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Catalytic Decomposition of Oil Slime in the Presence of Inorganic Salts

Yury. Yu. Kosivtsov*, Kirill V. Chalov, Yury. V. Lugovoy, Esther M. Sulman, Vladimir P. Molchanov

Tver Technical University, Dep. Biotechnology and Chemistry, A.Nikitina str. 22, 170026, Tver, Russia.
kosivtsov@science.tver.ru

In the present paper we report on the results of the process of heavy and residual hydrocarbons thermocatalytic processing with metals chlorides KCl, NaCl, $MgCl_2$, $AlCl_3$, $FeCl_2$, $FeCl_3$, $ZnCl_2$, $CoCl_2$ and $NiCl_2$. The pyrolysis process was carried out with an experimental pyrolysis set-up in a temperature range from 450 to 650 °C. The experimental pyrolysis set-up consists of a metal fixed-bed reactor heated with the electric furnace.

The study of the kinetics of the oil sludge pyrolysis process was carried out using the thermoscales TG 209 F1 (NETZSCH) with different heating rate (1, 5, 10, 15 and 20 °C/min). The oil-containing waste samples with the amount of crude oil 20 %wt. without a catalyst and with 5 %wt. $CoCl_2$ were used for the analysis.

1. Introduction

Oil production, transportation and storage as well as oil-products synthesis involve the formation of oil-containing waste (Bulatov et al., 2004). The world production of crude oil increases every year and amounts 49 billion tons per year. The contribution of the Russian Federation to the global oil recovery budget is about 500 million tons per year, besides the amount of the produced oil-containing waste can reach up to 10 % of the total volume of the produced oil (Kurochkin et al., 2010). Annually tens of thousands of tones of oil-slime are stored in sludge tanks showing irrational and ineffective use of fossil fuel. The significant pollution of the environment is the result of oil spill, waste disposal, and oil waste burning or dumping; that leads to the significant deterioration of the living conditions (Bokovikova et al., 2011). Oil-containing waste mainly consists of heavy and residual hydrocarbons of the oil-products, water and mineral components (sand, clay, metals oxides etc.) which account for their variable composition and complicate their disposal. This is the reason for the development of the green and ecologically friendly technology for oil waste processing mainly to the energy (Krasnogorsky et al., 2004).

The choice of the method of oil-slime processing and decontamination mostly depends on the amount and nature of oil-products part of oil-slime. The methods of treatment resulting in gaseous and liquid fuel formation by thermal treatment are economically more profitable (Shie et al, 2003). The methods of treatment resulting in gaseous (Rasul et al., 2012) and liquid (Braz and Crncovic, 2014) fuel formation by thermal treatment are economically more profitable. The use of the catalysts in the pyrolysis process of oil-slime allows obtaining products which can be used either as fuel (Shie et al, 2000) or raw material for the chemical industry (Barbarias et al., 2015). Compared to other methods of oil-containing waste thermal treatment, the catalytic pyrolysis has a number of advantages: (i) rather low process temperature (400 – 650 °C), (ii) low sensitivity to the feedstock composition and (iii) a closed circuit of processing that comply with the modern requirements of chemical production.

This paper focuses on the investigation of the influence of metal chlorides on catalytic pyrolysis of oil-containing waste. We demonstrate that the highest conversion of oil-containing waste into gaseous and liquid products was observed in the presence of iron subgroup metal chlorides, in particular $CoCl_2$.

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2. Experimental

Model oil-containing waste was prepared from silica sand (fraction 0.1 - 0.4 mm, Voronezh Region oil field, Russian Federation) and from oil from the Caspian field at various weight ratios. As the catalyst used metals chlorides KCl, NaCl, $ZnCl_2$, $MgCl_2 \cdot 6H_2O$, $AlCl_3 \cdot 6H_2O$, $FeCl_2 \cdot 4H_2O$, $FeCl_3 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$ and $NiCl_2 \cdot 6H_2O$.

The study of oil-slime pyrolysis was carried out in a fixed-bed reactor at a temperature range of 450-650^{0}C. The reactor was equipped with an outlet for inert-gas purging. The pyrolysis process was performed in nitrogen. During the experiments the weights of solid, liquid and gaseous products were estimated. In order to analyze the composition (hydrocarbons, CO, CO_2, H_2) and to estimate the heat capacity of the gaseous mixture, the state of-the-art analytic complex including 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.

Thermogravimetric analysis (TGA) was carried out using 209 F1 NETZSCH. The analyses were carried out in argon at a gas rate of 20 mL/min. The samples were heated at a constant rate of 10 ºC/min. When 600 ºC was achieved, the sample was kept under isothermal conditions for 50 minutes.

The analysis conditions were as follows. The sample was heated from 30 up to 500 °C at a heating rate 1, 5, 10, 15 or 20 °C/min with the following 2-hour hold at a temperature of 500 °C, and then it was heated up to 600 °C at the same rate. The analysis was carried out in argon at a gas rate of 20 mL/min.

The mathematical analysis of the experimental data on the thermogravimetric analysis (TGA) of the oil waste pyrolysis process was done using the program software «NETZSCH Thermokinetics 3.1» according to the model-independent methods of Friedman (differential method) and Ozawa-Flynn-Wall (integral method) (Kaisersberger et al., 1991), based on the isoconversion approach, when the reaction rate dα/dt at some degree of conversion is only the function of the temperature.

To determine the kinetic model of the destruction process the non-linear regression mode was used (Fillips et al., 2014; Kaisersberger et al., 1991; Brown et al., 2000). The non-linear regression allows the performance of the direct approximation to the experimental data without the transformations which change the errors structure.

3. Results and Discussion

3.1 Influence of oil-slime composition and the process temperature on the products yield

To estimate the influence of the metals chlorides under study on oil-slime pyrolysis it is necessary to compare the experimental data obtained while using chlorides with the similar data for a non-catalytic process.

During the research the influence of the pyrolysis process temperature on the conversion of the model oil-slime samples was revealed. As it is seen from the experimental data obtained (Figure 1) the optimal temperature of the process is 500 - 550 °C. At this temperature high conversion of oil-slime into gaseous and liquid products is achieved The increase of the process temperature from 550 °C to 650 °C results in a little increase of conversion by 8 %, while the temperature increase demands additional energy costs and thus does not make economic sense.

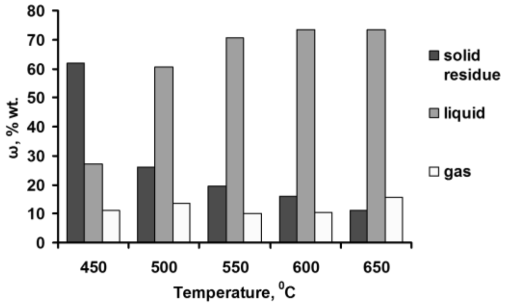

Figure 1: Dependence of oil-slime pyrolysis products weight percent on the process temperature in the working temperature range 450-650 °C

3.2 Influence of the catalysts on oil-slime conversion

At the next step of the research the influence of metals chlorides on the process of oil-slime pyrolysis was studied. The experimental data obtained showed that metals chlorides are highly active in the processes of hydrocarbon raw material pyrolysis (Rasul et al., 2012). In Figure 2 the data on model oil-slime conversion (oil fraction content 20 %wt.) in the presence of metals chlorides at the process temperature of 500 °C are presented. The metals chlorides of iron subgroup are the most active in oil-slime pyrolysis. The maximum increase of weight percent of gaseous and liquid products was observed in case of cobalt chloride and made 41.2 and 8.5 (wt.) accordingly in comparison with a non-catalytic process. Higher catalytic activity of iron group metals chlorides compared to the chlorides of the other metals studied can be explained by average relative acidity of the metals chlorides of iron subgroup in electrophilic processes.

Metals chlorides can be arranged in the following sequence according to the increase of acid sites strength: $KCl>NaCl>NiCl_2>ZnCl_2>CoCl_2>FeCl_2>MgCl_2>FeCl_3>AlCl_3$. The catalysts under study can be divided into 3 groups (Minsker et al., 1995):

a) catalysts with low acidity have low activity or they are not active in the pyrolysis process (KCl, NaCl);

b) catalysts with medium acidity reveal relatively high activity and selectivity ($NiCl_2$, $CoCl_2$, $ZnCl_2$, $FeCl_2$);

c) catalysts with high acidity have high activity but low selectivity ($MgCl_2$, $FeCl_3$, $AlCl_3$.).

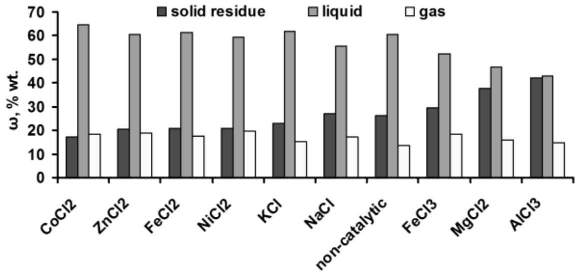

Figure 2: Weight percent of pyrolysis products with the catalysts added (10 % of raw material weight) at t = 500 °C

According to the data presented in Figure 2 the chlorides of alkaline metals showed low activity in the oil-slime pyrolysis. With the increase of electronegativity (within the group) the pyrolysis gaseous products weight increases and the liquid fraction weight decreases. In case of using sodium chloride as a catalyst the percent of gaseous products increased by 20 %wt and the percent of liquid products decreased by 8 %wt in comparison with pyrolysis and in the presence of potassium chloride.

In Figure 3 the dependence of the volume of the gaseous products (hydrocarbons C_1-C_4) formed on the relative acidity of the catalyst used is presented. In case of potassium chloride showing low relative acidity the composition and the volume of the gaseous products does not practically change. The use of the other metals chlorides studied resulted in more than 40 % increase of the gaseous products volume (normal conditions) compared to a non-catalytic process.

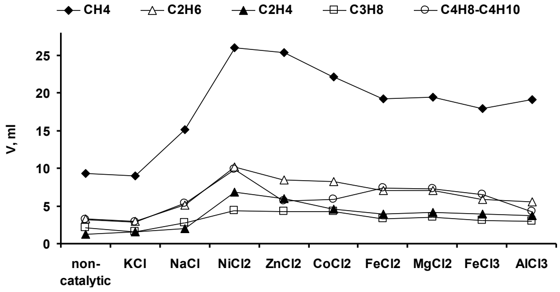

Figure 3: Dependence of the volume of the gaseous hydrocarbons C_1-C_3 (normal conditions) on the type of the catalyst used (10 % of the raw material weight) at t = 500 °C

In the presence of cobalt chloride and nickel chloride the volume of hydrocarbons C_1-C_3 increased by 2.4 and 2.9 times compared to a non-catalytic process.

Several factors can be singled out from the analysis of the influence of different metals chlorides on the yield of gaseous and liquid pyrolysis products (Figures 2, 3):

1) influence of the strength of metals chlorides aprotonic acid sites. According to data the activity and selectivity of the catalysts action in electrophilic processes (destruction, alkylation, hydrogenation and dehydrogenation, resin and coke formation. The catalysts with low acidity are less likely to show their catalytic properties in electrophylic processes while the catalysts with high acidity increase the number of side reactions.

2) influence of electronegativity of chlorides cations on oil-slime pyrolysis.

The heat of combustion of gaseous products is one of the most important characteristics. The influence of the catalysts discussed on this characteristic was studied to apply this method to the oil-slime disposal.

3.3 Study of the pyrolysis process by the methods of thermogravimetric analysis

The influence of cobalt chloride on the oil-slime thermal stability was studied using the method of thermogravimetric analysis (TGA). In the course of pyrolysis process cobalt chloride added increases its catalytic activity with the loss of crystallization water because of the increase of the catalyst acidity at calcinating (Figure 4). Three peaks (I – 124; II – 190; III -215 °C) correspond to the loss of crystallization water weight for the oil-slime sample with 5 % cobalt chloride content (curve 1) (Mishra et al., 1992).

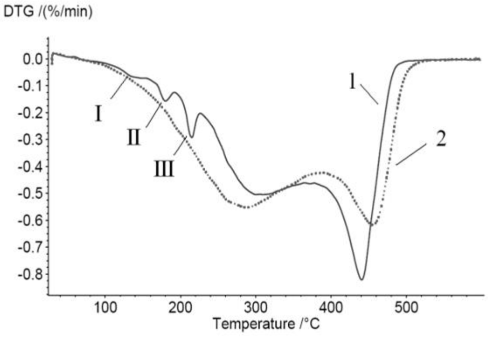

Figure 4: Differential curves of TGA for the studied samples at a heating rate of 10 K/мин: a – dm/dt on temperature; 1- catalyst $CoCl_2 \cdot 6H_2O$; 2 – non-catalytic

As it is seen in the differential curves (Figure 4), the maximum rate of the sample weight loss was observed with the catalyst at a temperature of 440 °C and without it at 465 °C. The use of cobalt chloride decreases the thermal stability of the oil-slime sample that results in the increase of the destruction rate compared to the sample without additions.

The oil-containing waste pyrolysis is the complex process consisting of numerous chemical reactions, so the study of the mechanism of the singular stage is a difficult task. Therefore the reaction order and kinetic parameters of Arrhenius equation are the conditional characteristics that show the sum of various chemical processes and are named the apparent parameters.

In the case of the multi-stage process using Friedman method the information can be obtained only for the initial field. In Figures 5a and 5b the dependences of the logarithm of the samples destruction rate on the reciprocal temperature are shown. In accordance to the given curves, the slope of the lines directly-proportional to the activation energy changes with the increase of the conversion; this can testify the proceeding of the multi-stage pyrolysis process both non-catalytically and in the presence of cobalt chloride. The lines connecting the experimental points in the range $0.02 \le \alpha \le 0.1$ have minor angle of the slope to the x-axis than the lines of isoconversion and, hence, the initial destruction can be described as diffusion-controlled reaction both in the case of non-catalytic and catalytic process.

On the base of isoconversion curves the value of the activation energy and the logarithm of pre-exponential factor were calculated using Friedman and Ozawa-Flynn-Wall methods. The values of kinetic parameters of the Arrhenius equation obtained by two methods are in high convergence. In figures 6a and 6b the kinetic parameters of both non-catalytic and catalytic oil-containing waste pyrolysis are shown. According to the curves the process activation energy depends on the conversion α, this fact verifies the hypothesis on the multi-stage process.

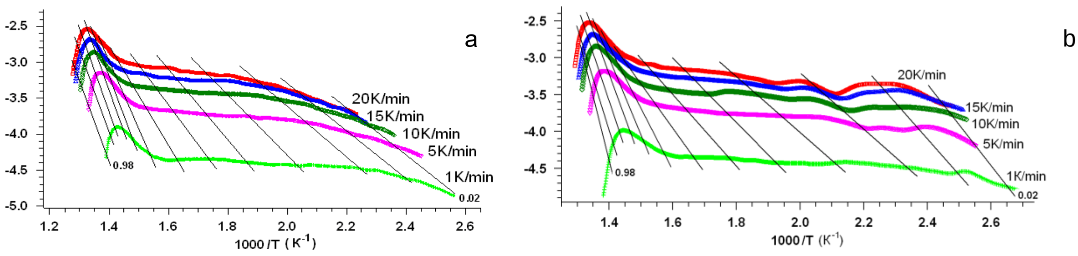

Figure 5: the curves of the rate of samples weight loss in the coordinates log dα/dt–1,000/T, obtained using Friedman method: a – oil-containing waste (non catalytic); b – oil-containing waste +$CoCl_2$ 5 %wt.

Analyzing the data (Figures 6a and 6b), one can suppose that the non-catalytic pyrolysis process of oil-containing waste passes through two stages because the minimum and the maximum of the activation energies at the conversion 0.5 and 0.9 respectively can be defined. In the case of catalytic process, pyrolysis can pass through three stages. It can be explained by the observation of two minima of activation energy at the conversion 0.2 and 0.5 respectively, and at the conversion close to 1.0 the activation energy value essentially increases and reaches more than 235 kJ/mol.

A number of kinetic models were tested taking into account the data of isoconversion analysis methods. The statistical analysis on the base of F-test showed the prevalence of one kinetic model to describe both the non-catalytic and catalytic oil sludge pyrolysis that satisfies the condition of $F_{exp} \leq F_{crit}$ with the value of significance 95 %. According to the obtained models, the non-catalytic pyrolysis process consists of three stages and the catalytic process passes through four stages (Figures 7a and 7b).

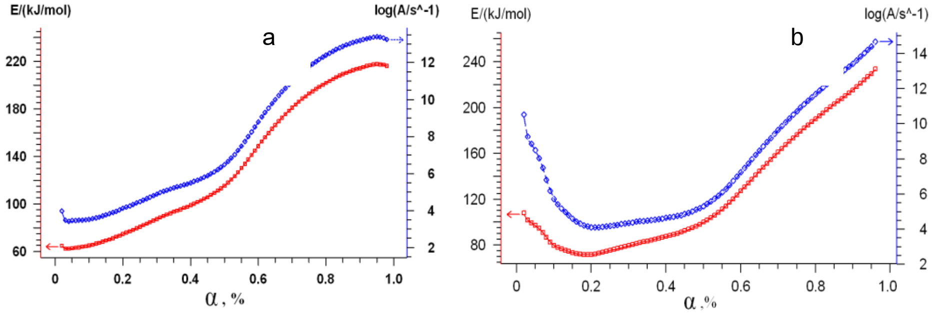

*Figure 6: the dependence of the activation energy and logarithm of the pre-exponential factor on the sample partial weight loss obtained using Ozawa-Flynn-Wall method: **a** – oil-containing waste (non catalytic); b – oil-containing waste +$CoCl_2$ 5 %wt)*

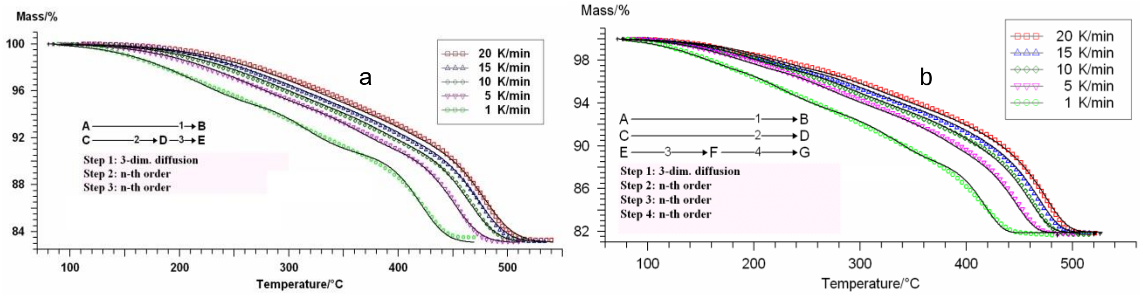

*Figure 7: the weight loss curves of oil-containing waste samples at different heating rates: 1, 5, 10, 15, 20 K/min; **a** – oil-containing waste (non catalytic); b – oil-containing waste +$CoCl_2$ 5 %wt) (Line – computed; symbol – experimental)*

The kinetic parameters are shown in Table 1. It is noteworthy that the obtained kinetic models have a formal character and the chemism of the oil slime pyrolysis process cannot be described only on the base of TGA data.

Table 1: Activation energies (E), pre-exponential factor logarithm (lgA), reaction orders (n) and weighting factors (F) for the models of oil-containing waste pyrolysis (non catalytic and catalytic)

Parameter		Step 1	Step 2	Step 3	Step 4
Ea, kJ/mol	non catalytic	-	72	105	219
	$CoCl_2$ 5 %	154	71	96	197
lgA, c^{-1}	non catalytic	-	3.46	5.89	13.46
	$CoCl_2$ 5 %	16.58	4.66	5.23	11.97
n	non catalytic	-	-	1.4	1.36
	$CoCl_2$ 5 %	-	2.5	1.1	0.9
F, %	non catalytic	-	0.28	0.39	0.33
	$CoCl_2$ 5 %	0.07	0.28	0.37	0.28

According to the data (Table 1), the use of $CoCl_2$ in the oil-containing waste pyrolysis process leads to the decrease of apparent activation energy of thermodestruction process in the two last stages approximately by 10 and 20 kJ/mol, respectively, as well as to the change of the reaction order that can be induced by the catalysis of the destruction process by $CoCl_2$.

4. Conclusions

The influence of metals chlorides on the oil-slime thermal destruction is explained by 2 factors:
- strength of the catalyst aprotonic acid sites;
- cation electronegativity.

Metals chlorides can be arranged in an ascending order according to the influence on the process of hydrogen formation: $MgCl_2$>KCl>NaCl>$FeCl_2$>$AlCl_3$>$FeCl_3$>$CoCl_2$> >$ZnCl_2$>$NiCl_2$.

Cobalt, zinc and nickel chlorides showed the highest catalytic activity in the oil-containing waste pyrolysis while the use of cobalt chloride resulted in the highest degree of conversion into gaseous and liquid products and allowed a 41.2 and 8.5 %wt. increase, respectively, compared to the non-catalytic process. In the presence of cobalt and nickel chlorides the volumes of the C_1-C_4 hydrocarbons increased by factors 2.4 and 2.9, respectively, compared to the non-catalytic process. Therefore, for the model oil-containing waste sample pyrolysis, we recommend catalytic process at 500 °C and at 5 %wt. of cobalt chloride of the oil-containing waste oil fraction weight.

The use of $CoCl_2$ in the oil-containing waste pyrolysis process leads to the change of the destruction mechanism and to the decrease in the process activation energy by 20 - 30 kJ/mol.

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