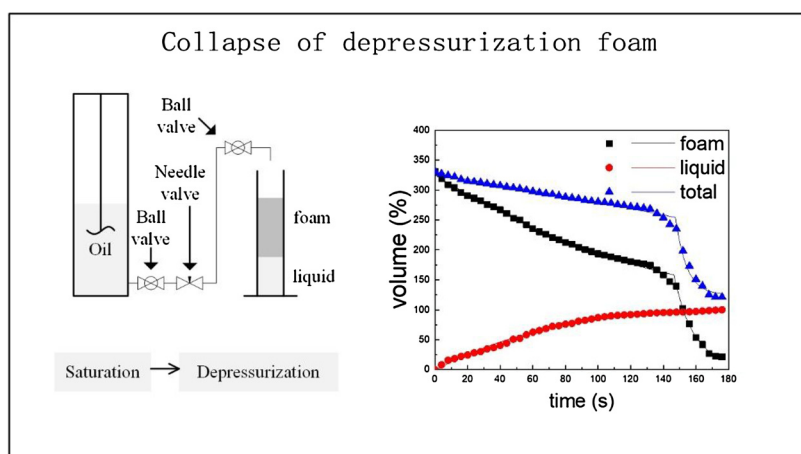# Foaming of crude oil: Effect of acidic components and saturation gas

Jianping Chen, Limin He*, Xiaoming Luo, Chunying Zhang

College of Pipeline and Civil Engineering, China University of Petroleum, Qingdao 266580, PR China

GRAPHICAL ABSTRACT

ABSTRACT

Foaming tendency of crude oil is diverse due to the variance in crude oil components. Crude oil viscosity, asphaltene, and resin contents have been studied in general, but the specific surfactant molecules that stabilize crude oil foam are not identified. Carbon dioxide oftentimes accompanies hydrocarbon gases in reservoirs rich in natural CO_2 and fields where CO_2 enhanced recovery is implemented. Crude oil acidic components and carbon dioxide may have considerable significance to foam formation and defoaming kinetics. We studied the effect of acidic components and saturation gas on foaming of crude oils with pneumatic and depressurization tests respectively. Foaminess, foamability and time to half collapse are used to characterize foaming of oils. We present a new piecewise model that can be divided into two segments with almost equal timescales to fit the collapse curve and we use parabola function and expdec1 function to model the two segments respectively. The *t* values at the intersection of two segments are approximately the same as time to half collapse. Model parameter *A* is close to foamability. Increase in the rigidity of the interface and viscosity of the bulk liquid may account for excellent foam stability of some acids/oil systems. Some acidic crude oil components, for example, naphthenic acids, long-chain fatty acids, increase foaminess significantly, suggesting that crude oil antifoams combined with reagents that will react with some acidic components may have better performance.

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* Corresponding author.
   E-mail address: upcmpfs@163.com (L. He).

1. Introduction

In the petroleum industry, the occurrence of foams can be beneficial as gas injection and especially CO_2 flooding can be used for the enhancement of oil recovery [1]. Foam-oil interactions, foam-particle interactions, propagation of foam front in porous media and comparison of surfactant performance at varying scales are some central issues raised by researchers [2–6]. However, foaming of crude oils may pose difficult problems in some other stages of petroleum production [7]. An unfavorable result of crude oil foaming is the decrease in separator capacity due to the increased residence time for foam breaking. Another disadvantageous result is inaccurate level measurement. Foaming can cause liquid carry-over through the gas line, which further causes contamination of solvents and damage to scrubbers and compressors [8]. Furthermore, foaming can lead to unwanted gas carry-over in the oil line, resulting in dangerous degassing and damage to pumps. Foam inhibition provides better process control over crude oil separation and distillation and thus lab test of crude oil foaming and antifoam performance is necessary [9,10].

The attempts to identify the factors affecting foamability of various crude oils have produced some acceptable results. Bulk viscosity, film elasticity, asphaltene content, the ratio of asphaltene to resin were found to affect foamability [11,12]. Previous studies reported that chemical-free crude oils from which organic acids were extracted have much lower foaminess compared to whole oil. These acidic extracts were analyzed by gas chromatography-mass spectrometry and the presence of straight-chain saturated carboxylic acids, cyclic carboxylic acids and benzoic acids in extracts was identified, which had all been well defined in petroleum [13]. Such conclusion is unsatisfactory because the extremely complicated procedure for separation and analysis of acidic surfactants from crude oil may have altered the components of crude oil in the first place. Until recently, there has been no reliable evidence that natural acidic compounds in crude oils are the reason that some crude oils have high foaming tendencies.

Much work has been dedicated to the design of the experimental program for testing foaming tendencies of crude oils. Several researchers developed their experiments based on the idea of decompression or depressurization [14–17]. Since depressurization has been considered the main reason why foaming of crude oil mainly occurs in onshore, offshore and subsea environments, these apparatus seems to be reasonably acceptable. We have performed similar depressurization test of crude oils both inside and outside the pressurized vessel ourselves. However, we only successfully performed tests on mineral oils because crude oils we obtained had low foamability under low saturation pressure. Thus, we performed pneumatic tests on oils with different additives. Our study aims to identify some acidic components in crude oil that are responsible for foaming. This study will help to address vital issues about the foam formation and defoaming kinetics regarding gas types and acidic oil components. Thus, the results could be beneficial for foam control in oil and gas industry.

2. Experimental program

2.1. Materials

We employed two crude oils as well as a mineral oil of different components as foaming systems. A third crude oil was created by mixing the two crude oils in 1:1 ratio. Signs of incompatibility, such as the apparition of solid deposits or the desolubilization of some asphaltene or resin components, were not found when we mixed the two crude oils. The properties of four oils are listed in Table 1. Viscosity was characterized by the rheometer (Anton Paar MCR302, concentric cylinder measuring system) at 20 °C. Oil sample 1# was light crude oil from Murban region. Sample 3# was slightly heavy crude oil from Changqing, China. We used paraffinic mineral oil in some tests as the oil phase to compare and contrast different result patterns. All crude

Table 1
Oil Properties: Density, API Gravity, and Viscosity.

oil	ρ at 20 °C (kg/m³)	API gravity (deg)	μ at 20 °C (mPa·s)
1#Murban	740	59.7	16
2#Murban/Changqing	799	45.6	65
3#Changqing	838	37.4	450
4#Mineral oil	851	34.8	17

oils showed Newtonian behavior when we measured the viscosity of the fluids except oil sample #3. Oil samples were stored in airtight containers to decelerate the alteration of the physicochemical properties of oils throughout the tests. CO_2 and CH_4 gases of 99.99% purity supplied by Tianyuan were used throughout. The acids and phenol are decanoic acid, octadecanoic acid, cyclohexanecarboxylic acid, 4-methylbenzoic acid and 4-methylphenol (analytical reagents, supplier Aladdin). The reagent bottles containing decanoic acid, cyclohexanecarboxylic acid and 4-methylphenol (melting point below 35 °C) were heated in the water bath at 40 °C. Then, the reagent fluids were added to the oils with the plastic dropper to the desired concentration. The granular octadecanoic acid or 4-methylbenzoic acid (melting point 69.6 °C and 180 °C) were added into the oil #4 directly. Then, the solid/liquid mixture was subjected to an agitating heater (60 °C and 95 °C) until the visible solid particles entirely dissolved. After the oil 4# with these two acid additives cooled, crystal particles were observed as the fluid changed from transparent to opaque.

2.2. Apparatus and procedures

We performed the depressurization test and pneumatic test with the apparatus illustrated in Fig. 1. The principle behind the depressurization test is the nucleation of bubbles from the entrapped gas inside the liquid phase. 250 mL of mineral oil was placed into the pressurized cell and saturated at 5 bar of saturation gas (CO_2, CH_4 or 1:1 mixture of CO_2 and CH_4) with the stirrer. The tightness of the pressurized cell was checked before the test and the typical saturation time was 120 min. Saturation temperature was kept at 30 °C. The cell was connected to a 100 mL graduated glass cylinder with detachable stainless steel tubing of inner diameter 3 mm. The first ball valve was to seal the liquid inside the saturation cell during the saturation. The needle valve at fixed position created a sufficient pressure drop to the flow of gas saturated oil to ensure comparability and reproducibility of the tests. Foam flow was abruptly cut off by the second ball valve when foam volume reached 40 mL ± 5 mL (shown in Fig. 2). The opening of the needle valve was predetermined to keep foam flow rate moderate so that both drained liquids from foam and shock against existing foam in the cylinder were avoided. The whole foam collapsing process was recorded with Canon digital camera at 1080p, 30 fps. All experiments were conducted at room temperature. Foam characterization parameters were calculated by averaging results of three consecutive runs for different saturation gases. The video was edited and processed to obtain the batch snapshots, which were then processed by self-written MATLAB code to output the evolution of foam and liquid volume over time in an Excel file. The algorithm for data manipulation uses the scale on the glass cylinder to calculate the scale of one pixel to the unit length of the foam column. Then, the code plots a bounding box around the contiguous foam region of the binary image. With this bounding box, both foam and liquid volume can be determined. Foamability Π is defined the same as Blazquez's article (Eq. (1)), where v_f^0 is the maximum quantity of foam that the system can create at the test conditions and v_l^{inf} is the total liquid volume when foam completely drains [16].

$$\Pi = \frac{v_f^0}{v_l^{\text{inf}}}$$

(1)