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Modeling of catalytic-cavitation processing of middle oil fraction (200–300 ºC)

Experiment planning is the optimal control of an experiment in the context of incomplete information about the process mechanism. Interest in the science of experiment is associated with a wide range of experimental studies and a significant economic effect from the optimal organization of the experiment. An optimal experiment is a way to save time and cash, increase reliability of results. Middle fraction of Kumkol oil (200–300 ºC) was used to study the cavitation effect on fuel oil. The following catalytic systems were used, namely, modified FeS_2, nanocatalysts ε-Fe_2O_3/SiO_2, α-Fe_2O_3/SiO_2 spherical catalyst, β-FeOOH, and $Fe(OA)_3$. By quantifying the individual composition of the middle fraction (200–300 ºC) of Kumkol oil, a general pattern of the effect of catalytic-cavitation processing on the hydrocarbon composition of the middle fraction (200–300 ºC) of Kumkol oil was established. The optimal conditions and a number of factors affecting the cavitation processing of the middle oil fraction (200–300 ºC) in the presence of a FeS_2 catalyst were determined. In accordance with the regression equation obtained, the optimal conditions for cavitation processing are the following: τ = 90–120 s, the amount of added catalyst is 0.7–1 g and the amount of added water is 1.5–2 ml.

Keywords: nanocatalytic systems, cavitation processing, Kumkol oil, experiment planning, middle fraction, iron (III) oxides, polymorphic modifications, hydrocarbon composition.

Introduction

A large number of experimental problems in chemistry and chemical technology are formulated as extremal problems: determining the optimal process conditions, the optimal composition and etc. Due to the optimal location of points in the factor space and the linear transformation of coordinates, it is possible to overcome the drawbacks of classical regression analysis, in particular the correlation between the coefficients of the regression equation. The choice of the experiment plan is determined by the formulation of the research problem and the features of the object. The research process is usually divided into separate stages. The information obtained after each stage determines the further strategy of the experiment. Thus, the possibility of optimal control of the experiment arises. Planning an experiment allows all the factors to be varied simultaneously and to obtain quantitative estimates of the main effects and interaction effects. The effects of interest to the researcher are determined with a smaller error than with traditional research methods. Ultimately, the use of planning methods significantly increases the efficiency of the experiment [1].

Middle fraction of Kumkol oil (200–300 ºC) was used to study the cavitation effect on fuel oil. The individual chemical composition of the middle fraction of Kumkol oil (200–300 ºC) is presented in Table 1.

Table 1

Individual chemical composition of the middle fraction (200–300ºC) of Kumkol oil

Exit time, min	Chemical composition	Content, %
1	2	3
2.477	Methylcyclodecane	0.46
3.589	2-Methyldodecanol	3.92
3.755	1,2,4-Trimethylbenzene	4.15
4.629	2-Hexyloctanol	10.87
4.758	2-Hexyldecanol	10.05
5.963	Cyclodecane	2.4
6.049	2-Ethyl-1,4-dimethylbenzene	2.56
7.912	Decane	5.87
9.129	Undecane	3.63

Continuation of Table 1

1	2	3
9.664	2,6,11-Trimethyldodecane	6.35
10.138	2,7-Dimethylnaphthalene	3.68
10.986	1-Hexadecene	3.4
11.620	2,3,6-Trimethylnaphthalene	4.3
12.357	2-Dodecyloxyethanol	2.34
12.517	Dodecane	2.82
13.304	Tridecan	10.62
13.390	2,6,10-Trimethyltetradecane	0.62
14.534	2-Methylheptadecane	1
14.768	1,1-Hydroxybishexadecane	13.05
15.635	2-Methylhexadecane	0.79
15.819	Tetradecane	2.33
16.194	8-Methylpentadecane	1.59
20.197	Pentadecane	3.1

The following catalytic systems were used, namely, modified FeS_2, nanocatalysts ε-Fe_2O_3/SiO_2, α-Fe_2O_3/SiO_2 spherical catalyst, β-FeOOH, and $Fe(OA)_3$.

Experimental

Experiments on the cavitation processing of the middle fraction of oil (200–300 ºC) were performed in a ultrasonic disperser MEF-92, which allows high-intensity processing of small volumes of liquids under laboratory conditions.

A sample of the treated liquid with a volume of 0.05 ml was subjected to a cavitation effect for 7–10 minutes. The amount of the introduced catalytic additive was 1 % of the volume of the treated substance. The parameters of the ultrasonic cavitator MEF-92 are as follows: the oscillation frequency is 22 kHz, the intensity of the ultrasonic effect is up to 250 W/cm^2, the power is 600 W.

The study of products of the middle fraction of oil (200–300 ºC) before and after cavitation processing was determined by gas chromatography-mass spectrometry using an HP 5890/5972 MSD instrument from Agilent (USA). Chromatography conditions are DB-XLB-5 column, 30 mm × 0.5 µm; gas — helium, 0.8 ml/min; in the temperature range of 50 ºC — 4 min, 50–150 ºC — 10 ºC/min, 150–300 ºC — 20 ºC/min, 300 ºC — 4 min; evaporator: 200–300 ºC. Identification of substances was carried out according to the NIST 98 mass spectral database.

Results and discussion

One of the ways to successfully solve the technological problem of cavitation processing of oil fuels is to determine the optimal process conditions, namely, the duration of the cavitation processing, the amount of catalyst added and water. As optimization parameters (y), the dynamic viscosity of the average fraction of oil was considered, since viscosity is the main physico-chemical parameter of the properties of oil fuels. The following factors have been chosen as independent factors, namely, z_1 is duration of cavitation treatment (s); z_2 is the amount of catalyst (g); z_3 is the amount of water added (ml).

The influence of various factors on the reduction of viscosity during cavitation processing of the middle fraction of oil (200–300 ºC) was determined by the method of full factorial experiment design [1]. To derive a linear regression equation, an extended planning matrix of the full factorial experiment of type 23 was used (the number of levels was 2, the number of factors was 3), where all possible combinations of factors were implemented at the levels chosen for the study [2]. The coordinates of the center of the plan, the intervals of variation and the levels of research are shown in Table 2.

Table 2

Experimental Conditions

	z_1	z_2	z_3
Main level, z^o_j	90	0.75	1.5
Variation interval, Δz_j	30	0.25	0.5
+1	60	1	2
–1	120	0.5	1

Table 3 presents the plan of the extended planning matrix of the full factorial experiment 2^3 on a dimensionless scale.

Table 3

Expanded matrix of planning full factor experiment 2^3

Experience number	x_0	x_1	x_2	x_3	x_1x_2	x_1x_3	x_2x_3	$x_1x_2x_3$	Y_{exp}, $Pa{\cdot}s$
1	+1	–1	–1	–1	+1	+1	+1	–1	2.52
2	+1	+1	–1	–1	–1	–1	+1	+1	2.34
3	+1	–1	+1	–1	–1	+1	–1	+1	2.4
4	+1	+1	+1	–1	+1	–1	–1	–1	2.28
5	+1	–1	–1	+1	+1	–1	–1	+1	2.37
6	+1	+1	–1	+1	–1	–1	–1	–1	2.4
7	+1	–1	+1	+1	–1	–1	+1	–1	2.26
8	+1	+1	+1	+1	+1	+1	+1	+1	2.16

Using the plan presented in Table 3, the coefficients of the full linear regression equation were calculated:

$$\hat{y} = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{23}x_2x_3 + b_{123}x_1x_2x_3 \, . \quad (1)$$

Any coefficient of the regression equation b_j is determined by the scalar product of the column y on the corresponding column x_j divided by the number of experiments in the planning matrix N:

$$b_j = \frac{1}{N}\sum_{i=1}^{N} x_{ji} y_i \, . \quad (2)$$

In accordance with equation (2), the following coefficients of the regression equation were obtained: $b_0 = 18.9$; $b_1 = –0.44$; $b_2 = –0.34$; $b_3 = –0.36$; $b_{12} = –0.89$; $b_{13} = –4.6$; $b_{23} = –0.16$; $b_{123} = 0.04$.

To determine the dispersion of reproducibility ($s^2_{\text{reprod.}}$) and check the significance of the regression coefficients and the adequacy of the equation, three additional experiments were put in the center of the plan and the following values of y were obtained:

$$y_1^0 = 2.42; \quad y_2^0 = 2.3; \quad y_3^0 = 2.37;$$

$$\overline{y}^0 = \frac{\sum_{u=1}^{3} y_u^0}{3} = 2.36;$$

$$s^2_{\text{reprod.}} = \frac{\sum_{u=1}^{3}(y_u^0 - \overline{y}^0)^2}{2} = 0.0016; \quad s_{\text{reprod.}} = 0.04 \, .$$

The diagonal elements of the covariance matrix are equal to each other; therefore all the coefficients of equation (1) are determined with the same accuracy:

$$s_{b_j} = \frac{s_{\text{reprod.}}}{\sqrt{\text{N}}} \, . \quad (3)$$

According to the formula (3):

$$s_{b_j} = 0.04/\sqrt{8} = 0.014 \, .$$

The significance of the coefficients of the regression equations was estimated by the Student's criterion using the formula:

$$t_j = \frac{|b_j|}{s_{b_j}} \quad (4)$$

According to the formula (4) $t_0 = 1334.1$; $t_1 = 31.05$; $t_2 = 24$; $t_3 = 25.4$; $t_{12} = 62.8$; $t_{13} = 324.7$; $t_{23} = 11.3$; $t_{123} = 2.82$. The tabular value of the student's criterion for the significance level $p = 0.05$ and the number of degrees of freedom $f = 2$ $t_p(f) = 4.30$. Consequently, the coefficient b_{123} is insignificant and should be excluded from the regression equation (1), and the equation takes the form:

$$\hat{y} = 18.9 - 0.44x_1 - 0.34x_2 - 0.36x_3 - 0.89x_1x_2 - 4.6x_1x_3 - 0.16x_2x_3\,. \quad (5)$$

The adequacy of the obtained regression equation (5) experiment was tested by the Fisher criterion:

$$F = s^2_{\text{residual}} / s^2_{\text{reprod.}}\,;$$

$$s^2_{\text{residual}} = \frac{\sum_{i=1}^{8}(y_i - \hat{y}_i)^2}{N - l} = 0.0225\,,$$

where l is the number of significant coefficients in the regression equation, equal to 4. Then $F = 0.0225 / 0.0016 = 14.06$. The tabular value of the Fisher criterion for $p = 0.05$, $f_1 = 1$, $f_2 = 2$, $F_{1-p}(f_1, f_2) = 18.5$, i.e. $F < F_{1-p}(f_1, f_2)$.

Consequently, the resulting regression equation (5) adequately describes the experiment.

In accordance with Figure, we find that according to the obtained mathematical calculations, the optimal conditions for cavitation processing are the following: τ = 90–120 s, the amount of added catalyst is 0.7–1 g and the amount of added water is 1.5–2 ml.

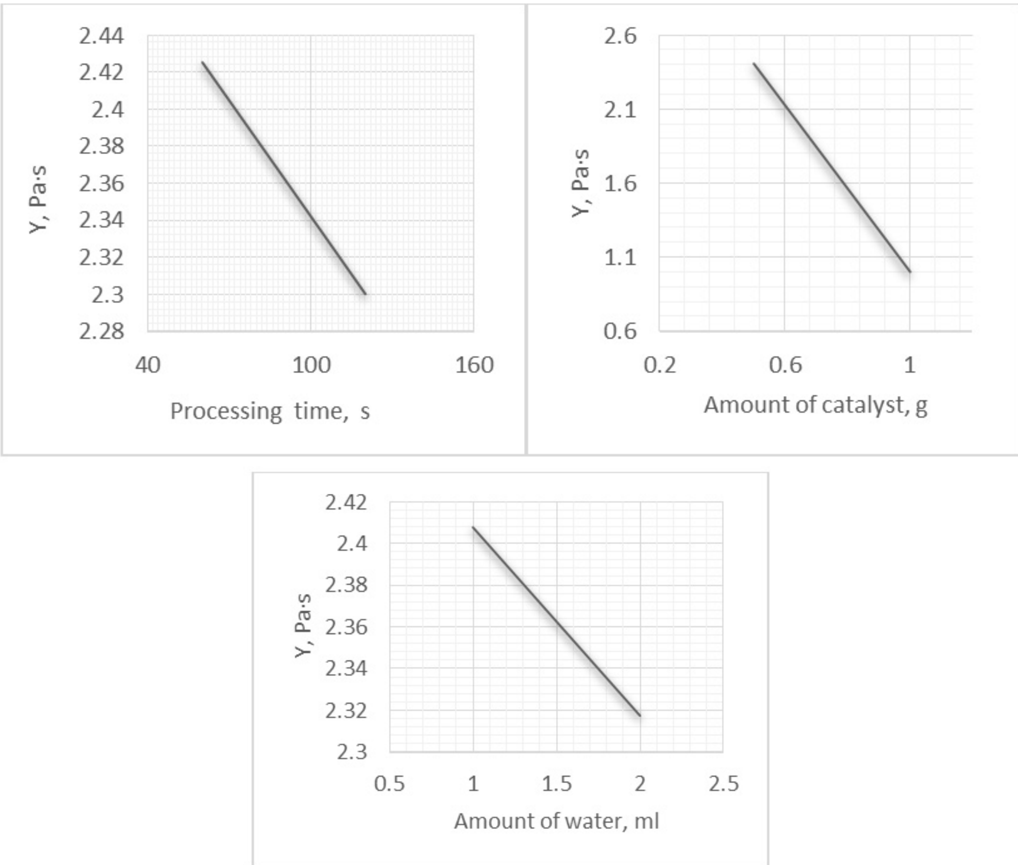

Figure. The influence of factors z_1, z_2, z_3 on the reduction of viscosity during cavitation processing of the middle fraction of oil (200–300 ºC)

Conclusions

Thus, optimal conditions and a number of factors affecting the cavitation treatment of the middle oil fraction (200–300 ºC) in the presence of a FeS_2 catalyst are determined. In accordance with the obtained regression equation, the optimal conditions for cavitation processing are the following: τ = 90–120 s, the amount of added catalyst is 0.7–1 g and the amount of water added is 1.5–2 ml.

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Мұнайдың орта фракциясын (200–300 ºС) каталитикалық-кавитациялық өңдеу процесін модельдеу

Экспериментті жоспарлау — бұл үрдіс механизмі туралы толық емес ақпарат арқылы экспериментті оңтайлы бақылау. Эксперименттік ғылымға деген қызығушылық эксперименталды зерттеулердің кең ауқымымен және тәжірибенің оңтайлы ұйымдастырылуынан айтарлықтай экономикалық әсерге байланысты. Оңтайлы эксперимент деп уақыт пен қаржыны үнемдеуді, нәтижелердің сенімділігін арттыруды айтады. Мұнай отындарына кавитациялық әсерді зерттеу үшін құмкөл мұнайының (200–300 ºС) орташа үлесі пайдаланылды. Келесі каталитикалық жүйелер қолданылды: модификацияланған FeS_2; ε-Fe_2O_3/SiO_2 нанокатализаторы; α-Fe_2O_3/SiO_2 сфералық катализаторы; β-FeOOH және $Fe(OA)_3$. Құмкөл мұнайының орта фракциясының (200–300ºС) жеке құрамын анықтау арқылы каталитикалық-кавитациялық өңдеудің көмірсутегі құрамына әсері анықталды. FeS_2 катализаторының қатысуымен мұнайдың орта фракциясын (200–300 ºС) кавитациялық өңдеуге әсер ететін оңтайлы жағдайлар мен бірқатар факторлар анықталды. Алынған регрессиялық теңдеуге сәйкес, кавитациялық өңдеудің оңтайлы шарттары мынадай: τ = 90–120 с, катализатордың мөлшері 0,7–1 г, ал қосылған судың мөлшері 1,5–2 мл.

Кілт сөздер: нанокаталитикалық жүйелер, кавитация үрдісі, құмкөл мұнайы, эксперименттік жоспарлау, орта фракция, темір (ІІІ) оксидтері, полиморфты модификациялар, көмірсутектік құрам.

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Моделирование процесса каталитическо-кавитационной обработки средней фракции нефти (200–300 ºС)

Планирование эксперимента — это оптимальное управление экспериментом в условиях неполной информации о механизме процесса. Интерес к науке об эксперименте связан с широкими масштабами экспериментальных исследований и значительным экономическим эффектом от оптимальной организации. Оптимальный эксперимент — это путь к экономии времени и средств, увеличению надежности и достоверности результатов. Для исследования кавитационного воздействия на нефтяные топлива была использована средняя фракция кумкольской нефти (200–300 ºС). В качестве каталитических систем были использованы: модифицированный FeS_2; нанокатализаторы ε-Fe_2O_3/SiO_2; α-Fe_2O_3/SiO_2 сферический катализатор; β-FeOOH и $Fe(OA)_3$. Путем количественного определения индивидуального состава средней фракции (200–300 ºС) кумкольской нефти была установлена общая закономерность влияния каталитическо-кавитационной обработки на углеводородный состав средней фракции (200–300 ºС) кумкольской нефти. Определены оптимальные условия и ряд факторов, влияющих на проведение кавитационной обработки средней фракции нефти (200–300 ºС) в присутствии катализатора FeS_2. В соответствии с полученным регресионным уравнением оптимальные условия для кавитационной обработки следующие: τ = 90–120 с, количество добавляемого катализатора 0,7–1 г и количество добавляемой воды 1,5–2 мл.

Ключевые слова: нанокаталитическая система, процесс кавитации, кумкольская нефть, экспериментальное планирование, средняя фракция, оксиды железа (III), полиморфные модификации, углеводородный состав.

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