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Modeling and optimization of naphthalene extraction from fuel oil, application of a mixture design

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Abstract : The aim of this work was to improve the performance of the liquid-liquid extraction of naphthalene from a fuel phase using a mixture composition as extractant. The composition of the extractant mixture was performed by implementing an experimental mixture design where the mixing proportions of the three components dimethyl sulfoxide, methanol and phenol, were studied. The response was the effect of the solvent on the extraction yield of naphthalene. The results treated in a statistic way were interesting and showed that the optimum conditions can enhance the yield of extraction until 84.56 % theoretically. An experimental validation of the model in the same conditions had given a yield of 83.48%.

Keywords : Naphthalene; Liquid-liquid extraction; Mixture design; Modeling; Optimization.

INTRODUCTION

The coke is a necessary component for iron melting in blast furnaces of steel plants. The coke gas as a byproduct is very important; it is used as a fuel or as an important source of raw materials. The naphthalene if present in the gas, may be deposited at room temperature due to its easy sublimation and can cause blockages in the circuits of industrial plants such as burners, valves, piping *etc.*, It may cause explosions, fires and frequent stops for maintenance. In steel plants, the washing of coke gas with fuel oil to remove naphthalene is one of the gas treatment processes. The amount of fuel used and discharged by the process is about 14.5 tons per day. To regenerate this fuel considered as industrial waste, it is essential to treat it for a possibly reuse. In this context, the work is primarily focused on the extraction of naphthalene which is also an undesirable product in the fuel for the same reasons mentioned above. This treatment would mainly, recycle the fuel oil, regenerate used solvents and produce a considerable amount of pure naphthalene.

The liquid-liquid extraction is a process of mass transfer between two fluid phases. It consists to extract one or more components from a solution by simple dissolution in contact with another solvent in

which the components are more soluble. This is also frequently used to separate components of a liquid mixture whose volatilities are low or very similar, as in the case of thermo-degradable compounds or azeotropic mixtures. Knowing, that the separation of such compounds by distillation is more difficult and certainly more expensive.

Solvent extraction is particularly well suited to the separation of components by chemical families. In the petrochemical industry, the use of selective solvents in liquid-liquid extraction does not date since very longtime[1-5]. This kind of treatment can eliminate some unwanted components present in oil in order to improve its characteristics and especially its lubricating qualities[5-7]. It is applied on a large scale especially for the dearomatisation of gas oils, the lubrification of oils, the deasphalting of heavy cuts and the extraction of BTX aromatics (benzene, toluene, xylene). In major industries such as hydrometallurgy, nuclear and organic chemistry, it is also widely used[8].

In previous works, the selective solvent dimethyl sulfoxide (DMSO) gave interesting results but the solvent regeneration and the recovery of pure naphthalene were difficult steps, and this was the major drawback of treatment with DMSO[9]. The treatment with methanol alone, although its regeneration by crystallization and precipitation of pure naphthalene were very easy, gave a low extraction efficiency. This is due to a low solubility of methanol in the fuel (5.3%) and a rapid saturation of naphthalene (6%) in methanol[10]. To achieve a more efficient extraction, a mixture of solvents namely DMSO, methanol and phenol, was chosen in order to improve the extraction efficiency. The solubility of methanol decreases in the fuel and naphthalene passes more easily in the extracting phase.

The design of experiments for mixtures is well known since the 50s of the last century by the initial work of Scheffe[11]. But the methodology was developed mainly during the 70s[12]. It proposes to study one or more variables in response according a mixture of components, the total amount remaining stable. It is then assumed that the measured response depends only on the proportions of the constituents present in the mixture. Mixture design factors are the proportions of the blend components[13,14]. However these components are not independent of each other. The sum of the proportions of a mixture is always 100%. The percentage of one component is imposed by the percentages of the other compounds. This is why mixture designs are treated separately. The use of special reduced polynomial models is common to adjust standard configurations such as networks Scheffe. Mixture designs are also characterized by many constraints that may influence the choice of the proportions of the constituents. For example, the concentration of a product must be at least x percent or the concentration may does not exceed a given value. Based on these constraints, the planning study is modified and must be adapted to each case[15-17]. Whatever their types[12-15,18-20], these constraints have the effect of reducing the experimental study field[21].

The main objective of this work was to improve the extraction yield of naphthalene from a fuel oil phase with the search for an optimal composition of a mixture of three solvents DMSO, methanol and phenol. Therefore, a mixture design with three components was applied to study the extraction yield of naphthalene as the response.

EXPERIMENTAL

Based on previous works[6,10,22,23], certain operating conditions were selected. The extraction of naphthalene was carried out by contacting an extractant mixture with a solution of simulated fuel charged with a definite concentration of naphthalene. These experiments were conducted with initial concentration of naphthalene (7.75%) comparable to that was determined by mass balance of the industrial process[9], with a ratio F/M equal to 0.5 (Fuel/extractant Mixture), a stirring speed of 100 rpm and during a contact time of 30 minutes. The three components of the extractant mixture were varied according to a mixture experimental design. The extraction of naphthalene from oil phase to the mixed phase involves a decrease in the concentration of naphthalene in the fuel, it was followed experimentally by the change of the oil phase refractive index. This index varies linearly according to the percentage of naphthalene in the fuel as shown by the calibration

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curve (Figure 1). The areas of the three components studied were chosen around the optimal values already obtained previously.

The mixture design method can give some information on the components, their influences separately and their possible interactions, reducing the number of experiments significantly and facilitating the study. The response depends on the proportions of the components used. Thus, for a mixture of three factors (DMSO, methanol and phenol) the sum of various volume fractions is equal to unity, they are dependent on each other.

The choice of upper and lower terminals of the individual components was based on previous studies[6,7,22,23], and preliminary tests of naphthalene extraction.

It is rare that proportions of all mixture components can vary in the interval freely {0-1}. In general, for technical, economic or regulatory reasons, they can vary within fairly narrow limits. In this study, the upper and lower imposed for three possible mixtures of constituent limits are shown in TABLE 1.

The study area was a triangle (simplex design). The experimental compositions of the extractant mixture were: three points vertices of the triangle indicating pure components, one for each component (DMSO, methanol and phenol), three mixtures containing all components with different proportions and a central point corresponding to the mean level of all components (Figure 2).

Concentrations of naphthalene in the fuel were determined by refractometry using the calibration curve prepared under the same operating conditions (Figure 1) and confirmed by infrared spectroscopy knowing that the characteristic band of naphthalene appears clearly at 780cm^{-1}. The extraction yield was calculated according to equation 1 as a function of the final concentration of naphthalene in the fuel oil after extraction.

$$Y(\%) = [1 - \frac{[Napht]_f}{[Napht]_0}] \times 100 \quad (1)$$

Where Y is the yield of the extraction, $(napht)_0$ and (napht) are the initial (7.75%) and the final percentages of naphthalene in the fuel respectively.

To overcome the temperature variation from one experiment to another, all refractive indices N_t at a given temperature (t) had been reported at 20°C (N_{20}) using equation 2 established experimentally.

$$N_{20} = N_t - 0.0004 \times (20 - t) \quad (2)$$

RESULTS AND DISCUSSION

Yield of extraction

Experimental tests were carried out according to a matrix of the mixture design and the results expressed by the extraction yield of naphthalene are summarized in TABLE 2.

Analysis of variance

TABLE 1 : Component ratios of the extractant mixture

N°	Component	Level	
		Min	Max
1	DMSO	0.1	0.2
2	Methanol	0.2	0.3
3	Phenol	0.6	0.7

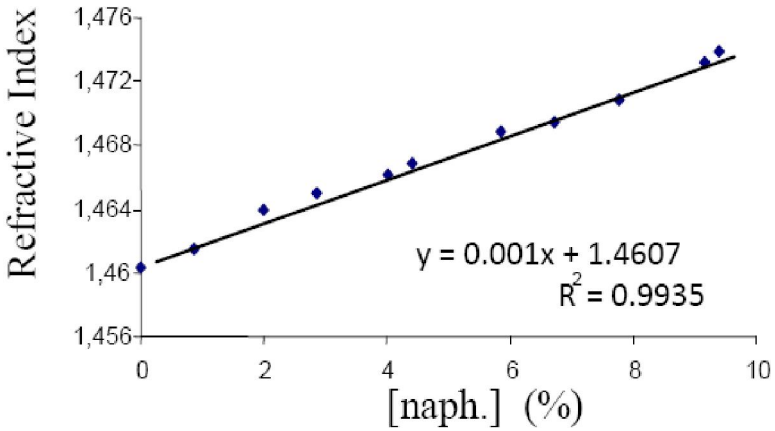

Figure 1 : Calibration curve fuel-naphthalene []

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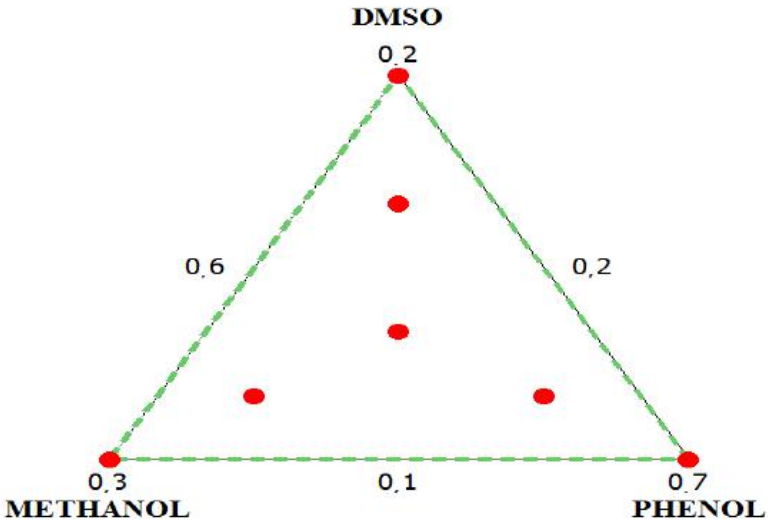

Figure 2 : Simplex design for DMSO-phenol-methanol

TABLE 2 : Experimental matrix of mixture design and results

Run	DMSO	Methanol	Phenol	N Ref.	N_B Mes.	Naph. (%)	Y (%)
1	0.1000	0.3000	0.6000	1.4521	1.4548	1.93	75.10
2	0.1167	0.2167	0.6667	1.4521	1.4554	2.36	69.55
3	0.1667	0.2167	0.6167	1.4511	1.4548	2.64	65.94
4	0.2000	0.2000	0.6000	1.4506	1.4550	3.14	59.48
5	0.1167	0.2667	0.6167	1.4529	1.4550	1.5	80.65
6	0.1333	0.2333	0.6333	1.4482	1.4511	2.07	73.29
7	0.1000	0.2000	0.7000	1.4526	1.4555	2.07	73.27

The statistical analysis was performed using a software program (Minitab 15). The modeling of the extraction yield was based on a polynomial regression with three selected components, the influence of the type of regression was first studied. Indeed, from TABLE 3 it is shown that the probability p-value (P) of interactions terms DMSO×Methanol and DMSO×Phenol were significant and the coefficients in the mixture indicate that Methanol (Coef.= -2006) and DMSO (Coef.= 2151) provided more significant level than Phenol (Coef.= 235).

Positive coefficients for two component mixture mean that the two components act synergistically and are complementary. That is why the response of the mixture is greater than that obtained by simply averaging the two responses of each pure mixture. Negative coefficients indicate that the two components are antagonistic. Thus, the mean response is less than that obtained by the simple average of the two responses. From TABLE 4, the linear and square are all significant factors on the extraction efficiency.

Mathematical modeling

The mathematical model applied to the response (extraction yield of naphthalene) is a quadratic model for three components with a total of six coefficients for a single response according to Equation 3.

$$Y(\%) = 2151 \times DMSO - 2006 \times Methanol + 235 \times Phenol + 6543 \times DMSO \times Methanol - 5691 \times DMSO \times Phenol + 2589 \times Methanol \times Phenol \quad (3)$$

The graphical representation of experimental esults based on estimated (theoretical) values (Figure 3) of extraction yields shows a very good linearity with a high correlation ($R^2 = 0.9998$).

Diagram of Cox (composition effect)

Figure 4 shows the trace of the performance Y(%) as response. In this figure, the vertical axis is the predicted response and the horizontal axis is the incremental change in each component. The reference mixture is shown as the point 0.000 on the horizontal axis. This graph clearly shows that the methanol is the most important to explain the performance. In fact,

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TABLE 3 : Estimated regression coefficients for extraction yield

Terms	Coefficients	Er-T Coef	T	P
DMSO	2151	165.69	*	*
Methanol	-2006	140.12	*	*
Phenol	235	25.74	*	*
DMSO×Methanol	6543	287.13	22.79	0.028
DMSO×Phénol	-5691	287.13	-19.82	0.032
Methanol×Phenol	2589	287.13	9.02	0.070

TABLE 4 : Analysis of variance (ANOVA) for extraction yield

Source	DF	SeqSS	adjSS	adjMS	F	P
Regression	5	280.760	280.7597	56.1519	869.31	0.026
Linear	2	220.226	30.7781	15.3890	238.24	0.046
Square	3	60.533	60.5335	20.1778	312.38	0.042
Residual Error	1	0.065	0.0646	0.0646		
Total	6	280.824				

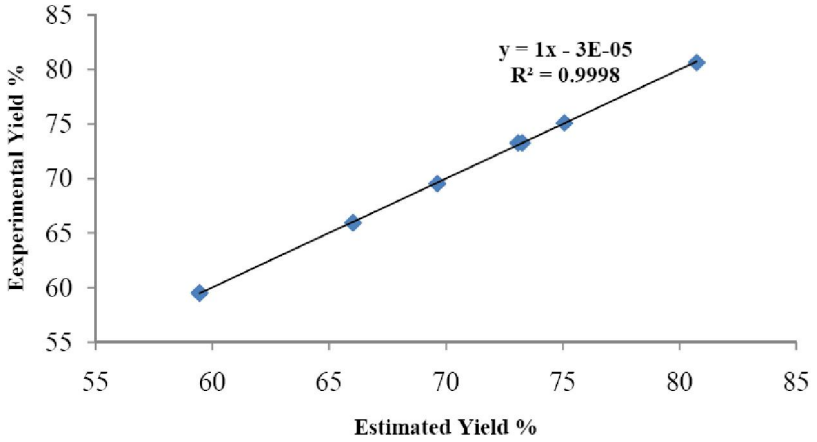

Figure 3 : Graphical representation of experimental yields versus estimated yields

when the concentration of methanol increases the value of performance also increases. On the other hand, the phenol has a strong negative effect that shows by the fall of performance value when the phenol concentration decreases, the same comments are observed for the DMSO; the performance decreases slightly when the proportion of DMSO decreases.

Response surface and contour

As for the design of experiments methodology[24-27], the Simplex method assumes that the system under study can be represented by a surface response limited to a well specific experimental field. Figures 5 and 6 show the contour graph and the response surface of the Yield based on three components (DMSO, methanol and phenol). The red outline on the bottom left of the triangle is the area where the best performance was obtained (yield> 80%). The response surface represented in a polyhedron is a triangle shape with a small convex particular shape on the top side of the phenol corresponding to the best yield of extraction

Optimization

The preceding analysis provides an interesting qualitative diagnosis in the study of mixtures. However, these criteria often have different interests: some variables should exceed a minimum threshold, others should be maximized. To reconcile all these constraints and to optimize the mixture, a mix of so-called "desirability" functions can be defined[28]. Then, several optimizations must be made in order to find a better response with a satisfactory desirability (TABLE 5). It was found that the theoretical response (Yield) is the same in all cases but optimized desirability changes with the change of

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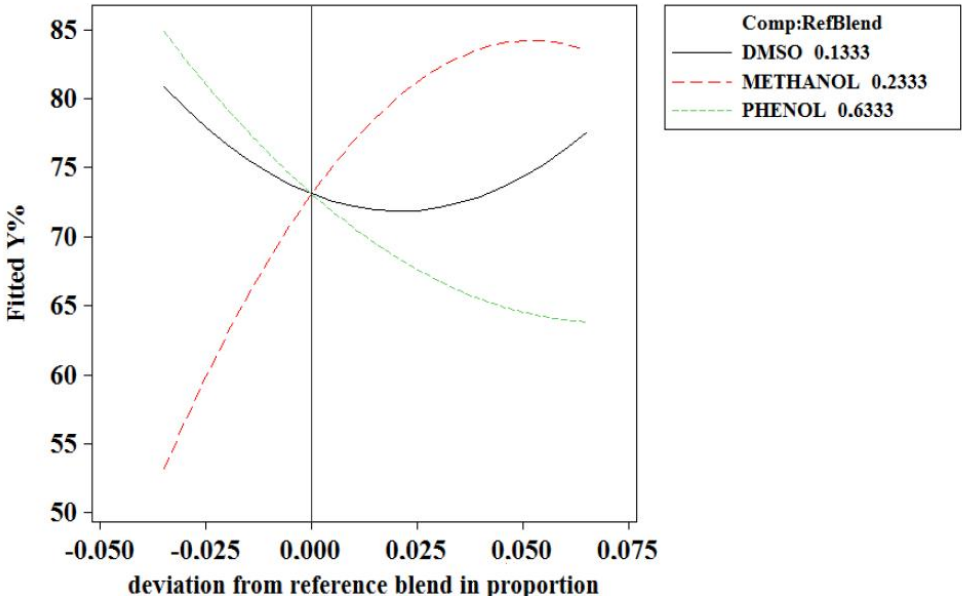

Figure 4 : Diagram of cox

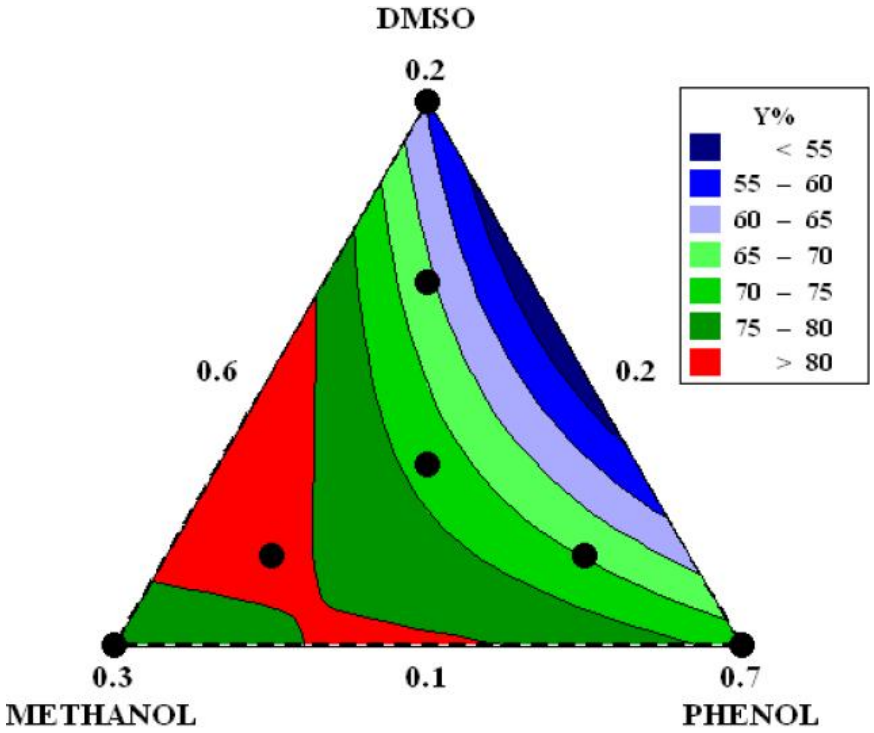

Figure 5 : Contour surface

the input parameters of the dialog box. A good desirability (97.05%) with a yield of 84.56% and a composition of DMSO (0.138), methanol (0.262) and phenol (0.600) was obtained finally.

Checking

The checking of optimum conditions obtained was performed using the same experimental setup: the temperature was 20°C, the initial concentration of naphthalene in fuel was 7.75%, the optimized extractant mixture determined above was used, the ratio of F/M was 0.5 and the stirring speed was100 rpm. The extraction of naphthalene from fuel had given a final concentration 1.28 % during 20 minutes corresponding to an extraction yield equal to 83.48 %. This value is comparable to the theoretical value (84.56 %).

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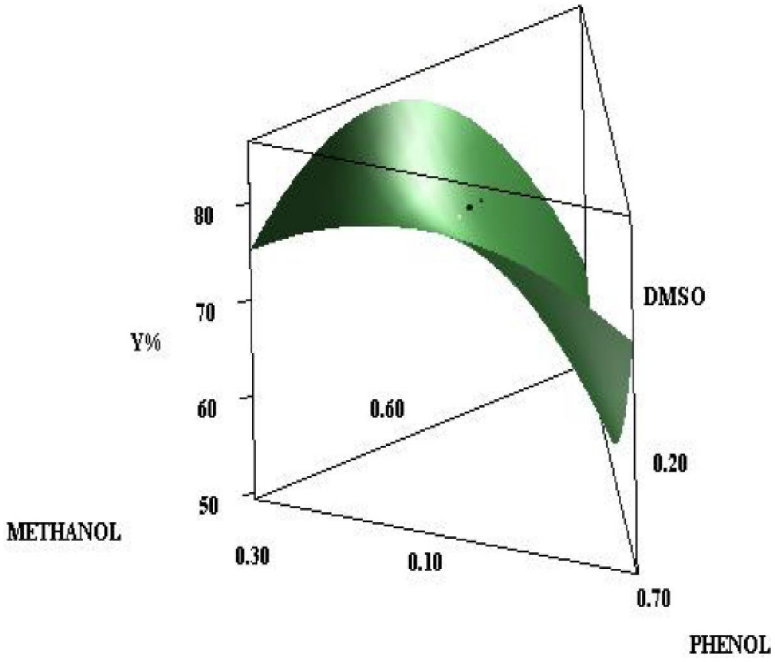

Figure 6 : Response surface

TABLE 5 : Criteria of optimization

Parameters	Inferior	Cible	Superior	Componennts	Y% Theor.	D
Optimization	70	85	100	DMSO = 0.138 Methanol = 0.262 Phenol = 0.6	84.557	0.970

CONCLUSION

As part of recycling a rejected fuel as an industrial waste for its possible reuse in the process of treatment of coke gas in the steel industry, the performance of the liquid-liquid extraction of naphthalene can be improved in the case of a mixture of three components DMSO, methanol and phenol as an extractant. An experimental area was defined and in which the three components were limited by explicit lower and implicit upper constraints. Using the method of mixture design, a linear model that relates the performance of the extraction as a response to various constituents, helped to build an array of experiences and propose formulations functions of targets set to determine the optimum conditions leading to a maximum of the extraction yield.

The analysis of variance showed that the linear effects and interactions were significant. The mathematical model was validated by comparing the experimental with theoretical yields. Indeed, the adjustment was almost perfectly linear with a constant of correlation equal to 0.999.

Optimization with better desirability (D = 0.97) gave an extractant mixture of the three components whose proportions were 0.138 (DMSO), 0.262 (methanol) and 0.600 (phenol) to a theoretical yield of 84 56%. In order to confirm and to validate the results obtained theoretically, a check for an additional experiment under the optimum conditions determined was performed and the yield obtained experimentally in the range of 83.48 % was compared to 84.56 %, corresponding to that was given by the model.

As perspective, this part of study should be followed by an optimization of operating parameters by another experiments design like central composite design. This would probably achieve higher yield extraction efficiency with the well optimized mixture.

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