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Pyrolysis conditions of biomass in fluidized beds for production of bio-oil compatible with petroleum refinery

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ABSTRACT

A predictive correlation of effective hydrogen to carbon ratio ($(H/C)_{eff}$) of bio-oils was satisfactorily developed to describe the general trends of bio-oil quality in fluidized beds of lignocellulosic biomass pyrolysis for production of bio-oils compatible with petroleum refinery. The correlation was based on an empirical relationship with operating parameters including fluidization hydrodynamics in fluidized bed pyrolyzers, which was derived from the data of this study and literature. The increment of $(H/C)_{eff}$ from feedstock to bio-oil during pyrolysis was a strong function of fluidization variables related with hydrodynamics and bed mixing such as fluidization number, bubble fraction and entrainment flux of bed materials. The predicted $(H/C)_{eff}$ of bio-oil based on the correlation well accorded to the experimental data. The prediction results indicate that the correlation can predict an optimum operating condition for balancing quality against bio-oil yield.

1. Introduction

Biomass energy sources are widely recognized as a potential future solution to the energy problem worldwide. Pyrolysis is the thermal degradation of materials in the absence of oxygen, which converts the biomass to bio-oil, char and gasses depending on the pyrolysis conditions [5]. It can be a promising option for biomass utilization, because bio-oils derived from biomass pyrolysis could act as a feedstock for producing hydrocarbons that may be readily integrated into the existing petroleum refineries or future biorefineries. Although bio-oils produced by the pyrolysis are a very promising technology, their direct applications as fuels are limited by the problems of high oxygen content, high viscosity, corrosion and thermal instability [23]. It is clear that the pyrolytic bio-oils would require refining and deoxygenation for application as fuels [16]. One of the most effective methods to improve the qualities of bio-oils into transportation fuels is to reduce the oxygen content by use of a catalyst [18]. The co-processing of the bio-oils with hydrocarbon feedstocks in a conventional refining scheme including the hydroprocessing and catalytic cracking processes, where they can play the role of non-conventional feedstocks, deserves consideration for upgrading the bio-oils by the catalyst use [3,23]. These have been attempted by means of hydrotreating or catalytic cracking in the gas phase. The hydroprocessing of bio-oils with catalysts at high temperature and high hydrogen pressure, similarly to processes in petroleum refining, leads to the release of oxygen as water and to the hydrogenation or hydrocracking of heavy molecular weight compounds. However, one of the inconveniences of these processes is their high cost from requirement of high hydrogen consumption. To reduce high hydrogen demand during upgrading of the bio-oils, it is required to produce bio-oil with low oxygen content in pyrolysis [23]. Meanwhile, the catalytic cracking untreated bio-oils over acidic zeolites produces deoxygenation leading to a mixture of hydrocarbons with high concentration of aromatics like in the fluid catalytic cracking (FCC) process, which is considered more economical than the hydroprocessing [32]. However, catalysts tend to deactivate easily by coking during crude bio-oil cracking owing to its high oxygen content [32]. It would be necessary to reduce the coke-forming potential, which could be mainly due to the significant concentration of heavy molecular weight oxygenated species [3]. In the sense, the hydroprocessing and FCC processes in existing refinery could be potential receivers, if the oxygenated compounds in the pyrolytic bio-oils could be removed by means of conditioning the pyrolysis operation [3,16] or introducing aliphatic alcohols as effective co-cracking reactants with biomass feedstock [33,34].

If upgrading or co-processing of bio-oils is intended into existing refineries, the effective hydrogen to carbon ratio ($(H/C)_{eff}$) can be a useful comparative parameter [8,3,23,32–34]. The higher $(H/C)_{eff}$

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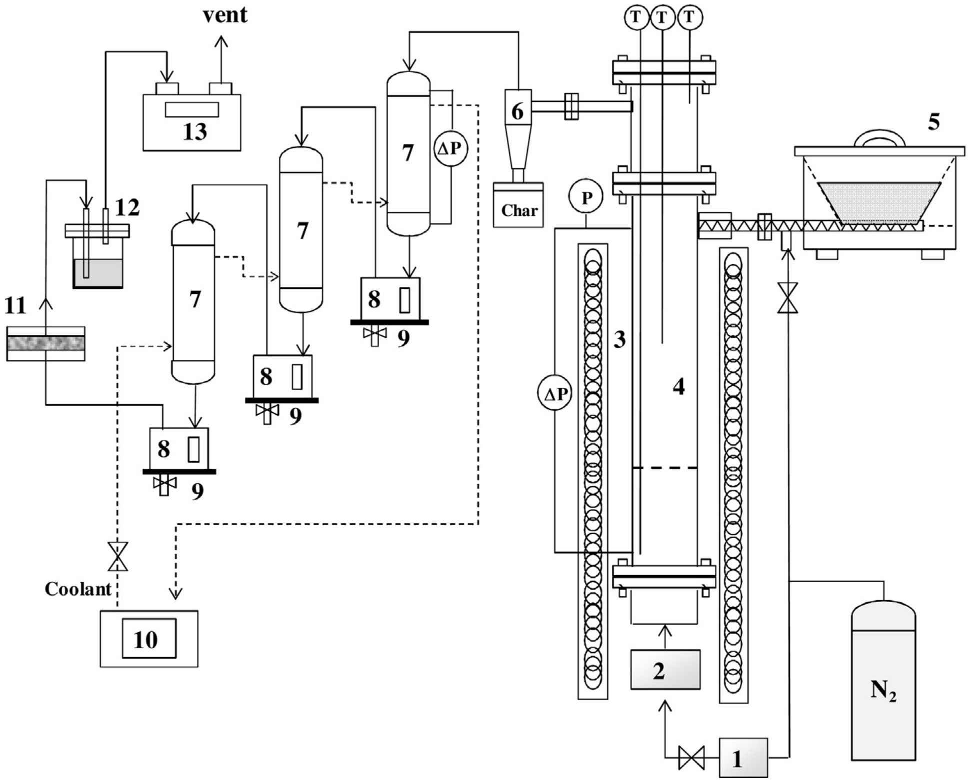

Fig. 1. Experimental apparatus.
(1) mass flow meter; (2) preheater; (3) furnace (electric heater); (4) fluidized bed reactor(pyrolyzer); (5) screw feeder; (6) cyclone; (7) condenser; (8) sampling pot; (9) heating plate; (10) chiller; (11) oil filter; (12) water trap; (13) accumulated gas flowmeter; P—pressure gauge; ΔP—differential pressure gauge; T—thermowell.

in the feedstock indicates more efficient conversion in refineries [9]. The ratio, which is defined by Eq. (1), denotes the neat H/C of a feedstock containing heteroatoms,

$$\left(\frac{\mathrm{H}}{\mathrm{C}}\right)_{\mathrm{eff}} = \frac{(\mathrm{H} - 2\mathrm{O} - 3\mathrm{N} - 2\mathrm{S})}{\mathrm{C}} \tag{1}$$

where H, C, O, N and S are the molar percentages of the corresponding elements on dry basis.

The $(\mathrm{H/C})_{\mathrm{eff}}$ values can be compared to those of petroleum-derived feeds, which range from slightly over 1 for highly aromatic residues to 2 for highly paraffinic feeds; heavy oils such as atmospheric residue, coal oil and shale oil, with high content of polar and aromatic compounds, have $(\mathrm{H/C})_{\mathrm{eff}}$ values between 1.4 and 1.7. In this respect, biomasses with $(\mathrm{H/C})_{\mathrm{eff}}$ less than 0.3 can be viewed as a hydrogen-deficient molecule as compared with petroleum-based feedstocks, and strategies for biomass conversion must take their $(\mathrm{H/C})_{\mathrm{eff}}$ value into account as a quality index to apply the pyrolytic bio-oil into the refineries [36,3].

A predictive correlation was developed to describe the general trends of bio-oil quality from biomass pyrolysis in fluidized bed for production of bio-oil compatible with petroleum refinery. The correlation was based on an empirical relationship between $(\mathrm{H/C})_{\mathrm{eff}}$ of bio-oils and operating parameters including fluidization conditions in fluidized bed pyrolyzers, which were derived from the data in experiments of this study and literature. A comparison between predicted results and experimental data was done to show its predictive capability for pyrolysis of various biomasses in fluidized beds.

2. Experimental

2.1. Experimental method

A sample of *Jatropha* (*Jatropha curcas* L.) seedshell cake (JSC) was acquired from an oil extraction plant in Indonesia. Elemental composition by ultimate analysis was obtained by an elemental analyzer of model EA 1108 (Fisons instruments) according to the ASTM D3176 standard procedures. The elemental analysis showed that JSC mainly consisted of carbon and oxygen as shown in Table 1. The HHVs (Parr-1261, Parr Instrument) of JSC was 20.8 MJ/kg, similar to that of typical biomass. The JSC sample was ground and sieved to an average size of 764 μm using an electric mixer and standard sieves. Silicon carbide ($d_p = 190\ \mu\mathrm{m}$, $\rho_s = 3210\ \mathrm{kg/m^3}$) particles were used as bed material in this study. The pyrolysis system consisted of a mass flow controller (MFC), main pyrolyzer, screw feeder, cyclone, three condensers, and accumulative flowmeter as shown in Fig. 1. The system was previously described in detail [18]. The flow rate of nitrogen (99.9%) for fluidization was controlled by the MFC and the volume of the product gas was measured by the accumulative flowmeter (G6R, GTEC Industry). Before entering the stainless steel fluidized bed reactor (0.102 m id. and 0.97 m high), the fluidizing N_2 gas was preheated in the air plenum to 450–600 °C. A distributor with 7 bubble caps, each with 4 orifices (holes of 1 mm), was fitted at the bottom of the reactor to allow an even distribution to be achieved. To prevent condensation of the pyrolysis vapor, the top of the reactor and the pipe connecting the reactor to the first condenser were maintained at 400 °C. The refrigerant was circulated in the shell of the condensers by a chiller system. The gas was sampled by a gas sampler to analyze its composition.

Pyrolysis tests were conducted at 390–520 °C with N_2 flow rates of 33 and 41 L/min at 25 °C (superficial gas velocities of 0.15–0.21 m/s depending on temperature), corresponding to ca.