ANNALS of Faculty Engineering Hunedoara
– International Journal of Engineering
Tome XIV [2016] – Fascicule 1 [February]
ISSN: 1584-2665 [print; online]
ISSN: 1584-2673 [CD-Rom; online]
a free-access multidisciplinary publication
of the Faculty of Engineering Hunedoara

1. Vladimir V. JOVANOVIĆ, 2. Nebojša MANIĆ,
3. Dragoslava D. STOJILJKOVIĆ, 4. Pavle HADŽIĆ

PRODUCTION OF BIODIESEL IN A BATCH REACTOR BY ALKALINE TRANSESTERIFICATION AT ROOM TEMPERATURE

1-3. University of Belgrade, Faculty of Mechanical Engineering, Belgrade, SERBIA
4. Gosa Institute, Belgrade, SERBIA

ABSTACT: Biodiesel is produced by the chemical reaction of lipids with alcohols (mainly methanol, ethanol or a mixture of lower alcohols) in the presence of a catalyst. The technology for producing biodiesel opens many opportunities for improvement and advancement of reaction parameters. Among the most important are certainly: the type of alcohol, the molar ratio of alcohol to vegetable oil, type and consistency of the catalyst, catalyst concentration, reaction temperature, reaction time and the method of mixing of the reaction mixture. The procedures generally accepted in small production usually represent a compromise between developed and defined laboratory procedures and procedures for easy implementation in practical terms. Performing transesterification process at room temperature (18-22°C) significantly simplifies the process of biodiesel production in a batch reactor. Here we report on the results acquired through experimental tests on real batch reactor and the results of performed analysis of the physical and chemical characteristics of biodiesel produced from native cold pressed sunflower, soybean and rapeseed oils and degummed rapeseed oil.
Keywords: biodiesel, batch reactor, reaction temperature, alkaline trans esterification

1. INTRODUCTION

In terms of chemical structure, biodiesel is a mixture of alkyl esters of fatty acids with monohydric alcohols, and as fuel is intended for use in diesel engines without any modifications of the engine. The process for obtaining biodiesel from vegetable oils that are composed of triglycerides of higher fatty acids, comprise transesterification by short chain alcohols (mainly methanol and ethanol; however, isopropanol or other alcohols or their mixtures are also acceptable), to produce the end product – fatty acid methyl esters (FAME) which are very similar to the conventional diesel fuel by their characteristics. The transesterification of triglycerides by alcohols is reversible chemical process and product yield depends on several factors. The factors determining the yield of the transesterification process are:

- ratio of used reactants (molar ratio of vegetable oil/alcohol),
- process temperature,
- duration of the process,
- type and amount of catalyst,
- validity of contact of the reactants during the reaction (the mixing of the reaction mixture),
- ability to remove certain products reactions during the process, and others.

Previous experiences [1] in biodiesel production in a batch reactor proved that it is possible to produce biodiesel of almost commercial quality (as defined by EN 14214) at process temperatures of 40 to 55°C. Providing this temperature is not easy task for small biodiesel producers, so the further investigations were focused on performing the process at reduced – room temperatures (18 to 22°C).

2. EXPERIMENT

2.1. Raw materials

As a raw materials, cold-pressed sunflower oil, soybean oil, rapeseed oil and degummed rapeseed oil (obtained from the manufacturer Victoria oil) were used. Other reagents used were anhydrous methanol (99+% Methanol complex Kikinda), sodium hydroxide of analytical grade (Superlab, Beograd) and Perfit PF 220 (aluminosilicate for use in the food industry, Termika Zrenjanin). Table 1 contains the basic characteristics of the raw materials.

Table 1. Basic characteristics of the raw materials [2]

Characteristic Oil	High heating value [kJ/kg]	Density at 15°C [kg/m³]	Viscosity at 40°C [mm²/s]
Sunflower	40.193	921	32,19
Soybean	40.562	921	31,26
Rapeseed	40.129	918	34,57
Degummed rapeseed	40.062	918	35,06

2.2. Experimental procedures

Biodiesel production was performed in two steps: the production of crude biodiesel and purification of the product. The base transesterification was performed by the following procedure [3]: The vegetable oil (100 kg), which was charged to the reactor, methanol (26 liters) was added in which the catalyst sodium hydroxide (750 g, 0.75% by weight of vegetable oil) was pre-dissolved. The total amount of alcohol in which the catalyst was dissolved was added in the oil at once at the beginning of the reaction. After two hours with stirring at room temperature (18-22°C) the reaction mixture was allowed during the following hour to separate the glycerol, which was discarded. The crude biodiesel was transferred to the vessel for rinsing and washed five times with 25 liters of tap water at a temperature of 15°C. After the last wash the crude biodiesel was left for twenty-four hours to gravitational separation of raw water and later analyzed.

Purification of biodiesel in one step after rinsing with water was carried out using a desiccant for clarification for the food industry based on aluminosilicate (Perfit PF 220, the manufacturer Termika Zrenjanin).

3. MEASUREMENT RESULTS

3.1. Requirements of acting standard

Biodiesel produced according to methodology described above was tested according to relevant standard (EN 14214). Review of requirements of this standards is given in Table 2.

Table 2. Requirements of standard EN 14214 [4]

EN 14214 - Property	Units	lower limit	upper limit	Test-Method
Ester content	% (m/m)	96,5	-	EN 14103
Density at 15°C	kg/m³	860	900	EN ISO 3675 / EN ISO 12185
Viscosity at 40°C	mm²/s	3,5	5	EN ISO 3104
Flash point	°C	> 101	-	ISO 3679
Sulfur content	mg/kg	-	10	-
Tar remnant (at 10% distillation remnant)	% (m/m)	-	0,3	EN ISO 10370
Cetane number	-	51	-	EN ISO 5165
Sulfated ash content	% (m/m)	-	0,02	ISO 3987
Water content	mg/kg	-	500	EN ISO 12937
Total contamination	mg/kg	-	24	EN 12662
Copper band corrosion (3 hours at 50 °C)	rating	Class 1	Class 1	EN ISO 2160
Thermal Stability	-	-	-	-
Oxidation stability, 110°C	hours	6	-	EN 14112
Acid value	mg KOH/g	-	0,5	EN 14104
Iodine value	-	-	120	EN 14111
Linoleic Acid Methyl ester	% (m/m)	-	12	EN 14103
Polyunsaturated (>= 4 Double bonds) Methyl ester	% (m/m)	-	1	-
Methanol content	% (m/m)	-	0,2	EN 14110
Monoglyceride content	% (m/m)	-	0,8	EN 14105
Diglyceride content	% (m/m)	-	0,2	EN 14105
Triglyceride content	% (m/m)	-	0,2	EN 14105
Free Glycerin	% (m/m)	-	0,02	EN 14105 / EN 14106
Total Glycerin	% (m/m)	-	0,25	EN 14105
Alkali Metals (Na+K)	mg/kg	-	5	EN 14108 / EN 14109
Phosphorus content	mg/kg	-	10	EN 14107

3.2. Test results of selected biodiesel properties

Only the most important properties defined by EN 14214 were tested and the results of these tests are presented in Table 3 [5].

Table 3. Results of measured properties of produced biodiesel

Property	Sunflower oil	Soybean oil	Rapeseed oil	Rapeseed oil (degummed)	Requirement of EN 14214
Ester content % (m/m)	97.8	93.0	96.7	97.5	min 96.5
Monoglyceride content % (m/m)	0.025	0.080	0.099	0.127	max 0.8
Diglyceride content% (m/m)	0.086	0.171	0.082	0.057	max 0.2
Triglyceride content % (m/m)	0.433	2.191	1.015	1.108	max 0.2
Free Glycerin % (m/m)	<0.0001	<0.0001	<0.0001	<0.0001	max 0.02
Total Glycerin % (m/m)	0.063	0.271	0.141	0.154	max 0.25
Polyunsaturated (>= 4 Double bonds) Methyl ester % (m/m)	0.22	0.11	0.24	0.24	max 1
Methanol content % (m/m)	<0.01	<0.01	<0.01	<0.01	max 0.2
Water content (mg/kg)	520	480	417	406	max 500
Iodine value (g I_2/kg)	128	129	111	111	max 120
Acid value (mgKOH/g)	0.11	0.11	0.18	0.16	max 0.5
Density at 15 °C (kg/m^3)	886.7	887.3	883.6	882.6	860-900
Viscosity at 40°C (mm^2/s)	4.5	4.6	4.4	4.5	3.5-5.0
Flash point (°C)	164	164	170	174	min 101
Copper band corrosion (3 hours at 50°C)	1a	1a	1a	1a	-
Heating value (kJ/kg)	38,631	39,567	40,041	36,705	-

4. ANALYSIS OF THE TEST RESULTS

The principal goal of biodiesel production, finalization of transesterification process, was successfully reached for three of four samples. Sunflower, rapeseed and degummed rapeseed oil provided biodiesel with more than 96.5% mass fraction of ester content. Only the soybean oil didn't reach this limit but it was very close to satisfying this requirement (93.0% per mass).

Glyceride content of mono and diglycerides of all samples is within required limits (less then mass fraction 0.8%, respectively 0.2%) but tryglicerides content for all biodiesel samples is significantly higher than required by the standard (from twice for sunflower oil biodiesel to 10 times for soybean oil biodiesel).

5. CONCLUSIONS

Experiments of transesterification process at room temperature (18-22°C) in a batch reactor performed in this investigation have proved that this method of biodiesel production is technologically justifiable. Starting with raw materials: cold-pressed sunflower oil, soybean oil, rapeseed oil and degummed rapeseed oil, using anhydrous methanol for transesterification process, sodium hydroxide as catalyst and Perfit PF 220 as a purification agent, biodiesel of almost commercial quality (according to acting EN standard) was produced.

Proposed production method provides a simple solution for biodiesel production in batch reactor, suitable for small producers in the field. Further investigations should be performed on a bench scale as to justify obtained results from these laboratory experiments.

Acknowledgment: The results presented in this paper are part of investigation performed within research activities in a project TR35042 financed by a Ministry of Education, Science and Technology of Serbia.

Note: This paper is based on the paper presented at The 12th International Conference on Accomplishments in Electrical and Mechanical Engineering and Information Technology – DEMI 2015, organized by the University of Banja Luka, Faculty of Mechanical Engineering and Faculty of Electrical Engineering, in Banja Luka, BOSNIA & HERZEGOVINA (29th – 30th of May, 2015), referred here as[6].

References

[1] Hadžić, P., Stojiljković, D., Manić, N., Jovanović, V. (2102). Individual biodiesel production - significant component of national defense policy, 5th International Scientific Conference on Defensive Technologies OTEH 2012, Belgrade

[2] Stojiljković, D., Jovanović, V.,Manić, N. (2012). Determination of Basic characteristics of raw vegetable oils, Internal report, University of Belgrade, Faculty of Mechanical Engineering, Fuels&Combustion Laboratory, Belgrade, 2012

[3] Hadžić, P. (2012). Procedure for transesterification process of raw vegetable oils, Internal report, Gosa Institute, Belgrade, Belgrade

[4] ***, EN 14214:2012, Automotive fuels. Fatty acid methyl esters (FAME) for diesel engines. Requirements and test methods

[5] Stojiljković, D., Jovanović, V., Manić, N. (2013). Properties of samples of biodiesel produced from raw vegatable oils, Internal report, University of Belgrade, Faculty of Mechanical Engineering, Fuels&Combustion Laboratory, Belgrade

[6] Vladimir Jovanović, Nebojša Manić, Dragoslava Stojiljković, Pavle Hadžić, Production of biodiesel in a batch reactor by alkaline transesterification at room temperature, Proceedings of the 12th International Conference on Accomplishments in Electrical and Mechanical Engineering and Information Technology – DEMI 2015, Banja Luka, Bosnia & Herzegovina