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CHEMISTRY

Synthetic Diesel Fuel Produced from Coal

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Abstract—The characteristics of synthetic diesel fuel are analyzed. The fuel consists of hydrocarbons C_3–C_{32}; the content of the middle fractions is 83.26 wt %. The IR spectrum of the synthetic diesel fuel contains deformational vibrations corresponding to paraffins and unsaturated hydrocarbons, as well as aromatic and heteroaromatic compounds. Synthetic fuel produced from coal is recommended as a raw material for DTZ commercial diesel fuel, suitable for use in winter.

Keywords: synthetic diesel fuel, hydrogenation of coal

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As oil and gas reserves shrink and the energy shortage becomes more serious, coal may be expected to play a major role in the global economy in the near and far future. Thanks to the numerous organic components in coal, it may serve as a source of electric power, gaseous and liquid fuels, chemical raw materials, blast-furnace coke, activated carbon, constructional materials, and much more [1]. With the growing demand for waste-free technologies in order to meet environmental and resource-conservation standards, it is important to identify the best uses of coal [2].

Estimates suggest that world coal reserves will last for 200 years, as against 40 years for petroleum and uranium-235 and 50 years for natural gas [3].

Therefore, in order to ensure the supply of fuels and of feedstocks for the chemical industry, we need to develop technologies for converting coal to a replacement for oil and natural gas. This is a particular priority for Kazakhstan, a coal-rich country. Today, around 400 coal basins and fields are being worked in Kazakhstan. In this context, the production of synthetic liquid fuels from coal is a high priority [4–6].

In the present work, we study synthetic diesel fuel produced by the hydrogenation of Karazhyra coal on natural zeolite catalysts.

According to technical analysis, the characteristics of the coal are as follows: $W^a = 8.0\%$, $A^a = 7.2\%$, $V^{daf} = 45.4\%$, $C^{daf} = 69.7\%$, $H^{daf} = 5.7\%$, $N^{daf} = 1.4\%$, $O^{daf} = 22.0\%$, $S^{daf} = 1.2\%$. The mineral composition is as follows: 59.0% SiO_2, 24.54% Al_2O_3, 5.04% Fe_2O_3, 2.24% CaO, 2.01% MgO, 1.35% TiO_2, 1.57% K_2O, 1.53% Na_2O, 1.83% SO_3, and 0.39% rare-earth metals. A paste is formed with the heavy petroleum fraction from the Karazhanbas field ($T_b > 773$ K). The catalyst in coal hydrogenation is Semei-Tau natural thermostable zeolite.

A Büchiglasuster high-pressure laboratory reactor is used for hydrogenation at 5 MPa and 420°C. The optimal parameters for the production of synthetic liquids from Karazhyra coal were determined in [7–9].

The characteristics of the synthetic diesel fuel are determined in the accredited (KZ.I.02.1572) and certified (certificate 03/14) laboratory for fuel analysis at the Research Institute for New Chemical Technologies and Materials, Al-Farabi Kazakh National University.

The cloud point, pour point, and limiting pour point of the diesel fuel are determined in accordance with the ISO 9001 standard on equipment development by the Kristall Institute. The flash point is established in a closed crucible in accordance with State Standard GOST 6356–75 on the ATV-21 automated system. The heat of combustion of the synthetic diesel fuel is determined on a V08MA automated calorimeter. The sulfur content is determined in accordance with State Standard GOST R 51947–2002 on a

Table 1. Characteristics of synthetic diesel fuel

Parameter	Value	Study method
Density at 20°C, kg/m^3	0.849	GOST 3900–85
Ash content, %	0.0126	GOST 1401
Coking properties, %	0.0056	GOST 19932
Spark point, °C	92	GOST 6356–75
Refractive index n_D	1.4300	GOST 18995.2–73
Cloud point, °C	–13.2	
Filtration point, °C	–16.3	ISO 9001
Pour point, °C	–20.1	
Sulfur content, %	0.428	GOST P 51947–2002
Fractional composition, °C:		
onset of boiling	183	
50% distillation	280	GOST 2177–99
90% distillation	357	
end of boiling	357	
Calorific value, kJ/kg	44754	GOST 21261–91

Spectroscan S system (ASTM D 4294–98). The fractional composition of the diesel fuel is determined in accordance with State Standard GOST 2177–99 on ARN-LAB-02 equipment. The ash content and coking properties of the synthetic fuel are determined in accordance with State Standards GOST 1401 and GOST 19932.

The liquid hydrogenation products of Karazhyra coal contain ~60% distillate fractions with T_b = 350°C, which may be used to obtain gasoline, diesel fuel, and pastes. Table 1 summarizes the characteristics of the synthetic diesel fuel.

Analysis of Table 1 indicates that the density and viscosity of the product are low. That means that it can be readily sprayed. With increase in density and viscosity, the droplet diameter increases, and their combustion is incomplete. As a result, the fuel consumption increases and the smoke content of the exhaust gases increases. The density and viscosity affect the cetane number of the fuel. The fuel consumption depends not only on the temperature at which boiling begins but also on the temperatures corresponding to 50% and 90% distillation.

In the samples, these values meet the requirements for DTZ diesel fuel; they are in the range 183–357°C. The fractional composition of the fuel is closely related to the spark point, at which the petroleum vapor forms a combustible mixture with air. The spark point of the synthetic diesel fuel is found to be 92°C. It determines the fire risk in transportation, storage, and use of the fuel. The classification of the diesel fuel is determined by the following temperatures: the pour point, –20.1°C; the cloud point –16.3°C; and the filtration point, –13.2°C.

The hydrocarbon composition of the fuel is determined on a Khromatek Kristall 5000 instrument, with the following results:

Hydrocarbon	content, wt %
C_3	0.005
C_4	0.002
C_5	0.013
C_7	0.093
C_8	0.188
C_9	0.721
C_{10}	2.578
C_{11}	4.895
C_{12}	8.147
C_{13}	8.415
C_{14}	9.665
C_{15}	11.018
C_{16}	11.070
C_{17}	9.715
C_{18}	7.120
C_{19}	7.990
C_{20}	5.225
C_{21}	3.960
C_{22}	3.190
C_{23}	2.025
C_{24}	1.650
C_{25}	1.085
C_{26}	0.660
C_{27}	0.240
C_{28}	0.235
C_{29}	0.070
C_{30}	0.015
C_{31}	0.005
C_{32}	0.005

Table 2. IR spectral characteristics of the synthetic diesel fuel

Wave number, cm^{-1} (wavelength μm)	Types of vibration (intensity)	Structural fragments
2955.82	ν_{as}(strong)	$-CH_3$
2924.46	ν_{as}(strong)	$-CH_2-$
2854.67	ν_s(strong)	$-CH_2-$
2360.26	ν(strong)	$R_2NH_2^+$
2341.99	ν(strong)	$R_2NH_2^+$
1698.99	ν(strong)	Aromatic
1638.28	tr.	C=C nonconjugate
1605.97	ν(strong)	C=C conjugate with C=O
1557.83	ν(strong)	Ketonic form $CO-CH_2-CO$
1541.34	ν(strong)	Ketonic form $CO-CH_2-CO$
1458.47	$\Delta_{as(}$medium)	$-CH_3$
1377.23	δ_s(strong)	$-CH_3$
1154.46	ν(weak)	$R-SO_2-R$
992.53	δ_{ns} nonplane	$HRC=CH_2$
965.57	δ_{ns} plane	HRC=CR'H
909.16	δ_{ns} plane	$HRC=CH_2$
886.63	δ_{ns} nonplane	$RR'C=CH_2$
811.42	δ_{ns} nonplane	RR'C=CR"H
748.09	ν(strong)	Thiophenes
722.32	ν(strong)	Thiophenes
618.73–668.04	ν(strong)	Heterocompounds

Chromatographic analysis of the hydrogenation products shows that it consists basically of the middle hydrocarbon fractions $C_{11}-C_{15}$ (42.14%) and $C_{16}-C_{20}$ (41.12%).[1] The content of light hydrocarbons is very slight: no more than 0.02% for the propane–pentane fraction and 3.58% for the other light paraffins. The total content of heavy hydrocarbons $C_{21}-C_{32}$ is only 13.14%. In Fig. 1, we plot the content of hydrocarbons with different numbers of carbon atoms in the molecule for the synthetic diesel fuel. This distribution is exponential, with a maximum at the mean hydrocarbon fraction (C_{16}).

In Fig. 2, we show IR spectrometric data for the synthetic diesel fuel produced from Karazhyra coal.

Analysis of the data in Fig. 2 and Table 2 indicates that normal and isostructural paraffins predominate in the sample: we note the presence of the functional groups $-CH_3$ and $-CH_2-$ with high-intensity deformational vibrations at 1377.23 cm^{-1}; high-intensity antisymmetric vibrations at 2955.82 cm^{-1}, 2924.46 cm^{-1}, and 2854.67 cm^{-1}; and medium-intensity antisymmetric deformational vibrations at 1458.47 cm^{-1}, corresponding to saturated hydrocarbons.

The fuel also contains amine salts with functional groups $R_2NH_2^+$ with strong absorption bands at 236.26 cm^{-1} and 2341.99 cm^{-1}; and heterocompounds

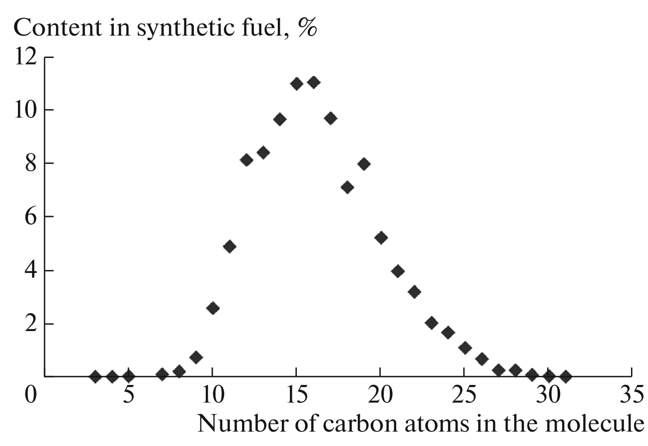

Fig. 1. Content of hydrocarbons with different numbers of carbon atoms in the synthetic diesel fuel.

[1] Here and in what follows, we use wt %.

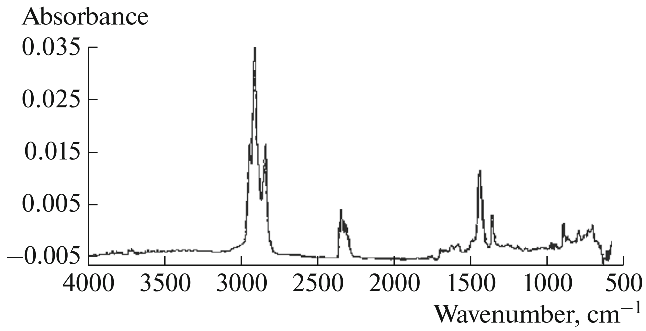

Fig. 2. IR spectrum of the synthetic diesel fuel.

with strong vibrations at 618.73–668.04 cm^{-1}. High-intensity bands corresponding to thiophene are seen at 748.09 cm^{-1} and 722.32 cm^{-1}, as well as low-intensity bands corresponding to sulfur compounds with the functional group $R–SO_2–R$ at 1154.46 cm^{-1}. We also detect aromatic compounds with intense vibrations at 1698.99 cm^{-1}. On interpretation of the spectrograms, we also find deformational vibrations of functional groups corresponding to unsaturated hydrocarbons at the absorption bands 1638.28 and 811.42–992.53 cm^{-1}. High-intensity valence vibrations correspond to ketones with wave numbers 1541.34–1605.97 cm^{-1}.

CONCLUSIONS

We have analyzed the characteristics of synthetic diesel fuel produced from Karazhyra coal (Eastern Kazakhstan). We find that the fuel consists of hydrocarbons C_3–C_{32}; the content of the middle fractions predominates.

The IR spectrum of the synthetic diesel fuel contains deformational vibrations corresponding to paraffins and unsaturated hydrocarbons, as well as aromatic and heteroaromatic compounds.

Synthetic fuel produced from coal is recommended as a raw material for DTZ commercial diesel fuel, suitable for use in winter.

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