THE PRODUCTION METHOD OF BIODIESEL FUELS BY USING LOW ENERGY WAVES AND RESEARCH PRODUCTS OF THEIR COMBUSTION

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Abstract

In this proceeding, the production process of methyl ethers of unrefined cottonseed, corn and sunflower vegetable oils by using amine containing compounds like diethylamine, triethylamine and p-phenylendiamine as catalyst, with 1:6 ratio of oil to methanol, at 65-70°C, in 15-45 mTl induction of magnetic field has been investigated. As a result of the process which had been done in 25mT induction of magnetic field for 30-45 minutes, it has been determined that the production yield is 97.1-98.8 % (by mass).

The content of the flue gases of the compositions those are produced by adding 5 and 10% of the manufactured methyl ethers to petroleum based diesel fuel has been determined.

It has been revealed that when 5% of methyl ethers of vegetable oils are added to diesel fuel, the amount of the carbon monoxide and the sulfur oxides in the flue gases decreases by 23.4-25.2% and 5.2-6.9% respectively

Key words: *biofuel, catalyst, magnetic field, combustion products, flue gases, carbon monoxide, sulfur oxides, nitrogen oxides, DSC spectra*

1. INTRODUCTION

The world energetics should prefer renewable and environmentally friendly energy carriers since the ecology is contaminated because of the dangerous waste materials those are produced as a result of the combustion process of petroleum based energy carries and released to atmosphere. In order to accomplish this process, a number of leading countries accept different programs and budget a high amount of money [1].

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, so what to use 25% of alternative renewable energy of the total energy resources until 2025. According to the calculations, it leads to save 35% of petroleum consumption (10 million barrel per day) until 2030, to reduce 80% of greenhouse gases and to be e leader for the climate changes in the world until 2050.

The similar program has been accepted in the European Union. By the Executive Center of the European Union, it is predicted that the usage of the alternative energy sources will be 20% and the amount of the contamination to the atmosphere will be reduced by 20% with respect to the pointers of 1990 until 2020. Since 2013, the plan that is called “20-20-20” has been providing the transfer of quota sale of the countries those are included in European Union for CO_2 contaminants [2-4].

The energy carriers those are manufactured on the basis of the bio-feedstock are the easiest to obtain, cost effective and widely used among the renewable energy carriers. If we take into consideration that the automobiles are the main consumers of energetics, the application of alternative biofuels to the transport is very essential [4].

The main advantages of the biofuels are that they are produced on the basis of the renewable feedstock, they do not contain sulfur and aromatics, they are safely broken up in environment during 2 months and they contain environmentally friendly waste gases. As a result of ethanol usage, the greenhouse gases (CO_2 equivalent) decreased by 8 million tonnes those are equal to the annual waste

gases of 1.21 million cars in the USA in 2008. As a feedstock of the greenhouse gases, biofuels are neutral since the amount of the CO_2 gases those are released to atmosphere as a result of their production and consumption is equal to the amount of the absorbed CO_2 gases by plants.

According to the "Encourage for the usage of biofuels" directive of the European Union, the following materials are considered as biofuel: bioethanol, biodiesel, biogas, biomethanol, the ether of biodimethyl, bio-ETBE (ethyl-tert-butyl ether) on the basis of bioethanol, bio-MTBE (methyl- tert-butyl ether) on the basis of biomethanol, synthetic biofuel, biohydrogen and vegetable oils.

Nowadays, biofuels are being used as an alternative fuel type for diesel engines. Biodiesel fuels consist of the methyl, ethyl and etc. ethers of oil acids those are produced as a result of the transesterification of miscellaneous vegetable oils with alcohols. These kinds of fuels provide to transfer oxygen to combusted solution at the end of the combustion cycle, during the deficiency of oxygen, since they contain oxygen molecules. By this way, the oxygen of the biodiesel fuel is used during the last steps of the combustion process and causes full burning. For instance, in the combustion products of B100 (100% biodiesel) and B20 (20% biodiesel and 80% conventional fuel) fuels, there are 56.3% and 11% of decrease for unburned hydrocarbons, 55.4% and 18% of decrease for solid particles and 43.2% and 12.6% of decrease for carbon dioxide respectively. If we take into consideration that the waste gases from the automobiles remain in the respiratory system of the human for a long time and cause cancer because of the high buildings and narrow streets of big cities, the burning products should be pure.

The improvement of the production methods of the biodiesel fuels is operated in several directions: searching new types of catalysts; enhancing the speed of the transesterification process under the influence of different waves (as well as the magnetic field) and etc. Under the influence of the magnetic field, the bonds of the molecules weaken as a result of the polarization/depolarization processes and the speed of the reaction increases [5-8].

2. EXPERIMENTALS

2.1. Materials and methods

In the presented work, the manufacturing process of the methyl ethers of the cottonseed (CSO), sunflower (SO) and corn oil (CO) by using different amine containing catalysts, with 6:1 methanol to oil ratio, at 65°C in the 15-45 mTl induction of magnetic field has been investigated. Diethylamine, trimethylamine and p-phenylendiamine those had been obtained from Sigma Aldrich company have been used as catalysts. The physical and chemical properties of the used unrefined vegetable oils are indicated in table 2.1 and the physical and chemical properties of diesel fuel are shown in table 2.2.

The name of the oil	Iodine number, g I_2/100 g oil	Total Acid Number, mg KOH/g oil	Density, at 20°C kg/m^3	Viscosity at 100°C, mm^2/s	T_{flash}, °C	$T_{freezing}$, °C	Refractive index
CSO	53,13	4,25	918,8	7,69	316	-18	1,4758
CO	54,09	4,09	922,7	6,84	306	-17	1,4762
SO	56,75	3,96	927,5	7,93	320	-16	1,4754

Table 2.1. The physical and chemical properties of used vegetable oils

Pointers	**Values**
Cetane number	47
Density, at 20°C kg/m^3	849,5
Fractional composition, ℃	
Initial boiling point	190
10% distillation temperature	210
50% distillation temperature	270
90% distillation temperature	335
96% distillation temperature	345
Hydrocarbon composition, %	
Aromatic	21,23
Paraffin -Naphthene	78,52
Unsaturated	0,25
Kinematic viscosity, at 20°C mm^2/ sec	2,23
Acidity, mg KOH/100 cm^3	0,01
Iodine number, g I_2/100 g	0,18

Table 2.2(a). The physical and chemical properties of used diesel fuel

Pointers	**Values**
Flash point, °C	73
Freezing point, °C	-36
Cloud point, °C	-28
Filtration Coefficient	1,2
Factual waxes, mg/100 cm^3	5
Total Sulfur Content, 10^{-3} %	12
Corrosion experiment on copper plate at 100°C during 3 hours	+
Coking of 10% residue, 10^{-3} %,	1
Ash content, 10^{-3} %	0,9
Caloricity, kC/kg	43290
Lubricity, mm	0,595
Antistatic ability, pS/m	8

Table 2.2(b). The physical and chemical properties of used diesel fuel

The content of the flue gases those have been produced as a result of the combustion of 5% and 10% composition of biodiesel ethers based on the cottonseed, corn and sulflower oil with diesel fuel has been analysed with “TESTO 350TM” probe. The smoking ability of them during the application of

these compositions as a fuel has been determined with "Smokemeter" 495-01 gas analyser (made in Italy) by optical measurement method in the Ecological Measurement Center of the Department of Ecology of SOCAR.

The heat-physical properties of 5% and 10% composition of biodiesel ethers based on the cottonseed, corn and sulflower oil with diesel fuel have been determined with DSC Q-20 device which is manufactured by "Intertech Corporation" of the USA by the differential scanning calorimetry method in the air and inert (nitrogen) system, with the heating speed of 10°C/minute.

3. RESULTS AND DISCUSSION

The yields of the methyl ethers of cottonseed, sunflower and corn oil and the duration of the processes according to used catalysts are presented in Table 3.1

Catalysts	**The yields of the methyl ethers of cottonseed, sunflower and corn oil, % mass.**		
	Used vegetable oil		
	cottonseed	**corn**	**sunflower**
	Under the influence of 25 mT magnetic field		
Diethylamine	78,2	73,6	75,4
Triethylamine	98,8	96,5	97,1
p-phenylenediamine	87,6	84,5	80,7
Duration of the reaction, min.	30	40	45
	Without the influence of magnetic field		
Diethylamine	60,2	57,6	52,5
Triethylamine	87,7	82,4	88,2
p-phenylenediamine	75,2	73,5	75,4
Duration of the reaction, hour	8	6	6

Table 3.1. The yields of the methyl ethers of cottonseed, sunflower and corn oil and the duration of the processes according to used catalysts

As it is obvious from Table 3.1, a production yield of 95-98% (by mass) of biodiesel ethers was observed during 30-45 minutes, however 6-8 hours are required for the same process with a production yield of 82.4-88.2% (by mass) by using conventional method. Triethylamine was the most active catalyst for this process.

The catalysts those are used in order to obtain the maximum production yield of biodiesel ethers irrespective of the types of the oils which is used for both conventional and the synthesis process under the magnetic field can be written in the following order: triethylamine > p-phenylendiamine > diethylamine.

The quality pointers of the methyl ethers of unrefined cottonseed, sunflower and corn oil are indicated in the Table 3.2.

Pointers	**Cottonseed oil**	**Sunflower oil**	**Corn oil**
Density, 20°C kg/m^3	888,5	887,5	889,8
Kinematic viscosity at 20°C mm^2/sec	3,15	3,45	3.38
Iodine number, g J_2/100g oil	94,08	97,4	90,7
Total Acid Number mg KOH/1 g oil	0, 29	0,35	0,32
Freezing point °C	-9	-6	-10
Cloud point, °C	-4	-2	-5
Flash point, °C	120	120	120
Experiment on the copper plate	+	+	+
Ash content, % mass	-	-	-
Total Sulfur Content, % mass	0,0001	0,0001	0,0001
Coking of 10% residue, 10^{-3} %, mass	0,12	0,12	0,14
Boiling range	250-355	255-355	260-355
Cetane number	52	52	52

Table 3.2. The quality pointers of the methyl ethers of vegetable oils

The content of the flue gases those are released as a result of the combustion of the 5% and 10% mixture of the produced methyl ethers of sunflower, corn and cottonseed oils with the diesel fuel has been determined.

	The content of flue gases, % mass		
	CO	**SO_2**	**NO_x**
Diesel fuel	0,575	0,058	0,051
	Diesel fuel +5% methyl ethers		
The methyl ethers of cottonseed oil	0,430	0,055	0,051
The methyl ethers of sunflower oil	0,440	0,055	0,051
The methyl ethers of corn oil	0,433	0,054	0,049
	Diesel fuel +10 % methyl ethers		
The methyl ethers of cottonseed oil	0,347	0,053	0,047
The methyl ethers of sunflower oil	0,351	0,053	0,047
The methyl ethers of corn oil	0,355	0,052	0,046

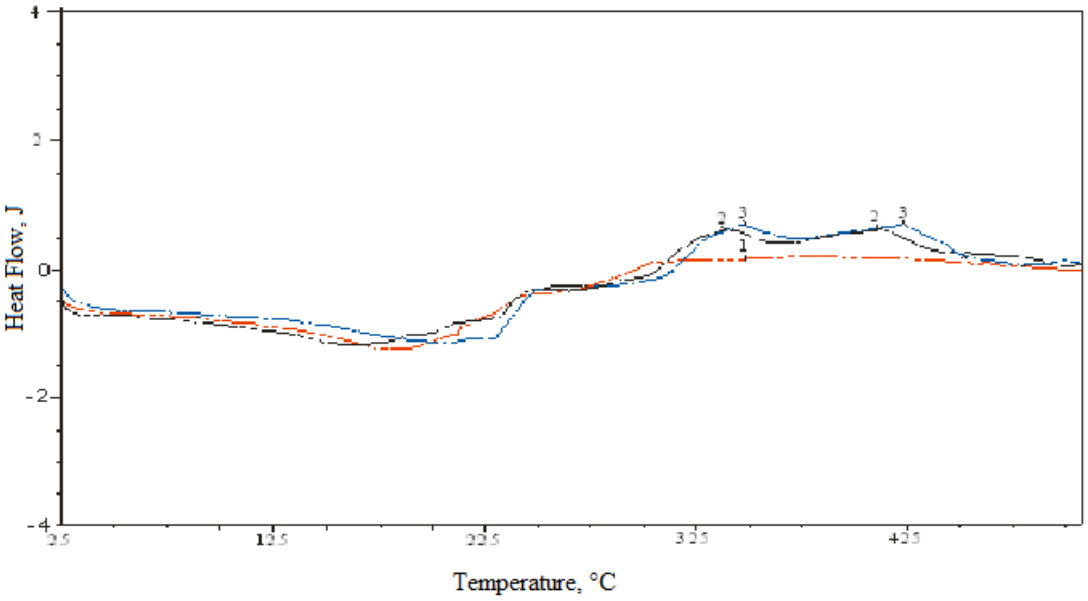
Table 3.3. The content of the flue gases those are released as a result of the combustion of the 5% and 10% mixture of the produced methyl ethers of sunflower, corn and cottonseed oils with the diesel fuel

It has been revealed that when 5% of methyl ethers of vegetable oils are added to diesel fuel, the amount of the carbon monoxide and the sulfur oxides in the flue gases decreases by 23.4-25.2% and 5.2-6.9% respectively by mass. The amount of nitrogen oxides does not change practically and it is

0.051-0.049% by mass. When 10% of methyl ethers of vegetable oils are added to diesel fuel, the amount of carbon monoxide decreases by 38.2-40.4% by mass.

On the other hand, it has been determined that the smoking ability of 10% (by mass) composition of the used diesel fraction with methyl ethers 44 % less than the initial diesel fraction. This is very vital for the big megalopolises.

The difference between the combustion processes of the 5% and 10% (by mass) compositions of methyl ethers of vegetable oils with diesel fuel and initial diesel fuel can be easily seen from the spectra of Differential Scanning Calorimetry (DSC) analysis. (Fig 3.1)



1. The DSC spectrum of the combustion of the initial diesel fuel
2. The DSC spectrum of the combustion of 5% composition of diesel duel with the methyl ethers of cottonseed oil
3. The DSC spectrum of the combustion of 10% composition of diesel duel with the methyl ethers of cottonseed oil

Fig.3.1. The DSC spectra of the combustion of diesel fuel and its 5-10% compositions with the methyl ethers of cottonseed oil

As it is obvious from the Fig.3.1, there is a small difference until 325°C temperature in the curve which shows the dependence of heat flow that characterizes the combustion of initial diesel fuel and its compositions on temperature. However, the characters of the curves change in the temperature interval of 325-425°C. In this interval, the curve which indicates the initial diesel fuel was nearly straight, whereas for compositions, two peaks were recorded.

The reason is that in 325-425°C temperature interval, there is as if a fractionation process for the composition based fuels. It is predicted that the additives carry extra oxygen those are not used for combustion at elevated temperatures. That is why, they let to provide oxygen for the last step of the combustion process which is characterized with the deficiency of oxygen. So, during the last steps of the combustion, the oxygen of the additives is used and provide full combustion process rather than the appropriate diesel fuel.

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