Catalytic fast pyrolysis of corn stover in a fluidized bed heated by hot flue gas: Physicochemical properties of bio-oil and its application

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Abstract: Fast pyrolysis of corn stover was performed at temperatures in the range of 450°C-525°C in a fluidized bed.   The chemical composition of the bio-oil acquired was analyzed by GC/MS, and its pH, kinetic viscosity and calorific values were determined.   In the pyrolysis system used in this experiment, some improvements to former pyrolysis systems were done. Two screw feeders were used to prevent jamming the feeding system, and the condenser was equipped with some nozzles and a heat exchanger to cool quickly the cleaned hot gas into bio-oil.   The results showed that the bio-oil yield increased with increasing pyrolysis temperature and then declined with a further increase in pyrolysis temperature.   The highest bio-oil yield of 43.3 wt.% was obtained at 500°C with the dolomite as bed material.   The char yield always decreased with the increase of temperature.   The major chemical compounds of bio-oil included acetol, butanone, acetic acid, propionic acid, ethylene glycol, phenol, etc.   Pyrolysis oil was completely immiscible in diesel, but homogeneous emulsions were obtained when mixing the pyrolysis oil, emulsifier with diesel in different ratios.

Keywords: corn stover, pyrolysis, bio-oil, fluidized bed, hot flue gas, GC/MS

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1   Introduction

Because of the global climate changes, environmental pollution and reduction of availability of fossil energy resources, there is increasing interest in biomass as a renewable resource with high potential for energy production.   Biomass can be converted to various forms of energy through numerous thermochemical conversion processes[1,2], depending upon the type of energy desired. Among the thermochemical processes, pyrolysis is a promising tool for providing bio-oil that can be used as fuel or chemical feedstock[3].

Depending on the operating conditions, the pyrolysis process can be divided into two classes: conventional pyrolysis and fast or flash pyrolysis[4].   Conventional pyrolysis is a known technology for producing charcoal (mainly) and chemicals such as methanol and acetic acid[5].   The main goal of fast pyrolysis is to convert the biomass into a liquid.   In practice, about 40%-75% of the biomass (on dry basis) is converted into pyrolytic oil, and about 10%-20% of the biomass is converted into

char[6].   Fast pyrolysis offers a flexible and attractive way of converting biomass into a liquid, which can be easily stored, transported and handled for the production of heat, power and chemicals.   In fast pyrolysis, biomass decomposes very quickly to generate mostly vapours and aerosols and some charcoal and gas.   After cooling and condensation, a dark brown homogenous mobile liquid is formed which has a heating value about half that of conventional fuel oil.   A high yield of liquid is obtained with most biomass feeds low in ash.   Principles and practice of biomass fast pyrolysis and applications for the liquid product were reviewed by Bridgwater[7].   Bio-oil has a number of undesirable characteristics as fuel, such as thermally unstable components leading to gum formation, low heating value due to the water content and highly oxygenated compounds, a corrosive organic acid component, and phase instability with a tendency towards phase separation[6,7].

Corn stover is one of the major agriculture biomasses produced in large quantities in developing countries.   In China, nearly 1.22-1.27 million tons of corn stover as residue is produced every year[8].   Part of these is consumed in a traditional way, such as fodder for livestock and household fuel for stoves.   Until recently, the majority of corn stovers have not been used and disposed of by burning in open fields, causing environmental and public health problems.   At present, China energy policies are strongly encouraging the use of corn stover for energy purposes, mainly owing to three aspects: economic and social development, elimination of wastes, and reduction of CO_2 emissions[9].   In this situation, fast pyrolysis of biomass, as a promising technology, constitutes an attractive option.

Comparing the density and energy content in the corn stover with rice straw, it has been found that the density of corn stover (220 kg/m^3) is higher than the density of rice straw (63.85 kg/m^3).   Furthermore, the energy content in the corn stover is 15.07 MJ/kg which is higher than the energy content of rice straw (13.62 MJ/kg)[10].   This clearly suggests that the bioenergy plant using corn stover will be more efficient than some straw available in the world.   Fixed carbon content and the volatile fraction in corn stover are higher than many agricultural

biomass[11].   And so it can be realized that pyrolysis oil from fast pyrolysis of corn stover has higher quality.   Fast pyrolysis of a large number of feedstocks, such as rice husk, rice straw, wood, cedar sawdust, coffee bean residue, sugarcane residue, cassava residue and many more, has been extensively studied[12-17].   In order to improve the quality of bio-oil, some catalytic pyrolysis tests were performed based on fixed bed reactor, and the catalyzers included red mud, HZSM-5 and metallic oxide[18-20].   However, there has been little information to produce bio-oil from fast catalytic pyrolysis of corn stover by fluidized-bed reactor.   In this study, fast pyrolysis of corn stover was investigated in a fluidized-bed reactor with dolomite as catalytic bed material and the effects of pyrolysis temperature and bed material on the product distribution were analyzed.   The chemical composition of the bio-oil acquired was analyzed by GC/MS, and its pH, kinetic viscosity and calorific values were determined.

2   Materials and methods

2.1   Biomass feedstock

Corn stover was used in this study as the representatives of agricultural residues.   The sample was first crushed and sieved.   Fractions in the size range of <1.0 mm were used in the pyrolysis experiments.   The main properties of corn stover are listed in Table 1.

Table 1   Main characteristics of corn stover

Proximate analysis/wt.%	Value
Moisture	6.35±0.12
Volatile matter	74.61±0.34
Fixed carbon	13.45±0.21
Ash	5.59±0.17
Ultimate analysis/wt.%	
Carbon	48.62±0.23
Hydrogen	5.86±0.09
Nitrogen	0.85±0.06
Oxygen (by difference)	44.67±0.25
Calorific value /MJ·kg^{-1}	17.3±0.65

2.2   Experimental apparatus and procedure

The fast pyrolysis experiments were performed in the fluidized-bed biomass fast pyrolysis liquefaction plant (Figure 1) located in Shandong Research Center of Engineering & Technology for Clean Energy (Zibo, China).   The experimental device mainly consists of a

hopper, two screw feeders, an electric heater, a fluidized bed reactor, two cyclones, two condensers, an oil pump, etc.   The hopper is used to contain corn stover feedstock. The two screw feeders have the same configuration and size; the first one is used to control the feeding rate and the second one operates at a relatively high speed to prevent jamming the feeding system.   The fluidized bed reaction tube has a height of 2 m and a diameter of 70 mm in which the corn stovers are rapidly heated for pyrolysis. The electric heater can ensure the reactor to maintain the required temperature.   The two cyclones are used to separate solid particles such as charcoal and ash from the hot gas.   The condenser is equipped with some nozzles and a heat exchanger.   The condenser can quickly cool the cleaned hot gas into a liquid.   An oil pump is used to pump the condensed liquid from the bottom of the condenser to the nozzles on the top of the condenser. Pumping the cooled liquid back into the condenser assists in the scrubbing and condensation process. Thermocouples and pressure meters are used to monitor and control the pyrolysis system.   The specification of the thermocouples is K Type, made from the alloy of Pt-Rh, measurement range from 0 to 815°C with measurement accuracy of the thermocouples of ±1°C. The specification of the pressure gauges has a range from 0 to 2.5 MPa, and the measurement accuracy of the pressure gauges is ±0.004 MPa.
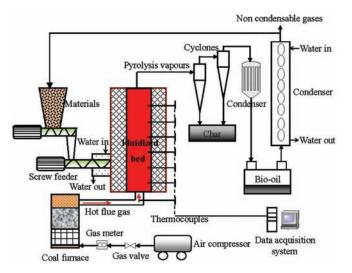

Figure 1   Experimental device of biomass pyrolysis experimental system

In the first experiment, some ethanol was put into the condenser for scrubbing the hot gas.   Therefore, the liquid obtained from the condenser actually consisted of a mixture of ethanol and pyrolysis oil pyrolysed from corn stover.   As ethanol has a high volatility, its concentration in the mixture would continually decrease during the experiments until the ethanol was completely gone. According to our experience, it can be considered that the mixture only consisted of the pyrolysis oil pyrolysed from corn stover if the experiment lasted for more than 10 h. Approximately 3 kg of ground corn stover particles were put into the reactor.   The flow rate of hot flue gas was kept 5.5 m³/h, and the hot flue gas was reheated to the setting temperature by preheater.   In the second condenser, the temperature was close to room temperature. After the experiment lasted for more than 10 h, ethanol was not detected by GC-MS in the pyrolysis oil. Besides pyrolysis oil, two by-products, namely charcoal and an un-condensable gas, could also be obtained when corn stover was pyrolyzed.   Corn stover was fast pyrolyzed in a fluidized-bed reactor and the pyrolysis temperature was between 450°C and 525°C.   The yield of pyrolysis oil could be determined from the condensed liquid.   The yield of charcoal could be determined from the charcoal collected from the two cyclones.   The yield of uncondensable gas could be determined from the fact that the sum of three product yields should equal 100%. All the experiments with different level were conducted in triplicate and the average values were reported.

The pH of bio-oil was measured by a PHS-2F digital pH meter.   Prior to the measurement, the instrument was calibrated with a liquid calibration standard of pH 7. The calorific value was obtained using a IKA C2000 automatic isoperibol calorimeter.   The bio-oil was analyzed by a Agilent 6890/5973N Gas Chromatograph–Mass Spectrometer (GC-MS).   For the GC separation, a capillary column DB-1701 (60 m×0.25 mm×0.25 μm inner diameter) was used.   Carrier gas was He with a flow rate of 59.7 mL/min.   The column oven programme was as follows: initial temperature of 40°C with a heating rate of 5°C/min to 240°C and held during 300 s.   The mass spectrometry operating parameters: electron impact (EI) ion source at 70 eV, the scanning range of m/z 12 to 550, ion source temperature was 150°C, the interface temperature is 240°C.   The heating injection volume

was 0.2 L, and the split ratio was 60:1. The water content of bio-oil was measured by Karl-Fischer titration using a Metrohm 870 KF Titrino Plus. The non-condensable gas was monitored by a infrared gas analyzer (GASBOARD 3100). The stability characteristics of pyrolysis oil were studied in terms of variation of viscosity over time. Viscosity measurements were done over a period of time under two different storage conditions, one stored at room temperature (18°C) and the other stored at ageing temperature (60°C), for each of the oil samples. The viscosity was measured according to the standard procedure (ASTM D-445-88).

3   Results and discussion

3.1   Pyrolysis product distribution

The pyrolysis product yields as a function of pyrolysis temperatures with quartz sand as bed material are present in Figure 2. The bio-oil yield increases from 31.5wt.% to 39.6wt.% with increasing pyrolysis temperature from 450°C to 500°C and then changes little with a further increase of pyrolysis temperature. The gas yield always decreases with increasing temperature until 500°C. Afterwards, the gas yield increases with a further rise of temperature. The increase in gas yield at higher temperatures is predominately attributed to secondary cracking or reactions of pyrolysis vapors[21]. The extent of secondary reactions can be affected by pyrolysis temperature. At higher temperatures, secondary reactions in the vapor phase are much faster, leading to over-cracking of pyrolysis vapors and an increase of the gas yield. Inorganic matters as K_2O, Na_2O, CaO and Fe_2O_3 may play a catalytic role in tar cracking and might help to increase the gas yield[21]. The char yield always decreases with the rise of pyrolysis temperature in the range of 450°C-525°C. The decrease in char yield with rising temperature could either be due to greater primary decomposition of raw materials at higher temperatures or through secondary decomposition of the char residue. The secondary decomposition of the char at higher temperatures may produce non-condensable gaseous products, which would also contribute to the increase in gas yield with the rise in temperature.
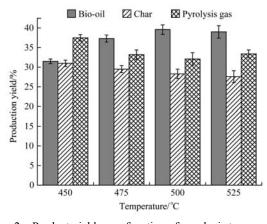

Figure 2   Product yields as a function of pyrolysis temperatures with quartz sand as bed material

The effects of pyrolysis temperature on the composition of gas products with quartz sand as bed material are displayed in Figure 3. CO_2, CO and CH_4 are the main gas products. The content of CO_2, CO and CH_4 in the pyrolysis gases accounted for more than 90%. As the temperature rises, the CO content in the product gases increases from 29.85vol% at 450°C to 33.95vol% at 525°C and the CH_4 content increased from 5.38vol% at 450°C to 8.82vol% at 525°C, while the CO_2 content exhibits the opposite trend. This is largely because the release of CO_2 is mainly caused by the cracking and reforming of carboxyl groups which can be easily decomposed at relatively low temperatures. Furthermore, the secondary reactions of volatiles at high temperatures generate mostly CO and CH_4 rather than CO_2[22,23]. The heating value of pyrolysis gases increased from 6.93 MJ/kg to 9.11 MJ/kg with increasing temperatures from 450°C to 525°C. The pyrolysis gases can be used as energy sources for pyrolysis processes or in other applications.
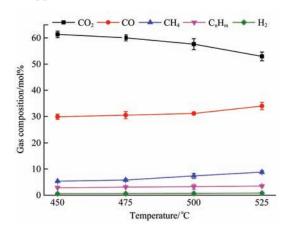

Figure 3   Effect of pyrolysis temperature on the composition of pyrolysis gases with quartz sand as bed material

The effects of bed materials on bio-oil yield and heavy oil percentage in the whole bio-oil are shown in the Figure 4. The highest bio-oil yield of 43.3wt.% is obtained at 500°C when dolomite is used as bed material. The heavy oil percentage in the whole bio-oil first increases and then decreases with the rise of temperature. For a given temperature higher than 450°C, calcined dolomite gives the lowest heavy oil percentage compared with quartz sand and aluminous soil. It is well known that the formation of tar has adverse effects on bio-oil production and pyrolysis system. It usually adheres to the internal walls of the pipes and reactors and is difficult to be cleaned. Calcined dolomite is favorable for bio-oil production below 500°C. A great quantity of CaO-MgO complexes, which are formed via the calcination of dolomite, have a positive effect on the catalytic cracking of biomass tars, leading to the increase of bio-oil yield.
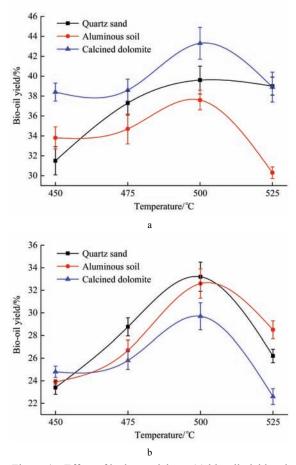

a

b

Figure 4   Effect of bed materials on (a) bio-oil yield and (b) heavy oil percentage in the whole bio-oil

3.2   Properties and compositions of the bio-oil

The bio-oil produced from fast pyrolysis of corn stover was a viscous and dark-brown organic liquid with a fairly strong smoky odour.

Table 2 gives the main physical properties of light bio-oil obtained from corn stover in relation to pyrolysis temperatures and bed materials. The pH of light oils ranged from 3.18 to 3.99. The kinetic viscosity ranges from 5.0 mPa·s to 5.9 mPa·s. The calorific value was very low which only ranged from 7.63 MJ/kg to 8.25 MJ/kg. The viscosity of the pyrolysis oil as produced can be greatly varied depending on the temperature, feedstock, water content of the oil, amount of light ends that have been collected and the extent to which the pyrolysis oil has aged. The viscosity of pyrolysis light oil produced from corn stover was found to be around 5.5 mPa·s at 18°C. This value was much lower than many pyrolysis oils and also lower than some hydrocarbon fuels[24]. In the application of liquid as fuel, the lower the viscosity of the oil is, the easier it is to pump and to atomize and achieve finer droplets. This is the major criterion upon which the oils are aged. Since the pyrolysis oil from corn stover was lower viscous than many other pyrolysis oils and hydrocarbon fuels[24], it was assumed that this pyrolysis oil can be used in the internal combustion engine for transportation and power generation.

Table 2   Physical properties of light oil from fast pyrolysis of corn stover

Bed material	Temperature /°C	pH	Kinetic viscosity /mPa·s	Calorific value /MJ·kg⁻¹
Quartz sand	450	3.40±0.17	5.3±0.1	7.68±0.12
	475	3.94±0.09	5.5±0.1	7.89±0.15
	500	3.71±0.23	5.5±0.2	7.73±0.23
	525	3.54±0.14	5.9±0.2	7.79±0.18
Aluminous soil	450	3.18±0.04	5.5±0.1	8.12±0.09
	475	3.68±0.08	5.5±0.3	8.09±0.21
	500	3.61±0.06	5.4±0.2	7.79±0.32
	525	3.77±0.09	5.5±0.5	7.82±0.15
Dolomite	450	3.29±0.12	5.2±0.3	8.15±0.18
	475	3.99±0.06	5.5±0.4	7.76±0.42
	500	3.74±0.13	5.5±0.3	8.25±0.19
	525	3.56±0.15	5.0±0.3	7.63±0.38

When the calcined dolomite was used as bed material, the bio-oil production was highest at 500°C, and the bio-oil was further analyzed. The properties and components of pyrolysis oil are presented in Tables 3 and 4.

From Table 3, it could be found that: (1) The energy density of the pyrolysis oil is much higher than that of the corn stover so that it is convenient for transportation and

utilization.   (2) The oxygen content of the pyrolysis oil is high.   The oxygen content of the pyrolysis oil depends on the raw material and the pyrolysis conditions.   The oxygen content of the corn stover was 44.67wt.% and the oxygen content of the pyrolysis oil must be higher than the oxygen content of the corn stover, because 20wt.%-30wt.% charcoal which was mainly made from carbon was produced when corn stover was fast pyrolysed.   Moreover maximum yields of pyrolysis oil were obtained at temperatures in the range 450°C-550°C and residence times of 0.5-5 s depending on the particular process[7] being typical conditions of fast pyrolysis.   In this case the pyrolysis oil was highly oxygenated.   The high oxygen content was indicative of the presence of many highly polar groups leading to high viscosities and boiling points as well as relatively poor chemical stability. As the table showed a significant fraction of the oxygen was present as water.   On account of their high oxygen content and hydrophilic character it was not surprising that fast pyrolysis oils were mostly insoluble in hydrocarbon solvents.   (3) The calorific value of the pyrolysis oil was 17.2 MJ/kg but the calorific value of diesel is 42.6 MJ/kg, the calorific value of coal is 29.3 MJ/kg, and the calorific value of gasoline is 44.0 MJ/kg. It revealed that the calorific value of the pyrolysis oil was much lower than the calorific value of fossil fuel because the oxygen content of the pyrolysis oil was high.

Table 3   Main properties of bio-oil derived from fast pyrolysis of maize stalk.

Elemental composition	Value
Carbon/wt.%	43.61±0.82
Hydrogen/wt.%	7.14±0.48
Nitrogen/wt.%	0.43±0.01
Oxygen (by difference)/wt.%	48.90±0.98
Water content/wt.%	23.53±0.52
Density/kg·m^{-3}	1220±68
Calorific value/MJ·kg^{-1}	17.23±0.62
pH	3.2±0.2

The main organic components of the bio-oil were identified with gas chromatography-mass spectrometry (GC/MS) technique.   Figure 5 shows the total ion current chromatogram of corn stover fast pyrolysis bio-oil. It can be found that more than 100 peaks were displayed in the chromatogram.   Most of the identified peaks are oxygenated compounds, which included acids, aldehydes,

ketones, esters, alcohols, furanics, pyranics, anhydrosugars, phenols, etc.   Since the oxygenated compounds in the bio-oil are nonpolar, it is not miscible with petroleum oil.   Nevertheless, the bio-oil could be blended with petroleum fuel via emulsification.   Table 4 lists the major chemical compounds in corn stover fast pyrolysis bio-oil as determined by GC/MS.   The major chemical compounds includes 1-hydroxy-2-propanone, acetic acid, ethanol, 1,2-Ethanediol, 2-Methyl-2-cyclopenten-1-one, benzenediol, levoglucosan, phenols, etc.   The perfect identification of all the peaks is not possible due to the complex composition of biomass pyrolysis oil and the difficulties in the identification are mainly due to overlapping peaks and low signal to noise ratios.
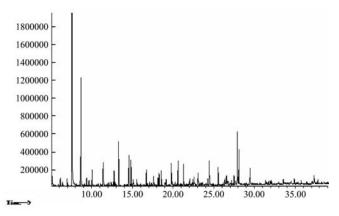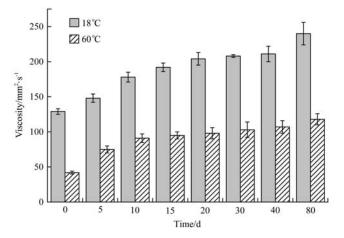

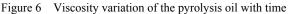Figure 5   Total ion current chromatogram of corn stover fast pyrolysis bio-oil

Table 4   Major chemical compounds in corn stover fast pyrolysis bio-oil as determined by GC-MS

No.	Retention time/min	Compound name	Percentage
1	5.506	Methyl Alcohol	3.048
2	6.403	Propanoic acid, anhydride	1.270
3	7.015	Acetaldehyde, hydroxy-	4.316
4	7.646	Acetic acid	18.853
5	8.747	2-Propanone, 1-hydroxy-	19.101
6	1.167	Propanoic acid	3.086
7	11.422	1-Hydroxy-2-butanone	5.079
8	12.775	Propanoic acid, 2-oxo-, methyl ester	1.772
9	13.307	Furfural	3.362
10	14.587	2-Furanmethanol	4.374
11	14.838	2-Propanone, 1-(acetyloxy)-	1.709
12	16.747	1,2-Cyclopentanedione	1.341
13	18.296	Furan, tetrahydro-2-methyl-	2.343
14	18.565	2(5H)-Furanone	1.303
15	19.802	2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	2.084
16	20.634	Phenol	2.401
17	21.289	Phenol, 2-methoxy-	1.561
18	24.466	Cyclopropyl carbinol	2.278
19	27.912	2-Propenoic acid, 3-(2-hydroxyphenyl)-, (E)-	2.768
20	29.473	Phenol, 2,6-dimethoxy-	1.535

3.3   Stability characteristics of the pyrolysis oil

The change of viscosity of pyrolysis oil at different storage conditions is presented in Figure 6.   The pyrolysis oil viscosity increases with increasing storage time, due to slow polymerization and condensation reactions, the increase of viscosity of pyrolysis oil are enhanced by higher temperature, and the rate of increase of viscosity of pyrolysis oil was found to reduce after some time.   This result is quite consistent with many reported results[25].   Hence though pyrolysis oil has certain instability, the instability is not too strong to use the pyrolysis oil.   If in the presence of inhibitors for example hydroquinone, the rate of increase of viscosity of pyrolysis oil can dramatically reduce, due to the suppression of thermal polymerization reactions by the inhibitors[26,27].

Figure 6   Viscosity variation of the pyrolysis oil with time

4   Conclusions

In the pyrolysis system used in this experiment, some improvements to former pyrolysis systems were done. Two screw feeders were used to prevent jamming the feeding system, and the condenser was equipped with some nozzles and a heat exchanger to cool quickly the cleaned hot gas into bio-oil.   The results showed that the bio-oil yield increased with increasing pyrolysis temperature and then declined with a further increase in pyrolysis temperature.   The highest bio-oil yield of 43.3wt.% was obtained at 500°C with the dolomite as bed material.   The char yield always decreased with the increase of temperature.   The major chemical compounds of bio-oil included acetol, butanone, acetic acid, propionic acid, ethylene glycol, phenol, etc.

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