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The factors influencing hydrogenation of a primary coal tar

Due to steady increase in prices for oil, the receiving of fuel and chemical products from coal and heavy oil gets the practical value that can be considered as one of the perspective directions in energetics and the petrochemical industry of the near future. Receiving liquid fuels from firm combustible minerals is reduced to destruction of molecules of initial raw materials, increase in the relative content of hydrogen, removal of oxygen, nitrogen, sulfur and cindery mineral substances. The method of planning the experiment with use of the composite plan of Boxing Wilson optimum conditions of carrying out process were determined, a hydrogenation of fraction of primary coal tar to 175 °C. It was established the influence of various factors, such as the process course temperature, reaction time, pressure of hydrogen and number of the added catalyst. The regression equation is calculated, the importance of the equation is estimated by parametrical criteria of statistics (Student and Fischer's criterion). It is defined that degree of a hydrogenation of fraction of primary coal tar from the end of boiling at 175 ºC rises with increase in temperature, duration and the maintenance of the added catalyst. It is established that the most optimum temperature of hydrogenation processes 420 °C, the initial pressure of hydrogen is 3,0 MPa and duration of carrying out process is 60 min.

Key words: hydrogenation, fraction of primary coal tar, temperature, hydrogen pressure, Nano catalyst.

A large number of experimental tasks in chemistry and chemical technology are formulated as extreme tasks: definition of optimum conditions of process, optimum structure of compositions, etc. Due to an optimum arrangement of points in factorial space and to linear transformation of coordinates, it is possible to overcome disadvantages of the classical regression analysis, in particular the correlation between coefficients of regression.

Planning of experiment allows varying all factors at the same time and allows receiving quantitative assessment of the main effects and the effects of interaction.

In works [1–3] the hydrogenation of model objects in the presence of the synthesized Nano dimensional catalysts on the basis of iron oxide is considered. It is established that the Nano catalyst Fe_3O_4 shows high activity and selectivity in comparison with other synthesized catalysts (β-FeOOH and Fe_2O_3) [4].

In the process of a hydrogenation of heavy hydro carbonic raw materials the main objective is an increase in an exit of liquid products due to transition of hydrogen to reactionary mix [5]. Various solvents, fractions of coal tar, oil products, high-viscosity oil and its fractions can act as the donor of hydrogen. Thermodynamic calculations allow establishing optimum degree of a saturation of donors molecules by hydrogen [6].

Experimental

Studying the process of a hydrogenation of high-molecular substances with their transformation in low-molecular [7] shows that this process depends on a number of factors including the main ones: pressure, temperature, heating duration at an experience temperature, the speed of heating and catalysts.

In this work the method of planning of multiple-factor experiments is applied to definition of optimum conditions of a hydrogenation of fraction of primary coal tar in the presence of the Nano catalyst [8]. During planning complete factorial experiment all possible combinations of factors are realizes at all chosen levels. The necessary number of N experiences is determined by a formula:

$$N = 2^k + 2k + n,$$

where n — number of levels; k — number of factors.

As factors on which depends, process of a hydrogenation of fraction of the primary coal tar (PCT), the following ones are chosen: z_1 — temperature,°C; z_2 — duration of hydrogenation process, min.; z_3 — number of the catalyst added to PCT fraction, %; z_4 — the initial pressure of hydrogen, MPa.

Results and discussion

Because the analysis of parametrical sensitivity of process was an objective in this research, the orthogonal plan of the second order was chosen as the plan of experiment, providing equality to zero all covariance's between coefficients in the regression equation. Coordinates of the center plan, intervals of a variation and levels of research are specified in Table 1.

Table 1

Levels of the studied factors

	Z_1	Z_2	Z_3	Z_4
Zj^0	400	50	0,2	1,5
ΔZj	20	10	0,1	0,5
1	420	60	0,3	2,0
–1	380	40	0,1	1,0
1,61	440	70	0,35	2,5
–1,61	360	30	0,05	0,5

The orthogonal plan of a matrix of the experiment is presented in Table 2.

Table 2

The plan of the matrix experiment fraction of PCT hydrogenation

№ experience	x_0	x_1	x_2	x_3	x_4	y
1	1	–1	–1	–1	–1	78,50
2	1	–1	0	0	0	77,00
3	1	–1	1	1	1	74,95
4	1	0	–1	0	1	79,60
5	1	0	0	1	–1	61,40
6	1	0	1	–1	0	69,40
7	1	1	–1	–1	1	77,30
8	1	1	0	0	–1	78,35
9	1	1	1	1	0	79,05
10	1	–1	–1	1	–1	73,75
11	1	–1	0	–1	0	77,10
12	1	–1	1	0	1	84,25
13	1	0	–1	1	0	76,55
14	1	0	0	–1	1	79,80
15	1	0	1	0	–1	82,60
16	1	1	–1	0	0	87,00
17	1	1	0	1	1	71,55
18	1	1	1	–1	–1	77,85
19	1	–1	1	–1	–1	73,75
20	1	1,61	0	0	0	91,03
21	1	–1,61	0	0	0	63,31
22	1	0	1,61	0	0	79,65
23	1	0	–1,61	0	0	51,73
24	1	0	0	1,61	0	90,78
25	1	0	0	–1,61	0	52,57
26	1	0	0	0	1,61	69,40
27	1	0	0	0	–1,61	61,40

Where y — extent of the extraction of liquid products, %.
Plan parameters: k — 4; n_0 — 3; α — 1,61; number of levels N — 27.

Thanks to orthogonality of a matrix the planning all regression coefficients are determined independently from each other by a formula:

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

According to the results of experiments regression coefficients and their error are calculated:

b_0 = 75,02	b_1 = 2,05	b_2 = 4,07
b_3 = –4,14	b_4 = –1,65	b_{11} = 47,86
b_{12} = –3,15	b_{13} = –5,05	b_{14} = 2,12
b_{21} = –3,15	b_{22} = 43,79	b_{23} = –2,19
b_{24} = –2,84	b_{31} = –0,18	b_{32} = –2,20
b_{33} = 45,82	b_{34} = 3,01	b_{41} = 2,12
b_{42} = –2,84	b_{43} = 3,01	b_{44} = 43,00
b_{1234} = –0,01		

The significance of the equation coefficients regression is estimated by Student's test according to the formula:

$$t_j = |b_j| / s_{b_j}.$$

Where b_j — regression equation coefficient; s_{b_j} — average square deviation the *j* of coefficient.

t_0 = 167,66	t_1 = 4,58	t_2 = 9,09
t_3 = –9,25	t_4 = –3,66	t_{11} = 106,96
t_{12} = –7,04	t_{13} = –11,29	t_{14} = 4,74
t_{21} = –7,04	t_{22} = 97,86	t_{23} = –4,89
t_{24} = –6,35	t_{31} = –4,04	t_{32} = –4,92
t_{33} = 102,4	t_{34} = 6,73	t_{41} = 4,74
t_{42} = –6,35	t_{43} = 6,73	t_{44} = 96,1
t_{1234} = –0,02		

Tabular criterion value of Student for the importance equation p = 0,05 and numbers of degrees freedom of $f = n_0 - 1 = 2$; $t_p(f) = 4{,}3$.

Thus, the coefficients b_3, b_4, b_{12}, b_{13}, b_{21}, b_{23}, b_{24}, b_{31}, b_{32}, b_{42}, b_{1234} aren't significant and they should be excluded from the regression equation. After an exclusion of insignificant coefficients the equation of regression is:

$$\hat{y} = 75{,}02 + 2{,}05x_1 + 4{,}07x_2 + 2{,}12x_1x_4 + 3{,}01x_3x_4 + 2{,}12x_4x_1 + 3{,}01x_4x_3.$$

In order to check the importance of coefficients of regression and adequacy of the equation parallel experiences were conducted in addition. Dispersion of reproducibility is counted by three experiences in the center of the plan:

$$\hat{y}^0 = \frac{\sum_{u=1}^{3} y_u^0}{3} = 81{,}33,$$

where y_1 = 79,8 %;
y_2 = 81 %;
y_3 = 83,2 %;
y_u = 244 %.

The checking of adequacy of the received equation was carried out by Fischer's criterion:

$$F = \frac{s_{ост}^2}{s_{воспр}^2}.$$

Dependences of influence of various factors (process temperature, duration of hydrogenation process, number of the catalyst added to PCT fraction and the initial pressure of hydrogen) upon process of a hydro up classing of PCT fraction are presented in Figures 1–4.

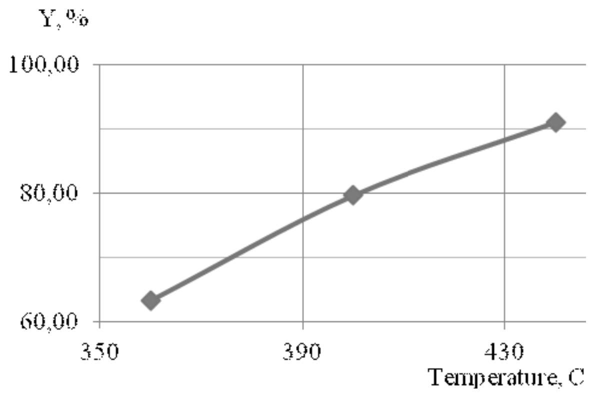

Figure 1. Influence of the temperature on degree of a hydrogenation of PCT fraction

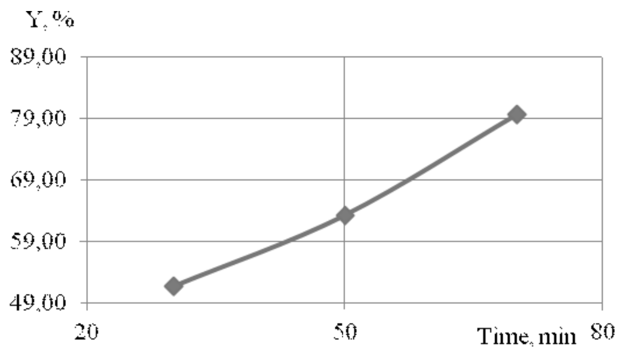

Figure 2. Influence of duration the interaction on degree of the hydrogenation of PCT fraction

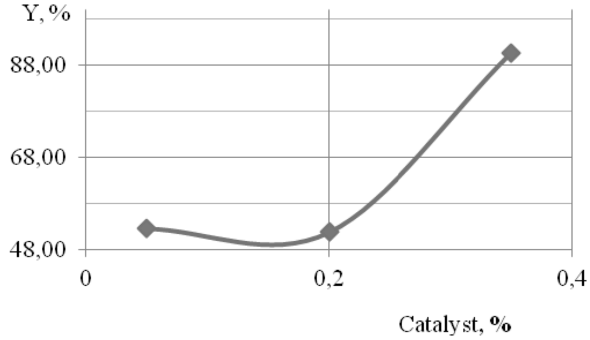

Figure 3. Influence of the maintenance the catalyst on degree of a hydrogenation the PCT fraction

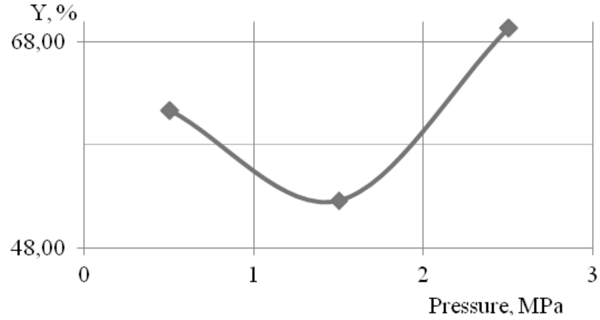

Figure 4. The effect of the hydrogen pressure on the degree of hydrogenation fraction PCT

These equations are adequate to experiment $F_{(calc)} = 6{,}55$. Tabulated values of Fisher criterion $F_{(tab)} = 19{,}45$ significance level $f_1 = 24$, $f_2 = 2$. Therefore, the resulting regression equation adequately describes the experiment.

The analysis of parametric sensitivity of the regression equation is shown in Figure 4. Calculations are made for the center of the plan. The degree of hydrogenation of fraction PCT increases with increasing temperature, length and content of the added catalyst (Fig. 1–3).

Thus, the hydrogenation of PCT fraction in the presence of the Fe_3O_4 Nano catalyst is carried out. Influence of such factors as the process temperature, process duration, number of the added Nano catalyst, and also initial pressure of hydrogen are analyzed. The optimal conditions for the hydrogenation process are established. The optimum conditions for the hydrogenation process PKS fractions are 420 ºC temperature, 60 minutes duration, the amount of catalyst added is from 0,1 to 0,5 % and an initial hydrogen pressure of 3 MPa.

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Біріншілік тас көмір шайырының гидрогенизациясына факторлардың әсері

Мұнай бағаларының үздіксіз жоғарлауы көмір мен ауыр мұнайдан отын және химиялық белгілеуіндегі өнімдерді алу тәжірибелі маңызды болады, бұл жақын болашақтағы энергетика мен мұнай химия өнеркәсіптеріндегі келешегі бар бағыттардың бірі ретінде қарастырылды. Қатты жанатын қазбалардан сұйық отындарды алу бастапқы өнімнің молекулалардың бөлінуіне, сутегі көлемінің біршама жоғарлауына, оттегіні, азотты, күкіртті және күлді минералды заттарды кетіруге әсер етеді. Бокс-Уилсон композиционды жоспарын пайдалана отырып, көп факторлы тәжірибені жобалау әдісімен нанокатализатор қатысында біріншілік тас көмір шайырының гидрогенизациясының тиімді жағдайлары анықталды. Бастапқы сутегі қысымы, қосылатын нанокатализатор көлемі, температура мен үрдіс уақыты сияқты факторлардың әсері зерттелді. Статистиканың параметрлік белгілері арқылы (Стьюдент және Фишер белгілері) регрессия теңдігі есептелініп, мәнділігі анықталды. 175 ºС дейінгі біріншілік тас көмір шайырының фракциясының гидрлеу дәрежесі температураның өсуімен, үрдістің уақытының жоғарлауымен, қосылатын катализатор мөлшерінен өсетіні анықталды. Ең тиімді жағдай ретінде температура 420 ºС, бастапқы сутегі қысымы 3,0 МПа және үрдіс уақыты 60 мин болатыны белгіленді.

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Факторы, влияющие на гидрогенизацию первичной каменноугольной смолы

В связи с неуклонным ростом цен на нефть практическое значение приобретает получение продуктов топливного и химического назначения из угля и тяжелой нефти, что может рассматриваться как одно из перспективных направлений в энергетике и нефтехимической промышленности ближайшего будущего. Получение жидких топлив из твердых горючих ископаемых сводится к разрушению молекул исходного сырья, увеличению относительного содержания водорода, удалению кислорода, азота, серы и зольных минеральных веществ. Методом планирования эксперимента с использованием композиционного плана Бокса-Уилсона были определены оптимальные условия проведения процесса гидрогенизации фракции первичной каменноугольной смолы до 175 ºС. Установлено влияние различных факторов, таких как температура протекания процесса, время протекания реакции, давление водорода и количество добавляемого катализатора. Рассчитано уравнение регрессии, значимость уравнения оценена параметрическими критериями статистики (критерий Стьюдента и Фишера). Определено, что степень гидрогенизации фракции первичной каменноугольной смолы с концом кипения 175 ºС возрастает с увеличением температуры, продолжительности и содержания добавляемого катализатора. Установлено, что наиболее оптимальная температура протекания процесса гидрогенизации составляет 420 ºС, начальное давление водорода 3,0 МПа и продолжительность проведения процесса 60 мин.