

Scientific bases of biomass processing into basic component of aviation fuel

V V Kachalov¹, V A Lavrenov¹, I I Lishchiner¹, O V Malova¹,
A L Tarasov² and V M Zaichenko¹

¹ Joint Institute for High Temperatures of the Russian Academy of Sciences, Izhorskaya 13
Bldg 2, Moscow 125412, Russia

² Zelinsky Institute of Organic Chemistry of the Russian Academy of Sciences, Leninsky
Avenue 47, Moscow 119991, Russia

E-mail: v.a.lavrenov@gmail.com

Abstract. A combination of feedstock pyrolysis and the cracking of the volatile pyrolysis products on the charcoal at 1000 °C allows to obtain a tarless synthesis gas which contains 90 vol% or more of carbon monoxide and hydrogen in approximately equal proportions. Basic component of aviation fuel was synthesized in a two-stage process from gas obtained by pyrolytic processing of biomass. Methanol and dimethyl ether can be efficiently produced in a two-layer loading of methanolic catalyst and γ -Al₂O₃. The total conversion of CO per pass was 38.2% using for the synthesis of oxygenates a synthesis gas with adverse ratio of H₂/CO = 0.96. Conversion of CO to CH₃OH was 15.3% and the conversion of CO to dimethyl ether was 20.9%. A high yield of basic component per oxygenates mass (44.6%) was obtained during conversion. The high selectivity of the synthesis process for liquid hydrocarbons was observed. An optimal recipe of aviation fuel B-92 based on a synthesized basic component was developed. The prototype of aviation fuel meets the requirements for B-92 when straight fractions of 50–100 °C (up to 35 wt%), isooctane (up to 10 wt%) and ethyl fluid (2.0 g/kg calculated as tetraethyl lead) is added to the basic component.

1. Introduction

Continuous growth of energy consumption is causes to search for ways to expand the raw material base for the liquid motor fuels production. Technology of integrated synthesis is an efficient method of syngas conversion into liquid motor fuel through intermediates such as methanol and dimethyl ether. The technology is especially interesting for the synthesis gas with a low H₂/CO ratio obtained by the thermal biomass conversion methods [1]. In this case the attractiveness of combined processes of methanol and dimethyl ether synthesis is significantly increased from a thermodynamic standpoint [2]. Integrated synthesis can be carried out with high efficiency even at relatively low pressure which makes the process very flexible.

Currently Russia does not have its own production of low-octane aviation fuel. Imports mainly represented by such fuel brands as Avgas 100LL or Avgas 100VLL, which is produced in accordance with ASTM D 910 and DEF STAN 91-90. These fuels are standard for a plenty of popular planes and helicopters: AN-2, Ka-26, Gessna aircrafts, Robinson helicopters and others, which is widespread in Russia. Making an analogue of Avgas 100LL or Avgas 100VLL, meeting the requirements of ASTM D 910 or DEF STAN 91-90 or Russian standard GOST



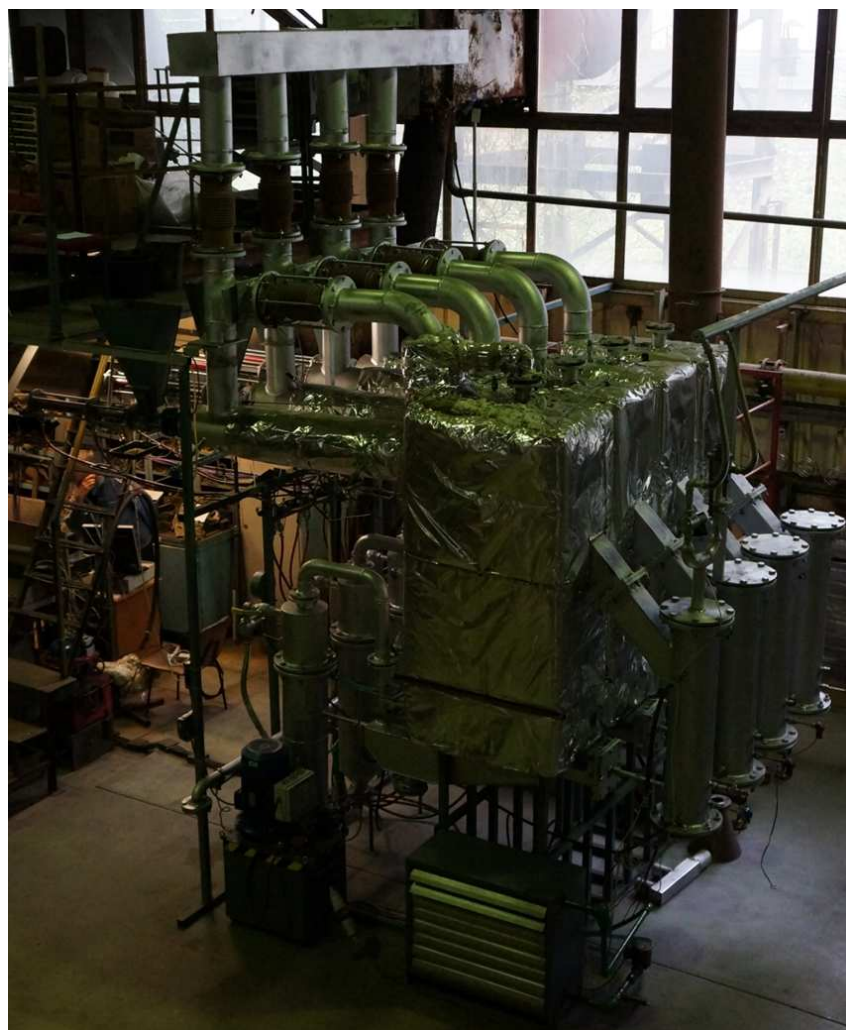


Figure 1. Biomass processing unit.

55493 developed on their basis is the main task of restoring the production of aviation fuel in Russia [3]. This article observes some scientific guidelines along which the production of aviation fuel from biomass can be organized.

2. Synthesis gas production

A method for the two-stage pyrolytic processing of various types of biomass into synthesis gas is described in detail in [4,5]. The two-stage thermal conversion of biomass into tarless synthesis gas is performed sequentially in two reaction volumes with specific temperature conditions. Whole the process is carried without access of oxidant. The first stage is pyrolysis. Biomass is heated up to 600 °C in hot wall reactor (the first reaction volume). There occurs the formation of pyrolysis products: charcoal and volatile. They are moved into the second reaction volume—cracking reactor. Here charcoal is heated up to 1000 °C. During the second stage volatile pyrolysis products are blown through the thick charcoal bed. The destruction of complex molecules of volatile (tars) on the surface of charcoal is occurred. The extended surface of charcoal promotes a considerable increase of the decomposition reactions rate. The biomass processing unit photo is shown in figure 1.

Table 1. Chemical composition of the synthesis gas.

Component	vol%
Hydrogen (H ₂)	46.8
Carbon monoxide (CO)	48.5
Methane (CH ₄)	0.35
Nitrogen (N ₂)	3.95
Carbon dioxide (CO ₂)	0.4

A certain thickness of the charcoal bed provides required duration of interaction for complete decomposition of pyrolysis tars. The main products of the decomposition process of volatile are carbon monoxide and hydrogen. Thus completely excluded the condensable fraction in synthesis gas. The entrainment of fly ash and carbon dust is almost absent due to the low syngas flow rate. The syngas is mid-calorific (about 10–12 MJ/m³).

A synthesis gas with a ratio of H₂/CO = 0.96 was obtained from wood biomass in two-stage thermal process and was used as a feedstock in the research. The chemical composition of the synthesis gas is shown in table 1.

3. Production of aviation fuel basic component from synthesis gas

The research was carried out using a laboratory installation composed of two reactors in tandem: R1 (a reactor for the synthesis of oxygenates) and R2 (a reactor for the synthesis of motor fuel basic component). A heated line between the reactors was fitted with a sampler to test the gas coming from the first reactor. The oxygenates-to-syngas synthesis involved the use of a two-layer catalyst. The upper layer (60 vol%) represented a methanol-synthesis catalyst composed as follows: ZnO—26.4, CuO—62.3, Al₂O₃—10.04 (wt%), and the lower layer (40 vol%)— γ -Al₂O₃ of the A-64 brand (Ryazan).

During the synthesis of the motor fuel basic component a zeolite-containing catalyst of the following structure was used:

- high-silica zeolite SiO₂/Al₂O₃ = 50 pentasil group—70.8 wt%;
- binding Al₂O₃—26.0 wt%;
- zink oxide—2.0 wt%;
- lanthanum oxide—1.2 wt%.

The reaction gas underwent an isothermal analysis at a temperature of 55 °C using a chromatograph (model 3700) coupled with a pair of packed columns HayeSep-Q (CO + H₂, CH₄, CO₂, CH₃OH and dimethyl ether), molecular sieves 5A (H₂, N₂, CH₄, CO), and a katharometer as a detector.

Liquid products were analyzed according to ASTM 6729 on a chromatograph (Kristall 4000) using a capillary column HP-1 100 m × 0.25 mm × 0.5 μ m and flame ionization detector.

Table 2 displays the mass balance of the oxygenate-synthesis reaction in R1 at 50 bar and GHSV (gas hourly space velocity) 4000 hr⁻¹.

The obtained result shows that dimethyl ether and methanol can be efficiently produced form the synthesis gas using the two-layer catalyst loading. Total conversion of CO to dimethyl ether and methanol per pass (using the syngas with a ratio of H₂/CO = 0.96) was 38.2%. Conversion of CO to CH₃OH was 15.3% and conversion of CO to dimethyl ether was 20.9%.

Table 2. The mass balance of the oxygenate-synthesis reaction in R1 at 50 bar and GHSV (gas hourly space velocity) 4000 hr⁻¹.

R1 inlet	l/hr	g/hr	vol%	wt%	R1 outlet	l/hr	g/hr	vol%	wt%
CO	194.0	242.5	48.5	85.66	CO	119.89	149.87	50.79	52.93
H ₂	187.2	16.71	46.8	5.90	H ₂	38.98	3.48	16.51	1.23
CO ₂	1.6	3.14	0.4	1.11	CO ₂	1.94	3.81	0.82	1.35
N ₂	15.8	19.75	3.95	6.98	N ₂	1.40	1.00	0.59	0.35
CH ₄	1.4	1.00	0.35	6.98	CH ₄	3.62	2.91	1.53	1.03
H ₂ O	0.0	0.00	0.00	0.00	CH ₃ OH	29.68	42.4	12.57	14.98
					DME ^a	40.55	79.64	17.18	28.13
TOTAL:	400.0	283.11	100	100	TOTAL:	236.07	283.11	100	100

^a Dimethyl ether.**Table 3.** The mass balance of the motor fuel basic component in R2 produced at 370 °C and 50 bar.

R2 inlet	g/hr	wt%	R2 outlet	g/hr	wt%
CO	149.87	52.9	CO	148.37	52.41
H ₂	3.48	1.2	H ₂	3.91	1.38
CO ₂	3.81	1.3	CO ₂	5.31	1.88
CH ₄	1.00	0.4	CH ₄	1.12	0.40
H ₂ O	2.91	1.0	C ₂ H ₆	0.17	0.06
CH ₃ OH	42.4	15.0	C ₂ H ₄	0.11	0.04
DME	79.64	28.1	C ₃ H ₈	2.20	0.78
			C ₃ H ₆	0.33	0.11
			i-C ₄	1.11	0.39
			n-C ₄	1.07	0.38
			C ₄ H ₈	0.29	0.10
			Basic component	54.37	19.20
			H ₂ O	59.34	20.96
			Reaction gas	5.42	1.91
TOTAL:	283.11	100	TOTAL:	283.11	100

Table 3 shows the mass balance of the motor fuel basic component produced in R2 from the oxygenates contained in the gas exiting from R1.

Research shows a high yield of the basic component of an aviation fuel per feed oxygenates (44.6%) and a high selectivity towards liquid hydrocarbons (90.9%). Table 4 presents the hydrocarbon composition of obtained basic component of aviation fuel.

The basic component contains very high-octane compounds such as aromatic hydrocarbons (51.47%) and isoparaffin hydrocarbons (29.79%).

Table 4. Hydrocarbon composition of obtained aviation fuel basic component.

Component	wt%
benzene	1.79
aromatic hydrocarbons	51.47
isoparaffin hydrocarbons	29.79
naphthene hydrocarbons	8.86
paraffin hydrocarbons	7.42
olefinic hydrocarbons	2.30

Table 5. Physical and chemical properties for the aviation fuel composition [3].

Index	CUTR ^a	B-92 ^b	B-92 ^c	Base component	Comp. No. 2	Test method
Fraction composition:						
init. boiling point (\geq °C)	—	40	40	39.1	41.9	GOST (State standards) 2177
10% distilled (\leq °C)	82	82	82	62.7	61.9	
50% distilled (\leq °C)	105	105	105	116.9	93.0	
90% distilled (\leq °C)	170	145	145	154.9	144.8	
97% distilled (\leq °C)	—	180	180	167.2	166.8	
Residue (\leq %)	1.5	1.5	1.5	1.4	1.0	
Loss (\leq %)	1.5	—	1.5	0.5	1.1	
Vapour pressure range (kPa)	29.3–49.0	29.326–47.988	29.3–49.0	52.5	45.7	GOST 1756
Calorific value (\geq MJ/kg)	—	42.737	42.737	42.150	43.500	GOST 21261
Motor octane number (\geq)	91	91.5	91.5	85.2	80.6	GOST R 52946

^a Customs Union Technical Regulation.^b Technical specifications.^c GOST project.

4. Development of an aviation fuel recipe

Upon consideration of a variety of compositions, the following composition for aviation fuel has been chosen. Prototype sample of the following structure was prepared:

- basic component—55 wt%;
- straight-run fraction 50–100 °C—35 wt%;
- reference isooctane—10 wt%.

The prototype was subjected to analysis of fraction composition, vapour pressure, calorific value and motor octane number (MON). These values was matched against the Technical Specs 38.401-58-47-92 for B-92 and the basic component, as shown in table 5.

The composition has unsatisfactory knock rating without ethyl fluid supplements. The MON value shall be increased by 11 units at least. Adding ethyl fluid to the maximum permissible concentration (2.0 g/kg calculated as tetraethyl lead) allows to increase MON up to 92.6 that satisfies Tech Specs requirements for aviation fuel B-92.

5. Conclusions

A method for the two-stage pyrolytic processing of various types of biomass into synthesis gas was described. It is a combination of feedstock pyrolysis at 600–700 °C and the cracking of the volatile pyrolysis products on the biomass charcoal at 1000 °C. According to the researches, biomass (vegetable origin) processing allows to obtain a synthesis gas which contains 90 vol% or more of carbon monoxide (CO) and hydrogen (H₂) in approximately equal proportions. Such a synthesis gas contains no tar and its calorific value is 10–12 MJ/Nm³.

Basic component of aviation fuel was synthesized in a two-stage process from gas obtained by pyrolytic processing of biomass. Methanol and dimethyl ether can be efficiently produced in a two-layer loading of methanolic catalyst and γ -Al₂O₃. The total conversion of CO per pass was 38.2% using for the synthesis of oxygenates a synthesis gas with adverse ratio of H₂/CO = 0.96. Conversion of CO to CH₃OH was 15.3% and the conversion of CO to dimethyl ether was 20.9%. A high yield of basic component per oxygenates mass (44.6%) was obtained during conversion. The high selectivity of the synthesis process for liquid hydrocarbons was observed.

An optimal recipe of aviation fuel B-92 based on a synthesized basic component of was developed. The prototype of aviation fuel meets the requirements for B-92 when straight fractions of 50–100 °C (up to 35 wt%), isooctane (up to 10 wt%) and ethyl fluid (2.0 g/kg calculated as tetraethyl lead) is added to the basic component.

Acknowledgments

The work was supported by the Ministry of the Russian Federation for Education and Science (project No. 14.607.21.0134, unique identifier RFMEFI60715X0134).

References

- [1] Batenin V M, Bessmertnykh A V, Kosov V F, Sinel'shchikov V A and Zaichenko V M 2010 *Therm. Eng.* **11** 946–952
- [2] Bushman A V, Lomonosov I V, Fortov V E and Khishchenko K V 1994 *Khim. Fiz.* **13**(5) 97–106
- [3] *Technical Regulations 013/2011 of the Customs Union "On the Requirements for Motor and Aviation Gasoline, Diesel and Marine Fuel, Propellants and Fuel Oil"* (Resolution No. 826 of the Customs Union)
- [4] Kosov V F, Kosov V V, Sinelschikov V A and Zaichenko V M 2014 *Proc. 5th Int. Conf. on Bioenvironment, Biodiversity and Renewable Energies (Chamonix)* 9–13
- [5] Kosov V F, Lavrenov V A and Zaitchenko V M 2015 *J. Phys.: Conf. Ser.* **653** 012031