

Co-Processing of Oil and Bio-Oil in the Medium of Supercritical Solvent Mixture

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Nowadays, the production of liquid motor fuel faces such problems as compliance of the final product with existing international standards (for the content of sulfur, oxygen and nitrogen) as well as the improvement of the feasibility of the existing technologies for fuel production. Biomass is one of the most perspective and widely spread sources for energy. The existing techniques for biomass conversion into the fuels are mainly based on the hydroprocessing and can be successfully applied in petroleum industry. The integrated processes involving both biofuel and oil conversion are of great interest. In this work, the novel hydrogen-free approach for co-processing of heavy oil fractions and bio-oil is described. The use of supercritical solvent mixture, which includes propanol-2 and n-hexane, allows full substrate conversion to be achieved for maximum 3 h. As a result, the hydrocarbon mixture consisting of aromatic and cyclic compounds was obtained with 99 wt. % yield.

1. Introduction

The steadily increasing demand for motor fuel, depletion of crude oil sources, decline in the quality of the produced oil, and the environmental problems associated with the emission of green-house gases make the producers to replace fossil fuels with alternative environmentally friendly energy resources, e.g. biomass. The existing liquid fuels from biomass (including bio-oil and biodiesel) do not always have good miscibility with the petroleum and require additional modification to meet fuel standards. This modification involves the removal of oxygen and isomerization of the resulting hydrocarbons in the presence of hydrogen (so-called hydrotreatment processes) (Peralta-Ruiz et al., 2018). The same conditions and catalysts are used in the hydrotreatment of fuels from biomass and in the hydrotreatment of oil (i.e. hydrodesulfurization, hydrocracking, hydroisomerization). The integration of biofuel upgrading processes in the existing technologies of crude oil refining is one of the promising directions for the production of liquid motor fuels (Wu et al., 2019).

Co-processing of biogenic raw material and oil fractions has recently become increasingly important. This process includes cracking, hydrogenation, hydrotreating of renewable and mineral feedstock for the production of gasoline, kerosene (Primo and Garcia, 2014) and diesel hydrocarbons (Tay et al., 2020). To date, the co-processing of oil fractions and biofuels is carried out in three main directions: 1) hydrotreatment of diesel fuel and vegetable oils (Chen et al., 2013); 2) hydrotreatment of gas oil and bio-oil (pyrolysis liquid or liquid products of hydrothermal wood processing) (Chen et al., 2018); 3) hydrocracking of vacuum gas oil and bio-oil (Al-Sabawi et al., 2012).

Existing technologies of co-processing of petroleum feedstock and biofuels are typically performed without the use of solvents in the flow mode with high consumption of gaseous hydrogen. Petroleum hydrocarbons in this case play the role of solvents. However, the high viscosity of petroleum hydrocarbons requires the use of high temperature that reaches up to 450 °C (Al-Sabawi et al., 2012). Low solubility of hydrogen in such mixtures leads to the use of high gas pressures for the processes (Bezergianni et al., 2018). This affects the efficiency and economy of the co-processing. Nowadays, the researches in the field of co-hydroprocessing of oil fractions and biofuels are performed in two main directions. The first one is the decrease in the process

temperature and hydrogen consumption. In order to decrease the cost of hydrotreatment processes, several approaches are applied. The use of supercritical solvents is one of such ways. This method, in addition to reducing the temperature of the process, can serve as the donors of atomic hydrogen and, are able to decrease the hydrogen consumption. Currently, there are several works on deoxygenation of components of vegetable oils and bio-oil using supercritical solvent, such as water (Dickinson et al., 2012), hexane, propane, carbon dioxide (Park et al., 2019), and alcohols (Shafaghat et al., 2019). According to the literature (Park et al., 2019), hexane and light alcohols are the most promising solvents, as they allow the process to be carried out under relatively mild conditions. However, there is no information on the use of supercritical fluids in co-treatment of biomass and oil fractions in the literature.

The second area is the search for novel catalysts which are stable for the rapid deactivation and cheap. Catalysts used in hydrotreatment are divided into two types: 1) transition metal compounds (sulfides, nitrides, phosphides) deposited on aluminum oxides (De Paz Carmona et al., 2019), silicon (Sauvanaud et al., 2018) or zeolites (Santillan-Jimenez et al., 2019), and 2) noble and rare earth metals (Pt, Pd, Re, Rh) deposited on carbon or oxide supports (Naik et al., 2015).

Hydrothermal synthesis is one of the ways to solve the problem of novel catalyst development. This approach allows the ultrafine crystalline metal oxides from their inorganic salts to be obtained (Lee et al., 2020), and does not require additional calcination. Currently, hydrothermal synthesis is used to produce noble metal based catalysts (Zhang et al., 2018) and transition metal oxide catalysts (Yang et al., 2019). Recently, we have shown that hydrothermal synthesis leads to the restructuring of the porous structure of the polymeric support and the formation of large mesopores, which is favorable for the conversion of high-molecular compounds (Stepacheva et al., 2019).

Taking into the account our previous studies and world practice, this work is devoted to the investigation of the joint conversion of heavy oil fractions and oxygen-containing biomass-derived compounds to produce high-quality fuel. The novelty of this work includes the use of supercritical approach as well as the use of supercritical solvent mixture for the upgrading of heavy oil fractions and bio-oil. Also, the use of hydrothermally synthesized catalysts in the joint conversion is described for the first time.

2. Experimental

2.1 Materials

Hypercrosslinked polystyrene (Macronet, MN-270, Purolight Inc., UK), cobalt (II) nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, c.g., Reackhim, Russia), nickel (II) nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, c.g., Reackhim, Russia), ruthenium (IV) hydroxochloride (RuOHCl_3 , c.g., Aurat, Russia) and distilled water were used for the catalyst synthesis. Anisol (c.g., Acros Organic, USA) was used as a bio-oil model compound. Anthracene (c.g., Acros Organic, USA) was used as model compounds of oil fractions. n-Hexane (c.g., Nevareactiv, Russia) and propanol-2 (c.g., Nevareactiv, Russia) were used as components of the supercritical solvent.

2.2 Catalyst synthesis and characterization

The bimetallic catalysts supported on the polymeric network of the hypercrosslinked polystyrene were synthesized by the simultaneous hydrothermal deposition. The catalysts were prepared as follows: 1 g of MN-270 with the particle size of 80 μm , ruthenium (IV) hydroxochloride calculated as 1 wt. % of ruthenium, cobalt or nickel nitrate calculated as 10 wt. % of metal and 15 mL of distilled water were fed into the high-pressure steel reactor (PARR-4307, Parr Instrument, USA). The mixture was heated up to 200 $^\circ\text{C}$ under a nitrogen pressure of 6 MPa. The catalyst synthesis was carried out for 15 minutes under the indicated conditions. The catalyst was filtered, washed with water, dried at 120 $^\circ\text{C}$ for 2 h, and reduced in a hydrogen flow at 300 $^\circ\text{C}$ for 5 h. The resulted catalysts were signed as 1 %-Ru-10 %-Co-MN-270 and 1 %-Ru-10 %-Ni-MN-270. The metal concentration in the catalysts was chosen based on our previous studies on the deoxygenation of fatty acids (Stepacheva et al., 2019) and bio-oil compounds. The catalyst characterization was performed using the low-temperature nitrogen physisorption, X-Ray photoelectron spectroscopy, transmission electron microscopy.

2.3 Hydrotreatment procedure

The experiments were carried out in a six-cell reactor Parr Series 5000 Multiple Reactor System (Parr Instrument, USA) equipped with a magnetic stirrer. 3 g of the model compound mixture (varied from 5 to 50 wt. % of anisole) was dissolved in 30 mL of the solvent. The solvent composition was varied from 0 to 50 vol. % of propanol-2 in n-hexane. The mixture was put into the reactor cell and 0.05 g of the catalyst was added. The reactor was sealed and purged with nitrogen three times to remove air. Then the nitrogen pressure was set as 3.0 MPa, and the reactor was heated up to 270 $^\circ\text{C}$. After the reaching of the reaction temperature, the pressure increased up to 7.5 - 9.5 MPa depending on the solvent composition. The

experiments were performed varying the process time (from 10 min to 3 h) in order to maintain the phase equilibrium.

The liquid phase was analyzed by GCMS using gas chromatograph GC-2010 and mass-spectrometer GCMS-QP2010S (SHIMADZU, Japan) equipped with chromatographic column HP-1MS with 30 m length, 0.25 mm diameter and 0.25 μm film thickness. The column temperature program was set as follows: initial temperature 120 $^{\circ}\text{C}$ was maintained for 5 min then the column was heated up to 250 $^{\circ}\text{C}$ with the rate of 5 $^{\circ}\text{C}/\text{min}$ and maintained at 250 $^{\circ}\text{C}$ for 5 min. Helium (volumetric velocity of 20.8 cm^3/s , the pressure of 253.5 kPa) was used as a gas-carrier. The injector temperature was 280 $^{\circ}\text{C}$, ion source temperature was 260 $^{\circ}\text{C}$; interface temperature – 280 $^{\circ}\text{C}$.

The quantitative estimation of the hydrotreatment process was performed for each model compound using substrate conversion and product yield calculated according to Eq(1) and Eq(2).

$$X = \frac{C_0 - C}{C_0} \cdot 100\% \quad (1)$$

$$Y = \frac{C_i}{\sum C_i} \cdot X \quad (2)$$

where X – substrate conversion, wt. %; C_0 – initial substrate concentration, mol/L; C – current substrate concentration, mol/L; Y – product yield, wt. %; C_i – product concentration, mol/L.

3. Results and discussion

3.1 Catalyst characterization results

To study the catalyst structure and morphology, the physic-chemical characterization was performed using such methods as low-temperature nitrogen physisorption, X-Ray photoelectron spectroscopy, transmission electron microscopy. The results of catalyst characterization are shown in Table 1. It is seen that the synthesized samples are characterized by a high surface area (over 800 m^2/g) and pore volume (ca. 1.0 cm^3/g). The analysis of the absorption-desorption isotherms (see Figure 1) shows the micro-mesoporous structure of the catalysts with the bimodal pore size distribution - about 4.5 and 10-20 nm (Thommes et al., 2015). It should be noted, that Ni-containing catalyst has a lower surface area in comparison with 1 %-Ru-10 %-Co-MN-270. This is due to the slight aggregation of metal-containing phase during the catalyst reduction (to compare, the surface area of as-synthesized catalysts was found to be 890 and 900 m^2/g for 1 %-Ru-10 %-Co-MN-270 and 1 %-Ru-10 %-Ni-MN-270). This is confirmed by the higher particle size of metal-containing phase for Ru-Ni catalyst (Table 1, Figure 2).

Table 1: Results of catalyst characterization

Catalyst	Surface area, m^2/g	Pore volume, cm^3/g	Metal particle size, nm
1 %-Ru-10 %-Co-MN-270	870 ± 5	0.99 ± 0.05	3.2 ± 0.05
1 %-Ru-10 %-Ni-MN-270	845 ± 5	0.98 ± 0.05	4.8 ± 0.1

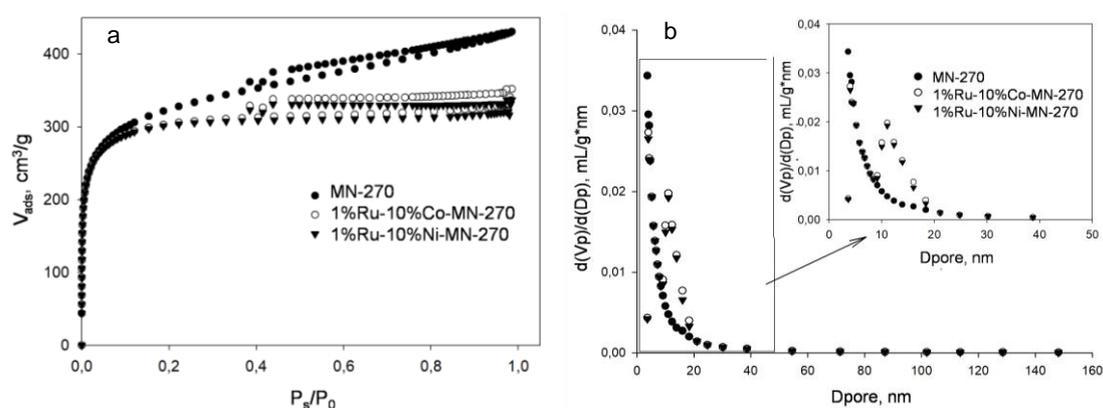


Figure 1: Nitrogen adsorption-desorption isotherms (a) and pore size distribution (b) for the synthesized catalysts

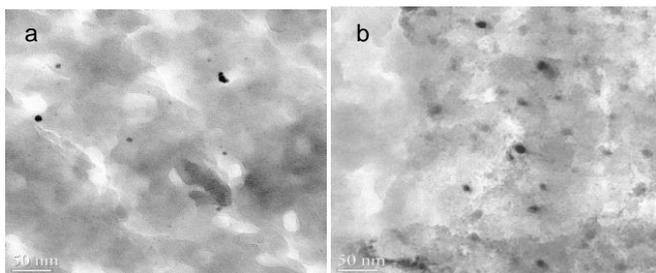


Figure 2: TEM images for 1 %-Ru-10 %-Ni-MN-270 (a) and 1 %-Ru-10 %-Co-MN-270 (b) catalysts

According to XPS analysis, the composition of the metal-containing phase of 1 %-Ru-10 %-Co-MN-270 was found to be presented by the mixed oxides of Co (II), Co (III) (Biesinger et al., 2011) and Ru (IV) (Morgan, 2015). For 1 %-Ru-10 %-Ni-MN-270 metal-containing phase consisted of Ni (II), Ni (III) (Biesinger et al., 2011) and Ru (IV) oxides (Morgan, 2015).

3.2 Influence of solvent composition

To estimate the influence of solvent composition on the conversion of model compounds of bio-oil and heavy oil fractions (anisole and anthracene), the experiments on the varying of propanol-2 concentration (from 0 to 50 vol. %) in n-hexane were performed. The results of the study of the solvent composition influence on the anisole and anthracene conversion are presented in Figures 3 and 4.

An increase in the propanol-2 concentration in the solvent increases the conversion degree for both anisole (Figure 3a) and anthracene (Figure 3b) in the non-catalytic process. The efficiency of the catalytic treatment of anisole practically does not depend on the solvent composition. The conversion degree, in this case, reaches up to 100 wt. % for both Ru-Co and Ru-Ni catalysts even if no alcohol was added. In contrast, propanol-2 concentration strongly affects the anthracene processing increasing conversion degree up to 100 wt. % as the alcohol content increases over 40 vol. %. Such results can be explained by the acceleration of cracking reaction through an increase in the H-atom concentration as well as an increase in the anthracene solubility.

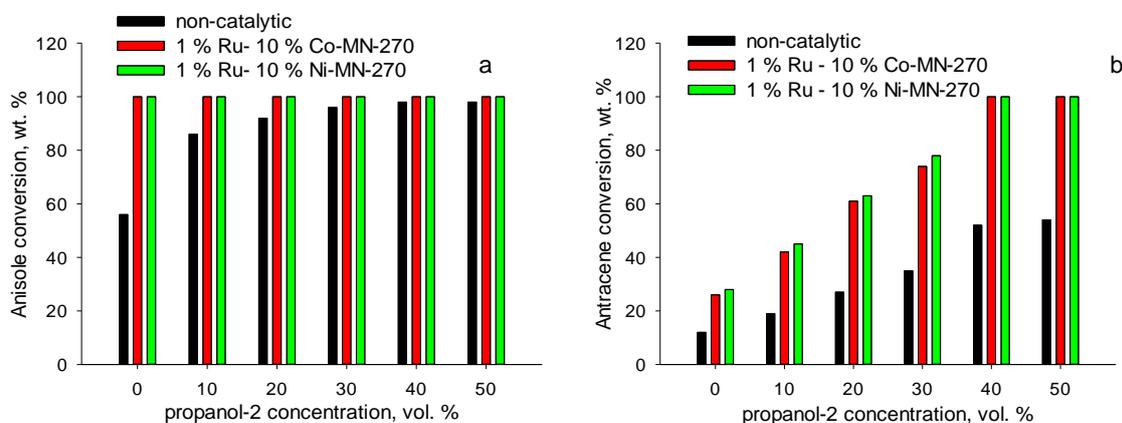


Figure 3: Solvent composition influence on anisole (a) and anthracene (b) conversion degree

However, propanol-2 concentration strongly affects the product yield in both anisole and anthracene processing (see Figure 4) because of an increase in the H-atom concentration. During the anisole treatment, phenol (up to 95 wt. %) was found to be the main product in non-catalytic conversion (Figure 4a). In this case, methanol was the major side product. The use of the catalysts results in the formation of hydrocarbons (mainly benzene). Cyclohexane was also observed among the products. It is noteworthy that the 1 %-Ru-10 %-Ni-MN-270 catalyst provides higher selectivity to cyclohexane (up to 40 %) in comparison with 1 %-Ru-10 %-Co-MN-270 (up to 15 %) due to the higher activity of nickel in hydrogenation.

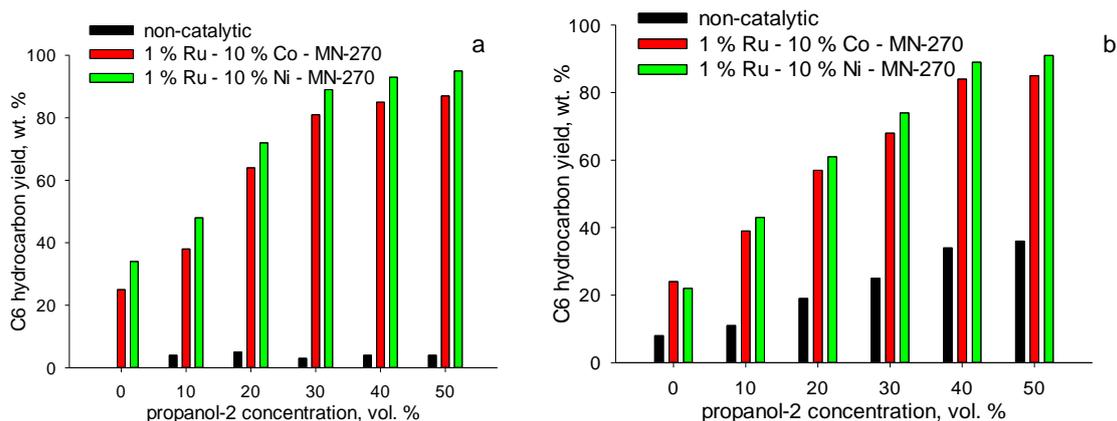


Figure 4: Solvent composition influence on the yield of aromatic hydrocarbons in anisole (a) and anthracene (b) conversion

In the case of anthracene, benzene, toluene and xylene were found to be the main products of non-catalytic process. The use of the catalysts (particularly 1%-Ru-10%-Ni-MN-270) results in the formation of benzene and cyclohexane with the maximum yield of up to 25 wt. % of cyclohexane and 55 wt. % of benzene. Based on the experiments, the solvent composition 40 vol. % propanol-2 and 60 vol. % n-hexane was chosen for further studies.

3.3 Influence of substrate composition

The study of the influence of substrate composition was performed using 1%-Ru-10%-Ni-MN-270 catalyst in the solvent consisting of 40 vol. % propanol-2 and 60 vol. % n-hexane. The results of the experiments are shown in Table 2. Anisole content in the substrate mixture was varied from 5 up to 50 wt. %. It is seen that the addition of anisole to anthracene increases the C₆ hydrocarbon yield up to 98 wt. % in comparison with the conversion of pure anthracene (about 90 wt. %). This can be explained by the synergetic effect of C-C and C-O bonds breaking during the process. Benzene and cyclohexane were found to be main product with the selectivity about 65 and 32 %.

Table 2: Substrate composition influence on the conversion and hydrocarbon yield

Anisole content, wt. %	Conversion, wt. %	C ₆ hydrocarbon yield, wt. %
5	100	90
15	100	93
30	100	97
50	100	98

4. Conclusions

In this work, the study of the co-processing of bio-oil and heavy oil model compounds was carried out in the supercritical solvent mixture (propanol-2 – n-hexane). Influence of solvent composition and substrate composition on the hydrocarbon yield was estimated. The solvent composition of 40 vol. % propanol-2, 60 vol. % n-hexane and the addition of minimum 30 wt. % of anisole provide the highest (up to 98 wt. %) yield of C₆ hydrocarbons at 100 % substrate conversion. Benzene and cyclohexane were found to be main products of anisole and anthracene co-processing in the presence of 1%-Ru-10%-Ni-MN-270 with the selectivity about 65 and 32 %.

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