Liquefaction of corn stover using industrial biodiesel glycerol

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Abstract: Corn stover was liquefied using an industrial biodiesel glycerol as a liquefying agent at atmospheric pressure and low temperature. It was found that the liquefaction yield increased with increasing glycerol-to-corn stover ratios. Sulfuric acid, added as a catalyst, was found to improve liquefaction yield. The hydroxyl number, moisture content, acid number, pH value, viscosity, density, elemental composition, and higher heating value of the liquefied corn stover samples were determined. The liquefied corn stover showed a high hydroxyl number of 270−310 mg KOH/g. Fourier transform infrared spectroscopy (FTIR) results revealed the functional groups and confirmed the existence of the OH group in the liquefied corn stover, indicating that the liquefied corn stover is indeed a source of polyols and a potential chemical stock for the synthesis of polymers.

Keywords: liquefaction, corn stover, industrial biodiesel glycerol, biopolyol
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1 Introduction

Biomass is an abundant renewable resource. Biomass based energy technologies offer potential solutions to environmental and sustainability issues in energy production and uses. Biomass and biomass-based energy is therefore receiving tremendous interest and attention. Current petroleum-based energy industry is much more mature than the biomass-based energy industry in terms of technology and economy. In addition to the liquid and solid fuels, an oil refinery can

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produce various polymeric materials from fossil fuels. However, materials derived from petrochemicals are unfriendly to the environment and often harmful to human health. Therefore, many efforts have been made by scientific communities and industries to develop renewable, biodegradable, and non-toxic polymer materials. Over the years, many biorenewable and biodegradable plastic polymers have been developed, such as polylactic acid (PLA), polyhydroxyalkanoate (PHA), polycaprolactone (PCL) and polyesteramide originally from biological conversion of biomass. Researchers are now seeking ways to produce bio-polyols from thermochemical conversion of biomass and then utilize the bio-polyols to develop useful polymers[1, 2].

Conversion of biomass to bio-based products is one of the promising ways to benefit agriculture, processing industries, and the environment. Lignocellulosic biomass could be liquefied to produce polyol products which contain multiple hydroxyl groups. Liquefaction is defined as a low temperature, high pressure thermochemical process with catalysts[3]. Liquefaction of corn stover using 90% ethylene glycol and 10% ethylene carbonate mixture as liquefying agents with catalyst at moderate temperature under atmospheric pressure and preparation of polyester from the liquefied corn stover has been studied[2]. The liquefaction of other biomass such as wood, cashew nut, corn cob, or paper pulp has also been reported. The solvents used as liquefying agents can be quite flexible, extensive, and expensive. Such liquefying agents include ethylene glycol, ethylene carbonate, propanol, butanol, poly-ethylene glycol, or water[4-14]. The production of glycerol increases rapidly as the biodiesel industry and market rapidly grow, and the cost of glycerol is dramatically decreased to as low as one cent per liter. Biomass liquefaction using glycerol could be a potential good way to utilize the abundant glycerol and produce liquid fuel or polymer feedstock at low costs. Although glycerol has been used as the liquefying agent, the high liquefaction temperature (around 550 K) was required to ensure satisfactory liquefaction yield with substantial amounts of alkali such as KOH or Na_2CO_3 added as catalyst[15], and glycerol was only used as a co-agent (5%−20% in total liquefying solvent)[1, 16].

The objective of this research was to liquefy corn stover using industrial biodiesel glycerol as the liquefying agent at atmospheric pressure and low temperature and evaluate the characteristics of liquefied corn stover with different glycerol/corn stover ratios. The performance of biodiesel glycerol was evaluated through comparison with that of chemical grade glycerol.

2 Materials and methods

2.1 Corn stover

Corn stover (collected from Waseca, MN, USA) used in this experiment was dried in air. It was pulverized mechanically by a Thomas-Wiley lab mill (Model No. 3375-E15, Thomas Scientific, USA) with a 1 mm screen.

2.2 Glycerol

The glycerol from a biodiesel production plant was supplied by the Agricultural Utilization Reserach Institute *(*AURI*)*, Waseca, MN, USA. The glycerol was brown with some visible impurities. It was purified through filtration using 10 to 20 wt% diatomaceous earth (Hyflo Super Gel, Sigma-Aldrich) to remove impurities. The filtered biodiesel glycerol was called purified biodiesel glycerol. Chemical grade glycerol (ReagentPlus) was purchased from Sigma-Aldrich.

2.3 Preparation of Liquefied Corn Stover (LCS)

The liquefaction apparatus consisted of a heater, a temperature controller, and a 1000 mL three-neck flask. The three-neck flask was equipped with a reflux condenser, a thermometer, and a motor-driven stirrer. Liquefying reagents and the catalyst sulfuric acid were first placed in the flask and preheated to 100℃, and then the ground corn stover was added into the flask. Liquefaction was carried out under reflux at 160℃ for 1−8 hours with continuous stirring. Table 1 shows the compositions of the liquefaction system.

Table 1 Compositions of the liquefaction system

Glycerol/Corn stover	Glycerol/g	Corn stover/g	Sulfuric acid/g
2:1	100	50	3
3:1	100	33	2
4:1	100	25	1.5
5:1	100	20	1.2

2.4 Measurement of Insoluble Residues Ratio (IRR) and Liquefaction Yield (LFY) of LCS

Two grams of liquefied corn stover (LCS) were diluted using 50 mL dioxane-water (4:1, V/V) and were shaken overnight at ambient temperature. The insoluble residues were filtered using a Buckner funnel and filter paper at a vacuum condition. The filter paper with insoluble residues was dried at 105℃ for 24 hours. Ten sheets of unused filter paper were dried under the same conditions to obtain the average water content of the filter paper. The insoluble biomass residues ratio (IRR) is given as follows:

$$IRR = \frac{w_2 - w_3}{w_1}$$

where w_1 is the weight of LCS before dilution with dioxane-water (2 g); w_2 is the weight of filter paper and residue left on filter paper after drying; w_3 is the weight of filter paper after drying.

The liquefaction yield is given as follows:

$$LFY\ (\%) = (1 - IRR \times w_4 / w_5) \times 100\%$$

where w_4 is the total weight of LCS and w_5 is the weight of the corn stover added in the liquefaction process.

2.5 Bio-polyol property test

1) Analysis of moisture content, viscosity, and pH value

The moisture content of bio-polyols was determined using a Schott Titroline automatic Karl Fisher titrator. The viscosity of the bio-polyols was measured using a Brookfield viscometer at 20℃ and 60% RH. The pH value of the bio-polyols was measured using a pH meter (Model 340, Corning Inc., NY) at 20℃ and 60% RH.

2) Elemental analysis

The elemental compositions, C, H, and N, of the bio-polyols were analyzed with a CE-440 elemental analyzer (Exeter Analytical, INC). The higher heating value (HHV) of each product was measured using a Bomb calorimeter.

3) Determination of acid value of bio-oils

A mixture of 2 g LCS sample and 40 mL dioxane-water solution (4/1, V/V) was titrated with a 1 mol/L NaOH to pH 8.3 using a pH-meter to indicate the end-point. Then the acid value was calculated using the formula below:

$$\text{Acid value (mg KOH/g)} = (C - D) \times N \times 56.1 / W$$

where C is the volume of NaOH standard solution consumed in sample titration, mL; D is the volume of NaOH standard solution consumed in blank titration, mL; W is sample weight, g; N is equivalent concentration of NaOH standard solution, mol/L.

4) Hydroxyl number

The hydroxyl numbers were determined according to JIS standard (JIS K1557). One gram of each polyol was weighed into a 150 mL beaker and 10 mL of phathalic anhydride solution was added (dissolving 150 g phathalic anhydride in 900 mL of dioxane and 100 mL pyridine). The beaker was covered with aluminum foil and put into a boiling water bath for 20 minutes. After cooling down, 20 mL of dioxane-water solution (4/1, V/V) and 5 mL of distilled water were added to the beaker and then titrated with 1 mol/L NaOH to pH 8.3 by using a pH-meter to indicate the end-point. The blank titration was conducted using the same procedure.

$$\text{Hydroxyl value (mg KOH/g)} = (B - S) \times N \times 56.1 / W + \text{Acid value}$$

where B is the volume of NaOH standard solution consumed in blank titration, mL; S is the volume of NaOH standard solution consumed in sample titration, mL; W is sample weight, g; N is equivalent concentration of NaOH standard solution, mol/L.

5) FTIR

FTIR spectroscopic analysis was performed using a Nicolet MAGNA-IR 750 model instrument (Thermo Electron Corporation, Madison, WI, USA) equipped with a deuterated triglycine sulphate (DTGS) detector and fitted with a potassium bromide beam splitter. The spectrometer was continuously purged with dry air. The area of the sample to be measured was selected visually, and the contact was made between the surface of the sample and the ATR crystal. Background spectra were obtained through the ATR element when it was not in contact with the sample. The number of readings taken was 32. The software used to analyze was OMNIC (6.1a)[17].

3 Results and discussion

3.1 Effect of glycerol/corn stover ratio on the

liquefaction process

Liquefaction of corn stover in pure and biodiesel glycerol was carried out at different glycerol-to-corn stover ratios. The results are shown in Table 2. When pure glycerol was used, corn stover could be liquefied in all the tested ratios ranging from 2:1 to 5:1. With the increase of the ratios, the LFY value increased and IRR decreased, indicating that more glycerol led to better liquefaction.

Table 2 Corn stover liquefaction results

Glycerol/corn stover		IRR/%	LFY/%	Hydroxyl number /mg KOH • g^{-1}
Pure glycerol	2/1	7.22	78.34	267
	3/1	4.36	82.56	290
	4/1	3.24	83.80	360
	5/1	1.98	88.12	346
Biodiesel glycerol	2/1	ND	ND	ND
	3/1	11.91	52.36	278
	4/1	9.75	51.25	307
	5/1	8.17	50.98	309

Note: ND means not determined.

Biodiesel glycerol could liquefy corn stover though its LFY was not as good as that of pure glycerol. Liquefaction of corn stover with biodiesel glycerol failed at the glycerol-to-corn stover ratio of 2:1. When the ratio was increased to above 3:1, around 50% LFY was achieved. Surprisingly, increasing glycerol-to-corn stover ratios to above 3:1 did not produce higher LFY.

The hydroxyl values of all LCS were very high, ranging from about 270 to 360 mg KOH/g, suggesting that the LCS had a large number of active hydroxyl groups and thus a great potential to be used as polymer feedstock compared with the reported 137 mg KOH/g for LCS with ethylene carbonate[1]. We know one glycerol molecule has three hydroxyl groups, so the resulting liquefied product will definitely have a high hydroxyl number when glycerol is used as the liquefying agent.

It is worthwhile to point out that unliquefied biomass residues may play a less important role if LCS is to be used as chemical building stocks for making polymers instead of liquid fuels. The insoluble residues in the LCS may react with other reagents to form polymers or act as "fillers" in the polymer morphology. Therefore the impact, whether negative or positive, of these unliquefied biomass residues on the performance of bio-polymers made from LCS should be evaluated in future studies.

3.2 Effect of reaction time on the liquefaction process

Figure 1 shows the time dependency of the insoluble biomass residues ratio (IRR) at the glycerol-to-corn stover ratio of 4:1. At the beginning of liquefaction, the stirrer spun only the middle portion of the mixture and pushed corn stover outward to the wall of the flask where corn stover was not well mixed with glycerol for the first two hours according to observation. Corn stover well mixed with the glycerol would be liquefied and have a decreased IRR within the first two hours. The corn stover adhered to the wall of the flask gradually mixed with the glycerol and liquefied corn stover. This portion of corn stover, before its degrading, might increase the insoluble residues in the volume being sampled, causing IRR fluctuation as shown in Figure 1. The observed increase in IRR during liquefaction may also be attributed to the recondensation of liquefied biomass components. Although glycerol may suppress recondensation of the degraded components, such a suppression effect may not occur in the presence of lignin[13] since corn stover contains about 19% lignin[14-16]. By using biodiesel glycerol, IRR decreased to a lower level at sixth hour and then increased, probably due to recondensation. The lowest level of IRR for pure glycerol was found at the fourth hour. Therefore four to six hours would be an appropriate liquefaction reaction time for pure glycerol and biodiesel glycerol at the glycerol-to-corn stover ratio of 4:1 at 160℃. Similar curves of IRR were observed at glycerol-to-corn stover ratios of 3:1 and 2:1.

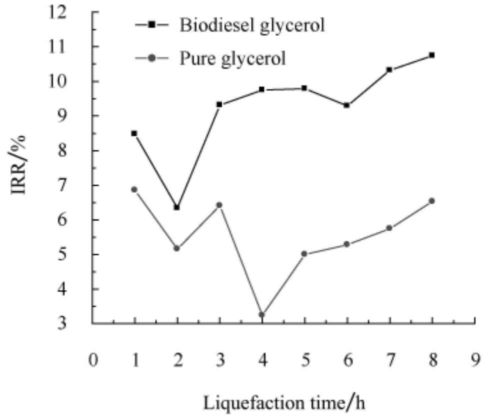

Figure 1 IRR curves of glycerol-to-corn stover ratio of 4:1

3.3 Effect of catalyst amount on the liquefaction process

The effect of catalyst content on the IRR and LFY was investigated. Figure 2 shows IRR and LFY of corn stover at the liquefaction conditions of four hours, 160℃, and a glycerol-to-corn stover ratio of 3:1. The LFY increased from 81% to 88% for pure glycerol and from 56% to 75% for biodiesel glycerol when the catalyst content was increased from 6% to 10%. The nearly 20% increase in LFY for the biodiesel glycerol indicates that catalyst played a more important role in affecting the liquefaction involving biodiesel glycerol rather than pure glycerol. For both biodiesel and pure glycerol liquefaction processes, when the catalyst content was less than 4% of the feedstock, some corn stover remained unliquefied after four hours. Liquefaction is essentially degradation of macromolecules into small molecules in the aqueous medium or an organic solvent[3]. The liquefaction reaction is called hydrolysis if water is used, or alcoholysis if alcohol such as glycerol or ethylene glycol is used. It is well known that acid or alkali can be used as catalysts in hydrolysis reactions. Hydrolysis and alcoholysis share the same mechanisms except that different acyl acceptors (water or alcohol) are involved. It is reasonable to believe that acid or alkali can catalyze the alcoholysis reaction similar to the way these catalysts promote hydrolysis. In this liquefaction process, both hydrolysis and alcoholysis occurred, with alcoholysis being more prominent than hydrolysis because the amount of glycerol is more than that of water.

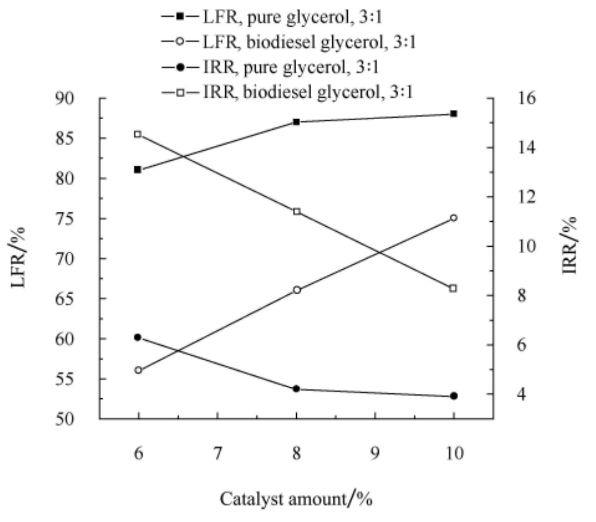

Figure 2 Effect of catalyst amount on the LFY and IRR

4 Characterization of LCS

4.1 Viscosity

Figure 3 shows the effect of glycerol-to-corn stover ratios on the viscosity of the liquefied polyols. The viscosity of both pure glycerol LCS and biodiesel glycerol LCS decreased drastically when the glycerol-to-corn stover ratio increased from 3:1 to 5:1. The viscosity was much higher for biodiesel glycerol LCS than pure glycerol LCS, especially at low glycerol-to-corn stover ratios. Although the biodiesel glycerol derived polyols had a very high viscosity, these polyols are still suitable for the preparation of polymers because of their high hydroxyl number.

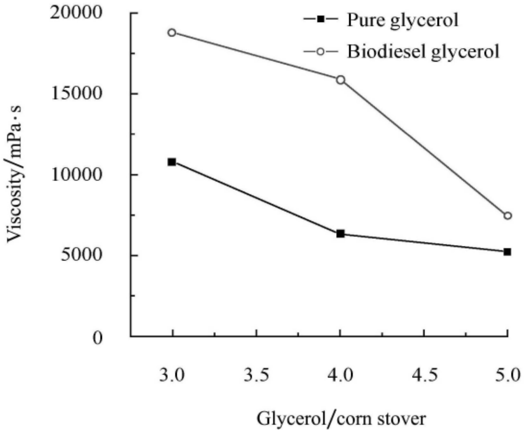

Figure 3 Effects of glycerol-to-corn stover ratios on the viscosity of liquefied corn stover.

4.2 Acid value

Acid values of the resulting polyols were used for the calculation of hydroxyl numbers. Figure 4 shows the changes of acid values in polyols as a function of glycerol-to-corn stover ratios. The polyols prepared with biodiesel glycerol had a relatively smaller acid value than the polyols made from pure glycerol. Acidic substances can be produced during the liquefaction of wood or starch[21]. The increase in acid values may be attributed to either the increase in acidic substances in depolymerized corn stover components or the oxidation of the saccharides during the liquefaction[13]. The lower acid value in the biodiesel glycerol LCS might be associated with the lower depolymerization of corn stover in biodiesel glycerol compared with that in pure glycerol.

In the meantime, according to the observation, the impurities in the biodiesel glycerol would react with sulfuric acid even without heating and thus might consume a certain amount of sulfuric acid leading to a lower acid value.

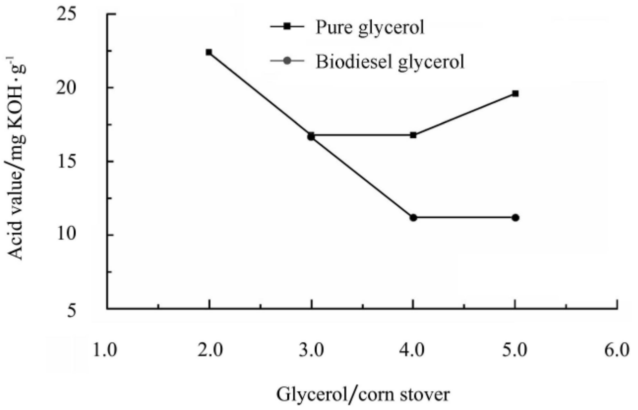

Figure 4 Acid values as a function of glycerol/corn stover ratios

4.3 Hydroxyl number

Hydroxyl numbers of liquefied corn stover increased with the increase of glycerol-to-corn stover ratios (Fig.5). This can be attributed to the high hydroxyl number of glycerol. The polyols made from pure glycerol had higher hydroxyl numbers than those made from biodiesel glycerol. This can be explained by a higher hydroxyl number in pure glycerol than that in biodiesel glycerol due to water content and impurities in biodiesel glycerol. After liquefaction, the hydroxyl number ranged from about 270 to 360 mg KOH/g. The hydrolysis reaction may break down the long chain of biomass molecules, producing extra free hydroxyl groups thus increasing the hydroxyl number. The alcoholysis reaction consumed one hydroxyl group of glycerol and in the meantime produced one free hydroxyl group on the broken down biomass molecule. The hydroxyl number decreased with the increase of reaction time. The results indicated that the decrease in the hydroxyl number during liquefaction should be attributed to an increased oxidation or dehydration reaction of the glycerol or depolymerized biomass components as reaction time increased. The decreased hydroxyl number observed with the increase of liquefaction time was also reported previously[22].

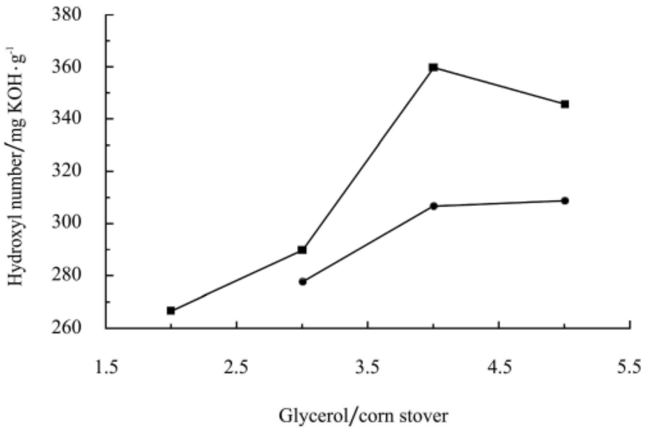

Figure 5 Hydroxyl number as a function of glycerol-to-corn stover ratios

4.4 Other characteristics

Other characteristics of liquefied corn stover were summarized in Table 3. As can be seen from the table, all LCS from pure glycerol and biodiesel glycerol as liquefying agents, had similar densities ranging from 1.23 to 1.28 g/mL. Considering the water content of 7.6% in corn stover and 0.63% in pure glycerol, the initial water contents of the reaction mixture should be 3.0%, 2.4%, 2.0% and 1.8% respectively for glycerol-to-corn stover ratios of 2:1, 3:1, 4:1, and 5:1. The water contents of polyols made from pure glycerol were similar at about 4%, which indicated that water was generated during liquefaction. This result confirmed the above stated oxidation or dehydration reactions of the glycerol or depolymerized biomass components during the liquefaction which would produce water and reduce hydroxyl value. The initial water content of the biodiesel glycerol mixture was about 8.9% with biodiesel glycerol containing 9.27% water. For biodiesel glycerol derived polyols, the water content was about 9.19% for glycerol-to-corn stover ratio of 5:1, 6.06% for a ratio of 4:1, and 4.19% for a ratio of 3:1.

Elemental analysis indicated that bio-polyols made from pure glycerol had more carbon than those made from biodiesel glycerol. Similar compositions of N and H were found in bio-polyols made from pure and biodiesel glycerol. The HHV of bio-polyols made with biodiesel glycerol were all about 1000 kJ/kg less than that of the bio-polyols made with pure glycerol.

Table 3　Properties of the seven liquefied corn stover samples

	Pure Glycerol-to-Corn Stover				Biodiesel Glycerol-to-Corn Stover		
	5:1	4:1	3:1	2:1	5:1	4:1	3:1
Density/g • mL^{-1}	1.28	1.27	1.27	1.23	1.27	1.27	1.26
Moisture Content/%	4.77	4.31%	4.01	ND	9.19	6.06	4.19
pH value	0.73	0.6	0.52	0.37	0.9	0.94	1.02
Elemental Analysis							
C/%	34.80	34.43	35.65	36.07	31.97	30.00	31.85
H/%	7.40	7.56	7.38	6.91	7.41	6.82%	7.20
N/%	0.85	0.08	0.34	0.08	0.80	0.50	0.15
Other*/%	56.94	57.93	56.63	57.03	59.82	62.69	60.80
HHV/kJ • kg^{-1}	18074	17626	17886	17735	15340	15780	16199

Note: ND: tests could not be done for ratio of 2:1, due to its high viscosity.　* The remaining percent was calculated to be other elements including O.

4.5　FTIR

The FTIR spectrum of pure glycerol, purified biodiesel glycerol, and unpurified biodiesel glycerol are shown in Figure 6. The three spectra were almost identical except at 1670 cm^{-1}. The FTIR spectrum of corn stover is also shown in Figure 6. The spectrum of glycerol is very similar to the spectrum of liquefied products (Figure 7 and 8). It indicates that there should be some glycerol remaining in the resulting LCS. The spectrum of corn stover is significantly different from that of LCS, indicating that the corn stover was digested into smaller molecules, though part of the liquefied corn stover remained in solid state. The functional groups identified from the FTIR spectrum of bio-polyols are shown in Table 4. As seen in Figure 7 and 8, the bio-polyols prepared from pure glycerol or biodiesel glycerol as liquefying agents almost perfectly overlapped each other. Similar functional group peaks were found in bio-polyols prepared from pure glycerol and biodiesel glycerol; however, the peak appearing at 1600−1700 cm^{-1} turned out to be less in the biodiesel glycerol derived bio-polyols. The functional group within this range could be C=O. The widespread and relatively large peak between 3300−2400 cm^{-1} corresponds to the -OH stretching vibrations, which is associated with free H_2O, -OH groups of non-bonded polyol. This again proved the bio-polyols contained a large amount of hydroxyl group. The peak between 2850−3000 cm^{-1} corresponded to a C-H stretching vibration, which indicates the presence of aliphatic hydrocarbons. The peaks occurring at 1700−1740 cm^{-1} may represent the C=O in aldehyde, ketone, and carboxylic acid. The peaks between 1000−700 cm^{-1} corresponded to a C-H out of plane bending caused by aromatic structure. The peaks between 1450−1600 cm^{-1} corresponded to a C=C stretching caused by aromatic structure. The aromatic rings can be determined between 700 and 850 cm^{-1} [23].

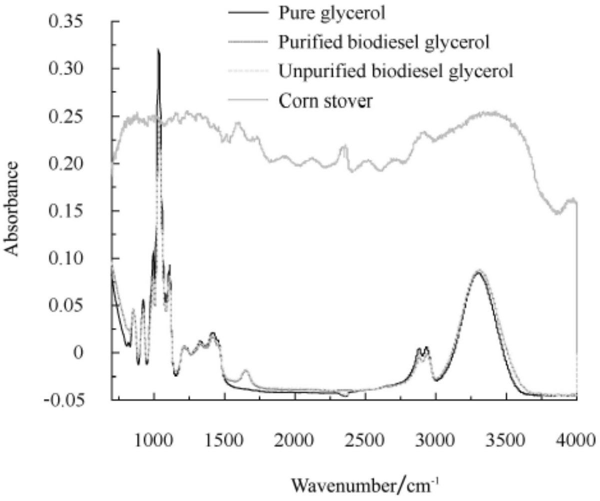

Figure 6　FT-IR spectra of glycerols and corn stover

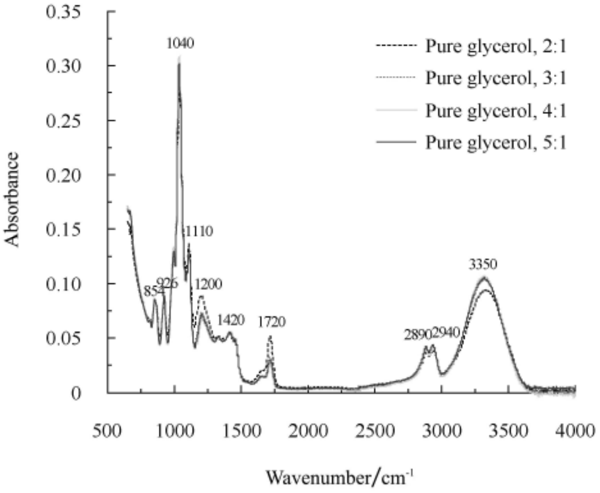

Figure 7　FT-IR spectrum of bio-polyols using pure glycerol as the liquefying agent

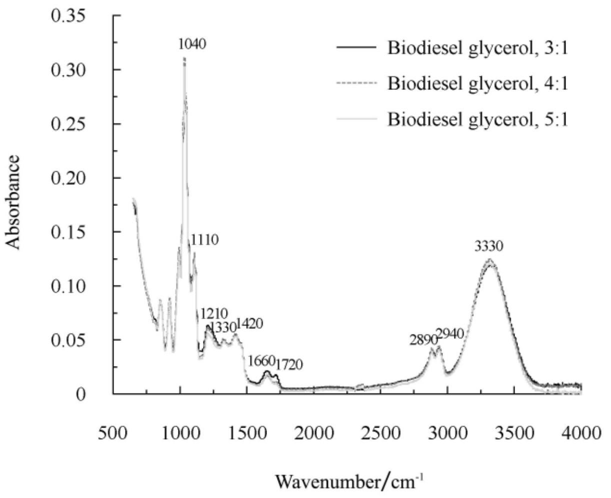

Figure 8 FT-IR spectrum of bio-polyols using biodiesel glycerol as the liquefying agent

Table 4 Functional groups in bio-oil according to the FTIR analysis

Functional groups	Type of vibration	Intensity	Wave numbers /cm^{-1}
-OH (associated)	stretching	m	3400～3200
-C-H (Alkanes)	stretch	s	3000～2850
-C-H (aromatics)	out of plane bend	s	1000～700
-C-H (Aldehyde)	stretching	w	2900～2800
C=C (Alkene)	stretching	m-w	1680～1600
C=C (aromatic)	stretching	m-w	1450～1600
C=O (Aldehyde)	stretching	s	1740～1720
C=O (Ketone)	stretching	s	1725～1705
C=O (carboxylic acid)	stretching	s	1725～1700
C-O Alcohols, ethers, esters, carboxylic acids	stretching	s	1300～1100
Aromatic rings			700～850

Note: s, strong; m, medium; w, weak.

5 Conclusions

Experimental results demonstrate that inexpensive industrial biodiesel glycerol can be used as a liquefying agent to liquefy corn stover at atmospheric pressure and low temperature. The liquefied corn stover (LCS) had a high hydroxyl value, making the LCS a potential biopolyol source for making biopolymer. In this study, the effects of glycerol-to-corn stover ratio, addition of catalyst, and reaction time were evaluated. Liquefaction yield increased with the increase of glycerol-to-corn stover ratios. Sulfuric acid, added as a catalyst, was found to improve the liquefaction yield, particularly when biodiesel glycerol was used as the liquefying agent. Near complete liquefaction of corn stover was achieved within four to six hours at 160℃. The moisture content, acid number, pH value, viscosity, density, elemental composition, and higher heating value of the LCS samples were also determined. FTIR results revealed the functional groups and confirmed the existence of the OH group in the LCS, thus verifying that they could be called polyols and have potential applications in the synthesis of polymers.

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