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Oil Residue Pyrolysis Process in the Presence of Aluminosilicates

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This paper presents a study of the pyrolysis process of oil residues in the presence of catalysts based on natural and synthetic aluminosilicates. The process of fast thermal decomposition was studied in a continuous reactor at a residence time of feedstock in the reaction zone less than 20 s. The optimum temperature of oil-sludge decomposition was determined taking into account the yield of gaseous and liquid pyrolysis products. The optimal pyrolysis temperature for the studied feedstock was found to be 600 °C. The study of the effect of the aluminosilicates on the oil-sludge thermal decomposition showed that among the studied catalysts, zeolites were found to be the most active. The highest yield of gaseous and liquid products was observed In the presence of three-dimensional porous pentasil zeolite H-ZSM-5. H-ZSM-5 was found to provide the 40 wt. % yield of liquid and 13.5 wt/ % of gaseous products during the fast oil-sludge pyrolysis at the optimal temperature. In order to reduce the cost of the catalyst used, a catalyst representing a mixture of zeolite H-ZSM-5 and bentonite clay was synthesized. This catalyst also showed high activity in the process of oil-containing residue composition providing 36 w. % yield of liquid products and 10 wt. % of gaseous products. It is interesting to note, that in the presence of the mixed catalyst the highest yield of light liquid fraction (50 wt. %) was obtained.

1. Introduction

Oil production and processing, as well as the synthesis of oil-related products, involve the formation of oil residue. Oil residue represents a complex mixture mainly consisting of saturated and non-saturated hydrocarbons, aromatics, resins, asphaltenes, and a mineral fraction (i.e. silica, alumina etc.) (Bokovikova et al., 2011).

However, oil-containing waste can be a valuable source of energy and chemicals. Among different methods of oil-sludge processing thermal decomposition methods such as pyrolysis (Lam et al., 2016), gasification (Moltó et al., 2013), combustion (Yaman et al., 2004) and co-pyrolysis (Deng et al., 2016) are the most investigated.

Compared to other methods of thermal treatment, catalytic pyrolysis has a number of advantages: low process temperatures (400 - 650 °C) (Kaminsky and Zorriqueta, 2007), and low sensitivity to the feedstock composition (Sulman et al., 2009). Valuable gaseous and liquid products, mainly hydrocarbons, are the main products obtained during the thermal destruction (AlHumaidan et al., 2015). The product composition depends on the nature of oil residue, process conditions and the presence of the catalyst (Barbarias et al., 2015).

Catalytic pyrolysis is one of the widely used methods of oil-containing residual thermal processing, because the use of catalysts promotes the growth of the effectiveness of organic compounds processing (Huber et al., 2006). The process is carried out at rather low temperatures (400–700 °C) (Barneto et al., 2014) mostly in nitrogen atmosphere (Conesa Moltó et al., 2014). The decrease in the process temperature is caused by the additional thermal conductivity of the solid catalyst. Natural aluminosilicates (Muraza, 2015), zeolites (Tripathi et al., 2015) and Ni-Mo-containing catalyst (Miskolczi et al., 2015) are used as catalysts.

Among the catalysts used in pyrolysis, zeolites demonstrate high catalytic activity in cracking and dehydrogenation reactions. Li et al. (2012) studied the process of waste pyrolysis using a ZSM-5 zeolite catalyst. The use of this type of zeolite leads to an increase in the yield of hydrocarbon products, including alkylated

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phenols and aromatic compounds. In another work (Antal et al., 2003), the effect of synthetic aluminosilicates (ZSM-5, Y, Mordenite) in the cracking process was studied. The use of the ZSM-5 catalyst led to an increase in the yield of light hydrocarbons in comparison with other studied catalytic systems. ZSM-5 and Mordenite showed high selectivity to the formation of aromatic and aliphatic hydrocarbons. The use of aluminosilicate catalysts in the cracking process leads to an increase in the yield of liquid products. ZSM-5 results in the increase in the yield of gasoline fraction, while Y and Mordenite, in contrast, increase the yield of the kerosene fraction (Mohan et al., 2006).

According to the literature, the study of the effect of catalysts based on aluminosilicates in the pyrolysis of oil residues is of scientific interest. In the current work, the catalytic activity of the synthetic aluminosilicates was studied and compared with that obtained for the natural aluminosilicates. In order to reduce the cost of the catalyst used, a catalyst representing a mixture of zeolite HZSM-5 and bentonite clay was also tested.

2. Experimental

Both natural aluminosilicates (kaolin, bentonite) and synthetic zeolites (H-Beta-25 and H-ZSM-5) were used as the catalysts for low-temperature fast pyrolysis of oil residue. The zeolites were purchased from Zeolyst International, USA, and used as received. The catalyst in the form of a mixture of natural (bentonite) and synthetic (H-ZSM-5) aluminosilicates was prepared by the mixing of aluminosilicates. To study the process of pyrolysis, samples of oil residue (fuel oil residue) were used. The main characteristics of the used material are presented in Table 1.

Table 1: Oil residue characteristics

Parameter	Value
Density at 15 °C (kg/m^3)	992
Dynamic viscosity at 100 °C (mm^2/s)	28
S (wt. %)	2.3
H_2O (wt. %)	1.1
Ash content (wt. %)	0.11

The study of oil residue pyrolysis was carried out with laboratory pyrolysis set up shown in Figure 1. 25 g of oil residue was loaded into the batch hopper 1. The system was sealed and purged by a flow of inert gas (nitrogen) during 4–5 min. The feedstock supply and its residence time in the reactor were controlled by the feeding screw. The residence time of the feedstock in the hot region of the reactor was less than 20 s. The temperature was varied in the range 500-750 °C and was maintained by the electric furnace 3 which heated the reactor 2. The solid carbon residue of pyrolysis was accumulated in discharge hopper 5. The formed gaseous products passed through condenser 7, and the condensed liquid fraction of pyrolysis products was collected in system 6. The laboratory setup allows separating liquid products into two oil fractions: light and heavy. The formed gaseous products were purified from the ash in filter 8. The refined gases were collected in eudiometer 9.

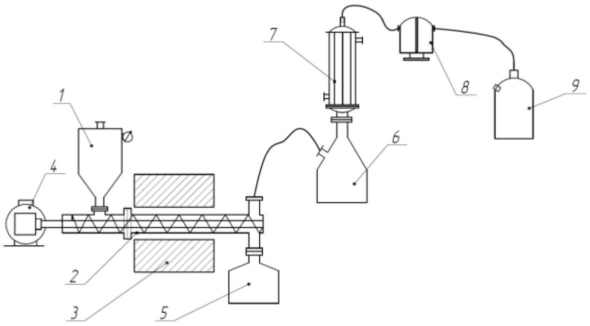

Figure 1: Experimental setup for oil residue pyrolysis: 1 – batch hopper; 2 – continuous reactor; 3 – electric furnace; 4 – electric motor; 5 – discharge hopper; 6 – collection system of liquid products; 7 – condenser; 8 – filter; 9 – eudiometer.

During the experiment, the rate of gaseous products evolution was controlled by eudiometer. At the end of the experiment, the weights of solid residue (according to the change of the reactor weight), liquid fraction (according to water trap), and gas (according to the difference of the initial sample and liquid and solid residue weight) were determined.

In order to analyze the composition (hydrocarbons, CO, CO_2, H_2) and to estimate the heat capacity of the gaseous mixture the gas chromatographs (Crystallux 4000M, GAZOKHROM 2000) and a specially developed analyzer of the specific heat of combustion on the base of a flame-temperature detector, were used. The chromatographic analysis of hydrocarbons in the gaseous mixture was carried out on the chromatograph Crystallux 4000M (Table 2).

Table 2: Chromatographic analysis conditions

Parameter	Value
Crystallux 4000M	
Consumption of gas-carrier (nitrogen)	120 mL/min
Gas-carrier pressure	1.5 kg s/sm^3
Duration of the analysis	30 min
Sample volume	1 mL
Carrier-silica gel	0.4 mm
Column length	1 m
column temperature	50 °C
detector temperature	150 °C
GAZOKHROM 2000	
the flow rate of the gas-carrier (helium)	30 mL/min
sample volume	0.5 mL
thermostat temperature	40 °C

3. Results and Discussion

Figure 2 shows the data of the yields of gaseous, liquid and solid pyrolysis products. As can be seen from the presented data, at a temperature of 500 °C the yield of gaseous products and solid carbonaceous residue were found to be the minimal (5 wt. % and 1 wt. % respectively). At this temperature, the yield of light oil fraction was about 22 wt. %, and heavy oil fraction was the main product.

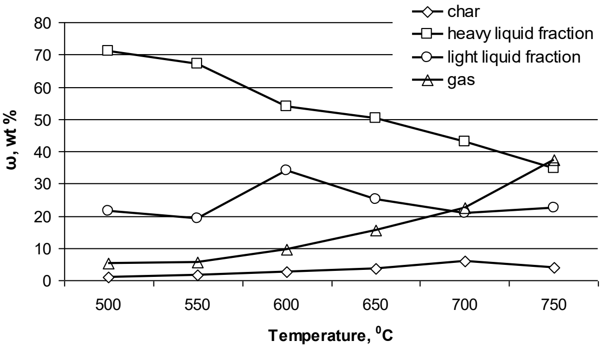

Figure 2: Dependence of oil residue pyrolysis products weight percent on the process temperature in the working temperature range 500-750 °C

The yield of solid carbon residue increases slightly from 1 % to 5 % (wt.) with temperature increase from 500 to 700 °C. The further increase in temperature does not lead to the changes in the solid residue yield. The increase in the process temperature leads to a smooth decrease in the yield of heavy petroleum fractions which is reduced by 2 times at a temperature of 750 °C. The dependence of the light oil fraction yield on the temperature has a parabolic character with a maximum at a temperature of 600 °C (the yield of the light fraction increases by 1.5 times compared to that obtained at a temperature of 500 °C). The yield of gaseous products also increases with the increase in the process temperature from 5 to 37 % (wt.) in the range 500-750 ºC. Based on the data of Table 3, with an increase in temperature up to 600 °C, the volume of gases produced increases by 2 times compared to the volume at a temperature of 500 °C, and at a temperature of 750 °C – by 5.8 times. Thus, the increase in the temperature leads to an increase in the rate of radical decomposition of oil hydrocarbons which, in turns, increases the yield of gaseous and light hydrocarbon fractions. The increase in the yield of the solid residue can be connected with the acceleration of the secondary resin and coke formation reactions.

Table 3: Dependence of the volume of the gas on the process temperature

Temperature, °C	V, L/g substrate
500	0.05
550	0.06
600	0.1
650	0.14
700	0.21
750	029

Analysis of gaseous products by gas chromatography showed that the main components were found to be saturated and unsaturated hydrocarbons C_1-C_4, hydrogen and nitrogen, which is a ballast gas. Since the process was carried out in an inert medium (N_2), the formation of carbon monoxide and dioxide was observed in trace amounts. Figure 3 shows the dependence of the hydrocarbon content in the resulting gas mixture on the process temperature.

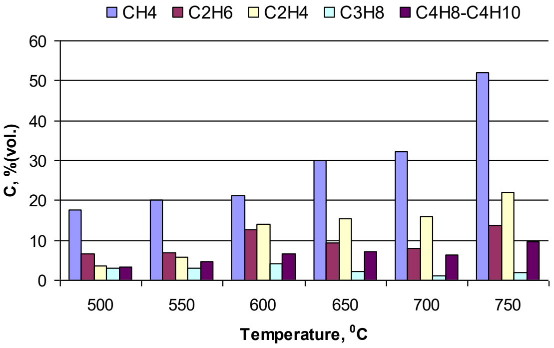

Figure 3: Dependence of the volume of the gaseous hydrocarbons C_1-C_4 on the process temperature

According to the data obtained the increase in temperature leads to the increase in the content of C_1-C_4 hydrocarbons in pyrolysis gas, and, accordingly, to the decrease in the nitrogen content. At a temperature of 600 °C, a significant increase in the content of unsaturated hydrocarbons (ethylene) in the gas was observed. It indicates the behavior of the radical decomposition reactions of hydrocarbons according to the Eq(1):

$$C_nH_{2n+2} \rightarrow C_mH_{2m} + C_pH_{2p+2}, \\ n = m + p \tag{1}$$

where n, m, p are the carbon number.

As the heat of the combustion of the gaseous products is important parameter, the influence of the temperature on the calorific value of pyrolysis gas was estimated. With an increase in the temperature of the process, an increase in the heat of combustion of gases was observed due to an increase in the content of combustible components (Figure 3). In the temperature range of 600 - 700 °C, the heat of combustion of the gas varies slightly and is about 35 MJ/m^3. The optimum temperature of the pyrolysis process was found to be 600 °C. The temperature increase is not cost-effective, since the heat of combustion of pyrolysis gases increases slightly, and the yield of the light oil fraction decreases.

The results on the temperature influence on the oil residue pyrolysis process correlate the data obtained in the previous studies (Schmidt et al., 2001). The increase in the temperature leads to an increase in the yield of gaseous and solid pyrolysis products (Wang et al., 2007). However, the difference in the reactor constriction and chemical composition of the feedstock used does not allow the quantitative comparison of the results.

The study of the effect of aluminosilicates on the process of thermal decomposition of oil residue was carried out at a temperature of 600 °C. Figure 4 show the effect of the catalysts on the yield of solid, liquid and gaseous products.

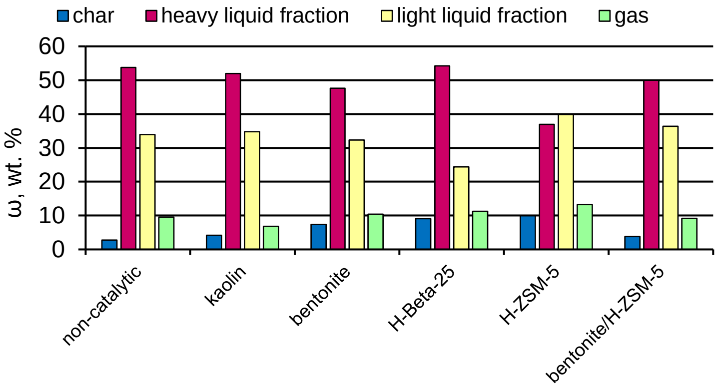

Figure 4: Weight percent of pyrolysis products depending on the catalysts

All studied catalysts increased the yield of solid carbon residue, which indicates the acceleration of the reaction of coke formation on the surface of aluminosilicates. The highest yield of gaseous and liquid products was observed in the presence of zeolite H-ZSM-5. In this case, the yield of gaseous products increased up to 37 wt. %, and light oil fraction increased up to 18 wt. % compared to the non-catalytic process. The yield of the heavy oil fraction, in contrast, was significantly reduced from 54 up to 37 wt. %. The mixed bentonite/H-ZSM-5 catalyst showed relatively high efficiency in the pyrolysis process increasing the yield of the light oil fraction by 8 wt. %.

Figure 5 shows the dependence of the calorific value of pyrolysis gases on the type of catalyst used in the process. According to the data obtained, the use of synthetic zeolites and a mixed catalyst (bentonite/H-ZSM-5) leads to an increase in the total calorific value of gaseous pyrolysis products. In the presence of H-ZSM-5, pyrolysis gases with the highest heat of combustion (by 1.15 times higher than that of the non-catalytic process) were formed.

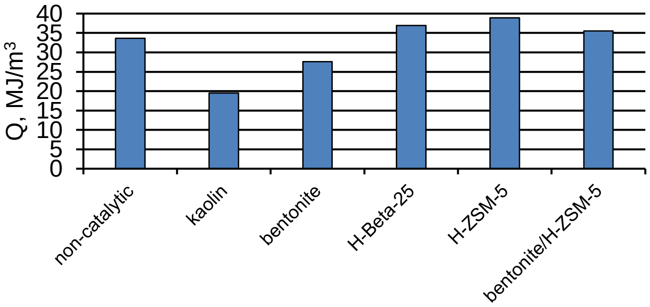

Figure 5: Dependence of the total heat of combustion of pyrolysis gaseous products on the type of the catalyst

Based on the estimation of the zeolite influence on the pyrolysis of the oil-containing residues it can be concluded that the use of zeolites increases the yield of liquid hydrocarbons and changes the composition of the products (Lin et al., 2017).

4. Conclusions

The optimum temperature of oil residue pyrolysis process was determined to be 600 °C. Synthetic aluminosilicates showed the highest activity in the process of oil residue thermal decomposition. These catalysts increased the yield of gaseous products and light oil fraction by the factor 1.5 and 1.3. It was found that the use of H-ZSM-5 zeolite catalysts leads to an increase in C_1-C_4 hydrocarbons concentration. The mixed catalyst had a lower activity than zeolite H-ZSM-5, but its application increases the yield of gaseous products and light oil fractions in comparison with the non-catalytic process. The introduction of bentonite clay into the catalyst reduces its cost, which makes catalytic pyrolysis with the use of a synthesized catalyst promising for industrial applications.

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References

Al Humaidan F, Hauser A, Rana M, Lababidi HMS, Behbehani M., 2015, Changes in asphaltene structure during thermal cracking of residual oils: XRD study, Fuel, 150, 558-564.

Antal M.J., Jr. Grønli M., 2003, The art, science, and technology of charcoal production, Industrial & Engineering Chemistry Research, 42, 1619–1640.

Balat M., Kirtay E., Balat H., 2009, Main routes for the thermo-conversion of biomass into fuels and chemicals. Part 1: Pyrolysis systems, Energy Conversion & Management, 50, 3147–3157.

Barbarias I, Artetxe M, Arregi A, Alvarez J, Lopez G, Amutio M, et al., 2015, Catalytic cracking of HDPE pyrolysis volatiles over a spent FCC catalyst, Chemical Engineering Transactions, 43, 2029–2034.

Barneto AG, Moltó J, Ariza J, Conesa JA., 2014, Thermogravimetric monitoring of oil refinery sludge, Journal of Analytical and Applied Pyrolysis, 105, 8–13.

Bokovikova T.N., Shperber E.R., Shperber D.R., 2011, Elaboration of application methods for trice oil emulsions and oil-slimes, NAFTA, 62(7-8), 253-256.

Conesa Moltó JA, Ariza J, Ariza M, Barneto AG., 2014, Study of the thermal decomposition of petrochemical sludge in a pilot plant reactor, Journal of Analytical and Applied Pyrolysis, 107, 101–106.

Deng S, Wang X, Tan H, Mikulcic H, Yang F, Li Zh, Duic N., 2016, Thermogravimetric study on the co-combustion characteristics of oily sludge with plant biomass, Thermochimica Acta, 633, 69–76.

Huber G.W., Iborra S., Corma A., 2006, Synthesis of transportation fuels from biomass: Chemistry, catalysts, and engineering, Chemical Reviews, 106, 4044–4098.

Kaminsky W., Zorriqueta I.-J.N., 2007, Catalytical and thermal pyrolysis of polyolefins, Journal of Analytical and Applied Pyrolysis, 79 (1-2), 368-374.

Kosov V., Zaichenko V., 2014, Experimental research of heterogeneous cracking of pyrolysis tars, Chemical Engineering Transactions, 37, 211-216.

Lam SS, Liew RK, Jusoh A, Chong CT, Ani FN, Chase HA., 2016, Progress in waste oil to sustainable energy, with emphasis on pyrolysis techniques. Renewable & Sustainable Energy Reviews, 53, 741–753.

Li X., Su L., Wang Y., Yu Y., Wang C., Li X., Wang Z., 2012, Catalytic fast pyrolysis of Kraft lignin with HZSM-5 zeolite for producing aromatic hydrocarbons, Frontiers of Environmental Science & Engineering, 6, 295–303.

Lin B., Wang J., Huang Q., Ali M., Chi Y., 2017, Aromatic recovery from distillate oil of oily sludge through catalytic pyrolysis over Zn modified HZSM-5 zeolites, Journal of Analytical and Applied Pyrolysis, 128, 291-303.

Miskolczi N, Ates F., 2015, Thermo-catalytic co-pyrolysis of recovered heavy oil and municipal plastic wastes, Journal of Analytical and Applied Pyrolysis, 117, 273-281.

Mohan D., Pittman C.U., Steele P.H., 2006, Pyrolysis of wood/biomass for bio-oil: A critical review, Energy & Fuels, 20, 848–889.

Moltó J., Barneto A.G., Ariza J., Conesa J.A., 2013, Gas production during the pyrolysis and gasification of biological and physicochemical sludges from an oil refinery, Journal of Analytical and Applied Pyrolysis, 103, 167–172.

Muraza O., 2015, Hydrous pyrolysis of heavy oil using solid acid minerals for viscosity reduction, Journal of Analytical and Applied Pyrolysis, 114, 1-10.

Schmidt H., Kaminski W., 2001, Pyrolysis of oil sludge in a fluidized bed reactor, Chemosphere, 45, 285-290.

Sulman M., Kosivtsov Yu., Sulman E., Alfyorov V., Lugovoy Yu., Molchanov V., Tyamina I., Misnikov O., Afanasjev A., Kumar N., Murzin D., 2009, Influence of aluminosilicate materials on the peat low-temperature pyrolysis and gas formation, Chemical Engineering Journal, 154, 355-360.

Tripathi AK, Ojha DK, Vinu R., 2015, Selective production of valuable hydrocarbons from waste motorbike engine oils via catalytic fast pyrolysis using zeolites, Journal of Analytical and Applied Pyrolysis, 114, 281–292.

Wang Zh., Guo Q., Liu X., Cao Ch., 2007, Low-temperature pyrolysis characteristics of oil sludge under various heating conditions, Energy & Fuels, 21, 957-962.

Yaman S., 2004, Pyrolysis of biomass to produce fuels and chemical feedstocks, Energy Conversion & Management, 45, 651–671.