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Hydrodeoxygenation of the aqueous fraction of bio-oil with Ru/C and Pt/C catalysts

Aimaro Sanna [a,d], Tushar P. Vispute [b,d], George W. Huber [c,d,*]

[a] School of Engineering & Physical Sciences, Heriot-Watt University, Edinburgh EH14 4AS, UK
[b] Praxair Technology Center, Praxair, Inc., 175 East Park Drive, Tonawanda, NY 14150, USA
[c] Department of Chemical and Biological Engineering, University of Wisconsin-Madison, 1415 Engineering Drive, Madison, WI 53706, USA
[d] Department of Chemical Engineering, University of Massachusetts, 686 North Pleasant Street, 159 Goessmann Lab, Amherst, MA 01003, USA

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ABSTRACT

In this paper we discuss the continuous flow hydrogenation of the water soluble fraction of bio-oil (WSBO) with Ru/C and Pt/C catalysts. Temparatures higher then 125 °C lead to homogeneous reactions within the aqueous phase of bio-oil. Low temperature hydrogenation (LTH) at 125 °C over Ru/C catalyst and with WHSV of 1.5–3 h^{-1} was required to stabilize the bio-oil so higher temperature hydrogenation (HTH) could occur. The main products from LTH were ethylene and propylene glycols and sorbitol. At these temperatures only small amounts of acetic acid (AA), levoglucosan, furanone, phenol and phenol substitutes were hydrogenated. In the HTH step, the sorbitol was hydrogenated to mono-alcohols and diols by hydrogenolysis and secondary hydrogenation reactions. Up to 45% carbon in WSBO was converted to useful products (gasoline-cuts and diols) in the HTH step over Pt/C catalyst at 250 °C and WHSV of 3 h^{-1}. The reactions product distribution can be controlled by modifying operating pressure and temperature. The production of gasoline range compounds (C4–C6 alkanes and C1–C6 alcohols) is favoured at low pressure (750 psi). Increasing the reaction pressure decreased the amount of carbon that was converted into gas phase products.

1. Introduction

Pyrolysis is a promising technology for conversion of biomass into liquid fuels mainly due to its low capital and operating cost advantages compared to competing technologies such as fermentation and gasification [1–6]. The liquid fuel produced by pyrolysis is called bio-oil or pyrolysis oil. The pyrolysis oil has half the energy content of a petroleum based liquid fuel, a high oxygen content (45–50 wt%), low pH and a complex composition. In addition the pyrolysis oil is unstable and undergoes phase separation with time [7,8]. These factors all limit the direct usage of pyrolysis oil as a liquid transportation fuel. Several options have been proposed to convert bio-oils using conventional crude-oil technologies such as thermal- catalytic- cracking, hydrotreating, hydrocracking and aqueous phase processing [9–15]. Hydrogen based processes are typically more expensive than thermal cracking but they have the advantage to possess a higher selectivity to liquid products, by minimizing light gas and coke formation. HDO involves the reaction of the bio-oil with hydrogen by four key classes of reaction (1) hydrogenation of C—O and C—C bonds, (2) dehydration of C—OH groups, (3) C—C bond cleavage by retro-aldol condensation and decarbonylation, and (4) hydrogenolysis of C—O—C bonds [1,16–18]. Typical process conditions for HDO include temperatures between 300 and 400 °C and hydrogen pressure between 507–4200 psi. However the high H$_2$ consumption and capital costs and low product selectivity render this method uneconomical [19,20]. Several previous papers have shown the challenge with obtaining high yields of products from HDO of bio-oil [12,19–23]. Direct hydrogenation (6 h) of bio-oil in batch reactors over Raney Ni (200 °C, 40 bar H$_2$) yielded only 30% organic liquid (pH 3.3) indicating that the direct hydroprocessing of bio-oils is difficult and produces large yield of coke and tar, which lead to deactivation issues [24].

One of the catalyst deactivation mechanisms that occur during HDO of bio-oil is carbon deposition on the catalyst surface. This deactivation represents a major limit of this technology because the catalyst has to be frequently regenerated. One approach that has been reported is to try and develop HDO catalysts that have low acidity and hence a lower rate of coke formation [1,16]. Elliott and co-workers have reported that two hydrogenation steps are

* Corresponding author at: Corresponding author at: University of Wisconsin Madison, Department of Chemical and Biological Engineering, 1415 Engineering Hall, Madison, WI 53706, USA. Tel.: +1 608 263 0346.
E-mail address: huber@engr.wisc.edu (G.W. Huber).

typically required for HDO of pyrolysis oil: (1) a low temperature step (100–140 °C) and (2) a high temperature step (200–300 °C) with final products containing 40% of the starting carbon [12,23]. The purpose of the low temperature step is to hydrogenate aldehydes and ketones and make the pyrolysis oil more stable [21,25]. This low temperature stabilization step does not completely deoxygenate the bio-oil. However, it does make the pyrolysis oil more stable and decreases the rate of coke formation in the high temperature HDO step. The improved stabilization of the resulting bio liquid by the low temperature hydrogenation also allows the bio-oil to be easier to handle and store for further upgrading and applications in existing crude oil refinery settings [1]. The first step in the low temperature hydrogenation of the bio-oil is hydrogenation of guaiacols, hydroxyacetaldehyde, furfural, levoglucosan, furanone and phenol into more stable corresponding alcohols over Pt, Pd, Ru and Rh catalysts supported on carbon [21–23]. Vispute and Huber indicated that 15% of the carbon is lost in solid and gas hydrogenating the bio-oil at 125 °C and that levoglucosan, sugars and aromatic rings are not fully converted to the corresponding alcohols at 125 °C [21]. Further, Li et al. converted an aqueous carbohydrate stream from maple wood into gasoline range products with carbon yield of 57% in a 2-step APP process over Ru/C catalyst (1st step) and Pt/ZrP catalyst (2nd step) [26]. These studies indicate that the challenge with WSBO hydrogenation is to minimize the H_2 consumption and carbon loss to the gas phase, while achieving high selectivity of the desired products. The use of continuous flow reactors is expected to improve the hydrogenation reaction due to higher concentration of hydrogen compared to batch reactors, since in the latter; the hydrogen availability is limited by the low H_2 solubility in water. Bio-oil aqueous phase hydrodeoxygenation (HDO) processes at moderate temperatures (≤250 °C) at which no catalyst coking or reactor plugging was observed were recently proposed to overcome the traditional hydro-treating limits and the single stage hydrogenation processes using moderate amounts of hydrogen and producing a range of products such as gasoline and feedstock for the chemical and polymer industries [14]. The current bio-oil hydro-deoxygenation state of the art indicates that there is a wide range of products formed and that the involved catalytic chemistry needs to be understood in more detail [18,21,25]. These studies also illustrate the need to understand the homogeneous reactions that can also occur in the hydrogenation process. It would be highly desirable to be able to speciate the individual intermediates and identify the important reaction classes that occur in HDO of bio-oil.

The objective of this paper is to study the hydrogenation and HDO of a well characterized water soluble bio-oil in a packed bed with Ru/carbon and Pt carbon catalysts and identify the important reaction pathways. This paper provides important molecular level data about the reactions that occur during HDO of the aqueous phase of bio-oil. This molecular level knowledge can be used to design improved catalytic processes for the conversion of pyrolysis oils into fuels and chemicals.

2. Experimental and materials

2.1. Bio-oil sample for APP

The bio-oil used was obtained from Mississippi State University. The bio-oil was produced by pyrolysis of dry pine wood in an auger reactor and was stored in a refrigerator to avoid aging. The bio-oil was separated into a water soluble bio-oil (WSBO) and water insoluble bio-oil (WIBO) fractions by the addition of water. About 112 g of distilled water was mixed with 28 g of bio-oil and then centrifuging at 10,000 rpm for 20 min until phase separation. The centrifuge used was the Fisher Scientific Marathon 2100. The aqueous solution used in the experimental work had a WSBO concentration of

12.5 wt%. Ash content of the bio-oil samples was 0.3 wt%, found by heating about 1 gm of sample in a muffle furnace in the presence of air at 600–750 °C for 6 h. Nitrogen and sulphur were not detected by elemental analysis done at Galbraith Laboratories, Knoxville, Tennessee.

2.2. Catalytic APP hydrogenation set-up

A schematic of the packed bed reactor is shown in Fig. 1. The reactors consist of a continuous flow reactor, a temperature controller system, a furnace and a hydrogen gas supply. The tubing connecting the sample flask to the reaction chamber was wrapped with silicone rubber insulated heating tape to maintain a temperature between 30 and 80 °C. The reactor was a 1/4″ in diameter tubing placed into a vertical furnace. Two different reactors were used in series during the experimental work, where the feed and hydrogen were added from the top of the reactors. A system of safety check valves and a back pressure regulator was installed for safety reasons. Digital mass flow controllers were used to control the gas flowrates.

The WSBO was analyzed by GC–MS, high performance liquid chromatography (HPLC) and total organic carbon (TOC) analyzer to establish its composition. A library of 28 individual compounds was established to identify and semi-quantify the WSBO. The levoglucosan, glucose and sorbitol standards were analyzed by HPLC while all the other standard compounds (levoglucosan included) were detected and quantified by HP gas chromatograph (Model 7890A) with a Restek Rtx-VMS column using a constant column linear velocity of 1.24 ml/s. Ultra high purity helium was used as a carrier gas and the injection temperature was 280 °C. The program involved a hold at 35 °C for 5 min, followed by a rise to 240 °C at 10 °C/min and a hold at 240 °C for 15 min. The HPLC was packed with a Bio-Rad's Aminex HPX-87H column with 0.0005 M sulphuric acid as mobile phase (flow rate of 1 ml/min) at 30 °C. The HP Gas Chromatograph (Model 7890A) was used to analyze the reactor effluent gas, the liquid feed and liquid products. The effluent gas was analyzed using a flame ionization detector (FID) maintained at 300 °C. A Restek RT-Q-BOND column was used with a helium carrier gas flowing at 4.24 ml/min. The column oven temperature programme involved a hold at 30 °C for 5 min, a ramp to 150 °C at 5 °C/min and a hold at 150 °C for 15 min. The liquid product was sampled every 4 or 8 h to be analyzed by GC-FID and HPLC. At least 3 liquid samples were collected at a particular set of operating conditions to ensure the steady state. The quantification of sugars, sugar/alcohols and levoglucosan was carried out using a Shimadzu HPLC system. A flame ionization detector (FID) was used on the GC to quantify all the other liquid products. A GC-TCD HP 5890 series II was used to analyse CO_2 and hydrogen with an Alltech HAYESEP DB 100/120 packed column with 1 ml/min of helium as carrier gas. The oven temperature was maintained at 75 °C and the injection ports at 160 °C and 120 °C for CO_2 analysis, respectively. Standards of methane, ethane, propane, butane, pentane (FID) and CO_2 (TCD) were used to identify and quantify the gas produced. The carbon content was analyzed by a Shimadzu 5000A total organic carbon (TOC) that was able to quantify carbon contents below 1000 ppm.

The aqueous phase hydrogenation experiments were carried out using a stainless tubular downward flow reactor heated by a Lindberg Blue M furnace. The temperature was maintained with an in-built temperature controller on the furnace. The catalysts used were (i) 5 wt% ruthenium/activated carbon (Strem Chemicals, Product No. 44-4059) and (ii) 5 wt% platinum/activated carbon (Strem Chemicals, Product No. 78-1509). Both catalysts were in wet form, about 50 wt% water, and were dried at 110 °C for 7 h using 3 l/min of nitrogen before every reaction cycle.

Between 0.8 to 1.6 g of catalyst was packed into the tubular reactor and secured using glass wool. The packing was important to