COMPARISON OF SULPHIDIC AND NON-SULPHIDIC CATALYSTS FOR PYROLYSIS BIO-OIL HYDROTREATING

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Abstract

In accordance with the energy directive RED II, EU countries must increase the production of second-generation biofuels from renewable sources, such as bio-oil. While the undesirable properties of bio-oil (high acidity, oxygen content) can be eliminated by conventional hydrotreatment using sulphided catalysts, this means that the bio-oil must be doped with extra sulphur to maintain catalyst activity. However, it also means that the final product may not then conform to fuel sulphur limits. In this study, we compared the composition and physicochemical properties of hydrotreated wheat straw bio-oil on sulphided NiMo/Al_2O_3 and non-sulphided Ni/Al_2O_3 and Co/Al_2O_3 catalysts. A continuous flow reactor with a fixed bed catalyst layer was used for bio-oil upgrading under the following conditions: 280-320 °C, 4 MPa, WHSV 1 h^{-1}. Simulated distillation was used to analyze the organic fraction composition and FTIR to determine the functional groups.

Introduction

Fuels from renewable resources are attractive nowadays due to several reasons. One of them is their potential to reduce carbon dioxide emissions. Biofuels can also partially replace petroleum distillates, can decrease the dependence of fuel markets on crude oil imports and support local rural economy value chains. By the proposed European Union directive RED II[1] establishing a policy to produce energy from renewable sources, EU countries should increase the use of advanced biofuels, called 2nd generation, and reduce the use of the 1st generation biofuels. Hence, advanced biofuels from non-food parts of crops, wood and agriculture waste, mainly lignocellulose-based, are preferred. The following technologies can be used for the production of advanced biofuels: torrefication, gasification, hydrothermal liquefaction and pyrolysis of biomass[2].

Pyrolysis[3] is a flexible technology that can handle different kinds of biomass and is not so sensitive to feedstock variation. Pyrolysis products can be divided into three following groups: liquid, solid and gaseous. Their yield depends on the type of pyrolysis (slow, intermediate and fast pyrolysis) which differs primarily in biomass residence time (RT) in the reactor.

To maximise the yield of the liquid product (up to 75 %, called bio-oil), which is favourable to produce transportation fuels, a fast pyrolysis is commonly used. The yields of by-products, gaseous and solid are typically 12-13 % each. This is achieved by very high heating rates and short RT (less than 1 s). Different types of fast pyrolysis reactors make this process flexible with respect to different feedstock. The most commercially used pyrolysis reactors include fluidized bed, hot-rotating cone, auger and ablative pyrolysis reactor[3,4].

Bio-oil consists of oxygenates with different functional groups: aldehydes, ketones, alcohols and carboxylic acids that are produced by the decomposition of cellulose, hemicellulose and lignin. The chemical composition of bio-oil is responsible for its instability. The other disadvantage of bio-oil is high water content due to partial deoxygenation and high polarity of bio-oil[5]. Due to these unfavourable properties, bio-oil cannot be used directly as a fuel and has to be upgraded. Main technologies, which provide good quality products, are catalytic hydrotreatment and catalytic cracking of bio-oil. Nevertheless, hydrotreatment seems to be more favourable process due to a better deoxygenation level and higher yields of upgraded products[9].

Many studies were dedicated to hydrotreatment of lignocellulosic pyrolysis bio-oil to fuels and other valuable products using different catalysts including metal nitrides, phosphates, carbides and sulphides on various supports such as C, SiO_2, TiO_2 and others. Catalytically active metals used for bio-oil upgrading can be divided into three categories: noble metals, transition metals and sulphided metals[10].

Noble metals (Pt, Pd, Rh) showed outstanding results[11] in bio-oil upgrading according to many publications, but their main disadvantage was the quick activity loss by poisoning by sulphur present in bio-oil. Moreover, the cost of the noble metal catalyst is prohibitively high. Due to this, transition metals (Ni, Co, Mo, Cu) in metallic and nitridic/phosphidic form were studied to reduce the cost of bio-oil upgrading[12]. Ardiyanti[7] tested a wide range of NiCu catalysts on different supports (SiO_2 and Al_2O_3) in a batch reactor. The degree of deoxygenation was in a range from 58 to 70 % for both supports for temperatures 150 and 300 °C respectively. But for NiCu/Al_2O_3, the reaction pressure was 10 MPa (not 20 MPa as for NiCu/SiO_2), which makes Al_2O_3 a more favourable support. The yield of the organic (hydrocarbon-like) product obtained over NiCu catalysts was typically between 35-42 wt. %. Transition metals can be also poisoned by sulphur as noble metals, but activity decrease is not so significant as for noble metals. A sulphided form of transition metals could also be active in hydrotreatment, but less than the respective metallic form.

To avoid the problem of catalysts poisoning by sulphur, metals in sulphide form, predominantly alumina-supported Ni/Co-Mo can be use directly. These catalysts were well studied[13] for bio-oil hydrotreatment under a wide range of reaction conditions (200-450 °C and 1-29 MPa). In contrast to the previously discussed catalysts, the sulphur content in bio-oil is too low for maintaining the activity of sulphided catalysts and an external sulphur source (H_2S, dimethyldisulphide etc.) has to be added[14].

The aims of this work are to (i) describe the hydrotreatment process over the sulphided $NiMo/Al_2O_3$ and non-sulphided Ni/Al_2O_3 and Co/Al_2O_3 catalysts and (ii) determine the composition and physicochemical properties of the bio-oil and upgraded products.

Experimental

Bio-oil hydrotreatment: For comparison sulphided and non-sulphided catalysts for bio-oil hydrotreatment wheat-barley (1:1 w/w) bio-oil mixed with 0.5 wt. % dimethyldisulphide (DMDS) has been used as feedstock. Bio-oil was upgraded in co-current fixed bed reactor under following reaction conditions: 280-320 °C, 4 MPa, WHSV 0.25 and 1 h^{-1} for non-sulphided and sulphided catalysts, respectively. As a sulphided catalyst, $NiMo/Al_2O_3$ was used, and as non-sulphided catalysts, Ni/Al_2O_3 and Co/Al_2O_3 were chosen.

$NiMo/Al_2O_3$ catalyst was sulphided from its oxide form in-situ via hydrogenated straight run gas oil containing 3 wt. % DMDS at 345 °C. The catalyst activation was followed by its stabilization with straight-run gas oil (0.23 wt. % of sulphur). Ni and Co catalysts were reduced from their oxide form to metal in-situ.

Elemental composition (C, H, N, S, O) was determined using a Vario EL Cube analyser (Elementar). A Merck stearic acid standard and a standard by Elementar Analysensysteme GmbH (C: 67.68 wt%, H: 4.95 wt%, N: 0.69 wt%, S: 0.81 wt%) were used for the instrument calibration. The oxygen content was calculated by difference.

The degree of deoxygenation was calculated according to oxygen content from elemental analysis of feedstock and products organic phase.

Density at 40 °C and a kinematic viscosity at 40 °C were determined by SVM 3000 Stabinger Viscometer (Anton Paar).

Micro Conradson Residue (MCR) was determined according to the ASTM D4530 standard method, by an NMC 420 device (NORMALAB ANALIS).

Water content was determined by a Karl Fischer volumetric titration according to the ASTM E203 using a METTLER TOLEDO DL38 device.

Carboxylic acid number (CAN) was determined by a titration method, where tetrabutyl ammonium hydroxide as a titrant, tetraethyl ammonium bromide as an electrolyte and isopropanol as a solvent were used.

FTIR spectra of feedstock and upgraded products were recorded using an infrared spectrometer IRAffinity-1 (Shimadzu, Japan) with Quest ATR accessory with a diamond crystal (Specac, USA). LabSolution IR software (Shimadzu, Japan) was used as an interface between the spectrometer and the control computer. The spectra were recorded in the 4000–650 cm^{-1} region using the spectral resolution of 4 cm^{-1} and 128 scans.

Bio-oil and all liquid organic products were characterized also by **simulated distillation**. Samples were dissolved in carbon disulphide (1 wt. % solution) and introduced to a TRACE ULTRA gas chromatograph (Thermo Scientific) equipped with an on-column injector, Agilent J&W CP-SimDist UltiMetal (10 m x 0.53 mm x 0.17 µm) column, a FID detector and an oven cryogenic cooling system.

Results and discussion

Organic liquid products obtained by bio-oil hydrotreating at different reaction temperatures and using different catalysts were compared with the feedstock in terms of their C/O and C/H ratio, shown on Figure 1. Low C/O ratio shows that the feed contains a significant amount of oxygenates (alcohols, carboxylic acids, aldehydes, phenols and others). With increasing reaction temperature the C/O ratio of all products significantly increased compared with the feed as a result of deoxygenation. At 280 and 300 °C, Ni and Co showed close C/O ratios, i.e. similar deoxygenation degree, but at 320 °C Ni showed much better results in terms of deoxygenation than Co (Figure 1). Nevertheless, NiMo exhibited the highest C/O ratios at all reaction temperatures, i.e. outperforming the non-sulphided catalysts. The biggest difference in deoxygenation between NiMo and Ni/Co can be seen at 320 °C, where C/O ratio was 7.15 over NiMo, but only 5.44 over Ni.

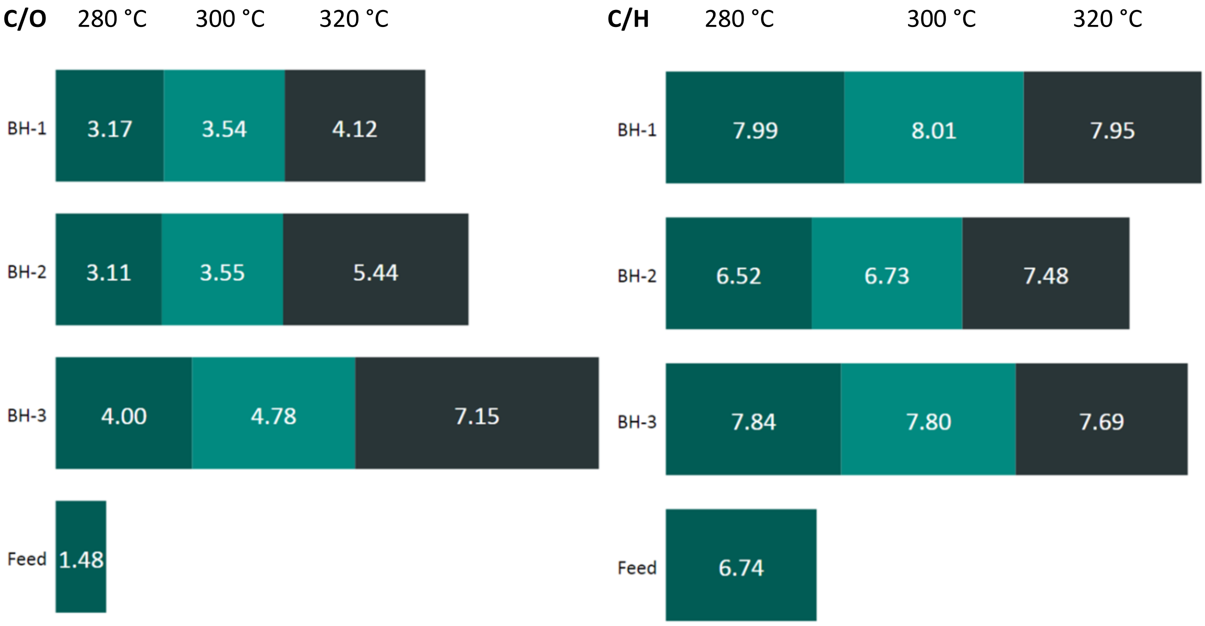

Figure 1. C/O and C/H ratio of feed and products. BH-1 Co/Al_2O_3, BH-2 Ni/Al_2O_3, BH-3 NiMo/Al_2O_3

The fractional composition of the upgraded products at 320 °C and the feed was measured by simulated distillation and the results are shown in Figure 2. The main challenge of bio-oil analysis using this method is the lower response factor of oxygenates and high water content that affects recovery values at FID detector of the GC. Nonetheless, products from bio-oil upgrading can be compared among themselves due to lower oxygen content and their hydrocarbon nature. For clarity, there are shown the final boiling point lines of gasoline (200 °C) and diesel (400 °C) in Figure 2 to allow a comparison of the recoveries (yields) of products. The highest recovery of the desired fuel fractions (gasoline and diesel) was obtained for the product from NiMo/Al_2O_3 bio-oil upgrading at 320 °C, they were 23 and 42 wt. %, respectively. Gasoline yield over Ni/Al_2O_3 was close to that over NiMo/Al_2O_3 product, but the diesel yield was lower, 38 wt. %. Bio-oil upgraded over Co/Al_2O_3 catalyst had the lowest overall yield of the desired fuel products. Gasoline and diesel yields were 16 wt. % and 41 wt. %. Consequently, non-sulphidic catalysts upgraded straw bio-oil to a product with a higher amount of high- boiling compounds (>400 °C) than sulphidic NiMo/Al_2O_3 catalysts which afforded a higher yield of fuel fractions.

An FTIR method was used for fast screening of the bio-oil upgrading level and for monitoring of changes in oxygen containing functional groups. Figure 3 depicts FTIR spectra of bio-oil and its upgraded products at 320 °C on Ni/Al_2O_3 and NiMo/Al_2O_3. Wavenumber 3650-3100 cm^{-1} encompasses bonds that can be attributed to O-H stretching in phenols, carboxylic acids, alcohols and water. The absorbance in this region was much lower for the product than for the bio-oil, which is in accordance with the higher C/O ratio of products than that of bio-oil. Methyl and methylene groups represented by wavenumbers 3100-2800 cm^{-1} were also more pronounced in products than in bio-oil. There were not any significant differences in these regions between products obtained over Ni catalyst and those obtained over NiMo catalyst. An interesting difference in absorbance between Ni and NiMo catalysts can be seen for wavenumbers 1750-1650 and 1620-1500 cm^{-1} that correspond to the stretching of the C=O groups and the stretching of the C=C bonds from aromatics or alkenes, respectively. Carbonyl group absorbance (reflecting the presence of acids, ketones and aldehydes) was lower for products obtained over NiMo catalyst, while double bonds absorbance was lower for products obtained over Ni catalyst. This agrees with elemental analysis and clearly, demonstrate the superior performance of the sulphided catalyst.

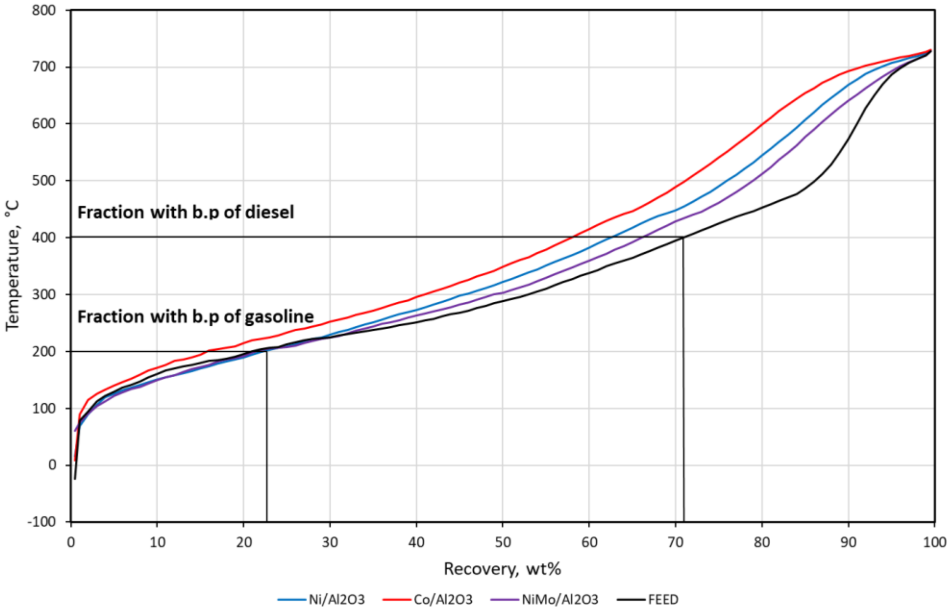

Figure 2. Simulated distillation of bio-oil feed and products from 320 °C

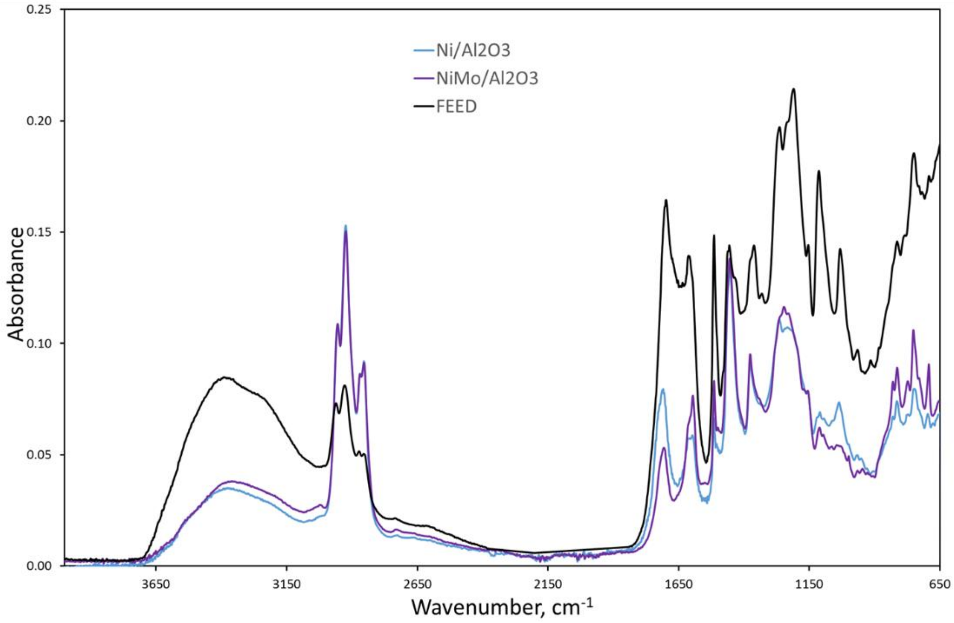

Figure 3. FTIR spectra of bio-oil and products upgraded on Ni/Al_2O_3 and NiMo/Al_2O_3 at 320 °C

Physical properties of the feed and products are summarized in Figure 4. The density of all products was lower than that of the feed and had a decreasing trend with increasing temperature. At 280 °C Ni/Al_2O_3 upgraded the bio-oil better than the other catalysts, but at 320 °C densities of the products obtained over Ni and NiMo were almost the same. The changes in kinematic viscosity with temperature were greater than those in density. The product obtained over Co catalyst had even a higher viscosity than the feed, plausibly due to the separation of the aqueous phase from the product. Again, Ni showed better results at lower temperatures, but at 320 °C the NiMo catalyst ensured the same reduction in viscosity of the products as the Ni catalyst.

Micro Conradson Residue that shows the tendency of the feedstock to form carbonaceous deposits was very high for the feed (15 wt. %) and was reduced to 4 wt. % over Ni and NiMo catalysts. The water content of the products obtained over Ni and NiMo catalysts at 320 °C was close to 2.5 wt. % and was significantly reduced in comparison with the feed bio-oil (22.6 wt. %).

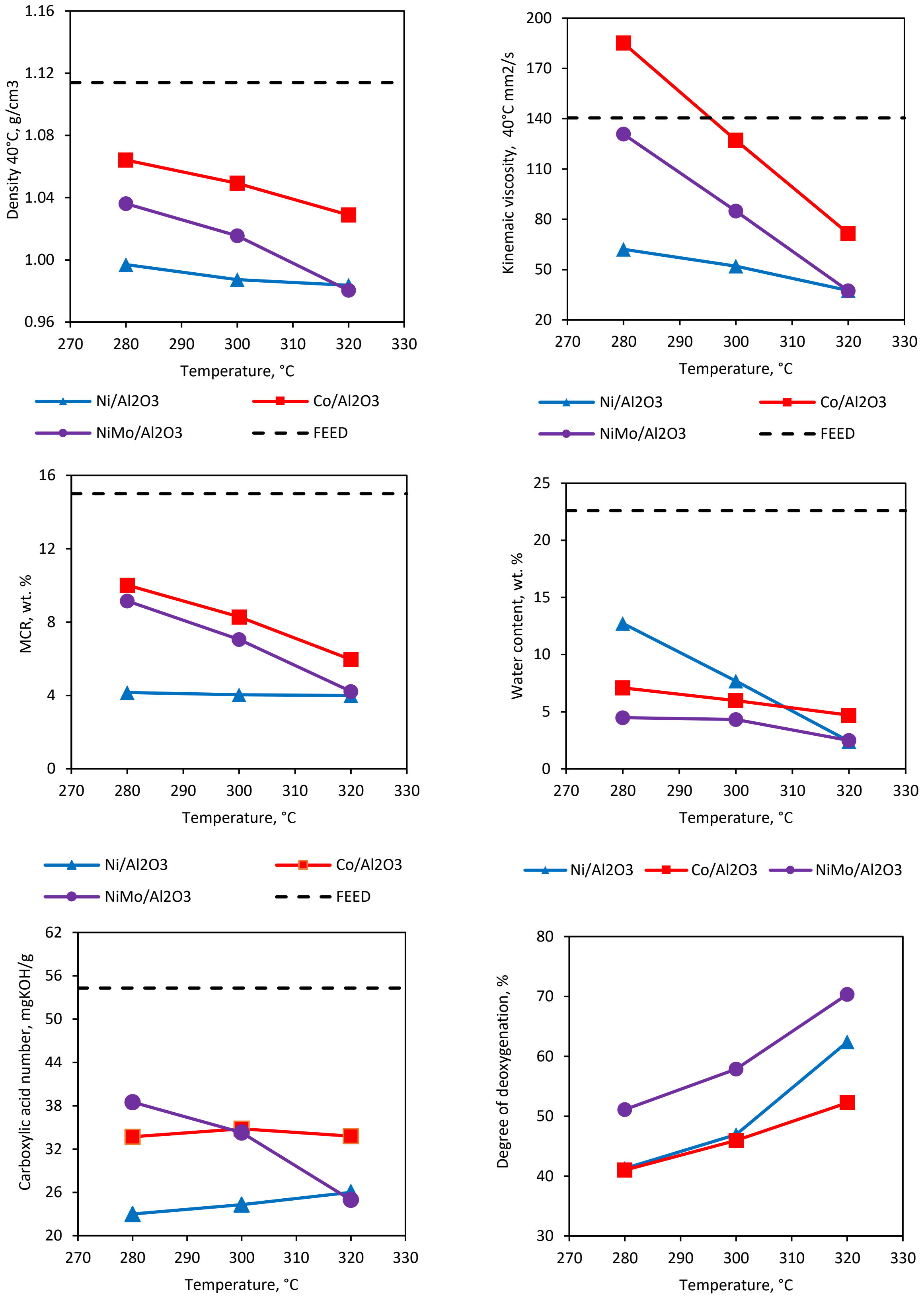

Figure 4. Properties of feedstock and upgraded products

The CAN of the hydrotreated products obtained over Ni and NiMo was reduced to the half of the feed value (56 mg KOH/g). However, while the CAN of the NiMo upgraded products had a decreasing trend with increasing temperature, the CAN of the Ni and Co upgraded products was constant or even showed a slightly increasing trend with the increasing reaction temperature. This can be attributed to the loss of catalytic activity with the increasing time on stream, and even the increased temperature did not compensate the activity loss for Ni/Al_2O_3 catalyst. The degree of deoxygenation (DOD) of all products obtained over NiMo was higher at all reaction temperatures than the DOD of products obtained over Ni or Co catalysts.

Conclusions

Straw bio-oil was upgraded in a co-current fixed bed reactor using a sulphided $NiMo/Al_2O_3$ and non-sulphided Ni/Al_2O_3 and Co/Al_2O_3 catalysts in the temperature range 280-320 °C and pressure 4 MPa. Bio-oil hydrotreating performed at higher reaction temperatures resulted in improved properties of the hydrotreated products. The increase in the C/O ratio of the products was greater over the $NiMo/Al_2O_3$ catalyst than over Ni/Al_2O_3 and Co/Al_2O_3 catalysts. FTIR results indicated that the NiMo catalyst possessed a better deoxygenation activity whereas the Ni catalyst showed a better hydrogenation activity. Physicochemical properties of the hydrotreated bio-oil products were significantly improved mainly at 320 °C using Ni/Al_2O_3 and $NiMo/Al_2O_3$ catalysts. Kinematic viscosity and Micro Conradson residue decreased from 140 to 38 mm^2/s and from 15 to 4 wt.%, respectively, due to hydrotreating. The carboxylic acid number was reduced to the half of the feed value. It can be concluded that sulphided $NiMo/Al_2O_3$ afforded products having better properties than Ni or Co catalysts. Also, the loss of catalytic activity was less pronounced over the NiMo catalysts than over Ni and Co catalysts.

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