

Catalytic hydroconversion of bio-oils: preventing macromolecules formation by solvent effect

Matthieu Ozagac^a, Céline Bertino-Ghera^a, Denis Uzio^a, Dorothée Laurenti^b, Christophe Geantet^b

^aIFP Energies Nouvelles, Rond-point de l'échangeur de Solaize, BP3, 69360 Solaize, France

^bUniversité de Lyon, IRCELYON, UMR5256, 2 avenue A. Einstein, 69626 Villeurbanne cedex, France

*Corresponding author: christophe.geantet@ircelyon.univ-lyon1.fr

Abstract: Conversion of pyrolytic bio-oils into biofuels requires a first stage in the upgrading which stabilizes the bio-oil and partly reduces the O content. The upgrading of a bio-oil was performed with a sulfide catalyst at various temperatures ($200^{\circ}\text{C} < T < 300^{\circ}\text{C}$) and a total pressure of 13 MPa (3Mpa of H_2 being introduced at RT). Our work has been focused on the macromolecules formation during the process as pyrolytic lignin but also macromolecules formed during the reaction from sugars condensation for instance. We evidenced that the presence of an oxygenated solvent such as guaiacol prevents the formation of undesired macromolecules.

Keywords: bio-oil, pyrolysis, hydroconversion, macromolecules

1. Introduction

Flash pyrolysis for liquid production has received a great interest since it can be used for energy or chemicals¹. The main product, liquid bio-oil, is obtained in yields of up to 75 wt.% on a dry-feed basis but has many drawbacks such as acidity, viscosity, O content for energy applications. Therefore upgrading methods are requested. A promising upgrading process is the catalytic hydroconversion that performs a significant oxygen removal before any downstream conventional refining process. Several literature studies^{2,3} show the occurrence of competitive reactions such as condensation and polymerization of very reactive oxygen containing compounds leading to humines formation. The understanding of the formation of resulting products is scarce. In a previous work, we have investigated the reactivity of model molecules mixtures including D-glucose, furfural or guaiacol under hydroconversion conditions⁴ and demonstrated the beneficial effect of the presence of guaiacol for preventing macromolecules formation from D-glucose or furfural. In the present study, we investigate the catalytic hydroconversion of a bio-oil (BO) with and without guaiacol in order to determine if the observed beneficial effect still remains in the presence of a complex and real matrix.

2. Experimental

The BO was purchased from VTT and Guaiacol (GUA) from Acros Organics (99+% purity). A proprietary NiMo/ γ - Al_2O_3 catalyst displaying hydrothermal resistance was supplied by Axens. Before each reaction, fresh catalyst was crushed and sieved to particle size from 1 to 2 mm and was reduced using a hydrogen flow ($0.30 \text{ m}^3 \cdot \text{h}^{-1}$) at atmospheric pressure and 400°C during 2 h. All catalytic reactions were carried out in an isothermal 500 cm^3 stainless steel autoclave equipped with an electromagnetic driven stirrer (Rushton impeller). For each run, 150 g of feed was introduced followed by 15 g of freshly reduced catalyst transferred in an argon vessel avoiding any post-oxidation. Two feeds will be considered: either 150 g of BO or 75 g of BO plus 75 g of GUA (mixture referred to BO+GUA). Considering non-catalytic reactions, 30 g of glass balls were introduced (2 mm diameter) representing the same volume than the NiMo catalyst. The

reactor was hermetically closed and purged by substituting air by N₂ and finally by H₂. The initial pressure of hydrogen or nitrogen was set to 3.0 MPa before temperature increase. The reaction temperatures ranged from 200 to 300°C. Analytical techniques (like SEC, NMR, GCxGC, HPLC) were used to characterize the liquid products.

3. Results and discussion

While chromatographic analyses were not able to characterize macromolecules production arising during the BO conversion, SEC analysis highlight structures beyond 5,000 g.mol⁻¹ PS eq.. For the BO hydroconversion at 250°C, macromolecules were produced in the organic phases and were particularly stable with reaction time. Nevertheless, elemental analysis and quantitative liquid state ¹³C NMR indicated the production of deoxygenated species mostly composed of aromatic rings as well as deoxygenated aliphatic compounds. As shown by SEC (see figure 1) and GC analysis, guaiacol reacted with the macromolecules precursors and limited their extension (up to 3,000 g.mol⁻¹ PS eq. into the organic phases). The hydroconversion temperature has an impact on the reactivity (characterized by ¹³C NMR and SEC analysis) and thus the textural properties of catalysts are also modified regarding the evolution of BET and porous volumes of the used catalysts. The presence of guaiacol strongly reduces coke formation.

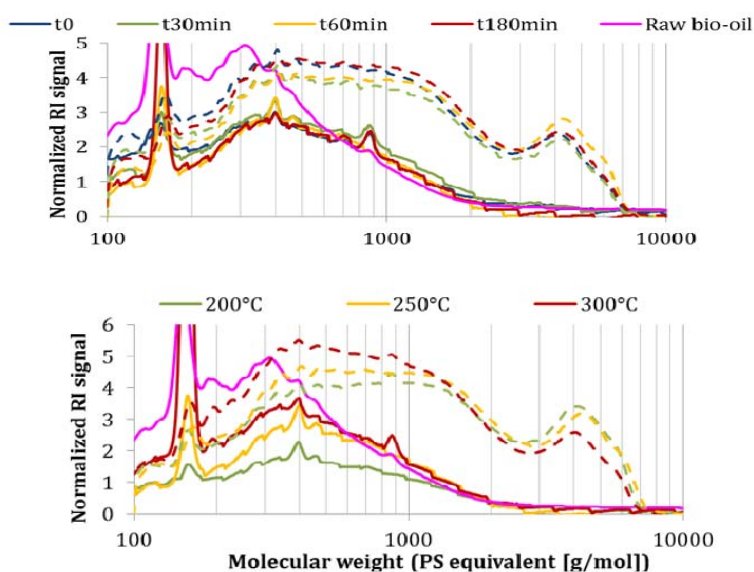


Figure 1. Impact of residence time at 250°C (top) and temperature at 1 h reaction (bottom) on SEC–RI analysis of heavy compounds obtained from hydroconversion of the bio-oil (dotted line) and BO+GUA.

4. Conclusions

The positive role of guaiacol for preventing the formation of undesired macromolecules, already established with model molecules, is now confirmed in the case of a bio-oil conversion. A strong analogy between macromolecules observed with model compounds and those issued from the BO conversion exists. These results bring new insights as regard to Venderbosch et al. [3] and Elliott et al. [2] studies on BO instability during the hydroconversion, as well as about solvent role introduced in pilot scale.

References

1. A. V. Bridgwater. *Biomass and Bioenergy.*, 38 (2012) 68-94
2. D. C. Elliott. *Energy Fuels.*, 21 (2007) 1792-1815
3. R. H. Venderbosch, A. R. Ardiyanti, J. Wildschut, A. Oasmaa, H. J. Heeres. *J.Chem.Technol.Biotechnol.*, 85 (2010) 674-686
4. M. Ozagac, C. Bertino-Ghera, D. Uzio, M. Rivallan, D. Laurenti, C. Geantet, *Biomass and Bioenergy*, 95 (2016), 182-193
5. M. Ozagac, C. Bertino-Ghera, D. Uzio, M. Rivallan, D. Laurenti, C. Geantet, *Biomass and Bioenergy*, 95 (2016), 194-205