

# Factors Contributing to Petroleum Foaming. 1. Crude Oil Systems

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Gas/oil separation can often be accompanied by unwanted foaming. To study this phenomenon, 20 crude oils were subjected to low-pressure foaming experiments. Eleven of the crudes were from offshore platforms where foaming occurs regularly. Two foaming parameters, foam volume (or foamability) and collapse slope (i.e. the rate of foam collapse in the absence of sparge gas), were compared with several crude oil properties, namely, density, bulk viscosity, surface tension, asphaltene and resin content, asphaltene and resin molecular weight, and asphaltene and resin heteroatom content. For asphaltenic crudes, collapse slope was found to correlate with asphaltene content as well as several other crude oil properties: density, viscosity, and surface tension. Foam volume did not relate to any asphaltenic crude oil property. However, for crudes having little to no asphaltenes, foam volume, not collapse slope, strongly related to crude oil surface tension. For low asphaltenic crudes, results further indicate that resin chemical composition plays a key role in determining foam volume and that larger foam volumes were associated with higher crude densities and viscosities. Finally, viscosity was found to play a major role in determining whether a crude oil will foam under the experimental conditions.

## Introduction

During the initial phases of surveying a potential field for oil and/or gas production, producers often determine beforehand various processing issues that might be encountered during full-scale production. A host of issues are considered pertinent, some of which include production line blockage due to wax, asphaltenes, scale, and hydrate deposition.<sup>1</sup> Additional crude oil production issues include corrosion, emulsions (both water-in-oil and oil-in-water), and foaming.<sup>2–4</sup> During development of a field, small amounts of crude are often available for characterization. Lab testing can often assist in determining the degree of severity for several or all of the flow assurance and processing problems.<sup>1</sup> As a result, test methods and characterizations that are able to identify important crude oil properties and how they relate to or predict process operations are valuable to the industry.

Depending on the nature of the crude oil and the type of separation scheme used, foaming problems can curtail crude oil production and even cause unwanted and unexpected process shutdowns. The first vessel typically encountered during the production of crude oil and gas is the high pressure separator, often followed by one or more separators operating at successively lower pressures. Foaming can occur in any separator, but the greatest severity is generally encountered in the first stage.<sup>5</sup> Larger separators are apparently not a solution to the problem,<sup>6,7</sup> and this consideration is not possible for many offshore platforms where space is limited. Foaming, which is often associated with liquid carry-over from the separator, can also be accompanied by unwanted gas carry-under to the next separator or other downstream vessel. The former problem results in liquid flooding of downstream vessels and equipment (e.g., compressors), while the latter problem causes reductions in separator capacity. Both events interfere with the desired separation of gas and oil.

During initial examination, the separator can be viewed as a wide point in the production line that permits the separation of crude oil and gas.<sup>4</sup> Optimization of separator design, which is typically accomplished via the introduction of various internal devices, is one way to examine and address foaming concerns.<sup>5,6,8</sup> A

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(4) Laurence, L. L. Foaming Crudes Require Special Separation Techniques. *World Oil* **1981** (November), 103.

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(6) Nilsen, F. P.; Davies, G. A. What is Wrong with Primary Separators. In *The 3rd Major Conference on Current Developments in Production Separation Systems*, April 23 and 24, 1996.

(7) Smith, R. F. Curing Foam Problems in Gas Processing. *Oil Gas J.* **1979** (July 30), 186.

second way to prevent foaming is via the addition of chemicals.<sup>8–11</sup> Both methods could greatly benefit by having a better understanding of what crude oil components and properties contribute to severe foaming at certain production sites. Such understanding could further explain why some facilities experience more manageable foam (i.e., less chemical demand and separation schemes that require few if any revisions). Furthermore, as additional wells or distant subsea reservoirs are added to existing production, the foaming situation can rapidly change from manageable to problematic. Many of these instances can likely be explained from the mixing of incompatible crudes.<sup>12,13</sup>

Significant progress has been made concerning the role that various crude oil components (namely, asphaltene and resins), their ratios, elemental composition, and molecular weights play in stabilizing another production problem, water-in-oil emulsions.<sup>14</sup> Asphaltene and resins comprise the two heaviest, most polar fractions of crude oil. These components have an inherent tendency to associate and often strongly influence crude oil properties.<sup>15</sup> By definition, asphaltene is the portion of crude that is insoluble in alkane solvents (typically *n*-pentane or *n*-heptane is used) but soluble in aromatic solvents (benzene or toluene).<sup>16</sup> Asphaltenes, while structurally quite complex, have several common features: a polynuclear aromatic core, some degree of saturated substituents, and noticeable levels of nitrogen, oxygen, and/or sulfur.<sup>17</sup> Resins, while less studied, can be viewed as low molecular weight versions of asphaltene with a higher degree of overall saturation, thus rendering them alkane soluble.<sup>18</sup>

This paper and the following paper (Part II<sup>13</sup>) will likewise approach crude oil foaming with regard to how certain crude oil constituents and their properties are involved in stabilizing foam. Part I, this paper, studies how foam generated from a series of crude oils relates to crude composition and physical properties. Twenty crudes were chosen for the study. The first nine crudes were selected from crudes used in previous emulsion

studies<sup>14</sup> and wax characterizations.<sup>19</sup> The remaining eleven, all from the Gulf of Mexico, were known to cause foaming problems in oil/gas separators. Part II<sup>13</sup> takes a different approach and focuses on synthetic crudes. By adding crude components, asphaltene and resins, to a solvent system where the aromatic/aliphatic ratio is varied, a more basic understanding of how components behave singularly and together was achieved.

Various approaches taken to understand the factors that stabilize nonaqueous foaming are reviewed by Callaghan.<sup>8</sup> Regarding specific components within crude oil, Callaghan and co-workers demonstrated that naturally occurring surfactants, specifically, short-chain carboxylic acids and phenols of molecular weight  $\leq 400$ , can stabilize foam.<sup>20</sup> Using various oilfield production data, Claridge and Prats<sup>21</sup> proposed a model where the asphaltene and resins for certain crudes adsorb onto gas bubbles as the pressure falls below the bubble point. As a result, a semirigid coating forms causing both foam stabilization and viscosity reduction.

Another study by Cassani and co-workers showed the foaming tendency or foam power to be proportional to the concentration of asphaltene.<sup>22</sup> When sparging crude oil samples with air, heavier crudes having 9.1–10.2% asphaltene had a high foaming power (1,400 mL of foam), a crude with 5.3% asphaltene had less foaming power (1,100 mL of foam), and samples with lower asphaltene contents had even less foaming power (around 600 mL of foam). Their results were explained by asphaltene acting as surface active agents tending to reduce the surface tension of the liquid and thus stabilize the bubbles. In effect, Cassani et al. are claiming a distinct relationship between asphaltene concentration and foaming tendency. However, with regard to measuring the surface tension of crudes at equilibrium, oils with higher asphaltene concentrations generally have higher surface tensions (e.g., see the **M** crudes listed in Table 2). This relationship could in part depend on the general observation that solutions with higher molecular weight have higher surface tensions.<sup>23</sup> Alternatively, crudes having higher asphaltene concentrations, with consequent proportions of resin solvation, may render resins less available to lower the surface tension. In addition to determining how specific crude components contribute to foam stabilization, a number of other correlations describing how certain physical properties (e.g., bulk viscosity,<sup>24,25</sup> surface viscosity,<sup>25,26</sup>

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(9) Pape, P. G. Silicones: Unique Chemicals for Petroleum Processing. *J. Pet. Technol.* **1983**, *35*, 1197.

(10) Owen, M. J. The Surface Activity of Silicones: A Short Review. *Ind. Eng. Chem. Prod. Res. Dev.* **1980**, *19*, 103.

(11) Callaghan, I. C.; Hickman, S. A.; Lawrence, F. T.; Melton, P. M. Antifoams in Gas-Oil Separation. *Spec. Pub.-R. Soc. Chem.* **1987**, *59* (*Ind. Appl. Surf.*), 48.

(12) For a general discussion on instability and incompatibility due to crude oil mixing, see: Speight, J. G. *The Chemistry and Technology of Petroleum*, 3rd ed.; Marcel Dekker: New York, 1998; pp 488, 818.

(13) See the second paper in this series (Part II): Kilpatrick, P.; Zaki, N. N.; Poindexter, M. K. Factors Contributing to Petroleum Foaming. 2. Synthetic Crude Oil Systems. *Energy Fuels* **2002**, *16*, 711. This work demonstrates how solvent changes can precipitate asphaltene and thus lead to radically different foaming characteristics. Similar effects have been noted in the field when mixing various crudes (unpublished results).

(14) McLean, J. D.; Spiecker, P. M.; Sullivan, A. P.; Kilpatrick, P. K. The Role of Petroleum Asphaltene in the Stabilization of Water-in-Oil Emulsions. In *Structures and Dynamics of Asphaltenes*, Mullins, O. C.; Sheu, E. Y., Eds.; Plenum: New York, 1998; p 377.

(15) Yen, T. F. Asphaltene: Types and Sources. In *Structures and Dynamics of Asphaltenes*, Mullins, O. C., Sheu, E. Y., Eds.; Plenum: New York, 1998; p 6.

(16) Speight, J. G. *The Chemistry and Technology of Petroleum*, 3rd ed.; Marcel Dekker: New York, 1998; p 32.

(17) Speight, J. G. *The Chemistry and Technology of Petroleum*, 3rd ed.; Marcel Dekker: New York, 1998; p 453.

(18) Speight, J. G. *The Chemistry and Technology of Petroleum*, 3rd ed.; Marcel Dekker: New York, 1998; p 471.

(19) Musser, B. J.; Kilpatrick, P. K. Molecular Characterization of Wax Isolated from a Variety of Crude Oils. *Energy Fuels* **1998**, *12*, 715.

(20) Callaghan, I. C.; McKechnie, A. L.; Ray, J. E.; Wainwright, J. C. Identification of Crude Oil Components Responsible for Foaming. *Soc. Pet. Eng. J.* **1985**, 171.

(21) Claridge, E. L.; Prats, M. A Proposed Model and Mechanism for Anomalous Foamy Heavy Oil Behavior. SPE Paper 29243; Presented at the International Heavy Oil Symposium of the Society of Petroleum Engineers, Alberta, 19–21 June 1995.

(22) Cassani, F.; Ortega, P.; Dávila, A.; Rodríguez, W.; Serrano, J. Evaluation of Foam Inhibitors at the Jusepin Oil/Gas Separation Plant, El Furrial Field, Eastern Venezuela. SPE paper 23681; Presented at the Latin American Petroleum Engineering Conference of the Society of Petroleum Engineers, Caracas, 8–11 March 1992.

(23) The trend that higher molecular weight species have higher surface tensions is often true for compounds within a given class (e.g., a series of normalalkanes, cyclic alkanes, aromatics, etc.); see: Speight, J. G. *The Chemistry and Technology of Petroleum*, 3rd ed.; Marcel Dekker: New York, 1998; p 320. Crude oil, being a complex mixture, has properties governed not only by molecular weight, but many additional interactions.

**Table 1. Crude Oil Properties for the Initial Nine Crudes**

crude oil	designation	density (g/mL)	viscosity (cP)	% asphaltenes	% resins	foamability (mL)	collapse slope (mL/min)
Alaska North Slope	ANS	0.8894	13	3.38	8.72	30	-9
Arab Berri	AB	0.8383	4	0.79	3.24	140	-220
Arab Heavy	AH	0.9460	34	6.68	7.46	200	-39
Canadon Seco	CS	0.9030	70	7.50	8.94	45	-8
Hondo	HO	0.9377	363	14.81	20.52	5	a
Malu Isan	MI	0.8448	38	0.18	4.86	75	-22
San Joaquin Valley	SJV	0.9792	1390	4.56	19.37	0	
Statfjord	SF	0.8328	3	0.09	4.02	120	-228
THUMS 1	T1	0.9516	152	5.09	18.70	0	

<sup>a</sup> Maximum foam volume was 5 mL. Upon terminating the gas flow, the foam immediately collapsed to 1 mL. A stable foam collar remained at 1 mL for the next 8 min.

**Table 2. Gulf of Mexico (GOM) Crude Oil Properties and Solvent Standards**

sample	designation	density (g/mL)	viscosity (cP)	surface tension (mN/m)	% asphaltenes <sup>a</sup>	% resins	foamability (mL)	collapse slope (mL/min)
GOM 1M	1M	0.8926	20	27.49	3.61	10.72	365	-80
GOM 2M	2M	0.9227	68	28.66	8.71	13.71	390	-19
GOM 3M	3M	0.8911	19	27.91	4.16	9.83	257	-74
GOM 4M	4M	0.9087	48	28.41	9.10	10.49	103	-30
GOM 1A	1A	0.8387	6	26.30	0.21	3.86	30	-88
GOM 2A	2A	0.8689	10	27.74	0.50	4.77	105	-94
GOM 3A	3A	0.8567	9	27.07	0.44	4.85	97	-97
GOM 4A	4A	0.8617	9	27.20	0.36	6.10	91	-106
GOM 5A	5A	0.8235	5	26.42	0.08	1.82	24	-76
GOM 6A	6A	0.8565	24	27.71	0.33	4.38	127	-106
GOM 7A	7A	0.8477	7	26.65	0.62	4.31	39	-108
toluene		0.8628	0.5 <sup>b</sup>	28.10	0	0	0	0
heptane		0.6804	0.3 <sup>b</sup>	19.91	0	0	0	0
octane		0.6991	0.4 <sup>b</sup>	21.30	0	0	0	0
mineral oil (heavy)		0.8772	68	31.32	0	0	126	-33

<sup>a</sup> As noted in the text, the GOM A crude asphaltenes are actually waxes. <sup>b</sup> Viscosities taken from the *Handbook of Chemistry and Physics*, 65th ed.; Weast, R. C., Ed.; CRC Press: Boca Raton, 1984-1985.

surface dilatation,<sup>20,27,28</sup> surface tension,<sup>29</sup> and surface activity<sup>30</sup>) relate to various types of nonaqueous foaming have also been studied.

Similar to the approach of Callaghan and co-workers<sup>20</sup> where certain chemical species were shown to correlate to a foaminess index, this study compares both foam volume and foam stability to various crude oil properties (density, bulk viscosity, and surface tension) and crude oil components (asphaltene and resins). Another objective of this paper is to demonstrate that "dead oils",<sup>5,31</sup> which are commonly received in labs for testing and evaluation, can be used to correlate with and help determine field foaming properties. By establishing such lab based trends, and coupling this knowledge with field foaming experiences, these relationships can be applied to new fields possessing oils with similar properties.

(24) For engine lubricating oils and medicinal grade paraffin oils, see: Brady, A. P.; Ross, S. J. The Measurement of Foam Stability. *J. Am. Chem. Soc.* **1944**, *66*, 1348.

(25) McBain, J. W.; Robinson, J. V. Surface Properties of Crude Oils. Technical Note No. 1844; National Advisory Committee for Aeronautics: Hanover, MD, 1949.

(26) For lubricating oils, see: Mannheimer, R. J. Surface Rheological Properties of Foam Stabilizers in Nonaqueous Liquids. *Am. Inst. Chem. Eng. J.* **1969**, *15*, 88.

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(28) Loglio, G.; Tesei, U.; Cini, R. Dilatational Properties of Monolayers at the Oil-Air Interface. *J. Colloid Interface Sci.* **1984**, *100*, 393.

(29) Scheludko, A.; Manev, E. Critical Thickness of Rupture of Chlorobenzene and Aniline Films. *Trans. Faraday Soc.* **1963**, *64*, 1123.

(30) For a description of how surface activity relates to surface tension, see: Ross, S.; Nishioka, G. Dynamic Foam: A Problem in Fractionation and Distillation Towers. *Chem. Ind.* **1981** (January), 47.

(31) Dead oils have little or no dissolved gas. For a formal definition, see Hyne, N. J. *Dictionary of Petroleum Exploration, Drilling, and Production*; PennWell: Tulsa, 1991.

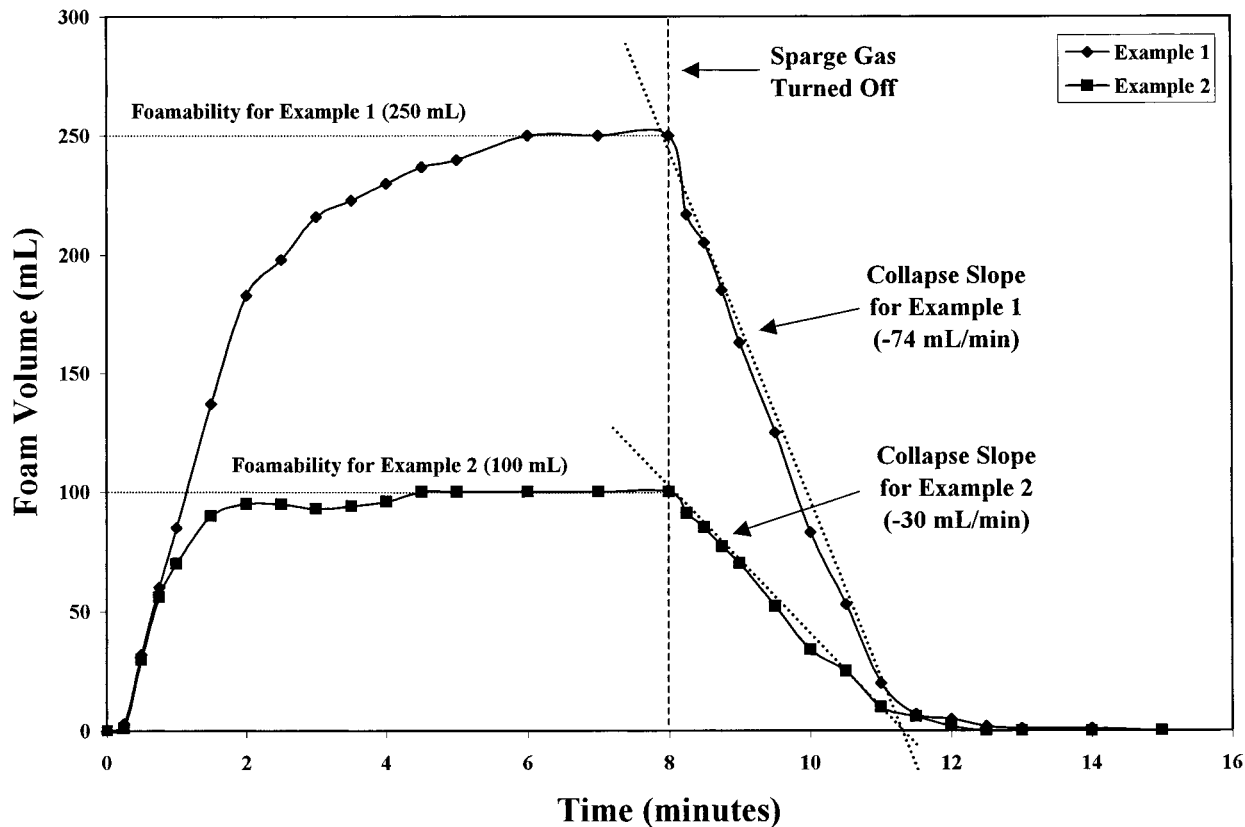
## Experimental Section

**Materials.** All solvents used were HPLC grade (acetone, methylene chloride, and toluene were from Burdick and Jackson; *n*-heptane was from EM Science; octane and heavy mineral oil were from Aldrich). Both antifoams, poly(dimethylsiloxane) VISC-60M and fluorosilicone FF160, were from GE Silicones. Crude oils from the field were chemical free (i.e. contained no antifoam) and used as received.

**Crude Oil Fractionation.** Separations for Alaska North Slope, Arab Berri, Arab Heavy, Canadon Seco, Hondo, Malu Isan, San Joaquin Valley, Statfjord, and THUMS 1 crudes were conducted according to the SARA (saturates, aromatics, resins, and asphaltene) procedure of McLean and Kilpatrick<sup>32</sup> (see Table 1 for resin and asphaltene results). Gulf of Mexico (GOM) crude oil separations (see Table 2) were conducted by the same procedure but with minor modifications. Specifically, 10 g of crude (weighed to the nearest 0.1 mg) were added dropwise to 400 mL of *n*-heptane and stirred overnight at room temperature. The solution was filtered simultaneously through both Whatman 1 and GF/B filter paper. The precipitated asphaltene was washed with *n*-heptane until the filtrate was colorless, then collected with methylene chloride, concentrated using rotary evaporation, dried in an argon-flushed vacuum oven (75 °C, 2 h), and weighed.

The filtrate (i.e., the saturates, aromatics, and resins, sometimes collectively referred to as the maltenes) was concentrated and then dissolved in 200 mL of methylene chloride. Activated silica gel (50 g, Davisil, 30-60 mesh from Aldrich) was added to the maltene solution, and the contents stirred at room-temperature overnight. The slurry was concentrated and dried in a vacuum oven (75 °C, 2 h). Using the column described by McLean,<sup>32</sup> 30 g of activated silica was

(32) McLean, J. D.; Kilpatrick, P. K. Comparison of Precipitation and Extrography in the Fractionation of Crude Oil Residua. *Energy Fuels* **1997**, *11*, 570.



**Figure 1.** Examples of foamability and collapse slope for two crudes.

added first followed by the silica loaded with maltenes. Saturates and aromatics were eluted first using *n*-heptane/toluene (68/32, v/v) followed by the resins using acetone/methylene chloride/toluene (40/30/30). The resins were concentrated, vacuum-dried (75 °C, 2 h), and weighed.

**Foaming Experiments.** Spurge experiments were conducted using a modified dynamic foam test.<sup>33</sup> The bottom of a 500 mL graduated glass cylinder was removed and fitted with a threaded glass connector (32 mm O. D. tube) from Ace Glass, Inc. The reservoir (or extension below the cylinder) ultimately held 46 mL of crude. A gas dispersion tube of medium porosity D (10–20  $\mu$ m) from Ace Glass was inserted through the bottom of the glass extension and held in place with a Teflon ferrule and nut assembly from Swagelok and a Teflon adapter (#25 thread) from Ace Glass. The top of the gas dispersion tube (distributor) was always positioned 44 mm above the bottom of the reservoir. This setup eliminated any interference caused by having a dispersion tube and associated tubing enter from the top of the cylinder.<sup>33,34</sup> The design also permits ease of gas dispersion tube replacement and exchange with tubes having different porosities, an advantage over the well-known Bikerman apparatus which has a permanently fixed porous plate.<sup>35</sup>

Nitrogen was used as the spurge gas. Related crude oil studies<sup>20,36</sup> have also used compressed air or natural gas. Gas rates were either 100 or 250 mL/min as measured by a Cole-Parmer 150-mm correlated flowmeter. Trace levels of moisture and oxygen were removed by passing the nitrogen through a

moisture trap model MT200-2 and an oxygen moisture trap model T3-2 (both from R&D Separations).

For each foam experiment, the gas rate was established at a predetermined rate (100 or 250 mL/min, depending on the crude under investigation) and diverted to an exit via a three-way valve. Before gas introduction, the attached reservoir was filled with crude oil such that the top of the liquid level was at the 0 mL mark of the foam cylinder. At the start of data recording, the gas flow was redirected to the spurge tube located in the hydrocarbon reservoir. Foam volume, measured at the air-foam interface, was visually recorded at 15 s intervals for the first minute of sparging, 30 s intervals for the next four minutes, and then each minute for the last three minutes (as depicted in Figure 1). At the eight minute mark, the gas flow was immediately terminated, and the foam allowed to collapse. The time intervals used to record foam volume during sparging were used to record foam volume during the collapse phase of the experiment.

It was determined that the same spurge tube should be used throughout the evaluation. To ensure good reproducibility, the tube was flushed immediately after crude oil foaming with the following order of solvents: toluene, acetone, toluene, and methylene chloride. After drying for 1 h at 100 °C, the tube was ready for reuse.

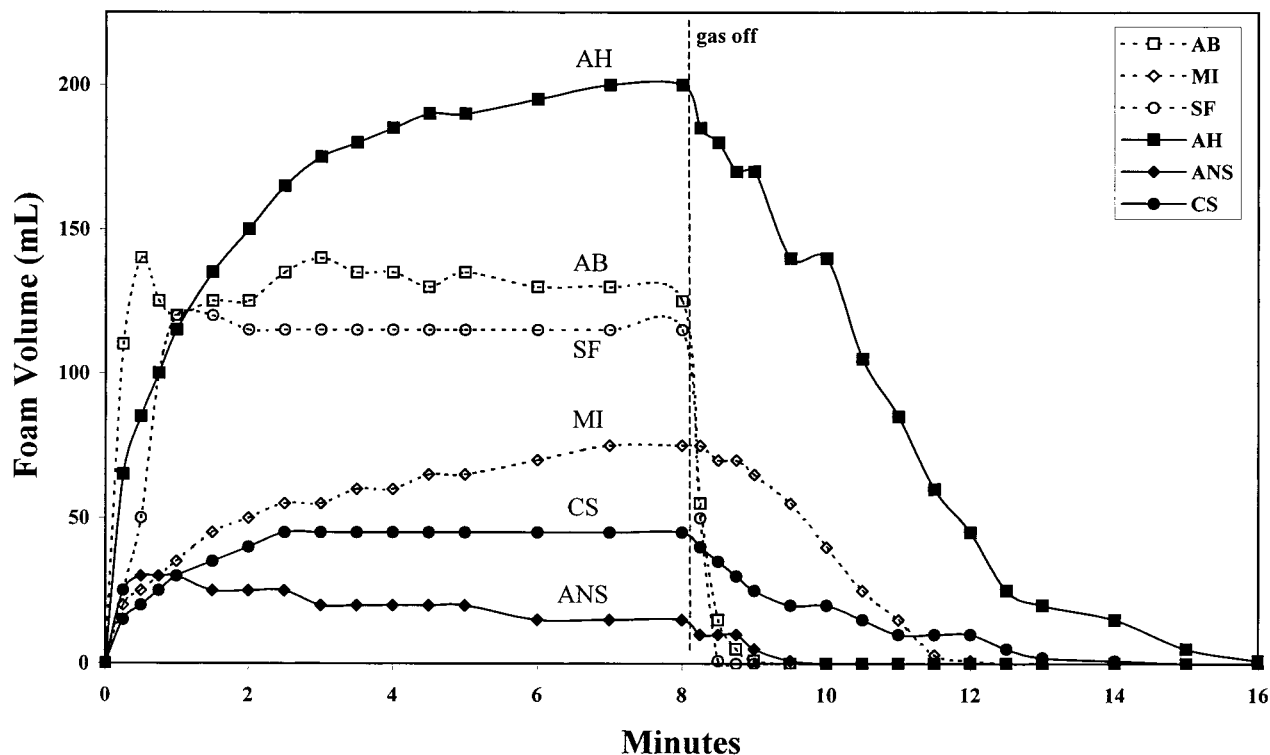
**Ancillary Measurements.** Crude oil surface tension measurements were performed on a Krüss K12 Tensiometer using a Wilhelmy plate made of platinum (width 19.9 mm, thickness 0.2 mm). Density was determined at 15.56 °C using a Paar Density Meter DMA 48. Viscosities at 37.8 °C were obtained using either a Brookfield Viscometer Model LVT with spindle no. 1 or a Brookfield Rheometer D-III+ with spindle SC4-18. Number-average molecular weights ( $M_n$ ) were determined on a UIC, Inc. 070 Vapor Pressure Osmometer (VPO) using toluene as the solvent (90 °C).<sup>37</sup> Three different concentrations of either asphaltenes or resins were used for each VPO analysis. <sup>1</sup>H NMR analyses were conducted on a 300 MHz Varian Unity Spectrometer using 5 mm sample tubes. Crude

(33) For a review of various, but related dynamic foam test apparatus and procedures, see: Schramm, L. L.; Wassmuth, F. In *Foams: Fundamentals and Applications in the Petroleum Industry*; Schramm, L. L., Ed.; Advances in Chemistry Series 242; American Chemical Society: Washington, DC, 1994; p 30.

(34) Kouloheris, A. P. Foam Destruction and Inhibition. *Chem. Eng.* **1970** (July 27), 143.

(35) Bikerman, J. J. *Foams*; Springer-Verlag: New York, 1973; p 83.

(36) Callaghan, I. C.; Neustadter, E. L. Foaming of Crude Oils: A Study of Non-Aqueous Foam Stability. *Chem. Ind.* **1981** (January), 53.



**Figure 2.** Time vs foam volume for initial crude study, nitrogen gas rate was 250 mL/min.

fractions were diluted in deuteriochloroform. To ensure complete relaxation, a total of 2,048 transients were acquired using a 30 s pulse delay and a 45° pulse width. Elemental analyses were performed by Galbraith Laboratories in Knoxville, Tennessee.

## Results and Discussion

**Foaming Response Variables.** Two key parameters, foam volume (or foamability) and collapse slope, were determined from each foam experiment where foam volume in milliliters versus time was recorded during and after sparging with gas. These parameters are illustrated for two examples in Figure 1. Foamability relates to the maximum foam volume achieved during a fixed period of time. For these studies, a sample of crude (46 mL) was sparged at a constant gas rate for eight minutes. Figures 2, 3, and 4, which represent 17 of the 20 crudes under investigation, show that in general the foam volumes are relatively stable after the first 2–3 min of sparging. Two crudes, Malu Isan (**MI**) and Arab Heavy (**AH**), in Figure 2 have foam volumes that continue to increase slightly over the eight minutes, while one crude, Alaska North Slope (**ANS**), reaches its maximum foam volume (30 mL) early in the run and then gradually drops to 15 mL. Similarly, the foam volume for Gulf of Mexico crude **2M** in Figure 3 increases throughout much of the gas sparge, while **1M** and **3M** just level out over the last few minutes.

Once the gas flow was terminated, the foam volume was measured over time. Previous work by McBain and Woods<sup>38</sup> used collapse slope to characterize a number of different lubricating oils. Using a similar method, the collapse slope for this study was determined by a least-

squares fit of the linearly decreasing part of the curve after termination of the sparge gas. Other researchers have characterized foam collapse by integrating the area beneath the curve once gas flow was stopped to obtain an average foam lifetime.<sup>39</sup> This method works well for liquids that collapse to zero or close to zero foam volume in a reasonable amount of time. However, as noted by other workers, some crude oil foams never fully collapse.<sup>11</sup> One Gulf of Mexico crude (**2M**, see Figure 3), which will be discussed shortly, falls into this category. Even after an hour of terminating the gas flow, a substantial foam volume still existed.<sup>40</sup> For crudes having this behavior, collapse slope is more appropriate and provides information that well characterizes the slow descent of the foam column. As described in Part II<sup>13</sup> of this series, collapse time was used to quantify the property of foam collapse in the absence of sparging. This technique works well for samples that collapse relatively quick.

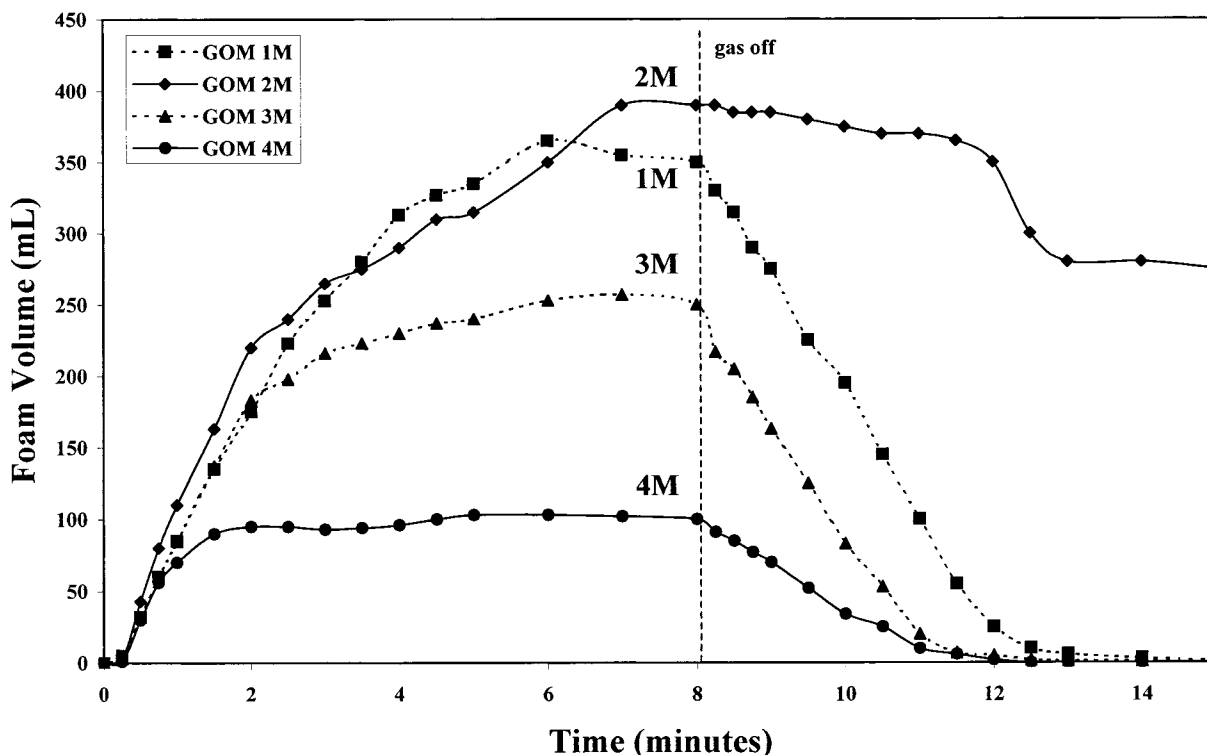
**Initial Screening of a Variety of Crudes.** The foaming studies started with nine crude oils possessing a fairly diverse range of chemical and physical properties (see Table 1). Three of the crudes (Hondo, San Joaquin Valley, and THUMS 1) generated little ( $\leq 5$  mL) to no foam when sparged with gas at 250 mL/min. These three samples were distinct from the other six crudes, having noticeably high viscosities (e.g., at 37.8 °C, 363 cP for Hondo, 1390 cP for San Joaquin Valley, and 152

(37) For a review on how temperature and solvent can influence VPO results, see: Altgelt, K. H.; Boduszynski, M. M. *Composition and Analysis of Heavy Petroleum Fractions*; Marcel Dekker: New York, 1994; pp 78–85.

(38) McBain, J. W.; Woods, W. W. Surface Effect of Various Compounds in Use with Airplane Engines upon Foaming of Aircraft Lubricating Oil. Technical Note No. 1843; National Advisory Committee for Aeronautics: Hanover, MD, 1949.

(39) Callaghan, I. C. Non-Aqueous Foams: A Study of Crude Oil Stability. In *Foams: Physics, Chemistry, and Structure*; Wilson, A. J., Ed.; Springer-Verlag: London, 1989; Chapter 7, p 95.

(40) Some researchers have introduced the term "foam collar" to describe residual amounts of foam that exist for prolonged periods of time after the sparge gas is terminated. See ref 38.



**Figure 3.** Time vs foam volume for Gulf of Mexico crude oils 1M–4M, nitrogen gas rate was 100 mL/min.

cP for THUMS 1). From these nine crudes, it was concluded that if the viscosity is approximately 150 cP or greater at 37.8 °C, then low pressure sparging will not generate foam. From the three nonfoaming crudes, Hondo was highly asphaltenic. Additionally, these three nonfoaming crudes have noticeably high levels of resins, near 20 wt %.

For the remaining six crudes, three have low asphaltene levels (Arab Berri, Malu Isan, and Statfjord) with correspondingly lower resin levels (ca. 3–5 wt %), and three have more moderate levels of asphaltenes (Alaska North Slope, Arab Heavy, and Canadon Seco) with a resin content between ca. 7–9 wt %. Two of the three low asphaltenic crudes (Arab Berri and Statfjord) have very steep collapse slopes (–220 and –228 mL/min, respectively). This behavior is readily seen in Figure 2. It is noteworthy that while these two crudes have the steepest collapse slopes of all those studied, they also have very low viscosities and densities. These short-lived foams are the result of rapid film drainage due to low bulk viscosity and low levels of foam stabilizing species such as resins and asphaltenes. Thus, once a foam column is formed, the bubbles rapidly coalesce after the gas source is removed. The other low asphaltenic oil, Malu Isan, produces a more stable foam column (–22 mL/min), behaving more like crudes having higher densities, higher viscosities, and higher asphaltene and resin contents (e.g., Alaska North Slope, Arab Heavy, and Canadon Seco).

A possible explanation accounting for Malu Isan's foam stability is its high paraffin wax content. Work by Musser and Kilpatrick<sup>19</sup> involving 16 different crudes, including those listed in Table 1, showed that Malu Isan had the highest degree of straight chain methylene groups. Thus, species such as asphaltenes, resins, or waxes which increase the bulk viscosity of the liquid tend to stabilize a foam column (see the following paper

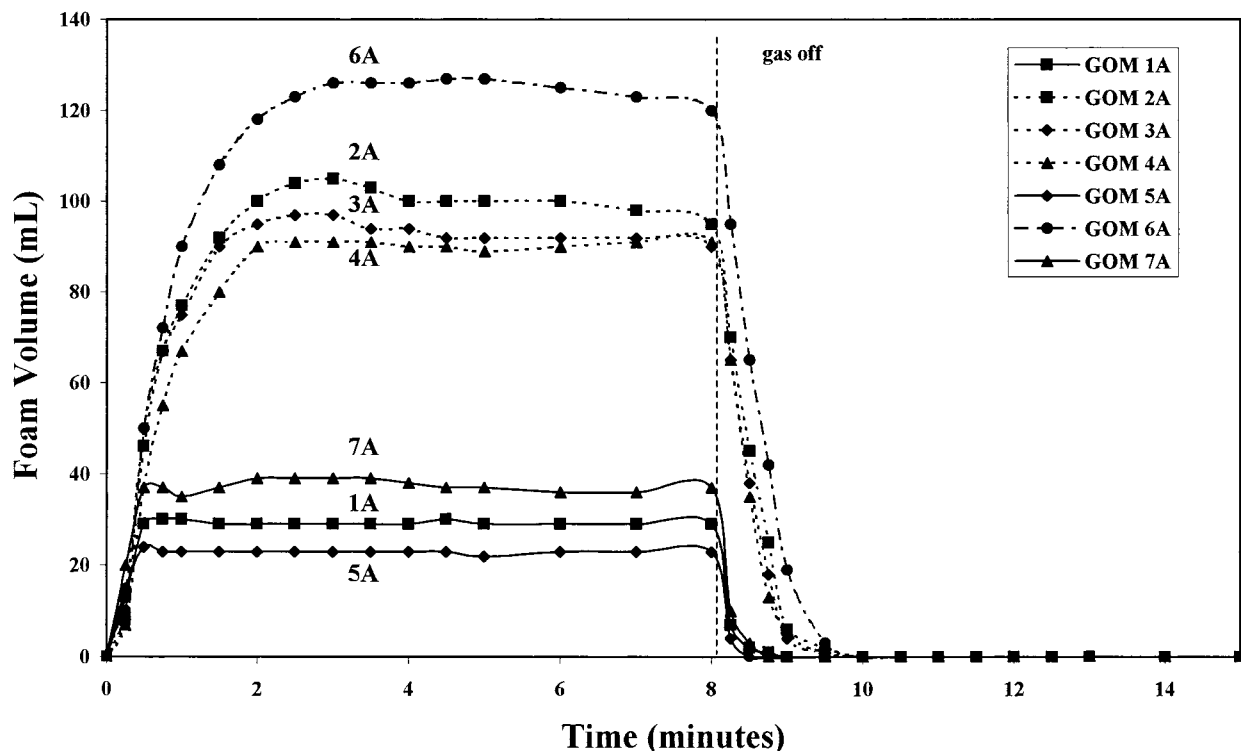
for a detailed study of this effect). This is seen when analyzing the remaining three crudes from Table 1 (Alaska North Slope, Arab Heavy, and Canadon Seco). Two of the three more asphaltenic crudes (Alaska North Slope and Canadon Seco) have very low collapse slopes (–9 and –8 mL/min, respectively), while Arab Heavy has a collapse slope (–39 mL/min) close to that of Malu Isan. Features detailing the collapse slopes of these three, more viscous crudes are seen in Figure 2. In addition to affecting the bulk viscosity, a portion of Malu Isan's wax content may also undergo surface crystallization (i.e., surface freezing) during introduction of gas. Surface wax films caused by this property of high molecular weight *n*-alkanes could readily stabilize foam as demonstrated in a number of model wax studies.<sup>41,42</sup>

While the collapse slope parameter relates to asphaltene, resin, and wax contents, which in turn relates to bulk viscosity, foamability does not seem to share such a strong relationship, particularly for the heavier crudes. As seen in Figure 2, the lighter or less asphaltenic crudes (AB, MI, and SF, see the dashed lines) have foam volumes that are more tightly grouped together (75 to 140 mL), while the heavier crudes (AH, ANS, and CS, solid lines) span a much greater range (30–200 mL). For these crudes, higher levels of asphaltenes did not lead to greater foam volumes as reported in the literature.<sup>22</sup> This same wide variability in maximum foam volume when compared to asphaltene content was seen in the next group of crude oils from the Gulf of Mexico.

**Foaming Asphaltenic Gulf of Mexico Crudes.** To further discern why collapse slope provided better correlations than foamability, eleven other crudes known

(41) Gang, H.; Patel, J.; Wu, X. Z.; Deutsch, M.; Gang, O.; Ocko, B. M.; Sirota, E. B. Macroscopic Manifestations of Surface Crystallization. *Europhys. Lett.* **1998**, *43*, 314.

(42) Sirota, E. B. Supercooling and Transient Phase Induced Nucleation in *n*-Alkane Solutions. *J. Chem. Phys.* **2000**, *112*, 492.



**Figure 4.** Time vs foam volume for Gulf of Mexico crude oils 1A–7A, nitrogen gas rate was 100 mL/min.

to cause foaming problems in Gulf of Mexico (GOM) oil/gas separators were chosen for further study (see Table 2). Four of the eleven crudes, hereafter labeled the **M** crudes, were from different wells feeding the same offshore platform. Gas sparge rates were lowered to 100 mL/min for these four crudes as higher rates (e.g. 250 mL/min as used previously) resulted in the foam column separating into two halves by a massive gas pocket, making accurate foam volume measurements impossible.

As shown from all the properties listed in Table 2, the four **M** crudes can be divided into two subgroups, with 1M and 3M forming one pair and 2M and 4M another pair. Crudes 1M and 3M are lower in density, viscosity, surface tension, and percent asphaltenes compared to crudes 2M and 4M. Resin contents for the four crudes are relatively close to one another. Additionally, crudes 1M and 3M (and likewise for 2M and 4M) pair up similarly with regard to collapse slope values ( $-80$  and  $-74$  mL/min versus  $-19$  and  $-30$  mL/min), but their foam volumes do not. For example, crudes 1M and 2M both have very large foam volumes (365 and 390 mL), while crudes 3M and 4M are noticeably lower (257 and 103 mL). Foam volume, in contrast to collapse slope, does not correlate with any crude property for these asphaltenic crudes. To illustrate these trends, Figure 5 plots one of the crude oil properties, percent asphaltenes, versus collapse slope. The same relationships between the collapse slope of 1M–3M (and 2M–4M) hold true for three other crude oil properties: density, viscosity, and surface tension. A summary of these linear correlations is provided in Table 3 where the *R*-squared values for both collapse slope and foam volume versus percent asphaltenes and resins, density, viscosity, and surface tension are listed.

**Characterization of Asphaltene-Free Gulf of Mexico Crudes.** Isolation of all **A** crude “asphaltenes”,

which existed in very low levels ( $\leq 0.62$  wt %), yielded material having a lighter brown color and a more waxy appearance compared to the **M** crude asphaltenes. Various analytical methods confirmed that the **A** crude *n*-heptane insoluble fractions were not asphaltenes but were waxlike. From vapor pressure osmometry (VPO) measurements, the **A** crude “asphaltenes” had number-average molecular weights ( $M_n$ ) that were noticeably low when compared with the **M** crude asphaltenes (see Table 4) which are more typical of literature values.<sup>37</sup> For four of the **A** crudes, the resin molecular weights were higher than their “asphaltene” counterpart molecular weights. These results suggest that the *n*-heptane insoluble fractions were likely not asphaltenes by any definition other than solubility class.<sup>43</sup>

The waxlike nature of these **A** crude fractions was further confirmed by elemental analysis (carbon and hydrogen). The high H/C atomic ratios (1.73–1.85, see Table 4) obtained for the *n*-heptane insoluble fractions were characteristic of paraffinic and/or microcrystalline material rather than asphaltenic<sup>44</sup> or even resinous material.<sup>45</sup> Also, the nitrogen content for each sample was less than 0.50 wt %. However, most asphaltenes have a nitrogen content which falls in a fairly consistent range from 0.6 to 3.3 wt %.<sup>46</sup> Nitrogen values for the **M** crude asphaltenes are within this range (see Table 4). <sup>1</sup>H NMR spectroscopy confirmed that the hydrogen

(43) Resin fraction molecular weights are substantially lower than their counterpart asphaltene molecular weights, see: Speight, J. G. *The Chemistry and Technology of Petroleum*, 3rd ed.; Marcel Dekker: New York, 1998; p 472.

(44) Asphaltene H/C (atomic ratios) typically vary from 0.98 to 1.56, see: Speight, J. G. *The Chemistry and Technology of Petroleum*, 3rd ed.; Marcel Dekker: New York, 1998; p 420.

(45) Resin H/C (atomic ratios) typically vary from 1.39 to 1.69, see: Koots, J. A.; Speight, J. G. Relation of Petroleum Resins to Asphaltenes. *Fuel* **1975**, *54*, 179.

(46) Speight, J. G. *The Chemistry and Technology of Petroleum*, 3rd ed.; Marcel Dekker: New York, 1998; p 421.

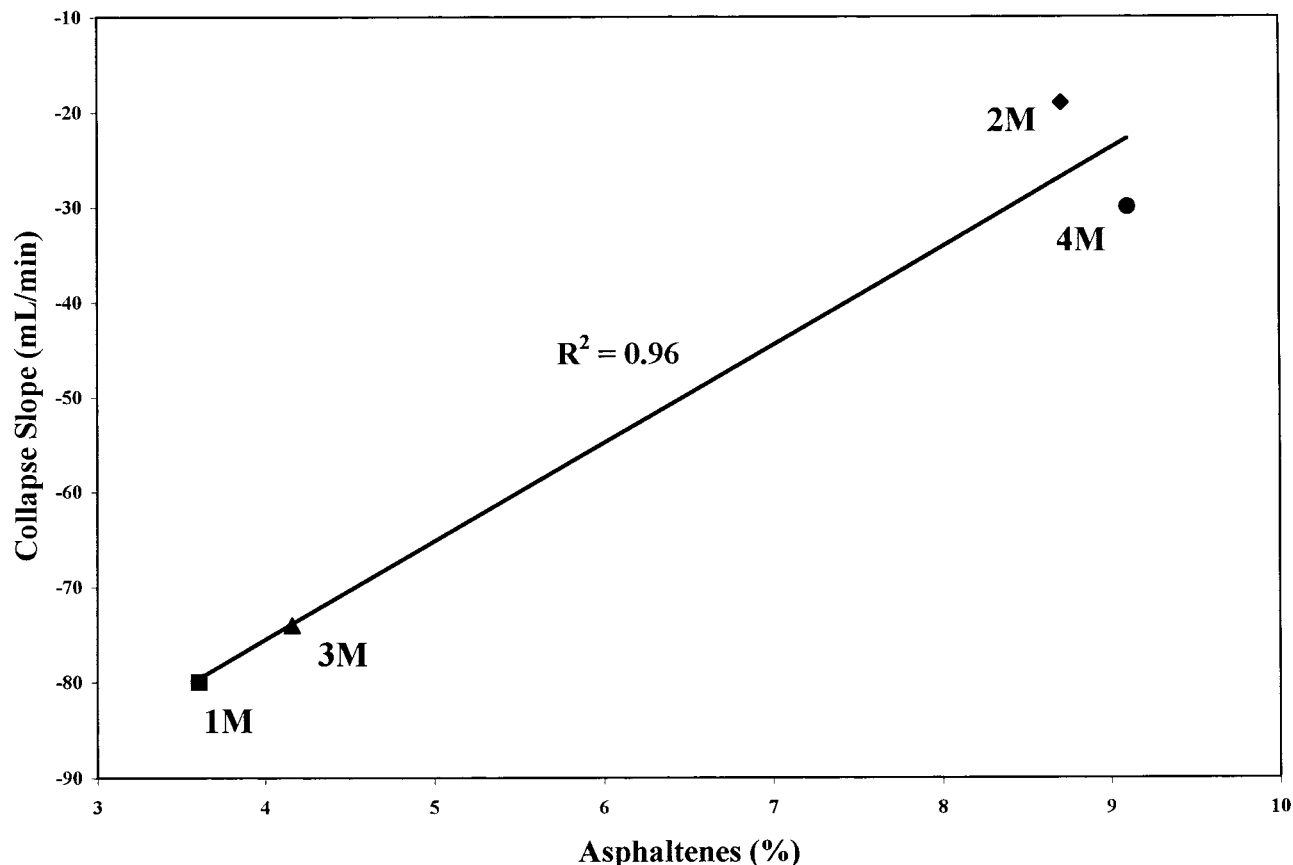


Figure 5. Percent asphaltenes vs collapse slope for the four Gulf of Mexico M crudes.

Table 3. Linear R<sup>2</sup> Correlations between Foam Parameters (Collapse Slope and Foam Volume) and Crude Oil Properties

	collapse slope	foam volume
crude oil "M"		
percent asphaltenes	0.96	0.13
percent resins	0.49	0.34
density	0.93	0.01
viscosity	0.95	0.00
surface tension	0.93	0.04
crude oil "A"		
percent n-heptane insolubles	0.56	0.13
percent resins	0.63	0.41
density	0.49	0.70
viscosity	0.25	0.60
surface tension	0.26	0.91

content was mostly aliphatic and not aromatic (see Table 5). The small aromatic hydrogen content (1.9–3.4%) corresponds to the aromatic content found in other waxes isolated from petroleum (0.3–5.0% in one study<sup>47</sup> and 0.23–0.65% in a second study<sup>19</sup>). Table 5 further shows that the wax fractions have similar amounts of methyl protons (integration from 0.4 to 1.0 ppm) and methylene/methine protons (1.0–1.9 ppm). Other chemical shifts, which were less descriptive and less prominent, are included in Table 5 for comparison. The <sup>1</sup>H NMR spectrum of crude 2A "asphaltenes" is shown in Figure 6 and is representative of the other corresponding A crude fractions. While minor in amount, the presence of these high molecular weight waxes reveals

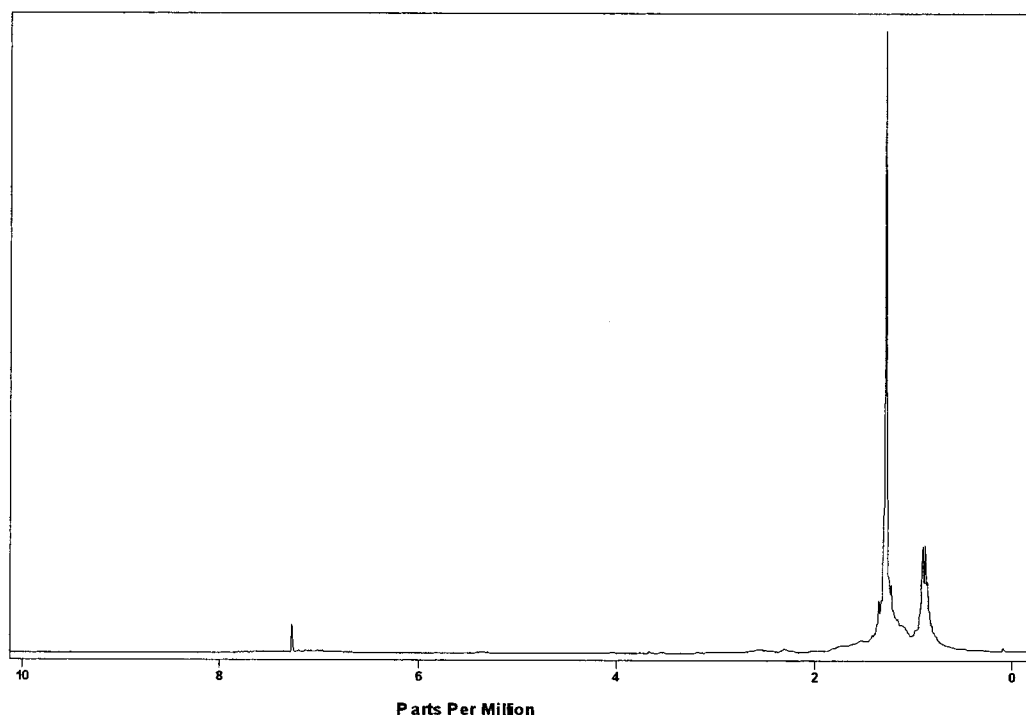
Table 4. Characterization of Gulf of Mexico Crude n-Heptane Insoluble Fractions and Resin Properties

crude	n-Heptane Insoluble Fractions					
	M <sub>n</sub>	wt % C	wt % H	wt % N	H/C	
1M	3994	81.17	8.80	0.94	1.30	
2M	4014	81.67	8.29	1.01	1.22	
3M	2796	81.65	8.71	0.99	1.28	
4M	4209	82.14	8.28	1.09	1.21	
1A	904	83.18	12.64	<0.50	1.82	
2A	838	83.79	12.10	<0.50	1.73	
3A	742	83.87	12.36	<0.50	1.77	
4A	989	83.27	12.77	<0.50	1.84	
5A	2451	84.02	12.83	<0.50	1.83	
6A	1648	82.80	12.78	<0.50	1.85	
7A	674	84.61	13.00	<0.50	1.84	
crude	Resin Properties					
	M <sub>n</sub>	wt % C	wt % H	wt % N	H/C	wt % (S+O) <sup>a</sup>
1M	1368	80.60	10.05	0.76	1.50	8.59
2M	1341	80.79	10.05	0.74	1.49	8.42
3M	1268	81.10	9.98	0.81	1.48	8.11
4M	1379	80.89	9.87	0.84	1.46	8.40
1A	799	79.13	10.73	<0.50	1.63	9.64 <sup>b</sup>
2A	1111	81.60	10.18	0.71	1.50	7.51
3A	1230	81.59	10.37	0.69	1.53	7.35
4A	1348	81.71	10.41	0.68	1.53	7.20
5A	757	80.33	10.90	0.56	1.63	8.21
6A	1136	81.77	9.98	0.77	1.46	7.48
7A	853	81.12	10.76	0.58	1.59	7.54

<sup>a</sup> Calculated by difference, wt % (S+O) = 100% - % C - % H - % N. <sup>b</sup> Assumed that % N = 0.50 wt % for calculation.

a drawback in isolating asphaltenes using most SARA separation methods. High molecular weight waxes can have solubility properties that begin to resemble as-

(47) Winschel, R. A.; Robbins, G. A.; Burke, F. P. Improvement in Coal Liquefaction Solvent Quality by Dewaxing *Fuel* 1987, 66, 654.



**Figure 6.**  $^1\text{H}$  NMR spectrum of Gulf of Mexico **2A** crude *n*-heptane insoluble fraction in deuteriochloroform.

**Table 5.**  $^1\text{H}$  NMR Analysis (%) of Gulf of Mexico **A** Crude *n*-Heptane Insoluble Fractions

crude	$\text{CH}_2/\text{CH}_3$ ratio	6.3–9.3 ppm <sup>a</sup>	5.1–5.5 ppm	3.0–4.3 ppm	1.9–3.0 ppm	1.0–1.9 ppm <sup>b</sup>	0.4–1.0 ppm <sup>c</sup>
<b>1A</b>	4.7	2.8	0.5	2.4	5.5	67.3	21.5
<b>2A</b>	4.2	2.5	0.1	0.6	6.3	66.7	23.8
<b>3A</b>	5.4	2.2	0.1	0.5	5.2	72.0	20.0
<b>4A</b>	5.7	1.9	0.1	0.6	5.0	73.3	19.1
<b>5A</b>	5.9	2.9	0.6	5.6	6.1	67.7	17.1
<b>6A</b>	5.1	2.5	0.1	1.0	6.1	69.8	20.5
<b>7A</b>	3.7	3.4	0	0.4	6.3	64.0	25.9

<sup>a</sup> Aromatic protons. <sup>b</sup> Methylene and methine protons. <sup>c</sup> Methyl protons.

phalthenes (i.e. having greater solubility in toluene than in *n*-heptane).<sup>48</sup>

#### Foaming Asphaltene-Free Gulf of Mexico Crudes.

Compared to the **M** crudes, the seven Gulf of Mexico **A** crudes are much lighter having no asphaltenes and lower densities, viscosities, and resin contents (see Table 2). Though chemically different, the **A** crudes provide another representation of oils that foam in oilfield separators. Like the **M** crudes, each of the **A** crudes are from different wells that are processed on the same platform. To make comparisons between the two Gulf of Mexico crude sets, the **A** crudes were also sparged at 100 mL/min.

During the foam collapse of the **A** crudes, all gave smooth and steep descents as seen in Figure 4. The foam collapse of these seven crudes had the same pattern as seen for the two lowest viscosity crudes in Figure 2, specifically, Arab Berri and Statfjord. When subjected to gas sparging, these crudes all produce polyhedral (dry) foams with a uniform, small bubble size distribution throughout the foam column. In comparison, the

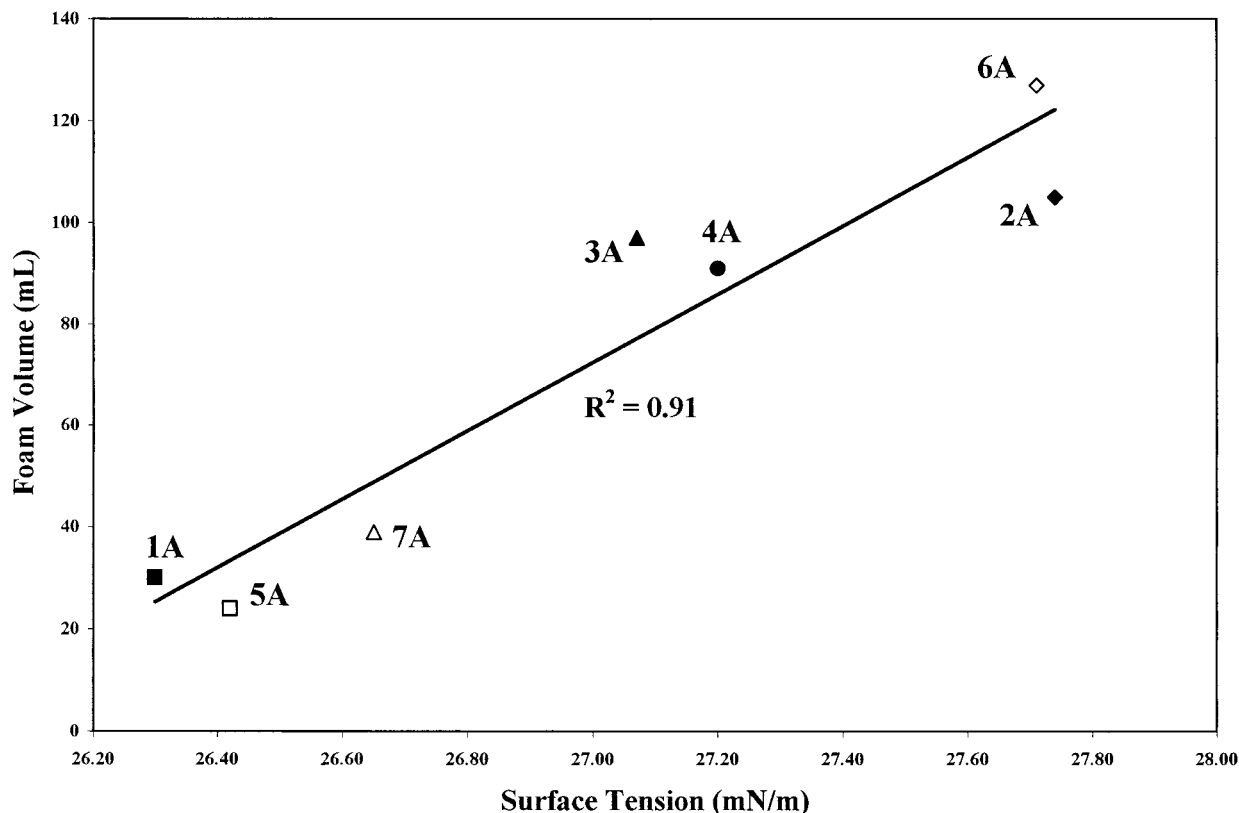
foam collapse for the heavier, more dense crudes (**AH**, **MI**, **CS**, **ANS**, and **1M-4M**) possess a somewhat irregular foam decline. This difference is attributed to the heavier crudes producing foams with a broad bubble size distribution, and like the **A** foams, the **M** foams also have polyhedral shaped bubbles. For the heavier crudes when a group of large bubbles coalesced, a noticeable drop in foam volume was seen, thus creating the periodic stepwise descent. Additional experiments were performed to further demonstrate that the foams created were in fact not gas dispersions, but true dry foams. As noted by Callaghan and co-workers, true gas dispersions (or wet foams) are not readily affected by the addition of an antifoam while polyhedral foams are.<sup>5</sup> When silicone-based antifoams were added to the foam column of each **M** and **A** crude, complete foam collapse was achieved.<sup>49</sup>

For the **A** crudes, the collapse slope values are all relatively close to each other and rather steep, ranging from  $-76$  to  $-108$  mL/min (see Figure 4 and Table 2). While the lower end of this range ( $-76$  mL/min for **5A**) overlaps with the collapse slope observed for two of the **M** crudes (**1M** and **3M**, which have collapse slopes of  $-80$  and  $-74$  mL/min, respectively), a noticeable difference between the **M** and **A** crudes exists. Crude **5A** collapses in about 15 s, while **1M** and **3M** collapse over significantly longer times, 4 and 3 min, respectively. These similar collapse slope values start from noticeably different foam volumes. The foam volume of **5A** is 24 mL, but **1M** and **3M** have volumes of 365 and 257 mL, respectively. Thus, the **M** and **A** crudes are in clearly distinct classes whether one makes foaming or compositional comparisons.

While collapse slope proved to be the most appropriate property characterizing the foam quality of the heavier **M** crudes, foam volume proved to be more descriptive

(48) Freund, M.; Csikós, R.; Keszthelyi, S.; Mózes, Gy. *Paraffin Products: Properties, Technologies, and Applications*; Mózes, Gy., Ed.; Developments in Petroleum Science 14; Elsevier Scientific: New York, 1982; p 124.

(49) Either a poly(dimethylsiloxane) or a fluorosilicone was employed at 50 parts per million based on the total volume of crude oil used.



**Figure 7.** Surface tension vs foam volume for the seven Gulf of Mexico A crudes.

for the lighter A crudes. As seen in Figure 4, the seven A crudes can be split into two subgroups – four higher foaming crudes (2A, 3A, 4A, and 6A) and three lower foaming crudes (1A, 5A, and 7A). For these lighter crudes, foam volume strongly relates to surface tension (see Figure 7). As surface tension is reduced, foam volume is reduced. Initially, this seems counter intuitive since in some texts,<sup>50</sup> it is generally taught that as surface tension is reduced the ability to foam is increased. However, as will be discussed shortly, the A crude resins are not identical to each other, and the solvency (aromatic/aliphatic character) of each crude is unique and will differ.

Tables 2 and 4 provide several trends and a plausible explanation regarding the relationship between the observed surface tension reduction and corresponding foam volume decrease. The number-average molecular weights of the seven A resins can be divided into two groups, those with  $M_n > 1100$  (A2, A3, A4, and A6; i.e., crudes with higher foam volumes), and those with  $M_n < 900$  (A1, A5, and A7; crudes with lower foam volumes). Additionally, the former four crudes have higher nitrogen contents (0.68–0.77 wt %), while the later three crudes have lower nitrogen contents ( $\leq 0.58$  wt %). If the percent remaining heteroatom content as calculated by difference is compared, the higher foaming crudes have less inferred sulfur/oxygen content (7.20–7.51%), while the lower foaming crudes have more sulfur/oxygen (7.54–9.64%). The nitrogen and sulfur/

oxygen concentrations are in opposition to each other; however, they consistently group themselves with regard to crudes having either larger or smaller foam volumes. Additional groupings are evident when comparing the larger foam volume A crudes to the smaller foam volume A crudes. The former group is consistently higher in density, viscosity, and resin concentration (Table 2). A summary of  $R$ -squared values for the A crudes is given in Table 3.

Apparently, resins which are both larger and have a particular heteroatom arrangement or distribution could conceivably form larger aggregates. Larger aggregates could in turn influence the viscosity (e.g., surface viscosity) or film elasticity enough to allow the buildup of higher foam columns during gas sparging. While the nature of the resins appears to effect foamability, the effect is not carried over to collapse slope when gas sparging is removed. The A crudes, having relatively low bulk viscosities, are not able to support the foam column once gas sparging is terminated. Rapid film drainage leads to steep collapse slopes.

**Additional Crude Oil Comparisons.** The bottom portion of Table 2 provides several hydrocarbon solvents that illustrate the behavior of well-defined fluids in the foaming apparatus. Subjecting these solvents to the foaming conditions of the M and A crudes reveals, as expected, that the low molecular weight pure solvents (toluene, heptane, and octane) do not foam. These low viscosity solvents produce gas dispersions as the bubbles exiting the gas distributor immediately burst when they reach the top of the reservoir. No polyhedral foam is generated. By increasing the gas flow to much higher rates ( $\geq 560$  mL/min) gas dispersions were created with volumes reaching 10–20 mL.

(50) While surface tension plays a role in foaming, see, for example, Schramm, L. L.; Wassmuth, F. In *Foams: Fundamentals and Applications in the Petroleum Industry*; Schramm, L. L., Ed.; Advances in Chemistry Series 242; American Chemical Society: Washington, DC, 1994; p 9, the authors teach that other factors are also important (e.g., surface elasticity and other rheological properties).

When the density, viscosity, and surface tension of an alkane-based solvent system are increased, as in the heavy mineral oil case, a stable foam results (bottom of Table 2). In fact, the foamability and collapse slope of mineral oil are both well within the range of the **M** crudes. When comparing mineral oil physical properties to the **M** crudes, its density is lower, viscosity is comparable, and surface tension is noticeably higher. Mineral oil, containing no asphaltene or resins, is able to generate and stabilize foam by high bulk viscosity and possibly by the surface crystallization of *n*-alkanes at the oil-air interface.<sup>41,42</sup> However, in many respects, it is not possible to make direct comparisons between mineral oil and any of the crude oils. Their compositions are radically different. In an attempt to make such comparisons, Part II<sup>13</sup> of this work studies the effect of adding crude oil constituents, asphaltene and resins, to several model solvent systems where the aromatic/aliphatic ratio is varied. This systematic approach allows investigation of constituent concentrations and their ratios (i.e. resin/asphaltene) not feasible from selecting even a wide range of crudes from the oilfield.

### Conclusions

Crude oils, sampled and depressurized in the field, were studied in low pressure lab foaming tests. Two foam parameters, foam volume and collapse slope, were found to correlate with certain commonly measured crude oil properties – density, bulk viscosity, surface tension, asphaltene and resin contents as determined by SARA analyses, resin molecular weights as measured by VPO, and heteroatom content of the resins. As a first indicator, viscosity plays a key role in determining whether foam generation is possible with the low-

pressure sparge test. Crudes having viscosities at or above 150 cP at 37.8 °C produce little or no foam. Thus, the sparge method run at room temperature is not adequate to study crudes of this nature.

For asphaltenic crudes, collapse slope was found to correlate with asphaltene concentration as well as crude oil density, viscosity, and surface tension. On the other hand, asphaltene and resin contents as well as crude oil density, viscosity, and surface tension did not relate to foam volume. In one case, a crude with few asphaltene (Malu Isan) but with high levels of wax was shown to behave like an asphaltenic crude.

For crudes having no asphaltene, foam volume was found to correlate with crude surface tension and the chemical nature of the resinous fraction. Crudes with resins having higher molecular weights and higher nitrogen content produced larger foam volumes. Higher foaming non-asphaltenic crudes also had higher densities, viscosities, and resin concentrations. Future work needs to determine if crudes having lower asphaltene levels than those studied (ca. 1–3%) would best be characterized by foam volume, collapse slope, or some combination of the two parameters.

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