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Studying the Effect of Hydrophobic Particles on Foam Formation in Fluid-contact Devices of a Petroleum Refinery

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Abstract

Foam formation in fluid-contact devices (e.g., refining, absorption, and reaction) operating with hydrocarbon liquids is undesirable because it decreases the volume required for mass and heat transfer inside the chemical device and, for example, in thermal cracking reactors, leads to cocking of the product and thus reduces the reaction performance. A practical study was conducted on the effect of operational conditions (surface velocities of gas and liquid, the volume of solid particles, volumetric percentage of particles loaded in the column, and the type of those particles) on foam formation in a column operating with a hydrocarbon liquid (kerosene), as well as a study to find a simple and inexpensive method to reduce foam. Experimental results revealed that the fluid hydrodynamics of reduction foam using solid particles can be accelerated to attack foam bubbles by converting the particles from hydrophilic to hydrophobic ones. It is also shown that a feasible method could be used to convert solid particles into hydrophobic ones. The water contact angle technique and FTIR analysis were utilized to predict this conversion. The foam's volume fraction was reduced from 0.8 to 0.15 when using hydrophobic particles with a diameter of 0.25 mm and a fluid velocity of 0.3 cm/s. The results of this study may have a wide application in the oil and petrochemical industries.

Keywords: three-phase columns, fluid flow, foam reduction, hydrophobic particles.

الخلاصة

الرغوة هي ظاهرة غي مرغوب بها في اجهزة تلامس الموائع (التكرير، الامتصاص، و التفاعل) التي تعمل بالسوائل الهيدروكربونية وذلك لان الرغوة تقلل الزمن اللازم لبقاء السائل داخل الجهاز وتؤدي مثلاً في مفاعلات التكسير الحراري الى تفحم المنتج وبالتالي تقلل من كفاءة اداء التفاعل. تم اجراء دراسة عملية لتاثير الظروف التشغيلية (السرعة السطحية للغاز والسائل، حجم الدقائق الصلبة، النسبة الحجمية للدقائق المحملة في العمود ونوع تلك الدقائق) على تكون الرغوة في عمود يعمل بسائل هيدروكربوني (كيروسين) وكذلك دراسة ايجاد طريقة بسيطة وغير مكلفة لتقليل الرغوة. من خلال البحث الحالي تم (يمكن تحفيزها لمهاجمة Hydrophilic استنتاج الاتي : ان تقليل الرغوة في عمود يستخدم الدقائق الصلبة المحبة للماء) (وقد استخدمت طريقة عملية Hydrophobic الى دقائق كارهه للماء Hydrophilic فقاعات الرغوة بتحويل الدقائق من) (للتأكد من عملية التحول تم استخدام تقنية قياس زاوية تلامس الماء مع الصلب Hydrophobic لتحويل الدقائق الصلبة الى) (Hydrophobic). تم تقليل الكسر الحجمي للرغوة من 0.85 الى 0.15 عند استخدام دقائق كارهه للماء (FTIR وكذلك تقنية) 0.3. ان نتائج هذه الدراسة يمكن ان يكون لها تطبيقات واسعة في مجال الصناعات cm/s ذات القطر 0.25 ملم وسرعة سائل النفطية والبتروكيمياوية.

الكلمات الافتتاحية: اعمدة ثلاثية الاطوار، جريان موائع، تقليل الرغوة، الدقائق الكارهة للماء.

1. Introduction

The activity and performance of petroleum contact devices (e.g., hydroconversion reactors, distillation columns, and absorption columns) highly rely on the hydrodynamics and operating conditions. The design and scale-up of fluidized bed reactors generally depend on the quantification of three main phenomena: mixing characteristics; heat and mass transfer characteristics; and chemical kinetics of the operating system. Thus, the published data confirm the requirement for an improved knowledge of the two or three-phase hydrodynamics and its effect on phase mixing, and exchange properties [1].

Foaming is an exciting phenomenon and has been an issue of the study for about two centuries [2]. It is significant to know the construction of foam to realize its behavior. The phenomena demanded in its structure decide how the foam interacts with a force. The structural elements can slip and change conformation or break. Foam is reported as a viscoelastic fluid. Because its structure is affected by the liquid part, so is its way of acting [3].

Foaming causes significant issues in many industrial operations. Weekman and Myers [4] found a high increase in pressure drop in the bulk for foaming fluids. Charpentier and Favier [5]; and Bartelmus and Janecki [6] presented flow maps for foaming. Foam might decrease products and separation efficiency or can even cause pollution of products because of the taking of foam from other vessels [7-8]. In hydrocracking and other foaming reactors, the foam rises to the upper section since it contains more gas fraction than the bubbly bulk from which it creates. The large percentage of foams is unwanted in petroleum reactors because it highly decreases the liquid residence time and in hydrocracking reactors also enhances the generation of coke [9].

The aim of the present work was to understand the role of fluidized particulates in a hydrocarbon stream flowing in a three-phase contactor and to develop a simple and inexpensive process for foam suppression which can be employed in the petroleum industries especially in the hydroconversion reactor without requiring excessive additional materials.

2. Material And Methods

2.1 Material

The silica sands of composition (0.7% max. Fe_2O_3 , 96% min. SiO_2 , and 1% max. Al_2O_3) were supplied by the state company for mining industries in Iraq. octanol ($\geq 99\%$) was supplied by Sigma- Aldrich, India. Glycerin ($\geq 99\%$) was purchased from Riedel-DeHAën AG, Germany. Kerosene and deionized water were purchased from local market

2.2 Methods

2.2.1 Experimental setup

Specifications of equipment and auxiliaries used during the current study are shown in Table

Table 1: Equipment used in the experimental setup

Item	Description
Column)	72 mm i.d x 1600 mm long), Plexiglas
Feeding pump	Centrifugal (KSB), Flow rate= $1\text{m}^3/\text{h}$, Head=20m, carbon steel
Feeding tank	Volume=100-Liter, PVC

Pressure gauge	Bourdon type gauge, 4 in. dial, 0- 200 mbar, stainless steel
Gas flow meter	Floating type flowmeter, 0- 800 L/min, glass made.
Flow meter for fresh liquid	Floating type flowmeter, 0- 40 L/min, glass made

The experimental set up is composed of a Plexiglas column equipped with six sampling taps located axially along the column; a feeding tank, a centrifugal pump using for fresh feed as shown in Fig. 1 (a & b). The feeding of liquid and air was at the bottom of column through a mixing chamber beneath a distributor grid (8.6 cm OD x 2 mm thickness) made of a stainless steel 316 perforated with 31 holes ($d_h = 1.0$ mm). Packings of ceramic and plastic Raschig were placed into the mixing chamber to enhance the distribution of liquid and gas. A compressor was used to supply an oil-free air to the column. The feeding gas and liquid are regulated via calibrated flow meters for the gas (F2) and the liquid (F1) respectively. Details of the column internals are shown in Fig. 1 (A & B). At the top of the column, a two-phase flow of air and liquid were discharged out of the system. Water is used, as the continuous phase. All the sampling taps were connected to a valve which facilitates the use of the taps for pressure measurement (connected to a pressure manometer, 0 – 200 mbar). Ranges of operating variables (i.e., average particle size, liquid flow rate, gas flow rate, and solid concentration) used in the present work are listed in Table 2.



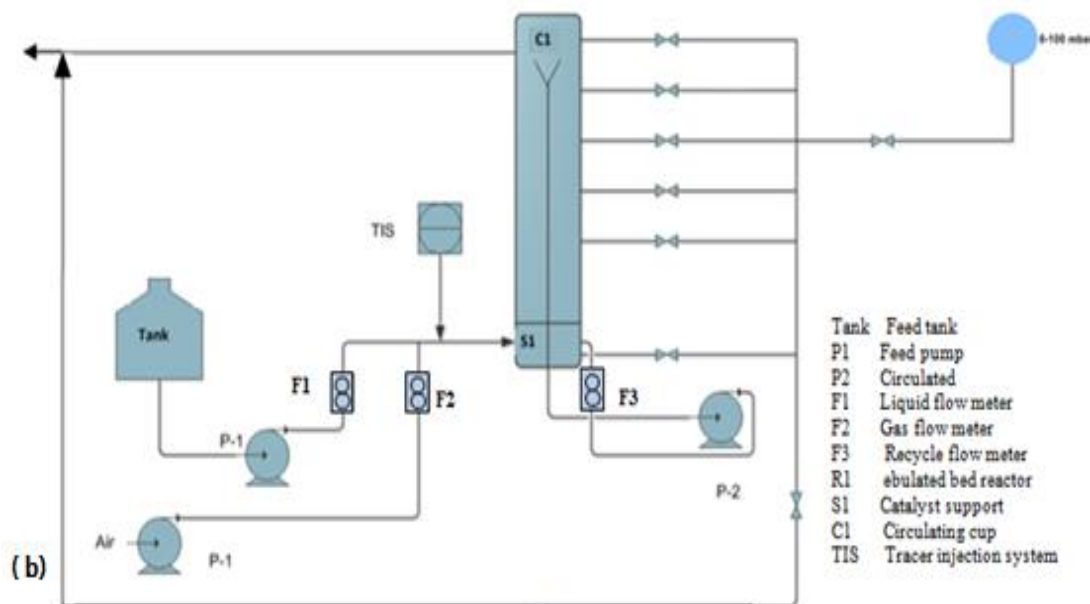


Fig. 1: Experimental setup

2.2.2 Surface modification of sands

Hydrophilic sands have been changed into hydrophobic using the technique of Maloney and Oakes [10] who revealed that sands that are hydrophilic substances are combined with hydrophobic aliphatic primary or secondary alcohol (e.g., octanol) with (C atoms > 8) in silica / hydrophobic alcohol weight ratio of about (0.25:1) and heated to a temperature above (100 °C) till the species react to generate the products. Maloney and Oakes reported that particulate siliceous materials having significant surface hydroxylation or surface silanol content can react chemically with hydrophobic alcohols to form hydrogen bonds which appear to be more stable at a high operating temperature that is equivalent to the operating temperature of the hydroconversion reactor.

In the present work, octanol was used as the liquid carrier of the solid particles. The resulting mixture was heated below the boiling point of octanol (i.e. 178 °C) for a time period of (4 hrs) which was sufficient to cause the silica to chemically react with the substantially hydrophobic alcohol.

The influence of surface modification on the silica particles was investigated by measuring the water-particle contact angle. The meter of contact angle model (CAM 110-Taiwan) was employed to quantify the contact angle of water (WCA); a 5 µL DI water was trickled on the silica particle. Moreover, The surface functional groups were predicted by Fourier transform infrared (FTIR) spectrophotometer (NICOLET, Nexus 870 FTIR, USA).

2.2.3 Experiments design

In the present work, the factorial design technique was utilized for arranging the experiments due to its validity in investigating the impacts and interactions among the studied parameters of the experimental system. The real values and their levels are shown in Table (2).

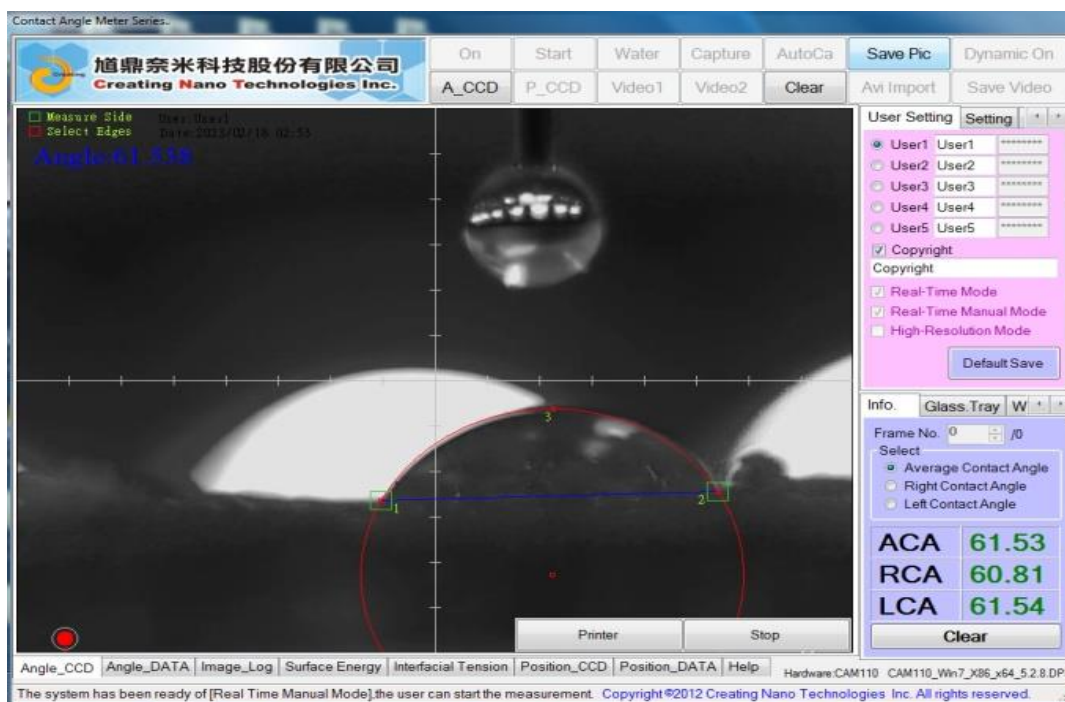
Table 2: Selected levels and factors

Variables	Levels and range		
	(-1)	(0)	(+1)
Average particle size (mm)	0.25	0.55	0.75
Liquid flow rate (L/min)	0.5	1	2
Gas flow rate (L/min)	20	40	70
Solid concentration % (V/V)	0	10	20

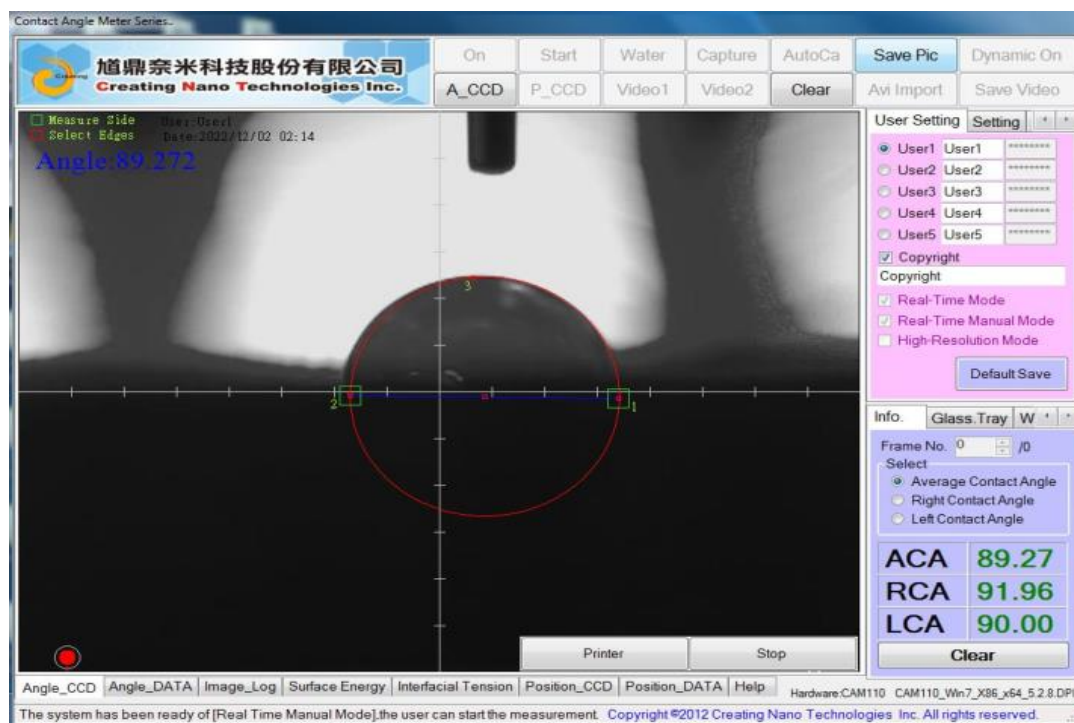
4. Result And Discussion

4.1 Surface morphology

Figure 2 (a, and b) displays the effect of the surface modification technique used in the present work on particle wettability. In Figure 3b it is shown that, after the surface treatment of silica particles, the contact angle attained a value of 91° meaning that a hydrophobic surface was obtained.



(a)



(b)

Figure 2. Water contact angle of Iraqi Silica used (a) before surface modification; (b) after surface modification

To investigate the influence of the chemical characteristics of microparticles on heavy oil viscosity, the surface microparticles were characterized utilizing FTIR. The FTIR images of the untreated and treated silica microparticles are seen in Figure 3 (a, and b), respectively. As can be observed in Figure 5b, the common oscillations of the siloxane and silanol groups could be noticed in all of the microsubstances. The bands at around 740 and 820 cm^{-1} represent the Si-O bond flexion, and the wide band between 845 and 955 cm^{-1} corresponds to the O-Si-O stretching oscillations. Additionally, the neighboring confronting band between 1100 and 1350 cm^{-1} exhibits identical bonds as asymmetric stretching [11]. Moreover, the existence of silanol groups is linked to the band between 2550 and 3850 cm^{-1} formed by the O-H bond oscillations. The band at 1650 cm^{-1} demonstrates OH scissoring [12].

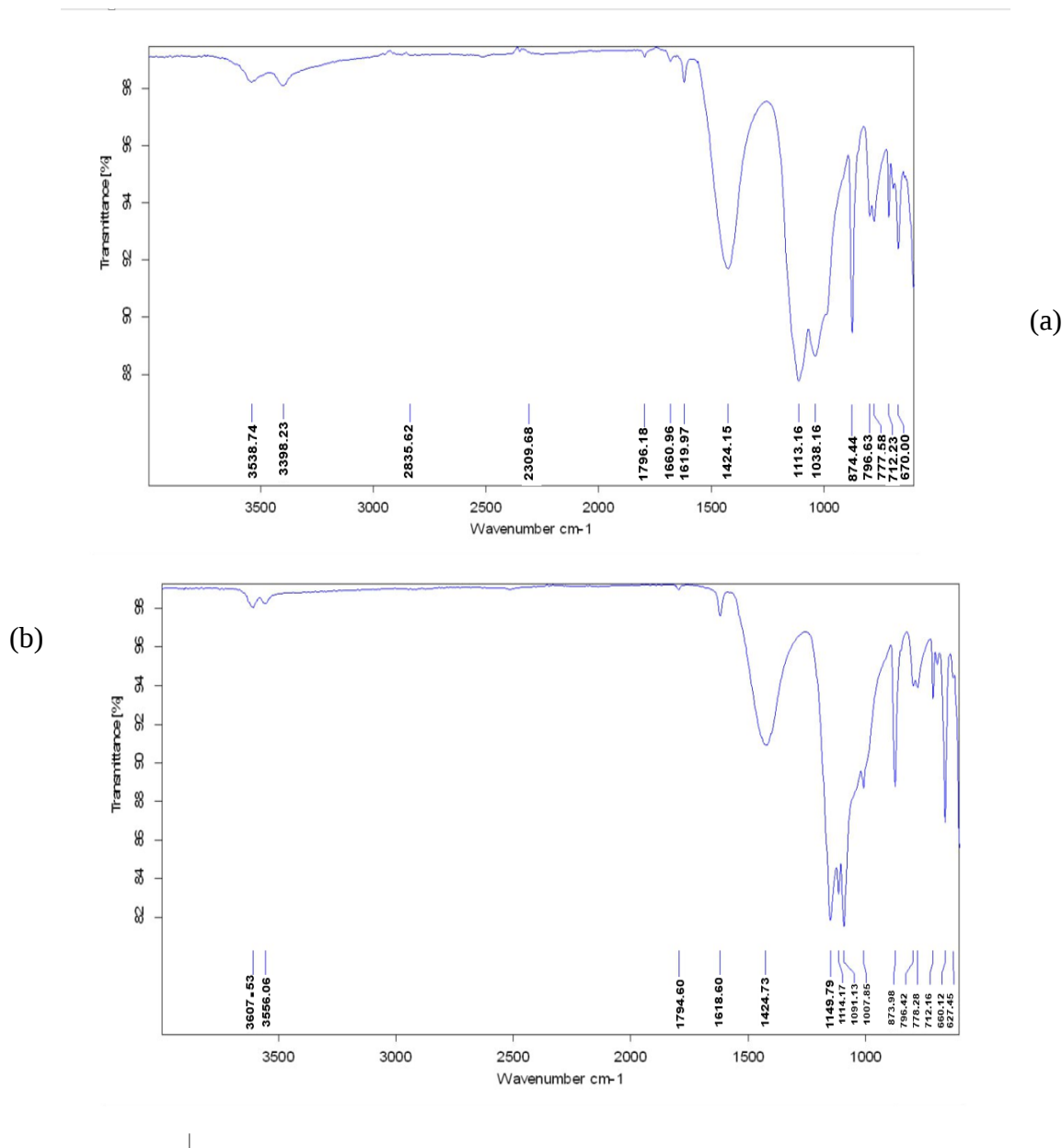
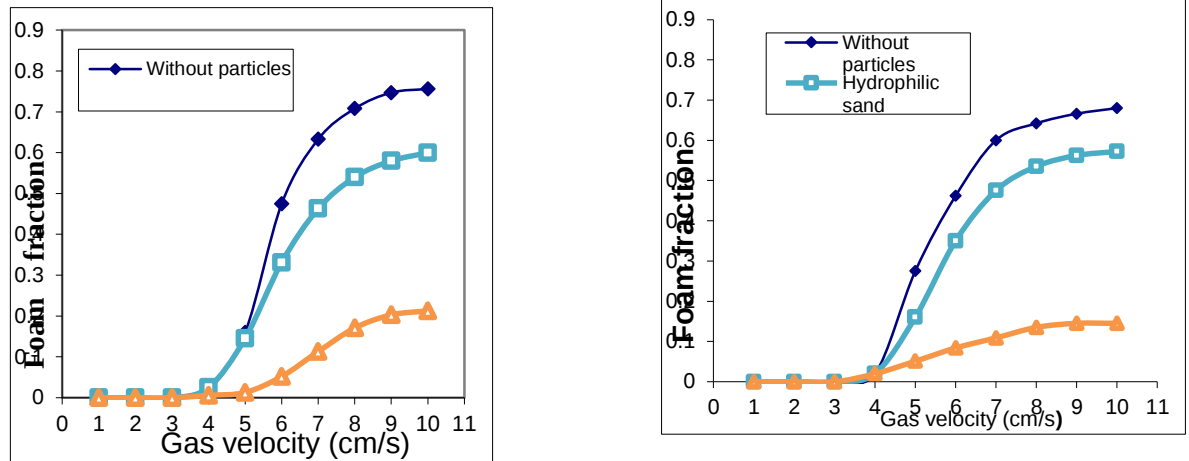


Fig. 3: FTIR spectra for silica particles (a) before surface modification; (b) after surface modification

4.2 Effect of operating variables on foaming

Figures (4-a) and (4-b) illustrate the foaming against the gas velocity at liquid velocity of 0.15 cm/s and 0.30 cm/s, respectively. It is shown that the hydrophobic particles reduced the foam more than the hydrophilic ones. The fluid mechanics of foam reduction with the hydrophilic particles are promoted by an attacking of foams by hydrophobic particles. This enhancement is due to the

reduction of the density of the hydrophobic particles in comparison with that of the hydrophilic ones leading in simple permeating into the foaming zone that existed at the upper section of the reactor.



(a) (b) **Fig. 4: Foam fraction against gas velocity, at a liquid velocity of (a) 0.15 cm/s and (b) 0.3 cm/s**

Figures (5-a) and (5-b) show the foam fraction as a function of the gas velocity at liquid velocities of 0.076 cm/s and 0.15 cm/s respectively, for the surfactant solution without particles and with a 10% volume fraction of hydrophilic and hydrophobic sand, with a mean size of (400-600). As expected, the hydrophobic particles decrease foam fraction better than their hydrophilic counterparts. As can be seen, increasing particle diameter has a proportional effect on the foam formation, while increasing liquid superficial velocity adversely impacts the foam formation. Our results agree well with previous published data of [13-14]

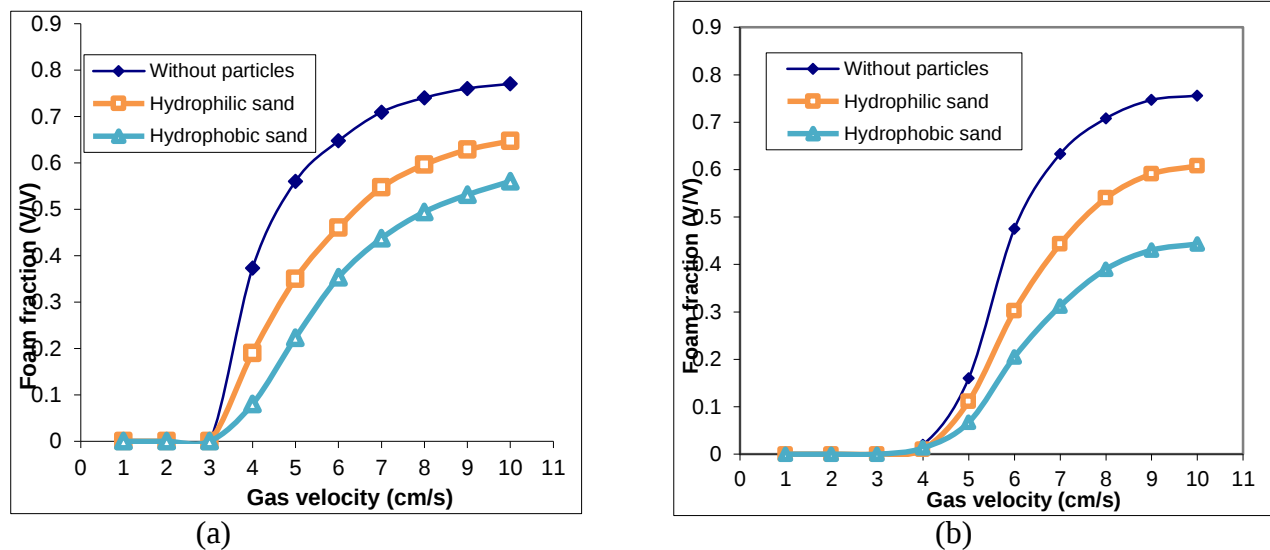


Fig.5 Foam fraction against gas velocity with a mean particle size of (400-600) μm and at a liquid velocity of (a) 0.076 cm/s and (b) 0.15 cm/s

In Figure (6), the foam fraction as a function of the gas velocity at a liquid velocity of 0.15 cm/s is compared for three mean size ranges; (200-300), (400-600), and (700-900) μm , for hydrophobic sand. As expected the smaller particles suppressed better the foam formation. The foam fraction seems to reach a plateau and even a change of slope in the foam curve at a gas velocity of approximately 8 cm/s. They expanded so well and penetrated the foam so easily, that a large accumulation of particles was observed at the top of the column.

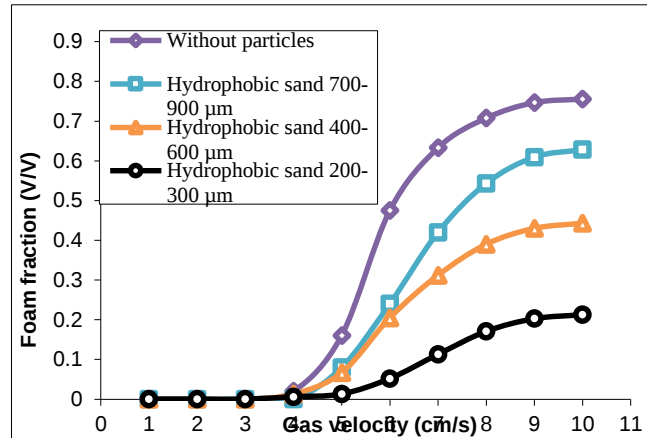


Fig. 6: Foam fraction against gas velocity with different sizes of hydrophobic particles and at liquid velocity of 0.15 cm/s

In Figure (7), two different volume fractions (10% and 20%) of the hydrophobic particles with an average size of (0.800) mm are compared for their effect on foam fraction at different gas velocities and constant liquid velocity of 0.15 cm/s. As seen in Fig.7, the foam reduction was enhanced by the use of the highest solid fraction. A visual observation of the bed expansion of the hydrophobic and hydrophilic particles was of interest. Hydrophobic particles have expanded more than the hydrophilic ones. More of the hydrophobic particles permeate the foam bed and elevate to the upper section of the column. Interestingly, as the gas and liquid flows are cut off, hydrophobic particles aggregate at the foam interface. This is attributed to the trapping of air by the hydrophobic particles as in a flotation process.

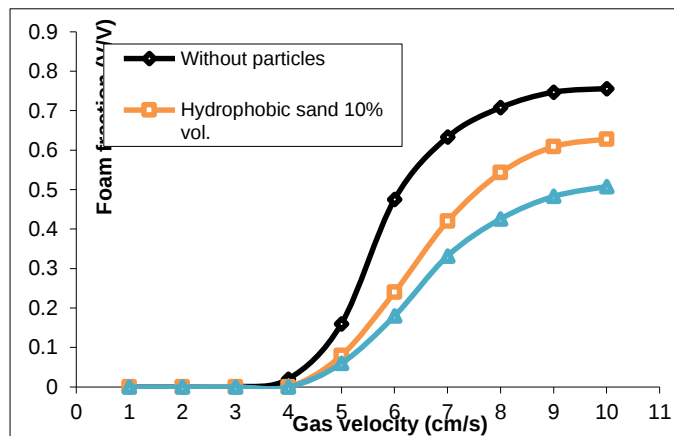


Fig. 7: Foam fraction against gas velocity at different particle concentrations and a liquid velocity of 0.15 cm/s.

Conclusions

Some remarks can be concluded from the present works;

In a three-phase fluidized bed with hydrophilic particles, foam reduction is promoted using hydrophobic particles. Hydrophobic particles are more functional in keeping breaking foam in liquid than the hydrophilic ones. This behavior may be beneficial in petroleum industries where hydrocarbon fluids are processed.

For a certain solid volume fraction (i.e. 10 vol.%), the average size of (250) μm hydrophobic particles is more effective in destroying foam than the other hydrophilic particles which have higher particle diameters.

The smaller particles expand well and permeate the foam bubbles, so the gathering of particles at the upper section of the device is formed. While increasing liquid superficial velocity has an adverse effect on the foam formation.

Competing interests

The authors have declared they have no conflict of interests with any organization or any person.

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