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Experimental: Thermochemical Dehydration of Oil Sludges of Different Origins.

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ABSTRACT

The paper studied the breaking of highly stable oil-water and water-hydrocarbon emulsions of natural and technogenic origin. The main factors are specified which determine the stability and an increased resistance of emulsions to the traditional destruction methods. The effectiveness of thermochemical treatment on various water-oil and water-hydrocarbon emulsions was tested. The demulsifier Rekod-118A was selected as the main reagent used on fields for the destruction of highly stable water-oil emulsions. It was shown that among five provided samples only one sample reduced the content of water to the required standard level after a thermochemical dehydration. It was established that thermochemical dehydration method is generally ineffective for the destruction of highly stable water-oil emulsions and may serve only as the means of preliminary emulsion treatment. It was shown that after thermochemical exposure at 60 °C the water content in IL, HPR, YS emulsions remained at an original level and in MOCW emulsion the water content decreased by 14% and made 19% wt. After the dehydration by thermochemical method, only one sample (LP) out five ones demonstrated the water content reduction to the required standard of performance. Optimum reagent dosage for this raw material made 800 g/t and the process temperature made 60 °C with settling duration of 24 hours.

Keywords: water-oil and water-hydrocarbon emulsions, crude oil, dehydration, demulsifier, thermochemical treatment

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INTRODUCTION

The development of petroleum, petrochemical industry and related fields of technology and economy takes place in the terms of constantly increasing demand for environmental standards of enterprises.

The problem of liquid crude oil, heavy pyrolysis resin, the mixture of oil waste disposal, etc., which are highly resistant water-oil emulsions is relevant, their formation and accumulation provide not only an environmental hazard but also causes a direct and an indirect economic losses to enterprises.

All considered types of crude oil are highly resistant water-oil and water-hydrocarbon emulsions, which are characterized by a low efficiency of conventional dehydration techniques based on aqueous phase sedimentation. On the average, such oil sludges contain 10-12% wt. of solids, 30-50% wt. of water and 30-50% wt. of hydrocarbon phase [1].

The increased stability of such emulsions is determined by the following factors:

- close densities of water and hydrocarbon phases [2];
- a high concentration of natural and manmade emulsifiers (asphaltenes, naphthenic acids, heterocyclic
- nitrogen compounds, resins, clay, oxygenated compounds, in general) [3, 4];
- the presence of inorganic salts (mainly sodium, magnesium, chlorides, carbonates and calcium
- sulfates, iron sulfides and oxides),
- abnormal viscosity of emulsions [5, 6].

The thermochemical method is most widely used to break the emulsions. Demulsifiers used for commercial purposes are such polymeric surfactants as copolymers of polyethylene and polypropylene or alkylphenol formaldehyde resins, dodecylbenzenesulfonic acids or various surfactant compositions [7, 8].

RESEARCH METHODOLOGY

In order to carry out the process of dehydration by thermochemical method the conditions were purposefully selected to ensure the maximum degree of water removal [8]. Rekod-118A was selected as the demulsifier, used on fields for the destruction of highly stable water-oil emulsions. All kinds of raw materials at initial stage had the same process conditions. Demulsifier dosage made 1000 g/t. The temperature mode of the process maintained at 60 °C through the use of a thermostat. Mixing time made 30 minutes. The mixing intensity made 200 rev/min. The settling time made a day. The amount of emulsion sample made 250 g.

If the some effectiveness of the thermal-chemical treatment was detected, then the variation of process conditions took place (temperature, reagent dosage, settling time) to determine the most optimal modes.

STUDY RESULTS AND THEIR DISCUSSION

The following emulsions were chosen as raw materials for the dehydratation process:

- The mixture of oil containing waste (MOCW)
- Emulsion of heavy pyrolysis resin (HPR)
- Yutazinsky sludge (YS)
- Intermediate oil layer (IL)
- The emulsion of liquid pyrolysis products (LP).

The mixture of oil containing waste (MOCW) is formed during cleaning and rinsing of tanks, rail and road tankers, vessel tanks and other equipment for the transportation and storage of petroleum products. Flushing waters with MOCW are discharged in special collecting ponds, where water is separated from oil due to the density difference. Only part of water is removed by collectors from MOCW. The mass fraction of water in MOCW after collectors varies from 20 to 50%. In order to perform the experiment MOCW emulsion was chosen obtained at washing and steaming station "Zeletsino" of OJSC "First freight company".

Heavy pyrolysis resin (HPR) and the emulsion of liquid pyrolysis products (LP) are the byproducts of the pyrolysis process at OJSC "Kazanorgsintez". They are formed during the pyrolysis stage in quenching-tempering devices at the stage of primary fractionation and in settling tanks. Emulsions are characterized by an increased resistance due to the high concentration of emulsion stabilizers (pyrolysis by-products obtained from polycondensation and polymerization, etc.). The hydrocarbon portion of these wastes may be used in the production of carbon black, coke, petroleum polymer dark resins, concrete superplasticizer and as fuel oil component.

The emulsion of intermediate layer (IL) is formed at the stage of crude oil preparation on the OGPD "Zyuzeevneft". In the treatment tanks of dehydration and desalting units on the boundary of oil and water phases organic and inorganic emulsion stabilizers (asphaltene, resin, paraffin compounds, mechanical impurities) are concentrated, they impart a high kinetic and aggregative stability for an intermediate layer. The involvement of IL emulsion in processing could provide oil industry with the additional sources of raw materials and expand the range of fuel oil.

Yutazinsky sludge (YS) is the collection of sludge, waste oil products, the waste obtained from the operation of motor vehicles and oil equipment, which accumulate in oil barns, oil storage tanks and settling ponds. The accumulation of such waste inevitably leads to air, lithosphere and the hydrosphere pollution, removes a large area of lands from application. The hydrocarbon phase extracted from sludge may be compounded with sales oil, or may provide the additional sources of fuel oil. Table 1 provides data on the types of used materials.

Table 1. Characteristics of raw materials

Raw material type	Density, kg/m^3	Water content, % wt.
Heavy pyrolysis resin (HPR)	950	32,03
Emulsion of liquid pyrolysis products (LP)	958	73,09
Yutazinsky sludge (YS)	970	34,83
The mixture of oil containing waste (MOCW)	947	21,79
Intermediate layer (IL)	964	21,21

The thermochemical method is based on thermal and chemical impact. During heating, the decrease of reinforcing layer around the water globules is observed due to the dissolution of some adsorbed paraffin molecules in an oil phase and the increase of water globule deposition rate due to hydrocarbon phase viscosity and density reduction. At the chemical impact by demulsifier reagent adsorbs itself at the water-oil boundary and lowers the surface tension, and thus the reduction of structural and mechanical strength of the water globules takes place.

Rekod-118A is used as a de-emulsifier. Demulsifier dosage made 1000 g/t. The process temperature made 60 °C. Mixing period made 30 minutes. The mixing intensity made 200 rev/min. The settling period made a day.

The results of thermochemical dehydration reflecting the initial and final water content are shown in Table 2.

As we see from the table, despite a relatively high temperature of dehydration and a high dosage of the de-emulsifier YS, IL and HPR emulsions showed resistance to its treatment. There is no partial water discharge. This is likely due to the fact that the presented emulsions have a high aggregate and kinetic stability due to the high concentration of natural emulsion stabilizers there, namely asphaltenes, resins, salts, etc.

Table 2. Thermochemical dehydration results

Raw materials	Original water content	Residual water content
HPR	32,03	32,02
LP	73,09	0,85
YS	34,83	34,80
MOCW	33,00	19,02
IL	21,21	21,07

MOCW emulsion shows lower resistance to a demulsifier. However, in this case, after the process the water cut of a product is maintained at a high level (19%). Since this raw material is obtained from washing of railway tanks for the finished oil products, some free water may be removed by a de-emulsifier treatment, at that the most part of the bound water remains in the emulsion.

De-emulsifier efficiency is revealed best of all concerning LP emulsion. According to the data of Table 2, in contrast to other types of considered raw materials, LP emulsion is characterized by lowest density indicators, salt content, kinematic and conditional viscosity, coking, the flash and freezing temperature. These indicators indirectly reflect the presence of emulsion stabilizers. Therefore, LP emulsion has a relatively lower resistance. The water content therein is reduced to 0.86% wt. This raw material does not require a deeper dehydration, the thermochemical process is a self-sufficient one. Further studies were held for LP emulsion in order to determine the optimal conditions for thermochemical demulsification. The dewatering curves at various conditions are shown on Figure 1.

Table 3. Physical and chemical characteristics of the product

Indicator name	Value
Viscosity at 50 °C Engler , °E Kinematic cSt	 1,61 7,398
Viscosity at 80 °C Engler, °E Kinematic cSt	 1,2 3,041
Viscosity at 100 °C Engler, °E Kinematic cSt	 1,1 1,994
Mass fraction of mechanical impurities	0,4
Mass fraction of water	0,86
The amount of water-soluble acids and alkalis	alkali
Sulfur mass fraction	3,84
Cokability	14,4
Flash point in open crucible, °C	66
Freezing temperature, °C	-16°C
Density at 20°C	950
Salt content, mg/l	170

According to Figure 1, the efficiency of thermochemical impact decreases dramatically when the process is carried out at 20 °C, despite a longer sedimentation period (72 hours). Dewatering process is performed significantly better at elevated temperatures (at 60 and 80 °C). It should be also noted that in order to achieve less than 1% of the water content in a product for two considered temperatures at the duration of sedimentation within a day the demulsifier dosage of 800 g/t is an optimum one. A further dosage increase is accompanied by a slight change of the residual water content in a product. One may conclude that an optimum process temperature for LP emulsion is 60 °C with the sedimentation duration of 24 hours and the reagent dosage of 800 g/t.

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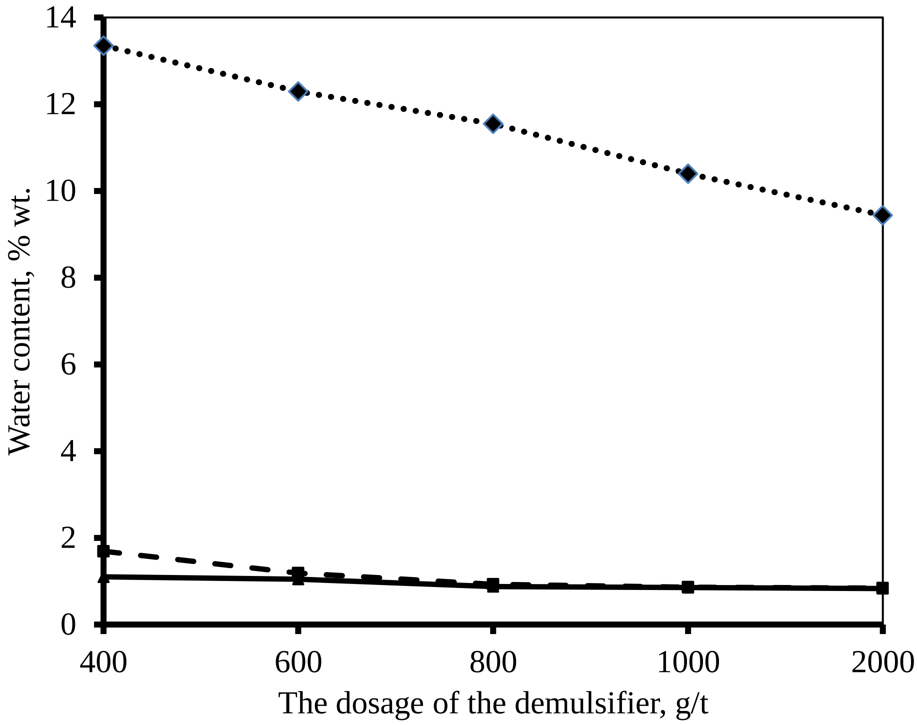

Fig. 1. The residual content of water in the LP emulsion under various conditions

CONCLUSIONS

The article studied the decomposition processes of highly stable oil-water and water-hydrocarbon emulsions of natural and technogenic origin by thermochemical method. The demulsifier Rekod-118A was selected as the main reagent used in the fields for the destruction of highly stable water-oil emulsions. The samples of water-hydrocarbon emulsions from petrochemical productions (HPR, LP), the emulsions forming from tank cleaning (MOCW), oil sludge from the oil storage tanks (YS), intermediate layers of oil treatment (IL). It was shown that after thermochemical exposure at 60 C° the water content in IL, HPR and YS emulsions remained at an original level, and for MOCW emulsion the water cut decreased by 14% and made 19% wt. In five samples of the above, after the thermochemical dehydration, only one sample (LP) out of 5 reduced water content to the required standard level. Optimum reagent dosage for this raw material is 800 g/m and the temperature of process performance makes 60 °C with the sedimentation duration of 24 hours.

SUMMARY

The processing of man-made waste oil currently requires a special attention since the volumes of their accumulation reached critical values on the territory of oil-producing, refining and petrochemical industries. Within this paper we studied the possibility of different liquid oil sludge dewatering by thermochemical method. All these raw materials are highly resistant water-oil emulsions. After the thermochemical treatment of 5 presented samples, only one reduced water content to the required standard values (LP). The remaining emulsion (HPR, YS, MOCW, IL) showed a relatively high resistance to the treatment of a demulsifier. This may be related to the fact that LP emulsion is an "oil-in-water" emulsion and its hydrocarbon phase has a low content of paraffinic hydrocarbons, low viscosity and a high content of light hydrocarbon fractions. It was also found that the thermochemical dehydration method is ineffective for the breaking of highly stable water-oil emulsions and may serve as the means of preliminary emulsion treatment.

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