Aviation Fuels of New Generation from Biological Raw Materials

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Abstract

Laboratory regularities for hydrocarbons synthesis by bioethanol are proposed. Samples of liquid hydrocarbon biofuel are obtained. Laboratory researches of the biofuels for establishment a correspondence to Technical requirements to alternative fuel for aviation gas turbine engines. One of the fuel samples corresponds to Technical requirements of GOST 10227-86 for jet fuel RT (unified Russian fuel for sub- and supersonic aircrafts).

Solar energy accumulated in biomass is a single alternative and inexhaustible source of energy due to reduction of the nonrenewable energetic resources (oil, coal, natural gas, uranium etc.). Now an efficient technology for engine fuel production (including jet fuels) from biological raw materials is one of the important problems.

Aviation freight and passenger aircrafts uses ~10% of world manufactured motor fuels [1]. Nevertheless intensive researches of synthetic jet fuels from non-oil raw materials (including biomass) are performed in USA and Europe [2-4].

Analysis of physical, chemical and operating properties of produced oxygen-containing synthetic biofuels (vegetable-derived alcohols and ethers) for reciprocating motors shows impossibility of their application in aviation gas turbine engines (AGTE) due to reduced heat of combustion as compared with aviation kerosene. The synthetic jet fuels should have hydrocarbon composition and be in competition with modern jet fuels produced from oil by the heat of combustion.

Technical requirements to synthetic jet fuel from alternative (non-oil) raw materials for AGTE have been developed in Central Institute of Aviation Motors n.a. P.I. Baranov (2008). First in Russia samples of liquid synthetic jet fuel from biological raw materials have been produced in Moscow University of Fine Chemical Technology in cooperation with CIAM (2009). Ethanol as widespread product of (inedible) biomass conversion is used for synthetic jet fuel production.

It is known that ethanol propagation through zeolites (with structure HZSM-5 (Si/Al)) leads to generation of aromatic and aliphatic hydrocarbons of different compositions [5]. New samples of catalysts have been used for the development of the laboratory regularities for hydrocarbons synthesis by bioethanol conversion. The catalysts are manufactured on base of zeolites of ZSM-5 type with different silicate modules and structured additives promoted by different metals and activated by thermal and mechanical methods.

Accounting results of the experimental researches, the zeolite-containing catalysts are chosen: 3%Zn/27%Al_2O_3/Fe-CKE-G50 (Si/Fe=550); SiO_2/Fe_2O_3=550MO (modified by mechano-chemical treatment); SiO_2/Fe_2O_3=550TPO (modified by thermal treatment). The most active zeolite-containing catalyst 3%Zn/27%Al_2O_3/Fe- CKE-G50 (Si/Fe = 550) with 0,2-0,5 mm particles is used for the experimental study of the ethanol conversion.

The rhenium-containing, platinum-containing, nickel-chrome-oxide, Co(Ni)-Mo/W-Al_2O_3, promoted by polyheterocompounds Mo and W are used for hydrogenising of ethanol conversion products. Rhenium- and platinum-containing catalysts show the most activity in the hydrogenising reaction.

The catalysts are prepared by standard methods including radiography, scanning electron microscope investigation and nuclear magnetic resonance.

The bioethanol conversion is studied with facilities of flow type at atmosphere and increased pressures (up to 0.6 MPa). Clear quartz reactor and stainless steel reactor are used for research under atmospheric and elevated pressures, respectively. Nitrogen is used for ethanol feeding under atmosphere pressure. The facilities have no principle differences.

The main part of facility is metallic reactor (3) located inside electric furnace (2) for heating up to 600°C.

Reactor includes the metallic pipe evaporator of 3 mm diameter. The catalyst hanging of 1 gram is located on the reactor grid. Pump (1) feeds the ethanol to the evaporator, after that vapor of the ethyl alcohol moves to the catalyst. Electric furnace (2) heats the reactor. Automatic thermoregulator controls temperature in the reactor. Pressure in the reactor is controlled by manometer (4). Throttling faucet supports the same value of pressure.

Fig. 1 represents scheme of facility for study ethanol conversion at elevated pressure.

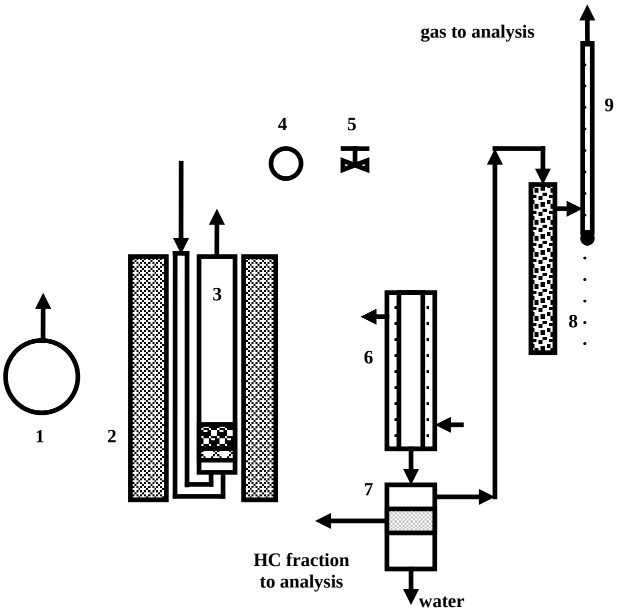

Fig.1**.** Scheme of experimental facility for fuel conversion at elevated pressures on stationary catalyst layer.
1 – pump- batcher; 2 – electric furnace;
3 – reactor block; 4 – manometer; 5 – throttling faucet; 6 – condenser;
7 – separator; 8 – scrubber; 9 – measuring device of gas flow

The reaction products come to condenser (6) cooled by running water. The products are separated on gas and liquid phases in separator (7). Liquid phase consisting of water and hydrocarbon fraction are collected in receiver. Separating funnel extracts the hydrocarbon fraction from the liquid reaction product. After scrubber (8) and measuring device of gas flow (9) gas fraction injects to atmosphere. Probe is used for analysis of gas products.

The researches of catalytic ethanol conversion are performed in the temperature range 350-450˚C, volume rate of nitrogen supply 2100-5700 h^{-1} and volume rate of ethanol supply 5000 h^{-1}.

In both cases the catalysts are treated in the nitrogen flow during 1 h at 600˚C. Gas and liquid products of the ethanol conversion are analyzed by gas chromatography and chromomatomass-spectrometry methods. The catalyst activity is estimated by the ethanol conversion and the reaction yield. Autoclave method is used for hydrogenising of products of the ethanol conversion. Fig. 2 represents the scheme of hydrogenising facility.

Rhenium-containing catalyst is used for hydrogenation under pressure 1.5 MPa and temperature 140^0C at active mixing during 30 hours with periodic hydrogen pumping. Hydrogenation of the bioethanol conversion products on platinum-containing catalyst is performed under pressure 10 MPa and temperature 250^0C during 3-4 hours. Obtained hydrocarbon product of the bioethanol conversion (synthetic oil) is distillate no containing sulfur and mazut fractions. Total recovery of the hydrocarbon products $C_1 – C_{10}$ from the bioethanol due to the developed laboratory regularities is approximately 30%.

Four samples of liquid hydrocarbon biofuel (in volume of 1 liter) are obtained from the synthetic oil produced in the laboratory:

- initial product of the bioethanol conversion (sample № 1);
- product of hydrogenation of sample № 1 (sample № 2);
- product of distillation of light fraction from sample №1, (sample №3);
- product of distillation of light fraction from sample №2, (sample №4)

All samples have been tested in accordance with Technical Requirements (TR of CIAM) for synthetic (non-oil) fuel for aviation gas turbine engines. Table represents the results of the testing. Here is shown rejected norm from the Technical Requirements.

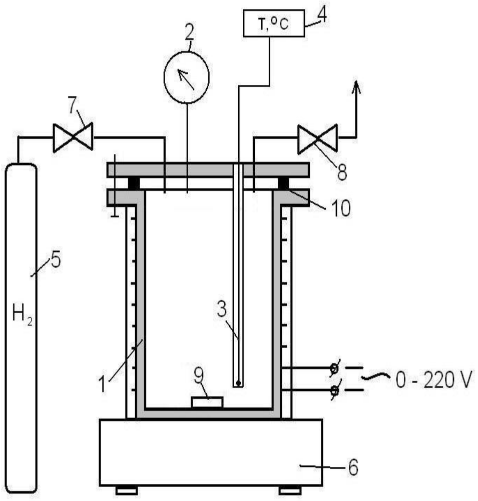

Fig.2. Scheme of facility for hydrogenising of fuel conversion products.
1 – reactor-autoclave; 2 – manometer; 3 – thermocouple; 4 – temperature sensor;
5 – hydrogen balloon; 6 – heating element; 7,8 – valves; 9 – magnetic mixer; 10 – packing.

Table

№	Parameter	TR	Sample №1	Sample №2	Sample №3	Sample №4
1	Density at 20^0C, kg/m^3, no less	755	775	755	855	790
2	Fractional composition: a) temperature of distillation start, ^{0}C, no more b) 10% is distilled at temperature, ^{0}C, no more c) 50% is distilled at temperature, ^{0}C, no more d) 90% is distilled at temperature, ^{0}C, no more e) temperature of the boiling finish, ^{0}C, no more	 135 175 225 270 280	 44,5 69,5 125 171,5 183	 56 90 127 166 196	 133 138 153 195 236	 135 144 153 166,5 196
3	Kinematic viscosity, cSt At 20^0C, no less At minus 20^0C, no more At minus 40^0C, no more	 1,25 8,0 16	 0,61 1,03 1,44	 0,83	 0,89 1,78 4,67	 1,09 2,19 3,7
4	Lower combustion heat, kJ/kg, no less	43100				43100
5	Height of sootless flame, mm, no less	25				31
6	Acidity, mg of KOH on 100 cm^3 of fuel, no more	0,7				0,1
7	Iodine number, gram of iodine on 100 gram of fuel, no more	0,5	10		8,23	0,26
8	Flash temperature measured in closed crucible, ^{0}C, no less	28				25
9	Freezing point, ^{0}C, no more	-60				Less -60
10	Thermal-oxidative stability under static conditions at 150^0C, no more a) concentration of deposit, mg on 100 cm^3 of fuel					

	b) concentration of soluble gums, mg on 100 cm^3 of fuel c) concentration of insoluble gums, mg on 100 cm^3 of fuel	6 30 3	9,6			2,0 5,5 3
11	Mass fraction of aromatic hydrocarbon, %, no more	22	51,2	18,6	51,4	6,9
12	Concentration of existent gums, mg on 100 cm^3 of fuel, no more	4	72		288	3,0
13	Mass fraction of sulfur, %, no more	0,1	absence			
14	Mass fraction of sour sulfur, %, no more	0,001	absence			
15	Mass fraction of sulphuretted hydrogen	absence	absence			
16	Test on copper plate at 100^0C during 3 h	tol.				tol.
17	Content of soap of naphthenic acids	absence				absence
18	Content of solid impurities and water	absence				absence
19	Mass fraction of naphthalene hydrocarbon, %, no more	1,5				0,06

All samples of hydrocarbon fuel are not satisfied to TR for the synthetic fuel for aviation gas turbine engines:

– sample № 1 by fractional composition, kinematical viscosity at 20^0C, concentration of aromatic hydrocarbons, iodine number, thermo-oxidation stability, gum concentration and a priori flash temperature due to light benzene fractions;

– sample № 2 1 by fractional composition, kinematical viscosity at 20^0C, concentration of aromatic hydrocarbons and flash temperature as sample № 1;

– sample № 3 by kinematical viscosity at 20^0C, concentration of aromatic hydrocarbons, iodine number and gum concentration;

– sample № 4 by kinematical viscosity at 20^0C and flash temperature.

Sample № 4 of the biofuel obtained by distillation of light fraction from sample № 2 seems to be more interesting. It should be noted that norm in TR by kinematical viscosity at 20^0C "not less than 1.25 cSt" is taken from TR for TS-1 fuel (GOST 10227-86) for reduction of viscosity influence on antiwear properties of the fuel.

Antiwear and antioxidative additives are added to Russian hydrogenation fuels (RT, T-8V, T-6). As contracted with virgin fuels, the hydrogenation fuels not contain natural heteroatomic antioxydizers and surface-active additives. Antiwear additive results in improvement of antiwear properties of the fuel and antioxydative additive leads to long-term preservation.

The same antiwear and antioxydative additives developed for RT fuel should be used for sample №4 obtained by deep hydrogenation. It results in good antiwear properties of the sample №4 in spite of decreased kinematical viscosity at 20^0C as compared with normative value. It should be noted that kinematical viscosity of the sample №4 (1,09 cSt at 20^0C) satisfies to demand of TR (GOST 10227-86) for wide-fractional T-2 jet fuel (not less 1,09 cSt). The T-2 fuel is reserve fuel for wide used TC-1 fuel.

T-2 fuel has low-boiling benzene fractions. As a result, the fuel has negative flash temperature (-18^0C).

Therefore, the parameter mismatch in kinematical viscosity at 20^0C and flash temperature is not rejected. This mismatch can be eliminated by change of TR or extraction of fractions with boiling temperature starting less 155 ^{0}C (maximum temperature of the boiling start for RT fuel from sample №4. In last case reduction of jet fuel output from the biomass is expected.

The part of synthetic jet fuel satisfying TR is ~ 10% of produced synthetic oil. Residual part hydrogenised conversion products of the synthetic oil can be used for benzene production, wide-fractional jet fuel such as T-2 (GOST10227-86) and also as raw materials for petrochemical industry.

Production cost of the synthetic jet fuel produced from ethanol and satisfying TR in modern experimental-industrial manufacture will be approximately in two times higher than production cost of standard jet RT fuel (at annual output of pilot facility of 500 metric tons of the synthetic oils and absence of excises on ethyl alcohol).

Russia is surrendered to advanced countries in replacement of traditional fuel on alternative ones. There are not pilot facilities for experimental-industrial production of the samples of alternative jet fuels. The half of produced oils

(~250 millions tons) is sell to foreign countries. However in future we should produce the alternative fuels and fueling by foreign alternative fuels in international airports.

The scientific researches in Russia should be continued for the next development of technical requirements to hydrocarbon biofuel synthesis for aviation gas turbine engine in order to increase the fuel output from biomass and decrease of its production cost. Except ethanol, it is necessary to consider application of other sources of biomass (for example, algae).

References

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