Utilization Efficiency of Aramide Polymeric Materials of the Cases of Solid-Propellant Missiles

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Abstract
Aramide polymeric wastes in the form of cases solid-propellant missiles were pyrolyzed in an externally heated fixed-bed reactor. The received mixture of liquid hydrocarbons has been subjected to cracking process with the purpose of alternative diesel fuel of wide fractional content production. The analysis of properties of this fuel and results of the diesel engine tests with this fuel, have shown a principal opportunity of such alternative fuel usage in diesel engines without modifying of their design.

Keywords: Processing; Aramide plastics waste; Alternative diesel fuel; Efficiency; Liquid hydrocarbons.

I. INTRODUCTION

At present Ukraine is a non-nuclear state, on which territory there is no nuclear weapons and means for its delivery. According with this status and international agreements Ukraine has transferred all its nuclear weapons to Russia and all means (equipment) for nuclear weapons delivery are to be destroyed.

Utilization of the polymer case of solid-propellant rockets presents most difficulty. These cases were designed so that they are able to resist various destroying factors. Therefore their utilization requires much power input and is very dangerous for the environment.

Team of researchers at State Design Bureau "Yuzhnoe" and National Shipbuilding University is currently working on project # 3963 funded by Ukrainian Scientific-Technological Center (USTC) and together developed an effective utilization technology for polymer cases of the solid-propellant missiles. Processes of controlled pyrolysis and cracking are in the basis of this technology; these processes lead to decomposition of the polymeric material into solid carbon residue and mixture of the liquid hydrocarbons.

Technological process' parameters can be optimized in such a way that techno-chemical properties of this mixture of the liquid hydrocarbons may become close to properties of diesel fuel. Such alternative fuel may be used in the modern stationary and transport internal combustion engines (ICE) with changes in the engines' design requiring only adjustment of the fuel delivery system.

Amount of alternative diesel fuel which is obtained during utilization of the polymer aramide composite is enough not only to cover energy expenses of the technological process but also to receive certain amount of commodity fuel.

II. EXPERIMENTAL

Aramide synthetic fiber – poly–para–phenylene terephtalamides (Kevlar) - is the base of the composite material of polymer cases of the solid-propellant rockets. This fiber consists of benzyl rings, connected via *–NH–CO–* group between one another. Strong intermolecular connections are formed between hydrogen and oxygen remaining which ensure high mechanical and thermal durability of the entire fiber. Aramide fiber structure is presented in the picture 1. In order to ensure needed properties aramide composite contains stuffing such as rubber, epoxide resin, capron thread, fluoroplastic film, and technical thread – bicarbolone.

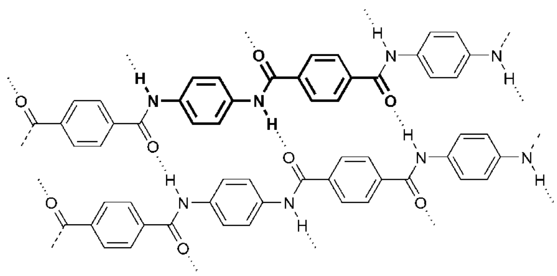

Fig.1 Para-aramide structure.

Controlled pyrolysis and cracking are in the basis of the main technological process, which secures obtaining of alternative diesel fuel with expected properties. Experimental work, which was carried our in the "Advanced Energy Technologies" Laboratory, less stable thermoplastic stuffing such as (epoxide resin, rubber and other polymeric materials) were first to disintegrate at pyrolysis' temperature between 800…900K; aramide fiber was last to decompose.

Pyrolysis' products may be divided into three groups: gases, liquid hydrocarbons and carbon residue.

Generalized chemical formula of the polymer compounds' mixture can be presented as $(C_6H_{10}O_5)_n$. In this case pyrolysis chemical reaction of these thermoplastic polymers may be presented as follows:

$$(C_6H_{10}O_5)_n \rightarrow$$
$$\rightarrow n\, C_{x1}H_{y1}O_{z1} + m\, C_{x2}H_{y2}O_{z2} + l\, C_{x3}H_{y3}O_{z3} + k\, H_2O\,,$$

where: $n\, C_{x1}H_{y1}O_{z1}$ – gaseous products; $m\, C_{x2}H_{y2}O_{z2}$ – liquid products; $l\, C_{x3}H_{y3}O_{z3}$ – solid carbon residue. In general cases, following chemical reactions take place:

$$C_6H_{10}O_5 + 0{,}5O_2 \rightarrow 6CO + 5H_2;$$
$$C_6H_{10}O_5 + H_2O \rightarrow 6CO + 6H_2;$$
$$C_6H_{10}O_5 + H_2 \rightarrow \text{mixture of liquid hydrocarbons} + H_2O;$$
$$C_6H_{10}O_5 + 12H_2 \rightarrow CH_4 + 5H_2O;$$
$$C_6H_{10}O_5 + CO + H_2O \rightarrow \text{mixture of liquid hydrocarbons}.$$

Hydrogen, that is a part of the compounds, may remain in a free state or become a part of hydrocarbons or water, as a result of these chemical reactions. According to all of the above, oxidizing and reduction reactions as well as Pyrolysis reactions' character depends on a number of factors; approximated gas' components are presented in Table I.

TABLE I
COMPONENTS OF PYPOLYSIS GAS

#	Components	%
1.	Ethylene	13,5
2.	Propylene	8,1
3.	Butane	7,2
4.	Pentane	3,8
5.	Isoprene	1,4
6.	Methane	20,3
7.	Ethane	17,4
8.	Propane	7,6
9.	Butane	2,7
10.	Pentane	1,0
11.	Hydrogen	13,5
12.	Carbon monoxide	2,4
13.	Carbon dioxide	1,1

Oxidation reactions give a mixture of liquid hydrocarbons, which presents row materials for obtaining alternative diesel fuel. Techno-chemical properties and content of these hydrocarbons are presented in the Table II.

TABLE II
TECHNO-CHEMICAL PROPERTIES OF LIQUID HYDROCARBONS

#	Properties	Units	Value
1.	Density	g/cm^3	0,9472
2.	Kinematics viscosity at 80^{o}C	mm^2/c	3,0
3.	Ash content	% mass.	0,1
4.	Flash point in open crucible	^{o}C	46
5.	Molar mass	g/mol	180
6.	Elementary content:		
	Carbon	% mass.	80,5
	Hydrogen	% mass.	9,4
	Nitrogen	% mass.	0,3
	Oxygen	% mass.	9,8
7.	Distillation test:		
	Start of distillation	^{o}C	70
	Distils at 100 ^{o}C	% vol.	11,0
	at 150 ^{o}C	% vol.	19,0
	at 200 ^{o}C	% vol.	36,0
	at 250 ^{o}C	% vol.	48,0
	at 300 ^{o}C	% vol.	62,5
	at 350 ^{o}C	% vol.	73,5
8.	Calorific value	MJ/kg	36,6

Disintegration of aramide fiber is taking place parallel to pyrolysis of thermoplastic polymers process. This fiber has high thermal resistance and its thermal decomposition is reduced to breakage of atomic bonds between hydrogen and nitrogen atoms, which are attached to the benzene rings, and also tear off of the oxygen atoms from benzene rings.

First, aramide fiber losses water (approximately 3.1% mass) and then it is disintegrated in two stages: tear off the hydrogen from nitrogen followed by tear off the hydrogen from the main structure. These fibers do not disintegrate at temperature under 480 ^{o}C and only when temperature exceeds 500 ^{o}C active pyrolysis process begins.

hydrogenation process take place during pyrolysis process.

Content of thermoplastic polymer materials in the cases of solid-propellant rockets is about 50%. About 1% of gaseous compounds, 21% of liquid hydrocarbons and 28% of solid carbon residue is formed in the result of these polymers' pyrolysis.

Sample of precipitated mixture of liquid hydrocarbons which are obtained from experimental unit as a result of aramide composite pyrolysis is presented in Fig. 2a. As becomes evident from the analysis, there are 12% of solid residue, which is presented by a mixture of heavy paraffins, 26% of water and 62% of mixture of liquid hydrocarbons fractions in the hydrocarbon product.

Residue of the liquid hydrocarbons is presented on Fig. 2b. Analysis of this product had shown that it consist of about 91% of diesel fractions, 8% of benzene fractions and 1% of non-identified light hydrocarbons.

a b

Fig. 2 Samples of liquid hydrocarbons that are obtained during aramide composite pyrolysis.

Precipitate of the liquid hydrocarbons mixture was subject to the cracking process in order to obtain alternative diesel fuel, with properties that allow this fuel to be used in diesel engines. Table III presents main techno-chemical properties of the alternative diesel fuel that is obtained in the result of cracking of aramide composite pyrolysis product and compared to standard diesel fuel.

Analyzing data presented, it becomes evident that alternative diesel fuel has properties that are similar to the properties of the standard diesel fuel and therefore alternative diesel fuel can be used in diesel engines.

Samples of solid residue that is obtained in the result of aramide composite pyrolysis are presented on Fig. 3. There are 90% of carbons and up to 10% of heavy solid hydrocarbons in the mixture.

In order to determine actual characteristics of diesel engine when using alternative diesel fuel, obtained in the result of aramide composite waste utilization, there were test conducted using diesel-generator 6ЧН12/14. Indicator diagrams of this engine's work using standard diesel fuel E590 and alternative fuel sample #1 and #2 were received. Engine's function when using alternative diesel fuel sample #2 is very similar when using standard diesel fuel.

TABLE III
TECHNO-CHEMICAL PROPERTIES OF LIQUID HYDROCARBONS

##	Quality requirements	Conventional Diesel Fuel	Alternative Diesel Fuel #1
1.	Cetane number	45	47
2.	Distillation test:		
	50% distils at temperature °C, not more	280	270
	96% distils at temperature °C, not more	360	350
3.	Kinematics viscosity at 20 °C, сСт	3,0–6,0	3,4
4.	Sulphur content, %, not more	0,2	0,1
5.	Copper plate corrosion test	OK	OK
6.	Pitches concentration in fact, not more	40	35
7.	Acidity, not more	5	7,5
8.	Iodine number, not more	6	6
9.	Ash, % not more	0,01	0,005
10.	Density at 20 °C, kg/m^3, not more	860	810


a b c
Fig. 3 Solid hydrocarbon residue.
a – highly dispersed fraction, b – large fragments,
c – incompletely pyrolysed fragment.

It is worth noting that alternative diesel fuel sample #2 differs from sample #1 by lower content of benzene fractions. Indicator diagrams (cylinder pressure) of the diesel engine 6ЧН12/14 for both operational regimes: with conventional diesel fuel (blue curve), with alternative diesel fuels #1 (red curve) and #2 (green curve) are presented in Fig. 4.

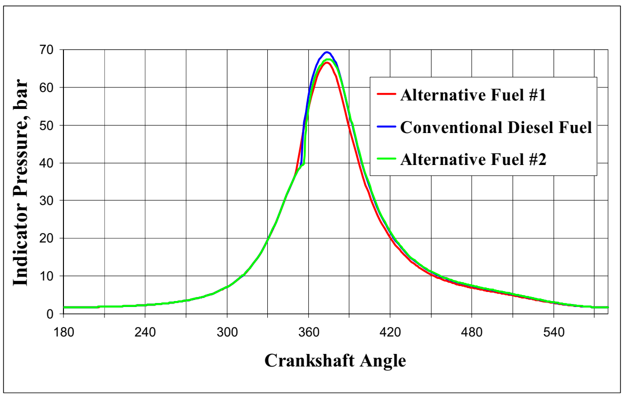

Fig.4 Indicator Diagrams for ICE Operating with Alternative Fuel from aramide composite.

Analysis of these diagrams allows to state, that changes in the pressure in engines' cylinders when using alternative diesel fuel obtained from aramide composite waste utilization process is not considerable different from pressure in engine's cylinders, when using standard diesel fuel. Observed premature ignition of the alternative diesel fuel as well as decrease of maximal pressure is explained by presence of easy-boiling benzene fractions.

The experimental researches prove that the satisfactory engine's operation may be reached by fuel equipments' tuning without additional changing in engine's construction. Engine's power, specific fuel consumption and ecological indexes were in the frame of the requirements.

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