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Catalytic pyrolysis of *Miscanthus* × *giganteus* over activated alumina

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ABSTRACT

The catalytic effects of activated alumina (Al_2O_3) on the pyrolysis of *Miscanthus* × *giganteus*, a new energy crop, were investigated. Catalytic pyrolysis experiments carried out under static and nitrogen atmospheres were performed in a fixed-bed reactor. The final pyrolysis temperature was kept constant at 550 °C in all of the experiments. The effect of catalyst loading (by weight of feedstock as 10%, 20%, 40%, 60%, 80% and 100%), heating rate (10 °C and 50 °C min^{-1}), nitrogen flow rate (50, 100, 150 and 200 $cm^3\ min^{-1}$) on the pyrolysis conversion and product yields were investigated. The results were compared with those obtained in non-catalytic pyrolysis. Activated alumina catalyst has a strong influence on the *Miscanthus* × *giganteus* pyrolysis product and conversion yield. Furthermore, the catalytic bio-oils obtained from catalytic pyrolysis under static and nitrogen atmospheres were examined using elemental analysis, column chromatography, Fourier transform infrared (FTIR) and nuclear magnetic resonance (^{1}H NMR) spectroscopy methods.

1. Introduction

Biomass is an attractive raw material that can be processed in many ways leading to a variety of products such as food, feed, fiber and some level of energy, fuels and chemicals. Biomass, as a renewable source for the production of fuels or useful chemicals, is attracting increasing interest (Adam et al., 2006; Demiral and Şensöz, 2006; Mohan et al., 2006; Corma et al., 2007; Qian et al., 2007). Today, it remains as an important component of national energy supplies in many countries (Antonakou et al., 2006). Biomass residues are abundant and offer many possible alternatives for practical utilization. The practical potential of biomass residues in the world will be 114 EJ/year, which is equivalent to one-third of commercial energy consumption in the world in 1990 (Yamamoto et al., 2001). In view of the increase in energy demand, the high costs of fossil fuels and disposal as well as the environmental concern about levels of CO_2 in the atmosphere, the use of biomass to provide partial substitution of fossil fuels for steam and power generation is of growing importance (Zhang et al., 2005; Mohan et al., 2006; Ryu et al., 2006; Qi et al., 2007; Huber et al., 2006; Huber and Corma, 2007).

It is necessary to develop biochemical and thermochemical technologies which make the conversion of biomass to valuable liquid, gaseous and solid fuels possible (Demirbaş et al., 2000; Mc Kendry, 2002; Şensöz, 2003; Basso et al., 2005; Ryu et al., 2006; Qi et al., 2007; Qian et al., 2007). The major challenge with biomass conversion strategies is how to efficiently remove the oxygen from hydrophilic biomass-derived feedstock and convert the biomass into a product with the appropriate combustion and thermochemical properties. Oxygen can be removed as CO, CO_2, or H_2O. Catalytic cracking and hydrotreating are very effective at removing oxygen from the biomass-derived feedstock. However, the oxygen is not always removed by the optimal pathway, and often undesired products such as coke or acids are formed during the conversion process (Huber and Corma, 2007). Amongst the thermochemical conversion processes (e.g. pyrolysis, gasification and combustion), pyrolytic process is recognized as the most promising one since it can be used either as an independent process for fuels and other valuable chemical products or an initial step to gasification or combustion (Mohan et al., 2006). Pyrolysis of biomass can be applied non-catalytically and catalytically to obtain fuels. A number of studies have been conducted to investigate the catalytic pyrolysis of biomass in both laboratory and industrial scales. (Samolada et al., 2000; Minkova et al., 2001; García et al., 2001; Ateş et al., 2005, 2006; Adam et al., 2006; Antonakou et al., 2006; Mohan et al., 2006). Homogeneous catalysts such as acids, bases and transition metal compounds are widely used in biomass pyrolysis processes. Very few study could be found on active alumina which is a solid acid catalyst (Samolada et al., 2000) Aluminas can show the presence of Lewis acid sites when they are calcined at temperature above 450 °C under these conditions, surface protons and aluminum cations become mobile and start to change their position in the lattice (Corma and Garcia, 2003). When stable stronger acidities are required, activated oxides can offer clear advantages. The 100 wt.% Al_2O_3 sample has the largest number of the acid sites having the highest strength, and consequently this should be the most active catalyst for acid-catalyzed

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reactions (Corma, 1995). These reactions proceed by breaking and formation of carbon–hydrogen bonds, on or next to double bond, and are catalyzed by the acid sites. (Corma, 1995; Huber et al., 2006) Brönsted acidity was responsible for cracking carbon–carbon bonds (Corma and Garcia, 2003). Pyrolysis liquids, containing large amounts of oxygen, are acidic, viscous, corrosive and thermally unstable and have poor fuel properties. Upgrading before use is desirable to give bio-oil product which can be used in a wider variety of applications (Zhang et al., 2005; Adam et al., 2006; Mohan et al., 2006; Qi et al., 2007). Oxygen removal and molecular weight reduction are necessary to produce usable hydrocarbon fuels (Ateş et al., 2006; Demiral and Şensöz, 2006). Removal of oxygen from the bio-oils has been achieved by a number of methods, most predominantly using either hydrotreating or catalytic cracking. The advantages of catalytic cracking are that no H_2 is required, atmospheric processing reduces operating cost, and the temperatures employed are similar to those used in the production of bio-oil. This offers significant processing and economic advantages over hydrotreating (Huber and Corma, 2007).

Energy crops as a biomass resources have a number of advantages for biomass energy systems. In particular, crops can be grown where they are needed, thus reducing transportation costs. Numerous energy crops have been proposed or are being tested for commercial energy farming (Lewandowski et al., 2000; Lewandowski et al., 2003; Fischer et al., 2005; Acaroğlu and Aksoy, 2005; Tuck et al., 2006). *Miscanthus* is a genus of C_4 perennial, rhizomatous grasses identified as potential biomass plants for renewable energy in the world. *Miscanthus* and particularly the variety *Miscanthus* × *giganteus* has been intensively investigated. *Miscanthus* × *giganteus* is in many ways an ideal energy crop. It is rapidly growing, having high biomass yield potential, widely and easily cultivated over a range of climates, and has genetic variability (Lewandowski et al., 2003; Price et al., 2004; Fischer et al., 2005; Tuck et al., 2006). The harvested stem of *Miscanthus* may be used as fuel for the production of heat and electric power or for conversion to other useful products such as transport fuels and ethanol (Lewandowski et al., 2000; Minkova et al., 2001; Yorgun and Şimşek, 2003; Price et al., 2004; Ryu et al., 2006). Studies on the growing of the energy crops are limited in Turkey. In a study, it was showed that the *Miscanthus* × *giganteus* is an appropriate energy crop for Turkey (Acaroğlu and Aksoy, 2005).

In this study, *Miscanthus* × *giganteus* was chosen as the raw material. Its catalytic pyrolysis was performed under different conditions in a fixed-bed reactor. Particulary, the effects of catalyst loading (by weight of feedstock as 10%, 20%, 40%, 60%, 80% and 100%), heating rate and nitrogen flow rate on the pyrolysis conversion, product yields and compositions were investigated. Furthermore, characterization of the bio-oil was also made in detail in relation to the process conditions.

2. Methods

2.1. Material

Miscanthus × *giganteus* used in this study as a raw material was obtained from central Anatolia-Konya region in Turkey. Prior to use, the sample was air dried, grounded in a high-speed rotary cutting mill and then screened to give the fraction of $0.425 < D_p < 0.6$ mm particle size for use in the catalytic pyrolysis experiments. Elemental analyses of the *Miscanthus* × *giganteus* and products were performed on a CARLO ERBA Model EA 1108 elemental analyzer. The elemental composition of *Miscanthus* × *giganteus* was C 53.15 wt.%, H 6.75 wt.%, N 1.69 wt.% and O (by difference) 38.41 wt.%. The H/C, O/C molar ratios and empirical formula were calculated from elemental composition as 1.52, 0.54 and $CH_{1.524}O_{0.542}N_{0.027}$, respectively. ASTM standard test procedures were applied for ash content (3.3 wt.%), ASTM D 1102-84; volatile matter content (71.4 wt.%), ASTM E 897-82; moisture content (6.8 wt.%), ASTM D 2016-74; and higher heating value (20.9 MJ/kg), ASTM D 3286. Fixed carbon content was obtained as 18.5 wt.% by finding the difference. The structural analyses were carried out by the related standard analytical methods. The TS 324 Turkish Standard test procedure was applied for cellulose content (45 wt.%). The ASTM standard test procedures ASTM D 1106-96 and ASTM D 1105-96 were applied for lignin content (17 wt.%) and extractive matter content (16 wt.%), respectively. In the method given by ASTM D 1105-96, the *Miscanthus* × *giganteus* is extracted with a mixture of ethanol and benzene, and then washed with alcohol and water. Extractives may include fats, some resins, gums, tannins, simple sugars, glycosides, starches, alkaloids, phenolics, terpenes, proteins, saponins, waxes and coloring matter. (Mohan et al., 2006). Hemicellulose content was obtained as 22 wt.% by finding the difference.

2.2. Catalyst

The Al_2O_3 catalyst was used in the catalytic pyrolysis experiments. The Al_2O_3 content was 93 wt.%, its bulk density was 0.706 g/cm^3, total pore volume was 0.35 cm^3/g, loss on ignition at 1100 °C was 6.6 wt.% and surface area was 200 m^2/g. A good contact between the catalyst and *Miscanthus* × *giganteus* is required. The Al_2O_3 catalyst was ground and sieved and the fraction of $0.600 < D_p < 0.850$ mm was used. It was activated at 550 °C and stored in a desiccator. The catalyst Al_2O_3 was directly added to *Miscanthus* × *giganteus* by dry mixing before pyrolysis.

2.3. Pyrolysis

The catalytic pyrolysis experiments were performed using a fixed-bed reactor. The 316 stainless steel reactor had a volume of 400 cm^3 (70 mm ID) and was externally heated by an electrical furnace in which the temperature was measured by a thermocouple inside the bed. The connecting pipe between reactor and the trapping system was heated up to 400 °C to avoid condensation of tar vapour. The pyrolysis system was also reported elsewhere (Yorgun and Şimşek, 2003).

The catalytic pyrolysis experiments were conducted at 550 °C in all experiments. This temperature was the optimum final pyrolysis temperature giving the maximum bio-oil yield resulted in the non-catalytical pyrolysis of *Miscanthus* × *giganteus* (Yorgun and Şimşek, 2003). The catalytic pyrolysis experiments were carried out in two series. The first group of the experiments were performed under the static atmosphere by dry mixing of the Al_2O_3 catalyst with the sample. The effects of the catalyst loading and the heating rate on the *Miscanthus* × *giganteus* pyrolysis conversion and yields were investigated. A 20 g of sample, having a particle size range of $0.425 < D_p < 0.600$ mm, was mixed with catalyst in different percentages. The applied catalyst loading values were between 10% and 100% (w/w). The temperature was raised at either 10 °C or 50 °C min^{-1} to the final pyrolysis temperature of 550 °C and the process was continued for 30 min at this temperature. The flow of released gas was measured using a soap film in the duration of the experiment. It was observed that no further release of gas occured at the end of 30 min in each of the experiments. The liquid products were collected in the stainless steel traps maintained at about 0 °C. The liquid products collected in the traps were removed by dichloromethane. These liquid products contained an aqueous phase and an oil phase (bio-oil) which were separated and then weighed. The amount of the solid (bio-char) was calculated by subtracting the amount of the Al_2O_3 catalyst from the amount of the total solid remaining in the reactor. The gas yield was calculated