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Synthetic liquid fuels obtained by thermolysis of animal waste

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Abstract

Modern methods of recycling organic waste are not considered viable today. Therefore, an important advantage of the proposed technology is to obtain mineral fuel products as an output. The technologies of high-temperature processing are based on thermal decomposition of waste without oxygen at high temperature. In pyrolysis, wastes are converted into gaseous, liquid and solid fuels. Thereby, the properties and composition of the liquid feedstock obtained by pyrolysis with a boiling temperature in the range of X.I. (38) - 180 °C, 180 - 320 °C and more than 320 °C were investigated . Residue with a boiling temperature over 320 ° C (52.4% vol.) is the main portion of the synthetic liquid fuels (SLF). It can be attributed to fuel oil grade 100 and used as boiler fuel or fuel oil additives according to the studied physicochemical parameters.

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1. Introduction

During the last decade, the volume of food production industry is steadily growing[1-3]. Disposal and recycling of organic wastes becomes a serious environmental problem for most of the processing enterprises in developing countries.

Organic wastes decompose during long time and produce a favorable environment for the development of harmful bacteria and parasites that contribute to their spread. According to the World Health Organization, organic animal waste may be a factor in the transfer of more than 100 infectious and parasitic diseases. Ammonia compounds contained in the biological waste which are characterized by high toxicity are also especially dangerous[3]. If the waste of livestock enterprises may be recycled and used as fertilizer in agriculture, for the food industry, producing meat and dairy products[1], the issues of waste management are even more relevant.

Disposal of waste will improve the ecology of the environment and help get green energy.

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Existing technology offers several solutions to the issue of biological waste disposal:

- Pressing and burial in the landfills;
- Biodegradation using bacteria and earthworms[4,5];
- High-temperature processing[6-12].

In most cases biological waste is used to produce methane. "Biogas" technology is based on the enzymatic decomposition of organic materials and the collection of emitted methane[4]. These processing plants require large areas of expensive equipment and, consequently, big investments. In winter, they need heating which leads to additional energy costs.

The technologies of high-temperature processing are based on thermal decomposition of waste without oxygen at a temperature of 600 – 800 °C. In pyrolysis wastes are converted into gaseous, liquid and solid fuels. The main advantages of using high-temperature processing method: processing industry is compact, highly efficient and has a high quality of waste treatment and environmental safety of the products[13].

The purpose of this research is to obtain and research the properties and composition of the liquid product of pyrolysis of animal waste to determine the possibility of using it as an alternative fuel.

2. Experimental

2.1. Technology for producing synthetic liquid fuels

As the object of research the liquid product of pyrolysis of animal waste produced on an experimental pilot plant Complex «GR» "Research and Production Enterprise" GEOCE" is chosen[13]. An experimental industrial plant capacity is 500 kg / h (fig. 1).

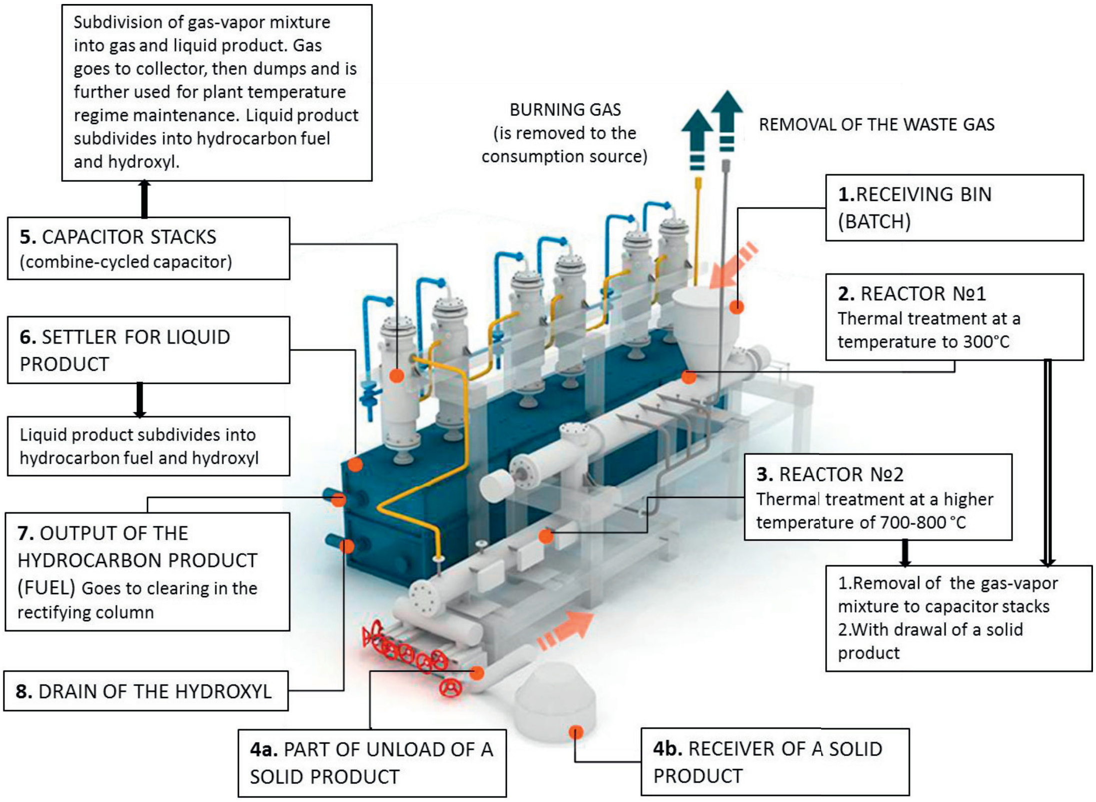

Figure 1. Scheme of the experimental plant “GR-1”

Feedstock (animal waste) is loaded into a receiving bin, and then it enters the reactor 1, where the thermal treatment occurs at a temperature of 300 °C. Further the mixture is decomposed at a higher temperature of 700-800 °C in the reactor 2. From both the reactors the gas-vapor mixture is removed to capacitor stacks during the heat treatment, and solid product is withdrawn to a receiver of solid product. Capacitor stacks contain subdivision of gas-vapor mixture into gas and liquid product. Gas goes to the collector, then dumps, and is further used for plant temperature regime maintenance. The liquid product subdivides into hydrocarbon fuel and hydroxyl in a settler for liquid product.

2.2. Analysis of synthetic liquid fuels and primary distillation products

The pyrolysis liquid product is a stable emulsion. For research, it is necessary to dehydrate the original synthetic liquid fuels. Dehydration was carried out in an autoclave with a demulsifying agent at 110 °C and a pressure of 12.5 MPa.

Physicochemical characteristics of the oils were determined according to appropriate ASTM methods: ASTM D4006-11, ASTM D287-92 (2006), ASTM D4294-10, ASTM D7042-11, ASTM D2892- 13, ASTM D5950-12a, ASTM D93- 11, ASTM D482- 07, ASTM D240- 09.

Organic liquids were analyzed by gas chromatography-mass spectrometry (GC-MS) using a TRACE DSQ gas chromatograph. Elemental composition (carbon, hydrogen, and nitrogen) was determined in an analyzer CHNS Flash2000.

3. Results and Discussion

3.1. Characterization of the Feedstock

Liquid mass has dark color, a pungent smell and looks like oil. Synthetic liquid fuel is a stable inverse emulsion – "water in oil", in which the original water content was 6.86 wt. %. The dehydration in an autoclave with the addition of a demulsifying agent "Separol" followed by heating with calcium chloride allowed water volume fraction to decrease to 0.58 % vol.

The analysis of the feedstock is presented in Table 1.

Table 1. The characteristics of the pyrolysis liquid product

Indicator	Test result
Content of water, % wt.	0.58
Density at 20 °C, kg/m^3	930.70
Kinematic viscosity of the emulsion at 20 C, mm^2/s	54.90
Kinematic viscosity at 20 C, mm^2/s	291.90
Mechanical impurities, % wt.	0.03
Content of sulfur, % wt.	0.34
Content of asphaltenes, % wt.	6.00
Content of resins, % wt.	27.50

The results of the elemental composition of the original SLF, selected resins, asphaltenes and selected mechanical impurities are shown in Table 2.

Table 2. Elemental composition

Sample name	Content of elements, % wt.			
	C	S	H	N
SLF	73.0	0,2	9.3	4.5
Resins	69.0	0.0	7.5	4.8
Asphaltenes	72.8	0.0	7.0	9.4
Mechanical impurities	66.9	0.0	6.9	7.9

Ratio of 100 H/C in the original sample SLF was 12.7, which identifies heavy oil. SLF is also present in significant nitrogen content, which is not typical for oil and can be explained by a high content of nitrogen in animal tissues, that goes through the process of pyrolysis into the core product. Ratio of 100 N/C of the resins and asphaltenes was 10.8 and 9.7, respectively. The values may indirectly confirm the presence of high molecular weight hydrocarbons in the original sample IGT.

The results of fractional composition of synthetic liquid fuels are shown in Table 3. Residue with a boiling temperature over 320 °C (52.4% vol.) is the main portion of SLF.

Table 3. Fractional composition

Indicator	Result, % vol.

IBP(38) – 180 °C	27,9
180 °C – 320 °C	16,3
remain > 320 °C	52,4
loss	3,4

3.2. Characteristics of primary distillation products

The fraction with a boiling temperature within X.I. (38) - 180 °C is similar to gasoline. Basic physical and chemical parameters are given in Table 4.

Table 4. Characteristics of fraction X.I. – 180 °C

Indicator	Test result
Mass fraction of water, % wt.	10.90
Density at 20 °C, kg/m^3	808.30
Kinematic viscosity at 20 °C, mm^2/s	0.99
Fractional composition	
IBP	38.00
50 %, °C	100.00
90 %, °C	175.00
Content of sulfur, % wt.	0.46
Water-soluble acids and bases	Alkaline
Test on copper plate	Class 1
Color	Vinous
pH	10

The fraction contains a large amount of water - 10.9 % vol. This fraction has an alkaline impact and high sulfur content. Values of viscosity and density with respect to the viscosity and density of gasoline that average 0.4-0.8 and 710.0 are accordingly inflated.

Analysis results of the hydrocarbon fraction using gas chromatography-mass spectrometry showed a high content of oxygenated compounds, such as phenol and xylene; nitrogen compound such as quinoline. The sample also contains saturated hydrocarbons, pentane, hexane, heptane, octane, nonane, decane, undecane, dodecane, tridecane; olefins: hexene, octene, decene, undecene, dodecene, tridecene; aromatic hydrocarbons, toluene, benzene, styrene. The molecular weight of the compounds of this fraction varies between 72 and 184 g/mol.

Fraction with a boiling temperature in the range 180 – 320 °C can be attributed to diesel boiled at a temperature no higher than 360 °C. Table 5 presents data on the definition of basic physical and chemical characteristics of this fraction.

Table 5. Characteristics of fraction 180 – 320 °C

Indicator	Test result
Cetane number	37.0
Content of water, % wt.	absent
Density at 20 °C, kg/m^3	865.0
Kinematic viscosity at 20 °C, mm^2/s	4.9

Fractional composition	
IBP	180.0
50 %, °C	250.0
90 %, °C	310.5
Content of sulfur, % wt.	0.2
Water-soluble acids and bases	absent
Freezing point, °C	-16.0
Flash point in closed crucible,°C	70.0
Limited temperature of filterability,°C	-13.0
pH	8.0
Color	Deep-brown

This fraction meets such requirements as: viscosity, sulfur content, melting point, flash point, limiting filterability temperature, water content and water-soluble acids and alkalis. Such indicators as density fraction and cetane number do not correspond to the established norms.

Analysis results of the hydrocarbon fraction using gas chromatography-mass spectrometry revealed the presence of mainly saturated and olefinic hydrocarbons having a molecular weight ranging from 162 to 254 g / mol. The sample also contains nitrogen compounds: quinolone, indole and a small amount of aromatic compounds: indene, fluorene. The results of the hydrocarbon analysis of gasoline and diesel fractions are consistent with hydrocarbon composition of oils[14,15].

The residue with boiling temperature more than 320 °C can be attributed to fuel oil grade 100. Basic physical and chemical parameters are given in Table 6.

Table 6. Characteristics of residue with a boiling temperature over 320 °C

Indicator	Test result
Content of water, % wt.	absent
Content of sulfur, % wt.	0.16
Kinematic viscosity at 80 °C, mm^2/s	17.30
Kinematic viscosity at 100 °C, mm^2/s	10.00
Flash point in open crucible,°C	246.00
Ash content, %	0.05
Freezing point, °C	12.00
Density, kg/m^3	970.00
Coking, %	19.4
Heat of combustion, kJ/kg	37449.00
Water-soluble acids and bases	absent
pH	6

The fraction satisfies such indicators as kinematic viscosity, density, pour point, flash ash, coking, the absence of water-soluble acids, and alkalis sulfur content.

4. Conclusion

Research of the properties and composition of the liquid product – the synthetic liquid fuels (SLF) obtained by pyrolysis and its fractions showed that animal waste may be used as an alternative source of fuel.

The fraction with a boiling temperature within X.I. (38) – 180 °C and 180 - 320 °C due to the fact that this fraction do not meet the requirements by almost all indicators and in the heating process has unpleasant pungent odor, it is recommended for use only after additional processing.

The residue with a boiling temperature more than 320 °C according to the studied physicochemical parameters can be attributed to fuel oil grade 100 and used as boiler fuel or fuel oil additives. Work is performed as a part of the state Russian Government Project "Science" 1.13.10.2014.

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References

1. Wang, L.J. Production of bioenergy and bioproducts from food processing wastes: A review. *Transactions of the ASABE* 2013. p. 217-229.
2. Serio M., Kroo E., Florczak E., Wójtowicz M., Wignarajah K., Fisher J. A prototype pyrolysis/oxidation system for solid waste processing. *SAE Technical Papers 2005 35th International Conference on Environmental Systems*, ICES 2005; Rome; Italy: 11 July 2005 through 14 July 2005; Code 85861.
3. Demirbaş, A. Biomass resource facilities and biomass conversion processing for fuels and chemicals. *Energy Conversion and Management* 2001; p. 1357-1378.
4. Lorenz, H. , Fischer, P., Schumacher, B., Adler, P. Current EU-27 technical potential of organic waste streams for biogas and energy production. *Waste Management*. 2013; p. 2434-2448.
5. Marculescu, C. Stan, C. Non-oxidant thermal treatment for organic waste neutralization. *Energy Procedia* 2012. p. 545-551.
6. Balat, M. Mechanisms of thermochemical biomass conversion processes. Part 1: Reactions of pyrolysis. *Energy Sources, Part A: Recovery, Utilization and Environmental Effects.* 2008; p. 620-635.
7. Serio, M.A., Bassilakis, R., Kroo, E., Wójtowicz, M.A Pyrolysis processing of animal manure to produce fuel gases. *ACS Division of Fuel Chemistry, Preprints.* 2002; p. 588-592.
8. Michael A. Serio, Rosemary Bassilakis, Erik Kroo, and Marek A. Wójtowicz. Pyrolysis processing of animal manure to produce fuel gases. *Fuel Chemistry Division Preprints*. 2002; p. 588-592.
9. Sánchez, M.E., Martínez, O., Gómez, X., Morán, A. Pyrolysis of mixtures of sewage sludge and manure: A comparison of the results obtained in the laboratory (semi-pilot) and in a pilot plant. *Waste Management.* 2007; p. 1328-1334.
10. A. Chaala, C. Roy. Recycling of Meat and Bone Meal Animal Feed by Vacuum Pyrolysis. *Environ. Sci. Technol.* 2003; p. 4517-4522.
11. Cascarosa, E. , Gea, G., Arauzo, J. Thermochemical processing of meat and bone meal: A review. *Renewable and Sustainable Energy Reviews* 2012. p. 942-957.
12. Yoshiyuki Shinogia, Yutaka Kanri. Pyrolysis of plant, animal and human waste: physical and chemical characterization of the pyrolytic products. *Bioresource Technology.* 2003; p. 241-247.
13. Scientific production enterprise GEOCE http://geoce.ru/en/about/
14. Goncharov, I.V., Oblasov, N.V., Smetanin, A.V., Samoilenko, V.V., Fadeeva, S.V., Zhurova, E.L. Genetic types and nature of fluid of hydrocarbon deposits south-east of Western Siberia. *Neftyanoe Khozyaistvo – Oil Industry Issue.* 2012; p. 8-13.
15. Strel'mikova E.B. , Goncharov, I.V., Serebrennikova, O.V. Concentration and distribution of oxygen-containing compounds in crude oils from the southeastern part of Western Siberia. *Petroleum Chemistry.* 2012; p. 278-283.