



Effects of chemical inhomogeneity of corn stalk on solvolysis liquefaction

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ABSTRACT

Structural characterization of corn stalk (CS) fractions including whole stalk, ear husk, leaf blade, stem bark and stem pith was conducted. Different fractions were liquefied by solvolysis liquefaction method. Acid number, hydroxyl number and insoluble residues ratios (IRR) of liquefied products from CS fractions were monitored. Results showed chemical compositions of CS fractions had remarkable difference. Cellulose, hemicellulose and lignin accounted for 36.9–41.43%, 21.77–37.3% and 3.38–7.52% of the raw material, respectively. Acid numbers increased with increasing time from 30 to 90 min, whereas hydroxyl numbers decreased gradually, IRR decreased and then increased. However, properties of liquefied products differed remarkably. Higher acid number, higher hydroxyl number, and lower IRR were detected from ear husk liquefied products. This is coincident with the higher content of hemicelluloses in ear husk. This work proved that whole utilization process is unsatisfactory in solvolysis liquefaction and different fractions of CS should be given themselves optimum applications.

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1. Introduction

Lignocellulosic resources utilization receives much attention in recent years due to its renewable properties, which offer important economic and environmental benefits. The quantity of lignocelluloses such as woody wastes, agriculture wastes and waste paper is very large. Only agriculture waste in China is amounted up to 700 million tons annually (China Statistical Yearbook of Agriculture, 2010). They are often incinerated or discarded in the environment, which are harmful to the environment. How to convert them into useful materials such as chemicals, bio-oil, pharmaceuticals have been researched for several decades. The chemical conversion or solvolysis liquefaction, which is using the specific organic reagents to convert the biomass into liquid products, is a promising approach and has been intensively studied in the recent years. The liquefaction processes of biomass such as wood (Kurimoto, Koizumi, Doi, Tamura, & Ono, 2001; Lee & Wang, 2005), grapevine cane (Alma & Basturk, 2006), wheat straw (Chen & Lu, 2009), bagasse (Ge et al., 2003), cotton stalk (Wang, Pan, Li, & Yang, 2008), western red cedar (Nakamura, Miyafuji, & Saka, 2010) and bamboo (Yip, Chen, Szeto, & Yan, 2009) have been researched.

The liquefaction of corn stalk (CS) has obtained more attention than other agriculture wastes due to its abundance, over 200 million tons annually in China (China Statistical Yearbook of Agriculture, 2010). The solvent plays an important role

during CS liquefaction process, which influences the product yield. Ethyleneglycol, polyethyleneglycol, and glycerol as liquefied agent to convert CS have been studied by Yan, Pang, Yang, and Liao (2008) and Wang, Zhang, Chen, and Hu (2007). The effects of reaction temperature and reaction time on the liquefied products were also investigated (Wang et al., 2007). Liu, Xie, Ren, and Sun (2012) has evaluated CS liquefaction in sub- and super-critical ethanol. The products were analysis by means of gas chromatography–mass spectrometry (GC/MS). The main products including volatile organic compounds, water-soluble oil and heavy oil are comprised a mixture of esters, phenols, acids, furans and their derivatives. The product properties of CS liquefied with water as liquefaction solvents have been discussed by Du and Li (2009). The liquefaction technology of CS was optimized by Liang, Liang, Xu, and Teng (2009).

Results from Demirbas (2000) indicated that there is a strong correlation of lignin content and the yields of products. With an increase of lignin content, the char yield increased, and however the oil yield decreased. The researches of Kurimoto and co-workers also had suggested that the higher content of lignin, the easier the biomass was liquefied (Kurimoto, Takeda, Doi, & Tamura, 1999). Compared with hemicelluloses and cellulose, lignin was easier to be liquefied. Lignin also accelerates the appearance of recondensation polymerization in the later liquefaction stage to form the indigestible residues. However, only the liquefaction of whole straw was studied in these previous works. Up to now, little attention has been paid to the liquefaction properties of the every fraction of CS.

In fact, the chemical compositions of CS fractions such as whole stalk, ear husk, leaf blade, stem bark and stem pith are different,

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which can result in the difference of liquefaction process. Chen, Li, and Liu (2011) have reported that differences of chemical compositions of CS parts including leaf, shell, core and node affect enzymatic hydrolysis and fermentation performances. In our early studies (Wang et al., 2008a,b), it has found that ethylene carbonate (99.90%, w/w) and sulfuric acid (97%, w/w) are effective solvent and catalyst respectively in liquefaction CS. In this paper, the fractions of CS including whole stalk, ear husk, leaf blade, stem bark and stem pith are selected and liquefied respectively with ethylene carbonate (99.90%, w/w) as the solvent and sulfuric acid (97%, w/w) as the catalyst at a reaction temperature of 160 °C. The chemical composition of each fraction will be analyzed. The characteristic of products including hydroxyl number, acid number and insoluble residue ratio (IRR) will be measured and analyzed, respectively.

2. Materials and methods

2.1. Materials and chemicals

Corn stalk (CS) was harvested in 2010 and collected from a local farm in Beijing suburb of China and stored in plastic bags, and had moisture content from 8% to 10%. The CS sample was divided up manually into whole stalk, ear husk, leaf blade, stem bark and stem pith. Each individual fraction was milled and the fractions under 20 meshes were used for the liquefaction experiments, respectively. The whole stalk was aboveground components of corn plant, comprised of leaves 25 wt.%, stalks (including stem bark, stem pith and node) 47 wt.%, ear husk 24 wt.% and others 4 wt.%.

Sulfuric acid (97%, w/w) was used as the catalyst. Ethylene carbonate (99.90%, w/w) was used as the solvent in the liquefaction process. All chemicals used were reagent grade and were obtained from commercial sources.

2.2. Liquefaction of CS morphological fractions

Each oven-dried individual fraction flour 10 g, ethylene carbonate 50 g and sulfuric acid 1 g were placed in a three-neck flask (250 ml) equipped with a reflux condenser, a thermometer, and a motor-driven stirrer, refluxed at 160 °C with continuous stirring. The reaction time changed at a range of 30–90 min of a 15 min interval. Then the flask was immersed into cold water to quench the reaction and the liquefied products including all the components in three-neck flask were collected for later analysis.

2.3. Chemical component analysis of CS morphological fractions

The method of Van Soest, Robertson, and Lewis (1991) was employed to determine hemicelluloses content, cellulose content and lignin content by means of fibertec system 2010.

2.4. Characteristics measurements of liquefied product

The method of Kurimoto et al. (2000) was employed to determine hydroxyl number and acid number.

Insoluble residues ratios (IRR) were determined as follows. A mixture of 2 g liquefied corn stalk (LCS) was diluted using 50 ml dioxane–water (4:1, v/v) and the insoluble residues were filtered using a Buckner funnel and tared filter paper (the weight was marked). The residues rinsed thoroughly with the dioxane and 10 blank filter papers were heated for 24 h at 105 °C. The average content of water in blank filter paper was calculated. The IRR is given as follows:

$$\text{IRR} = \frac{w_2 - w_3}{w_1} \quad (1)$$

Table 1

Chemical component with different fractions of corn stalk.

Sample name	Hemicellulose/wt.%	Cellulose/wt.%	Lignin/wt.%
Stem bark	21.77 ± 1.68	41.43 ± 2.51	7.52 ± 0.73
Ear husk	37.30 ± 1.42	38.70 ± 1.73	3.38 ± 0.12
Stem pith	24.81 ± 2.13	36.90 ± 3.02	4.78 ± 0.35
Leaf blade	23.74 ± 2.28	38.77 ± 2.65	7.15 ± 0.68
Whole stalk	25.73 ± 2.02	37.25 ± 1.98	6.81 ± 0.52

where w_1 = LCS weight (g); w_2 = filter paper and insoluble residues weight (g); w_3 = filter paper weight (g).

3. Results and discussion

3.1. Chemical composition of CS fractions

The chemical compositions with different fractions of CS were shown in Table 1. The ear husk has a noticeable difference from other fractions in view of hemicelluloses content with maximum value of 37.30%. The hemicelluloses content in stem pith, leaf blade, stem bark and whole stalk is 24.81%, 23.74%, 21.77% and 25.73%, respectively. The cellulose content in the stem bark was the maximum, 41.43%. That was 38.77%, 38.70%, 36.90% and 37.25% in the leaf blade, ear husk, stem pith and whole stalk, respectively. The lignin content of 7.52% in the stem bark was the maximum. The next was 7.15% in the leaf blade and 6.81% in the whole stalk. In contrast, low lignin content was detected in ear husk and stem pith, which was 3.83% and 4.78%, respectively. The results of chemical components of different fractions of CS in the study were some differences from other researchers (Chen et al., 2011; Templeton, Sluiter, Hayward, Hames, & Thomas, 2009; Weiss, Farmer, & Schell, 2010). In fact, there are important effects of some factors such as environmental conditions and crop maturity on the chemical components of CS (Pordesimo, Hamies, Sokhansanj, & Edens, 2005; Templeton et al., 2009). So it is difficult to reach the same components of CS collected by one researcher from other researchers.

3.2. Effects of chemical inhomogeneity on the IRR

Fig. 1 showed the effects of chemical inhomogeneity on IRR. Although all curves have a similar trend of decreasing and then increasing, there are noticeable differences. It suggested that chemical inhomogeneity of CS fractions had important effects on the liquefied process and reaction time played a significant role in the liquefied process to all raw materials. IRR of liquefied ear husk was the least at a range of reaction time, indicating that the liquefaction of ear husk was the easiest than other fractions. IRR leveled off after 45 min, suggesting the ear husk could be liquefied completely in 45 min. As for liquefied whole stalk, IRR reached its least

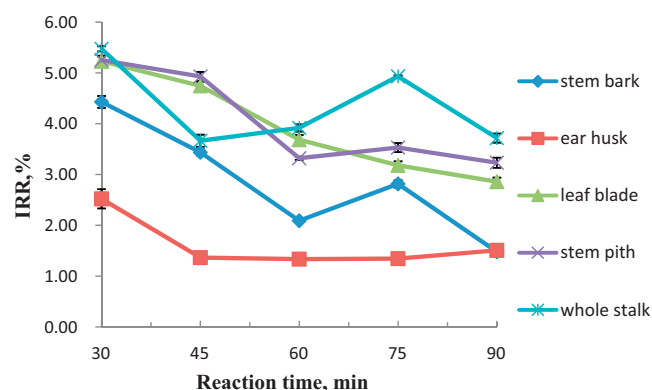


Fig. 1. IRR of liquefied product from different fractions of CS.

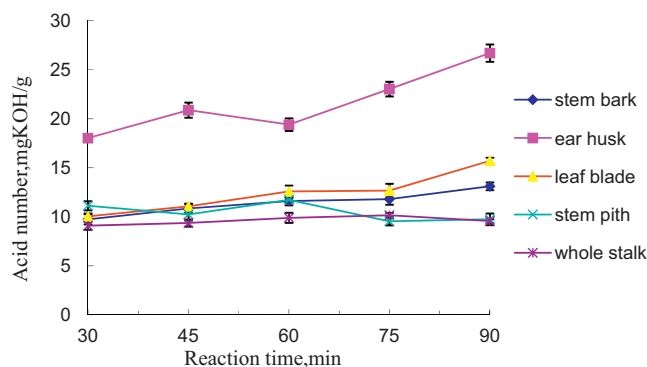


Fig. 2. Acid number of liquefied product from different fractions of CS.

value of 3.67% at 45 min. Along the further reaction, IRR increased rapidly to 4.93% at 75 min and then decreased to 3.72% at 90 min. The trends of stem bark and stem pith were similar. IRRs reached their lowest values of 2.09 and 3.32% at 60 and 75 min respectively, and increased to 2.82% and 3.53% in 90 min respectively.

Lignocelluloses are converted into small molecular weight compounds during solvolysis liquefaction, resulting in decrease of IRR. However, the small molecular weight compounds could be carbonized to form carbon at high temperature, which induced the increase of the IRR in return. The various IRR evolution behaviors could be attributed to the difference of chemical composition of fractions. The explanation of ear husk is vulnerable to liquefaction could be that hemicelluloses has smaller molecular weight and sensitive to solvent.

3.3. Effects of chemical inhomogeneity on acid number

The effects of chemical inhomogeneity on acid numbers from different fractions of CS were shown in Fig. 2. As could be seen in the figure, the trends of five curves were similar, the acid numbers increased with increasing reaction time. But notable difference could be found when each of the five curves was considered singly. The acid numbers of liquefied ear husk were the largest and of liquefied whole stalk were the least at the range of times. The acid number of liquefied ear husk was 18 mg KOH/g at a reaction time of 30 min and was 98.2% higher than the whole stalk's at the same reaction time. At 90 min, that was 26.7 mg KOH/g from ear husk and was 179% higher than from whole stalk. The acid numbers of liquefied leaf blade, stem bark and stem pith were similar at the reaction time of 30 min. However, there was a rapid increase of leaf blade's than the stem bark's with increasing time from 30 min to 90 min.

The researches of Yamada and Ono (2000) have indicated that alcoholysis reaction, oxidation reaction and condensation reaction occurred when polyol was used as liquefaction solvent to transfer the lignocellulose. At starting stage, the alcoholysis reaction takes the leading role. Increasing reaction time resulted in the appearance of oxidation reaction and condensation reaction. The increase of oxidation reaction or condensation reaction is one of main reasons of acid number increase. So, with an increasing of reaction time, the acid number increased. In addition, the different kind of lignocellulose results also in the difference of acid number (Ge, 2003). In other words, the chemical compositions of lignocelluloses are also a significant effect on the acid number. It is well known, the main chemical compositions of CS are cellulose, lignin, hemicellulose and other polysaccharides. But the ratio of these compositions was different in every fraction (Table 1). Leaf blade, stem bark and ear husk contained more cellulose and lignin. The hemicelluloses content in ear husk was the maximum. Due to better chemical reaction activity, the hemicellulose could be converted easier than cellulose into little molecular weight compounds, which resulted in

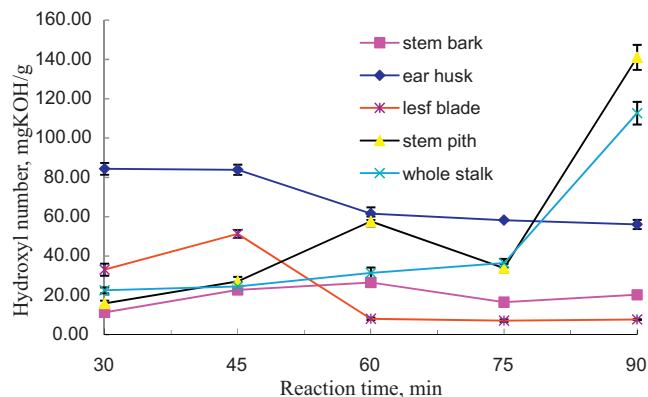


Fig. 3. Hydroxyl number of liquefied product from different fractions of CS.

occurrence of oxidation reaction and condensation reaction. Similar hemicelluloses content of stem pith, stem bark, leaf blade and whole stalk resulted in similar acid number.

3.4. Effects of chemical inhomogeneity on hydroxyl number

The effects of chemical inhomogeneity on hydroxyl numbers of liquefied products from different fractions of CS were shown in Fig. 3. As could be seen in the figure, the trends of five curves were remarkable different. The hydroxyl number of liquefied ear husk decreased with an increase of reaction time. The largest value 84 mg KOH/g was observed at a reaction time 30 min. The hydroxyl numbers of liquefied whole stalk and stem pith increased and reached their largest value of 113 mg KOH/g and 141 mg KOH/g, respectively. As for liquefied leaf blade and stem bark, the hydroxyl numbers increased and then decreased. But the turning-point of reaction time was different: 45 min and 60 min, respectively. These suggested that reaction time played a significant role in the liquefied process of CS fraction and each CS fraction had an important effect on the liquefied process.

The research of Yamada and Ono (2000) has also indicated that alcoholysis reaction is contributed to increasing hydroxyl number. However, with prolongation of reaction time, the oxidation reaction and condensation reaction become active, result in the increasing of acid number. So, with an increase of reaction time from 30 min to 75 min, the hydroxyl number decreased. However, the hydroxyl numbers from all samples except of liquefied ear husk at 90 min were higher than the values at 75 min, especially liquefied stem pith and whole stalk. This could be due to depolymerization of compounds from condensation reaction. Higher hydroxyl numbers of liquefied ear husk than others samples could be due to higher hemicelluloses content.

4. Conclusion

Chemical components of every fraction of CS were different remarkable. Hemicelluloses content in ear husk was the maximum, and cellulose content in the stem bark was the maximum. Higher acid number, higher hydroxyl number, and lower IRR were detected from ear husk liquefied products, and acid number from whole stalk was the least. These suggested that chemical compositions of CS fractions had important effects on the properties of liquefied products. Meanwhile, reaction time also played a significant role in the liquefaction process of CS fractions. With an increase of reaction time, IRR decreased firstly and then increased, and acid numbers increased, and hydroxyl number decreased. This work proved that it should be given attention various performances of CS fractions in

solvolysis liquefaction and different fractions of CS should be given themselves optimum applications.

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