



Research paper

Mild hydrotreatment of the light fraction of fast-pyrolysis oil produced from straw over nickel-based catalysts

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ABSTRACT

Upgrading bio-oils for the production of transport fuel and chemicals is a challenge that has recently attracted a lot of attention. As one of the most prominent approaches, hydrodeoxygenation (HDO) was used in this work to upgrade the light phase of a pyrolysis oil produced from straw in the bioliq[®] pilot plant in Karlsruhe. A mild hydrotreatment was performed in a batch autoclave at 250 °C under hydrogen atmosphere (8.0 MPa at room temperature) in the presence of various nickel-based catalysts using different loadings and supports. Their catalytic performances, measured in term of hydrogen consumption, were similar but inferior to Ru/C (used as benchmark). The oxygen content was significantly decreased in the upgraded oils (20–26 wt%) as result of hydrodeoxygenation reactions and of the repartition of more apolar compounds in the upgraded oil. Using gas chromatography, the typical biomass platform molecules were detected and some reaction trends were identified. The conversion of phenol and the product selectivity was different whether this molecule was investigated in the pyrolytic mixture or as model compounds, indicating that the complex composition of the light phase or the probable deactivation of the catalyst plays a significant role. Quantitative ¹H-NMR analysis was a useful method for gaining an overview about the reactivity of the different molecular functional groups present in the bio-oil.

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1. Introduction

In the last two decades, the pronounced depletion of the common mineral oil has been the driving force of many studies aimed to increase the competitiveness of renewable resources in the energy market. Biomass represents a renewable carbon-based source, from which the production of fuels and chemicals is possible via suitable conversion techniques [1,2]. Among them, fast pyrolysis permits to convert lignocellulosic biomass [3], which is not in competition with the food production, preferentially into a high-energy liquid mixture, called pyrolysis oil or bio-oil [4,5]. However, the qualities of a bio-oils are not suitable for the direct use in specific applications [6], e.g. as transport fuel or as source of chemicals, and an upgrading is required [7,8]. Since its elemental composition is rather similar to biomass (high oxygen content)

instead of fossil fuels, the bio-oil is consequently not miscible with crude oil and it cannot be used or processed in the same facilities together [9–11]. The high oxygen content represents the main issue, since the functional groups containing oxygen are responsible for several characteristics of a bio-oil, such as the polarity, the acidity, the relative low heating value, the viscosity and the reactivity, parameters that influence overall its phase stability [8]. In addition, some of the compounds tend to polymerize, the water content in the pyrolysis oil has a negative influence on the heating value and the phase separation, and the high acidity of a number of constituents represents a problem in terms of material corrosion during transport, storage and processing [8].

In order to increase the stability and decrease the oxygen content of the pyrolysis oil, catalytic hydrodeoxygenation (HDO) is one of the most studied and most promising upgrading methods, which can provide a combustible mixture with a higher heating value and stronger resemblance to fossil fuels [8,12–16]. The reaction is carried out under high hydrogen pressure, preferentially in the

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presence of a catalyst able to activate hydrogen and to cleave the C–O bond, removing the oxygen in form of water. Depending on the process temperature, it is possible to differentiate between *mild HDO* (or mild hydrotreatment), generally up to 250 °C and mainly used for bio-oil stabilisation, and *deep HDO*, up to 400 °C for obtaining a high deoxygenation degree [17]. The difference between these two conditions is the grade of deoxygenation achieved in the products, which is proportional to the hydrogen consumption [17].

Hydroprocessing of bio-oils has been largely studied with pioneering studies already in the eighties and recently reviewed for example by D.C. Elliott [16]. Nowadays it is becoming more important as demonstrated by the increasing number of articles in literature that reported experiments using different catalysts, reaction conditions and reactor types [8,12–15]. The current challenge is still to find a catalyst with good stability in the aggressive bio-oil environment, with a long lifetime, with a good conversion at relative low temperature (in order to minimise the coke formation) and that is available and cheap for minimising the costs of a scale-up plant.

Catalysts for hydrodesulfurization (HDS) of crude oil, such as CoMo/ γ -Al₂O₃ and NiMo/ γ -Al₂O₃ in sulphide form, have been tested in HDO obtaining satisfying results in term of oxygen removal but not in terms of catalyst stability [8,18–20]. A reason of deactivation of these catalysts is due to the low amount of sulphur present naturally in the pyrolysis oil [7,8] and to the high content of oxygen that constrains the supply of an additional sulphur source in order to keep the catalyst active. However, one of the most important and not completely resolved problem is associated to the deposition of carbonaceous species on the catalyst surface [7,8,21]. Water, present originally in the bio-oil and as the main HDO product, can also limit the stability of the support and decreases the catalytic activity by competitive adsorption on the active catalyst surface [21]. On the other hand, some studies in literature report that in suitable operating conditions the catalyst can resist relative long period. For example M.V. Olarte et al. [22] reported a lifetime of a proprietary sulfided catalyst of over 700 h in a two-stage fixed bed reactor after an appropriated bio-oil pre-treatment over a non-sulphide catalyst.

Supported noble metals, like Pt, Pd and Ru, have been studied by several groups with model compounds [23] and pyrolysis oil [17,24,25], identifying Ru/C as the most active metal in HDO. The main problems related to noble metals are the price/availability, a high consumption of hydrogen not only due to HDO but also to the concurrent hydrogenation of unsaturated bonds (such as aromatic rings) and their tendency to get easily poisoned by the low amount of sulphur in the bio-oil [26,27].

Nickel-based catalysts is another category that has recently gained interest, because of its high abundance and thus lower price, a potentially lower consumption of hydrogen compared to noble metals [11] and a supposed higher stability in the reaction conditions than HDS catalysts. Especially, nickel catalysts that allow a synergy between the active metal and the acidity of the support appear attractive: nickel acts as active centre for hydrogen adsorption while the metal oxide promotes the coordination of oxygen and the subsequent deoxygenation via dehydration (Lewis acid) [28]. The mechanism is still debated and it seems that also nickel is able to coordinate the oxygen group [8]. Related studies with model compounds in the literature have described HDO with nickel catalysts as an attractive route [19,29–35], however only few of them have been carried out with real bio-oils [11,28,33].

In this work, we investigated HDO reactions performed with a bio-oil in the presence of nickel-based catalysts. The catalysts that we used were selected from studies reported in the literature by different authors performing catalysed HDO of model compounds

and/or of bio-oils. Various supports and eventually promoters, which demonstrate an improvement in the conversion, were chosen: NiW/AC (supported on activated carbon) [19], NiCu/Al₂O₃ [11,28,33], Ni/ZrO₂ [34], Ni/SiO₂ [34], Ni/TiO₂ [34], Ni/Al₂O₃ [34] were tested under mild HDO conditions at 250 °C in a 200 ml batch reactor. As benchmark, a Ru/C catalyst was used in the same condition, in order to compare the activity of the two different classes.

The bio-oil under investigation was produced in the bioliq[®] pilot plant in Karlsruhe from fast pyrolysis of wheat straw in a twin-screw mixer reactor [36,37]. Differently from the majority of the articles reported in literature, this work aims to study the hydro-treatment of a bio-oil produced from straw instead of one from wood, therefore its composition (the different inorganic content in the biomass can drive to different fragmentation reactions during pyrolysis) and its properties can differ significantly [38,39]. In our specific case, we employed the light fraction of the original bio-oil, focussing in this way on the reactivity of more polar and lower molecular weight compounds like sugar derivatives, lignin-derived monomers, acids and ketones. The original feed and the products were characterized by different techniques, with a special focus on gas chromatography (GC) and quantitative hydrogen nuclear magnetic resonance (¹H-NMR). We evaluated the main changes induced by the HDO reaction on the general properties of the bio-oil and we monitored the reactivity of some single representative components.

2. Materials and methods

2.1. Pyrolysis oil production

The bio-oil under investigation was produced from the pyrolysis of wheat straw at 500 °C and derived from a one-week experimental pyrolysis campaign of bioliq[®] pilot plant in December 2011. After storage for several days, the bio-oil underwent a natural phase separation and two phases were formed, which are called in this paper “light phase” and “heavy phase” with respect to their densities. According to the observation with an optical microscope, the light phase is homogeneous while the heavy phase is a heterogeneous complex system containing higher molecular weight compounds and solids. In addition, the light fraction contains more polar compounds with lower molecular weight and higher oxygen content, and also higher water content in comparison to the heavy phase.

The HDO tests which are reported in this paper were performed with the light phase due to a narrower product range and the possibility to understand this “simplified” system and identify more easily some reaction trends.

2.2. Characterisation of the bio-oil and the products

The light fraction (denoted in this work also *feed*) of the bio-oil and the upgraded products were analysed by the same techniques. Different types of products were collected: gas, an aqueous phase (lighter-density liquid phase), an upgraded oil (heavier-density liquid phase) and solids.

The density of the feed was determined by a density meter DMA 450 M from Anton Paar and the pH was measured by 691 pH Meter (Metrohm). The water content was determined by a Karl-Fischer titration using a direct titration system Titrando 841 and the Oven Sample Processor 774 from the company Metrohm.

The elemental analysis was performed in an external institute (FM-VEA, KIT) following the standard method DIN51721 for carbon and hydrogen determination and DIN51722 for nitrogen content. The oxygen content was calculated by difference. Since the nitrogen

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