

Co-processing of Biomass Waste and Heavy Oil Fraction as an Effective Way for Fuel Production

Anastasia A. Dmitrieva^a, Antonina A. Stepacheva^{b,*}, Elena O. Schipanskaya^a, Mariia E. Markova^b, Valentina G. Matveeva^b, Mikhail G. Sulman^b

^aTver State University, Zhelyabova str., 33, Tver, 170100

^bTver State Technical University, A. Nikitin str., 22, Tver, 170026
a.a.stepacheva@mail.ru

The integration of biofuel upgrading processes in the existing technologies of crude oil refining is considered to be one of the promising directions for the production of liquid motor fuels. In this work, the co-processing of bio-oil obtained from biomass waste and heavy oil fractions in the supercritical solvent was studied. The bio-oil was obtained by the slow pyrolysis of birch and pine wood sawdust in the presence of a Fe-containing zeolite-based catalyst. The influence of the catalyst on the yield and composition of liquid products was studied. To find the optimal reaction conditions, the co-processing of the model compounds (anisole – eicosane – dibenzothiophene) was carried out by varying the solvent, reaction temperature, and the initial nitrogen pressure. Full removal of oxygen and sulfur as well as a decrease in the concentration of heavy and polyaromatic compounds from the feedstock were observed under the following process parameters: solvent – propanol-2, reaction temperature – 260 °C, initial nitrogen pressure – 1.5 MPa, total pressure – 7.2 MPa.

1. Introduction

Fossil fuels are considered to be the main energy source. The modern tendencies require the involvement of renewable fuels in the transportation sector. Among the existing fuels derived from biomass, bio-oil seems to be a promising source of energy (Isa and Ganda, 2018). Bio-oil is the liquid product obtained by the pyrolysis of different feedstock including biomass waste. It is a complex mixture containing aromatic and aliphatic compounds. The high oxygen content in bio-oil makes it inappropriate for direct use as a fuel.

The existing fuels obtained from biomass do not always meet the fuel standards and are needed to be upgraded. The upgrading of biofuels implies the hydrotreatment processes which are effectively used for obtaining fuels from heavy oil fractions (Zhang et al., 2021). The co-processing of bio-oils and petroleum in existing petroleum refineries seems to be the prospective way (Pontes et al., 2021). It can minimize the capital cost associated with bio-oil upgrading and avoid several issues of this process (Wu et al., 2020). In co-processing, two main directions are currently studied: fluid catalytic cracking (Choi et al., 2018), and hydrotreatment (Wang et al., 2021).

The co-hydrotreatment of fossil fuels and bio-oil in supercritical fluids is a novel approach for the production of fuels (Santillan-Jimenez et al., 2019). In spite of the numerous studies on co-processing, the use of supercritical technologies in this direction was not previously investigated. The preliminary results on anisole-anthracene mixture conversion in supercritical solvent were recently reported by Stepacheva et al. (2020). In this work, for the first time, the results on the co-processing of the bio-oil obtained by the wood waste pyrolysis and straight-run diesel in a supercritical solvent are described.

2. Experimental

2.1 Pyrolysis catalyst synthesis

Commercial zeolite H-ZSM-5 (Zeolyst, Netherlands) was chosen as a support for the pyrolysis catalyst. The catalyst was synthesized by the wet impregnation as follows: 5 g of zeolite was mixed with 10 mL of an

aqueous solution containing 3.6075 g of iron nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, c.g., Reachim, Russia). The suspension was continuously stirred for 30 min, filtered, and dried at a temperature of 100 ± 5 °C. The dried sample was calcined at 500 ± 5 °C for 5 h. The calcination temperature and time was chosen on the basis of the previous studies (Lugovoy et al., 2018).

2.2 Pyrolysis of wood waste

To obtain the bio-oil, two types of wood waste were used – pinewood sawdust, and birch sawdust. The bio-oil was obtained by the slow-pyrolysis process of the sawdust. Thermal decomposition of the wood waste was carried out in a developed laboratory set-up (Chalov et al., 2017) using nitrogen as a carrier gas. For the pyrolysis, 3 g of the sawdust were mixed with 0.3 g of the zeolite-based catalyst and put in the heating zone of the reactor. The process was carried out under the following conditions: the size of the feedstock fractions - 1-2 mm, the temperature – 500 ± 2 °C, the pyrolysis time – 25 minutes. The yield of the bio-oil was calculated as a mass fraction of gaseous, liquid, and solid products. The composition of the obtained liquid was studied GCMS-QP2010S (Shimadzu, Japan) according to the procedure described by Chalov et al. (2017).

2.3 Co-processing catalyst synthesis

The Ni-containing catalyst deposited on schungite was used for the co-processing of petroleum and bio-oil. Schungite is a fullerene-like natural carbonaceous material with high sorption ability and high reductive properties. Schungite powder (Zazhogino field, Karelia Republic, Russia) with the humidity of 10 wt. % was used as the catalyst support. The schungite was preliminarily washed with hexane and acetone to remove the organic contaminants and dried at 70 ± 3 °C. Dry support was milled and sieved and the fraction with the particle size above 150 μm was chosen for catalyst preparation.

Nickel acetate ($\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, c.g.) was purchased from Aurat (Russia) and used as received as a metal precursor. The deposition of nickel was carried out by the precipitation of the pre-calculated amount of the salt in the medium of the subcritical water using a high-pressure reactor Parr 4307 (Parr Instrument, USA). For the synthesis, 1 g of schungite powder, 0.4274 g of nickel acetate, and 15 mL of distilled water were used. The synthesis was carried out at the temperature of 200 ± 2 °C and the nitrogen pressure of 6.0 MPa for 15 min (Stepacheva et al., 2021). The resulting catalyst was filtered and dried at a temperature of 120 ± 5 °C. The obtained catalyst sample was heated in a nitrogen flow at 300 ± 5 °C for 3 hours to form the nickel oxide phase.

2.4 Experiments on the co-processing

Anisol (c.g., Acros Organic, USA) was used as a bio-oil model compound. Eicosane (c.g., Acros Organic, USA) and dibenzothiophene (c.g., Acros Organic, USA) were used as model compounds of oil fractions. n-Hexane (c.g., Nevareactiv, Russia), methanol (c.g., Nevareactiv, Russia), and propanol-2 (c.g., Nevareactiv, Russia) were used as solvents. The experiments on the co-processing of petroleum and bio-oil model compounds were carried out in a six-cell reactor Parr Series 5000 Multiple Reactor System (Parr Instrument, USA) equipped with a magnetic stirrer. A mixture containing 1 g of each model compound was dissolved in 30 mL of the solvent used. The resulting solvent and 0.1 g of the catalyst were put into the reactor cell. The reactor was sealed and purged with nitrogen three times to remove air. Then the working nitrogen pressure was set (1.0 – 5.0 MPa), and the reactor was heated up to the required temperature (240 – 300 °C). The moment the reaction temperature reached was chosen as a reaction beginning. The process was performed for 3 h. The samples of the liquid and gaseous phase were taken after the cooling of the reactor to maintain the phase equilibrium.

For the co-processing of bio-oil and straight-run diesel, the experiments were carried out according to the same procedure as it was used for the model compounds under the chosen reaction conditions.

2.5 Co-processing product analysis

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 50 °C was maintained for 5 min then the column was heated up to 270 °C with the rate of 10 °C/min and kept at 270 °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 °C, the ion source temperature was 260 °C; the interface temperature – 280 °C.

The gas-phase analysis was carried out using gas chromatograph "Crystallux 4000M", equipped with a flame ionization detector and katharometer. To separate the components of the gas mixture, a 2.5 m long and 3.0 mm diameter Packed column filled with granules of polymer adsorbent MN-270 (Purolight Inc., UK) with a fraction of 125-250 μm was used. The gas-phase analysis was carried out under the following conditions: initial temperature of the column 40 °C, maintained for 4 min, then, the temperature was raised to 250 °C at a

heating rate of 15 °C/min; a temperature of the evaporator and the detector 260 °C; carrier gas – helium; total flow He 30.0 mL/min. For the quantitative analysis, the calibration curves in terms of the dependence of reaction mixture compound concentration on the peak area were used.

3. Results and discussion

3.1 Wood waste pyrolysis and the bio-oil composition

To study the influence of the catalyst on the wood waste pyrolysis, the experiments were carried out without the catalyst, in the presence of pure zeolite, and in the presence of Fe-ZSM-5 obtained according to Section 2.1. The comparison of the product yield and the composition of bio-oil for both pine wood and birch sawdust was performed. Figure 1 presents the yields of the gaseous, liquid, and solid products obtained at 500 °C.

The presence of catalyst strongly affects the formation of gaseous and liquid products of the pyrolysis increasing their yield for both birch and pines wood. A decrease in the solid residue yields while using the catalyst in the pyrolysis was noted by different scientists (Huber et al., 2006). Besides, an increase in the calorific value of pyrolysis gases was observed when the zeolite and the catalyst were added to the feedstock. For example, the heat of the combustion for gases obtained in the birch sawdust pyrolysis increased from 6.2 to 8.1 kJ/L because of an increase in methane concentration (from 3.4 up to 7.2 wt. %). For pinewood sawdust, the calorific value of gases increased from 8.7 to 10.1 kJ/L when methane concentration rose from 2.3 to 3.4 wt. %.

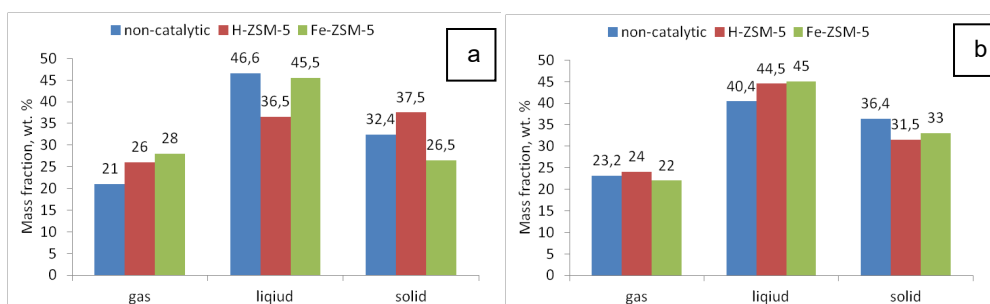
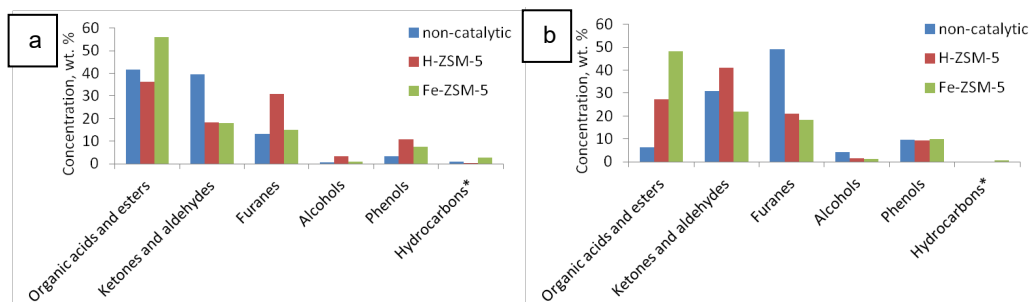


Figure 1: Yield of gaseous, liquid, and solid products of the pyrolysis: (a) birch sawdust, (b) pinewood sawdust

Analysis of the pyrolysis liquid showed that the presence of zeolite and the synthesized catalyst (Figure 2) increases the concentration of lignin decomposition products (anisole, guaiacol, ethyl guaiacol, acetogvayacol, syringol, etc.), as well as low-molecular oxygen-containing products of cellulose and hemicelluloses decomposition (acetic acid and its derivatives, ketones) (Isa and Ganda, 2018). A negligible amount of monoaromatic (benzene, toluene) and polyaromatic (naphthalene, methyl naphthalene) compounds were observed in the presence of the catalyst (2.8 and 0.5 wt. % for birch and pine wood respectively).



*Mainly mono- and polyaromatics

Figure 2: Bio-oil composition dependence on the catalyst presence: (a) birch sawdust, (b) pinewood sawdust

The zeolite-based catalyst seems to accelerate the decomposition of the lignin component in wood leading to an increase in both gas and liquid yield and reducing the weight of the solid residue.

3.2 Model compound conversion

To determine the optimal conditions for the co-processing of bio-oil and petroleum, the experiments were carried out using the mixture of the model compounds (anisole – eicosane – dibenzothiophene 1:1:1 by mass). First, the solvent allowing the maximum conversion and gasoline- and diesel-range hydrocarbons to be reached was chosen. Three solvents in the supercritical state were used: n-hexane ($T_c = 234.7\text{ }^\circ\text{C}$, $P_c = 3.03\text{ MPa}$), methanol ($T_c = 240\text{ }^\circ\text{C}$, $P_c = 7.95\text{ MPa}$), propanol-2 ($T_c = 235.6\text{ }^\circ\text{C}$, $P_c = 5.37\text{ MPa}$). The process was carried out at $250\text{ }^\circ\text{C}$ and the initial nitrogen pressure was 1.5 MPa . After reaching the reaction temperature, the pressure increased up to $6.5\text{--}8.2\text{ MPa}$.

The use of the supercritical hexane led to the formation of BTX (benzene-toluene-xylene) products from anisole, while eicosane tended to be converted into decane and decene (see Table 1). The dibenzothiophene conversion products were nonsaturated and saturated branched hydrocarbons with the carbon number 7-10. These results are in contrast to the common dibenzothiophene conversion product – biphenyl (Ates et al., 2014). The conversion degree of the model compounds used did not exceed 85, 62, and 48 wt. % for anisole, dibenzothiophene, and eicosane respectively. When using alcohols as a solvent, the conversion rose to 92 wt. % for all compounds in propanol-2 and up to 87 wt. % in methanol. This can be explained by the polar nature of the alcohols allowing better interaction of the reaction mixture with the hydrophilic surface of the catalyst and better reactants adsorption in its pores. Being the hydrogen donors, alcohols also led to the formation of saturated linear hydrocarbons (decane) from eicosane, while anisole and dibenzothiophene were converted in BTX. Also, small concentrations of cyclohexane, methylcyclohexane, and cyclohexanols were observed in the reaction mixture. Propanol-2 was chosen as the optimal solvent because of the highest conversion of the model compounds. In the chosen solvent, the experiments on the influence of the reaction temperature and pressure on the conversion of the model compound mixture were carried out.

Table 1: Solvent influence on the model compound mixture conversion

Solvent	Conversion, wt. %				Product yield, wt. %		
	anisole	eicosane	dibenzothiophene	BTX	C ₇ -C ₁₀ alkanes	C ₇ -C ₁₀ alkenes	Cyclohexanes
n-Hexane	84.8	48.0	61.9	29.1	8.7	27.0	0.0
Methanol	96.7	85.1	87.2	61.0	27.8	2.7	3.5
Propanol-2	98.2	91.8	92.4	59.3	30.4	0.5	4.2

The studies on the temperature influence on the conversion of the model compound mixture were carried out at the initial nitrogen pressure of 1.5 MPa . The temperature varied from $240\text{ to }280\text{ }^\circ\text{C}$. The mixture of the model compounds consisted of anisole – eicosane – dibenzothiophene 1:1:1 by mass. The results obtained are presented in Table 2.

Table 2: Temperature influence on anisole – eicosane – dibenzothiophene mixture co-processing

Temperature, $^\circ\text{C}$	Conversion, wt. %				Product yield, wt. %		
	anisole	eicosane	dibenzothiophene	BTX	Decane	Decene	Cyclohexanes
240	87.4	82.3	84.6	56.0	27.3	2.5	1.3
250	98.2	91.8	92.4	59.3	30.4	0.5	4.2
260	100.0	98.6	99.2	58.4	32.8	0.0	7.9
270	100.0	100.0	100.0	57.4	33.3	0.0	9.3
280	100.0	100.0	100.0	54.1	33.3	0.0	12.6

The data obtained show that an increase in temperature leads to an increase in conversion of model compounds reaching 100 wt. % at $270\text{ }^\circ\text{C}$. As the decane yield was found to reach the constant values, the eicosane was proposed to proceed through the cracking, while BTX is the product of the conversion of anisole and dibenzothiophene. The hydrogenation of both unsaturated and aromatic products takes place when the reaction temperature rises. This can be explained by the faster dehydrogenation of propanol-2 over the catalyst used at the higher temperature. Based on the experiment results, $260\text{ }^\circ\text{C}$ was chosen to be the optimal temperature for anisole – eicosane – dibenzothiophene mixture co-processing as it allows almost 100 % removal of oxygen and sulfur from the feedstock also providing the high yield of C₆-C₁₀ hydrocarbons.

The studies on the initial nitrogen pressure influence on the conversion of the model compound mixture were carried out at a temperature of $260\text{ }^\circ\text{C}$. The mixture of the model compounds consisted of anisole – eicosane – dibenzothiophene 1:1:1 by mass. The initial nitrogen pressure varied from $1.5\text{ to }3.0\text{ MPa}$. The total pressure in the reactor was $7.5\text{--}11.0\text{ MPa}$. The results obtained are presented in Table 3.

Table 3: Initial nitrogen pressure influence on anisole – eicosane – dibenzothiophene mixture co-processing

Nitrogen pressure, MPa	Conversion, wt. %			Product yield, wt. %			
	anisole	eicosane	dibenzothiophene	BTX	Decane	Decene	Cyclohexanes
1.5	100.0	98.6	99.2	58.4	32.8	0.0	7.9
2.0	100.0	100.0	100.0	60.1	33.3	0.0	7.6
2.5	100.0	100.0	100.0	59.7	33.3	0.0	7.2
3.0	100.0	100.0	100.0	59.4	33.3	0.0	6.9

When the pressure increases, a slight decrease in cyclohexane formation is observed. This can be explained by the lower rate of hydrogen formation through the dehydrogenation of propanol-2 and, thus, the lower rate of aromatic product hydrogenation. The pressure influence on the reaction is negligible and serves mainly for providing the solvent supercritical state. An increase in nitrogen pressure over 1.5 - 2.0 MPa is not desirable.

3.3 Co-processing of bio-oil and straight run diesel

For the study of co-processing of the real feedstock, the bio-oil obtained by the pyrolysis of birch and pine wood sawdust in the presence of Fe-ZSM-5 catalyst as well as the straight run diesel were used. The composition of bio-oil is presented by mainly oxygen-containing compounds (97.2 and 99.5 wt. % for birch and pine wood sawdust respectively) (see Figure 2). The composition of the straight-run diesel fraction is represented by n- and isoparaffin hydrocarbons (57%), naphthenic compounds (12%), monoaromatic compounds (20%), polyaromatic hydrocarbons (8.5%), and benzo- and dibenzothiophene derivatives (2.5 %). The processing was carried out at the reaction conditions chosen in the study of model compound mixture conversion: solvent – propanol-2, reaction temperature – 260 °C, initial nitrogen pressure – 1.5 MPa, total pressure – 7.2 MPa. First, the conversion of straight-run diesel and bio-oil was studied separately to identify the main products. The analysis of the liquid and gaseous phase of bio-oil conversion using propanol-2 as a solvent showed the formation of benzene, toluene, phenols, alcohols, and light hydrocarbons. The oxygen removal reached values above 85 % after 180 min of the process (see Figure 3).

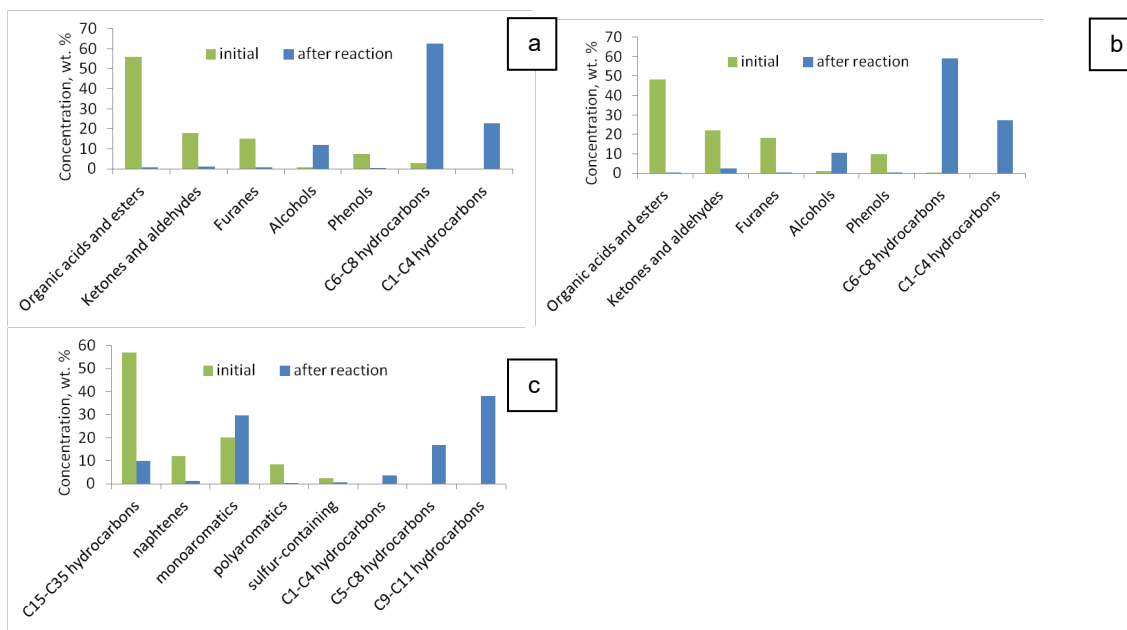


Figure 3: Bio-oil composition dependence on the catalyst presence: (a) bio-oil from birch sawdust, (b) bio-oil from pinewood sawdust, (c) straight run diesel

For straight-run diesel, partial hydrogenation of mono- and polyaromatic compounds was observed, and an increase in the light fraction (including monoaromatic compounds) was also observed. The concentration of sulfur-containing hydrocarbons was found to decrease by 70 %. The maximum of linear and isomeric hydrocarbons was found to be for C₉-C₁₁ alkanes (Figure 3c).

When the co-processing was carried out, the mixture contained 1 g of bio-oil and 1 g of straight-run diesel in 30 mL of propanol-2. The process conditions were the following: reaction temperature – 260 °C, initial nitrogen

pressure – 1.5 MPa, total pressure – 7.2 MPa, catalyst mass – 0.1 g. No oxygen- and sulfur-containing compounds, as well as heavy and polyaromatic hydrocarbons, were observed in the reaction mixture after 3 hours of the experiment. The resulting product contained 39.3 wt. % of C₉-C₁₁ hydrocarbons, and 54.9 wt. % of C₅-C₈ hydrocarbons including BTX. BTX content was found to be 31.8 wt. %. Also, 5.9 wt. % of light gaseous alkanes were obtained. Thus, the co-processing of bio-oil and heavy petroleum can be considered a promising approach for the production of high-quality liquid fuel.

4. Conclusions

The studies presented in this work showed that the co-processing of bio-oil and heavy petroleum is a prospective way for liquid fuel production. The use of supercritical propanol-2 allows the full conversion of the feedstock to be reached for 3 hours. Based on the experimental data the optimal reaction conditions for the co-processing of bio-oil obtained by the pyrolysis of wood waste and straight run diesel were found: solvent – propanol-2, reaction temperature – 260 °C, initial nitrogen pressure – 1.5 MPa, total pressure – 7.2 MPa, catalyst mass – 0.1 g. At these conditions, the resulting product of the co-processing contains 39.3 wt. % of C₉-C₁₁ hydrocarbons, and 54.9 wt. % of C₅-C₈ hydrocarbons including BTX. For the further studies, the possibility of the application of the developed technology for other feedstock (i.e. vegetable oil, bio-diesel, vacuum gasoil) will be investigated. Also, the analysis of the economic and environmental impact of the co-processing in comparison with the crude oil will be performed.

Acknowledgments

The authors thank the Russian Science Foundation (grant 19-79-10061) for the financial support.

References

- Ates A., Azimi G., Choi K.-H., Green W.H., Timko M.T., 2014, The role of catalyst in supercritical water desulfurization, *Applied Catalysis B: Environmental*, 147, 144–155.
- Chalov K., Lugovoy Y., Kosivtsov Y., Stepacheva A., Sulman M., Molchanov V., Smirnov I., Panfilov V., Sulman E., 2017, Petroleum-containing residue processing via Co-catalyzed pyrolysis, *Fuel*, 198, 159-164.
- Choi Y.S., Elkasabi Y., Terves P.C., Mullen C.A., Boateng A.A., 2018, Co-cracking of bio-oil distillate bottoms with vacuum gas oil for enhanced production of light compounds, *Journal of Analytical and Applied Pyrolysis*, 132, 65-71.
- Huber G.W., Iborra S., Corma A., 2006, Synthesis of transportation fuels from biomass: chemistry, catalysts, and engineering, *Chemical Reviews*, 106, 4044–4098.
- Isa Y.M., Ganda E.T., 2018, Bio-oil as a potential source of petroleum range fuels, *Renewable and Sustainable Energy Reviews*, 81, 69-75.
- Lugovoy Y.V., Chalov K.V., Sulman E.M., Kosivtsov Y.Y., 2018, Thermocatalytic refining of gaseous products produced by fast pyrolysis of waste plant biomass, *Chemical Engineering Transactions*, 70, 385–390.
- Pontes N.S., Silva R.V.S., Ximenes V.L., Pinho A.R., Azevedo D.A., 2021, Chemical speciation of petroleum and bio-oil coprocessing products: Investigating the introduction of renewable molecules in refining processes, *Fuel*, 288, 119654.
- Santillan-Jimenez E., Pace R., Morgan T., Behnke C., Sajkowski D.J., Lappas A., Crocker M., 2019, Co-processing of hydrothermal liquefaction algal bio-oil and petroleum feedstock to fuel-like hydrocarbons via fluid catalytic cracking, *Fuel Processing Technology*, 188, 164-171.
- Stepacheva A., Markova M., Gavrilenko A., Dmitrieva A., Sulman M., Matveeva V., Sulman E., 2020, co-processing of oil and bio-oil in the medium of supercritical solvent mixture, *Chemical Engineering Transactions*, 81, 169-174
- Stepacheva A.A., Markova M.E., Schipanskaya E.O., Matveeva V.G., Sulman M.G., 2021, Highly effective schungite-based catalyst for deoxygenation of biomass components, *Chemical Engineering Transactions*, 88, 283-288.
- Wang H., Meyer P.A., Santosa D.M., Zhu C., Olarte M.V., Jones S.B., Zacher A.H., 2021, Performance and techno-economic evaluations of co-processing residual heavy fraction in bio-oil hydrotreating, *Catalysis Today*, 365, 357-364.
- Wu L., Qi Z., Wang Y., Zheng L., 2020, Multi-objective Optimization of co-processing of bio-oil and vacuum gas oil: a survey of gasoline selling price and bio-oil co-processing ratio, *Computer Aided Chemical Engineering*, 48, 1717-1722.
- Zhang M., Hu Y., Wang H., Li H., Han X., Zeng Y., Xu C.C., 2021, A review of bio-oil upgrading by catalytic hydrotreatment: Advances, challenges, and prospects, *Molecular Catalysis*, 504, 111438.