



# The influence of recycling non-condensable gases in the fractional catalytic pyrolysis of biomass

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## ABSTRACT

In this study, the effect of recycling the non-condensable gases (NCG) in the catalytic pyrolysis of hybrid poplar using FCC catalyst was investigated. A 50 mm bench scale fluidized bed reactor at 475 °C with a weight hourly space velocity (WHSV) of 2 h<sup>-1</sup> and a gas recycling capability was used for the studies. Model fluidizing gas mixtures of CO/N<sub>2</sub>, CO<sub>2</sub>/N<sub>2</sub>, CO/CO<sub>2</sub>/N<sub>2</sub> and H<sub>2</sub>/N<sub>2</sub> were used to determine their independent effects. Recycling of the NCG in the process was found to potentially increase the liquid yield and decrease char/coke yield. The model fluidizing gases increased the liquid yield and the CO<sub>2</sub>/N<sub>2</sub> fluidizing gas had the lowest char/coke yield. The <sup>13</sup>C-NMR analysis showed that recycling of NCG increases the aromatic fractions and decreases the methoxy, carboxylic and sugar fractions. Recycling of NCG increased the higher heating value and the pH of the bio-oil as well as decreased the viscosity and density.

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## 1. Introduction

Catalytic fast pyrolysis technology is one of the thermochemical platforms that are used to produce high quality bio-oil and chemicals from biomass feedstocks (Adjaye and Bakhshi, 1995; Agblevor et al., 2010a; Williams and Horne, 1995). The process involves the rapid heating of biomass under inert atmosphere in the presence of a suitable catalyst. The technology has been extensively reviewed in the literature by Huber and Corma (2007), Park et al. (2011) and Taarning et al. (2011). In catalytic pyrolysis, a large fraction of the biomass is converted into non-condensable gases (NCG) at the expense of the liquid product. The gas product yield obtained on a dry biomass feed is about 20–50% depending on the type of catalyst used (Agblevor et al., 2010a; Lappas et al., 2009; Mante et al., 2011; Williams and Horne, 1995; Zhang et al., 2009). It mainly consists of carbon oxides, methane, hydrogen and minor hydrocarbons (Huber and Corma, 2007; Stefanidis et al., 2011; Williams and Horne, 1994). These gases can be usefully recycled back into the reactor to assist in fluidization or could be combusted to provide process heat for large scale operations. The concept of recycling the NCG helps to reduce operational cost and eliminates further downstream processes of the gas stream. Studies have shown that with efficient condensation systems and compressors,

the NCG can be effectively recycled back to replace the initial inert fluidizing gas (Agblevor et al., 2010b; Bridgwater, 1999).

Theoretically, recycling the NCG for fluidization could possibly influence the catalytic pyrolysis of biomass as these gases are capable of acting as co-reactants in the process. Studies have shown that the reductive gas stream (CO, H<sub>2</sub>, and hydrocarbons) and mild oxidative gas (CO<sub>2</sub>) affect the thermal decomposition of biomass (Butterman and Castaldi, 2009a; Butterman and Castaldi, 2007; Butterman and Castaldi, 2009b; Carlson et al., 2009; Jindarom et al., 2007; Meesuk et al., 2011; Scahill and Diebold, 1988; Thangalazhy-Gopakumar et al., 2011; Zhang et al., 2011). Zhang et al. (2011) investigated the effect of N<sub>2</sub>, CO<sub>2</sub>, CO, CH<sub>4</sub> and H<sub>2</sub> as carrier gases on the fast pyrolysis of corncob in a fluidized bed reactor. They reported that the liquid yield was dependent on the type of gas used and more oxygen was converted to CO<sub>2</sub> and H<sub>2</sub>O in the presence of CO and H<sub>2</sub>. Meesuk et al. (2011) also reported that lower liquid yields were achieved in H<sub>2</sub> atmosphere from the fast pyrolysis of rice husk in a fluidized bed reactor with or without the use of CoMo/Al<sub>2</sub>O<sub>3</sub> and Ni/LY catalyst. A study by Thangalazhy-Gopakumar et al. (2011) also reported a reduction in carbon yield when the thermogravimetric studies of pine wood chips under He was changed to H<sub>2</sub>. However, they did not observe any significant change in the yield when the experiment was conducted with a ZSM-5 zeolite catalyst. Studies by Carlson et al. (2011) on the production of green aromatics and olefins from wood sawdust via catalytic fast pyrolysis using ZSM-5 zeolite showed that co-feeding light hydrocarbons (C<sub>2</sub>–C<sub>3</sub>) with wood increases gasoline

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yields. An earlier work by *Scahill and Diebold (1988)* also explored the effect of recycling olefins over HZSM-5 zeolite catalyst in the upgrading of pyrolysis vapors from wood. Most of the literature reports are on only the effect of individual gases on the pyrolysis of biomass. Currently, there are no reported findings on the influence of recycling the pyrolysis gas on catalytic pyrolysis of biomass.

In this study, the effect of recycling the NCG from the fractional catalytic pyrolysis of hybrid poplar wood using FCC catalyst on the product yields and properties of the bio-oils was investigated. The FCC catalyst which contains Y-zeolite has been shown to have a different effect on the catalytic pyrolysis of wood when compared with ZSM-5 zeolite catalyst (*Carlson et al., 2009; Lappas et al., 2002; Williams and Horne, 1994*). The FCC catalyst typically produces lower bio-oil yields and forms large amounts of coke due to its pore size and acidity (*Carlson et al., 2009; Lappas et al., 2009; Mante et al., 2011; Samolada et al., 2000; Williams and Horne, 1995*). It is therefore hypothesized that recycling of the NCG with the FCC catalyst would enhance the catalytic process. Two sets of experiments were conducted to understand the effect of recycling the NCG. In the first trial, the NCG was recycled continuously throughout the run. In the second experiment, the effect of the individual gases (CO, CO<sub>2</sub> and H<sub>2</sub>) on the product distribution and bio-oil composition was determined.

## 2. Methods

### 2.1. Materials

The hybrid poplar wood samples were prepared by air drying and grinding to pass a 1-mm screen in a Wiley mill prior to all experiments. The moisture content was determined to be 8 wt.% using an HG53 Halogen Moisture analyzer (Mettler Toledo, Greifensee, Switzerland). The elemental composition and calorific value of the hybrid poplar wood was performed by Galbraith Analytical Laboratory (Knoxville, TN, USA). The hybrid poplar wood had carbon (C), oxygen (O) and hydrogen (H) contents of 49.30%, 43.57% and 5.69% respectively. The nitrogen content was less than 0.5% and sulfur was less than 0.05%. The ash content was 0.94 wt.% and the higher heating value (HHV) was 18.4 MJ/kg. The commercial FCC catalyst (Al<sub>2</sub>O<sub>3</sub>=38.86 wt.%, RE<sub>2</sub>O<sub>3</sub>=5.54 wt.%, Zeolite surface area = 404 m<sup>2</sup>/g, Matrix surface area m<sup>2</sup>/g = 112, Micropore Volume = 0.258 cm<sup>3</sup>/g), water gas shift catalyst (FeCrCu) and the CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst used for the trials were supplied and characterized by BASF Catalysts LLC (Iselin, NJ, USA). The FeCrCu and the CoMo/Al<sub>2</sub>O<sub>3</sub> were added to the FCC catalyst at 20 wt.% level.

### 2.2. Fractional catalytic pyrolysis of hybrid poplar

The catalytic pyrolysis of hybrid poplar at 475 °C and a weight hourly space velocity (WHSV) of 2 h<sup>-1</sup> was carried out using a bench scale pyrolysis unit (*Fig. 1*) which consisted of a K-Tron volumetric feeder (K-Tron Process Group, Pitman, NJ), a fluidized bed reactor, hot gas filter, two chilled water condensers, an electrostatic precipitator, coalescing filter and a compressor. A detailed description of the pyrolysis unit and the fractional catalytic process used has been reported elsewhere (*Agblevor et al., 2010a*) and will not be repeated here. The reactor was externally heated with a three-zone electric furnace (Thermcraft, Winston-Salem, NC) and the temperatures were measured and controlled by three K-thermocouples inserted into a thermal well in the reactor. The temperatures across the reactor, hot gas filter and condensers were controlled and monitored using the OMB-Multiscan 1200 acquisition system (Omega Engineering, Inc.) with TempView 2.1 program.

The nitrogen gas flow rate was controlled with a mass flow controller. A total of 6.5 L/min of N<sub>2</sub> gas was used to fluidize the

catalyst bed and entrain the biomass into the reactor. The catalytic cracking experiments were performed at apparent average vapor residence times of 3 s and 6.5 s. The apparent average vapor residence time was defined as the total volume of fluidized catalyst divided by gas flow rate at reactor conditions. For all recycling experiments, the NCG that exited the coalescing filter was continuously returned to the reactor using an oil-less diaphragm compressor/pump (GAST WLS71272 pump). The initial flow rate of the N<sub>2</sub> fluidizing gas was reduced appropriately to maintain the same vapor residence time. For the gas chromatography analysis, a stream of non-condensable gases from the coalescing filter at flow rate of 0.1 L/min was connected to a Varian 490 micro GC (Agilent Technologies, Inc. Santa Clara, CA USA) to determine the concentration of the gases during the run. The gases were automatically analyzed online every 3.25 min for the duration of the experiment. The micro GC was equipped with two modules, a 10 m Molsieve (MS) 5 Å column and a 10 m porous polymer (PPU) column. Each module had a thermal conductivity detector. The MS column was used to analyze hydrogen, methane and carbon monoxide. Carbon dioxide and C<sub>1</sub>–C<sub>5</sub> gases were analyzed by the PPU column. The model gas experiments were conducted with the following synthetic gas mixtures: 10 mol% CO in N<sub>2</sub>; 10 mol% CO<sub>2</sub> in N<sub>2</sub>; 5 mol% H<sub>2</sub> in N<sub>2</sub>; and 4.5 mol% CO + 7 mol% CO<sub>2</sub> in N<sub>2</sub>. The composition of the inlet gas was taken into consideration in the determination of the gases produced in the pyrolysis process.

### 2.3. Bio-oil analysis

A Thermo Scientific Flash 2000 organic elemental analyzer (ThermoFisher Scientific, Cambridge, UK) was used to determine the C, H, N, O, and S of the bio-oil fraction. The higher heating values (HHV) were determined using IKA C2000 basic bomb calorimeter (IKA® Works, Inc, NC, and U.S.A.) according to ASTM D2015. The pH was measured using a Mettler Toledo pH Meter and probe (Mettler-Toledo GmbH, Switzerland). The pH data were obtained after 5–10 min stabilization of the mechanically stirred oil. The viscosity and density of the bio-oils were measured at 40 °C with a SVM 3000 Stabinger viscometer (Anton Parr, Graz, Austria). The results were consistent with viscosities determined by the ASTM D445 method. A Metrohm 701KF Titrino (Brinkmann Instruments, Inc, N.Y, U.S.A) and a 703 titration stand setup were used for the Volumetric Karl Fischer titration. Hydranal® Composite 5 reagent was used. 50 ml of methanol was placed in the titration vessel and conditioned. About 60–100 mg of oil sample was loaded into a hypodermic plastic syringe and weighed. The sample was injected into the titration solvent and the syringe was weighed again. The water content was titrated volumetrically and the resulting mass was recorded.

The <sup>13</sup>C-NMR spectra were recorded on a JOEL 300 MHz NMR spectrometer (JEOL Ltd, Tokyo, Japan). About 1.0 g of oil was dissolved in 0.7 ml of dimethyl sulfoxide-d<sub>6</sub> in a 5 mm sample tube. The NMR solvent, DMSO-d<sub>6</sub> [99.9 atom% D, containing 1% (v/v) tetramethylsilane (TMS)] was obtained from Sigma-Aldrich (Sigma-Aldrich, St. Louis, MO, USA). The observing frequency for the <sup>13</sup>C nucleus was 100.58 MHz. The pulse width was 10 μs, the acquisition time was 1.58 s, and the relaxation delay was 2 s. The spectra were obtained with 4000 scans and a sweep width of 20.0 kHz.

## 3. Results and discussion

### 3.1. Product yields

The product distribution in terms of organic, water, gas and char/coke from the fractional catalytic cracking of hybrid poplar pyrolysis vapors are shown in *Table 1*. From the results, it can be

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