



The Effect of Fly Ash and Tween 20 Combination in Water-In-Crude Oil Emulsions Treatment

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Abstract

The petroleum industry is in demand of effective techniques for breaking stable emulsions. In order to develop a low-cost, green and effective demulsifier, fly ash taken from the local power plant was applied to water-in-oil emulsions of various concentrations and conditions. A thorough analysis of crude oil composition and ash sample structure was carried out. Emulsion separation kinetics demonstrated that the optimal temperature for the crude oil emulsions was 60 °C, but the demulsification efficiency was not satisfactory. To improve separation efficiency Tween 20 was applied to the emulsions in combination with grinded coal fly ash. This resulted in a higher demulsification efficiency (100% for some emulsions) and was justified by the microphotographs before and after demulsification. The optimal conditions found were as follows: 60 °C, Tween 20 (1600 ppm), and grinded coal fly ash (1 wt%). Finally, the demulsification process was investigated with FT-IR analysis to justify the proposed mechanism.

Keywords: Crude oil emulsion; Water-in-oil emulsion; Coal fly ash; Oil emulsion breaking; Green demulsifier.

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1. Introduction

One of the main issues of the oil production industry is the separation of water from crude oil. The crude oil extracted from the wellbore is naturally in an emulsion form.^[1,2] The formation of water-in-oil emulsion happens once the heterogenous mixture flows in the piping valves and porous rocks and endures turbulence at high temperatures or high pressure.^[3,4] Emulsions are extremely stable due to the presence of interface-active species such as surfactants, asphaltenes, resins, naphthenic acids, and fine solids.^[5-7] The formation of highly stabilized emulsion with saline water causes numerous problems during oil processing and transportation, including an increase in viscosity related to the presence of tiny water droplets in crude oil, obstruction during transit, the high cost of pumping and transportation as well as pipelines corrosion and catalysts poisoning throughout the refining process.^[8-10] The emulsion must be split into two

phases or demulsified to maintain a smooth refining process in the oil production industry. Therefore, elaborating the efficient and qualitative method of reducing the stability of water-in-oil emulsions is the primary concern among oilfield researchers.

Several demulsification techniques were developed in recent years for the separation of crude oil emulsions such as chemical, biological,^[11-13] membrane,^[14-16] electrical^[17-19] and microwave irradiation.^[20-22] Chemical treatment is the most widely used demulsification method, which involves the addition of demulsifying chemicals to improve emulsion separation.^[1,23,24] Demulsifiers should have a higher interfacial activity than natural emulsifiers and less mechanical strength of the interfacial film that facilitates the coalescence of water droplets. The demulsification mechanism involves replacing surface active natural stabilizers with demulsifier molecules from the water-oil interface.^[25,26] In recent years, plentiful research studies have been dedicated to using various types of chemical additives to estimate the influence of demulsifiers' composition, structure, concentration and molecular weight on demulsifier effectiveness.^[3,27-30] Chemical demulsifiers are well-known for their effective separation of oil from water as well as for reducing the operational and disposal costs. However, they are associated with environmental pollution as a result of the discharge of demulsified water (removed from the crude) into the environment and contamination of the

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separated product.^[31] In addition, it is necessary to select or optimize the demulsifying agent regarding the composition of crude oil emulsion which can be varied depending on the oil field and depth of production prior to separation.^[25]

The coal fly ash (CFA) could be considered as the auspicious alternative to chemical additives. Recently, several studies have reported the CFA as a promising demulsifying agent for stable W/O emulsions due to the high content of silica, iron and alumina oxides.^[32] The main advantage of CFA compared to chemical demulsifiers is that it can be easily removed from the water phase after breaking the emulsion and recycled, thus, reducing the operational costs.^[33] Furthermore, CFA is the waste product of thermoelectric power stations,^[34] making it relatively cheap and available, and its implementation in the petroleum industry may be beneficial both for the economy and ecology since CFA can result in issues with the skin, eyes, respiratory, cardiovascular, and neurological and even cause cancer.^[35] Fly ash is usually stored in open ash dumps and contributes to the content of PM_{2.5} particles (inhalable particles with diameters of 2.5 μm and smaller) in the air.^[36] Also, the use of ash is a waste-free process and may reduce the burden on the environment of large cities in Kazakhstan. Fly ash's demulsifying capabilities have recently been studied in Kazakhstan,^[37] but more research is still needed to determine how it affects oil emulsions with different compositions and stability.

In this work, highly stable water-in-crude oil emulsions were treated under different temperatures in the presence of CFA. The correlation between particle size distribution of coal fly ash and demulsify/cation efficiency was revealed. In addition, the combination effect of CFA with a surface-active agent Tween 20 was investigated and the separation mechanism of CFA was described.

2. Experimental section

2.1 Materials

Crude oil samples are taken from North-West Qonys oilfield in Kyzylorda region, Kazakhstan. The selected properties of crude oil were determined and are presented in Table 1.

Table 1. Crude oil of North-West Qonys oilfield characteristics.

Characteristic	Value	Determination method
Asphaltenes	0.19 wt%	GOST 11858-66, ASTMD 6560
Waxes	0.69 wt%	GOST 11858-66, ASTMD 6560
Paraffines	11.5 wt%	GOST 11851-85
Dynamic viscosity	52.8 mPas (at 30 °C)	Brookfield digital rheometer DV-III+
Density	843 kg/m ³	GOST 33364-2015
API Gravity	36.35°API	ASTM D-287
Water content	6% (vol.)	ASTM D-4006

Tween 20 was used as a surface-active agent. Tween 20 – polyoxyethylene (20) sorbitan monolaurate (Fig. 1). The

hydrophilic properties of Tweens are provided by ethylene oxide groups - (CH₂CH₂O) - and a carboxylic acid polyester, and the lipophilic properties are provided by polysorbitan.

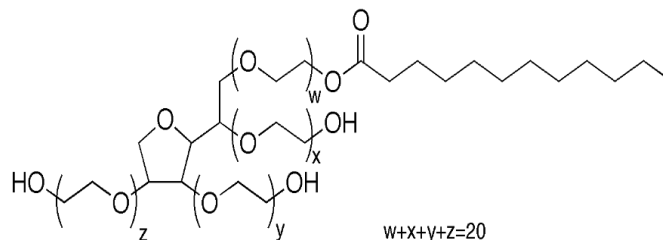


Fig. 1 Tween 20 structural formula.

2.2 Methods

The CFA samples were taken from thermal power station № 2 in Almaty city, Kazakhstan. CFA was dried at 105 °C for 2 hours and sieved using vibratory sieve shaker Analysette 3 with the smallest mesh size of 63 μm and labelled as CFA-1. The sieved fraction of CFA was then milled in a planetary ball mill (SQM-0.4 L) at 400 rpm for 10 minutes. The grinded CFA sample was labelled as CFA-2.

Emulsions were mixed with 1 wt% of coal fly ash powders and homogenized for 5 minutes. This amount of CFA is found as an optimal weight for demulsification.^[38] Afterwards, emulsions with ash were thermostated at various temperatures for different periods of time and then were centrifuged for the ash particles sedimentation. The laboratory centrifuge CM-6M at 1500 rpm during 5 min was used for centrifugation of W/O emulsion.

The demulsification efficiency (DE) was studied using the bottle test method at different temperatures.^[39] The crude oil model emulsion was transferred into 50 ml graduated glass test tubes and placed into a thermostat. The aqueous phase separation was visually monitored at regular time intervals. DE was calculated according to the equation taking into account the initial volume of water in crude oil:

$$DE = \frac{\text{Volume of separated water}}{\text{Total volume of water in the crude oil emulsion}} \times 100\%$$

X-ray diffraction patterns of samples were obtained on Dron-4 diffractometer in digital form using copper radiation. Sample recording modes are as follows: X-ray tube voltage 35 kV, tube current 20 mA, goniometer movement step 0.05° 2θ, and intensity measurement time at a point - 1.5 sec. During the shooting, the sample rotated in its own plane at a speed of 60 rpm. The phase analysis was carried out using the PCPDFWIN and EVA programs with the PDF-2 diffraction database.

Scanning electron microscopy (SEM) images were derived via Quanta 3D 200i system and microphotographs were obtained via optical microscope Leica DM 6000 M at Kazakh National university's National nanotechnology laboratory of open type.

The Fourier Transform Infrared Spectra (FT-IR) of crude oil samples were measured on PerkinElmer Spectrum 65 and zeta potential measurements were carried out using Anton Paar zeta potential analyzer.

The particle size analysis was determined via the laser scattering particle size distribution analyser Partica LA-960. The dynamic viscosity measurements were analysed via Brookfield digital rheometer model DV-III+. The water content was defined through Dean-Stark distillation method (ASTMD-4006).

3. Results and discussion

3.1 Determination the physicochemical characteristics of coal fly ash particles

In the first stage of this work, the characteristics of CFA particles were studied. According to the XRD analysis results (Fig. 2, Table 2), CFA is mainly represented by crystals of mullite and quartz with insignificant amounts of aluminium and iron (III) oxides. This result correlates with other research papers dedicated to fly ash.^[40–42] Conforming to the ASTM C-618 standard, CFA belongs to the F type. Measured zeta potential was equal to -25mV and it can be explained by the presence of aluminum oxide carrying the negative charge.

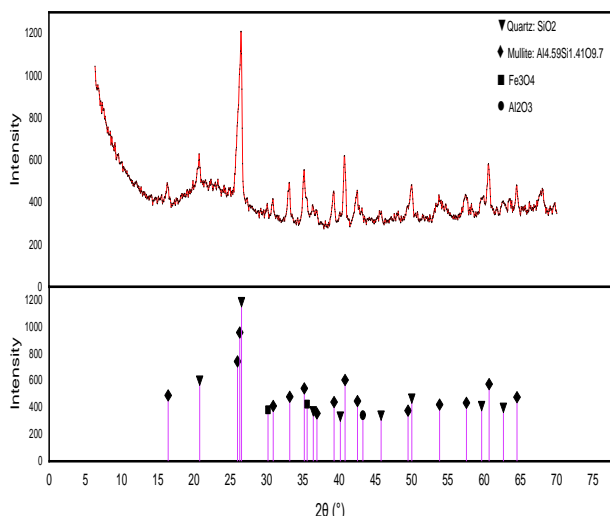


Fig. 2 XRD analysis of CFA.

Table 2. Mineral composition of CFA.

Mineral	Weight composition (%)
Mullite	67.3
Quartz	25.8
Al ₂ O ₃	3.7
Fe ₃ O ₄	3.2

According to the SEM image (Fig. 3) CFA-1 is represented mainly by spherical and polydispersed particles with sizes from less than 1 μm to 15 μm.

From Fig. 4 it is evident that the ash grinding leads to a shift of the peak maxima in the particle size distribution curve from 11.5 to 4.4 μm. It favors increasing in the specific surface area of CFA powder and more uniform distribution of ash particles in crude oil emulsion. During grinding, the particles become finer and more monodisperse, which correlates well with SEM image of CFA-2 (Fig. 5). Finally, the ash particle's shape is altered from a spherical to a more irregular form.

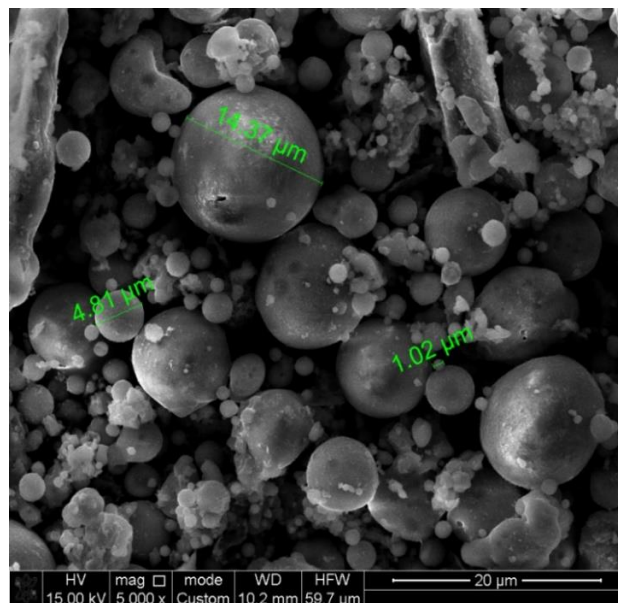


Fig. 3 Scanning electron microscopy image of CFA-1.

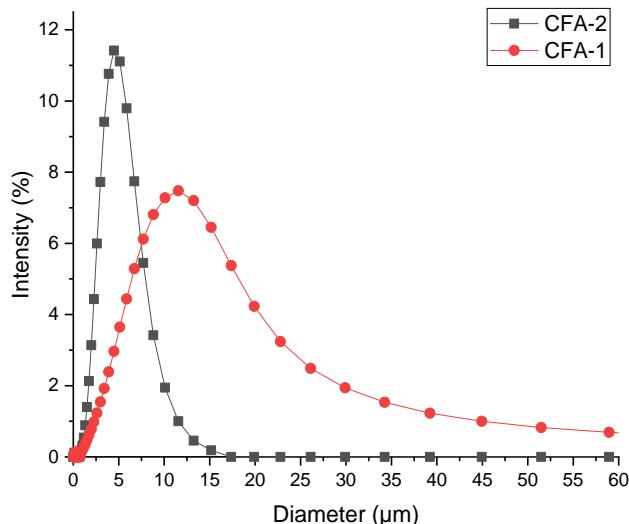


Fig. 4 Particle size distribution curve of CFA.

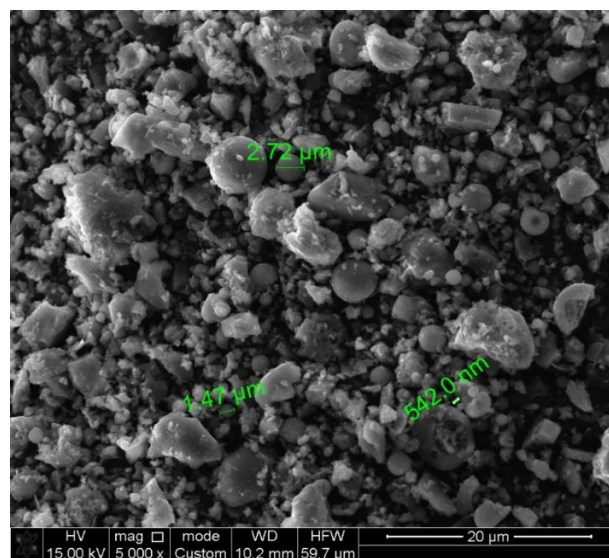


Fig. 5 Scanning electron microscopy image of CFA-2.

3.2 Demulsification performance of the coal fly ash particles

W/O emulsions of various concentrations from 10% to 50% (vol.) were stable at room temperature, and the phase separation was not observed. Natural water-in-oil emulsions are usually produced during oil extraction and transportation. Water content of the emulsions varies between 30-50% (vol.) according to Zolfaghari et al. and 60-80% (vol.) according to Fingas and Fieldhouse.^[6,43] This is why water concentration from 10% to 50% (vol.) were chosen. In addition, the watering degree of w/o emulsions of Kazakhstan oilfields varies closed to these concentrations.^[44-46] W/o emulsions treatment with CFA at room temperature did not yield in any phase separation. This is why thermal treatment was decided to apply. Optimal temperature of 60 °C was chosen due to the highest DE for 50% (vol.) w/o emulsion which is the closest to the natural emulsions by water content. Moreover, due to the high stability of crude oil emulsions, temperatures below 50-60 °C are not applied and the application of higher temperatures is not justified due to evaporation of light oil fractions. The emulsions were thermostated for 90 minutes and then they were centrifuged. The effect of the thermal treatment was investigated on w/o emulsions, and it was clear that temperatures from 50 °C to 60 °C are optimal and yield the highest DE. Nevertheless, thermal treatment is not enough for the dewatering of the w/o emulsion, because the DE did not exceed 20% at the optimal temperature.

To study the demulsification in the presence of CFA particles, w/o emulsions were treated with the fly ash powder under different temperatures and concentrations of emulsions, and the results are presented in Fig. 6. Fig. 6 shows that DE rises with higher water content in the emulsions and reaches nearly 80% for 40% (vol.) w/o emulsion, whereas for 20% (vol.) and 10% (vol.) does not exceed 60%. It is noteworthy that demulsification of 10% and 20% w/o emulsions at different time intervals happened suddenly. It can be explained by the fact that phase boundary was not clear first 20-50

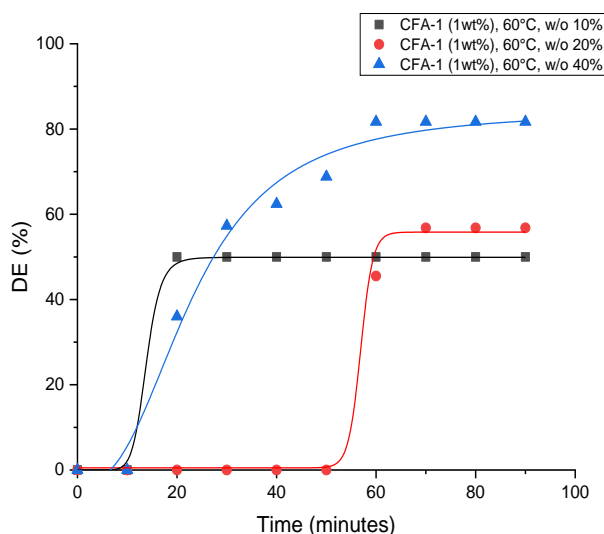


Fig. 6 DE of CFA-1 at 60 °C.

minutes, but values after 50 minutes were visible and reached the plateau.

Particle size decrease positively affects DE as shown in Fig. 7. For example, CFA-2 applied at the same conditions to 20% (vol.) w/o emulsion increases the DE nearly by 10% compared with CFA-1. Nevertheless, DE was improved nearly by 1% for 40% (vol.) w/o using CFA-2.

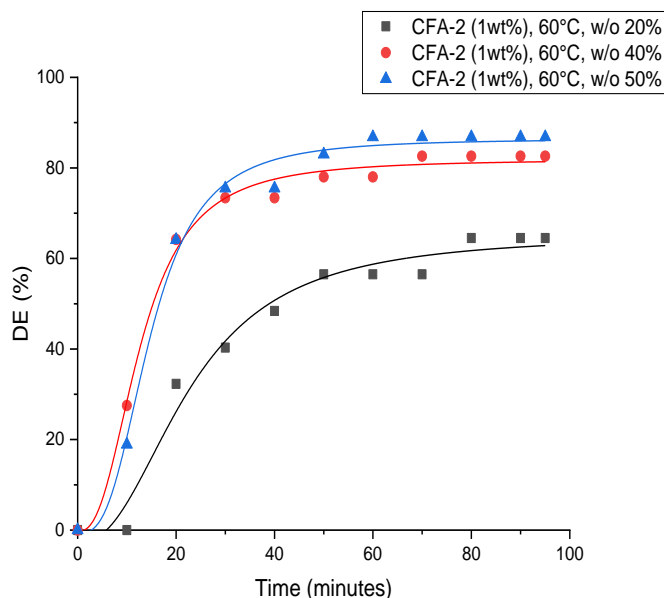


Fig. 7 DE of CFA-2 at 60 °C.

Effect of temperature in combination with CFA-2 addition was measured onto w/o emulsions of various concentrations. Table 3 displays that increasing the temperature higher than 50-60°C leads to lowering of DE. Some results deviate from the general trend due to the absence of clear phase boundary observed during the experiments.

Table 3 DE (%) of CFA-2 (1 wt%) for w/o emulsions at 90th minute.

Water content	10%	20%	40%	50%
Temperature				
50 °C	64.9	80.6	91.7	75.5
60 °C	-	64.5	82.6	86.8
70 °C	52	56.5	62.2	71.7

Microphotographs (Fig. 8) illustrate that 50% (vol.) w/o emulsion with water droplet diameter from 1.3 to 22 μm was broken after 1-hour treatment with CFA-2 at 60 °C. Complete breaking of the crude oil emulsion can be justified by the absence of water droplets on the microphotograph image. The demulsification via CFA-2 yields higher DE, but causes the transition of fine CFA-2 particles suspended in the oil phase. However, it is known that fine ash particles (up to 75 μm) mixed with fluids in the gaps of the pumping unit's bearings and bushings cause increased vibrations and subsequent jamming.^[47] Therefore, the centrifugal treatment of w/o emulsions was applied after thermostating stage.

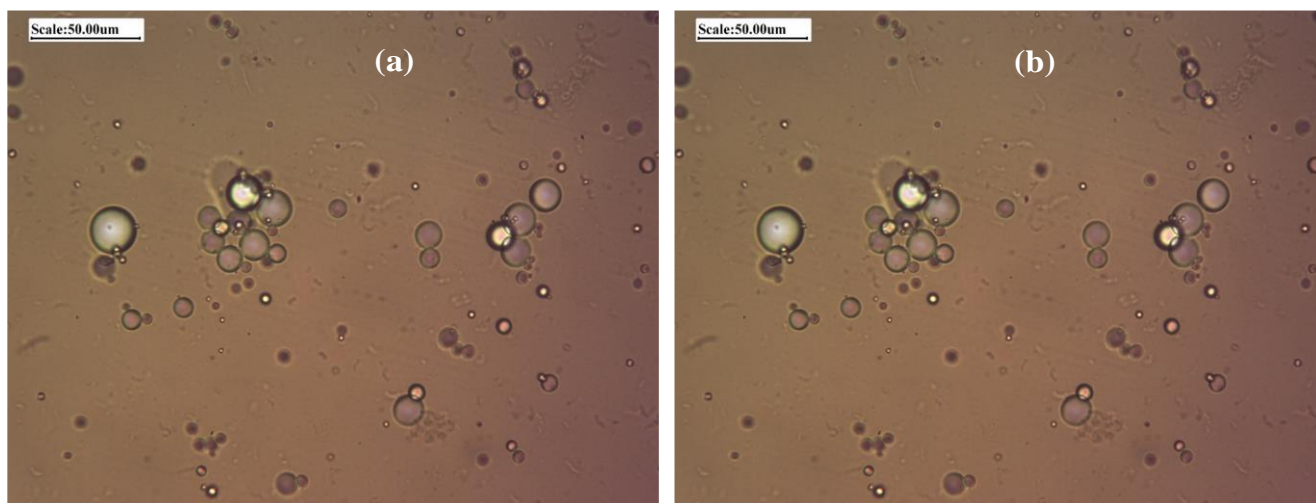


Fig. 8 Microphotographs of a) - 50% w/o emulsion; b) - 50% w/o emulsion after demulsification by CFA-2 at 60 °C.

Surface active agents are widely used to split the w/o emulsions into two phases. For instance, the group of researchers applied Tweens onto w/o emulsions at various concentrations, and the effective concentrations varied from 700 ppm to 800 ppm.^[48] As a result of their natural fatty acid and sugar alcohol origins, Tweens are acknowledged as green emulsifiers, detergents, and dispersion agents for food, cosmetic, and personal care applications.^[49] The demulsifying effect of Tweens is based on the fact that they contain a sufficiently large number of ethylene oxide groups, for Tween 20 it equals to 20. Polymeric non-ionic surfactants are used in practice mainly to destabilize the water-in-oil emulsion. Tween 20 has the highest HLB value among Tweens.^[48] Polymeric demulsifiers with high HLB values can be adsorbed at the water-oil interface and destroy the adsorption layer of emulsifiers. That is, they have a developed hydrophilic part that can penetrate into the interfacial layer around the water globule.

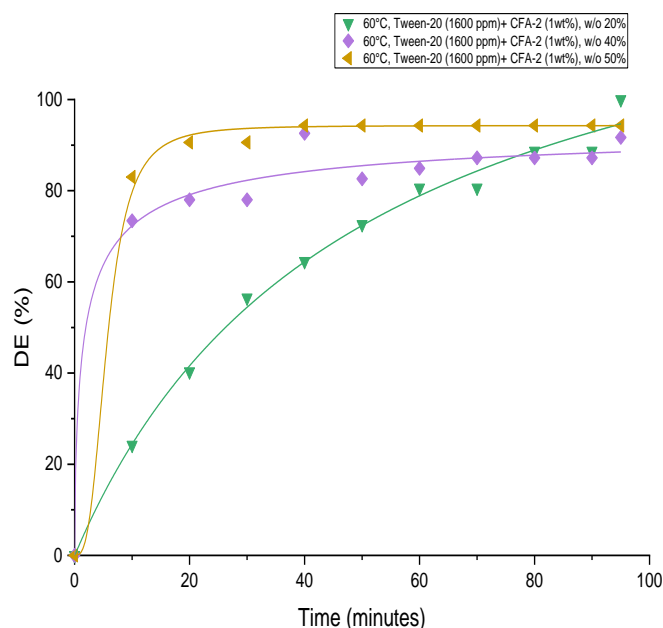


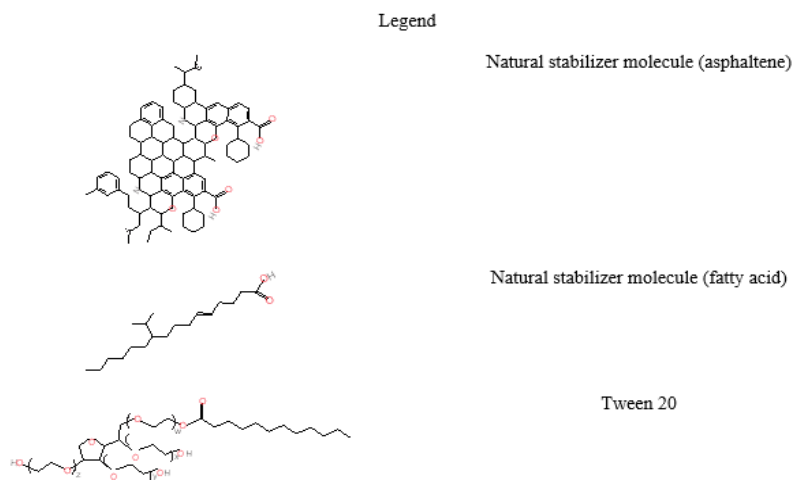
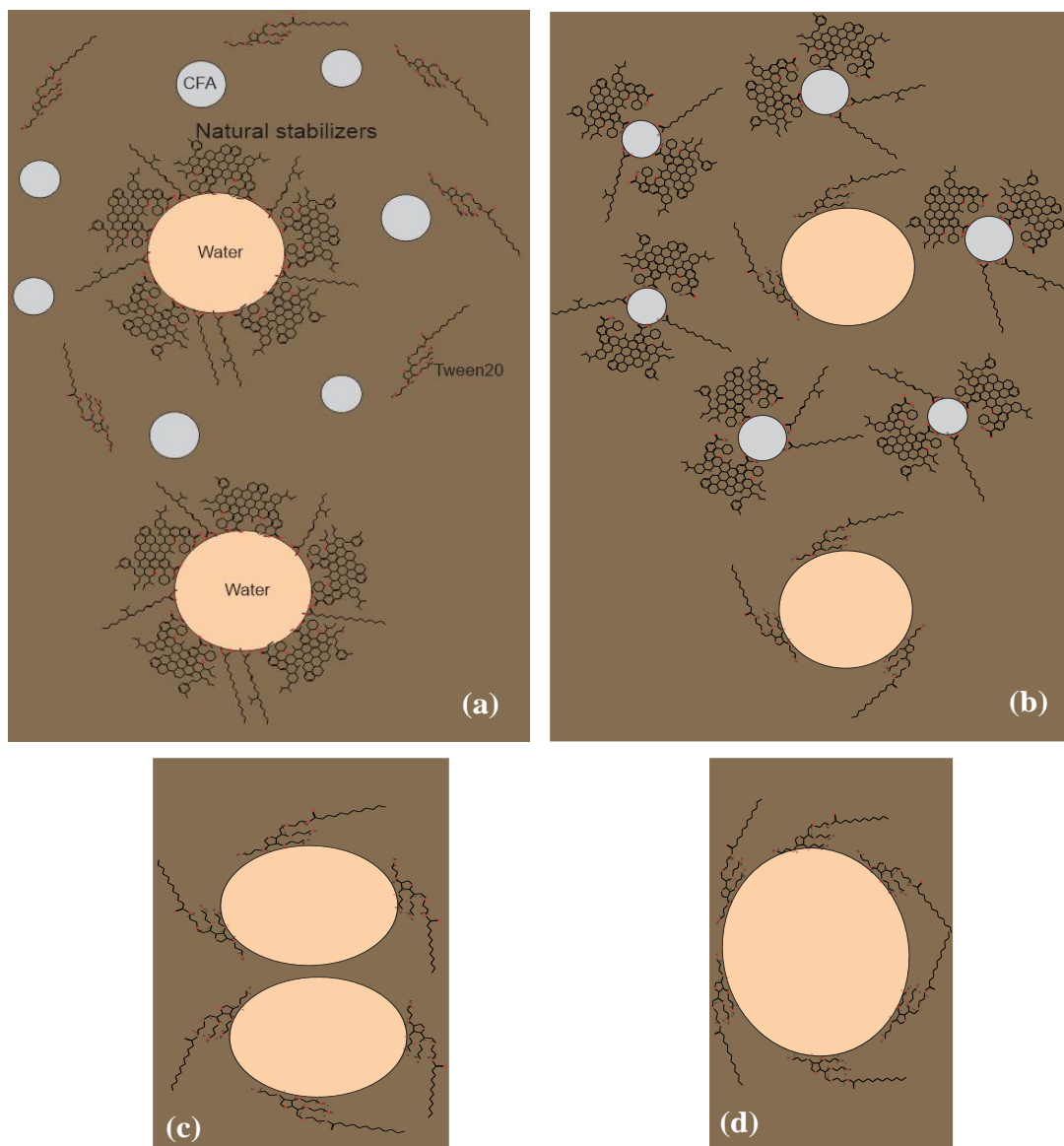
Fig. 9 Cumulative effect of Tween 20 (1600 ppm) and CFA-2.

In the current investigation, Tween 20 was applied onto w/o emulsions at concentrations of 800 ppm and 1600 ppm. At concentrations of 800 ppm and room temperature, Tween 20 was not effective and did not show two separate phases. Heating up to 60 °C and increasing the concentration of Tween 20 to 1600 ppm allowed to reach DE of 3.8% only. Fig. 9 demonstrates that the Tween 20 has a significant impact on the DE in combination with CFA-2. The combined effect of Tween 20 and CFA-2 was studied. DE reached 100% at 1600 ppm of Tween 20 and 1% wt of CFA-2 for 20% (vol.) w/o emulsion, while for 40% and 50% (vol.) w/o emulsions DE was around 90%.

3.3 The demulsification mechanism of CFA particles

The combination of Tween 20 and CFA-2 led to the highest DE even with the lowest water content emulsions at 60 °C. The consistent explanation of this could be the effects of adsorption of natural stabilizers on the surface of CFA-2 (Figs. 10a, b) and the subsequent replacement of the residual stabilizers by Tween 20 (Fig. 10c). Electrostatic interaction between the negative charge of CFA particles and positively charged nitrogen heteroatoms from asphaltene molecules could be a reason for the adsorptive properties of CFA. Thus, the interfacial film became less stable and water droplets are coalesced (Figs. 10 c, d). The proposed separation mechanism is illustrated in the Fig. 10.

To justify the concept of adsorptive action of CFA-2, the FT-IR spectra were measured. Fig. 11 displays the FT-IR spectrum of crude oil sample, pristine CFA-2 and CFA-2 used to treat 40% w/o emulsion. CFA-2 sample after using it for dewatering the 40% w/o emulsion was collected from the bottom of a test tube and did not contain the water as it was oily already. As shown in Fig. 11c, the crude oil sample produce the strongest bands that correlates with aliphatic C-H stretching and could be related to methyl, methylene and methine groups attached to the heteroatoms such as O and N and aromatic rings (largest bands at about 2850 and 2925 cm⁻¹) in asphaltene and resins aggregates. Same patterns of bands



* oil phase is shown as the brown medium

Fig. 10 The suggested demulsification mechanism of CFA action. a) representation of stable w/o emulsion with CFA introduced; b) natural stabilizers adsorption on CFA; c) Formation of water droplets stabilized by Tween 20 molecules and their approaching; d) water droplets coalescence.

observed were found and described by Asemani et al.^[50] These bands were detected in CFA-2 sample after using it for oil emulsion dewatering (Fig. 11b), while they were not spotted in pure CFA-2 sample (Fig. 11a).

The cost-effectiveness of the proposed method involves various factors including assessment of cost and availability of fly ash and Tween 20. Fly ash is a waste product on thermal power plants and its price is relatively low. Prices of fly ash can range from \$14 to \$26 per ton, depending on location and particle size distribution. Almaty Thermal Power Plant #2 can be considered as a potential supplier. Tween 20 is a surfactant that is more expensive than ash. The price of Tween 20 depends on the purity and quantity purchased. Usually, Tween 20 costs around \$8 to \$108 per kilogram (kg). Consumption of Tween 20 and fly ash, when converted to 1 ton of the crude oil emulsion, is (the water content of crude oil emulsion is assumed to be very high and density of the emulsion is close to 1g/l) 1.56 kg (1600 ppm) and 10 kg (1% wt.) respectively. Thus, fly ash and Tween 20 prices per 1 ton of emulsion may vary from \$12.64 to \$167 in total. Also, the final cost of the proposed method depends on labour, equipment and energy costs. Finally, potential scale-up implies the multiplication of costs by several times. Even though, the price of the oil separated and ecological benefits overweight the expenses.

To benchmark the effectiveness of fly ash and Tween 20 combination several studies were compared. Ramalho et al. investigated the effect of commercial poly(ethylene oxide-b-propylene oxide) demulsifier on the separation efficiency of

water-in-crude oil emulsions and the maximum water separation index was 57.2% with 50 ppm demulsifier concentration.^[51]

Similarly, Adilbekova et al. tested the effect of commercial demulsifiers represented as block copolymers in which the central polypropylene glycol group is flanked by two polyethylene glycol groups and yielded a separation efficiency of 96% for 30% (vol.) water-in-crude oil emulsion.^[52]

Hajivand and Vaziri have evaluated the plethora of commercial demulsifiers present on the market and justified that separation efficiency did not exceed 60% for various oil- and water-soluble demulsifiers applied to water-in-oil emulsions at 70 °C, pH 5.5 and demulsifier concentration 10-5 volume fraction.^[53] Obviously, the degree of separation depends on the oil type and other conditions like temperature, treatment time and demulsifier concentrations.

4. Conclusions

The study is dedicated to investigating coal fly ash dewatering ability of water-in-oil emulsions. Fly ash samples were collected from the local power plant in Almaty city, Kazakhstan and characterized using various techniques. Fly ash was represented mainly by silica and aluminium oxides with an average particle diameter of 11.5 μ m. The utilization of a planetary ball mill for dispersion caused a change in the peak maximum of the curve representing the distribution of particle sizes, moving it from 11.5 to 4.4 μ m.

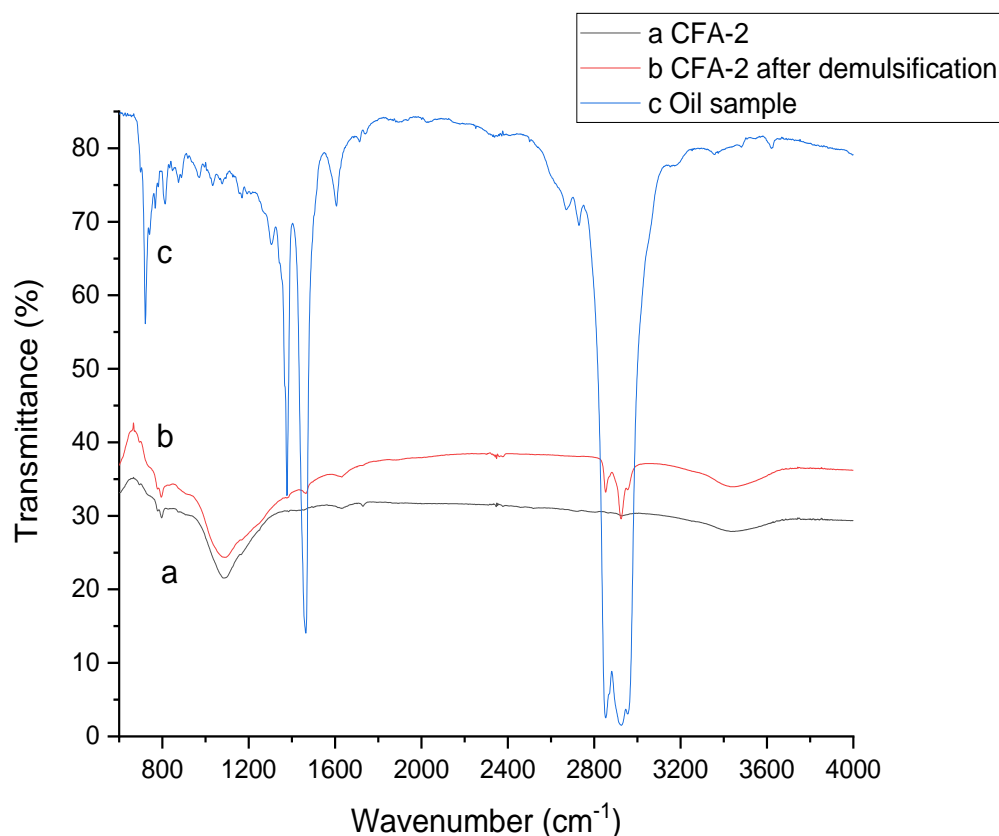


Fig. 11 FT-IR spectroscopy of a) CFA-2; b) CFA-2 after treating 40% w/o emulsion, c) crude oil sample.

Stable water-in-oil emulsions were prepared and treated with dispersed CFA-2 at different temperatures and concentrations. The role of centrifugation was determined as an additional treatment for producing the clear phase boundary and increase of demulsification degree. The effect of thermal treatment with and without CFA-2 was explored. The optimal conditions for CFA-2 (1 wt%) were 60 °C and 1-hour treatment with the DE of about 80%. The cumulative effect of CFA-2 and Tween 20 at 60 °C was observed with the DE higher than 90% in less than 1 hour. It has been noticed also that with the raise in the water content in the emulsions, the DE increases at any applied conditions.

The rationale for selecting grinded CFA in demulsification is based on several factors such as chemical composition, high surface area, adsorption capacity, availability, cost-effectiveness and environmental benefits. According to the American Society for Testing and Materials CFA is classified into C type and F type based on its chemical composition.^[54] The main difference between C and F types is the amount of calcium oxide (more than 20% wt. in class C). Therefore, utilizing C class CFA should consider the interaction of calcium oxide with the water and oil phase. In particular, fatty acids present in minor amounts and playing a surfactant role in w/o emulsions may precipitate when reacted with calcium oxide resulting in destabilization of emulsions. Additionally, water present in emulsions can react with calcium oxide to produce calcium hydroxide which is slightly soluble in water and increase the temperature of the emulsion. In contrast, insoluble particles produced may lead to the formation of Pickering emulsions. Finally, C class CFA may have potential as a demulsifier as well as F type and requires additional attention.

Crude oil differs by type and chemical composition from one well to another well. Furthermore, the presence of impurities in crude oil is not an obstacle because using fly ash in combination with Tween 20 considers the flexibility of the method due to the demulsification mechanism proposed.

Tween 20 is a surfactant that is commonly stated as inexpensive, non-toxic, environmentally friendly and water-soluble. Nevertheless, some studies show its disruptive properties onto some plant membranes at concentrations from 0.001% (v/v) to 0.01% (v/v).^[55,56]

A possible mechanism of CFA-2 and Tween 20 combination action was proposed. The combination of Tween 20 and dispersed CFA-2 results in the adsorption of natural stabilizers on the CFA surface and the subsequent substitution of the natural stabilizers by Tween 20.

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Conflict of Interest

There is no conflict of interest.

Supporting Information

Not applicable.

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