Volver

STATISTICAL MODELING FOR DEMULSIFIERS DEVELOPMENT

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Abstract

Demulsifiers are the most used chemical in production segment. These chemicals are added to crude oil in order to break the stable emulsion generated by the natural surfactants present in the oil like asphaltenes, naphthenic acids and others, getting a final separation of water and oil phases. Usually higher treating temperature and residence time favors a better demulsification process with cleaner water and drier oil. There are thousands of molecules that are claimed to be good demulsifier agents like alkoxylated alkyl phenol formaldehyde, polyalkylene glycols and others, each one giving its particular responses on the final treating. To formulate all these chemicals "*Bottle Testers*" still see this concept more like an art instead of science, achieving suitable formulations using try and error methodology and their own experience. At this work it is proposed a new way to formulate these chemical agents, using the concept of design of experiments and statistical modeling. The factors are the chemical agents used and the responses for the model are water drop speed, residual water and emulsion (BS&W) and interface quality. Correlations could be seen like the synergy and antagonism of certain chemicals for a considered response. At the end, of this study a final demulsifier agent was developed trough statistical modeling consuming just 66 experiments and 3 days of work instead of conventional weeks of labor and lack of knowledge about the effects generated by the chemicals used.

1. Introduction

The process of separating the undesired matter from crude oil might include the removal of water, salt, sand and sediments. Basically the process is based on decanting the water present in the emulsion from the reservoir considering an increase in the residence time of the fluid passing through various tanks such as three-phase separation tanks, where free water, oil and gas are separated, or the free water knock out vessel, where only non-emulsified water and oil are separated. In oil treating tanks heat is applied and the de-emulsifying action is favored for the separation of heavy emulsion and finally in an electrostatic treater, which generates an electric field on the fluid allowing greater speed of coalescence of water droplets in the oil phase. These tanks are present in most of the processes of water and oil separation. A scheme of this type of process is illustrated in Figure 1.

The demulsifying agent may be applied before the passage of fluid in either of these tanks, although its action is most favored if applied before the oil treating tank or electrostatic vessel.

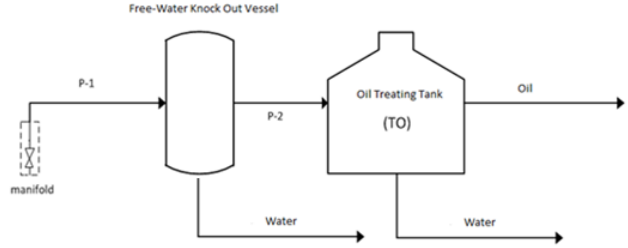


Figure 1. Simplified scheme of a system for separation of water in oil

The law governing the process of demulsification is basically Stoke's Law (Equation 1), where the demulsifier chemical acts directly on the size of water droplet and at the speed of coalescence, allowing the terminal velocity to increase. As in process tanks, the goal is to decrease the velocity of the droplets due to the increase in residence time, increasing the terminal velocity of an individual droplet facilitates its deposition at the bottom of the tanks, increasing the phase separation between the two phases.

$$v = \frac{2 \cdot g \cdot R^2 \cdot (\rho_w - \rho_o)}{9 \cdot \mu_o} \qquad \text{(Equation 1)}$$

Where:

v: Sedimentation velocity of a water drop with spherical shape;
g: Gravitational acceleration
R: Radius of water drop;
ρw:Water specific gravity;
ρo: Oil specific gravity;
μo: Oil viscosity;

The characteristics for a demulsifier to have a good performance are described below in general terms:

- Be very attracted to the oil / water interface;
- Compete successfully with natural emulsifiers in oil / water interface;
- Flocculate and coalesce water droplets;
- Be a good wetting agent.

Factors related to the emulsion break, are correlated to the breakup of the film around the water droplets to coalesce and produce even larger particles. Theoretically, if time was unlimited, the entire emulsion would separate into oil and water naturally, but as the residence time in the tanks is limited there is a need to add demulsifier agents together heat and in some cases also an electric field.

For demulsifiers development usually a huge number of experiments are needed, mainly because there are several types of molecules suitable for demulsification. Most of these chemicals are formulated "taylor made" for the specific oil field in consideration.

To give one idea about the potential number of experiments to be done just considering a combinatory analysis some calculations are made below.

- For typical combinations of 1:1; 1:3 and 3:1 parts of chemicals with 2 components considering 18 molecules available for the demulsifier development it is possible to make 459 formulations.

$$\frac{C_{(18,2)}}{(1:1)} + \frac{C_{(18,2)}}{(1:3)} + \frac{C_{(18,2)}}{(3:1)} = 459 \text{ possibilities}$$

- For typical combinations of 1:1:1; 2:1:1; 1:2:1; 2:2:1; 1:2:2; 1:1:2 parts of chemicals with 3 components considering 18 molecules available for the demulsifier development it is possible to make 4896 formulations.

$$\frac{C_{(18,3)}}{(1:1:1)} + \frac{C_{(18,3)}}{(2:1:1)} + \frac{C_{(18,3)}}{(1:2:1)} + \frac{C_{(18,3)}}{(2:2:1)} + \frac{C_{(18,3)}}{(1:2:2)} + \frac{C_{(18,3)}}{(1:1:2)} = \underset{\text{possibilities}}{4896}$$

As a result of the calculations above, it is possible to achieve with typical formulation ratios using 2 and 3 components with just 18 molecules more than 5000 formulations. This represents an enormous amount of *bottle tests* that can be done.

The mixture design supports experiments with factors that are ingredients in a mixture. The properties of this mixture are almost always a function of the relative proportions of the ingredients rather their absolute amounts. In experiments with mixtures, the value of a factor is its proportion in the mixture, which falls between zero and one. The sum of the proportions in any mixture recipe is equal to 1 (100%).

Designs for mixture experiments are fundamentally different from those for screening. Screening experiments are orthogonal. This means that over the course of an experiment, the setting of one factor varies independently of any other factor. Thus, the interpretation of screening experiments is relatively simple, because the effects of the factors on the response are separable.

With mixtures, it is impossible to vary one factor independently of all the others. When the proportion of one ingredient changes, the proportion of one or more other ingredients must also change to compensate. This simple fact has a profound effect on every aspect of experimentation with mixtures, like the factor space, the design properties, and the interpretation of the results.

Because the proportions sum to one, mixture designs response takes the form of a simplex. The plane where the sum of the three factors sum to one forms a ternary plot.

2. Materials and Methods

To evaluate the best demulsifiers for each type of crude oil, it is usually conducted "*bottle tests*" where the real dehydration process is simulated in laboratory conditions. Although crude oil treatment is a continuous process, with large residence time, bottle tests are conducted in a static way. Depending on the "*bottle tester*" the test to be conducted is pretty much the same, but sometimes there are some variations in terms of agitation rate, sampling point for interface evaluation and others.

The experimental procedure for a conventional "*bottle test"* is described below. At this test, analysis of water and sediments (BS&W) is considered for the treated oil by centrifugation method according to ASTM D 96.

<u>Equipments and Reagents</u>

- Glass syringes (50 and 25 ml)
- Heating bath
- Analytical scale
- Centrifuge

- 100 ml graduated glass tubes
- Graduated centrifuge tubes
- Transfer pipettes - 50, 500, 1000 µL
- Glass bottles, 15 ml
- Thermometer (-10 to 120 °C)
- Kerosene
- Technical grade Xylene
- Technical grade Ethanol

Crude Oil Preparation

The crude oil sample from the field must be representative of the current dehydration process. The actions below are very important for good testing reproducibility.

- Sample collection without demulsifiers contamination used in field.
- Removal of free water before starting the test itself.
- Blending of oil samples produced in several fields representing the real oil composition of the dehydration plant

Laboratorial Procedure

First the demulsifier samples must be diluted at 2% concentration in active content. To achieve the desired proportion, solids analysis can be conducted using a microwave automated scale to measure solvent concentration before and after dilution. Dilution is made using ethanol.

"*Bottle test"* itself consists taking crude oil sample and placing it in 100 ml graduated bottles. The demulsifier agent is added using a micropipette with respective volume in microliters to give the final dosification required in the bottle, usually in ppm levels. The bottles are shaken and let it rest in a heated bath considering the process temperature of oil treater. Measurements of water drop are taken in a pre determined space of time.

To determine the Total Water and BS for the crude oil, approximately 10 ml of treated oil sample is taken and transferred into a centrifuge bottle graduated in percentage, with half of its volume filed with oil. The volume is completed with kerosene and homogenized. Centrifugation is done for 5 min at 3000 rpm and then readings of water separation at the bottle are done. This number should be multiplied by two and results are recorded in a worksheet as W1. Three drops of the "Slug" demulsifier are added to the bottle and mixed well again. Centrifugation is done one more time for 3 min at speed of 5000 rpm. The amount of water obtained at the bottom multiplied by two is recorded as W2. BS is basically the difference between W2 and W1.

In a design of experiments (DOE), tests are conducted in a planned sequence, where the factors (or controlled variables) are amended so as to assess their impact on the response variable. This can allow further statistic analysis with results obtained as well as to use previous data obtained for better modeling of the phenomenon adding more data in another DOE.

The first design of experiment elected to be conducted was the Simplex Centroid Design. The ternary plot obtained with this design is shown at Figure 2.

This design mainly consists:

- All combinations of two factors at equal levels
- All combinations of three factors at equal levels
- A center point run with equal amounts of all the ingredients is included.

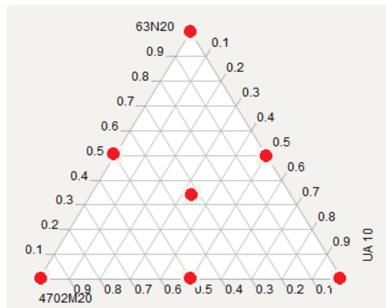


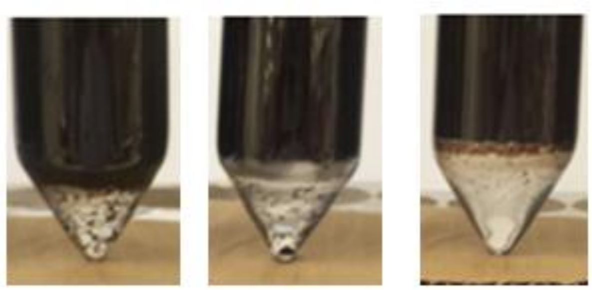
Figure 2. Ternary plot for the ingredients compositions in a mixture design simplex centroid

The main response variables for the *bottle test* experiments can be considered as below:

Water drop (ml/min): Represents the amount of water found at the bottom of the bottle after some time in the heating bath.

Water Quality: The water quality is classified according to visual assessment: 1-5 (1 - poor 5 - good) Cloudy / Clear.

Interface Quality: The quality of the interface is classified according to visual assessment: 1-5 (1 - poor 5 - good) Rough / diffuse / Sharp



Interface rough Water Cloudy | Interface diffuse Water Cloudy | Interface Sharp Water Clear

Figure 3. Representation of water and interface quality obtained

Thief Grind-out: It corresponds to the evaluation of the interface water / oil. After removing the water from the bottom of the bottle, a sample is withdrawn at the bottom for BS&W analysis.

Composite Grind-out: It corresponds to evaluation of oil obtained after the test. After removing the sample for "Thief" analysis, the bottles are shaken again and another sample is taken for BS&W analysis.

W1: This refers to the volume of water found in the centrifuge tubes after centrifuging. A treatment that can reduce W1 to minimum levels with no residual emulsion indicates that good dryness was achieved.

W2: This refers to the volume of water found in the centrifuge tubes after second centrifuging. W2 indicates the total amount of water (free water plus emulsion) after treatment.

EM: This is the amount of emulsion observed visually after the centrifuging operation.

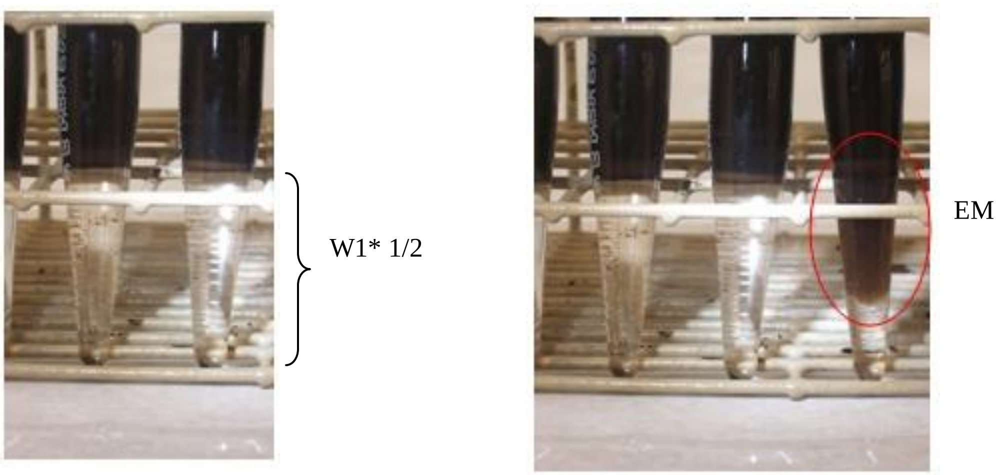


Figure 4. Representation of the value found for "W1" and "EM"

BS: It is the difference between the values of W1 and W2 respectively found at the first centrifuging and second centrifugation with the addition of demulsifier "Slug." Basically this is the value that represents how much water in emulsion phase remained after the treatment with the studied demulsifier.

For the study here proposed just the variables Water Drop Speed, Interface Quality, BS and W1 are considered for statistical modeling.

3. Results and Discussion

A crude oil sample from a Brazilian off-shore field was taken for a demulsifier development. The total residence time of the testing was considered 30 minutes and treating temperature around 60 ^{o}C. All the tests are run considering the dosage curve of incumbent demulsifier. The concentration where desired performance is achieved is fixed for all further tests in order to eliminate the dosification parameter as one more variable at the study.

Table 1. Incumbent Dosage curve

Products	Dosage	Water Drop (mL/minutes)					Treated oil Quality										
							WATER QUALITY	INTERFACE QUALITY	BSW THIEF GRINDOUT				BSW COMPOSITE GRINDOUT				
									Without Slug		With Slug	BS	Without Slug		With Slug	BS	H2O Total
	ppm	0	5	10	15	30			W1	EM	W2		W1	EM	W2		
Blank	#	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	42.0	34.0	34.0	1.2	40.8	34.0	32.8	34.0
Incumbent	300	26.0	32.0	32.0	32.0	34.0	1.0	2.0	0.0	0.0	0.0	0.0	1.2	0.0	1.6	0.4	35.1
Incumbent	350	28.0	32.0	32.0	34.0	34.0	1.0	3.0	0.0	0.0	0.0	0.0	0.6	0.0	0.6	0.0	34.3
Incumbent	400	28.0	30.0	32.0	34.0	34.0	1.0	4.0	0.0	0.0	0.0	0.0	0.4	0.0	0.4	0.0	34.3
Incumbent	450	26.0	30.0	30.0	32.0	34.0	1.0	4.0	0.0	0.0	0.8	0.8	0.2	0.0	0.2	0.0	34.1
Incumbent	500	22.0	28.0	28.0	28.0	34.0	1.0	3.0	0.0	0.0	1.0	1.0	0.2	0.0	0.2	0.0	34.1
Incumbent	550	26.0	30.0	30.0	32.0	34.0	1.0	4.0	0.0	0.0	0.6	0.6	0.2	0.0	0.2	0.0	35.1
Incumbent	600	26.0	30.0	32.0	34.0	34.0	1.0	4.0	0.0	0.0	0.8	0.8	0.0	0.2	0.2	0.2	35.1
																	34.5
Blank	#	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.4	43.6	40.0	37.6	1.2	42.8	36.0	34.8	36.0
Incumbent	300	20.0	32.0	36.0	36.0	36.0	1.0	3.0	0.4	1.6	1.6	1.2	0.2	2.2	2.4	2.2	37.5
Incumbent	350	26.0	36.0	36.0	36.0	38.0	1.0	2.0	0.0	0.0	0.2	0.2	0.4	0.4	0.4	0.0	37.3
Incumbent	400	28.0	34.0	36.0	36.0	36.0	1.0	3.0	0.0	0.0	0.2	0.2	0.4	0.4	0.8	0.4	35.5
Incumbent	450	32.0	34.0	36.0	36.0	36.0	1.0	3.0	0.0	0.0	0.2	0.2	0.4	0.0	0.4	0.0	36.3
Incumbent	500	8.0	34.0	36.0	36.0	36.0	1.0	3.0	0.0	0.0	0.2	0.2	0.8	0.4	1.2	0.4	35.8
Incumbent	550	5.0	32.0	34.0	36.0	38.0	1.0	3.0	0.0	0.0	0.2	0.2	0.4	0.4	0.6	0.2	37.4
Incumbent	600	5.0	32.0	34.0	36.0	38.0	1.0	4.0	0.0	0.0	0.2	0.2	0.4	0.4	0.6	0.2	36.4

In Table 1 it is observed the dosage curve for the incumbent material replicated in order to verify the experimental error of the testing and to elect the best dosage to run further tests. The concentration of 400 ppm was found to be the most suitable for next experiments as demulsifier performance was considered suitable in all response parameters.

Bottle tests were conducted for the single individual components in the first step of the experimental design. These individual tests will give the information about the chemicals that can give the best performance for each of the response variables to be used in further ternary plots for synergy search.

Table 2. *Bottle Test* run for all the individual intermediates at fixed dosage of 400 ppm

Products	Dosage	Water Drop (mL/minutes)					Treated oil Quality										
							WATER QUALITY	INTERFACE QUALITY	BSW THIEF GRINDOUT				BSW COMPOSITE GRINDOUT				
									Without Slug		With Slug	BS	Without Slug		With Slug	BS	H2O Total
	ppm	0	5	10	15	30			W1	EM	W2		W1	EM	W2		
Blank	#	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.8	31.2	28.0	25.2	2.0	42.0	36.0	34.0	36.0
Incumbent	400	26.0	32.0	34.0	34.0	34.0	1.0	3.0	0.0	TR	0.0	0.0	0.4	0.4	0.8	0.4	34.5
Demulsifier 1	400	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	TR	0.0	0.0	26.0	18.0	38.0	12.0	38.0
Demulsifier 2	400	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	TR	0.0	0.0	14.0	28.0	36.0	22.0	36.0
Demulsifier 3	400	8.0	24.0	26.0	26.0	28.0	1.0	3.0	0.8	7.2	8.0	7.2	8.0	4.0	10.0	2.0	35.2
Demulsifier 4	400	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2	1.0	1.6	1.4	12.0	28.0	38.0	26.0	38.0
Demulsifier 5	400	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.0	2.0	2.0	2.4	43.6	36.0	33.6	36.0
Demulsifier 6	400	0.0	0.0	1.0	2.0	2.0	1.0	0.0	0.0	2.0	2.0	2.0	8.0	2.0	8.0	0.0	38.6
Demulsifier 7	400	0.0	5.0	16.0	28.0	34.0	1.0	0.0	0.0	0.4	0.6	0.6	1.2	2.0	3.2	2.0	36.1
Demulsifier 8	400	0.0	0.0	0.5	3.0	6.0	1.0	0.0	0.0	TR	0.2	0.2	20.0	0.0	20.0	0.0	37.6
Demulsifier 9	400	26.0	26.0	28.0	28.0	28.0	1.0	0.0	1.2	2.0	2.8	1.6	7.0	5.0	12.0	5.0	34.9
Demulsifier 10	400	30.0	32.0	32.0	32.0	32.0	1.0	1.0	2.0	0.0	16.0	14.0	4.4	0.0	4.6	0.2	33.6
Demulsifier 11	400	0.0	10.0	14.0	16.0	16.0	1.0	1.0	0.8	16.0	2.0	1.2	0.2	19.8	20.0	19.8	36.0
Demulsifier 12	400	0.0	6.0	6.0	8.0	10.0	1.0	0.0	0.0	TR	0.2	0.2	4.8	2.2	6.0	1.2	34.2
Demulsifier 13	400	4.0	7.0	7.0	8.0	10.0	1.0	0.0	0.0	5.2	4.4	4.4	1.6	24.4	22.0	20.4	36.0
Demulsifier 14	400	0.0	0.5	5.0	20.0	26.0	1.0	0.0	0.2	0.0	0.8	0.6	0.8	1.2	2.0	1.2	35.3
Demulsifier 15	400	1.5	32.0	34.0	32.0	34.0	1.0	1.0	0.4	0.0	0.4	0.0	1.6	TR	1.6	0.0	33.6
Demulsifier 16	400	28.0	30.0	30.0	30.0	30.0	1.0	0.0	0.4	0.0	0.4	0.0	2.0	TR	2.0	0.0	32.4
Demulsifier 17	400	0.0	14.0	20.0	20.0	28.0	1.0	4.0	8.0	0.0	8.0	0.0	9.0	0.0	9.0	0.0	33.6
Demulsifier 18	400	22.0	32.0	32.0	32.0	34.0	1.0	4.0	0.4	0.0	0.4	0.0	0.8	0.0	1.2	0.4	33.8
Demulsifier 19	400	4.0	26.0	30.0	30.0	30.0	1.0	5.0	3.6	0.0	3.6	0.0	4.4	0.0	4.4	0.0	33.8

Considering the responses water drop speed, interface quality, BS and W it was chosen the products that gave better performance for each one of these variables. A summary of the best chemicals for each response is shown below in order of best to worst results:

<u>Faster water drop speed</u>

Demulsifier 03
Demulsifier 15
Demulsifier 16
Demulsifier 09
Demulsifier 10

<u>Lower BS</u>

Demulsifier 07
Demulsifier 15
Demulsifier 09
Demulsifier 14

<u>Better Dryness (Lower W1)</u>

Demulsifier 07
Demulsifier 15

<u>Higher Interface Quality</u>

Demulsifier 03
Demulsifier 17

After determining the best individual product for each response, ternary mixtures are made considering the simplex centroid design. The objective is to have in each ternary plot a product with good performance for all the responses considered.

Table 3. Mass fraction of each component in a simplex centroid design.

Intermediate 1	Intermediate 2	Intermediate 3
1	0	0
0	1	0
0	0	1
0.5	0.5	0
0.5	0	0.5
0	0.5	0.5
0.33333333	0.33333333	0.33333333

It is proposed 6 ternaries combinations to make the DOE where 6 models will be generated giving already some information about synergies and antagonisms among chemicals for each response and even showing some potential formulations, although not yet refined.

The combinations below were chosen trying to get an overall good performance for all response variables just considering the individual bottle tests done.

Model 1 – Demulsifier 03 / Demulsifier 07 / Demulsifier 15

Model 2 – Demulsifier 09 / Demulsifier 07 / Demulsifier 15

Model 3 – Demulsifier 10 / Demulsifier 16 / Demulsifier 07

Model 4 – Demulsifier 16 / Demulsifier 15 / Demulsifier 07

Model 5 – Demulsifier 15 / Demulsifier 10 / Demulsifier 14

Model 6 – Demulsifier 03 / Demulsifier 10 / Demulsifier 16

Bottle tests are run again considering the binary combinations and the tertiary combination for each model described in table 3. The individual components data can be considered the previous one obtained from initial screening with pure components. Concentration is still fixed as 400 ppm. For these 6 models only 24 additional bottle tests are required. For better understanding and avoid repeating concepts just model 3 is explained in details in this study. The analogous methodology is used for the other models.

At the pictures below, it is described the ternary plots for Model 3 after modeling in JMP® statistical software. It is possible to see clearly the regions where the response factors are higher or lower varying the mixture composition.

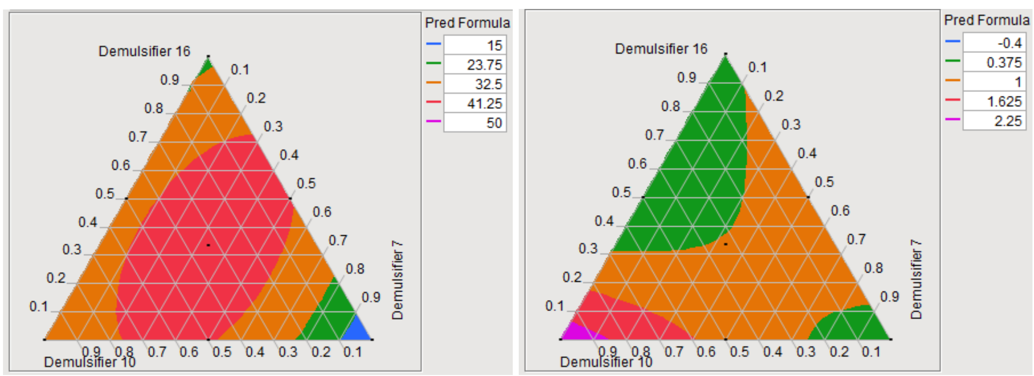


Figure 5. Water drop speed and Interface quality ternary plots for Model 3

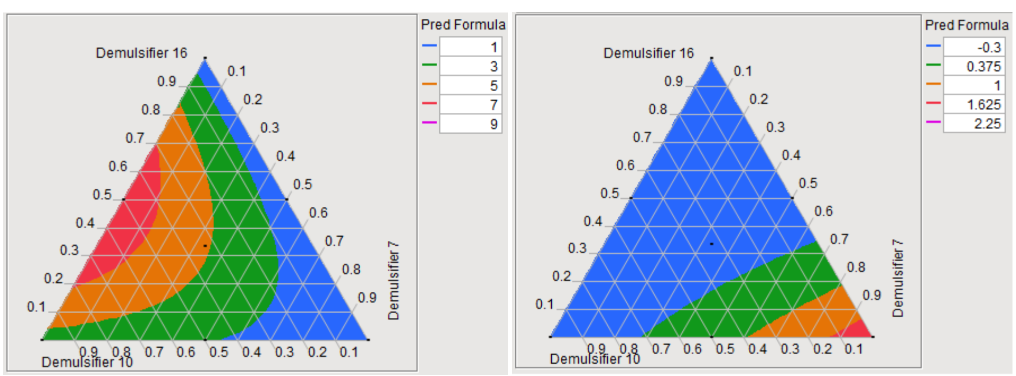
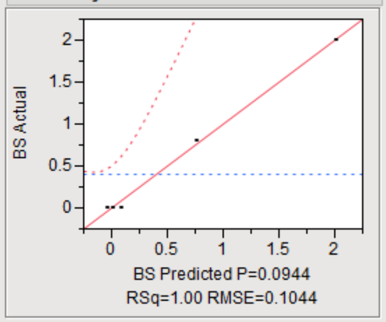


Figure 6. Dryness (W1) and BS ternary plots for Model 3

It is possible to see synergisms and antagonisms among the components present in a specific model. For model 3 it is shown the model fit and effects estimate for response BS in Figure 7.

Response BS



Sorted Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Demulsifier 7	2.0090909	0.10405	19.31	0.0329*
Demulsifier 16*Demulsifier 7	-4.181818	0.478289	-8.74	0.0725
Demulsifier 10*Demulsifier 7	-0.981818	0.478289	-2.05	0.2886
Demulsifier 10*Demulsifier 16	-0.181818	0.478289	-0.38	0.7687
Demulsifier 10	0.0090909	0.10405	0.09	0.9445
Demulsifier 16	0.0090909	0.10405	0.09	0.9445

Figure 7. Modeling fit and Effects estimate for response BS in Model 3.

By the response obtained from the software, there was a good modeling fit expressed by the adjustment of the experimental data into the prediction formula. It is expressed the sorted magnitude of the effects considering the components of the blend. It can be seen that for BS response, Demulsifier 07 had a positive response effect with considerable statistical confidence (p-value lower than 0.05) which means that Demulsifier 07 alone does not contribute for BS reduction. However the mixture of Demulsifier 07 and Demulsifier 16 shows a negative effect in the response, meaning that there is a potential good synergy between these chemical as they contributes to minimize this response variable with p-value equal to 0.0725.

Considering the prediction formula for each response it is possible to find the optimal proportion of chemicals maximizing water drop and interface quality and minimizing the residual amount of BS&W for each model.

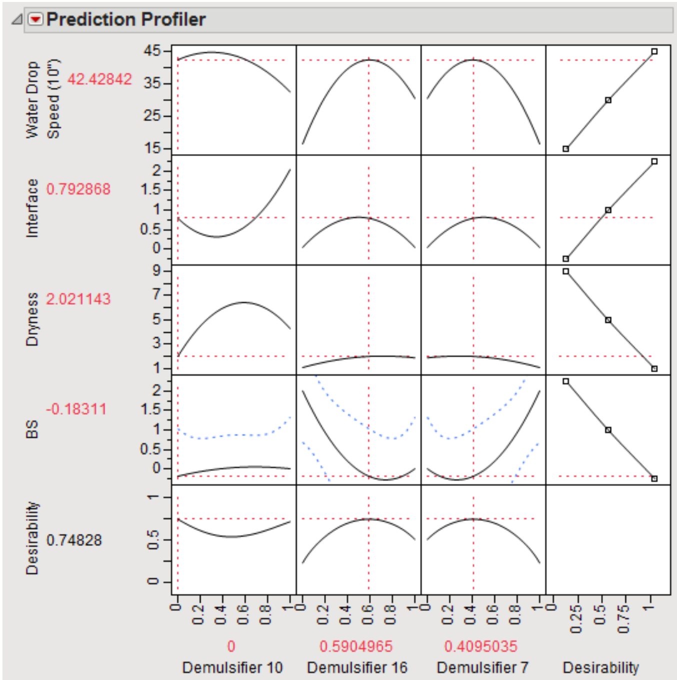


Figure 8. Prediction Profile for Model 3

A potential formulation is already identified using the prediction profiler maximizing the desirability of the model. This formulation consists of 40% Demulsifier 07 and 60% Demulsifier 16. The contribution of Demulsifier 10 is negligible to enhance final performance of this blend.

After running all the models and finding potential good formulations and synergies available, it is possible to run a final ABCD modeling with 4 components.

The demulsifiers below showed good synergy levels and low antagonism for the responses of the 6 models studied.

- Demulsifier 15
- Demulsifier 16
- Demulsifier 10
- Demulsifier 07

ABCD modeling generates a screening design for mixtures devised by Snee (1975). This is a well balanced designed for 4 components and the testing points are basically indicated in table 4. One of the advantages of using this design after the simplex centroid is that some of the data points are already available.

Table 4. ABCD design representing mass fraction of the experiments for each demulsifier

Intermediate 1	Intermediate 2	Intermediate 3	Intermediate 4
1	0	0	0
0	1	0	0
0	0	1	0
0	0	0	1
0.5	0.5	0	0
0.5	0	0.5	0
0.5	0	0	0.5
0	0.5	0.5	0
0	0.5	0	0.5
0	0	0.5	0.5
0.625	0.125	0.125	0.125
0.125	0.625	0.125	0.125
0.125	0.125	0.625	0.125
0.125	0.125	0.125	0.625
0.25	0.25	0.25	0.25

Considering the first models using the simplex centroid design, the individual components as well as the 50% / 50% binary components data are already available. This means that for the 15 experiments required, 10 data points are already available from previous tests and a refining in modeling terms is constructed using ABCD with 5 more experiments.

For the proposed combination of Demulsifier 15, Demulsifier 16, Demulsifier 10, Demulsifier 07 an ABCD modeling is done. After experiments are concluded, getting the final equation for each response JMP® software maximize the desirability for all the responses analyzed (maximizing water drop speed and interface quality and minimizing BS and W) proposing a formulation.

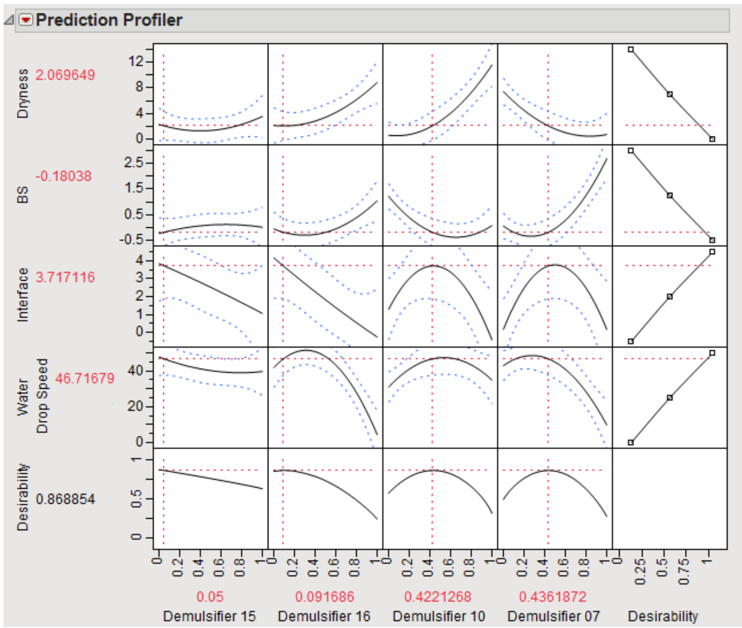


Figure 9. Prediction Profiler of ABCD modeling

The final Demulsifier Model_ABCD formulation proposed consists of:

- 5% Demulsifier 15
- 10% Demulsifier 16
- 42% Demulsifier 10
- 43% Demulsifier 07

To validate performance of the final formulation achieved a comparative *bottle test* is conducted comparing the performance of the new product with the current one in use in field in a dosage curve.

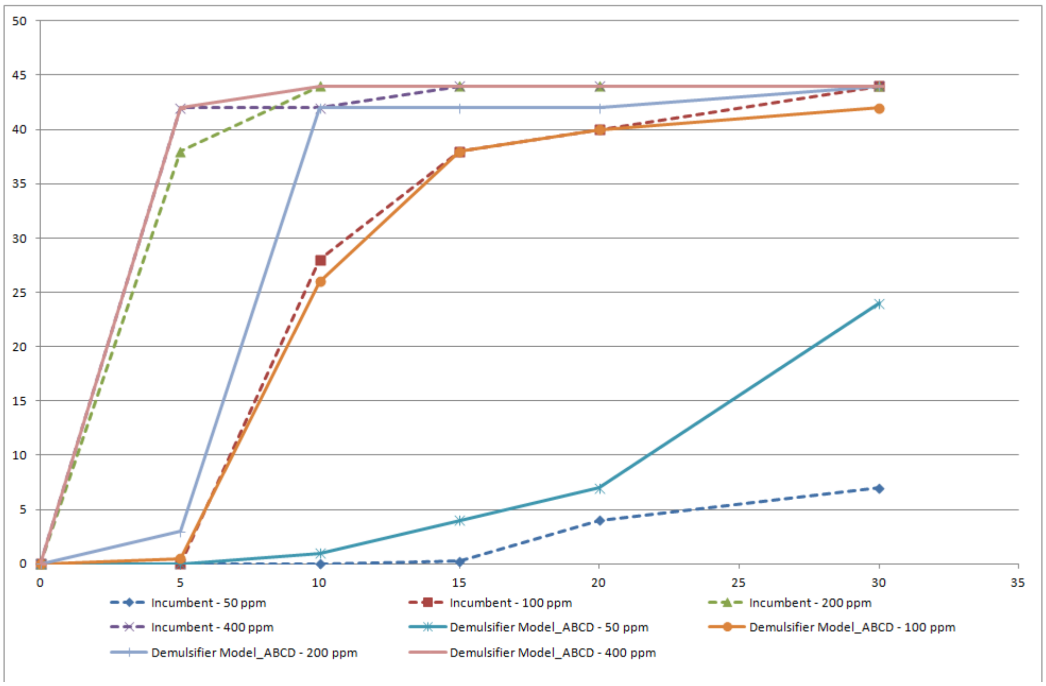


Figure 10. Water Drop curves for incumbent and Demulsifier Model_ABCD formulation

The dotted line is the incumbent and the solid line the new Demulsifier Model_ABCD formulation proposed. The new product performed very similar to the incumbent for higher dosage levels but showing some faster water drop. The main significant difference is related to lower dosages where the new formulation got considerable better performance.

BS&W test were conducted to check residual emulsion and free water levels after treatment. The results are illustrated in Figure 11.

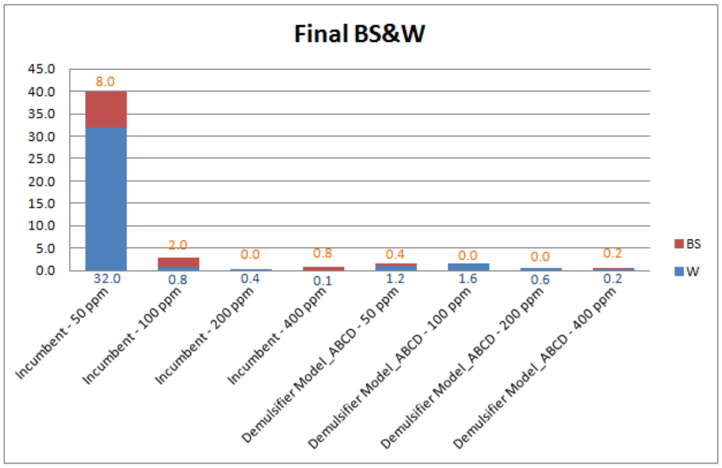


Figure 11. BS&W results for incumbent and Demulsifier Model_ABCD

Confirming what has been seen in Figure 10, for lower dosages until 100 ppm, Demulsifier Model_ABCD formulation gave better BS&W results comparing to incumbent. The performance for higher dosages were similar but yet Demulsifier Model_ABCD gave slightly better behavior.

Interface quality for all dosage levels for incumbent and Demulsifier Model_ABCD formulation were satisfactory.

4. Conclusions

A new demulsifier formulation was obtained using regular *bottle test* technique with performance superior to incumbent considering a statistical approach. The advantages of using a design of experiments are mainly related to:

- Reduction of the number of proposed experiments,
- Find synergies and antagonisms,
- Get formulation prediction
- Reduce try and error experiments very common for bottle testers.

Among the enormous amount of experiments possible, to run all the required tests and to get the final formulation desired just 66 experiments were conducted not considering the final comparative dosage curve. As the tests were done in a planned way, more sophisticated models can be constructed using the previous information obtained. However it is critical to make the experiments as fast as possible to avoid oil ageing and changes in the emulsion characteristics.

5. References

TREATING OILFIELD EMULSIONS, fourth edition, Petroleum Extension Service, The University of Texas at Austin, 1990.

SALL J., CREIGHTON L., LEHMAN A., JMP® Start Statistics, Third Edition, SAS institute Inc., 2005.

SNEE R.D., Experimental Designs for Quadratic Models in Constrained Mixture Spaces, Technometrics Volume 17, Issue 2, 1975.