



Kraft-lignin pyrolysis and fractional condensation of its bio-oil vapors



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ABSTRACT

Kraft lignin has been pyrolyzed in a modified bubbling bed reactor coupled with an internal stirrer, and the resulting bio-oil vapors have been fractionated using a series of three condensers maintained at different temperatures. The temperatures of the condensers have been optimized in order to selectively separate most of the water present in the bio-oil vapor stream and increase the quality of the remaining bio-oil. The condenser train comprised of an electrostatic precipitator-cum-condenser (C-ESP) installed between two cyclonic condensers. The fractionated bio-oil was found to be rich in phenolic compounds with a water content of less than 1 wt%. The effect of pyrolysis temperature on the fractionated bio-oil yield and characteristics is also discussed.

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1. Introduction

Lignin is the second most abundant biomass component, and is the largest source of aromatics in nature. Kraft lignin is a by-product of the Kraft pulping, which is the predominant chemical process used by the pulp and paper industry. Kraft lignin is usually burned as a low-grade fuel in recovery boilers. Because of its availability in large quantities and its large aromaticity, Kraft lignin is considered as a valuable biomass source for the potential production of renewable fuels and chemicals [1,2].

In the last 30 years, there have been major developments in the fast pyrolysis technology, which converts solid biomass to energy-dense, transportable liquid, together with solid co-products (bio-char) and non-condensable hydrocarbon gases. Fast pyrolysis can produce high liquid yields of up to 75% [3], based on the type of biomass, through rapid thermal decomposition of lignocellulosic biomass in the absence of oxygen. However, fast pyrolysis of lignin is not widely investigated because of the difficulties faced during the continuous feeding and processing of lignin in fluidized bed reactors. Due to its low melting point (between 150 and 200 °C), lignin is usually found to melt even before entering the reactor, causing blockage of the feeding systems. Other problem encountered during lignin pyrolysis is the slow reactivity, resulting in the formation of a liquid phase in the reactors leading to the bed agglomeration and subsequent defluidization. The liquid yield

resulting from the condensable vapors from the lignin pyrolysis is quite low and is reported in the range of 20–37 wt% [4,5].

Fast pyrolysis liquid, also called bio-oil, has tremendous potential as a fuel oil substitute. The heating value of raw bio-oils is around 17 MJ/kg [3], which is equivalent to approximately 40% of the heating value of diesel. The relatively low heating value of the bio-oil is due to its high water concentration (typically in the range between 15 and 30 wt%) and high oxygen content (35–40%). Bio-oils also have other undesirable properties for fuel application, such as low thermal stability, high corrosiveness and high acidity. The upgrading of bio-oils is crucial to convert bio-oils into stable liquid fuels [6,7].

The heating value, corrosiveness and the phase stability of the bio-oils can be greatly improved by decreasing the water content of the bio-oils. Lately, researchers around the world have been extensively investigating the fractional condensation method for the separation of the constituents of the bio-oil [8–11]. In the fractional condensation process, the bio-oil vapor stream from the fast pyrolysis reactor is passed through a series of condensers maintained at different, gradually decreasing temperatures to allow the collection of liquid fractions of different physical and chemical properties in each condenser.

The objective of the present work is to obtain dry bio-oil, i.e. with very low water content, from the pyrolysis of Kraft lignin in order to generate a high value and stable feedstock for the possible production of phenols and fuel products. Kraft lignin is pyrolyzed in a modified bubbling fluidized bed equipped with an internal mechanical stirrer, and the resulting bio-oil vapors are fractionated using a three-condenser train to obtain a dry bio-oil. The effect of

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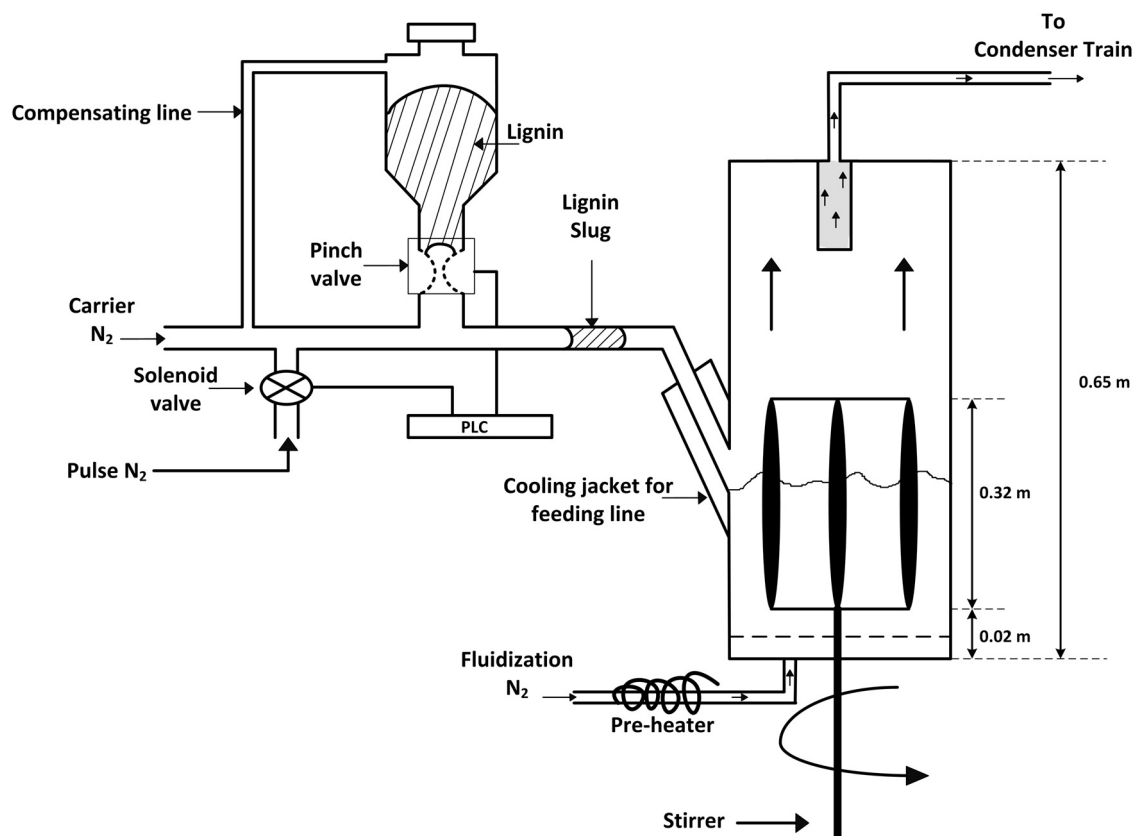


Fig. 1. Schematic of bubbling fluidized bed setup used for the pyrolysis of lignin.

reactor temperature on the yield and characteristics of dry bio-oil will also be studied.

2. Materials and methods

2.1. Materials

Kraft lignin was used as the feedstock. The Kraft lignin was pyrolyzed without any pre-treatment. The bulk density and the higher heating value of Kraft lignin were 330 kg/m^3 and 26 MJ/kg , respectively. The proximate and ultimate analyses of Kraft lignin are reported in Table 1. The sulfur detected in the Kraft lignin results from the Kraft process.

Inert silica sand with a Sauter-mean diameter of $180 \mu\text{m}$ was used as the bed material in the bubbling fluidized bed. The bed mass was 800 g.

Table 1
Proximate and ultimate analyses of Kraft lignin.

	Kraft Lignin
Proximate analysis (% wet basis)	
Fixed carbon	61
Volatile	24
Ash	10
Moisture	5
Ultimate analysis (% dry and ash free basis)	
C	63.2
H	4
N	2
O	20
S	0.8

Nitrogen was used as the inert fluidization gas. Nitrogen was also the gas used in the pulsating feeder used to introduce the Kraft lignin into the bubbling bed.

2.2. Bubbling fluidized bed setup

The fluidized bed reactor is made of Inconel 600, 0.075 m in diameter, with a 0.65 m long cylindrical section [5]. The reactor is heated by three irradiative electric heaters, covering the dense sand bed and the freeboard sections. The heaters are independently controlled using Watlow PID digital controllers, to set a constant temperature profile along the axis of the reactor. The temperature feedback for the Watlow controllers is provided through type K thermocouples placed within the bed at the same height as the heaters. The reactor is equipped with an internal stirrer, made with three blades of Inconel, to break the agglomerates formed by char and sand during the pyrolysis of lignin [4]. The nitrogen fluidization gas enters the bed through a perforated distributed plate located at the bottom of the reactor. Before entering the bed, the nitrogen is heated using a 400 W in-line air process heater (Omega AHP-5052).

The ICFAR biomass “slug injector” is used to feed lignin into the bubbling bed reactor [12]. As shown in Fig. 1, a hopper filled with lignin discharges through a pneumatically activated pinch valve. The pinch valve opens periodically (usually every 10 s), for short periods of time (0.4 s), allowing small amounts of lignin to fall into a horizontal injector tube. During each cycle, the lignin forms a slug, which is propelled into the reactor by intermittent pulses of nitrogen and a continuous stream of carrier gas (nitrogen). The continuous nitrogen prevents any solids settling in the injector tube. A solenoid valve is used to deliver this gas pulse. The pinch valve and the solenoid valve are controlled and synchronized with a programmable logic controller (PLC). The flow rates of the fluidization and carrier nitrogen are metered and controlled with two Omega

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