

Catalytic pyrolysis of heavy and residual hydrocarbons in the presence of metal chlorides

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Abstract—In the present paper we report on the results of the process of heavy and residual hydrocarbons thermocatalytic processing with metals chlorides KCl, NaCl, MgCl₂, AlCl₃, FeCl₂, FeCl₃, ZnCl₂, CoCl₂ и NiCl₂. The higher yield of liquid and gaseous hydrocarbons was obtained in the presence of iron subgroup metal chlorides. On the base of the experimental data the optimal parameters of oil-containing waste pyrolysis were defined as follows: temperature – 500 °C; catalyst – CoCl₂ with the catalyst loading 5% (wt.) of the substrate weight. The kinetic investigation of the pyrolysis process at the optimal conditions was carried out. The activation energy of the catalytic pyrolysis decreased by 20-30 kJ/mol in comparison with non-catalytic process.

Keywords— Thermocatalytic processing, pyrolysis, heavy and residual hydrocarbons, metals chlorides, gaseous hydrocarbons.

I. INTRODUCTION

THE main source of the heavy and residual hydrocarbons is the waste of oil crude refining. The world crude oil production increases every year and at present amounts to 49 billions tons per year. The contribution of the Russian Federation to the global oil recovery budget is about 500 millions 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 [1], [2]. The significant pollution of the environment is the result of oil spill, waste disposal, oil waste burning or dumping; that leads to the significant deterioration of the living conditions. The oil-containing waste can be obtained at all the stages of processing, storage, transportation and the use of oil. It also requires the vast area for the earthen containers and sludge collectors, resulting in the energy carrier price rise [2]-[6].

The existing methods of oil-containing waste processing can be divided into physical, chemical, physicochemical, thermal and biological [7], [8]. The choice of the method of oil-containing waste processing and decontamination mostly depends on the amount and nature of oil-products in oil-containing waste. The methods of oil-containing waste

processing used in industry are quite expensive and time consuming, so the volume of oil-containing waste processing is much lower than the volume of its formation [7]. The thermal treatment resulting in gaseous and liquid fuel formation is considered to be the most economically beneficial [8], [9]. Besides oil waste sensible utilization can be an essential step towards the development of resource-saving technology on the basis of the integrated use of oil raw material.

Thus, non-catalytic pyrolysis of oil-containing waste was studied for many years [10]-[13], but high energy consumption and other shortcomings made this process unappealing. Catalytic pyrolysis of oil-containing waste allows obtaining hydrocarbons which can be used either as fuel or raw material for the chemical industry [8], [9], [14]. Compared to other methods of oil-containing waste thermal treatment, catalytic pyrolysis has a number of advantages: (i) rather low process temperatures (400-650 °C), (ii) low sensitivity to the raw material composition and (iii) a closed circuit of processing that comply with the modern requirements of chemical production. The use of the catalysts in the pyrolysis process allows increasing the yield and quality of valuable products and decreasing the process reaction temperature [15]-[17]. The practical application of this method will contribute to the solution of the problem of oil waste disposal and thus to the development of thermal catalytic processing of organic waste with obtaining valuable final products.

Catalytic pyrolysis of a number of organic compounds (wood, polymers, hydrocarbons) has been recently studied with metal chlorides as catalysts [18]-[20]. However, to the best of our knowledge, no catalytic studies of metal chlorides in pyrolysis of oil-containing waste have been published.

This paper focuses on the study 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 for CoCl₂. The substantial increase of the conversion into gaseous and liquid products for this metal salt indicates that the catalytic pyrolysis of oil-containing waste is promising for industrial exploration.

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II. EXPERIMENTAL

A. Materials

THE chemical grade metals chlorides KCl, NaCl, ZnCl₂, MgCl₂·6H₂O, AlCl₃·6H₂O, FeCl₂·4H₂O, FeCl₃·6H₂O, CoCl₂·6H₂O and NiCl₂·6H₂O were purchased from Reakhim (Moscow) and used as received.

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. The oil used possesses the following characteristics: the oil density (at 20 °C) is 860±2 kg/m³; the dynamic viscosity (at 20 °C) is 3.39 MPa·s; the sulphur content is 0.16%; the paraffin content is 20.04 wt. %; the tar content is 5.2% (wt.); the asphaltene content is 0.94% (wt.); the fraction yield (according to the true boiling point) is 19.0% (wt.) up to 200 °C and 45.0% (wt.) up to 360 °C.

B. Pyrolysis procedure

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, a gas sampler, a water trap for collecting liquids, and a eudiometer for collecting gas. The reactor was equipped with an outlet for inert-gas purging. The pyrolysis process was performed in nitrogen. Inert gas purging was carried out before the experiment. The weight of the oil-containing waste studied was varied depending on the oil fraction concentration. Oil fraction weight was constant (2 g). The oil-fraction content in oil-containing waste varied from 10 up to 100% (wt.) due to the change of mineral fraction weight. The catalyst content of oil-containing waste was from 1 up to 10% (wt.) of the oil-fraction weight. The catalyst was introduced into the oil-containing waste in the form of solid salt. The duration of the experiment was an hour and a half. Each procedure was repeated at least three times to insure reproducibility of the results.

After the completion of the experiment the following parameters were determined: solid residue weight according to the change of the reactor weight; liquid fraction weight according to water trap and sampler weight; gas weight according to the difference of the initial sample and liquid and solid residue weight. Standard deviation for the pyrolysis products is ±0.5% (wt.) from weight measurements. In order to analyze the composition (hydrocarbons, CO, CO₂, H₂) 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. The chromatographic analysis of hydrocarbons in the gaseous mixture was carried out on the chromatograph Crystallux 4000M under the following conditions: the consumption of gas-carrier (nitrogen) 120 mL/min; gas-carrier pressure

1.5 kg·s/sm³; 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 100 °C. Volume concentrations of nitrogen, carbon oxide and methane were analyzed on the chromatograph GAZOKHROM 2000. The flow rate of the gas-carrier (helium) was 30 cm³/min; sample volume of the gas analysed was 0.5 cm³; thermostat temperature was 40 °C.

C. Characterization

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.) CoCl₂ were used for the analysis.

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) [21], based on the isoconversion approach, when the reaction rate $d\alpha/dt$ at some degree of conversion is only the function of the temperature:

$$\frac{d\alpha}{dt} = A \cdot \exp\left(-\frac{E}{RT}\right) \cdot f(\alpha) \quad 1$$

where A – pre-exponential factor, E – activation energy, R – gaseous constant, T – temperature.

To determine the kinetic model of the destruction process the non-linear regression mode was used [22-24]. The non-linear regression allows the performance of the direct approximation to the experimental data without the transformations which change the errors structure.

The regression value is calculated by the quintic method of Runge-Kutta with the use of embedded formula of Prince-Dormand for the automatic optimization of the quantity of significant figures. To minimise the deviation and its sum of squares the upgrade version of hybrid procedure was used [25].

The statistical comparison of different models was done using F-test where the requirement $F_{\text{exp}} < F_{\text{crit}}$ must be valid, F_{exp} – F-test, F_{crit} – statistical fractal.

The metal content was determined by X-ray fluorescence analysis (XFA) measurements performed with a Spectroscan – Maks – GF1E spectrometer (Spectron, St-Petersburg, Russia) equipped with Mo anode, LiF crystal analyzer and SZ

detector. The analyses were based on the Co K α line.

III. RESULTS AND DISCUSSION

To estimate the influence of the metal chlorides under study on oil-containing waste pyrolysis, we compared the pyrolysis data with such catalysts as KCl, NaCl, ZnCl₂, MgCl₂·6H₂O, AlCl₃·6H₂O, FeCl₂·4H₂O, FeCl₃·6H₂O, CoCl₂·6H₂O and NiCl₂·6H₂O and without them.

A. Influence of oil-containing waste composition and the process temperature on the products yield in the non-catalytic process

Large figures and tables may span both columns. Place First, the non-catalytic pyrolysis with oil-containing waste containing 20% (wt.) of oil was studied. The pyrolysis temperature was varied between 450 and 650 °C. Figure 1 shows that below 500 °C, the product contains a high fraction of solid residue. At the 500-550 °C high conversion of oil-containing waste into gaseous and liquid products is achieved. The increase of the process temperature from 550 to 650 °C results in an 8% increase of conversion, however, this temperature increase requires additional energy, making it economically unfavorable. Thus, the 500-550 °C can be considered as an optimal pyrolysis temperatures.

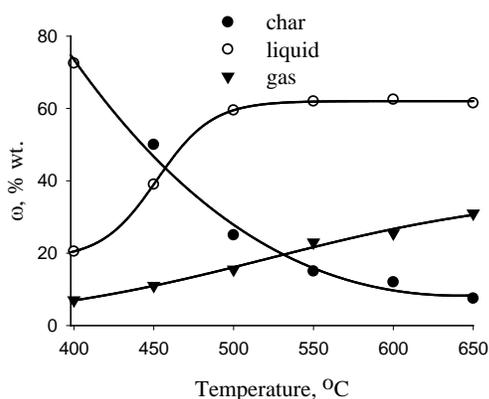


Fig.1 dependence of oil-containing waste pyrolysis products weight percent on the process temperature in the working temperature range 450-650 °C.

Oil-containing waste contains mineral components such as silica and small amounts of metals such as Fe and Cu, which were detected by of XFA (Table 1). Apparently, trace amounts of these metals come either from sand, or from oil. In the pyrolysis process mineral components with metal inclusions can play the role of active sites enhancing the flow of the reactions of cleavage, dehydrogenation, condensation, and coking [26]. Thus, even without the added catalyst some catalytic influence from trace metals is possible.

On the other hand, mineral components containing more than 90% (wt.) of SiO₂ of oil-containing waste can play role of a heat carrier that increases heat conductivity of the system and accelerates thermal degradation (heat conductivity coefficients of SiO₂ (0% humidity) is 0.33 W/m·K, while for oil (an

average value), it is 0.13 W/m·K) [27]. It results, mainly, in the increase in the gaseous product yield due to the increase of the sample heating rate as is demonstrated in Fig. 2. The highest yield of the gaseous and solid products was observed in the pyrolysis of the mixture containing 10-20% (wt.) of the oil fraction.

Table 1. Elemental analysis of oil-containing waste solid components

Solid residue	Determined element, % (wt)				Undetermined component, % (wt)
	Silica (SiO ₂)	Fe	Cu	Co	
Initial component	99.93	0.02	0.04	-	-
Without a catalyst 450 °C	87.88	0.04	0.03	-	12
Without a catalyst 500 °C	94.74	0.03	0.03	-	5.2
Without a catalyst 600 °C	96.15	0.02	0.03	-	3.8
Catalyst CoCl ₂ 500 °C	96.13	0.06	0.04	0.57	3.2

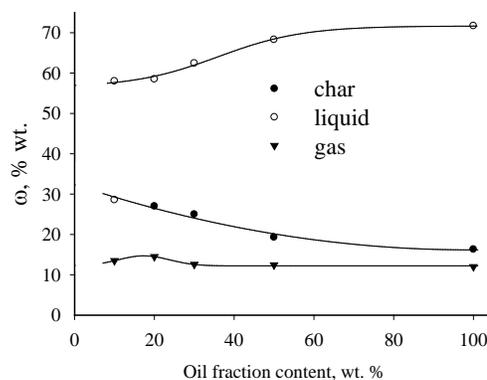


Fig. 2 dependence of pyrolysis products weight percent on oil fraction content (t=500 °C).

The increase in the solid residue yield can be attributed to the increase of the dehydrogenation reaction rate and the formation of unsaturated hydrocarbons contributing to coking [26].

B. Influence of the catalyst type on the oil-containing waste conversion

We studied the influence of metals chlorides on the oil-slime pyrolysis. It is known that metals chlorides are highly active in hydrocarbon raw material pyrolysis [17]. Fig. 3 displays the model oil-containing waste conversion (oil fraction content of 20% (wt.)) in the presence of metal

chlorides at the pyrolysis temperature of 500 °C. It clearly shows that the metals chlorides of the iron subgroup are the most active in oil-containing waste pyrolysis. The highest increase of the weight fraction of gaseous and liquid products was observed in the case of cobalt chloride and was 41.2 and 8.5% (wt.), respectively, in comparison with the non-catalytic process. The higher catalytic activity of the iron subgroup metal chlorides compared to the other metal chlorides studied can be explained by higher relative acidity of the former metals chlorides in electrophilic processes [8]. Here we assume that solubility of metal chlorides is low for all salts studied, thus the influence of solubility is neglected.

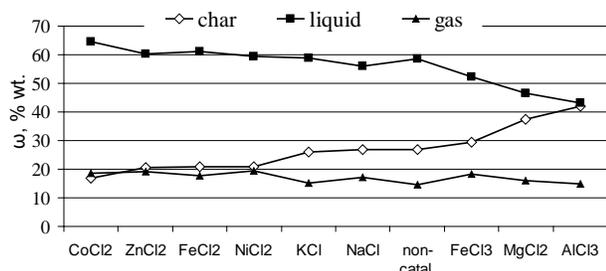


Fig.3 weight percent of pyrolysis products with the catalysts added (10 % of raw material weight) at $t = 500\text{ }^{\circ}\text{C}$

In the series $\text{NaCl} \rightarrow \text{MgCl}_2 \rightarrow \text{AlCl}_3$ the increase of the solid carbon-containing residue was observed compared to the non-catalytic process. This fact can be explained by the increase of the strength of the Lewis acid sites [23]. The strength of the acid sites accounts for high activity of the catalyst which contributes both to C-C bond breaking with the formation of volatile products and the reactions of resin and coke formation [16].

The catalysts under study can be divided into three groups [26]:

- catalysts have low acidity or they are not active in the pyrolysis process (KCl, NaCl);
- catalysts with medium acidity reveal relatively high activity and selectivity (NiCl_2 , CoCl_2 , ZnCl_2 , FeCl_2);
- catalysts with high acidity have high activity but low selectivity (MgCl_2 , FeCl_3 , AlCl_3).

Compared to the non-catalytic process the solid residue weight increased while using FeCl_3 , MgCl_2 and AlCl_3 by 14, 44 and 61% (wt.), respectively. Thus the use of these catalysts is inappropriate as it can lead to the increase in the corrosive influence on the equipment and to the decrease of the process efficiency because of the high yield of the solid residue.

According to the data presented in Fig. 3 the chlorides of alkaline metals showed low activity in the oil-containing waste pyrolysis. This low activity can be due to low electronegativity and low acidity. Table 2 shows the pKa and electronegativity values for all the catalysts. Indeed, KCl and NaCl have lowest values of electronegativity. In the majority of metal chlorides studied, with the increase of electronegativity the pyrolysis conversion to gaseous and liquid products increases,

demonstrating the influence of this parameter on catalytic properties.

Table 2. Metals chlorides acidity [15] and electronegativity [17] values

Catalyst	Acidity value pKa	Cation electronegativity	
		According to Pauling	According to Allred and Rochow
KCl	-	0.82	0.91
NaCl	-	0.93	1.01
MgCl_2	+7.1	1.31	1.23
AlCl_3	-22	1.61	1.54
ZnCl_2	+17.0	1.65	1.66
FeCl_3	-	1.83	-
CoCl_2	+13.8	1.88	1.70
NiCl_2	+14.5	1.91	1.75
FeCl_2	-10	1.96	-

In Fig. 4 the dependence of the volume of the gaseous products (C_1 - C_4 hydrocarbons) formed on the relative acidity of the catalyst is presented. In the case of potassium chloride showing low relative acidity, the composition and the volume of the gaseous products is nearly the same as that of the non-catalytic process. The use of the other metal chlorides studied resulted in more than 40% volume increase of the gaseous products in normal conditions. In the presence of cobalt and nickel chlorides the volume of the C_1 - C_4 hydrocarbons increased by factors of 2.4 and 2.9, respectively, compared to the non-catalytic process.

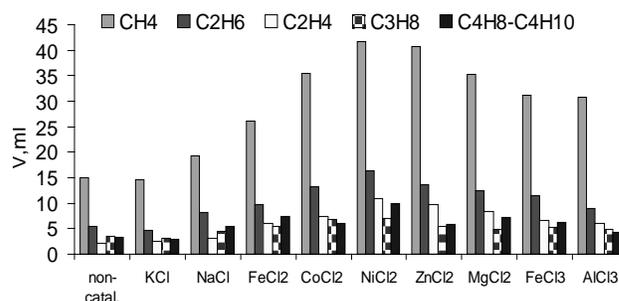


Fig. 4 dependence of the volume of the gaseous hydrocarbons C_1 - C_4 (normal conditions) on the type of the catalyst used (10% of the raw material weight) at $t = 500\text{ }^{\circ}\text{C}$.

The highest increase of the fraction of hydrocarbons which are the components of the pyrolysis gaseous products was observed in the presence of cobalt, nickel and zinc chlorides showing medium relative acidity.

Zinc chloride as well as nickel chloride shows high catalytic activity resulting in a considerable increase of the C_1 - C_4 hydrocarbon (Fig. 4) compared to the non-catalytic process. High activity of zinc chloride is likely to be explained by a higher solubility of water which is a part of oil-containing waste, compared to other chlorides [28].

Based on the above, two factors could be identified from the analysis of the influence of different metal chlorides on the yield of gaseous and liquid pyrolysis products (Fig. 3, 4). The first factor is the influence of the hardness of aprotic acid sites of metal chlorides. According to [16], [17], [26], the activity and selectivity of the catalysts in electrophilic processes (degradation, alkylation, hydrogenation and dehydrogenation, resin and coke formation) is determined by acidity. The catalysts with low acidity are less likely to show catalytic properties in electrophilic processes while the catalysts with high acidity increase the number of side reactions. The second factor is the influence of electronegativity of metal chloride cations on oil-containing waste pyrolysis.

The heat of combustion of gaseous products is one of the most important characteristics from the view point of practical applications. That is why the influence of the catalysts on this characteristic is essential for applicability of this method of oil-containing waste utilization.

According to the data presented in Table 3 the use of the metal chlorides results in the increase of the total heat of combustion of the pyrolysis gaseous products. The use of nickel chloride allowed for the highest value of the total gas heat of combustion. It is three times higher than the value obtained in similar conditions for the non-catalytic process.

Because cobalt chloride showed the highest yield of liquid and gaseous products, it was chosen as the catalyst for studying these products as well as the influence of the catalyst amount on pyrolysis.

Table 3. Influence of the catalysts on the total heat of combustion of the oil-containing waste pyrolysis gaseous products at T=500 °C. The oil fraction content is 20% (wt.)

Catalyst	Q, J/g substrate
non-catalytic	1810
KCl 10%	1680
NaCl 10%	2800
MgCl ₂ 10%	3160
AlCl ₃ 10%	3180
FeCl ₂ 10%	3380
FeCl ₃ 10%	3800
CoCl ₂ 10%	4130
ZnCl ₂ 10%	4870
NiCl ₂ 10%	5400

C. Influence of the cobalt chloride content on oil-containing waste pyrolysis

Considering that the use of cobalt chloride resulted in the highest degree of oil-containing waste conversion into liquid and gaseous products, the influence of the catalyst content on the weight distribution of the pyrolysis products was studied with this catalyst. The results of the influence of the catalyst concentration on oil-containing waste conversion are presented in Fig. 5.

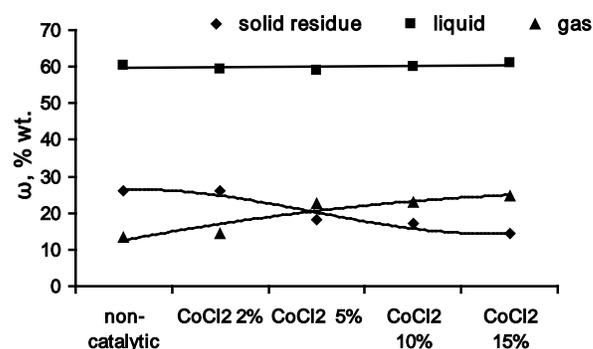


Fig. 5 influence of the catalyst content (wt. % of the oil-fraction weight) on the weight distribution of the oil-containing waste pyrolysis products at T=500 °C, oil fraction content 20% (wt.)

Upon addition of 2% (wt.) of cobalt chloride no changes were observed in the amount of liquid and gaseous products. The introduction of 5% (wt.) of CoCl₂ increased the amount of liquid and gaseous products by 15% compared to the non-catalytic process. The further increase of CoCl₂ content from 5 to 15% leads to a small decrease of the solid residue weight and therefore to the small increase of the amount of liquid and gaseous products. This is explained by the loss of crystallization water from the crystal hydrate. Based on the above, the optimal content of the catalyst is 5% (wt.) of the oil fraction weight.

D. The kinetic study of the oil-containing waste pyrolysis process by thermogravimetry method

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. Depending on the chemical composition of oil sludge, reaction medium, the catalyst presence and process temperature, various reactions of destruction proceed. 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.

The curves of the function $\frac{\log d\alpha}{dt} = f\left(\frac{1}{T}\right)$ (Fig. 6a and 6b) were plotted basing on the weight loss of the samples of oil-containing waste at different heating rates. 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.

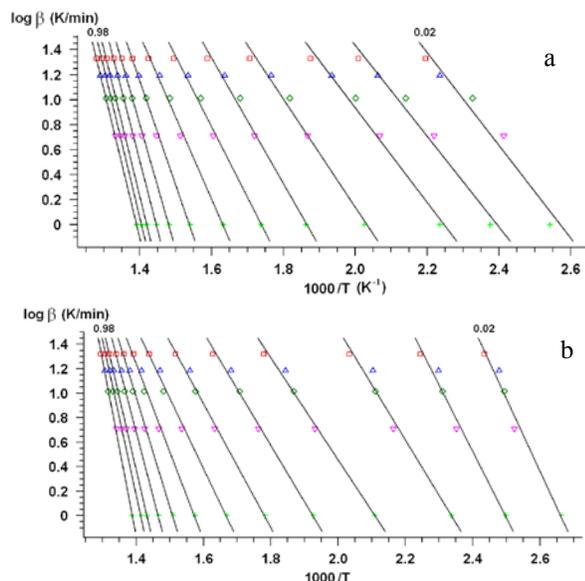


Fig. 6 the rates of the samples weight loss in the coordinates $\log da/dt-1000/T$, obtained using Ozawa-Flynn-Wall method:
 a – oil-containing waste (non catalytic);
 b – oil-containing waste + CoCl_2 5% (wt.)

In the case of the multi-stage process using Friedman method the information can be obtained only for the initial field. In Fig. 7a and 7b the dependences of the logarithm of the samples destruction rate on the reciprocal temperature are shown. The lines connecting the experimental points in the range $0.02 \leq \alpha \leq 0.1$ 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 (Fig. 6 and 7) 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 Fig. 8a and 8b 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.

Analyzing the data (Fig. 8a and 8b), 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.

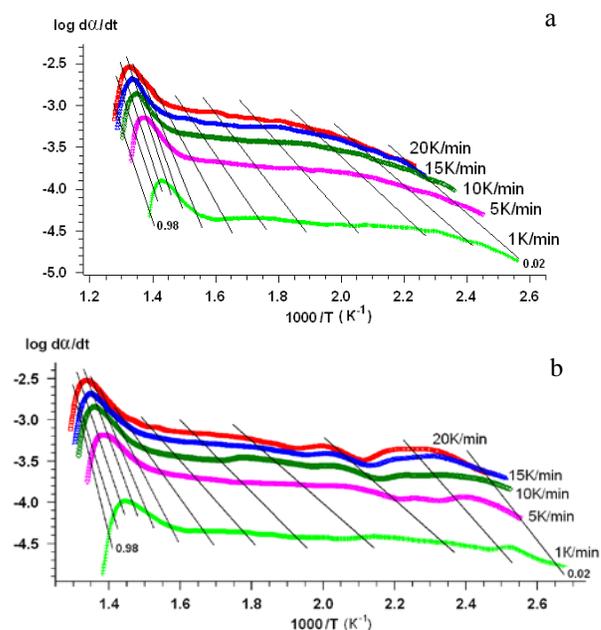


Fig. 7 the curves of the rate of samples weight loss in the coordinates $\log da/dt-1000/T$, obtained using Friedman method: a – oil-containing waste (non catalytic);
 b – oil-containing waste + CoCl_2 5% (wt.)

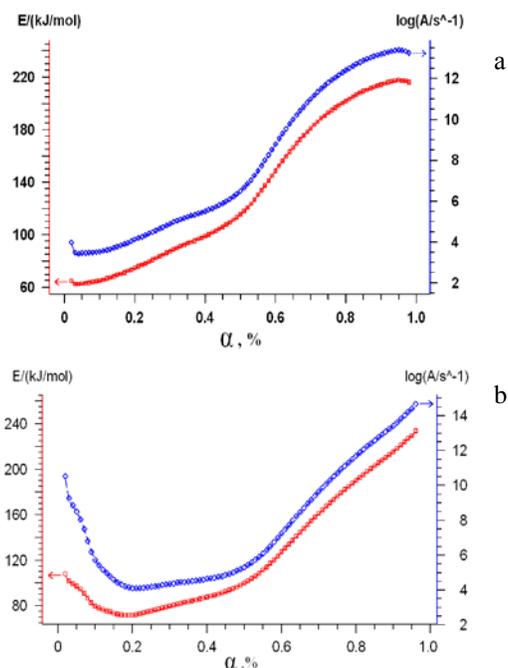


Fig. 8 the dependence of the activation energy and logarithm of the pre-exponential factor on the sample partial weight loss obtained using Ozawa-Flynn-Wall method:
 a – oil-containing waste (non catalytic);
 b – oil-containing waste + CoCl_2 5% (wt.)

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 (Fig. 9a and 9b).

The kinetic parameters are shown in Table 4. It is noteworthy that the obtained kinetic models have a formal character and the chemism of the oil slime pyrolysis process can not be described only on the base of TGA data.

Table 4. 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

The statistical analysis of the obtained kinetic parameters of both non-catalytic and catalytic pyrolyses of oil-containing waste is shown in Table 5.

Table 5. The statistical analysis of kinetic parameters

Parameter	Value	
	non catalytic	CoCl ₂ 5%
Sum of least squares	$2.71 \cdot 10^{-2}$	$3.95 \cdot 10^{-2}$
Correlation coefficient	0.999625	0.999561
Standard deviation	$2.96 \cdot 10^{-3}$	$3.59 \cdot 10^{-3}$

According to the data (Table 4), the use of CoCl₂ 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 CoCl₂.

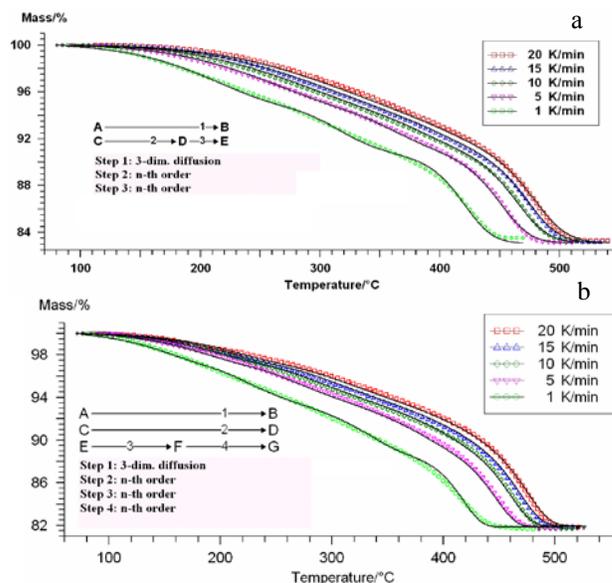


Fig. 9 the weight loss curves of oil-containing waste samples at different heating rates: 1, 5, 10, 15, 20 K/min; a – oil-containing waste (non catalytic); b – oil-containing waste +CoCl₂ 5% (wt.) (Line – computed; symbol – experimental).

IV. CONCLUSION

THE influence of metals chlorides on the oil-containing waste thermal degradation is explained by two major factors: (i) strength of the catalyst aprotic acid sites and (ii) cation electronegativity.

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 C₁-C₄ 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 CoCl₂ 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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