

# Influence of the crude oil and water composition on the quality of synthetic produced water.

*Marcin Dudek<sup>1</sup>, Eugénie Kancir<sup>2</sup> and Gisle Øye\*<sup>1</sup>*

<sup>1</sup> Ugelstad Laboratory, Department of Chemical Engineering, Norwegian University of Science and Technology (NTNU), Sem Sælandsvei 4, 7491 Trondheim, Norway

<sup>2</sup> National Graduate School of Engineering (ENSICAEN), 6 Boulevard Maréchal Juin, 14000 Caen, France

Keywords: Produced water, crude oil, water quality, water characterization, oil characterization.

## ABSTRACT

Produced water originates from the crude oil production. It is a mixture of organic and inorganic compounds and its composition is highly oilfield-dependent. The present study was carried out to increase the understanding of the relations between the crude oil properties and the composition of the aqueous phase on the produced water quality. Brines with different compositions and pH levels were mixed with five crude oils. Initially, the physicochemical properties and composition of the crude oils were determined, while the quality of the synthetic produced water samples were described by parameters such as the total oil concentration and organic carbon, pH, the drop size distribution and the Sauter mean diameter. The characterization part revealed that crude oils fell into two categories: light and heavier oils.

Most parameters like density, viscosity, total acid number (TAN) or composition reflected this division. A similar pattern was sustained for the water quality analyses. Water produced with heavier crude oils generally contained higher concentration of emulsified oil with the biggest and most polydispersed droplets. Light oils had a tendency to create water-in-oil emulsion between the oil and water phase, which impeded the phase separation, resulting in less free water. The Sauter mean drop diameters increased with pH of the water phase. However, the presence of calcium at the highest pH decreased the droplet size and the amount of free water, compared to the brine without divalent ions, which is in agreement with the interfacial role of the naphthenic acids in the crude oil emulsions. The results showed the significance of both the water and oil composition on the quality of the produced water. This can lead to improved fundamental perception of the produced water treatment process.

## **Introduction**

During crude oil and gas production, the largest by-product during the extraction process is produced water. The water cut depends on the location of the reservoir and the age of the production wells. It can vary from a few percent in the beginning of the exploitation to more than 95% in the last phases of the production. Global estimates say that for every barrel of crude oil, three barrels of water are produced<sup>1</sup>.

There are two main paths for disposal of the produced water. One is discharge of the water to the sea. Before the water can be disposed of, it needs to undergo treatment processes to reach a certain quality level, specified by local environmental regulations. Depending on the location, the maximum average oil in water (OIW) content for disposal is between 30 and 40 ppm<sup>2</sup>. The second disposal option, reinjection, can be carried out by pumping the water into a disposal or a production reservoir. The latter would be more desired from a technological and economical point of view, as it can sustain the production pressure of the reservoir<sup>3</sup>. Produced water reinjection is also likely to be preferred way of handling the water in subsea production and processing facilities. However, the process also carries several risks, for instance reservoir souring or formation damage due to injectivity decline. Furthermore, emulsified oil droplets and suspended solid particles in the produced water can block the pores in the reservoir and decrease the permeability of the formation. This means that the requirements for the quality of the produced water are strict both for the reinjection and discharge options<sup>4</sup>.

The produced water treatment methods can be divided into three types. The primary separation relies on the bulk phase separation of gas, crude oil and water, using a conventional or modified gravity separator. In this step, the OIW concentration in the outlet water can range from 100 ppm to 1000 ppm<sup>5</sup>. The secondary treatment usually consists of hydrocyclones or gas flotation units. Both those processes are capable of lowering the oil in water concentration below the discharge limit<sup>6-8</sup>. A tertiary treatment (or water polishing step) can be performed to

reduce the concentration of dissolved components through media filtration or adsorption processes<sup>6, 9-10</sup>. Novel techniques such as ultrafiltration<sup>11</sup>, nanofiltration and reversed osmosis<sup>12-13</sup> or biological treatment<sup>1, 14</sup> are also considered to be promising water polishing methods.

The produced water contains dissolved salts, dispersed solids, dissolved and dispersed crude oil components, as well as traces of heavy metals and radioactive materials<sup>9</sup>. Additionally, chemicals added during different stages of the production affect the quality and properties of the produced water<sup>15-16</sup>. The composition of the produced water is field-dependent, as the location of the reservoir determines its conditions (pressure, temperature), reservoir rock and the type of the produced oil. The conditions of the reservoir will mostly affect the water solubility of salts dissolved from the rock formation, gases and indigenous crude oil compounds. What is more, the conditions of the reservoir also change with the progress of the oil production, especially when seawater is injected or enhanced oil recovery techniques are employed.

The chemical composition of the crude oil has an effect on the produced water quality, with respect to both dispersed and dissolved components. Typically, crude oil is characterized by physical properties like density and viscosity, and chemical properties, such as the total acid and base number and SARA (Saturates, Aromatics, Resins, Asphaltenes) composition. The interfacial activity of components in the crude oils will be affected by these parameters and can lead to increased emulsion stability and problems with separation<sup>17-18</sup>. It has been shown that the interfacial properties can influence the coalescence of oil droplets<sup>19</sup> and the stability of oil-in-water emulsions<sup>20-21</sup>. Once in contact with an aqueous phase, water-soluble hydrocarbons in the crude oil will partition into the water phase<sup>22-24</sup>, adsorb at the gas-water interfaces and influence the oil removal efficiency by gas flotation<sup>25-26</sup>. The characteristics of the produced

water also depends on the properties, like pH<sup>27-28</sup>, ionic strength<sup>29</sup> and the presence of divalent ions<sup>30</sup>.

The aim of this work was to investigate the effect of the water and crude oil properties on the quality of produced water. First, the physicochemical and interfacial properties of five crude oils were studied. Then the oils were mixed with water with different pH and ionic composition. After separation, the quality of the synthetic produced water (i.e. free water) was determined in terms of the total organic carbon, pH, the total oil concentration and the drop size distributions of the dispersed oil. The preparation conditions were kept the same for all the samples in order to enhance the influence of the crude oil properties and the water composition on the synthetic produced water quality.

## **Materials and methods**

### ***Crude oil characterization.***

*Crude oils.* Five dead (i.e. stored at ambient pressure and temperature) crude oils from the Norwegian Continental Shelf were analyzed and used as received.

*Density measurements.* The density of the crude oils was measured at 20°C, using a DMA 5000 laboratory density meter (Anton Paar, Austria).

*Viscosity measurements.* The viscosity of the crude oils was measured at 20°C, using a MCR 301 laboratory rheometer (Anton Paar, Austria) with a cylindrical geometry (CC-27).

*Total acid and base number measurements.* The analysis of the total acidic number (TAN) was performed according to the D664-95 ASTM method<sup>31</sup>. The total base number (TBN) was evaluated with a similar method to the one presented by Dubey and Doe<sup>32</sup>. Both methods were described in details previously<sup>33</sup>. In short, TAN was determined by titrating the solution of crude oil in a 100:99:1 (v/v) mixture of toluene/isopropanol/water with 0.1 M solution of tetrabutylammonium hydroxide in a 10:1 mixture of isopropanol and methanol (Sigma-Aldrich). To measure the TBN, the solution of crude oil dissolved in methylisobutyl ketone was titrated with 0.025 M solution of perchloric acid in acetic acid. In both cases the titration was controlled by a Titrand unit (Metrohm, Switzerland), connected to a 6.0229.100 LL solvotrode.

*HPLC fractionation.* The procedure for fractionation of the crude oils into saturates, aromatics, resins and asphaltenes (SARA) was previously reported by Hannisdal et al.<sup>34</sup>. 4 g of crude oil were dissolved in 160 ml of n-hexane (Chromanorm® for HPLC, VWR). The mixtures were mixed overnight and then filtered with a 0.45 µm membrane filter (Millipore HVLP) to isolate the asphaltene fraction. A HPLC system with two columns (unbounded silica and amino) was used to fractionate the filtered maltenes into saturate, aromatic and resin

fractions. After controlled evaporation of the solvent in N<sub>2</sub> atmosphere, the weight percentages of the fractions were determined gravimetrically.

*Interfacial tension measurements.* The interfacial tension (IFT) measurements were performed using a pendant drop tensiometer (PAT-1M, Sinterface Technologies, Germany). Images of a crude oil drop, immersed in a brine solution were recorded over time. The measurements lasted until the near-equilibrium values were reached. This usually took less than 7 hours for the light oils, while often exceeded 16 hours for the heavier crude oils (an example of the dynamic interfacial tension evolution was shown in Figure S1 in Supporting Information). The interfacial tensions were calculated by fitting the drop profiles to the Young-Laplace equation. The reported IFT values were an average of at least two measurements. All the measurements were performed at room temperature (22°C).

*Elemental composition analysis.* The content of carbon, hydrogen, nitrogen, oxygen and sulphur was determined for the crude oils and each of their SARA fractions. The analyses were performed using an elemental analyser EA 1108 (Fisons Instruments) at the Oil and Gas Institute – National Research Institute in Cracow (Poland).

*Water content.* The amount of water in the as-received crude oils was analysed by Karl Fischer titration, using a KF Coulometer 831 (Metrohm, Switzerland).

***Preparation and characterization of synthetic produced water.***

*Brine solutions.* Two types of brines were used during this study in order to simulate high salinity conditions and to study the influence of divalent ions on the produced water quality. The first contained only NaCl (Emsure®, Merck Millipore) and is referred to as Na-Brine. The other was a mix of NaCl and CaCl<sub>2</sub>·2H<sub>2</sub>O (p.a., Sigma-Aldrich), with a molar ratio of sodium to calcium equal to 35:1, and is referred to as NaCa-Brine. The ionic strength was kept the same in both the brines (I=0.59 M). The salt concentration was similar to the seawater conditions, however the produced waters from the Norwegian Continental Shelf were reported

to be of comparable salinity<sup>35</sup>. The solutions were adjusted to pH 3 and 10, using solutions of diluted HCl (AnalaR, VWR) and dissolved NaOH (AnalaR, VWR). The natural pH of the brines ranged from 5,9 to 6,4 and is later referred to as pH 6. Deionized water (Millipore Simplicity Systems, Germany) was used to prepare all solutions.

*Produced water preparation.* 100 ml brine and 100 ml crude oil were poured into a 250 ml aspirator bottle and mixed for 8 min at 20 000 rpm, using an Ultra-Turrax S25N-10G homogenizer (IKA, Germany). The samples were left to phase separate for two hours, before the water phase was collected through the bottom outlet of the aspirator bottle. The amount of free water after 2 hours was recorded. From the collected water phase (later referred to as the synthetic produced water), the drop size distributions, the total oil concentration and pH in this synthetic produced water were determined. Each sample was prepared and analyzed at least three times. All of the steps were performed at room temperature (22°C).

*Drop size measurements.* The drop sizes in the water phase were analyzed within 5 minutes after sampling, using a Nikon LV 100D microscope. 10 to 12 pictures were captured per sample and the Image-Pro Plus 5.0 software was used to determine drop size distributions and the Sauter mean diameters, which were calculated according to Equation 1:

$$d_{32} = \frac{\sum d_i^3}{\sum d_i^2} \quad (1)$$

where  $d_{32}$  is the Sauter mean diameter and  $d_i$  is the diameter of the drop, detected by the software. Only drops below 30  $\mu\text{m}$  were considered.

*Total oil concentration.* Appropriate amount of methylene chloride (HiPerSolv CHROMANORM for HPLC, VWR) was added to the water phase and shaken, in order to extract the dispersed and dissolved crude oil components into the organic phase. The two phases were then separated in a separation funnel. The organic phase was collected and UV analysis was performed to determine the amount of oil, using UV-VIS spectrophotometer (UV-

2401PC, Shimadzu, Japan). Calibration curves, prepared individually for each crude oil, were used to calculate the oil concentration from the absorbance at 259 nm.

*pH measurements.* The pH of the water phases were measured using a pH meter (SevenEasy pH, Mettler Toledo, Switzerland). Prior to the measurements, the oil drops were removed by centrifugation (Heraeus Multifuge X3R, Thermo Scientific, USA).

*Total Organic Carbon (TOC) analysis.* Approximately 50 ml of brine and 50 ml of crude oil were poured into Schott bottles and put on a vertical shaker (200 rpm) for 24 hours in order to saturate the water phase with the water-soluble oil components. Subsequently, the aqueous phase was sampled, centrifuged (Heraeus Multifuge X3R, Thermo Scientific, USA) and acidified to  $\text{pH} < 2$  with sulphuric acid (95-97% p.a., Sigma-Aldrich). The TOC analyses were then determined using a TOC-L<sub>CPH</sub> Analyser (Shimadzu, Japan). The analyses were performed at GIG Research Institute in Katowice (Poland).

## Results and discussion

### *Crude oil characterization.*

The physicochemical properties and the composition of the crude oils are presented in Table 1. Based on the API gravities, the crude oils were divided into light oils, with the API values ca. 36-38 (B,D,E), and heavier oils with the API values 19.2 and 23 (A,C). The heavier oils were characterized by significantly lower saturate fraction and higher TAN numbers (above 2 mg KOH/g oil) than the other oils. Furthermore, their substantial content of polar components (resins and asphaltenes) provided higher density and viscosity. The light oils consisted of low amounts of acidic and basic components. In addition, they had similar values of the density and the viscosity, the lowest water content and some variations in the saturate, aromatic and resin contents.

More detailed insight into crude oils composition was provided by the elemental analysis of all the fractions, as previously demonstrated by Gawel et al.<sup>33</sup>. The C/H atomic ratios of the crude oils are shown in Fig. 1. The division into light and heavier crude oils was also noticed here, as crude oils A and C had higher C/H ratio (0.62 and 0.59 respectively) than the remaining crude oils (ca. 0.55). The C/H atomic ratio in the saturate fractions was slightly higher for the heavier crude oils (0.52-0.53) than for the light oils (ca. 0.5). The saturate fractions are usually expected to contain straight-chained, branched or cyclic aliphatic hydrocarbons, but this could suggest that the heavier crude oils also contained some compounds with unsaturated moieties. The aromatics and resins fractions had comparable values of the C/H ratio in most of the oils, which indicated similar aromaticity with an analogous extent of methylene moieties in both fractions. The biggest variation was observed for the asphaltenes. Crude oils A and C had the highest aromaticity in this fraction, while it was lower for the lighter crudes. The surprisingly low value for crude oil E may be due to oxidation of the sample (see below).

Fig. 2 shows the amount of nitrogen, oxygen and sulphur in the complete crude oils and their SARA fractions. The amount of nitrogen in the crude oil D was considerably higher than for the rest of the oils (Fig. 2A). No nitrogen was detected in the saturate fractions of the crude oils, whereas the aromatic and resin fractions contained similar amounts of nitrogen. The asphaltene fractions contained the highest nitrogen amounts for crude oil A and C. For the lighter oils, however, the highest nitrogen content was seen in the resin fraction. The oxygen content was similar in all the crude oils (Fig. 2B). Furthermore, the saturate and aromatic fractions had comparable and relatively low amounts of oxygen, while the two most polar fractions contained significantly more of this element. Most of the light crude oils had higher amount of oxygen in the asphaltenes than in the resin fractions, which agrees with observations made by Gawel et al.<sup>33</sup>. The crude oils with the highest viscosity (A and C) tended to have larger amounts of sulphur (Fig. 2C). This trend was also seen in the SARA fractions, where all fractions of the heavier crudes contained more sulphur, with an exception of crude oil B, which had very high content of sulphur in the aromatics fraction. Similarly to nitrogen, no sulphur was detected in the saturate fractions of all of the crude oils.

The IFT values of the crude oils varied from 19 to 20.5 mN/m against the Na-Brine and from 16.2 to 19.9 mN/m for the NaCa-Brine. The lowering of the IFT when calcium was present in the aqueous phase suggested that acidic components played some role for the interfacial properties, as dissociated acids can form complexes with  $\text{Ca}^{2+}$ <sup>36-37</sup>. However, no quantitative relations were found between the IFT and the TAN. The asphaltenes are also known to reduce the IFT<sup>38</sup>. An interesting observation in this respect was that slightly lower interfacial tension values were obtained for the two crude oils (D, E) with the highest content of nitrogen. These crude oils also had significantly higher share of oxygen in their asphaltene fractions. An inversed dependence was observed for sulphur, as crude oils A, B and C had the highest values of the IFT. These observations were in agreement with previous findings<sup>39</sup>.

### *Separation*

Fig. 3 displays that the total amount of free water after two hours of gravity separation varied between the samples, but generally increased when the initial pH of the Na-Brine increased. A similar trend was noticed for the NaCa-Brine (Figure S2 in Supporting Information). The amount of recovered water was higher for the samples with heavier crudes than for the samples prepared from the lighter crude oils at the two lowest pHs. This was likely due to the formation of stable water-in-oil emulsion layers that reduced the amount of recovered water in the latter samples, however size distributions of the water drops might also have played a role. A similar trend was not seen at the highest pH, where the difference in the amount of recovered water varied less between the samples. Furthermore, while the amount of recovered water was more or less independent of the ionic composition at the lowest pHs, the amount of recovered water decreased in the presence of calcium ions at pH 10, as seen in Table 2. The reduction ranged from a few (A, D) to almost 30 percent (C, E).

The higher water-in-oil emulsion stability for the systems with the lighter crude oils was explained by the high saturate and low aromatic contents in these oils. This can facilitate increased interfacial activity, as well as the aggregation of asphaltenes, resulting in rigid interfacial layers that enhanced the emulsion stability<sup>19,38,40</sup>. It was also argued by other authors that wax particles, often found in light crude oils, can increase the emulsion stability<sup>41</sup>. pH of the aqueous phase also influenced the rigidity or viscoelasticity of the interfacial films and thereby the emulsion stability. At low pH, competitive adsorption of protonated naphthenic acids and molecules of resins and asphaltenes had been reported to form rigid interfacial layers that oppose the coalescence of crude oil drops<sup>42</sup>. Increased pH caused dissociation of the naphthenic acids, which enhanced their interfacial activity and their water solubility. Replacement of molecules causing interfacial rigidity by dissociated naphthenic acids has been proposed as a reason for decreased emulsion stability<sup>42</sup>. Furthermore, partitioning of the

naphthenic acids into the aqueous phase has also been found to reduce interfacial film stability<sup>43</sup>. Here, the presence of divalent ions increased the emulsion stability at the highest pH. This indicated that sufficient dissociated acids at the interface underwent complexation with calcium and strengthened the interfacial film. As mentioned above, another contributing factor for the differences in the stability of water-in-oil emulsions might have been the size distribution of water droplets. Crude oils with higher viscosity require longer mixing time, in comparison with less viscous oils, to reach a comparable water droplet size distribution<sup>44</sup>. As the mixing time here was constant for all of the samples, it is possible that large enough water droplets were present in the heavier crude oils to give higher amount of recovered water due to faster sedimentation.

#### *Produced water quality*

The total organic carbon content, representing the water soluble crude oil components, in the synthetic produced water from NaCa-Brine varied from about 20 to 70 ppm between the samples, as seen in Fig. 4. Similar trends, with slightly lower TOC values, were observed in the samples from the Na-Brine (Figure S3 in Supporting Information). The highest values of TOC were found in the synthetic produced water prepared from crude oil D and E. Notably, those crude oils stood out with a considerably higher oxygen content in the asphaltene fractions than the other oils. This could suggest improved water solubility of the smallest compounds in the asphaltene fractions<sup>21</sup>. Similar observations were made previously<sup>45</sup>, where the amount of oxygen in the asphaltene fraction affected their water solubility.

The composition of the crude oil also had an impact on the pH of the synthetic produced water (Fig. 5). When the initial pH of the brine was 3, most of the samples displayed a slight increase of the pH. For the produced water from crude oil A, however, the pH was noticeably higher. The significantly higher TBN in the corresponding crude oil may promote more extensive partitioning of the basic components into the aqueous phase. When the initial pH of

the brine was 6, the produced water samples experienced either a small decline or a small increase of the final pH value. However, in this pH range even the smallest concentration of dissociated species can cause a noticeable change in the pH. The effect of the dissolved CO<sub>2</sub> would also be most noticeable in this range. All water samples experienced a considerable decrease of pH (down to 6-7), when the brine was initially at pH 10. This agrees with the higher water solubility of the acidic components in the crude oils<sup>27</sup>. It is worth pointing out that the water produced with crude oil C showed a lower pH value than the other samples with brines pH 6 and 10, corresponding with a high TAN value for this crude oil. Overall, these results showed that the type of compounds that partitioned into the aqueous phase depended on the initial pH of the brine for all the crude oils. When the pH was low, the solubility of the basic components increased, while the brines with higher pH levels raised the water-solubility of the molecules with acidic groups. The results also resembled a study on the mass transfer between crude oil and water performed by Hutin et al<sup>24</sup>. The authors introduced a model for quantifying the effect of the acidic and basic components partitioning from the oil phase, on the final pH of the aqueous phase. Generally, the results indicated that acidic components were more water-soluble in the tested pH range and were in agreement with the mentioned paper. Even when the TAN values of the crude oils were low (0.5 mg/KOH or less), the final pH of aqueous phase dropped from 10 to 6-7. Similar observations were not made for the TBN values. At the low initial pH only crude oil A had significant partitioning of basic components into the aqueous phase. This crude oil not only had the highest TBN value, but also contained the highest amount of asphaltenes and resins. Furthermore, it had the highest nitrogen content in the asphaltene fraction, which could explain the increase in pH.

As seen in Fig. 6, a marked difference in the oil in water concentration was observed between the produced waters from the light and heavier oils. The water from the heavier crude oils usually contained between 100 and 500 ppm of oil, while the light crude oils gave water with

less than 100 ppm of oil. The increased amount of oil in the produced water from the heaviest crude oils was only seen at high pH when calcium was present. Both of those crude oils had significantly higher TAN, traditionally used as an indicator of the naphthenic acids content. As discussed previously, increased pH causes dissociation of the naphthenic acids and their enhanced interfacial activity. The presence of calcium enabled the formation of complexes, which could accumulate at the oil/water interface and stabilize the system. The relatively high standard deviations in the produced water samples from the heavier oils (A, C) was due to difficulties when sampling the water phase after separation. The viscous crude oils tended to get stuck in the outlet and distorted the oil in water concentration results.

Representative microscopy pictures of selected produced water samples are shown in Figure 7. The produced water sample prepared from the heavy crude oil A (Figure 7A) contained more and larger drops than the sample produced from the light crude oil E (Figure 7B). This also represented the major difference between the produced water samples from the heavy and light crude oils.

The corresponding drop size distributions are shown in Figure 8. The drop size distribution in the synthetic produced water from the crude oil A was broad. Even though the overall number of drops bigger than 10  $\mu\text{m}$  is low (less than 10% of the total number of detected drops), they had a considerable contribution in the volume distribution (ca. 50%). The water samples produced with crude oil E had a narrower size distribution, where the great majority of drops (number-wise, more than 70%) were smaller or equal to 5  $\mu\text{m}$ . Furthermore, the volume contribution of drops larger than 10  $\mu\text{m}$  was negligible. The increased polydispersity in the emulsions, when the viscosity of the dispersed phase was higher, agreed with other reports<sup>20, 46</sup>, even though the measurements were done subsequent to two hours of gravity separation. When the viscosity of the dispersed phase increases, the drop breakage regime may shift from bursting to stretching, which may lead to broadening of the size distribution<sup>46</sup>, observed in this

study. Additionally, the increased content of polar components in the oils A and C could have played a role in the stabilization of larger crude oil droplets in the water phase.

The Sauter mean diameters of the oil drops were generally lowest in the synthetic produced water at low pH and increased with pH, as seen in Figure 9. This trend was less clear for the samples prepared with the NaCa-Brine (Figure S4 in Supporting Information). The average Sauter diameter of drops in the produced water from the heaviest crude oils (A and C) was 20-50% larger than for the samples prepared with the light oils. Higher creaming velocity of drops created with the light crude oils (due to the higher density difference between the dispersed and continuous phases) could have contributed to that difference. Furthermore, as mentioned previously, at higher pH levels naphthenic acids are deprotonated and govern the interfacial activity of the crude oils, resulting in significantly lower values of IFT (Figure S5 in Supporting Information). The less clear trend with NaCa-Brine could be further evidence for the role of calcium in the interfacial film rigidity. Samples with calcium in most samples experienced a drop of the Sauter mean diameter between pH 6 and 10. Moreover, when comparing the Sauter mean diameter values between brines at pH 10, for most of the oils one could notice smaller droplets, when calcium was in the system. Possibly, the accumulation of the hydrophobic complexes of calcium at the oil/water interface negatively influenced the coalescence, resulting in smaller sized drops.

## **Conclusions**

The influence of the properties of crude oils and water composition on the synthetic produced water quality was studied. The quality of the synthetic produced water samples was highly dependent on the composition and the properties of the crude oils. The light crude oils gave higher water quality in terms of the total oil concentration, even though the amount of free water obtained from the samples was significantly lower. Additionally, the initial pH was of importance to the properties of the synthetic produced water. The amount of free water was lowest at low pH and increased with the pH. What is more, the size of the emulsified droplets increased with the initial pH of the brines. The effect of calcium was mostly seen at the highest pH, where it created complexes with dissociated naphthenic acid molecules and stabilized emulsions. The results indicated the complexity of the crude oil emulsions and the severity of the separation issues that may occur during the produced water treatment. The interfacially active components found in the crudes may experience different behavior, e.g. increased water solubility or interfacial rigidity that can affect phenomena such as creaming or coalescence and in the end lead to differences in the quality of the produced water.

### **Acknowledgements**

This work was carried out as a part of SUBPRO, a Research-based Innovation Centre within Subsea Production and Processing. The authors gratefully acknowledge the financial support from SUBPRO, which is financed by the Research Council of Norway, NTNU and major industrial partners (ABB, Aker Solutions, DNV GL, ENGIE, Lundin, Shell and Statoil). We additionally thank ENGIE, Shell and Statoil for providing us with crude oil samples.

## References

1. Fakhru'l-Razi, A.; Pendashteh, A.; Abdullah, L. C.; Biak, D. R.; Madaeni, S. S.; Abidin, Z. Z., Review of technologies for oil and gas produced water treatment. *J Hazard Mater* **2009**, *170* (2-3), 530-51.
2. Igunnu, E. T.; Chen, G. Z., Produced water treatment technologies. *International Journal of Low-Carbon Technologies* **2014**, *9* (3), 157-177.
3. Muggeridge, A.; Cockin, A.; Webb, K.; Frampton, H.; Collins, I.; Moulds, T.; Salino, P., Recovery rates, enhanced oil recovery and technological limits. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences* **2014**, *372* (2006).
4. Paige, R. W., Sweeney, F.M., Produced Water Re-Injection: Understanding the Problems. In *Water Management Offshore Conference*, Aberdeen, 1993.
5. Arthur, J. D.; Langhus, B. G.; Patel, C. *Technical Summary of Oil & Gas Produced Water Treatment Technologies*; ALL Consulting, LLC.: 2005.
6. *Technical Assessment of Produced Water Treatment Technologies*; Colorado School of Mines: Golden, CO, 2009.
7. Rawlins, C. H., Flotation of Fine Oil Droplets in Petroleum Production Circuits. *Recent Advances in Mineral Processing Plant Design* **2009**, 232.
8. Saththasivam, J.; Loganathan, K.; Sarp, S., An overview of oil–water separation using gas flotation systems. *Chemosphere* **2016**, *144*, 671-680.
9. Hansen, B. R.; Davies, S. H., Review of potential technologies for the removal of dissolved components from produced water. *Chemical Engineering Research and Design* **1994**, *72* (A2), 176-188.

10. Dastgheib, S. A.; Knutson, C.; Yang, Y.; Salih, H. H., Treatment of produced water from an oilfield and selected coal mines in the Illinois Basin. *International Journal of Greenhouse Gas Control* **2016**, *54*, Part 2, 513-523.
11. Li, Y. S.; Yan, L.; Xiang, C. B.; Hong, L. J., Treatment of oily wastewater by organic–inorganic composite tubular ultrafiltration (UF) membranes. *Desalination* **2006**, *196* (1), 76-83.
12. Xu, P.; Drewes, J. E., Viability of nanofiltration and ultra-low pressure reverse osmosis membranes for multi-beneficial use of methane produced water. *Separation and Purification Technology* **2006**, *52* (1), 67-76.
13. Piemonte, V.; Prisciandaro, M.; Mascis, L.; Di Paola, L.; Barba, D., Reverse osmosis membranes for treatment of produced water: a process analysis. *Desalination and Water Treatment* **2015**, *55* (3), 565-574.
14. Berdugo-Clavijo, C.; Gieg, L. M., Conversion of crude oil to methane by a microbial consortium enriched from oil reservoir production waters. *Frontiers in Microbiology* **2014**, *5* (197).
15. Veil, J. A.; Puder, M. G.; Elcock, D.; Redweik, R. J., Jr. *A white paper describing produced water from production of crude oil, natural gas, and coal bed methane*; Argonne National Laboratory for the U.S. Department of Energy, National Energy Technology Laboratory: 2004.
16. Dickhout, J. M.; Moreno, J.; Biesheuvel, P. M.; Boels, L.; Lammertink, R. G. H.; de Vos, W. M., Produced water treatment by membranes: A review from a colloidal perspective. *Journal of Colloid and Interface Science* **2017**, *487*, 523-534.

17. Sjöblom, J.; Aske, N.; Harald Auflem, I.; Brandal, Ø.; Erik Havre, T.; Sæther, Ø.; Westvik, A.; Eng Johnsen, E.; Kallevik, H., Our current understanding of water-in-crude oil emulsions.: Recent characterization techniques and high pressure performance. *Advances in Colloid and Interface Science* **2003**, *100–102*, 399-473.
18. Zolfaghari, R.; Fakhru'l-Razi, A.; Abdullah, L. C.; Elnashaie, S. S. E. H.; Pendashteh, A., Demulsification techniques of water-in-oil and oil-in-water emulsions in petroleum industry. *Separation and Purification Technology* **2016**, *170*, 377-407.
19. Gawęł, B.; Lesaint, C.; Bandyopadhyay, S.; Øye, G., Role of Physicochemical and Interfacial Properties on the Binary Coalescence of Crude Oil Drops in Synthetic Produced Water. *Energy & Fuels* **2015**, *29* (2), 512-519.
20. Silset, A.; Flåten, G. R.; Helness, H.; Melin, E.; Øye, G.; Sjöblom, J., A Multivariate Analysis on the Influence of Indigenous Crude Oil Components on the Quality of Produced Water. Comparison Between Bench and Rig Scale Experiments. *Journal of Dispersion Science and Technology* **2010**, *31* (3), 392-408.
21. Poteau, S.; Argillier, J.-F.; Langevin, D.; Pincet, F.; Perez, E., Influence of pH on Stability and Dynamic Properties of Asphaltenes and Other Amphiphilic Molecules at the Oil–Water Interface†. *Energy & Fuels* **2005**, *19* (4), 1337-1341.
22. Faksness, L.-G.; Grini, P. G.; Daling, P. S., Partitioning of semi-soluble organic compounds between the water phase and oil droplets in produced water. *Marine Pollution Bulletin* **2004**, *48* (7–8), 731-742.
23. Stanford, L. A.; Kim, S.; Klein, G. C.; Smith, D. F.; Rodgers, R. P.; Marshall, A. G., Identification of Water-Soluble Heavy Crude Oil Organic-Acids, Bases, and Neutrals by Electrospray Ionization and Field Desorption Ionization Fourier Transform Ion Cyclotron

Resonance Mass Spectrometry. *Environmental Science & Technology* **2007**, *41* (8), 2696-2702.

24. Hutin, A.; Argillier, J.-F.; Langevin, D., Mass Transfer between Crude Oil and Water. Part 1: Effect of Oil Components. *Energy & Fuels* **2014**, *28* (12), 7331-7336.

25. Eftekhardakhah, M.; Øye, G., Induction and Coverage Times for Crude Oil Droplets Spreading on Air Bubbles. *Environmental Science & Technology* **2013**, *47* (24), 14154-14160.

26. Eftekhardakhah, M.; Aanesen, S. V.; Rabe, K.; Øye, G., Oil Removal from Produced Water during Laboratory- and Pilot-Scale Gas Flotation: The Influence of Interfacial Adsorption and Induction Times. *Energy & Fuels* **2015**, *29* (11), 7734-7740.

27. Havre, T. E.; Sjöblom, J.; Vindstad, J. E., Oil/Water-Partitioning and Interfacial Behavior of Naphthenic Acids. *Journal of Dispersion Science and Technology* **2003**, *24* (6), 789-801.

28. Hutin, A.; Argillier, J.-F.; Langevin, D., Influence of pH on Oil-Water Interfacial Tension and Mass Transfer for Asphaltenes Model Oils. Comparison with Crude Oil Behavior. *Oil Gas Sci. Technol. – Rev. IFP Energies nouvelles* **2016**, *71* (4), 58.

29. Nour, A. H., Yunus R. M., Stability Investigation of Water-in-Crude Oil Emulsion. *Journal of Applied Sciences* **2006**, *6* (14), 6.

30. Brandal, Ø.; Hanneseth, A. M. D.; Hemmingsen, P. V.; Sjöblom, J.; Kim, S.; Rodgers, R. P.; Marshall, A. G., Isolation and Characterization of Naphthenic Acids from a Metal Naphthenate Deposit: Molecular Properties at Oil-Water and Air-Water Interfaces. *Journal of Dispersion Science and Technology* **2006**, *27* (3), 295-305.

31. ASTM D664-95 Standard Test Method for Acid Number of Petroleum Products by Potentiometric Titration. ASTM International: West Conshohocken, PA, 2001.
32. Dubey, S. T.; Doe, P. H., Base Number and Wetting Properties of Crude Oils. **1993**.
33. Gawęł, B.; Eftekhardakhah, M.; Øye, G., Elemental Composition and Fourier Transform Infrared Spectroscopy Analysis of Crude Oils and Their Fractions. *Energy & Fuels* **2014**, *28* (2), 997-1003.
34. Hannisdal, A.; Hemmingsen, P. V.; Sjöblom, J., Group-Type Analysis of Heavy Crude Oils Using Vibrational Spectroscopy in Combination with Multivariate Analysis. *Industrial & Engineering Chemistry Research* **2005**, *44* (5), 1349-1357.
35. *Produced Water: Technological/Environmental Issues and Solutions*. Springer US: 1992; Vol. 46, p 632.
36. Tichelkamp, T.; Teigen, E.; Nourani, M.; Øye, G., Systematic study of the effect of electrolyte composition on interfacial tensions between surfactant solutions and crude oils. *Chemical Engineering Science* **2015**, *132*, 244-249.
37. Farooq, U.; Simon, S.; Tweheyo, M. T.; Øye, G.; Sjöblom, J., Interfacial Tension Measurements Between Oil Fractions of a Crude Oil and Aqueous Solutions with Different Ionic Composition and pH. *Journal of Dispersion Science and Technology* **2013**, *34* (5), 701-708.
38. Langevin, D.; Argillier, J.-F., Interfacial behavior of asphaltenes. *Advances in Colloid and Interface Science* **2016**, *233*, 83-93.

39. Eftekhardadkhah, M.; Øye, G., Correlations between crude oil composition and produced water quality: A multivariate analysis approach. *Industrial and Engineering Chemistry Research* **2013**, *52* (48), 17315-17321.
40. Spiecker, P. M.; Gawrys, K. L.; Kilpatrick, P. K., Aggregation and solubility behavior of asphaltenes and their subfractions. *Journal of Colloid and Interface Science* **2003**, *267* (1), 178-193.
41. Stockwell, A.; Taylor, A. S.; Thompson, D. G., The Rheological Properties of Water-in-Crude-Oil Emulsions. In *Surfactants in Solution: Volume 6*, Mittal, K. L.; Bothorel, P., Eds. Springer US: Boston, MA, 1986; pp 1617-1632.
42. Arla, D.; Flesinski, L.; Bouriat, P.; Dicharry, C., Influence of Alkaline pH on the Rheology of Water/Acidic Crude Oil Interface. *Energy & Fuels* **2011**, *25* (3), 1118-1126.
43. Brandal, Ø.; Sjöblom, J., Interfacial Behavior of Naphthenic Acids and Multivalent Cations in Systems with Oil and Water. II: Formation and Stability of Metal Naphthenate Films at Oil-Water Interfaces. *Journal of Dispersion Science and Technology* **2005**, *26* (1), 53-58.
44. Clark, P. E.; Pilehvari, A., Characterization of crude oil-in-water emulsions. *Journal of Petroleum Science and Engineering* **1993**, *9* (3), 165-181.
45. Eftekhardadkhah, M.; Kløcker, K. N.; Trapnes, H. H.; Gaweł, B.; Øye, G., Composition and Dynamic Adsorption of Crude Oil Components Dissolved in Synthetic Produced Water at Different pH Values. *Industrial & Engineering Chemistry Research* **2016**, *55* (11), 3084-3090.
46. Calabrese, R. V.; Chang, T. P. K.; Dang, P. T., Drop breakup in turbulent stirred-tank contactors. Part I: Effect of dispersed-phase viscosity. *AIChE Journal* **1986**, *32* (4), 657-666.

## Legend of Tables and Figures

Table 1: Physicochemical properties and composition of crude oils

Table 2: The amount of recovered water after mixing crude oils and brines at pH 10.

Figure 1: C/H atomic ratio of the crude oils and their fractions.

Figure 2: Nitrogen (A), oxygen (B) and sulphur (C) content in complete crude oils and SARA fractions.

Figure 3: The percentage of free water 2 hours after mixing the crude oils with Na-Brine at various pH.

Figure 4: Total organic carbon content for water samples produced with different crude oils (NaCa-Brine).

Figure 5: pH of the synthetic produced water prepared using Na-Brine. The dotted lines indicate the initial pH of the brine.

Figure 6: Total oil concentration in the synthetic produced water samples prepared using NaCa-Brine.

Figure 7: Pictures of dispersed droplets in water of crude oil A (left) and crude oil E (right) in Na-Brine at pH6.

Figure 8: Number (left) and volume (right) size distributions of oil drops for crude A and E in Na-Brine (pH 6).

Figure 9: The Sauter mean diameters in the synthetic produced water samples prepared from the Na-Brine.

TABLES

Table 1: Physicochemical properties and composition of crude oils

Crude oil		A	B	C	D	E
API gravity [°]		19.2	35.8	23.0	36.3	37.9
Density at 20°C [g/cm <sup>3</sup> ]		0.935	0.841	0.911	0.839	0.831
Viscosity at 20°C [mPa*s]		354.4	14.2	74.4	10.3	8.3
TAN [mg KOH/g oil]		2.2	<0.1	2.7	0.2	0.5
TBN [mg KOH/g oil]		2.8	1.0	1.1	1.1	0.4
SARA	Saturates [% (w/w)]	50.6	84.0	64.9	71.5	74.8
	Aromatics [% (w/w)]	31.2	13.4	26.3	23.1	23.2
	Resins [% (w/w)]	15.7	2.3	8.4	5.1	1.9
	Asphaltenes [% (w/w)]	2.5	0.3	0.4	0.3	0.1
Water content [ppm]		590.9	85.4	535.8	202.4	333.4
IFT [mN/m]	Na-Brine (pH 6)	20.4 ±0.6	20.5 ±0.2	22.2 ±0.6	19.0 ±0.5	19.9 ±0.1
	NaCa-Brine (pH 6)	18.6 ±0.8	19.9 ±0.2	18.9 ±0.7	16.2 ±0.4	17.4 ±0.4

Table 2: The amount of recovered water after mixing crude oils and brines at pH 10.

		Recovered water [%]				
		A	B	C	D	E
Brine	Na	83.3% ±4.7%	70.0% ±0%	66.7% ±4.7%	56.7% ±9.4%	70.0% ±16.3%
	NaCa	76.7% ±4.7%	56.7% ±17%	43.3% ±4.7%	46.7% ±9.4%	46.7% ±12.5%

## FIGURES

Figure 1: C/H atomic ratio of the crude oils and their fractions.

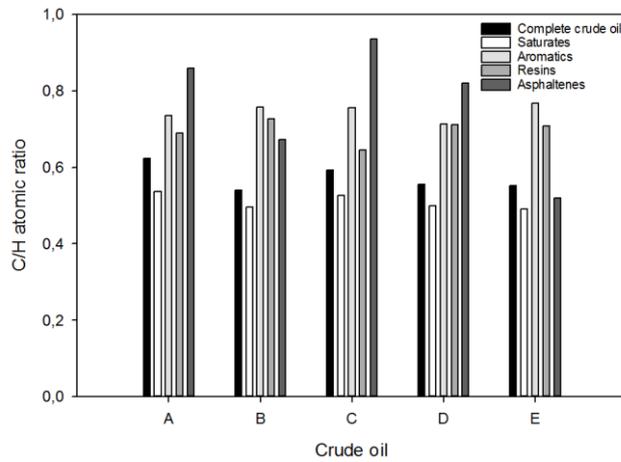


Figure 2: Nitrogen (A), oxygen (B) and sulphur (C) content in complete crude oils and SARA fractions.

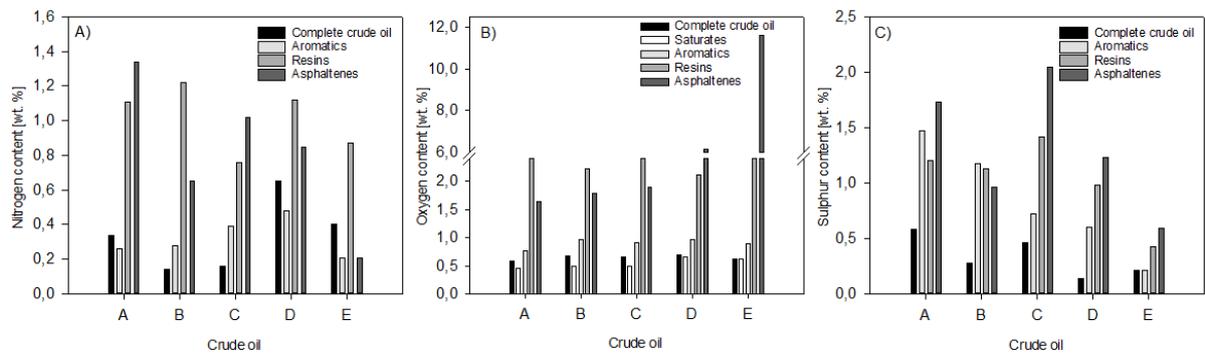


Figure 3: The percentage of free water 2 hours after mixing the crude oils with Na-Brine at various pH.

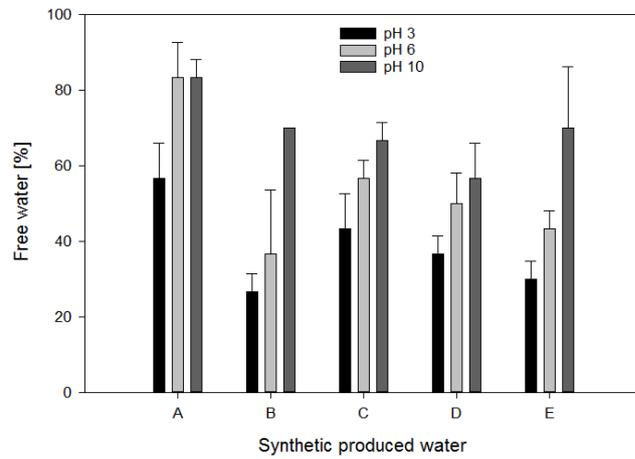


Figure 4: Total organic carbon content for water samples produced with different crude oils (NaCa-Brine).

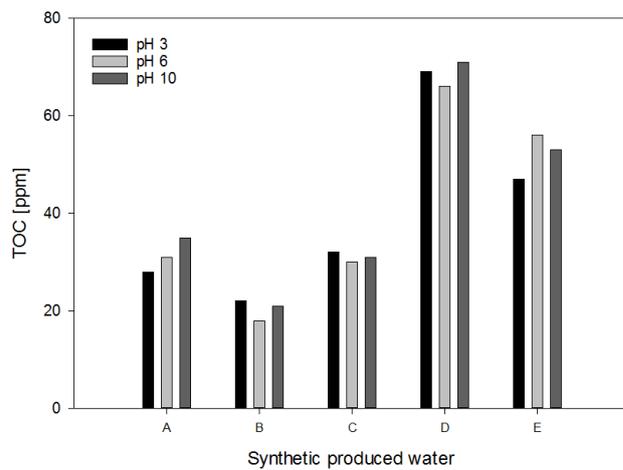


Figure 5 pH of the synthetic produced water prepared using Na-Brine. The dotted lines indicate the initial pH of the brine.

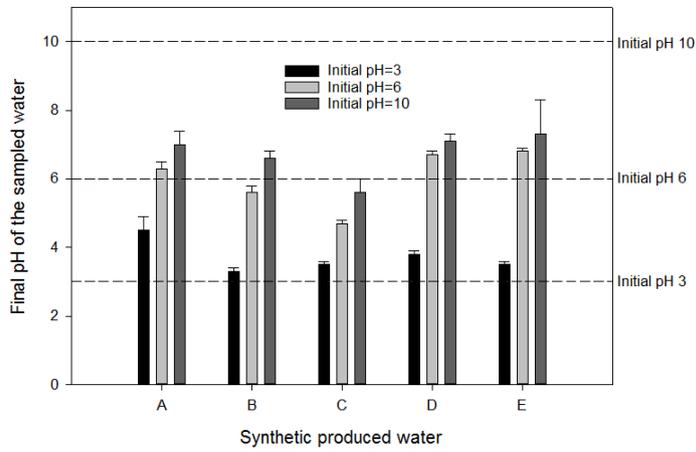


Figure 6 Total oil concentration in the synthetic produced water samples prepared using NaCa-Brine.

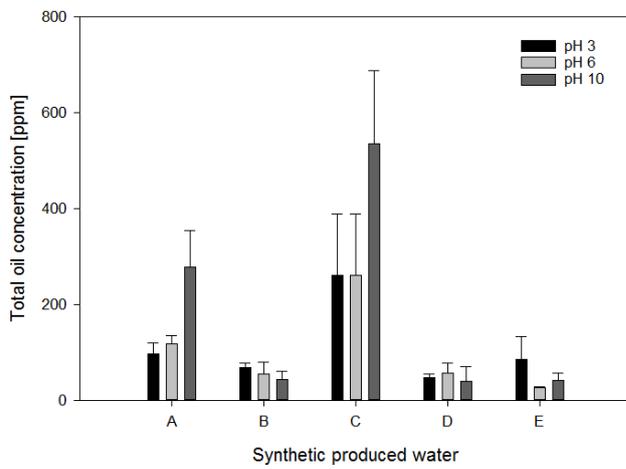


Figure 7 Pictures of dispersed droplets in water of crude oil A (left) and crude oil E (right) in Na-Brine at pH6.

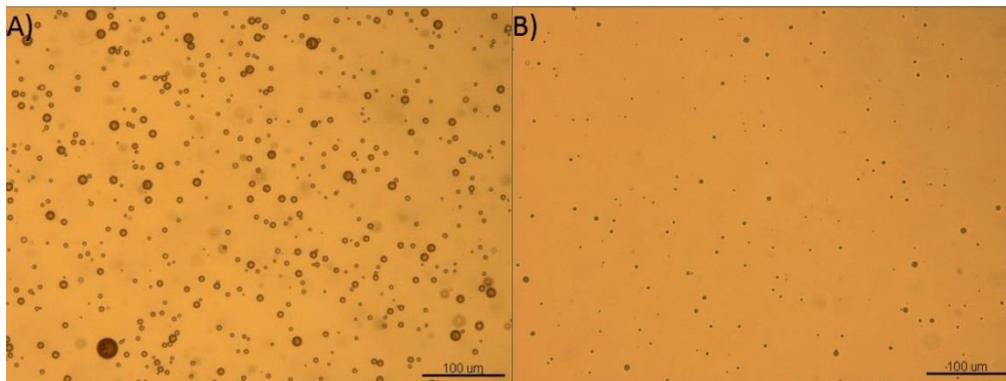


Figure 8 Number (left) and volume (right) size distributions of oil drops for crude A and E in Na-Brine (pH 6).

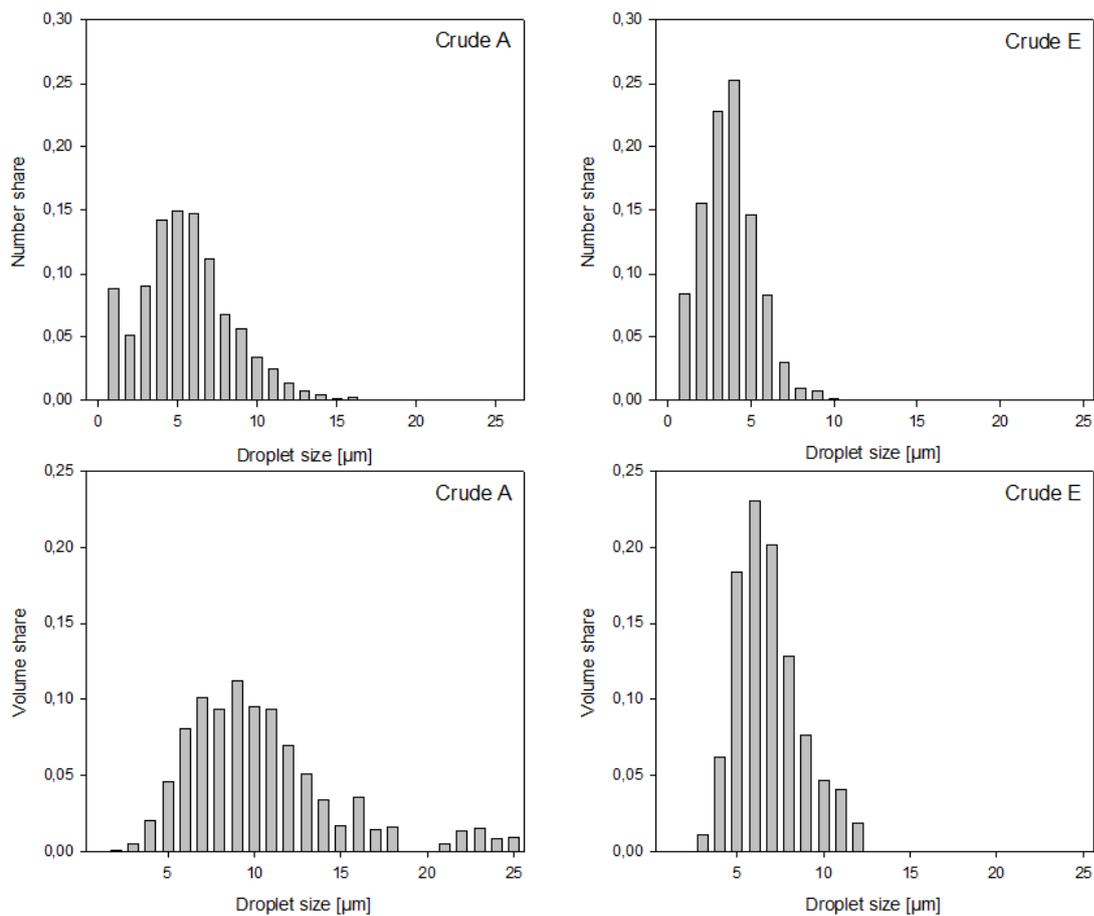
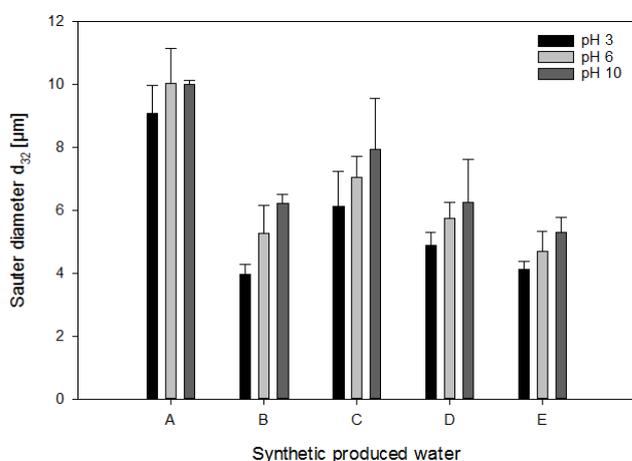


Figure 9 The Sauter mean diameters in the synthetic produced water samples prepared from the Na-Brine.



#### AUTHOR INFORMATION

**Corresponding author:** Telephone: +47 735 94 135. E-mail: [gisle.oye@ntnu.no](mailto:gisle.oye@ntnu.no)

#### ASSOCIATED CONTENT

Figure S1: Dynamic interfacial tension between crude oil A and B, and Brine-Na at pH 6.

Figure S2 The percentage of free water 2 hours after mixing the crude oils with NaCa-Brine at various pH.

Figure S3 Total organic carbon content for water samples produced with different crude oils (NaCa-Brine).

Figure S4 The Sauter mean diameters in the synthetic produced water samples prepared from the NaCa-Brine.

Figure S5 Interfacial tensions of crude oils in Na-Brine (left) and NaCa-Brine (right).