Chemical Engineering Journal 238 (2014) 219–226

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Influence of metals chlorides on oil-slime thermocatalytic processing

K.V. Chalov, Yu.V. Lugovoy, V.Yu. Doluda, A.I. Sidorov, M.G. Sulman, Yu.Yu. Kosivtsov, O.P. Tkachenko, E.M. Sulman *

Tver State Technical University, 1 – Zelinsky Institute of Organic Chemistry (ZIOC RAS) Russia, Leninsky prospekt, 47, Moscow 119991, Russian Federation

HIGHLIGHTS

- Catalytic pyrolysis of oil-containing waste with metals chlorides is presented.
- Cobalt and nickel chlorides showed the most catalytic activity in the oil-slime pyrolysis.
- The use of $CoCl_2$ resulted in the highest degree of conversion.
- The optimal temperature of the model oil-slime sample is 500 °C.
- The optimal catalyst content – cobalt chloride 5% (wt.).

ARTICLE INFO

Article history:
Available online 18 September 2013

Keywords:
Catalytic pyrolysis
Oil-containing waste
Metals chlorides
Gaseous hydrocarbons

ABSTRACT

The goal of this research is the development of the method of oil-slime recycling. In the present paper we report on the results of the process of oil-containing waste catalytic pyrolysis with such metals chlorides as 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 highest conversion of oil-slime into gaseous and liquid products was observed in the presence of iron subgroup metals chlorides. The maximum conversion was obtained in the presence of $CoCl_2$. The increase of the conversion into gaseous and liquid products in the presence of $CoCl_2$ was 41.2 wt.% and 8.5 wt.%, respectively, compared to a non-catalytic process. The optimal conditions of the oil-slime pyrolysis process are 500 °C and cobalt chloride content of 5 wt.%.

1. Introduction

Oil production, transportation and storage as well as 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 [1]. More than that, the storage of oil-containing waste in sludge tanks endangers the environment [2].

Oil-slime is bulk waste the formation of which takes place at all stages of oil production, processing and transportation. Oil-slime mainly consists of oil-products, water and mineral constituents (sand, clay, metals oxides etc.) which accounts for their variable composition and complicates their disposal. That is why the development of environmentally clean technology for oil-slime processing is of paramount importance [2–5].

The existing methods of oil-slime processing can be divided into physical, chemical, physicochemical, thermal and biological [6,7]. 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 [6]. The thermal treatment resulting in gaseous and liquid fuel formation is considered to be the most economically beneficial [6–8]. 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-slime was studied for many years [9,10,8], but high energy consumption and other shortcomings made this process unappealing. Catalytic pyrolysis of oil-slime allows obtaining hydrocarbons which can be used either as fuel or raw material for the chemical industry [7,8,11]. Compared to other methods of oil-slime 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 [12–14]. The practical application of this method will contribute to

* Corresponding author. Tel.: +7 (4822) 44 93 17/(499) 137 2944; fax: +7 (4822) 44 93 17/(499) 135 5328.
E-mail addresses: sulman@online.tver.ru, secretary@ioc.ac.ru (E.M. Sulman).

1385-8947/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.cej.2013.09.048

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 [15–17]. However, to the best of our knowledge, no catalytic studies of metal chlorides in pyrolysis of oil-slime 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-slime into gaseous and liquid products was observed in the presence of iron subgroup metal chlorides, in particular for $CoCl_2$. The substantial increase of the conversion into gaseous and liquid products for this metal salt indicates that the catalytic pyrolysis of oil-slime is promising for industrial exploration.

2. Experimental

2.1. Materials

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.

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 the sulfur 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.

2.2. 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 an 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 in 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 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, 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. 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 kgs/sm^3; duration of the analysis 30 min; sample volume 1 mL; carrier-silica gel 0.4 mm; column length 1 m; column temperature 50 °C; detector temperature 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 cm^3/min; sample volume of the gas analyzed was 0.5 cm^3; thermostat temperature was 40 °C.

2.3. Characterization

FTIR-spectra of diffuse reflection (DRIFT) were recorded at room temperature on a NICOLET "Protege" 460 spectrometer using the diffuse reflection attachment within the range of 6000–400 cm^{-1} with a step 4 cm^{-1}. CD_3CN was used as a test for acidity; it was adsorbed at room temperature. Before acetonitrile adsorption the catalysts and carriers were treated in vacuum at room temperature for 3 h and at 450 °C for 2 h with the heating rate of 5°/min.

The determination of the specific surface areas and pore distributions of the pyrolysis solid residues was performed by low-temperature adsorption of liquid nitrogen on Beckman Coulter SA 3100 at −196 °C and ps/p^0 adsorption 0.9814. In the analysis, t-plot model was used. To process the adsorption data, the Harkins and Jura equation was applied.

Thermogravimetric analysis (TGA) was carried out using 209 F1 NETZSCH. Differential scanning calorimetry (DSC) was performed using 204 F1 NETZSCH firm. 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 °C/min. When 600 °C was achieved, the sample was kept under isothermal conditions for 50 min.

Liquid products of oil-slime pyrolysis (at 500 °C and oil fraction content 20 wt.%) were analyzed by gas chromatography-mass spectroscopy (GC–MS) on a PQ-GCMS-2010S instrument (SHIMADZU). The conditions of the analysis were as follows: thermostat temperature was 40 °C for 15 min, heating up to 280 °C at a rate of 5 °C/min, holding up time 20 min at 280 °C; injector temperature 280 °C; column flow 1 mL/min (high purity He); interface temperature 280 °C; IonSource temperature 260 °C; m/z 15÷500 atomic mass unit.

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 Kα line.

3. Results and discussion

To estimate the influence of the metal chlorides under study on oil-slime pyrolysis, we compared the pyrolysis data with and without catalysts such as 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 $NiCl_2{\cdot}6H_2O$.

3.1. Influence of oil-slime composition and the process temperature on the products yield in the non-catalytic process

First, the non-catalytic pyrolysis has been studied with oil-slime containing 20 wt.% of oil. The pyrolysis temperature was varied between 450 and 650 °C. Fig. 1 shows that below 500 °C, the product contains a high fraction of solid residue. At the 500–550 °C 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 8% increase of conversion, however, this temperature increase requires additional energy, making it economically