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Importance of hydrogen and bio-oil inlet temperature during the hydrotreatment of bio-oil

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ABSTRACT

This paper reports the effects of hydrogen and bio-oil inlet temperature on the coke formation and product distribution during the hydrotreatment of bio-oil. A bench scale continuous hydrotreatment fixed-bed reactor set-up was used with pre-sulphided NiMo/γ-Al_2O_3 as the catalyst. The temperature of hot fluidised sand bath in which the hydrotreatment reactor was immersed was set at 390 °C while the pressure at the reactor exit was kept at around 70 bar. An LHSV of 1 h^{-1} (on the basis of organics in the bio-oil feed) was used. Our results show that the presence of hot hydrogen in the injection point of bio-oil to the reactor reduced the coke formation and reactor blockage for prolonged catalyst activity. This was due to the enhanced cracking and minimised polymerisation of bio-oil fragments when hot hydrogen was used to heat and activate the catalyst at the injection point. Moreover, lighter products with less coking propensity and smaller aromatic ring systems were formed when the injection point was maintained at a higher temperature with the use of hot hydrogen. These results indicate that the coke formation during hydrotreatment is at least partly because of the slow heating up of the bio-oil and the resulting bond breakage not being matched by the supply of active hydrogen from the catalyst.

1. Introduction

Biomass is an attractive option for the production of renewable liquid fuels. Pyrolysis converts biomass into bio-oil. Because bio-oil is very unstable, acidic and has high oxygen content and high concentrations of heavy components, bio-oil needs to be upgraded in order to be used a fuel in vehicle engines [1–3]. The catalytic hydrotreatment of bio-oil under mild conditions (150–450 °C and pressure > 50 bar) is one of the main routes to upgrade the bio-oil. Various types of reactions could take place during the hydrotreatment of bio-oil. The composition and properties of the hydrotreatment products would strongly depend on reaction conditions. The formation of coke, as an undesirable product, and the consequent blockage of the reactor are the main challenge in the hydrotreatment of bio-oil, which can also depend on reaction conditions [4,5]. Therefore, the knowledge about the effects of reaction conditions on coke formation and product distribution is essential for the development of a bio-oil hydrotreatment technology.

It is believed that the formation of coke, including the formation of large aromatic ring systems that could be considered as the precursors of coke, during hydrotreatment could be at least partly due to the slow heating up of bio-oil where the bond breakage in bio-oil is not matched by the availability of active hydrogen whose supply from the relatively cold catalyst is rather limited [6]. In other words, the bonds in bio-oil can break at a very low temperature level at which the catalyst is not sufficiently active to produce the active hydrogen required to stabilise the broken bonds (free radicals) [6]. Different types of reactions including hydrogenation, hydrocracking, hydrodeoxygenation and recombination can take place between radicals. All these reactions could occur simultaneously. The provision of active hydrogen could reduce the formation of coke as well as large aromatic ring systems that can be the precursors of coke.

In our recent work, a variety of reaction conditions including bio-oil feeding rate and temperature were studied [7,8]. The results demonstrated that the feeding rate of bio-oil and reaction temperature could drastically alter the formation of coke and its precursors (including large aromatic ring systems) in the product [7,8].

Further fundamental studies are required to understand the effects of process conditions on the coke formation and product composition. Various parameters including catalyst activity and availability of hot active hydrogen to stabilise radicals produced from the bond breakage of big molecules in bio-oil should be studied in details. Unfortunately, insufficient direct data have been reported in literature on this matter.

Fixed-bed reactors are commonly used for the hydrotreatment of bio-oil [4,5]. In conventional fixed-bed reactors, temperature gradient cannot be avoided, especially at the feeding point where cold bio-oil and hydrogen are introduced into the reactor. Bio-oil would be gradually heated up as it flows along the reactor length. For catalysts such as NiMo, the bond breakage in the bio-oil would become significant before

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the bio-oil can come into contact with a hot catalyst at temperatures at which catalyst is sufficiently active to generate active hydrogen to stabilise the broken bonds (radicals). The recombination of radicals could thus lead to coke formation in the reactor or larger molecules in the products. It is hypothesised that one way to overcome this undesirable temperature profile is to heat up the hydrogen and injecting the hot hydrogen into the reactor so that the bio-oil would come into contact with the catalyst that is already at high temperature and thus active. It is believed that the enhanced supply of active hydrogen could decrease the formation of coke (and its precursors) inside the reactor and also stabilise the broken bonds (free radicals) [6].

Therefore, the purpose of this paper is to demonstrate the effects of the injection of hydrogen at different temperatures to the upper section of the reactor, where bio-oil is injected, on the stabilisation of the radicals and consequently the amount of coke formation inside the reactor. For a better understanding of coke formation, efforts have been made to monitor the deterioration of hydrotreatment products, especially the formation of large aromatic ring systems, during the hydrotreatment of bio-oil.

2. Experimental

2.1. Bio-oil sample

The bio-oil used in this study was obtained from the pyrolysis of mallee wood in a grinding pyrolysis reactor at 450 °C [9]. Commercial pre-sulphided NiMo/Al_2O_3 catalyst (hereafter referred as NiMo catalyst) supplied by Eurecat was used for the hydrotreatment. The catalyst was ground and sieved to obtain the particles in the size range of 600–800 μm for the hydrotreatment process. Other chemicals were purchased from Sigma Aldrich.

2.2. Hydrotreatment

The hydrotreatment of the mallee wood bio-oil was carried out in a fixed-bed reactor. More details on the system have been reported elsewhere [10]. The reactor was made from 1-inch stainless steel 316 straight tubing (0.125″ wall thickness) with a length of 30 cm (as shown in Fig. 1). During the experiment the reactor was immersed inside a hot fluidised sand bath. The bio-oil sample was fed into the reactor at a specified liquid hourly space velocity (LHSV) of 1 h^{-1} on the basis of organics in the inlet bio-oil.

A simple way to heat up the bio-oil feed rapidly was to feed the bio-oil directly into the hot catalytic bed in the reactor. The bio-oil to be hydrotreated was mixed with 2 L/min hydrogen gas before it was fed into the reactor. In other words, the liquid bio-oil was entrained with hydrogen before it was carried through a thin tube (1/8 in. or 1/4 in.) into the hot catalyst bed in the reactor (at the sand bath level, Fig. 1). The entrainment of liquid bio-oil by the hydrogen gas ensured that the bio-oil would spend a very short period of time (around 0.6 ms) in the thin tube before it met the hot catalyst particles, during which the bio-oil would not have been heated up appreciably. The linear velocity of the bio-oil/hydrogen in the feeding line at room temperature was 8.1 m/s. This can effectively reduce (not yet eliminate, see below) the coke formation inside the feeding tube.

Based on our hypothesis (see Introduction), the upper section of the reactor was kept hot to make the catalyst active enough to stabilise the radicals from the bond breakage of the molecules present in bio-oil. One way to keep the upper section of the reactor hot is to bring the heat from an external source. In these experiments, to keep the upper section of the reactors hot, 4 L/min hydrogen was pre-heated (to various temperatures – see below) and fed from the top of the hot zone (Fig. 1). The heater was made of 1 in. tubing filled with 600–800 μm NiMo catalyst particles and immersed in a separate heated fluidised sand bath. It should be noted that the reactor shown in Fig. 1 was used for this fundamental research. A reactor configuration for practical application can be found in Ref. [6].

The hydrotreated bio-oil product, together with hydrogen and other gases such as steam and hydrotreating gaseous products (CO, CO_2, CH_4 etc), would exit the reactor via a central thin tube (1/4 in.) positioned in the centre of the reactor with an inlet at the bottom of the reactor. This minimised the time the hydrotreated bio-oil would spend at high temperature without being in contact with the catalyst. Moreover, it transferred some heat back to the upper section of the reactor from the bottom.

All experiments were done by setting the temperature of the fluidised-bed bath (T_{sand}) at 390 °C and the outlet pressure (P_{outlet}) at around 70 bar. In each experiment the temperature at 3 cm into the hot zone (i.e. 3 cm below the sand bath level, Fig. 1) was kept at different temperatures and recorded continuously. The temperature at this

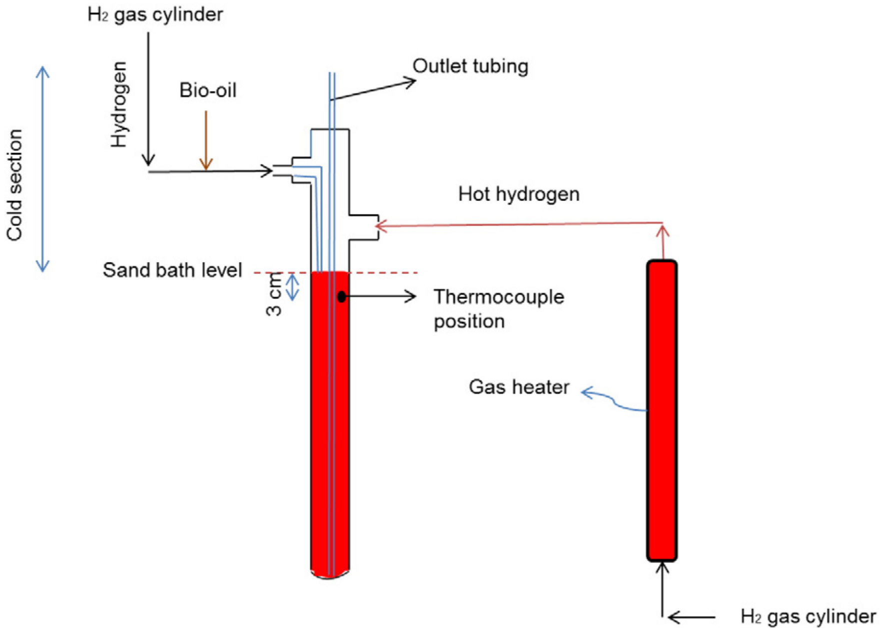

Fig. 1. A schematic diagram showing the reactor configuration and the heating system.