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Research paper

Influence of feedstock, catalyst, pyrolysis and hydrotreatment temperature on the composition of upgraded oils from intermediate pyrolysis

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ABSTRACT

Hydrodeoxygenation (HDO) of bio-oils obtained from intermediate pyrolysis with hot vapor filtration was investigated over Ru/C and $NiCu/Al_2O_3$ catalysts as a function of several parameters: feedstock (beech wood, wheat straw), pyrolysis temperature, catalyst and hydrotreatment temperature. Beech wood was found to be a suitable feedstock for HDO due to its low heteroatom content, whereas the high sulfur content in the wheat straw bio-oil caused irreversible poisoning of the catalysts. Ru/C generally consumed more hydrogen than $NiCu/Al_2O_3$, showing higher hydrogenation/HDO activity with higher selectivity towards alcohols and hydrocarbons, whereas $NiCu/Al_2O_3$ resulted in a higher concentration of ketones. The pyrolysis temperature affected the fragmentation degree; higher temperatures resulted in a higher quality pyrolysis oil with low oxygen mass fraction, but with decreased mass yield. By varying the hydrotreatment temperature (80, 150, 250, 350 °C), different classes of compounds were converted and different deoxygenation degrees were achieved. Overall the results indicate that intermediate pyrolysis with hot vapor filtration is a valid alternative to the more commonly used fast pyrolysis for decentralized (or small-scale) applications, especially for heterogeneous feedstocks with high ash content.

1. Introduction

Biomass represents the main renewable carbon resource and biomass conversion into higher value products has been the subject of much research in recent years [1]. However, this subject still constitutes a significant challenge due to the highly complex chemical structure of biomass. Among several conversion technologies, fast pyrolysis followed by upgrading is considered an economical and energetically valuable route to produce transport fuels and eventually chemicals [2]. Besides fast pyrolysis, intermediate pyrolysis in screw reactors is an emerging technology [3–5], which can also be used for bio-oil production. Intermediate pyrolysis shows longer vapor residence times than fast pyrolysis (order of minutes vs seconds), and usually two condensates are obtained (an aqueous phase and an organic phase defined as bio-oil). Although the yield of bio-oil is lower compared to fast pyrolysis, the bio-oils produced from intermediate pyrolysis are more stable, contain less oxygen ([6]) and exhibit lower molecular weight substances. The process is easier to control [4] and can be a valid alternative to fast pyrolysis in a decentral to central biomass-to-fuels framework, especially for heterogeneous feedstock with high ash content [6]. However, the technology is relatively new and therefore requires deeper understanding of the process and evaluation of the feasibility of upgrading the bio-oils produced. According to the authors' knowledge, no studies have been previously performed related to the upgrading of intermediate pyrolysis oils, which is necessary for the subsequent production of transportation fuels and chemicals due to their higher oxygen mass fraction [2]. Hydrodeoxygenation (HDO), which can be also indicated as hydrotreatment in this context, offers a potential strategy to decrease the oxygen content, since it can provide higher upgraded oil yield, with higher carbon recovery and better quality in comparison to alternative methods such as zeolite cracking [2,7–9].

In this work, a systematic analysis on intermediate pyrolysis and HDO was carried out in order to understand the influence of different parameters on the composition of the upgraded oils, including: biomass feedstock [10,11], catalyst type, pyrolysis temperature and hydrotreatment temperature. Experiments related to intermediate pyrolysis were carried out in the screw reactor STYX (Institute for Technical

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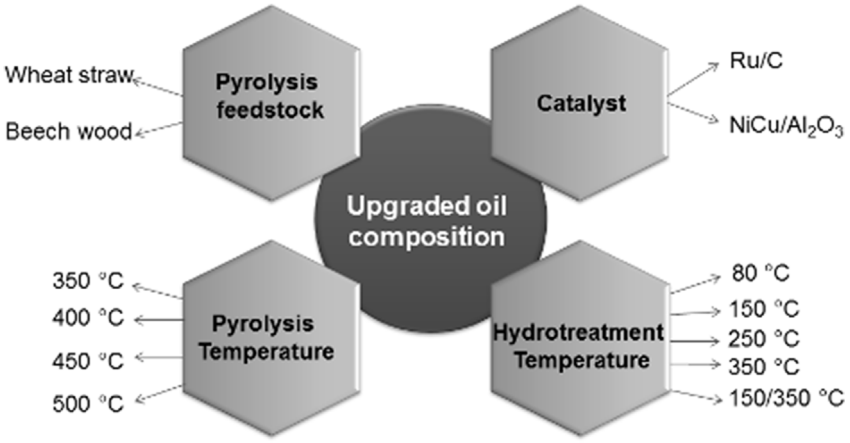

Fig. 1. Different parameters affecting the composition of the upgraded oils and conditions tested in this study.

Chemistry, Karlsruhe Institute of Technology), which implements hot vapor filters integrated with the pyrolysis unit for removal of solids, heavy tar substances and minerals [5]. A summary of the experimental parameters of interest to evaluate the potential of intermediate pyrolysis with integrated hot vapor filtration as basis for fuels/chemical production is shown in Fig. 1. The chosen biomass feedstock influences the bio-oil composition, which in turn can affect the upgraded oil composition and the catalyst performance. Herein beech wood and wheat straw were chosen as feeds for intermediate pyrolysis, as representative of hard wood and herbaceous species respectively. Concerning the upgrading process, Ru/C was chosen as a noble metal catalyst and $NiCu/Al_2O_3$ as an alternative HDO nickel-based catalyst, whereby differences in activity and product selectivity are expected [12,13]. The pyrolysis temperature has a known influence on the fragmentation degree of the molecules, producing oils with different composition and molecular weight. Four bio-oils were therefore produced using beech wood and different pyrolysis temperatures: 350, 400, 450 and 500 °C. The hydrotreating temperature was investigated using the bio-oils from beech wood and wheat straw produced at 450 °C, which optimizes the mass and carbon yields of the oils. Four HDO temperatures (80, 150, 250 and 350 °C) were used in order to see the reactivity of different functional groups and the deoxygenation degree (DOD) over $NiCu/Al_2O_3$ and Ru/C. The influence of the stabilization step at 150 °C was also studied for HDO at 350 °C. A detailed analysis of the products by the combination of GC-MS, ^{1}H NMR, elemental analysis and Karl Fischer titration was chosen to provide more detailed on understanding the reaction pathways and elaborate a general reactivity scale of bio-oil components over Ru/C and $NiCu/Al_2O_3$ catalysts. Finally, analysis of the spent catalysts is presented to obtain information about deactivation processes on the catalysts surface.

2. Materials and methods

2.1. Production of the bio-oils

Four bio-oils derived from beech wood and one from wheat straw were produced in the so-called STYX reactor. The beech wood was bark-free with chips particle size between 2.0 and 4.5 mm (Fagus Sylvatica, Räuchergold® delicatessen from J. Rettenmaier und Söhne GmbH & Co. in Rosenberg, Germany). More information about elemental composition is reported in Ref. [5]. The wheat straw derived from winter straw (triticum aestivum, cultivar "Tommi") sown in October 2012 on fields near "Urspring" in Germany (latitude 48.546764 °N, longitude 9.896208 °E), harvested in August 2013 and stored as rectangular bales in an open storage shed and delivered to the pyrolysis plant in July 2014. It was stored in a closed storage in KIT Campus North until being used in 2016.

The intermediate pyrolysis bench scale reactor (STYX) was developed by the Institute for Technical Chemistry (ITC) at Karlsruhe Institute of Technology (KIT) and was previously described by Tomasi Morgano et al. [5]. STYX consists of a screw reactor with an integrated hot gas filtration, i.e. ceramic filter candles displaced within the vessel of the reactor. Hot gas or vapor filtration enables the elimination of char particles and minerals from the final bio-oil, producing a feed more suitable for HDO. Two-step condensation was employed: the first at 80 °C and the second at 15 °C, including an electrostatic precipitator for the removal of organic aerosols. The feedstock materials were continuously fed to the reactor with a mass flow rate of 2 kg h^{-1}. The bio-oils from beech wood were produced at temperatures of 350, 400, 450 and 500 °C (denoted in this study beech 350 °C – beech 500 °C), and the one derived from wheat straw at 450 °C (named straw 450 °C). The

Table 1
Bio-oil yield from the intermediate pyrolysis process as mass fraction and chemical compositions of the bio-oils used in this study.

	beech 350 °C	beech 400 °C	beech 450 °C	beech 500 °C	straw 450 °C
Bio-oil yield from pyrolysis process (%)	9.1	12.8	14.3	12.9	13.1
pH	2.5	2.6	2.7	3.0	3.8
Water mass fraction (%)	17.8	14.6	12.4	11.5	23.7
Element mass fractions, as received; water free (%)					
C	49.3; 60.0	52.2; 61.1	55.4; 63.2	58.9; 66.6	49.7; 65.1
H	7.7; 7.0	7.6; 7.0	7.1; 6.5	7.2; 6.7	8.5; 7.6
O	43.0; 33.1	40.2; 31.9	37.5; 30.2	33.9; 26.8	40.6; 25.6
N	< 0.3; < 0.3	< 0.3; < 0.3	< 0.3; < 0.3	< 0.3; < 0.3	1.2; 1.5
S	< 0.005; < 0.005	< 0.005; < 0.005	< 0.005; < 0.005	< 0.005; < 0.005	0.3; 0.4
Higher heating value (HHV) as received; water free (MJ/kg)	21.1; 25.7	22.5; 26.3	23.4; 26.7	25.1; 28.4	22.2; 29.1