



Research paper

Impact of guaiacol on the formation of undesired macromolecules during catalytic hydroconversion of bio-oil: A model compounds study



M. Ozagac^a, C. Bertino-Ghera^{a,*}, D. Uzio^a, M. Rivallan^a, D. Laurenti^b, C. Geantet^b

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

^b IRCELYON, UMR5256 CNRS-UCBL, 2 avenue A. Einstein, 69626, Villeurbanne cedex, France

ARTICLE INFO

Article history:

Received 21 June 2016

Received in revised form

23 September 2016

Accepted 30 September 2016

Keywords:

Biofuels

Macromolecules characterization

Pyrolysis bio-oil

Guaiacol

D-glucose

SEC

ABSTRACT

Although catalytic hydroconversion of pyrolysis bio-oils has been studied for many years, side reactions such as condensation or oligomerization leading to high molecular weight compounds still need comprehensive studies. In this work, the catalytic hydroconversion of D-glucose, furfural, acetic acid and guaiacol representative of pyrolysis bio-oils was investigated separately before testing a 5-component mixture. Thanks to a detailed analytical strategy (i.e. SEC, ¹³C NMR, GC, HPLC), this paper focuses on the effect of guaiacol conversion on sugar-like macromolecules. The study of single D-glucose and furfural revealed the fast production of high molecular weight compounds (up to 700 g mol⁻¹) that were proven to further precipitate (from D-glucose). Guaiacol addition led to a decrease of the solid production through solubilizing and/or reacting with macromolecules. This phenomenon produced larger soluble macromolecules (up to 5000 g mol⁻¹). Results show that guaiacol and its hydroconversion products formed soluble macromolecules at short reaction times and low temperatures.

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1. Introduction

Lignocellulosic biomass is a promising feedstock that could be used as a renewable and CO₂-neutral source of energy and is expected to be an important resource for liquid transportation fuels or chemicals in a near future. Lignocellulose is commonly composed of three major fractions: 40–45 wt% of cellulose (dry composition), 25–35 wt% of hemicelluloses, 15–30 wt% of lignin and up to 10 wt% of other compounds (such as minerals) [1]. The most widely studied softwood feedstock are pine (or spruce), and cork or oak as regard to hardwoods. Flash pyrolysis is a thermochemical process used to transform these resources into liquid [1,2]. However, the obtained pyrolysis bio-oils have limited end-user application due to their acidity (Total Acid Number or TAN between 70 and 120), their low heat capacity (compared to fossil fuels), their immiscibility with hydrocarbons and their thermal instability resulting from high oxygen content [3]. Oxygen is present in organic compounds but also as free water which can represent up to 30 wt% of the raw bio-oil. Since the last three decades, many laboratories have tried to

perform deoxygenation process inspired from petroleum feedstock catalytic hydroconversion [4]. However, upgrading biomass-derived oils from flash pyrolysis liquefaction to hydrocarbons requires a significant oxygen removal (and consequently a high H₂ consumption) before any final conventional refining process.

Also called upgrading, those thermo-chemical processes deal with operational temperatures up to 400 °C. Nevertheless, several literature studies [4,5] showed the occurrence of fast competitive reactions such as condensation or oligomerization which are prone to produce solid residues even at low temperature. This phenomenon is detrimental for the process because it leads to extensive plugging of the reactor and catalyst deactivation. This coking ability especially due to the bio-oils thermal instability is a process limitation and needs an in-depth comprehension before any industrial scaling-up. Venderbosch [5,6] and Elliott [7] published studies describing the competition between hydroconversion pathways and the production of high molecular weight compounds also referred as soluble macromolecules [8–10]. To avoid those pathways, they recommended a two-step process to firstly convert macromolecules precursor at low temperatures (from 150 to 200 °C) followed by a deep hydrodeoxygenation (up to 350 °C). So far, the involved reaction mechanisms are not well described and

* Corresponding author.

E-mail address: celine.bertino-ghera@ifpen.fr (C. Bertino-Ghera).

literature is largely lacking of rationalization of the chemical mechanisms.

The pyrolytic degradation products of lignin were generally represented by aromatic model compounds [10–12] such as guaiacol, anisole or phenol derivatives. On the one hand, carbohydrates, acids, ketones and furans derivatives were commonly used to represent the contribution of cellulose and the hemicellulose [12,13] fractions in the flash pyrolysis liquefaction. Levoglucosan [14,15] and D-glucose [16] are typically adopted as representative compounds. Even if levoglucosan would be the model of choice as it is present in high quantity in pyrolysis bio-oils, it is readily converted to D-glucose in hydroconversion conditions and in acidic water medium [15–17]. On the other hand, it is well established [18,19] that hemicelluloses flash pyrolysis produces furanic and carboxylic acid compounds in large amounts. Besides well identified molecules, heavier molecules including macromolecules are also present in the bio-oil (including pyrolytic lignin) and those macromolecules usually precipitated by water addition. These oligomers were characterized by typical aromatic fragments arising from lignin [10,20]. Our purpose in this study is to investigate the macromolecules production from light molecules during the hydroconversion reaction.

Numerous studies deal with representative model molecules of bio-oils composition which result from lignocellulose [11] degradation during the pyrolysis step. Because of the high diversity of oxygenated compounds in a bio-oil, it is mandatory to consider at least a mixture of representative compounds even if very few studies were proposed in the literature. For a catalysts screening, Elliott [21] developed a three-compound mixture made of guaiacol, furfural, acetic acid and water. More than thirty by-products were quantified but no crossed-interactions between those compounds were discussed. More recently, Runnebaum [22] has studied the catalytic conversion of four compounds representing a pyrolyzed lignin fraction. Nevertheless, none of those experimental studies complied with the comprehension of the high molecular compounds production.

In this paper, we have chosen D-glucose as the ex-cellulose model molecule and arising compounds from hemicellulose flash pyrolysis were represented by furfural and acetic acid. In a previous work [23] we investigated the catalytic hydroconversion of D-glucose and furfural and we observed the fast and extensive production of high molecular weight compounds even at 200 °C. This trend was followed by SEC analysis and carbon balances including GC-quantified compounds. Those so called macromolecules were proven to arise from furanic and aromatic compounds that were extensively produced by D-glucose dehydration and furfural hydrolysis/hydration. In the present work, we report the catalytic hydroconversion of a mixtures constituted by D-glucose, furfural and guaiacol. Through an increase of the complexity of the mixtures and using a multi-technique characterization strategy (SEC, ¹³C NMR, GC, HPLC, etc ...), this study highlights the main routes responsible for the formation of high molecular compounds and the effect of the presence of guaiacol on macromolecules.

2. Materials and methods

2.1. Material

The D-glucose (>99.5%), furfural (99%) and acetic acid (99%) were purchased from Sigma Aldrich and guaiacol (>99%) from Acros Organics and n-hexadecane (99%) from Alfa Aesar. Those compounds were used as received.

To promote the hydroconversion reactions, various mono- and bi-metallic active phases were investigated. Noble metal based catalysts such as Pt, Pd or Ru exhibit high performances but remain

expensive. Less performing Ni/alumina-based catalysts [24–26] are nevertheless an economically suitable solution for an industrial process. A proprietary NiMo/γ-Al₂O₃ catalyst (9.2 wt% Ni, 5.4 wt% Mo) displaying hydrothermal resistance was provided 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 m³ h⁻¹) at atmospheric pressure and 400 °C during 2 h.

2.2. Experimental procedures

All catalytic reactions were carried out in an isothermal 500 cm³ stainless steel autoclave equipped with an electromagnetic driven stirrer (Rushton impeller). The methodology used and the reproducibility of the experiments are described in [Supplementary Fig. S1 and S2](#). For each run, 150 g of feed were introduced followed by 15 g of freshly reduced catalyst transferred in a basket in an argon vessel avoiding any post-oxidation. The reactor was hermetically closed and purged by substituting air by nitrogen and finally by hydrogen. The initial pressure of hydrogen was set to 3.0 MPa before temperature increase.

The reaction temperature ranged from 200 to 300 °C. In order to limit the catalytic reactions during the heating ramp (15 min to reach 250 °C), the feed was vigorously stirred (1200 RPM) only once the reaction temperature was reached. This procedure was adopted in order to limit the D-glucose conversion during the heating time. Stirring is maintained during cooling down. The hydrogen addition was set to maintain a constant total pressure of 13.0 MPa during the run. This procedure has been applied considering the maximization of the hydrogen consumption during the catalytic hydroconversion of an aqueous D-glucose (20 wt%) solution. Considering those stirring rates and catalyst beads size, no external hydrodynamic limitations have been observed [23].

Once the reaction time was reached, H₂ introduction was stopped and the reactor was cooled down to room temperature (10 min to cool down from 300 to 100 °C). Then gaseous, liquid and solid products were totally collected and separately analyzed. Gases were collected using an auxiliary vessel and sampled in vacuum TEDLAR[®] bags for subsequent off-line gas chromatography (GC-FID/TCD) analysis. While the reactor was purged by nitrogen and unlocked, the catalytic basket was removed. The liquid phases and the solid residues were separated by centrifugation at 4000 tr min⁻¹ during 20 min. Subsequently, aqueous and organic phases were separated in a separatory funnel referred respectively as “aqueous phase” and “organic phase”. The recovered catalyst was washed using a Thermo Scientific™ Dionex™ (ASE 150) extractor heated at 60 °C and under a 10 MPa acetone pressure. The catalyst and the solid residues were dried at 70 °C under atmospheric pressure during 12 h. Acetone was used as a washing solvent also to clean the reactor and the impeller and was further removed by a vacuum rotary evaporator. The obtained liquid phase will be referred as “washed phase”.

2.3. Analytical procedures

Considering the complexity of the products, an analytical strategy was set to characterize each effluent (see [Supplementary Fig. S3](#)). Each phase was analyzed separately in order to determine the repartition of the carbon and to identify a maximum of compounds.

Gases were analyzed by GC (Agilent 7890A) equipped with a Flame Ionization Detector (FID) and two Thermal Conductivity Detectors (TCD). Three parallel columns were used: HP-Plot Q (30 m × 0.32 mm i.d × 20 μm), HP-Plot 5A (30 m × 0.32 mm i.d × 1 μm) and PONA (50 m × 0.2 mm i.d × 0.5 μm). The carrier gas was helium. Standards were periodically injected for alkanes (C1 to

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