UDC 577.05, 665.3

[1]A.S. Belgibayeva*, [1]S.M. Kozbakarova, [1]B.M. Ashim,
[1]Ye.K. Ongarbayev, [2]S. Farrell

[1]Faculty of Chemistry and Chemical Technology, Al-Farabi Kazakh National University, Almaty, Kazakhstan
[2]Rowan University (USA)
*E-mail: belgibayeva@mail.ru

A comparative analysis of biodiesels produced from vegetable oils and their waste

This article shows the results of synthesis and investigation of biodiesel from canola and corn oils and waste feedstock. Tests on the diesel engine for an estimation of quality of the received products also were carried out.
Keywords: biodiesels, vegetable oil, canola oil, corn oil.

Introduction

Biodiesel is a biofuel on the basis of vegetative or animal fats (oils), and also the products of their etherification. Process of production of biodiesel fuel is rather simple. Vegetable oil is a mixture of triglycerides, ethers conjugated to a glycerin molecule. Major task of the biodiesel production consists in removing glycerin by replacing it with alcohol. This process is called re-esterification. The result of esterification is the formation of ethers of fatty acids (biodiesel) and a by-product of re-esterification - triatomic alcohol - glycerin (its unrefined condition is called glycerol) [1].

According to definition of the USA standard, biodiesel fuel implies the monoalkyl ester fatty acids obtained from vegetative or animal oils and to be used in diesel engines. Major task to be solved is the replacement of the oil refining products by naturally renewable resources. Thus, fast strengthening of positions of biofuel is accounted for the efforts to support agricultural manufacturers.

Raw material for biodiesel fuel is the rapeseed, sunflower, palm and other vegetable oils, and pork fat. Introduction of non-processed oils in fuel, which is often practiced, is undesirable. The matter is that they are characterized by high viscosity and rather low heating capacity which reduces capacity of the engine by 15 % on average; also, they have poor startability at low temperatures, and because of presence of free acids they are badly combined with constructional and sealing materials and tend towards oxidation at storage. Therefore the oils are alkylated into monoesters of corresponding acids. Products of alkylation are characterized with better low-temperature properties and lower viscosity. Thus, cetane index increases from 30-40 to 50-80 units [3].

The most popular for the production of methyl ethers is the use of methanol. In course of re-esterification (approximate proportion of 1 ton of oil and 200 kilo of methanol + potassium or sodium hydroxide) the oils and fats react with methyl alcohol in presence of a catalyst (alkali) as a result of which compound ethers (biodiesel) are produced, and a glycerol phase (the so-called "black" glycerin) which contains 45-56 % of glycerin, 4 % of methanol (not reacted), 13 % fatty acids, 8 % water, 9 % inorganic salts, and 10 % ethers. The mixture obtained as a result of the reaction to be separated in separators or sediment bowls [5].

For production of qualitative product a number of requirements should be met [6]:

1. Upon completion of re-esterification the content of methyl ethers should be above 96 %.
2. For fast and full re-esterification, methanol should be taken in plenty, therefore methyl ethers should be cleared of it.
3. The use of methyl ethers as fuel for diesel machinery without preliminary purification of products of saponification is inadmissible. Soap will litter the filters and form sedimentation, and pitches in the combustion chamber. Separation and

centrifugation are not enough. Purification demands water or a sorbent.

4. Final stage includes drying of methyl ethers of fatty acids. For water leads to development of microorganisms in biodiesel and promotes formation of free fatty acids which cause corrosion of metal details.

5. Storing of biodiesel for more than 3 months is not recommended – it decays.

Biodiesel is easy to transport and use. Besides, biodiesel is flammable - the ignition temperature equals to 150°C while the ignition temperature of diesel equals to 77°C. This fact gives a number of advantages. Biodiesel is biologically dissolved, like sugar, and 10 times less toxic than table salt. At burning of biodiesel in the engine there is no typical smell of the exhaust gases formed at burning of typical diesel fuel. Instead there is a normal smell typical for process of preparation of a fried potato or popcorn.

Biodiesel has considerable advantages in respect of environmental impact, for example it promotes global warming to a lesser degree, and it has a lower level of emissions, and gives positive effect on agriculture. The use of biodiesel allows lowering considerably the emissions of CO2 (by 65-90 % less than at the use of traditional fuel), and reducing emission of firm particles with the exhaust gases and other harmful emissions. Biodiesel contains a very small quantity of sulphur which is highly oleiferous and the fats in it are biologically destructible. All the above listed advantages are confirmed by the research of various EU Commissions, and the tests made by independent research institutes [4].

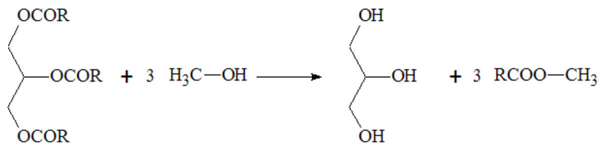
In special cases the waste vegetable oils can become raw material for production of biodiesel. Besides reduction of emissions of the waste oils, they are competitive and favorable in respect of low quantity of emissions of CO2 by way of transformation of the wastes in energy for transport vehicles.

Additional reduction of harmful emissions reduces quantity of problems connected with human health.

According to experiments made, biodiesel being put in water does not cause any harm to plants and animals. Besides, it is exposed to almost complete biological degradation: in soil or in water the microorganisms process 99 % of biodiesel within 28 days which allows speaking about minimization of pollution of rivers and lakes. Flammability point for biodiesel exceeds 100 °C which allows calling the biofuel a rather safe substance.

For production of biodiesel all kinds of vegetable oils can be used - sunflower, rapeseed, linen, etc. And biodiesels made from different oils have some differences. For example, biodiesel obtained from rapeseed oil has the highest caloric content, and also the highest temperature of filterability and hardening. Biodiesel produced from rapeseed oil concedes the palm biodiesel by caloric content; however it better stands cold weather and therefore is more applicable in cold climate.

In our tests we used the canola and corn oils, and the waste oils of these vegetative cultures. Process of production of biodiesel went through the reactions as follows:



Triglycerides Metanol (3) Glitserol Ethers

Material and methods

The essence of the biodiesel production process consists in reduction of viscosity of a vegetable oil which is achievable in different ways. Any vegetable oil is a mixture of triglycerides (ethers connected to a glyceride molecule) and triatomic alcohol. Glycerin gives viscosity and density to the vegetable oil. Therefore, production of biodiesel demands removal of glyceride by replacing it with alcohol. This process is called trans-etherification. Sodium hydroxide acts as catalyst.

. In case that we use the waste vegetable oil as initial raw material, preliminary filtration is required for removal of impurity and water. If water had not been removed, a triglyceride hydrolysis would take place instead of trans-etherification. As a result we will obtain not biodiesel but salts of fatty acids.

In the course of reaction the oil in the beginning heats up to 45-500 °C (for acceleration of the reaction), and then a catalyst and alcohol are added in it. With application of methanol, methyl ether is produced. Acid also can be used to accelerate the reaction. The mixture is stirred for certain time at 45-50 °C and precipitates. After precipitation the mixture stratifies with the formation of biodiesel in the top layer (chemically called "ether"), then a layer of soap, and glycerin at the bottom. Then glycerin and the soap layer are removed and biodiesel is washed out in different ways for removal of the rests of soap, catalyst and other possible impurities. After washing it is drained for removal of the rests of water, for example with magnesium sulphate. Then the dehydrator is removed by simple filtration. One ton of vegetable oil and 111 kilo of alcohol (in presence of 12 kilo of catalyst) gives approximately 970 kilo (1100 lt) of biodiesel and 153 kilo of primary glycerin.

Results and discussion

In the course of experiment we compared quantity of the consumed electric power of the biodiesel production process by means of a wattmeter. It turned out that in course of time the production of biodiesel from canola oil demands much less electric power than from corn oil, therefore it is more economic. However, the production of biodiesel from the waste oils demands more electric power than for the above mentioned oils (Fig.1).

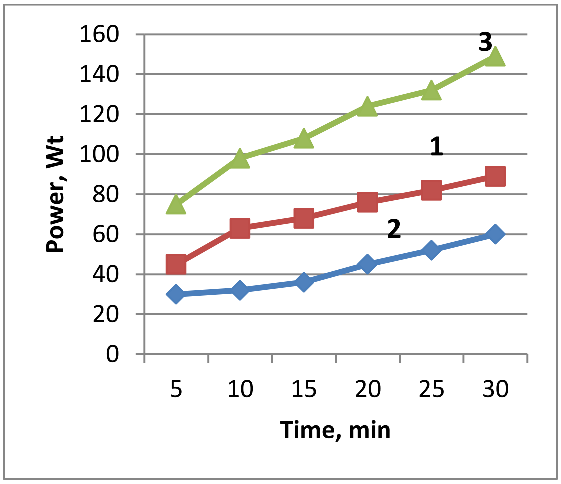


Figure 1 – Dependence of capacity of the consumed electric power on time of the biodiesel production.
Note: 1 – corn oil; 2 – canola oil; 3 – waste oil.

Upon completion of reaction, glycerin deposits at the bottom. Biodiesel should be colored as honey, glycerin should be of darker color (Fig.2).

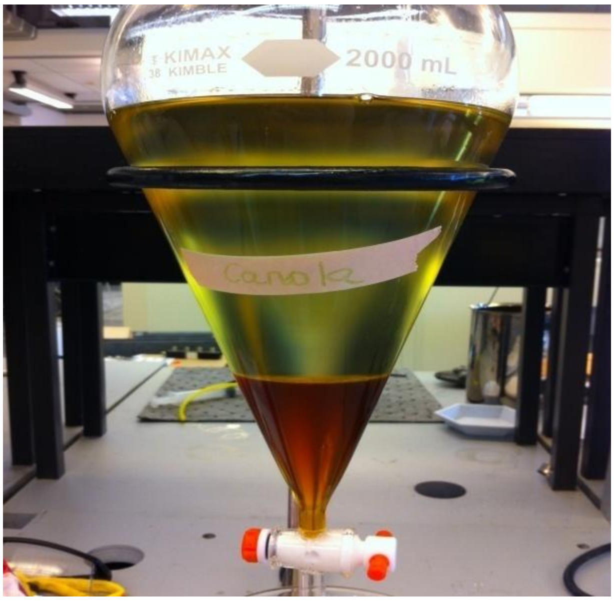


Figure 2 - Separation of biodiesel and glycerin.

With temperature maintained at some 380 °C glycerin remains in liquid state and can be easily removed from below the mixing tank by a separate hose. Glycerin obtained from the waste oils usually is brown and hardens at 380 °C, glycerin from fresh oils remains in liquid state at lower temperatures. It can be used as a by-product after preliminary evaporation of methanol from it by heating up to 65-50°C.

Similar method we used for production of biodiesel from waste oil. As we know, the majority of fast food restaurants utilize the remained oil after frying which could be processed into biofuel for fuelling of motor vehicles. This resource finds a good and worthy application and has a number of advantages to environment. Characteristics of such biofuel concede nothing to biodiesel produced from pure oils, and even surpass it by the product yield. However the waste oil should be exposed to initial clearing process which includes oil filtration, drying and titration.

Upon formation, biodiesel arrives in process of washing from residual water and not-reacted products. Washing is carried out by mixing of biodiesel and warm water, with further sedimentation and separation. The process is implemented until water becomes transparent with neutral environment. The second way of clearing of biodiesel is transmittance of substances through a column filled with rubber balls - sorbents.

As a result the yield of biodiesel from canola oil is bigger than that from corn oil which speaks for a clear advantage of the first. However the yield of biodiesel from the waste oils is bigger than that of the above mentioned oils. It can be connected with deeper purification of oil and influence of properties of original plant.

Quality of the obtained product is defined, first of all, by visual examination and checking of pH. By sight the biodiesel should look as pure sunflower-seed oil. Any suspensions, impurity, particles or opacification are not allowed. Opacity means the presence of water to be removed by heating. After the first application of biodiesel it is necessary to check up the fuel filters.

Also, we checked quality of biodiesels in the engine. It was established that the amount of harmful atmospheric emissions is much less when using biodiesel. Combustion of biodiesel produces exactly the same amount of carbon dioxide as is consumed from the atmosphere by a plant, which is initial raw material for production of oil, for its entire lifetime. Biodiesel, in comparison with typical diesel fuel, almost does not contain sulfur which is good in terms of ecology. Biodiesel is characterized by good lubricant properties which prolongs lifetime of the engine. This is caused by its chemical composition and content of oxygen in it. In operation of the engine on biodiesel, its mobile parts are greased as a result of which, according to the tests, service lives of the engine and a fuel pump increase by 60% on average.

Table 1 – Total results of production of biodiesels.

Names of samples	Mass balance, %	Losses, %	The yield, %	Mass balance after clearing, %	Losses after clearing, %	The yield after clearing,%
Biodiesel from the canola oil	95,13	4,87	100,66	89,84	10,16	83, 75
Biodiesel from the corn oil	94,45	5,55	100,42	87,11	12,89	78, 23
Biodiesel from the waste oils	96,22	3,78	100,99	90,46	9,54	95, 73
Glycerin from the canola oil	11,32	1,25	99,65	-	-	-
Glycerin from the corn oil	10,65	1,46	98,54	-	-	-
Glycerin from the waste oil	9, 41	0,78	97,38	-	-	-

Table 2 – A comparative table of contents of sulfur and the atmospheric gas exhausts.

Contents %	Diesel	Biodiesel from the clean oil	Biodiesel from the waste oil
S	0,2-0,01	0,2	0,1
CO2	9,0	1,35	1,25
CO	142,1	83,4	80,1
NO	24,6	13,8	12,6
NO2	3,9	3,1	3.1
NOx	28,1	22,5	21,9

The world practice limits a number of components of the exhaust gases, they are: carbon monoxide CO, unburned hydrocarbons, nitrogen oxides NOx and carbon char. Advantages of biodiesel as per parameters of combustion products are obvious: carbon monoxide, hydrocarbons, residual particles and carbon char.

Conclusions

According to experts, the next decades anticipate further decrease in production of traditional power sources including oil production. The renewable types of biofuel can be used widely in motor-and-tractor diesel engines, also in the diesels used at the railroad or on a water transport.

The results of work allow noting the advantage of biodiesel produced from the waste oil, in raw materials being wastes for further utilization, quality of the product and high productivity. However it concedes to biodiesel produced from pure vegetable oils on such economic expenses as costs of electric power, costs of additional stages of purification, time of carrying out of the experiment. The main point is that the analysis of methods of assessment and ways of decrease in negative ecological impact of diesels on the environment shows that today the main direction would be the use of alternative fuels.

References

1 R.G. Vasilov. Prospects of development of the biofuel production. Report 1 // The Reporter of biotechnology and physical and chemical biology named after Y.A. Ovchinnikov. – 2007 . – T. 3 . – No. 1. – P. 47-54.

2 Dolinsky A.A., Grabov L.N., Skoree V.I., Kusok A.I. Production of the energy carriers from renewable vegetable raw materials // Power industry and electrification. The Scientific Magazine. – 2008, No. 9.

3 Mironenko V. Biodiesel production technologies: [a course of lectures for students of agricultural institutes // V. Mironenko, B.O. Dubrovin, V. M. Popishchuk, S. V. Dragnev - M: Holtekh, 2009. - P.100

4 Polischuk V.N. Application of biofuel in diesel engines // V. M. Polischuk, S.V. Dragnev, I.I. Ubozhenko, M.Y. Pavlenko, O. V. Polischuk // The Scientific Reporter of the National Agrarian University. - K : NAU, 2008. - No. 125. – P. 315-318.

5 Production and use of biodiesel: reference book // A.R. Ablayev, etc. – M: Agrarian and industrial complex and PPRO, 2006. – P.80

6 Rapeseed – the planting of the 21st century: aspects of use as food, fodder and energy // A collection of scientific reports at the International Scientific and Practical Conference on July 15-16, 2005 – Lipetsk, 2005.