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Canada Centre
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CHARACTERIZATION AND DEMULSIFICATION STUDIES
OF OIL AND WATER EMULSIONS

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JOB DESCRIPTION

In my most recent work term in association with the University of Victoria Chemistry Co-op, I was employed by Energy, Mines and Resources, Canada in the Western Research Laboratory in Edmonton. The laboratory was engaged in research for the energy industry. One field of research in which the laboratory was involved was the separation of oil in water and water in oil emulsions.

The definition of an emulsion which fits the work done most closely is "emulsions are intimate mixtures of two immiscible liquids, one of them being dispersed in the other in the form of fine droplets". In an oil in water emulsion, the oil is dispersed in the water in fine droplets; in a water in oil emulsion, the water is dispersed in the oil.

INTRODUCTION

The work described in this report involved emulsions obtained from the Athabasca tar sands and Alberta heavy oil deposits. The oil in water emulsions came from the Texaco pilot plant at Fort McMurray where in-situ recovery methods were tested on tar sands. The water in oil emulsions were obtained from Petro-Canada which was working on in-situ recovery of heavy oil. The purpose of the work was to find a more efficient and cheaper alternative to breaking the emulsions than presently used. The study consisted of two parts: the first part was the determination of the size of the droplets and the oil and water content in the sample. The second part of the study was the testing of chemical demulsification reagents to determine which reagent was best at breaking the emulsion.

DETERMINING DROPLET SIZE DISTRIBUTION WITH COULTER COUNTER

a) Theory

The sample to be analyzed is placed in an electrolyte and forced through a small aperture in a glass tube. Electrodes are placed on opposite sides of the aperture and a current is passed between the electrodes. When the particles pass through the aperture, the resistance between the electrodes changes. This creates a current pulse which is related to the particle volume. The duration and magnitude of these current pulses are sized into sixteen channels where the particles were counted and separated by size.

b) Procedure

Most emulsions undergo some separation after preparation, therefore the emulsions were passed through a 400 mesh screen to remove the coarse portion of the oil which was weighed and added to the oil content. Since the emulsion obtained from Texaco had a very high clay and sand content and a relatively high oil content, the emulsion was diluted after screening so the aperture did not get clogged. The dilution factors, particle distribution and aperture size was entered into the computer which determined particle size distribution and oil content for the oil in water emulsions. The Petro-Canada water in oil emulsions could not be tested on the Coulter Counter because the emulsions did not conduct electricity; also, there would have been sampling problems and aperture clogging.

WATER CONTENT DETERMINATION

a) Dean and Stark

i) Theory

The Dean and Stark method is used to determine the water content

for water in oil emulsions. The process involves distillation of a sample which has been diluted with toluene. The vapours pass over a side arm into a water cooled condenser and receiver. The condensed water is collected and measured, the condensed toluene overflows back into the distillation flask.

ii) Procedure

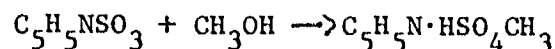
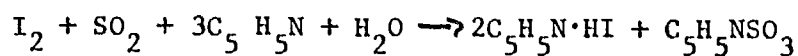
About 400 ml of toluene and approximately 100 g of sample weighed to the closest mg were added to a 1000 ml distillation flask with boiling chips. The flask was then placed onto an electric heater, the condenser and receiver were attached, and cold water circulated through the condenser. Heat was then applied and adjusted so that approximately 15 ml of distillate was condensed per minute. Distillation was continued until the volume of water in the receiving flask remained constant for five minutes. The water was then emptied from the receiver and its volume was recorded. The distillation would continue until approx. 300 ml of toluene was distilled from the flask. The remaining sample in the flask was transferred to a preweighed aluminum dish and allowed to dry in the fume hood for 24 hours. The weight of the remaining sample was taken as that of the bitumen.

This method of water determination was used only for water in oil emulsions because the oil in water emulsions consisted of approx. 85% water, and therefore the time of distillation would be extremely long.

b) Mitsubishi Moisture Meter

i) Theory

Since the Dean and Stark method of water determination was very time consuming and needed very large samples an alternative method of determining H_2O content was needed. One such method employs the Mitsubishi Moisture Meter, which uses the Karl Fischer titration reagent. This reacts with water as follows.



The sample was added to the titration vessel which has a pyridine-methanol solution with I^- and SO_2 as principle components.

The iodine produced at the anode was allowed to react with the water. The iodine was produced in direct relationship with the quantity of electricity according to Faraday's Law. Based on the quantity of electricity required for complete electrolysis of the water the moisture meter gave a direct reading in μg of H_2O . From the reading the % H_2O was calculated as follows:

$$\% H_2O = \frac{\mu g \text{ measured}}{mg \text{ injected}} \times 10^{-4} \times \text{dilution Factor}$$

ii) Procedure

The samples analyzed by Mitsubishi were first diluted at least one hundred fold with tetrahydrofuran. For oil in water emulsions, 1 g of the oil layer was diluted and for water in oil emulsions 5 g of the oil layer was diluted. From the diluted sample a .5 ml aliquot was taken and weighed. The .5 ml was then injected into the titration vessel where a digital reading in μg of H_2O was obtained. The Mitsubishi method of H_2O determination was very useful for testing the oil layer of both types of emulsions after they had undergone demulsification tests, because the volume of the oil layer in the culture tube was too small to use the Dean and Stark method, and also because the time required for a Mitsubishi test was very short. The Mitsubishi test could also be used for quick analysis of Petro-Canada samples.

OIL IN WATER DEMULSIFIER TESTS

a) Introduction

The emulsions obtained from the Texaco pilot plant at Fort McMurray were more stable than conventional oil field emulsions, due to the presence of solid matter at the oil/water interface. Due to this increased stability, the addition of large quantities of demulsification chemicals was needed to separate the two liquids. The chemicals were supplied by different chemical companies who were doing research in that field.

b) Procedure

Once every two months, a shipment of oil in water emulsions were received from the pilot plant in Fort McMurray. The emulsions were shipped in 2 l containers, three of those containers were received from each of the test wells. The oil in water emulsions which appeared to have a high oil content were used for the demulsification tests. Two of the three containers were emptied into a five gallon bucket, and the last container was kept from each site for tests to be carried out later. Once enough emulsion was collected in the five gallon bucket for the experiment, the emulsion was stirred until homogenous. The oil content of the five gallons of emulsion was determined by Coulter Counter and Mitsubishi Moisture meter (by difference). *etc.*

Once the emulsion was analyzed the experiment began. The method used for testing the Bayer chemicals was the same as used for all previous projects. First a 0.3% solution of reagent was prepared and allowed to sit over night. In the morning the water baths were turned on, so that the water temperature would be 60°C for the experiment. Once the temperature reached 60°C the emulsion was vigorously stirred so that a representative sample of 200 ml was obtained for each reagent to be tested that day. Six culture tubes were needed for each reagent to be tested so that one would be straight emulsion, and the other tubes would contain 0, 50, 100, 200 and 400 ppm of reagent based on the volume of emulsion. Those solutions were prepared as follows:

Culture Tube#	Emulsion (ml)	Solvent (ml)	Reagent (ml)
1	30	-	-
2	30	4.0	-
3	30	3.5	.5
4	30	3.0	1.0
5	30	2.0	2.0
6	30	-	4.0

Those solutions were then capped and hand shaken 10 times. Then 5 ml of toluene was added to all culture tubes, except the one with emulsion only. The tubes were then recapped and placed in the water bath holding rack and shaken 10 times. Next the culture tubes were placed in the heated aquarium in front of the camera and photographed (usually a picture was taken at 15 sec, 30 sec, 1 min, 5 min, 10 min, 15 min, 30 min, 1 h, 2 h, and 4 h). If the reagent was successful at separating the emulsion, more pictures were taken. After the 4 h picture was taken, the culture tubes were placed in the second water bath for the night.

The following day, a 24 h photograph was taken and the emulsions were allowed to cool. Once the culture tube was cool enough to touch the volume of each layer was determined by measuring each layer with a ruler. Two or three separate layers were usually discernible.

For the reagents which were successful in separating the emulsion, an aliquot was taken from the oil layer and from the water layer. From those aliquots the oil content in the water layer was determined by Coulter Counter and the water content of the oil layer was determined by Mitsubishi.

WATER IN OIL DEMULSIFIER TESTS

a) Introduction

Once a month four 5 gallon samples of heavy oil emulsions were delivered by Petro-Canada. The samples consisted of one steam group, one air test and two well head samples. A 500 ml representative sample

was obtained by vigorously stirring, and placed in a glass jar. A photograph of the sample was taken immediately; more photographs were taken after 2, 4 and 24 h to record the stability of the sample. After the sample had been sitting for 24 h the water content in the oil layer* was determined by Dean and Stark. Once the water content was determined for all four samples, the emulsion which had the highest water content in the stable oil phase was used for the demulsification tests.

b) Procedure

A 0.45% solution of demulsifying reagent was prepared, and the emulsion to be used was diluted with toluene so that a 1:8 toluene to bitumen ratio was obtained. This was done to reduce the viscosity, so the sample was easier to handle.

Seven culture tubes were needed for each reagent tested. The tubes were designated as follows:

Culture tube#	Emulsion (ml)	Solvent (ml)	Reagent (ml)
1-Emulsion	25	-	-
2-0 ppm	25	8.0	-
3-100 ppm	25	7.5	0.5
4-200 ppm	25	7.0	1.0
5-400 ppm	25	6.0	2.0
6-800 ppm	25	4.0	4.0
7-1600 ppm	25	-	8.0

The procedure followed was to add reagent and solvent to the culture tube first, and then 25 ml of diluted emulsion was poured on top. The culture tubes were then hand shaken 10 times and placed into a heated (60°C) water bath for 24 h. After this a single picture was taken. Also, after each set of chemicals was tested, the water content of the emulsion (culture tube #1) was determined. The water content of the oil layer was determined for the 0 ppm and other culture tubes if some separation was evident.

*Petro-Canada emulsions show some separation of phases with no chemical addition.

VIDEO EQUIPMENT

Recently, video equipment has proven itself very useful for industrial applications. One of those applications was the monitoring of the rate of demulsification for the oil in water emulsions. The procedure for preparing the samples and concentration of demulsifying reagent was the same as stated earlier in this report.

When using video equipment, the setting up of the equipment was of prime importance. Before the reagent and emulsion were mixed, all the equipment was turned on. Next the camera was focused on full zoom and then the zoom was retracted so that all culture tubes would be in the field of view. Then a tape was placed in the recorder and set up in the record mode with the pause button engaged so that the pause button only had to be released to start recording. Next the color balance for the camera was adjusted with the vertical bars on the monitor. Just before the emulsion and reagent were mixed, the white balance switch was activated so the camera would program itself to the proper shades of colors. Next the samples were prepared and when the samples were being shaken the recording was started and all room lights were turned off and the camera lights were turned on. The samples were then placed into the heated (60°C) aquarium and the digital timer was zeroed. Once the recording had started, the video could be left unattended for up to 96 hours depending on the recording speed.

When the video was not in use all the equipment was turned off and covered to keep the dust off the equipment. Before the camera was covered, the lens cap was placed over the lens and the iris was set to "C" and the lens filter adjusted to "0".