Catalytic processing of distillate fractions of a resin in the presence of finely dispersed catalysts

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Abstract. The article describes the catalytic cracking of heavy oil residue in the presence of a finely dispersed catalyst. It was determined that in the processing of high molecular weight hydrocarbons, catalysts are effective, which are uniformly distributed in the volume of raw materials and are introduced into the technological process in the form of small particles. Coke tar mainly consists of 27.00 wt.% asphaltenes, 60.00 wt.% of polyaromatic hydrocarbons that have been studied and identified as a potential source of raw materials to produce motor fuels in the future.

1 Introduction

The increased demand for motor fuels requires further development of deep processing of high molecular weight petroleum feedstock, as well as solid combustible minerals (coal, shale, peat). Coal (coking) tar, consisting mainly of condensed aromatic hydrocarbons and other high-molecular compounds refers to hard-processed raw materials. In industry, the tar is subjected to dehydration and distillation into separate fractions, from which benzene, naphthalene, phenols, pyridine bases and other chemical products are obtained by the methods of alkaline and acid extraction, crystallization, hydro-treatment. At present, the increasing requirements for product quality require the improvement of technological schemes, as well as methods of processing high molecular weight raw materials.

Saryarka Spetskoks LLP uses Chinese technology to produce 30 thousand tons of resin and 300 thousand tons of special coke per year during coal processing. This resin is not currently undergoing any processing. The process of partial coking of coal is carried out at a temperature of 500-550 °C. The volatiles generated in the process do not pass completely through the zone heated by the furnace to a temperature of 700-750 °C, and are less susceptible to secondary high-temperature pyrolysis. Therefore, the quality of the resin released in the process matches the quality of the primary resin. Therefore, the object of the study was a coke-chemical tar obtained by semicoking coal from the Shubarkol deposit [1].

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2 Experimental

The process of cracking the distillate products obtained by hydrogenating the resin to 320°C is carried out at a much lower temperature of 400-450 °C compared to the high temperature of 550-560°C, which is produced by industrial enterprises at a pressure of 3.0 MPa. Dispersion of raw materials with a mass of Na_2SiO_3 catalyst is carried out in a disperser with a rotation speed of 1800 rpm. The experiments were carried out in a high-pressure laboratory setup with a 0.25 dm^3 hollow reactor and a stirring device. A mixture of resin with a catalyst and sulfur addition, heated to 70–80 °C, was loaded into a reactor, which was preliminarily purged with argon and filled with hydrogen at an initial pressure of 2–3 MPa. The heating of the reactor was switched on, and upon reaching 150 °C, the stirring device. The temperature was measured with a thermocouple and automatically maintained with an accuracy of ± 2 °C. The working pressure of hydrogen was 5.0 MPa, the temperature was 350–450 °C, and the reaction time was 15 min. A hydrogen pressure of 5.0 MPa was selected as effective on the basis of experimental data [2] and the results obtained in [3].

In the course of the study, a fraction boiling at temperatures above 350 °C, obtained at a vacuum distillation unit at the PetroKazakhstan Products refinery, was used as a hydrogen donor-pasteurizer.

3 Results and discussion

Were determined the physicochemical properties of coke tar for further production of motor fuels (Table 1).

Table 1. Physical and chemical properties of coke tar

Indicator name	Indicator
1	2
Mass fraction of water, %	3.420
Density at 20°C, kg/m^3	1.085
Mass fraction of insoluble substances in toluene, %	1.310
Mass fraction of insoluble substances in quinoline, %	0.210
Ash content	0.110
Fractional distillation:	
Initial boiling point, °C	130
Up to 180 ° C	2.610
180-230°C	11.25
230-280°C	8.17
280-330°C	10.55
Above 330 ° C + residue	68.12
Elemental composition, wt. %:	
C	91.90
H	5.65
S	0.47
N	0.78
O	1.62
Analysis of pitch after resin distillation:	
Softening temperature, °C	68.10
Volatile matter yield,%	83.05
Ash content, %	0.215

1	2
Mass fraction of insoluble substances in toluene, %	11.35
Mass fraction of insoluble substances in quinoline,%	0.32
Mass fraction of phenols, %	18.31
Mass fraction of naphthalene, %	0.44
Flash point, °C	121.05
Calorific value, kcal/kg	8385
Conditional viscosity at 80°C, °VC	1.67
Coke,%	2.30-3.45
Mass fraction of sulfur, %	0.055
Resins, acphaltenes, %	27.05
Polyaromatic hydrocarbons,%	60.10
Correlation index	108-128
Boiling point, °C	112-122
Mass fraction of ions Na^-, %	0.015-0.025
Mass fraction of ions K^-, %	0.030-0.040
Melting point, °C	20.10

The influence of the weight and temperature of the catalyst on the process was studied in order to reduce the operating pressure of the hydrotreating process and to determine the optimal conditions for the cracking of coke distillate products (Table 2).

Table 2. Results of cracking of distillate resin fractions in the presence of $Na_2SiO_3 \cdot 10H_2O$ catalyst

Catalyst	T, °C	The yield of liquid products, wt.%			∑L.P.	Gas output, wt.%	Resid ue, wt.%	Loss, wt.%
		Up to 180 °C	180-250 °C	250-320 °C				
Without cat.	400	9.8	8.6	15.7	34.3	17.9	27.7	14.0
	420	6.3	10.5	17.2	33.9	22,9	35,0	8.2
	450	9.3	14.3	34.0	57.6	13.9	15.1	13.4
1.0 wt.% Na_2SiO_3 10H2O	400	12.6	17.3	18.6	48.5	27.7	18.1	5.8
	420	11.3	18.4	20.8	50.5	24.5	17.4	7.6
	450	13.7	24.0	20.7	58.4	17.3	10.9	13.4
2.0 wt.% Na_2SiO_3 $10H_2O$	400	14.6	25.3	20.6	60.5	10.7	19.1	9.7
	420	13.3	26.4	25.8	65.5	14.5	10.0	9.8
	450	15.7	34.0	26.7	68.4	12.3	8.0	11.3
3.0 wt.% Na_2SiO_3 $10H_2O$	450	14.6	28.3	23.6	66.5	7.7	16.1	9.7
	450	13.7	34.0	20.7	68.4	7.3	11.9	12.4
	450	17.3	30.4	30.8	78.5	4.5	9.1	7.9

As can be seen from the table, during the process at a temperature of 450°C and an increase in the amount of the catalyst $Na_2SiO_3 \cdot 10H_2O$ from 1.0 wt. % up to 2.0 wt. % the yield of liquid products in comparison with those obtained without catalyst increases from 57.60 wt. % up to 60.50 wt. %, including gasoline fraction from 9.30 wt. % increased by 15.70 wt.%. At the same temperature, with an increase in the amount of catalyst by 1.0 wt. %, the yield of the liquid products from 68 wt. % increased by 78.50 wt. %, and the gasoline fraction from 15.70 wt. % increased by 17.30 wt. %. At 450 °C, the yield of liquid products in the presence of 3.0 wt. % the amount of catalyst is 78.50 wt. %, including gasoline fraction 17.30 wt. %, and the output of the diesel fraction at a boiling point of 180-320 °C is 61.20 wt. %. Fig. 1 compares the yield of liquid products at temperatures of 400, 420 and 450 °C.

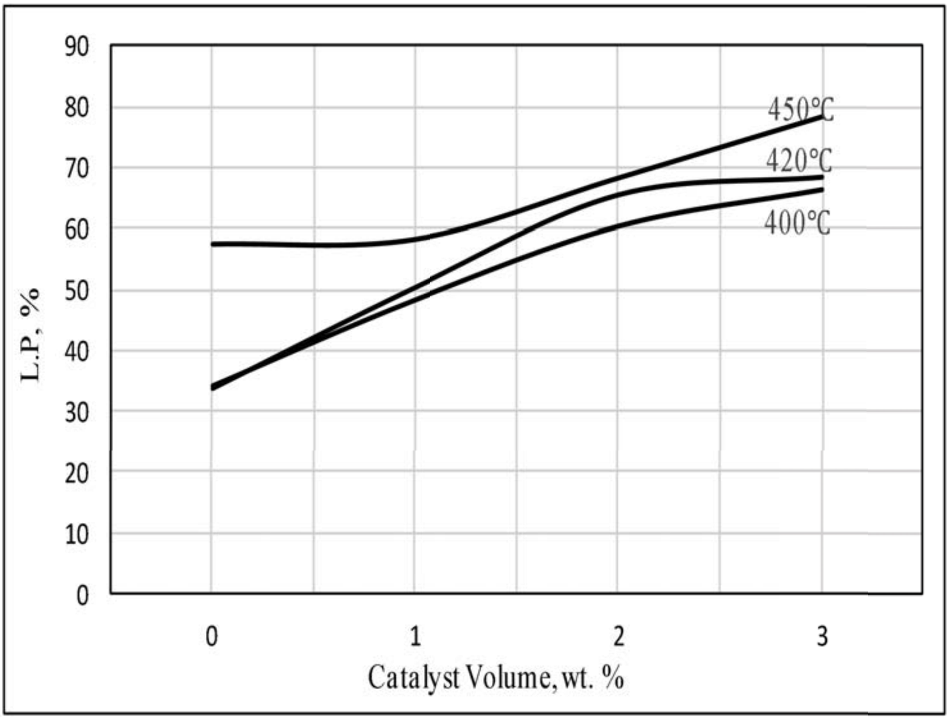

Fig. 1. Comparison of the yield of liquid products at different temperatures

As can be seen from the figures, the optimal process conditions are a temperature of 450°C and 3.0 wt. % of the catalyst $Na_2SiO_3 \cdot 10H_2O$, at which the yield of the liquid products increased from 57.6 to 78.5%. The mass balance of the cracking process of coke-chemical distillate products is shown in Table 3.

Table 3. Material balance of the cracking process of coke-chemical distillate products (P = 3 MPa, T=450°C, catalyst is $Na_2SiO_3 \cdot 10H_2O$)

Raw material	Wt. g	Wt. %	Product	Wt. g	Wt. %
Feedstock + Paste former	28.60	95.30	Liquid products obtained by catalytic cracking	23.55	78.50
Catalyst			0-180 °C 180-250 °C above 250°C	5.19 9.12 9.24	17.30 30.40 30.80
	1.40	4.70	Gas Water+loss	1.35 5.1	4.5 17
Total	30.0	100	Total	30.0	100

4 Conclusions

It was found that when heating the emulsion of the feedstock with the catalyst solution, the nanosized crystallites of the catalyst are uniformly distributed in the volume of the feedstock due to the transition from the emulsion to the phase of water vapor and cracking of the feedstock. During the cracking of coke-tar fractions boiling at 180-320 °C under conditions of 450 °C temperature and a pressure of 5 MPa, the yield of liquid product was 78.5 wt. % including the yield of gasoline fractions 17.3 wt. % Thus, Coke tar is identified as a potential source of raw materials for the production of motor fuels in the future.

References

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