Fuel Processing Technology 148 (2016) 175–183

Contents lists available at ScienceDirect

Fuel Processing Technology

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

Research article

# Effects of temperature on the hydrotreatment behaviour of pyrolysis bio-oil and coke formation in a continuous hydrotreatment reactor

Mortaza Gholizadeh [a], Richard Gunawan [a], Xun Hu [a], Ferran de Miguel Mercader [b], Roel Westerhof [a], Weerawut Chaitwat [a,1], Md Mahmudul Hasan [a], Daniel Mourant [a], Chun-Zhu Li [a,]*

[a] Fuels and Energy Technology Institute, Curtin University of Technology, GPO Box U1987, Perth, WA 6845, Australia
[b] Scion, Private Bag 3020, Rotorua 3020, New Zealand

ARTICLE INFO

*Article history:*
Received 17 December 2015
Received in revised form 28 February 2016
Accepted 1 March 2016
Available online 11 March 2016

*Keywords:*
Hydrotreatment
Bio-oil
Coke
Heavy components
Aromatics

ABSTRACT

In this study, we investigated the effects of temperature on the hydrotreatment behaviour of bio-oil from the pyrolysis of mallee wood with a special focus on coke formation. The experiments were carried out in a continuous hydrotreatment reactor with pre-sulphided NiMo/γ-$Al_2O_3$ as the main catalyst over a nominal temperature range from 375 to 450 °C while the outlet pressure was set at 70 bar. GC-MS, TGA, UV-Fluorescence spectroscopy, elemental analysis and FT-Raman spectroscopy were used to characterise the reaction products and spent catalyst. While an upstream Pd/C catalyst bed had some effects of stabilising bio-oil, it was insufficient to ensure long-term operation under all conditions. Aromatic ring growth and polymerisation could take place continuously even under the overall dominating hydrotreatment/hydrocracking conditions. Temperature drastically affected the hydrotreatment product quality and coke formation. Increasing temperature favours the polymerisation for the formation of coke. At high temperature (e.g. 450 °C), the coke formation could be so severe that the reactor was blocked before the heavy liquid could reach the end of the reactor. The coke formed mainly from heavy liquid showed very different properties (different aromatic ring systems) from the coke formed mainly from the light species.

## 1. Introduction

Biomass is the only carbon-containing renewable resources that can be used directly to produce liquid transport fuels. The pyrolysis of biomass would produce a liquid bio-oil and a solid biochar together with a combustible gaseous product that would be burned in situ to meet the energy demand of pyrolysis itself. However, the crude bio-oil is not suitable to be used directly as a fuel in internal combustion engines due to its high oxygen content (20–50 wt%), low pH value (1.5–3.8) and thermal instability. Bio-oil requires further upgrading [1,2]. One of the bio-oil upgrading methods is the catalytic hydrotreatment, mainly hydrodeoxygenation, under high hydrogen pressure and elevated temperature to convert bio-oil into a liquid fuel that can be used in the existing vehicles.

In early research papers, sulphided NiMo/γ-$Al_2O_3$ and/or CoMo/γ-$Al_2O_3$ were used as catalysts based on the experience from the hydrotreatment, especially the hydrodesulphurisation, of petroleum. The reactor temperature was varied between 200 and 450 °C at pressures between 100 and 200 bar. The liquid hourly space velocity (LHSV) of bio-oil varied from 0.05 up to 2 $h^{-1}$ [3]. The most important finding of these earlier experiments was that bio-oil could not be processed in the same way as petroleum. The blockage of reactor due to coke formation has been the single biggest hurdle in upgrading bio-oil via hydrotreatment [4–7].

One approach to overcome this coke formation problem was to use a two-stage hydrotreatment process. In the first stage, the low-temperature (150–250 °C) hydrotreatment was applied using a noble catalyst like Ru/C or Pd/C to “stabilise” the bio-oil by hydrotreating the most unstable components in bio-oil [4,8,9]. In the second stage, more severe conditions of higher temperatures (350–450 °C) and high pressures (100–200 bar) was used for further deoxygenation. It was found that sulphided NiMo/$Al_2O_3$ and CoMo/$Al_2O_3$ catalysts became active especially at temperatures higher than 330 °C [10–12]. Nevertheless, no success has been reported that this two-stage approach has resolved the notorious coke formation problem. Additional evidence for this problem will be reported in this work. The use of carbon as a support in the Pd/C (or similar) catalysts means that these catalysts once deactivated by coke formation cannot be easily re-generated using the normal combustion method, which will greatly limit their use in the hydrotreatment of bio-oil.

Much further fundamental knowledge is required in order to develop a technology/strategy to overcome the coke formation problem. This requires the detailed consideration of various types of reactions

---

* Corresponding author.
*E-mail address:* chun-zhu.li@curtin.edu.au (C.-Z. Li).

[1] Present address: Environmental Engineering and Disaster Management Program, Mahidol University, Kanchanaburi Campus, Saiyok, Kanchanaburi, Thailand.

http://dx.doi.org/10.1016/j.fuproc.2016.03.002
0378-3820/

taking place during hydrotreatment. The breakage of weaker bonds is the first step of all hydrotreatment reactions. The radicals could then undergo many different types of reactions. For example, the radicals could be further hydrogenated, (hydro) cracked or hydro-deoxygenated to form stable molecules. The radicals could also re-combine, i.e. to polymerise, into bigger molecules; polymerisation can continue and finally form coke [13]. These different types of reactions occur simultaneously, in series and in parallel, in the vapour phase, in the liquid phase and on the catalyst surface to form a complicated reaction network during the hydrotreatment of bio-oil.

Obviously, the activation energies for different type of reactions in the reaction network will cover a wide range. Therefore, changing temperature would alter the relative reaction rates of different reactions and thus completely change the outcomes of the competitions among various reactions within the above-mentioned network. It is obvious that a balanced approach must be taken in choosing an operating temperature for a commercial process. For example, at higher temperatures, the deoxygenation rate is nearly 100% [9,14]. However, the hydrogenation of aromatics will also intensify to result in increases in hydrogen consumption. The effects of temperature are clearly important knowledge for the development of an effective hydrotreatment technology. Unfortunately, there are insufficient data reported in the literature, particularly on the continuous hydrotreatment.

Much has been done on the hydrotreatment of various model compounds [12], which are thought to represent the typical structures in bio-oil. These model compounds are normally simple compounds of low molecular masses. However, bio-oil is a lot more complicated than the model compounds. In particular, the knowledge about the behaviour of model compounds cannot possibly be used to predict the behaviour of heavy bio-oil molecules. Firstly, a big bio-oil molecule would have multiple reactive functional groups, each can be a centre or initial point of reaction, which cannot be easily predicted a priori, at least due to the complicated 3-D configuration of the molecule. Secondly, at best, only a small part of a big bio-oil molecule can be adsorbed on the catalyst surface whose behaviour would surely differ from that of a simple model compound. Unfortunately, very little is available in the literature about the mechanisms of coke formation during the hydrotreatment of a true bio-oil, as opposed to that of model compounds.

The purpose of this work is to investigate the effects of temperature on the hydrotreatment behaviour of bio-oil with a particular focus on coke formation. A better understanding about the effects of temperature on coke formation is gained by simultaneously tracing the hydrotreatment product structure, including its aromatic structures that are likely the precursors for coke formation. The structural features of the coke formed in the catalyst were also characterised with FT-Raman spectroscopy.

## 2. Experimental

### 2.1. Bio-oil sample

The bio-oil for these experiments was produced in a grinding pyrolysis reactor at 450 °C using mallee wood as feedstock [15]. 5 wt% palladium supported on activated carbon (Pd/C) and industrial pre-sulphided nickel-molybdenum supported on $Al_2O_3$ (NiMo/$Al_2O_3$) were purchased from Sigma-Aldrich and Eurecat, respectively. The Pd/C catalyst was sieved to the 25–75 μm particle range. The NiMo/$Al_2O_3$ (hereafter termed simply as NiMo catalyst) was ground and sieved to the 600–800 μm particle size range.

### 2.2. Hydrotreatment

The details of the continuous catalytic hydrotreatment reactor can be found elsewhere [7,16]. Briefly, the hydrotreatment reactor (Fig. 1) was made of 3/4 inch stainless steel 316 tubing with a length of 40 cm, which was packed into two parts of 10 and 20 cm lengths with the Pd/C and NiMo catalysts, respectively, in the same reactor. The last 10 cm of the reactor at the outlet side was not used in the experiment as the outlet tubing was put at the end of NiMo catalyst bed (see Fig. 1). The reactor was heated externally with a hot fluidised sand bath. The reactor part containing the Pd/C catalyst bed was not immersed in the sand bath while that containing the NiMo catalyst was immersed directly in the sand bath.

Two dual-syringe pumps were used to feed the bio-oil continuously into the reactor system. The hydrogen gas flow rate was constant at 4 L/min measured under ambient conditions. The bio-oil and hydrogen were pre-mixed before entering the reactor. The reaction products were continuously condensed and collected into one of two pressurised traps that were cooled with ice water. The traps were alternated every 45 min to collect the hydrotreated liquid products into

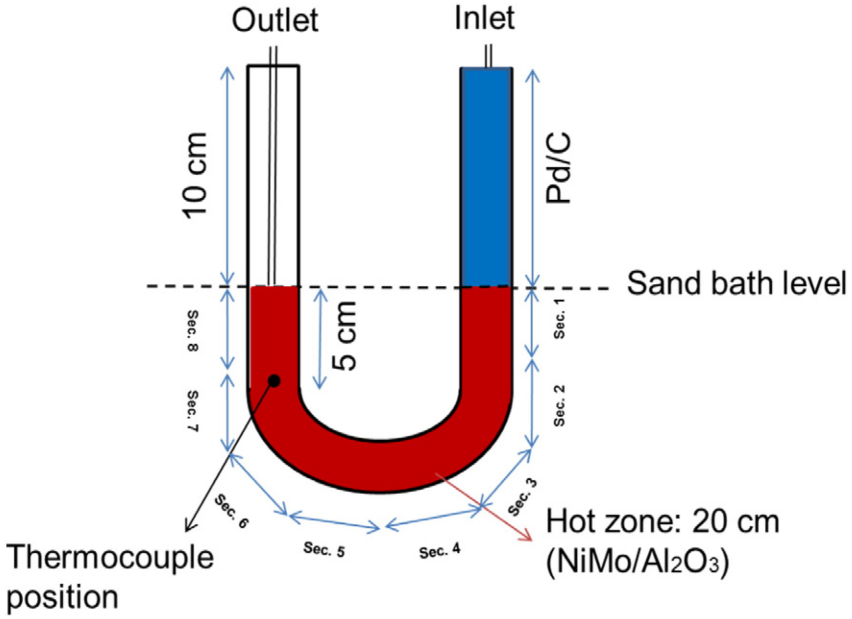

**Fig. 1.** A schematic diagram of the reactor configuration.