RESEARCH PAPER

Influence of Solvents on The separation of Water From The bitumen Emulsions Using Alginite.

Sangar S.Ahmed
Department of Chemistry, College of Science, Salahaddin University-Erbil, Kurdistan Region, Iraq

A B S T R A C T:
The impact of various diluents on the removing of water from bitumen emulsions for the distillation feed (bitumen) using alginite as a demulsifier was investigated. Alginite as a natural rock is able to remove water from the bitumen emulsion. The results demonstrated that the alginite can be enhanced by adding solvents. The separation of water without adding diluents using 0.5 wt.% was about 84 %. In contrast, the addition of 2.0 mL 1-butanol can significantly improve the process resulting in water removal of 98.3 %. Furthermore, at the highest volume of hydrocarbon solvent, which was a kerosene fraction (2 mL), this yields an increase in the last water separated from 73.5 % to nearly 81.3 % in the bitumen emulsion. Consequently, the results confirmed that applying toluene, hydrocarbon solvents, and medium-chain alcohols can enhance the destabilization process when they are used together with alginite. Thereafter, changing the physical characteristics of an emulsion with the addition of diluent leads to a decrease in the viscosity of the oil phase and contributes to the coalescence of water droplets.

KEY WORDS: Bitumen, Emulsion, Alginite, 1-butanol, Toluene.
DOI: http://dx.doi.org/10.21271/ZJPAS.33.2.5
ZJPAS (2021) , 33(2);51-58.

1. INTRODUCTION:

Bitumen (tar sands) consists of a large number of oil resources in Canada. Although, due to oil sands unconsolidated deposits of very heavy hydrocarbon bitumen and this require many stages of processing before refining (Jiang et al., 2007). Bitumen is exploited using in-situ thermal operations corresponding to steam-assisted gravity drainage (SAGD) and cyclic steam stimulation and utilizing surface mining, wherever the bitumen is separated from reservoir sand and clay using hot water and a froth flotation operation.

Due to low mobility and flow which are closed to ambient temperature, the complex composition of heavy crude oil and bitumen would be difficult and expensive to produce and transport through pipelines. Furthermore, their high asphaltene and paraffin contents stimulate pipe clogging, pressure drops, and consequently a lower production rate rather than lighter crude oils (Martínez-Palou et al., 2013) and (Yarranton et al., 2000). Nevertheless, these two operations involve the production of viscous emulsion (Elsayed Abdelfatah et al., 2019). The emulsion is droplets of water or brine which are distributed in an exceedingly continuous phase of crude oil and that they are recognized as water-oil emulsions (W/O) (Saad et al., 2019).

Moreover, high viscosity and enormous contents of resins and asphaltenes contribute to
stabilize the water droplets which spread in oil, that making petroleum demulsification harder and also the development of new dehydrating agents is necessary. For the droplets to flocculate and coalesce, the additives should reduce this steric repulsion by softening the rigid skin. Highly interfacially active demulsifiers compared to asphaltene can compete effectively for the interface and soften the interfacial asphaltene film. (Elsayed Abdelfatah et al., 2019) A lot of techniques such as mechanical, chemical, thermal, and electrical have been applied to resolve the emulsion phenomenon. Also, combinations of these methods have been conducted for a good demulsification achievement. (Cendejas et al., 2013)

However, bitumen density is almost the same as the density of water, and without the addition of a light hydrocarbon diluent (e.g., naphtha), froth treatment is not possible. Diluting the froth with a light hydrocarbon decreases the stage of oil density, that making separation of water from diluted possible bitumen. Gravity settlers, centrifuges, and/or cyclones are applied in all operating plants. Therefore, the addition of a diluent reduces the oil phase viscosity, and further support in the removal of the water and solids (Czarnecki and Moran, 2005).

The impact of solvent is also very essential to the stability of diluted water-bitumen emulsion. The stability of the bitumen emulsion was decreased with the rise of the dilution ratio. The diluted bitumen film between water droplets and oil phase, which becomes less stable. Besides, the physical properties of the oil phase such as density, viscosity will affect with using the dilution ratios. (Jiang et al., 2011) Light hydrocarbon such as Naphtha and paraffinic diluent are widely used in froth treatment operations. Hence, a diluent that has the capability of destabilizing the bitumen emulsion would be a breakthrough. Meanwhile, adding conventional demulsifiers requires the addition of volatile organic solvents such as toluene and alcohol as a carrier for the demulsifier. This poses significant environmental issues and complicates the process. Environmentally friendly demulsifiers and diluents are essential for the oil industry. (Salam et al., 2013)

Consequently, the objective of the current work is to go beyond what was performed previously work (Hippmann et al., 2018) and aims to study the influence of various types of solvents on the demulsification of the water-bitumen emulsion prepared with a residual distillation feed oil using alginite as eco-friendly demulsifier. The effects of solvents with alginite on the rheology and water droplets of the bitumen emulsion were also investigated. Alginite is a natural rock out of the oil shale family and it descents from the Gérce mine in- Hungary. The essential ingredients of alginite are high of organic matter (19 %), clay (54 %), and limestone content (22 %) (Hippmann et al., 2018).

2. EXPERIMENTAL SECTION

2.1. EQUIPMENT AND MATERIALS

Vacuum residual distillation feed (bitumen), which was a residue from Khurmala oil field, was utilized to prepare water-bitumen emulsions. It was obtained from Erbil in the (Kurdistan Region of Northern Iraq). All used solvents were of analytical grade and purchased from Fluka (USA).

The density (using the pycnometer), entire sulfur content % (using the X-ray sulfur meter models RX-360SH, Japan), kinematic viscosity (using the SCHOTT CT 52 viscometer), and flash point (using the Automated Cleveland Open cup Flash Point Tester aco-8/8 as) of the bitumen were analyzed. The typical characteristics of bitumen are listed in Table 1. Alginite, which was given by Terra Natural Resources GmbH with a grain size of 3 mm that used as a demulsifier and prepared in powder form of particle size less than 100 µm.

Table 1: Physical properties of bitumen sample.

| Test Description       | Method       | Sample Results |
|------------------------|--------------|----------------|
| Density g/cm³          | ASTM D-70    | 0.9937         |
| Sp.gr @ 15.5 °C        | ASTM D-1217  | 0.9935         |
| API Gravity            | ASTM D-287   | 10.93          |
| Total sulphur content wt % | ASTM D-4294 | 4.8034         |
| Flashpoint °C          | ASTM D-92    | >120           |
| Viscosity cSt 50 °C    | ASTM D-445   | 2498           |

Also, the physical properties of diesel and gasoline samples are illustrated in Table 2 and Table 3 respectively.
Table 2: Physical properties of diesel sample.

| Test description          | Unit  | Results |
|--------------------------|-------|---------|
| Flash point              | ºC    | 67      |
| Pour Point               | ºC    | -9      |
| Density at 15.5 ºC       | g/ml  | 0.8485  |
| Kinematic Viscosity @40 ºC | mm²/sec | 3.5 |
| Water content            | vol%  | 0.0     |
| Cetane Number            |       | 47      |
| Cetane Index             |       | 50      |
| Total Sulfur Content     | mass% | 0.645   |

| Test description          | Unit  | Results |
|--------------------------|-------|---------|
| Initial Boiling Point, IBP | ºC    | 158     |
|                         |       |         |

Distillation temperature

| Test description          | Unit  | Results |
|--------------------------|-------|---------|
| 10% Recovered, vol%      |       | 196     |
| 50% Recovered, vol%      | ºC    | 272     |
| 90% Recovered, vol%      |       | 320     |

Final Boiling Point, FBP

| Test description          | Unit  | Results |
|--------------------------|-------|---------|
| Recovered                | vol%  | 97      |
| Evaporated               | vol%  | 1       |
| Residue                  | vol%  | 2       |
| Aniline point            | ºC    | 70      |
| Diesel Index             |       | 55.7    |

Table 3: Physical properties of gasoline sample.

| Test description          | Unit  | Results |
|--------------------------|-------|---------|
| Density at 15 ºC         | g/ml  | 0.7312  |
| Specific Gravity@15.5 ºC |       | 0.7320  |
| API Gravity              |       | 61.78   |
| Water content            | vol%  | 0.0     |
| Initial Boiling Point, IBP | ºC    | 50      |

Distillation Temperature

| Test description          | Unit  | Results |
|--------------------------|-------|---------|
| 10% Recovered, vol%      |       | 76      |
| 50% Recovered, vol%      | ºC    | 114     |
| 90% Recovered, vol%      |       | 192     |

Final Boiling Point, FBP

| Test description          | Unit  | Results |
|--------------------------|-------|---------|
| Recovered                | vol%  | 92      |
| Evaporated               | vol%  | 6.5     |
| Residue                  | vol%  | 1.5     |
| Total Sulfur Content     | mass% | 206     |
| Research octane number, RON |       | 92.1    |
| Motor octane number, MON |       | 82.9    |
| Antiknock Index, AKI     |       | 87.5    |

For preparing the water in oil emulsion, an intensive mixer Citenco F.H.P. motors LC9, (England) was applied. Demulsification experiments were carried out using a magnetic mixer by IKA, Germany. The water content after demulsification was measured by the Karl-Fisher titration using a V20 by Mettler-Toledo, USA. The optical Microscopy was performed using a microscope PrimoStar by Zeiss, Germany, which was equipped with a digital camera DCMC310 and software ScopePhoto (Ver. 3.1.615) by ScopeTek, China. Conversely, the rheology investigations were accomplished by using a rheometer model RN 4.1 with a spindle type Rotor S1 by RHEOTEST, Germany, and a thermostatic bath Alpha RA12 by Lauda, Germany.

2.2 preparation of water-bitumen emulsion

Making a density difference between bitumen and water, it is better to decrease the viscosity of bitumen, toluene at a volume ratio of 3:1 that was used as a solvent to create the continuous stage. Bitumen was transferred to a beaker and diluent was added. The mixture diluent–bitumen (Dilbit) was stirred to homogenize for 15 minutes at 1500 rpm using a mechanical stirrer (Citenco F.H.P. motors, model LC9, England). Emulsions samples were prepared by slowly adding brine solution (3% NaCl) to diluted bitumen (mass ratio 1:1) and kept mixing at 4500 rpm for 45 minutes. The stability of the prepared emulsion was measured under gravity sedimentation using a test tube at laboratory temperature. The water content of the stable bitumen emulsion was measured over time (more than one year) and the amount of emulsified water remained constant over time in the emulsion. Furthermore, without adding alginate using 2 mL of diluents like toluene, butanol, hexadecyl amine, n-heptane, there was no water separated.

2.3 demulsification of water-oil emulsion

The demulsification tests of prepared water-bitumen emulsion were carried out as follow:

50 ml of the water-bitumen emulsion was used into a beaker and it was stirred before adding alginate and diluent at constant stirred 1200 rpm for 5 min. using a magnetic stirrer. Then, alginate and diluent were added to the bitumen emulsion at 60 ºC temperature and stirred at 1200 rpm for 30 minutes. Then, the influence of solvents on the demulsification process was investigated. After the demulsification process, the water content of the treated bitumen emulsion was measured by the Karl-Fisher method using a Mettler-Toledo V20.
(Germany) and reported as a weight percentage. The result was reported as a weight percent and it was calculated by using Equation 1.

\[
\text{Water removal } \% = \left(1 - \frac{\text{Water content of sample}}{\text{Water content of initial emulsion}}\right) \times 100
\]

\[\text{Equation 1}\]

2.4. Optical microscopy

The optical microscopy technique was utilized to visualize the emulsion droplet sizes. Also, it was used to study the influence of alginate as well as diluents on the size of water droplets in the emulsion. A drop of the emulsion (ca. 50 μL) with a diluent and alginate was placed on a glass slide and followed by a cover slide. The optical microscopy images were captured using a microscope equipped with the digital camera DCMC 310 and a Scope Photo (Ver. 3.1.615) image analysis software.

2.5. Determination of viscosity

Dynamic viscosity of prepared water-bitumen emulsion at a constant speed of rotation (1000 rpm) and temperature (60 °C) using a rheometer was measured. A spindle type Rotor S1 was used to measure the emulsion viscosities with a cell containing 35mL of a sample. The rheometer was connected with a water bath thermostat using a Lauda thermostat. After that, the same procedure was applied to study the effect of alginate and diluents on the viscosity of the water-bitumen emulsion.

3. RESULTS AND DISCUSSION

3.1. Effect of toluene

For the treatment of bitumen emulsion, the solvent was initially applied to form driving forces for the demulsification of water-in-bitumen emulsions by raising the different densities between the oil and water phases and, simultaneously, reducing oil phase viscosity. Since asphaltenes have been recognized as exactly involved in the stabilization of bitumen emulsions, solvent aromaticity should play an essential role in the demulsification of bitumen emulsions, considering that the phase of behavioral asphaltenes depends on solvent aromaticities. (Mullins, 2007) Figure 1 shows the degree of demulsification of the bitumen emulsion as a function of different amounts of toluene. The experimental evidence shows that when the bitumen emulsion is diluted with 2.0 mL of toluene, more than 87 % of water was separated from the emulsion using 0.5 wt.% of alginate.

![Figure 1: Effect of toluene on water removed using 0.5 wt. % alginate.](image)

The results revealed that the solvent effect was very crucial to the stability of diluted bitumen emulsion. Increasing aromaticity of the emulsion causes enhancing asphaltene solubility allowing asphaltene molecules to be freer to leave their sites at the oil-water interfacial film. This ruptures the film and permits small water droplets to coalescence and grows, eventually separating into an aqueous phase (Zhang et al., 2005).

3.2. Effect of hydrocarbon solvents

Figure 2 shows the impacts of the blending different hydrocarbon solvents with toluene on water removed% from the bitumen emulsion. Depending on diluent blended types with the bitumen emulsion, 78 % of water was separated from the emulsion without using diluents. Moreover, 80.2%, 76.2%, 78.1%, and 78.6% of water were removed from the bitumen emulsions using 2.0 mL of gasoline, n-hexane, n-octane, and n-decane respectively.

![Figure 2: Effect of hydrocarbon solvents on water removed using 0.5 wt. % alginate.](image)

In general, gasoline and kerosene fractions, which include a combination of paraffinic, naphthenic, and aromatic components),
as compared to a light aliphatic solvent, it can achieve more demulsification of bitumen emulsions. Without aromatic and naphthenic constituents, lighter solvents (e.g., n-pentane) were detached water from the emulsion less than heavier solvents (e.g., gasoline and kerosene) with aromatic and naphthenic compounds in their fractions. The same results were observed by (Mullins, 2007). Moreover, the solvent with higher aromaticity (toluene) accelerates water resolution from the oil stage marginally more than the solvent with lower aromaticity (hydrocarbon solvents) (see Figure 1).

3.3. Effect of different type of solvents
Since n-heptane and n-hexane, which have been used in the froth treatment, are greatly volatile solvents, the damage of solvent through the two hours of interface equilibrating should carefully be considered (Czarnecki and Moran, 2005). Consequently, it is important to find and investigate a solvent with high efficiency for destabilizing the water-bitumen emulsion. To study the effect of various solvents on the water-bitumen emulsion, four different solvents such as toluene, butanol, hexadecyl amine, n-heptane were investigated. From Figure 3, it is seen that the addition of 2.0 mL of n-heptane destabilizes the water-bitumen emulsions, while with the same amount of butanol more than 98% of water was removed from the emulsion.

![Figure 3: Effect of different solvents on water removed using 0.5 wt. % alginite.](image)

As it can be noticed that from Figure 3, extended aromaticity of the bitumen emulsion helps to solubilize the asphaltenes and reduce the emulsion stability. Moreover, most destabilization was achieved when the dispersed phase is diluted with medium-chain alcohols. This attribute to using 1-butanol the asphaltene monolayer becomes more flexible at the interfacial film between water and oil stages. It can be clearly seen that 1-butanol molecules entered the interfacial film and these led to weakening the interfacial film between asphaltenes molecules and water, thereby, leading to less-rigid the film. (Abdurahman H. Nour et al., 2007)

On the other hand, the addition of 2.0 mL hexadecylamine results in a separation of 90.8% of the water from the bitumen emulsion. The observation of amine solvent co-demulsifier efficiency was due to the high molecular weight of hexadecylamine, which drives as flocculants in adsorption of amine compounds in the interfacial film and interaction activity. (Abdurahman H. Nour et al., 2007)

3.4. Effect of alcohol solvent
Alcohol solvents contain both hydrophobic and hydrophilic parts in their structure. The alcohol molecules are located at the tail (hydrophobic part) at the surface of the interfacial film, whereas, the tail is penetrating the interfacial film of the bitumen emulsion. Therefore, having alcohol molecules in the monolayer, it diminishes the interactions among asphaltenes molecules which may lead to a less-rigid interfacial film. (Zhang et al., 2005)

Figure 4 gives the effect of different blended alcohol solvents on the stability of the bitumen emulsions. It is seen that the highest demulsification efficiency was obtained with 1-butanol was 98% using 0.5 wt.% of alginite, whereas, with the same amount of ethanol, 1-propanol, 1-hexanol, and 1-decanol, water separation efficiency was 79.5%, 93.0%, 97.4%, and 95.9%, respectively.

![Figure 4: Effect of different alcohol solvents on water removed using 0.5 wt. % alginite.](image)
Nevertheless, four carbon alcohols and higher, having much lower water solubility. This can be illuminated by considering the way that water molecules can spread solute molecules into a solution. The polar water molecules are attracted to the hydroxyl group by hydrogen bonding that happens between the hydrogen of water molecules and the oxygen in the alcohol molecules. As the hydrocarbon portions of the alcohol become more extensive, they could be in a higher molecular weight (Abdurahman H. Nour et al., 2007). Additionally, medium-chain alcohols such as 1-butanol and 1-hexanol have an entirely different concentration dependence upon destabilization of the bitumen emulsion. The medium-chain alcohols are soluble in both the aqueous phase and the bulk crude oil in the interfacial region. Diffusion/partitioning between these sites will adjust the interfacial properties of the system in such a way that the film becomes less rigid, and hence more dynamic, allowing more accentuated fluctuations to occur. Such processes will directly improve the possibilities of an effective overlap between dissimilar adjoining droplets, and thus strongly favour coalescences (Sjöblom, H. Söderlund, S. Lindblad, E. J. Johansen and I. M. Skjärvö, 1990).

3.5. Effect of the diluent on the water droplets

To understand more about the effect of diluents specially 1-butanol and alginate on the water-bitumen emulsion, the microscopic technique was applied. As can be distinctly seen from Error! Reference source not found.A that without using alginate particles and diluents, the emulsion was stable and no water was separated from the emulsion. On the other hand, as illustrated in Error! Reference source not found.C, after mixing alginate with the emulsion, the drops of water start to separate from the emulsion. Also, using 1-butanol with the particles of alginate, the water was separated immediately from bitumen emulsion (see Error! Reference source not found.B).

From the current results, it can be concluded that utilizing 1-butanol besides alginate particles initiates the rise of water droplets in the bitumen emulsion system, thus, extends to an increase in the coalescence of the water droplets.

3.6. Effect of alginate and solvent on the viscosity of the emulsion

The viscosity of the treated and untreated bitumen emulsion was measured to investigate the effect of alginate with diluent and alginate on the rheology of the water-bitumen emulsion. The viscosity test was carried out at temperature 60 °C and constant rotational speed (1000 rpm). As presented in Figure 6, the viscosity was reduced after adding alginate to the emulsion immediately. The viscosity of untreated emulsion has remained constant without adding alginate. The result shows that alginate has great power efficiency in decreasing the interfacial tension of the adsorption film in the emulsion, which makes the deformation of the distributed phase easier. Moreover, the viscosity of bitumen emulsion instantly reduced to 10mPa.s after 2 mL of 1-butanol and 0.5 wt.% of alginate was added to the emulsion. This means that water was completely broken from the bitumen emulsion. This can be attributed to the fact that alginate with 1-butanol has the power to split water in the bitumen emulsion. Altering the physical characteristics of an emulsion with the addition of diluents leads to a decrease in the viscosity of the constant stage and provides a coalescence of water droplets. On the other hand, the increase in viscosity of the untreated bitumen emulsion after 600 sec. is mainly due to the increase of interaction bonds,
which is formed between water and functional groups of bitumen. This is leading to reduce in the molecular distances of the emulsion, thereby, a rise of resistance to flow and increase the dynamic viscosity.

![Image](304x810 to 549x828)

**Figure 6**: Effect of alginate on the viscosity of water-bitumen emulsion.

From the current results discussed, it can be noticed that 1-butanol made an increase of water droplet sizes and reduce viscosity in the emulsion system after adding to alginate. This demonstrates that the complete distribution of the alginate molecules on the interfacial film is between water and bitumen emulsion.

4. CONCLUSIONS

This work indicates the addition of diluents with alginate was essential to obtain high results. Therefore, alginate can be used as a new powerful demulsifier in both the petroleum industry and the environmental field. The percentage separation of water without adding diluents using 0.5 wt.% was about 84 %. The addition of 2.0 mL 1-butanol can significantly improve the process resulting in water removal becoming 98.3 %. The highest volume of hydrocarbon solvent, which was kerosene fraction (2 mL), this yields an increase in the last water separated from 73.5 % to nearly 81.3 % in the bitumen emulsion. The results revealed that the solvent has a crucial effect on stabilising the diluted bitumen emulsion. Increasing aromaticity of the emulsion with adding toluene to the emulsion can enhance asphaltene solubility while allowing asphaltene molecules to be freer to leave their sites at the W/O interfacial film. This ruptures the film and permits small water droplets to coalescences and grows, and eventually separating into an aqueous phase.

Acknowledgements

The author wishes to thank his advisor, Prof. Dr. rer. Nat. habil. Martin Bertau the head of the Chemical Technology Institute at the Freiberg University of Mining and Technology for his guidance, hospitality, and support throughout this work. Also, thanks to Sebastian Hippmann for his help in performing laboratory experiments. Further thank Terra Natural Resources GmbH, Bonn, Germany for kindly providing alginate material.

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