

Separation and Characterization of Biomass Components (Cellulose, Hemicellulose, and Lignin) from Corn Stalk

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Representative hemicellulose, milled wood lignin (MWL), and cellulose were directly separated from corn stalk, and their main chemical content was determined using NREL methods. The chemical elements, chemical groups, and molecular structure of corn stalk biomass components (hemicellulose, MWL, and cellulose) were analyzed by elemental analysis, Fourier transform infrared, and nuclear magnetic resonance spectroscopy analyses. The results showed that the purity of the biomass components separated from corn stalk was high, the degree of damage was relatively small, and their own structural characteristics were relatively intact. The hemicellulose that was separated from corn stalk was mainly composed of L-arabino- β -(1 \rightarrow 4)-D-glucuronoxylan units. There were also sugar residues attached to the main chain in the form of side chains, such as D-glucopyranose, galactose, glucuronic acid, and galacturonic acid. The isolated cellulose consisted of glucosyl linked by β -(1 \rightarrow 4)-glucosidic bond. The MWL separated from corn stalk has a GSH-type of β -O-4 structure, and the contents were as follows, in order of more to less: guaiacyl (G), p-hydroxyphenyl (H), and syringyl (S) units. Biomass components with high purity were separated from corn stalk, and their respective structure and composition were understood, which provides a foundation for the subsequent high-value utilization of corn stalk.

Keywords: Corn stalk; Cellulose; Hemicellulose; MWL; Separation

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INTRODUCTION

The efficient conversion and utilization of renewable lignocellulosic biomass is a hot global research interest. It is generally recognized that lignocellulosic biomass is composed of three polymers (hemicellulose, lignin, and cellulose) (Zhang *et al.* 2019a), a small amount of organic matter, and mineral substances (Yang *et al.* 2006; Ruffell *et al.* 2010). The polymers in the first three main categories usually account for more than 95% of biomass mass (Ragauskas *et al.* 2006). They are not a simple physical combination, but rather combined by a variety of complex chemical bonds, such as ether bond, glycoside bond, acetal bond, ester bond, hydrogen bond, Van der Waals forces, and so on. Generally, the molecular chain length and relative molecular weight of each biomass component are large. In the process of liquefaction, the structural properties of the three main polymers determine the properties of the liquefaction products, and the liquefaction characteristics of the biomass components show great differences due to their different chemical structures. In the process of catalytic liquefaction, the lignocellulosic biomass with

complex composition is degraded, alcoholized, and polymerized to produce liquefaction products with more complex composition and structure. Therefore, understanding the structure and composition of corn stalk biomass components can lay a foundation for further research of the liquefaction mechanism (Zhang *et al.* 2019b), and make a large number of corn stalk resources achieve high value-added utilization.

The separation methods of biomass components have a great impact on researchers all over the world. There has been increased attention by researchers to overcome the shortcomings of separating lignin, hemicellulose, and cellulose from plant stalk under harsh high temperature and high pressure conditions, along with the low purity and recovery efficiency of the separated components.

Corn stalk was pretreated with ethanol and nitric acid at atmospheric pressure, then steamed using dilute alkali solution and treated by hydrogen peroxide. Efficient separation and recovery of lignin, hemicellulose, and cellulose components were expected (Ma *et al.* 2015). The results revealed that the content of organic matter in the waste liquid produced in the separation process was much smaller than that of other methods that only recover cellulose. The waste liquid mainly consisted of inorganic salts, and the waste liquid treatment was relatively simple. This method overcame the disadvantages of the current atmospheric pressure separation process, such as inability to realize the separation and recovery of the whole component (Kim and Lee 2006; Gao *et al.* 2009), low purity of the obtained components, lack of quantitative analysis of component purity, and a non-environmentally friendly process (Nawshad *et al.* 2012).

At present, knowledge regarding the reaction processes of non-wood biomass components liquefaction is vague and needs to be further researched. In this work, representative hemicellulose, lignin, and cellulose were directly separated from corn stalk, and then the main chemical content, functional groups, and organic structures of biomass components were systematically analyzed using National Renewable Energy Laboratory (NREL) methods, elemental analysis (EA), Fourier transform infrared spectroscopy (FTIR), cross-polarization/magic angle spinning carbon-13 nuclear magnetic resonance spectra (CP/MAS ^{13}C -NMR), proton nuclear magnetic resonance spectra (^1H -NMR), and carbon nuclear magnetic resonance spectra (^{13}C -NMR). This study's objectives were the following: further understand the chemical structures of the biomass components isolated from corn stalk; provide theoretical guidance for the subsequent analysis of the liquefaction and deconstruction rules and the formation mechanism of liquefaction products from the structural level; and promote the efficient utilization of biomass resources and the development of biomass-based products. At the same time, this separation method has some merits, such as mild reaction conditions, environmentally friendly character, simple operation, and its availability as a practical way of classification using corn stalk.

EXPERIMENTAL

Materials

Corn stalk was taken from farmland in Tanggu, Tianjin, China, crushed (20 to 80-mesh). The moisture content was balanced through equilibration, and then the material stored until further use. The chemical composition of corn stalk was summarized as follows: cellulose 36.89%, hemicellulose 20.42%, lignin 17.38%, ash 2.43%, cold water extract 19.40%, hot water extract 20.43%, ethanol extract 13.80%, and 1% NaOH extract 36.89%.

Analytically pure reagents (concentrated hydrochloric acid, glacial acetic acid, sodium chlorite, acetone, and potassium hydroxide) and chromatographic pure reagents (deuterated dimethyl sulfoxide, heavy water, potassium bromide, D-(+)-glucose, L-(+)-arabinose, and D-(+)-xylose) were purchased from Sinopharm Chemical (Shanghai, China) and Cambridge Isotope Laboratories Inc. (Tewksbury, MA, USA), respectively.

Separation and Purification of Corn Stalk Biomass Components

Corn stalk powder was extracted in anhydrous ethanol (99 °C water bath, 9 h) and air-dried, and then separated by biomass components. The separation process is shown in Fig. 1.

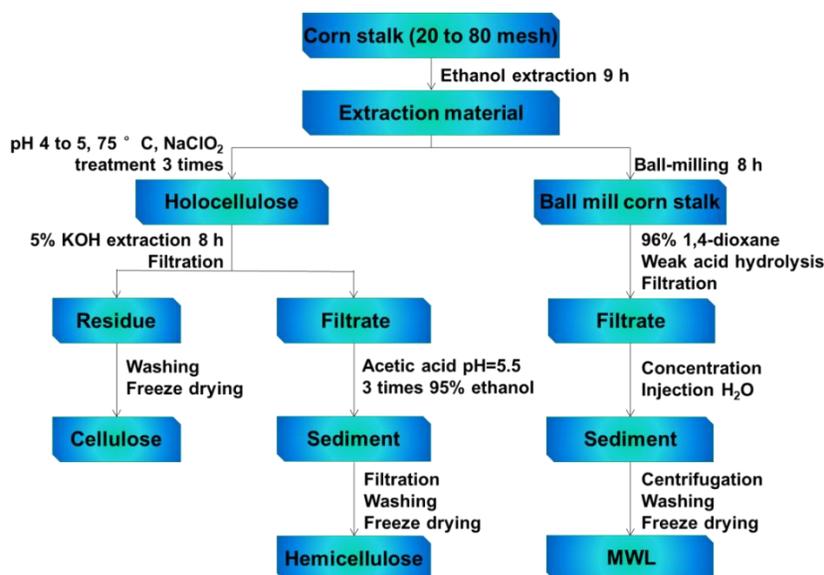


Fig. 1. Schematic for separation of hemicellulose, cellulose, and MWL from corn stalk

Separation of MWL

The extracted and air-dried corn stalk powder was ground in a ball mill tank (20 revolutions/min, 8 h), and the moisture was measured after equilibrium. A total of 8 times of water-dioxane solvent (9:1) was added into the milled corn stalk powder, and then a small amount of hydrochloric acid was injected, making the concentration 0.2 mol/L. The solution was stirred at room temperature for 36 h, filtered, concentrated to 3 to 5 mL, injected with 2000 mL H₂O, precipitated, and let stand until further use. The supernatant was removed by siphon method. The precipitated MWL was centrifuged, washed 3 to 5 times, and then freeze-dried.

Separation of hemicellulose

A total of 10 g (absolute dry weight) extracted corn stalk powder and 325 mL deionized water were injected into a 500-mL conical flask, shaken well, and glacial acetic acid was added to make the pH value of the mixture within the range of 4 to 5. Subsequently, 3 g of NaClO₂ (according to 100%) was poured, shaken, covered with a 100-mL conical flask, and the whole device was placed in a water bath at 75 °C. After 1 h, glacial acetic acid and NaClO₂ were added. The lignin was completely removed after three times of operation until the corn stalk powder turned white. Finally, the holocellulose was obtained by filtration, washing, and drying.

Holocellulose was extracted with 5% KOH solution (solid-liquid ratio 1:15, room temperature, and 8 h). The filtrate was neutralized with glacial acetic acid until the pH value of the solution was approximately 5.5. Then, the hemicellulose was precipitated with 3 times volume of 95% ethanol. After standing, siphoning, and centrifuging, the solid was washed with ethanol and deionized water 3 times. Finally, the hemicellulose component was obtained after freeze-drying.

Separation of cellulose

This process was done following a previous study by Lv and Wu (2012). The solid residue obtained after extraction and filtration of the holocellulose was washed to neutral (pH = 7) with deionized water, and then washed with acetone 3 times and freeze-dried.

Analysis of Main Components of Biomass Components

Determination of cellulose and hemicellulose content

The content of cellulose and hemicellulose in corn stalk was determined by NREL method (Yang *et al.* 2007; Peng and Wu 2010). A total of 300 ± 10 mg of the extracted and dried corn stalk powder (m_0 , g, oven-dry) was transferred into a 10-mL centrifuge tube. Next, 3 mL of 72% sulfuric acid was added and shaken well, then hydrolyzed in a water bath at 30 °C for 1 h. It was transferred to a 100-mL conical flask, 84 mL of ultrapure water was injected and weighed. The resulting mixture was sealed, sterilized (121 °C, 1 h), filtered, and the filtrate pH was adjusted to 1 to 3. The concentrations of glucose (C_{glu} , mg/mL), arabinose (C_{ara} , mg/mL), and xylose (C_{xyl} , mg/mL) were determined by high-performance liquid chromatography (HPLC, 1200 series; Agilent Technologies, Palo Alto, CA, USA). Substituting them into Eqs. 1 and 2, respectively, the content of cellulose (C , %) and hemicellulose (H , %) in corn stalk can be calculated:

$$C (\%) = \frac{C_{glu} \times 87 \times 10^{-3} L \times 0.90}{m_0} \times 100 \quad (1)$$

$$H (\%) = \frac{(C_{xyl} + C_{ara}) \times 87 \times 10^{-3} L \times 0.88}{m_0} \times 100 \quad (2)$$

Determination of acid insoluble lignin content

The content of acid insoluble lignin was measured by NREL method (Sluiter *et al.* 2010). The residue obtained from two-step acid hydrolysis was washed with hot distilled water until the filtrate was neutral. It was placed in an oven at 105 °C for constant weight, m_1 (g), and then carbonized, burned in a muffle furnace at 575 °C for 4 h, cooled and weighed, m_2 (g). The content of acid-insoluble lignin in corn stalk was calculated by Eq. 3:

$$L (\%) = \frac{m_1 - m_2}{m_0} \times 100 \quad (3)$$

Determination of acid soluble lignin content

A small amount of hydrolysate was taken, and its absorbance at 320 nm was measured with a DR6000 ultraviolet spectrophotometer (HaCH Corporation, Loveland, CO, USA) to determine the content of acid soluble lignin (ASL, %). The calculation formula is shown in Eq. 4,

$$ASL (\%) = \frac{UV \times V \times n}{\varepsilon \times m \times P} \times 100 \quad (4)$$

where UV is optical density, V is volume of hydrolysate (mL), m is the hydrolysate weight (g), n is dilution ratio, ϵ is the absorption coefficient, 25 L/(g·cm), and P is color plate thickness (cm).

Elemental Analysis

The mass percentage of organic elements, such as C, H, N, and S, in corn stalk and its biomass components were tested using the Vario MACRO cube elemental analyzer (Elementar, Heraeus, Germany). The content of element O was calculated by subtraction. Then, the calorific value, or higher heating value (HHV) of the sample was estimated by Dulong Eq. 5 (Sun *et al.* 1998):

$$HHV \text{ (MJ/kg)} = 0.3383Z_C + 1.422 (Z_H - Z_O/8) \quad (5)$$

Chemical Group Analysis

The 650 Fourier transform infrared spectrometer (Bruker, Karlsruhe, Germany) was used to detect the chemical groups of biomass components. The scanning range was 4000 to 400 cm^{-1} , the resolution was 4 cm^{-1} , the scanning time was 16, and the mass ratio of sample to KBr was 1:100 (Zhang *et al.* 2018).

Molecular Structure Analysis

CP/MAS ^{13}C -NMR analysis of cellulose

Cellulose was difficult to dissolve in NMR reagent, so it was characterized using CP/MAS ^{13}C -NMR (Infinityplus 300, Varian Inc., Palo Alto, CA, USA).

^1H - and ^{13}C - NMR analysis of hemicellulose

The hemicellulose with a mass of approximately 30 mg was dissolved in 0.55 mL D_2O for the determination of ^1H -NMR (AV III 400M, Bruker, Karlsruhe, Germany) with a frequency of 16 scans.

Approximately 140 mg hemicellulose was soluble in 1.1 mL D_2O to carry out the ^{13}C -NMR (AV III 400M; Bruker, Karlsruhe, Germany), with about 20000 times scanning frequency.

^1H - and ^{13}C - NMR analysis of MWL

Approximately 30 mg MWL was dissolved in 0.5 mL DMSO-d_6 , and the frequency was scanned 8 times. Approximately 200 mg MWL was soluble in 0.5 mL DMSO-d_6 and scanned about 20000 times. ^1H - and ^{13}C - NMR were recorded using an AV III 400M spectrometer (Bruker, Karlsruhe, Germany).

RESULTS AND DISCUSSION

Analysis of Main Components of Biomass Components

The contents of the main components in hemicellulose, cellulose, and MWL obtained directly from corn stalk are displayed in Table 1. As shown, the contents were 82.50% cellulose, 12.17% hemicellulose, and 0.64% acid soluble lignin in the cellulose sample, which indicated that the cellulose isolated from corn stalk contained a small amount of hemicellulose, almost no lignin, and its separation purity was high. The hemicellulose sample contained 76.32% hemicellulose, 2.89% cellulose, and 1.63% acid

soluble lignin. It manifested that there was a minimal amount of cellulose and lignin in the separated hemicellulose. There were measurable amounts of cellulose (1.99%) and hemicellulose (2.27%) in MWL sample, including 88.86% acid insoluble lignin and 1.24% acid soluble lignin. In other words, more than 90% of lignin was present in the MWL sample. In general, the purity of the biomass components separated from corn stalk in this work was high, and they can be used as raw materials alone for subsequent scientific research.

Table 1. Main Components Contents of Cellulose, Hemicelluloses, and MWL

Sample	Cellulose Content (%)	Hemicellulose Content (%)	Acid-insoluble Lignin Content (%)	Acid-soluble Lignin Content (%)
Cellulose	82.50	12.17	-	0.64
MWL	1.99	2.27	88.86	1.24
Hemicellulose	2.89	76.32	-	1.63

Elemental Analysis

The contents of organic elements C, H, O, N, and S in corn stalk and its biomass components, and their associated HHV are summarized in Table 2. As shown in Table 2, the highest content of each element in biomass components was the following: the content of H in cellulose was 7.07%, the content of O in hemicellulose was 57.07%, and the content of C in MWL was 60.89%. Its C content was considerably higher than that in corn stalk, cellulose, and hemicellulose, resulting in the maximum HHV of MWL, which was related to the special C₃-C₆ structure of MWL. The high content of C was also the main factor that caused MWL to generate coke during biomass pyrolysis.

Table 2. Elemental Analysis of Corn Stalk and Its Biomass Components

Sample	Element Content (%)					HHV (MJ/kg)
	C	H	O	S	N	
Corn Stalk	41.24	6.04	51.46	0.86	0.40	13.39
Cellulose	44.07	7.07	48.78	-	0.09	13.53
Hemicellulose	36.64	6.20	57.07	-	0.09	13.72
MWL	60.89	6.09	32.23	0.21	0.58	17.67

Chemical Group Analysis of the Biomass Components

FTIR analysis of cellulose

Figure 2 presents the FTIR of cellulose obtained from corn stalk. As can be seen in Fig. 2, the absorption peak at 901 cm⁻¹ was originated from the bending vibration of C₁-H, corresponding to β-(1→4)-glucosidic bond. The bending vibration absorption peak of C-O linkage in glucosidic bond appeared at 1061 cm⁻¹. The absorption peaks in the 1375 to 1310 cm⁻¹ region were caused by the skeleton vibration of C-C and C-O. At 1159 cm⁻¹, the absorption peak corresponded to C-O-C stretching vibration connection with β-(1-4)-glycosidic bond. The absorption peaks appearing at 1425 and 2905 cm⁻¹ were derived from the stretching or bending vibration of methyl or methylene. The absorption peaks at 1105, 1634, and 3416 cm⁻¹ represented a stretching vibration of the inner ring, C=O stretching vibration, and O-H stretching vibration, respectively.

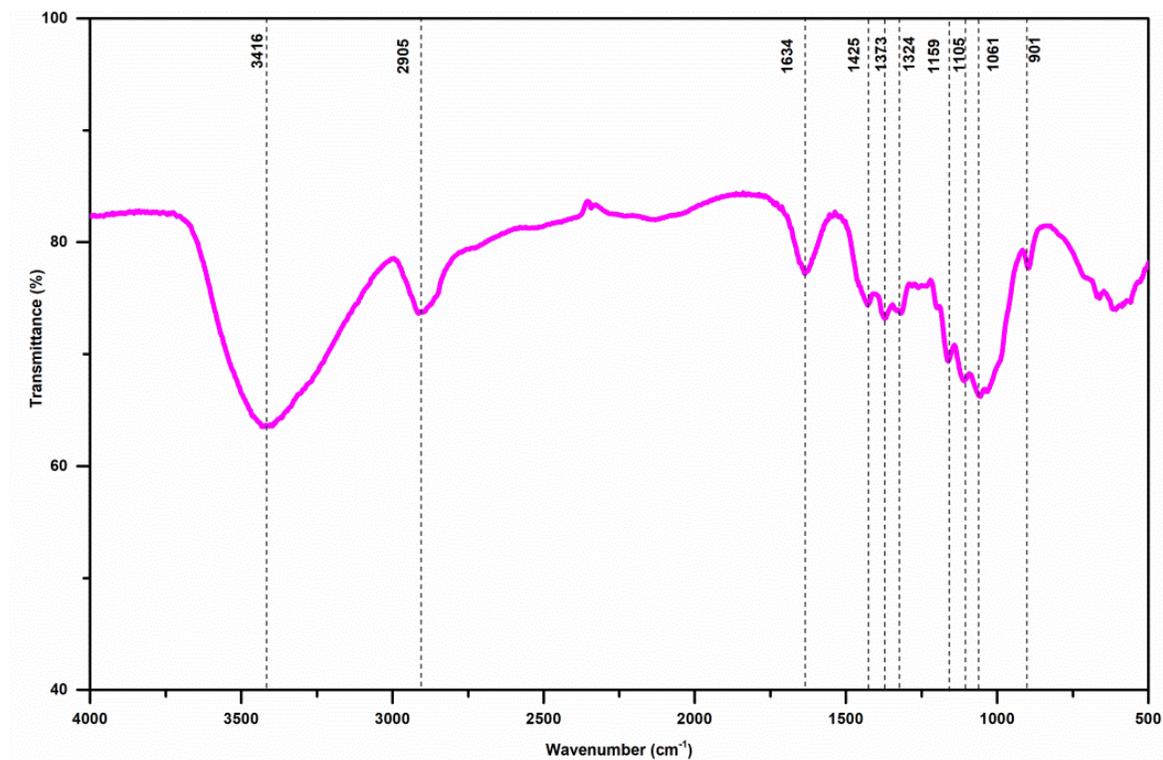


Fig. 2. FTIR spectra of corn stalk cellulose

FTIR analysis of hemicellulose

The FTIR spectrum of hemicellulose is displayed in Fig. 3. It is well known that cellulose and hemicellulose have some similar oxygen-containing functional groups, but the FTIR spectrum of hemicellulose had its own unique structural characteristics to a certain extent (Yang *et al.* 2007). As shown in Fig. 3, the characteristic absorption peaks of glycosyl units in hemicellulose were mainly concentrated in the region of 1600 to 800 cm^{-1} (Sun *et al.* 1998; Peng *et al.* 2010). There was a strong absorption peak at 897 cm^{-1} , which was attributed to the frequency vibration of C-1 group, indicating that the sugar units of hemicellulose were connected by β -glycosidic bonds. Absorbance peaks appeared at 990, 1043, and 3399 cm^{-1} , which were agreeable with vibrational xylosyl C₃-H bending, C-O-C stretching, and O-H stretching in sugar units, respectively. The broad band between 1170 and 1000 cm^{-1} was assigned to the typical characteristic absorption of xylan, and there was a strong absorption peak in this region. These findings imply that the hemicellulose was mainly composed of xylose with pyran ring (Teleman *et al.* 2000). At the same time, a weak absorption peak at 1159 cm^{-1} was attributed to arabinose side chain.

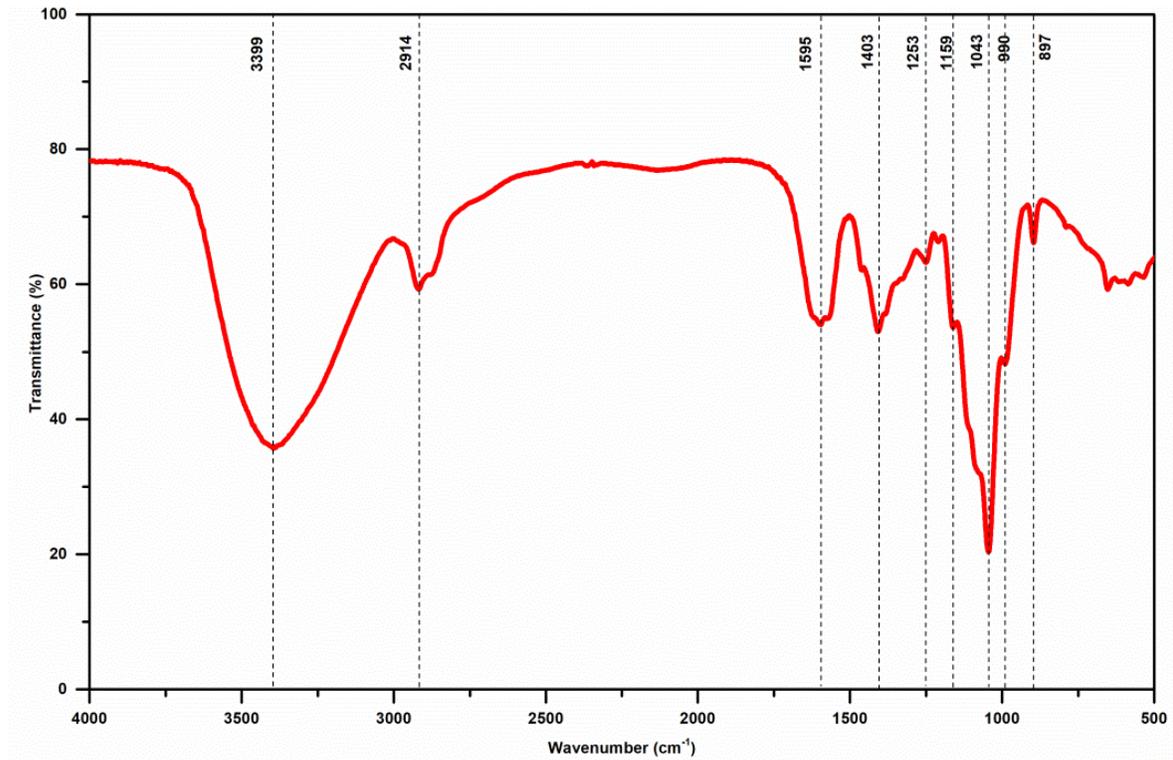


Fig. 3. FTIR spectra of corn stalk hemicellulose

FTIR analysis of MWL

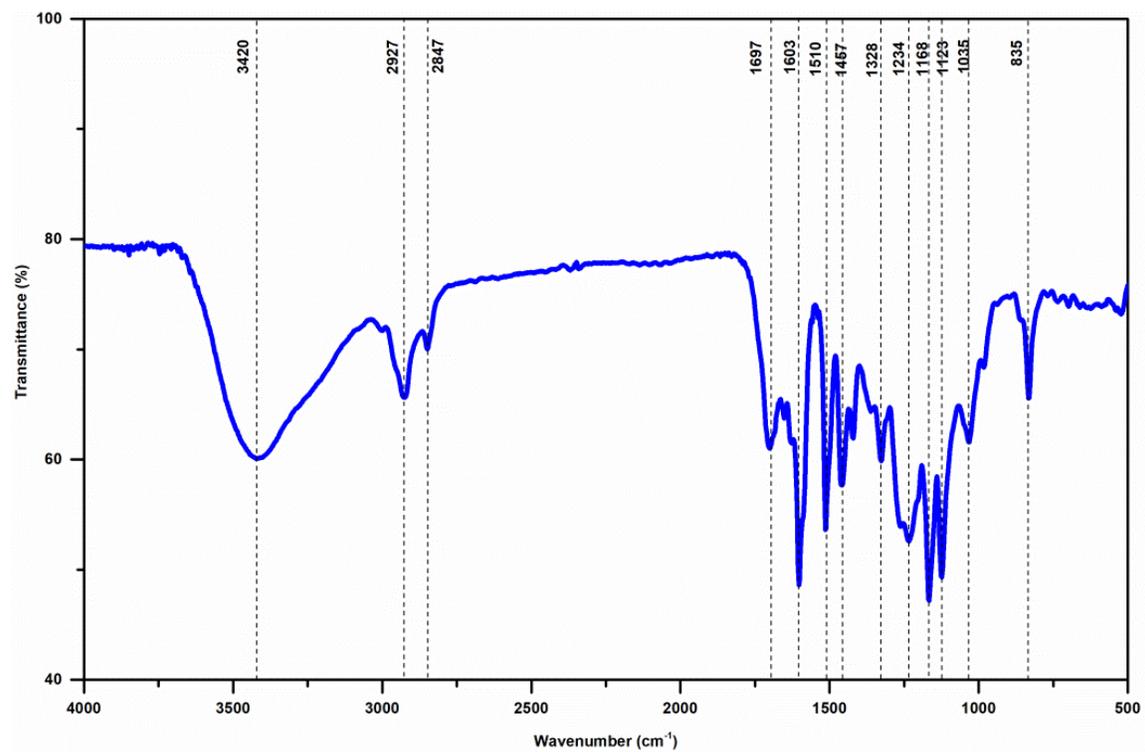


Fig. 4. FTIR spectra of corn stalk MWL

The FTIR spectrum of MWL is presented in Fig. 4. Strong absorption peaks were observed at 1603 and 1510 cm^{-1} , which arose from the aromatic ring C=C skeleton vibration. These are the characteristic absorption peaks of MWL (Li *et al.* 2014), suggesting that the benzene skeleton structure of MWL was not damaged clearly during the separation process and was well preserved. The C-O and C-O-C stretching absorption peak of MWL phenolic ether bond at 1234 cm^{-1} could also be found. The absorption peaks at 1123, 1168, and 1328 cm^{-1} corresponded to C-H vibration in S or G units. Meanwhile, the absorption peak caused by out of plane deformation vibration of C-H in H unit was observed at 835 cm^{-1} . These results indicated that there were G, S, and H units in the MWL isolated from corn stalk.

Molecular Structure Analysis of the Biomass Components

CP/MAS ^{13}C -NMR analysis of cellulose

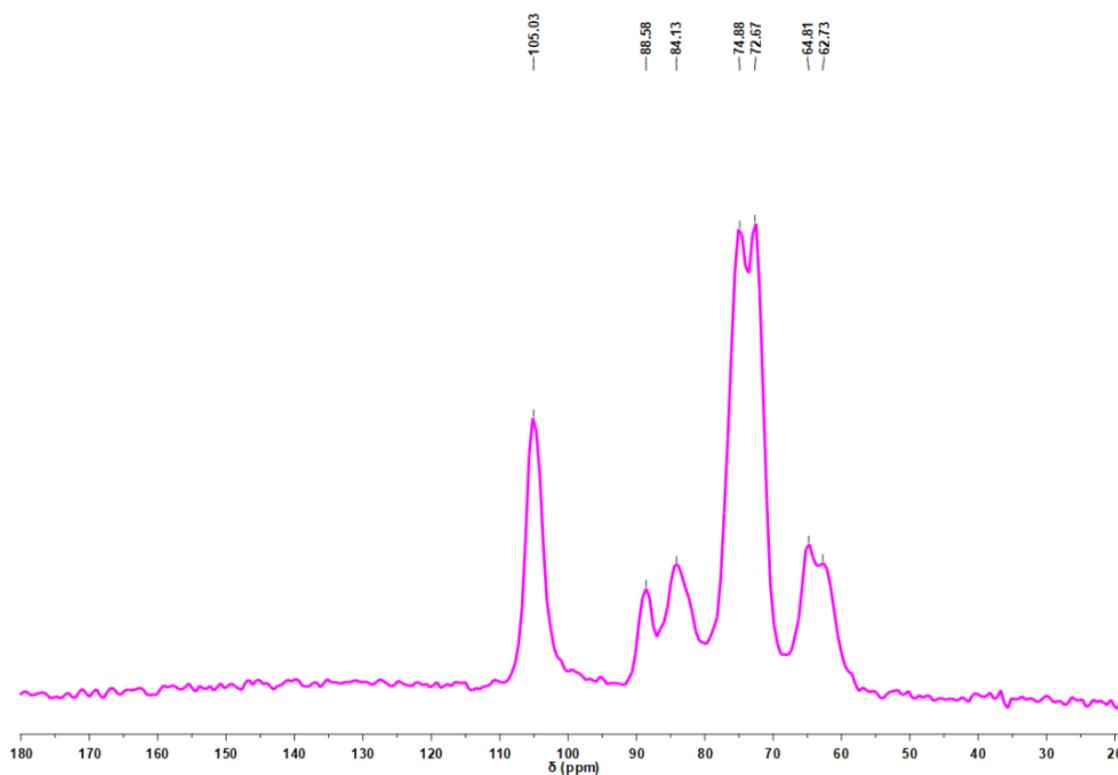


Fig. 5. CP/MAS ^{13}C -NMR spectrum of corn stalk cellulose

Figure 5 illustrates the CP/MAS ^{13}C -NMR signal positions of cellulose produced by corn stalk. The signals were mainly observed in the range of δ 110.0 to 60.0 ppm. The C-4 and C-6 spectra of cellulose were divided into two parts, namely, the sharp narrow low field corresponding to the crystalline region and the wide high field corresponding to the non-crystalline region. The C-4 signals between 92.0 and 82.0 ppm belonged to I_α , I_β , and quasi-crystalline phases of cellulose (Sun *et al.* 2004). Among them, the strong signals at δ 88.58 and 84.13 ppm respectively came from C-4 in the crystalline and amorphous region. It is worth noting that the crystallinity of various samples was generally estimated according to the intensity of the C-4 signal in the crystallization zone (Horii *et al.* 1982). The signals in the range of 60.0 to 66.0 ppm correspond to the C-6 of cellulose. The signals

at δ 64.81 and 62.73 ppm were respectively assigned to the C-6 of crystalline and amorphous cellulose. In addition, the signal was at δ 105.03 ppm, belonging to cellulose C-1. At δ 74.88 and 72.67 ppm gave rise to C-2, C-3, and C-5 of cellulose, and there was a certain overlap (Tang *et al.* 2000).

¹H- and ¹³C- NMR analysis of hemicellulose

The ¹H-NMR spectrum of hemicellulose isolated from corn stalk is illustrated in Fig. 6. The signals were mainly concentrated at δ = 6.0 to 1.0 ppm. The proton signals at δ 5.34 and 5.24 ppm were caused by α -D-furanoarabinose end group attached to the C-3 of the main chain xylose group. The signals in the δ = 4.5 to 4.1 ppm band corresponded to the protons agreeable with β -D-xylose end groups linked to the C-2 or C-3 in the main chain (Sun and Hughes 1998). Signals originating from proton on C-5 of the alkane hydroxyl sugar unit (δ 3.86, 3.74, and 3.50 ppm) were visible in the spectrum. In the region of δ 3.5 to 3.0 ppm signals were identified as proton on the arabinose and β -D-xylose of the hemicellulose side chains. It was considered that the branched chain glycosyl of hemicellulose isolated from corn stalk were β -D-xylopyranose and α -L-furanoarabinose. The signals at δ 3.41 and 1.96 ppm were originated from the methyl protons, corresponding to 4-O-methyl-D-glucuronic acid and acetyl group, respectively. Strong signal strength (δ 1.86 ppm) revealed that most of the acetyl groups were well preserved by mild alkali treatment during the separation of hemicellulose from corn stalk. Moreover, considerable solvent (D₂O) signal was seen near δ 4.70 ppm.

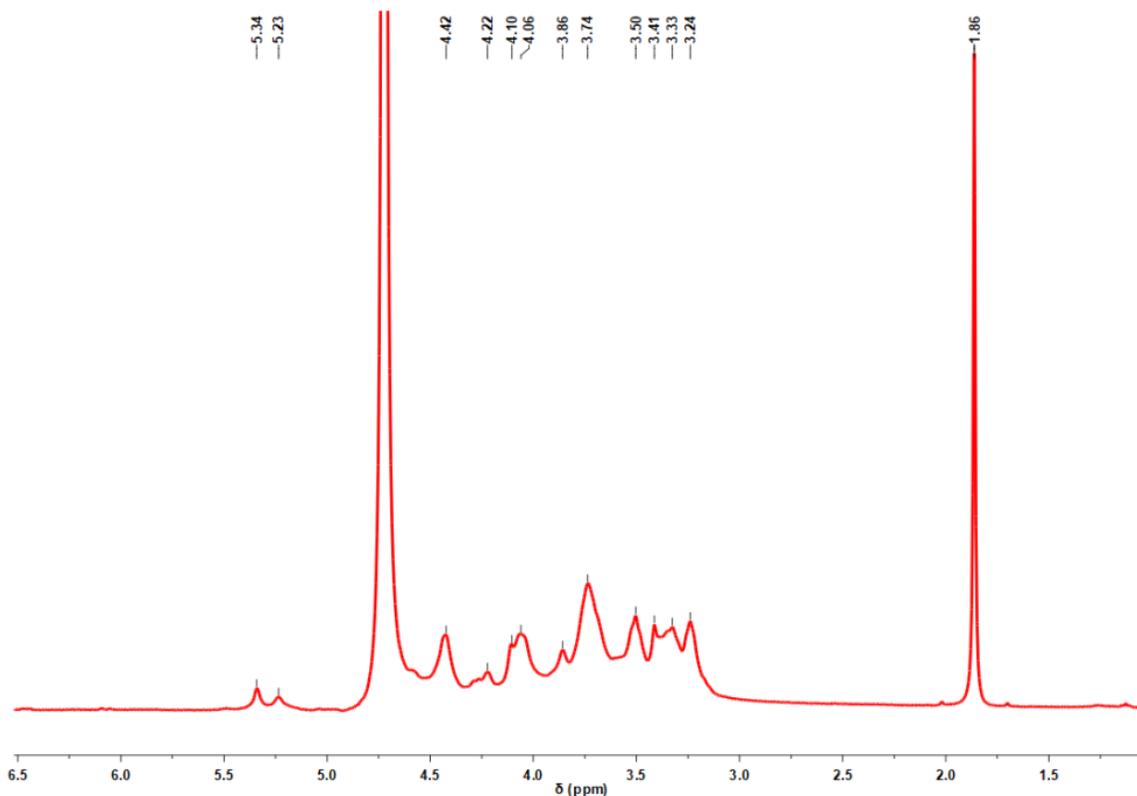


Fig. 6. ¹H-NMR spectrum of corn stalk hemicellulose

The ¹³C-NMR spectrum of corn stalk hemicellulose is listed in Fig. 7. The carbon signals predominantly appeared from δ 110.0 to 60.0 ppm. The signals of C-1, C-4, C-2,

C-3, and C-5 in α -L-arabinofuranose were located at δ 107.87, 86.72, 82.27, 80.63, and 61.28 ppm, respectively. The signals at δ 101.77, 76.46, 75.62, 73.78, and 63.24 ppm were respectively ascribed to C-1, C-4, C-3, C-2, and C-5 on the β -D-xylopyranose (Lv *et al.* 2010). The weak signal of carbon atom in galactose side chain was found at δ 102.04 ppm. The signals were respectively derived from C-1, C-4, C-3, and C-2 of 4-O-methylglucuronic acid at δ 98.38, 84.78, 72.62, and 70.92 ppm. The carbon atoms of -COOH, C=O, and -OCH₃ on uronic acid appeared at δ 181.17, 177.02, and 59.64 ppm, respectively. The strong signal at δ 23.33 ppm again confirmed the presence of a large number of acetyl groups in hemicellulose. Furthermore, there was no obvious signal in the δ 170.0 to 110.0 ppm band, representing the absence of lignin in the separated hemicellulose (Sun *et al.* 2005), which fit in with the determination results of the main components of hemicellulose mentioned above. Therefore, the hemicellulose isolated from corn stalk was mainly composed of β -D-xylose, α -L-furan arabinose, galactose, and uronic acid, which was not only consistent with the results of FTIR and ¹H-NMR analysis of hemicellulose, but also in accordance with the typical characteristics of gramineae hemicellulose (Peng and Wu 2010).

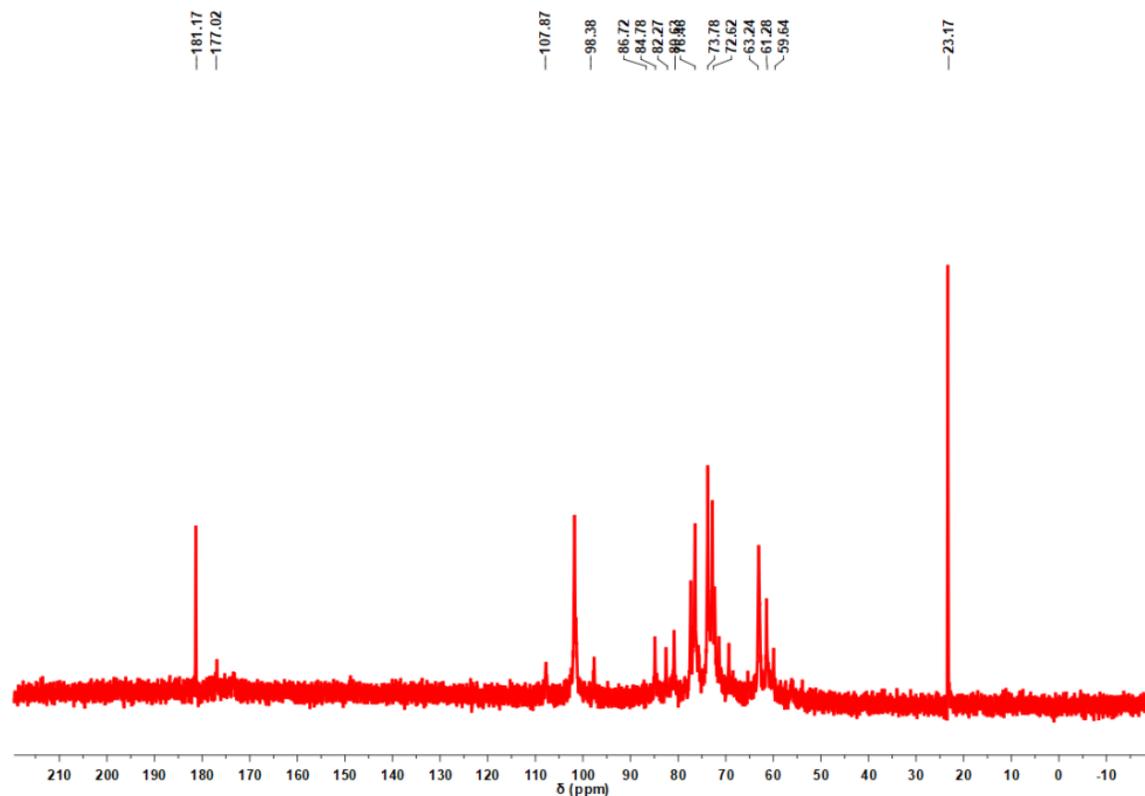


Fig. 7. ¹³C-NMR spectrum of corn stalk hemicellulose

¹H- and ¹³C- NMR analysis of MWL

¹H-NMR spectrum of corn stalk MWL was expressed in Fig. 8. The proton signals were mainly located in the wide band of δ 12.0 to 0.0 ppm. At δ 10.06 ppm, the weak signal was assigned to carboxyl or aldehyde group protons. The signals within δ 8.0 to 6.0 ppm belonged to the aromatic protons in G and S units, and there was an obvious signal at δ 7.48 ppm, corresponding to aromatic protons of p-coumaric acid or p-ferulic acid, which

was usually found in gramineous MWL. The signals at δ 4.91 and 4.39 ppm were respectively agreeable with H α and H γ of the β -O-4 bond (Lapierre *et al.* 1982). Conspicuous signals of protons from -OCH₃ were detected at δ 3.76 and 3.45 ppm. The signals appeared at 1.5 to 0.8 ppm were attributed to aliphatic protons (Tejado *et al.* 2007). In addition, a strong signal at δ 2.54 ppm was in keeping with DMSO-d₆.

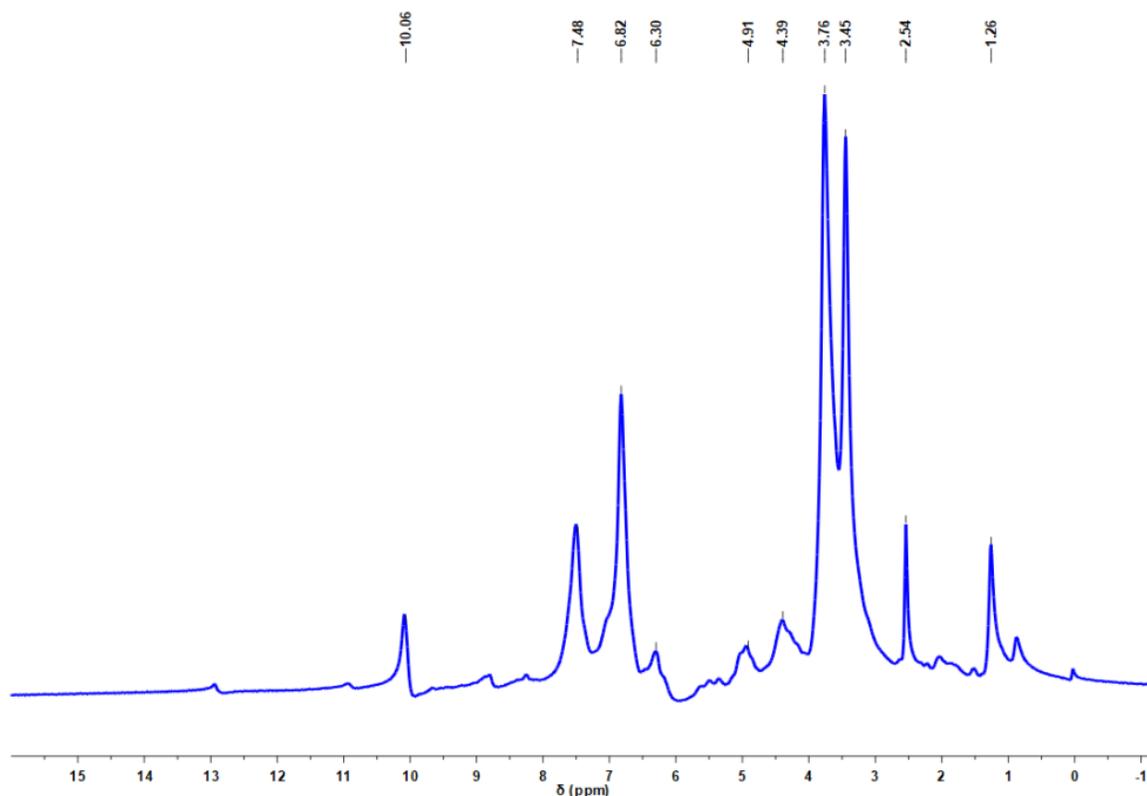


Fig. 8. ¹H-NMR spectrum of corn stalk MWL

The ¹³C-NMR spectrum of MWL isolated from corn stalk is exhibited in Fig. 9. The carbon of aliphatic carboxyl group signal was present at δ 166.84 ppm. The signals at 90.0 to 67.0 and 61.0 to 57.0 ppm corresponded to the carbon atoms of β -O-4 structure, which were important characteristic structural units of corn stalk MWL. In particular, C- β , C- α , and C- γ of β -O-4 signals were present at δ 84.00, 72.73, and 64.00 ppm in turn. The signals at δ 149.81, 148.00 (etherified C-3), 147.73, 147.51, 147.29 (etherified C-4), 145.46, 144.80 (unetherified C-4), 134.87 (etherified C-1), 119.90 (C-6), 114.58 (C-5), and 111.62 ppm (C-2) were in accordance with the carbon atoms related to the G unit of MWL. The carbon signals reflected on S unit were distributed at δ 153.17, 152.72 (C-3/C-5), 147.81, 147.63, 147.25 (unetherified C-3/C-5), 138.36 (etherified C-4), 134.86 (etherified C-1), and 104.37 ppm (C-2/C-6). The carbon atoms associated with the H unit were represented by signals of δ 130.74 (C-2/C-6), 125.54 (C-5/C-5'), and 116.34 ppm (C-3/C-5). Additionally, the carbon signals were respectively revealed at δ 115.35 and 56.39 ppm for p-coumarate ester and -OCH₃. No strong absorption signal was found in the area of 100.0 to 90.0 ppm, which indicated that the MWLn-linked carbohydrates were well degraded in the mild acid hydrolysis stage, so as to obtain high-purity MWL. In the meantime, this ¹³C-NMR spectrum confirmed that the MWL of corn stalk belonged to GSH type, in which G

unit was the most abundant, followed by H unit, and S unit was the least abundant. This result matched the conclusion of ^{31}P -NMR analysis by Wang *et al.* (2006).

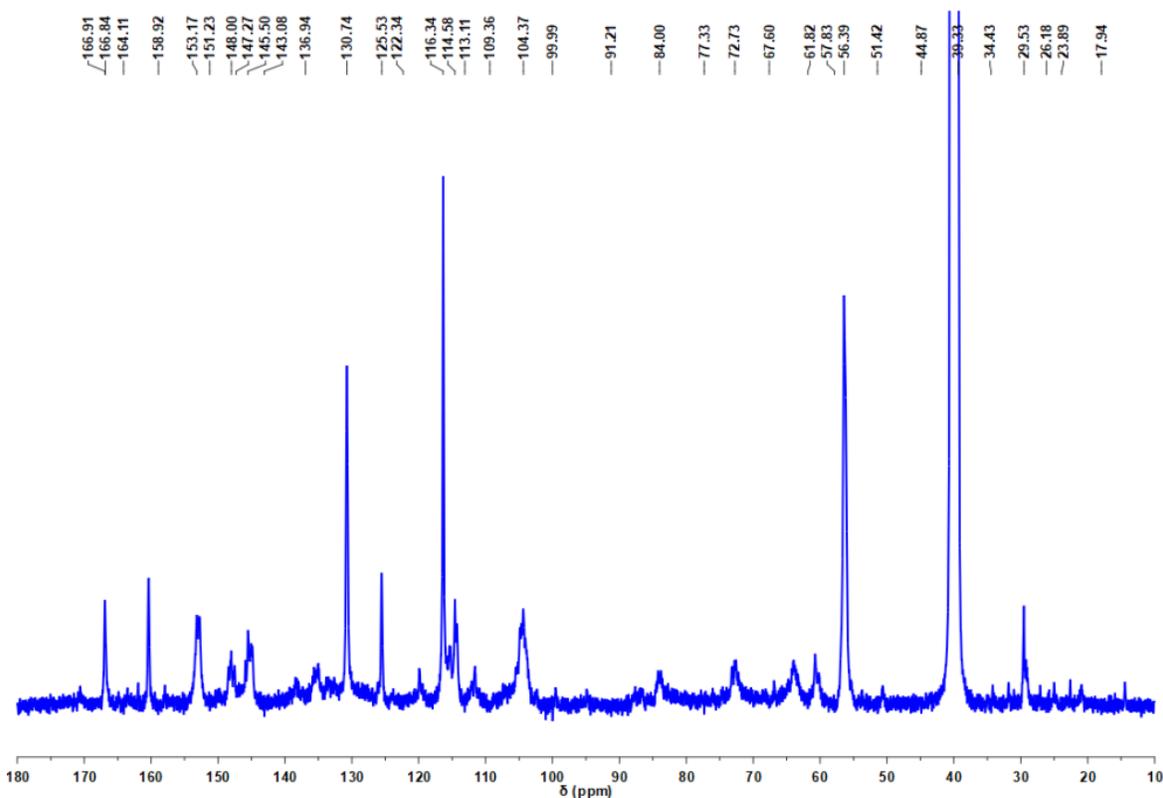


Fig. 9. ^{13}C -NMR spectrum of corn stalk MWL

CONCLUSIONS

1. In this study, the purity of cellulose, hemicellulose, and milled wood lignin (MWL) separated from corn stalk was very high, which was suitable for the subsequent investigation of their liquefaction.
2. The contents of H, O, and C were respectively the highest in cellulose, hemicellulose, and MWL, which were 7.07%, 57.07%, and 60.89%. The HHV of MWL was the largest among the biomass components.
3. The hemicellulose isolated from corn stalk was mainly composed of L-arabino- β -(1 \rightarrow 4)-D-glucuronoxylan units and a small amount of branched chain sugar units (such as galactose, D-glucopyranose, galacturonic acid, glucuronic acid) linked with the main xylose group.
4. The β -O-4 structure of MWL separated from corn stalk was G-S-H type, and the content of MWL was G, H, and S units in order from high to low.

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