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Synergetic effect during co-pyrolysis/gasification of biomass and sub-bituminous coal

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ABSTRACT

In this work, the co-pyrolysis of Indonesian coal (sub-bituminous) and two types of biomass, rice straw and *Leucaena leucocepha* wood, was studied using a drop tube fixed-bed reactor. The gasification reactivity of the obtained co-pyrolyzed char with steam was examined using a rapid heating thermobalance reactor. In the co-pyrolysis, a synergetic effect, in terms of higher gas yield and lower tar and char yields, was manifested especially at a biomass and coal ratio of 1:1. This synergetic effect could be explained by the transferring of active OH and H radicals from the biomass to the coal as well as the catalytic role of potassium (K) from the biomass. In the steam gasification, the *in situ* pyrolyzed char from the coal/biomass blend exhibited a higher reactivity than that from the coal or the biomass. This could be related to the increased surface area and pore volume of chars from the blend as well as the influence of volatile K released from the biomass. In addition, the biomass type appeared to have a significant influence not only on the magnitude of the synergetic effect during the co-pyrolysis but also on the reactivity of the resultant chars.

1. Introduction

Gasification is a promising technology for producing gaseous fuel ("synthesis gas") from hydrocarbon-based materials. The produced gas can be applied for electricity generation or/and petrochemicals production, such as methanol, dimethyl ether (DME) or/and Fisher–Tropsch processes for producing synthetic fuel oil. Coal, biomass, polymer/plastic and municipal wastes are typical sources used for the gasification processes. At present, coal is the main feedstock used for the gasification process because of its large reserves, and it is expected to be applied as the energy resource for many decades ahead. However, the use of coal has been more concerned because of the environmental impacts that caused from the emission of toxic gases (H_2S, SO_x and NO_x) and the fused-ash slagging problem forming inside the gasifier. In contrast, biomass is a renewable energy resource of interest as a replacement for coal to reduce the environmental impact and fossil fuel usage. Thailand is an agricultural based country with a corresponding large supply of biomass resources. Most such biomass, such as rice straw, rice husk, bagasse, palm oil waste and wood chips, have been utilized for energy purposes, such as combustion and gasification [1]. Unfortunately, gasification of any individual biomass normally encounters several problems such as their seasonal harvesting rather than all year round availability, high transportation costs and lower fuel-qualification characters. Furthermore, the relatively high tar content in most biomass leads to corrosion in the piping and a reduction in the overall gasification efficiency.

The co-utilization of coal and biomass is an interesting way to solve these problems. In recent years, a number of studies have reported a synergetic effect in the co-processing of coal and biomass, in particular co-pyrolysis and co-gasification [2–9]. This synergy during the co-processing is likely to be due to the higher hydrogen and carbon molar ratio (H/C) of biomass compared with coal which could facilitate coal decomposition [2–4,9].

Nevertheless, some studies have reported a lack of any significant synergetic effect when using coal/biomass blends [10–14]. This apparent discrepancy might depend on the operating parameters used, such as temperature, pressure, heating rate, type of reactor, type of coal, type of biomass and biomass blending ratio [2,9,10,15–17]. In a conventional thermobalance reactor, the devolatilization of coal and biomass particles takes place at different time due to the slow heating rate of ~10 °C min^{-1} [13]. The rapid heating rate in a fluidized bed reactor could shorten the time lag of devolatilization but the contact time between the pyrolytic products from coal and biomass is relatively short [14]. This likely explains why no synergetic effect was observed in those studies.

Therefore, in this study the co-pyrolysis of Indonesian sub-bituminous coal and two types of biomass, rice straw (RS) and *Leucaena leucocepha* wood (LN) was carried out in a drop tube fixed-bed reactor. The samples (coal, biomass and coal/biomass blends) were instantly

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Table 1
Proximate and ultimate analysis results of the samples.

Sample	Indonesian coal (Coal)	Rice straw (RS)	*Leucaena leucocepha* (LN)
Proximate analysis (wt.%, as received)			
Moisture	12.41	6.43	8.89
Ash	8.39	11.22	2.59
Volatile matter	36.84	61.95	62.21
Fixed carbon	42.36	29.25	26.31
Ultimate analysis (wt.%, daf)			
Carbon	72.13	45.30	48.39
Hydrogen	6.67	6.93	7.11
Nitrogen	1.4	0.92	0.29
Sulfur[a]	0.22	0.14	0.14
Oxygen (by difference)	19.58	46.71	44.07
H/C molar ratio	1.11	1.84	1.76
O/C molar ratio	0.20	0.77	0.68
Element analysis (wt.%, db)[b]			
Sodium (Na)	0.034	0.064	0.219
Potassium (K)	0.126	1.892	0.823
Calcium (Ca)	0.788	0.844	1.108
Magnesium (Mg)	0.171	0.139	0.186
Silicon (Si)	4.00	11.81	1.00
Iron (Fe)	1.645	0.075	0.165
Gross heating value (kJ/g)	22.66	14.95	12.76

[a] By Bomb washing method (ASTM 3177).
[b] By X-ray fluorescence (XRF).

dropped so that the heating rate of the particles was higher than other typical fixed-bed reactors. The contact time of the pyrolytic products was also presumably longer than that in fluidized-bed reactors, owing to the fixed-bed section. The influence of the biomass blending ratio and biomass type on the product distribution was studied. Their interactions, in terms of the product distribution and gas composition, were described by comparing experiments of coal or biomass alone to coal/biomass blends. The pyrolytic tar and char were characterized with Brunauer–Emmitt–Teller (BET), scanning electron microcopy (SEM) and gas chromatography–mass spectrometry (GC–MS) techniques. In addition, the synergetic effect on the *in situ* char steam gasification rate was investigated using a rapid heating thermobalance reactor.

2. Experimental

2.1. Fuel samples

Indonesian sub-bituminous coal (referred to as coal hereafter), rice straw (RS) and *L. leucocepha* (LN) were ground and sieved into particle sizes of 150–250 μm. To remove the effect of varying moisture contents, the samples were oven-dried at 110 °C for 1 h and then stored in a desiccator before testing. Proximate and elemental analysis results of the samples are shown in Table 1. Coal/biomass blends were prepared by physical mixing at biomass and coal weight ratio of 0:1, 1:3, 1:1, 3:1 and 1:0, respectively.

2.2. Pyrolysis in a drop tube fixed-bed reactor

Pyrolysis of coal, biomass (RS or LN) at the different ratio of coal/biomass blends was performed in a drop tube fixed-bed reactor, as illustrated schematically in Fig. 1. The quartz-tube reactor, which had an inner diameter of 20 mm and a length of 580 mm, was heated externally by a Nabertherm RS 8013001M electric furnace. The heating zone (340 mm length) was located in the middle of the reactor tube. N_2 was used as the carrier gas at a total gas flow rate of 120 mL min^{-1}. After the reactor was heated to 800 °C and held for 1 h, 4 g of sample was instantly dropped into the reactor. The fast pyrolysis immediately took place within the short residence time. The char was produced over a quartz wool filter, which was subsequently weighed for calculating the char yield. Some of the heavy tars were condensed by an iced-tar trap filled with isopropanol and round glass beads of 6 mm in diameter to enhance its capability for recovering condensable compounds.

The chemical structure of the condensed tar was characterized by GC–MS analysis (Section 2.3). The produced gases were collected in a 2-L gas bag and further quantitatively analyzed by GC with a thermal conductivity detector (TCD–GC). The gas collection bag was changed

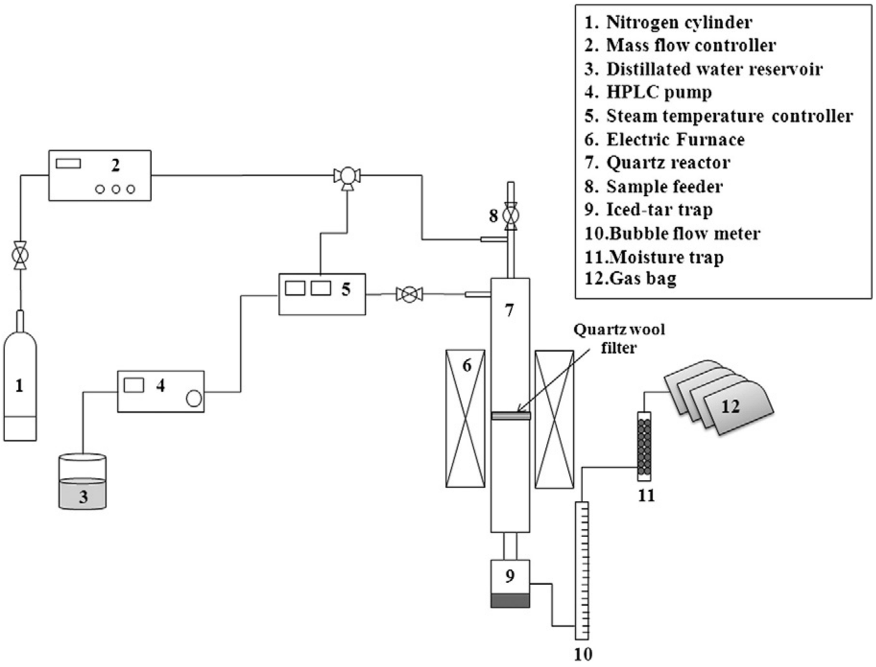

Fig. 1. Schematic image of the drop tube fixed-bed reactor.