Colloid chemistry and experimental techniques for understanding fundamental behaviour of produced water in oil and gas production

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Abstract:

Due to increasing volumes of produced water and environmental concerns related to its discharge, water treatment has become a major challenge during the production of crude oil and natural gas. With continuously stricter regulations for discharging produced water to sea, the operators are obliged to look for ways to improve the treatment processes or re-use the water in a beneficial way, for example as a pressure support during oil recovery (produced water re-injection). To improve the knowledge of the underlying phenomena governing separation processes, detailed information of the composition and interfacial properties of produced water is undoubtedly useful and could provide valuable input for better understanding and improving separation models. This review article summarizes knowledge gained about produced water composition and the most common treatment technologies, which are later used to describe the fundamental phenomena occurring during separation. These colloidal interactions, such as coalescence of oil droplets, bubble-droplet attachment or partitioning of components between oil and water, are of crucial importance for the performance of various technologies and are sometimes overlooked in physical considerations of produced water treatment. The last part of the review deals with the experimental methodologies that are available to study these phenomena, provide data for models and support development of more efficient separation processes.

Contents

1. Introduction

Produced water (PW) is a natural by-product from oil and gas production. The composition of PW changes over the production life of the field and is highly dependent on the location and age of the reservoir, together with the water injection history. Composition can also be affected by various processes taking place in the reservoir, such as chemical (scaling), physical (sedimentation, biofilm attachment) or microbial (reservoir souring, degradation of organics and formation of biomass). Water injection is nowadays a normal process for increasing recovery of hydrocarbons and extending the lifetime of oilfields, where water is injected to increase pressure and improve the oil recovery. PW is therefore often a mix of formation and injection water, which is extracted from the reservoirs together with the hydrocarbons. Seawater and treated produced water are the normal sources for injection water offshore, while injection water onshore can be freshwater (groundwater, surface water) or seawater. The composition is complex, containing both dispersed and dissolved components of organic and inorganic nature, as well as microorganisms from the source. Some are indigenous components (hydrocarbon- and reservoir-related) and others are added chemicals needed in the production (scale- and corrosion inhibitors, emulsion breakers, sulphide scavengers etc.) or necessary for improving water treatment (flocculants).

The amount of produced water required to be treated keeps going up. In 1990, the production of crude oil and water was approx. 65 and 190 million barrels per day, respectively. Almost 30 years later, the daily worldwide production of oil has increased to more than 80 million barrels, whereas the water production has gone up to almost 320 million barrels per day. This means that the often-cited number of 3 barrels of water produced per barrel of oil [1] is nowadays probably closer to 4 to 1. During the 50 years history of oil and gas production at the Norwegian Continental Shelf (NCS), oil production reached the peak already after 25 years (1995: 180 million m^3 of oil and 90 million m^3 of PW). In 2018, the oil production was ca. 90 million m^3, whereas water production was close to 180 million m^3. This is supported by the data in Figure 1, where a typical production profile for an oilfield at the NCS is presented. During the first couple of years, the production of oil and water is relatively stable, and the water cut (percentage of water in the total produced fluid volume) is low. Later, the oil recovery steadily declines, whereas the amount of water increases. Within 10 years or so, the production of water is already higher than the volume of produced hydrocarbons. Although

93 the water production eventually starts to decrease, the water cut keeps increasing, as

94 indicated by the black line in Figure 1. Before decommissioning, the water cut can become as

95 high as 95% [2].

96 Produced water is typically either re-injected, disposed into a waste well or discharged. The

97 water must be treated to an acceptable quality prior to disposal. The continuously increasing

98 water cut requires increased water treatment capacity. This can therefore become a

99 bottleneck for prolonging the production. At the same time, the required treated water

100 quality must meet stricter environmental regulations and reservoir requirements. Currently,

101 the removal of dispersed oil is the primary objective during most of the produced water

102 treatment processes, as the discharge limits are based on the concentration of dispersed oil

103 [1]. Local and international regulations bind the oil producers to decrease the potential

104 damage to the marine environment by limiting the discharge of harmful components (Figure

105 2). At the NCS and other regions covered by OSPAR (Oslo-Paris Convention or the Convention

106 for the Protection of the Marine Environment of the North-East Atlantic), discharge limit for

107 oil is set to 30 ppm [3], but European operators are experiencing a push towards an emission

108 production limit of 15 mg/l on existing installations and zero discharge on new facilities [4].

109 New standards for monitoring dispersed oil in water has reduced the amount of oil

110 components included in the monitoring method, and good performance of PW treatment

111 offshore has given authorities confidence that the operators can meet such stringent

112 emission limits.

113 Environmental Risk Assessment, applied at the NCS for many years and recently implemented

114 in OSPAR, introduced the Environmental Impact Factor (EIF). EIF changes the focus from

115 dispersed components (hydrocarbons and reservoir related) to dissolved compounds.

116 Production chemicals in produced water are also receiving more attention. The concentration

117 and composition of dissolved components will depend on a number of factors, including

118 produced water volume, type of produced oil, maturity of the field and process conditions

119 (temperature, water pH, pressure) [5]. The growing awareness about the environmental

120 impact of the produced water makes it necessary for the operators to perform more in-depth

121 analyses of the produced water composition, leading to better understanding of its chemistry.

122 Currently produced water is mostly discharged to the sea or evaporation ponds and is treated

123 as a waste product. This way of dealing with produced water accounts for 40% of the total

124   PW volume [1]. At the Norwegian Continental Shelf, more than 75% of the water produced is
125   also discharged to the sea [6]. Nowadays, oil producers try to find other, more beneficial ways
126   of dealing with this by-product. In offshore production, this typically means re-injecting
127   produced water to reservoirs for production support, or to disposal formations to avoid
128   contamination. Previously, only seawater was used for pressure support in the secondary
129   recovery stage, but currently more oil producers consider re-injection of PW instead, both for
130   environmental and economic reasons [7]. In contrast to seawater, produced water contains
131   low amounts of sulphates, which decreases the activity of sulphate reducing bacteria (SRB)
132   and reduces the risk of reservoir souring through H_2S production. A major limitation for
133   implementing produced water re-injection, however, is often the risk of uncontrolled
134   injectivity decline. The presence of particles (both oil and solids, including scale particles and
135   biomass from pipelines, tubing and vessels – Figure 3) is the main cause for this, and their
136   removal before re-injection is desirable. Re-injection of PW is often considered to be the
137   preferable solution for new field developments as well as for mature fields upon
138   implementation of chemical enhanced oil recovery methods. It is also likely to be the
139   preferred way of handling water in subsea production and processing facilities.

140   The increasing amounts of water to be treated and the need for cleaner water must lead to a
141   more holistic approach where oil recovery, produced water treatment and reservoir
142   management become more integrated. In order to achieve this, better fundamental
143   understanding of how the fluids behave in the reservoir and in the various production and
144   processing stages is essential. In this review, we will focus on how microscopic phenomena,
145   such as breakage and coalescence of droplets, flocculation and attachment of droplets to
146   bubbles can influence various produced water treatment processes. Fundamental
147   understanding of such phenomena is an important, but sometimes overlooked part of
148   improving and optimizing produced water treatment. Better knowledge about interactions
149   between dispersed droplets, solids and bubbles, and how interfacial properties can affect
150   these, can provide better descriptions of the processes. Subsequently, this can make
151   separation models more accurate and improve the description and prediction of actual
152   treatment processes, including better understanding of the partitioning of chemicals between
153   oil, gas and water phases in the PW treatment train.

Produced water, its composition and treatment methods had been reviewed by other authors [1, 5, 8-10]. Some colloidal aspects of produced water were also discussed in the review paper by Dickhout et al., however in connection with membrane treatment [11]. Research tools relevant to colloidal systems in oil-continuous systems were summarized by Sjöblom et al. [12, 13], while Kamp et al. reviewed experimental and modelling approaches for studying drop coalescence [14]. Therefore, the aim of this review article is twofold: (1) describe how large-scale produced water treatment processes are linked to microscopic dispersions and interfacial phenomena, and (2) provide an overview of experimental methods that can be used to study fundamental aspects of produced water. In the first two parts, an overview of the vital steps in petroleum production and processing, and the composition and treatment methods for produced water are given. The colloid chemistry of produced water is described in part 4, while an overview of analytical methods is outlined in the last part.

2. Petroleum production and processing

Crude oil is created from sedimented and decomposed organic matter trapped under thick layers of rock over hundreds of millions of years [15]. The high pressure and temperature conditions allowed the long-term thermal reactions, catalysed by clay particles, to convert incompletely decayed plankton, plants and animal remains into petroleum. Typically, crude oil is composed of predominantly saturated, but also non-saturated, cyclic and aromatic hydrocarbons. More complex molecules also contain heteroatoms such as nitrogen, oxygen and sulphur, and to lesser extent also metals, e.g. nickel, vanadium or copper [16]. Crude oil can be found in underground reservoirs both onshore and offshore. The composition and properties of petroleum highly depend on the biological origin of crude oil, the geological formation (thermal conditions, reservoir rock type), its age and exposure to microorganisms. Crude oils are often characterized in terms of the SARA fractions, meaning the weight percentages of **s**aturates, **a**romatics, **r**esins and **a**sphaltenes. This classification is based on the polarity of the first three fractions, also called maltenes, and the (in)solubility of asphaltenes in aliphatic solvents. Saturates and aromatics have less complex structure and are considered the most valuable products of petroleum. The two most polar groups, resins and asphaltenes, consist of molecules that can adsorb at various interfaces, therefore can be considered surface-active. This may result in flow assurance and separation problems like stable emulsions or asphaltene aggregation and deposition. The acidic or basic nature of

185 crude oils can also be characterized by total acid number (TAN) and total base number (TBN).
186 It should also be pointed out that the composition of the crude oil greatly influences both its
187 physicochemical and interfacial properties, as well as the quality of the produced water [17].

188 Produced water is any water co-produced with petroleum and is often a mix of water from
189 different sources [18], adding to its complexity. The main source is the formation water, which
190 the geological formation was saturated with before the hydrocarbons migrated there.
191 Another source is the water injected to aid the recovery process, i.e. freshwater, seawater or
192 treated produced water. Typically, the salinity of produced water varies between the
193 seawater salt concentration and almost completely saturated brine (30-35% wt.). The ionic
194 composition of produced water is often unique for a given field and is modified during the
195 production cycle. It also contains a range of dissolved and dispersed organic and inorganic
196 components that can influence the petroleum production process (detailed description is
197 given later).

198 During petroleum production, the high pressure of the formation initially sustains a steady
199 flow of hydrocarbons without additional energy input. Up to 15% of the hydrocarbons
200 originally in place can be retrieved during this primary recovery. After expansion of gas and
201 subsequent reduction of pressure in the reservoir, the formation will require additional
202 support to maintain production. Then, injection of additional fluid is needed for a pressure
203 boost in the formation, which marks the beginning of the secondary recovery stage. The water
204 injected into the reservoir can either be treated produced water or raw/purified seawater. At
205 the Norwegian Continental Shelf, this secondary process can recover up to 50-60% of all
206 hydrocarbons in the formation. Still, slightly less than half of the oil remains, predominantly
207 trapped by capillary forces in small, micron-sized pores. This is when the enhanced oil
208 recovery (EOR or tertiary recovery) often are utilized. These methods can be categorized into
209 gas (foam) injection, chemical injection or thermal displacement.

210 ## 2.1. Offshore crude oil and natural gas production

211 The example below describes a typical offshore production process of petroleum at the NCS,
212 either on a platform or on a FPSO (Floating Production, Storage and Offloading) unit, which is
213 a ship designed for both production and transportation of crude oil and natural gas. In an

offshore facility, several oil wells are usually connected to a production manifold, from which the fluids flow topside for further processing (Figure 4).

Initially, the fluids enter a gravity separator, where three-phase separation (gas, oil and water) takes place. Due to the turbulent flow, significant pressure drops (e.g. in chokes or manifolds) and the presence of resins and asphaltenes, foams and emulsions (oil- and water-continuous) may be formed. These can negatively impact the separation. Most of the free gas is removed during the three-phase separation. The gas phase typically contains some water, acid gases (H_2S and CO_2) and longer hydrocarbons (>C_4), and must be processed before compression and export. The oil and water are separated by sedimentation and creaming of the dispersed phases. Larger solid particles also settle in the gravity separator, whereas fine solids will follow the fluid streams. After initial separation, crude oil is treated in a second-stage and sometimes third-stage separator, where the oil usually reaches export quality (<0.5% of water in oil). Finally, the produced water undergoes treatment in order to reach discharge or re-injection quality. This will be described in section 3.2.

2.2. Subsea production and processing

The oil reserves in easily accessible locations are slowly running out. To meet the demand for petroleum products, the oil producers are developing production facilities in less accessible reservoirs. Typically, this entails reservoirs far from the existing infrastructure and/or located in deep waters (>2000 m). Furthermore, the conditions in such locations are usually more extreme, which increases the health and environmental concerns of the operations. Examples include oil and gas fields in the Barents Sea or deep-water oil supplies in the Gulf of Mexico and off the coast of Brazil. Subsea production can aid in development of such fields. In addition, it can increase the recovery from mature fields with already existing infrastructure (so-called brown fields) with high water cuts [19].

The idea behind subsea separation is to move as much of the crude oil, natural gas and produced water treatment facilities to the sea floor to de-bottleneck production capacity or even completely remove the need for manned production platforms. Many of the existing and planned subsea separators focus on the removal of free water from the fluid stream to increase the production rate of hydrocarbons that can later be processed topside. There are several additional requirements regarding subsea processing, compared to standard topside

equipment. Commonly, subsea systems are divided into modules for easier installation, replacement and decommissioning. For this reason, the units should be compact. The fluid behaviour in high pressure and temperature conditions might also be quite different, which creates the need for additional research in the fundamental aspects of production and separation. Nonetheless, the benefits of subsea separation may outweigh the additional process requirements. The proximity to the well can reduce the wellhead pressure and help stabilize the flow of the produced fluids. In addition, higher pressure and temperature of the production stream will result in lower viscosity, higher density difference, and less problems with asphaltene or wax precipitation, all of which should enhance the separation. Regarding water treatment, partial or complete removal of water at the seabed offers more compact topside facilities, reduced use of chemicals and decreased backpressure on the reservoir [20]. Higher pressure during treatment will also keep the CO_2 in the water phase, preventing the increase of pH and subsequent adsorption of acids to interfaces or even partitioning into the water phase [21]. This should decrease scaling and corrosion problems of the water lines and reduce the amount of dissolved components in the produced water. Subsea-treated produced water will also require less pumping energy for re-injection. All in all, the idea of a complete subsea factory, envisioned by several oil producers, should lead to reduced CAPEX, increased hydrocarbon recovery and reduced environmental footprint.

Operators have already gained field experience through a number of subsea installations, for example: bulk separation of gas, oil and water (Equinor's Troll Pilot and Tordis SSBI at the Norwegian Continental Shelf), gas-liquid separation (Petrobras' Marlim Field in Brazil, Total's Pazflor in Angola, Equinor's Åsgard Field in Norway), and desanders and hydrocyclones in Petrobras' Marlim Field (Brazil). Qualification of other types of separators, mostly focused on the treatment of produced water (flotation units, settling tanks, biological treatment), is under way.

3. Produced water

The composition of produced water is complex and varies from field to field. Some general properties of produced water and a comparison to seawater are given in Table 1. The major constituents of produced water are typically divided into the following categories : dissolved inorganic and organic compounds, dispersed hydrocarbons, dissolved gases, production chemicals and suspended solids.

275 In the next section, an overview of the dispersed and dissolved components in produced

276 water is given. Subsequently, several established produced water treatment methods are

277 described.

278   3.1.   Composition of produced water

279   3.1.1. Dispersed oil

280 Crude oil becomes dispersed in produced water as micron-sized droplets as a result of shear

281 forces, which induce mixing between oil and water. This typically occurs across the choke,

282 valves, in pipelines etc. Most PW treatment methods rely on gravity separation, and therefore

283 the size distribution of oil drops is important. Large oil droplets (>100 μm) will be removed in

284 the gravity separator, while hydrocyclones or gas flotation units aim at removing smaller

285 droplets. Notably, most produced water treatment processes are currently only targeting

286 removal of dispersed oil.

287   3.1.2. Dissolved organics

288 Some crude oil components have partitioned into the formation water in the reservoir, while

289 some become water-soluble during the production process. The concentration and

290 composition of dissolved components in produced water will depend on numerous factors,

291 including produced water volume, type of oil produced, maturity of the field, water cut and

292 process conditions (temperature, water pH, pressure) [5]. Several papers reported the

293 complexity of the dissolved organics found in produced water [22, 23]. Figure 5 illustrates the

294 ratio of different organic species in the PW samples from the Norwegian Continental Shelf

295 [6].

296 Most of the dissolved organic components are polar. Organic acids are typically much more

297 water-soluble than other constituents of crude oil. In addition, the presence of inorganic salts

298 causes the salting-out effect, which can decrease the solubility of pure hydrocarbons,

299 compared to the polar ones [24]. The acids present in PW are mostly short-chained, with 1 to

300 5 carbons in their chain, meaning they will be fully water-soluble regardless of the conditions.

301 Longer acids are in the literature often termed as naphthenic acids, although this description

302 is not accurate [25]. Per definition, naphthenic acids should contain a naphthene ring,

303 however in practice all organic acids found in crude oil (or all acids with more than 5 carbons)

304 are included in that category. The water solubility of these acids will heavily depend on the

pH, temperature and salinity of the water phase [26]. Certain production chemicals, such as scale inhibitors or de-oilers can also contribute to the presence of organic acids [27], but the indigenous acidic species are predominant in the dissolved organic matter of produced water [8, 27].

Out of all the dissolved organics in produced water, the low molecular weight aromatic components such as benzene, toluene, ethyl benzene and xylenes (BTEX), polycyclic aromatic hydrocarbons (PAH), other heterocyclic aromatic species and phenols are considered the most toxic [28]. PAHs are also slowly biodegradable and have high affinity to oil and fat, which results in increased removal in efficient oil/water separation systems, but also increased bioaccumulation, and acute and chronic effects on the marine organisms if discharged. The most abundant type of organics of the dissolved organic components, the short acids (or volatile fatty acids - VFA), are usually relatively harmless as they are readily biodegradable by the microorganisms in the seawater [29]. They can, however, contribute to the corrosion of the process equipment [30] and lead to increased biofilm formation in the process equipment [31]. The naphthenic acids in the water phase, which are of more environmental concern, are characteristic for process waters from the production of bitumen from oil sands [32, 33], where the water phase is recycled, leading to continuous increase of concentration of these acidic species if not treated. However, a growing number of conventional oilfields are also found to be acidic in nature. This means that the presence of naphthenic acids in the discharge waters will soon become of equal importance as other dissolved organic material. BTEXs are quite volatile and typically evaporate from water rather quickly [34], although this is affected by the water temperature. In addition, some metals like cadmium, cobalt, copper, lead, mercury and nickel, or naturally occurring radioactive materials (e.g. ^{226}Ra and ^{228}Ra) can also increase the toxicity of produced water [5]. Lastly, some of the chemicals added during crude oil production can also end up in the discharged water stream and contribute to the harmful consequences on the marine environment [35]. It should be noted, however, that the acute toxic effects can occur only in the direct vicinity of the discharge pipes and when the dilution is less than 100-fold, as shown both by direct measurements and dispersion modelling [36, 37]. In addition, the discharge of produced water has not been linked to any irreversible or significant negative ecological effects on the marine environment [38]. The reader is kindly

335 referred to other sources for a comprehensive description of the studies on toxicity and
336 impact of dissolved species in produced water, for example [28, 36, 39, 40].

3.1.3. Solid particles

338 The solid particles dispersed in produced water come from different sources, for example
339 formation solids, inorganic scale, gas hydrates and microorganisms (dead or alive) [9]. Their
340 concentration is often expressed as the total suspended solids (TSS). The solids can contribute
341 to the stabilization of emulsions [41] or flow assurance problems [42]. The partitioning of
342 particles between the water stream, oil stream and oil-water interface will depend on their
343 wettability, size and density. The number of particles can be controlled to some extent with
344 production chemicals (wax, scale, hydrates, corrosion inhibitors, flocculants) or adequate
345 treatment of the injection water to reduce bacteria growth or scale formation.

3.1.4. Dissolved minerals

347 The location and type of the reservoir will largely determine the salinity and composition of
348 the formation water. Table 2 provides an overview of different ions typically found in the
349 North Sea produced water, in comparison to seawater.

350 Produced water also contains heavy metals (zinc, lead, copper, cadmium) and sometimes
351 even naturally occurring radioactive materials [9], but their concentration should not exceed
352 tens of ppm. The information about the ionic composition of the brine is vital for process and
353 environmental reasons. The presence of certain cations and anions can lead to inorganic scale
354 formation in production equipment or in the reservoir. On the other hand, produced water
355 can contain harmful levels of heavy metals or naturally-occurring radioactive materials, which
356 adds to the toxicity of the discharged fluids [36].

357

358

3.1.5. Production chemicals

360 During crude oil production, various additives are injected to maintain, aid and secure the
361 integrity of the production process and facilities. These production chemicals can be divided
362 into four groups [43]: (1) inhibitors against fouling and deposition; (2) chemicals to improve

363 separation (3) corrosion inhibitors to maintain process integrity and (4) chemicals added for
364 other purposes, for example environmental reasons or increased oil recovery. The type and
365 concentration of the additives varies from field to field. Depending on the application,
366 production chemicals can be oil- or water-soluble, and in some cases both. The production
367 chemicals that can be found in produced water include corrosion, hydrate and scale
368 inhibitors, H_2S and O_2 scavengers, and flocculants. Their concentration typically does not
369 exceed tens of ppm, but in some cases (e.g. gas hydrate inhibitors) it can be quite substantial
370 with concentrations over 1 g/L [8]. At the Norwegian Continental Shelf, operators are
371 encouraged to use chemicals from "green" or "yellow" list, which classifies them as having no
372 or minor effect on the natural environment [44].

373 Production chemicals discharged with produced water, similarly to the other dissolved
374 components, may have local effects close to the discharge points, and their disposal is
375 regulated at the national level. These include all additives used during drilling and production
376 operations. Discharges of chemicals are largely related to drilling activities. In 2016, almost
377 70% of the discharged chemicals originated from drilling operations at NCS [6]. Chemicals that
378 are not discharged, are deposited below the seabed or transported onshore and treated as
379 hazardous waste. Norway established a zero-discharge target for hazardous substances
380 released as a result of petroleum activities in 1997, which, according to the Norwegian
381 Environmental Agency was achieved in 2010, but the regulations are getting stricter and new
382 targets are being defined [45] together with the OSPAR.

383 ### 3.1.6. Dissolved gases
384 Produced water can contain dissolved gases, like volatile hydrocarbons, CO_2, O_2 and H_2S. Their
385 concentration highly depends on the process conditions (pressure, temperature) and is rather
386 insignificant during the topside PW treatments conducted at low pressure. If, however, the
387 separation is to be performed at higher pressures (e.g. subsea), the dissolved gases can cause
388 flow assurance problems such as free gas release or hydrate formation during pressure drops
389 [20].

390 ### 3.2. Produced water treatment

391 The water downstream the gravity separators contains dispersed oil droplets, solids and
392 dissolved organics that to various extents need to be removed. The water phase can contain

393   up to 1000 ppm of oil-in-water (OiW) and up to 350 ppm of TSS [46]. Most oil droplets will be

394   (significantly) smaller than 100-150 µm in size [47], whereas solid particles will typically not

395   be larger than 50 µm [48]. Some of the most commonly applied produced water treatment

396   methods used by the operators are described in the following. For more comprehensive

397   descriptions of the techniques, please refer to other reviews [1, 9, 10].

398   Produced water treatment (PWT) can typically be divided into three categories: (1) primary

399   PWT, predominantly gravity-based separation and aimed at removing dissolved gas, the

400   largest dispersed oil droplets and suspended particles; (2) secondary PWT that aims at further

401   reduction of dispersed oil content, and (3) tertiary PWT, often called water polishing step,

402   which also targets the dissolved components in produced water.

403   Using a second gravity separator (skimmer) is considered a primary PWT method. This process

404   is predominantly used onshore, as it requires long residence times (hours). Skimmers can

405   have either horizontal or vertical configuration. The specific design will depend on the need

406   for solid removal or limitation of slugging. In a horizontal setup, the water phase enters the

407   separator from one side. The lower density of oil causes the droplets to rise to the oil-water

408   interface, where they form an oil layer. Conversely, the solid particles sediment to the bottom

409   of the separator. The skimmed oil passes over a baffle and is removed from the skimmer,

410   whereas water (and particles) is forced downwards to the water outlet. The performance of

411   the skimmer is relatively insensitive to the inlet OiW concentration, but requires high

412   retention times (i.e. low flowrate or large volume) for necessary separation. The footprint of

413   a skimmer can be reduced by introducing plate coalescers. These internal plates capture

414   droplets on horizontally inclined plates and decrease their rising distance, which leads to

415   more efficient coalescence between droplets. The plate coalescers can reduce the minimum

416   removed drop size from approximately 100-150 µm to 20-40 µm [49].

417   Another primary PWT, more common offshore, are hydrocyclones, which utilize the

418   centrifugal force to remove the dispersed oil droplets from the water. Produced water enters

419   the separator through an axial or tangential inlet, which creates a swirling flow towards the

420   bottom part of the unit. The dispersed oil is pushed towards the centre and is combined with

421   the reject flowing upwards. The cleaner water phase exits the hydrocyclone from the bottom.

422   The gravitational acceleration is multiplied by the centrifugal forces in this process. The

423   acceleration increases with the narrowing of the liner, which facilitates gradual removal of

droplets of different sizes. The largest droplets are removed in the upper part, whereas smaller drops can be separated in the lower, narrower section. Hydrocyclones can remove droplets down to 5-15 μm in size [47], and significantly reduce the OiW concentration. Their compact size and robustness make them attractive for offshore produced water treatment. Typically primary water treatment reduces the content of dispersed oil to between 50 and 200 ppm [7]. If used in series, they can lower the oil-in-water content close to the discharge limit.

A secondary treatment technique is gas flotation, although it can also be used in series as both primary and secondary water treatment. Gas flotation relies on dispersing small gas bubbles in the water phase and their attachment to the oil droplets. The combined bubbles and droplets have lower density than water and typically large size, which increases their rising velocity and benefits separation. In the dissolved gas flotation (DGF), the gas bubbles are generated through nucleation in super saturated water and oil phases. Part of the recycle water passes through a saturation vessel, where it is pressurized with gas. Afterwards, the water flows back to the separation vessel, where the lower pressure forces the gas to nucleate and form very fine bubbles, typically below 100 μm [50]. Additionally, some gas is already dissolved in the fluids, which further enhances the nucleation of bubbles upon pressure reduction. During the induced gas flotation (IGF) process, the gas bubbles are formed by mechanical dispersion. One way to disperse gas bubbles is with eductors, where the flow of recycled water and gas through a nozzle creates a jet of dispersed gas bubbles ejected to the separator. Another way is to use motor-driven rotors that draw gas from above the liquid and disperse it in the water phase. The average bubble size range in the induced gas flotation is usually between 100 and 1000 μm [50].

The IGF is more frequently used in the produced water treatment systems at NCS, being a more robust technology and less sensitive to parameter changes (droplet size or pressure level). In most cases, natural gas is used as the gas phase, being the most abundant and safest gas available due to lack of oxygen. Gas flotation performance can be enhanced with the addition of water treatment chemicals, which improves the attachment efficiency between bubbles and droplets [50]. This process can effectively reduce the concentration below the discharge limit and can even serve as a single water treatment technology if used in series.

454   Offshore water treatment processes often include a gas flotation unit. This unit can be either

455   dissolved or induced gas flotation, or a combination of both if the water to be treated is

456   supersaturated. In the NCS fields, most of the gas flotation units are more compact than

457   traditional flotation cells used onshore, and are called compact flotation units (CFU). For the

458   CFUs operating as IGFs, the induced gas is dispersed into the water through a shearing device

459   (various designs) to give small bubble sizes. However, often low pressure drops are required

460   in the production process, leading to a compromise in bubble size distribution. The compact

461   flotation units have internals that makes the fluid distributions more optimal, both in the bulk

462   water flow and for handling of the gas/oil reject (e.g. swirling flow). For the latest

463   developments of CFUs, full performance for the residence time of 30 seconds or less have

464   been documented. Most CFUs are fully dependent on the coalescence/attachment

465   mechanism acting between oil droplets and gas bubbles to be efficient (explained in detail in

466   the next section). Any interference of this mechanism, like changing production chemicals

467   (types and/or dosing), adding new wells, changing pressures/temperatures, may strongly

468   impact the performance. Many vendors have entered the market since Epcon launched the

469   first commercial CFU for offshore water treatment in the 90-ties, but all of them are based on

470   the same fundamental mechanisms to be efficient. CFU technology is also currently

471   undergoing qualification process for subsea produced water treatment.

472   Recently, also membrane separation was suggested as an alternative for secondary produced

473   water treatment [11]. Micro- and ultrafiltration with membranes following primary

474   treatment can reduce the oil-in-water concentration below 5 ppm [51]. Ceramic membranes

475   are typically preferred over the polymeric membranes for produced water treatment due to

476   their higher resistance against fouling and better performance at elevated temperatures [52].

477   However, in practice the application of membrane technology for produced water separation

478   is still hindered by the risk of reversible and irreversible clogging of pores with oil droplets,

479   solid particles, and biofouling which can greatly reduce the performance and safety of the

480   process. Currently water treatment using membrane technology at the Norwegian

481   Continental Shelf is used only at gas/condensate fields.

482   For most production facilities, the treatment of produced water stops with the secondary

483   PWT. At NCS, many facilities have a degasser tank for removing supersaturated fraction of gas

484   from the water phase before discharging or re-injecting. It can operate in a similar manner as

485   dissolved gas flotation, which removes additional dispersed oil droplets. Degassers are

486   considerably larger than CFUs, with a residence time of few minutes. If the water must be of

487   higher quality (<10 ppm), it can also undergo a water polishing step. This typically includes

488   almost complete removal of the dispersed oil and considerable reduction of the dissolved

489   organic and/or inorganic components from the water phase. Walnut shell filtration,

490   coalescing filters, gas stripping, biological treatment, liquid-liquid extraction or high-G

491   centrifugation are examples of such treatment processes, however mostly used onshore [8,

492   9].

493   As it can be seen, most of the produced water operations is focused on the crude oil-related

494   contaminants. Solid particles (formation solids, corrosion products, microorganisms)

495   however, can also cause significant problems during production. Examples include

496   stabilization of emulsions, settling in or erosion of the processing equipment or formation

497   damage during re-injection [7]. Solid management can be performed on several levels [48].

498   The sand production can be minimized as a result of production limitation (lowest inflow

499   without solid particles in the stream), sand retention at the well, solid separation process or

500   incorporating a solid separation step during fluid separation.

501   At NCS, the solid particles are typically settling in the separators during three-phase

502   separation or further water treatment steps. These are later removed through e.g. sand jets

503   or manually during scheduled maintenance. While larger solids usually settle in the gravity

504   separator, finer solids (<25 µm) can follow either water or oil stream, depending on their

505   wettability. The particles in crude oil are typically not treated and add to the impurities of

506   crude oil (basic sediment and water – BS&W). The water-wetted particles, however, need to

507   be removed to avoid damaging the equipment or, later, the reservoir. This can be done with,

508   for example, desanding cyclones, sand traps or filtration [48].

509   **4. Colloidal aspects of produced water**

510   Colloidal systems and their interfacial aspects are crucial at almost every stage of crude oil

511   production. The knowledge on these fundamental phenomena can often help prevent

512   separation problems, reduce flow assurance issues, enable more cost-efficient process

513   designs and improve the overall quality of hydrocarbons and produced water. Interestingly,

514   the reservoir fluids are, to some extent, stratified in the formation. Therefore, it is the

515   production process that creates the need for separating dispersed bubbles and droplets from

516   the gas, oil and water phases later. Fundamentally, these fluid particles are kinetically-

517   stabilised, meaning that they will separate into the individual phases given enough time.

518   However, since the residence time in gravity separators is typically insufficient to achieve

519   complete phase separation, additional treatment processes must be used to remove the

520   remaining dispersed or dissolved components. Therefore, especially for offshore production,

521   the increasing environmental awareness, reduced footprint of the processing units and

522   dynamically changing composition of the fluids collected from several tie-ins force better

523   understanding of what is happening during the process.

524   As mentioned above, the dispersions are predominantly created during the petroleum

525   extraction process. The flow and pressure of fluids passing through the well and wellhead is

526   controlled by choke valve(s). They can also be installed upstream any kind of separator, both

527   in the oil and water treatment trains to ensure correct parameters of the flow. The pressure

528   reduction releases huge amount of energy, transformed into shear forces and turbulence in

529   the produced fluids, which can create dispersions of various degree of complexity. Many

530   fundamental studies performed decades ago showed that the higher the shear forces, the

531   smaller the size of generated droplets. The size distribution will of course depend on more

532   factors, such as temperature or the type of oil and the volume fractions of fluids, however

533   these parameters cannot be controlled. Since many separators are based on some form of

534   gravity separation, smaller droplets will obviously take much longer to separate. Improved

535   knowledge on the breakage phenomena led to the design of low shear valves. Further

536   development included low-shear pumps, another element that could apply strong shear

537   forces to fluids.

538   While the lack of small droplets, generated at the choke valve, will in fact improve the quality

539   of produced water, it still requires further treatment, for example with gas flotation. The

540   latest generation of highly efficient compact flotation units bears little resemblance to

541   flotation cells, originally adapted for produced water treatment in 1970s from flotation

542   columns used for mineral processing. Attachment of gas bubbles to small oil droplets, the

543   underlying phenomena of gas flotation, multiplies their rising velocity through increased size

544   and density difference. Simple observation of the process and fundamental research using

545   single bubbles and droplets or lab-scale flotation devices allowed to understand the

behaviour of fluid particles in various conditions (oil/water composition, droplet/bubble size distribution, aging effects, temperature etc.). Consequently, the correlation between the microscopic phenomena and performance of the process motivated the oilfield industry to introduce innovative changes to flotation units, such as centrifugal flow or reduced generation of extremely small bubbles.

Even deeper colloidal knowledge is required for understanding of the effects of production chemicals, added during petroleum processing. These specialized products, with often custom-tailored chemistry, must be extensively tested before being applied in the field. Often dosed at low-ppm level, they can promote growth or aggregation of particles (flocculants), mitigate separation issues (defoamers, de-emulsifiers), inhibit precipitation and/or deposition of various materials in pipelines (asphaltene, scale or wax inhibitors) or improve reservoir recovery rates (surfactants or polymers). They can also have undesired effects, for example stabilization of dispersions (often the case with corrosion inhibitors) or interacting with other chemicals or components that can compromise their efficiency. Lack of understanding on how they work and affect the produced fluids at any given stage of separation might lead to serious consequences, ranging from manageable separation problems to even temporary production shut-down.

These are just a few examples where the colloidal chemistry of produced fluids has a high impact on the process. Clearly, the efficiency of the water treatment processes, which are the focus of this review, will depend on many factors that affect the interactions of bubbles and droplets (i.e. process conditions, equipment design and fluid properties). Here, we will primarily focus on the fluid composition and elucidate how this can affect size distributions through breakage, flocculation and coalescence of the dispersed phases.

4.1.   Droplet break-up and coalescence

The dispersed oil in produced water constitutes an o/w emulsion. Formation of emulsions is a multi-step process that can be divided into three stages [53]: 1) Deformation of the two immiscible phases (oil and water) into coarse drops; 2) Disruption and break-up of the drops into smaller drops; 3) Counterbalance of the drop break-up by coalescence of drops. These three stages can occur simultaneously or successively, and they can influence each other. Furthermore, the adsorption of surface-active components originating from crude oil at the

interface between the oil and water can affect these stages by lowering the interfacial tension (IFT), giving rise to interfacial tension gradients (Marangoni effects) and formation of interfacial layers. The first phenomena will generally promote breakage of drops, while the latter two can stabilize the drops towards coalescence. Also, for this reason, the droplets with "fresher" interface will coalesce more readily. Mathematical expressions for both breakage and coalescence are the foundation of population balance equations [54], which can be used to model the evolution of size distributions and separation during treatment.

During the break-up of droplets, the hydrodynamic conditions and the interfacial properties between oil and water are important. Even though reliable models for predicting drop size distributions are not available, mechanistic models for estimating maximum stable drop sizes in given hydrodynamic conditions have been established [55]. These models normally account for the cohesive and disruptive stress acting on a drop. The cohesive stress depends on the IFT, the viscosity of the dispersed phase and the radius of the drop. The disruptive stress, on the other hand, is governed by the viscosity of the continuous phase, the radius of the drop and the type and intensity of the flow. A drop is stable if the disruptive stress is smaller than the cohesive stress. The breakage of droplets in dispersions was first described by Kolmogorov [56] and Hinze [57], but since then many other models have been developed [58]. The breakage in mathematical terms is often described with breakage frequency and the number and size of droplets created through the breakage of the original droplet. Both functions, characterizing the frequency of breakage and its outcome, are necessary in the population balance models used for simulation separation processes [59].

Coalescence is the main mechanism of droplet growth in produced water. The film drainage model is often used to describe this phenomenon [60]. It defines collisions and merging of drops as a multistage process. Initial approach of droplets results in a thin liquid film between them. This is followed by drainage of the thin film and finally the film ruptures at a critical thickness of the film and the drops merge into a larger drop. Each stage is depicted in Figure 6. The film drainage depends on the drop size, fluid parameters and surface forces, which effect is described below. Typically, the initial film thickness is in the range of hundreds of nanometres [61], whereas the critical thickness is at least an order of magnitude lower [62]. Furthermore, the rupture time is usually considerably faster than the drainage time [63]. This means that the drainage of the aqueous film is the rate-determining step in the process, and

607 it is important to understand and control the factors influencing it. It should also be
608 mentioned that not all collisions will end up in coalescence. If the average contact time
609 between droplets is shorter than the drainage time required for them to merge, the droplets
610 will detach without coalescence. This can occur, for example, when the thin film is extremely
611 stable (repulsion dominating) or when the emulsion is mixed due to high turbulence (very
612 short contact time).

613 Collisions between drops depend on the flow regime and can occur through different
614 mechanisms. The most important are turbulent fluctuations (mixing), velocity field gradients,
615 single eddy capture, buoyancy differences and wake interactions [60]. The resulting collisions
616 will involve forces that affect the rate of film drainage. Many drainage models consider these
617 forces purely as a function of the flow conditions (i.e. local shear rate) and some basic physical
618 properties of the fluids. However, at the distances comparable to the thin film thickness (tens
619 to hundreds of nanometres), the so-called surface forces will become significant. These forces
620 have molecular origin and can be attractive or repulsive. The relative magnitude of the
621 attractive and repulsive forces will vary with separation distance between droplets (i.e. film
622 thickness). The resulting difference between pressure within the film and in the bulk is called
623 the disjoining pressure. If the attractive forces dominate, giving rise to negative disjoining
624 pressure, the drainage of the thin film will be spontaneous. If, on the other hand, the repulsive
625 forces dominate (i.e. positive disjoining pressure), additional forces are necessary for the thin
626 film to drain.

627 The attractive surface forces include the van der Waals forces and the so-called hydrophobic
628 forces. The van der Waals forces are due to interactions between permanent and induced
629 dipoles in the molecules constituting the droplets and will always be present. Another
630 characteristic of these forces is that they become strong at short separation distances. The
631 hydrophobic forces between dispersed entities can be divided into two categories [61]:
632 structuring of water molecules in the vicinity of hydrophobic surfaces and interactions caused
633 by the presence of the dissolved gas. In the latter case, dissolved gas molecules preferentially
634 adsorb at hydrophobic surfaces, and induce the formation of nanobubbles that can form
635 gaseous bridges, pulling the surfaces together and facilitating coalescence [64]. These forces
636 are normally longer ranged than the van der Waals forces.

The repulsive surface forces include double-layer electrostatic forces, steric forces and hydration forces. Electrostatic repulsion occurs when the electrical double layers of similarly charged interfaces start to overlap each other. These interactions are, however, negligible in produced water, since the electrical double layers are efficiently supressed in high salinity environments. Steric repulsion takes place when interfacial active species are present at the interface and provide a steric hindrance for close approach. These can typically be resins, asphaltenes and added production chemicals containing surfactants or polymers. Finally, the hydration effect will give rise to repulsion when water molecules are attached to approaching interfaces [65].

In addition to the disjoining pressure, Marangoni effect will also influence the film drainage process. When the aqueous film is drained, it also pulls the molecules at the interfaces along with it and creates a concentration gradient at the interface. The result is a flux of components from the high concentration region towards the low concentration region, as illustrated in Figure 7, which will slow down the film thinning rate [61]. Furthermore, the adsorption of resins and asphaltenes can result in formation of elastic interfacial layers and change the interfacial rheology at the oil-water interface. This will also impact the Marangoni effect and further alter the film drainage [66].

The stability of drops against coalescence can be affected by other dissolved and dispersed components in the produced water [11], such as small particles at the interface (so-called Pickering emulsions), low-molecular organic species, multivalent inorganic ions or production chemicals [67]. For example, the addition of flocculants can neutralize the charge on the surfaces of droplets, reducing the repulsive forces, or promote bridging between them. This will lead to increased coalescence or, if the film is stable against rupture, aggregate formation. If overdosed, the flocculant can lead to increased stability against coalescence and worse treatment performance.

4.2. Drop-bubble attachment

Oil removal by gas flotation relies on the similar fundamental description as above [68, 69]: approach of bubbles and droplets by various forces, followed by drainage and rupture of the thin aqueous film arising between the bubble and droplet (Figure 8). However, some differences exist as well.

667 The size ratio between bubbles and droplets is an important aspect during flotation. The
668 collision mechanisms will largely depend on the relative size between bubble and drop sizes
669 [70], as summarized by Niewiadomski et al. [69]. Encounters by gravity occur because of the
670 large buoyancy difference between bubbles and oil droplets. The interception mechanism
671 dominates when the droplets are larger, and the droplet is trapped in the water streamlines
672 passing the bubble. Inertial impacts occur when the droplet is not following the water
673 streamlines due to its inertia, but it is considered to play a small role during gas flotation of
674 oil droplets. Finally, in turbulent motion the bubbles and drops tend to become located in the
675 centre of turbulent eddies, which should increase the chance of encounter.

676 Once thin films between droplets and bubbles are formed, the disjoining pressure and
677 Marangoni effect will play a similar role for the film drainage as described above. The
678 adsorption of resins and asphaltenes at the oil-water interface will influence the film thinning
679 rate. In addition, dissolved oil components in the produced water will adsorb onto gas-water
680 interfaces [71, 72] . This has been shown to slow down the drainage of the thin film [73] and
681 reduce the oil removal efficiency during gas flotation [74].

682 Oil can be removed by gas flotation whether the film ruptures or not. If the film does not
683 rupture, drops can become attached to rising bubbles, entrapped in the hydrodynamic wake
684 of rising bubbles (Figure 9a) or pushed upwards by a "pillow" of flocculated bubbles (Figure
685 9b) [75]. These mechanisms are, however, vulnerable to turbulence and collisions, which can
686 result in detachment of the droplets and bubbles. The critical thickness when the aqueous
687 film ruptures is often quoted to be around 100 nm [76, 77]. When it ruptures, two
688 mechanisms are possible (Figure 9c, d): 1) the oil spreads around the gas bubble and forms
689 an oil film. This mechanism is considered the most stable and ensures efficient flotation of
690 the droplets. Furthermore, additional droplets can coalesce with the oil-coated bubbles,
691 forming thicker oil films. 2) The oil forms a lens inside the bubble, which is more unstable than
692 the previous, since the oil can detach from the bubble due to for example turbulence. A simple
693 and convenient method to determine the type of attachment is to consider the spreading
694 coefficient (S_{ow} – Equation 1) [78]:

$$S_{ow} = \gamma_{wg} - \gamma_{ow} - \gamma_{og} \qquad (1)$$

where γ_{wg} is the interfacial tension between water and gas, γ_{ow} is the interfacial tension between oil and water, and γ_{og} is the interfacial tension between oil and gas. If the value of the spreading coefficient is positive, the spreading of oil on gas will be favourable from a thermodynamic point of view. If the spreading coefficient is negative, the oil droplets will not spread over the surface. For most gas flotation processes in produced water treatment, however, the spreading coefficient will be positive [68]. The time of the spreading can also be significant [69, 73].

During dissolved gas flotation, bubbles can also nucleate at the oil droplet surfaces. While this will not have a large effect on the buoyancy of the droplet, it can lead to improved flocculation between droplets and/or other bubbles through additional attractive (hydrophobic) forces. The presence of these nanobubbles was observed to aid the flotation of both solid particles [79] and oil droplets [80].

4.3. Interactions between solid particles

The wettability and wettability alterations of the various solids in produced water will influence their tendency to aggregate, sediment and form particle-stabilized emulsions [81-83], and ultimately increase the separation difficulties. The surface properties of particles can be altered by adsorption of interfacially active components from the crude oil [84] or by adsorption of water-soluble crude oil components in the produced water. This adsorption often provides steric repulsion that slows down the aggregation or flocculation of the solids. It can also lead to attachment of particles at emulsion droplets, which can inhibit coalescence between droplets [85].

5. Research tools for studies concerning produced water

Many aspects of produced water, from unique chemical composition and environmental concerns to optimization of treatment processes, require specific research methodologies to provide insight into the fluids and the treatment process. In this section we present experimental methods to study interfacial properties, drop breakage, coalescence and flocculation of droplets, bubbles and solids, and composition of PW. Many of the techniques are well established and have been used for years, whereas some are relatively new and not yet widely utilized.

5.1.   Interfacial properties

The interfacial tension and rheology are of great importance in coalescence and breakage processes. These can be investigated with drop tensiometers, where a drop of dispersed phase is immersed in a continuous phase and recorded over time. Pendant and spinning drop techniques are commonly used in the produced water field. In the pendant drop method, a drop is immersed in a bulk phase from a capillary. Images of the drop profile are used to convert the shape parameters to the interfacial tension. Due to its simplicity and versatility, this method is frequently used to measure the IFT between the crude oil and water phase [86, 87], also at high pressure and temperature conditions [88, 89]. In addition, high-frequency oscillations of the volume drop allow calculations of the elastic (E') and viscous (E'') moduli and have been used for characterization of the viscoelastic properties of oil/water interfaces [90-92]. In spinning drop tensiometer, a drop is placed in the centre of a rotating capillary due the centrifugal force. The elongation of the drop is imposed by the capillary rotation speed, physical properties of the phases and the interfacial tension. The technique is especially useful for measuring extremely low values of the IFT, even down to 10^{-6} mN/m, for example in high pH conditions or with a surfactant in a system [93, 94].

Depending on the composition of the produced water, it can exhibit different surface tension values. This is often measured with the du Noüy ring [95], the pendant drop [96] or the maximum bubble pressure method [72, 97]. The bubble pressure method is a useful technique to study the surface tension as a function of the surface age, also allowing to calculate the kinetics of surfactant diffusion.

5.2.   Droplet break-up

Droplet break-up studies require the possibility of following the events in dynamic conditions. Such experiments are typically performed in a static mixer, a pipe flow or a stirred tank, using high speed cameras to obtain the breakage time and the number and size of droplets. The stirred tank (Figure 10) is probably the most common out of the three, due to its simplicity and good control over the parameters, although the turbulence distribution is not as homogenous as for the other two. The pipe flow experiments are usually the closest to the process reality of crude oil production, however are also quite difficult to follow. The literature on the breakage of crude oil drops in water with visual methods is very scarce.

754 During our literature search we only found one paper that dealt with the breakup of crude oil

755 droplets in a stirred tank [98]. Other authors, such as Maaß et al. [99] or Solsvik and Jakobsen

756 [100], used kerosene or other model hydrocarbons in their studies, which, although

757 petroleum-derivatives, do not really represent the complexity of a crude oil. Many efforts are

758 undertaken to precisely describe and model the breakage process [101] and probably for this

759 reason the use of real crude oil products is sporadic. Regardless, more comprehensive

760 descriptions of mostly visual-based methods for model oil droplet breakup studies were

761 reported elsewhere [99, 100].

762   5.3.   Drop-drop interactions and coalescence

763 The visual methods for following coalescence can roughly be divided into two types: (1) quasi-

764 static, where the fluid particles are slowly pushed against each other or allowed to rise to an

765 interface, and (2) dynamic, where the interactions are followed during flow. The first type of

766 methodology is typically easier to work with and offers much better control over the

767 experiment, however the latter allows to study interactions between droplets in similar, to

768 some extent, conditions as the water treatment process. Starting with the static methods,

769 Flumerfelt et al. presented a method based on the spinning drop technique, where two oil

770 droplets in a rotating capillary were first allowed to age and then came into contact [102].

771 This technique was later utilized by Peru and Lorenz to determine the coalescence time of

772 crude oil drops in alkaline water, also at elevated temperatures [103]. In another approach, a

773 pendant drop was used to study the coalescence between the drop and interface [104, 105]

774 (Figure 11a). A drop of oil was released from a hook and rose to a layer of oil on top of the

775 water phase. After sufficient time, the thin film broke and the droplet merged with the

776 interface. The entire experiment was recorded and analysed to determine the drainage time.

777 Further modification of this technique included adding another capillary to generate two

778 single drops simultaneously, and observe their binary coalescence with a camera. The setup

779 of Ata et al. [106] allowed to follow the coalescence of two ca. 2 mm drops of kerosene in

780 temperatures up to 75°C (Figure 11b). Gaweł et al. used a droplet bubble micro manipulator

781 (DBMM) to study the coalescence between droplets of different crude oils [66]. In contrast to

782 the techniques presented so far, DBMM relies on measuring capillary pressure, rather than

783 image analysis (Figure 11c). A similar setup, with a better control over the approach velocity

784 between two drops and video image analysis, was presented by Ayirala et al., who

785   systematically studied the effect of inorganic ions in the water phase on the coalescence times

786   of crude oil drops [107]. Finally, microscopy can be useful for determining coalescence of

787   crude oil drops [108, 109], but it provides coalescence rates, rather than coalescence times.

788   All of these experimental techniques require static environments, which makes the timescale

789   of the phenomena significantly longer than in dynamic conditions.

790   New possibilities for studying coalescence of droplets during flow emerged after recent

791   advances and popularization of high-speed imaging. This also altered the measured timescale

792   of coalescence times from tens of seconds for static to tens or hundreds of milliseconds for

793   dynamic conditions. Kamp and Kraume [110], Villvock et al. [111] and Gebauer et al. [112]

794   developed a cell for single drop coalescence investigations. Although model fluids were used,

795   their work provided interesting insights into the importance of inorganic ions and the

796   direction of mass transfer (from or to the continuous phase). Coalescence kinetics of crude

797   oil droplets in alkali-surfactant-polymer solutions using high-speed imaging was also studied

798   by Luo et al. [113].

799   Recently, microfluidic methodology has become a useful tool to study fundamental aspects

800   of emulsions [114]. Microfluidics enables control of fluids in small channels, where at least

801   one of the dimensions is in the micrometre size range. The flow can be manipulated and

802   observed by auxiliary equipment or with internal sensors and valves. The possibility of

803   combining various tools in one small device lead to the name 'Lab-on-a-Chip' (LOC).

804   Microfluidics combines the advantages of visual observations in dynamic conditions with high

805   throughput, short measurement times and small droplet size, often relevant for industrial

806   applications. While the application of microfluidics for petroleum-related research keeps

807   growing, the main focus is directed towards fluid analysis and behaviour [115], rather than

808   separation aspects. However, some groups reported the microfluidic methods for studying

809   coalescence in water-in-crude oil systems [116, 117]. For oil drops in water, microfluidic

810   devices were used for studying both coalescence dynamics (frequency) [118] and kinetics

811   (coalescence time) [119, 120]. Krebs et al. also presented a microscopic method to study

812   coalescence of oil under enhanced gravity (i.e. simulating hydrocyclone conditions) [121].

813   Following their work, Dudek et al. presented a method to study the coalescence of model oils

814   at higher pressure [122]. It was later used to study coalescence of crude oil droplets in

815   synthetic produced water [123, 124] (Figure 12). In contrast to the DBMM studies done in our

816 group, the microfluidic method allowed to follow coalescence in dynamic conditions and with

817 (monodisperse) droplets 1-2 orders of magnitude smaller, which is more relevant for

818 produced water treatment processes. The study, however, used only light crude oils due to

819 method limitations.

820 While visual observation methods are useful for investigating single droplets or dilute

821 systems, light scattering and transmission techniques allow to follow the bulk behaviour of

822 dispersions over longer periods of time. The light scattering techniques can follow the

823 dynamic changes of size distributions, and thereby provide information about the extent of

824 coalescence or breakage in the systems (Figure 13). These methods were used to study the

825 dynamic changes of oil droplet size distribution in water, influenced by various parameters,

826 such as mixing time and speed [125, 126], volume fraction of the dispersed phase [127],

827 presence of EOR chemicals [128] and water composition [129]. Furthermore, flocculation of

828 oil drops upon addition of polymeric flocculants was studied by Fernandes et al. [130].

829 Turbidity measurements can also be used to follow the sedimentation or creaming of

830 dispersions. This method relies on the detection of transmitted light (for some cases also the

831 detection of back-scattered light) through a dispersion. However, the method is better suited

832 for studying sedimentation, creaming or massive changes due to flocculation [82, 131], rather

833 than subtle changes in the particle sizes.

834 For more in-depth analysis of forces occurring between single drops or particles, another class

835 of instruments can be used. Atomic force microscopes (AFM) scan a surface with a sharp,

836 flexible cantilever, which movement is detected and converted into the force of interaction.

837 It allows measurements of not only the mechanical properties of a surface, but also the

838 interaction forces between a surface and the cantilever tip. The precision of the instrument

839 is high enough to measure the forces in the Ångström range. It was used for the measurement

840 of the van der Waals forces [132] and hydrophobic interactions between surfaces in water

841 phase [133]. In petroleum research, AFM was successfully used to measure interaction forces

842 applicable for the bitumen extraction process [134] and asphaltene-covered surfaces [135].

843 5.4.   Gas flotation and bubble-droplet interactions

844 Starting with bench scale instrumentation, gas flotation processes are frequently investigated

845 using columns for batch flotation. Depending on the process, these are open or closed

columns, made from glass, plastic or steel, with the total volume in the range of litres. In the case of induced gas flotation, the gas is typically dispersed through a sparger or stirrer, whereas the dissolved gas flotation requires prior pressurization of the water phase. Strickland Jr. published a thorough report on the effect of various parameters on the performance and characteristics on the induced gas flotation process [68]. He showed the effect of salinity on the bubble size distribution, the influence of oil type and concentration, together with water pH and process temperature, on the oil recovery. Later, Sylvester and Byeseda reported a detailed study on a multi-stage IGF process [136]. The number and size of oil droplets were determined at the inlet and the outlets of each flotation cell. It was shown that droplets smaller than 2 μm were produced during mechanical dispersion of gas and were hardly removed during the gas flotation. An interesting concept was also reported by Bai et al., who improved the hydrocyclonic separation by introducing dispersed gas bubbles to the process [137], bearing some similarities to the CFUs. da Silva et al. combined the gas flotation with a photo-Fenton process, which further reduced the oil content through photochemical degradation [138]. Eftekhardadkhah et al. compared the laboratory gas flotation column tests with experiments in a pilot-scale flotation rig [74], where the large-scale equipment was run in induced, dissolved or combined induced-dissolved gas flotation mode. The dissolved gas flotation was also studied by several research groups. Multon and Viraraghavan [139] reported the removal of dispersed oil and suspended solid particles from two produced water samples from heavy oil operations with DGF, with and without polymeric additives. Etchepare et al. [80] and Oliveira et al. [140] focused on the application of nanobubbles to dissolved gas flotation and understanding their impact during separation process. While batch flotation is a simple way of studying the effect of various parameters (bubble/droplet size, water/oil composition, temperature etc.) on the treatment performance, it should be noted that most flotation units are dynamic systems. It is also relatively difficult to describe the mechanisms of bubble-droplet interactions, unless the process is followed with high-speed imaging or the experiments are combined with more fundamental investigation on individual fluid particles, as described next.

Oliveira et al. studied the separation of model oil from water containing different concentrations of salt and surfactant by dissolved gas flotation [76]. They also used a bubble-drop instrument to measure the induction time between a gas bubble and an oil droplet. It

877　was shown that both the induction time and the interfacial properties of the system (i.e.
878　spreading coefficient) had significant impact on the performance of gas flotation. Chakibi et
879　al. investigated the effect of salt on the flotation process and showed that the salinity level
880　has a positive effect on the separation performance up to certain level, above which it no
881　longer affected the separation [141]. Furthermore, they also reported a simple, but effective
882　setup for determining the induction time between an oil drop and planar air-water interface
883　with high accuracy (Figure 14). The measurements obtained on the microscale complemented
884　well the flotation column results. While the hydrodynamic conditions of the fundamental and
885　batch scale experiments were quite different, the observed trends were similar and proved
886　that the underlying attachment mechanisms are of great importance to the efficiency of gas
887　flotation.

888　Nikolov et al. used a capillary force balance technique to probe the stability of thin films
889　between oil and gas interfaces [142]. They found that by adding a de-emulsifying agent, the
890　stability of the film decreased, which should aid in the separation efficiency by gas flotation.
891　A custom-built setup was used to measure the induction time between a gas bubble and a
892　bitumen-covered surface [143, 144]. The method relied on the generation of a microbubble
893　and slow approach and retraction towards and from a bitumen-coated plate. The induction
894　time can be found through progressively increasing the contact time between the bubble and
895　the surface. The drop-bubble micromanipulator technique was also used to measure the
896　drainage and coverage times between crude oil drops and air bubbles (Figure 15) [73].
897　Microfluidic experiments of the induced gas flotation were performed by Dudek and Øye,
898　who systematically studied the attachment of crude oil droplets to gas bubbles in various
899　conditions [95]. Monodisperse drops and bubbles were generated and pumped through a
900　coalescence channel, where they could get in contact and interact. High-speed imaging
901　allowed to determine the number for oil droplets attached to gas bubbles during flow in a
902　microchannel. Recently, also AFM was used to measure the interaction forces between
903　bitumen and gas bubbles [145].

904　　5.5.　　　Size distributions

905　Knowledge of the distribution of dispersed particles and drops is crucial for the treatment of
906　produced water. Since the droplets or particles are often in the micrometre size range,
907　microscopic analysis is one of the easiest ways to measure the size of dispersed matter [17,

83, 128] (Figure 16a and b). A sample is put on a glass slide or in a cuvette, and analysed with a microscope, which is often coupled with a camera. Later, these pictures can be processed with an image analysis software to obtain average drop sizes or drop size distributions. Furthermore, confocal microscopy can be used to obtain distribution of droplet sizes in water [146, 147]. Microscopic analysis, is however a static technique and the results greatly depend on the appropriate and consistent sampling methods.

Size distributions measurements can also be performed with light scattering techniques. Particles of different sizes scatter light at specific angles. The intensity of the scattered light at different angles can later be transformed into a size distribution. In contrast to microscopy, light scattering instruments can be coupled in a flow system (for example, a stirred tank) and allow to directly follow the dynamic changes of drop sizes during the experiment. Flow and turbulence cause the droplets to continuously break up, collide and coalesce with each other, which bears much more resemblance to the actual process of produced water treatment. Light scattering methods are popular tools to measure the distribution of both oil droplets in water [125, 128] and suspended particles [42, 82, 148]. It should be noted, however, that due to the risk of multiscattering, the studied systems must be quite dilute. In addition, some instruments used for dynamic light scattering also allow to measure the surface charge (zeta potential) of the dispersed matter [147, 149].

Coulter counters can also be used to measure the particle size distributions. The apparatus contains a cell with two chambers filled with an electrolyte, connected with a microchannel. When a drop or particle passes through the channel, it causes a change of the electrical resistance, proportional to the volume of the particle, which is detected by the instrument. These types of devices were used to determine the size distribution of solid particles [82] and oil droplets [131, 150] in petroleum-related research. However, the method works best when the particles are of near-spherical shape [151], which is often not the case for solid particles.

5.6.   Oil-in-water analysis

The definition of dispersed oil depends on the local regulators [5]. For example, in the US, the Environmental Protection Agency sets the limit for discharge to sea to 29 mg/L monthly average and 42 mg/L daily maximum of oil and grease, which is defined as the materials extracted with *n*-hexane and not evaporated at 70°C. Meanwhile, OSPAR specifies dispersed

oil as all compounds extractable with *n*-pentane and not adsorbed on Florisil® (a magnesium silicate-based adsorbent), with chromatographic retention time values between *n*-heptane (C_7) and *n*-tetracontane (C_{40}). These differences in definitions and sample preparation can lead to considerable differences in the acquired oil concentration values. Regardless of the definition, the standard techniques for determination of OiW concentration can be classified into three types [152]: gravimetric, infrared (IR) absorption and gas chromatography with flame ionisation detection (GC-FID). All methods require acidification and extraction of oil from water with a solvent. In the gravimetric method, the solvent (e.g. *n*-hexane) is separated from water and evaporated, leaving the extracted oil in the flask for weighing. The IR absorption technique relies on the use of chlorofluorocarbons as solvent to avoid interference with the sample absorbance, which is proportional to the concentration of the oil in the solvent. In the last method, the oil extracted to the solvent (*n*-pentane or *n*-hexane) is fed to a GC column, which separates the oil components based on their boiling point and polarity. Then, they are carbonized and detected by a flame ionization detector. This method gives information about the concentration, as well as the type of hydrocarbons extracted from the water phase. It should be noted that in the last two methods, the most polar crude oil components that are dissolved (not dispersed) in the water phase could significantly influence the results. These components are often removed after extraction (e.g. with Florisil® [27]) or excluded *post factum* (based on the retention times in the GC column).

There are also other, novel techniques for OiW analysis that have been proposed recently. For example, Fan et al. used confocal laser fluorescence microscopy [146]. Their procedure correlated well with a reference method and was also tested in more realistic conditions, i.e. at different pH levels, in the presence of solid particles, at high salinity and at high temperature [147]. Wagner et al. reported a nuclear magnetic resonance (NMR) method for assessment of oil-in-water concentration [153], which later was improved to enable separate quantification of aliphatics and aromatics in the water phase [154]. Lastly, Ottaviano et al. determined the OiW concentration with fluorescence measurements after treating the oily water with flocculants [149].

5.7.   Dissolved components

5.7.1. Inorganics

968   The total salinity of water can roughly be estimated by density, conductivity or with γ-ray

969   measurements [155]. For more comprehensive data on the ionic composition of produced

970   water, spectroscopic techniques are used. The concentration of common cations, such as

971   sodium, potassium, magnesium, calcium, barium or iron, can be determined with inductively

972   coupled plasma atomic emission spectroscopy (ICP-AES) [36, 37], mass spectrometry (ICP-MS)

973   [39, 156], direct current plasma optical emission spectrometry (DCP-OES) [156, 157] or ion

974   chromatography (IC) [158]. Other cations (e.g. heavy metals), for example cadmium, cobalt,

975   lead, nickel or zinc are commonly detected with atomic absorption spectrometry (AAS) [22,

976   159, 160], but also ICP-OES [161] or ICP-MS [162]. The concentration and type of anions can

977   be measured with IC [156, 163]. An interesting microfluidic alternative to ICP-MS for

978   determination of boron in produced water was reported by Floquet et al. [164]. The authors

979   coupled ion exchange with colorimetric analysis to obtain a precise concentration of the

980   element in a complex mixture.

981   ### 5.7.2.   Organics

982   The composition of the dissolved organic components in produced water is more complex

983   than the inorganic components. The species partitioned from the crude oil have a

984   hydrocarbon-based structure, relatively low molecular weight (<600 g/mol [23]) and different

985   levels of polarity. The total organic carbon (TOC) is probably the most basic parameter to

986   quantify the organic pollution in PW and other types of wastewater [165]. TOC is commonly

987   measured by high-temperature catalytic oxidation or low-temperature photooxidation that

988   converts the organic matter into carbon dioxide. The quantification of CO_2 is typically

989   performed with an IR detector. This method is quite popular to describe the concentration of

990   dissolved components in produced water [17, 37, 166]. It is often possible to run the total

991   nitrogen (TN) measurement on the same instrument. A big advantage of this method is the

992   possibility of running analysis directly on water samples. Nonetheless, it does not provide any

993   information on the composition of the organics. UV analysis (ultraviolet-visible spectroscopy)

994   can also be used to measure the level of TOC in water samples [165, 167]. However, this

995   method can underestimate the concentration of some components since aliphatic

996   hydrocarbons, acids and many other organic components are undetectable with UV analysis.

997   Another technique, gas chromatography, requires first to extract the dissolved components

998   from water to organic phase (typically dichloromethane). The GC analysis allows not only to

999   measure the total concentration of dissolved hydrocarbons, but also enables to identify their

1000   structure (in combination with mass spectrometry). This, together with the low boiling

1001   temperatures of the water-soluble species found in water, have made it a well-established

1002   technique for in-depth analysis of produced water. Still, GC techniques have some limitations,

1003   such as the need to use specific type of columns for different kinds of components.

1004   For simplicity, the classification of dissolved organics in this review is as follows: BTEXs, PAHs,

1005   phenols, acids and bases (like the one presented in Figure 5 in the introduction). Although

1006   harmful to the environment, aliphatic hydrocarbons are scarcely water-soluble and are often

1007   associated with the dispersed oil [34]. Produced water samples are often fractionated based

1008   on the size of molecules and/or chemical properties. This is commonly performed with liquid

1009   chromatography techniques (in the past with open columns, nowadays with high-

1010   performance liquid chromatography – HPLC) [163, 168]. Benzene, toluene, ethyl benzene and

1011   xylenes, are quite volatile compounds and can be separated with purge-and-trap systems

1012   before entering the GC column [37, 39, 159]. The rest of the dissolved organics fractions, i.e.

1013   PAHs and phenols, are injected separately and with the use of different GC programmes (oven

1014   temperature, ramp). After the column, the solutes can be identified and quantified with MS

1015   [168-170] or FID [22, 40, 171] (Figure 17), the latter technique being more useful for

1016   quantification purposes. The fractions can also be quantified by gravimetric [168, 171] or IR

1017   analyses [163, 171]. Even though GC is the dominating technique when it comes to analysis

1018   of dissolved organic components, there are other methods for obtaining supplementary

1019   information about the functional groups or the average molecular weight. These include

1020   nuclear magnetic resonance [37]; Fourier transform ion cyclotron resonance mass

1021   spectrometry (FT-ICR) [172] or spectroscopy (FT-IR) [97]; and electrospray-ionization mass

1022   spectrometry (EI-MS) [71].

1023   The most polar components of produced water are the acids and bases. Their water solubility

1024   is highly affected by the water pH – dissociated acids or protonated bases have a higher

1025   affinity to the aqueous phase. The most abundant components in the polar fraction of

1026   produced water are short-chained organic acids (VFA) [34]. Their presence and concentration

1027   can be determined with isotachophoresis [22, 36], ion chromatography [163, 171], IR

1028   spectroscopy [173] or direct gas-liquid chromatography FID of water [27]. The water-soluble

1029   naphthenic acids (longer than C_5) also require comprehensive analysis due to their

complexity, but with different methodologies. Most analyses can only be performed with organic solvents, therefore acidification and extraction of the dissolved components to a hydrocarbon-based solvent is often necessary. Spectroscopic methods (e.g. FT-IR) for characterization of naphthenic acids were reported, but give little information about the molecular composition of the acidic fraction and can overestimate their quantity in the sample [174]. When it comes to the structural analysis of naphthenic acids, mass spectroscopy techniques like FT-ICR MS [175-177] and GC-MS (or two-dimensional GC-GC-MS) [32, 178, 179] are used, although other methods, such as Orbitrap [180] and Orbitrap/HPLC system [177] were used as well. FT-ICR MS analyses of naphthenic acids typically give high mass accuracy, resolution and selectivity in the measurements due to limited fragmentation of the molecules [175]. In addition, it provides the information about the presence and abundance of heteroatoms in the molecular structure of naphthenic acids. Nevertheless, the instrumentation is expensive and requires advanced expertise [181]. This prompted the development of GC-MS methodology, as a less complicated alternative for the analysis of acids in water. To improve the quality of the spectrum and avoid excessive fragmentation of the aliphatic chains, a derivatization agent is added to convert acids to esters, which allows to resolve the mixture and obtain molecular mass and structure of the species in the sample, as described by St. John et al. [182] and others [26, 179].

Before probing the composition of the crude oil-indigenous species in the water phase, one must transfer them from the oil phase. A large portion of the water-soluble crude oil components are short-chain acids that are easily biodegradable and rather harmless to the marine environment. However, the dissolved aromatic hydrocarbons are significantly more harmful, even though their concentration is typically low. The fraction of these components will depend on couple of factors, such as the temperature, pressure, crude oil and water composition (including pH) and flow characteristics. For this reason, studies on the partitioning of water-soluble components from crude oil to water phase are also important. Many tests involving partitioning typically include the use of the shake flask method [183], however, as the crude oil contains surface-active components and tends to create emulsions, this method is scarcely used for crude oil-related experiments. Instead, gentle shaking [26, 184, 185] or mixing [21, 186, 187] of the two phases over an extended period is the preferred way of promoting mass transfer from one phase to another. With the former, the extraction

1061 process can be quite lengthy due to low interfacial area, while the latter cannot be used if
1062 interfacially-active components are in the system, due to the risk of emulsion formation and
1063 sampling issues. An interesting setup to study partitioning in high-pressure and temperature
1064 conditions was developed by Bennett and Larter [188]. They used segmented flow in a long
1065 steel coil to induce faster equilibration through increased interfacial area and better mixing.
1066 The coil was placed in an oven to control the temperature of measurements, whereas
1067 pressure was regulated with valves. The setup was later upgraded to use live oil (i.e. crude oil
1068 with dissolved natural gas) in addition to dead oil [189] (Figure 18), and work in lower
1069 temperature range, simulating subsea oil production conditions [190]. Considering the flow
1070 rates and tubing diameters, this idea bears some resemblance to microfluidic extraction
1071 methodologies, for example presented by Breisig et al., who studied droplet-based liquid-
1072 liquid extraction [191]. Although the mass transfer studies in microfluidics are considerably
1073 faster and more efficient, and have already been used for studying extraction in crude oil
1074 systems [192, 193], to the best of our knowledge, these tools have not yet been applied to
1075 study mass transfer between crude oil and water. More on microfluidic extraction methods
1076 can be found in other reviews [194, 195].

6. Conclusions

1078 The amount of generated produced water will only continue to increase in the future,
1079 therefore efficient water treatment processes are crucial for the oil and gas production. The
1080 environmental regulations of acceptable quality of produced water discharged are becoming
1081 stricter. This makes alternative ways of disposal (e.g. re-injection) more appealing. Better
1082 understanding of produced water composition and properties plays a key role in these
1083 processes. Fundamental phenomena, such as coalescence or partitioning, has a significant
1084 impact on the separation performance and, in the end, the discharged produced water
1085 quality. Since these fundamental processes can be affected by several factors during
1086 petroleum production, it is paramount to perform experimental measurements to obtain
1087 knowledge on the decisive (chemical and colloidal) aspects impacting performance during
1088 produced water treatment.

References

1096 [1] Igunnu ET, Chen GZ. Produced water treatment technologies. International Journal of Low-
1097 Carbon Technologies. 2014;9:157-77.
1098 [2] Kaur G, Mandal AK, Nihlani MC, Lal B. Control of sulfidogenic bacteria in produced water from the
1099 Kathloni oilfield in northeast India. Int Biodeterior Biodegrad. 2009;63:151-5.
1100 [3] OSPAR. Discharges, spills and emissions from offshore oil and gas installations. 2010.
1101 [4] European Commission. Best Available Techniques Guidance Document on upstream hydrocarbon
1102 exploration and production. In: Limited WEISU, (editor). Luxembourg: Publications Office of the
1103 European Union; 2019.
1104 [5] Zheng J, Chen B, Thanyamanta W, Hawboldt K, Zhang B, Liu B. Offshore produced water
1105 management: A review of current practice and challenges in harsh/Arctic environments. Mar Pollut
1106 Bull. 2016;104:7-19.
1107 [6] gass No. Environmental Report 2017. Norsk olje & gass; 2017.
1108 [7] Paige RW, Murray LR. Re-injection of produced water - Field experience and current
1109 understanding. Society of Petroleum Engineers; 1994.
1110 [8] Hansen BR, Davies SH. Review of potential technologies for the removal of dissolved components
1111 from produced water. Chem Eng Res Des. 1994;72:176-88.
1112 [9] Fakhru'l-Razi A, Pendashteh A, Abdullah LC, Biak DR, Madaeni SS, Abidin ZZ. Review of
1113 technologies for oil and gas produced water treatment. J Hazard Mater. 2009;170:530-51.
1114 [10] Jiménez S, Micó MM, Arnaldos M, Medina F, Contreras S. State of the art of produced water
1115 treatment. Chemosphere. 2018;192:186-208.
1116 [11] Dickhout JM, Moreno J, Biesheuvel PM, Boels L, Lammertink RGH, de Vos WM. Produced water
1117 treatment by membranes: A review from a colloidal perspective. J Colloid Interface Sci.
1118 2017;487:523-34.
1119 [12] Sjöblom J, Skodvin T, Holt Ø, Nilsen FP. Colloid chemistry and modern instrumentation in
1120 offshore petroleum production and transport. Colloids Surf Physicochem Eng Aspects. 1997;123-
1121 124:593-607.
1122 [13] Sjöblom J, Aske N, Harald Auflem I, Brandal Ø, Erik Havre T, Sæther Ø, et al. Our current
1123 understanding of water-in-crude oil emulsions.: Recent characterization techniques and high
1124 pressure performance. Adv Colloid Interface Sci. 2003;100–102:399-473.
1125 [14] Kamp J, Villwock J, Kraume M. Drop coalescence in technical liquid/liquid applications: a review
1126 on experimental techniques and modeling approaches. Rev Chem Eng. Vol. 332017. p. 1.
1127 [15] Speight JG. The Chemistry and Technology of Petroleum. 4th Edition ed. Boca Raton, USA: CRC
1128 Press; 2006.
1129 [16] Gaweł B, Eftekhardadkhah M, Øye G. Elemental Composition and Fourier Transform Infrared
1130 Spectroscopy Analysis of Crude Oils and Their Fractions. Energy Fuels. 2014;28:997-1003.
1131 [17] Dudek M, Kancir E, Øye G. Influence of the Crude Oil and Water Compositions on the Quality of
1132 Synthetic Produced Water. Energy Fuels. 2017;31:3708-16.
1133 [18] Ray JP, Engelhardt FR. Produced Water: Technological/Environmental Issues and Solutions:
1134 Springer US; 1992.
1135 [19] Ruud T, Idrac A, McKenzie LJ, Høy SH. All Subsea: A Vision for the Future of Subsea Processing.
1136 Offshore Technology Conference; 2015.

1137   [20] Bringedal B, Ingebretsen T, Haugen K. Subsea Separation and Reinjection of Produced Water.
1138   Offshore Technology Conference. Houston, Texas: Offshore Technology Conference; 1999.
1139   [21] Hutin A, Argillier J-F, Langevin D. Mass Transfer between Crude Oil and Water. Part 1: Effect of
1140   Oil Components. Energy Fuels. 2014;28:7331-6.
1141   [22] Røe Utvik TI. Chemical characterisation of produced water from four offshore oil production
1142   platforms in the North Sea. Chemosphere. 1999;39:2593-606.
1143   [23] Stanford LA, Kim S, Klein GC, Smith DF, Rodgers RP, Marshall AG. Identification of Water-Soluble
1144   Heavy Crude Oil Organic-Acids, Bases, and Neutrals by Electrospray Ionization and Field Desorption
1145   Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. Environ Sci Technol.
1146   2007;41:2696-702.
1147   [24] Endo S, Pfennigsdorff A, Goss K-U. Salting-Out Effect in Aqueous NaCl Solutions: Trends with
1148   Size and Polarity of Solute Molecules. Environ Sci Technol. 2012;46:1496-503.
1149   [25] Grewer DM, Young RF, Whittal RM, Fedorak PM. Naphthenic acids and other acid-extractables
1150   in water samples from Alberta: What is being measured? Sci Total Environ. 2010;408:5997-6010.
1151   [26] Bertheussen A, Simon S, Sjöblom J. Equilibrium Partitioning of Naphthenic Acid Mixture, Part 1:
1152   Commercial Naphthenic Acid Mixture. Energy Fuels. 2018;32:7519-38.
1153   [27] Tibbetts PJC, Buchanan IT, Gawel LJ, Large R. A Comprehensive Determination of Produced
1154   Water Composition. In: Ray JP, Engelhardt FR, (editors). Produced Water:
1155   Technological/Environmental Issues and Solutions. Boston, MA: Springer US; 1992. p. 97-112.
1156   [28] Bakke T, Klungsøyr J, Sanni S. Environmental impacts of produced water and drilling waste
1157   discharges from the Norwegian offshore petroleum industry. Mar Environ Res. 2013;92:154-69.
1158   [29] Brendehaug J, Johnsen S, Bryne KH, Gjøse AL, Eide TH, Aamot E. Toxicity Testing and Chemical
1159   Characterization of Produced Water — A Preliminary Study. In: Ray JP, Engelhardt FR, (editors).
1160   Produced Water: Technological/Environmental Issues and Solutions. Boston, MA: Springer US; 1992.
1161   p. 245-56.
1162   [30] Derungs WA. Naphthenic Acid Corrosion —An Old Enemy Of the Petroleum Industry. Corrosion.
1163   1956;12:41-6.
1164   [31] Moiseeva LS, Kondrova OV. Biocorrosion of Oil and Gas Field Equipment and Chemical Methods
1165   for Its Suppression. I. Prot Met. 2005;41:385-93.
1166   [32] Wilde MJ, Rowland SJ. Naphthenic acids in oil sands process waters: Identification by conversion
1167   of the acids or esters to hydrocarbons. Org Geochem. 2018;115:188-96.
1168   [33] Wu C, De Visscher A, Gates ID. On naphthenic acids removal from crude oil and oil sands
1169   process-affected water. Fuel. 2019;253:1229-46.
1170   [34] Neff J, Lee K, DeBlois E. Produced Water: Overview of Composition, Fates and Effects. In: Lee K,
1171   Neff J, (editors). Produced Water: Environmental Risks and Advances in Mitigation Technologies.
1172   New York, NY: Springer New York; 2011. p. 3-54.
1173   [35] Henderson SB, Grigson SJW, Johnson P, Roddie BD. Potential Impact of Production Chemicals on
1174   the Toxicity of Produced Water Discharges from North Sea Oil Platforms. Mar Pollut Bull.
1175   1999;38:1141-51.
1176   [36] Strømgren T, Sørstrøm SE, Schou L, Kaarstad I, Aunaas T, Brakstad OG, et al. Acute toxic effects
1177   of produced water in relation to chemical composition and dispersion. Mar Environ Res.
1178   1995;40:147-69.
1179   [37] Somerville HJ, Bennett D, Davenport JN, Holt MS, Lynes A, Mahieu A, et al. Environmental effect
1180   of produced water from North Sea oil operations. Mar Pollut Bull. 1987;18:549-58.
1181   [38] Beyer J, Bakke T, Lichtenthaler R, Klungsøyr J. Environmental effects of offshore produced water
1182   discharges evaluated for the Barents Sea. Oslo, Norway: Norsk Institutt for Vannforskning; 2019.
1183   [39] Niu H, Lee K, Robinson B, Cobanli S, Li P. Monitoring and modeling the dispersion of produced
1184   water on the Scotian Shelf. Environmental Systems Research. 2016;5:19.
1185   [40] Lofthus S, Almås IK, Evans P, Pelz O, Brakstad OG. Biodegradation in seawater of PAH and
1186   alkylphenols from produced water of a North Sea platform. Chemosphere. 2018;206:465-73.

1187 [41] Kralova I, Sjöblom J, Øye G, Simon S, Grimes BA, Paso K. Heavy Crude Oils/Particle Stabilized
1188 Emulsions. Adv Colloid Interface Sci. 2011;169:106-27.
1189 [42] Deng S, Yu G, Chen Z, Wu D, Xia F, Jiang N. Characterization of suspended solids in produced
1190 water in Daqing oilfield. Colloids Surf Physicochem Eng Aspects. 2009;332:63-9.
1191 [43] Kelland MA. Production Chemicals for the Oil and Gas Industry. Boca Raton: CRC Press; 2014.
1192 [44] OLF. 2007 Environmental Report. 2007.
1193 [45] Miljødirektoratet. Work towards the zero discharge goal on discharges to sea in the petroleum
1194 offshore sector. Miljødirektoratet; 2016.
1195 [46] Mueller J, Cen Y, Davis RH. Crossflow microfiltration of oily water. J Membr Sci. 1997;129:221-
1196 35.
1197 [47] Arnold K, Stewart M, Stewart MI, Stewart MI. Surface Production Operations: Design of Oil-
1198 Handling Systems and Facilities. Second ed. Woburn: Gulf Professional Publishing; 1999.
1199 [48] Rawlins CH. Sand Management Methodologies for Sustained Facilities Operations. Society of
1200 Petroleum Engineers; 2013.
1201 [49] Judd S, Qiblawey H, Al-Marri M, Clarkin C, Watson S, Ahmed A, et al. The size and performance
1202 of offshore produced water oil-removal technologies for reinjection. Sep Purif Technol.
1203 2014;134:241-6.
1204 [50] Saththasivam J, Loganathan K, Sarp S. An overview of oil–water separation using gas flotation
1205 systems. Chemosphere. 2016;144:671-80.
1206 [51] Weschenfelder SE, Louvisse AMT, Borges CP, Meabe E, Izquierdo J, Campos JC. Evaluation of
1207 ceramic membranes for oilfield produced water treatment aiming reinjection in offshore units.
1208 Journal of Petroleum Science and Engineering. 2015;131:51-7.
1209 [52] Zsirai T, Al-Jaml AK, Qiblawey H, Al-Marri M, Ahmed A, Bach S, et al. Ceramic membrane
1210 filtration of produced water: Impact of membrane module. Sep Purif Technol. 2016;165:214-21.
1211 [53] Walstra P. Principles of emulsion formation. Chem Eng Sci. 1993;48:333-49.
1212 [54] Ramkrishna D. The Status of Population Balances. Rev Chem Eng. Vol. 31985. p. 49.
1213 [55] Tadros TF. Emulsion Formation and Stability: Wiley; 2013.
1214 [56] Kolmogorov AN. On the disintegration of drops in a turbulent flow. Dokl Akad Nauk SSSR.
1215 1949;66:4.
1216 [57] Hinze JO. Fundamentals of the hydrodynamic mechanism of splitting in dispersion processes.
1217 AIChE J. 1955;1:289-95.
1218 [58] Liao Y, Lucas D. A literature review of theoretical models for drop and bubble breakup in
1219 turbulent dispersions. Chem Eng Sci. 2009;64:3389-406.
1220 [59] Solsvik J, Tangen S, Jakobsen Hugo A. On the constitutive equations for fluid particle breakage.
1221 Rev Chem Eng. Vol. 292013. p. 241.
1222 [60] Liao Y, Lucas D. A literature review on mechanisms and models for the coalescence process of
1223 fluid particles. Chem Eng Sci. 2010;65:2851-64.
1224 [61] Danov KD. Effect of Surfactants on Drop Stability and Thin Film Drainage. In: Starov V, Ivanov I,
1225 (editors). Fluid Mechanics of Surfactant and Polymer Solutions. Vienna: Springer Vienna; 2004. p. 1-
1226 38.
1227 [62] Chesters AK. The modelling of coalescence processes in fluid-liquid dispersions: a review of
1228 current understanding. Chem Eng Res Des. 1991;69:259-70.
1229 [63] Chen J-D. A model of coalescence between two equal-sized spherical drops or bubbles. J Colloid
1230 Interface Sci. 1985;107:209-20.
1231 [64] Ninham BW, Lo Nostro P. Molecular Forces and Self Assembly in Colloid, Nano Sciences and
1232 Biology. 1 ed. Cambridge: Cambridge University Press; 2010.
1233 [65] Gregory J. The Role of Colloid Interactions in Solid-Liquid Separation. Water Sci Technol.
1234 1993;27:1-17.
1235 [66] Gaweł B, Lesaint C, Bandyopadhyay S, Øye G. Role of Physicochemical and Interfacial Properties
1236 on the Binary Coalescence of Crude Oil Drops in Synthetic Produced Water. Energy Fuels.
1237 2015;29:512-9.

1238   [67] Zangaeva E. Produced water challenges. Influence of production chemicals on flocculation.
1239   [Master thesis]. Stavanger, Norway: University of Stavanger; 2010.
1240   [68] Strickland WT, Jr. Laboratory Results of Cleaning Produced Water by Gas Flotation. Soc Pet Eng
1241   J. 1980:175-81.
1242   [69] Niewiadomski M, Nguyen AV, Hupka J, Nalaskowski J, Miller JD. Air bubble and oil droplet
1243   interactions in centrifugal fields during air-sparged hydrocyclone flotation. Int J Environ Pollut.
1244   2007;30:313-31.
1245   [70] Nguyen AV, Schulze HJ. Colloidal Science of Flotation. Boca Raton: CRC Press; 2003.
1246   [71] Eftekhardadkhah M, Øye G. Dynamic Adsorption of Organic Compounds Dissolved in Synthetic
1247   Produced Water at Air Bubbles: The Influence of the Ionic Composition of Aqueous Solutions. Energy
1248   Fuels. 2013;27:5128-34.
1249   [72] Eftekhardadkhah M, Reynders P, Øye G. Dynamic adsorption of water soluble crude oil
1250   components at air bubbles. Chem Eng Sci. 2013;101:359-65.
1251   [73] Eftekhardadkhah M, Øye G. Induction and Coverage Times for Crude Oil Droplets Spreading on
1252   Air Bubbles. Environ Sci Technol. 2013;47:14154-60.
1253   [74] Eftekhardadkhah M, Aanesen SV, Rabe K, Øye G. Oil Removal from Produced Water during
1254   Laboratory- and Pilot-Scale Gas Flotation: The Influence of Interfacial Adsorption and Induction
1255   Times. Energy Fuels. 2015;29:7734-40.
1256   [75] Rawlins CH. Mechanisms for Flotation of Fine Oil Droplets. SME Annual Meeting and Exhibit.
1257   Denver, Co2011.
1258   [76] Oliveira RCG, Gonzalez G, Oliveira JF. Interfacial studies on dissolved gas flotation of oil droplets
1259   for water purification. Colloids Surf Physicochem Eng Aspects. 1999;154:127-35.
1260   [77] Masliyah J, Zhou ZJ, Xu Z, Czarnecki J, Hamza H. Understanding Water-Based Bitumen Extraction
1261   from Athabasca Oil Sands. The Canadian Journal of Chemical Engineering. 2004;82:628-54.
1262   [78] Bergeron V, Cooper P, Fischer C, Giermanska-Kahn J, Langevin D, Pouchelon A.
1263   Polydimethylsiloxane (PDMS)-based antifoams. Colloids Surf Physicochem Eng Aspects.
1264   1997;122:103-20.
1265   [79] Schubert H. Nanobubbles, hydrophobic effect, heterocoagulation and hydrodynamics in
1266   flotation. Int J Miner Process. 2005;78:11-21.
1267   [80] Etchepare R, Oliveira H, Azevedo A, Rubio J. Separation of emulsified crude oil in saline water by
1268   dissolved air flotation with micro and nanobubbles. Sep Purif Technol. 2017;186:326-32.
1269   [81] Simon S, Theiler S, Knudsen A, Øye G, Sjöblom J. Rheological Properties of Particle-Stabilized
1270   Emulsions. J Dispersion Sci Technol. 2010;31:632-40.
1271   [82] Dudášová D, Sjöblom J, Øye G. Characterization and Suspension Stability of Particles Recovered
1272   from Offshore Produced Water. Industrial & Engineering Chemistry Research. 2014;53:1431-6.
1273   [83] Gaweł B, Nourani M, Tichelkamp T, Øye G. Influence of the wettability of particles on the
1274   morphology and stability of crude oil–particle aggregates in synthetic produced water. Journal of
1275   Petroleum Science and Engineering. 2016;139:198-204.
1276   [84] Dudášová D, Simon S, Hemmingsen PV, Sjöblom J. Study of asphaltenes adsorption onto
1277   different minerals and clays: Part 1. Experimental adsorption with UV depletion detection. Colloids
1278   Surf Physicochem Eng Aspects. 2008;317:1-9.
1279   [85] Hannisdal A, Ese M-H, Hemmingsen PV, Sjöblom J. Particle-stabilized emulsions: Effect of heavy
1280   crude oil components pre-adsorbed onto stabilizing solids. Colloids Surf Physicochem Eng Aspects.
1281   2006;276:45-58.
1282   [86] Farooq U, Simon S, Tweheyo MT, Øye G, Sjöblom J. Interfacial Tension Measurements Between
1283   Oil Fractions of a Crude Oil and Aqueous Solutions with Different Ionic Composition and pH. J
1284   Dispersion Sci Technol. 2013;34:701-8.
1285   [87] Hutin A, Argillier J-F, Langevin D. Influence of pH on Oil-Water Interfacial Tension and Mass
1286   Transfer for Asphaltenes Model Oils. Comparison with Crude Oil Behavior. Oil Gas Sci Technol – Rev
1287   IFP Energies nouvelles. 2016;71:58.

1288   [88] Moeini F, Hemmati-Sarapardeh A, Ghazanfari M-H, Masihi M, Ayatollahi S. Toward mechanistic
1289   understanding of heavy crude oil/brine interfacial tension: The roles of salinity, temperature and
1290   pressure. Fluid Phase Equilib. 2014;375:191-200.
1291   [89] Lashkarbolooki M, Ayatollahi S. Evaluation of effect of temperature and pressure on the
1292   dynamic interfacial tension of crude oil/aqueous solutions containing chloride anion through
1293   experimental and modelling approaches. The Canadian Journal of Chemical Engineering.
1294   2018;96:1396-402.
1295   [90] Poteau S, Argillier J-F, Langevin D, Pincet F, Perez E. Influence of pH on Stability and Dynamic
1296   Properties of Asphaltenes and Other Amphiphilic Molecules at the Oil–Water Interface†. Energy
1297   Fuels. 2005;19:1337-41.
1298   [91] Yarranton HW, Sztukowski DM, Urrutia P. Effect of interfacial rheology on model emulsion
1299   coalescence: I. Interfacial rheology. J Colloid Interface Sci. 2007;310:246-52.
1300   [92] Quintero CG, Noïk C, Dalmazzone C, Grossiord JL. Formation Kinetics and Viscoelastic Properties
1301   of Water/Crude Oil Interfacial Films. Oil & Gas Science and Technology - Rev IFP. 2009;64:607-16.
1302   [93] Hutin A, Argillier J-F, Langevin D. Mass Transfer between Crude Oil and Water. Part 2: Effect of
1303   Sodium Dodecyl Benzenesulfonate for Enhanced Oil Recovery. Energy Fuels. 2014;28:7337-42.
1304   [94] Tichelkamp T, Teigen E, Nourani M, Øye G. Systematic study of the effect of electrolyte
1305   composition on interfacial tensions between surfactant solutions and crude oils. Chem Eng Sci.
1306   2015;132:244-9.
1307   [95] Dudek M, Øye G. Microfluidic Study on the Attachment of Crude Oil Droplets to Gas Bubbles.
1308   Energy Fuels. 2018;32:10513-21.
1309   [96] Ghorbanizadeh S, Rostami B. Surface and Interfacial Tension Behavior of Salt Water Containing
1310   Dissolved Amphiphilic Compounds of Crude Oil: The Role of Single-Salt Ionic Composition. Energy
1311   Fuels. 2017;31:9117-24.
1312   [97] Eftekhardadkhah M, Kløcker KN, Trapnes HH, Gaweł B, Øye G. Composition and Dynamic
1313   Adsorption of Crude Oil Components Dissolved in Synthetic Produced Water at Different pH Values.
1314   Ind Eng Chem Res. 2016;55:3084-90.
1315   [98] Gopalan B, Katz J. Break Up of Viscous Crude Oil Droplets Mixed With Dispersants in Locally
1316   Isotropic Turbulence. 2008:53-8.
1317   [99] Maaß S, Kraume M. Determination of breakage rates using single drop experiments. Chem Eng
1318   Sci. 2012;70:146-64.
1319   [100] Solsvik J, Jakobsen HA. Single drop breakup experiments in stirred liquid–liquid tank. Chem Eng
1320   Sci. 2015;131:219-34.
1321   [101] Herø EH, Forgia NL, Solsvik J, Jakobsen HA. Determination of Breakage Parameters in Turbulent
1322   Fluid-Fluid Breakage. Chemical Engineering & Technology. 2019;42:903-9.
1323   [102] Flumerfelt RW, Catalano AB, Tong C-H. On the Coalescence Characteristics of Low Tension Oil-
1324   Water-Surfactant Systems. In: Shah DO, (editor). Surface Phenomena in Enhanced Oil Recovery.
1325   Boston, MA: Springer US; 1981. p. 571-94.
1326   [103] Peru DA, Lorenz PB. The Effect of Equilibration Time and Temperature on Drop-Drop
1327   Coalescence of Wilmington Crude Oil in a Weakly Alkaline Brine. Chem Eng Commun. 1989;77:91-
1328   114.
1329   [104] Kourio MJ, Gourdon C, Casamatta G. Study of drop-interface coalescence: Drainage time
1330   measurement. Chemical Engineering & Technology. 1994;17:249-54.
1331   [105] He Y, Howes T, Litster JD, Ko GH. Experimental study of drop-interface coalescence in the
1332   presence of polymer stabilisers. Colloids Surf Physicochem Eng Aspects. 2002;207:89-104.
1333   [106] Ata S, Pugh RJ, Jameson GJ. The influence of interfacial ageing and temperature on the
1334   coalescence of oil droplets in water. Colloids Surf Physicochem Eng Aspects. 2011;374:96-101.
1335   [107] Ayirala SC, Yousef AA, Li Z, Xu Z. Coalescence of Crude Oil Droplets in Brine Systems: Effect of
1336   Individual Electrolytes. Energy Fuels. 2018;32:5763-71.
1337   [108] Yarranton HW, Urrutia P, Sztukowski DM. Effect of interfacial rheology on model emulsion
1338   coalescence: II. Emulsion coalescence. J Colloid Interface Sci. 2007;310:253-9.

1339 [109] Hirasaki GJ, Miller CA, Raney OG, Poindexter MK, Nguyen DT, Hera J. Separation of Produced
1340 Emulsions from Surfactant Enhanced Oil Recovery Processes. Energy Fuels. 2011;25:555-61.
1341 [110] Kamp J, Kraume M. Influence of drop size and superimposed mass transfer on coalescence in
1342 liquid/liquid dispersions – Test cell design for single drop investigations. Chem Eng Res Des.
1343 2014;92:635-43.
1344 [111] Villwock J, Gebauer F, Kamp J, Bart H-J, Kraume M. Systematic Analysis of Single Droplet
1345 Coalescence. Chemical Engineering & Technology. 2014;37:1103-11.
1346 [112] Gebauer F, Villwock J, Kraume M, Bart H-J. Detailed analysis of single drop coalescence—
1347 Influence of ions on film drainage and coalescence time. Chem Eng Res Des. 2016;115:282-91.
1348 [113] Luo X, Huang X, Yan H, Yang D, Zhang P, He L. An experimental study on the coalescence
1349 behavior of oil droplet in ASP solution. Sep Purif Technol. 2018;203:152-8.
1350 [114] Bremond N, Bibette J. Exploring emulsion science with microfluidics. Soft Matter.
1351 2012;8:10549-59.
1352 [115] Bao B, Riordon J, Mostowfi F, Sinton D. Microfluidic and nanofluidic phase behaviour
1353 characterization for industrial CO2, oil and gas. Lab Chip. 2017;17:2740-59.
1354 [116] Nowbahar A, Whitaker KA, Schmitt AK, Kuo T-C. Mechanistic Study of Water Droplet
1355 Coalescence and Flocculation in Diluted Bitumen Emulsions with Additives Using Microfluidics.
1356 Energy Fuels. 2017;31:10555-65.
1357 [117] Lin Y-J, Perrard A, Biswal SL, Hill RM, Trabelsi S. Microfluidic Investigation of Asphaltenes-
1358 Stabilized Water-in-Oil Emulsions. Energy Fuels. 2018.
1359 [118] Krebs T, Schroën K, Boom R. Coalescence dynamics of surfactant-stabilized emulsions studied
1360 with microfluidics. Soft Matter. 2012;8:10650-7.
1361 [119] Krebs T, Schroen K, Boom R. A microfluidic method to study demulsification kinetics. Lab Chip.
1362 2012;12:1060-70.
1363 [120] Dudek M, Fernandes D, Helno Herø E, Øye G. Microfluidic method for determining drop-drop
1364 coalescence and contact times in flow. Colloids Surf Physicochem Eng Aspects. 2020;586:124265.
1365 [121] Krebs T, Ershov D, Schroen CGPH, Boom RM. Coalescence and compression in centrifuged
1366 emulsions studied with in situ optical microscopy. Soft Matter. 2013;9:4026.
1367 [122] Dudek M, Muijlwijk K, Schroen CGPH, Øye G. The effect of dissolved gas on coalescence of oil
1368 drops studied with microfluidics. J Colloid Interface Sci. 2018;528:166-73.
1369 [123] Dudek M, Bertheussen A, Dumaire T, Øye G. Microfluidic Tools for Studying Coalescence of
1370 Crude Oil Droplets in Produced Water. Chem Eng Sci. 2018;191:448-58.
1371 [124] Dudek M, Chicault J, Øye G. Microfluidic investigation of crude oil droplet coalescence: effect
1372 of oil/water composition and droplet ageing. Energy Fuels. 2019.
1373 [125] Angle CW, Hamza HA. Drop sizes during turbulent mixing of toluene–heavy oil fractions in
1374 water. AlChE J. 2006;52:2639-50.
1375 [126] Angle CW, Hamza HA, Dabros T. Size distributions and stability of toluene diluted heavy oil
1376 emulsions. AlChE J. 2006;52:1257-66.
1377 [127] Angle CW, Dabros T, Hamza HA. Predicting sizes of toluene-diluted heavy oil emulsions in
1378 turbulent flow. Part 1—Application of two adsorption kinetic models for σE in two size predictive
1379 models. Chem Eng Sci. 2006;61:7309-24.
1380 [128] Deng S, Bai R, Chen JP, Yu G, Jiang Z, Zhou F. Effects of alkaline/surfactant/polymer on stability
1381 of oil droplets in produced water from ASP flooding. Colloids Surf Physicochem Eng Aspects.
1382 2002;211:275-84.
1383 [129] Angle CW, Hamza HA. Effects of sand and process water pH on toluene diluted heavy oil in
1384 water emulsions in turbulent flow. AlChE J. 2009;55:232-42.
1385 [130] S. Fernandes R, González G, F. Lucas E. Assessment of polymeric flocculants in oily water
1386 systems. Colloid Polym Sci. 2005;283:375-82.
1387 [131] Silset A, Flåten GR, Helness H, Melin E, Øye G, Sjöblom J. A Multivariate Analysis on the
1388 Influence of Indigenous Crude Oil Components on the Quality of Produced Water. Comparison
1389 Between Bench and Rig Scale Experiments. J Dispersion Sci Technol. 2010;31:392-408.

1390　[132] Hutter JL, Bechhoefer J. Measurement and manipulation of van der Waals forces in atomic-
1391　force microscopy. Journal of Vacuum Science & Technology B: Microelectronics and Nanometer
1392　Structures Processing, Measurement, and Phenomena. 1994;12:2251-3.
1393　[133] Ishida N, Sakamoto M, Miyahara M, Higashitani K. Attraction between Hydrophobic Surfaces
1394　with and without Gas Phase. Langmuir. 2000;16:5681-7.
1395　[134] Liu J, Xu Z, Masliyah J. Colloidal forces between bitumen surfaces in aqueous solutions
1396　measured with atomic force microscope. Colloids Surf Physicochem Eng Aspects. 2005;260:217-28.
1397　[135] Liu J, Zhang L, Xu Z, Masliyah J. Colloidal Interactions between Asphaltene Surfaces in Aqueous
1398　Solutions. Langmuir. 2006;22:1485-92.
1399　[136] Sylvester ND, Byeseda JJ. Oil/Water Separation by Induced-Air Flotation. Soc Pet Eng J. 1980.
1400　[137] Bai Z-s, Wang H-l, Tu S-T. Oil–water separation using hydrocyclones enhanced by air bubbles.
1401　Chem Eng Res Des. 2011;89:55-9.
1402　[138] da Silva SS, Chiavone-Filho O, de Barros Neto EL, Foletto EL. Oil removal from produced water
1403　by conjugation of flotation and photo-Fenton processes. J Environ Manage. 2015;147:257-63.
1404　[139] Multon Lance M, Viraraghavan T. Removal of Oil from Produced Water by Dissolved Air
1405　Flotation. Pract Periodical Hazard, Toxic, Radioact Waste Manage. 2008;12:25-9.
1406　[140] Oliveira HA, Azevedo AC, Etchepare R, Rubio J. Separation of emulsified crude oil in saline
1407　water by flotation with micro- and nanobubbles generated by a multiphase pump. Water Sci
1408　Technol. 2017;76:2710-8.
1409　[141] Chakibi H, Hénaut I, Salonen A, Langevin D, Argillier JF. Role of Bubble–Drop Interactions and
1410　Salt Addition in Flotation Performance. Energy Fuels. 2018;32:4049-56.
1411　[142] Nikolov AD, Randie M, Shetty CS, Wasan DT. Chemical Demulsification of Oil-in-Water
1412　Emulsion using Air-Flotation: The Importance of Film Thickness Stability. Chem Eng Commun.
1413　1996;152-153:337-50.
1414　[143] Gu G, Xu Z, Nandakumar K, Masliyah J. Effects of physical environment on induction time of
1415　air–bitumen attachment. Int J Miner Process. 2003;69:235-50.
1416　[144] Wang L, Sharp D, Masliyah J, Xu Z. Measurement of Interactions between Solid Particles, Liquid
1417　Droplets, and/or Gas Bubbles in a Liquid using an Integrated Thin Film Drainage Apparatus.
1418　Langmuir. 2013;29:3594-603.
1419　[145] Ren S, Masliyah J, Xu Z. Studying bitumen–bubble interactions using atomic force microscopy.
1420　Colloids Surf Physicochem Eng Aspects. 2014;444:165-72.
1421　[146] Fan J, Sappington EN, Rifai HS, Rodrigues DF. Confocal microscopy as a new real-time
1422　quantification method for oil content in produced water. Journal of Petroleum Science and
1423　Engineering. 2018;167:54-63.
1424　[147] Fan J, Louie SM, Rodrigues DF. The Influence of Salinity, pH, Temperature and Particles on
1425　Produced Water Oil Quantification Precision and Accuracy with Confocal Laser Fluorescence
1426　Microscopy. Energy Fuels. 2018;32:6978-89.
1427　[148] Dudášová D, Flåten GR, Sjöblom J, Øye G. Study of asphaltenes adsorption onto different
1428　minerals and clays: Part 2. Particle characterization and suspension stability. Colloids Surf
1429　Physicochem Eng Aspects. 2009;335:62-72.
1430　[149] Ottaviano JG, Cai J, Murphy RS. Assessing the decontamination efficiency of a three-
1431　component flocculating system in the treatment of oilfield-produced water. Water Res.
1432　2014;52:122-30.
1433　[150] Clark PE, Pilehvari A. Characterization of crude oil-in-water emulsions. Journal of Petroleum
1434　Science and Engineering. 1993;9:165-81.
1435　[151] Salama AIA, Mikula RJ. Particle and Suspension Characterization. Suspensions: Fundamentals
1436　and Applications in the Petroleum Industry. Vol. 251: American Chemical Society; 1996. Chapter 2. p.
1437　45-106.
1438　[152] Yang M. Measurement of Oil in Produced Water. In: Lee K, Neff J, (editors). Produced Water:
1439　Environmental Risks and Advances in Mitigation Technologies. New York, NY: Springer New York;
1440　2011. p. 57-88.

1441   [153] Wagner L, Kalli C, Fridjonsson EO, May EF, Stanwix PL, Graham BF, et al. Quantitative produced
1442   water analysis using mobile ^{1}H NMR. Meas Sci Technol. 2016;27.
1443   [154] Wagner L, Kalli C, Fridjonsson EO, May EF, Zhen J, Johns ML. Simultaneous quantification of
1444   aliphatic and aromatic hydrocarbons in produced water analysis using mobile ^{1}H NMR. Meas Sci
1445   Technol. 2018;29.
1446   [155] Holstad MB, Johansen GA. Produced water characterization by dual modality gamma-ray
1447   measurements. Meas Sci Technol. 2005;16:1007.
1448   [156] McMahon PB, Kulongoski JT, Vengosh A, Cozzarelli IM, Landon MK, Kharaka YK, et al. Regional
1449   patterns in the geochemistry of oil-field water, southern San Joaquin Valley, California, USA. Appl
1450   Geochem. 2018;98:127-40.
1451   [157] Warner NR, Darrah TH, Jackson RB, Millot R, Kloppmann W, Vengosh A. New Tracers Identify
1452   Hydraulic Fracturing Fluids and Accidental Releases from Oil and Gas Operations. Environ Sci
1453   Technol. 2014;48:12552-60.
1454   [158] Kadnar R. Determination of alkali and alkaline earth metals in oilfield waters by ion
1455   chromatography. J Chromatogr A. 1998;804:217-21.
1456   [159] Dórea HS, Bispo JRL, Aragão KAS, Cunha BB, Navickiene S, Alves JPH, et al. Analysis of BTEX,
1457   PAHs and metals in the oilfield produced water in the State of Sergipe, Brazil. Microchem J.
1458   2007;85:234-8.
1459   [160] Freire AS, Santelli RE. Trace elements determination in high salinity petroleum produced
1460   formation water by high-resolution continuum source graphite furnace atomic absorption
1461   spectrometry after matrix separation using Chelex-100® resin. Spectrochimica Acta Part B: Atomic
1462   Spectroscopy. 2012;71-72:92-7.
1463   [161] Penha TR, Almeida JR, Sousa RM, de Castro EVR, Carneiro MTWD, Brandão GP. Multielement
1464   analysis of crude oil produced water by ICP OES after acid digestion assisted by microwave. J Anal At
1465   Spectrom. 2015;30:1154-60.
1466   [162] Oliveira EP, Yang L, Sturgeon RE, Santelli RE, Bezerra MA, Willie SN, et al. Determination of
1467   trace metals in high-salinity petroleum produced formation water by inductively coupled plasma
1468   mass spectrometry following on-line analyte separation/preconcentration. J Anal At Spectrom.
1469   2011;26:578-85.
1470   [163] Bostick DT, Luo H, Hindmarsh B. Characterization of Soluble Organics in Produced Water. Oak
1471   Ridge National Laboratory; 2002.
1472   [164] Floquet CFA, Sieben VJ, MacKay BA, Mostowfi F. Determination of boron concentration in
1473   oilfield water with a microfluidic ion exchange resin instrument. Talanta. 2016;154:304-11.
1474   [165] Thomas O, El Khorassani H, Touraud E, Bitar H. TOC versus UV spectrophotometry for
1475   wastewater quality monitoring. Talanta. 1999;50:743-9.
1476   [166] Eftekhardadkhah M, Øye G. Correlations between crude oil composition and produced water
1477   quality: A multivariate analysis approach. Ind Eng Chem Res. 2013;52:17315-21.
1478   [167] Bourgeois W, Burgess JE, Stuetz RM. On-line monitoring of wastewater quality: a review.
1479   Journal of Chemical Technology & Biotechnology. 2001;76:337-48.
1480   [168] Mills MA, McDonald TJ, Bonner JS, Simon MA, Autenrieth RL. Method for quantifying the fate
1481   of petroleum in the environment. Chemosphere. 1999;39:2563-82.
1482   [169] Faksness L-G, Grini PG, Daling PS. Partitioning of semi-soluble organic compounds between the
1483   water phase and oil droplets in produced water. Mar Pollut Bull. 2004;48:731-42.
1484   [170] Lu J, Wang X, Shan B, Li X, Wang W. Analysis of chemical compositions contributable to
1485   chemical oxygen demand (COD) of oilfield produced water. Chemosphere. 2006;62:322-31.
1486   [171] McFarlane JB, Debra T., Luo H. Characterization and modeling of produced water. Council
1487   Produced Water Conference. Colorado Springs2002.
1488   [172] Lewis AT, Tekavec TN, Jarvis JM, Juyal P, McKenna AM, Yen AT, et al. Evaluation of the
1489   Extraction Method and Characterization of Water-Soluble Organics from Produced Water by Fourier
1490   Transform Ion Cyclotron Resonance Mass Spectrometry. Energy Fuels. 2013;27:1846-55.

1491   [173] Sirivedhin T, Dallbauman L. Organic matrix in produced water from the Osage-Skiatook
1492   Petroleum Environmental Research site, Osage county, Oklahoma. Chemosphere. 2004;57:463-9.
1493   [174] Scott AC, Young RF, Fedorak PM. Comparison of GC–MS and FTIR methods for quantifying
1494   naphthenic acids in water samples. Chemosphere. 2008;73:1258-64.
1495   [175] Headley JV, Peru KM, Barrow MP, Derrick PJ. Characterization of Naphthenic Acids from
1496   Athabasca Oil Sands Using Electrospray Ionization: The Significant Influence of Solvents. Anal Chem.
1497   2007;79:6222-9.
1498   [176] Mapolelo MM, Rodgers RP, Blakney GT, Yen AT, Asomaning S, Marshall AG. Characterization of
1499   naphthenic acids in crude oils and naphthenates by electrospray ionization FT-ICR mass
1500   spectrometry. Int J Mass spectrom. 2011;300:149-57.
1501   [177] Sun C, Shotyk W, Cuss CW, Donner MW, Fennell J, Javed M, et al. Characterization of
1502   Naphthenic Acids and Other Dissolved Organics in Natural Water from the Athabasca Oil Sands
1503   Region, Canada. Environ Sci Technol. 2017;51:9524-32.
1504   [178] Merlin M, Guigard SE, Fedorak PM. Detecting naphthenic acids in waters by gas
1505   chromatography–mass spectrometry. J Chromatogr A. 2007;1140:225-9.
1506   [179] Bertheussen A, Simon S, Sjöblom J. Equilibrium Partitioning of Naphthenic Acid Mixture Part 2:
1507   Crude Oil-Extracted Naphthenic Acids. Energy Fuels. 2018;32:9142-58.
1508   [180] Headley JV, Peru KM, Fahlman B, Colodey A, McMartin DW. Selective solvent extraction and
1509   characterization of the acid extractable fraction of Athabasca oils sands process waters by Orbitrap
1510   mass spectrometry. Int J Mass spectrom. 2013;345-347:104-8.
1511   [181] Holowenko FM, MacKinnon MD, Fedorak PM. Characterization of naphthenic acids in oil sands
1512   wastewaters by gas chromatography-mass spectrometry. Water Res. 2002;36:2843-55.
1513   [182] St. John WP, Rughani J, Green SA, McGinnis GD. Analysis and characterization of naphthenic
1514   acids by gas chromatography–electron impact mass spectrometry of tert.-butyldimethylsilyl
1515   derivatives. J Chromatogr A. 1998;807:241-51.
1516   [183] OECD. Test No. 107: Partition Coefficient (n-octanol/water): Shake Flask Method1995.
1517   [184] Shiu WY, Bobra M, Bobra AM, Maijanen A, Suntio L, Mackay D. The water solubility of crude
1518   oils and petroleum products. Oil and Chemical Pollution. 1990;7:57-84.
1519   [185] Spildo K, Høiland H. Interfacial Properties and Partitioning of 4-Heptylbenzoic Acid between
1520   Decane and Water. J Colloid Interface Sci. 1999;209:99-108.
1521   [186] Page CA, Bonner JS, Sumner PL, Autenrieth RL. Solubility of petroleum hydrocarbons in
1522   oil/water systems. Mar Chem. 2000;70:79-87.
1523   [187] Sterling MC, Bonner JS, Page CA, Fuller CB, Ernest ANS, Autenrieth RL. Partitioning of Crude Oil
1524   Polycyclic Aromatic Hydrocarbons in Aquatic Systems. Environ Sci Technol. 2003;37:4429-34.
1525   [188] Bennett B, Larter SR. Partition behaviour of alkylphenols in crude oil/brine systems under
1526   subsurface conditions. Geochim Cosmochim Acta. 1997;61:4393-402.
1527   [189] Bennett B, Aplin AC, Larter SR. Measurement of partition coefficients of phenol and cresols in
1528   gas-charged crude oil/water systems. Org Geochem. 2003;34:1581-90.
1529   [190] Jaggi A, Snowdon RW, Stopford A, Radović JR, Oldenburg TBP, Larter SR. Experimental
1530   simulation of crude oil-water partitioning behavior of BTEX compounds during a deep submarine oil
1531   spill. Org Geochem. 2017;108:1-8.
1532   [191] Breisig H, Schmidt M, Wolff H, Jupke A, Wessling M. Droplet-based liquid–liquid extraction
1533   inside a porous capillary. Chem Eng J. 2017;307:143-9.
1534   [192] Bowden SA, Monaghan PB, Wilson R, Parnell J, Cooper JM. The liquid-liquid diffusive extraction
1535   of hydrocarbons from a North Sea oil using a microfluidic format. Lab Chip. 2006;6:740-3.
1536   [193] Bowden SA, Wilson R, Parnell J, Cooper JM. Determination of the asphaltene and carboxylic
1537   acid content of a heavy oil using a microfluidic device. Lab Chip. 2009;9:828-32.
1538   [194] Assmann N, Ładosz A, Rudolf von Rohr P. Continuous Micro Liquid-Liquid Extraction. Chemical
1539   Engineering & Technology. 2013;36:921-36.
1540   [195] Ciceri D, Perera JM, Stevens GW. The use of microfluidic devices in solvent extraction. Journal
1541   of Chemical Technology & Biotechnology. 2014;89:771-86.

1542 [196] Dudášová D. Characterization of solid particle suspensions with organic coatings in oilfield
1543 produced water. Trondheim, Norway: Norwegian University of Science and Technology; 2008.

1544

1545 TABLES

1546 Table 1 Basic properties of produced water and seawater. Based on [8, 9, 18]

Parameter	Produced water		Seawater
	North Sea	World	
Density [kg/m^3]	1 014 – 1 085	1 014 – 1 140	1 020 – 1 029
Temperature [°C]	3 – 80	N/D	3 – 17
pH	6 – 7.7	4.3 – 10	7.6 – 8.3
Surface tension [mN/m]	N/D	43 – 78	72 – 73
Total Organic Carbon [mg/L]	0 – 1 500		0 – 1
Total dissolved solids [g/L]	Similar to seawater	0.1 to 300	Ca. 35

1547

1548

1549 Table 2 Concentrations of inorganic ions in produced water and seawater. Based on [27].

Ion	Concentration [mg/dm^3]	
	Produced water	Seawater
Cl^-	12 400-81 000	18 800-20 800
HCO_3^-	420-1430	134-155
SO_4^{2+}	18-1 650	2 810-2 960
Na^+	5 000-43 600	10 700-11 500
K^+	160-744	472-564
Mg^{2+}	25-791	1 180-1 322
Ca^{2+}	151-5 700	393-427
$Fe^{2+/3+}$	1-33	0-0.5
Ba^{2+}	1-218	0-0.1

1550

1551 FIGURE CAPTIONS

1552 Figure 1 Crude oil and water production profiles for the Heidrun oilfield in the North Sea.

1553 Based on [196]

1554   Figure 2 Offshore discharge of produced water. Discharge point is typically located under

1555   the platform (a), 10-20 m below the sea level. High dispersed oil concentration in the

1556   discharged waters can lead to an oily layer on the surface of the sea (b). Pictures courtesy of

1557   Eilen Arctander Vik, Aquateam COWI, anonymous sites 2008 & 2009.

1558   Figure 3 Micrographs of produced water from the production separator. Pictures from

1559   Aquateam COWI, anonymous site 2009.

1560   Figure 4 Schematic of an offshore crude oil, natural gas and water processing.

1561   Figure 5 Distribution of organic species (left) and detailed distribution of organic acids in PW

1562   samples (right), based on [6]. BTEX – Benzene, Toluene, Ethylbenzene, Xylene; PAH –

1563   Polycyclic aromatic hydrocarbon.

1564   Figure 6 Consecutive stages of coalescence: approach, contact, film rupture and formation

1565   of a new droplet.

1566   Figure 7 Illustration of the Marangoni effect during film drainage between two oil droplets

1567   in water.

1568   Figure 8 Snapshots of a droplet spreading around a bubble. From left to right: approach

1569   (first two pictures), contact, thin film breakage, spreading and an oil-coated bubble.

1570   Figure 9 Bubble-droplet attachment mechanisms.

1571   Figure 10 Image sequences of a drop breakup in a stirred tank. Figure reprinted from [100],

1572   Copyright (2015), with permission from Elsevier.

1573   Figure 11 Various coalescence measurement setups: (a) drop-interface, (b) drop-drop with

1574   optical detection and (c) drop-bubble micromanipulator (DBMM) with optical detection and

1575   capillary pressure measurements. Figure 11a reprinted from [105], Copyright (2002), with

1576   permission from Elsevier. Figure 11b reprinted from [106], Copyright (2011), with

1577   permission from Elsevier. Figure 11c reprinted with permission from [73], Copyright (2015)

1578   American Chemical Society.

1579   Figure 12 Microfluidic chip and setup for studying coalescence of crude oil drops. Figure

1580   reprinted from [123], Copyright (2018), with permission from Elsevier.

1581 Figure 13 Mixing apparatus for following the evolution of drop size distribution with light

1582 scattering technique. Figure reprinted from [144], Copyright (2006), with permission from

1583 Wiley.

1584 Figure 14 Setup for studying spreading of oil droplet on air-water surface. Figure reprinted

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1586 Figure 15 Drop-bubble micromanipulator for studying interactions between bubbles and

1587 crude oil droplets. Figure reprinted with permission from [73], Copyright (2013) American

1588 Chemical Society.

1589 Figure 16 Microscopic pictures of crude oil droplets in water: (a) covered with $BaSO_4$

1590 particles and (b) after alkaline/surfactant/polymer flooding. Figure 16a reprinted from [83],

1591 Copyright (2016), with permission from Elsevier. Figure 16b reprinted and adapted from

1592 [128], Copyright (2002), with permission from Elsevier.

1593 Figure 17 Extracted ion chromatograms with increasing mass ranges. Figure reprinted with

1594 permission from [179], Copyright (2018) American Chemical Society.

1595 Figure 18 Setup for measuring partition coefficients between water and crude oil. Figure

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1605 FIGURES
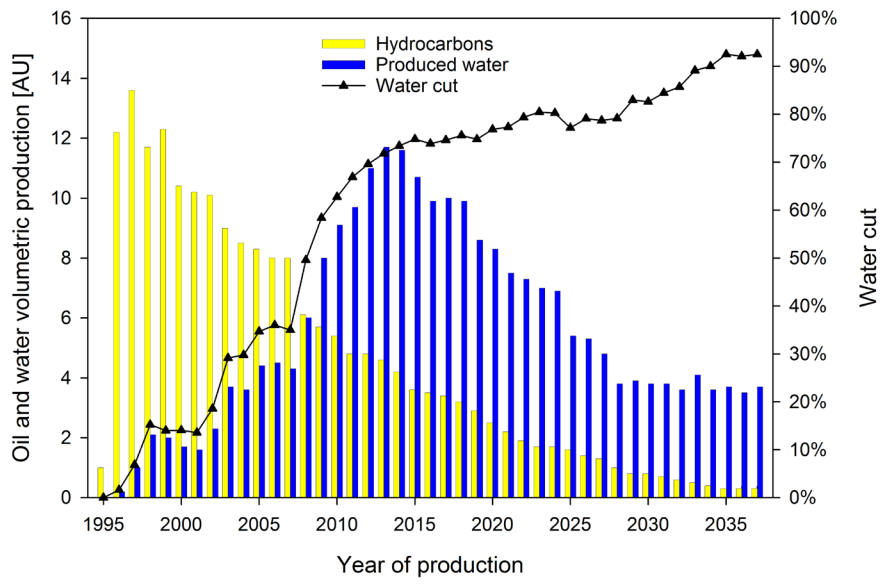
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1607   Figure 1
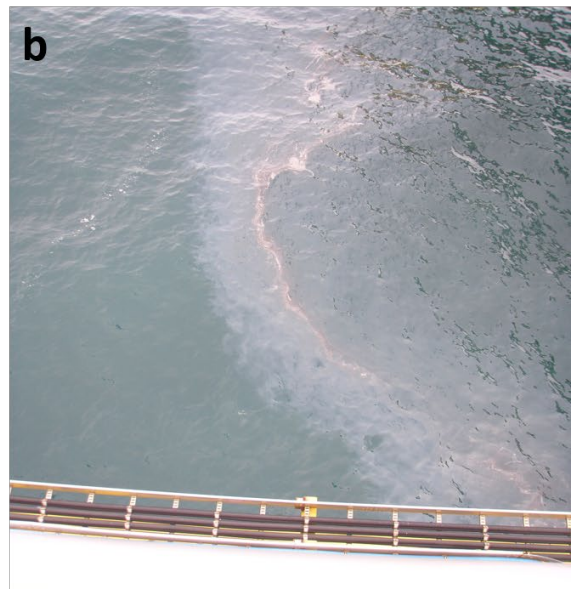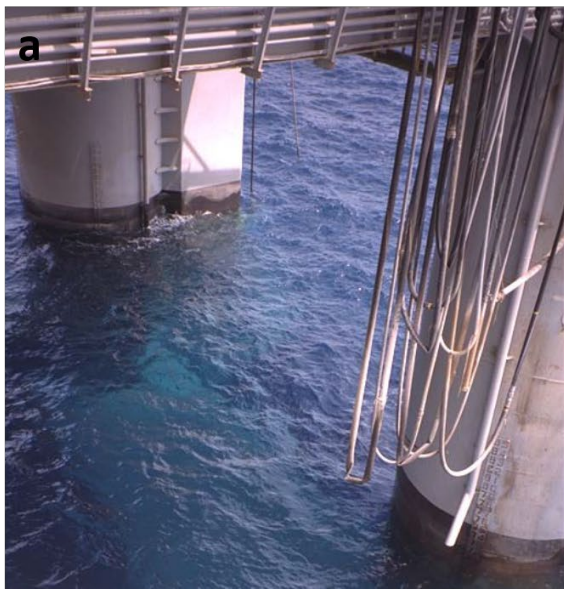
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1609   Figure 2

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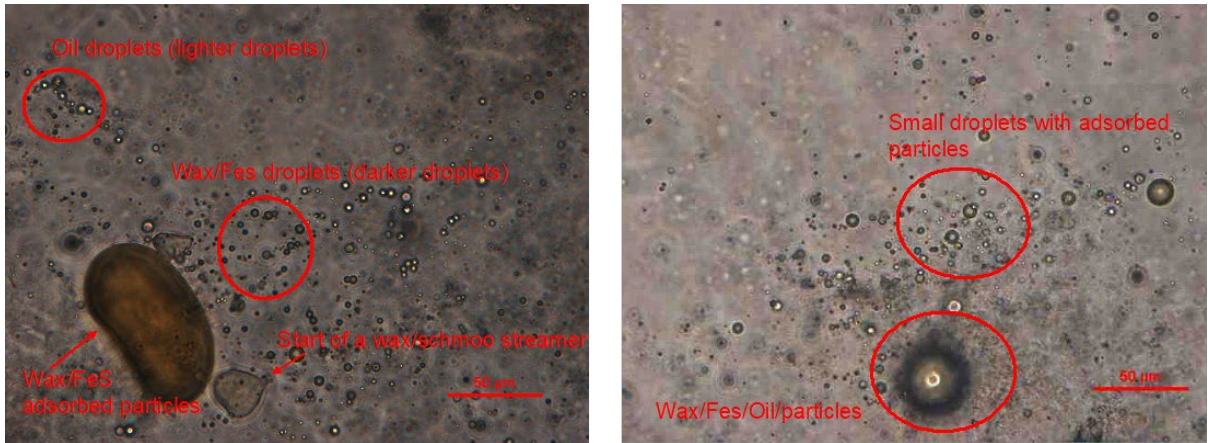
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1613   Figure 3

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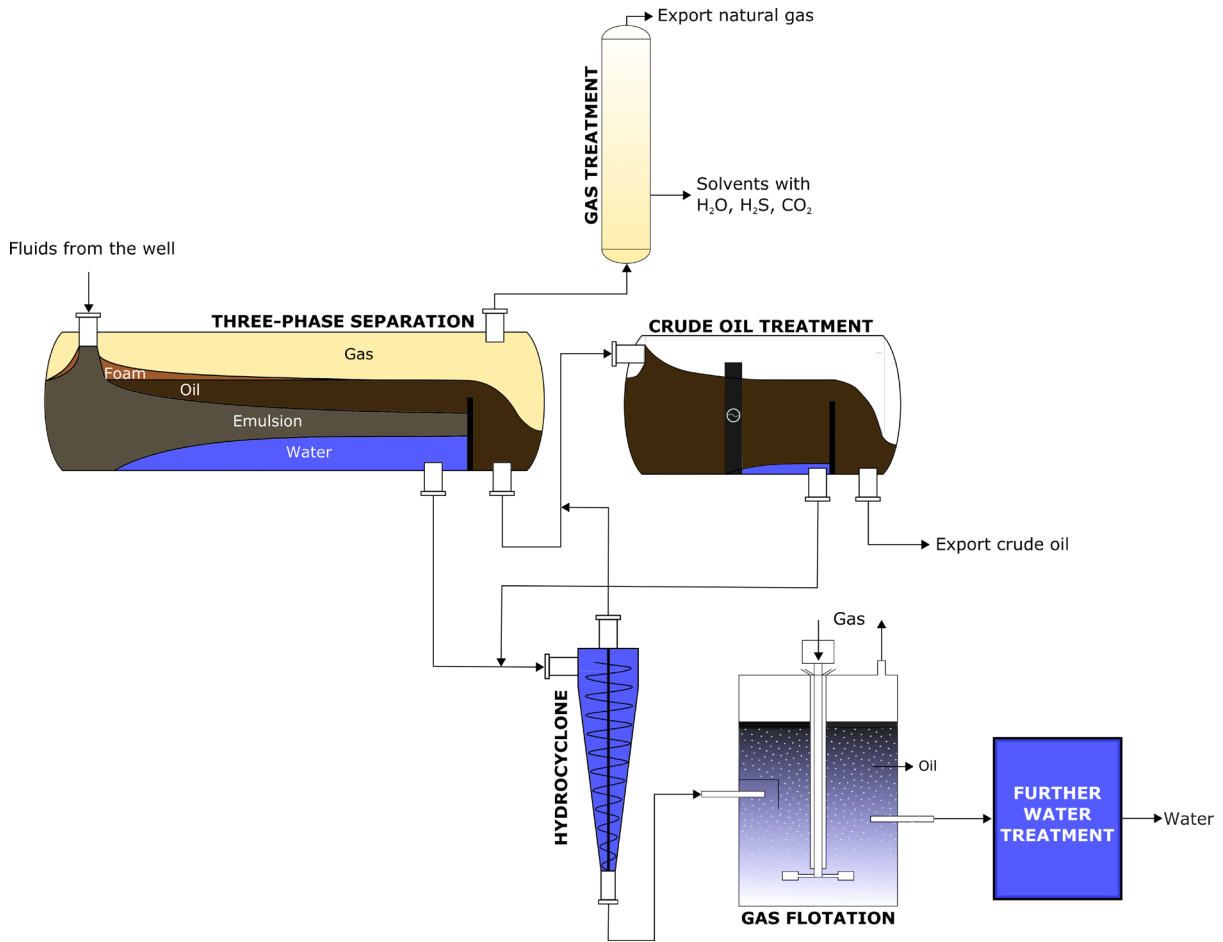
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1616   Figure 4

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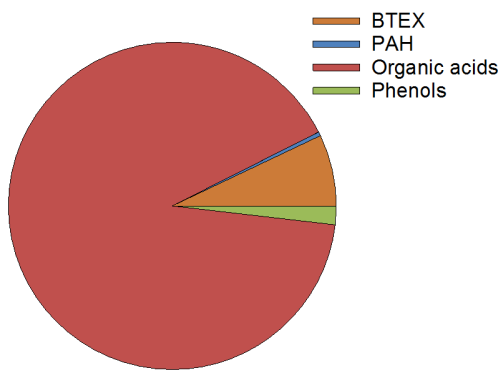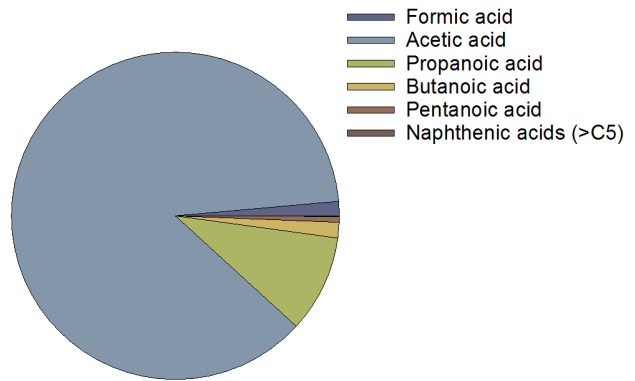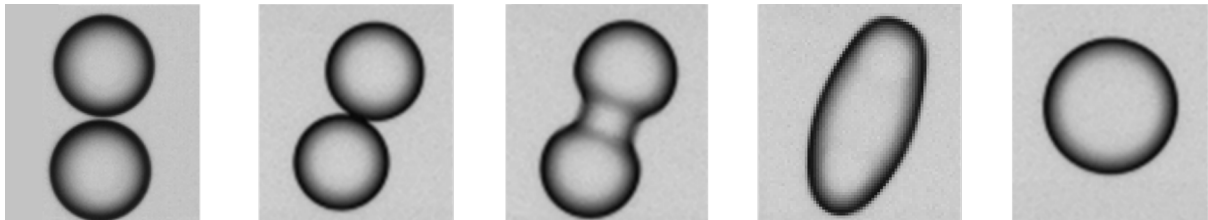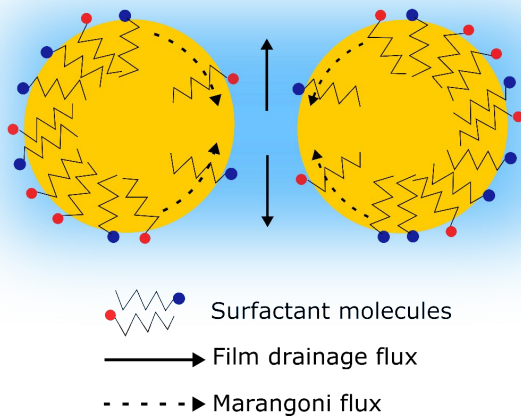
Figure 5
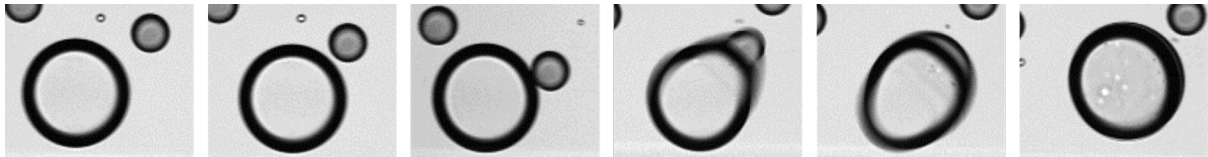
Figure 6

Figure 7

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1628   Figure 8

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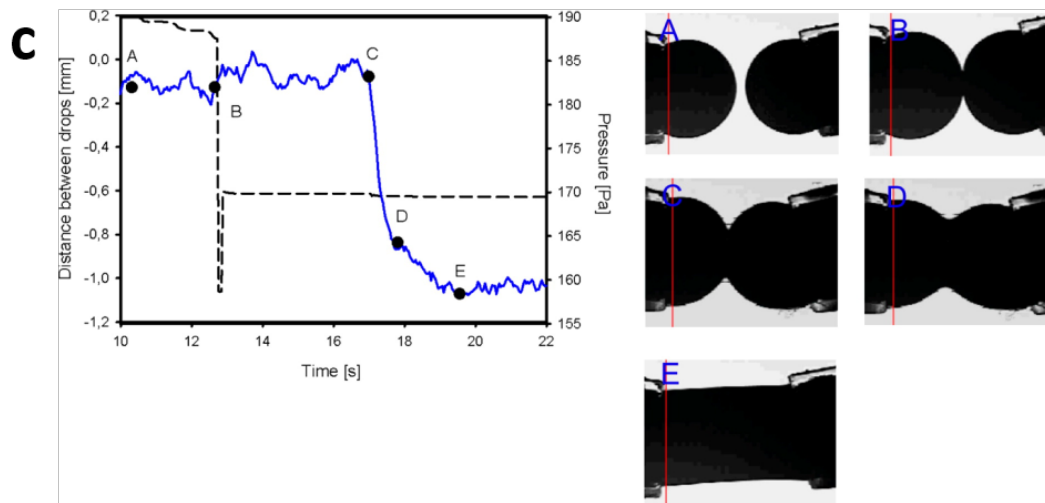a) Wake entrapment   b) Gas bubble cluster   c) Oil film   d) Oil lens
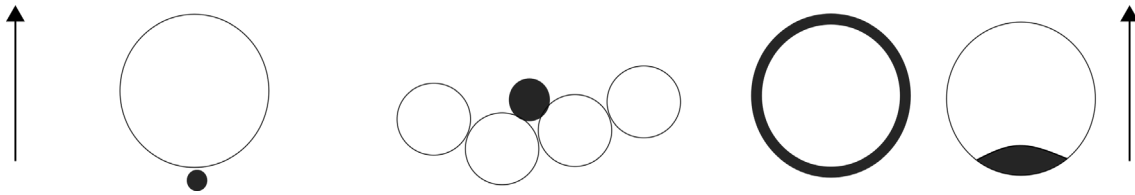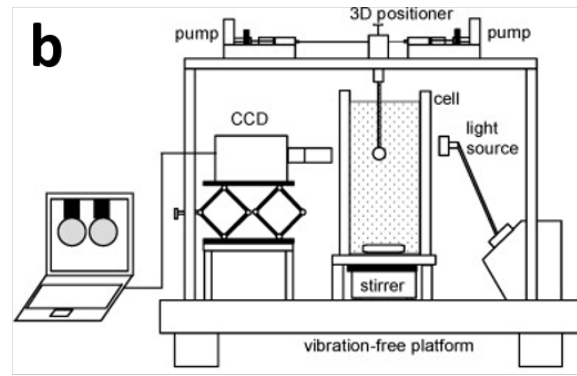
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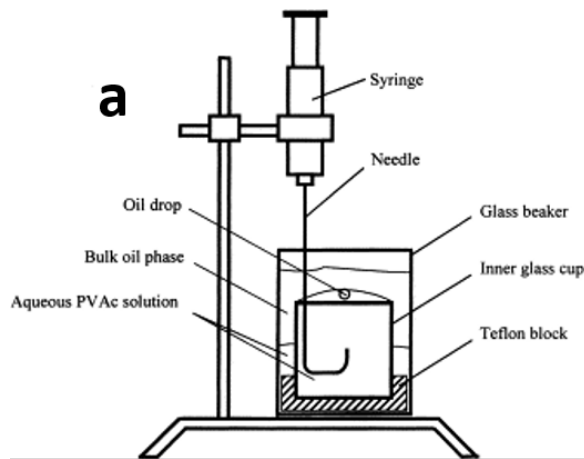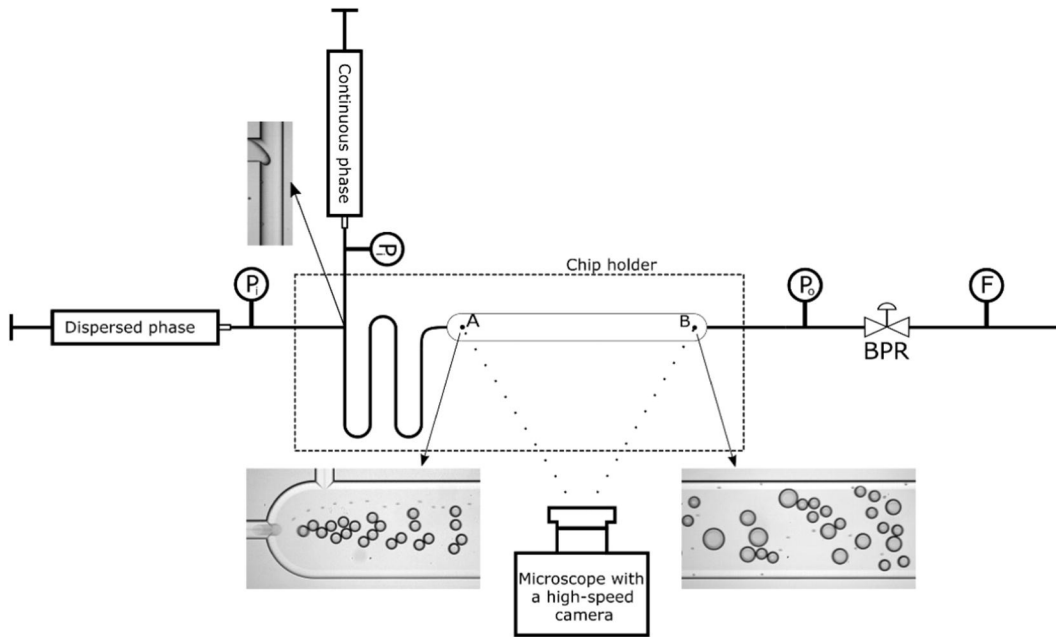
1631   Figure 9

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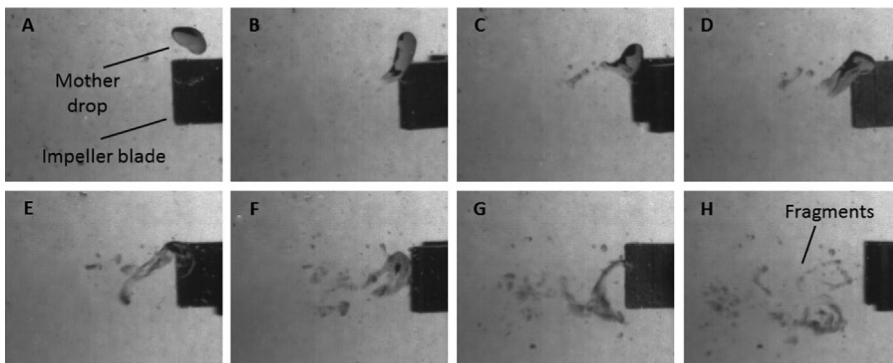
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1634   Figure 10
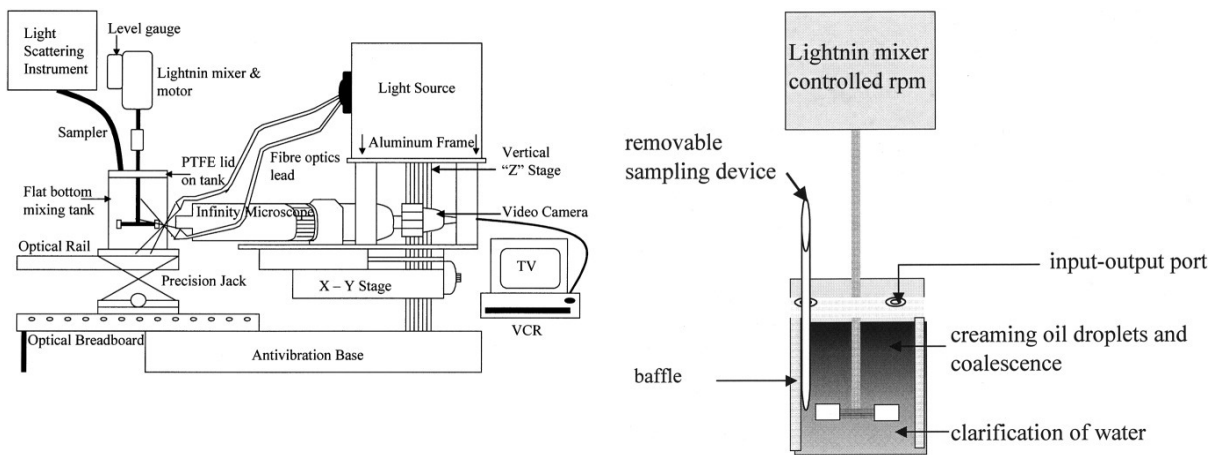
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1636   Figure 11
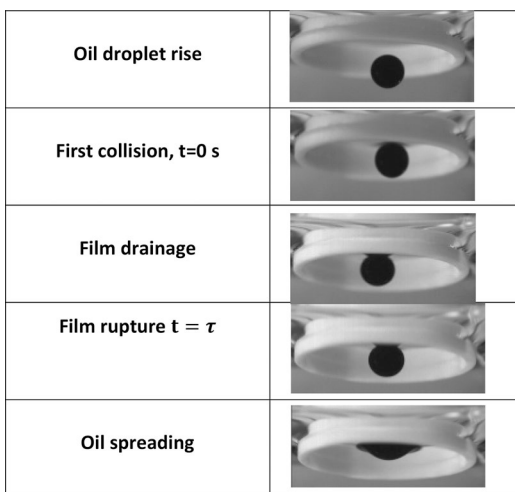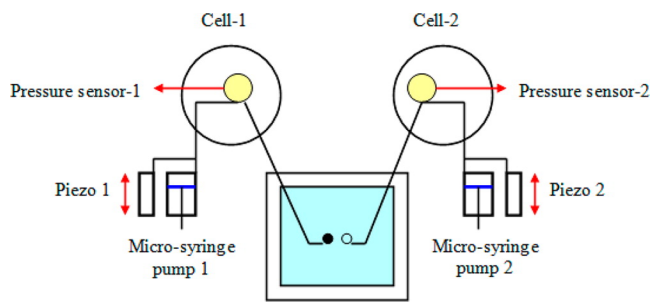
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Figure 12

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Figure 13

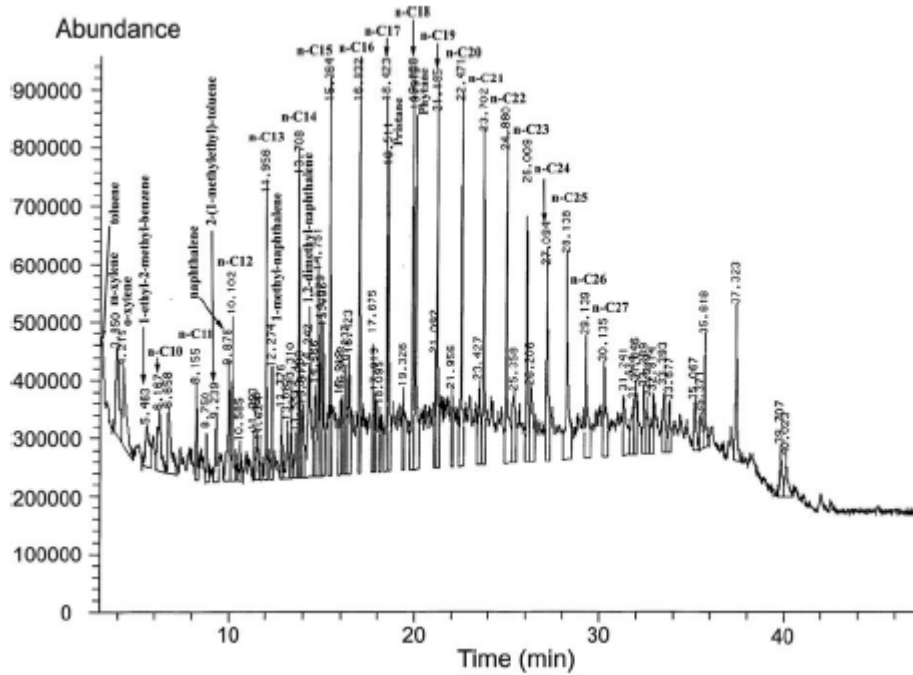|	
Oil droplet rise	
First collision, t=0 s	
Film drainage	
Film rupture t = τ	
Oil spreading	

1642
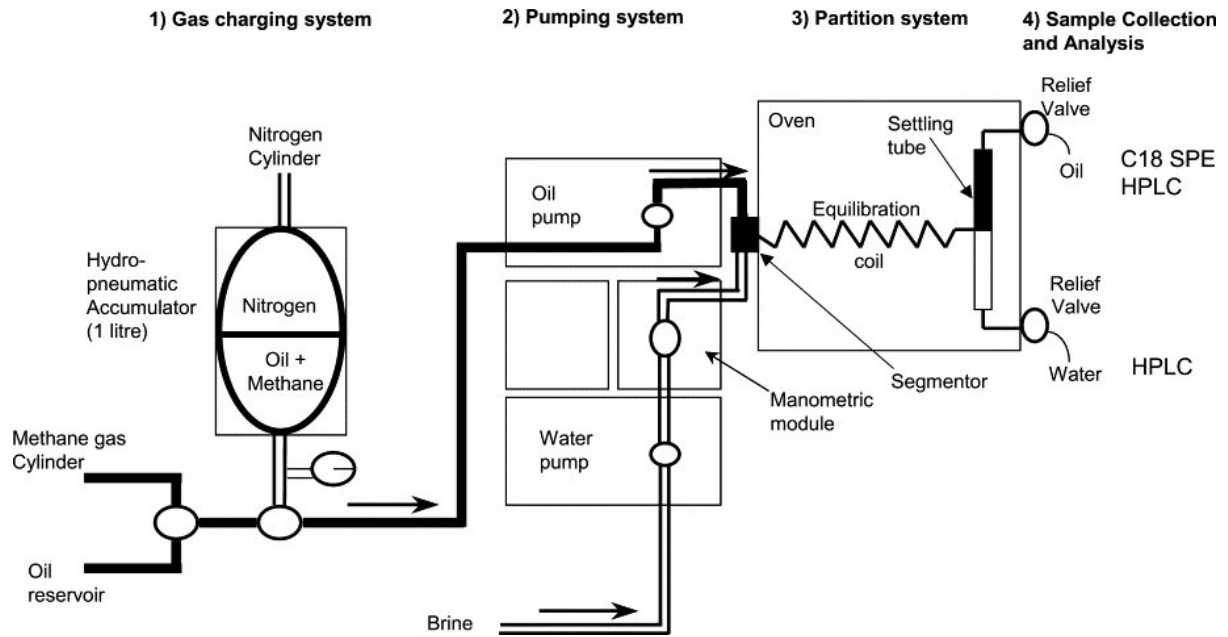
Figure 14

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Figure 15

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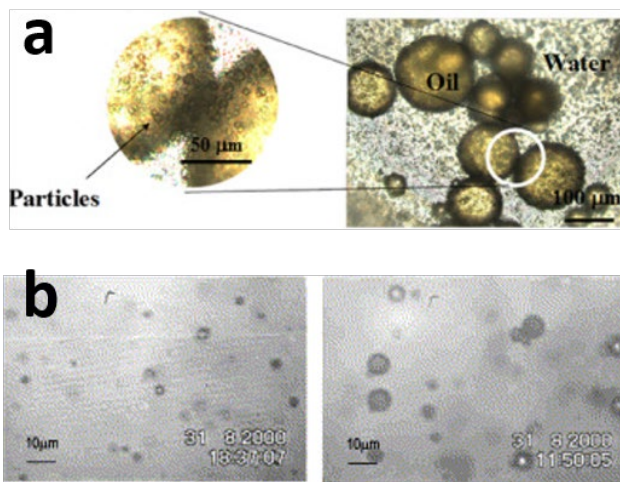
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1649   Figure 16

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1651   Figure 17

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1654   Figure 18