

## Thermodynamic and economic analysis of lignocellulosic bio-oil upgrading by hydrogenation

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**Abstract:** The catalytic hydrogenation of lignocellulosic derived bio oil has been assessed from the thermodynamic simulation perspective. The thermodynamic model has been applied to perform a detailed sensitivity analysis of the water-soluble bio-oil hydrogenation at reaction temperatures between 50 and 250 °C, pressures from 10 to 150 bar and 1:1 H<sub>2</sub>/bio-oil feed molar ratio. The thermodynamic model has quantified how the operating conditions affect the reaction in terms of yield, while the preliminary economic evaluation identified the conditions where there the process is profitable. The results indicate that sorbitol (25% yield) and propanediol (15%) are the main products at 50°C for the WBO hydrogenation. A maximum EP of \$5.5 ± 0.5 billion/y at pressure between 55-150 bar and temperature from 50 to 75 °C was obtained for the WBO-HD.

**Keywords:** bio-oil, thermodynamic model, catalysis; hydrogen, bio-fuels.

### 1 Introduction

The catalytic hydrodeoxygenation (HDO) of biomass- derived fast pyrolysis oil represents a fascinating route for production of liquid transportation fuels and commodity chemicals [1]. The path for the conversion of biomass into petroleum-compatible product through pyrolysis/HDO can be divided into a series of steps including feed purification, chemical modification and products separation. In refineries, the hydrogenation reactions are common operations to limit the presence of oxygen, nitrogen, sulphur, olefins and aromatics.

Despite the increased interest in bio-oil hydrogenation, there have been very limited studies on the thermodynamic simulation of the bio-oil chemical functionalities behaviour under different process conditions.

The thermodynamic models have been used to describe different process [2-5]. Resende *et al.*[4] studied the steam reforming of simulated bio oil aqueous fraction varying the reaction temperature and the steam/feed ratio, trying different reaction pathways.

Therefore, the aim of this study is to evaluate the overall performance of a bio-oil hydrogenation process system and explore the appropriate operation variables by a thermodynamic model studying the spontaneity of the process. This work is performed using Aspen Plus software based on the simulation of the hydrogenation reactions of the water-soluble bio-oil process system, with a feedstock processing capacity of 10Mt/y. Afterwards, the thermodynamic model outputs have been used to calculate the economic potential of the hydrogenation plant.

### 2 Methodology

A suitable simulation model for an industrial hydrogenation plant was developed in order to predict the reactions behaviour during the upgrading process. In this regard, first, a reaction network responsible for the hydrogenation of the bio-oil is proposed and then, physical and empirical correlations are applied.

The bio-oil composition of the feed considered in this work was simplified using only the most representative compounds of the different bio-oil functionalities. The thermodynamic model was developed using Aspen Hysys (v9) simulator. The process capacity was assumed to be 10 millions ton per year. The Economic Potential (EP) was calculated taking into consideration available values for the produced chemicals and starting raw materials.

### 3 Results and discussion

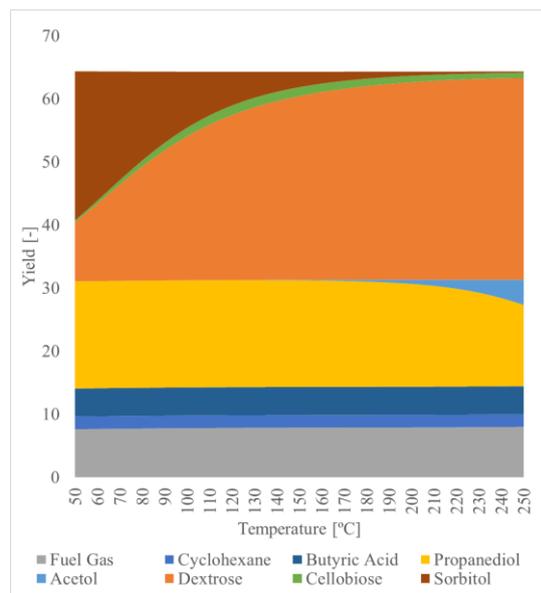
#### 3.1 Influence of temperature reaction

The HDO of bio-oil was studied in term of product yields, by varying the reaction temperature between 50 and 250 °C, at pressures from 10 to 150 bar using a 1:1 H<sub>2</sub>/bio-oil feed molar ratio. Furthermore, the sorbitol yield has been investigated, as the reaction is strongly thermodynamic limited.

The HDO reaction for WBO involves ten reactions, of which, three of them with thermodynamic equilibrium. In particular:



The eq.s (1) and (3) are favored at low temperature and high pressure (exothermic reaction). On the contrary, reaction (2) is favoured at high temperature. To study the effect of the temperature reaction in term of yield, the HDO was carried out at 70 bar, feed molar ratio H<sub>2</sub>/WBO = 1 and at temperatures between 50 and 250 °C, as shown in Fig. 1. Remembering that cyclohexane and butyric acid are produced by irreversible reactions, without thermodynamic limit, their yields are constant varying the reaction temperature.



**Figure 1** Influence of temperature at 70 bar and feed molar ratio H<sub>2</sub>/WBO = 1

The thermodynamic study indicates that sorbitol (25% yield), propanediol (15%) and dextrose (10%) are the main products at 50°C, while dextrose yield increases as the temperature increases at the expense of sorbitol yield and propanediol yield decreases at temperatures higher than 200°C. Therefore, to improve the

sorbitol production, low temperatures will be necessary. In case of propanediol, its yield decreases at high temperature, when there is an increment of acetol yield due to reaction (1).

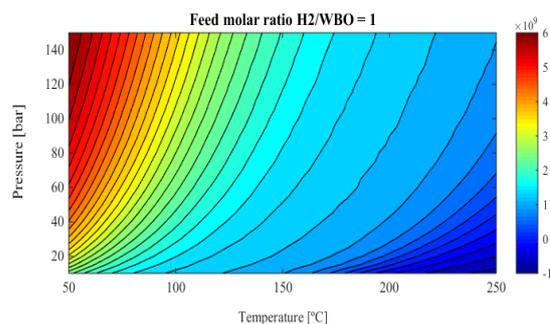
The high water content (H<sub>2</sub>O/Cellobiose about 10) ensures a constants cellobiose yield ≈ 1.5 %, while dextrose yield increases as the temperature increases, at the expense sorbitol yield.

#### 3.2 Economic evaluation

The success of a chemical process depends from its economic potential (EP), since the objective is to have products with high added economic value than the raw material. Usually, the raw materials purchase represents from 33 to 85 % of total processing costs [6].

Fig.2 evaluates the EP at the different operating conditions for WBO –HDO process at different feed molar ratios. The EP has good performance in terms of \$/y with a reaction temperature < 100 °C, reaction pressure > 20 bar.

The maximum EP for WBO-HD resulted in \$5.5 ± 0.5 billion /y at pressure between 55-150 bar, temperature from 50 to 75 °C and H<sub>2</sub>/WBO molar ratio between 1. The above mentioned EP can be only obtained if the reactions products (diols, mono-alcohols etc.) are separated from the water solution and not considered as drop-in fuels but sold as chemical commodities. Also, the EP does not take into consideration separation costs, which can be considerable.



**Figure 2** Economic Potential [\$/yr] HDO- WBO, H<sub>2</sub>/WBO feed molar ratio= 1

### 4 Conclusions and recommendations

The thermodynamic study of the WBO hydrogenation indicate that sorbitol (25% yield) and propanediol (15%) are the main products at 50°C, while dextrose yield increases as the temperature increases at the expense of sorbitol and propanediol yield. An increase of

pressure results in the increase of sorbitol at the expenses of dextrose.

The maximum EP for the WBO-HD resulted in  $5.5 \pm 0.5$  billion /y at pressure between 55-150 bar between 50 and 75 °C. However, the EP did not take into consideration organics/water separation costs, which can be considerable.

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## Presenting author biography

Giuseppe Bagnato is a PhD student at Heriot-Watt University. His project's aim is to integrate catalytic membrane reactors into bio-refineries. In 2014 he obtained a MEng in Chemical Engineering at University of Calabria (Italy) with

the thesis "Experimental and modelling analysis of the Water Gas Shift Reaction in dense Pd-Ag membrane reactor for hydrogen production" in collaboration with the Institute on Membrane Technology of the Italian National Research Council (ITM-CNR).

Dr Aimaro Sanna was awarded a Heriot-Watt University Fellowship (tenure track) in June 2014. His research team (Advanced Biofuels Lab) is developing new generation catalytic systems for understanding and controlling the chemical transformation of biomass and wastes to fuels and chemicals and on bio-CCS technologies.