

Staged liquefaction: reaction pathway and mechanism of corn stalk hemicellulose in 1,2-propylene glycol / diethylene glycol under acid catalysis

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Research Article

Keywords: Hemicellulose, Liquefaction, Bio-oil, Residue, Polyol

Posted Date: October 20th, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-10198824/v1>

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Additional Declarations: No competing interests reported.

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2 hemicellulose in 1,2-propylene glycol / diethylene glycol under acid
3 catalysis

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18
19 **ABSTRACT**

20 To promote full-component utilization of lignocellulosic biomass and reduce petrochemical reliance for
21 “dual carbon” goals, this experiment studied the liquefaction of hemicellulose directly separated from
22 corn stalk by 1,2-propylene glycol (PG) and diethylene glycol (DEG) mixture with acid catalysis at
23 different reaction times. By investigating the variations in composition, structure, and distribution of
24 liquefaction products under varying reaction times, the study aimed to elucidate the formation
25 pathways of active functional groups and the liquefaction reaction mechanisms, thereby establishing
26 the fundamental reaction patterns of the process. The time-dependent analysis revealed that the

liquefaction reaction of hemicellulose proceeded in stages (the highest liquefaction yield of 87.02% at 0 min). Notably, '0 min' indicated the moment when the target temperature of 170 °C was reached. The hemicellulose degradation process was dominant and primarily completed during the heating phase (prior to 0 min), while polymerization reaction predominantly occurred during the holding phase (0–150 min). In the heating stage, hemicellulose degraded into pentoses/hexoses, then into oligosaccharides/monosaccharides under acid. These sugars formed corresponding PG/DEG-glycosides, further transformed into low molecular weight (LMW) compounds such as furfural and levulinic acid. In the holding stage, abundant degradation-generated LMW organics (alcohols, ketones, aldehydes, acids, ethers, esters, hydrocarbons, etc.) underwent polymerization among themselves, intermediates, and PG/DEG, forming higher molecular weight substances (liquefaction residue).

Keywords: Hemicellulose; Liquefaction; Bio-oil; Residue; Polyol

Summary

- Hemicellulose liquefaction for biomass utilization and carbon goals.
- Staged process: degradation during heating, polymerization during holding.
- Highest liquefaction yield of 87.02% was achieved at 0 min.
- Sugars form PG/DEG-glycosides, then convert to furfural and acids.
- Holding stage polymerizes LMW organics into higher molecular residue.

1. Introduction

Based on the rapid development of industrial production and the continuous growth of global fuel demand, there was an urgent need to utilize more renewable resources in order to alleviate the fuel shortage and environmental crisis [1,2]. Lignocellulosic biomass was the world's most abundant renewable resource, among which hemicellulose accounted for 20%~35% of its main components (cellulose, hemicellulose, lignin) [3–6]. Hemicellulose, unlike cellulose, had a complicated structure and was a polysaccharide made up of multiple monosaccharides (pentoses and hexoses) [7]. The logical and effective synthesis and exploitation of hemicellulose were both difficult and crucial [8].

Research had demonstrated that lignocellulosic materials may be used in a variety of methods, including hydrolysis, fast pyrolysis, liquefaction, and gasification [9]. These techniques enabled them to transform their lignocellulosic resources into syngas, bio-oil, and biomass polyols, which may then be turned into useable chemicals via various routes [10–14]. Among these methods of resource utilization, liquefaction was one of the simplest and most successful [15,16]. It was an efficient way to turn lignocellulose into a valuable liquid product [17,18]. There were two common types of liquefaction, one was liquefaction without catalyst at high temperature and pressure. Phaiboonsilpa used the hydrothermal method in the liquefaction of xylan from corn cob under pressure with nitrogen and carbon dioxide [19]. The alternative method was acid-catalyzed liquefaction, which employed a suitable solvent and catalyst at a moderate temperature and atmospheric pressure, such as polyol and phenol as liquefied solvents [20,21].

Atmospheric liquefaction had attracted extensive attention because of its mild reaction conditions and high liquefaction efficiency, especially regarding the liquefaction of one component, hemicellulose, which had already been reported [22,23]. Shi et al. [24] and Wang et al. [25] two research teams respectively used xylan to study the liquefaction of hemicellulose with ethylene glycol (EG). The results indicated that xylan had undergone degradation and been converted into liquid bio-oil, which contained EG and its derivatives, alcohols, ketones, aldehydes, esters, and acids.

Our team conducted preliminary research on the presence of alcohols (over 90% content), acids, ethers, esters, ketones, and other compounds in the bio-oil obtained from hemicellulose separated from corn stalk through phosphoric acid catalysis, 1,2-propylene glycol (PG) and diethylene glycol (DEG) liquefaction, with over 80% of the compounds having a carbon number below 25 [26]. These compounds were formed through condensation, cyclization, and other reactions between polyol

radicals and intermediate small molecule radicals generated by the liquefaction of hemicellulose. Additionally, hemicellulose could be degraded into various glycosides through liquefaction, which were then converted into furfural derivatives. As the reaction proceeded, these derivatives underwent degradation and polymerization reactions to generate LMW soluble substances and insoluble residues.

The xylose in lignocellulose usually existed in the form of furanose, pyranose or ring-opening. Research had displayed that furfural was mainly generated through the degradation and conversion of xylose, a type of pyranose, while liquefied products (formic acid, lactic acid, acetone aldehyde, glyceraldehyde, etc.) were produced by the transformation of xylose (ring-opening form) [27]. When studying the impact of lignocellulose on the generation and composition of bio-oil, the results showed that the properties of bio-oil produced through the reaction of xylose and glucose were similar, indicating that the reaction processes experienced by glucose and xylose were close [28].

In recent decades, excessive consumption of fossil fuels had gradually worsened the energy and environmental crises. Atmospheric liquefaction technology enabled the preparation of sustainable bio-oil from lignocellulose. However, current research on the polyol liquefaction mechanism remained incomplete and superficial, with limited theoretical and technological support for existing liquefaction techniques, especially regarding the reaction mechanisms of individual components during the liquefaction process [29]. Particularly, there were even fewer studies on the reaction mechanism of the actual components of lignocellulosic biomass[30]. In this paper, acid-catalyzed polyols PG/DEG liquefaction experiments were performed on hemicellulose, one of the major components isolated from corn stalk, during different liquefaction reactions. The changes of chemical groups, chemical structures, molecular weights and pyrolysis characteristics of liquefied products were analyzed by infrared spectroscopy (FT-IR), nuclear magnetic resonance (NMR), gel permeation chromatography (GPC), and thermogravimetric analysis (TGA). This reflected hemicellulose structural changes during the liquefaction system, inferring its liquefaction reaction pathways, thereby improving the liquefaction mechanism of lignocellulosic biomass and promoting the high-value utilization of its entire components.

2. Materials and methods

2.1. Materials.

Corn stalk with a mesh size of 20 to 80 was collected from a farm near Henan, China. After drying at 105 °C for 24 h, it was placed in a desiccator for use. The hemicellulose was extracted directly from corn stalk powder and kept for subsequent use, as shown in **Figure 1** [31]. And the extracted hemicellulose included 3.89% glucose and 82.58% xylose and arabinose.

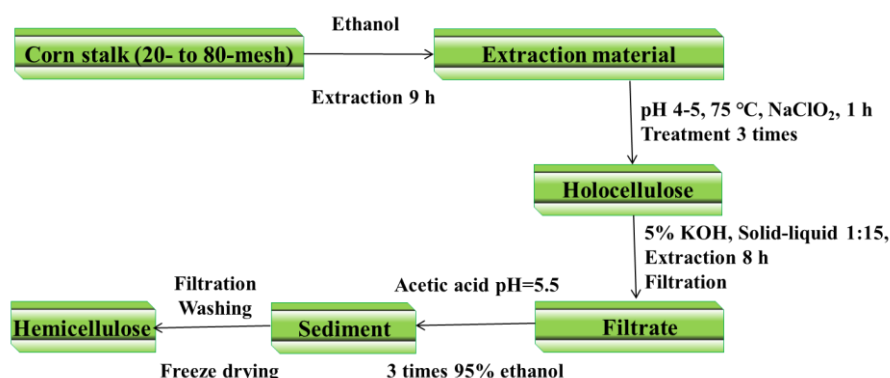


Figure .1. The flow chart for the separation of hemicellulose from corn stalk.

Concentrated phosphoric acid (≥ 85.0 wt%), DEG, PG, 1,4-dioxane, sodium chlorite, potassium hydroxide, glacial acetic acid were analytical purity, and potassium bromide was chromatographic purity. Sinopharm Chemical (China) was the supplier of these solvents. Cambridge Isotope Laboratories Inc. (USA) provided acetone- d_6 (chromatographic purity).

2.2. Liquefaction of hemicellulose.

Based on the liquefaction conditions obtained from the previous experiments of our research group. To liquefy oven-dried hemicellulose m_1 (g), DEG blended PG (1:2) with a 5/1 liquid-solid ratio (mass ratio of the liquefying agent PG/DEG to the hemicellulose) and 10% phosphoric acid dosage (mass percentage of H_3PO_4 and PG/DEG) at 170 °C were utilized. Reaction time was set as 0, 15, 45, 75 and 150 min (holding stage). The heating stage was from room temperature to 170 °C, and the holding stage was for the reaction time from 0 until 150 min.

2.3. preparation of bio-oil and liquefaction residue.

Liquefied product was diluted in an adequate amount of 80% 1,4-dioxane combination before centrifuging. A TGL-20M high-speed chilled centrifuge was used to separate the saturated liquefaction products into solid and liquid (10000 r/min, 10 °C, 15 min). To remove the solvent and create a bio-oil,

the upper liquid layer was exposed to spin evaporation at a temperature of 40 °C. The bottom solid layer was washed, filtered, and dried to a constant mass m_2 (g) to obtain liquefied residue. The liquefaction yield of hemicellulose Y (%) was based on Eq.1 [32].

$$Y(\%) = \frac{m_1 - m_2}{m_1} \times 100\% \quad (1)$$

2.4 Liquefied products characterization.

The M_1 (g) bio-oil was carbonized under aerobic conditions for 20 min and then burned at a temperature of 775 °C for 8 h (M_2 (g)). The char yield, Q (%), was calculated by Eq.2.

$$Q(\%) = \frac{M_2}{M_1} \times 100\% \quad (2)$$

About determination of solid content. A total of 1.0~1.5 g (0.0001 g) bio-oil, G (g), in a weighing bottle with constant weight, W (g), was placed in an oven at 105 °C, until the sample had a constant weight, W_1 (g). The solid content in bio-oil, Z (%), was calculated according to Eq.3.

$$Z(\%) = \frac{W_1 - W}{G} \times 100\% \quad (3)$$

Chemical groups of bio-oil and liquefaction residue were detected on a Fourier transform infrared spectrometer (FTIR-650, Bruker, Germany). The resolution was 4 cm^{-1} with 4000~400 cm^{-1} wavelength area, and there were 16 scans. The sample to KBr mass ratio was 1:100 (W/W) [33].

The bio-oil's molecular weight and its polydispersity were determined by GPC, (Waters-1515, Agilent, USA) with a -G.2000 HHR chromatographic column and a -G.1000 gel column [34]. The detector was a refractive index detector calibrated with polystyrene. The measurement period was 25 min, and the frequency was 1.0 mL/min. 10 mg bio-oil was dissolved in tetrahydrofuran (10 mL) by a volume injection of 50.00 μL .

Bio-oil (about 10 mg) was dissolved in solvent acetone- d_6 (0.5 mL). Its ^1H -NMR was detected on AV III 400M nuclear magnetic resonance spectrometer (Bruker, Germany) and scanned 8 times [32].

The bio-oil (100 mg) was dissolved in acetone- d_6 (0.5 mL), and was used to test ^{13}C -NMR with the scanning frequency of 20000 scans (30° pulse, sampling time 1.4 s, relaxation time 2 s, scanning time 12 h) [28].

The TGA-Q50 thermogravimetric analyzer (Shimadzu, Japan) was used to conduct TGA of sample (5~10 mg bio-oil or residue) from 30 to 600 or 800 °C (nitrogen atmospheres, heating rate 10 °C/min) [35].

3. Results and discussion

3.1. Effect of reaction time on liquefaction efficiency of hemicellulose.

The effects of reaction time on liquefaction yield, char yield and solid content were presented in **Figure 2**. As the increase of reaction time, liquefaction yield and char yield presented a tendency of first rising and then falling, or first decreasing and then increasing, respectively, reaching a peak value at 0 min (87.02% or 11.93%), while the solid content increased. In the heating stage, as the reaction time prolonged, the contact and mixing of hemicellulose, catalyst H_3PO_4 and liquefied solvents PG/DEG became more complete, leading to an acceleration of reaction speed and facilitating hemicellulose liquefaction process, which was dominated by the degradation reaction of hemicellulose in this stage [29]. In the holding stage, the liquefaction yield of hemicellulose dropped as reaction time rose, whereas char yield and solid content increased. Because the polymerization reaction between the liquefied products or with PG/DEG intensified with the reaction time extension, and too long liquefaction time might facilitate the formation trend of residue and gas [26]. At this stage, polymerization was the main reaction. This indicated that degradation reaction of hemicellulose completed basically in the heating stage, while in the holding stage, the polymerization process was primarily used to create compounds with a higher molecular weight.

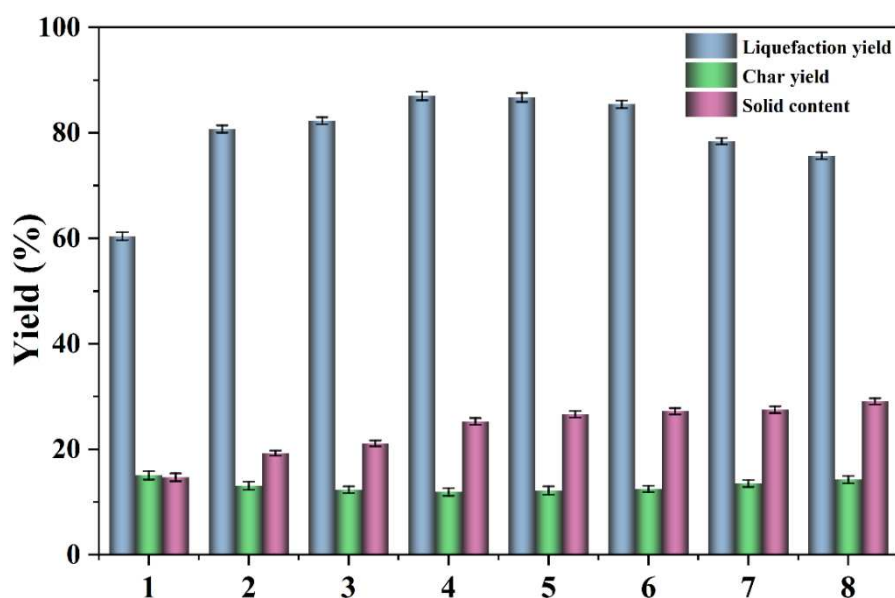


Figure 2. Effect of reaction time on liquefaction efficiency of hemicellulose. (1, 2, 3 respectively represented the heating stage of 20, 40, 60 min, while 4, 5, 6, 7, 8 respectively represented the holding stage of 0, 15, 45, 75, 150 min.)

3.2. Changes of chemical groups in bio-oil.

The FT-IR spectra of hemicellulose and the its bio-oils obtained with reaction time of 0, 15, 45, 75 and 150 min was displayed in **Figure 3**. The bio-oil's FT-IR spectra produced at various reaction periods were highly similar and exhibited the similar structures and compositions [36]. However, they were very different from the FT-IR spectra of hemicellulose, indicating that the liquefaction process played an important role in the modification or destruction of hemicellulose.

As a control group, the signals of sugar unit in the hemicellulose spectrum were mostly focused on the fingerprint area of $1650\sim800\text{ cm}^{-1}$ [31]. At 897 cm^{-1} , there was a strong signal caused by $1,4\text{--}\beta\text{--}$ glycosidic bonds between xylopyranose units in the backbone of xylan [37]. Bands at 1170 to 1000 cm^{-1} represented the canonical specific absorption of xylan, such as the very strong signal at 1045 cm^{-1} , and signal near 987 cm^{-1} could be put down to the bending of xylosyl $\text{C}_3\text{--H}$, representing that the composition of this hemicellulose was mainly xylose. The weak signal at 1160 cm^{-1} indicated that the hemicellulose contained arabinosyl side chains. These characteristic signals were not present in the bio-oil spectra, which proved once again that hemicellulose had basically completed the liquefaction degradation reaction in the heating stage [38].

In the holding stage, with the prolongation of reaction time, the O--H stretching vibration signal became broad and gentle near 3396 cm^{-1} , and the signal intensity increased slightly [39,40]. The strength of saturated C--H bending vibration signal near 1457 cm^{-1} also increased slightly, indicating that alcohols and alkanes in bio-oil increased slightly[41]. However, C--O--C stretching vibrations at 1132 and 1011 cm^{-1} , uncoupled C=O stretching vibration at 1718 cm^{-1} , and C=C stretching vibration at 1615 cm^{-1} were all nearly identical in intensity, it suggested that the contents of ethers, aldehydes, ketones, acids, esters and olefin compounds in bio-oil remained nearly constant [35,42,43].

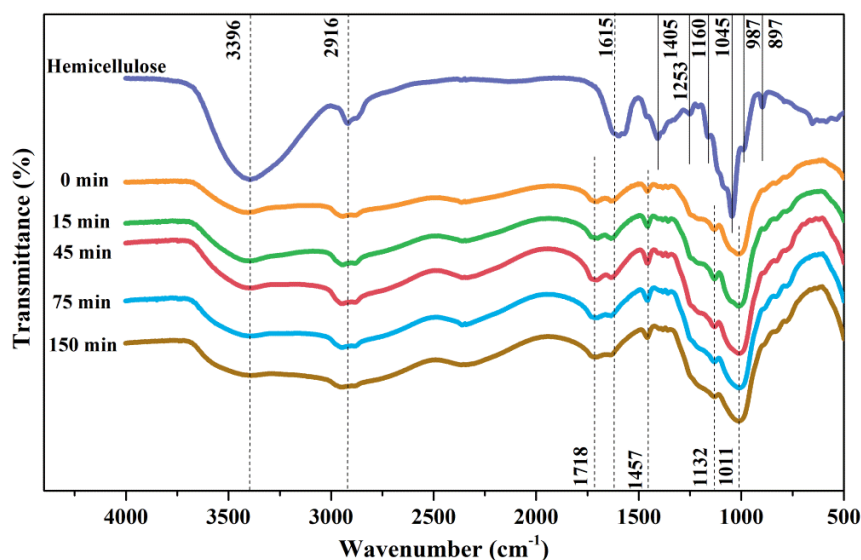


Figure.3. FT-IR spectra of bio-oil at different reaction times.

3.3. Molecular weight of bio-oil and its polydispersity.

Table 1 Average molecular weight and polydispersity of bio-oil at different reaction times.

Reaction time (min)	0	15	45	75	150
M_n (g·mol ⁻¹)	169	173	170	167	170
M_w (g·mol ⁻¹)	228	267	278	284	310
M_w/M_n	1.35	1.54	1.64	1.70	1.82

The average molecular weight and polydispersity (M_w/M_n) of bio-oil synthesized from hemicellulose at different reaction times was summarized in **Table 1**. As shown, the number-average molecular weight (M_n) of bio-oil remained relatively stable at approximately 170 g/mol, while the weight-average molecular weight (M_w) increased from 228 to 310 g/mol with increasing reaction time. The polydispersity rose from 1.35 to 1.82. These results suggested that the bio-oil produced through H_3PO_4 -catalyzed liquefaction of polyols PG/DEG contained a high proportion of long-chain components and exhibited a broad molecular weight distribution [44]. It was expounded that with the progress of the liquefaction reaction, the LMW produced by the degradation of hemicellulose were relatively decreased, while the larger molecular weight produced by polymerization between the degradation

product and PG/DEG were increased [45]. Furthermore, the degradation of hemicellulose has been completed in the heating stage. Therefore, in the process of liquefaction, the polymerization of degradation products was the main process in the insulation stage [46].

3.4. ¹H-NMR changes of bio-oil.

Figure 4a showed ¹H-NMR spectroscopy of bio-oil at reaction times of 0, 15, 45, 75, and 150 min.

From the comparison of five groups of bio-oil hydrogen spectrum, bio-oil was a complicated mixture. Although their ¹H-NMR spectra were generally similar, there were still some differences. At 2.07 ppm, the proton signal was assigned to the solvent (acetone-d₆) [34]. The hemicellulose bio-oil at 0 min had proton signal of hydrocarbon substances such as -CH₂- in the signal δ 1.50 to 0.85 ppm, indicating that hemicellulose had been degraded to a large extent during the heating process [36]. Their signal areas averaged 5.84, 5.27, 4.90, 4.83, and 4.01 protons as time passed, in other terms, with the liquefaction reaction progress, the signal intensity in this area steadily reduced. It was considered that -CH₂- and other hydrocarbon compounds generated from hemicellulose degradation in the liquefaction heating stage can be combined with PG/DEG or other polymerization reactions to generate macromolecules in the liquefaction heating stage. The characteristic signal of β-D-xylose matrix was not found in the δ 3.27 and δ 4.66 ppm of the five groups of hemicellulose bio-oils. Meanwhile, the signal bands (δ 3.80-3.20 ppm) of the five groups originated from protons of esters, ethers alcohols, etc. (**Figure 4b**) [32]. Which may be attributed to the violent degradation of hemicellulose in the liquefaction heating stage and the transformation of xylose unit structures into compounds such as esters, ethers, and alcohols in the liquefaction heating stage [47,48]. C_γ-H, C_β-H and C_α-H were found at δ 4.60-4.00 ppm of all samples. It indicated that γ, β and α substitution reactions appeared in LMW compound and PG/DEG formed by hemicellulose liquefaction degradation regardless of the length of reaction time. In addition, there were multiple signals resonated at 3.64 and 3.54 ppm, which was due to the diversity of degradation products of hemicellulose, which was the result of the superposition of multiple products.

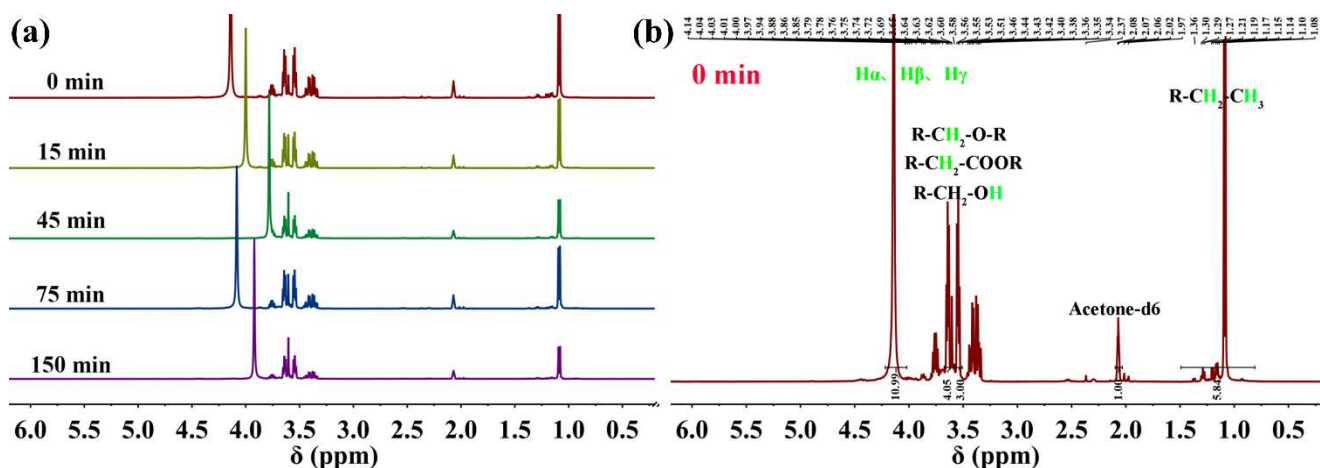


Figure.4. ¹H-NMR spectra of bio-oil (a) at 0, 15, 45, 75 and 150 min, and (b) at 0 min.

3.5. ¹³C-NMR changes of bio-oil.

¹³C-NMR spectra of bio-oil produced at different reaction times were illustrated in **Figure 5**. According to the **Figure 5a**, the carbon spectra of five bio-oil were relatively close, indicating that there were numerous commonalities in the molecular structures of the bio-oil obtained from hemicellulose during the liquefaction and heating stage. The signals at δ 206.62 and 29.26 ppm were originated from the reference substance acetone-d₆ [32].

Signals in the range of δ 180-160 ppm were attributed to the carboxyl carbon. There was no obvious signal at δ 160-120 ppm, which demonstrated that there was no lignin of isolated hemicellulose[49]. The signal of bio-oil mainly existed at the 80-60 ppm, it proved that hemicellulose degraded into complex oligosaccharides or monosaccharides in PG/DEG system catalyzed by H₃PO₄, and oligosaccharides were changed into furfural compounds and levulinic acid in acid [50]. For example, The signals were discovered near δ 148.71, 112.59, 122.08, 153.02, 177.93 ppm, as well as δ 177.93, 29.06, 38.10, 206.23, 24.52 ppm, correspond to characteristic chemical shifts of C-5, C-4, C-3, C-2, and C-1 in furfural and levulinic acid, respectively (**Figure 5b**) [51]. The characteristic signal of alkanes (-CH₂- and -CH₃) was detected at 40-10 ppm, indicating that a large number of alkanes or LMW alkanes were generated and reacted with PG/DEG during the liquefaction degradation.

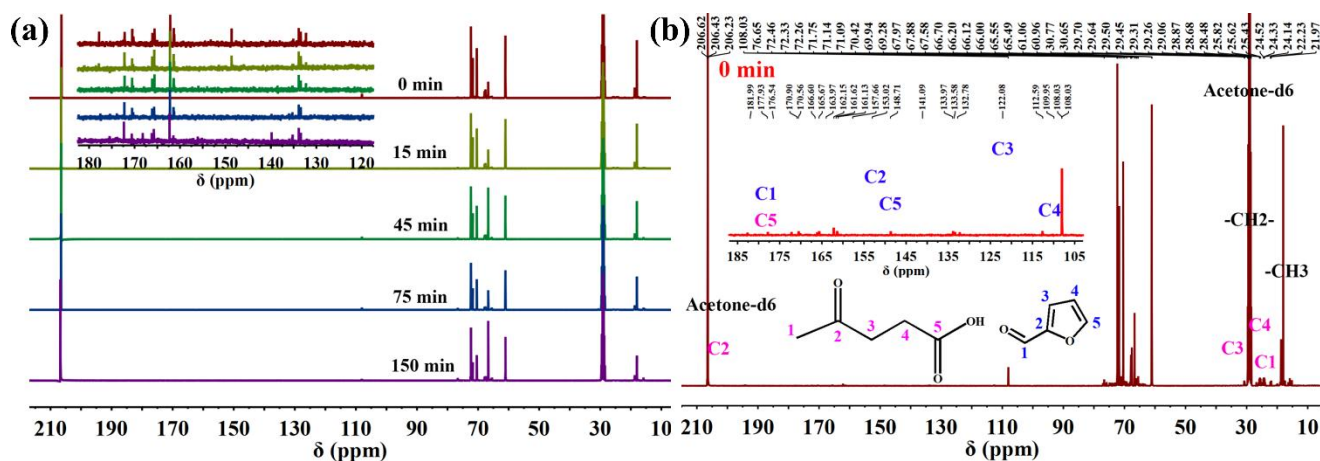


Figure 5. ^{13}C -NMR spectra of bio-oil (a) at 0, 15, 45, 75 and 150 min, and (b) at 0 min.

3.6 Changes in TGA of bio-oil.

The bio-oil's boiling point distribution could be estimated by thermogravimetric (TG) [52]. TG and derivative thermogravimetric (DTG) curves of bio-oil obtained at liquefaction time of 0, 45 and 150 min were exhibited in **Figure 6 (a)** and **(b)**, respectively. In the curves **(a)**, the bio-oil's mass loss with the liquefaction time of 0, 45 and 150 min were about 40%, 37% and 32% at 30~150 °C, decreasing successively. At 150~350 °C, the mass loss were about 45%, 49% and 55%, increasing successively [53]. It proved that the compounds (e.g., naphtha gas oil and refinery oil) having less than ten carbon atoms decreased while the compounds with $\text{C}_{10}\text{--C}_{25}$ (e.g., diesel, kerosene and heavy oil) increased in hemicellulose liquefaction, which also verified that the polymerization at this stage was the main reaction in the process of the liquefaction [36,54,55]. As could be seen in curves **(b)**, the maximum mass loss rate signal in the three curves shifted to the high temperature area, demonstrating that the carbon number of chemicals present in bio-oil had a distinct dispersion, in general, as the reaction time prolonged, the carbon chain in bio-oil increased [32]. This conclusion was consistent with the result of GPC detection. At 350~600 °C, less than 5% of the three groups of bio-oils were decomposed. In addition, the carbonaceous residue yields of the three groups of bio-oil were 10.5%, 11.5% and 12.4%, respectively. This meant that there were a few substances in the bio-oil with a carbon number greater than 25. Summarily, more than 85% of the substances with carbon number lower than 25 were present in bio-oil obtained from the liquefaction of hemicellulose.

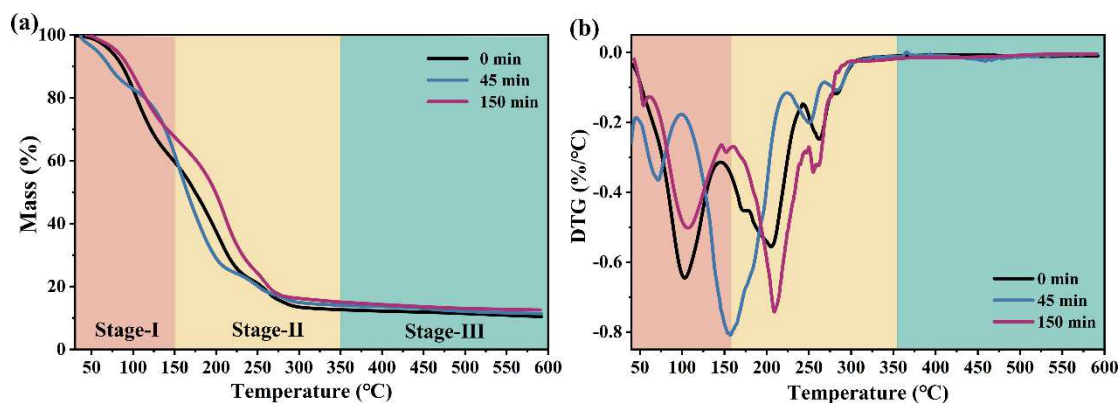


Figure 6. TG curves (a) and DTG curves (b) for bio-oil at various reaction times.

3.7 Changes of chemical groups in liquefaction residue.

Figure 7 showed the FT-IR spectra of hemicellulose and its liquefaction residue generated at 0, 15, 45, 75 and 150 min. As shown, FT-IR spectra of hemicellulose during the liquefaction reaction were significantly different ascribing to damaged or modification of hemicellulose under PG/DEG liquefaction catalyzed by H_3PO_4 . Sugar unit vibrational O—H stretching generated the high absorption signal at 3400 cm^{-1} . At 2920 cm^{-1} , the absorption signal was owing to vibration C—H stretching of alkyl group, both of which were present in hemicellulose and all residue. Hemicellulose glycosyl unit absorption signals were mostly localized between 1600 and 800 cm^{-1} [56]. There was an O—H in-plane bending vibration signal near 1405 cm^{-1} . Regarding the β -glycosidic linkages between sugar units, the absorption signal near 897 cm^{-1} was due to C-1 group frequency vibration [48]. The absorption signal of about 1045 cm^{-1} came from the sugar unit C—O—C stretching. Signal represented xylan, side chain arabinose group, at $1170\sim 1000$ and 1160 cm^{-1} , respectively [31]. the signal at 987 cm^{-1} was from $\text{C}_3\text{—H}$ bending vibration of xylose. However, those were not observed in the liquefaction residue, indicating that the liquefaction residue had become a new substance under PG/DEG liquefaction. In general, the chemical structure of hemicellulose had changed in the liquefaction heating stage and polymerization became dominant in the liquefaction system. The signal of hemicellulose at 1604 cm^{-1} was divided into 1705 (unconjugated C=O stretching) and 1604 cm^{-1} (conjugated C=O stretching) in the liquefaction residue spectrum, the intensity of these two signals increased with the prolongation of reaction time, suggesting that the degradation products were polymerized to form carboxyl or carbonyl groups [33,43].

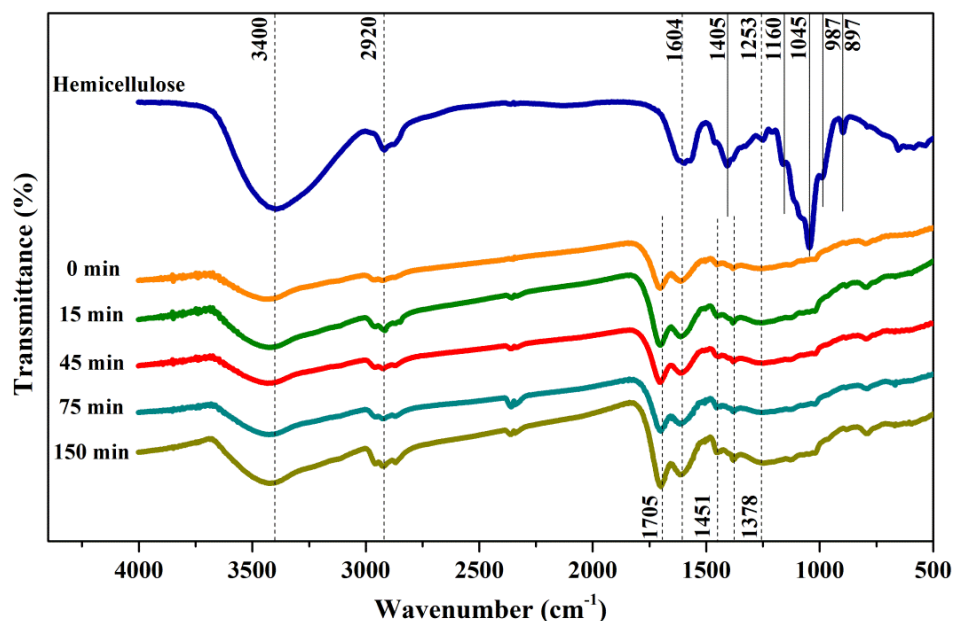


Figure 7. FT-IR spectra of liquefaction residue at different reaction times.

3.8 TGA changes of liquefaction residue.

The TGA curves of hemicellulose and its liquefaction residue obtained under different reaction times were seen in **Figure 8**. As shown, TG-DTG curves of the three liquefaction residue were identical. At around 100 °C, it was found that all samples exhibited dehydration peaks in their DTG curves, due to the moisture removal [57]. However, there were significant differences in the thermal degradation behavior of hemicellulose and its liquefaction residues within the range of 150~650 °C. The main loss revisits the area of hemicellulose (as a control group) and liquefaction residue was at 150-350 and 250-650 °C, which showed that the liquefaction residue had a larger main loss revisit the area and a higher termination reaction temperature. The reason was that some polymers with high molecular weight and melting point were formed in the liquefaction process [58]. The maximum mass loss rate signals of the three liquefaction residues were found at 400 °C, and the final mass loss rate was about 52%, which was significantly lower than hemicellulose (77%). The results expounded that hemicellulose degradation was almost complete during PG/DEG liquefaction, the liquefaction residue was a polymerization generated by polymerization between degradation products produced by hemicellulose or between PG/DEG. Its chemical structure changed significantly, so the pyrolysis of hemicellulose liquefaction residue also became different.

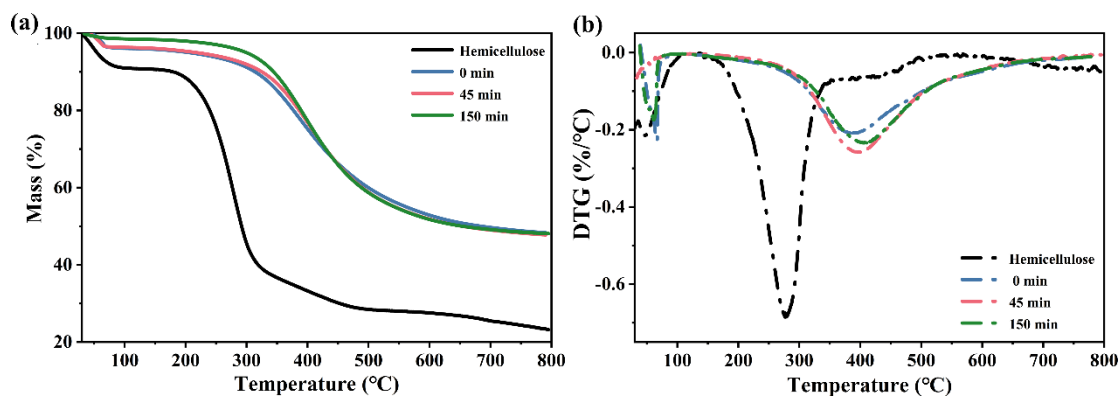


Figure.8. TG (a) and DTG (b) curves of liquefaction residue at various reaction times.

3.9 Mechanism analysis of polyols in hemicellulose liquefaction.

According to the above various detection and analysis of liquefied product, it was speculated that PG/DEG degradation of hemicellulose was intense and had been almost completed in the heating stage. **Figures 9** and **10** expressed reaction paths of hemicellulose in H_3PO_4 and PG/DEG liquefaction. As seen in **Figure 9**, hemicellulose can be transformed into furfural substances catalyzed by H_3PO_4 , which had relatively active chemical properties due to a furan ring and an aldehyde group and it can be converted into furfural derivatives, levulinic acid, tetrahydrofurfural, 5-hydroxymethylfurfural (HMF), etc [59–61]. As shown in **Figure 10**, the chains of hemicellulose macromolecules were broken for hydrolysis by H_3PO_4 , providing a considerable amount of pentosan and hexosan, which were then translated into different glycosides by PG/DEG, and PG/DEG glycosides of LMW are further degraded into furfural derivatives and alcohols, acids, esters, and ketones (aliphatic ketones and cyclopentanones) [62,63]. These derivatives can be degraded to soluble LMW compounds, and can also be polymerized with hemicellulose degradation products to form insoluble liquefaction residue.

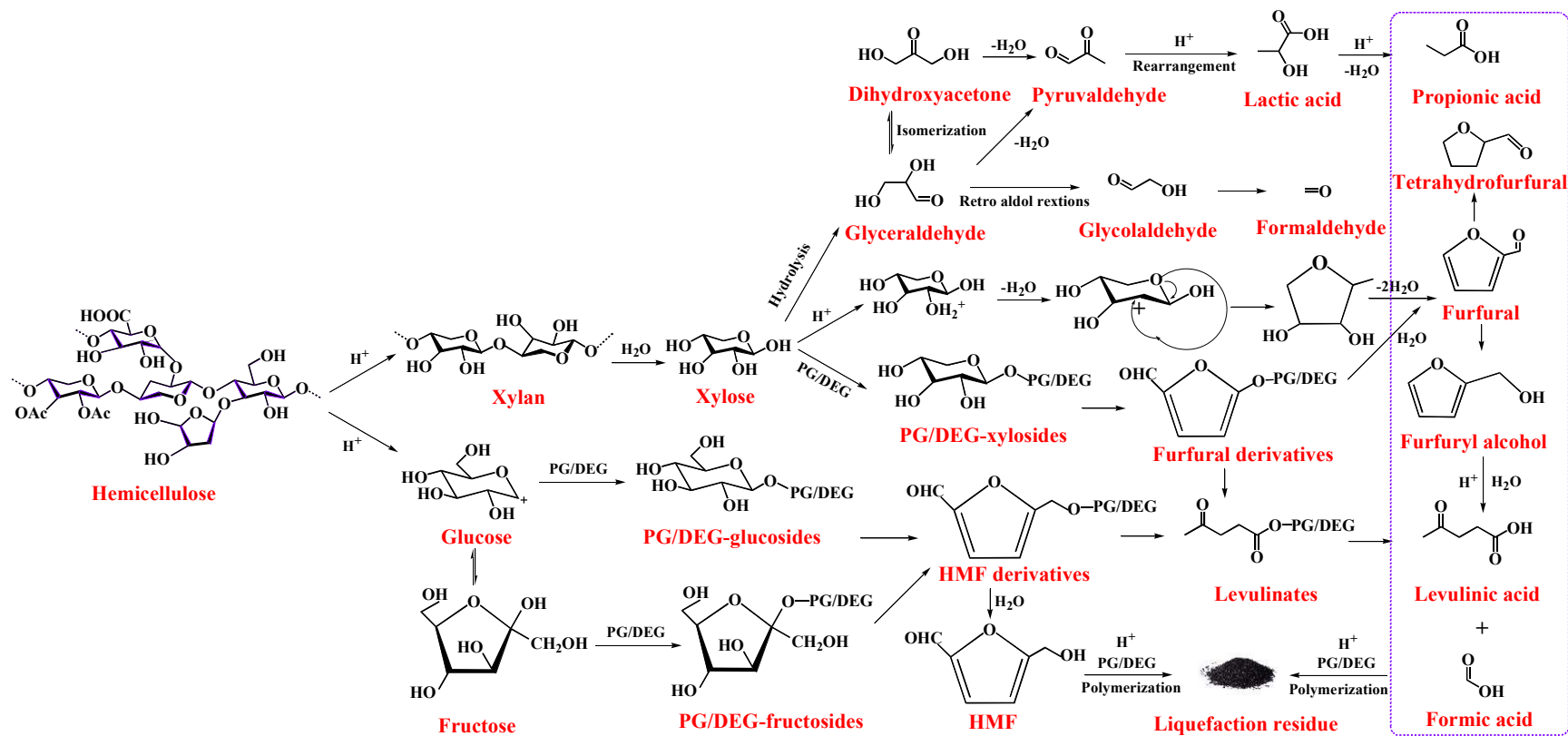


Figure .9. Hemicellulose degradation process in PG and DEG liquefaction.

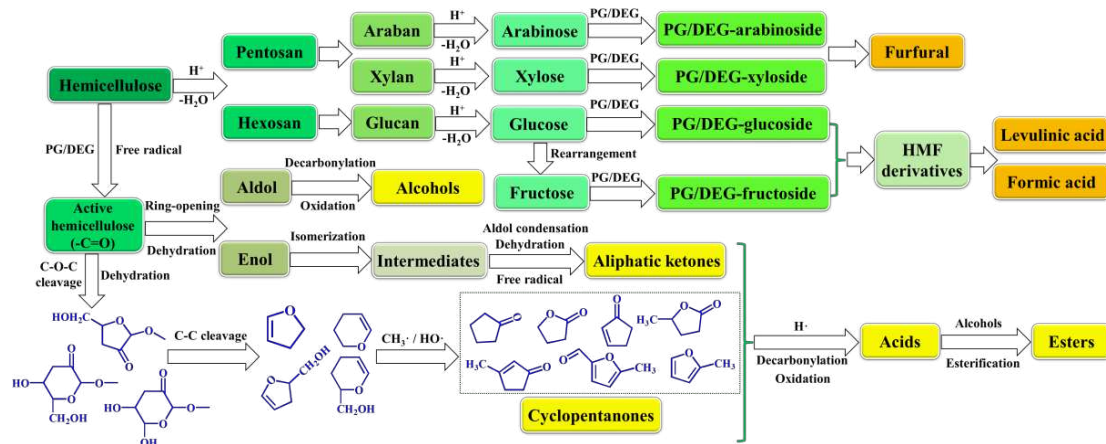


Figure .10. Hemicellulose degradation process in PG and DEG liquefaction.

In conclusion, Chemical reactions such as polymerization and cyclization can occur between PG/DEG free radicals and intermediate products generated by hemicellulose degradation, such as small molecular free radicals, to inhibit the re-degradation of LMW intermediate products to produce gas or solid products. As a result, tiny molecule fragments can be coupled with PG/DEG free radicals to produce small molecular substances (ethers, alcohols, ketones, acids, esters, etc.). Under the catalysis of H_3PO_4 , PG/DEG can be polymerized with LMW from hemicellulose degradation or degradation transformation. For example, at the liquefaction holding stage, levulinic acid and glycoside degraded from hemicellulose interacted with PG/DEG to produce macromolecules, which was one of the primary routes of liquefaction residue generation.

4. Conclusion

The liquefaction degradation of corn stalk hemicellulose via PG/DEG catalyzed by H_3PO_4 was explored in this article. The degradation of hemicellulose was completed in the liquefaction heating stage, while in the liquefaction holding stage, the polymerization reaction mainly generated substances with larger molecular weight. With the development of liquefaction reaction, both the molecular weight polydispersity (1.35-1.82) and M_w (228-310 g/mol) of bio-oil obtained from hemicellulose liquefaction increased, indicating a wide molecular weight distribution and a gradual increase in the composition of long-chain molecules. In other words, compounds with carbon numbers less than 10 were decreased, while those with

carbon numbers between 10 and 25 were increased. Hemicellulose was destroyed or modified under the liquefaction of PG/DEG catalyzed by H_3PO_4 , and liquefaction residue was the repolymerization product created by polymerization reaction between degradation products produced by hemicellulose or with PG/DEG, and its chemical structure changed substantially, resulting in the formation of a new molecule. Hemicellulose was dominated by polymerization during the liquefaction reaction.

Author Contributions

Yan Zhang: conceptualization (lead), data curation (lead), formal analysis (lead), funding acquisition (lead), investigation (lead), methodology (lead), project administration (lead), writing – original draft (lead), writing – review and editing (lead). **Xu Chen:** methodology (supporting), software (supporting), supervision (supporting), validation (supporting), visualization (supporting). **Jianfeng Ji :** methodology (supporting), supervision (supporting), validation (supporting), visualization (supporting). **Zhuangzhi Gao:** methodology (supporting), software (supporting), validation (supporting). **Huifang Zhao:** methodology (supporting), supervision (supporting), validation (supporting), visualization (supporting). **Zhong Liu:** methodology (supporting), supervision (supporting), validation (supporting), visualization (supporting).

Acknowledge

This investigation was supported by the Natural Science Foundation of Zhejiang Province (LQ23C160001), and Tianjin Key Laboratory of Pulp & Paper (Tianjin University of Science & Technology), P. R. China (No. 202604).

Data Availability Statement

Data are contained within the article.

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Graphical abstract

