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Preparation of liquid fuels from chark chemical tar

Abstract. In the course of study the optimal conditions of conduction of the process hydrogenization are found. Optimal temperature for preparation of motor oils from chark chemical tar is 400^0C. On the increase of temperature from 350^0C to 400^0C the yield of liquid products on Mo-containing catalyst increases from 47.1 mass. % to 65.2 mass. % compared to the yield of liquid products obtained without the catalyst. The yield of gasoil fraction constitutes 15 mass. %. Optimal quantity of catalyst for preparation of liquid products from the tar is 0.05 mass. %. According to the results of study the catalytic effect of synthesized from emulsion catalyst appears at low concentration of molybdenum (0.05 mass.%). But the double increase of concentration of molybdenum weakly effects the improvement of indicators of the process.
Keywords: suspension, catalyst, chark chemical tar, hydrogenization, motor fuel, emulsion, liquid products, hydrocarbon source.

Introduction

In order to obtain chemical products from charcoal destructive thermal processes are used. Chark formation and partial chark formation belong to the group of such thermal processes. Chark chemical tar is basically composed of condensed aromatic hydrocarbons and other high molecular structural units belonging to sources which are hard to be processed. In the majority of cases the products from chark chemical tar are produced, where every step leads to consumption of large amounts of reagents, consumption of heat and loss of other valuable products. There is a high amount of compounds in the structure of tar which preserve their reactivity with increasing the production temperature. There are works carried out in Russia devoted to preparation of liquid fuels with participation of catalytic suspensions leading to hydrogenation of tar followed by active stabilization of reactive compounds [1-4].

Results and Discussion

Such works have the objective of preparation of motor fuels from chemical chark tar by hydrogenation using laboratory setups at hydrogen pressure of 5.0MPa, with participation of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ catalytic suspension. Distillate fraction of oil with boiling temperature of $>320^0$C was used as a carrier of hydrogen in the role of donor.

As the experimental object in present work the primary tar obtained from half coking of charcoal was used from the "Sary-arka speckoks" company. The effects were studied of temperature and mass of the catalyst on the process of hydrogenation of charkchemical tar with the aim of preparation of motor fuels and determination of optimal conditions of this process.

The effect of temperature on the process of hydrogenation of tar using the catalytic suspension is shown is shown in Table 1.

As can be seen from the table the general yield of liquid products increases from 47.1 mass % to 65.2 mass.% on addition to the reactive media of 0.05 % mass. % $(NH_4)_6Mo_7O_{24} \cdot 10H_2O$ catalyst. The yield of liquid products decreases from 65.2 mass.% to 31.6 mass.% on increase of temperature from 400^0C to 450^0C. The decrease of yield of liquid products with the increase of process temperature can be explained by the deep cracking processes leading to the increase of gas-phase products. Nickel, cobalt, and iron sulfides are widely used for hydrogenation of charcoal and hydrocracking of heavy oil fractions. On heating the initial mixture taken for catalytic purposes to the decomposition temperature, there occurs sulfidization of products of decomposition, which leads to the formation active catalytic phase of necessary composition (Figure 1).

Table 1 – The effect of temperature on the hydrogenation of chark chemical tar in the presence of catalytic suspension

Catalyst	Temperature, °C	The yield of liquid products, mass. %			∑L.P	Gas yield,mas. %	Residue, mas.%	Yield, mas. %
		below 180°C	180-250°C	250-320°C				
The effect of temperature on the yield of liquid products								
Without the catalyst	400	7,80	15,30	24,0	47,1	7,25	27,0	17,5
0,05 мас. % $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$	350	4,25	6,45	23,3	33,9	4,00	44,2	15,8
	400	14,7	18,7	31,7	65,2	10,80	17,5	6,00
	450	10,3	7,60	13,7	31,6	27,00	27,3	13,0

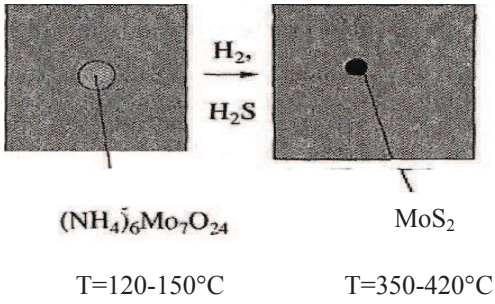


Figure 1 – Formation of MoS2 upon heating the tar to the temperature of experiment

The reactions occurring under conditions of the process are:

$$H_2O_{(c)} + (NH_4)_6MoO_4 \rightarrow H_2O_{(г)} + NH_{3(г)} \rightarrow MoO_{3(к)} \quad (1)$$

$$H_2O_{(c)} + (NH_4)_2MoS_4 \rightarrow H_2O_{(г)} + NH_{3(г)} + S_{(c)} + H_2S_{(г)} + MoS_{2(к)} \quad (2)$$

$$(R\text{-}COO)_2\,MoO_{2(c)} + 7\,H_{2\,(г)} + H_2S_{(г)} \rightarrow MoS_{2(к)} + 2\,R\text{-}CH_{3(c)} + 6H_2O_{(г)} \quad (3)$$

On heating the raw material to the experimental temperature solid particles interact with the components of the gas phase (hydrogen and hydrogen sulfide) and the new phase of molybdenum sulfide forms [5-8].

Finally, according to the experimental results the optimal temperature for preparation of liquid fuels from charkchemical tar is determined to be 400^{0}C. Along with these studies the effect of the amount of catalyst on the yield of liquid products was studied. The results of study are shown in Table 2.

Table 2 – Effect of catalyst on the yield of liquid products obtained from chark chemical tar

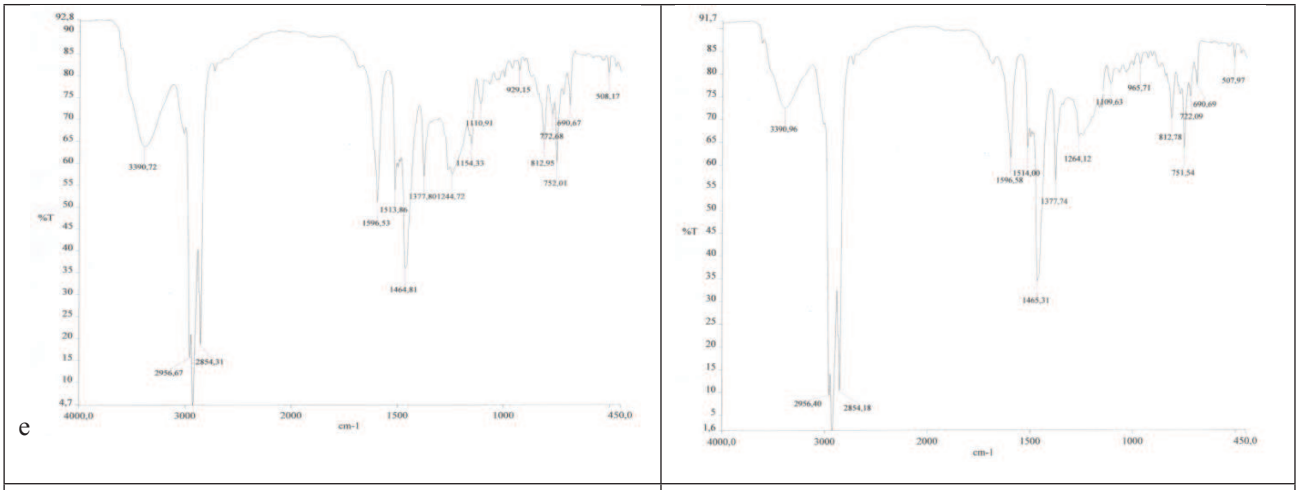
Catalyst	Tempera-ture, °C	Yield of liquid products, mas. %			∑L.P	Yield of gas, mas, %	Yield, mas,%	Yield, mas, %
		Below 180°C	180 – 250°C	250 – 320°C				
The effect of the amount of catalyst on the yield of liquid products, mas. %								
Without the catalyst	400	7,80	15,3	24,0	47,1	7,25	27,0	17,5
0,05 mas. % $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$	350	4,25	6,45	23,3	34,0	4,00	44,2	15,8
	400	14,7	18,7	31,7	65,2	10,8	17,5	6,00
	450	10,3	7,60	13,7	31,6	27,0	27,3	13,0
0,1 mas. % $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$	350	3,90	5,81	22,32	32,03	4,20	46,68	15,89
	400	10,6	22,0	29,0	60,1	4,60	11,2	23,4
	450	6,29	7,13	11,6	25,0	26,0	33,0	16,0

As can be seen from the table, the increase of the catalyst from 0.05 mass.% to 0.1 mass.% at the temperature of 350^{0}C the general yield of liquid products decreases from 34,0 mass. % to 32,03 mass. %, among them the gasoil fraction - from 4,25 mass. % to 3,9 %, at 400^{0}C - from 65,2 mass. % to 60,1 mass %, among them the gasoil fraction - from 14,7 mass. % to 10,6 mass. %, and at 450^{0}C from - 31,6 mass. % to 25,0 mass. %, among them the gasoil fraction decreases from 10,3 mass. % to 6,29 mass %.

The decrease of the yield of liquid products with the increase of the temperature of the process can be explained by the substantial formation of gas-phase products. As a result, according to the analysis of experimental results the optimal amount of the $(NH_4)_6Mo_7O_{24}\cdot 4\ H_2O$ catalyst is determined to be 0.05 mass %.

It is shown that according to the results obtained in the course of research there is proposed a new method of processing of the charkchemical tar by catalytic suspension, which is shown to be one of the main directions of fuels and chemical industry. Similarly, the proposed method of synthesis of catalyst is simple for realization, has simple technological structure and is possible to be realized using typical industrial setups.

In the proposed work the chemical structure of motor fuels and physical-chemical indicators were studied. Based on the results of IR-spectral analysis the chemical composition of studied samples was determined. The IR-spectra of gasoil fraction directly transformed from chark chemical tar and obtained with the help of the catalyst are shown in Figure 2.



1 – IR-spectrum of the fraction boiling at 180°C obtained without the catalyst;	2 – IR-spectrum of the fraction boiling at 180°C obtained with participation of the catalyst

Figure 2 – IR-spectra of obtained samples

If in case of the absence of the catalyst in charkchemical processing directed towards the preparation of gasoil fraction the lines are visible of COC simple ethers in the region of 1034,3 cm^{-1} and 113,0 cm^{-1} , 1230-1160 cm^{-1} - aromatic aldehydes, then in the composition of gasoil fraction obtained in the presence of the catalyst among different aromatic hydrocarbons asymmetric deformational vibrations are visible equivalent to alkylbenzene derivatives in the region of 1464,81 cm^{-1}, along with symmetric deformational vibrations at 1377,4 cm^{-1} equivalent to CH_2 methylated benzene derivatives, and in the same row, in the region of 1596,53 cm^{-1}, 1513,86 cm^{-1} intensive absorption lines are observed corresponding to –CH aromatic groups.

Similarly in the region of 812,95 cm^{-1} deformational vibrations equivalent to 1,2,4 three substituted benzene derivatives are observed, in the field of 772,0 cm^{-1} , 752,01 cm^{-1} the medium intensity lines are determined corresponding to 1,3 two substituted benzene derivatives

Due to the decrease of the content of aromatic hydrocarbons and oxygen-containing compounds in the composition of gasoil fraction obtained in the results of catalytic processing of charkchemical tar in the presence of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ the conditions required for motor fuels are not satisfied.

Therefore it is impossible to use liquid products obtained from tar directly as motor fuels. In spite

of this, tar distillates can still be used for further processing. Individual and group composition of hydrocarbons provides additional information about the level of catalytic hydrogenation process. The group hydrocarbon composition along with physical-chemical properties of the hydrogenated tar distillates of Mo containing catalytic suspensions are shown in Table 3.

Table 3 – Physical-chemical indicators and group composition of tar distillates hydrogenated by Mo-containing catalytic suspensions

Indicators	Fractions of the distillate		
	80 - 180^{0}C	180 - 250^{0}C	250 - 320^{0}C
Gasoline fraction obtained without the participation of the catalyst			
Density, 20^{0}C, g/cm^3	1,01	1,08	1,23
Refractive index, n_d^{20}	1,6558	1,5923	1,6725
Hydrocarbon group composition, % Alkane Iso-alkane Aromatic Naphthenes Olefins	 55,4 10,14 17,2 1,4 2,3	 16,02 14,65 55,40 10,85 3,08	 16,42 13,75 47,40 11,98 1,443
Sulfur content, %	0,07	0,09	0,11
Iodine number J_2/100	43,5	42,35	10,47
0,05 mas. % $(NH_4)_6Mo_7O_{24}\cdot 4\,H_2O$			
Density, 20^{0}C, г/см^3	0,90	1,00	1,12
	2	3	
Refractive index n_d^{20}	1,48	1,43	1,55
Hydrocarbon group composition, % Paraffin Isoparaffin Aromatic Naphthene Olefins	 10,22 32,3 37,6 0,68 1,42	 20,94 27,23 35,5 15,25 1,08	 17,82 25,36 40,40 16,03 0,388
Sulfur content, %	0,02	0,08	0,03
Iodine number J_2/100	42,67	36,57	32,51

As shown in the table, gasoline fraction obtained from the tar distillates represents a complex mixture. The density and refraction index of tar distillates obtained without the catalyst acquire high values with the increase of the temperature. This can be explained by the presence of heavy hydrocarbons with high boiling temperatures and incomplete transformation of tar. The amount of sulfur: 0.07% in the fraction obtained in the interval of 80-180°C, 0.09% in the fraction obtained in the interval of 80-180°C, 0.11% in the fraction obtained in the interval of 250-320°C. Iodine number: for the fraction between 80-180°C 43.5, for the fraction between 180-250°C 42.35, for the fraction between 250-320°C 10.47 mass %.

Comparison of the composition of distillate with the gasoil fraction obtained at 80-180°C in the result of catalytic direct reforming of chark-chemical tar with participation of 0.05 mass % of the $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ catalyst has shown that the content of aromatic hydrocarbons increased from 12.17 % to 37.6 mass. %, isoalkanes – from 10.14 mass. % to 32.3 mass.%, naphthenes – decreased from 1.4 % to 0.68 mass.%, unsaturated hydrocarbons - from 2.3 mass. % to 1.42 mass.%. Such changes in the presence of 0.05 mass.% $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ catalyst can be explained by the processes of hydrocracking, isomerisation, cyclization.

Conclusion

Finally, the possibility is shown for preparation of liquid fuels rich in aromatic and naphthene hydrocarbons by hydrogenation of charkchemical tar distillates with participation of 0.05 mass % $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ catalysts. The group composition of gasoil fraction is shown in Table 4.

Table 4 – Hydrocarbon composition of gasoil fraction

Hydrocarbons	Gasoline fraction obtained without the catalyst	Gasoline fraction obtained with the use of the catalyst
Alkane	55,4	10,22
Isoalkane	10,14	12,3
Aromatics	12,7	37,6
Naphthenes	1,4	0,68
Olefins	2,3	1,42
Cycloolefines	0,48	-
Dienes	-	-

As can be seen from the table, the composition of gasoil fraction undergoes substantial changes in the presence of the catalyst. These changes, in turn lead to the increase of octane number of gasoil.

Finally, the possibility is shown of obtaining liquid fuels by processing of charkchemical tar in the presence of catalytic suspension and their physical-chemical indicators and hydrocarbon composition is studied.

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Коксохимиялық шайырдан сұйық өнімдер алу

Зерттеу барысында гидрогенизациялау процесінің оңтайлы жағдайлары анықталды. Коксохимиялық шайырдан мотор отындарын алудағы оңтайлы температура 400°С. Мо-құрамды катализатор қатысында сұйық өнімдер шығымы процестің температурасын 350°С-тан 400°С-қа арттырған сайын катализатор қатысынсыз алынған сұйық өнімдер шығымымен салыстырғанда 47,1 мас. % -дан 65,2 мас. %-ға жоғарылаған. Бензин фракциясының шығымы – 15 мас. %. Синтезделген катализатордың каталитикалық эффектісі молибденнің аз концентрациясында (0,05 мас. %) байқалады. Молибден концентрациясын 2 есе арттырған сайын процесс көрсеткіштерінің нашарлайтындығы көрсетілді.

Түйін сөздер: суспензия, катализатор, коксохимиялық шайыр, гидрогенизация, мотор отыны, эмульсия, сұйық өнімдер, көмірсутектік шикізат.

Ж.К. Каирбеков, Н.Т. Смагулова, А.Ж. Каирбеков

Получение жидких продуктов из коксохимической смолы

В ходе исследования найдены оптимальное условия проведения процесса гидрогенизации. Установлена оптимальная температура для получения моторных топлив из коксохимической смолы 400^0C. При увеличении температуры от 350°С до 400°С выход жидких продуктов на Мо-содержащем катализаторе по сравнению с выходом жидких продуктов без катализатора увеличился от 47,1 мас. % до 65,2 мас. %. Выход бензиновой фракции составляет 15 мас. %. Оптимальное количество катализатора для получения жидких продуктов из смолы составляет 0,05 мас. %. По результатам исследования каталитический эффект синтезированного из эмульсии катализатора проявляется уже при низкой концентрации молибдена (0,05 мас.%). Однако возрастание концентрации молибдена в 2 раза мало сказывается на улучшении показателей процесса.

Ключевые слова: суспензия, катализатор, коксохимическая смола, гидрогенизация, моторное топливо, эмульсия, жидкие продукты, углеводородное сырье.