Co-Pyrolysis of Peat and Petroleum Containing Waste on Ni and Co Containing Catalysts

Yury Yu. Kosivtsov*, Kirill V. Chalov, Yury V. Lugovoy, Esther M. Sulman, Antonina A. Stepacheva

Tver Technical University, A.Nikitina st., Tver, 22170026, Russian Federation
kosivtsov@science.tver.ru

The goal of this research is the development of the method of oil-slime recycling. In this work the influence of natural and synthetic aluminosilicates, metal chlorides of iron subgroup on the peat low-temperature pyrolysis and co-pyrolysis of peat with oil-slime and polymeric waste was studied in a variety of conditions (t = 350 – 650 ºC, catalyst loading: from 1 up to 30 % wt.). The use of bentonite clay (30 % wt.) at 460 ºC as a catalyst in peat pyrolysis resulted in the increase in weight of gaseous and liquid products from 23 up to 30 % wt. and from 32 up to 45 % wt. Co-pyrolysis of peat and oil-slime in the presence of bentonite clay resulted in the increase in gaseous product weight from 18 up to 26 % wt. and liquid fraction yield from 45 up to 55 % wt. in comparison with precalculated value. The use of metal chlorides of iron subgroup (2 % wt. concentration) at 500 ºC in the co-pyrolysis of peat and polymeric waste led to optimal conversion of substrate in desired products, 15 % increase of total weight of gaseous and liquid products formed during the pyrolysis process and simultaneous decrease of char formation.

1. Introduction

Oil production, transportation and storage as well as the syntheses of oil related products involve the formation of oil-containing waste. Oil-containing waste (oil-slime) is one of the most hazardous pollutants of surface and ground water, terrain and atmospheric air. Annually tens of thousands of tons of oil-slime are stored in sludge tanks demonstrating ineffective use of fossil fuel (Wang et al., 2007). More than that, the storage of oil-containing waste in sludge tanks endangers the environment (Kuriakose and Manjooran, 1994).

Oil-slime is bulk waste the formation of which takes place at all stages of oil production, processing and transportation (Shie et al., 2003). Oil-slime mainly consists of oil-products, water and mineral constituents (sand, clay, metals oxides etc.) which account for their variable composition and complicate their disposal (Bokovikova et al., 2011). That is why the development of environmentally clean technology for oil- slime processing is of paramount importance (Shie et al., 2002).

The existing methods of oil-slime processing can be divided into physical, chemical, physicochemical, thermal (Bokovikova et al., 2011) and biological (Shie et al., 2000). The choice of the method of oil-slime processing and decontamination mostly depends on the amount and nature of oil-products in oil-slime. The methods of oil-slime processing used in industry are quite expensive and time consuming, so the volume of oil-slime processing is much lower than the volume of its formation (Bokovikova et al., 2011). The thermal treatment resulting in gaseous and liquid fuel formation is considered to be the most economically beneficial (Karayildirim et al., 2006). Besides oil waste sensible utilisation 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-slime was studied for many years (Shie et al., 2000), but high energy consumption and other shortcomings made this process unappealing (Fonts et al., 2009). Catalytic pyrolysis of oil-slime allows obtaining hydrocarbons which can be used either as fuel or raw material for the chemical industry (Rulkens, 2008). Compared to other methods of oil-slime thermal treatment, catalytic

pyrolysis has a number of advantages: (i) rather low process temperatures (400 – 650 °C) (Kaminsky and Zorriqueta, 2007), (ii) low sensitivity to the raw material composition (Sulman et al., 2009) and (iii) a closed circuit of processing that comply with the modern requirements of chemical production (Zou et al., 2007). The use of the catalysts in the pyrolysis process allows increasing the yield and quality of valuable products and decreasing the process reaction temperature (Zou et al., 2007). 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 (biomass (Blasi et al., 2008), wood (Bennadji and Fisher, 2014), polymers (e.g. ABS (Junwon et al., 2005), polyethylene (Lima et al., 2012)), hydrocarbons (Shilina et al., 2008), bio-oil (Suh et al., 2014)) has been recently studied with metal chlorides as catalysts. However, to the best of our knowledge, no catalytic studies of metal chlorides in the pyrolysis of oil-slime have been published.

The methods of energy recovery from renewable biogenic raw materials are of great importance due to the limited amount of natural energy resources, such as oil and gas. Thus thermochemical conversion technologies, e.g. pyrolysis (Demirbas, 2000), gasification (Heermann et al., 2001) and combustion (Yaman, 2004) are studied extensively. The application of biomass as an energy source can be considered as sustainable since the biomass is causing almost zero net emissions of CO_2, which is in turn a primary contributor to the global greenhouse effect.

Here we report on the low-temperature catalytic pyrolysis of peat with the addition of natural and synthetic alumosilicates, and metal chlorides of iron subgroup. Besides, co-pyrolysis of peat with polymeric waste and oil slime was investigated.

2. Experimental

The samples of eriophorum-sphagnum peat with the degree of decomposition of 30 % and ash content of 5% were used as the feed stock for low-temperature catalytic pyrolysis.

The natural aluminosilicates (kaolin, bentonite) and synthetic zeolites (cambrian clay and clay mergel marked as H-Beta-25 and H-Mord) were purchased from Zeolyst International, USA. It is important to mention that zeolite catalysts were modified with Fe using repeated ion exchange (the iron precursor is ferric nitrate). Both natural aluminosilicates and synthetic zeolites were used as the catalysts for low-temperature pyrolysis of peat.

Natural alumosilicates were also used as catalysts of co-pyrolysis of peat and oil-slime. The oil products concentration in oil slime was about 20 % wt., the catalyst loading was varied from 1 to 10 % wt.

Iron sub-group metal chlorides were used as the catalysts of polymeric cord co-pyrolysis with peat. The catalytic activity of metal chlorides in the processes of thermal destruction of protonogenous and sulphur-containing compounds, which are part of polymeric cord produced during the processing of used automobile tires, is well known (Mohan et al., 2006). The choice of iron sub-group metal chlorides is based on the catalytic activity of metal cations in the processes of organogenic raw materials pyrolysis. The positive effect is due to the acceleration of reactions of olefin C-C bond destruction with the formation of hydrogen, low molecular weight alkanes and alkenes (Mohan et al., 2006).

The study of the pyrolysis process was conducted at varying the temperature in the range of 400 – 600 °C and catalyst concentration.

Catalytic efficiency was estimated considering the total amount of the gaseous mixture produced during pyrolysis, the concentration of hydrocarbons (methane, ethane, ethylene, propane) in gaseous mixtures and the heat of combustion of combustible gases.

The chemical grade 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 $NiCl_2 \cdot 6H_2O$ were purchased from Reakhim (Moscow) and used as received.

The model oil-slime 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/m^3; 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.

The pyrolysis process was carried out using 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-slime studied was varied depending on the oil fraction concentration. Oil fraction weight was constant (2 g). The oil-fraction

content of oil-slime varied from 10 up to 100 % wt. due to the change of mineral fraction weight. The catalyst content of oil-slime was from 1 up to 10 % wt. of the oil-fraction weight. The catalyst was introduced into the oil-slime in the form of a solid salt. The duration of the experiment was an hour and a half. Each procedure was repeated at least three times to insure the reproducibility of the results.

3. Results and Discussions

3.1 Catalytic pyrolysis of peat

Preliminary experiments showed that the addition of 2 % of synthetic zeolites and of 30 % of natural alumosilicates to peat was optimal.

The gaseous mixture obtained during peat pyrolysis was found to consist of carbon monoxide, carbon dioxide, saturated and unsaturated hydrocarbons and hydrogen. Carbon dioxide was formed mostly as a result of thermal decomposition of humic acids of peat. CO_2 is incombustible part of the gaseous mixture, thus, its concentration should be decreased in the combustible gaseous mixture.

As a result of the investigations it was found that in the presence of the catalysts the heat of combustion of gaseous mixture noticeably increased from 8.52 up to 23.88 kJ/mol (Figure 1), which was due to the higher content of lower hydrocarbons. The yield of methane increased by 1.4 – 1.7 times, ethane – by 1.5 – 1.9, ethylene – by 2.2 – 3.4 and propane by 1.8 – 2.4 times.
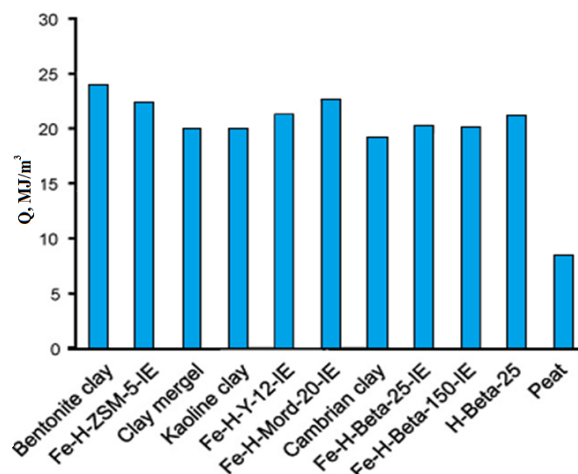

Figure 1: The heat of combustion of the gaseous mixture obtained during the peat pyrolysis

Bentonite clay was found to be the most active catalyst of peat pyrolysis. The highest heat of combustion (23.88 MJ/m^3) was reached at 460 °C. In the case of non-catalytic peat pyrolysis the heat of combustion was only 8.52 MJ/m^3. The average value of the specific heat of combustion was higher approximately by 2.6 – 2.8 times in comparison with the data obtained for non-catalytic process.

Besides, in the presence of such catalysts as Fe-H-Mord-20-IE, Fe-H-ZSM-5-IE, Fe-H-Beta-150-IE and clay mergel the amount of CO_2 evolved was 51 – 52 % vol. of the total amount of gases and decreased by 1.1 – 1.2 times in comparison with the non-catalytic process.

It is noteworthy that significant distinction in percentage of optimal amount of aluminosilicate component in reaction mixture between natural and synthetic aluminosilicates was likely due to the different structures of these compounds. Moreover, natural aluminosilicates when present in significant amounts in the reaction mixture, besides having a catalytic function also acted as heat-carriers, considerably increasing the heat conductivity of the mixture, thus promoting more uniform heating. Depending on aluminosilicates concentration the factor of heat conductivity of reaction mixture can be varied from 0.08 up to 0.182 W/(m·K).

The increase in the bentonite clay concentration was found to result in the increase in the volume of the gaseous mixture by 1.15 times, the amount of hydrocarbons by 2.6 – 2.9 times, carbon dioxide and hydrogen by 1.5 and 2.2 times, respectively, while the amount of carbon monoxide decreased by 1.31 times. The influence of the temperature on the heat of combustion of the gas mixture was also investigated (see Figure 2).
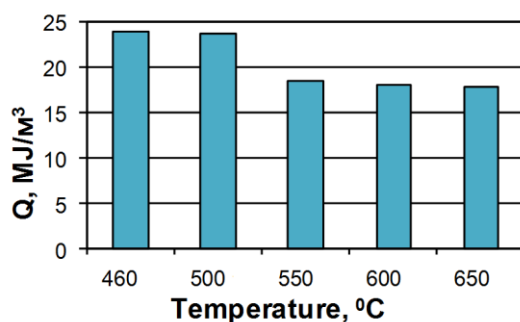
Figure 2: The influence of the temperature on the heat of combustion of the gaseous mixture in the presence of 30 % wt. of bentonite clay

The experimental data show that the increase in the temperature leads to the decrease in the heat of combustion of a gaseous mixture.

3.2 Co-pyrolysis of peat and oil-containing waste

During the experiments weights of char, liquid and gaseous products were determined, and also the qualitative and quantitative analyses of pyrolysis gaseous products were carried out. X-ray analysis of aluminosilicates (see Table 1) showed the presence of titan in the structure of bentonite clay that can influence the catalytic activity.

Co-pyrolysis of peat and oil-slime in the presence of bentonite clay resulted in the increase of gaseous product weight from 18 up to 26 % wt., and liquid fraction – from 45 up to 55 % wt. in comparison with the precalculated value. Besides, the use of metal-containing alumosilicate (bentonite clay) allowed obtaining higher concentration of $C_1 - C_3$ (up to 10 – 20 %) of a gaseous mixture.

Table 1: Investigation of elemental composition of clay by X-ray analysis

Catalyst	Metal	Concentration of metal, % wt.
Bentonite clay	Ti	0.5
	Fe	2.4
Kaolin clay	Fe	0.3
Cambrian clay	Fe	4.3
Clay mergel	Fe	2.2

3.3 Catalytic co-pyrolysis of peat and polymeric waste

In the case of polymeric cord pyrolysis, the catalytic activity (degree of the substrate conversion) increased from iron to nickel ($FeCl_2 \rightarrow CoCl_2 \rightarrow NiCl_2$). Nevertheless such dependence of the activity does not affect the gaseous hydrocarbons formation as in the case of $CoCl_2$ the highest volume of gaseous hydrocarbons was observed. Cobalt chloride was the most selective catalyst possessing the intensive formation of both gaseous hydrocarbons and liquid fraction during the pyrolysis. This difference between catalytic properties of the chosen metals can be explained by secondary periodicity in electron structure of the elements. Though the weights of gaseous and liquid products were rather close for $NiCl_2$ and $CoCl_2$ (see Table 2), the use of $CoCl_2$ was effective for the obtaining of combustible gases with higher calorific value. It is noteworthy that the increase in cobalt chloride concentration higher than 2 % wt. showed almost no benefit for the pyrolysis process. Moreover, it influenced the hydrogen yield and decreased the heat of combustion of the gaseous products.

Thus the best result was observed while using $CoCl_2$, in the presence of which the rate of hydrocarbons formation increased almost twice. The volume of gaseous products was higher (up to 25 %) in comparison with non-catalytic process that is likely due to the higher yield of low molecular weight compounds (methane, ethane, ethylene, propane and hydrogen).

Table 2: The dependence of the weight distribution of polymeric cord pyrolysis products on the reaction temperature

T,ºC	Products, % wt.	non-catalytic	FeCl$_2$ 2 %	CoCl$_2$ 2 %	NiCl$_2$ 2 %
	gas	12.4	13.5	15.1	16.2
400	liquid	22.1	27.2	31.5	32.8
	solid	65.5	59.3	51.4	51.0
	gas	16.5	18.1	20.3	20.8
450	liquid	32.3	37.2	39.1	40.2
	solid	51.2	44.7	39.6	39.0
	gas	18.1	19.4	21.1	21.6
500	liquid	38.3	39.3	40.2	41.9
	solid	43.6	41.3	38.7	37.5
	gas	20.2	21.5	23.0	23.0
600	liquid	43.4	42.5	41.7	42.5
	solid	35.9	36.0	35.3	34.5

4. Conclusions

The use of co-pyrolysis of peat, polymeric waste and oil-containing waste allows increasing considerably the rate of pyrolysis processes with the production of gaseous and liquid fuels. The search of the catalytic system for the co-pyrolysis processes of organic raw materials demands an individual approach in each case.

Co-pyrolysis of peat and oil-slime in the presence of bentonite clay resulted in the increase of the yield of gaseous products from 18 up to 26 % wt., and liquid fraction – from 45 up to 55 % wt. Besides, the higher yield of C$_1$ – C$_3$ hydrocarbons (up to 10 – 20 %) was observed.

The use of metal chlorides of iron subgroup (2 % wt. concentration) at 500 ºC in the process of co-pyrolysis of peat and polymeric waste resulted in the optimal conversion of the substrate in desired products. A total weight of gaseous and liquid products was increased up to 15 %, and at the same time the amount of char decreased.

Thus we have found that the use of catalytic systems does not only decrease the pyrolysis temperature but intensifies the processes of refining and ennobling of low-grade natural raw material.

Acknowledgements

References

Bennadji H., Fisher E., 2014, Influence of the Grain Direction on the Low-temperature Pyrolysis of Large Wood Particles, Chemical Engineering Transactions, 37, 61-66.

Blasi C.D., Branca C., Galgano A., 2008, Products and Global Weight Loss Rates of Wood Decomposition Catalyzed by Zinc Chloride, Energy Fuels, 22(1), 663-670.

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.

Bokovikova T.N., Shperber D.R., Shperber E.R., 2011, Application of oil-slimes in road base and surface construction, NAFTA, 62, 11-12, 383-385.

Demirbas A., 2000, Biomass resources for energy and chemical industry, Energy Edu Sci Technol, 5, 21-45.

Fonts I., Kuoppala E., Oasmaa A., 2009, Physicochemical Properties of Product Liquid from Pyrolysis of Sewage Sludge, Energy Fuels, 23, 4121–4128.

Heermann C., Schwager F. J., Whiting K.J., 2001, Pyrolysis & Gasification of Waste: A worldwide technology and business review, Juniper Consultancy services LTD, Uley, Gloucestershire, England.

Junwon J., Jinhwan K., Jin-Young B., 2005, Effects of Lewis acid-type transition metal chloride additives on the thermal degradation of ABS, Polym. Degrad. Stab., 88(2), 324-332.

Kaminsky W., Zorriqueta I.-J.N., 2007, Catalytical and thermal pyrolysis of polyolefins, J. of Anal. Appl. Pyrol., 79(1-2), 368-374.

Karayildirim T., Yanik V, Yuksel V, Bockhorn H., 2006, Characterisation of products from pyrolysis of waste sludges, Fuel, 85, 1498–1508.

Kuriakose P., Manjooran S.K.B., 1994, Utilization of refinery sludge for lighter oils and industrial bitumen, Energy Fuels, 8, 788-792.

Lima A., Canto E., De Souza Jr M., Valle M.L., 2012, Using simulated distillation or density to maximize lubricants production from low density polyethylene (LDPE) pyrolysis, Chemical Engineering Transactions, 26, 219-224.

Mohan D., Pittman Ch.U. Jr., Steele Ph.H., 2006, Pyrolysis of wood/biomass for bio-oil: A Critical Review, Energy Fuels, 20, 848-889.

Rulkens W., 2008, Sewage Sludge as a Biomass Resource for the Production of Energy: Overview and Assessment of the Various Options, Energy Fuels, 22(1), 9–15.

Shie J.-L., Chang C.-Y., Lin J.-P., Lee D.-J., Wu C.-H., 2002, Use of Inexpensive Additives in Pyrolysis of Oil Sludge, Energy Fuels, 16, 102-108.

Shie J.-L., Chang Ch.-Y., Lin V, Wu Ch.-H., Lee D.-J., 2000, Resources recovery of oil sludge by pyrolysis:kinetics study, J. Chem. Technol. Biotechnol., 75, 443-450.

Shie J.-L., Lin J.-P., Chang C.-Y., Lee D.-J., Wud C.-H., 2003, Pyrolysis of oil sludge with additives of sodium and potassium compounds, Resour. Conserv. Recycl., 39, 51-64.

Shilina M.I., Bakharev R.V., Smirnov V.V., 2008, Aluminum halide-cobalt halide polynuclear complexes active in low-temperature conversion of alkanes: formation, molecular structures, and IR spectra, Russ. Chem. Bull., 57(11), 2251-2260.

Suh D.J., Choi J.H., Woo H.C., 2014, Pyrolysis of Seaweeds for Bio-oil and Bio-char Production, Chemical Engineering Transactions, 37, 121-126.

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-temperaturepyrolysis and gas formation, Chem. Eng. J., 154, 355-360.

Wang Z., Guo Q., Liu X., Cao C., 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 Convers. Manage., 45, 651-671.

Zou X., Yao J., Yang X., Song W., Lin W., 2007, Catalytic Effects of Metal Chlorides on the Pyrolysis of Lignite, Energy Fuels, 21, 619-624.