Introduction

Asphaltenes are the heaviest, most polar and most surface active species of crude oils which are insoluble in n-alkanes (e.g. n-hexane, n-heptane) and soluble in light aromatics (e.g. toluene, xylene) [1]. Asphaltenes have a high molecular weight and contain large polycyclic aromatic hydrocarbons with peripheral aliphatic chains which are embedded with a small amount of heteroatoms such as sulfur, oxygen and nitrogen [2]. They also consist of trace moieties of metals (in ppm) such as iron, nickel, and vanadium which can be appeared in porphyrin or non-porphyrin structures[2]. Based on asphaltene concentrations in crude oils, the asphaltene molecules are dispersed in the oleic phase with a size range of ~1.5 to ~5 nm in width [3]. It is widely believed that the asphaltene nano-aggregates will either flocculate to form larger particles which can flow through a channel (e.g. pipeline, porous media) or deposit on the surfaces. In many oil reservoirs, asphaltenes are fairly stable in the oil, however a small variation in pressure, composition, and temperature can cause asphaltene phase instability and alteration in their solubility parameter [4], and they can precipitate and aggregate out of the crude oil, leading to expensive deposition problems in pipelines, wells and porous media. Asphaltene related researches have become more intensive in recent years because of a growth in the production of high asphaltene heavy oils and gas injection based enhanced oil recovery (EOR) techniques. However, it is interesting to mention that there are many reports that mention light oils which are easy to flow with very low asphaltene content have more asphaltene deposition problems than crude oils with high asphaltene contents. Hence in order to set a suitable plan for removing asphaltene related flow assurance issues, finding the source of these problems and the capability to estimate the thermodynamical behaviour and fluid flow characteristics of crude oils including asphaltene molecules are so crucial. The EOR methods generally divided into different categories including thermal, chemical, gas and water injection techniques. The first action to be undertaken, when the oil reservoir pressure is depleted through primary and secondary oil production, is to restore the pressure within the reservoir or improve oil production rate as a tertiary recovery or enhanced oil recovery (EOR) methodology. In this regard, the CO₂ injection, water injection, water alternating gas (WAG) injection and carbonated water injection (CWI) can be ideal EOR approaches in many cases. Since the late 70’s, the gas injection (especially CO₂ injection) is one of the most promising approaches which has been gained great attention and success worldwide. Besides additional economic benefit through different EOR processes, environmentally safe and employing at least part of the existing infrastructure in injection methodologies (CO₂/Water/WAG injection/CWI), some of them might have some disadvantages such as asphaltene precipitation and deposition in heavy oil reservoirs which may lead to permeability reduction and wettability alterations of rock surface towards oil/mixed wet state. Therefore, it is crucial to meticulously investigate the influences of different EOR techniques on asphaltenes behaviour in oleic phase at real field representative conditions which has remained a gap in the literature. The aim of this research study is to investigate the effects of different gas injection scenarios and water flooding with various ionic strengths on asphaltene precipitation and deposition during the gas injection and/or WAG-EOR processes. Additionally, our research work could shed light on the main drivers behind the low salinity water flooding and denotes how critical a role water molecule perform at fluid-solid interfaces.

Experimental Methods

The quartz crystal microbalance is a very sensitive equipment for measuring and detecting the adsorption of very small amounts (nanogram range) of solids to the surface of piezoelectric quartz crystal by monitoring the alterations in resonance frequency. This device is mainly utilized for biological studies. Researchers at Heriot-Watt University have started the using of QCM in petroleum industry since 1992, covering various applications like saturation point and hydrate dissociation point determinations, evaluation of anti-depositional paint coatings, choosing the best chemical treatment for cleaning solids adhering to the pipeline surfaces and determination of asphaltene onset and the effect of variety of inhibitors on asphaltene deposition [5]. QCM technique can be utilized to determine the asphaltene stability by n-C₇₇ titration which is used in ASTM D7157. The advantage of QCM rather than ASTM D7157 is that there is no need to use an optical device in QCM technique. In this study, we have
developed a new prototype small volume multi-tasking QCM rig. Herein, the QCM experiments were conducted using AT-cut (optimized for 90 °C) 5 MHz quartz crystal coated with gold purchased from Testbourne Ltd. The diameter of the crystal is 25.4 mm, while the front electrode diameter is 12.7 mm, the crystal thickness is 333 μm, and the crystal surface roughness is 50 Å. Figure 1 depicts the picture of the high pressure-high temperature (HPHT) QCM setup.

**Figure 1.** Picture of HPHT-QCM setup employed in this study.

In this work, dead crude oil was mixed with different gases including CO\(_2\), CH\(_4\), Mix.A (20.05 mole% N\(_2\); 41.3 mole% CH\(_4\); 38.65 mole% CO\(_2\)) and natural gas (NG) (1.84 mole% N\(_2\); 89.94 mole% CH\(_4\); 0.91 mole% CO\(_2\); 5.32 mole% C\(_2\); 1.45 mole% C\(_3\); 0.2 mole% iC\(_4\); 0.2 mole% nC\(_4\); 0.07 mole% iC\(_5\); 0.06 mole% (nC\(_5\) + C\(_6\))) to illustrate the influences of these gases on asphaltene instability in crude oil. In order to investigate the effects of water molecules on asphaltene precipitation and deposition during water alternating gas injection process, we have employed freshly deionised (DI) water in which various combinations of NaCl, KCl, CaCl\(_2\), and MgCl\(_2\) (all purchased from Sigma-Aldrich; analytical grade, purity >99.5%) were dissolved. Different brines with ionic strength range of 100 mM-1 M have been prepared to represent the low salinity water and sea water which are flooded into the reservoirs for improving oil recovery.

**Results and Discussion**

The QCM resonant frequency (RF) was monitored during the gas injection process to detect the asphaltene onset pressure. The RF is inversely proportional to the mass of QCM crystal surface. As depicted in figure 2.a, the asphaltene onset points (AOPs)/Gas oil ratio (GOR) were detected by HPHT-QCM at ~1040 psia/17.9 mol%, ~1651 psia/26.1 mol%, ~2082 psia/32.2 mol%, and ~2360 psia/34.9 mol% for the injected CO\(_2\), natural gas, CH\(_4\), and Mix.A gases, respectively. The AOP are much lower for the crude oil with injected CO\(_2\) compared to other injected gases. The effects of added gases on reducing asphaltene stability in the crude oil used in this work are found in the following order: CO\(_2\) > Natural gas > CH\(_4\) > Mix.A. Figure 2.b shows the influences of injected gas type on incrementing asphaltene deposition rate onto the QCM surface after AOP for the crude oil employed in this work are found as the following order: CO\(_2\) (-1424.6 HZ/hr) > Natural gas (-609.2 HZ/hr) > CH\(_4\) (-351.9 HZ/hr) > Mix.A (-177.1 HZ/hr). Clearly, it is the same order as for aforementioned asphaltene instability in crude oil. We have also performed the experiments with injection of NG and oil in various gas/oil ratios (GORs) in presence of water micro-emulsions for representing the WAG-EOR conditions and determined the asphaltene onset point (AOP) and deposition rate onto the QCM surface.
Figure 2. a) The effect of injected gas type on asphaltene onset point obtained by HPHT-QCM technique; b) Change in RF vs. time which is representing asphaltene deposition rate affected by various injected gas types.

In figure 3.a, the diagram indicates change in RF versus pressure for NG and oil at various GORs in presence of DI water with/out different salt contents and ion valences to monitor the AOP alterations. The pressure at which the RF begins to drop signifies the AOP which is \(~954\) psi at GOR of \(~15.6\) mol\% for the blank crude oil. As can be observed in figure 3a, a distinct AOP shift is recognised in presence of high salinity (HS) brine for which the AOP/GOR is \(~1221\) psia/21.8 mol\%.

The AOP/GOR is \(~1360\) psia/23.9 mol\% for 0.1M MgCl\(_2\), \(~1706\) psia/27.7 mol\% for 0.1M CaCl\(_2\), \(~1820\) psia/28.9 mol\% for low salinity (LS) brine, \(~1914\) psia/30.1 mol\% for 0.1M NaCl, \(~1990\) psia/31.2 mol\% for 0.1M KCl, and \(~2554\) psia/36.4 mol\% for DI water. Figure 3.b denotes the effects of brines with various ionic strengths on the asphaltene deposition rate after the AOP which is RF-decline versus time for the crude oil with/out brine micro-emulsions at various salts contents. There is a remarkable difference in the plotted curves between the blank oil without any water micro-emulsion and with presence of DI water, high and low salinity brines. DI water decreased the deposition rate from \(~708.7\) to \(~99.8\) Hz/hr. HS and low salinity brines suppressed the asphaltene deposition rate down to \(~286.5\) Hz/hr and \(~229.6\) Hz/hr, respectively. One of the potential mechanisms of deposition rate reduction is that the water/brines build a thin film layer surrounding the QCM surface and hinder asphaltene aggregates from depositing onto the solid surface. To investigate this hypothesis, we have monitored the micro-wettability changes of the QCM gold surface owing to the ion valency/content alterations using environmental scanning electron microscope (ESEM). Figures 3c-g show the micrographs of water droplets onto the solid surface with existence of different ions and respective average contact angle (\(\theta_{av}\)) values. It can be inferred that the \(\theta_{av}\) incremented with incrementing the brines ionic strength. The \(\theta_{av}\) in existence of low salinity brine denoted an increase from \(15^\circ\) to \(\approx 34^\circ\). The only significant district was observed between low and high salinity brines that is \(\approx 28^\circ\), from \(34^\circ\) to \(\approx 62^\circ\). This clearly shows how critical the roles of ion type and valency are in wettability alteration phenomenon during water flooding or water alternating gas injection EOR processes.
Figure 3. The influence of water with/out various ionic strengths on (a) AOP shifting and related GOR alterations, and (b) asphaltene deposition rate onto the QCM surface. ESEM micrographs of micro-droplets of water on gold plate of QCM surface in presence of (c) DI water, (d) 0.1M LS brine, (e) no water, plain surface, and (f) 1M HS brine. The white scale bar depicted in images is 20 µm. (g) the average contact angle values of water micro-droplets on the surface with/out presence of brines with different salinities and ion types. The picture is from the latest Authors’ publication [6].

Conclusions

The following conclusions from this research study can be drawn:
- It is proved that Quartz Crystal Microbalance (QCM) technology can also be used as a flow assurance tool besides its use in biological studies. It can be a reliable technique for investigation of asphaltene deposition during pressure depletion, gas/water injection EOR processes.
- During the gas injection process which is one of the most important EOR techniques, the severity of asphaltene precipitation phenomenon and amount of asphaltene precipitates extremely high rely on the amount of gas which is combined with oil.
- It can be concluded that water films on reservoir rock surfaces may prevent the deposition of asphaltene on the rock surfaces. It needs to be investigated further for different water chemistries.

There are some new approaches for simultaneously asphaltene precipitation prevention and improving oil recovery such as specific ionic liquids injection. These techniques should be developed and studied further in the future.

References