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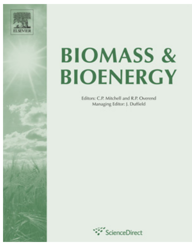

Oxidative pyrolysis of kraft lignin in a bubbling fluidized bed reactor with air

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ABSTRACT

Fast pyrolysis of kraft lignin with partial (air) oxidation was studied in a bubbling fluidized bed reactor at reaction temperatures of 773 and 823 K. The bio-oil vapors were fractionated using a series of three condensers maintained at desired temperatures, providing a dry bio-oil with less than 1% water and over 96% of the total bio-oil energy.

Oxygen feed was varied to study its effect on yield, composition, and energy recovery in the gas, char and oil products. The addition of oxygen to the pyrolysis process increased the production of gases such as CO and CO_2. It also changed the dry bio-oil properties, reducing its heating value, increasing its oxygen content, reducing its average molecular weight and tar concentration, while increasing its phenolics concentration. The lower reaction temperature of 773 K was preferred for both dry bio-oil yield and quality.

Autothermal operation of the pyrolysis process was achieved with an oxygen feed of 72 or 54 g per kg of biomass at the reaction temperatures of 773 and 823 K, respectively. Autothermal operation reduced both yield and total energy content of the dry bio-oil, with relative reductions of 24 and 20% for the yield, 28 and 23% for the energy content, at 773 and 823 K.

1. Introduction

Lignin is usually treated as a waste product in the pulping industry and mainly used as a low grade fuel for energy recovery. Building on its large availability from the paper mill industry, "the advent of bio-refineries that convert cellulosic biomass into liquid transportation fuels will generate substantially more lignin than necessary to power the operation" [1]. Therefore, it is important to develop technologies that convert lignin into value-added products, e.g., low-cost carbon fiber, engineering polymers, polymeric foams, fungible fuels and commodity chemicals. In fact, the conversion of lignin to chemicals is considered to be an important factor in improving the overall economics of an integrated bio-refinery [2].

Thermochemical treatment (mainly pyrolysis) is one of the important strategies for the production of fuels and aromatic chemicals from lignin. However, due to the complex structure and presence of various linkages between the monomers, the conversion of lignin to value-added compounds is substantially more difficult than that of carbohydrates. The thermal instability of the lignin fragments makes its processing even

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more challenging [3]. Despite the numerous studies on pyrolysis of woody biomass, fast pyrolysis of lignin, especially kraft lignin, is only sporadically reported for pilot plant operations. Most of the studies are focused on Py-GC-MS or TGA-FTIR characterizations for the pyrolysis of lignin [4–7].

Biomass fast pyrolysis is an endothermic process [8] and heat is typically provided by heat transfer either to a fluidized bed of inert sand, or alternatively, to circulating sand particles that are reheated in a separate burner [9–11]. Autothermal pyrolysis is of great interest for large-scale bio-oil production because it does not require any external energy input. Once the reactor has been preheated to the target reaction temperature, energy produced from the pyrolysis process is able to maintain the reactor at the desired temperature. An obvious benefit of an autothermal pyrolysis process is a greatly simplified reactor design since it does not require complex equipment to provide external heat to the process.

Oxidative pyrolysis of biomass and autothermal operation based on partial oxidative pyrolysis of biomass have been previously studied by several research groups and the results can be found in several publications [12–15]. These studies suggest that carefully controlled partial oxidative pyrolysis with low oxygen concentrations will improve the bio-oil quality by increasing the concentration of monomers, and reducing the concentration of oligomers or pyrolytic lignin. An advantage of the fractional condensation system is that the water produced by oxidation does not affect the dry bio-oil.

The objective of this study is to provide a systematic study for lignin pyrolysis in a bubbling fluidized bed reactor with fractional condensation. The effect of oxygen feed rate on dry bio-oil yield and quality is investigated for the pyrolysis temperatures of 773 and 823 K, which are known to be near the optimum for bio-oil production [16].

2. Experimental

2.1. Materials

Kraft lignin extracted from black liquor in Domtar's Plymouth, North Carolina mill, with a wood source of Southern Pines (including *Pinus taeda* L., *Pinus palustris* Mill., *Pinus echinata* Mill., and *Pinus elliottii* Engelm.), was used as the feedstock for the ICFAR bubbling fluidized bed pyrolysis pilot plant illustrated in Fig. 1. The higher heating value of the lignin powder was 25.9 MJ kg^{-1}. Proximate and ultimate analysis results are summarized in Table 1. The quantities are mass fractions of (a) material as received – proximate analysis (%) and (b) of dry material atomic composition – ultimate analysis.

The bed consisted of 0.8 kg of inert silica sand with a Sauter-mean diameter of 70 μm and an apparent particle density of 1430 kg m^{-3}. Nitrogen was used as the inert fluidization gas as well as the carrier and pulse gas for the injection of lignin powder slugs into the bubbling fluidized bed reactor using a pulsating feeder [17]. Compressed air was used as oxygen source (O_2). The flow rates of the air and nitrogen that were used for fluidization were controlled by pressure regulators, calibrated sonic nozzles and mass flow controllers.

2.2. Bubbling fluidized bed setup coupled with fractional condensation

A schematic of the experimental setup is shown in Fig. 1. It mainly consists of the biomass feeder, the pyrolysis reactor and the fractional condensation train.

2.2.1. Biomass feeder

The ICFAR biomass “slug injector” feeder [17] illustrated in Fig. 1 was used to feed kraft lignin powders into the bed at 0.15 m above the gas distributor through a 45° inclined line. Kraft lignin particles were discharged from the hopper through a pneumatically activated pinch valve. The pinch valve opened periodically (every 5 s) for short periods of time (0.35 s), allowing small amounts of biomass particles to fall into a horizontal injector tube. During each cycle, the biomass formed a slug, which was propelled into the reactor by intermittent pulses of nitrogen and a continuous stream of nitrogen carrier gas. The continuous carrier gas and the intermittent pulses prevented any solids from settling inside the injector tube. The pinch valve used to discharge biomass and the solenoid valves used to generate the pulse flow were synchronized and controlled with a programmable logic controller (PLC).

The flow rate of the carrier nitrogen was metered and controlled with an Omega mass flow meter, while the amount of pulse gas was calculated from the pressure and volume of a buffer tank and the pulse frequency.

2.2.2. Bubbling fluidized bed reactor

The 0.078 m i.d., 0.58 m high reactor was made of Inconel® 600. The reactor was heated by three radiant electric heaters, covering both the dense fluidized sand bed and the freeboard sections. The heaters were independently controlled using Watlow PID controllers so that a constant temperature was maintained everywhere along the axis of the reactor during the pyrolysis process. Temperature feedback for the PID controllers was provided through type-K thermocouples placed within the reactor at the same height as the heaters. The reactor is equipped with a mechanical stirrer, made with three blades of Inconel® 600, to break the agglomerates formed by liquefied lignin and sand during the pyrolysis process [16].

Fluidization gas (nitrogen and air) entered the pyrolysis reactor through the perforated gas distribution plate located at the bottom of the reactor. Before entering the fluidized bed, the fluidization gas was preheated to 573 K using a 400 W inline tube heater (Omega AHP-5052) with PID temperature control and its flow rate was metered and controlled with an Omega mass flow meter. This simulates the preheating of the fluidization gas which, in a commercial process, would likely be performed by recovering heat from the exhaust gases and vapors.

When the biomass particles were injected into the fluidized bed reactor, they were immediately mixed with the hot sand bed, melting and forming foam. The mechanical stirrer increased the mixing between the hot sand and the lignin foam, and prevented the formation of large agglomerates, consequently ensuring better conditions for the fast pyrolysis. During all the experiments, the mechanical stirrer was