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Vasyl Stefanyk Precarpathian
National University

ФІЗИКА І ХІМІЯ ТВЕРДОГО ТІЛА
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V.I. Kyrychenko[1], V.V. Kyrychenko[2], V.S. Ribun[3], M.B. Skladaniuk[3]

Alternative Fuels from Vegetable Oils: Innovative Methods and Technologies of Production and Usage

[1]Khmelnytsky National University, Khmelnytskyi, Ukraine, vikirich@ukr.net
[2]Pacell LLC, Kyiv, Ukraine, Kyrychenkovk@gmail.com
[3]Vasyl Stefanyk Precarpathian National University, Ivano-Frankivsk, Ukraine, ribun.vika@gmail.com, skladanyuk16@gmail.com

Traditional methods of biofuel production using vegetable oils and aliphatic alcohols (alcoholysis) have a number of disadvantages. A new method of transesterification of vegetable oils with alkyl acetates (esterolysis) is proposed. Esterolysis solves the problem of alcohol content in biofuels. It is not necessary to remove alkyl acetates from biofuels because they act as promoters of diesel fuel combustion. A method of improving both technology of alcoholysis and esterolysis by modifying the temperature range is proposed. Chemical and technological bases of two-stage process of vegetable oil transesterification are developed. In the first stage, the oils are treated with glycerol (glycerolysis) in order to convert tri-acyl-glyceros of oil into mono-acyl-glycerols. The second stage is alcoholysis of mono-acyl-glycerols with ethanol (ethanolysis) or esterolysis of mono-acyl-glycerols with ethyl acetate. The temperature range of the transesterification process is improved using heat-transfer solvents. Comparison of material balances of technologies of one- and two-stage ways of ethanolysis and esterolysis showed a significant increase in the selectivity of the process, yield and quality of biofuels. Analysis of the obtained biofuels and mixtures, which contain 20 % of biofuels and 80% of diesel fuel showed the best physical, chemical and operational characteristics. Therefore, the blended fuels are promising area of biofuel technology.

Key words: rapeseed oil, ethanolysis, esterolysis, tri-acyl-glycerol, mono-acyl glycerol, biofuel, blended fuel.

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Introduction

One of the ways to solve the current problem of energy and resource support of the state economy, as well as environmental safety is to develop new, effective methods and technologies of renewable raw material conwersion into products with high biodegradability, which can be used as components for blended fuels and lubricants. Using vegetable oils makes possible to produce basic biocomponents for fuels and lubricants, in particular: a) biofuels for blended diesel or jet fuels; b) basic components for the production of composite lubricants (biooils, oil dispersion media, technical bioliquids, lubricants and coolants for metal treatment processes) [1, 2, 5]. It is known that pure vegetable oils cannot be used as fuel due to the significant difference in the properties of oils and traditional motor fuels. For example, oils have high values of molecular mass (M = 890), density, viscosity, crystallization, boiling and flash point [1, 2, 9, 11]. That is why the processing of base oils into fuel biocomponents is considered an urgent problem in the development of effective methods for the conversion of oil molecules into products whose properties are related to the properties of mineral fuels.

The currently known methods of processing rapeseed oil into biofuels are based on chemical reactions of transesterification of tri-acyl-glycerol molecules with alcohols (alcoholysis) or acetates of those alcohols (esterolysis). The aim of such reactions is to replace the glycerol residuemin oilmolecule with simpler alkoxyl group -OAlk, for example, $-OCH_3$ or $-OC_2H_5$ to form a methyl or ethyl ester of higher fatty acids having general formula R-C(O)-OAlk [1, 3, 4, 5].

Today, the most technologically developed and implemented in production are the processes based on the transesterification of oils with methanol and ethanol. Biofuel production by traditional methods has significant disadvantages of their technologies, which are mainly caused by two factors: a) the factor of reversibility of heterogeneous reactions under limited temperature (75 - 80 °C); b) a factor of specific tri-acyl-glycerol structure of vegetable oil molecules with three ester groups, which have different energy stability [2, 5].

In addition, the practice of diesel engine operation on biofuel based on higher fatty acid methyl esters shows that use of biofuel as a motor fuel has a negative impact on both engine performance and operation of its individual components [1, 4, 9]. That is why blended fuels containing 10 - 20 % of biofuel and 80 - 90 % mineral diesel fuel are considered to be more more desirable to use [1, 4, 8, 9].

I. Experimental

The use of the first proposed method of esterolysis of oils with ethyl acetate can only partially eliminate the adverse factors of alcoholysis. In particular, the following are achieved: a) the reaction medium is homogeneous from the beginning to the end of the process; b) reduction of excess ethyl acetate in product and the ability to leave it in the biofuel as a combustion promoter; c) absence of hydrophilic OH-containing by-products (harmful to fuels). However, esterolysis has other disadvantages similar to alcoholysis.

Comparison of chemical and technological bases of both one-stage methods of transesterification shows their similarity in low values of such leading indicators of the effectiveness of their technologies as selectivity, yield and quality of biofuels. It is important to take into account the influence of physical and chemical characteristics of raw materials and products on ethanolysis and esterolysis:

a) rapeseed oil $[RC(O)-]_3-O_3C_3H_5$, $M \approx 886$, $d_4^{20} = 915$ кg/m^3 , $\nu_{40^\circ C} = 34 - 37$ mm^2/s, does not dissolve alcohols, but dissolves ethyl acetate, mineral and biofuels, benzene well;

b) the main product - biofuels, ethyl esters of higher fatty acids $R-C(O)-O\,C_2H_5$, $M \approx 310$, $d_4^{20} = 865$ кg/m^3, $t_{boiling} = 205^\circ C$, $t_{freezing} = -15…-25^\circ C$;

c) by-products that are a mixture of oil esters, glycerol derivatives, and glycerol $M_{av} \approx 480 - 550$.

Material calculations were performed taking into account the following conditions: a) 1 kg of rapeseed oil was consumed; b) conversion of raw materials and yield of the final product both are equal to 80 %; c) the reaction mass has been heated with constant stirring

Table 1

Comparison of traditional methods of alcoholysis and esterolysis

Alcoholysis of rapeseed oil with ethanol C_2H_5OH (M=46 g/mol, d_4^{20} = 789 кg/m^3, $t_{boiling} = 78^\circ C$, $P_{saturated\ vapor\ pressure}$ = 9,7 кPa, V_1 = 0,058 l)	Esterolysis of rapeseed oil with ethyl-acetate $CH_3C(O)C_2H_5$ (M=88 g/mol, d_4^{20} = 900 кg/m^3, $t_{boiling} = 77^\circ C$, $P_{saturated\ vapor\ pressure}$ = 13,3 кPa, V_1 = 0,098 l)
Alcoholysis equation	Esterolysis equation
$3[RC(O)-]_3-O_3C_3H_5 + 6C_2H_5OH \leftrightarrow$ $\leftrightarrow 6\ R-C(O)-O\ C_2H_5$ (MAIN PRODUCT) + $[RC(O)-CH_2]_2-CH-OH$ (BY-PRODUCT 1, M = 620) + $RC(O)-CH_2-C_2\ H_3-(OH)$ (BY-PRODUCT 2, M = 356) + $C_3H_5(OH)_3$ (GLYCEROL, M = 92)	$3[RC(O)-]_3-O_3C_3H_5 + 6\ CH_3-C(O)-OC_2H_5 \leftrightarrow$ $\leftrightarrow 6\ R-C(O)-O\ C_2H_5$ (MAIN PRODUCT) + $[RC(O)-CH_2]_2-CH-OC(O)CH_3$(BY-PRODUCT 1, M = 662) + $[RC(O)-CH_2]_2-CH-OC(O)R$ (BY-PRODUCT 2, M = 440) + $[RC(O)-]_3-O_3C_3H_5$(TRIACETIN, M = 218)

Table 2

Material calculations of ethanolysis and esterolysis

Consumption of non-oil raw material	
Ethanol (200% excess): V_{et} = 0,393 l, m = 0,310 кg	Ethyl-acetate(100% excess): $V_{et.\ ac.}$ = 0,412 l, m = 0,397 кg
Excess of non-oil raw material in the mass of products	
V_{et} = 0,288 l, m = 0,235 кg	$V_{et.\ ac.}$ = 0,264 l, m = 0,258 кg
The excess of rapeseed oil in the mass of products $m_{rapseed\ oil}$ = 0,200 кg	
The mas of products: a) the main product - biofuel (bio.f.)	
$m_{bio.f.}$ = 0,560 кg (65,8%)	$m_{bio.f.}$ = 0,560 кg (63%)
б) by-products (by-pr. 1, 2)	
$m_{by-pr.}$ = 0,294 кg (34,4%)	m_{by-pr} = 0,332 кг (37%)
$V_{glycerol}$ = 0,022 l, $m_{glycerol}$ = 0,028 кg	$V_{triacetin}$ = 0,057 l, $m_{triacetin}$ = 0,066 кg

(heterogeneous in the case of ethanolysis and homogeneous in the case of esterolysis) at a temperature of 80 - 85 °C for 8 - 10 hours.

The properties of by-products, which are formed as a result of each method reactions are quite different from the properties of biofuels, as they are oil products. Both processes are influenced by the following technological factors:

1) reversibility of chemical reactions (↔), which requires a shift of chemical equilibrium towards the formation of biofuels using a significant excess of non-oil reagents or changing the process temperature;

2) low selectivity and yield of biofuels (63 - 68 %) and bad quality of the obtained product, due to the formation of a mixture of by-products, which are soluble in biofuels well;

3) separation of pure biofuels, which may remain unwanted by-products in the range of 2.0 - 4.0 % is time-consuming and costly;

4) phase state of the reaction media: heterogeneity and as a consequence turbulent mixing using significant ethanol excess (250 – 400 %) and homogeneity and respectively laminar mixing using less excess ethyl acetate (50 – 150 %) than ethanol excess.

1.1. Features of separation technology of products

In the separation process of products into components, there are four stages:

- distillation (85 - 95℃) of excess residual reagents: ethanol V_{et} = 0.288 l or ethyl acetate $V_{et.ac}$ = 0.155 l;
- distillation of by-products under vacuum: after ethanolysis of 0.022 l of glycerol, and after esterolysis - 0.057 l of triacetin;
- biofuels with mass m = 0.560 kg and volume V = 0.640 - 0.647 l are distilled off under vacuum;
- in residue there is a technical oil product (t. oil), which consists of by-products and rapeseed oil. For ethanolysis $m_{t.oil}$. = 0.494 kg, and for esterolysis $m_{t.ol.}$ = 0.532 kg.

Since the considered one-stage methods of processing rapeseed oil into biofuel (traditional ethanolysis and new - esterolysis) are similar in main indicators, namely, low level of selectivity for biofuels and limited heating range (~ 80 °C), both can be estimated only on the basis material balance of ethanolysis (Table 3).

Table 3

Material balance of the technological process of obtaining biofuel using the traditional method of rapeseed oil ethanolysis

Raw materials	Mass, кg	Volume, l	The amount of substance, mol	Products	Mass, кg	The amount of substance, mol	Yield, Y, %
Rapeseed oil	1,000	1,093	1,13	Biofuel: theoretical actual	0,700 0,560	2,26 1,81	100 80
Ethanol: from reaction equation under 200% excess	0,104 0,312	0,10.390,331	2,26 6,78				
Catalyst C_2H_5ONa 1,5% of mass of reaction	0,020	-	0,34	By-products: mono - i diacylglycerols	0,294 0,028	0,60 0,30	-
				Raw material: ethanol rapeseed oil catalyst	0,235 0,200 0,020	5,11 0,23 0,34	-
Total	1,332	1,486	8,25	Total	1,337	8,35	

Table 4

Material calculations of two-stage technology of ethanolysis and esterolysis

Consumption of non-oil raw material under the condition of 92% conversion and 25% excess.	
Ethanol V_{et} = 0,219 l	Ethyl-acetate $V_{ey.\ ac.}$ = 0,278 l
Excess of non-oil raw material in the mass of products	
V_{et} = 0,058 l Rapeseed oil $m_{rapeseed\ oil}$ = 0,071 кg mono-acyl-glycerol $m_{m-ac-gl}$ = 0,080 кg	$V_{et.\ ac.}$ = 0,264 l Rapeseed oil $m_{rapeseed\ oil}$ = 0,071 кg mono-acyl-glycerol $m_{m-ac-gl}$ = 0,080 кг
The mas of products: a) the main product - biofuel (bio.f.) if yield of bio.f. = 92%	
$m_{bio.f.}$ = 0,862 кг, $V_{bio.f.}$ = 0,997 l	$m_{bio.f.}$ = 0,862 кг, $V_{bio.f.}$ = 0,997 l
б) water-soluble by-productsc	
$V_{glycerol}$ = 0,068 l, $m_{glycerol}$ = 0,085 кg	$V_{monoacetin}$ = 0,309 l, $m_{monoacetin}$ = 0,373 кg

Comparison of chemical equations of ethanolysis and esterolysis shows that the esterolysis with ethyl acetate has certain advantages over ethanolysis, namely, homogeneous medium, hydrophilic OH-containing by-products are absent in the product mass, usage of ethyl or methyl acetate as a promoter additive to blended fuels. However, the main unfavorable factors, namely the low level of selectivity of reactions to biofuels, limited temperature range are unresolved. In order to increase the efficiency of ethanolysis and esterolysis technologies significantly, it was necessary to develop a method of their chemical modification, which would eliminate the whole set of adverse factors.

1.2. Two-stage method of rapeseed oil transesterification

An innovative approach to the development of such a method should eliminate the main reason for the low selectivity of these technologies, namely, to modify the triacyl-glycerol structure of oil molecules, which determines the multidirectionality of transesterification reactions. At the same time there are three ways of interaction between 1,2,3-ester parts of glycerols of oils and non-oil reagents (alcohols, esters):

- interaction with three fragments, which leads to the formation of biofuel $RC(O)-OC_2H_5$;
- transesterification between only two parts (1,3- or 1,2-) of glycerols and non-oil reagents to form mono-acyl-glycerols $RC(O)-OCH_2-C_2H_3(OH)_2$, M-356;
- interaction between only one part of glycerols and non-oil reagents to form diacyl-glycerols $[RC(O)-OCH_2]-CH-OH$, M 620. This polydirectional interaction leads to the accumulation of up to 30 - 35 % of by-products of oil structure and hydrophilic by-products harmful to motor fuels in general [2, 10, 11].

It is obvious that for transesterification of vegetable oils and obtaining biodiesel using these methods, it is first necessary to transform tri-acyl-glycerol oil molecules (M = 886) into mono-acyl-glycerol molecules $RC(O)-OCH_2-C_2H_3(OH)_2$. This transformation can be implemented by a rather simple technologically and efficient method of glycerolysis of oils, that is alcoholysis with glycerol in a molar ratio of 1: 2 (~ 2.2). Moreover, glycerolysis is considered as a general first stage of a two-stage method of vegetable oil treatment. The second stage is actually the chemical reactions of the ethanolysis or esterolysis of mono-acyl-glycerols, which is highly selective and efficient methods of biofuel production.

Another innovation is the proposed method of adjusting the unfavorable temperature conditions in one-stage technologies (less than 80 ° C) using inert solvents such as diphenyl oxide (DFO) or diphenylmethane (DFM). Due to the rather favorable functional properties of DFO and DFM, in particular: $t_{boiling} > 200$ ° C, $t_{freezing} \approx$ 26 - 28 °C, good solubility in oils, esters, alcohols, bio- and mineral fuels, benzene, temperature conditions of both stages can be carried at a temperature range within 130 - 160 °C. Moreover, the use of DFO or DFM in two-stage technology provides not only the optimal temperature, but also the homogeneity of the reaction media, in particular at the stage of glycerolysis, as well as the simplicity of the operation of regeneration of the used solvents.

1.3. Chemical-technological bases of two-stage processes of ethanolysis and esterolysis

Common to both processes is the stage of glycerolysis of rapeseed oil in an inert heat-transfer solvent diphenylmethane (DFM) to transform tri-acyl-glycerol molecules of rapeseed oil into mono-acyl-glycerol, which are well soluble in bio- and mineral fuels. Glycerolysis is carried out using alkaline catalysis at a temperature of 160℃, it can be described by the following equation:

$$[RC(O)-]_3-O_3C_3H_5 + 2C_3H_5(OH)_3 \leftrightarrow$$
$$\leftrightarrow 3\ RC(O)-OCH_2-C_2H_3(OH)_2 \qquad (1.1)$$

The calculated amounts of all reagents are placed in 0.700 kg of heat-transfer solvent DFM or DFO heated to 50℃: 0.893 kg of rapeseed oil, 0.183 l (0.230 kg) of glycerol, 0.017 g (1.5 % by weight) of C_2H_5ONa catalyst. Heat the homogeneous reaction mass with constant stirring for 4 hours at a temperature of 160 °C. Under such conditions, 90 - 95 % level of raw material conversion and 90 - 95 % yield of mono-acyl-glycerols are achieved, that is ≈ 0.050 - 0.058 kg of rapeseed oil and 0.015 - 0.018 l of glycerol remain in the product mass.

The next stage of the two-stage process is ethanolysis or esterolysis of mono-acyl-glycerols in an inert heat-transfer solvent DFM (boiling point > 200 °C) to obtain ethyl esters of higher fatty acids $R-C(O)-O-C_2H_5$, which are biofuels. Technological features of the second stage processes are: usage of intermediate product mass, which contains an inert heat-transfer solvent (0.700 kg DFM), immediately after glycerolysis, to provide a high temperature of reaction ≈ 160℃ with constant stirring the mass for 5 hours; the reaction masses stay homogeneous in the reactor during the process; calculations are based on the consumption of 0.893 kg of rapeseed oil or 1.000 kg of mono-acyl glycerols and 25 % excess of non-oil raw materials (ethanol or ethyl acetate) and 1,5 % of the corresponding catalyst; high selectivity of both methods relative to the main product - biofuels, 90 - 95 % level of conversion of raw materials, 90 - 95 % yield of biofuels of high quality are achived; the product masses of each methods contains only one water-soluble compound, respectively glycerol or monoacetin.

Material calculations are based on the consumption of the corresponding non-oil raw materials under the condition of 92% conversion and 25 % excess.

Separation of final products to release biofuels consists of the following stages: distillation of etanol or ethyl acetate; cooling of food masses to 8 - 10℃ for 5 - hours and filtering the crystallized solvent; washing the residual mass with water at 30℃ to remove glycerol or monoacetin; distillation of biofuel under vacuum; the residue is a mixture of unreacted rapeseed oil and mono-acyl glycerols.

Thus, both innovative methods of production of biofuels from rapeseed oil are similar in the main favorable factors, in particular: the direction of transesterification reactions, the homogeneity of the media in the solvent, high temperatures, and so on. That is why the technical and economic evaluation of both methods can be estimated using material balance of one of them, for example, the ethanolysis of rapeseed oil (Table 5).

Analysis of the material balance data of two-stage eganolysis of rapeseed oil (Table 5) shows that the technology of oil processing in heat-transfer solven is more effective than one-stage technologies because of a number of favorable factors namely: homogeneuous

Table 5

Material balance of biofuel production using a new two-stage method of ethanolysis of rapeseed oil in a heat-transfer solvent medium

Raw materials	Mass, кg	Volume, l	The amount of substance, mol	Products	Mass, кg	The amount of substance, mol	Yield, Y Contents, C, %
1. The stage of glycerolysys							
Rapeseed oil	0,893	0,976	1,01	Main product			
Glycerol:				mono-acyl-			
under chemical	0,184	0,146	2,00	glycerols:	1,071	3,00	Y-100%
equation	230	0,183	2,5	theoretical	1,000	2,80	Y-93%
under 25% excess				actual			
	0,017	-	0,25	Excess of raw			
Catalyst				materials:			
C_2H_5ONa,1,5%	0,700	-	-	glycerol	0,046	0,50	C-7%
of reaction mass				rapeseed oil	0,063	0,07	C-7%
heat-transfer solvent				Catalyst	0,017	0,25	-
$(C_6H_5)_2CH_2$-ДФМ				heat-transfer	0,700	-	-
				solvent			
Total	1,840	1,129	3,76	Total	1,830	3,05	
2.The stage of mono-acyl-glycerol ethanolysis							
mono-acyl-glycerols	1,000	1,058	2,80	Main product			
ethanol:				biofuels:	0,862	2,78	B-93%
under chemical	0,138	0,174	3,00	By-products:			
equation	0,173	0,219	3,76	glycerol		0,93	Bм-
under 25% excess	0,006		0,09	raw materials:	0,085		7,0%
Catalyst		-	-	ethanol		1,00	
C_2H_5ONa,1,5%	0,700	-	-	rapeseed oil	0,046	0,07	-
of reaction mass				mono-acyl-	0,063	0,23	-
heat-transfer solvent				glycerols	0,070		-
$(C_6H_5)_2CH_2$-ДФМ				heat-transfer		-	
				solven	0,700		-
Total	1,179	1,277	6,65	Total	1,126	5,0	

Table 6

Systematization of rapeseed oil transesterification methods and features of their technologies

<table>
<tr><td colspan="2">Alcoholysis is catalytic (alkali) transesterification of vegetable oil molecules with alcohols:
-water-soluble methanol or ethanol, boiling point <80˚ C;
-hardly water-soluble butanols or amyl alcohols, boiling point > 110˚C</td><td colspan="2">Esterolysis - catalytic (acidic) transesterification of oil esters with acetates of alcohols:
-acetates of methyl or ethyl alcohols - methyl- or ethyl acetates, boiling point <86℃;
-n-butyl-, isobutyl-, n-amyl-, isoamyl-, 2-ethyl-hexyl-acetates, boiling point> 116˚C;</td></tr>
<tr><td colspan="4">The ways of technological processes implementation by appropriate methods</td></tr>
<tr><td>One-stage method of alcoholysis of triacylglycerols of vegetable oils to biofuels or bioliquids</td><td>Two-stage method using a heat-transfer solvent medium (DFO or DFM), t ~ 160˚C:
-glycerolysis of triacylglycerol of vegetable oils to monoacylglycerols
-alcoholysis of monoacylglycerols with alcohols to biofuels</td><td>One-stage method of esterolysis of triacylglycerols of vegetable oils to biofuels or bioliquids</td><td>Two-stage method using a heat-transfer solvent medium (DFO or DFM), t ~ 160˚C:
-glycerolysis of triacylglycerol of vegetable oils to monoacylglycerols
-esterolysis of monoacylglycerols with alcohols to biofuels</td></tr>
</table>

Table 6
(continuation)

Features of obtained products:			
Methanolysis - ethanolysis of oils: -heterogeneity -significant excess of alcohols -limited heating (70-80℃) -low selectivity for biofuels and bioliquids, low yield and quality of biodiesel.	Glycerolysis of oils - ethanolysis of monoacylglycerols in heat-transfer solvent medium (DFO or DFM): -homogeneity - insignificant excess of alcohols -heating up to t ~ 160˚C -high selectivity for biofuels and bioliquids, low yield and quality of biodiesel.	Esterolysis of oils with ethyl acetate: -homogeneity -high excess of ethyl acetate -limited heating (70-80℃) -low selectivity for biofuels and bioliquids, low yield and quality of biodiesel.	Glycerolysis of vegetable oils - esterolysis of monoacylglycerols ethyl acetate in DFO or DFM: -homogeneity; - insignificant excess of ethyl acetate -heating up to t ~ 160˚C; -high selectivity for biofuels and bioliquids, low yield and quality of biodiesel.

Table 7

Physical, chemical and operational properties of diesel fuel, biodiesel and blended fuel

Properties (standarts)	Diesel, DSTU 3868-2005	Biodiesel, DSTU 7178-2009, EN 14214		Blended fuel DSTU 6345-2014
		traditional one-stage technology	new two-stage technology	
Density at 20˚C, кg/m^3 (DSTU ISO 12185)	840-860	880-890	870-876	860-865
Viscosity at 20˚C, mm^2/s (DSTU-GOST 33)	3,0-6,0	8,5-9,5	7,0-7,5	4,5-5,5
Cetane number (CN), more than (DSTU ISO 5165)	50	48	51	51
Flash point,˚C (DSTU ISO 2719) not less than Cloud point,˚C, less than Cold filter plugging point,˚C, less than	65 -10 -5	125-135 -9 -7	110-115 -7 -10	75-80 -9 -6
Fractional composition,˚C, less than -50% об -90% об	280 340	- -	- -	260 320
Acid number (AN), mgKOH/g, less than (DSTU 14104)	0,03	0,65	0,50	0,12
Iodine number (IN), mgI$_2$/100 g, less than (DSTU EN 14111)	5,0	125	120	15-25
Coking capacity of 10% of distillation residue, %, less than (GOST 199932)	0,3	0,45	0,35	0,32
Sulfur content, %, less than	0,01	-	-	0,009
Corrosion, test on the Cu^0 plate at 50˚C, 3 hours (GOST 6321)	Stand, class1	Does not stand	Does not stand	Stand, class
Mass fraction of glycerides and glycerol, %, less than (DSTU EN 14105)	-	3,50	0,35	0,30
The fuel composition, ratio of C: H	6,9	6,7	6,4	6,7
Air consumption, air kg /fuel kg	12,5-12,7	14,2-14,5	13,5-14,2	13,0-13,3
Low heat value, MJ/кg	43	33	35	41
Biodegradability, test CEC-L-33A-94, %	25	85	85	45
Antifriction properties, diameter of wear spots, mm (the friction mashine, GOST 9490-75)	0,45	0,65	0,50	0,45

media at optimized temperature (150 - 160 °C), high levels of selectivity, high yield and quality of biodiesel.

Table 7 shows the main properties of biofuels obtained in different ways, as well as blended fuel, which is a mixture of diesel fuel containing 20 % biofuel and 80% of mineral diesel fuel [9, 10, 11, 12].

Comparison of the properties of the two types of biofuels (Table 7) shows that the fuel obtained by the two-stage technology has better properties than the fuel obtained by the one-stage technology. In accordance with the requirements of DSTU 7178-2009 fuel obtained by the two-stage technology has lower glyceride content, viscosity, acid and iodine number etc. Ehe data in Table 7 confirm the advantages of the two-stage method of ethanolysis in a heat-transfer solvent medium. Such advantages relate to a number of technologically favorable factors, namely, homogeneous reaction medium, high selectivity of chemical reactions of both stages, high process temperature, state of chemical equilibrium [4, 8, 9, 10, 13].

Conclusions

It is confirmed that traditional technologies of biofuel production are low-selective corresponding to biofuels and bioliquids, low yield of biofuels and their quality.

The method for the biofuel production by esterolysis of vegetable oils with alkyl acetates has been developed. It is shown that the technology of esterolysis solves the problem of excess alcohol content in biofuels. Alkyl acetates do not need to be removed from biofuels because they act as promoters of diesel fuel combustion.

An innovative method of two-stage alcoholysis and esterolysis is proposed. At the first stage rapeseed oil is modified by glycerolysis. The temperature conditions of the process is modified due to the use of heat-transfer solvent, which allows to increase the process temperature and causes high selectivity of the chemical reactions, biofuel yield and quality.

Kyrychenko V.I. – professor, Dr of Sc;
Kyrychenko V.V. – specialist;
Ribun V.S. - lead engineer of Chemistry Department;
Skladaniuk M.B.- PhD, assistant professor of Chemistry Department.

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В.І. Кириченко[1], В.В. Кириченко[2], В.С. Рібун[3], М.Б. Складанюк[3]

Альтернативні палива із технічних олій: інноваційні методи і технології одержання та використання

[1]*ДВНЗ «Хмельницький національний університет», м. Хмельницюкий, Україна,* *vikirich@ukr.net*
[2]*ТОВ «Пейселл», м. Київ, Україна,* *Kyrychenkovk@gmail.com*
[3]*ДВНЗ «Прикарпатський національний університет імені Василя Стефаника», м. Івано-Франківськ, Україна,*
ribun.vika@gmail.com, *skladanyuk16@gmail.com*

Традиційні способи виготовлення біопалива з рослинних олій та аліфатичних спиртів (алкоголіз) мають ряд недоліків. В даній роботі запропоновано новий метод переестерифікації рослинних олій алкіл ацетатами (естероліз). Естероліз усуває проблему вмісту спиртів у біопаливі. Алкілацетати не потрібно виділяти з біопалива, оскільки вони виконують роль промоторів згоряння дизельного палива. Запропоновано спосіб удосконалення технологій алкоголізу та естеролізу шляхом модифікації температурного режиму. Розроблено хіміко-технологічні основи двостадійного процесу переестерифікації рослинних олій. На першій стадії здійснюють алкоголіз олій гліцерином (гліцероліз) з метою перетворення три-ацил-гліцеролів олій на моно-ацил-гліцероли. На другій стадії проводять алкоголіз етанолом (етаноліз) чи естероліз моно-ацил-гліцеролів. Оптимізовано температурний режим процесу переестерифікації шляхом використання розчинників-теплоносіїв. Порівняльний аналіз наведених матеріальних балансів технологій одно- і двостадійних способів етанолізу та естеролізу показав значне зростання селективності процесу, виходу і якості біопалива. Аналіз отриманих біопалив та їх 20 % сумішей з дизельним паливом показав, що найбільш раціональним напрямком використання біопалива є формування композиційних палив.

Ключові слова: ріпакова олія, етаноліз, естероліз, три-ацил-гліцероли, моно-ацил-гліцероли, біопаливо, композиційне паливо.