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THE RESEARCH INTO REACTION OF TRANSESTERIFICATION OF VEGETABLE OILS WITH C_1 - C_4 ALCOHOLS IN TERMS OF HYDRODYNAMIC CAVITATION

Z.M. Aliyeva

Acad. Y. H. Mammadaliyev Institute of Petrochemical Processes
National Academy of Sciences of Azerbaijan
Baku AZ 1025, Baku, Khojaly ave,30
Fax: (+99412) 490-24-76. e-mail: zulfiya_aliyeva@inbox.ru

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Abstract: *The process of transesterification of cotton, sunflower, corn, soybean and palm vegetable oils with simple alcohols, including methanol, ethanol, iso-propanol and butanol under hydrodynamic cavitation conditions was studied with the use of amine-containing compounds as catalysts and among them are triethylamine (TEA), phenylenediamine (FDA), diphenylamine (DFA), iso-propylamine (IPA), tert-butylamine (TBA). It revealed that when carrying out the process in terms of hydrodynamic cavitation with an alcohol: oil ratio of 6: 1 and the process duration of 10-12 min for obtaining high yields of methyl and butyl esters of vegetable oils fatty acids when the content of TEA, FDA, DFA and TBA catalysts is 2.5% mass. and 3.0% the mass for obtaining ethyl and isopropylamine esters.*

Keywords: *vegetable oils, alcohol, transesterification, hydrodynamic cavitation, amine-containing compounds, catalysts, optimal conditions*

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Introduction

At present a number of physical effects are used to speed up chemical reactions and make them change the structure of the substance using the substance's internal reserves without applying larger external energy. Electric, electromagnetic, magnetic, vibration and acoustic fields may be external influences affecting the structure of the substance. These methods are more promising, for they are economical, efficient and affordable [1-6].

One of the used physical factors is hydrodynamic cavitation. This type of cavitation is formed by high velocity and fluctuating trajectories in fluids. The fluctuating trajectory means that fluid may have fluctuating diameters. For example. the narrowing and re-expansion of the diameter of the pipe in the fluid direction may add the cavitation effect to the process. Hydrodynamic cavitation occurs where the pressure of the fluid along the movement direction is lower in its critical pressure (P_{kr}) (for real liquids. saturated vapor pressure of liquid at that temperature equals P_{kr}).

For ideal homogeneous fluids, the formation of cavities as a result of disruption of the fluid continuity can occur only at high tensile stresses. For example the durability of the theoretical strain for water is $1.5*10^8$ Pa. This Fig. is even lower for real liquids. In reality, the effect is slightly down from saturated vapor pressure because they contained microscopic gas particles, damaged solid particles. and other admistures. They, in turn, are rapidly expanding along the flow of fluid when entering the zone where the pressure is below the critical pressure while gas pressures in them increases and the cavity zone filled with moving cavities is formed. As a result of compression and explosion of cavities in the cavitation zone, the bands in the molecule are weakened and broken down rapidly thus exceeding manifold the reaction rate [7-10].

Having regard to the above, the work analyzed the process of transesterification of cotton, sunflower, corn, soybean and palm vegetable oils with simple alcohols, including methanol, ethanol, iso-propanol and butanol

under hydrodynamic cavitation conditions with a view of producing the biodiesel fuel.

Experimental part and rezults

The transesterefication process of sunflower (SFL), corn(CORN), soybean (SOY) and palm (Palm) oils with methanol, ethanol, i-propanol and butanol alcohols in terms of hydrodynamic cavitation at a boiling temperature. Triethylamine (TEA), phenylenediamine (FDA), diphenylamin (DFA), isoprpopylamine (IPA), tert-butylamine (TBA) were used as catalysts.

The studies were carried out on a specially designed device equipped with a tank for raw materials, a rotary pump, a pipe of the corresponding diameter and a tank for the target products (Fig. 1). The feed rate was 7-8 m / s. ; processing time was regulated by the processing of raw materials in the system.

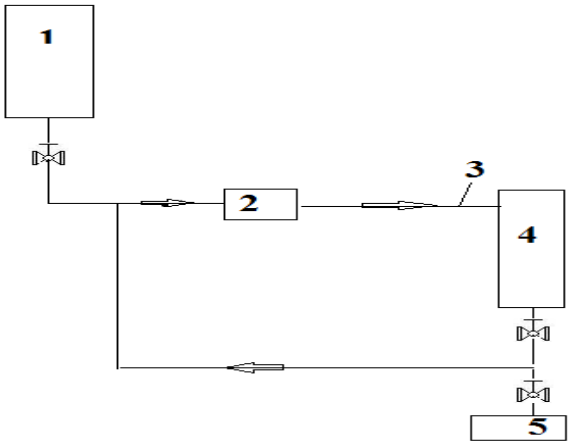


Fig. 1. Scheme of hydrodynamic cavitation installation: 1-raw material capacity, 2-pump, 3-tube of varying diameter, 4-vessel for circulating reaction product, 5- vessel of finished products

When the amount of the catalyst used was first taken, 3% hydrodynamic cavitation of the reaction solution was examined at 1: 4-1: 8 molar ratio of alcohol to oil within 10 minutes. The obtained results are given in Table 1.

Table 1. Yields of alkyl esters based on corn oil in hydrodynamic cavitation conditions in the presence of DFA, FDA, TEA, IPA and TBA catalysts depending on alcohol: oil molar ratio

Catalysts	Alcohol:oil, molar ratio		
	4:1	6:1	8:1
	Yield of methyl esters of corn oil, %		
DFA	92.2	98.6	98.8
FDA	92.3	98.3	98.5
TEA	94.1	99.2	99.0
IPA	87.5	97.5	98.0
TBA	92.5	97.0	97.8
	Yield of ethyl acids of corn oil, %		
DFA	90.3	97.3	97.6
FDA	89.2	97.1	96.9
TEA	91.7	98.0	98.1
IPA	78.2	84.4	87.1

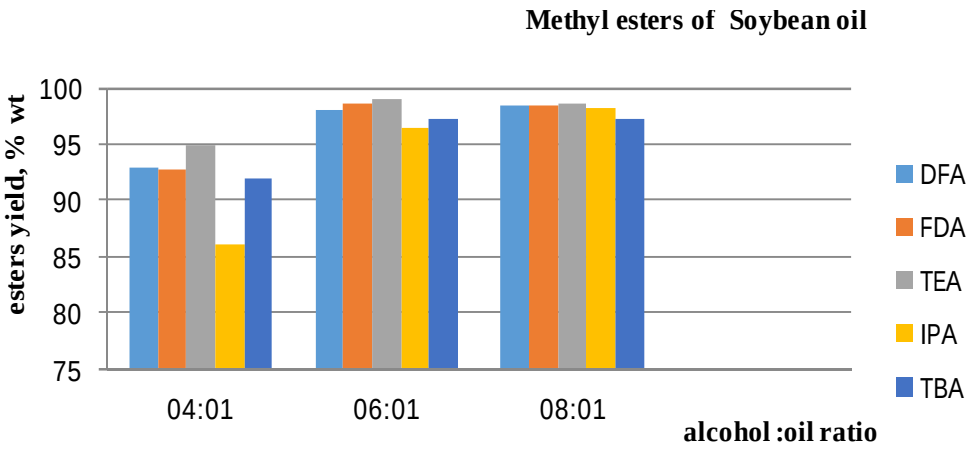
TBA	90.1	97.1	97.1
	Yield of iso-propyl esters of corn oil, %		
DFA	74.1	90.2	94.1
FDA	75.9	91.4	94.6
TEA	81.5	92.6	95.8
IPA	67.7	81.5	88.7
TBA	77.9	87.1	95.2
	Yield of butyl acids of corn oil, %		
DFA	93.1	98.0	98.2
FDA	92.6	98.3	98.6
TEA	93.5	98.7	99.0
IPA	86.1	94.2	97.4
TBA	90.8	97.8	97.8

As is seen from Table 1, the yield of methyl esters of corn oil in terms of hydrodynamic cavity with the presence of catalysts DFA, FDA, TEA and TBA: alcohol molar ratio of 4: 1 is not more than 92.1-94.1%. The slightly lower yields are observed in the presence of IPA catalyst and equalling 87.5%.

Note that in the presence of all the catalysts at the ratio of alcohols: oil molar ratio 4:1 in hydrodynamic cavitations yields were lower than the requirements of EN 14214, so the ratio of alcohol to oil rose to 6: 1. In this case the output of alkyl esters is 97.0-98.6% for methyl esters in the presence of DFA, FDA,TEA and TBA catalysts is 97.1-98.0% for ethyl ester; 97.8-98.7% for butyl ester; so the results obtained can be considered as good.

In this case, the rise in alcohol is a follows: oil molar ratio 8:1 does not have the same effect on the output, so the ratio of alcohol:oil 6:1 can be taken as optimum ratio.

The results obtained for methyl and isopropyl esters in the presence of catalyst only in the proportion of alcohols to oil 6:1 are not satisfactory making up 80.4% for ethyl esters and 81.5% for iso-propyl esters. In this case, the molar ratio alcohol is 8: 1 of oil to be recorded as optimal ratio. Approximately the same results were obtained from the use of other vegetable oils, and the output of methyl-, ethyl-, i-propyl- and butyl ester of soybean oil in the same process is shown in Fig.2 .



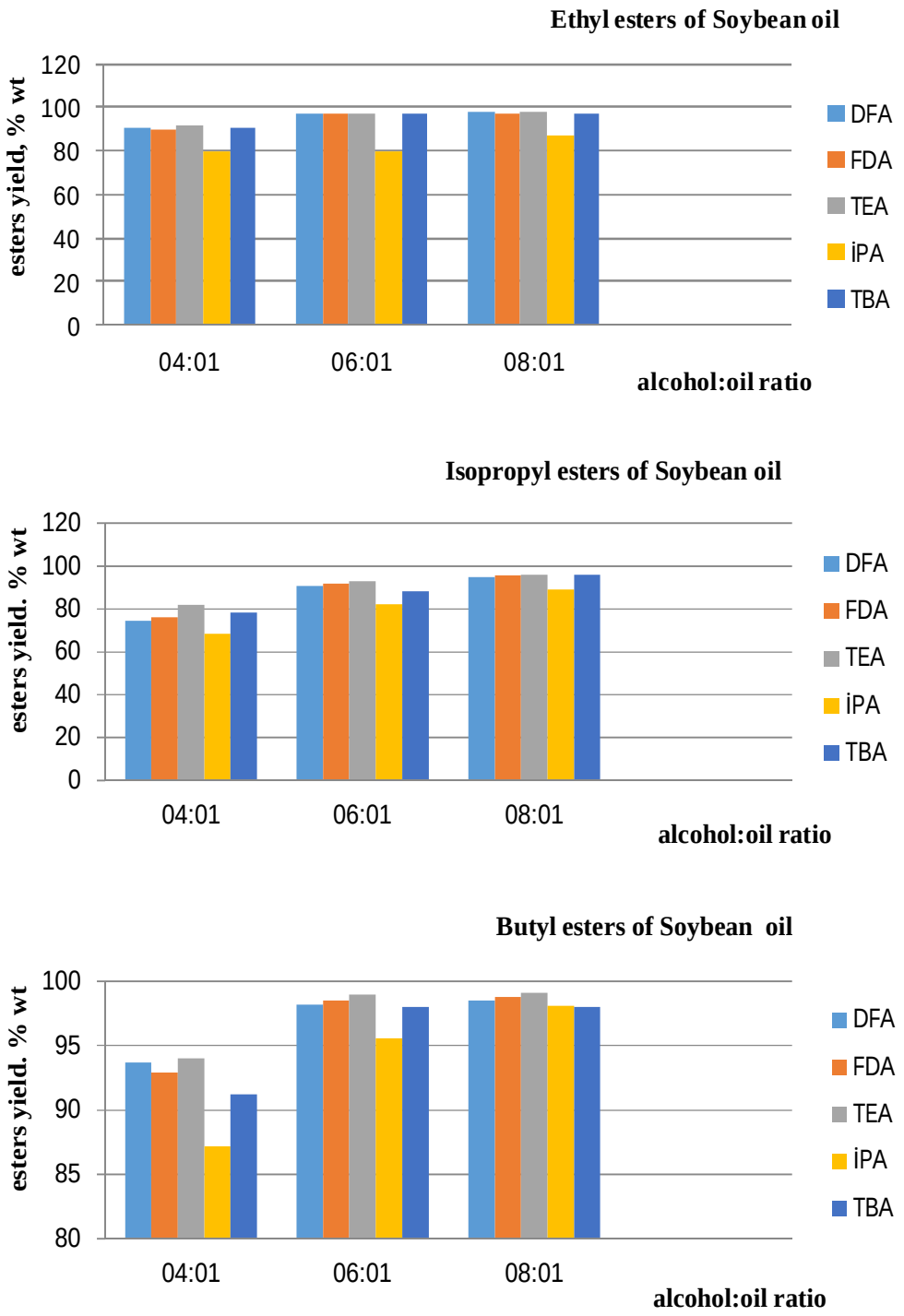


Fig. 2. Dependence of yields of methyl, ethyl, i-propyl and butyl ester based of soybean oil on alcohol: oil molar ratio

In the next step, the optimal concentration of the amino acid catalysts DFA, FDA, TEA, IPA and TBA was determined.

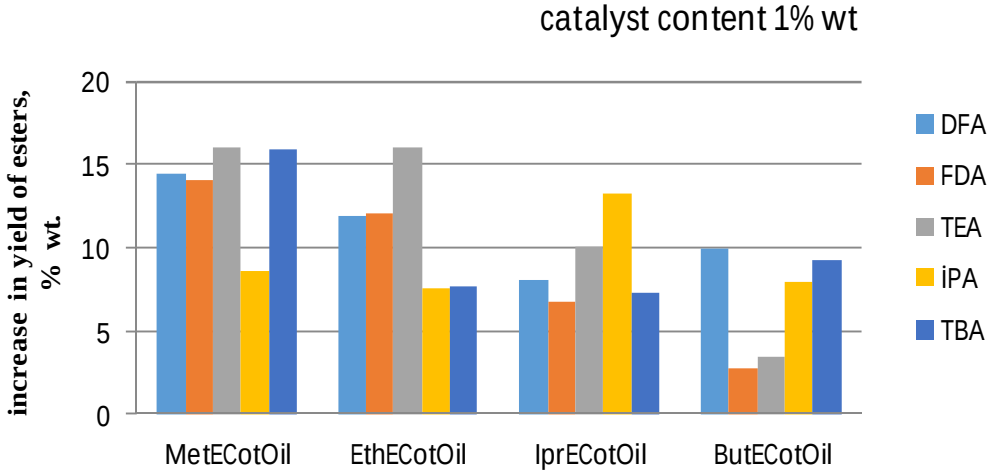
Experiments with alcohol using DFA, FDA, TEA and TBA catalysts at alcohol:oil molar ratio 6:1 in the presence of the catalyst of IPA at ratio 8: 1 for i-propyl esters, at boiling temperatures of the used alcohols were conducted for 10 minutes in the system. In Table 2 the obtained results are shown.

Table 2. The dependence of corn oil-based esters yields on the nature of amine catalyst in the hydrodinamic cavity

Catalysts	Amount of catalysts.% wt. (according to oil)				
	1.0	1.5	2	2.5	3.0
	Yield of methyl esters of corn oil				
DFA	62.1	81.6	94.1	98.6	99.0
FDA	66.7	83.2	94.3	98.3	99.0
TEA	70.3	85.4	93.8	99.0	99.0
IPA	44.2	58.1	75.3	92.6	98.0
TBA	60.1	78.3	94.5	97.4	98.0
	Yield of ethyl esters of corn oil				
DFA	52.2	67.5	80.4	97.4	98.5
FDA	56.7	66.3	81.6	97.2	98.3
TEA	58.3	71.2	83.5	98.3	98.7
IPA	36.2	47.6	64.7	80.6	89.5
TBA	46.4	64.1	78.1	96.9	97.1
	Yield of i-propyl esters of corn oil				
DFA	46.7	61.2	68.4	88.3	94.3
FDA	48.4	64.3	74.6	83.6	94.8
TEA	54.3	66.2	76.1	91.6	96.0
IPA	34.8	40.7	61.2	85.1	89.0
TBA	42.4	50.8	72.3	86.8	96.0
	Yield of butyl acids of corn oil				
DFA	56.7	82.8	93.6	98.1	98.6
FDA	54.6	85.2	94.3	98.5	98.7
TEA	56.1	86.4	95.2	99.1	99.2
IPA	38.6	57.4	83.4	95.0	96.2
TBA	50.8	68.4	92.1	97.5	97.2

To obtain methyl, ethyl and butyl esters of corn oil acids in the presence of DFA, FDA, TEA and TBA catalysts, a 2.5% amine catalyst is sufficient. It should be noted that studies on the effect of hydrodynamic cavitation show an increase in the same temperature and alcohol: oil content, but not in the conventional conditions (ie, the separation process without the use of cavitation effect).

For example, when using 1% DFA, FDA, TEA, and TBA catalysts, an increase in the yield of corn oil methyl esters is 9.2-19.1%, and when using an IPA catalyst, this increase is 8.6-11.0% wt.



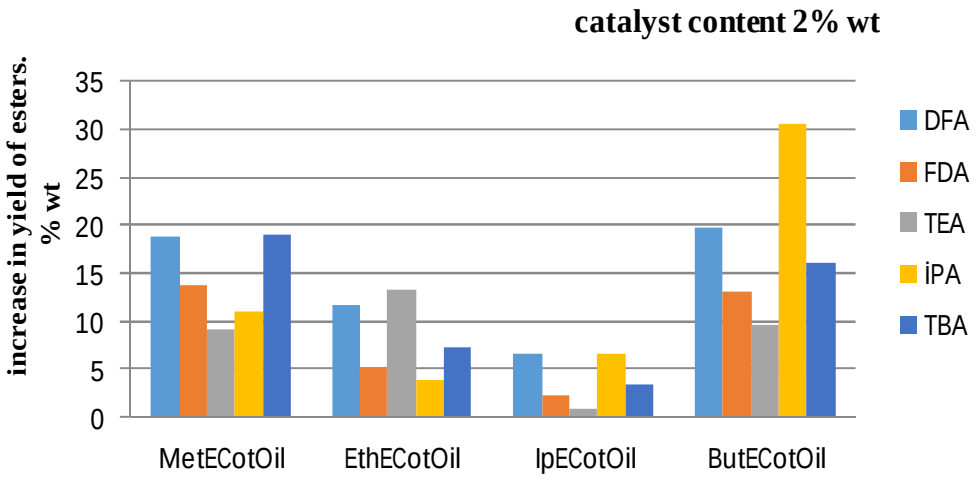


Fig. 3. Increases observed in the output of monoalkyl esters of corn oil acids when the amount of catalysts in hydrodynamic cavitation is 1% and 2% wt (by oil)

Approximately the same regularity is observed in other cases airway (Fig. 3). It is clear from the presented data that the highest increase in catalyst concentrations is observed for methyl esters of cotton oil acids, and 2% is recorded for both methyl and butyl esters.

Thus, the amount of DFA, FDA, TEA and TBA catalysts is 2.5% in the synthesis of methyl and butyl ester of cotton oil acids under hydrodynamic cavitation, while the concentration of these catalysts is about 3.0 % in the production of ethyl- and i-propyl esters. The optimum retention time was determined by the above mentioned catalyst additives and alcohol: oil ratio in hydrodynamic cavitation conditions for obtaining methyl-, ethyl-, i-propyl- and butyl esters of different vegetable oils acids. Obtained results are shown in Table 3.

According to the information given in Table 3 it can be said that 98.5-99.1% yield of the target products are obtained for 10 minutes under the hydrodynamic cavitation effect of the reaction solution with participation of catalysts DFA, FDA,TEA and TBA of methyl-, ethyl- and butyl esters of sunflower, corn, soybean and palm oils acids. Under these conditions, the IPA catalyst has slightly less activity, so that the reaction time for targeted ester should be at least 10 min. In the case of the isopropyl esters of the used vegetable oils, the optimum reaction time should be 12 minutes, which is a great advantage compared to the usual process (6-8 hours).

Conclusions

Thus, carrying out the reaction of transesterification of vegetable oils with alcohols C_1-C_3 in the conditions of hydrodynamic cavitation allows you to reduce the process time by 48-50 times compared with conventional conditions while maintaining high yields of biodiesel. According to the information given in this Table it can be said that 98.5-99.1% yield of the target products are obtained for 10 minutes under the hydrodynamic cavitation effect of the reaction solution with participation of catalysts DFA, FDA,TEA and TBA of methyl. ethyl and butyl esters of sunflower. corn. soybean and palm oils acids. Under these conditions, the İPA catalyst has slightly less activity, so that the reaction time for targeted ester should be at least 10 min. In the case of the isopropyl esters of the used vegetable oils, the optimum reaction time should be 12 minutes, which is a great advantage compared to the usual process (6-8 hours).

Table 3. Optimal synthesis period of methyl, ethyl, i-propyl and butyl esters of vegetable oils acids in the hydrodynamic cavitation conditions

Esters	Catalysts														
	DFA			FDA			TEA			IPA			TBA		
	Time of obtaining esters, min.														
	5	10	12	5	10	12	5	10	12	5	10	12	5	10	12
MetECotOil	82.4	99.3	-	87.4	99.0	-	88.2	99.0	-	83.4	96.0	98.6	85.7	99.1	-
MetESunFOil	81.2	98.8	-	86.3	98.5	-	87.6	99.0	-	82.8	94.5	98.4	84.9	98.7	-
MetECornOil	83.3	99.0	-	88.5	98.4	-	88.1	99.0	-	84.5	93.8	98.5	84.3	98.7	-
MetEPalOil	83.1	99.0	-	88.4	99.0	-	88.5	99.0	-	85.7	95.0	98.2	86.2	98.2	-
MetESoyOil	82.4	99.0		87.6	99.0	-	87.7	99.0	-	85.4	94.6	98.2	85.4	98.4	-
EthECotOil	72.1	98.5	98.7	74.5	98.0	-	72.4	98.4	98.7	55.6	89.5	98.0	72.3	97.1	-
EthESunFOil	71.8	98.1	98.4	73.9	98.0	-	73.2	98.4	98.7	54.8	87.5	98.0	71.9	98.6	-
EthECornOil	71.6	98.4	98.7	74.7	98.0	-	73.7	98.4	98.7	55.6	86.4	98.0	72.4	98.2	-
EthEPalOil	71.4	98.7	98.7	75.0	98.0	-	74.5	99.1	99.4	54.4	74.8	98.0	72.6	97.9	-
EthESoyOil	71.5	98.5	98.4	75.1	99.0	-	73.5	99.0	99.4	55.0	75.6	98.0	72.5	98.3	-
IprECotOil	50.6	94.3	98.7	60.8	94.8	98.0	62.5	96.0	98.0	40.7	89.0	98.5	62.5	96.0	97.8
IprESunFOil	51.4	92.9	98.0	61.2	92.6	97.5	62.8	95.9	98.0	41.9	90.1	98.6	62.4	95.2	97.6
IprECornOil	52.0	91.5	97.8	62.6	93.4	97.7	62.8	93.4	98.0	41.6	91.2	98.7	63.3	95.4	97.0
IprEPalOil	51.7	93.5	98.1	62.7	92.6	98.0	63.0	94.1	98.0	42.2	91.3	98.5	62.8	95.8	97.1
IprESoyOil	52.2	93.1	98.4	62.5	94.7	98.1	63.2	94.2	98.0	42.4	91.0	98.5	63.0	95.0	98.0
ButECotOil	84.3	98.6	-	90.8	98.7	-	86.7	99.0	-	64.8	96.2	98.6	80.9	98.6	-
ButESunFOil	85.5	98.4	-	90.6	98.2	-	86.5	99.0	-	63.6	95.2	98.4	80.5	98.2	-
ButECornOil	85.7	99.0	-	90.0	99.0	-	86.3	99.0	-	64.7	95.3	98.0	81.4	99.0	-
ButEPalOil	86.0	98.7	-	91.5	98.6	-	87.4	99.0	-	65.3	96.0	98.0	82.3	98.5	-
ButESoyOil	85.8	98.8	-	91.1	98.4		87.1	99.0	-	65.7	95.8	98.5	82.0	98.7	

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BİTKİ YAĞLARININ C_1-C_4 SPİRTLƏRİ İLƏ TRANSEFİRLƏŞMƏ REAKSİYASININ HİDRODİNAMİK KAVİTASİYA TƏSİRİNDƏ TƏDQİQİ

Z.M. Əliyeva

AMEA Akad. Y.H. Məmmədəliyev adına Neft-Kimya Prosesləri İnstitutu, Bakı
Az 1025. Bakı, Xocalı prospekti 30
Fax: (+99412) 490-24-76. e-mail: zulfiya_aliyeva@inbox.ru

Təqdim olunan məqalədə trietilamin (TEA), fenilendiamin (FDA), difeniamin (DFA), izoprpopilamin (İPA), üçlübutilamin (ÜBA) amintərkibli birləşmələrdən katalizator kimi istifadəsində pambıq, günəbaxan, qarğıdalı, soya və palma yağlarının sadə metanol, etanol, i-propanol və butanol spirtləri ilə transefirləşmə prosesi hidrodinamik kavitasiya şəraitində tədqiq olunmuşdur. Təyin edilmişdir ki, bitki yağlarının monoalkil efirlrinin alınması prosesi hidrodinamik kavitasiya səraitində spirt:yağ nisbəti 6:1. prosesin davamlığı 10-12 dəq təşkil etdikdə metil və butil efirlərinin alınmasında DFA, FDA, TEA və ÜBA katalizatorlarının lazım olan qatılığı 2.5% küt. təşkil edir, etil və i-propil efirlərin alınmasında isə bu katalizatorların qatılığı 3.0% küt. təşkil edir.

Açar sözlər: *bitki yağları, spirt, transefirləşmə, hilrodinamik kavitasiya, amintərkibli birləşmələr, katalizator, optimal şərait.*

ИССЛЕДОВАНИЕ РЕАКЦИИ ТРАНСЭТЕРИФИКАЦИИ РАСТИТЕЛЬНЫХ МАСЕЛ С C_1-C_4 СПИРТАМИ В УСЛОВИЯХ ГИДРОДИНАМИЧЕСКОЙ КАВИТАЦИИ

З.М. Алиева

Институт Нефтехимических Процессов им. акад. Ю.Г. Мамедалиева
Национальной АН Азербайджана
AZ 1025, проспект Ходжалы, 30

Fax: (+99412) 490-24-76, e-mail: zulfiya_aliyeva@inbox.ru

Изучен процесс трансэтерификации хлопкового, подсолнечного, кукурузного, соевого и пальмового растительных масел с простыми спиртами - метанол, этанол, изо-пропанол и бутанол в условиях гидродинамической кавитации при использовании в качестве катализаторов аминсодержащих соединений, таких как триметиламин (ТМА), фенилендиамин (ФДА), дифениламин (ДФА), изо-пропиламин (ИПА), третбутиламин (ТБА). Выявлено, что при проведении процесса в условиях гидродинамической кавитации при мольном соотношении спирт:масло 6:1 и продолжительности процесса 10-12 мин для получения высоких выходов метиловых и бутиловых эфиров жирных кислот растительных масел содержание катализаторов ТМА, ФДА, ДФА и ТБА составляет 2.5% масс., а для получения этиловых и изопропиловых эфиров 3.0% масс.

Ключевые слова: *растительные масла, спирт, трансэтерификация, гидродинамическая кавитация, аминосодержащие соединения, катализаторы, оптимальные условия.*