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Effect of emulsified water on the wax appearance temperature of water-in-waxy-crude-oil emulsions☆

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ABSTRACT

The article concentrates on the effect of emulsified water on the wax appearance temperatures (WATs) of water-in-waxy-crude-oil emulsions. Water-in-oil (w/o) emulsion samples with various water volume fractions (WVFs) were prepared by mixing a waxy crude oil with deionized water at three different stirring speeds. The WAT of each sample was attained via differential scanning calorimetry and was compared with that of the dehydrated crude. In addition, the effects of the WVF and the mean droplet size on the WAT of the emulsions were theoretically evaluated based on the relationship between the wax solubility in the crude oil and the Gibbs free energy concept. The results indicate a sharp increase in the WAT with the presence of water in the system, regardless of the volume of water. Greater deviations became apparent at higher WVFs and rotational speeds, which resulted in the formation of a larger number of droplets.

1. Introduction

In recent decades, emulsions have become a major research subject of interest in various industries, such as the cosmetics, pharmaceutical, food, combustion, chemical and petroleum industries due to the profound role of emulsions in enhancing the quality of the final products [1–5]. In the petroleum industry, emulsions are very common, and often problematic [6]. From the early stages of petroleum production, oil and water coexist within porous media, and when these reservoir fluids move toward producing wells, the existing vigorous shear forces create a high degree of agitation, leading to the formation of an emulsion [7]. The presence of such emulsions can impair the efficiency of production and jeopardizes the profitability of all parties involved in the petroleum industry, i.e., the producer, transporter and refiner [8]. Moreover, progressive achievements in exploration and drilling technology have recently made it feasible to explore and develop new remote deep-water fields, which have been unobtainable until now. The extracted crude oils are transported via long-distance subsea multiphase pipelines to reach various target destinations. Accordingly, production and transportation under these circumstances are subject to severe flow assurance problems, such as the formation and/or deposition of paraffin wax crystals in wells, flowlines or production facilities. These problems are further exacerbated by an incremental growth in the water cut and alterations in the characteristics of the fluids over time. The laboratory determination of parameters such as the wax appearance temperature (WAT) and viscosity are thus better made using representative emulsions rather than the dry crude. WAT which is also known as cloud point is defined as the temperature at which the first wax crystal appears in a crude oil when the oil is subjected to cooling [9,10] and heavy paraffinic components start to precipitate out of the crude oil [11].

The emulsion type, by and large, is governed by two main factors, namely, polar interactive forces and the molecular structure [8]. The first factor determines the emulsion type based on the tendency or reluctance of bipolar molecules (molecules that possess partial solubility in both phases) existing within crude oils to interact with the polar phase (water). Accordingly, water-in-oil (w/o) emulsions are more likely to be formed if the bipolar molecules possess strong polar groups, whereas oil-in-water (o/w) emulsions are often associated with the presence of weak polar groups. The second factor, however, relates to the configuration of the nonpolar groups of the bipolar molecules. As a rule of thumb, bipolar

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molecules with highly branched alkyl groups (nonpolar groups) or ring structures participate in the formation of w/o emulsions, while bipolar molecules with linear alkyl groups take part in the generation of o/w emulsions [8] A w/o emulsion is reported to be the most prevalent type in the petroleum industry, despite the possibility of the formation of a variety of emulsion types (i.e., o/w, w/o and water-in-oil-in-water) [12,13]. This is an unfortunate reality for petroleum engineers because w/o emulsions exhibit viscosities substantially greater than those found in crude oils at the same temperature [13]. Furthermore, the physical properties of emulsions (e.g., density, viscosity, thermal conductivity, pour point, specific heat and solubility) differ from those of the oil or water individually. Consequently, the fluidity in flow lines is also affected by such changes in the physical properties of fluids, resulting in higher pressure drops as well as production rate declines in most cases [14].

In waxy crudes, the wax constituents are long-chain solid alkanes (C20–C50) dissolved in the lighter components of the crudes [15]. These components can precipitate out of solution in the form of solid crystals when their solubility is disturbed and the oil temperature during the course of production and transportation declines below a specific value known as the WAT [16,17]. Such a precipitation of solid wax crystals may bring about severe flow obstructions with a deposition of only 2% of the total wax present in the system [18]. Additionally, when water and waxy crude oil flow in a pipeline concurrently, the extracted wax crystals diffuse into the medium (w/o emulsion) and are adsorbed by the existing dispersed water droplets. Thereafter, a rigid gel-like structure known as an emulsion gel is formed as the wax crystal networks grow across the system and entrap more emulsified water droplets [19]. This phenomenon can further boost the stability and viscosity of the gelled emulsion, which effectively reduces the fluidity. This explains the importance of considering the precise value of the WAT and maintaining operation conditions well above this temperature to avoid the extra cost incurred to compensate for the loss of fluidity.

The oil solubility of wax components within a crude oil extract depends on the degree of oil saturation, which is highly temperature sensitive. This fact can be thermodynamically explained and mathematically measured based on the molar Gibbs free energy equation. To date, the equation has been widely applied to binary systems in which two substances are present, and one is dissolved by the other. However, the emulsion of water in waxy crude oil is a ternary system, in which wax can be dissolved in the lighter components of crude oil, while water droplets existing in the bulk act as impurities.

To date, many publications have appeared in the literature documenting the parameters that affect the formation [12,20–23], rheology [6,24,25] and stability [26] of w/o emulsions encountered in the petroleum industry. Despite considerable efforts dedicated to understanding the concept of w/o emulsions, the effect of water, as an impurity within crude oil, on the WAT and the crystallization process has seldom been considered. The studies pertaining to waxy crude oils, however, have revealed that the WAT is influenced by several parameters, including kinetics, the oil (solvent) and wax composition, polydispersity, pressure, cooling rate and the presence of impurities [27,28]. Regarding the influence of impurities, a change in the crystallization mechanism due to the presence of any impurities has been widely reported [29–31]. This fact has been attributed to the free available surfaces provided by the impurities inside the system, known as nucleation sites, on which the crystal embryos can be formed more readily. To come into such conclusion, they all investigated the changes in the supercooling degree before and after the existence of the impurities by carefully studying the cooling and heating thermograms. The supercooling degree shows the tendency of the liquid to be crystalized at a lower temperature than the standard melting temperature under which crystal homogeneous nucleation occurs. This degree reduces by addition of nucleation sites in the system which changes the crystallization process into heterogeneous crystal nucleation. Therefore, any type of impurity existing in a hydrocarbon system causes variation in the value of the WAT. This phenomenon can also be extended to the field study of oil/water two-phase flow systems wherein waxy crudes are selected as the oil phase and w/o emulsion is a part of the flow, especially at temperatures near the WAT. In these studies, the WATs of the dehydrated oils are measured and are assumed to be representative of the entire system (i.e., w/o emulsion or wet crude oil), despite the possible effect on the WAT of the presence of water. Based on these assumptions, the presence of wax crystals in the designed systems is expected only at temperatures below the WAT of the dehydrated crude oils, which may not represent the real case in the oilfield. The measurements and results in these situations may lead to substantial errors. Li and Gong [32] are among the few researchers who have recently acknowledged the effect of water cut on the WAT. According to their results, the change in WAT for different water cuts did not exceed 0.15 °C, which indicates that the effect of water cut on the WAT is insignificant. Nevertheless, these research results did not provide adequate rationale for these investigators to put forth conclusions based on their findings; therefore, they merely reported the results.

In the present study, the effect of the presence of water, i.e., the water volume fraction (WVF) and the mean droplet size (MDS), on the WAT of water-in-waxy-crude-oil emulsions was experimentally investigated. To conduct the investigation, a thermal analysis was applied to elucidate the mechanism influencing this phenomenon by taking into consideration the Gibbs free energy concept. The results lead to a better understanding of oil and water transportation in pipelines in harsh environments such as low temperatures and over very long distances, which would enable designers and producers to more accurately create an appropriate pipeline for oil transportation.

2. Materials and measurements

2.1. Materials

The crude oil used in the experiment was a dead waxy crude oil obtained from Terengganu Crude Oil Terminal (TCOT), located on the East Coast of Peninsular Malaysia. The collected crude oil was thermally treated first, to redissolve potential wax crystals within the crude; second, to reduce the water content to a minimum of 0.05% of the total volume; and third, to evaporate the existing light ends in the crude oil. The treatment involved simultaneous heating and stirring of the crude oil at 80–85 °C in an unsealed beaker via an electric hot plate and a mechanical stirrer with a maximum speed of 1200 rpm for about 2 h. These conditions were applied to avoid further evaporation of the oil components during and after emulsification and thus eliminating the potential effects of light ends evaporation on the WAT measurement results. Subsequently, gas chromatography–mass spectrometry (GCMS) was applied and the results showed the existence of components with a carbon number of minimum eight within in the crude (see Table 1 in the Supporting Information). It should be noted that all the experimental procedures and measurements have been conducted after the aforementioned thermal treatment. Even though the temperature was not exceeding 85 °C at any stages of this study and additional evaporation of the crude oil was unlikely below this temperature, further precaution was taken to keep the samples sealed during the course of the experiments and preparation of the emulsion samples. Table 1 presents the physical properties of the crude oil measured after dehydration in Universiti Teknologi Malaysia's accredited lab-