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ACTIVATION OF THE TRANSESTERIFICATIONS PROCESS OF VEGETABLE OILS TRIGLYCERIDES WITH METHANOL UNDER THE INFLUENCE OF MAGNETIC FIELD

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ABSTRACT

The process of producing mono-alkyl esters of fatty acids from cottonseed and sunflower oils under the influence of the magnetic field with intensity 15-45 mT was investigated . It was revealed that the use of the energy of magnetic field allows to reduce the reaction time to 10 times, the excess of used alcohol to 2 times while maintaining high yield of the desired product.

Indexing terms/Keywords

Diesel fuel; fatty acids; cavitation; magnetic field; transesterification; vegetable oils.

Academic Discipline And Sub-Disciplines

Chemistry

SUBJECT CLASSIFICATION

Oil chemistry

TYPE (METHOD/APPROACH)

Experimental

1.INTRODUCTION

Expanding worldwide production of renewable fuels, primarily associated with the stringent environmental standards for motor fuels and products of combustion. To date, precisely biodiesel, which is representing alkyl esters of higher carboxylic acids of plant or animal origin, which have significantly cleaner exhaust in comparison with conventional petroleum diesel fuel significantly contributes to the development of the market of renewable motor fuels. [1,2].

A significant increase in production efficiency and quality of the products, including existing installations can be achieved through the use of non-traditional ways of influence to the hydrocarbon feedstock. In this regard, wave reagentless methods which are implemented on the basis of physical principles such us: electrical, magnetic, radiation, acoustic, microwave, vibration and laser, are increasingly used. The energy of the explosion, low-density plasma, barrier discharge, ionizing radiation are also used. These methods of physical influence should be considered as energy, which provides transfer of required amount of energy to the reaction mass by the above types of impacts. Thus, there are significant changes in the chemical and structural state of the hydrocarbon system, its activation and the change in the rheological and physico-chemical properties.

2. EXPERIMENTALS

2.1 The conditions of the experiment

Taking the above into account, we set a goal to activate the process of transesterification of the vegetable oil triglycerides by simple C_1-C_3 alcohols with the usage of magnetic field to produce alkyl esters of fatty acids of cotton and sunflower oils which are currently used as an alternative diesel fuel [1-5]. Potassium hydroxide was used as a catalyst. The magnetic field with the tension of 15-45 mT created by an electromagnet. The conditions of the experiment and the yield of monoalkyl esters of fatty acids shown in Table 1.

Table 1. The conditions of the experiment and the yield of monoalkyl esters of fatty acids under the influence of the magnetic field

	Without magnetic field		**With magnetic field**	
	cotton	**sunflower**	**cotton**	**sunflower**
Reaction time, h	6	6	0,6	0,6
The amount of catalyst,% (on oil)	0,5	0,5	0,3	0,3
The ratio of oil: alcohol	1 : 6	1 : 6	1 : 3	1 : 3
The reaction temperature, ° C	70	70	70	70
Yield of alkyl esters	98	98	95	96

As seen from the above results, the use of magnetic energy allows to reduce the reaction time to 10 times, the excess of used alcohol to 2 times while maintaining high yield.

3.RESULTS AND DISCUSSION

Composition of trans-esterification products of these triglyceride oils with methanol produced by the influence of magnetic field analyzed with ^{1}H and ^{13}C NMR spectroscopy (Fig. 1 a, b).

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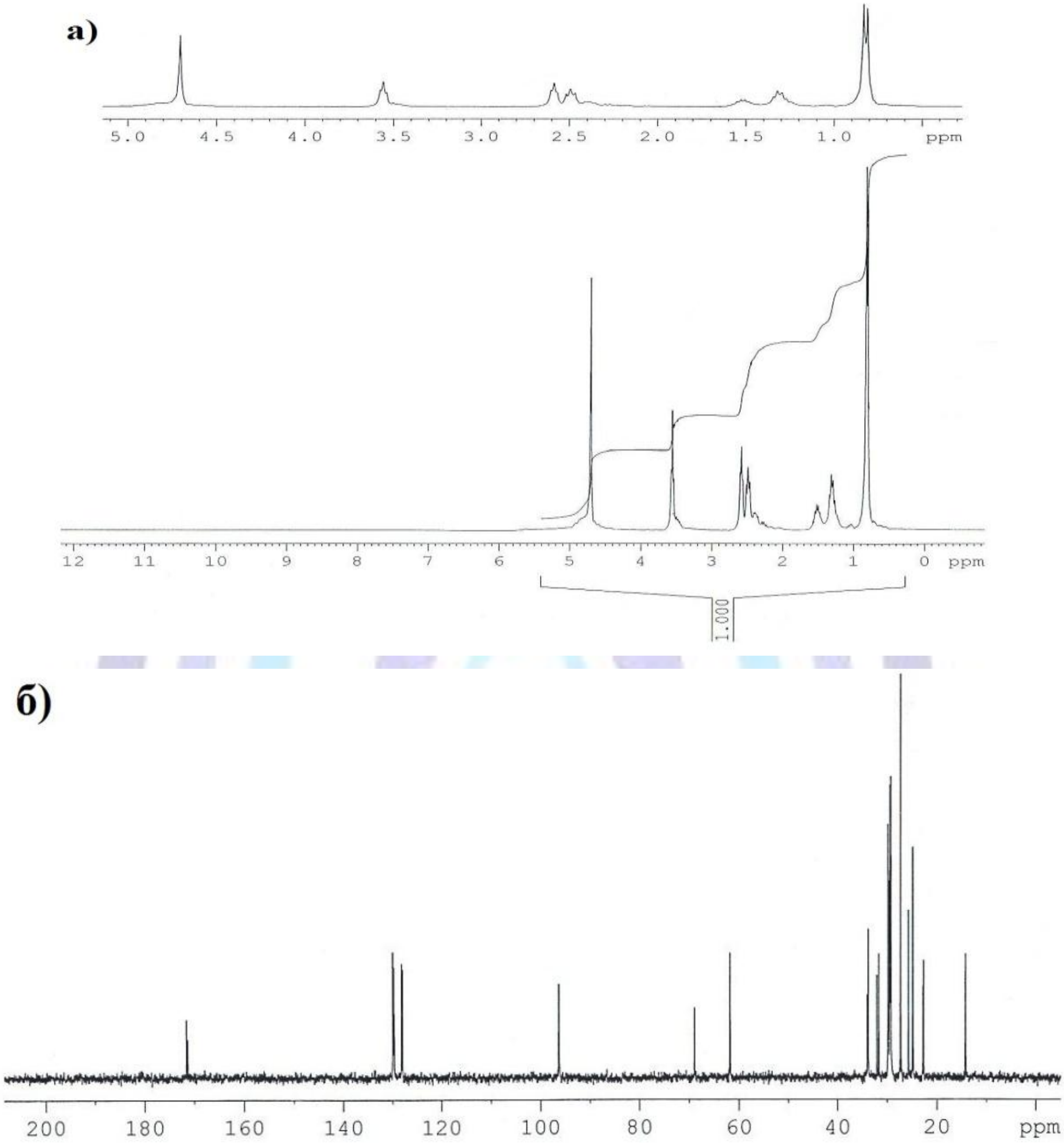

Fig. 1: [1]H (a) and [13]C NMR spectra of the products of the reaction of trans-esterification of cottonseed oil with methanol under the influence of the magnetic field

On the [1]H NMR spectra the signals of the methyl groups are 0.85 (3H, CH_3), 1, 30-1, 5 ppm (20H, CH_2) fragments in the fatty radicals, 2.1-2.2 ppm (4H, CH_2-C = C) fragments in allyl radicals and acyl group at δ = 3, 75 ppm (3H, OCH_3).

On the [13]C NMR spectra, the following chemical shifts were observed (δ, ppm): 19 (CH_3), 25 (CH_2), 27.4 (CH_2), 29.2 (CH_2), 29.5 (CH_2), 29 7 (CH_2), 29.9 (CH_2), 32.1 (CH_2), 33.8 (CH_2), 94.4 (OCH_3), 128.05, 128.2, 129.8, 130 (CH_2-C = C and C = C).

Studies of the reaction products of trans-esterification of triglycerides cotton and sunflower oils with methanol were carried out in accordance with EN 14214 (Table. 2). As seen from the results obtained methyl esters of sunflower and cottonseed oils fully meet the requirements of EN 14214 (fatty acid methyl esters (FAME) for diesel engines).

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Table 2. Quality parameters of methyl esters of the cottonseed oil obtained in a pilot plant

Index name	**Value of the index according to EN 14214**	**Methyl ester of cottonseed oil**	**Methyl ester of sunflower oil**
Cetane number, no less than	51	53	52
Kinematic viscosity at 40 ^{0}C mm2 / SC	3,5-5,0	3,99	3,22
Density at 15 ^{0}C, kg / m^3	860-900	889,7	882,3
Flash point in a closed crucible, ^{o}C,	120	125	125
Sulphur content, mg / kg	10	1	1
Coking behavior of 10 % residue, no more than	0,3	0,1	0,1
Ash content wt.%, no more than	0,02	0,01	0,01
Water content, % mg / kg	500	-	-
Mass fraction of ethers, %	96,0	96,0	98,5-99
Oxidation resistance, h, no less than	6,0	6,0	6,0
Acid number mg KOH / 1 g, no more than	0,5	0,34	0,26
Iodine number, g J_2 / 100 g, no more than	120	80,65	83,48
Mass fraction of methanol, %, no more than	0,2	0,01	0,01
Mass fraction of monoglycerides,%, no more than	0,80	0,3	0,3
Mass fraction of diglycerides,%, no more than	0,2	0,1	0,1
Mass fraction of triglycerides,%, no more than	0,2	0,1	0,1
Mass fraction of glycerol,%, no more than	0,25	0,18	0,15
Content of mechanical impurities mg / kg, no more than	500	-	-

The analysis of the obtained esters composition was carried out by chromatography according to ASTM Method D 6584 on the chromatograph Agilent 78A (capillary column Zebron ZB-5HT Inferno, the active phase of 5% phenyl - 95% dimethylpolysiloxane, 15 m $\times$ 0.32mm $\times$10 µm, the carrier gas - nitrogen) .

The composition of methyl esters of sunflower and cottonseed oils obtained in the pilot plant is given in the Table 3.

Table 3.The composition of the methyl esters of sunflower and cottonseed oils

Methyl esters of fatty acids	**Composition of methyl esters, % wt.**	
	Sunflower oil	**Cottonseed oil**
methyl ester of lauric acid (C12: 0)	0,7	-
methyl ester of palmitic acid (C16: 0)	10,0	20,5
methyl ester of stearic acid (C18: 0)	2,50	2,4
methyl ester of oleic acid (C18: 1)	40,0	32,1
methyl ester of linoleic acid (C18: 2)	43,4	36,4
methyl ester of linolenic acid (C18: 3)	2,0	6,2
Methyl ester of eicosenoic acid (C19: 1)	0,60	0,1
Methyl ester of eicosanoic acid (C19: 0)	0,10	0,7
Methyl ester of docosanoic acid (C22: 0)	0,5	1,1
Methyl ester of tetracosanova acid (C23:0)	0,20	0,5

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4. CONCLUSION

As seen from the above results, though to a sunflower, and cottonseed vegetable oils composed of obtained esters prevailing content of methyl esters of oleic and linoleic fatty acids, however the content of the above esters which were obtained from cottonseed oil is somewhat less than when we use sunflower oil (32.1 and 36.4 wt.%, respectively).

In addition, when we use cottonseed oil, the content of methyl ester of palmitic acid is almost two times higher than when we use sunflower oil.

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