Chemical Engineering and Processing 98 (2015) 112–122

Contents lists available at ScienceDirect

Chemical Engineering and Processing: Process Intensification

journal homepage: www.elsevier.com/locate/cep

Study of the formation and breaking of extra-heavy-crude-oil-in-water emulsions—A proposed strategy for transporting extra heavy crude oils

Rafael Martínez-Palou, Jesús Reyes, Ricardo Cerón-Camacho, Mario Ramírez-de-Santiago, Diana Villanueva, Alba A. Vallejo, Jorge Aburto*

Dirección de Investigación en Transformación de Hidrocarburos, Instituto Mexicano del Petróleo, Eje Central Lázaro Cárdenas 152, 07730 México D.F., Mexico

ARTICLE INFO

Article history:
Received 8 June 2015
Received in revised form 23 September 2015
Accepted 25 September 2015
Available online 4 November 2015

Keywords:
Extraheavy crude oil
Oil-in-water emulsion
Surfactants
Pipelining of crude oil

ABSTRACT

At present, many petroleum copmpanies in the world are facing processing problems about crude oil extraction, production and refining. For example, conventional pipelines are not suitable for pipelining of extra heavy oils and bitumen from the reservoirs to the refineries. According to the aforesaid, a procedure was developed for the formation of an oil-in-water emulsion employing a Mexican crude oil and its subsequent phase separation as a strategy for the pipelining of extra heavy crude oils. An O/W emulsion considerably decrease the viscosity of an extra heavy crude oil and facilitating its transport through pipelines, but crude oil must be dehydrated before further processing. We carried out a screening of commercial and synthetic surfactants for emulsion preparation as well as for breakage. The emulsion was characterized by calorimetry, optical techniques, particle size and dynamic viscosity. The stability of emulsions was evaluated by the kinetics of water separation in the presence of surfactants and heating. We also developed a factorial 2^k design to study emulsion breakage with factors such as temperature, surfactant concentration and pH. All surfactants developed by ours are low toxic and full biodegradable since they atre synthesized from glucose and glycine, respectively. Thus, we developed an environmental friendly approach to facilitate crude oil transport through pipelines.

1. Introduction

Nowadays, most of the world's oil countries are facing the challenge of processing increasingly heavier crudes. Particularly in Mexico, more than 50% of the proven reserves are heavy (less than 20 API) and extra-heavy (less than 10 API) crude oils. The complex composition of these crude oils makes them difficult and expensive to be transported through pipelines due to their high viscosity and low mobility and flowability [1]. Moreover, these crudes contain a high content of high molecular weight hydrocarbons and asphaltenes with a strong tendency to precipitate in the pipelines and also act as emulsifiers, favoring the formation of water-in-oil (W/O) emulsions, which increase significantly the viscosity of these oils. Thus, the development of an environmentally friendly technology, technically and economically feasible for the transportation of heavy and extra heavy crude oil is needed urgently.

Several technologies for transporting heavy crude oil have been described: dilution of heavy oil with light hydrocarbon fractions, upgrading, use of flow improvers, heating of subsea pipelines and core annular flow [2], but one of the most promising alternative is the formation of oil-in-water emulsions (O/W emulsions) by means of a surfactant [3,4]. Moreover, the formation of stable inverse emulsions promotes both an important viscosity reduction and pressure drops and it is a technological alternative for improving the fluidity of heavy crudes which due to their high densities and viscosities are difficult to be transported. The emulsion stability is strongly affected by the nature of interfacial films and the surfactant adsorption mechanisms.

An important aspect to be taken into account in this technology is that water must be removed from oil before any further process or refining. By minimizing the water level in oil, corrosion is reduced, which maximizes the use of pipelines by eliminating severe operational problems. Hence, this transport strategy should involve both the formation and breaking of emulsions and removal of water from oil after being transported and before the crude oil is refined.

Most works on the demulsification of crude oil emulsions have been done for W/O emulsions, which are the most abundant and

* Corresponding author.
E-mail address: jaburto@imp.mx (J. Aburto).

http://dx.doi.org/10.1016/j.cep.2015.09.014
0255-2701/

naturally formed in the crude oil [5–8] however few reports have been published on the demulsification of O/W emulsions [9,10].

Ideally, the emulsion should break naturally within the time elapsed between the transportation and processing of heavy crude oil, but it is very difficult to have a strict control over the emulsion stability; this process is carried out commonly by using a surfactant as a demulsifier [11]. Many attempts have been done to correlate the efficiency of the demulsifiers with their chemical and surface properties [12–16], but until now, this knowledge is still limited and the tools for the prediction of a demulsifier performance for a given type of crude oil are of low reliability, thus, the selection of chemicals for this purpose continues being based essentially on empirical criteria.

In this work, a procedure to prepare O/W emulsions from Mexican Extra-Heavy Crude Oil (EHCO) and their subsequent breakdown as a strategy for transporting EHCO was studied. Different parameters (i.e., temperature, stirring time and rate, oil/water ratio, and emulsifier and demulsifier concentrations) were studied for the formation and breaking of emulsions. The screening of commercial emulsifiers and demulsifiers and other surfactants synthesized in our laboratory was carried out to develop a comprehensive methodology for the formation of emulsions from EHCO and their subsequent breakdown.

The formation of O/W emulsions decreases considerably the viscosity of EHCO, which for transportation purposes behaves as a non-Newtonian liquid. The emulsions were characterized by DSC, optical microscopy, particle size and Zeta potential measurements. The stability of emulsions was evaluated by the kinetics of water separation by using demulsifiers and heat. For the screening of demulsifiers, a factorial 2^k design was employed and demulsification parameters such as temperature, demulsifier concentration and pH were studied in order to develop an integral strategy for the transportation of EHCO by using low toxicity surfactants as emulsifiers and demulsifiers, respectively.

2. Experimental

2.1. Materials and equipment

All reagents were purchased from Aldrich Chemical Co. The differential scanning calorimetry (DSC) were carried out by means of a Shimadzu model DSC-60A. A Karl Fisher titrator (model Orion AF-8) equipped with a double platinum electrode was employed during the water-content determination tests. Micrographs were taken in a Nikon Eclipse E800 optical microscope. The particle size measurements were performed with a freshly prepared emulsion using a counter and particle size analyzer PPS-Accusizer 780. Zeta potential measurements of the nanoemulsions were estimated from electrophoretic mobility (μ_E) measurements using phase analysis light scattering (PALS) in the Brookhaven ZetaPALS setup. A dip-in (Uzgiris type) electrode with 4-mL-polystyrene cuvettes was used and measurements were carried out at 25 °C. Henry's equation, valid for the $0.01 \leq \kappa d \leq 100$ condition (κ being the Debye parameter or inverse Debye length and d being the droplet diameter), was used to calculate the zeta potential (ζ) using either Smoluchowski's or Hückel's approximation [17].

2.2. Crude oil characterization

The EHCO sample used in this study was provided by the Mexican Petroleum Company (PEMEX) from a marine well drilled in the south of the Gulf of Mexico. The samples were characterized by the following standard procedures: API gravity (ASTM D-287), pour point (ASTM D97), kinematic viscosity (ASTM D-445), salt content (ASTM-D-3230), paraffin content (UOP-46), water content (ASTM D-4006), and saturated, aromatic, resin and asphaltene (ASTM D-2007) contents. Total sulfur was determined in an Antex 9000S, employing the ASTM D 5453-05 standard procedure: standard test method for determination of total sulfur in light hydrocarbons, motor fuels and oils by ultraviolet fluorescence. The cloud points for NPE in salty solutions were determined in accordance with the ASTM D 2024-09 standard procedure.

2.3. O/W Emulsion preparation

The optimized procedure developed in this study is described below.

Synthetic sea water (total salt content of 40,750 mg/L, standard method D-1995) was used to prepare O/W emulsions using the alkyl polyglucoside H4C14 (1500 mg/L) and nonylphenol ethoxylated (500 mg/L) as emulsifier, dissolved in 15 mL of sea water. The solution was poured into a jacketed glass reactor with water recirculation at 75 °C. The mixer propeller was fixed in order to keep it submerged in the aqueous phase and the solution was stirred at 8000 rpm using an IKA Labortechnik homogenizer. 35 g of EHCO, previously heated at 50 °C to increase the fluidity, were then added slowly from the top of the glass reactor. The surfactant sea water solution and EHCO were stirred for mixing at 75 °C for 3 min (Fig. 1). The formation of an O/W emulsion was confirmed by dispersing an emulsion drop in water, DSC analysis and optical microscopy.

2.4. Differential scanning calorimetry (DSC) measurements

These tests were carried out under N_2 atmosphere at a flow rate of 20 mL/min. Every emulsion was weighed accurately (ca. 10 mg) on an aluminum pan which was tightly sealed. The sample cooling cycle from 50 to −60 °C was scanned at a rate of 10 °C/min. The characterization of emulsions by DSC was performed twice on the same day the emulsions were prepared.

2.5. Synthesis of emulsifiers

Emulsifiers H4C12 and H4C14 where prepared under microwave irradiation in a CEM Discover microwave reactor [18] and their critical micelle concentrations (CMC) were determined as previously described [19,20].

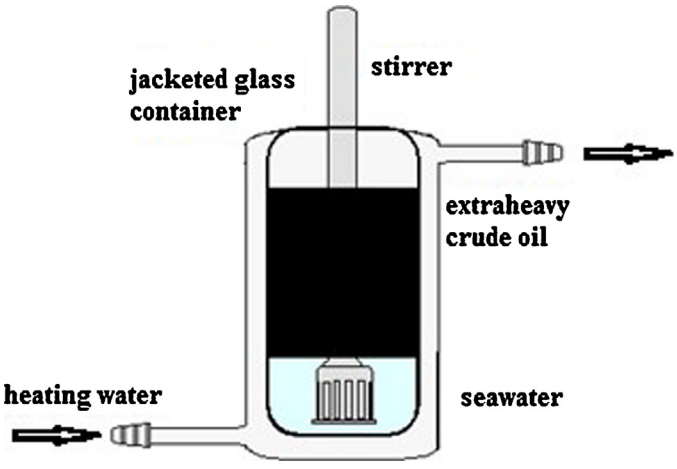

Fig. 1. Equipment for the preparation of O/W emulsions.