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METHANOL TRANSESTERIFICATION OF DIFFERENT VEGETABLE OILS

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Abstract:
The result of the investigation on methyl esters obtained on the basis of used sunflower oil, rapeseed oil and soybean oil are given in this paper. Transesterification reaction conditions that affect yield and purity of the product esters including oil quality, type and concentration of catalyst, temperature and reaction time were examined. Methanol esterification of different oils at 60 0C with 1-10 % (v/v) sodium met-oxide was studied. With appropriate percent of sodium met-oxide, temperature 60 0C and 1 hour, all investigated oils were sufficiently transesterified and could be used as fuel in diesel engines.

Key words: Biodiesel, Used frying, rapeseed oil, soybean oil, Reaction conditions

1. Introduction

Biodiesel fuel is an alternative to classic fossil fuel. It consists of methyl esters of vegetable oils and belongs to ecological fuels because of its qualitative composition (carbon 77 %, hydrogen 12%, oxygen 11% and traces of sulfur and nitrogen). As fuel of biological origin, it is recommended by the European Union and classified as a future fuel.

The production of methyl esters of used frying oil available as waste materials from restaurants and households is an interesting problem. However, most of the used oils are still waste material and ecological problems [1].

The used frying oils have properties different from the properties of refined and crude oils. The presence of heat and water accelerates the hydrolysis of triglycerides and increases content of free fatty acid in oil [1,2]. Oxidation stability of the mixtures is disturbed because of the contact of hot oil with food, and peroxide value of oil increases. Viscosity of oil increases considerably, because of the formation of polymeric acids and glycerides [3,4]. Molecular mass of oil and iodine number decreases, and saponification value and density increases [5,6] .

2. Experimental

Used frying oil, rapeseed oil and soybean oil (150 ml) and an appropriate volume of methanol (22-28 ml) with alkaline catalyst (sodium met-oxide) (12-15 ml) were placed into a dry reaction flask equipped with reflux condenser and magnetic stirrer. Reaction mixture was mixed for 1 hour at a temperature of 60^{o}C. The ester layer was separated from the glycerol layer in a separating funnel. Crude ester layer consisted of methyl ester, unreacted oil and methanol, of glycerol and catalyst residue, and small amount of produced soap. In the separating funnel, this layer was washed with hot water (30 ml), until the washings were neutral. This ester was dried and filtered.

The final product quality for methyl esters is generally described by means of acid value, saponification value and iodine value. The density was estimated by EN ISO 3675, the viscosity was

estimated by EN ISO 3104+AC. The methods for estimation of other characteristics of methyl esters are shown in table 1.

Table 1. The properties of vegetable oils.

Oil	Density (kg/m^3)	Viscosity (mm^2/s)	Cetane index	Acid Value mgKOH/g	Peroxide Value gI2/100g	Saponification Value mgKOH/g	Iodine Value gI2/100g
A	933	64,1	49,1	3,82	20,2	196	117
B	921	35,9	47,5	2,88	22,2	177	109
C	922	31,7	47,8	2,67	21,7	169	106

A – Used sunflower oil, B – Rapeseed oil, C – Soybean oil

3. Results and discussion

Properties of used vegetable oils are shown in table 1. Experiments were designed to determine how variations in oil quality, amount of alkaline catalyst, time and temperature of reaction affected the yield and properties of esters.

The results obtained in our investigations show that the quality of used frying oil does not have an essential effect on the quality of produced methyl esters, if optimal conditions of methanol transesterification process are chosen (table. 2). It is also obvious that methanol esters have much lower viscosities than used frying oil (tables 1 and 2).

Table 2. Effect of oil quality on ester properties /molar ratio = 4.5:1; temperature 60^0C; time 60 min; catalyst = 9 % $NaOCH_3$/.

Oil	Ester properties							
	Density (kg/m^3)	Viscosity ($mm^2/s.$)	Cetane index	Acid value mgKOH /g	Peroxide Value gI2/100g	Saponification value gI2/100g	Iodine value gI2/100g	Yield of crude ester (% on oil basis)
A	886	5,5	58	0,032	25	196	110	85.5
B	884	4,4	60	0,018	24	188	96	86.5
C	885	4,7	59	0,025	28	191	103	86.0

A – Used sunflower oil, B – Rapeseed oil, C – Soybean oil.

As a catalyst in the process of alkaline methanol transesterification, sodium met-oxide has used in the concentration of 1% (v/v) to 10 % (v/v) of oil. The results obtained from methanol transesterification of vegetable oils show that the type of catalyst has an important role. Namely 9 %(v/v) sodium met-oxide has given the best yields and viscosities of the esters (table. 3). Also, eventual soap formation, which appears as a consequence of increased concentration of catalyst, has been avoided.

The chemical composition of biodiesel fuel makes complete combustion in diesel engines possibly as well as a decrease in the emission of visible gas pollutants (smoke, soot and hard suspended particles), carbon monoxide, unburned hydrocarbons, sulfur and lead oxides in relation to classical diesel fuel. The decrease is more significant if methyl esters have been produced by soybean oil.

Table 3. Effect of various catalyst concentration on B ester properties /molar ratio = 4.5:1; temperature 60 ^{0}C; time 60 min/.

Ester properties	Various catalyst concentration									
	1 %	2 %	3 %	4 %	5 %	6 %	7 %	8 %	9 %	10 %
Peroxide value	29	27	27	26	25	25	25	25	24	24
Acid value, mg KOH/g	0,024	0,023	0,023	0,022	0,022	0,021	0,020	0,019	0,018	0,018
Cetane index	59	59	59	59	59	59	59	59	60	60
Viscosity ($mm^2/s.$)	4,6	4,6	4,5	4,5	4,5	4,5	4,5	4,5	4,4	4,4
Yield of crude ester, %	85	85	85	85	85	85.5	85.5	86	86.5	86.5
Iodine value, gI2/100g	105	103	102	101	101	100	98	97	96	96
Saponification value, mg KOH/g	195	195	195	193	192	192	190	190	188	188

4. Conclusions

1. The methyl esters obtained in this way can be used as a fuel in diesel engines, because of satisfying properties that could be compared with standard methyl esters [7].
2. Biodiesel of good quality can be produced from these three types vegetable oils in subsequent reaction conditions: 9 % (v/v) sodium met-oxide, temperature at 60 ^{0}C and 1 hour. The increase of the quantity of catalyst does not contribute to the growth of the yield and the quality of the esters.
3. Methanol transesterification of different vegetable oils and production of biodiesel is another possibility for producing cheap alternative fuels, which could reduce pollution and protect the environment.

5. References

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