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## Studying breaking of inverted emulsions with thermolysis purification TD<sub>600</sub>

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**Abstract** Currently, emulsions are used in many branches of industry and agriculture. It explains significant attention paid to issues in production, stabilization and breaking of emulsion. Besides, producing steady emulsions is of importance in many processes; the reverse problem, that of demulsification, is important as well in oil production and treatment of oil emulsion waste water. This paper studies the breaking (demulsification) of inverted emulsions with the help of thermolysis purification TD<sub>600</sub>, produced by thermal modification of purification, a large-scale waste of the sugar industry.

### 1. Introduction.

Demulsifying is used in such common processes as separation of emulsified water from crude oil and tar, deoiling of condensate, as well as removal of surfactants from water-based washing solutions used in wool scouring, etc.

Methods of emulsion breaking vary and may include the following stages:

- 1) reduction in strength and breaking of solid emulsifier membranes on the surface of water drops;
- 2) collision of water globules with each other and with hydrophilic particles, leading to coalescence;
- 3) lamination and separation of the broken emulsion into its phases after introduction of special surfactants.

Different methods are applied to break the protective membranes on the globules' surfaces: mechanical stimulus, application of chemicals (inorganic acids, aluminum salts, natural inorganic sorbents, organic compounds); electric methods, centrifugation, thermal methods (heating or freezing); filtration through different substances based on preferential wetting of petroleum products or powdered solids [1].

The filter bed, through which the emulsion is filtered, may be made of an excelsior, [2], clean sand [3], fossil flour, clay or marble [4], Fe<sub>2</sub>O<sub>3</sub> or amphibole [5], porous mass of crushed Al<sub>2</sub>O<sub>3</sub>[6], a layer of silica, pyrites and other [7-16]

### 2. Materials and methods

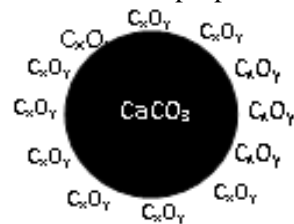
The targets of research into the model system are high-purity liquids; the studied oils had low dielectric permeability and high electric resistance. Distilled water was used and diesel fuel oil was clarified by Petrov's method and twice distilled T<sub>boil</sub> ~ 300°. Thermolysis purifying was used as a solid emulsifier and emulsion stabilizer.



The paper [1] contains a thorough study of purification, a calcium carbonate-containing waste from sugar production. It is a fine-dispersed calcium carbonate ( $\text{CaCO}_3$ ), which surface organic compounds are absorbed during the cleaning of sugar beet diffusion juice: pectines, sucrates, organic acids, saponin, nitrogen-free and nitrogen compounds, lime in the form of various salts and other mineral substances.

Thermolysis purification ( $\text{TD}_{600}$ ) was produced from initial purification by thermal treatment at  $600^\circ\text{C}$  without access of air in a SNOL electric furnace.

At the temperature of  $600^\circ\text{C}$ , a volumetric coloration of the initial purification happens: it turns black due to soot formation on the surface of the  $\text{CaCO}_3$  particles (Figure 1). Characteristics, physical and chemical properties of the initial purification were thoroughly studied in the paper [1].



**Figure 1:** A particle of  $\text{TD}_{600}$

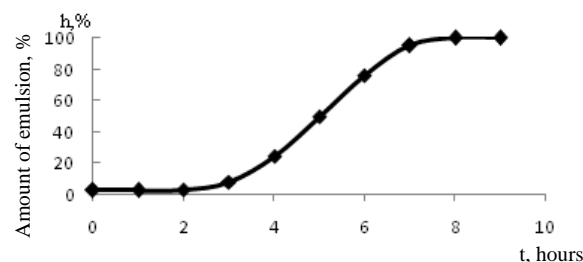
The chemical composition of the soot at the surface of  $\text{CaCO}_3$ : carbon 99.65%; hydrogen 0.28%; oxygen 0.08%; inorganic substances (ash) 0.01%. Carbon at the surface of the  $\text{CaCO}_3$  particles appears as crystallites ( $\text{C}_x\text{O}_y$ ). The specific surface of the thermolysis purification is  $22.2\text{ m}^2/\text{g}$  [1].

Hydrophobic emulsions were produced in the laboratory by dispersing distilled or technical water in the diesel fuel oil, diesel fuel, crude oil inside a T-302 homogenizer complete with a paddle mixer inside a steel liner with the volume of  $250\text{ cm}^3$ . Following some experimentations, an optimal method for preparation of concentrated emulsions was selected: mixing time is 30 min; mixer rotation speed is 3000 rpm.

### 3. Studying the breaking of inverted emulsions with the thermolysis purification

The inverted emulsions that the authors have developed consist of organic and inorganic substances; the main component is water. During the operation, the emulsion amasses a significant number of petroleum products (up to  $100\text{ g/l}$ ). Following its end of life, the emulsion may be treated together with other wastes at effluent water treatment facilities. To prevent ingress of significant volumes of petroleum products to the waste waters with the spent emulsion, it is necessary to utilize methods to break the emulsion and separate the petroleum products.

At this stage, experiments were conducted in breaking model emulsions with  $\text{TD}_{600}$  by residue size. A qualitative characteristic of an emulsion's aggregate strength is its lamination speed. It was determined by measuring the height (volume) of the separated phase at certain intervals after production of the emulsion. As an example, Figure 2 shows a dependency of daily residue of an inverted emulsion with a concentration of the dispersed phase ( $\text{Ph}=0.5$ ) on the concentration of  $\text{TD}_{600}$ .



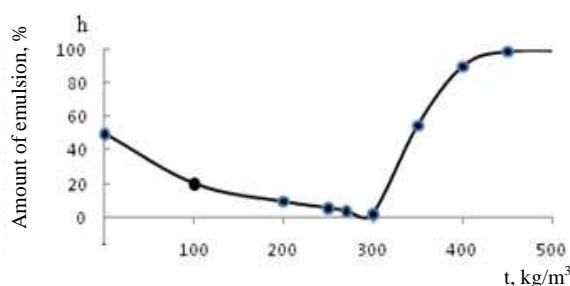
**Figure 2:** Daily residue of a  $\text{Ph}=0.5$  emulsion as a function of  $\text{TD}_{600}$  concentration

The data in Figure 2 show that when emulsifier concentration increases, the stability of the emulsion also increases, until it reaches a limit (maximum at  $C_d = 300\text{ kg/m}^3$ ) and starts breaking the emulsion instead; the emulsion is completely broken at the emulsifier's concentration of  $350\text{ kg/m}^3$  with complete release of water. Thus, it is necessary to note that depending on its concentration,  $\text{TD}_{600}$  may serve as a stabilizing emulsifier or as an emulsion breaker for inverted emulsions. As an example,

studies in dynamics of emulsion breaking are shown (Figure 3) and an electron photomicrograph (Figure 4), where  $h$  is the percentage of emulsion residue for certain moment  $\tau$ .



**Figure 3.** Dynamics of demulsification of an emulsion with  $\Phi=0.5$  and stabilized with  $TD_{600}$



**Figure 4:** Electron photomicrograph of an emulsion with  $\Phi=0.5$ , with  $TD_{600}$  concentration of 400 kg/m<sup>3</sup>

From Figures 3 and 4, one may conclude that the dynamics of emulsion breaking under the action of emulsifier depends on the amount of emulsifier added and the emulsion's dispersed phase concentration ( $\Phi$ ). The higher  $\Phi$  is, the faster the emulsion breaking is for the same emulsifier concentration, while for the same value of  $\Phi$ , dynamics of breaking increases significantly with increased concentration of  $TD_{600}$  (Figure 2). In Figure 4, it is evident that an initial coalescence of the drops of the emulsion happens there.

After settling an emulsion for a month, a complete breaking is observed. Due to the fact that these demulsifying methods lead to a large volume of sediment and the process takes a lot of time; filtration through a grainy bed was selected as a method for breaking the "water - diesel fuel oil" model inverted emulsions. The filter bed consists of layers of thermolysis purification  $TD_{600}$  and sand.

A model emulsion, containing 46.6 mg/l of petroleum products, passed through the two-layer filter, the height of each layer of  $TD_{600}$  and each layer of sand ( $SiO_2$ ) was 350 mm.

Comparative data for the filtering effect depending on weight ratio of the filtering materials are given in Table 1.

**Table 1.** Results of determining an effect of filtering as a function for the filtering load weight ratio

| Filtering material                                     | Weight ratio | Petroleum products, mg/l |                      | Degree of purification |
|--|--------------|--------------------------|----------------------|------------------------|
|  |              | in initial water         | after the filtration |                        |
| Thermolysis purification ( $TD_{600}$ ) and Volsk sand | 3:1          | 46.6                     | 9.32                 | 80.0                   |
|  | 2.5:1        |                          | 7.46                 | 84.0                   |
|  | 2:1          |                          | 3.64                 | 92.2                   |
|  | 1.5:1        |                          | 1.96                 | 95.8                   |
|  | 1:1          |                          | 1.31                 | 97.2                   |
|  | 0.5:1        |                          | 4.61                 | 90.1                   |

Comparing the data on results of purification (Table 1) allow concluding, that at a ratio of the filtering material less than 1:1, there is no further increase in the purification degree due to the fact that with the lower amount of de-emulsifier, the large-molecule sorption capacity becomes depleted, and these molecules cannot be absorbed by the mineral sorbent ( $\text{SiO}_2$ ). When the filtering materials ratio is larger than 2:1, the sorbent's capacity is not used to its full extent, leading to increased consumption of the sorbent and, as a result, to increased costs for the purification process. Thus, the best result for removal of petroleum products was obtained for the 1:1 ratio of the filtering materials.

The results of the physical and chemical indicators for purification of petroleum emulsions with demulsifier  $\text{TD}_{600}$  are shown in Table 2.

**Table 2.** Physical and chemical indicators of petroleum emulsion waste effluent before and after purification

| Indicator's name,<br>Unit | Before<br>purification | After purification with<br>$\text{TD}_{600}$ | Efficiency<br>of purification, % |
|---------------------------|------------------------|--|----------------------------------|
| pH                        | 10.0                   | 7.80   | –                                |
| COD, mgO/l                | 350.0                  | 18.7   | 94.6                             |
| Suspended matter (mg/l)   | 179.4                  | 0.056  | 99.9                             |
| Petroleum products, mg/l  | 46.6                   | 1.30   | 97.2                             |

As the results of the research show, when using  $\text{TD}_{600}$  to break petroleum emulsion effluents, concentration of suspended material after filtration is practically zero, that is, the purification from the suspended material is complete, COD is reduced by up to 94.6%; petroleum concentration - by up to 97.2%; pH is reduced from 10 to 7.8–7.6, while the refractive index of the filtrate  $n$  is equal to that of tap water.

#### 4. Conclusions

The experiments on breaking the model emulsions show that when emulsifier concentration increases, the stability of the emulsion also increases, until it reaches a limit (maximum at  $C_{II} = 300 \text{ kg/m}^3$ ) and starts breaking the emulsion; the emulsion is completely broken with the emulsifier's concentration of  $350 \text{ kg/m}^3$  with complete release of water. Depending on its concentration,  $\text{TD}_{600}$  may serve as a stabilizing emulsifier or as an emulsion breaker for inverted emulsions.

To accelerate the breaking of petroleum emulsions, filtering through layers of granular load was selected with the layers consisting of  $\text{TD}_{600}$  and sand. The best result for removal of petroleum products was obtained for the 1:1 ratio of the filtering materials. The optimum parameters for the granular layer filtration process were obtained: load height is 7 cm, filtration time is 110 min, filter capability is 0.043 l/h. It was found out that application of demulsifier  $\text{TD}_{600}$  for purification of concentrated petroleum emulsion effluents reduced initial concentrations of petroleum products to the values that are within the permitted limits for the water used in circulating water supply (15–20 mg/l). Thus, it is recommended to use 60% of the purified water for recirculation.

#### 5. Acknowledgment

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