

A novel perspective on emulsion stabilization in steam crackers



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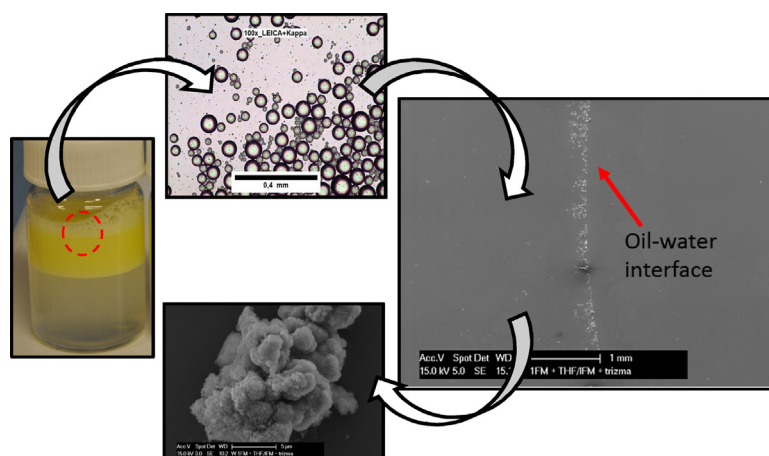
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HIGHLIGHTS

- Species soluble in water and in organic solvents were extracted from emulsions formed in steam crackers.
- The most stabilizing fraction at pH 5.5 and 8.5 was the fraction soluble in organic solvents.
- Stable interfaces were dominated by particles containing iron and sulfur, unstable interfaces contained mainly carbon.
- Compressional film rigidity and surface charge did not explain the different stabilizing effect of the fractions analyzed.
- Interfacial activity did not dictate the differences in the stability of the systems studied

GRAPHICAL ABSTRACT



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ABSTRACT

Fouling issues in steam crackers may arise due to a number of reasons, including emulsion formation in the quench water tower. Freeze-drying according to a protocol developed in-house was used to extract species potentially capable of stabilizing emulsions from process water sampled from a quench tower. Such species were subsequently fractionated into solubility classes: water soluble, and soluble in organic solvents (polar and apolar). Liquid chromatography/mass spectrometry analyses indicated differences in the chemical composition of these fractions, with molecules bigger and richer in oxygen in the fraction soluble in polar organic solvents compared to those detected in the water soluble fraction. Bottle tests demonstrated that the interfacial material soluble in polar organic solvents was the most effective in stabilizing water-in-gasoline and gasoline-in-water emulsions. When the water soluble fraction was added to these stable emulsions it acted as demulsifier, with the most marked effects observed at low pH. In the absence of the water soluble fraction emulsion stability was largely pH-independent. The role of electrostatic forces in emulsion stabilization was investigated by conducting zeta potential measurements. With the organic soluble fraction only added to the oil phase and at pH 5.5, emulsions were stable and the zeta potential was close to zero, proving that electrostatic forces did not play a role in stabilizing this system. With the water soluble fraction added to the water phase and at alkaline pH, emulsions were stable and the zeta potential was negative, suggesting that electrostatic stabilization mechanisms cannot be discounted in the presence of

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the water soluble fraction. Scanning Electron Microscopy (SEM)/Energy Dispersive X-Ray Spectroscopy (EDX) were used to probe the morphology and elemental composition of the Langmuir–Blodgett films extracted from the gasoline–water interface. SEM images highlighted the presence of particles at the gasoline–water interface, suggesting Pickering stabilization mechanisms. Dynamic interfacial tension measurements showed that the decrease of the interfacial tension measured for gasoline–water interfaces upon addition of interfacial material was relatively low and similar for all fractions, supporting this hypothesis. SEM/EDX data further reveal the strong correlation between interfacial film composition and emulsion stability, with high densities of particles containing sulfur and iron associated with significant emulsion stability. The compressional visco-elastic moduli of interfacial films were determined using a pulsating drop rheometer. Measurements were done at pH 5.5 and 8.5, with the individual solubility fractions added. Film rigidity was similar with all fractions, indicating that it did not dictate the differences in their stabilizing properties.

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1. Introduction

Emulsion formation represents a significant issue in the oil and gas industry, in either the upstream or the downstream sectors. In the upstream sector emulsions can form during bitumen extraction and liberation. In the downstream sector, problematic emulsions may form during thermal cracking of feedstocks, and specifically during steam cracking. Steam cracking of a variety of feedstocks is one of the technologies used to produce olefins such as ethylene, propylene, and butenes. In the cracking process hydrocarbons are decomposed at high temperature, and the hot stream is subsequently cooled in transfer line exchangers and a quench water towers. Water is an effective heat transfer medium, but mixing between hydrocarbons and water can lead to the formation of stable emulsions. When the hydrocarbon–water separation is incomplete fouling material present in the water phase is entrained to the units downstream of the quench tower, potentially leading to fouling issues.

Emulsions can be stabilized by surfactants [1], polymers [2], particles [3] or a combination of the above [4,5]. Emulsion stabilization can arise due to electrostatic, steric, electro-steric or hydration repulsion between droplets, formation of rigid films, Pickering stabilization mechanisms, and Marangoni effects [6,7]. The type of mechanism involved in emulsion stabilization largely depends on the types of stabilizing species that partition at the hydrocarbon–water interface, and identifying such species is therefore crucial to resolve emulsion issues. A variety of methods can be exploited to probe the importance of the different stabilization mechanisms, including electrophoretic measurements to estimate the ζ potential of droplets [8], Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM), and Brewster Angle Microscopy (BAM) to gain insights about interfacial film structure and the role of steric forces [9], and compressional and shear rheology to probe film rigidity [9,10].

In the upstream sector, significant efforts have been made to identify the species responsible for emulsion stability. Research has shown that bitumen consists of a complex mixture of macromolecules, which can be divided into solubility classes each having different stabilizing properties [11,12]. It is widely recognized that the asphaltene fraction stabilizes emulsions by creating rigid films around droplets, by contributing steric repulsive forces between approaching droplets and by forming a gel-like network that impedes film drainage [9]. Conversely, addition of the resin fraction to an asphaltene stabilized emulsion reduces the stability of that emulsion [12]. Recent studies have further indicated that an asphaltene sub-fraction, rather than the whole asphaltene fraction, is responsible for emulsion stabilization [13]. Additionally, a wealth of research has been devoted to elucidating the chemistry of asphaltenes [14–17].

In the downstream industry, efforts have been made to establish chemical or mechanical methods to separate oil in water emulsions within the context of hydrocarbon cracking and processing [18–20]. However, to date, the mechanisms and the species responsible for emulsion stabilization in quench water towers of chemical crackers have not been fully elucidated.

The goal of this work is to progress the understanding of emulsion stabilization mechanisms in the context of hydrocarbon cracking, drawing from the knowledge and techniques utilized to investigate emulsion stability in the upstream sector. This study is unique in that this interdisciplinary approach has not been adopted before. To the best of our knowledge this is the first study that investigates the role of different solubility fractions of interfacially active species on the stability of emulsion formed in the quench water tower of a steam cracker, and analyzes the importance of the mechanical properties, structure, electric charge and chemical composition of the interfacial films formed by such fractions within this context.

2. Materials and methods

2.1. Water and pyrolysis gasoline

In all experiments conducted the water used was purified using a Millipore system and had a conductivity of 18.2 M Ω cm at 25 °C and gasoline was pyrolysis gasoline. Pyrolysis gasoline is a product of high temperature cracking of naphtha in steam crackers, and it contains heavy aromatic, olefins and paraffins comprised of 5–12 carbon atoms.

2.2. Extraction and fractionation of the stabilizing material from the gasoline–water interface

Fouling material was extracted from quench water samples with freeze-drying using a VaCo 5 II (Zirbus Technology). The samples were transferred to round bottom flasks, which rotated in acetone dry-ice to create a thin ice layer on the outer flask wall. The flasks were subsequently connected to the freeze-drier at 0.09 mbar and –98 °C. The low temperature at which freeze-drying was conducted allowed extracting the interfacial material without altering the sample or evaporating volatile fractions, which could instead evaporate if the concentration process were carried out at elevated temperatures.

Freeze-dried interfacial material was subsequently fractionated in three solubility classes: 1. Water soluble material; 2. Material soluble in polar organic solvents (i.e. tetrahydrofuran, THF) but not in water; 3. Material soluble in an apolar organic solvent (i.e. toluene), but not in water or THF. The procedure adopted in the fractionation is as follows. First, the material was soaked in milli-Q

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