LIQUID-LIQUID EXTRACTION OF NAPHTHALENE. APPLICATION OF A MIXTURE DESIGN AND OPTIMIZATION

<u>Farida. Bendebane^a</u>, Lamya. Bouziane^b, Fadhel. Ismail^b* ^aDepartment of Chemistry, ^cDepartment of Processes Engineering, University Badji-Mokhtar of Annaba Email : bendefarida@yahoo.fr ; ismail.fadhel@univ-annaba.org

Abstract

Coke gas treatment process requires fresh fuel oil to remove naphthalene. At the Coke plant of Annaba in Algeria, an amount of about 14.5 tons/day of fuel oil is used as washing oil. At the end of the process the released fuel is charged of naphthalene (7-10%) as impurities. This creates serious environmental problems in the region due to the environmental pollution by this industrial waste.

In order to regenerate the fuel, a liquid-liquid extraction of naphthalene by a mixed solvent extraction was performed. The efficiency of extraction of naphthalene from an organic phase depends primarily on the choice of the extractant and can also be improved by optimizing the various operating parameters.

The aim of this work was to improve the performance of the liquid-liquid extraction of naphthalene from a phase fuel by the research for an optimal composition of a three solvents mixture as the extractant. From preliminary tests, the amount of fuel from the extractant mixture (F / M), stirring speed and the concentration of naphthalene in the fuel oil were fixed. The composition of the extractant mixture was performed by implementing an experimental mixture design where the mixing proportions of the three components dimethyl sulfoxide (DMSO), methanol and water, were studied,. The response was the effect of the solvent on the extraction yield of naphthalene. This yield was determined by the amount of naphthalene in the fuel oil phase which was followed by refractometry and confirmed by infrared spectroscopy.

The use of this design is very effective to evaluate and to model the effects of these components by developing polynomial regression equations that describe the interdependencies between the input parameters and the yield response. The results treated in a way statistics are very interesting and can finally determine the optimum conditions for a maximum yield of extraction.

Keywords: naphthalene, liquid-liquid extraction, mixture design, ternary diagrams, modeling and optimization

1. INTRODUCTION

The coke is an essential fuel in smelting-furnace of steel plants. The gas by-product of the coke is very important; it is processed for use as a fuel or as an important source of raw materials. Naphthalene present in this gas can deposit at ambient temperature because of its easy sublimation, and may cause blockages in the circuits of industrial installations such as burners, valves, pipes and so on. This leads to the risk of explosions, fires and frequent stops for interviews. To remove naphthalene the scrubbing of the coke gas by a fuel oil is one of the methods of its treatment.

The fuel oil amount used and released by the process as an industrial waste is in the range of 14.5 tons per day. It is charged and saturated with 7-10% of naphthalene. Naphthalene is also an undesirable product in the fuel oil for the same reasons above mentioned. To valorize this waste, it is imperative to recovery the fuel oil in order to reuse it eventually. In this context, the work focuses mainly on the extraction of naphthalene from fuel oil with the mixture DMSO-methanol-water. This treatment would lead to the recovery the fuel oil principally, the regeneration of solvents, and the production a considerable amount of pure naphthalene.

The liquid-liquid extraction is an operation of mater transfer between two liquid phases. It consists of extracting one or more components from a solution by simple dissolution in contact with another solvent in which the constituents are more soluble. This is also used frequently to separate from liquid mixture, components whose volatilities are low or very similar as in the case of thermo-degradable compounds or azeotropic mixtures. Especially since the separation of such compounds by distillation is more difficult and more expensive.

Extraction with solvents is particularly well suited to separate components by chemical families. In the field of oils, it is applied since long time and in a very large scale especially for the desaromatization of diesel fuels and lubricating oils, the deasphalting of heavy fractions and extraction of aromatics BTX (benzene, toluene and xylene). In major industries such as hydrometallurgy, nuclear and organic chemistry liquid-liquid extractions are widely used [1]. In the petrochemical industry, the use of selective solvents in liquidliquid extraction doesnøt date very long time. This kind of treatment can eliminate some unwanted components in a given oil to improve its characteristics and especially its lubricating qualities. Among these selective solvents, dimethyl sulfoxide (DMSO) gave interesting results but the regeneration of solvent and the recuperation of pure naphthalene seem as difficult steps, and present the major inconvenient of treatment with DMSO [2]. Treatment with methanol alone gives a low extraction efficiency although its recovery by crystallization and the precipitation of naphthalene are very easy. This is due to a solubility of 5.3% methanol in the fuel and a rapid saturation of 6% of naphthalene in methanol [3]. To reach more efficient extraction, a mixture of solvents composed of DMSO, methanol and water, was chosen in order to improve the efficiency of extraction. The solubility of the methanol in the fuel decreases, and the naphthalene goes into the extractant phase more easily.

The design of experiments for mixtures was well known since the fifteen¢s of last century by the early work of Scheffé [4]. But the methodology was developed mainly during the seventeen' years [5].

The methodology consists on the study of one or many variables as response according to the change of the mixture composition, the total of constituents is remaining stable. This assumes that the measured response depends only on the proportions of the constituents present in the mixture. The fact that the sum of proportions is always equal to the unity, particular and reduced polynomial models are indicated and it is common to adjust settings on conventional networks such as of Scheffe.

The factors of study for mixture design are the proportions of the constituents of the mixture [6-7]. However, these components are not independent on each other. The sum of the proportions of a mixture is always equal to 100%. The percentage of the last component is imposed by the sum of the percentages of the other compounds. That's why mixture designs are treated separately.

Mixture designs are also characterized by many constraints that can influence the choice of the proportions of constituents. For example, the concentration of a product must be at least x percent or the concentration may not exceed a given value. Based on these constraints, the planning of the study was modified and must be adapted to each case. The objectives of a problem formulation can be of different natures:

É The search for components that must be introduced in a real formula is a problem of screening. This objective involves the design of experiments to study the effects of factors. They have usually two ways to specify the presence or absence of the grantor. É Once we have the components to be included in a formula, we can have an objective knowledge of the value of a response at each point of the experimental domain defined by the changes imposed on the proportions of the constituents. This objective refers to the use of a general polynomial model to arrive at a plot of response surface and / or iso-response curves in the field

É Another objective may be to find an optimum for a response or to find a compromise between different responses using for example the use of desirability functions. É Finally, it is common in the industries of the formulation that we have a reference mixture. The purpose of a study may be to estimate the effect of changes in proportions of the constituents around the reference mixture. This approach is similar to a problem of screening, however, call of specific methods based on the exploitation of polynomial models for the determination of special effects. Previous work suggested a pragmatic approach to address the problem of interactions [8-10].

The main objective of this work is to improve the extraction yield of naphthalene from a phase fuel oil by the search for an optimal composition of a mixture of tree solvents DMSO-methanol-water using an experimental mixture design.

2. MIXTURE DESIGN

Simplex designs were used to study the effects of mixture components on the response variable. If q represents the number of ingredients in the system under study and x_i represents the proportion of ith constituent in the mixture, then

$$\sum_{i=1}^{q} x_i = x_1 + x_2 + \dots + x_q = 1.0; \ x_i > 0; \ i = 1, 2, 3, \dots, q$$
(1)

In mixture problems, the purpose of the experiments is to model the blending surface with some forms of mathematical equations so that predictions of the response for any mixture or combination of the ingredients can be made empirically where the measure is the influence of each component alone and the combination of together all components on the response. When the mixture is composed of three components, the mixture space is a triangle with vertices corresponding to formulations that are pure blends (mixtures that are 100% of a single component) [11]. The mixture blend representing the three components can be conveniently represented on tri-linear coordinate paper. Each of the three sides of the triangle represents a mixture that has none of one of the three components (the component labeled on the opposite vertex). The standard forms of the mixture models that are in widespread use are [12]:

$$\text{Linear}: Y = \sum_{i=1}^{n} \beta_i x_i \tag{2}$$

Quadratic: $Y = \sum_{i=1}^{q} \beta_i x_i + \sum_{i=1}^{q} \beta_{ij} x_i x_j$ (3)

Full cubic :

$$Y = \sum_{i=1}^{q} \beta_i x_i + \sum \sum_{i< j}^{q} \beta_{ij} x_i \ x_j + \sum \sum_{i< j}^{q} \delta_{ij} x_i \ x_j (x_i - x_j) + \sum \sum_{i< j< k}^{q} \beta_{ijk} x_i \ x_j x_k \quad (4)$$

Special cubic:

$$Y = \sum_{i=1}^{q} \beta_{i} x_{i} + \sum_{i < j} \sum_{k=1}^{q} \beta_{ij} x_{i} x_{j} + \sum_{i < j < k} \sum_{k=1}^{q} \beta_{ijk} x_{i} x_{j} x_{k}$$
(5)

Special quartic:

$$Y = \sum_{i=1}^{q} \beta_{i} x_{i} + \sum_{i < j} \sum_{k=1}^{q} \beta_{ij} x_{i} x_{j} + \sum_{i < j < k} \sum_{k=1}^{q} \beta_{iijk} x_{i}^{2} x_{j} x_{k} + \sum_{i < j < k} \sum_{k=1}^{q} \beta_{iijk} x_{i} x_{j}^{2} x_{k} + \sum_{i < j < k} \sum_{k=1}^{q} \beta_{ijkk} x_{i} x_{j} x_{k}^{2}$$

$$(6)$$

Where Y represents the yield or output variable of the process. i represents the expected response to the pure blend $x_i = 1$ and $x_j = 0$ when j \tilde{N} i. The potion $\sum_{i=1}^{q} \beta_i x_i$ is called the linear blending portion. When there is curvature arising from nonlinear blending between component pairs, the parameters is represent either synergistic or antagonistic blending. Higher-order terms are frequently necessary in mixture models because the phenomena studied may be complex and the experimental region is frequently the entire operability region and is therefore large, requiring an elaborate model. The simplex lattice and simplex centroid designs are boundary point designs. To make predictions about the properties of

complete mixtures, it would be highly desirable to have more runs in the interior of the simplex. This can be done by augmenting the usual simplex designs with axial runs and the overall centroid, if the centroid is not already a design point.

3. EXPERIMENTAL

I In order to improve the naphthalene extraction efficiency from the organic phase "fuel oil", a mixture design of three components namely, DMSO, methanol and water was carried out on only one response that is the yield of extraction.

Based on previous work to optimize the extraction of naphthalene from a fuel oil phase [3, 13-15], some operating conditions were chosen. Preliminary tests have shown that the use of a percentage up to 5% of water with DMSO had no effect on the naphthalene extraction yield which reveals that the use of an amount of water reduces the amount of solvent and this can be interressant economically.

The extraction of naphthalene consisted in contacting a solution of simulated fuel charged with a certain specific concentration of naphthalene (6%) and a ratio of Fuel / Mixture equal to 0.5. The stirring velocity was 100rpm during 30 minutes as the contact time. The three components of the mixture extractant were varied according to a mixture design. These experiments were conducted with initial concentrations of naphthalene in the fuel comparable to those determined from the mass balance of the industrial unit coke [2]. The extraction of naphthalene from the fuel phase into the mixture phase implies a decrease in the concentration of naphthalene in the fuel and this was followed by the variation of the refractive index of the fuel phase knowing experimentally that this index varies linearly with the percentage of naphthalene in the fuel as shown by the calibration curve (Fig 2). The areas of the three components studied were selected around the optimum values previously obtained earlier.

The method of mixture designs helps to obtain many informations on the components taken separately and their influences on their possible interactions. It reduces the number of experiments and facilitates the study significantly. The objective is to obtain mixtures with optimal response or some requirements that might be fixed preliminary. The response depends on the desired proportions of the mixtyre constituents. Thus, for a mixture of three factors (DMSO, methanol and water) taken in different volume proportions, their sum is equal to the unity that is why they are dependent on each other.

The choice of low and high levels of different constituants was based on previous works [15,16] and preliminary tests on the naphtalene extraction. It is not frequent that all constituants vary from 0 to 100%. Generally and for economic or reglementary raisons inteval limits are very week. In this work the levels are mentionned in table 1.

N°	Component	level	
		Low	High
1	DMSO	0.5	1
2	Methanol	0	0.5
3	Water	0	0.1

Table 1: Limit proportions of components

The area of study is a triangle. The experimental points are located at the vertices and mid edges (6 tests) and three points in the center of the triangle (test points) are used to validate the applied model. This gives a total of 9 points correspondent to 9 experimental tests.

To take consideration of the temperature variation from an experiment to another, all refractive indexes N_t at a given temperature t, are reduced to 20 °C(N_{20}) using Eq. (7) that was obtained from experimental linear curves of the refractive index variation according to the temperature for different fuels (Equations. (8), (9) and (10)).

$N_{20} = N_t - 0.0004 \times (20 - t)$		(7)
Fresh Fuel $N_t = -0.0004 \times t + 1.4687$	$R^2 = 0.9951$	(8)
Simulated Fuel $N_t = -0.0004 \times t + 1.4795$	$R^2 = 0.9904$	<mark>(</mark> 9)
Charged Fuel $N_t = -0.0004 \times t + 1.4726$	$R^2 = 0.9932$	(10)

In absence of naphthalene, the refractive index of the fuel oil is affected by the presence of the mixture due to its weak solubility. So a refractive index N_b correcting experimental 0% of naphthalene, was measured for each experience in the same operator conditions. Then the percentage of naphthalene was determined from Eq. (11) according to the calibration curve (Fig. 1).

$$[Naph.] = \frac{(N_m - N_b)}{0.0014} \tag{11}$$

where N_m is the refractive index measured of the fuel oil solution. The yield of extraction was then calculated using Eq. (12):

$$Y(\%) = \left[1 - \frac{[Napht]_t}{[Napht]_0}\right] \times 100$$
(12)

where $[Naph.]_t$ and $[Naph.]_0$ represent the concentrations of naphthalene in fuel oil solution at equilibrium and initial times respectively.



Fig 1: Calibration curve fuel-naphthalene.

The extraction of naphthalene was also followed by infrared spectroscopy. The naphthalene presents at 780 cm⁻¹ a characteristic band which varies according to its concentration. The IR spectra obtained on a \div Shimatzu IR 408, 200-91506øapparatus showed clearly the presence of naphthalene in the fuel oil charged and rejected by the industrial unit (Fig. 2). Moreover, we can notice that the band corresponding to the naphthalene in rejected fuel oil was more pronounced compared to the simulated fuel (6% of naphthalene). Indeed, the calculation by mass balance of the naphthalene concentration in the charged fuel rejected by the industrial unit gave about 8% [16].



Fig. 2 : Infrared spectra of different fuels. A : Fresh; B: simulated (6%); C: rejected

4. **RESULTS AND DISCUSSION**

4.1 Yield of extraction

Experimental tests were performed according to the matrix proposed by the program Minitab 15. The results expressed by the extraction yields of naphthalene are summarized in Table 2.

Run	DMSO	Methanol	water	Y%
1	0.8125	0.1125	0.075	60.66
2	0.9000	0.0000	0.100	76.16
3	0.8625	0.1125	0.025	77.33
4	1.0000	0.0000	0.000	62.00
5	0.6125	0.3125	0.075	58.33
6	0.5000	0.5000	0.000	87.00
7	0.7250	0.2250	0.050	66.66
8	0.6125	0.3625	0.025	83.33
9	0.5000	0.4000	0.100	63.16

Table 2: Yield of extraction (mixture design)

4.2 Analysis of variance

The statistical analysis was performed using specialized software Minitab 15 experimental design. To determine the polynomial regression model performance of the extraction Yield% based on the three selected components, the influence of types of regression was first studied. Indeed, from Table 3 it can be observed that the probability p-value (P) interaction terms are significant.

Positive coefficients for mixtures of two components mean that the two components act synergistically and are complementary. Thus, the response of the mixture is higher than that is obtained simply by calculating the average of two responses corresponding to each pure mixture. Negative coefficients indicate that both components are antagonistic. Thus, the mean response is lower than that both obtained by calculating the simple average of two responses. The mixture of all components two by two gives significant results. And this is confirmed by ANOVA (Table 4) which shows that all linear and quadratic terms are significant.

Terms	Coefficients	Er-T coef	Т	Р	VIF
DMSO	62	1.26	*	*	5
Methanol	-1525	130.32	*	*	7097
Water	60882	4759.96	*	*	463443
DMSO*Methanol	3274	260.00	12.59	0.001	9198
DMSO*Water	-67422	5282.69	-12.76	0.001	3006994
Methanol*Water	-68242	5282.69	-12.92	0.001	39747

Table 3: Estimated regression coefficients for yield

Source	DL	Sc Seq.	CM adjust	F	Р
Regression	5	896.214	179.243	104.75	0.001
Linear	2	343.168	171.584	100.28	0.001
Quadratic	3	642.219	214.073	125.11	0.001
Error residual	3	5.133	1.711		
Total	8				

 Table 4: Analysis of variance for yield ANOVA.

4.3 Polynomial regression

Low values of the probability P obtained in Table 3 show that all linear and quadratic terms are significant and important. The mathematical model expressing the efficiency of the extraction must take into account all the terms, thus a first degree quadratic model can be given by Equation 13.

 $Y\% = 62 \times DMSO \circ 1525 \times methanol + 60882 \times Water + 3274 \times DMSO \times Methanol$

4.4 Validation of model

To validate the model, three additional experiments were performed three tests that correspond to tests 7, 8 and 9 of Table 6. The results are summarized in Table 5. The difference between measured and calculated values is not significant; the model is then valid.

Run N°	Yield (exp.) (%)	Yield (theor.) (%)	(Yield) (%)
7	66.66	68.38	1.72
8	83.33	83.34	0.01
9	63.16	63.24	0.08

Table 5: Validation of the model by test points

In addition, the graphical representation of theoretical responses according to estimated responses shows a very good linearity with a high correlation constant ($R^2 = 0.9943$).



5. Optimization of mixing proportion for response

I

I.

The above analysis provides interesting qualitative diagnosis in the study of mixtures, but the main objective is to find the optimal mixture combining all the desired properties. However, these criteria often have different interests: some variables should exceed a minimum threshold, others should be maximized. To reconcile all these constraints and optimize the mixture, a function called "desirability" can be defined [17]. The statistical treatment of the mathematical model obtained from experimental results leads to the desirability of the naphthalene extraction efficiency corresponding to the three variables DMSO, methanol and water (Fig. 4). This figure shows that when the value of desirability is high (close or equal to 1), the response for the theoretical yield of 99.0% is better and close to the value of the optimal for a mixture of three components whose proportions are 0.7416, 0.2247 and 0.0337 for DMSO, methanol and water respectively.



Fig 4: Optimization and composite desirability for the response of extraction yield

I

I

6. Conclusion

The liquid-liquid extraction of naphthalene from a fuel oil was carried out with three components DMSO, methanol and water as an extractant mixture. The objective was to recycle the rejected fuel oil (14.5 tons /day) that was used in the coke gas treatment for a possible reuse. An experimental design has been defined and three components of a extractant mixture have been limited by constraints. Using the mixture design, a linear model that connects the extraction efficiency as a response to various constituents, has built a set of experiences and propose formulations to determine the optimum conditions leading to maximum efficiency of extraction. Analysis of variance showed that the linear and interaction effects are significant. The mathematical model was validated by comparing the resulting theoretical yields and the results obtained experimentally. Indeed, the fit was almost perfect and the linear correlation constant was 0.9943. The optimization with perfect desirability (d = 1) gave an extractant mixture of three components whose proportions are 0.7416. 0.2247 and 0.0337 for DMSO, methanol and of water respectively, corresponding to a theoretical yield of 99.0%. Indeed, to confirm and to validate the results obtained theoretically a check for an additional experiment under optimal conditions was performed and the yield obtained experimentally was in the range of 98.80% compared to 99% that was given by the model. In addition, the presence of about 3.37% of water in the extractant mixture is one of the practical conditions; this result is interesting in the sense that water is a pervasive and unavoidable in industrial circuits that are generally open to the air moist. This work will be followed by a study of the regeneration of the various products especially and the recovery of pure naphthalene that should be a production source of pure naphthalene.

References

- [1] MATAR. S., Chemistry of petrochemical processes, 2nd ed. Lavoisier, chapitre 2, p 149, (2001).
- [2] BOUHROUM S., Recyclage du fuel rejeté par løUnité Cokerie de Annaba, Thèse de Magister, Université de Annaba (1998).
- [3] ISMAIL. F., Zga. N., Tifouti. L., Traitement du fuel rejeté par la cokerie SIDER-Annaba 6^{ème} Congrès de la SAC, Sétif, 14-16 Mai, (2002).
- [4] SCHEFFÉ. H., Experiment with mixtures. Journal of the Royal Statistical Society, Series B, 344-360, (1958).
- [5] CORNELL. J A, Experiment with mixtures : Designs, Models, and the analysis of mixture Data, Edition Wiley, Interscience, New York, 632p, (1990).
- [6] GOUPY. J., Plans døexpériences : les mélanges. Dunod, collection Technique et Ingénierie, (2001).

- [7] TINSSON. W., Plans dæxpérience : constructions et analyses statistiques. Collection Mathématiques et Applications, Vol. 67, Springer, (2010).
- [8] PIEPEL. G.F., Hicks. R.D., SZYCHOWSKI. J.M., LOEPPKY. J.L., Methode for curvature and interaction in mixture experiments, Technometrics, Vol.44, N°2, 161-172, (2002).
- [9] LOUVET. F, 40 ans de plans de mélange : bilans et perspectivesí , 30 ans de Méthodologie de la Recherche Expérimentale, Aix en Provence, 2-3 Juin (2005).
- [10] BOX. G.E.P. et DRAPER. N.R., Response surfaces, mixtures and ridge analyses, John Wiley et Sons, New York (2007).
- [11] MONTGOMERY. D.C., Design and Analysis of Experiments, 7th ed., John Wiley and Sons, 2008.
- [12] CORNELL. J.A., Experiments with Mixtures: Designs, Models and the Analysis of Mixture Data , 3rd ed., Wiley, 2002.
- [13] ZGA. N., Traitement du fuel rejeté par la cokerie SIDER-Annaba, Thèse de Magister, Département de Chimie, Université de Annaba, (2000)
- [14] ISMAIL. F., Recyclage du fuel de lavage des gaz de coke. Etude de la polymérisation par métathèse du cyclopentène et de la microstructure du polypentenamère, Thèse de Doctorat døEtat, département de Génie des Procédés, Université Badji-Mokhtar Annaba (2006).
- [15] BENDEBANE. F., BOUZIANE. L., ISMAIL. F., Extraction of naphthalene. Optimization and application to an industrial rejected fuel oil, Journal of Industrial and Engineering Chemistry, 16, 3146320, (2010).
- [16] ISMAIL. F, BENDEBANE F., Retraining of fuel-oil rejected by the coke industrial unit of Annaba, CIME 07, Annaba, April 23625, (2007).
- [17] MATHIEU. D., PHAN-TAN-LUU. R., planification døxpériences en formulation, Techniques de løngénieur, doc. J 2 241 et J 2 242, (2000).