



# Separation of Water-in-Crude Oil Emulsions by Non-Ionic Tweens and Coal Fly Ash Powder at Thermal Treatment and Centrifugation

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## Abstract

The study aimed to investigate the separation of water-in-crude oil emulsions by non-ionic Tweens and coal fly ash powder at thermal treatment followed by centrifugation. Two samples of crude oil from different oilfields of Kazakhstan were taken (sample 1 and sample 2). For sample 1 the heating followed by centrifugation resulted in formation of intermediate layer emulsion. The use of Tweens for the sample 1 showed demulsifying ability close to 60 % and prevented the formation of an intermediate layer. The results of IR-spectroscopy confirm the mechanism of demulsification of coal fly ash based on an adsorption of stabilizing components of crude oil and their interaction with coal fly ash particles. The combination of coal fly ash and non-ionic amphiphile Tween 60 showed a slight increase of DE (68 %) for sample 1, and the formation of the intermediate layer emulsion was not observed. While for sample 2 the separation in the presence of coal fly ash and non-ionic Tween 60 was higher than 85 %, and 92 % for combination of Tween 80 and 2 % of coal fly ash. It has been shown that demulsification by fly ash and non-ionic surfactants depends on the nature and stability of crude oil emulsion.

*Keywords:* Separation; Water-in-crude oil emulsion; Coal fly ash; Thermal treatment; Centrifugation; Tweens.

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## 1. Introduction

Demulsification (separation of water from extracted crude oil) is one of the key processes of crude oil preparation to the oil processing. Water mixed with crude oil during the extraction leads to the formation of highly stable water-in-crude oil emulsion, which causes operational difficulties, such as corrosion of equipment or poisoning of catalysts. The problem of water separation requires new effective approaches that will be effective, inexpensive, and contribute to the sustainable development goals to get affordable and reliable energy, reducing the environmental impact and maintaining efficiency.<sup>[1,2]</sup>

Nowadays, numerous methods are available for the demulsification of crude oil emulsions (physical, chemical, biological dewatering).<sup>[3,4]</sup> The physicochemical properties, composition of crude oil, and stability of w/o crude oil emulsion depending on the reservoir, rate of demulsification and environmental protection regulations must be carefully

taken into account when choosing a demulsification technique.<sup>[5]</sup> Therefore, the development of effective, simple, and ecologically friendly demulsifiers based on natural raw materials for the separation of crude oil emulsions is still an important research field.<sup>[6,7]</sup> Currently, a new method has been developed where chemical demulsifiers are replaced by more available and cheaper solid demulsifiers based on fly ash which is usually a byproduct of coal combustion.<sup>[8,9,10,11]</sup>

Coal is still used extensively as a power source despite the emergence of alternative energies due to its availability, low cost and growing energy demand. As a result, a significant amount of coal fly ash (CFA) is produced worldwide as a combustion byproduct of coal. About 19 million tons of CFA are produced in Kazakhstan each year, and more than 300 million tons have accumulated at the nation's approved ash disposal sites.<sup>[12]</sup> The methods used for disposing of CFA are harmful to the environment due to its leaching ability, radioactivity, and toxicity. It causes significant contamination in the soil and natural water sources. The utilization rate of CFA in Kazakhstan is significantly lower, at under 10%,<sup>[12]</sup> compared to India (38%), China (45%), the USA (65%) and European Union countries (more than 80%).<sup>[13]</sup>

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The oxides that are present in coal fly ash include  $\text{Fe}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{Na}_2\text{O}$ ,  $\text{TiO}_2$ ,  $\text{MnO}$ ,  $\text{P}_2\text{O}_5$  and a high content of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  specifically.<sup>[14]</sup> It should be noted that mass content of chemicals presented in CFA is different for each country, and depends on power plants, boiler configuration, type of coal that was burned, and burning conditions.<sup>[13,15]</sup> The color of CFA is determined by the amount of unburned carbon that is present after the combustion and could range from dark brown to light gray. Particle size and surface area are also key physical characteristics of CFA. Regarding the morphological characteristics, CFA particles tend to be mainly spherical or oval in shape, and can be either solid, hollow, or amorphous, depending on the quality of the coal.<sup>[16]</sup> The spherical form of particles is determined by the technological mode of the thermal power plant: under the influence of high temperature in the furnace, the smallest oxides contained in the coal melt and are subsequently rapidly cooled at the outlet. Numerous studies have confirmed that coal fly ash always contains mullite and quartz.<sup>[8,17-19]</sup> The research conducted identified that the main phases in CFA samples taken from Kazakhstan powerplants located in Astana and Oskemen cities are mullite, quartz and magnetite/hematite, while the major elements containing in raw fly ash being Si, Al, Fe and alkaline metals. The results of particle size analysis showed that 90% of particles are less than  $419\ \mu\text{m}$ .<sup>[11]</sup>

It has been found that powders of ash have ability to reduce and break the stability of water-in oil emulsions. The first study was reported by Adewunmi *et al.*,<sup>[20]</sup> where they showed that coal fly ash works as a demulsifier for formulated stable w/o emulsions (crude oil to water volume ratio 4:6). The demulsification efficiency (DE) of different CFA quantities (1 to 7%) resulted in the water separation from the oil phase. The emulsion containing 7% CFA demonstrated the highest DE of 96.67%. It was found that DE was superior to the DE of a commercial demulsifier poloxamer 407. The interfacial tension measurements show that CFA particles tend to reduce the interfacial tension crude oil and water phases due to the ability of CFA adsorb at the oil-water interface.

Moreover, Adewunmi *et al.*<sup>[21]</sup> developed demulsification method based on application of palm oil fuel ash (POFA), a low-cost waste material from oil palm processing. Treatment by means of POFA resulted in the formation of three phases: oil phase, aqueous phase and solid phase of POFA particles that sedimented to the bottom of the separated water phase. The mechanism of palm fly ash action was explained by strong interaction of ash particles with natural emulsifiers (asphaltenes and resins) due to the mixing of POFA with oil emulsions and breaking of stabilizing film at the water-oil interface. According to the research, the addition of 3 wt % POFA promoted the high degree of demulsification and achieved 99.8 % for formulated crude oil emulsion where the ratio of oil to sea water was 3:7. The same authors showed the demulsifying effect of the alkaline treated fly ash on a 60% w/o emulsion with DE of 93%.<sup>[22]</sup>

The effectiveness of coal fly ash was studied regarding the

synthesized w/o emulsion of volume ratio of oil phase to water phase 0.6: 0.4 with various dosage of CFA which demonstrated good demulsification ability due to removal of asphaltenes from oil emulsions by CFA particles of 40 microns. The authors emphasize that the use of industrial waste material has importance for the improvement of environmental state of the country.<sup>[23]</sup>

Besides CFA, there are works studying the use of a demulsifier from natural rice husks which was prepared by a simple carbonization using a muffle furnace. Dehydration efficiency reached 96.99 % with 600 mg/L at  $70^\circ\text{C}$  during 80 min. According to Fan Ye *et al.* the interfacial activity of a rice husk carbon (RHC), content of silica and oxygen containing groups causes the high DE of RHC which is an attractive, environmentally friendly biomass resource of low cost, that is easy to prepare and is characterized by a special porous structure and several chemical components.<sup>[24]</sup>

To sum up, provided studies demonstrate the CFA as an effective demulsifying agent that is able to break stable W/O emulsions. Moreover, utilization of CFA in oil industry at the global scale may solve the problem with waste deposits of coal fly ash that is produced by power plants.<sup>[25]</sup> However, the lack of research regarding the demulsifying ability of CFA is the main obstacle that does not allow to implement CFA in oil industry, therefore more studies need to be done. In addition, as can be seen, most studies reported relate to the model emulsions formulated artificially; there are practically no works concerning naturally occurring crude oil emulsions.

The aim of this work is to study the demulsification ability of CFA in combination with non-ionic surface-active agents Tweens in relation to the natural crude oil emulsion taken from two different oilfields located in the territory of the Republic of Kazakhstan. Non-ionic surfactants are the most effective demulsifiers of oil emulsions and, according to Roodbari *et al.*<sup>[26]</sup>, do not have a strong corrosive impact compared to other classes of surfactants. In this work, for the first time, we tested the combined effect of nonionic Tweens and solid demulsifier CFA to increase the efficiency of dewatering of oil emulsions, because both CFA and Tween's macromolecules cause the weakening and breaking of adsorption layer surrounding the water droplets dispersed in the oil phase. The study will clarify the mechanisms of demulsification depending on the physicochemical properties of crude oil emulsions.

## 2. Experimental section

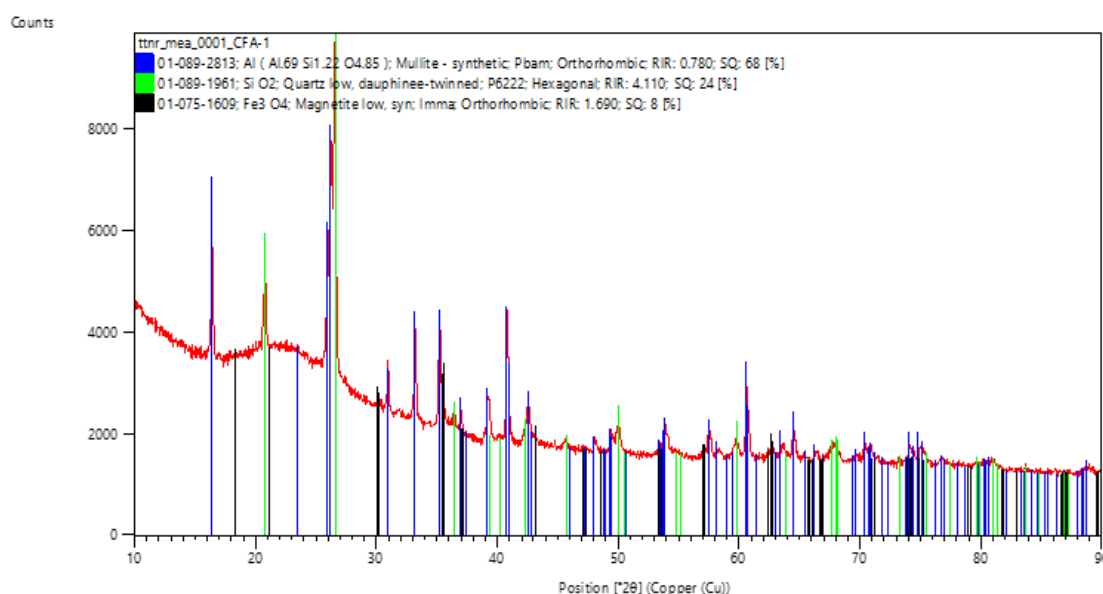
### 2.1 Materials and methods

Two samples of crude oil were taken from an oilfield of Atyrau region and Kyzylorda region, Kazakhstan. The physicochemical characteristics of oil samples are presented in Table 1.

Coal fly ash powder samples were collected from the local power plant (Almaty city, Kazakhstan). Mineralogical characterization of CFA was obtained by means of XRD analysis (Fig. 1) on a PANalytical X'Pert PRO MPD powder

**Table 1:** Crude oil physical-chemical properties.

Properties	Crude oil of Atyrau region oilfield, sample 1	Crude oil of Kyzylorda region oilfield, sample 2	Methods of measurements
Water content, %	25	13,5	GOST 2477-2014, ASTM D-4006
Density, kg/cm <sup>3</sup>	900	846	GOST 33364-2015
Kinematic Viscosity, mm <sup>2</sup> /s at 30 °C	41.4	6.2	ST RK ASTMD 445
Mechanical impurities, %	0.58	0.36	GOST 6370-2018
Chloride salts, mg/L	344.56	415.36	GOST 21534-76
Asphaltenes content, wt. %	1.89	0.2	GOST 11858-66, ASTM D 6560

**Fig. 1:** XRD spectrum of CFA.

diffractometer in Bragg-Brentano  $\theta/\theta$  geometry of 240 mm of radius (Cu  $K\alpha$  radiation:  $\lambda = 1.5418 \text{ \AA}$ , 45 kV, 40 mA). Active length =  $3.347^\circ$ ,  $\theta/2\theta$  scan from  $4,5$  to  $100^\circ 2\theta$  with step size of  $0.026^\circ$  and measuring time of 100 seconds per step. The sample of CFA was prepared in cylindrical standard sample holders of 16 millimetres of diameter and 2.5 millimetres of height. Phase identification was made using the PDF (*Powder Diffraction File*) database, ICDD-JCPDS (*International Centre for Diffraction Data – Joint Committee of Powder Diffraction Standards*, 2019). All analyses were repeated, and the average values are presented. It was found that CFA is mainly composed of mullite (68%) and quartz (24%) crystals, and iron (III) oxides, which is 8%.

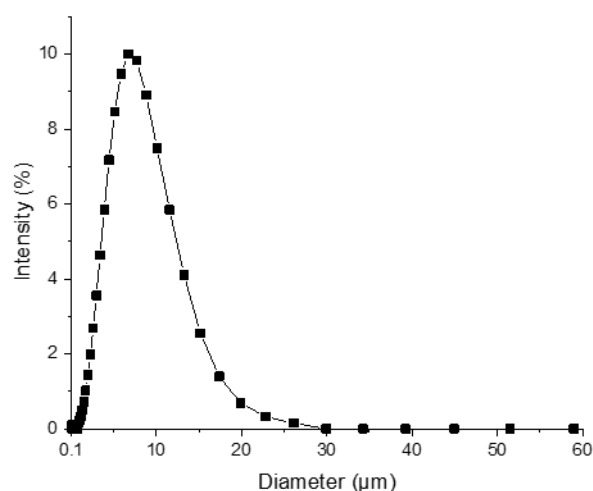
Specific surface area value measured by BET multi point method is equal to  $8.554 \text{ m}^2/\text{g}$  for dispersed fly ash powder. The bulk density of CFA was  $0.55 \text{ g}/\text{cm}^3$ . Total pore volume and the average pore diameter of CFA were measured by the BJH desorption methods and were equal to  $0.0196 \text{ cm}^3/\text{g}$  and  $9.1882 \text{ nm}$ , respectively.

For the demulsification tests the CFA powder was dried at  $105^\circ \text{C}$  for 2 hours and sieved by means of vibratory sieve shaker Analysette 3 with the smallest mesh size of  $63 \mu\text{m}$ . The sieved fraction of CFA was then milled in a planetary ball mill (SQM-0.4 L) at 400 rpm for 10 minutes. The particle size analysis after milling was determined by a laser diffraction particle size analyzer Horiba Partica La-960, HORIBA Ltd., Japan (Fig. 2).

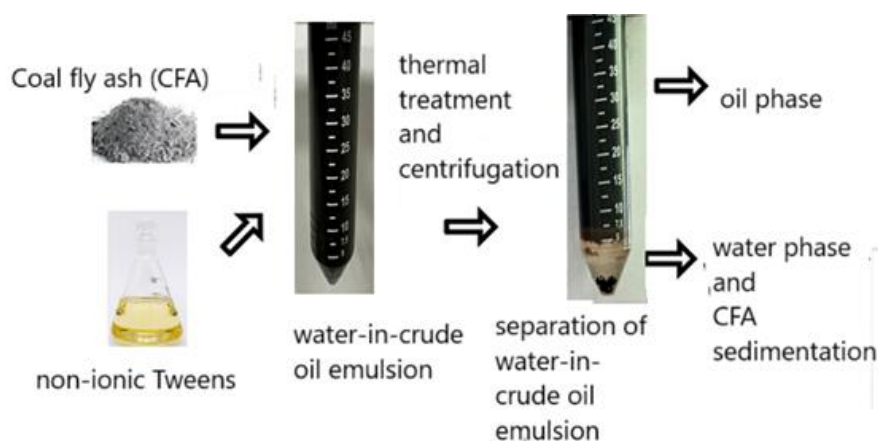
Tween-20 (polyoxyethylene sorbitan monolaureate), Tween-60 (polyoxyethylene sorbitan monostearate), Tween-80 (polyoxyethylene sorbitan monooleate), Sigma Aldrich; these surfactants are related to non-ionic amphiphiles, which have no charged hydrophilic groups, HLB of Tween 20 = 16.7, HLB of Tween 80 = 15.0, HLB of Tween 60 14.9.<sup>[26]</sup>

## 2.2 Methods

Water-in-oil emulsions were treated with different combinations of Tweens (800 ppm, 1600 ppm, 3200 ppm) and CFA samples (1 %, 2%). Various concentrations of CFA and



**Fig. 2:** The particle size distribution of CFA



**Fig. 3:** The scheme of separation of water-crude oil emulsion at thermal treatment and centrifugation is reported.

Tweens were added to the 50 ml of crude oil in plastic tubes and homogenized during 5 min to be thoroughly mixed. After homogenization, samples were placed into the thermostated water bath at 60 °C during 90 min, after thermostating, samples were centrifuged at 1500 rpm for 5 minutes to observe the phase separation (Fig. 3). The observation temperature of 60 °C as the treatment temperature was selected because it is representative of oilfield conditions.<sup>[27-28]</sup>

Demulsification efficiency (DE) was determined by the percentage of water separated from crude oil emulsion according to the Eq. (1):<sup>[29]</sup>

$$DE = \frac{V}{V_0} \times 100\%, \quad (1)$$

where V – is the volume of demulsified water separated from crude oil emulsion

$V_0$  – is the total volume of initially emulsified water in crude oil emulsion.

All measurements were repeated three times with each sample of crude oil emulsion; the results were expressed as the mean value  $\pm$  standard deviation.

SEM images of CFA powder were taken via Quanta 3D 200i at National Nanotechnology Laboratory of Open Type,

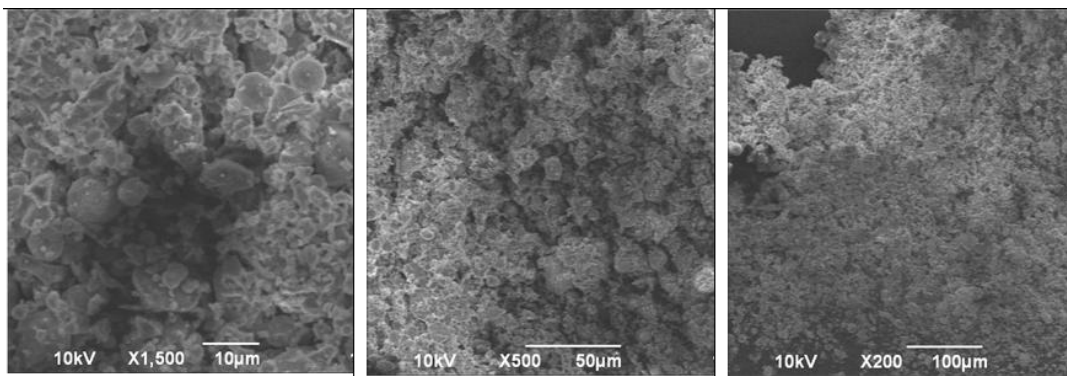
Al-Farabi Kazakh National University.

Microphoto of an intermediate emulsion layer (ILE) was obtained using the optical microscope Leica DM 6000 M at National Nanotechnology Laboratory of Open Type, Al-Farabi Kazakh National University.

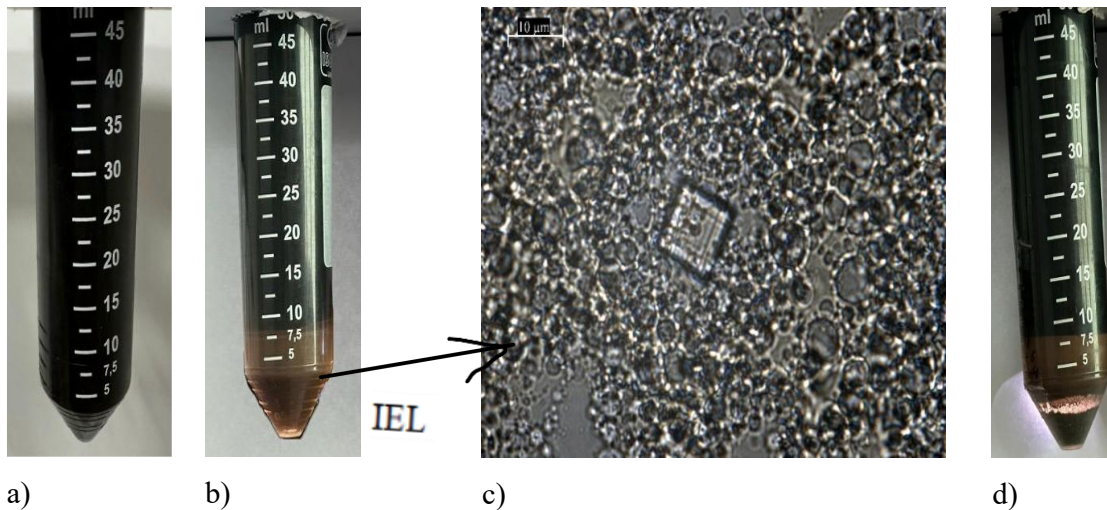
The IR-spectroscopic analysis was conducted for investigated samples on Fourier IR spectrometer «Spectrum - 65» (Perkin Elmer) at 4000 – 450  $\text{cm}^{-1}$  diapason.

### 3. Results and discussion

As mentioned above, the advantage of using CFA is that it is an industrial byproduct, making fly ash powder a cost-effective alternative to traditional chemical demulsifiers. Application of CFA for demulsification gives a beneficial utilization for this waste material, effectively reducing environmental contamination associated with its use. The powder of CFA, according to the results of electron microscopy, have mainly non-uniform surface morphology, particles of irregular and spherical shape (Fig. 4). The regular spherical shapes of some particles of CFA is explained by the fact that during coal combustion technology, high temperatures cause ash particles to sinter and take a regular



**Fig. 4:** The scanning electron microscopy image of CFA under various magnifications.



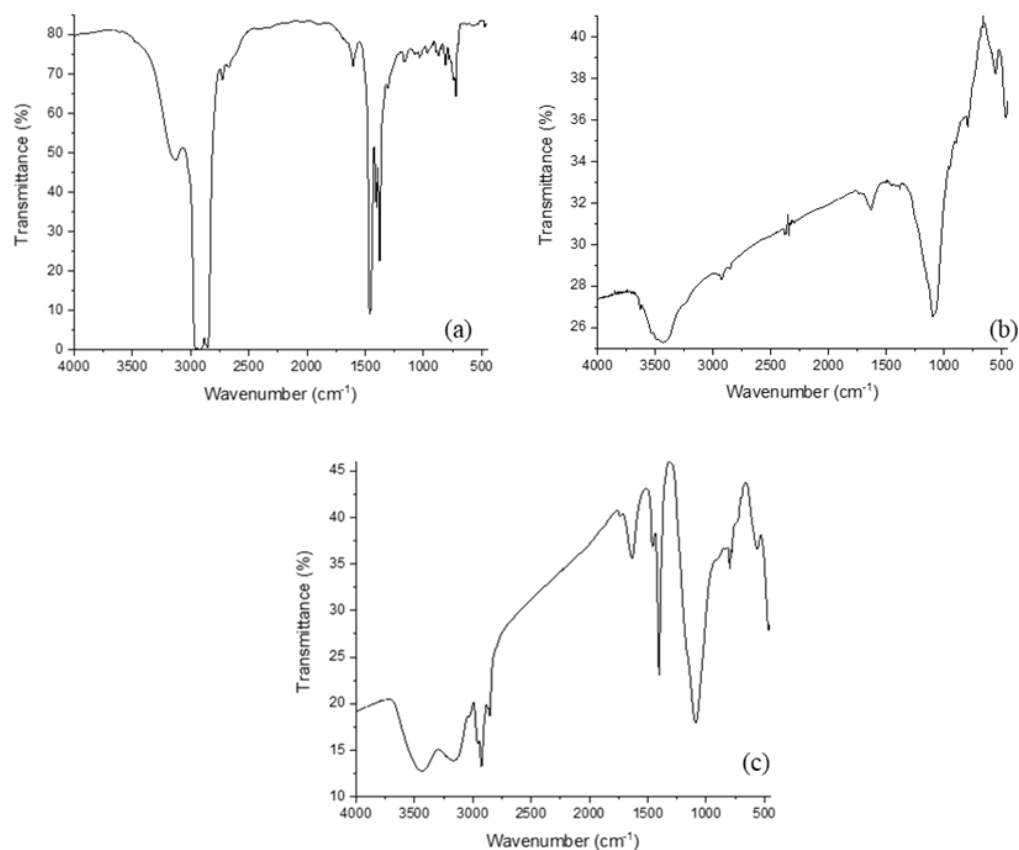
**Fig. 5:** Photo of the crude oil emulsion (sample 1) before and after demulsification. (a) crude oil, sample 1. (b) crude oil, sample 1 after heating at 60 °C and centrifugation with an intermediate emulsion layer settled to the bottom of a tube. (c) the optical microscopy image of intermediate layer. (d) separation effect of CFA powder on the intermediate emulsion layer.

rounded shape.<sup>[16,23]</sup> The electron microscopy image shows that the CFA particles after dispersion in a planetary ball mill are evaluated as polydisperse microparticles; particles with sizes around 10 μm and less are observed in Fig. 4. The particle size distribution curve correlates with SEM of CFA and shows that the particle sizes were within the range of 0.1-20 μm (Fig. 2), with the peak centered close to 10 μm. In the aforementioned studies, particles of fly ash have predominantly the similar sizes varying from 0.1-45 μm.<sup>[21]</sup> The dispersion was carried out to increase the dispersion degree and the specific surface area (8.554 m<sup>2</sup>/g) of the ash powder to increase the interaction of ash particles with the natural oil stabilizers such as asphaltenes and resins.

The sample 1 of crude oil emulsion (Fig. 5a) was heated at 60°C and centrifuged, while the formation of intermediate emulsion phase of brown color was observed, (Fig. 5b). The centrifugation of a sample 1 did not result in the water separation. The microscopic image of this intermediate layer is presented in Fig. 5c. According to the microimage, this phase can be evaluated as an intermediate emulsion layer (IEL)<sup>[28]</sup> contained a lot amount of water droplets and

mechanical impurities (Fig. 5c)

The concept of the formation of IEL is mentioned by Romanova *et al.*<sup>[30]</sup> When various demulsifiers are used, intermediate emulsion layer is formed; this is waste that needs to be utilized. It is extremely difficult, and occasionally impossible, to fully separate oil from water in such emulsions using conventional techniques. The formation of difficult-to-break water-in-oil emulsions or intermediate emulsion layer, is one of the complications during the process of oil production. IEL must be continuously discharged in sludge storage pits and recycled in order to lessen their detrimental effects on the environment. The ecological conditions in areas that produce oil and gas are negatively impacted by the existence of such waste storage and the requirement for its processing. During the breaking down, the water-in-oil mixture cannot separate immediately, there is a gradual increase of water droplets in a water layer until their coalescence. Kuzmina *et al.*<sup>[31]</sup> describe that the formation of an intermediate layer depends on the content asphaltenes, mechanical impurities, iron that adsorb at the water/oil interface. The content of mechanical impurities in the sample usually caused by the centrifugation of crude oil and studied



**Fig. 6:** IR spectra for samples of crude oil a), original CFA b), and CFA after using for demulsification.

is higher than it should be according to the standards (Table 1).

The intermediate emulsion phase (industrial layer) is occupying an intermediate position between oil phase and produced water phase. The presence of an IEL is usually observed both in samples from the wells and in the devices of the oil treatment unit. The formation of stable IEL at the wellhead entails economic losses associated with its ballast pumping, and the presence and accumulation of the industrial layer in the devices of the oil treatment, tanks lead to the failure of oil preparation to the required quality, formation of trap oil and oil sludges, clogging of process pumps. All this leads to more serious risks and economic costs for crude oil processing.<sup>[32]</sup> Therefore, in this work attention was paid to the breaking of intermediate layer formed after centrifugation of the crude oil sample.

As mentioned above, the CFA is an industrial byproduct and has a promising demulsifying effect. The addition of CFA for the crude oil emulsion sample resulted in decrease of the intermediate emulsion layer and separation of water phase, and CFA sedimented to the bottom of the test tube. This separation of the intermediate emulsion layer was observed after addition of CFA powder and heating to 60°C, then the sample was centrifuged. The decrease in the thickness of intermediate layer can be explained by the disruption of interfacial films at the interface under the action of CFA and the aggregation of water droplets. In accordance with the

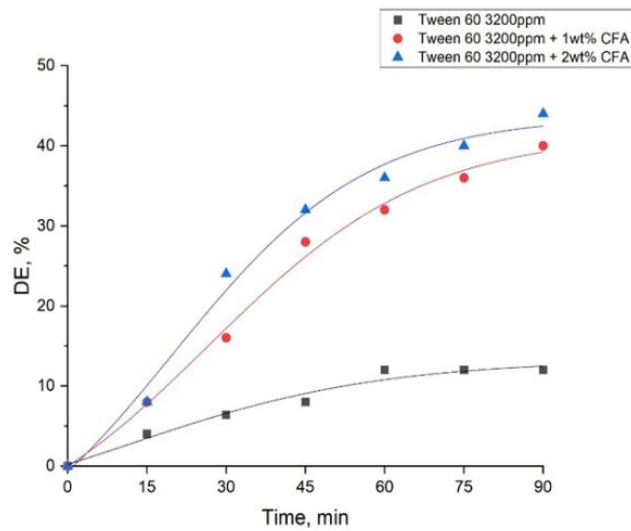
works of Adewunmi *et al.*<sup>[20,21]</sup> it was speculated that the demulsification mechanism is based on intensive interaction between CFA microparticles and asphaltenes followed by their sedimentation, CFA particles cause the disruption of stabilizing interfacial film and coalescence of water droplets.

The demulsification of crude oil studied (sample 1) under the action of CFA is not high and does not exceed 23%. However, it resulted in the breaking of the intermediate layer by almost two times by measurement of the height of this layer before and after treatment, while the ash particles settled at the bottom of the tube (Fig. 5d).

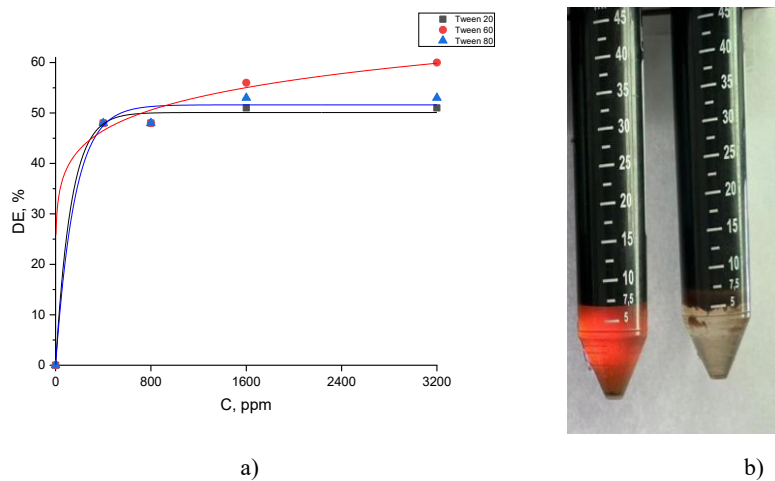
IR-spectra of crude oil (sample 1), CFA powder and CFA after demulsification confirms the interaction of CFA and crude oil components (Fig. 6).

The following absorption bands are characteristic for the IR spectrum of the oil sample 1: a band at 722.4 cm<sup>-1</sup>, corresponding to the deformation pendulum vibrations of the methylene group. The bands in the region of 1377-1450 cm<sup>-1</sup> correspond to symmetric and antisymmetric deformation vibrations of the methyl and methylene groups, 2927-2854 cm<sup>-1</sup> also correspond to paraffin groups. Vibrations of aromatic fragments appear in different parts of the spectrum, they correspond to bands with frequencies of 1604 cm<sup>-1</sup>, 1156-811 cm<sup>-1</sup>.<sup>[31]</sup>

In the IR spectrum of ash, an absorption band at 3400-3500 cm<sup>-1</sup> is characteristic of the stretching vibrations of the



**Fig. 7:** Kinetics of crude oil emulsions breaking (sample 1) in the presence of Tweens and CFA powder at T=60 °C, time of the treatment is 90 min.



**Fig. 8:** Relation between DE (%) and concentration of Tweens (ppm) at T=60 °C, time of the treatment 90 min (heating followed by centrifugation), sample 1.

OH groups of water molecules adsorbed, bands are observed in the region of 1100  $\text{cm}^{-1}$  characteristic of the stretching vibrations of the Si-O-Si (Al) group. A weak absorbance band in the 1650  $\text{cm}^{-1}$  region can indicate that a carbonyl group (C=O) is present as a product of coal burning. The region of 1600  $\text{cm}^{-1}$  shows the presence of  $\nu$  Si-O-Si, and the region of 800  $\text{cm}^{-1}$  corresponds to ( $\nu$ SiO<sub>2</sub>), minor peaks at 800  $\text{cm}^{-1}$  corresponds to aluminosilicates functional groups.<sup>[12,34]</sup>

The IR spectrum of CFA after demulsification shows absorption bands that were specific to both initial CFA sample and the functional groups of crude oil (2925.10  $\text{cm}^{-1}$ , 1636.22  $\text{cm}^{-1}$ , 1403  $\text{cm}^{-1}$ , 1088  $\text{cm}^{-1}$ , 797.2  $\text{cm}^{-1}$ ). For instance, 2925  $\text{cm}^{-1}$  corresponds to alicyclic compounds, and 1636  $\text{cm}^{-1}$  to aromatic groups. The band at 1403.65  $\text{cm}^{-1}$  denotes C-H bond deformation vibrations in methylene (CH<sub>2</sub>) and/or methyl (CH<sub>3</sub>) groups.<sup>[35]</sup> A peak around 797.2  $\text{cm}^{-1}$  indicates the presence of certain vibrations of bonds that may be associated with cyclic structures or the presence of aromatic hydrocarbons, which are characterized by these specific

bending vibrations. These changes in the IR-spectrum can be caused by the adsorption of oil components, including emulsifying components such as asphaltenes and resins. In addition, the appearance of a wide absorption band in the region of 3434  $\text{cm}^{-1}$  characteristic of the stretching vibrations of hydroxyl groups -OH is noticeable.

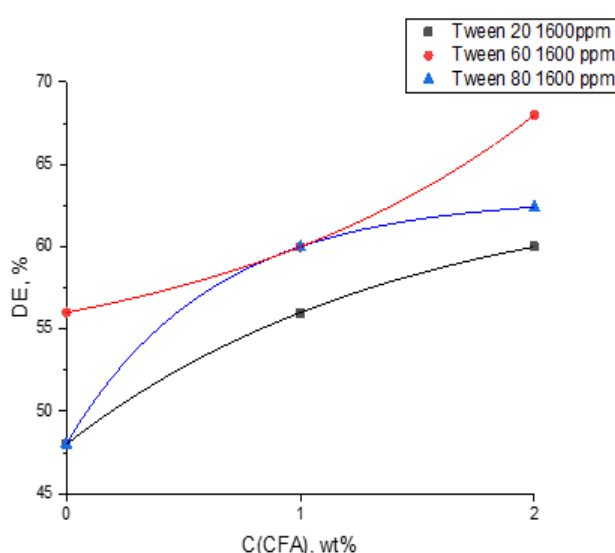
In order to investigate the breaking of crude oil emulsion, non-ionic surfactants, such as Tweens, were taken into consideration. Tweens are non-ionic class of surfactants and their demulsification effect on heavy crude water/oil emulsion was shown by Roodbari *et al.*, 2016.<sup>[26]</sup> Non-ionic Tweens are considered as “green demulsifiers” due to their biodegradability,<sup>[36]</sup> they are amphiphilic compounds. Tweens do not have charged counter ions, and their neutrality does not promote the corrosion effect relating to equipment at demulsification treatment of oil emulsions.

The demulsification performance of Tweens of different weight (ppm) were investigated, they were added to the water-in-crude oil emulsion and then emulsions were subjected to

the thermal treatment (60 °C), and followed by centrifugation. The thermal treatment alone does not produce the high effect of water separation (Fig. 7). Therefore, after thermal treatment, the centrifugation of samples was conducted and led to the decreasing of DE, in Fig. (8, 9) the DE values are shown including the results of centrifugation.

Demulsification by Tweens led to separation of pure water phase avoiding the formation of an intermediate emulsion layer. The non-ionic polysorbitans showed the DE close to 60 % (Fig. 6(a)), however they prevent the formation of the intermediate layer (Fig. 8b). The increase of a dosage of surfactants promoted the slight increase of DE.

The Fig. 9 shows the results of combination destabilization effect of Tweens and CFA.



**Fig. 9:** Relation between DE (%) and concentration of Tweens in combination with CFA powder at T=60 °C, time of the treatment 90 min (heating followed by centrifugation), sample 1.

The demulsifying effect of Tweens is explained by their ability to adsorb at the water/oil interface displacing the natural emulsifiers of crude oil.<sup>[26]</sup> The DE of Tween 60 regarding the crude oil emulsions is higher compared to other surfactants and reaches 60 % (Fig. 6). It should be noted that in the case of Tween 60, Tween 80 the separated water has the light brown color, as well as for Tween 20 the released water phase does not have color. Roodbari *et al.*,<sup>[26]</sup> mentioned the same observation for Tween 80 for water-in-oil emulsion dehydration. This effect can be explained by the low HLB value for Tween 60 and Tween 80 compared to Tween 20. The lower HLB amount, the more hydrophobicity of a surfactant molecule, it leads to the more intensive interaction of Tween macromolecule with oil components due to their affinity, natural emulsifiers will be displaced by non-ionic amphiphilic molecules. It is known that demulsifiers depending on the nature and composition of a crude oil can affect the water/oil

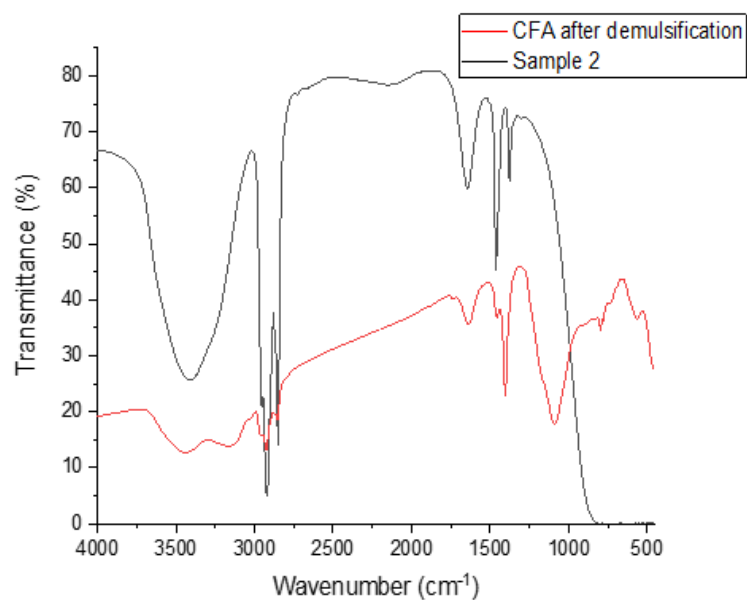
interface in different ways: some disrupt the stability of the emulsion, facilitating the separation of water without capturing oil components, while others cause the destruction of the emulsion with partial transfer of hydrocarbons into the aqueous phase.<sup>[37]</sup> This can lead to the desorption of organic substances (including resins, asphaltenes, and small droplets of oil) into water, which causes the coloration of the aqueous phase. Tween 60/80, due to the greater hydrophobicity of the macromolecule compared to Tween 20, can interact with the components of the oil and transfers them into the aqueous phase, influencing the quality of the separated phase.

The combination of Tweens and CFA increases the DE slightly and results in the pure water phase separation without the intermediate layer formation. The starting point in Fig. 9 corresponds to DE of Tweens added into the crude oil emulsion without CFA powder.

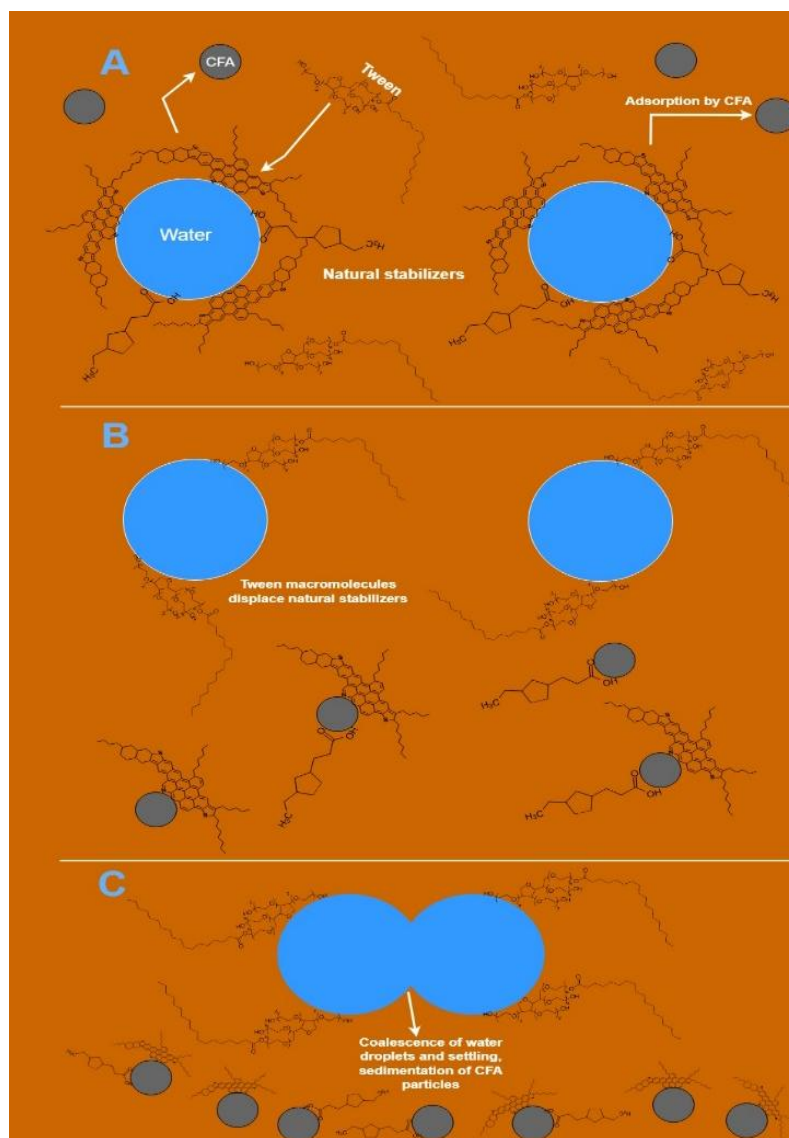
It should be mentioned, that the demulsifying action of CFA and its combination with Tweens depends on the nature of crude oil and content of stabilizers. For example, the sample 2 of crude oil from oilfield of Kyzylorda region have been studied regarding the dewatering using CFA. Sample 2 is differed by low concentration of asphaltenes compared to sample 1 (Table 2). The content of asphaltenes has a major impact on the stability of water-in-crude oil emulsions. The emulsion becomes more stable as the concentration of asphaltenes increases because of their adsorption and aggregation at the interface.<sup>[38]</sup> It was found out that the high degree of separation for sample 2 occurs at a concentration of Tweens equals to 800 ppm in comparison with the sample 1. The thermal treatment of the sample 2 at 60°C DE reaches 85 % at the combination of Tween 60 (800 ppm) and 2 %, and 92 % at the addition of Tween 80 and CFA at the same concentrations of the surfactant and the solid demulsifier. CFA powder performed demulsifying separation is equaled to DE of non-ionic surfactants (Table 2).

**Table 2:** Demulsification efficiency of CFA and Tweens at 60 °C, time of the treatment 90 min following by centrifugation. Sample 2.

	Concentration of surfactant, ppm	Concentration of CFA, %	DE, % ±SD
Crude oil emulsion "blank test"			31±1
CFA		2	46±0
Tween 20	800		39.3±0.58
Tween 60	800		46±0
Tween 80	800		46±0.57
Tween 20 + CFA	800	2	68.3±0.51
Tween 60 + CFA	800	2	85±0
Tween 80 + CFA	800	2	92±0.57



**Fig. 10:** IR spectra for crude oil sample 1 and CFA after using for demulsification.



**Fig. 11:** The suggested demulsification mechanism of CFA action.

The difference in DE, % can be explained by the different content of stabilizing components, for example, asphaltenes (Table 1). Also, as is seen in Table 2, the crude oil emulsion (sample 2) showed less stability because it separated the water phase at the heating followed by centrifugation while for sample 1 the formation of intermediate layer emulsion was observed. IR- spectra of the sample 2 and CFA after using for dewatering of the crude oil showed the same tendency performing the interaction of CFA with the oil components leading to the destabilization of crude oil (Fig. 10).

Consequently, the mechanism of emulsion breaking is based on adsorption of asphaltenes due to intensive interaction between CFA and asphaltenes,<sup>[20,21,25]</sup> and macromolecules of Tweens are displacing natural stabilizers, causing the disruption of stabilizing interfacial film and coalescence of water droplets. The centrifugation results in settling of CFA particles and water droplets (Fig. 11).

#### 4. Conclusion

The search for new materials and technologies that will make demulsification of crude oil emulsions more effective and easier is intensively continuing. Therefore, the development of novel materials to accomplish the successful separation of emulsions is relevant. In this study we investigated the using of CFA and non-ionic surfactants Tweens for separation of two crude oil samples from oilfields of the Atyrau region (sample 1) and the Kyzylorda region (sample 2), Kazakhstan. For sample 1 the heating of water-in-crude oil emulsion followed by centrifugation resulted in the formation of an intermediate layer emulsion, which causes the complications during oil processing. The results indicate that the addition of CFA leads to the dewatering of crude oil emulsion and decreasing of the intermediate layer. The use of Tweens for sample 1 of crude oil emulsion, Atyrau region, showed demulsifying ability close to 60% and prevented the formation of an intermediate layer. According to the results of IR spectroscopy, the mechanism of demulsification of CFA occurs due to the adsorption of stabilizing components of crude oil and their intensive interaction with CFA particles. The combination of CFA and non-ionic amphiphiles Tweens showed a slight increase of DE (68%), and the formation of the intermediate layer emulsion was not observed. It has been shown that demulsification depends on the nature and stability of crude oil emulsion due to the content of asphaltenes. For sample 2 the DE in the presence of CFA and non-ionic Tweens was higher than 85%. Two samples of crude oil emulsions had different physicochemical properties, including the percentage of asphaltenes. The results obtained from this study confirmed the possibility of joint use of CFA and non-ionic Tweens. Thus,

it can be concluded that the development and characterization of cost-effective CFA-based demulsifiers, particularly the combination of CFA and eco-friendly non-ionic amphiphilic substances, have high potential for improving emulsion dewatering and scalability in the petroleum industry. Besides, the utilization of CFA with optimized dosage for crude oil demulsification can promote better environmental sustainability and lower production costs.

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#### Conflicts of Interest

There are no conflicts to declare.

#### Supporting Information

Not applicable.

#### CRedit Statement

**Akbota Adilbekova** analyzed the data and wrote the manuscript, **Erik Sailaubay** and **Indira Kadyrbai** performed the experiments with calculations, **Saidulla Faizullayev** carried out analyses and contributed to the interpretation of the results, **Moldir Kerimkulova** contributed to the writing of the manuscript. All authors discussed the results and contributed to the final manuscript.

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