



Study on Sawdust Dissolution and Component Separation in NaOH/Thiourea/H₂O System

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The dissolution of sawdust in alkaline solvent system composed of NaOH/thiourea/H₂O was reported and the separation of the lignocellulosic ingredients combined with acid precipitation and ethanol extraction methods was proposed. Structures of the component separated were elucidated by the combination of fourier transform infrared spectroscopy (FT-IR), nuclear magnetic resonance (NMR), X-ray diffraction (XRD) and scanning electron microscope (SEM). The spectra of FT-IR and ¹³C NMR demonstrated that the residual after the treatment with alkali solvent was lignin, the precipitate by the acid precipitation of the liquor was cellulose, the solid precipitate by adjusting pH to 12 and ethanol extraction of the liquor which achieved by above operation was hemicellulose. X-ray diffraction patterns revealed that new crystals were formed or some crystals were redirected after the treatment in alkali system. Molecular structure has changed and intra-molecular rearrangement occurred after treatment in alkali system and by acid precipitation and alcohol extraction. The optimal dissolution conditions were determined by single-factor experiment as follows: the liquid-solid ratio, dissolution temperature and dissolution time was 30:1, 70 °C and 2 h, respectively. The lignin, cellulose, hemicellulose recovery yield can achieve to 88.3, 95.2 and 85.6 % under the optimal dissolution conditions.

Keywords: Lignocelluloses, Alkali solvent system, Dissolution, Component separation.

INTRODUCTION

The current social economic development and daily life are strongly depended on petroleum, coal and other traditional mineral resources, mankind is facing multiple pressure including resources shortage, energy crisis and environmental pollution brought about by the fast consumption of these mineral resources. Therefore, the development and utilization of renewable resources and energy which is high efficiency, green, low cost has become the key problem in sustainable development¹⁻³, while efficient components separation of renewable biomass is the most important to the complex utilization of the renewable resources. Lignocelluloses are the richest natural polymers on the earth. Making full use of them to produce various valuable products can not only protect the environment from pollution, but also save the limited petroleum resources^{4,5}.

At present, most fractionation processes of lignocelluloses were physicochemical pretreatment to increase the reactivity of the lignocellulosic structure, followed by one or more separation and purification stages to isolate products. Alkali treatment is one of the most popular and effective methods to pretreat lignocellulose⁶, including NaOH⁷, ammonia water immersing⁸,

ammonia recovery immersion⁹ and lime¹⁰ treatment. Sodium hydroxide treatment is one of the most commonly used methods. Isogai and Atalla¹¹ reported that all kinds of microcrystalline celluloses can completely dissolved when a 8 to 9 % sodium hydroxide solution is used as the solvent, then frozen it at -20 °C and thawed at room temperature, diluted it to the concentration to 5 %. They concluded that the dissolution process didn't change the crystallization morphology and crystallization index of celluloses. Kamide *et al.*¹²⁻¹⁴ and Laszkiewicz & Cuculo¹⁵ reported that an alkali-soluble cellulose can be dissolved in aqueous solution of NaOH at low temperature and prepared a solution from wood pulps and method of regeneration process. It is founded that only cellulose with lower degree of polymerization could be dissolved in this solvent and this solution is easy to gelation. A kind of new solvent system of cellulose has developed by Zhang *et al.*¹⁶, such as use 7 % NaOH /12 % urea solution can quickly dissolve cellulose whose weight-average molecular weight is 1.2×10^5 when the temperature is -12 °C. At present, the new solvent system has passed the pilot equipment and was used to spin successfully to obtain a new type of regenerated cellulose fiber with good performance. This system has several advantages such as easily available solvent, low cost, free pollution, but

its ability of dissolving is limited and cellulose solution obtained from this system is easy to form irreversible gel. Sun *et al.*¹⁷ reported that a combined process of wheat straw steam-exploded and sequential alkaline peroxide post-treatment with recovery of lignin being 92.4-99.4 % of the original lignin from wheat straw, but the separation of other components is not mentioned. Lignin separation and fractionation by ultra-filtration is reported by Toledano and his coworkers¹⁸. Thus so far there has been few reports with regard to the all components separation of lignocellulose, particularly on separation of the three components in sawdust.

This paper concerns the dissolution of sawdust in alkaline solvent system composed of NaOH/thiourea/H₂O and is focused on the separation of the lignocellulosic ingredients combined with acid precipitation and alcohol extraction procedures.

EXPERIMENTAL

The sawdust with content of cellulose, hemicellulose, lignin, ash is 23.2, 21.3, 51.3 and 4 % was shattered to 80 mesh. Sodium hydroxide (96 %), thiourea (99 %), hydrochloric acid ($f = 18.3\%$), ethanol (98 %) and distilled water were of analytical grade and purchased from Changchun Jintai chemical reagents company.

Dissolution and separation process: Take a certain amount of dry sawdust into 250 mL three-neck round-bottom flask with temperature control, stirring and reflux device, then add the alkaline solvent (6 % NaOH / 5 % thiourea / 89 % H₂O) into three-neck round-bottom flask according to the designed liquid-solid ratio, dissolution starts when the temperature inside the flask achieves the set value. Upon completion, the residue rich in lignin was filtered off and washed thoroughly with water until the residue was neutral and dried in an oven at 60 °C for 12 h, weighed and labelled as A_L.

The combined supernatant was acidified to pH 2 with HCl ($\phi = 18.3\%$), a large amount of fine precipitate produced, separated the precipitation by centrifugation at 6000 rpm for 10 min. Then the precipitate obtained dried at 60 °C in a drying oven, weighed and labelled as A_C. The filtrate rich in hemicellulose was concentrated in a rotary evaporation under reduced pressure to 50 mL, then adjust pH to 12 with NaOH (0.1 M/L) and mixed with three volumes of 98 % ethanol. The precipitated fraction was centrifuged and washed with 70 % ethanol, until the washing ethanol became colorless. The fraction obtained was further freeze-dried, weighed and labelled as A_H. Scheme for dissolution and component separation of sawdust are shown in Fig. 1.

It can be seen from Fig. 1 that the recovery ethanol could be reused for ethanol extraction. Carbon dioxide gas induced by acid precipitation was released into the air. In the process of industry production, cyano was considered to be introduced according to eqn (2), (3) with the H₂S generated to resynthesize thiourea, so as to achieve the recycle of solvent. The NaCl and NH₄Cl in residual solvents (eqn 1, 4) can be removed by recrystallization process.

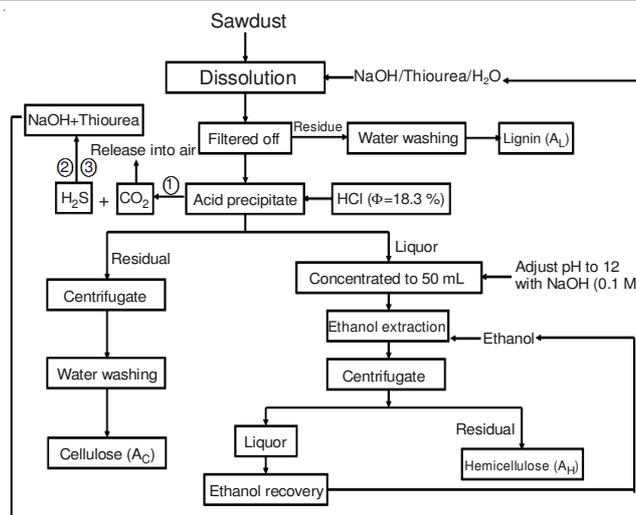
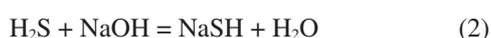
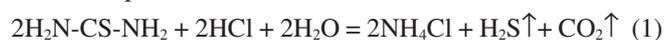


Fig. 1. Scheme for dissolution and component separation of sawdust



Recovery yield of components in sawdust: The recovery yield of lignin, cellulose and hemicellulose corresponding to ω_1 , ω_2 and ω_3 were calculated from following equation, respectively.

$$\omega_1 = \frac{m_1 - m_2}{m_0 \times \omega'_1} \times 100\% \quad (5)$$

$$\omega_2 = \frac{m_3}{m_0 \times \omega'_2} \times 100\% \quad (6)$$

$$\omega_3 = \frac{m_4}{m_0 \times \omega'_3} \times 100\% \quad (7)$$

where m_0 is the mass of sawdust added before dissolution, m_1 , m_2 , m_3 and m_4 are the mass of solid residual after dissolution, ash of sawdust, cellulose precipitate after acid precipitation and hemicellulose extraction by ethanol and ω'_1 , ω'_2 and ω'_3 are the percentage of the lignin, cellulose and hemicellulose in sawdusts, respectively.

FT-IR analysis: The raw as well as chemically treated sawdust were analyzed as KBr pellets using a FT04-035 FT-IR spectrometer (Thermo Technology Co., LTD, USA) at room temperature. All spectra were recorded with an accumulation number of 32 scans and a resolution of 4 cm⁻¹ in the range from 4000 to 400 cm⁻¹.

CP/MAS ¹³C NMR analysis: The NMR spectra were acquired with a Bruker AV 500 spectrometer (Bruker company, Switzerland) in dimethyl sulphoxide (DMSO)-*d*₆ for ¹³C NMR at 60 °C. The scan number was up to 10,000.

X-Ray diffractometry analysis: XRD patterns were obtained on a Philips X'Pert Pro X-ray diffractometer using CuK_α radiation (Philips company, Netherlands). The XRD patterns with CuK_α at 40 kV and 30 mA were recorded in the region of 2θ from 5 to 40°.

SEM analysis: The SEM micrographs were taken on a JSM-6480LV scanning electron microscope (JEOL technology co., LTD, Japan). The samples were glued to the sample stage

and were sputtered with gold, then observed the fracture surface and photographed.

RESULTS AND DISCUSSION

Effect of dissolution parameters on lignin, cellulose and hemicellulose recovery yield in sawdust

Dissolution temperature: The effect of dissolution temperature on lignin, cellulose and hemicellulose recovery yield in sawdust were shown in Fig. 2. It could be seen that the recovery yield of three components increase significantly with increasing dissolution temperature for the saponification of intermolecular ester bonds cross-linking lignin and part of the hemicellulose began, material porosity were increased and reach a plateau when the temperature was above 70 °C due to the dissolution of cellulose and hemicellulose were sufficient enough and few cellulose and hemicellulose were dissolved over 70 °C. 70 °C was selected to be the optimal dissolution temperature.

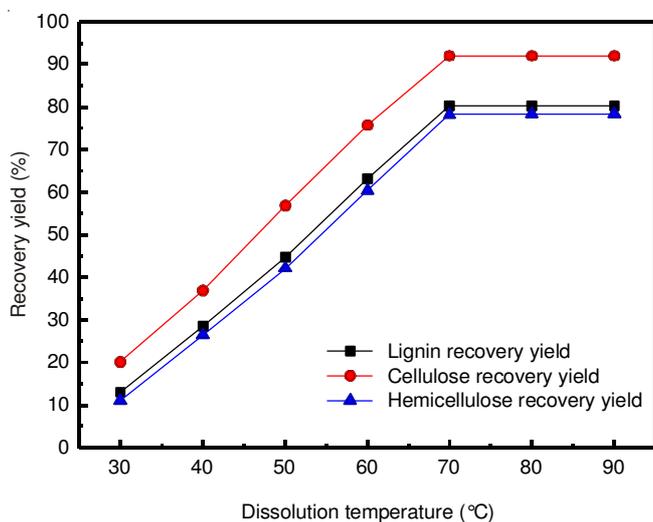


Fig. 2. Effect of dissolution temperature on lignin, cellulose and hemicellulose recovery yield in sawdust. (dissolution time 1 h, ratio of liquid to solid 20:1)

Dissolution time: The effect of dissolution time on lignin, cellulose and hemicellulose recovery yield in sawdust were shown in Fig. 3. With an increase of the dissolution time, the recovery yield of lignin, cellulose and hemicellulose rapidly increased, because NaOH synergies with thiourea played a role to break intra-molecular and intermolecular hydrogen bond of cellulose and the intra-molecular hydrogen bond of polysaccharides, cellulose and hemicellulose were dissolved gradually. Then it reached a plateau at 2 h, further dissolution of cellulose and hemicellulose were not observed. 2 h was selected to be the optimal dissolution time considering the efficiency of the process.

Ratio of liquid to solid: The effect of liquid to solid ratio on lignin, cellulose and hemicellulose recovery yield in sawdust were shown in Fig. 4. The recovery yield of three components increased significantly with increasing liquid to solid ratio and almost kept unchanged when the ratio reached to or above 30. Liquid to solid ratio 30 is chosen for the further dissolution experiments.

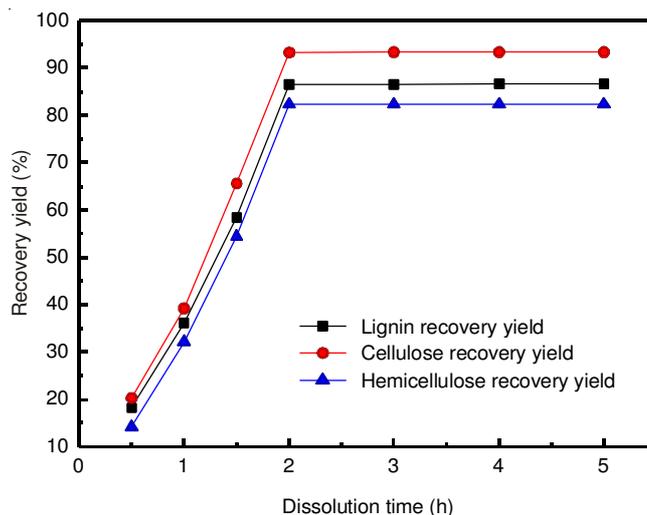


Fig. 3. Effect of dissolution time on lignin, cellulose and hemicellulose recovery yield in sawdust. (dissolution temperature 70 °C, ratio of liquid to solid 20:1)

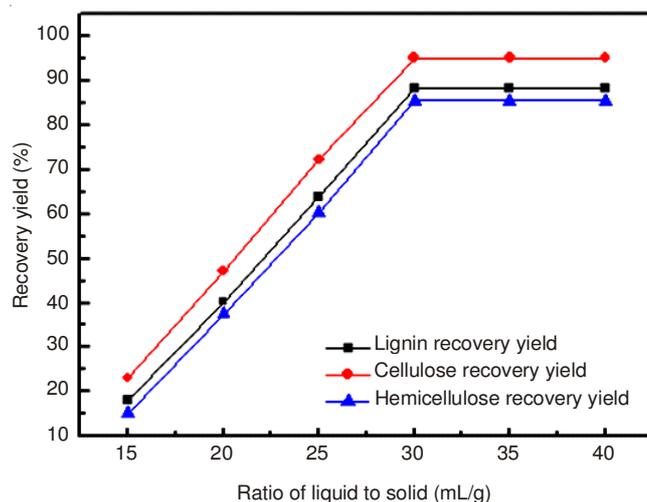


Fig. 4. Effect of liquid to solid ratio on lignin, cellulose and hemicellulose recovery yield in sawdust. (dissolution temperature 70 °C, dissolution time 2 h)

As shown in the experiment above, the optimal dissolution conditions were determined by single-factor experiment as follows: the liquid-solid ratio 30:1; dissolution temperature 70 °C; dissolution time 2 h. At this condition, the lignin, cellulose and hemicellulose recovery yield was 88.3, 95.2 and 85.6 %, respectively.

Principle and process consideration: The purpose of this present work was to isolate and characterize the cellulose, hemicellulose and lignin degraded in the alkaline solvent system treatment, acid precipitation and ethanol extraction with a view to elucidate their structures. The mechanism of alkaline hydrolysis is related to the saponification of intermolecular ester bonds cross-linking lignin and part of the hemicellulose. The reduction of this cross-linking tends to increase the material porosity¹⁹. Alkali hydrolysis proved to be the most effective method for breaking the ester bonds between lignin, hemicellulose and cellulose and avoiding fragmentation of the hemicellulose polymers²⁰. It could increase the solubility of solvent to material and solution stability by adding a small

amount of thiourea as cosolvent and forming synergies with NaOH owing to thiourea contains C=S which had strong polarity and -NH- groups, easily to form intermolecular hydrogen bond with cellulose molecules in order to break intramolecular and intermolecular hydrogen bond of cellulose and the intramolecular hydrogen bond of polysaccharides²¹.

FT-IR analysis: Fig. 5 shows the IR spectra of sawdust, A_L, A_C and A_H. The FT-IR spectra of sawdust and residuals after the treatment, acid precipitation and ethanol extraction were very similar, indicating similar structure of the residues. They were characterised by a dominant O-H stretch band (3422 cm⁻¹) and a C-H band (2977 cm⁻¹) corresponding to the aliphatic moieties in lignin (curve a and b) or polysaccharides [cellulose (curve a and c) and hemicellulose (curve a and c)]²². The absorption band at 1737 cm⁻¹ in curve a and b is attributed to the ester linkage of carboxylic group of the ferulic and *p*-coumaric acids of lignin.

The aromatic C=C stretch from aromatic ring of lignin gives two peaks at 1510 and 1429 cm⁻¹ in curve a and b, but it become very weak in the curve c and d as a result of the elimination of lignin. The band at 881 cm⁻¹ in the curve c which is indicative of the C-1 group frequency or ring frequency, is characteristic of β-anomer or β-linked glucose polymers and the characteristic absorption band of cellulose. It can be seen that the sediment by the acid precipitation of the liquor is cellulose. All the spectra had a specific band maximum at 1049 cm⁻¹, especially in the curve d and there are several weak peak in the 1200-1100 cm⁻¹, which are typical of xylans. This region is dominated by ring vibrations overlapped with stretching vibrations of (C-OH) side groups and the (C-O-C) glycosidic bond vibration. The results suggested that the main residual after the treatment in alkali solvent was lignin, the sediment by the acid precipitation of the liquor was cellulose and the precipitation after ethanol extraction of the liquid treated by acid precipitation and adjusting pH to 12 was hemicellulose.

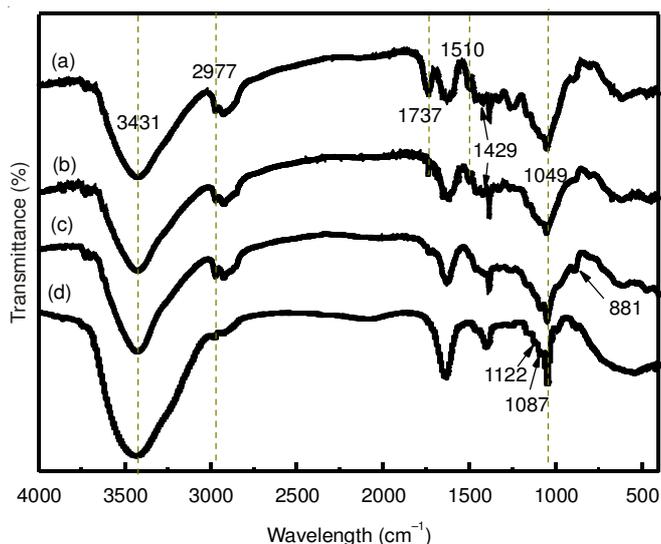


Fig. 5. FT-IR spectra of sawdust (a), A_L (b), A_C (c) and A_H (d)

CP/MAS ¹³C NMR analysis: The CP/MAS ¹³C NMR spectra of the sawdust, A_L, A_C and A_H are shown in Fig. 6.

Cellulose is semicrystalline biopolymer with ordered crystalline and disordered amorphous regions. Lignocellulose

is polymorph crystal of different forms, most of the crystal structure is cellulose. As shown in the Fig. 6a, the signal of C1 appeared at δ 105.2 and the signals at δ 88.8 and δ 83.5 could be assigned to C4. Resonances of the C6 were visible at δ 65.1 and δ 56.1, resonance peak overlap of C2, C3, C5 was detectable at δ 72.6. The signal at δ 88.8 resulted from the vibration of crystal cellulose, while resonance of irregular state fiber was visible at δ 83.5^{23,24}. The peak for C6 of crystal cellulose was appeared obviously in Fig. 6a and similar trend of vibration were occurred compared with C6. The signals at δ 21.0 and δ 170.9 were disappeared in Fig. 6b compared with Fig. 6a. It could be concluded that acetylation was happened after treatment by alkali system, hemicellulose and cellulose were eliminated and the crystal structure of cellulose was destroyed. The signals at δ 136.8 and δ 153.2 resulted from residual lignin and hemicellulose filled in the cellulose crystals. The signals at δ 136.6, δ 153.3 and δ 170.9 disappeared or weaken in Fig. 6c compared with Fig. 6a. It could be suggested that hemicellulose was eliminated completely after the acid precipitation and the residual filtrate was cellulose. In the Fig. 6d, the signal at δ 101.5 (C1) of β-D-xylose units and other signal from C3 and C4 of xylose units are observed at δ 74.6. The signal at δ 62.8 are characteristic C5 of the α-L-arabinofuranosyl residues that are (1→3)-linked to the β-D-xylans. It could be indicated that the residual after ethanol extraction is hemicellulose, which is mainly composed of most xylose and a small amount of arabinose.

XRD analysis: X-ray diffraction patterns of sawdust, A_L, A_C and A_H were shown in Fig. 7.

Lignocellulosic fibers are composed of three major components namely cellulose, hemicellulose and lignin. Crystalline microfibrils of cellulose are surrounded by amorphous hemicellulose and the whole is embedded in the matrix of lignin. Crystalline structure of cellulose and hemicellulose exhibits variability in both structure and constitutes.

Compared curve a with b, it can be seen, the diffraction peaks of the residual after the treatment in alkali solvent are shaper than the diffraction peaks of sawdust, the diffraction peaks appears at 2θ angle at 16°, 23°, 35°, indicating that new crystals were formed or some crystals were redirected after the treatment of alkali system²⁵. It can be explained by crystalline structure of lignocellulose changed after treatment in alkali solvent and is due to more efficient removal of non-cellulosic polysaccharides and dissolution of amorphous zones²⁶. Curve c shows the X-ray diffraction pattern of the filtrate by the acid precipitation of the liquor. Two sharp crystal peaks whose 2θ are 26° and 33° are recognized. It suggested that some intra- and inter-molecular hydrogen bonding were destroyed after these treatments which led to the amorphous area to be destroyed. So molecular structure has changed and intra-molecular rearrangement reaction has occurred after treatment by alkali system and acid precipitation. Curve d shows the X-ray diffraction pattern of the residual of ethanol extraction. The peaks at 26° and 33° are almost invisible, indicating that the residual turn to the amorphous, curve d shows a narrow peak at 33°, which may be due to heavy loading of chemicals.

SEM micrograph: The SEM micrographs of sawdust, A_L, A_C and A_H are shown in Fig. 8. It can be seen by comparing

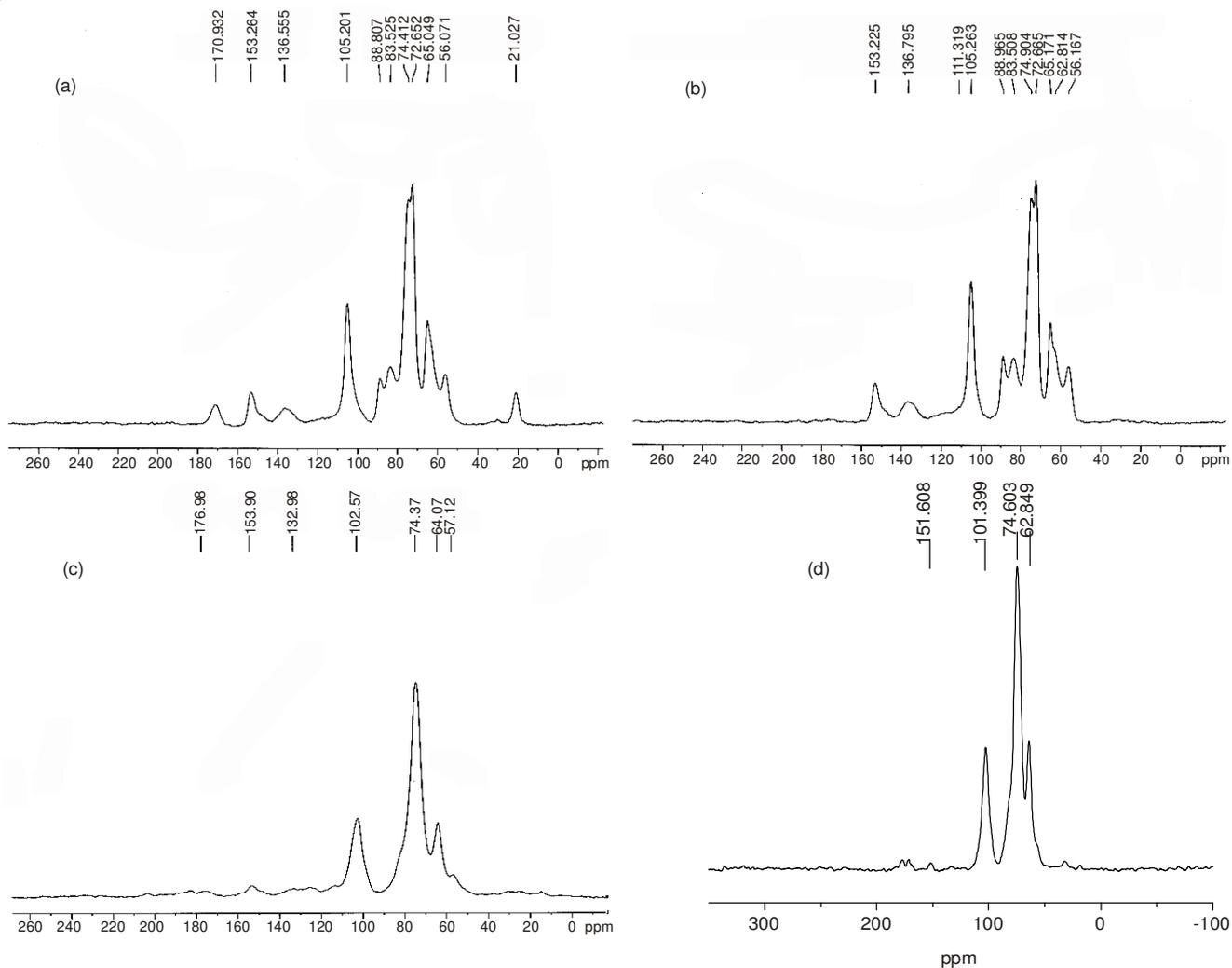


Fig. 6. ¹³C NMR spectrum of sawdust (a), A_L (b), A_C (c) and A_H (d), (Liquid to solid ratio 10:1, 60 °C, 2 h)

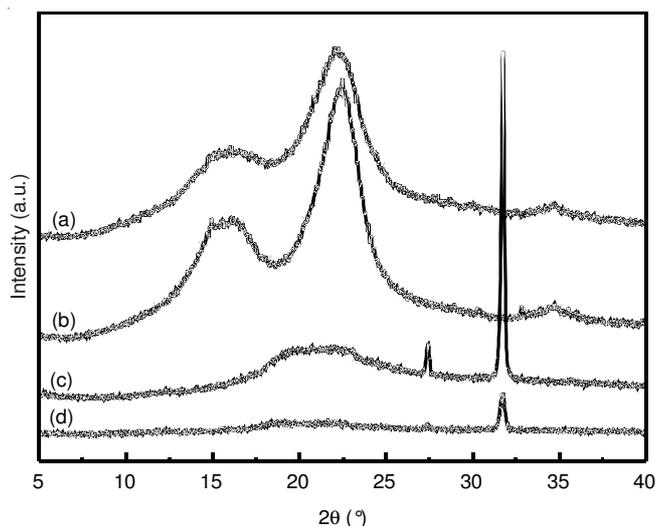


Fig. 7. X-ray diffraction pattern of sawdust (a), A_L (b), A_C (c) and A_H (d), (liquid to solid ratio 10:1, 60 °C, 2 h)

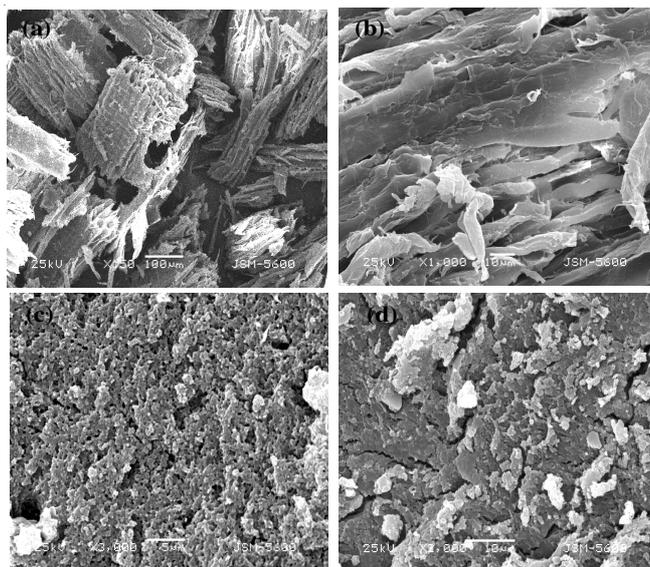


Fig. 8. SEM micrograph of sawdust (a), A_L (b), A_C (c) and A_H (d)

Fig. 8a-d, sawdust display on column fiber whose surface is flat and exist columnar fiber. After treatment by alkali system, there have been some fractures on the surface which is flat originally. Though column fiber can be seen, many tiny cracks

on its surface are appeared. It can be concluded that the surrounded structure of cellulose was destroyed. The surface of the filtrate after acid precipitation is very loose and a lot of holes can be seen. It could be demonstrated the cellulose is

released into the solution after treatment by alkali system and precipitated after the acid precipitation. When the liquid after acid precipitation is extracted by ethanol, a lot of voids appear, all residuals are in random order, it could be suggested that the residuals extracted by ethanol are more unstable in structure.

Conclusion

It has been shown by the experiments that the alkaline solvent system composed of NaOH/thiourea/H₂O have a good dissolvability to sawdust and the component separation of lignocellulose was achieved by combining with the acid precipitation and ethanol extraction methods. It is proven by the analysis of structure that the residual after the treatment in alkali solvent was lignin, the filtrate by the acid precipitation of the liquor was cellulose, the solid precipitation by adjusting pH to 12 and ethanol extraction of the liquid which achieved by above operation was hemicellulose. The optimal dissolution conditions were determined by single-factor experiment as follows: the liquid-solid ratio, dissolution temperature and dissolution time was 30:1, 70 °C and 2 h, respectively. The optimal recovery yield of lignin, cellulose and hemicellulose was 88.3, 95.2 and 85.6 %, respectively under the optimal dissolution conditions. The dissolution and component separation process to sawdust has the advantages of easy operation, low cost cost and high efficiency.

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