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TECHNOLOGY

PRODUCTION OF MOTOR FUELS FOR COLD CLIMATES WITH SIMULTANEOUS REFINING OF VEGETABLE AND CRUDE OIL STOCK

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The feasibility of incorporating synthetic oil produced by the Fischer—Tropsch process from synthesis gas of a wood-biomass gasification process into the production of class K5 alternative low-pour-point fuels by processing in a blend with straight-run diesel distillate employing a two-stage scheme (first stage, hydrofining in the presence of conventional hydrofining catalyst Co-Mo/Al_2O_3; second, hydroisodewaxing) is investigated. It is shown that a nickel-molybdenum-containing hydroisodewaxing catalyst based on a binary mixture of zeolites (high-silica low-alkali zeolite TsVN of pentasil structure and mordenite) enables the production of diesel fuel for Arctic conditions (limit filterability temperature –45°C) and aviation kerosene with an initial crystallization temperature of –63°C. A mixture of boron and lanthanum oxides was used as the promoter; a mixture of amorphous aluminum silicate and γ-alumina, as the binder.

Keywords: *low-pour-point motor fuels, wood biomass gasification, synthetic oil, Fischer—Tropsch synthesis, straight-run diesel distillate, hydrofining, hydroisodewaxing.*

Oil and natural gas are currently the most popular energy sources. However, renewable energy must be developed because fossil-fuel reserves are limited and global problems with ecological safety due to a constantly increasing demand for energy by the world economy must be resolved [1, 2].

The use of plant biomass that does not interfere with the food sector is one way of resolving the search for alternative renewable energy sources for transportation. In particular, utilization of wastes from

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lumber mills and the paper industry is very critical for Russia because it solves the problem of complex waste-free plant biomass processing with simultaneous production of an additional amount of valuable fuels.

Fischer—Tropsch (FT) synthesis is one of the most common of several known global technologies that can compete with oil refining for the production of motor fuels and includes a synthesis-gas (syngas, mixture of CO and H_2) production step [3-7]. The feedstock for syngas production can be coal, natural gas, or biomass. Co-containing catalysts are usually used to produce middle distillates (kerosene-gasoline) [8]. Subsequent hydrofining of the obtained synthetic oil can produce various types of alternative motor fuels [7, 9].

Fouling of acidic centers on the catalyst surface by resin and coke and disintegration of the support in the acidic medium at elevated temperatures are important problems for hydrofining middle distillates of synthetic-oil fuel fractions [10, 11]. One solution could be simultaneous processing of synthetic- and crude-oil fractions [12].

FT synthetic oils produced on a Co catalyst contain primarily normal and slightly branched alkanes with 15-29 C atoms. They typically have high cloud and gel points, which are responsible for the poor low-temperature properties of synthetic motor fuels.

Increased production of motor fuels designed for use in cold climates is the most critical problem for Russia considering its climate and geography. The demand for them is 40% of the total production volume.

Modern hydroisodewaxing processes that use domestic catalysts can alleviate the shortage of diesel fuels for cold and Arctic climates and produce high-quality aviation kerosene. Fuel with the required low-temperature parameters can be produced in high yield because the catalysts are highly active for isomerization of high-boiling waxy hydrocarbons and minimize hydrocracking [13-17].

Herein, results from studies of simultaneous processing of plant and oil feedstocks by a two-stage scheme combining hydrofining and hydroisodewaxing in order to produce diesel fuel for Arctic conditions and aviation kerosene are presented.

Table 1

Indices	Synthetic oil middle distillates	Straight-run diesel distillate
Boiling range, °C	140 – 350	180 – 360
Density at 15°C, kg/m^3	754	851
Kinematic viscosity at 40°C, mm^2/s	1.5	3.4
Sulfur content, mg/kg	–	2800
Cloud point, °C	4	– 13
Limit filterability temperature, °C	6	– 11
Pour point, °C	–2	– 16
Acidity, mg KOH/100 cm^3	12.0	6.1
Iodine number, g I_2/100 g	33.4	4.0
Group hydrocarbon composition, wt. %		
paraffinic (including *n*-alkanes)	83.8 (63.9)	53.3 (22.8)
naphthenic	1.1	16.1
olefinic	15.1	4.1
aromatic (including polycyclic)	–	26.5 (7.9)

The oil component was straight-run diesel distillate (SDD); the alternative component, medium distillate of synthetic oil (SO) produced by the FT method. Feedstock for FT hydrocarbon synthesis on Co catalyst was produced by gasification of wood biomass. Therefore, this component could be considered to be of plant origin. Table 1 presents the physicochemical characteristics of the feedstock components.

Chromatography—mass-spectrometry analysis of the group composition of the feedstock showed that SO hydrocarbons were mainly long-chain unbranched alkanes. These were mostly responsible for the poor low-temperature properties (limit filterability temperature, cloud and gel points) as compared with other groups of compounds. It is also noteworthy that the SO had low viscosity and density.

An advantage of the SO middle distillate over crude-oil distillate was its higher ecological safety due to the lack of S-containing compounds and aromatic hydrocarbons. This made it promising for producing alternative motor fuels. However, the high concentration of olefinic hydrocarbons and oxygenated acidic compounds, as indicated by the iodine and acidity parameters, necessitated catalytic hydrofining of SO in order to produce commercial motor fuels.

Industrial AKM hydrorefining catalyst ($CoMo/Al_2O_3$) in the sulfide form AGKD-400 was used for hydrofining of the SO fraction.

The acidity parameter was chosen as the criterion of hydrogenation of oxygenated compounds because, according to the literature, they (acids and phenols) prevail in SO and have the greatest negative effects on the traditional sulfided hydrorefining catalyst.

Two types of experiments were performed in order to avoid catalyst activity losses due to carbonization and replacement of S in the sulfide structure by oxygen during hydrofining of the SO fraction:

IB – hydrofining of pure SO with added dimethyldisulfide (DMDS) to maintain the catalyst S-form;

IIB – hydrofining of SO mixed with crude-oil distillate. Preliminary investigations showed that 30 vol% of SO in the mixture was optimal for producing diesel fuel with a normal density at 15°C.

Both types of hydrofining were carried out at 6 MPa, 360°C, feedstock volume flow rate 1 h^{-1}, and HCG/feedstock recirculation rate 500 norm. m^3/m^3. These were chosen as the optimal process parameters based on experimental results for the effect of the hydrofining conditions on the amount and quality of the products with respect to contents of S, olefins, and acidic oxygenated compounds.

Table 2 presents results for hydrofining of pure FT SO middle distillate and that mixed with crude-oil distillate. The target product was kerosene-gasoline fraction 135-360°C. Samples were analyzed by standard methods in order to assess the feasibility of using it as a motor-fuel component.

The catalyst activity was markedly less for hydrofining of pure SO middle distillate (IB). The acid number decreased by 95%; the degree of hydrogenation of unsaturated hydrocarbons, 88%. Simultaneous processing of synthetic and crude-oil feedstocks (IIB) reduced significantly the load on the catalyst because the acidity of the starting feedstock and the iodine number were decreased by 3.1 and 1.5 times, respectively. This gave a higher degree of hydrogenation of unsaturated hydrocarbons and a lower product acidity of 98 and 100%, respectively. Furthermore, adding an S-containing agent to SO degraded the product quality with respect to S content as compared with the product from the IIB process.

The results showed that the kerosene-gasoline fraction from simultaneous processing of SO and SDD satisfied the requirements of GOST 32511-2013 for the main parameters of DT-L-K5 fuel, had a large margin for the cetane index and PCA content, and could be used as a component of K5 class summer diesel fuel.

The target product from hydrofining of pure SO middle distillate must be compounded with traditional oil products in order to satisfy the density parameter. This type of processing is economically less attractive

Table 2

Indices	IB		IIB		Standard of GOST 32511 for DT-L-K5
	feedstock	product	feedstock	product	
Fractional composition, °C					
IBP	132	133	143	142	
10 vol. %	157	152	186	184	
50 vol. %	215	212	273	262	
90 vol. %	322	319	335	324	
95 vol. %	357	350	351	342	≤360
EP	358	354	359	352	
distills at 250°C, vol. %	64	65	39	44	≤65
distills at 350°C, vol. %	94	95	95	98	≥85
Density at 15°C, kg/m^3	754	752	822	821	820-845
Sulfur content, mg/kg	880[*]	14	2040	9	≤10
Aromatic hydrocarbons (including polycyclic), wt. %	–	–	18,6 (5,5)	17,6 (1,6)	≤8
Acidity, mg KOH/100 cm^3	12.0	0.6	7.9	-	–
Iodine number, g I$_2$/100 g	33.4	4.0	10.4	0.2	–
Cetane index (calc.)	66.5	64.3	55.9	53.2	
Limit filterability temperature, °C		5		- 6	Type A – ≤5 Type C – ≤ -5

Note. [*] Considering DMDS addition.

with respect to the need to expand the existing refinery infrastructure in order to introduce new capabilities for hydrogenation of SO.

The use of hydrogenation processes directed at transformation of *n*-paraffinic hydrocarbons into isoparaffins and *n*-paraffins of lower molecular mass is a more rational approach to improving the low-temperature characteristics of kerosene-gasoline hydrofining fractions in order to produce motor fuel components for cold climates.

Therefore, wet mixing was used at ARRIOR to synthesize IZO hydroisodewaxing catalysts with various combinations and contents of active components such as zeolites (15-60 mass%), hydrogenating metal oxides (6.5-21.0), promoters (2-4), and binder (remainder, to 100 mass%).

The acidic components were high-silica zeolites with high specific surface areas or their mixtures, zirconium tungstate, and amorphous aluminosilicates with various mass ratios of SiO_2 and Al_2O_3. The hydrogenation—dehydrogenation was provided by molybdenum, nickel, tungsten, and iron oxides.

A mixture of amorphous aluminosilicate and γ-aluminum oxide was used as the binder for creating the optimal porous structure and providing mechanical strength to the catalyst. It also had a significant effect on the formation and dispersion of the active phases.

Oxides of phosphorus, boron, and lanthanum were added as promoters (modifiers) in order to increase the process selectivity and stabilize the catalyst operation and also to improve its texture and strength.

The acidic properties of the synthesized catalysts were investigated using thermally programmed ammonia desorption starting with a model of one acidic center corresponding to one adsorbed ammonia molecule, i.e., the amount of desorbed ammonia corresponded to the number of sample acidic centers.

Porous structure parameters (specific surface area, average pore volume and diameter) were studied using low-temperature physical adsorption—desorption of N_2 at 77 K on an ASAP 2010 surface and porosity analyzer (Micromeritics, USA).

Series of investigations were carried out on a flow-through laboratory hydrogenation apparatus in order to establish trends in the effects of the hydroisodewaxing process parameters for middle distillate oil and synthetic feedstock and the composition (chemical) of the synthesized catalysts on the yield and quality of the target products. The catalyst volume loading for the reactor tests was 20 cm^3 (0.5-1.0-mm fraction). The reactor was a cylindrical tube of inner diameter 1 cm that was sealed with steel-alloy nozzles.

The quality assessment criterion of hydrogenate obtained from the apparatus was a gel point less than –55°C.

The constant process parameters were a pressure of 3 MPa and H_2/feedstock ratio of 600 v/v. These were optimal for hydroisomerization of normal alkanes.

The feedstock temperature and volume flow rate were the variables. The starting values were the minimal ones for carrying out the target reaction, i.e., 260°C and 1.5 h^{-1}. The temperature was increased in steps of 5°C in order to reach the required hydrogenate quality. The feedstock volume flow rate was increased in steps of 0.5 h^{-1} after the optimum temperature was reached in order to attain the maximum possible production.

The feedstock was the product from simultaneous hydrofining of SO and SDD fractions (product IIB).

The hydrogenate from the apparatus was fractionally distilled into gasoline (<135°C) and target fractions (>135°C) in order to isolate the middle distillates.

Table 3 presents results from selected tests of the synthesized IZO hydroisodewaxing catalysts.

Table 3

Sample type and composition, wt. %	Process temperature, °C	Feedstock volume feed rate, h^{-1}	Hydrogenate quality			Yield of target feedstock fraction, wt. %
			density at 15°C, kg/m^3	cloud point, °C	pour point, °C	
IZO -1 (Fe, Mo/ TsVN)	290	3.0	799.1	–49	–58.6	89.0
IZO -2 (Ni/ZSM-22,USY)	340	1.5	792.0	n/c	–49.8	90.8
IZO -3 (Ni/TsVN, Beta, ZSM-12)	300	3.0	751.4	n/c	<–72	76.9
IZO -4 (Ni, Mo/ mordenit, TsVN)	270	1.5	787.0	n/c	<–72	83.5
IZO -5 (Ni, Mo, W/ mordenit ZSM-12)	330	1.5	791.3	n/c	–70.5	85.0
IZO -6 (Ni, W/TsVN, USY)	310	2.0	785.1	–39	–57	91.0
IZO -7 (Ni, Mo/ TsVN, Beta)	265	3.0	792.3	n/c	< —69.0	89.9
IZO -8 (Ni, Mo/ TsVN, Beta)	320	3.0	789.5	n/c	<–64.0	85.0
IZO -9 (Ni, Mo/ TsVN, mordenit)	310	2.0	788.3	n/c	<–72.0	91.7
IZO -10 (Ni, Mo/мordenit, USY,WO_4/ZrO_2)	335	1.5	749.0	–43	–67.0	71.0

Note. n/c, – not cloudy

Table 4

Indices	Kerosene fraction 135-230°C	
	Actual data	Standard of GOST 10227-2013 for PT fuel
Density at 20°C, kg/m^3	787.0	≥ 775
Fractional composition, °C		
IBP	142	≥ 135
98 vol. %	241	≤ 155
		≤ 280
Flash point (closed cup), °C	35	≥ 28
Chilling point, °C	– 63	≤ – 60
Lower combustion heat (calc.), kJ/kg	43180	≥ 43120

The catalytic activity, selectivity, and operating stability of the catalysts were determined by the contents and characteristics of the acidic component included in the catalyst, i.e., geometry, zeolite channel size, number and strength of acidic centers, and functioning of the hydrogenating component.

Table 3 shows that the hydrogenates had lower densities at 15°C (749.0 and 799.1 kg/m^3) than the starting feedstock (821 kg/m^3). The hydrogenate cloud point varied from –39°C (sample IZO-6) to –49°C (samples IZO-1, 6, 10). The hydrogenate yields were 96.0-97.3 mass%.

Cloud points were not observed for samples IZO-2, 3, 4, 5, 7, 8, and 9, i.e., waxy hydrocarbon crystals did not precipitate. Therefore, the cloud points could not be determined.

The yield of target middle distillate >135°C with the required hydrogenate quality could be considered an indirect selectivity criterion of the hydroisodewaxing catalyst, i.e. high isomerizing and low cracking activity.

The results of selected tests showed that sample IZO-9, which was synthesized from a two-component mixture of mesoporous TsVN zeolite of pentasil structure and macroporous zeolite mordenite, gave the highest yield of kerosene-gasoline fraction (91.7 wt. %) under the optimum process conditions (310°C, feedstock volume flow rate 2 h^{-1}). The hydrogenating transition metals were Ni and Mo oxides; promoter, a mixture of B and La oxides; binder, a mixture of amorphous aluminosilicate and г-aluminum oxide. This catalyst was characterized by predominantly acidic centers of moderate strength (67%) with specific surface area 281 m^2/g and average pore radius 3.9 nm.

Chromatography—mass-spectrometry of the target fraction showed that the contents of linear waxy hydrocarbons C_7-C_{22} decreased by 32 mass% during hydroisodewaxing over catalyst IZO-9; the kerosene fraction (C_7-C_{13}), by 35.6 mass%; the diesel fraction (C_{10}-C_{22}), by 34.8 mass%.

Tables 4 and 5 present the principal quality parameters of aviation kerosene (135-230°C) and diesel fuel (>230°C and >180°C) produced during hydroisodewaxing using catalyst IZO-9 as compared with regulatory requirements for motor fuels used in cold and Arctic climates.

The actual data for the quality of the target products show that the hydroisodewaxing catalyst synthesized at ARRIOR provided the required low-temperature characteristics for aviation kerosene (135-230°C) and diesel fuel (180-360°C). The heat capacity of aviation kerosene that was calculated from the aniline point satisfied regulatory requirements.

Table 5

Indices	Diesel fraction		
	Actual data		Standard of GOST R 55475-2013 for winter/arctic diesel fuel (Z-32/A-44)
	230–360°C	180–360°C	
Density at 15°C, kg/m^3	859.0	842.5	800-855
Sulfur mass fraction, mg/kg	9	7	for К5 <10
Fractional composition			
distills before 180°C, vol. %	0	7	≤ 10
95 vol% distills at temperature, °C	345	343	≤ 360
Flash point in closed crucible, °C	65	58	≤ 40/30
Limit filterability temperature, °C	-32	– 45	≥ –32/– 44
Cloud point, °C	n/c	n/c	≤ –22/–34
Cetane index (calc.)	46.4	45.2	≥ 46.0/43.0

The residual from aviation kerosene production (230-360°C) with limit filterability temperature –32°C can be used as a component of winter diesel fuel Z-32.

Thus, the studies of two-stage simultaneous hydrogenation of plant and oil feedstocks found that incorporation of up to 30 vol. % of middle distillate of FT SO prepared using syngas from wood-biomass gasification during production of low-pour-point motor fuels was in principle possible. This enabled the hydrocarbon feedstock base to be expanded and an ecological problem with production of transportation fuel using the existing refinery infrastructure to be solved.

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