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Determining the optimal conditions for the catalytic hydrogenation of a mixture of Tian Shan coal and a wide fraction of heavy oil residues with an end-boiling point of 300°C

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Abstract. The shortage of natural resources in the power industry combined with their increasing usage, price, and negative impact on the environment necessitates the search for new techniques of producing liquid fuel. One such possibility is the production of fuel and chemical products from coal via hydrogenation. The transformation of coal into liquid fuel is a complex technical process that requires saturating the initial substance with oxygen. Therefore, the purpose of this study is to determine the optimal conditions for the catalytic hydrogenation of a mixture of coal, Primary Coal Tar (PCT), and heavy oil residues with an end-boiling point of 300°C. The results show the optimal conditions for producing liquid fuel. The proposed technique allows achieving complete homogenization of all components and producing a highly stable coal paste. This technique also allows significantly reducing the negative impact on the environment.

1. Introduction

Coal is usually hydrogenated over a catalyst under hydrogen pressure in a medium of paste-formers with hydrogen-donor properties at elevated temperatures. There are a number of methods for coal hydrogenation [1] over powdered iron ore as a catalyst or over an iron-containing waste from ore processing activated by sulfur additives or sulfur-containing compounds [2]. Of particular interest is the development of nano-textured catalysts [3,4]. The coal conversion increases when the catalysts and sulfur are co-processed in energy-intensive mills. The disadvantage of the above methods is the increased sulfur content of the resultant distillate fractions. A method similar to the introduced approach implies coal hydrogenation, whose process includes the preparation of carbon-oil paste from coal, a paste-former, and an iron-containing catalyst subjected to mechanical and chemical treatment with sulfur, paste heating under elevated pressure in a hydrogen medium, followed by the isolation of desired products. The high-boiling fraction of carbon hydrogenation product was used as a paste-former after thermal cracking in a water vapor medium on iron oxides at a temperature of 450-500°C, followed by mixing the paste-former with the catalyst before preparing the carbon-oil paste [5]. The disadvantage of this method is the low quality of target products, caused by the increased sulfur content in the

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distillate fractions. Hydrogenated products cannot be used as components of motor fuels without additional hydrotreatment. Besides, this method has another drawback-duration and insufficient degree of catalyst dispersion in the viscous paste-former by mechanical stirring.

Our goal is to improve the quality of distillate fractions of liquid coal hydrogenation products by reducing the sulfur content without reducing the output.

Due to the increasing need for petroleum products and the cost of extraction and transportation of oil and environmental measures, the search for new approaches to the production of various liquid fuels remains relevant [6,7]. Synthetic oil is produced by direct hydrogenation of solid and heavy hydrocarbon feedstock [8-10].

Therefore, in addition to developing the theory and technology of hydrogenation of solid hydrocarbon feedstock and heavy oil residues, it is crucial to determine the principles for managing this process [11-13]. During coal hydrogenation, carbon radicals are stabilized by hydrogen donors, whose hydrogenating properties are restored via their hydrogenation and whose activation can take place on the catalyst [11,14,15].

The purpose of this study is to determine the optimal conditions for the catalytic hydrogenation of a mixture of Tian Shan coal and a wide fraction of heavy oil residues with an end-boiling point of 300°C.

The study examines the hydrogenation of Tian Shan coal in the presence of a standard hydrogen donor (paste former)-tetralin and a catalytic additive-iron oxide with elemental sulfur.

2. Experimental

One of the solutions to the technological problem of solid and heavy hydrocarbon feedstock is to determine the optimal conditions for this process: the optimal paste former to feedstock ratio, temperature, initial hydrogen pressure, amount of added catalyst, and exposure time. Hydrogenation is a multi-step process that includes the hydrogenation of the initial feedstock and its subsequent cracking under the effect of hydrogen.

A set of complementary research methods was used to achieve the set goal, including analysis, analytical and numerical computations, and generalization of Kazakh and foreign experience on the subject at hand.

The experiments were carried out in an autoclave. Experiments on the PCT-and-coal mixture hydrogenation were carried out in a high-pressure reactor with an internal mixer (autoclave) of 0.5-liter capacity.

The pre-mixed starting materials were placed in an autoclave. Then, it was closed and purged with hydrogen under elevated pressure. The autoclave was heated to the required temperature and kept like that for a predetermined time. The rate of autoclave heating was 10°C/min. After that, it was cooled to room temperature. The autoclave was opened 24 hours later. The hydrogenation products were carefully washed with benzol.

The application of a standard hydrogen donor (tetralin) for large-scale production of synthetic fuel from alternative sources (coal, peat, slate, heavy oil residues and their fraction, etc.) is unprofitable [16-18]. Therefore, a wide fraction of heavy oil residues with an end-boiling point of 300°C was chosen as the hydrogen donor (paste former). The choice was made based on the studies [11-15], implying that this fraction could be potentially used as a hydrogen donor (paste former) for Tian Shan coal (well no. 3). The β-FeOOH synthesized nano-catalyst was used as the catalyst [6].

3. Results and discussion

The effects of various factors on the hydrogenation output (fraction up to 300°C) during the hydrogenation of a mixture of Tian Shan coal and a wide fraction of heavy oil residues with an end-boiling point of 300°C were determined by factor planning of the experiment [19-21].

To that end, four main factors that affect such an output (fraction up to 300°C) during the hydrogenation of a mixture of Tian Shan coal and a wide fraction of heavy oil residues with an end-boiling point of 300°C were studied.

Table 1 shows the levels of the factors under consideration and variation levels. The number of factors is $k = 4$; the number of levels is $n = 2$.

Table 1. Levels of studied factors.

Factors	**Levels**	
	1 minimum	**2 maximum**
A - Temperature (°C)	400	450
B - Process duration (min)	60	120
C - Amount of catalyst added to coal (%)	0,5	2
D - Hydrogen donor (paste former) to coal mass ratio	1.5:1	3:1

Table 2. Plan of matrix L_8 (2) for the experiment of hydrogenation of a mixture of coal and a wide fraction of heavy oil residues with t_b 300°C.

Experiment number	***A***	***B***		***C***			***D***	$\boldsymbol{Y_E}$ **(%)**^{a}
	1	**2**	**3**	**4**	**5**	**6**	**7**	
1	1	1	1	1	1	1	1	24.2
2	1	1	1	2	2	2	2	33.4
3	1	2	2	1	1	2	2	27.5
4	1	2	2	2	2	1	1	32.1
5	2	1	2	1	2	1	2	29.3
6	2	1	2	2	1	2	1	34.0
7	2	2	1	1	2	2	1	21.4
8	2	2	1	2	1	1	2	26.5
I_f	117.2	120.9		102.4			111.7	
II_f	228.4	107.5		126			116.7	
$\text{I}_m = \text{I}_f/4$	29.3	30.2		25.6			27.9	
$\text{II}_m = \text{II}_f/4$	57.1	26.9		31.5			29.2	
I_m-II_m	-27.8	3.3		-4.9			-1.3	

$^a Y_E$ (%) is the output of the fraction up to 300°C; A, B, C, and D are factors that affect the hydrogenation of a mixture of Tian Shan coal and a wide fraction of heavy oil residues with an end-boiling point of 300°C.

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

Equations used to determine the effect of factors A, B, C, and D on the output of the fraction up to 300°C during the hydrogenation of coal and a wide fraction of heavy oilresidues with an end-boiling point of 300°C are presented below:

$$Am_1 = 1/4\left(Y_{E1} + Y_{E2} + Y_{E3} + Y_{E4}\right) = 29.3, \quad (1)$$

$$Am_2 = 1/4\left(Y_{E5} + Y_{E6} + Y_{E7} + Y_{E8}\right) = 27.8, \quad (2)$$

$$Am_1 - Am_2 = 29.3 - 27.5 = 1.5 > 0, \quad (3)$$

$$Bm_1 = 1/4\left(Y_{E1} + Y_{E2} + Y_{E5} + Y_{E6}\right) = 30.2, \quad (4)$$

$$Bm_2 = 1/4\left(Y_{E3} + Y_{E4} + Y_{E7} + Y_{E8}\right) = 26.9, \quad (5)$$

$$Bm_1 - Bm_2 = 30.2 - 26.9 = 3.3 > 0, \quad (6)$$

$$Cm_1 = 1/4\left(Y_{E1} + Y_{E3} + Y_{E5} + Y_{E7}\right) = 25.6, \quad (7)$$

$$Cm_2 = 1/4\left(Y_{E2} + Y_{E4} + Y_{E6} + Y_{E8}\right) = 31.5, \quad (8)$$

$$Cm_1 - Cm_2 = 25.6 - 31.5 = -5.9 < 0, \quad (9)$$

$$Dm_1 = 1/4\left(Y_{E1} + Y_{E4} + Y_{E6} + Y_{E7}\right) = 28.1, \quad (10)$$

$$Dm_2 = 1/4\left(Y_{E2} + Y_{E3} + Y_{E5} + Y_{E8}\right) = 29.2, \quad (11)$$

$$Dm_1 - Dm_2 = 28.1 - 29.2 = -1.1 < 0. \quad (12)$$

Eqs. (1), (2), (4), (5), (7), (10), and (11) were used to determine the effect of factors A, B, C, and D on the output of the fraction up to 300°C during the hydrogenation of coal and a wide fraction of heavy oil residues with an end-boiling point of 300°C.

Based on Table 1, according to the obtained mathematical calculations, the optimal hydrogenation conditions are presented as follows: $T = 400 - 420$°C, $\tau = 60 - 90$ minutes, the amounts of a catalyst added to coal is 0.5-1%, and hydrogen donor to coal ratio is 2:1.

By using the matrix plan, it is possible to assess the mutual effect of the factors on the hydrogenation of the mixture of coal and a wide fraction of heavy oil residuals with an end-boiling point of 300°C.

The mutual effect of factors $A \times B$, $A \times C$, and $B \times C$ on the output of hydrogenation (fraction up to 300°C) is presented in Table 3.

The mutual effect of factors was calculated based on the following formulas:

$$A \times B = 1/4\left(Y_{E1} + Y_{E2} + Y_{E7} + Y_{E8}\right) - 1/4\left(Y_{E3} + Y_{E4} + Y_{E5} + Y_{E6}\right) = -4.3, \quad (13)$$

$$A \times C = 1/4\left(Y_{E1} + Y_{E3} + Y_{E6} + Y_{E8}\right) - 1/4\left(Y_{E2} + Y_{E4} + Y_{E5} + Y_{E7}\right) = 1.5, \quad (14)$$

$$B \times C = 1/4\left(Y_{E1} + Y_{E4} + Y_{E5} + Y_{E8}\right) - 1/4\left(Y_{E2} + Y_{E3} + Y_{E6} + Y_{E7}\right) - 1.2. \quad (15)$$

Table 3. Mutual effect of factors $A \times B$, $A \times C$, and $B \times C$ on the output of hydrogenation (fraction up to 300°C).

Factors	A	B	$A \times B$	C	$A \times C$	$B \times C$	D
	1	**2**	**3**	**4**	**5**	**6**	**7**
I_f	117.2	–	–	–	–	–	–
–	–	120.9	–	102.4	–	–	111.7
II_f	228.4	–	–	–	–	–	116.7
–	–	107.5	–	–	–	–	–
1/4 (I_f-II_f)	-27.8	3.35	-4.3	-5.9	1.5	-1.1	-1.25

By using the data shown in Table 3, it is possible to determine a series of factors that affect the output of the hydrogenation:

$$B > D > C > A.$$

The results of mathematical planning and the effect on the output of the fraction up to 300°C obtained during the hydrogenation of a mixture of coal and a wide fraction of heavy oil residuals with an end-boiling point of 300°C showed that the dominating factors were the duration of the process, the hydrogen donor (paste former) to coal mass ratio, and the amount of catalyst added to coal. Based on the determined series of factors, the following ones were chosen as factors on which the output of the fraction up to 300°C depended:

- z_1-process duration (60-120 minutes);
- z_2-amount of catalyst added to coal (0.5-2%);
- z_3-hydrogen donor (paste former) to coal mass ratio (1.5:1-3:1).

In order to derive the linear regression equation, an extended planning matrix of a full factor experiment of the 2^3 type was used (the number of levels was 2, while the number of factors was 3), which realized all the possible combinations of factors on the levels chosen in this study [20].

Table 4 shows the plan of the 2^3 extended planning matrix of a full factor experiment on a dimensionless scale.

The plan presented in Table 4 was used to calculate the coefficients of the full linear regression equation:

$$\hat{y} = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{23}x_2x_3 + b_{123}x_1x_2x_3. \tag{16}$$

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

$$b_j = \frac{1}{N}\sum_{i-1}^{N} x_{ji}y_i. \tag{17}$$

In accordance with Eq. (16), the following coefficients of the regression equation were obtained: $b_0 = 28.55$; $b_1 = 2.95$; $b_2 = -1.68$; $b_3 = -0.75$; $b_{12} = -0.53$; $b_{13} = -0.50$; $b_{23} = -2.18$; and $b_{123} = 0.63$.

Three additional experiments were conducted at the center of the plan to determine the error mean square (s_m^2) of the regression coefficient significance check and equation adequacy; the following values of y were obtained:

$$y_1^0 = 32.1, \qquad y_2^0 = 33.1, \qquad y_3^0 = 32.8, \tag{18}$$

$$y^0 = \frac{\sum_{u=1}^{3} y_u^0}{3} = 32.7, \tag{19}$$

Table 4. 2^3 extended planning matrix of a full factor experiment.

Experiment number	x_0	x_1	x_2	x_3	x_1x_2	x_1x_3	x_2x_3	$x_1x_2x_3$	y_{exp} (%)[a]
1	+1	−1	−1	−1	+1	+1	+1	−1	24.2
2	+1	+1	−1	−1	−1	−1	+1	+1	33.4
3	+1	−1	+1	−1	−1	+1	−1	+1	27.5
4	+1	+1	+1	−1	+1	−1	−1	−1	32.1
5	+1	−1	−1	+1	+1	−1	−1	+1	29.3
6	+1	+1	−1	+1	−1	−1	−1	−1	34.0
7	+1	−1	+1	+1	−1	−1	+1	−1	21.4
8	+1	+1	+1	+1	+1	+1	+1	+1	26.5

[a] y_{exp} (%) is the output of the fraction up to 300°C.

$$s_m^2 = \frac{\sum\limits_{u=1}^{3} \left(y_u^0 - \bar{y}^0\right)^2}{2} - 0.27, \tag{20}$$

$$s_m = 0.52. \tag{21}$$

The diagonal elements of the covariance matrix are equal, which is why all coefficients of Eq. (16) are found with identical accuracy:

$$s_{b_j} = \frac{s_m}{\sqrt{N}}. \tag{22}$$

According to Eq. (17):

$$s_{b_j} = \frac{0.52}{\sqrt{8}} = 0.2. \tag{23}$$

The significance of the regression equation coefficients was assessed using Student's t-test according to the following formula [6]:

$$t_j = \frac{|b_j|}{s_{b_j}}. \tag{24}$$

According to Eq. (18), $t_0 = 142.75$; $t_j = 14.75$; $t_2 = 8.4$; $t_3 = 3.75$; $t_{12} = 2.65$; $t_{13} = 2.5$; $t_{23} = 10.9$; and $t_{123} = 3.15$.

The reference value of Student's t-test for the significance level is $p = 0.05$, while the numbers of degrees of freedom are $f = 2t_p(f) = 4.30$. Hence, coefficients b_3, b_{12}, b_{13}, and b_{123} are insignificant and should be removed from regression equation (Eq. (16)), after which the equation will be as follows:

$$\hat{y} = b_0 + b_1x_1 + b_2x_2 + b_{23}x_2x_3. \tag{25}$$

The adequacy of the obtained regression equation (Eq. (19)) for the experiment was verified using Fisher's exact test [20]:

$$F = s_r^2/s_m^2, \tag{26}$$

$$s_r^2 = \frac{\sum\limits_{i=2}^{8} \left(y_i - \hat{y}_i\right)^2}{N-1} = 2.96, \tag{27}$$

where i is the number of significant coefficients in the regression equation, which is 4. Then, $F = 2.96/0.27 = 10.96$. The reference value of Student's t-test for the significance level is:

$$p = 0.05, \qquad f_1 = 4, \qquad f_2 = 2,$$

$$F_{1-p}(f_1, f_2) = 19.3, \quad \text{i.e.,} \quad F < F_{1-p}(f_1, f_2). \tag{28}$$

Thus, the obtained regression equation (Eq. (26)) describes the experiment adequately.

4. Conclusion

This study determined the optimal conditions for the catalytic-cavity treatment of heavy oil residuals in the presence of an FeOOH heterogenic catalyst:

- Temperature: −40 - 45°C;
- Amount of added water: −11-12 volume%;
- Emulsion droplet radius: −2.0-2.5 μm;
- Amount of added catalyst: −3.0-3.5 volume%;
- Treatment duration: −3.0-4.0 minutes.

It was shown that the treatment of a mixture of oil and a fraction of heavy oil residues with an end-boiling temperature of 300°C in a cavitator allowed achieving complete homogenization of both components of the mixture and producing a highly stable coal paste.

Thus, factorial experiment revealed the main factors that affect the output of liquid products. Thus, the optimal conditions for the hydrogenation of Tien-Shan coal mixture and a wide fraction with the end-boiling temperature point of up to 300°C were established. Moreover, the regression equation coefficients were calculated.

With the ever-increasing price of oil production and the existence of vast reserves of coal, our study offering a relatively new source of liquid motor fuels will obviously be able to alleviate the pressure on the oil industry and mitigate price fluctuations and market volatility, thereby contributing to the common good of humankind.

The resultant product can potentially serve as a raw material for motor fuels and is characterized by low-content sulfur and other harmful components.

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