

Production of Hydrogen and Alkanes by Aqueous Phase Processing of Aqueous Fraction of Bio-oil

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Introduction

Non-edible lignocellulosic biomass is the preferred feedstock for producing bio-fuels. Bio-oil (BO) is the liquid product obtained from the fast pyrolysis of lignocellulosic biomass and contains large fraction of biomass energy (60-75%). It is a complex mixture of more than 400 different compounds [1]. Currently bio-oil cannot be used as transportation fuel due to several of its drawbacks including: high viscosity, acidic nature, low heating value, high water and oxygen content and incompatibility with conventional fuels. An upgrading process to convert bio-oil to tangible fuels is hence necessary. Hydroprocessing [2] and zeolite upgrading are two widely studied bio-oil upgrading approaches. These upgrading routes suffer from drawbacks such as catalyst deactivation, coking, use of external hydrogen and harsh reaction conditions.

Dumesic and coworkers [3,4] have produced hydrogen and alkanes with high selectivity from the aqueous solutions of oxygenated hydrocarbons such as ethylene glycol and sorbitol through aqueous phase reforming and dehydration/hydrogenation. A large fraction of bio-oil is water soluble and the compounds present in its aqueous fraction are mainly oxygenated hydrocarbons. In this presentation we show that the concept of aqueous phase processing can be used to produce hydrogen and alkanes from the aqueous fraction of bio-oil.

Materials and Methods

Oak wood BO obtained from Renewable Oil International® was used in our studies. BO is mixed with distilled water and the aqueous and non-aqueous layers are separated by decanting. The aqueous fraction was then hydrogenated in a Parr bench top reactor with a 5wt% Ru/C (Strem Chemicals) catalyst. A packed bed up-flow reactor was used for the reforming reactions. For reforming the catalyst was a 1wt% Pt/Al₂O₃ (from UOP). Dehydration/hydrogenation catalyst used was 4wt% Pt/SiO₂-Al₂O₃. Both catalysts were calcined in air and reduced in flowing hydrogen before the reaction. Gaseous products from the reactor are analyzed online by gas chromatographs equipped with TCD (for CO₂ and H₂) and FID detector (for alkanes). Liquids are analyzed by GC-MS, GC-FID, HPLC (RI Detector) and Shimadzu TOC 5000A.

Results and Discussion

About 62wt% of the BO is water soluble. The major BO components present in the aqueous fraction are acetic acid, hydroxyacetone, furfural, 2-furanone, guaiacols, levoglucosan, and sugars (glucose, xylose). In hydrogenation, all the functionalities in the Water Soluble Bio-oil (WSBO) are converted to corresponding alcohols. The products after hydrogenation are ethylene glycol, propylene glycol, 1,4-butanediol, γ-butyrolactone, 1,2-cyclohexanediol and sorbitol. In addition to hydrogenation, C-C bond cleavage reactions also occur in the hydrogenation step leading to smaller polyols. A hydrogen selectivity of 70% was obtained for aqueous-phase reforming of the aqueous BO fraction at a gas phase conversion of 21 %. In

addition to hydrogen, alkanes were also formed. The gas phase conversion increased to 46% at a lower space velocity which gave a H₂ selectivity of 60%.

Alkanes are produced by passing the hydrotreated aqueous solution of bio-oil (HT-WSBO) over a bi-functional (metal and acid sites) 4wt%Pt/SiO₂-Al₂O₃ catalyst. At a gas phase carbon conversion of 35% the alkane selectivity was 45% at a WHSV of 0.96 h⁻¹. Similar alkane selectivity (42%) was obtained with higher carbon conversion (50%) when WHSV was reduced to 0.2 h⁻¹. A distribution of C1 to C6 alkanes was produced from the bio-oil as shown in Figure 1. The alkane distribution shifts to heavier alkanes when hydrogen is supplied externally. Alkane selectivity can be increased further (to 55-60%) by addition of small amount of HCl to the aqueous fraction of bio-oil.

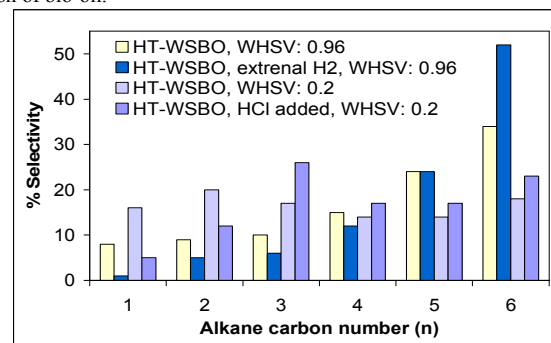


Figure 1. Individual alkanes selectivity for production of alkanes from HT-WSBO
T: 260°C, P: 750psi

Methane formation is suppressed upon HCl addition or external H₂ supply. High selectivity towards larger alkanes at high WHSV implies that C-C bond breaking reactions are present at low WHSV. Some catalyst de-activation is observed for both catalysts. Future work should be focused towards increasing the carbon conversion to gas phase while maintaining high selectivity.

Significance

Currently, bio-oil cannot be used as clean, high-quality fuel for transportation or any other purpose. This work is of immense industrial significance as we present a new route for conversion of bio-oil to tangible fuels such as H₂ and alkanes. Our process can be an integral part of bio-refinery where lignocellulosic biomass is converted to bio-oil by fast pyrolysis. Alkanes and H₂ are produced from WSBO and part of the H₂ produced is used to hydrotreat Water Insoluble Bio-oil (WIBO) to produce liquid fuel.

References

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