19 Monitoring the Demulsification of Crude Oil Emulsions by Using Conductivity Measurements

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CONTENTS

19.1 INTRODUCTION

The selection and performance evaluation for demulsifiers is commonly based on the bottle test, which, to date, is the most common and well-accepted method in the crude oil production industry worldwide. The method relies on the visual observation of phase separation of fresh crude oil emulsions in standard graded bottles. Interpretation is based on the speed of separation as well as on visual appearance. It is a hands-on method that is time consuming and an experienced engineer is required to perform the test in order to interpret the results and select an effective demulsifier.

The development of the method described in this chapter was driven by the idea to find an electronic, measurable signal, which stands quantitatively and qualitatively in relation with the demulsification process. With this background an automated demulsification monitoring method was developed.

In the following sections, first a short review of methods for monitoring of demulsification is given. We then present the method for monitoring the demulsification process by means of conductivity measurements. The principle, test equipment, and test procedure are described. Experimental results, where the demulsification monitoring by the new method is compared to the bottles test, are reported and discussed.

19.2 EXPERIMENTAL TECHNIQUES FOR DEMULSIFICATION MONITORING

Crude oil emulsions have been known since the start of crude oil production. The use of demulsifiers for separating the emulsified water and its development started in the beginning of the twentieth century.

The classical way for selecting an effective demulsifier has always been the bottle test, a method with a long tradition, which is still the most common way for demulsifier selection. The bottle test is described by several authors, for example by Lissant [1] and Becker [2]. The disadvantage with the bottle test is that it is time consuming and it relies on the subjective reading of the engineer.

As a result of attempts to remove subjective interpretation in the bottle tests, various methods for the investigation of the demulsification process have been presented in the literature, many of which use highly sophisticated techniques.

Many of the techniques presented to determine the separation speed of emulsions are based on light transmission [3]. One of these is a laser dispersant tester (Turbiscan), which can be used for the monitoring of emulsion separation [4,5]. During the test, a near infrared laser scanner moves along the height of the test tube and analyzes transmission and back scattering of light over the whole sample length at given time intervals. As water separates, the transmission increases at the lower part of the sample and the separation can be monitored. The advantage of this technique is that it provides an objective and accurate measure of the separation process. The instrument is also rather small (20 kg) and can be transported to remote oilfield locations [6]. However, the relative small diameter of the test tubes ($\sim$1 cm) can be of influence on the demulsification process. This laser dispersant tester is also limited to perform only one test at a time.

An alternative technique to the Turbiscan is presented under the commercial name Lumifuge [7,8]. This instrument is based on the same principle, with the additional advantage of accelerated tests through centrifugation. It is capable of performing up to eight tests at the same time, but with a weight of 38 kg is certainly not what the traveling service engineer would like to carry during a field visit!

It has been demonstrated that the water content in a crude oil emulsion can be determined by the use of an electroacoustic method [9,10]. In this method an ultrasonic field is applied to the emulsion and the electric field is measured. The decrease in water as the emulsion separates can then be monitored.

Above is presented techniques that are based on measuring how fast water is separated from an emulsion by means of light or electrical measurements. The separation process is the same as for the bottle test; it is the monitoring method that makes them different. There is also a range of other techniques that more indirectly assess the emulsion stability, and which can be used to determine the effectiveness of demulsifiers. Examples of such are methods based on critical electric field [11], high frequency spectroscopy [12], correlation to microemulsion phase behavior [13], or studies of Langmuir films [14]; just to mention a few.

Although many of these methods have provided valuable insights in the demulsification mechanism, they are costly, and few of them can be adapted for use in the field and even fewer would survive the trips to the remote locations, which have become the center of attention in our industry.

Another frequent disadvantage of the methods mentioned above is that they are commonly only capable of dealing with one or very few samples at the same time.

19.3 A NEW CONCEPT: THE DEMCOM METHOD

The target of the development of the new method was to find an electronic, measurable signal that stands quantitatively and qualitatively in relation with the demulsification process. In the method development, the criteria and the benefits of the traditional bottle test should be respected.

The solution was found in measuring conductivity of the separated water by a novel approach. In this section, the principle, apparatus, and test procedure of the new method are described. In the next section the experiments performed with one measuring cell are reported. This new method may lead to future advantages in demulsifier selection.

19.3.1 PRINCIPLE OF THE METHOD

The method is based on the idea that the conductivity of the emulsified water is a constant and the same for the first as well as for the last separated drop of water. However, if the separated water is continuously mixed with a known amount of water of a different, known conductivity, the conductivity of the mixture will change proportionally with the amount of separated water. The same principle has been used for many years in crude oil washing processes where the amount of salt separated from the crude oil can be monitored by measuring the increase in conductivity of the washing water [15,16].

Measuring the conductivity of the water phase continuously as a function of time, and by using data logging, a suitable program, and a personal computer, the demulsification process can be registered automatically. Objective data of how fast the water separates are obtained and can be used to determine the performance of demulsifiers.

We have named the method DEMCOM, which is an acronym for “***de***mulsification ***m***onitoring by ***co***nductivity ***m***easurement.”

19.3.2 TEST EQUIPMENT

The DEMCOM apparatus consists of standard equipment. The set-up is presented schematically in Figure 19.1. The apparatus consists of a vessel (~70 ml) with a thermostatic jacket, magnetic stirrer, and an electrode placed in the water phase. The probe must be placed such that the oil phase does not come in contact with the measuring electrode. The electrode is connected to a conductivity meter, which again is connected to a device that registers the signal as a function of time, such as a personal computer.

19.3.3 TEST PROCEDURE

In order to generate a measurable change in the conductivity versus time, the difference in conductivity of the mixing water and the emulsified water should be large. Typically, the emulsified water has a relatively high conductivity and demineralized water will be suitable for mixing. In those cases where the conductivity of the separated water is relatively low, mixing water with a high conductivity may be used.

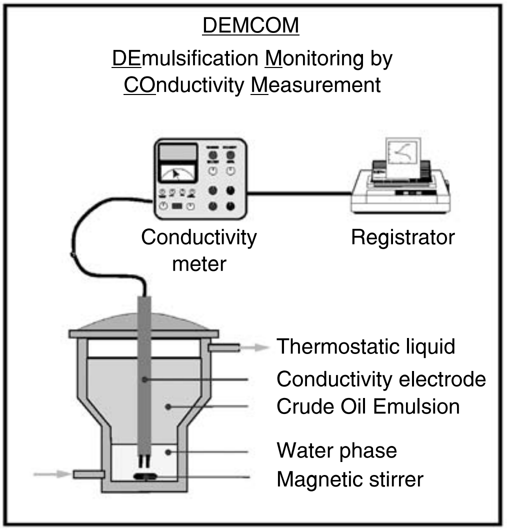

FIGURE 19.1 Scheme of the DEMCOM apparatus.

19.3.3.1 Calibration

In order to be able to convert the measured conductivity into the amount of separated water it is necessary to know the relationship between the measured signal and the ratio of each aqueous phase.

Measuring the conductivity of prepared ratios of each water quality allows a calibration curve to be drawn. For the resulting curve, a linear trend line and its formula can be determined. The formula is then used for calculating the separated amount of water. In Equation 19.1 the conductivity, Y, is shown as a linear function of the fraction X, in percent, of separated water in the water bulk phase.

$$Y = \alpha \cdot X + C \tag{19.1}$$

where α and C are constants determined by the curve fitting. Based on the measured conductivity and the calibration function, the fraction X of separated water in the water bulk phase is determined. However, the parameter of interest is the amount of separated water in percent of the initially emulsified water, Z. The parameter Z can be calculated using Equation 19.2 where $M_{emul,i}$ is the amount of initially emulsified water and $M_{bulk,i}$ is the amount of bulk water before the separation starts.

$$Z = \frac{X}{(100 - X)} \cdot \frac{M_{bulk,i}}{M_{emul,i}} \cdot 100 \tag{19.2}$$

As will be shown later in this chapter it may be sufficient to measure the conductivity of each of the water phases and then assume a linear calibration line.

19.3.3.2 Performing the Test

The procedure for adding the demulsifier is the same as for the bottle test. The crude oil emulsion is heated to the test temperature and the demulsifier under investigation is added and mixed into the emulsion by shaking.

The test cell (Figure 19.1) is filled with a measured quantity of water for mixing and thermostated to the test temperature. Once the conductivity electrode is installed in the water phase, the crude oil emulsion is poured carefully on top of this layer. In order to avoid disturbing of the reliability of the measuring signal, the electrode should not be contacted by the oil phase.

The magnetic stirrer is started at a moderate speed to obtain a fast and reliable signal response. Care has to be taken to ensure that the preconditioned water will not function as wash water for the crude. Formation of a vortex has to be avoided. Moderate agitation also occurs in practice where the crude oil emulsion in a separator always is under a slight movement.

The measuring starts from time zero and will continue as long as the monitored and logged signal indicates that the separation is still in progress.

19.4 EXPERIMENTAL RESULTS AND DISCUSSION

In the following we show experimental results obtained when using the DEMCOM method. We first determine the reproducibility of the calibration needed to convert the measured conductivity into separated water. The effectiveness of demulsifiers is then studied and the DEMCOM results are compared to results obtained using the traditional bottle test.

19.4.1 Calibration Results

Demineralized water was used for mixing with the separated water. The water separated from eight samples of one crude oil emulsions where used to make eight different calibration curves. The average values, with standard deviation, of the constants α and C in Equation 19.1 were determined to be 0.106 ± 0.006 and 0.23 ± 0.06, respectively.

By making the calibration formula based only on the measurement of the conductivity of each of the water phases, α and C are determined to be 0.108 and 0.2, respectively. This is in agreement with the values obtained by making various blending ratios. Since produced water normally primarily consists of strong electrolytes, the conductivity will be linearly dependent on the mixing ratio and it would be sufficient to determine the conductivity of each water phase. Figure 19.2 shows the experimental points used for the calibration. The line is drawn between the measuring points for each of the two water phases.

19.4.2 Demulsification Experiments

For the investigation in the research of this method, crude oil emulsions from one origin were used. The demulsifiers used were selected based on bottle test results and represent both good and bad performing products for this crude oil.

The amount of deionized water used for mixing with the separated water was 10 g. Twenty-eight grams of crude oil emulsion was added on top of this water. The water cut in the prepared emulsions varied from 38 to 54%. All experiments were performed at 40 °C.

Products A, B, C, D, E1, E2, and E3 was dosed at 30 ppm to the crude oil emulsion. The separation was studied by the bottle test and the DEMCOM method and the results are presented in Figures 19.3 to 19.7 where the amount of separated water from the emulsion is plotted as a

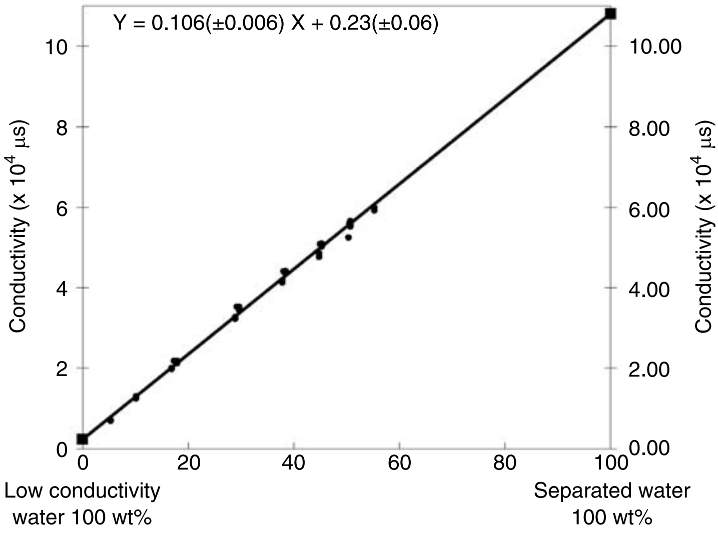

FIGURE 19.2 Conductivity calibration data for mixtures of separated water and low conductivity water. The line is drawn between measuring points for each of the two water phases. The points are determined conductivities for various mixing ratios.

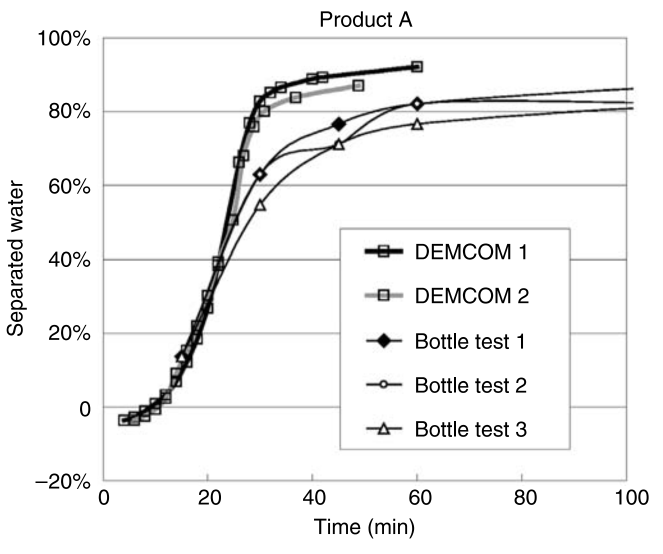

FIGURE 19.3 Amount of separated water versus time, as determined with the bottle test and the DEMCOM method, for a crude oil emulsion treated with 30 ppm of product A.

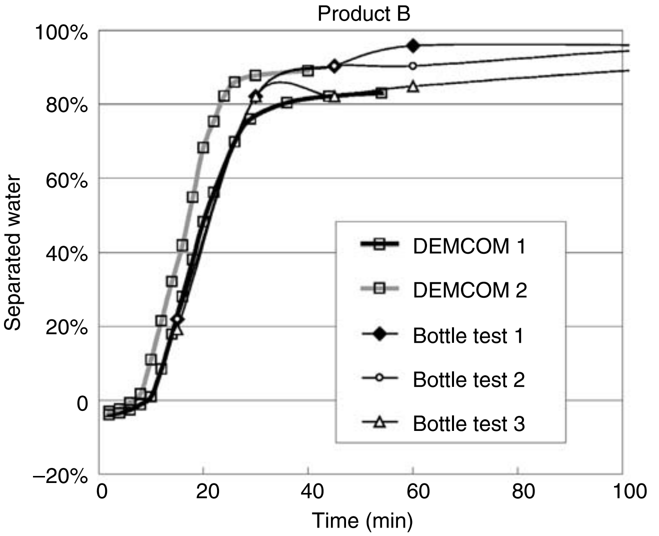

FIGURE 19.4 Amount of separated water versus time, as determined with the bottle test and the DEMCOM method, for a crude oil emulsion treated with 30 ppm of product B.

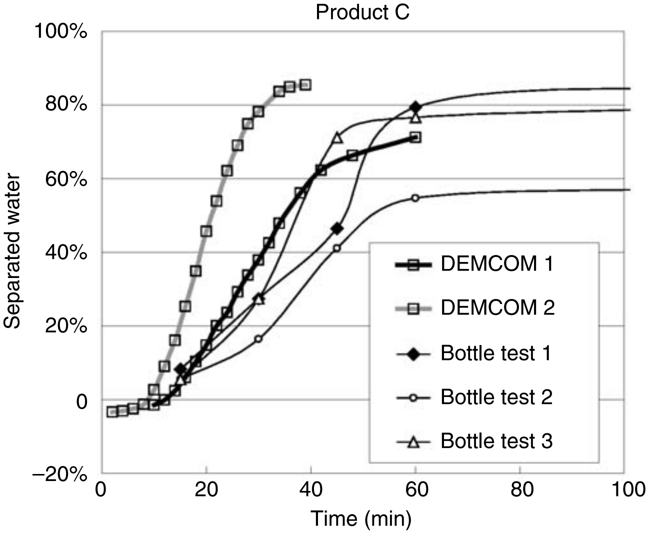

FIGURE 19.5 Amount of separated water versus time, as determined with the bottle test and the DEMCOM method, for a crude oil emulsion treated with 30 ppm of product C.

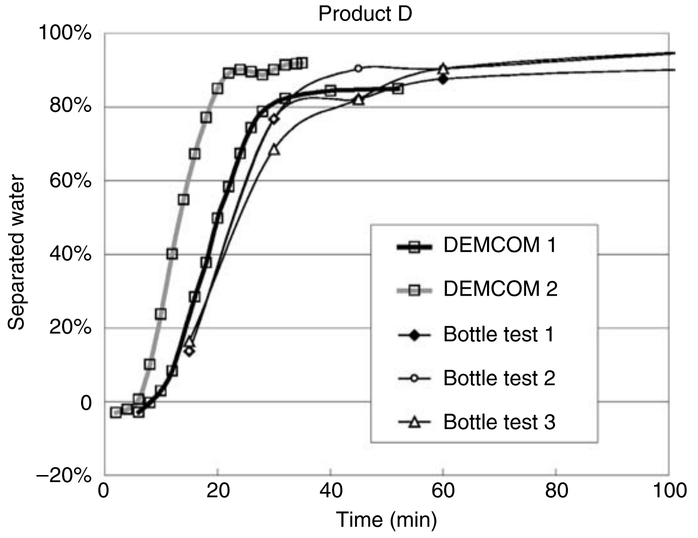

FIGURE 19.6 Amount of separated water versus time, as determined with the bottle test and the DEMCOM method, for a crude oil emulsion treated with 30 ppm of product D.

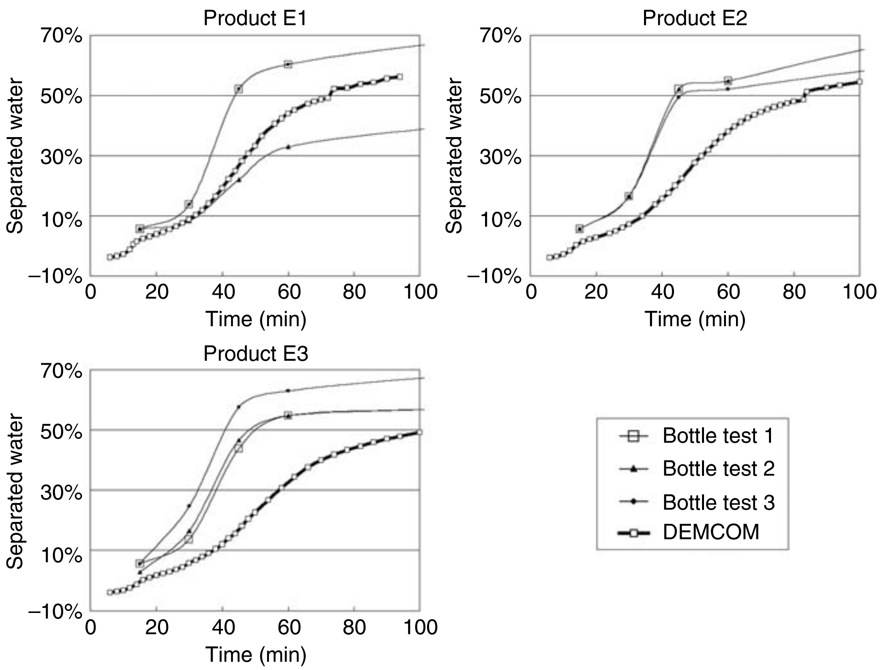

FIGURE 19.7 Amount of separated water versus time, as determined with the bottle test and the DEMCOM method, for a crude oil emulsion treated with 30 ppm of products E1, E2, or E3.

function of time. Bottle tests were performed in triplicate for each system and the DEMCOM tests were performed singly or repeated.

When comparing the bottle test with the DEMCOM test there is no consistent trend in which method that shows the higher amount of water separated. In the tests where products A and C are used as demulsifiers, the DEMCOM method indicates slightly higher amount of water separated than the bottle test (Figures 19.3 and 5). When products B and D are used, the amount of separated water at a given time is the same for the two methods (Figures 19.4 and 6). However, for products E1 to E3 the bottle tests show a higher amount of separated water than the DEMCOM tests (Figure 19.7).

Some factors can contribute to a difference in the results for the two methods. In the DEMCOM method, an agitated water phase is present from the start of the experiment. This may have an influence on the separation speed when compared to the bottle test. The interface between crude oil emulsion and water may be difficult to read with the naked eye, and this will lead to a random or systematic error in the estimated amount of water separated for the bottle test.

The results obtained by the DEMCOM method are not always exactly the same as the results obtained by the bottle test. Nevertheless, it is clear that the DEMCOM test generates the same trend of the effectiveness of the demulsifiers as the bottle test. The products found to be effective in the bottle test were also good in the DEMCOM method. Looking at the results presented here, it is seen that products A, B, and D are highly effective in destabilizing the current crude oil emulsion, product C is moderately effective, and products E1 to E3 show limited performance. Neither with the bottle test nor with the DEMCOM test was it possible to perform a more detailed ranking based on these results; i.e., to get an exact ranking of the products E1 to E3 or A, B, and D in terms of performance.

The shape of the lines is representative for the demulsifying characteristic; this is the same in both tests. However, the resolution of each curve is much higher with DEMCOM and the separation profile becomes clearer.

An idea of the reproducibility for each of the test methods can be found by looking at the duplicate runs for the DEMCOM method and comparing with the triplicate for the bottle test. It is clear that the reproducibility of the DEMCOM test is at least as good as for the bottle test. The experiments reported here were performed with the aim of proving that the DEMCOM principle can be used for demulsification monitoring. It is believed that further work with the experimental set-up and test procedure can result in improved reproducibility.

During the performance of the DEMCOM method no unexpected difficulties occurred. Once the operator is familiar with the procedure it is an effective and efficient method.

19.5 ADVANTAGES AND DISADVANTAGES WITH THE DEMCOM METHOD

The main incentive for developing the DEMCOM method has been to find an alternative for demulsification monitoring, especially when selecting demulsifier products at field locations. Today this is more or less always done by bottle testing. In the following we discuss advantages and disadvantages that can be identified when comparing the DEMCOM method with the traditional bottle test.

Obviously, a major advantage of the bottle test is that the equipment needed is limited to graded bottles. For the DEMCOM method a more advance instrument set-up is needed. However, the DEMCOM apparatus consists of low cost parts and it would be possible to design it so that it can be easily transported to field locations. This makes the DEMCOM method unique when compared to other automated demulsification monitoring techniques. In order to work accurately with the DEMCOM method, a balance with an accuracy of ±0.01 g is necessary, an apparatus which could also be very helpful for the bottle test.

In our experiments we have used one single measurement cell. For the DEMCOM method to work as an alternative to the bottle test in demulsifier screening it will be absolutely necessary to have multi-cell equipment available. Further developments have to be made before the DEMCOM method will have a portable form for experiments in the field. Once this is done, the DEMCOM method will be able to compete with the bottle test.

The DEMCOM method needs some extra preparation in respect to the generating of the calibration curve. However, for a bottle test it is also necessary to check the salt content of the crude oil emulsion. The cleaning of the DEMCOM apparatus after the test will be somewhat more laborious than for the bottle test, while the preparation of the emulsion is the same for both methods.

One of the main advantages with the DEMCOM method is that when the experiment is running, the demulsification process is registered automatically and accurately without any interference by the operator. While for the bottle test a series of tests has to be started at the same time, with the DEMCOM method each test can be performed on its own. During the course of the test it can be decided to continue or to stop. The latter can be done if the extrapolation of the curve is not predicting a good result. After terminating the test, a new experiment can immediately be prepared. For the bottle test it will only be practical to start a series of experiments at the same time.

The amount of crude oil emulsion for one DEMCOM test is about 30 ml, which is less than for the bottle test. This can be an advantage when a crude oil emulsion sample is limited in amount or difficult to obtain.

It is of a great advantage to generate a demulsifier characteristic and to have it directly available in an electronic data system. Comparing a great number of results in a demulsifier selection process is much easier this way. The generated data gives accurate information regarding the demulsifier performance, the initial activity, the demulsification rate, and what can be expected in respect to the end separation effect. While for the bottle test there will be limitations in how often a measuring point can be recorded, the DEMCOM apparatus can be set to collect data points as often as the operator decides.

Given the measuring principle and its accuracy it is expected that a rest water content determination of the separated crude will not be necessary for the DEMCOM method.

To summarize the comparison of the bottle test with the DEMCOM test it is clear that the great advantage of the bottle test is the simple equipment needed. Less work is also required for preparation of the separation vessels. On the other hand, the advantages of the DEMCOM method are its automatic and objective collection of separation data. It is our belief that the DEMCOM method can be developed so that it will be a good alternative to the bottle test for demulsifier screening.

19.6 CONCLUSIONS AND RECOMMENDATIONS

The name chosen for the described method is "The DEMCOM method," which is an acronym for "***de***mulsification ***m***onitoring by ***co***nductivity ***m***easurement."

The data generated with the DEMCOM method can be considered as the demulsifying characteristic of a particular demulsifier for a particular crude. This characteristic describes information such as the initial activity, the progress in separating water, and the effectiveness in respect to rest water and rest salt in the crude. Having the data directly available in an electronic data system makes the comparison of a great number of results much easier.

The precision of the method is good and is the same for the first as well as for the last separated drop of water; therefore the determination of the rest water or rest salt in the crude oil after finishing the separation process is no longer required.

Crude oil emulsions containing just a few percent of water, which are almost impossible to test in the classical bottle test, can be easily tested by this method. This will be of interest for refineries and for monitoring the wash process for the crude.

The DEMCOM method can be used for quality control of supplied demulsifier batches to crude oil producers.

The first experimental results with this newly developed DEMCOM method are very promising. The method is based on a well-known principle and is simple to perform. It is expected that once a multi-cell unit is developed with suitable data logger and software a very accurate method will be available for field use.

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