



Catalytic pyrolysis of oak via pyroprobe and bench scale, packed bed pyrolysis reactors

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ABSTRACT

The pyrolytic conversion of oak sawdust at 500 °C in flowing He over eight proprietary catalysts is described and compared to the control bed material, quartz sand. The reactions were conducted and compared in two reactors, an analytical, μg -scale pyroprobe reactor and a bench, g-scale packed bed reactor. The catalysts examined were modified acid catalysts, dealuminated-zeolite Y, β -zeolite, a naturally occurring metal hydroxide containing mineral, mordenite, and a mesoporous aluminosilicate molecular sieve. The packed bed reactor allowed the collection of three bulk product fractions, char, liquid, and gas, all of which could not be obtained from the μg -scale pyroprobe reactions. The catalysts effect on the mass balance of the bulk fractions tended toward more chars and less liquid compared to the sand control. The catalysts' effects on the liquid products obtained in both reactors shifted away from acetic acid, furfural and higher molecular weight phenolics obtained with sand to lower molecular weight aromatics. This halved the total acid number of the liquid fraction and raised the pH by up to 1.4 units. The modified catalysts' effects on the gas products from both reactors did not follow a specific trend. Instead, specific catalysts were able to enrich specific gas species up to a factor of 15 while suppressing the formation of others compared to the sand control. Two catalysts, β -zeolite and a naturally occurring metal hydroxide containing mineral, were regenerated and recycled up to five times with no loss of activity.

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1. Introduction

The thermochemical conversion of biomass has been reported as a near- to mid-term option for the development of renewable energies, fungible fuels, and chemical products [1]. The pyrolysis of biomass produces char, oil, and gas fractions each of which contains inherent energy and chemical product components. The pyrolysis process can be optimized (e.g. feedstock, feed rate, residence time and temperature) to enhance the formation of a particular fraction and modify the chemical make-up of the various fractions [2]. Unfortunately, the direct replacement of fossil-based fuels and chemicals with pyrolysis products is not without its challenges. For example, because of its high oxygen content and acidity pyrolysis oil requires additional processing to be suitable for use in the petroleum refining industry or it must be cracked or steam

reformed to be useful as lower molecular weight synthesis gasses [3]. Additionally, several economic factors will impact the conversion of biomass to fungible fuels and chemicals on an industrial scale.

Economic analyses have been conducted on direct-firing, co-firing, gasification and pyrolysis of biomass as stand-alone unit operations [2,4]. While these data suggest that stand-alone thermochemical plants may not be competitive with existing power generation facilities that burn fossil fuels, selective design of feedstock and thermochemical processing logistics can improve a pyrolysis plant's economic feasibility. One model proposes the implementation of small, mobile, skid-mounted pyrolysis units for converting biomass feedstocks on site at the farm [5]. The pyrolysis gasses are used to sustain the pyrolyzer's operation, the char is used for soil amendment, and the pyrolysis oil is transported to a centralized processing facility for upgrading. On-site conversion of the low density biomass feedstock to higher density pyrolysis oil requires lower volume farm-site storage and significantly reduces the transportation costs of materials to the refining facility.

This distributed thermochemical processing model with farm-site conversion of biomass and subsequent centralized refining requires an easily operated, small to medium scale, on-site, fast pyrolyzer. One pilot-scale pyrolyzer design consists of a fluidized

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bed reactor wherein the biomass is heated. Volatile products and char can be carried over in the inert gas stream to a series of cyclones to trap the char followed by a series of electrostatic condensers and chillers to collect the condensable bio-oil. The non-condensable gasses are vented at the end of the process [6–8]. The standard heat transfer material used in the fluidized bed of this continuous feed pyrolyzer is quartz sand [2,8]. The biomass feedstock is fed into the fluidized bed at a rate of 1–5 kg h⁻¹ where it is exposed to 450–500 °C sand for 0.5–5 s (fast pyrolysis). The typical product ratio of fast pyrolysis is 15–25 wt% char, 60–75 wt% bio-oil (containing 15–30 wt% water), and 10–20 wt% noncondensable gasses, depending on the pyrolysis parameters and feedstock [2,9].

Fast pyrolysis conditions have been optimized for bio-oil formation. Pyrolysis bio-oil is a dark, viscous liquid that contains many (>300) highly oxygenated (30–40 wt%) organic compounds, is corrosive, has a low heating value (~20 MJ/kg, 50% of petroleum fuels), low pH, and is chemically unstable, tending to gel upon standing. These properties render pyrolysis bio-oil unsuitable for use as a liquid transportation fuel, although it can be burned directly in stationary turbines [9]. Extensive work has been conducted on catalytic upgrading of pyrolysis bio-oil. Methods similar to petroleum refining are the primary areas of this research. Deoxygenation is accomplished by hydrotreating with conventional catalysts containing Co, Mo, and Ni on alumina and hydrocracking (zeolites), though the practicality and economic feasibility of such methods are still being debated [3,10,11]. More recent studies have investigated the use of less conventional inorganic catalysts such as CeO₂, carbon nanotube-supported Pd, and homogenous RuCl₂(PPh₃)₃ in water/toluene emulsions for upgrading bio-oil [12–14].

Alternatively, less studied is the *in situ* use of the catalysts during pyrolysis to affect change of the bio-oil [15–18]. Here the catalyst and feedstock are in intimate contact during the pyrolysis reaction. For the fluidized bed reactor discussed above, the catalyst essentially replaces the sand as the heat transfer agent. Unfortunately, the low density, fine-powder nature of the typical catalysts and supports (e.g. alumina silicates and zeolites) are problematic for a fluidized bed pyrolyzer since they are easily carried over from the reactor to the cyclones in the inert gas stream. A possible solution to this problem is extruding the catalyst powders into higher mass pellets for use in the fluidized bed; however, the effects the extrusion process on the catalysts' activities are unknown. Herein, we examined the *in situ* use of extruded catalysts for the pyrolysis of oak. Two small scale pyrolysis methods, a pyroprobe (μg scale) and a packed bed reactor (g scale), were used to screen the modified catalysts. The liquid and gas fractions from the two methods were determined and compared in an attempt to evaluate which method would best predict catalyst functionality in a large scale, fluidized bed pyrolyzer.

2. Materials and methods

2.1. Biomass and catalysts

Oak pellets were obtained from the U.S. Department of Energy and ground in a Glen Mills Model No. 92-1614 grinder and sieved to 0.710 mm using ASC Scientific Standard, ASTM E11 specified sieves. The empirical content of the oak sawdust was 45.52 ± 0.12% C, 5.88 ± 0.12% H, 0.09 ± 0.08% N (*n* = 3 trials), and 51.49 ± 0.32% O (by difference). The ash content of the oak was 0.36 wt% and the moisture content was 5.10 wt%.

The extruded catalysts obtained from Honeywell-UOP (Des Plaines, IL) were provided as pellets. The pellets were ground to small granules with a mortar and pestle prior to use. The proprietary catalysts were identified as follows: low acid catalyst (G), moderate acid catalyst (H), high acid catalyst (I), dealuminated-

zeolite Y (L), β-zeolite (M), a naturally occurring metal hydroxide containing mineral (N), mordenite (O), and mesoporous aluminosilicate molecular sieve (P).

2.2. Packed bed reactor

The previously described pyrolysis unit and reaction conditions [15] were used with the following modifications. The reaction cell, constructed of 0.5 mm thick stainless steel, was 12.0 cm tall by 0.9 cm diameter, resulting in a volume of 7.6 cm³. The total gas flow and volume were measured using a Ritter Milli-Gas Counter (maximum gas flow 100 mL/min) monitored with Rigamo-1CH V2.01-Beta Channel Signaling software (Calibrated Instruments Inc., Hawthorne, NY).

Samples were prepared as 1:5 ratio of oak sawdust to catalyst. The oak sawdust and catalyst were intimately mixed and loaded into the cell between plugs of quartz wool. The cell was purged with 300 mL of He before heating. Each run was performed in at least duplicate and major compounds were quantitatively analyzed (see below).

2.3. Gas chromatography with thermal conductivity detector (GC-TCD)

Gas samples from the packed bed reactions were analyzed on a HP 6890 GC fitted with a TCD operating at 220 °C. Gas separation was accomplished using a Poropack Q column (Restec, Bellefonte, PA) with He as the carrier gas. The column was heated as follows: 40 °C for 3 min followed by a 15 °C/min ramp to 180 °C, which was held for 5 min. Gas products were quantified vs. calibration of a standard gas mix consisting of ~3% (w/v) each H₂, CH₄, CO, CO₂, C₂H₆, and C₂H₄ (Linde North America Inc., Murray Hill, NJ). Due to the TCD signal damping effect of He on H₂, a standard curve for H₂ was prepared from home-made mixtures ranging from 3% to 50% (v/v), resulting in a calibration curve of $y = 24x^{1.5}$ ($R^2 = 0.997$).

2.4. GC-mass spectrometry (GC-MS)

GC-MS analyses of the condensed volatiles from the packed bed reactions were performed using an Agilent 6890N gas chromatograph with a 5973 network mass selective detector. Separation of products was accomplished on a Supelco Petrocol DH 50.2 column (50 m × 0.2 mm diameter × 0.2 μm film thickness). The oven program was 65 °C for 2 min followed by a heating ramp of 10 °C/min to 270 °C. The Wiley Mass spectral library was used, along with retention times of known standards, for component identification.

2.5. High performance liquid chromatography (HPLC)

HPLC analyses of the condensable volatiles from the packed bed reactions were performed on a Spectra Systems chromatograph equipped P4000S pumps, SCM 1000 Vacuum degasser, AS 3000 autosampler, and Finnegan Surveyor RI Plus detector (35 °C). Twenty microliter samples were analyzed on a Biorad Aminex HPX-87H (300 mm × 7.8 mm) ion exchange column developed with a 24 min, 0.8 mL/min isocratic flow of 500 mM H₂SO₄, prepared with Millipore 0.20 μm Nylon membrane filtered deionized H₂O. Samples were prepared as 1:20 dilutions with mobile phase containing 40 mM isopropanol used as an internal standard. Separated compounds were quantified against standard curves of 0.15 mg/mL to 30 mg/mL of analytes, lowest $R^2 = 0.9996$.

2.6. Pyroprobe GC-MS

Flash pyrolysis experiments were conducted using a Pyroprobe 2000 (CDS Analytical, Oxford, Pa) coupled to an Agilent HP 6890N

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