Fuel Processing Technology 181 (2018) 1–7

Contents lists available at ScienceDirect

Fuel Processing Technology

journal homepage: www.elsevier.com/locate/fuproc

Research article

Co-pyrolysis of lignin and low rank coal for the production of aromatic oils

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ARTICLE INFO

Keywords:
Co-pyrolysis
Hydrolysis lignin
Low rank coal
Aromatic oils
Toxic effect
Synergistic effect

ABSTRACT

The co-pyrolysis of hydrolysis lignin and low rank coal was studied in a drop-tube fixed bed reactor. Baganuur (BN) coal blending into hydrolysis lignin with mass ratio of 50:50 decreased the yields of oil and gas significantly, and then increased the yield of char compared to their predicted values after the co-pyrolysis at 450 °C. This toxic effect was explained by the easier coupling reaction of BN coal derived poly-aromatic radicals with hydrolysis lignin (HL)-derived aromatic compounds to form solid product - char. However, when the amount of BN coal in the blend decreased from 50% to 30%, the toxic effect decreased, and experimental yields of char, oil and gas approached to their predicted values. In case of HL-AC (50:50) blend, a synergistic effect was observed during the co-pyrolysis of hydrolysis lignin and Aduunchuluun (AC) coal. The oil yield slightly increased, and the yields of gas and char decreased compared to their predicted values after the co-pyrolysis at 450 °C. Amount of aromatic hydrocarbons in acetone soluble of the oil was close to its predicted value, and several kinds of aliphatic alcohols, aldehydes and ketones were detected in toluene soluble of the oil product, even though there were no such compounds existed in the toluene soluble from the pyrolysis of single feed-AC coal. It was supposed that additional hydrogen was produced by the secondary water-gas shift reaction of CO gas evolved from AC coal with large amount of inherent alkali and alkali earth metals during the HL-AC co-pyrolysis. It was also supported by the larger H/C ratios of oil and char compared to their predicted values after the co-pyrolysis of HL-AC blend.

1. Introduction

Due to increasing energy production concern and climate change, woody biomass has reached the most attention of the researchers as a potential resource of renewable energy since it has high yield of volatile matter, possibility of being converted into liquid fuels and chemicals, low contents of sulfur and nitrogen as well as emitting relatively low CO_2 content [1,2]. Woody biomass (on a dry basis) is mainly composed of three components: 30–40 wt% cellulose, 20–30 wt% hemicellulose and 20–30 wt% lignin with the remaining 5–10 wt% ash. Undesirable characteristics of woody biomass, such as low HHV in comparison with fossil fuel, high volatile content, and high transportation cost, has limited its utilization as a feedstock for renewable energy production. However, co-processing woody biomass with coal (i.e. pyrolysis, liquefaction, gasification, combustion) is one of the most promising choices to keep off these drawbacks emerging from biomass utilization. The co-processing not only removes the disadvantages of biomass and coal, but also adds some advantages to them. The co-pyrolysis process of coal and biomass can produce char, tar and gas. Due to synergistic effect of co-pyrolysis of coal and biomass, there has been growing interest for research in this area recently [2,3]. The high content of hydrogen and carbon ratio (H/C) in woody biomass in comparison with coal can be addressed as synergistic effect of co-pyrolysis [4,5]. Nevertheless, a lack of any significant synergistic effect on coal and biomass also has been reported with some researchers [7,8]. This could happen in co-pyrolysis by enhancing different operating conditions i.e. temperature, pressure, heating rate, type of reactor, type of biomass and biomass blending ratio [9–11]. The co-pyrolysis of Indonesian coal (sub-bituminous) and two types of biomass, rice straw and *Leucaena leucocepha* wood using a drop tube fixed-bed reactor, was studied by Krekkaiwan et al. [12] and a synergistic effect, in terms of higher gas yield and lower tar and char yields, was reported especially at a biomass and coal ratio of 1:1. In an another work by Li et al. [13] co-pyrolysis behaviors of saw dust and Shenfu bituminous coal in a drop tube furnace and a fixed bed reactor at different temperatures were studied, by using six different biomass/coal ratios. Synergistic effect was reported in gaseous phase, which was mainly caused by the secondary reactions in co-pyrolysis. It was also described that in co-pyrolysis of Thai lignite and corncob CH_4 formation was 3 times higher than calculated value at 400 °C, by Sonobe et al. [3]. Guo and Bi [14]

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https://doi.org/10.1016/j.fuproc.2018.09.008
Received 29 May 2018; Received in revised form 2 August 2018; Accepted 9 September 2018

reported the synergistic effect in volatiles during the co-pyrolysis process of Fugu subbituminous coal and corn stalk, which made the yield of tar and light-tar increased. A study by Zhang et al. [4] was performed on co-pyrolysis of biomass (legume straw) and coal (Dayan lignite) in a free fall reactor under atmospheric pressure at temperature range 500–700 °C, with nitrogen as balance gas, and different blending ratio of biomass in mixtures from 0 to 100 wt%. They have reported the positive effects in the co-pyrolysis of biomass and coal. Under the higher blending ratio of biomass, the char yields were lower than the theoretical values calculated on the basis of pyrolysis yields of each individual fuel, and consequently the liquid yields were higher. Moreover, they showed that the compositions of the gaseous products from blended samples were not all in accordance with those of their parent fuels. It was summarized by Hassan et al. [6] that during the co-pyrolysis, biomass may act as a hydrogen donor and produced large amounts of volatile compounds, which could enhance the “gas-lignite” contact, secondary tar cracking, char gasification and gaseous phase contact. Until now, several researchers examined only the effect of biomass feed types on the co-pyrolysis of biomass and coal. With a viewpoint of natural heterogeneous resource of coal, an effect of its type should play an important role in product yield and composition of the co-pyrolysis of biomass and coal.

Our research work aimed to investigate co-pyrolysis of two kinds of Mongolian low rank coal (Baganuur and Aduunchuluun coal) with a hydrolysis lignin using drop tube fixed bed reactor in temperature range 450–650 °C and two different mass ratios (70:30 and 50:50) depending on the coal types in the first time. Effects of coal type, its blending ratio and pyrolysis temperature on characteristics of aromatic oils obtained from the pyrolysis were examined.

2. Experimental

2.1. Samples

Two kinds of Mongolian low rank coals were used as research samples. Baganuur coal (BN) is deposited in the northern central area of Mongolia. Its resource is estimated by approximately 500 million tons, and mainly utilized as a fuel for power plants. Another coal deposit of Aduunchuluun (AC) is located in the eastern part of the country. Its resource is about 600 million tons, and utilized as a fuel in local area. The results of their proximate and ultimate analysis were listed in Table 1.

The hydrolysis lignin (HL) used in this study, obtained from FPInnovations, was derived from Aspen wood that is composed of 30–55 wt% cellulose, 15–35 wt% hemicellulose and 5–31 wt% lignin. HL is a residue produced in FPInnovations's TMP-Bio process [15], and has the following textural compositions: 56.7 wt% lignin, 29.8 wt% carbohydrates, 1.2 wt% ash and 12.3 wt% others. ACS reagent-grade acetone and toluene, purchased from Caledon Laboratory Chemicals (ON, Canada) were used as the reactor rising/washing solvent for product separation.

Hydrolyzed lignin and coal samples were mechanically mixed with the weight ratios of 50:50 and 70:30. Powder mesh size of the samples was 150–75 μm.

Table 1
Proximate and ultimate analysis of low rank coals and hydrolysis lignin.

Sample	Volatile (wt%, daf)	Fixed C (wt%, daf)	Ash (wt%, db)	C	H	N	S	O	H/C
				(wt%, daf)					(−)
BN	41.6	78.5	7.45	66.1	4.9	0.85	0.57	27.6	0.89
AC	47.1	73.3	10.6	62.9	4.83	0.66	1.49	30.1	0.92
HL	71.4	26.7	1.89	49.8	6.45	0.33	0	43.5	1.56

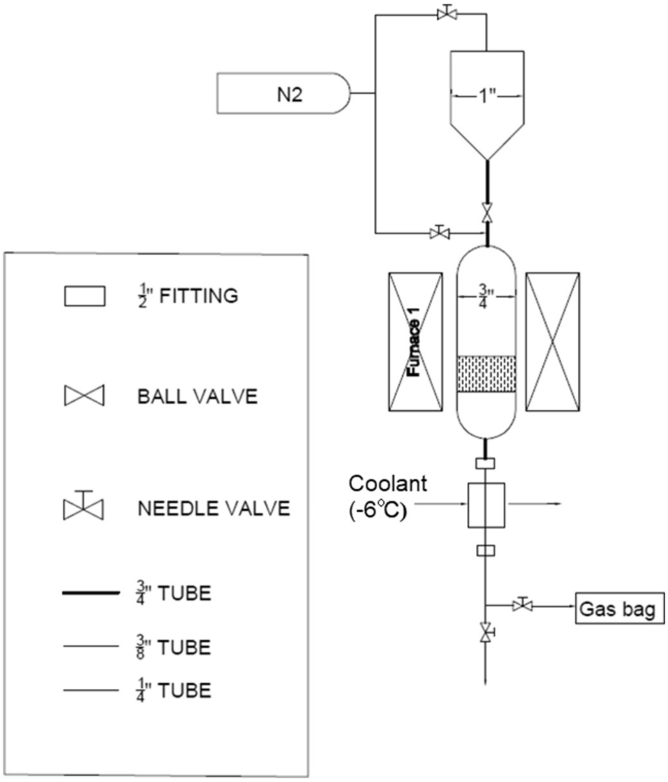

Fig. 1. Scheme of the drop-tube fixed bed reactor for pyrolysis experiments.

2.2. Co-pyrolysis experiments

Co-pyrolysis experiments were carried out in a drop-tube fixed bed reactor made of SS 316L tube (3/4″ O.D., 26.5″ length). The schematic diagram of the reactor is shown in Fig. 1.

The reactor was heated in an electric furnace whose temperature was controlled by a temperature controller. The bed temperature was measured by putting a thermocouple inside the bed, and the uniform temperature zone with the length of 6″ is located in the mid-section of the reactor. The reported value for temperature is the actual value inside the bed. The nitrogen flow rates through the biomass feeder and reactor was set and controlled with Brokenhorst High-Tech mass flow controller meter (EL-FLOW). In a typical run, hydrolysis lignin (HL) and coal were carried out at the temperature range from 450 to 650 °C with sweeping N_2 gas at a flow rate of 97 ml/min. 1.5 g of HL and 1.5 g coal were completely mixed and loaded into the feeder (1″ OD tube) above the reactor separated from the reactor by a ball valve, and approximately 0.4 g of quartz wool was put in the bottom of the reactor as sample-bed holder on top of which 3 g of feed sample was loaded in the tubular reactor positioned in the hot-zone of the furnace, as illustrated in Fig. 1. During the pyrolysis process 0.4 g of quartz wool was loaded on the top of the sample. Leak proof was ensured with high pressure nitrogen gas. Before starting the reaction the reactor and the feeder were vacuumed/purged thrice repeatedly to eliminate air inside the reactor system. The difference between the temperature inside the reactor and the set temperature by controller was measured (10 °C) by putting a thermocouple inside the reactor and it was already considered in all the temperatures. The reactor was then heated up to desired temperature at a heating rate 10–20 °C/min in 97 ml/min N_2, and after the reactor temperature reached to specified temperature, biomass and coal in the feeder were fed into the reactor rapidly by opening the ball valve by gentle tapping. Assuming negligible change in total gas flow rate (97 ml/min N_2) during the pyrolysis experiments, the residence time of the vapor inside the 3 g sample was estimated to be < 0.5 s. Mass balances upon pyrolysis experiments fell within a reasonable