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Research paper

Understanding macromolecules formation from the catalytic hydroconversion of pyrolysis bio-oil model compounds

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ABSTRACT

Catalytic hydroconversion of pyrolysis bio-oils is a promising process that can greatly contributes to their deoxygenation. Other simultaneous reactions such as condensation or oligomerization leading to heavy molecular weight compounds are detrimental to the process and still not well understood. This study deals with the hydroconversion of D-glucose and furfural in a batch reactor with a NiMo/alumina catalyst. Considering the carbon balances and SEC-RI analysis of hydroconversion products, we describe fast reaction pathways leading to soluble macromolecules (up to 700 g mol^{-1}) that are further precipitated into the solid phase. From the D-glucose conversion, ^{13}C NMR analysis of residues revealed significant amounts of aromatic carbons. Also detected by FTICR-MS analysis of a liquid effluent, those structures were likely formed through dehydration reactions. Finally, a high water content in the feed demonstrated that D-glucose was preserved from dehydration reactions contrary to furfural which is prone to be hydrolyzed into soluble macromolecules precursors.

1. Introduction

In order to meet the growing demand in transportation fuels and chemicals, lignocellulosic biomass could be used as a renewable and CO$_2$-neutral source. The most widely studied softwood feedstock are pine or spruce and cork or oak as regards hardwoods. 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). Flash pyrolysis is a thermochemical liquefaction process that can be used to transform solid biomass into liquid [1,2]. However, the pyrolysed bio-oils have limited end-user application due to the acidity, their low heat capacity (compared to fossil fuels), their immiscibility with fossil hydrocarbons and their thermal instability due to their high oxygen content. 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 30 years, many laboratories [3] have tried to perform upgrading process inspired from petroleum feedstock catalytic hydroconversion (HDC). However, upgrading biomass-derived oils from flash pyrolysis to produce hydrocarbons requires a significant oxygen removal before any subsequent conventional refining process.

In parallel to the deoxygenation reactions, several literature studies [3,4] show the occurrence of competitive reactions such as polymerization, condensation or oligomerization which promote the production of solid residues. This phenomenon is detrimental to the process because it leads to severe plugging of the equipment and to the catalyst deactivation. The coking ability especially due to the bio-oils thermal instability is a process limitation and needs an in-depth comprehension prior to any industrial scaling-up. Venderbosch [4,5] and Elliott [6] published studies describing the competition between hydroconversion pathways and the formation of liquid soluble high molecular mass compounds (also called macromolecules). However, the involved reaction mechanisms are not fully depicted. So far, those soluble compounds are also poorly identified by currently available analytical techniques [7,8]. To get an insight of soluble macromolecules contained into upgraded pyrolysis oil, Hoekstra [9] and more recently Castellvi [10] used the size exclusion chromatography (SEC) to detect molecular weights up to 1000 g mol^{-1} PS eq. (Polystyrene equivalent). Those compounds are also called "pyrolytic lignin", which corresponds to the water insoluble fraction of bio-oils and exhibit a highly aromatic structure [11].

To get a better molecular insight, some studies attempted to use

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model molecules representative of bio-oils composition. The thermal degradation products of lignin are generally represented [1,12] by phenolic species such as guaiacol, anisole or phenol derivatives [13]. On the other hand, carbohydrates and furans derivatives are commonly used to represent compounds resulting from flash pyrolysis liquefaction of cellulose and hemicelluloses respectively [14].

Contrary to representative ex-lignin compounds, carbohydrates and their derivatives have not been extensively studied in HDC conditions. Levoglucosan [15,16] and D-glucose [17] are typically chosen as representative compounds. Even if levoglucosan is present in high amount in pyrolysis bio-oils, it is readily converted to D-glucose in hydroconversion conditions [16–18]. Thus, in this work, D-glucose was chosen as the cellulose-derivative model molecule.

At a molecular level, many works deal with the conversion of aqueous diluted D-glucose solutions [19–24]. They distinguished a catalytic pathway involving sorbitol and a thermal pathway to furanic species such as 5-(Hydroxymethyl)furfural (5-HMF). Girisuta et al. [25] observed the predominance of the pathway involving furans when organic acids were introduced in the feed and Wildshut [26] studied the D-glucose hydroconversion with Ru/C and Pd/C catalysts. However, none of them complies with the corresponding carbon balances or attempts to describe the macromolecules formed by condensation reactions also called “humins” referring to water-insoluble organic compounds in aquatic systems. Buffle [27] reviewed in detail studies about physical and chemical properties of “humins” and their precursors such as humic and fulvic acids. Kleinhempel [28] presented a 3D molecular modelling involving the polymorphic condensation of oxygenated aromatics, aliphatics, ketones, nitrogen groups and non-organic compounds (mineral and metal compounds). Nevertheless, comparison between such macromolecules and those produced during a sugar-like compound hydroconversion has never been investigated so far. In order to avoid the extensive formation of “humins”, the catalytic hydroconversion of sorbitol was studied [29]. Detected products were found to result not only from hydrogenation reactions but also from several parallel reactions such as dehydration, retro-aldol condensation or dehydrogenation followed by decarbonylation [30]. Macromolecules was assumed to arise from hydrated furans such as 2,5-dioxo-6-hydroxy-hexanal (reported as DHH) leading to macromolecular structures [31,32] through aldol condensations. More recently, Hu [33] compared the formation of soluble macromolecules during the catalytic hydroconversion of 5-HMF using water or methanol as a solvent. In this case, methanol reacted with acidic compounds (levulinic acid for instance) through esterification reactions which prevent undesirable pathways.

Furfural reactivity in hydroconversion process has been deeply investigated [34] as model molecule arising from hemicellulose flash pyrolysis [14]. Kubickova et al. [35] extensively reported furfural hydroconversion in presence of various catalytic active phases. By studying furfural hydroconversion between 210 and 250 °C with a Pd-based catalyst, decarbonylation and hydrogenation routes were also observed as the two main pathways by Sitthisa et al. [36–38]. The decarbonylation reaction needs higher activation energy than hydrogenation reaction which, explains its predominance at higher temperature. In addition, furfural was also studied as precursors for resins production. Identified reactions were alkylation with phenol [39], enzymes catalyzed aldol reaction [34,40] or polymerization with furan [41].

Nevertheless, in all these works, carbon balances were very low or even not reported, underlining the lack of products characterization and the need to strengthen our efforts on this critical point. A better understanding of carbohydrate macromolecules production would be a key factor to ensure an industrial development of pyrolysis oil hydroconversion. In this study, the macromolecules formation during the catalytic hydroconversion of D-glucose and furfural, chosen to mimic compounds resulting from degradation of cellulose and hemicelluloses respectively, was investigated. The effect of reaction time and temperature as well as the presence of free water on macromolecules formation have been investigated.

2. Materials and methods

2.1. Material

The D-glucose (purity >99.5%) and furfural (purity 99%) were purchased from Sigma Aldrich (USA) and were used without any further treatment. N-hexadecane (purity 99%) was obtained from Alfa Aesar (USA) and will be referred as n-C16. Tetrahydrofuran (purity 99.7% min) was obtained from VWR.

A commercial NiMo/γ-Al_2O_3 catalyst was supplied by Axens. Prior to catalytic test, the fresh catalyst was crushed and sieved to a particle size from 1 to 2 mm and subsequently reduced at 400 °C under H_2 flow (0.030 m^3 h^{-1}) at atmospheric temperature and pressure for 2 h.

2.2. Experimental procedures

All catalytic tests 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 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 N_2 and finally by H_2. The initial pressure of H_2 was set to 3.0 MPa before temperature increase. The reaction temperature varied from 200 to 300 °C. To investigate water effect and in order to limit the thermal degradation of reactants during the heating ramp (15 min to reach 250 °C), the feed was vigorously stirred (1200 tr min^{-1}) either from the beginning of the experiment or only once the reaction temperature was reached. For comparison, some experiments where the feed was stirred during the heating ramp are also reported. This optimization has been done considering the maximization of the H_2 consumption during the catalytic hydroconversion of an aqueous D-glucose (20 wt%) solution. Those stirring rates and catalyst granulometries were chosen in order to optimize H_2 consumption (see Supplementary Figs. S2 and S3).

The H_2 addition was set to maintain a constant total pressure of 13 MPa during the run. Once the reaction time was reached, H_2 introduction was stopped and the reactor was cooled down to room temperature (10 min to cool down from 300 to 100 °C). The separation procedure is fully described in Supplementary Fig. S1. 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 N_2 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 (when n-hexadecane was introduced) 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