

Thermolysis of oil sludge with metal chlorides as a catalyst

E. M. SULMAN*, K.V. CHALOV, YU. V. LUGOVOY, YU. YU. KOSIVTSOV,
I.S. SMIRNOV

Department of biotechnology and chemistry
Tver State Technical University
A.Nikitin Str., 22, 170026, Tver
RUSSIA

Abstract: - Oil sludge utilization is an important economical and ecological problem which solution can be an essential step towards the development of resource-saving technology on the basis of the integrated use of oil raw material. Catalytic influence of KCl, NaCl, ZnCl₂, MgCl₂·AlCl₃, FeCl₂, FeCl₃, CoCl₂ and NiCl₂ on the thermolysis of oil sludge had been studied. The optimal process parameters such as temperature, amount of catalyst, ratio of oil sludge to sand, residence time of the black sludge inside reactor were also explored. The most attractive conditions were dined as follows: catalyst – CoCl₂ 5 wt. %, oil content – 20 wt. %, temperature – 500 °C. Besides NiCl₂ and ZnCl₂ also showed a high level of conversion. As a result of CoCl₂ influence the activation energy of thermolysis decreased by 20-30 kJ/mol; the presence of C₁-C₄ hydrocarbons in gaseous product increased in 2.4; a percent degree of conversion of oil sludge into gaseous and liquid products increased by 37% and 7% , respectively, compared to non-catalytic treatment.

Key-Words: - catalytic pyrolysis, oil sludge, metal chlorides, gaseous hydrocarbons, liquid hydrocarbons

1 Introduction

Nowadays petroleum products are being widely used in all area of modern life of humanity. More than 4 billion metric tons were consumed in 2014 [1]. The oil sludge has been produced during oil production, storage and transportation. Approximately 5% of whole oil becomes a waste in other words, about 210 million metric tons of waste every year. Moreover the oil sludge is a very dangerous contaminator for air, ground and especially for water. However, due to an ineffective using of fossil fuel and high cost of treatment, huge amount of oil sludge still has being stored in a sludge tanks and endangers the environment [2].

The oil sludge is a tar-like substance which generally consists of water, sand, clay, metal oxides, oil products etc. The exact composition depends on the origin place of waste: groundwater, demersal sludge or storage tank that makes the recycling of oil waste more complicated issue [3]. Therefore there are many different methods of treatment such as microwave pyrolysis; screw and augur kilns; vacuum pyrolysis; fixed, bubbling, circulated bed fluid; microbiological degradation, different extraction techniques and so on [4, 5]. However these methods did not become a widespread due to a high cost, high level of time consumption, and

relatively low economic prices of oil waste dumlping.

Among whole recycling methods the most attractive is a thermal catalytic treatment [6, 7]. Catalytic thermolysis of oil sludge allows utilizing waste and obtaining gaseous and liquid products, which further can be used as a raw material or fuel [8, 9]. This type of treatment in comparison with other methods has the following advantages:

- fairly low process temperatures (400-650 °C);
- low sensitivity to the fuel composition;
- a closed circuit of processing that comply with the modern requirements in chemical production [10].

Also the thermolysis process can be approached by using of catalysts which allow increasing the yield and quality of target products and decreasing the process reaction temperature. The choice of catalyst was based on the consideration and comparison of a number of experiments with organic materials (hydrocarbon, wood, polymers) [11, 12].

This paper is devoted to the description of influence of metal chlorides (such as KCl, NaCl, ZnCl₂, MgCl₂·AlCl₃, FeCl₂, FeCl₃, CoCl₂ and NiCl₂) and definition the optimal process conditions.

2 Experimental

2.1 Materials

The metals chlorides (KCl, NaCl, ZnCl₂, MgCl₂·6H₂O, AlCl₃·6H₂O, FeCl₂·4H₂O, FeCl₃·6H₂O, CoCl₂·6H₂O and NiCl₂·6H₂O) were received from Reakhim (Moscow) and used as a standard.

Feeds of oil sludge were consisted of a silica (the size range 0.1-0.4 mm, Voronezh Region oil field, Russian Federation) and oil from the Caspian field at various weight ratios. The oil characteristics are: density (at 200 °C) is 860±2 kg/m³; dynamic viscosity (at 20 °C) is 3.39 MPa·s; sulphur content is 0.16 wt. %; the paraffin content is 20.04 wt. %; tar content is 5.2 wt. %; asphaltene content is 0.94 wt. %; fraction yield (according to the true boiling point) is 19.0 wt. % up to 200 °C and 45.0 wt. % up to 360 °C.

2.2 Apparatus and methods

The thermolysis process was carried out with an experimental thermolysis reactor in a temperature range from 450 to 650 °C. The experimental thermolysis reactor consists of a metal fixed-bed reactor heated by the electric furnace, a gas sampler, a water trap for collecting liquids, and an eudiometer for collecting gas. The reactor is equipped with an outlet for inert-gas purging.

Before the tests the oil sludge feed was placed into the fixed bed reactor. Than the system had been purged by a low flow of nitrogen during 4-5 min. After that the heating was carried out, temperature was ranged from 450 °C to 650 °C (450, 500, 550, 600 and 650 °C). The duration of the test was an hour and a half and each test was repeated at least 3 times.

The definition of optimal ratio of oil and silica for the preparation of oil sludge feed was implemented as an experiment without catalyst. The oil sludge feed consist of two parts: oil containing and silica. The weight of oil was always constant – 2 g, the weight of sand feeds were varied: 0, 2, 6.67, 10, 20 g, in other words prepared feeds contained 100 wt. %, 50 wt. %, 30 wt. %, 20 wt. % and 10 wt. % of oil.

The optimal ratio of oil and silica are used further as a standard composition for next tests. Than the standard composition was mixed with 10 wt. % of metal chloride (KCl, NaCl, ZnCl₂, MgCl₂·6H₂O, AlCl₃·6H₂O, FeCl₂·4H₂O, FeCl₃·6H₂O, CoCl₂·6H₂O and NiCl₂·6H₂O) and tested. The most attractive catalyst was chosen. Then the optimal amount of

catalyst was detected by tests with 0 wt. %, 2 wt. %, 5 wt. %, 10 wt. % and 15 wt. % of additive.

2.3 Analysis

When a test had been done and reactor had been cooled the following parameters were measured: weight of solid residue according to the weight change of the reactor, weight of liquid products according the weight change of water trap, weight of gas determined as a difference between the initial weight of feed and weights of liquid and solid products. Standard deviation of the weight measurement was ±0.5 wt. %.

The analysis of the gaseous composition (CO, H₂, CO₂ hydrocarbons) and the evaluation of the heat capacity of thermolysis products were performed by the gas chromatographs Crystallux 4000M and GAZOKHROM 2000; the specific heat capacity was measured by specially designed analyzer based on flame-temperature detector.

The hydrocarbon analysis of gaseous products was performed by Crystallux 4000M, the following parameters were used: consumption of gas-carrier (N₂) – 120 mL/min; N₂ pressure 1.5 kg s/sm³; duration of the analysis – 30 min; sample volume – 1 mL; column: carrier – silica gel 0.4 mm; column length – 1 m; temperature – 50 °C; detector temperature – 100°C. Volume concentrations of methane, carbon oxide and hydrogen were measured by GAZOKHROM 2000, the following parameters were used: flow rate of the gas-carrier (He) – 30 cm³/min; sample volume – 0.5 cm³; thermostat temperature – 40 °C.

The acidity of catalyst samples was estimated by NICOLET “Protege” 460 spectrometer (FTIR-spectra of diffuse reflection (DRIFT)), the diffuse reflection range was 6000-400 cm⁻¹ with a step 4 cm⁻¹. Acetonitrile (CD₃CN) was used as a test for acidity at ambient temperature. Before adsorption of CD₃CN the catalysts were treated in vacuum at room temperature for 3 hours and at 450 °C for 2 hours with the heating rate of 5 °/min.

The metal content was determined by X-ray fluorescence analysis (XFA) implemented by the 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.

3 Results and discussion

2.1 Influence of oil sludge composition and temperature during non-catalytic pyrolysis

The influence of temperature on non-catalytic process has been estimated for the 20 wt. % oil sludge feed. Process temperatures were varied: 400, 450, 500, 550, 600 and 650 °C. As it can be seen on Fig. 1 below 500 °C the high yield of solid residue is observed. The high yield of liquid and gaseous products takes place at 500-550 °C. The further heating up to 650 °C is not a beneficial because promotes only 8% increasing of total conversion herewith requires an additional energy and makes a process more expensive. Thus, the 500-550 °C is a most optimal temperature.

The mineral and metal components of oil sludge were detected by XFA and represented in Table 1. Perhaps, the presence of metals is caused by composition features of a sand or/and from oil. These metals can provide the appearance of active sites which can be involved in coking, dehydrogenation, condensation and cleavage reactions [13]. Thus even without special additives of catalyst there is some catalytic effect from the trace amount of metals.

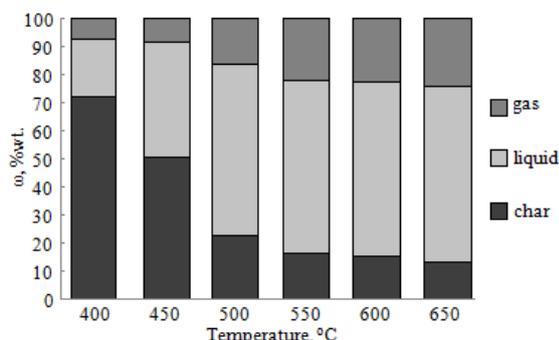


Fig. 1. Temperature dependence of the oil sludge conversion

However, since the 90 wt. % of mineral components is a silica (heat conductivity of oil and SiO₂ is 0.13 and 0.33 W/m·K, respectively) the heat conductivity of system increases thus the degree of thermal degradation also increases. This feature leads to the increasing of gaseous product yield for high silica containing feed as it can be seen in Fig. 2.

Table 1 Elemental analysis of oil-slime 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

The highest gaseous product yield was received at 10-20 wt. % of the oil fraction (90 and 80 wt. % of SiO₂, respectively). The increase of solid residue yield can be caused by the rise of dehydrogenation rate and the formation of unsaturated hydrocarbons contributing to coking [14].

Also the possible influence of silica acidity had been studied by the DRIFT technique; the received spectra can be seen on Fig. 3. If there is some influence of silica acidity, it can be observed as a trace of CN absorption (from CD₃CN). This interaction typical is represented by the isolated silanol group (≡Si-OH) (weak Brønsted acid sites) with the characteristic wave number around 3740 cm⁻¹.

On current spectra there is no sign of the silanol group, therefore the acidity influence of silica on the thermal dehydration is insignificant. The other three bands mentioned on the Fig. 3 at 3380, 3620 and 3695 cm⁻¹ correspond to the vibrations of hydrogen bonded and bridged (Si(OH)Si) OH groups [14, 15].

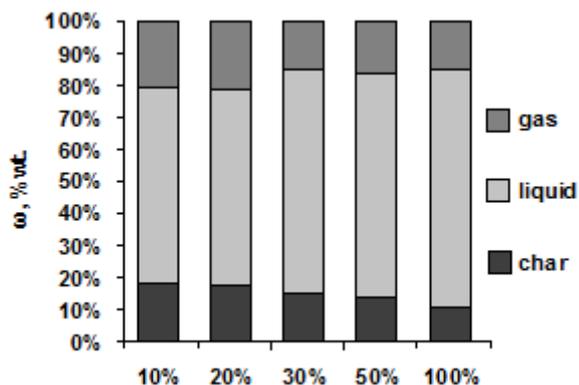


Fig. 2. Dependence of thermolysis product yields on oil content expressed in wt%

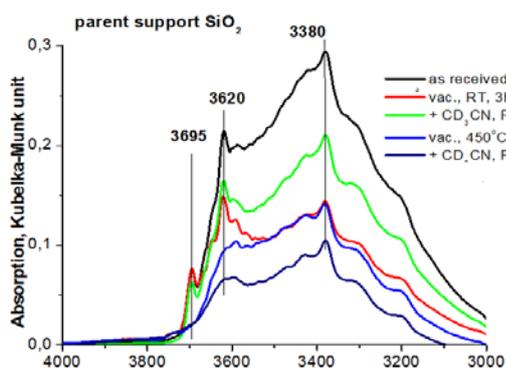


Fig. 3. DRIFT spectra of hydroxyl (OH) – groups on the parent silica (SiO_2) before and after acetonitrile- d_3 (CD_3CN) adsorption.

2.2 Catalytic influence of different metal chlorides on thermolysis process

The influence of different metal chlorides (10 wt. % of catalyst was added) was studied at the optimal conditions: temperature – 500 °C, the oil sludge feed content 20 wt. % of oil.

As it can be seen from Fig. 4 the highest products yield was received in the presence of CoCl_2 , which increased the yield of gaseous and liquid products by 37 and 7 wt. % compared to non-catalytic pyrolysis. However there are three more catalysts ZnCl_2 , FeCl_2 and NiCl_2 showed significant conversion ability. This can be explained by relatively high acidity of these catalysts, which plays a catalytic role in a present electrophilic process [16]. The solubility of all catalysts is assumed as low therefore its influence is not considered.

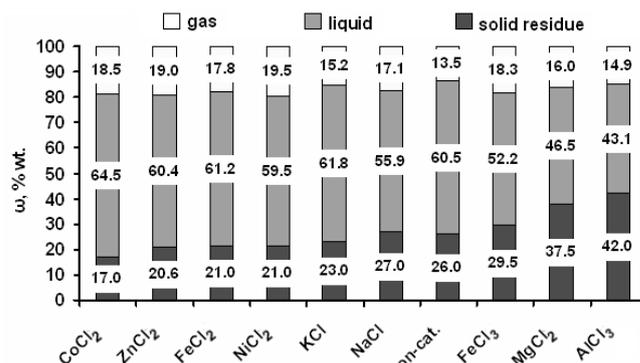


Fig. 4. Dependence of thermolysis product yield on the catalyst

In the series $\text{KCl} \rightarrow \text{FeCl}_3 \rightarrow \text{AlCl}_3$ the share of solid residue increases successively compared to thermolysis without catalyst. It can be due to the growth of strength of Lewis acid sites [16]. These sites promote two types of reactions: coke and resin formation; breaking of C-C bond followed by the formation of gaseous products.

According to the catalytic influence the metal chlorides can be grouped as:

- Catalysts which activity is either low or absent (KCl , NaCl);
- Catalysts with a moderate acidity contributed to the high selectivity and activity (CoCl_2 , MgCl_2 , NiCl_2 and FeCl_2);
- Catalysts with a strong acidity which promote high conversion level but selectivity of conversion is low (AlCl_3 , FeCl_3 and MgCl_2)

Although the catalysts consisted of NiCl_2 , MgCl_2 and FeCl_2 promote a higher yields of liquid and gaseous products, nevertheless the yield of solid residue also increases compared to the best catalyst – CoCl_2 . The formation of solid residue is undesirable because it has an effect on equipment, decreases productivity of the treatment. That is why among b) group catalysts the best one is CoCl_2 .

As it can be seen on Fig. 4 KCl and NaCl show a low activity during the oil sludge treatment. It can be explained by low acidity and low electronegativity of alkali metals (Table 2).

Indeed, alkali metal chlorides show the lowest values of electronegativity and low activity. Therefore there are considered the higher electronegativity the higher conversion of oil sludge to gaseous and liquid products.

The influence of catalyst type on the volume of gaseous products ($\text{C}_1\text{-C}_4$ hydrocarbons) can be seen on Fig. 5.

Table 2 Metal chlorides acidity and electronegativity [17, 18]

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	-

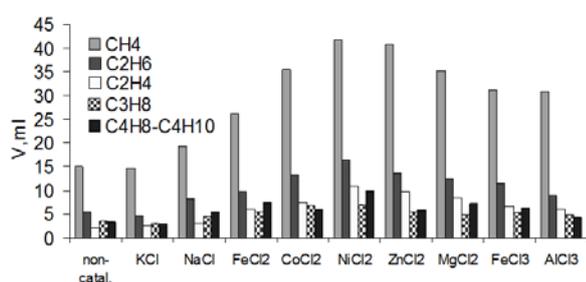


Fig. 5. Dependence of the volume yield of C₁-C₄ hydrocarbons

Fig. 5 shows the influence of metal chlorides on the oil sludge conversion to C₁-C₄ hydrocarbons. In the cases of potassium and sodium chlorides the degree of conversion is almost the same as for test without catalyst. Other catalysts at the optimal condition promote the increase of gaseous product yield by 40%.

The high degree of the conversion was observed during the tests with CoCl₂, NiCl₂ and ZnCl₂ which have a medium relative acidity. The acidity of catalytic systems was estimated by the DRIFT spectroscopy. The DRIFT spectra of CD₃CN adsorbed on CoCl₂, NiCl₂ and ZnCl₂ supported on sand are represented on Fig. 6-8.

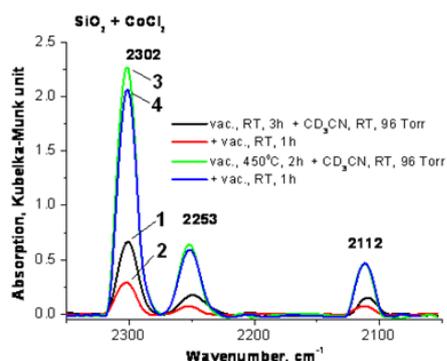


Fig. 6. DRIFT spectra of CD₃CN adsorbed on CoCl₂ sample supported on SiO₂

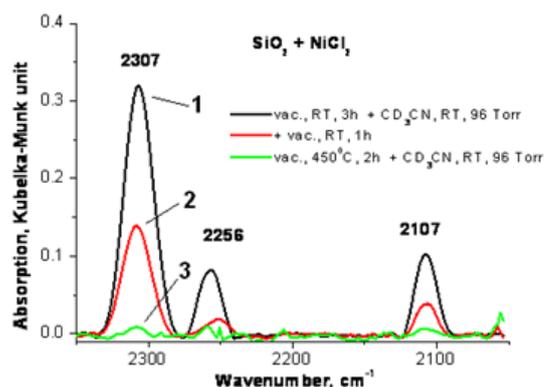


Fig. 7. DRIFT spectra of CD₃CN adsorbed on NiCl₂ sample supported on SiO₂

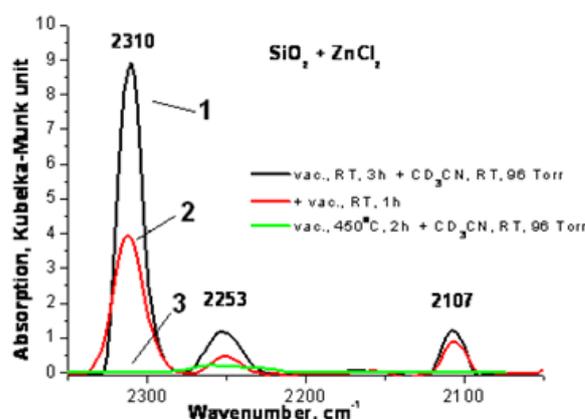


Fig. 8. DRIFT spectra of CD₃CN adsorbed on ZnCl₂ sample supported on SiO₂

The adsorption of CD₃CN on the Lewis acid sites goes through the formation of C≡N bond, which appears on DRIFT spectra at 2302-2310 cm⁻¹. After the samples undergone desorption in vacuum at room temperature during 1 h the decrease of C≡N band intensities is observed.

Unusual behavior is shown in the case of CoCl₂. Even after high temperature vacuum pretreatment (450 °C) Lewis acid sites were found on the surface and amount of these sites increased (line 3 on Fig.6).

Also the use of b) group metal chlorides leads to the increase of gaseous hydrogen yield compared to non-catalytic reactions (Fig. 9). In the series FeCl₂→CoCl₂→NiCl₂ hydrogen yield increases in 1.7, 2.1 and 2.8 times, respectively. During the non-catalytic reaction there are two competitive reactions: breaking of the C-C bond and C-H bond. The catalysts make the second reaction more probable by catalyzing water-gas shift reaction [5]. ZnCl₂ as well as NiCl₂ demonstrates an increase of C₁-C₄ hydrocarbon and hydrogen yield due to high catalytic activity as it can be seen on Fig. 5 and Fig. 9. However the high catalytic activity of ZnCl₂ can

be related to a higher solubility on water which is a part of oil sludge compared to other metal chlorides [19].

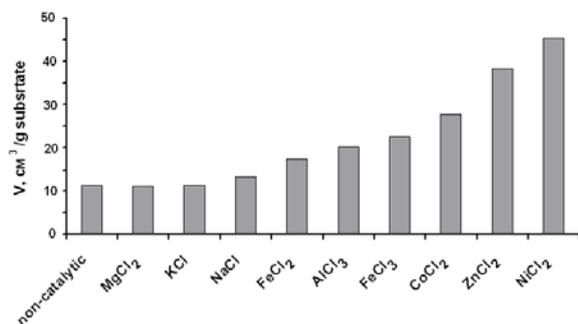


Fig. 9. Influence of catalysts on the volume of hydrogen at the optimal conditions

According to the information received from analysis, there are two main factors involved in catalytic thermolysis of oil sludge (Fig. 4 and 5). The first factor is related to the influence of aprotic acid sites of catalysts. According to [10, 11, 20], the activity and selectivity of the catalysts in electrophilic processes (degradation, alkylation, hydrogenation and dehydrogenation, resin and coke formation) are determined by acidity. So the first factor can be rephrased as the higher acidity the higher catalytic activity. The second factor is the influence of electronegativity of metal chloride cations on oil sludge thermolysis. Finally, the most important characteristic of thermolysis process is heat capacity of combustion. Exactly heat capacity determines the applicability of catalysts, process conditions and so on.

Fig. 10 presents the dependence of an eliminated heat during the thermolysis using different catalysts.

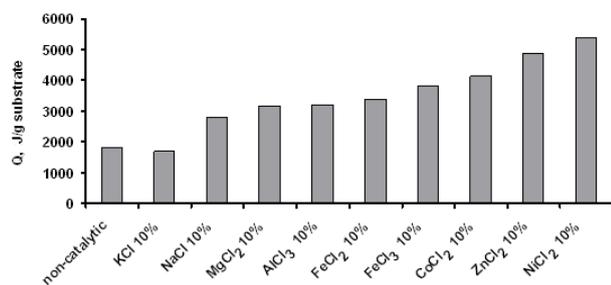


Fig. 10. influence of the catalysts on total heat of combustion of oil sludge treatment

Obviously the presence of catalysts significantly increases the heat of combustion. For example, NiCl₂ promotes the heat emission that a three time higher than the heat emission during the non catalytic process.

Since CoCl₂ had demonstrated the highest yield of gaseous and liquid products, cobalt chloride was chosen as the best catalyst based on chloride for further.

2.3 Investigation of influence of CoCl₂ content on oil-sludge thermolysis

The weight dependence of CoCl₂ catalytic activity was studied through the number of tests which were performed with a different amount of catalyst – 0, 2, 5, 10 and 15 wt. % (Fig. 11).

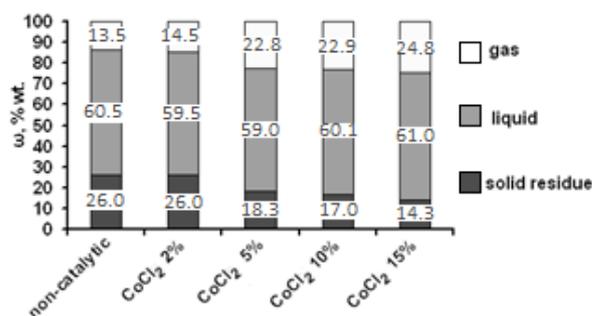


Fig. 11. Influence of the CoCl₂ content on oil sludge conversion

Significant changes in comparison with non-catalytic process occur at tests with ≥ 5 wt. % of catalyst. The addition of 5 wt. % CoCl₂ increases the yield of gaseous and liquid products by 15%. During tests with 10 and 15 wt. % additions the insignificant reduction of solid residue was observed, therefore the conversion of oil sludge to gaseous and liquid products increased. It can be explained by the loss of crystallization water from the crystal hydrate of CoCl₂. Based on the above, the 5 wt. % CoCl₂ was chosen as an optimal amount.

4 Conclusion

Thermolysis of oil sludge at the presence of metal chlorides such as potassium chloride (KCl), sodium chloride (NaCl), zinc chloride (ZnCl₂), magnesium chloride (MgCl₂·6H₂O), aluminum chloride (AlCl₃·6H₂O), iron (II and III) chloride (FeCl₂·4H₂O, FeCl₃·6H₂O), cobalt chloride (CoCl₂·6H₂O), and nickel chloride (NiCl₂·6H₂O) as well as without catalyst was performed and studied. The following parameters of catalysts were discovered as the most influential:

- 1) the strength of the catalyst aprotic acid sites and

2) cation electronegativity.

CoCl₂, NiCl₂ and ZnCl₂ had showed the highest catalytic activity during the oil sludge thermolysis. These catalysts allowed obtaining the highest conversion of waste into gaseous and liquid products and increase in 41.2 and 8.5 wt. %, respectively, compared to the non-catalytic process. In the presence of CoCl₂ and NiCl₂ the volumes of the C₁-C₄ hydrocarbons increased by factors 2.4 and 2.9, respectively, compared to the non-catalytic process. The use of CoCl₂ also minimized the activation energy of the oil sludge treatment in 1.2 times and decreased the thermal decomposition temperature up to 30 °C.

Therefore, for the model oil-sludge sample pyrolysis, we recommend catalytic process at 500 °C and at 5 wt. % of cobalt chloride of the oil-sludge oil fraction weight.

References:

- [1] M.S. Alam, S.R. Paramati Do oil consumption and economic growth intensify environmental degradation? Evidence from developing economies, *Applied Economics*, ahead-of-print, 2015, P. 1.
- [2] C.Yu. Chang Major products obtained from the pyrolysis of oil sludge, *Energy & fuels*, Vol. 14, No. 6, 2000, P. 1176.
- [3] N. Charon Multi-technique characterization of fast pyrolysis oils, *Journal of Analytical and Applied Pyrolysis*, Vol. 116, 2015, P. 18.
- [4] D. Fytli, A. Zabaniotou Utilization of sewage sludge in EU application of old and new methods – a review, *Renewable and Sustainable Energy Reviews*, Vol. 12, No. 1, 2008, P. 116.
- [5] J.P. Diebold *A review of the chemical and physical mechanisms of the storage stability of fast pyrolysis bio-oils*, Golden, CO: National Renewable Energy Laboratory, 2000.
- [6] M.G. Rasul, M.I. Jahirul Recent Developments in Biomass Pyrolysis for Bio-Fuel Production: Its Potential for Commercial Applications, *Recent Researches in Environmental and Geological Sciences*, 2012, P. 256.
- [7] J.-L. Shie, C.-Y. Chang, J.-P. Lin, C.-H. Wu, D.-J. Lee Resources recovery of oil sludge by pyrolysis: kinetics study, *J Chem. Technol. Biotechnol.*, Vol. 75, 2000, P. 443.
- [8] J.-L. Shie Pyrolysis of oil sludge with additives of sodium and potassium compounds, *Resources, conservation and recycling*, Vol. 39, No. 1, 2003, P. 51.
- [9] T. Karayildirim Characterization of products from pyrolysis of waste sludges, *Fuel*, Vol. 85, No. 10, 2006, P. 1498-1508.
- [10] V. Matveeva Metals Chlorides in Oil-sludge Thermocatalytic Processing.
- [11] J. Junwon, K. Jinhwan, B. Jin-Young Effects of Lewis acid-type transition metal chloride additives on the thermal degradation of ABS, *Polym. Degrad. Stab.*, Vol. 88, No 2, 2005, P. 324.
- [12] Qi Zhang Review of biomass pyrolysis oil properties and upgrading research, *Energy conversion and management*, Vol. 48, No. 1, 2007, P. 87.
- [13] K.S. Minsker, V. A. Babkin, G. E. Zaikov *Acidic force of proton donors in complexes of non-transition metals halogenides as the measure of activity of electrophilic polymerization catalysts*, 1994.
- [14] C.M. Jinesh Operando DRIFT spectroscopy on unprecedented influence of Cu 2+ over NiAl LDHs for isomerization of eugenol, *Catalysis Communications*, Vol. 28, 2012, P. 100.
- [15] G.R. Ford *The chemist's companion: a handbook of practical data, techniques and references*, John Wiley & Sons. New York. 1972.
- [16] T. Karayildirim, J. Yanik, M. Yuksel, H. Bockhorn Characterization of products from pyrolysis of waste sludges, *Fuel*, Vol. 85, 2006, P. 1498.
- [17] W. Kaminsky, I.-J. N. Zorriquet Catalytical and thermal pyrolysis of polyolefins, *J. of Anal. Appl. Pyrol.*, Vol. 79, No 1-2, 2007, P. 368.
- [18] N. Shimada, H. Kawamoto, S. Saka Different action of alkali/alkaline earth metal chlorides on cellulose pyrolysis, *Journal of Analytical and Applied Pyrolysis*, Vol. 81, No. 1, 2008, P. 80.
- [19] P. Patnaik *Handbook of Inorganic Chemicals*, The McGraw-Hill. New York. 2002.
- [20] Yu.V. Lugovoy Effect of iron-subgroup metal salts on polymer cord pyrolysis, *RSC Advances*, Vol. 5, No. 70, 2015, P. 56460.

**Creative Commons Attribution License 4.0
(Attribution 4.0 International, CC BY 4.0)**

This article is published under the terms of the Creative Commons Attribution License 4.0

https://creativecommons.org/licenses/by/4.0/deed.en_US