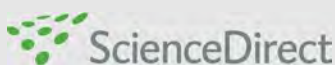


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Article (Dedicated to Professor Yi Chen on the occasion of his 80th birthday)

AlCl₃ catalyzed conversion of hemicellulose in corn stover

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ABSTRACT

The selective conversion of the hemicellulose in corn stover (stalk) by AlCl₃ as catalyst under hydrothermal conditions at low temperature was investigated. The effect of reaction temperature, reaction time, and AlCl₃ amount was investigated. The biomass samples before and after reaction were characterized by chemical titration, X-ray diffraction, and scanning electron microscopy. The conversion of the hemicellulose in the corn stover at 140 °C for 1 h reached 85.1%, while keeping a high proportion of the cellulose and lignin components unreacted with the conversions of 10.7% and 23.9%, respectively. Xylose and a small amount of acetic acid, and furfural were obtained from the filtrate from the hemicellulose conversion. Further reaction of the filtrate significantly improved the conversion of xylose. This was performed in a H₂O-tetrahydrofuran solvent system, and large amounts of levulinic acid, formic acid, and furfural were obtained. The γ-Al₂O₃/SO₄²⁻ solid acid catalyst selectively promoted the formation of furfural in the H₂O-tetrahydrofuran solvent system.

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1. Introduction

Dwindling petroleum resources combined with economic and environmental concerns over the petroleum-based economy make it imperative to develop new feedstocks for the production of fuels and chemicals [1–3]. Renewable biomass, which include agricultural residues such as corn stover (stalk), wheat straw, and other lignocellulosic materials, have the potential to be a sustainable feedstock for future fuels and chemicals [4,5]. Biomass has a complex structure consisting of three main polymeric components, namely, hemicellulose, cellulose, and lignin. Hemicellulose is the second most abundant polysaccharide in plants. It is usually bonded to various cell wall components such as cellulose, cell wall proteins, lignin, and other phenolic compounds by covalent and hydrogen bonds [6]. A wide variety of monosaccharides such as xylose, arabinose, galactose, and mannose are contained in hemicellulose [1,7], which can be converted to ethanol and other value-added

chemicals, such as 5-hydroxymethylfurfural (HMF), furfural, levulinic acid, and xylitol [8–15].

Currently, a common problem encountered in the production of value-added chemicals from the hemicellulose in biomass is that the physical and chemical properties of the hemicellulose, cellulose, and lignin in biomass are significantly different [16], which make it difficult to separate by fractionation the hemicellulose from the cellulose and lignin. When they are not separated, then in a conversion of hemicellulose, the cellulose and lignin components in biomass would also be degraded, and different liquid products would be obtained with low selectivities. Consequently, an extra separation of the products is necessary and difficult. To extract hemicellulose from biomass, the most common methods adopted include organic solvent treatment, alkaline extraction, alkaline peroxide extraction, liquid hot water extraction, and steam explosion-based extraction [17,18]. However, the practical pretreatment processes often involve the use of organic solvent and mineral acid (HCl,

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H₂SO₄), which cause waste formation, corrosion, and safety problems and require severe reaction conditions. [19]. To overcome the disadvantages of pretreatment, the selective conversion of hemicellulose while avoiding significant degradation of the cellulose and lignin would be an ideal method. The reaction residue that would then contain mainly cellulose and lignin can be used as the raw material for the production of value-added chemicals like 5-HMF and phenolic compounds [20–23]. The efficient and selective conversion of biomass by a fractional route was presented in our previous works [24,25]. So far, very few research on the selective conversion of the hemicellulose component in biomass has been reported. The selective conversion of hemicellulose in biomass to furfural using maleic acid with microwave heating was reported by Eurick et al. [11]. Stein et al. [26] reported a method for the selective catalytic depolymerization of hemicellulose using oxalic acid as the catalyst in a biphasic system (H₂O/2-MTHF). In our previous work [27], the selective conversion of hemicellulose in pubescens was achieved in a H₂O-cyclohexane (v/v = 1/1) system, and 86.6% hemicellulose conversion was obtained without significant degradation of the cellulose. The main liquid products from the hemicellulose conversion were formic acid and acetic acid.

The objective of this work is the selective conversion of the hemicellulose present in corn stover to obtain value-added chemicals like furfural and levulinic acid, while most of the cellulose and lignin components were to be unreacted and would remain in the reaction residue. AlCl₃ was used as the catalyst. It is cheap, abundant, and much safer than a mineral acid.

2. Experimental

2.1. Material and catalyst preparation

Corn stover sample was ground into powder (20–60 mesh) and dried in an oven at 110 °C overnight before use. AlCl₃ and solvents were obtained from commercial sources and used without further purification. γ -Al₂O₃ was calcined at 400 °C for 3 h before use. HZSM-5 was calcined at 550 °C for 6 h before use. ZrO₂ and γ -Al₂O₃/SO₄²⁻ were prepared according to the method reported in the literature [28,29].

2.2. Selective conversion of the hemicellulose in corn stover

The hydrothermal treatment of the corn stover was carried out in a 250 ml stainless steel autoclave reactor equipped with a stirrer. For a typical run, 3.0 g corn stover and the required amount of AlCl₃ were placed in the reactor with 100 ml high purity water. Air in the reactor was removed by flushing with pure nitrogen three times. Under 2.0 MPa of initial nitrogen pressure, the reaction system was heated from room temperature to the designated temperature. After reaction, the reactor was taken out from the electric furnace and cooled to room temperature. The gaseous products were collected in an evacuated gas bag, and they were then analyzed by gas chromatography (GC) with a thermal conductivity detector (TCD). The

content remaining in the autoclave, which was a mixture of water, liquid product, and solid residue, was collected by simply pouring it out and washing the reactor with high purity water three times. The collected mixture was filtered. The residue remaining was dried in an oven at 110 °C overnight and weighted for conversion calculation. It was then analyzed by X-ray diffraction (XRD), scanning electron microscopy (SEM), and chemical titration. The liquid products were quantitatively analyzed by GC with FID and high performance liquid chromatography (HPLC, Ultimate_3000) with a refractive index detector using calibration curves from standard samples. The yield (wt%) of liquid product was defined as: Yield = liquid product content (g)/hemicellulose contained in corn stover (g) × 100%.

2.3. Further reaction of the filtrate

After the removal of the hemicellulose in the corn stover, the further reaction of the filtrate (from the reaction of the corn stover catalyzed by 1 g AlCl₃ at 140 °C for 1 h) was performed in a H₂O/THF (50/50, v/v) solvent system. The operation and product analysis were similar to those in Section 2.2.

2.4. Characterization of the solid residue

The components (hemicelluloses, cellulose, and lignin) in corn stover and the unconverted part of the samples after reaction were analyzed using classical chemical titration methods. The experimental details of the analysis were previously given in reference [30].

The crystalline forms of the corn stover and residues obtained after liquefaction for different reaction times were examined by XRD measurement on a Dandong Fangyuan DX-1000 instrument. The diffracted intensity from Cu K α radiation ($k = 0.1540$ nm; 40 kV and 25 mA) was measured over the range from 4° to 40°. The crystallinity index (CI) of the cellulose part in samples was determined by $CI = (I_{002} - I_{AM}) / I_{002}$, where I_{002} is the peak intensity corresponding to the (002) ($2\theta = 22^\circ$) lattice plane of the cellulose, and I_{AM} is the peak intensity observed at 2θ of 18°. I_{002} represents both crystalline and amorphous material while I_{AM} represents only amorphous material [27]. SEM (FEI Inspect F, at an acceleration voltage of 20 kV) was used to characterize the surface morphology of the raw material and the residue after reaction.

3. Results and discussion

3.1. Selective conversion of the hemicellulose in corn stover

3.1.1. Effect of reaction temperature

Liquefaction of the corn stover using AlCl₃ as catalyst in aqueous solution was conducted at different reaction temperatures (100–180 °C). The results are shown in Table 1. At a low reaction temperature (100 °C), most of the hemicellulose (84.2%) contained in the corn stover were unreacted, and the cellulose and lignin components remained unchanged. With increasing reaction temperature from 100 to 140 °C, the conversion of corn stover significantly increased. The conversion

Table 1

Effect of reaction temperature on the conversion of the different components in corn stover.

<i>t</i> (°C)	Hemicellulose		Cellulose		Lignin	
	<i>R</i> ^a (%)	<i>C</i> ^b (%)	<i>R</i> ^a (%)	<i>C</i> ^b (%)	<i>R</i> ^a (%)	<i>C</i> ^b (%)
Raw material	18.8	0	46.1	0	17.3	0
100	14.4	15.8	37.0	1.0	14.2	0.6
120	9.1	46.7	36.1	3.5	12.7	11.1
140	2.6	85.1	33.4	10.7	10.9	23.9
160	1.4	91.8	30.9	17.4	12.0	16.0 ^c
180	0.4	97.8	19.1	49.1	13.4	6.3 ^c

Reaction conditions: corn stover 3.0 g, solvent H₂O 100 ml, reaction time 1 h, AlCl₃ 1.0 g.^a Remaining percentage in the reaction residue.^b Conversion of different components.^c Lignin content from chemical titration was higher than the actual value because of the formation of char at high temperatures (160–180 °C).

of the hemicellulose component in the corn stover reached 85.1% at 140 °C, while the conversions of cellulose and lignin components were 10.7% and 23.9%, respectively. On further increasing of the reaction temperature from 160 to 180 °C, the conversion of hemicellulose increased slightly. However, the conversion of cellulose quickly increased with increasing reaction temperature and reached 49.1% at 180 °C. Table 1 indicated that the conversion of the lignin in the corn stover increased to 23.9% with increasing reaction temperature to 140 °C, while it decreased to 6.3% at 180 °C. The decrease of lignin conversion at 160 and 180 °C was attributed to erroneous chemical titration. This was because of the formation of char at higher temperatures (160–180 °C), which caused the chemical titration of lignin to give in Table 1 a value that was higher than the actual value. This was confirmed by the presence of some phenolic compounds in the liquid products at 180 °C, which indicated that the lignin in the corn stover was degraded. These results indicated that the three components in corn stover have distinct reaction dependence on temperature, which was attributed to their different chemical and physical properties. Thus, the separation and selective conversion of the hemicellulose component in the corn stover can be achieved by using the appropriate reaction temperature. In our reaction system, the hemicellulose can be selectively converted at 140 °C without significant conversion of cellulose and lignin.

3.1.2. Effect of reaction time

The effect of reaction time on the conversion of corn stover is presented in Fig. 1. The reaction time 0 h means that the liquefaction reaction was immediately stopped when the temperature had increased from room temperature to the desired temperature. The conversion of cellulose and lignin gradually increased with increasing reaction time up to 4 h. It is remarkable that the effect of reaction time on the conversion of the hemicellulose in the corn stover was significantly different from the effects on the conversions of cellulose and lignin. With increasing reaction time to 1 h, the conversion of hemicellulose increased quickly, and most of the hemicellulose was converted after 1 h. On further increasing the reaction time from 1 to 4 h, the conversion of hemicellulose increased slowly. This implied that the conversion of hemicellulose was much easier than those of cellulose and lignin. Hemicellulose is non-cellulosic

and comprises short branched chain hetero-polysaccharides. Its average degree of polymerization is in the range of 80–200, which is much lower than that of cellulose [6]. Thus, the hemicellulose contained in the corn stover can be nearly converted within 1 h at a low temperature, when the conversions of cellulose and lignin were limited.

3.1.3. XRD measurement

In order to investigate the crystal structure of the cellulose in the corn stover after reaction, XRD analysis of the samples before and after reaction were carried out. The XRD patterns and calculated crystallinity index are given in Fig. 2. Corn stover is a lignocellulose complex in which hemicellulose, cellulose and lignin are connected to each other by ether links or glucosidic linkage [11]. As shown in Fig. 2(a), the corn stover exhibited diffraction peaks at $2\theta = 16.5^\circ$, 22.2° , and 34.8° , corresponding to the (101), (002), and (040) characteristic planes of cellulose I [27]. With increasing of the reaction time to 2 h, a significant increase in the CI from 82.67% to 89.33% was observed, which was ascribed to the removal of the hemicellulose and easily degradable lignin that had existed as amorphous materials [27]. This indicated that the structure of the cellulose in the corn stover was not destroyed by the reaction. This result agreed well with the result of the chemical titration. As

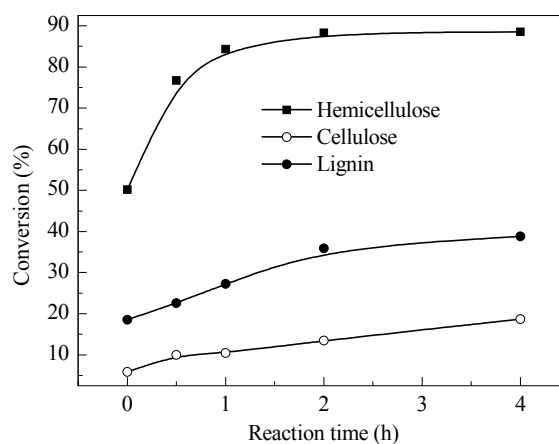


Fig. 1. Effect of reaction time on the conversion of the different components in corn stover. Reaction conditions: corn stover 3.0 g, solvent H₂O 100 ml, reaction temperature 140 °C, AlCl₃ 1.0 g.

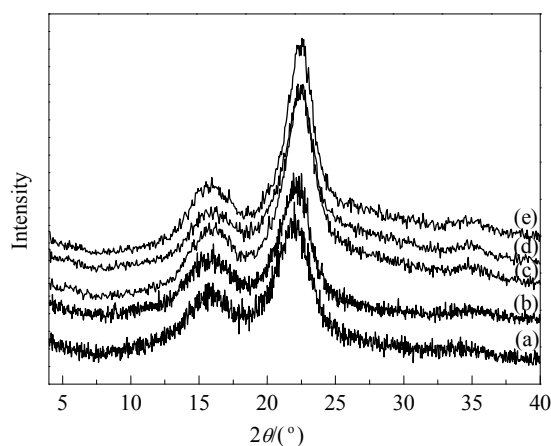


Fig. 2. XRD patterns of the corn stover and residues obtained after different reaction times. (a) Corn stover, CI = 82.67%; (b) 0 h, CI = 85.68%; (c) 0.5 h, CI = 87.89%; (d) 1.0 h, CI = 89.10%; (e) 2.0 h, CI = 89.33%.

reported by Wan et al. [31], when hemicellulose was extracted from paper pulp with 8% NaOH, fibrils appeared that aggregated and formed a more compact structure.

3.1.4. SEM characterization

The SEM analysis of the samples before and after reaction are shown in Fig. 3. As shown in Fig. 3(a), obvious cellulose bundles with a rough surface were observed, which was attributed to the coating of cellulose fibers by non-cellulosic materials, that was, a hemicellulose-lignin composite [32]. Spherical droplets were observed on the surface of the residue at 0 h, which suggested that some hemicellulose composite was peeled off from the cellulose bundles, while the cellulose bundles remained. In Fig. 3(c), the cellulose bundles are more iso-

lated while the hemicellulose composite has been mostly degraded. The comparison of Fig. 3(a), (b), and (c) showed that the hydrothermal treatment and catalysis by AlCl_3 achieved the removal of hemicellulose without significant degradation of cellulose and lignin, which agreed well with the chemical titration and XRD results.

3.1.5. Effect of reaction time on the distribution of liquid products

The effect of reaction time on the yields of liquid products is illustrated in Fig. 4. Xylose, furfural, and acetic acid were the main liquid products from the conversion of hemicellulose. Xylose was produced from the hydrolysis of xylose oligomers in the hemicellulose contained in the corn stover. Furfural was produced in a two step process consisting of the hydrolysis of xylose oligomers followed by the dehydration of xylose monomers [10]. Acetic acid was probably produced from the hydrolysis of acetylated xylose oligomers. With increasing of the reaction time to 1 h, the yield of xylose sharply increased. Due to the further dehydration to furfural, the xylose amount quickly decreased after 1 h, and there was little xylose at 4 h [33]. The yield of furfural and acetic acid gradually increased with reaction time up to 2 h and then decreased slightly with increasing reaction time from 2 to 4 h. These results confirmed that the hemicellulose component in corn stover was nearly completely converted after 1 h in this reaction system. The gas products were mainly C_2H_6 (42.8%), CO_2 (25.6%), H_2 (22.3%), and CO (9.3%).

3.1.6. Effect of AlCl_3 amount

To investigate the catalytic effect of AlCl_3 , a control experiment was conducted in the absence of AlCl_3 . The result indicated that only 31.3% hemicellulose was converted after 1 h.

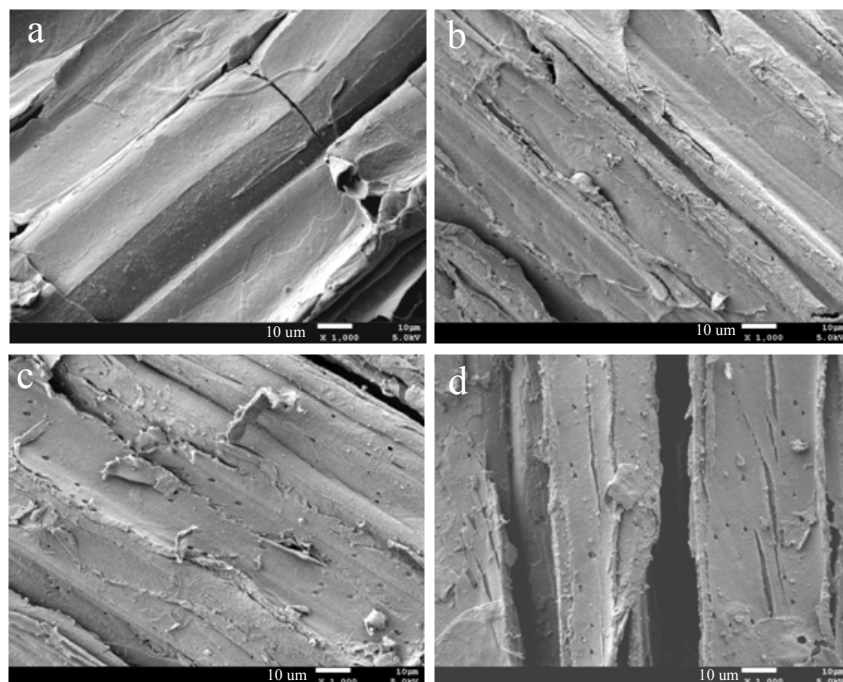


Fig. 3. SEM micrographs of the residues. (a) Raw material; (b) Treated for 0 h; (c) Treated for 1.0 h; (d) Treated for 2.0 h.

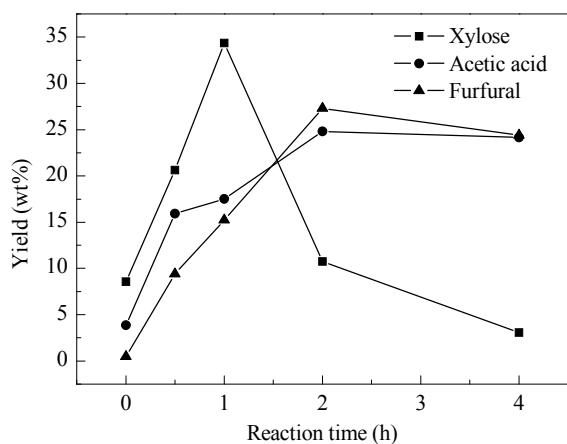


Fig. 4. Effect of reaction time on the distribution of liquid products from hemicellulose conversion based on the hemicellulose content in corn stover. Reaction conditions: corn stover 3.0 g, solvent H₂O 100 ml, reaction temperature 140 °C, AlCl₃ 1.0 g.

With increasing amount of AlCl₃, the conversion of the hemicellulose in the corn stover significantly increased. The hemicellulose was nearly completely converted with 2 g AlCl₃ added, and the percentage conversion reached 97.9%. However, the increase in the AlCl₃ amount did not cause an increase in the conversion of the cellulose and lignin components. The amount of AlCl₃ significantly affected the distribution of liquid products. As shown in Fig. 5, with increasing amount of AlCl₃, the yield of xylose significantly increased when this was less than 0.5 g, and then there was quick decrease because of the further conversion to furfural. The yield of furfural and acetic acid gradually increased with increasing amount of AlCl₃. This indicates that the conversion of xylose was efficiently catalyzed by AlCl₃. Yang et al. [28] also pointed out that AlCl₃ significantly promoted the conversion of xylose to furfural. The yield of glucose gradually decreased with increasing amount of AlCl₃, which implied that AlCl₃ was effective for the further conversion of glucose.

3.2. Further reaction of the filtrate

From Fig. 4, it can be found that the yield of furfural was limited when the reaction was carried out for 1 h, and a large amount of xylose was present in the filtrate. To further convert the xylose and its oligomers to higher value-added chemicals like furfural and to prevent damage to the carbohydrate, the further reaction of the filtrate obtained from the reaction at 140 °C for 1 h was carried out. The results are shown in Table 2. Xylose in the filtrate was nearly completely converted by direct heating to 160 °C for 2 h, which implied that AlCl₃ in the filtrate efficiently catalyzed the conversion of xylose and its oligomer at the increased temperature. Zhang et al. [34] indicated that AlCl₃ was more efficient than a mineral acid for producing furfural from xylose in an ionic liquid. However, the increase in furfural in our reaction system was quite limited (from 16.29% to 19.12%) during the further reaction of the filtrate, which was ascribed to the formation of some char under the hydrothermal conditions at the relatively high temperature.

Our previous work pointed out that a high yield of furfural

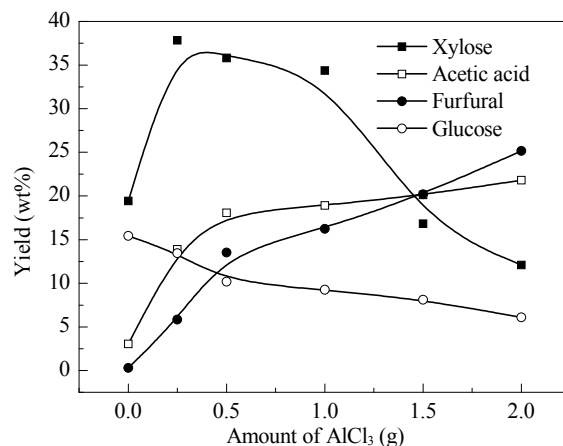


Fig. 5. Effect of AlCl₃ amount on the yield of different liquid products from hemicellulose conversion. Reaction conditions: corn stover 3.0 g, solvent H₂O 100 ml, reaction temperature 140 °C, 1 h.

from xylose can be obtained using a H₂O/THF medium containing AlCl₃ as catalyst. Thus, an equivalent volume of THF was employed as a co-solvent in the further reaction of the filtrate. The result indicated that the yield of furfural was significantly improved in the H₂O-THF reaction system with the use of AlCl₃, and there was almost no char formation. This indicated that the addition of THF was favorable for the production of furfural. Meanwhile, the yield of formic acid and levulinic acid also increased, and the yield of acetic acid showed no obvious change in the further reaction of the filtrate. Levulinic and formic acid are usually formed with a ratio of 1:1 by the hydrolysis of 5-HMF, which comes from the dehydration of hexose like glucose and fructose [5]. However, the yield of formic acid was much higher than that of levulinic acid in the H₂O-THF reaction system. This suggested that the formic acid mainly came from the hydrolysis of the carboxylic groups of uronic acid, and a lot of formic acid was obtained from the conversion of hemicelluloses in pubescens in our previous work [27]. To investigate the origin of the formation of levulinic acid, a control experiment was carried out using xylose as the raw material. The result indicated that 6.2% levulinic acid was obtained with 9.42% formic acid. Dumesic and co-workers [33] pointed out that levulinic acid is formed from furfuryl alcohol, which was produced by the reduction of furfural. Therefore, the formation of levulinic and formic acid in our reaction system was from two pathways. One pathway was by the further conversion of the hexose in the hemicellulose of the corn stover to 5-HMF, which was further hydrolyzed to levulinic and formic acid. The other pathway was by the reduction of furfural to furfuryl alcohol, which was further hydrolyzed to levulinic acid.

Generally, the production of furfural from xylose and its oligomers is catalyzed by mineral acids such as H₂SO₄ and HCl [6]. However, the use of a mineral acid causes serious equipment corrosion and environmental pollution. To further improve the yield of furfural, several solid acid catalysts were studied with the H₂O-THF system. As shown in Table 2, the yield of furfural was slightly promoted by the addition of γ -Al₂O₃, and the yield of acetic acid was also increased. HZSM-5 exhibited a similar effect to γ -Al₂O₃ for the promotion of furfural yield, but inhib-

Table 2

Distribution of liquid products for the further reaction of the filtrate.

Sample	Liquid product distribution (%)					
	Glucose	Xylose	Formic acid	Acetic acid	Levulinic acid	Furfural
Filtrate ^a	4.13	34.37	1.00	21.01	1.12	16.29
H ₂ O ^b	3.38	1.60	3.02	21.61	2.09	19.12
H ₂ O/THF ^c	—	—	37.81	24.52	13.43	26.59
ZrO ₂ ^d	0.71	—	24.84	21.75	14.83	19.92
γ-Al ₂ O ₃ ^d	1.78	—	37.99	29.84	15.13	28.99
HZSM-5 ^d	5.02	—	31.14	22.20	14.29	29.88
γ-Al ₂ O ₃ /SO ₄ ²⁻ ^d	2.01	—	35.51	20.04	15.00	35.88

^aThe filtrate for the first reaction at 160 °C for 2 h.^bFurther reaction of filtrate by heating the filtrate to 160 °C.^cFurther reaction of filtrate in H₂O/THF (v/v = 1:1) solvent.^dFurther reaction of filtrate in H₂O/THF (v/v = 1:1) solvent catalyzed by solid acid catalyst.

ited the formation of formic acid. This implied that the added solid acid catalyst had a pore structure and acidity that was favorable for the production of furfural. However, both the formation of furfural and formic acid was significantly inhibited by the addition of ZrO₂, which was possibly due to its smaller pore volume [29]. The yield of furfural was much increased by γ-Al₂O₃/SO₄²⁻, which had increased acidity over γ-Al₂O₃, implying that γ-Al₂O₃/SO₄²⁻ is an efficient catalyst for the conversion of xylose to furfural.

Based on these experimental results, it can be deduced that AlCl₃ as a Lewis acid selectively promoted the conversion of the hemicellulose in corn stover at low temperature. Much xylose was obtained in the filtrate, which implied that AlCl₃ catalyzed the depolymerization of hemicellulose to yield the monomer. However, AlCl₃ did not catalyze well the further conversion of xylose to furfural. In the further reaction of the filtrate, the yield of furfural was significantly improved by increasing the acidity of the solid acid catalyst added. The selective conversion of the hemicellulose in corn stover to furfural can be achieved by combining AlCl₃ and a solid acid catalyst in a two-step process.

4. Conclusions

The selective conversion of the hemicellulose in corn stover was achieved without significant degradation of the cellulose and lignin by using AlCl₃ as the catalyst under hydrothermal conditions at a low temperature, which eliminated expensive pretreatment processes and simplified product separation. The further reaction of the filtrate by increasing the reaction temperature promoted the conversion of xylose and its oligomers. By the addition of an equivalent volume of THF to form a co-solvent, the yield of furfural, levulinic, and formic acid was significantly improved. γ-Al₂O₃/SO₄²⁻ significantly increased the yield of furfural in the H₂O/THF reaction system. This method allowed the selective conversion of the hemicellulose in corn stover to furfural, while the reaction residue contained mainly cellulose and lignin that can be further used as raw materials to produce fuels and value-added products.

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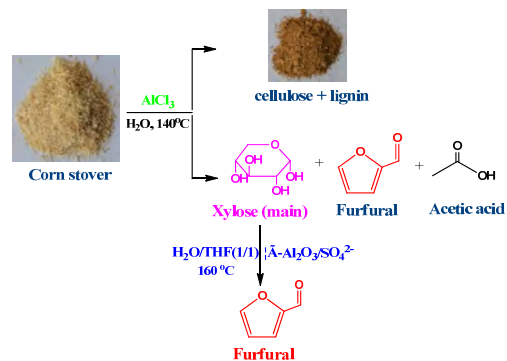
Graphical Abstract

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AlCl₃ catalyzed conversion of hemicellulose in corn stover

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The selective conversion of the hemicellulose in corn stover was achieved using AlCl₃ as the catalyst under hydrothermal conditions. γ -Al₂O₃/SO₄²⁻ efficiently catalyzed the formation of furfural in a H₂O/THF system used for the further reaction of the filtrate.



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AlCl₃催化玉米秸秆中半纤维素的选择性转化

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摘要: 研究了AlCl₃ 催化剂作用下, 水热体系中玉米秸秆中半纤维素组分在温和条件下的选择性转化. 详细考察了反应温度、反应时间和AlCl₃用量对半纤维素选择性转化的影响. 原料及反应后的固体残渣分别采用化学滴定、X射线衍射和扫描电镜进行表征. 结果表明, 140 °C下反应1 h可转化玉米秸秆中的大部分半纤维素, 转化率为85.1%; 而玉米秸秆中的绝大部分纤维素和木质素组分仍保留在固体残渣中, 此时纤维素和木质素的转化率分别为10.7%和23.9%. 半纤维素转化的主要液体产物为木糖, 同时含有一些乙酸和糠醛. 升高温度, 将滤液进行进一步反应可促进木糖的转化. 在水/四氢呋喃反应体系中, 滤液的进一步反应有利于乙酰丙酸、甲酸和糠醛的生成. 固体酸催化剂 γ -Al₂O₃/SO₄²⁻的加入可进一步提高糠醛的收率.

关键词: 玉米秸秆; 半纤维素; 选择性转化; 三氯化铝; 糠醛

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