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RESEARCH INTO THE PRODUCTION PROCESS OF BIODIESEL ETHERS BY USING AMINE-CONTAINING CATALYST IN MAGNETIC FIELD

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The production of biodiesel esters by transesterification of corn and sunflower oil with methanol has been analyzed using 1,3-bis (isopropylamino)-propan-2-ol catalyst in 15-45mT magnetic field, at 65°C temperature and 6:1 molar ratio of methanol to oil. Experiments were carried out in three-neck round-bottom flask which is placed in magnetic field produced by electromagnets and equipped with a thermometer, a mixer and a dropping funnel. The yield of the biodiesel ester was 95-97% (by mass) and the duration of the process was 4.5 times shorter with magnetic field when the catalyst is used at 3% by weight relative to oil.

***Keywords**: biodiesel, transesterification, amine-containing catalysts, magnetic field*

INTRODUCTION

Nowadays, approved petroleum reserves of the world are 157 billion tons and according to estimates, it will meet energy requirement for 40-50 years. In consdering the fact that the poisonous waste are those produced due to the combustion of petroleum-based energy carriers which deteriorate the ecology, the world energetics should use renewable and more environmentally-convenient fuels [1].

In order to accomplish the process, a number of leading countries are accepting various programs and a budget of high amount of money [2,].

For instance, 1.5 billion dollars of public investment will be spent during the upcoming decade for the development of bioeconomics in the United States of America. The purpose of this investment is 25/25, i.e. to use 25% of alternative renewable energy of total energy resources until 2025. According to estimates, it may save 35% of petroleum consumption (10 million barrel per day) until 2030; reduce 80% of greenhouse gases and thus lead climate changes in the world until 2050.

The similar program has been accepted in the European Union (EU). Executive Center of the EU predicts the usage of the alternative energy sources reaching to 20% and the amount of the contamination to the atmosphere being reduced by 20% by 2020 with respect to the pointers of 1990. Since 2013, the plan that is called "20-20-20" has been providing the transfer of quota sale of the EU members for CO_2 contaminants [2].

The manufacture of energy carriers from the biological feedstock is the easiest and the most cost effective process, and widely used among other renewable energy sources. Considering that the major part of the fuel energy is consumed by automobiles, the application of alternative biofuels in the transportation industry becomes very essential [3-5].

The main advantages of the biofuels are their production from renewable feedstock, being sulfur free and rich in aromatics, biodegradibility (most feedstock degrade in about 2 months) and environmentally friendly gaseous waste. As a result of ethanol usage, the greenhouse gases (CO_2 equivalent) decreased by 8 million tonnes, which equalled to the total annual emissions of 1.21 million cars in the USA in 2008 [1]. Greenhouse gases emitted from renewable biosources do not contribute to the global CO_2 growth in the atrmosphere since the amount of the CO_2 released into the atmosphere corresponds to the amount absorbed by the plants. EU's "Encourage for the usage of biofuels" directive specifies following components as biofuel: bioethanol, biodiesel, biogas, biomethanol, the ether of biodimethyl, bio-ETBE (ethyl-tert-butyl ether) produced from bioethanol, bio-MTBE (methyl- tert-butyl ether) produced from biomethanol, synthetic biofuel, biohydrogen and vegetable oils.

Nowadays, biofuels are already being used as an alternative fuel for diesel engines. Biodiesel consists of alkyl esters of fatty acids produced by transesterification of various vegetable oils with alcohols. These kinds of molecules provide oxygen into combustion products in the oxygen-deficient environment as they contain the oxygen atoms. By this way, the oxygen atoms in biodiesel are used during the combustion process to cause complete burning. For instance, switching to B100 (100% biodiesel) from conventional diesel, causes 56.3% decrease of incompletely burned hydrocarbons, 55.4% decrease of solid particles and 43.2% decrease of carbon dioxide. Considering that the incompletely burned gaseous waste from automobile emissions get into the human respiratory system for a long time and risk potentially causing the lung cancer, especially in big cities where the emissions are high, the combustion products have to be purified.

Currently, the most widespread method for preparing biodiesel is the transesterification of vegetable oils (or fatty acids obtained from them) with alcohols in the presence of alkaline catalyst in mixing batch reactor. Despite being simple in technology, this process has some disadvantages. The most important one is that the feedstock need to be dried, otherwise it will cause saponification, lowering the yield of the desired products. Produced soap hinders the separation process of ester/glycerol phases as a surfactant and raises the production cost by up to 30% [6-8].

The production of biodiesel esters is optimized in a number of ways, including testing new catalysts capable of preventing saponification, increasing rates of the transesterification process by using electromagnetic and magnetic waves, etc. Note that the use of magnetic field weakens chemical bonds in the molecules as a result of polarization/depolarization processes which accordingly raise the reaction rate [9,10].

Results of various studies utilizing amine-containing catalyst for the transesterification of fatty acids is given in Table 1 [11-15].

Table 1. Relative activity of miscellaneous amine-containing compounds as transesterification catalyst.

Catalyst	Amount,% by mass, according to oil	Reaction time, hour	pK_a	The yield of alkyl ethers, % by mass
1,5,7-triazabicyclo[4,4,0]dec-5-ene (TBD) [5,6]	1	1	25,9	89
1,5,7-triazabicyclo[4,4,0] dec-5-ene (TBD)	2	1	---	91
1,5,7-triazabicyclo [4,4,0] dec-5-ene (TBD)	3	1	---	93
Tris-(dimethylamino)methyliminophosphorane (Me_7P) [7]	1	1	27.5	63
1,8 -diazabicyclo[5,4,0]undec-7-ene (DBU)	1	1	24.32	32

[5,7,8,9]				
1,1,3,3–tetramethylguanidine (TMQ) [10-12]	1	1	23.30	18
1,5 diazabicyclo[4,3,0] non-5-ene (DBN) [7,9]	1	1	23.79	45

As is seen from the Table 1, TBD and Me_7P catalysts show highest activities among other tested amines for transesterification process. For example, when 1,5,7-triazabicyclo[4,4,0] dec-5-ene is used (oil:alcohol ratio 1:4, temperature 70°C) the 1% and 3% of catalyst yielded 91% and 93% of biodiesel esters, respectively. In order to obtain 98-99% yield by using conventional KOH and NaOH catalysts, amine containing catalysts should be used above 3% by mass.

EXPERIMENTALS

In this proceeding, we examined the production process of the biodiesel esters from corn and sunflower oils and methanol using 1,3-bis (isopropylamino)-propan-2-ol catalyst in 15-45mT magnetic field and at 65°C temperature. Methanol to oil ratio was set at 6:1. The experiments were carried out in three-neck round-bottom flask equipped with a thermometer, a mixer, and a dropping funnel and placed in the magnetic field produced by electromagnets. Amount of catalyst (relative to oil) varied in the interval of 1-3%. Refined corn and sunflower oils and unrefined sunflower oil were used as vegetable oils.

RESULTS AND DISCUSSION

Yields of biodiesel ethers produced by using 1,3-bis (isopropylamino)-propan-2-ol as catalyst are given in Table 2.

Table 2. The dependence of the yields of biodiesel ethers on the duration of process by using 1,3-bis (isopropylamino)-propan-2-ol as catalyst with and without* magnetic field

Duration of process	Refined sunflower	Unrefined sunflower	Refined Corn
	Yields of biodiesel ethers with 1% catalyst		
40 minutes	40/22*	45/26	41/ 24
2 hours	62/ 45	68 / 48	60 / 43
4 hours	72 / 58	81/ 62	75 / 60
	Yields of biodiesel ethers with 3% catalyst		
40 minutes	95 / 61	97 / 65	96 / 62
2 hours	96 / 71	98 / 75	98 / 75
4 hours	98 / 89	98 / 91	98 / 90

Note that the yield of biodiesel esters varied at 22-26% (by weight) interval after 40 minutes in normal conditions when the 1% catalyst was used by weight. However, when the magnetic field was applied, the yields were doubled within the same duration to make up 43-46%. Also, yields of biodiesel esters were 43-48% and 58-62% during 2 and 4 hours of the conventional process, respectively, whereas they increased to 62-68% and 72-81%, respectively, with magnetic field. The yield has reached to 95-97% by weight in 40 minutes and under magnetic field when the amount of the catalyst rose to 3%. However, under standard conditions, an appropriate yield was 61-65% and even after 4 hours, it only reached to 90-91%. The purity of synthesized methyl esters of sunflower and corn oils have been verified by using ^1H and ^{13}C NMR spectroscopy methods (Figure 1).

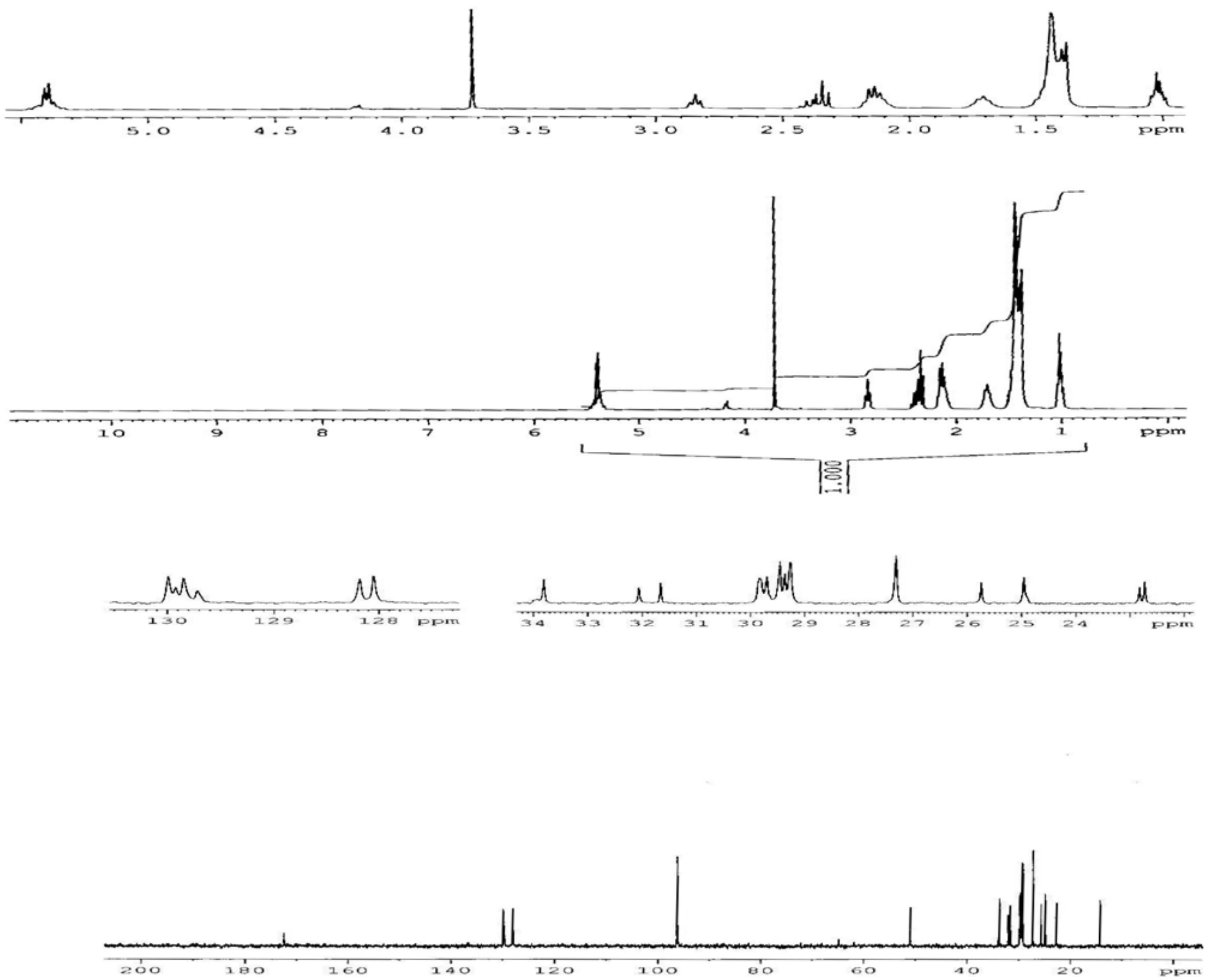

Fig.1 ^1H, ^{13}C NMR spectra of the methyl ether of sunflower oil

Note that protons of methyl and methylene groups, as well as those belonging to unsaturated hydrocarbon radicals have been observed in 1.35 (3H, CH_3) and 1.35-1.5 (20H, 10 CH_2) ppm, however, the allyl protons of allyl group and the protons of metoxy group have been recorded in 2.1-2.2 (4H, $2CH_2C{=}C$) and 3.75 (3H, OCH_3) ppm.

Signals according to the following chemical shift have been recorded via NMR ^{13}C spectrum: 22.8 (CH_3), 24.8 (CH_2), 27.4 (CH_2), 29.2 (CH_2), 29.5(CH_2),29.7(CH_2), 29.9(CH_2), 31.6(CH_2), 32.1(CH_2), 33.8(CH_2), 61.6(CH_2), 68.8 (OCH_3),128.05,128.2, 129.8, 130 (CH2=C and C=C).

RESULTS

Following the experiments in question, it was revealed that synthesized 1,3-bis (isopropylamino)-propan-2-ol might be used as catalyst for the transesterification process of both refined and unrefined vegetable oils with methanol if it is taken with 3% (by mass) according to oil. Advantages of this catalyst are that it is soluble in methanol as a solid substance to create a precipitation during the usage of alcohol in reaction and may be reused, for it is easily separated from the reaction products. When the process runs under the influence of 15-45mT magnetic field, the duration of the reaction decreases 4.5 times.

It should be mentioned that at the beginning of the transesterification process, 3-bis (isopropylamino)-propan-2-ol, which is used as catalyst is dissolved in methanol and led to the reaction environment, whereas at the end, when the methanol is used and the excess amount is dismissed, it precipitates as a crystal and may be reused as catalyst by removing from products very easily.

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ИССЛЕДОВАНИЕ ПРОЦЕССА ПОЛУЧЕНИЯ БИОДИЗЕЛЬНЫХ ЭФИРОВ С ИСПОЛЬЗОВАНИЕМ АМИНСОДЕРЖАЩЕГО КАТАЛИЗАТОРА В МАГНИТНОМ ПОЛЕ

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Исследован процесс синтеза биодизельных эфиров путем переэтерификации кукурузного и подсолнечного масла метанолом с использованием в качестве катализатора 1,3-бис(изопропиламино)-пропан-2-ола в магнитном поле интенсивностью 15-45 мТ, температуре 65 ° С и молярном соотношении метанол:масло 6:1. Эксперименты проводились в оборудованной термометром, смесителем и капельной воронкой трехгорлой круглодонной колбе, помещаемой в магнитное поле, создаваемое электромагнитами. Выход биодизельного эфира составил 95-97% масс. при использовании катализатора в количестве 3% масс. При этом продолжительность реакции уменьшилась в 4.5 раза по сравнению с процессом, проводимом без использования магнитного поля.

Ключевые слова: *биодизель, переэтерификация, аминсодержащие катализаторы, магнитное поле*

BİODİZEL EFİRLƏRİNİN AMİNTƏRKİBLİ KATALİZATOR VƏ MAQNİT SAHƏSİ TƏSİRİNDƏ ALINMASI PROSESİNİN TƏDQİQİ

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Biodizel efirlərinin sintez prosesi qarğıdalı və günəbaxan yağlarının metanolla transefirləşməsilə 1,3-bis (isopropilamino)-propan-2-oldan katalizator kimim iştifadə etməklə 15-45mT maqnit sahəsində, 65°C temperaturda və spirt:yağ nisbəti 6:1 olduqda tədqiq edilmişdir. Təcrübələr termometr, qarıştırıcı və damcılayıcı qıfla təchiz olunmuş və elektromaqnitlər vasitəsilə yaradılmış maqnit sahəsində yerləşdirililmiş üç boqazlı kolbada aparılmışdır. Katalizatorun miqdarı yağa görə 3% olduqda biodizel efirilərinin çıxımı 95-97% (kütlə) təşkil etmiş və bu zaman prosesin aparılma müddəti maqnit sahəsinin təsiri olmadan aparılan proses ilə müqayisədə 4.5 azalmışdır.

Açar sözlər: *biodizel, transefirləşmə, amin tərkibli katalizator, maqnit sahəsi*

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