Characteristics of Cotton Stalk Torrefaction Catalyzed by Magnesium Chloride

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Abstract

Multistep fast pyrolysis of magnesium chloride ($MgCl_2$)–impregnated biomass materials offers a promising way to obtain a value-added chemical-rich liquid product. In this work, cotton stalk with $MgCl_2$was pyrolyzed in a thermogravimetric analyzer and a fixed-bed reactor at 260°C. The feedstock characteristics, product distribution, and liquid-phase compositions were analyzed. The presence of $MgCl_2$ changed the product distributions and liquid-phase composition. Only two targeted chemicals were successfully collected for the purpose of chemical production. The effect of catalyst loading on pyrolysis behavior for furfural and acetic acid production was studied. The furfural and acetic acid contents in the water-free liquid phase were about 28 and 51 percent, respectively, whereas the $MgCl_2$ content was 18.54 percent.

Torrefaction is a thermal process that involves heating the biomass to temperatures between 200°C and 280°C in an inert environment. The process can be called mild pyrolysis, as it occurs at a lower temperature range of the pyrolysis process, corresponding to the decomposition range of the hemicellulose component in biomass. After the torrefaction process, the moisture of raw biomass and the oxygen-to-carbon ratio are reduced, leading to the energy density of the torrefied biomass being increased by 8 to 36 percent, depending on the torrefaction conditions. About 90 percent of the energy of biomass was attained (Chen and Kuo 2011). The efficiency of the next thermochemical process is enhanced because ignitability and reactivity is improved. The fibers of biomass become brittle, improving grindability and reducing the cost and energy of grinding. In general, torrefaction is a promising technique to improve the performance of biomass for energy utilization.

Today, studies on torrefaction focus mainly on improving the properties of biomass by upgrading its heating value and the qualities of bio-oil derived from the main pyrolysis stage (Aziz et al. 2012, Hilten et al. 2013). Much less attention has been given to the properties of the liquid product from torrefaction itself. The liquid phase of biomass torrefaction can be divided into three subgroups: water, organics, and lipids (Tumuluru et al. 2011). The latter two subgroups contain kinds of value-added chemicals that can be used as feedstocks in the fine chemical industry. Although these chemicals are easily available through the torrefaction process, they have not been utilized effectively. The main challenge in upgrading the liquid phase for chemicals is that the liquid phase is a complex mixture, and most of the chemicals in it are of low content. Therefore, the commercialization of the liquid phase for value-added chemicals requires the production of a specific liquid phase with a high content of target products. For this purpose, several conversion techniques have been developed (Duan and Savage 2011, Mortensena et al. 2011). Among these processes, catalytic pyrolysis was considered the most promising technique and was introduced into biomass pyrolysis to produce the desired chemicals and high-quality fuels. Many studies have focused on the catalytic activity of alkali/alkaline earth hydroxide on biomass torrefaction and

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pyrolysis for the purpose of fuel production (Pushkaraj et al. 2011, Foster et al. 2012). In addition, torrefaction temperature should be strictly controlled, close to the hemicellulose final decomposition temperature and cellulose temperature, which ensure the liquid phase of torrefaction mainly from the hemicellulose decomposition. Previous studies (Pierre 2012) have shown that the liquid phase from the mixture of cellulose and hemicellulose pyrolysis is more complex than that from hemicellulose torrefaction and that the content of target chemicals is lower than that obtained in the latter process. This leads to the separation process being very expensive and not economically efficient.

The purpose of this work was to investigate the properties of solid fuel and liquid phases from biomass catalytic torrefaction. The torrefaction characteristics of cotton stalks impregnated with magnesium chloride ($MgCl_2$) was researched using a thermogravimetric analyzer (TGA) to determine the torrefaction temperature. Gas chromatography–mass spectrometry (GC-MS) was used to evaluate the liquid-phase composition from the fixed-bed reactor.

Materials and Methods

Materials

Cotton stalk samples were collected from Shandong province, China, and used in this study. All samples were ground to a particle size range of 40 to 60 mesh after being washed to have the soil or dirt removed and then oven-dried at 105°C to a constant weight.

$MgCl_2$, purchased from Sinopharm Chemical Reagent Co., Ltd., was used in this study by using the incipient wet impregnation method. Cotton stalk samples were impregnated by three different concentrations of $MgCl_2$ solution. Different concentration solutions were added to the cotton stalk and then stirred for 2 hours at room temperature. The theoretical weight ratio of metal ions to pine bark was 0.05, 0.1, and 0.2. After impregnation, the actual $MgCl_2$ loading was 4.89, 9.02, and 18.54 percent.

Equipment and procedure

The moisture content, ash content, and volatile matter content were determined following the procedures given in ASTM D4442 (ASTM International 1992), ASTM E1534 (ASTM International 2006), and ASTM E872 (ASTM International 1982) standard methods, respectively. Fixed carbon content was calculated as the difference between the total content and the sum of moisture and volatile matter. The ultimate analysis, which measured the carbon, hydrogen, nitrogen, oxygen, and sulfur content, was carried out by a CHNS analyzer (Elementar Vario EL III). The oxygen content was calculated as the difference between the total content and the sum of carbon, hydrogen, nitrogen, and sulfur. Analysis of the chemical composition of samples was performed according to the method given by Phanphanich and Mani (2011). The results are presented in Table 1. The solid product and liquid phases were obtained by weighing the components before and after the experiments, and the gases were obtained by the difference.

Torrefaction characteristics of cotton stalks were analyzed using a TGA (Mettler TGA/DSC1/1600HT). About 10 mg of unimpregnated sample was placed on a thermobalance at a heating rate of 50°C /min up to 600°C at a steady nitrogen flow of 50 mL/min.

Table 1.—Proximate, ultimate, and chemical analysis of cotton stalk material.

Properties[a]	Content (%)
Proximate analysis	
Moisture	9.07
Volatile matter	69.75
Fixed carbon (by difference)	16.73
Ash	4.45
Chemical analysis	
Hemicellulose	22.86
Cellulose	38.36
Lignin	25.05
Ultimate analysis	
C	43.56
H	6.08
O (by difference)	49.36
N	0.86
S	0.14

[a] C = carbon; H = hydrogen; O = oxygen; N = nitrogen; S = sulfur.

The pyrolysis processes were carried out in a stainless steel tube reactor with a diameter of 40 mm and a length of 500 mm using a fixed-bed reactor to collect the liquid phase. A nitrogen carrier gas was passed through the reaction tube to keep the reaction system in an inert environment and to remove volatile products from the biomass pyrolysis system. An external furnace was used to provide heat to the reactor. A vapor condenser system was used to cool the pyrolysis vapor and condense the tar.

The condensed bio-oil was analyzed using GC-MS (US VARIAN 3800/2200). The GC capillary column CP-SIL5, used for separation, was 30 m by 250 μm with a 0.25-μm film thickness. The MS detector was set at a scan mode with a mass-to-charge range from 40 to 500 amu. Standard electron impact ionization at 70 eV was used. The ion source temperature was 240°C. The GC oven temperature was initially held at 60°C for 2 hours, ramped at 3 K/min to 260°C, and then held at 260°C for 15 minutes. The injector and detector temperatures were set at 250°C and 235°C, respectively. The injector split ratio was fixed at 20:1. Helium (99.9999%) was used as a carrier gas with a constant flow of 1.0 mL/min. The pyrolysis–oil sample was prepared as 5-wt% solutions dissolved in dichloromethane filtered through a 0.45-μm polytetrafluoroethylene filter. One microliter of pyrolysis–oil solution was injected for each analysis.

Results and Discussion

Determination of torrefaction temperature

The pyrolysis behavior of raw cotton stalk was carried out, and TGA and differential thermal gravity (DTG) curves are given in Figure 1. Similar to the conclusion on biomass pyrolysis from another study (Peng and Wu 2009), there are two main weight-loss stages in our investigated temperature range. The first stage was around 50°C to 110°C, corresponding to the dewatering process. The second stage, between 230°C and 400°C, was the main weight-loss stage and represented 60 percent weight loss. This stage is owing mainly to the decomposition of cellulose. The shoulder is at about 260°C and can be attributed to the decomposition of hemicellulose (Bridgeman et al. 2008). This conclusion was

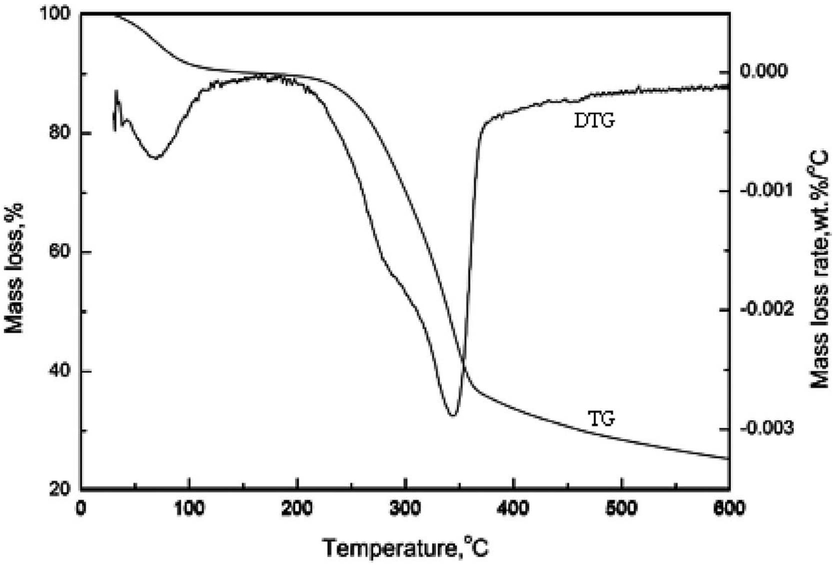

Figure 1.—Thermogravimetric (TG) analyzer and differential thermal gravity (DTG) curves of raw cotton stalk.

consistent with the results of the chemical composition analysis of samples. The hemicellulose composition of the samples decreased from 22.86 to 1.89 percent after torrefaction treatment. On the other hand, the cellulose and lignin content increased from 38.36 and 25.05 percent to 52.07 and 35.46 percent, respectively. Thus, 260°C was chosen as the torrefaction temperature in this work because most of the hemicellulose component was decomposed at this point. In order to verify the reasonableness of the temperature chosen in this study, a higher temperature pyrolysis (280°C) was also conducted. About 68 compounds detected from the liquid phase pyrolyzed at 280°C using GC-MS, whereas 12 compounds from the liquid phase pyrolyzed at 260°C. The difference between the composition of these two liquid phases indicated that more cellulose and lignin components were pyrolyzed at 280° C. Similar results were obtained by a previous study (Pushkaraj et al. 2011).

Fixed-bed torrefaction results

Product yield.—The yields of the product phases (in wt% calculated from the initial amount of raw material) are given in Table 2. The yield of the liquid phase is much higher than the yield from noncatalytic runs, with the increase of $MgCl_2$ loading from 0 to 18.54 percent and the liquid-phase yield increasing from 5.98 to 16.26 percent. On the contrary, the char decreased with the increasing of $MgCl_2$ content, which is opposite to the conclusion from biomass pyrolysis at higher temperature. This trend can be attributed to the following two opposite catalytic effects in the process of biomass catalytic pyrolysis. On the one hand, the addition of $MgCl_2$ catalyzed the decomposition of the cellulose component by lowering the cellulose temperature and accelerated the cellulose pyrolysis reaction; on the other hand, the catalytic effect changed the product distribution of hemicellulose decomposition and catalyzed the charring reactions, leading to more solid and less volatile products. The first catalytic effect should be ascribed to the decreased solid phase and increased liquid yield at the investigated temperature. The second catalytic effect should be responsible for solid-phase formation. In this work, the char formation reaction catalyzed by $MgCl_2$ could be neglected because the pyrolysis temperature is relatively low (Chen and Kuo 2011).

Table 2.—Product distribution of cotton stalk pyrolysis with different catalysts loading at 533 K.

	Distribution (wt%) at a catalyst loading of:			
Product	0%	4.89%	9.02%	18.54%
Noncondensable gas (by difference)	11.15	11.57	11.33	14.39
Pyrolysis–oil	5.98	8.38	10.32	16.26
Solid product	82.87	80.05	78.35	69.35

Chemical composition of the liquid phase.—The composition of the liquid phase (water free) was characterized using GC-MS. The GC area percent of detected compounds in different liquid phases is given in Table 3. About 38 compounds in the liquid phase were detected by GC-MS from the noncatalytic process. In the catalytic process, only two dominant compounds (furfural and acetic acid) were detected from GC-MS analysis, and most of the chemicals greatly decreased or disappeared. This indicated that $MgCl_2$ changed the liquid-phase composition significantly. Acetic acid and furfural content increased from 38.93 and 7.49 percent to 50.99 and 28.19 percent, respectively, with 18.54 percent $MgCl_2$ impregnation. This trend was consistent with the results of Wan et al. (2009) and Prins et al. (2006). The $MgCl_2$ exhibited high selectivity on furfural production (Wan et al. 2009). Results from Prins et al. (2006) showed that the liquid rich in acetic acid could be produced during carbonization or torrefaction of biomass at temperatures lower than 300°C (Patwardhan et al. 2011).

In the process of hemicellulose pyrolysis, the formation of acetic acid is involved in the primary elimination reaction of the active O-Ac groups in the side chain of *O*-acetyl xylan (Guo et al. 2011). The cleavage of the O–C5 or C2–O chain on the arabinose in the side chain also contributed to the formation of acetic acid. The formation of acetic acid is comparatively dominant over the latter since the acetyl

Table 3.—Pyrolysis liquid compounds identified by gas chromatography–mass spectrometry (GC-MS).[a]

Retention time (min)	Peak name	GC area (wt%) at a catalyst loading of: 0%	4.89%	9.02%	18.54%
1.417	Chloride		9.78	11.69	16.46
1.423	1-Butanol	3.27			
1.495	Acetic acid, methyl ester		2.14	2.09	
1.473	Formic acid	3.45	5.32	4.94	5.79
1.556	Acetic acid	38.93	45.97	49.53	50.99
1.672	1 2-Propanone, 1-hydroxy-	5.87	2.84	2.11	1.69
1.938	1-Hydroxy-2-butanone	4.12			
2.088	Cyclotrisiloxane, hexamethyl-		0.60		
2.204	Furfural	7.49	18.84	20.46	28.19
2.271	2-Furanmethanol	1.11			
2.315	1,2-Ethanediol, diacetate	1.17			
2.614	2(5*H*)-Furanone	1.38	1.33	1.06	0.66
3.789	*sec*-Butylamine	2.08			
3.922	Levoglucosenone		2.71	1.37	4.13
4.465	1,2-Benzenediol	1.80			
4.830	Cyclobutane, methyl-				1.17
5.102	3,4-Dihydroxyacetophenone	1.22			
5.938	Pentanoic acid, 3-methyl-4-oxo-	1.05			

[a] Only the chemicals with a GC area percentage of greater than 1 percent are listed.

groups are in larger proportion than the 4-*O*-methylglucuronic acid units in the hemicellulose structure.

Furfural is obtained through the cleavage of the bond between O–C5 and ring formation between the C2 and C5 positions on the main chain of xylan (Shen et al. 2010). The other two pathways for furfural formation are related to the decomposition of 4-*O*-methylglucuronic xylan along with the release of CO_2 and methanol. One is the ring-opening reaction of the depolymerized xylan unit through the cleavage of the hemiacetal bond (between oxygen and C-1 on the pyran ring), followed by dehydration between the hydroxyl groups on the C2 and C5 positions. The other is the cleavage of the 1,2-glycosidic bond between the xylan unit and the 4-*O*-methylglucuronic acid unit, followed by the ring-opening reaction and rearrangement of the 4-*O*-methylglucuronic acid after the elimination of CO_2 and methanol. Accordingly, it was found that the *O*-acetylxylan unit did not contribute to the formation of furfural (Shen et al. 2010).

Unfortunately, few studies have been done on the catalytic mechanism of $MgCl_2$ on hemicellulose decomposition, and further studies need to be carried out to investigate the decomposition routes of hemicellulose with the addition of catalysts.

Conclusions

In this work, cotton stalk impregnated with different concentrations of $MgCl_2$ was pyrolyzed in a TGA and a fixed-bed reactor. The biomass was torrefied at 260°C to ensure that the hemicellulose in a cotton stalk is the only component to be decomposed. The presence of $MgCl_2$ changed the liquid-phase composition by inhibiting the formation of most of the compounds, leaving the furfural and acetic acids as the two dominant compounds. The yield of furfural and acetic acid was affected by $MgCl_2$ content. The furfural and acetic acid contents in the water-free liquid phase were about 28 and 51 percent, respectively, whereas the $MgCl_2$ content was 18.54 percent.

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