



Catalytic and atmospheric effects on microwave pyrolysis of corn stover



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HIGHLIGHTS

- ▶ Reaction performance under N₂ atmosphere was better than under CO₂ atmosphere.
- ▶ Metal-oxide catalysts increased the maximum temperature and mass reduction ratio.
- ▶ The gas most produced was CO under N₂ atmosphere but CO₂ under CO₂ atmosphere.
- ▶ Liquid product should be less toxic due to less PAHs formation.
- ▶ More liquid but less gas produced may be due to the Fischer–Tropsch synthesis.

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ABSTRACT

Corn stover, which is one of the most abundant agricultural residues around the world, could be converted into valuable biofuels and bio based products by means of microwave pyrolysis. After the reaction at the microwave power level of 500 W for the processing time of 30 min, the reaction performance under N₂ atmosphere was generally better than under CO₂ atmosphere. This may be due to the better heat absorbability of CO₂ molecules to reduce the heat for stover pyrolysis. Most of the metal-oxide catalysts effectively increased the maximum temperature and mass reduction ratio but lowered the calorific values of solid residues. The gas most produced was CO under N₂ atmosphere but CO₂ under CO₂ atmosphere. Catalyst addition lowered the formation of PAHs and thus made liquid products less toxic. More liquid products and less gas products were generated when using the catalysts possibly due to the existence of the Fischer–Tropsch synthesis.

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1. Introduction

Bioenergy is a sustainable and renewable energy and includes both traditional uses for cooking and heating and modern uses to produce electricity, heat, and biofuels (Kim and Dale, 2004). Like solar energy, wind power, and hydropower, bioenergy is clean, green, and inexhaustible. Bioenergy is the fourth largest energy source after oil, coal, and natural gas, and it accounts for about 13% of the world's total final energy consumption (IEA, 2011). Recently, bioenergy is getting intensive attentions owing to various reasons including energy security, oil price, global warming, and climate change. Biomass materials with high energy potential include agricultural residues such as crop straw, sugarcane bagasse, coffee husks, rice husks, coconut shells, and corn stover as well as residues from forest-related activities such as wood chips, sawdust, and bark (Werther et al., 2000).

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Corn is a major crop in the United States and many other countries, so its residues from harvesting, the corn stover, can be seen as an abundant potential feedstock for the production of green fuels and chemicals. The average annual production of corn in the United States is about 320 million tonnes (USDA, 2012). Since one mass unit of corn stover can be generated per mass unit of corn harvested (Kim and Dale, 2004), the annual production of dry corn stover in the United States can be approximately 269 million tonnes with an assumption that 16% of corn stover is moisture content. In fact, corn stover is the most abundant agricultural residue in the United States. Thus, it will be an enormous waste if the corn stover is not properly and completely utilized.

Nowadays, many methods that can be mainly divided into thermochemical and biochemical categories have been developed to convert biomass into valuable biofuels and biobased products. Thermochemical conversion technologies primarily include combustion, gasification, and pyrolysis. Depending on the operating conditions, the pyrolysis processes can be divided into three subclasses: conventional pyrolysis, fast pyrolysis, and flash pyrolysis (Maschio et al., 1992). Compared with conventional heating,

microwave (dielectric) heating can provide several benefits. In conventional heating methods, heat is transferred into materials by convection, conduction, and radiation to material surfaces. On the contrary, microwave energy is delivered directly into materials within an electromagnetic field. Therefore, energy is transferred by thermal gradients in the conventional heating, but microwave heating is the conversion of electromagnetic energy into molecular kinetic energy rather than heat transfer. This difference can result in many potential advantages of using microwaves for processing of materials (Thostenson and Chou, 1999).

There have been several researches to study the microwave pyrolysis of biomass-related feedstocks such as oil shale (El harfi et al., 2000), oil-palm stone (Guo and Lua, 2000), paper (Miura et al., 2001), plastic waste (Ludlow-Palafox and Chase, 2001), sewage sludge (Menendez et al., 2002), rock phosphate (Bilali et al., 2005), scrap tire (Appleton et al., 2005), coffee hulls (Dominguez et al., 2007), wood (Chen et al., 2008), rice straw (Huang et al., 2010), corn stalk bale (Zhao et al., 2010), oil palm biomass (Salema and Ani, 2011), and microalgae (Hu et al., 2012). According to these researches, the microwave pyrolysis of biomass-related feedstocks can produce various biofuels and biobased products such as bio-oil, biochar, syngas, and hydrogen depending on factors including operating parameters, reaction atmosphere, and biomass characteristics (Huang et al., 2012). However, the reaction performance, productivity, and pilot- and full-scale data of the technology are still necessary to be further researched to promote its commercial applicability. A practical way is the addition of catalysts. Catalytic biomass pyrolysis is gaining increasing interest, and the use of catalysts or additives to improve the yield or quality of gaseous or liquid fuel from biomass is still in its infancy (Chen et al., 2008). Catalytic pyrolysis usually produces additional water and coke-solid residues and thus reduces the yield of organic phase in bio-oils. According to the work of Wan et al. (2009), some catalysts improved bio-oil yields, and chloride salts in particular simplify the chemical compositions of the resultant bio-oils and therefore improve the product selectivity of the pyrolysis process.

Since corn stover is an abundant source of bioenergy and microwave pyrolysis possesses many advantages over conventional methods, this study aimed to research the reaction performance and product of microwave pyrolysis of corn stover by using different catalysts and atmospheres. Solid, liquid (condensable), and gas (incondensable) products were separately collected and analyzed to discuss their characteristics and applicability.

2. Methods

2.1. Corn stover

The corn stover was obtained from vegetable markets. Before relevant tests, the corn stover was shredded and sieved by a 60-mesh screen. The composition and characteristic analyses of corn stover are listed in Table 1. The moisture fraction of the as-received stover was about 5%. Most of the stover was volatile matter and the fraction was about 97%. The fractions of fixed carbon and ash content were much lower. The stover was primarily composed of three elements, C, H, and O, whose fractions were about 46%, 7%, and 45%, respectively. The extractives, hemicellulose, cellulose, and lignin fractions of stover were about 3%, 31%, 48%, and 14%, respectively. Thus, about 80% of the stover was composed of polysaccharides. The calorific value of stover was 18.20 MJ/kg.

2.2. Metal-oxide catalysts

This study chose four metal oxides, NiO, CuO, CaO, and MgO, as catalysts for the microwave pyrolysis of corn stover. Table 2 lists

Table 1

The composition and characteristic analyses of corn stover.

| | |
|--|-------|
| Moisture (wt.%) | 4.96 |
| Calorific value (MJ/kg) | 18.20 |
| <i>Proximate analysis (wt.%)^a</i> | |
| Volatile matter | 97.14 |
| Fixed carbon | 0.18 |
| Ash | 2.69 |
| <i>Elemental analysis (wt.%)^b</i> | |
| C | 46.32 |
| H | 6.57 |
| N | 0.37 |
| S | 0.77 |
| O | 44.54 |
| <i>Lignocellulosic analysis (wt.%)^b</i> | |
| Extractive matter | 3.28 |
| Hemicellulose | 31.37 |
| Cellulose | 48.30 |
| Lignin | 14.46 |

^a Dry basis.

^b Dry ash free basis.

Table 2

The purchasing details of commercial metal oxides.

| | Particle size | Appearance | Supplier | CAS # |
|-----|---------------|----------------------|-------------|-----------|
| NiO | 0.5–6 mm | Dark gray granular | May & Baker | 1313-99-1 |
| CuO | 1–4 mm | Black granular | J.T. Baker | 1317-38-0 |
| CaO | <20 mesh | White powder | Alfa Aesar | 1305-78-8 |
| MgO | 3–6 mm | Transparent granular | Alfa Aesar | 1309-48-4 |

the purchasing details of commercial metal oxides. Compared with the X-ray diffraction (XRD) peaks of original metal oxides, the peaks of metal oxides irradiated by microwaves did not shift. Therefore, the microwave irradiation would not affect the crystal-line structures of metal oxides.

2.3. Experimental apparatus and procedure

This study used a microwave processing device at 2.45 GHz frequency that was described elsewhere (Huang et al., 2010). Its irradiation manner was single mode (focused). The catalyst was added into the shredded and sieved corn stover for the additive ratios of 3%, 5%, and 10%. The mixed sample was filled in a quartz crucible, and then it was placed inside a quartz tube and precisely in the pathway of microwaves. In order to maintain anoxic circumstances and to purge out the vapor generated during microwave pyrolysis, inert gas (N₂/CO₂) was purged into the system with a flow rate of 50 mL/min. After enough purging, the power supply of microwave device was turned on and switched to the designated microwave power level (500 W) for the designated processing time (30 min). Reflection microwave power levels were controlled to be less than 10% of incident ones during the whole experiment period. After passing through a condenser, the vapor generated by microwave pyrolysis was divided into two parts: liquid (condensable) and gas (incondensable). When the designate processing time was reached, the power supply was turned off and the carrier gas was shut down, and then the liquid and gas collectors were removed and sealed. After self-cooling down to room temperature, the solid residues remained in the crucible were removed and placed in a desiccator.

2.4. Product analysis

The analysis of gaseous product was carried out by a PerkinElmer AutoSystem XL gas chromatography-thermal conductivity

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