGO and CMF from biomass corroborated using the literature [17,21].

Dobele et al. demonstrated that the obtained bio-oil contained a 6.5% (relative %) LGO using GC-MS analysis [9]. The conversion of birch wood for the synthesis of LGO was carried out using a screw-type pyrolysis reactor. Prior to conversion, biomass was hydrothermally processed for 1 h at 180 °C and 6.6 bar pressure. The treated biomass was then impregnated with $H_3PO_4$ (5 wt%) for 6 h at room temperature. The chloroform extraction of bio-oil and subsequent distillation produced fractions containing 79.14% LGO. Additionally, they found that the generation of LGO in the reactor is half that of Py-GC/MS/FID from the same biomass [9]. Another research from the group reported 19.8% and 21.8% yields of LGO (relative %) using 3 wt% and 3.7 wt% $H_3PO_4$ impregnated birch wood, respectively, in a flash pyrolyser [22]. Prior to $H_3PO_4$ impregnation and use in a flash pyrolyser, the biomass was treated with steam explosion (156 °C, 4.5 bar for 1.5 h) [45]. Suian et al. utilize sugarcane bagasse treated with 4.3 wt% $H_3PO_4$ and 0.05 M $H_2SO_4$ (equivalent to 4.28 wt% acid loading), agitated for 20 h, then dried at 60 °C for 4 h and 105 °C for 12 h before using it to produce LGO using a quartz tube pyrolyzer set to 290 °C. It resulted in a 36.1% yield of bio-oil and a 5.53% yield of LGO therein, implying that 1.99 g of LGO was generated from 100 g of sugarcane bagasse [37]. Onkarappa and Datta [24] synthesized CMF from glucose and sucrose in the presence of aqueous HCl-1,2-dichloroethane and Benzyl-tributylammonium chloride (BTBAC) as a phase transfer catalyst in a biphasic batch reactor. The reaction was carried out for 3 h at 90 °C. Following the process, a 64% yield of CMF was obtained from glucose in the presence of BTBAC. Without BTBAC, the maximum amount of CMF yield was 47%. Sucrose resulted in a 73%

yield of CMF when combined with BTBAC [46]. Chen et al. [23] used a deep eutectic solvent (3c-DES) for the manufacture of CMF from bamboo and bamboo pulp at 120 °C in less than 30 min, yielding 15% and 22% CMF, respectively [47]. Mascal and Nikitin's investigation yielded the highest CMF production ever reported in the literature at 80.2% from corn stover's hexose content. The experiment included treating powdered corn stover with strong hydrochloric acid (70 mL) and 1,2-dichloroethane (140 mL) and heating the combination vigorously in a closed system at an oil bath temperature of 80 °C [17].

No research that we are aware of has reported the formation of CMF from woody biomass. Our current work establishes a proof of concept and an unique route for the production of two important platform chemicals, LGO and CMF, using acid gas from woody biomass. The LGO and CMF derived from biomass shown in Figure 8 were produced directly from biooil without additional extraction, distillation, or purification.

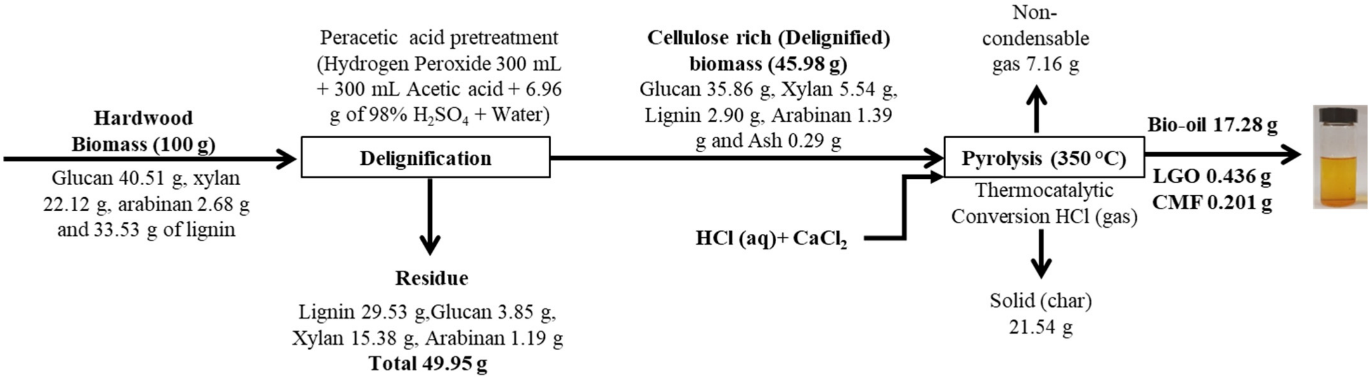

**Figure 8.** Process diagram of peracetic acid pretreatment and LGO production from hardwood biomass one-step thermochemical process (350 °C).

Figure 8 displays the process flow diagram based on the thermochemical conversion of hardwood biomass using data from the compositional analysis, sugar content, and LGO production. The overall amount of bio-oil produced from a single-step thermochemical conversion of 100 g biomass was 17.28 g. Conversion in the presence of hydrogen chloride gas resulted in LGO generation of 0.436 g per 100 g of hardwood biomass with 0.20 g of CMF at 350 °C. Around 63% of chlorine ion was utilized to generate CMF, and the remaining may have been used to catalyze the reaction. Thermchemical conversion of hardwood biomass at 350 °C resulted in the production of 0.058 g of furfural from 100 g of biomass. The conversion process also resulted in char and non-condensable gas production as byproducts. The non-condensable gas was calculated by difference with generated bio-oil and char during the conversion of biomass. The gas Analysis of HW-Delignified biomass at 350 °C detected CO (56.88%), CO2 (41.59%), and CH4 (1.52%) as non-condensable gas on a N2-free basis. A few studies focused on the production of $H_2$ gas from biomass using a high heating rate and high temperature [21,22]. In this study, the gas analysis took into consideration to identify the gas composition whether it is not the objective of this study. Thus, under the above conditions it is possible to produce a high purity of platform chemicals even though further optimisation is possible. The current results will assist in the adjustment of conditions and the design and construction of a scalable continuous reactor, enabling us to improve the platform chemical yields.

## 4. Conclusions

The study demonstrated the successful biomass conversion to platform chemicals, LGO and CMF, in a fluidized bed reactor. Thermochemical conversion, with and without HCl presence, were conducted in a small-scale fluidized bed reactor with four types of biomass—HW-raw, HW-delignified, SW-raw, and SW-delignified. Delignified biomass showed higher platform chemical concentration compared to raw biomass. Thermochemical conversion, in the absence of HCl, of raw biomass, produced a range of other chemicals with a low concentration of LGO below 500 °C, and no LGO was found at 500 °C. Both delignified biomasses are promising candidates to produce LGO through the thermochemical conversion. Among these, HW-delignified biomass presented a higher concentration of platform chemicals during thermochemical conversion with and without the presence of HCl. This study describes that the use of HCl gas as a reactant and catalyst to produce LGO and CMF. The highest concentration of LGO (27.70 mg/mL of bio-oil) was found at 350 °C, and CMF (19.24 mg/mL of bio-oil) was obtained at 400 °C in the fluidized bed reactor. Further increase of temperature resulting in a low concentration of the platform chemicals of interest. One might infer that a one-step reaction in the presence of HCl gas can provide two essential platform chemicals from biomass feedstock. Our current effort focuses on developing and scaling up the process using a continuous fluidized bed reactor capable of converting 3–5 kg of delignified biomass per hour.

**Supplementary Materials:** The following are available online at https://www.mdpi.com/article/10.3390/catal12020206/s1, Figure S1: Furnace calibration by using three external thermocouples, Figure S2: GC-MS analysis of bio-oil obtained from the thermochemical conversion of HW-raw biomass at 350 °C in small-scale fluidized bed reactor (RT 5.92: Furfural, and RT 11.08: LGO), Figure S3: Mass spectrum (*m/z*) of standard LGO (a), HMF (b), and CMF (c), Figure S4: GC-MS analysis of bio-oil obtained from the thermochemical conversion of HW-delignified biomass at 350 °C in small-scale fluidized bed reactor (RT 5.84: Furfural, and RT 10.98: LGO), Figure S5: GC-MS analysis of bio-oil obtained from the thermochemical conversion of HW-delignified biomass at 400 °C in small-scale fluidized bed reactor in the presence of HCl gas (RT 5.88: Furfural, RT 11.07: LGO, and RT 11.90: CMF), Table S1: Furnace calibration.

**Author Contributions:** Conceptualization, C.K. and S.B. (Sankar Bhattacharya); methodology, C.K., formal analysis, C.K.; writing—original draft preparation, C.K.; editing, S.B. (Saheli Biswas), M.A.K. and S.B. (Sankar Bhattacharya); visualization, S.B. (Saheli Biswas); supervision, S.B. (Sankar Bhattacharya). All authors have read and agreed to the published version of the manuscript.

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