

У статті описані нові технології виробництва біодизеля з використанням вищих ЖК. Дана технологія дозволяє знизити кислотне число, за рахунок використання кислотного катализатора при етерифікації ЖК з утворенням бутилових естерів

Ключові слова: біодизель, бутилові естери жирних кислот, переетерифікація, катализатор

В статье описаны новые технологии производства биодизеля с использованием высших ЖК. Данная технология позволяет снизить кислотное число, за счет использования кислотного катализатора при этерификации ЖК с образованием бутиловых эфиров

Ключевые слова: биодизель, бутиловые эфиры жирных кислот, переэтерификация, катализатор

In this paper a new technologies of biodiesel producing with using the high FFA are described. Present technique makes possible reducing the acid value; through using an acid catalyst by the FFAs esterify with butyl esters formation

Keywords: Biodiesel, butyl esters, FFA, Transesterification, Catalyst

DEVELOPMENT OF TECHNOLOGY OBTAINING FATTY ACID OF BUTYL ESTERS

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Introduction

Energy is the most basic necessity of all industrial activities in civilized societies. Consumption of fossil fuels has increased to a greater extent and the use of these energy resources is seen as having major environmental impact. Thus, looking for an alternative way to develop a substitute of diesel is an imperious task for humans.

Biodiesel, defined as "an alternative fuel for diesel engines" that is derived from the oils and fats of plants and animals, is worthy of continued study and optimization of production procedures because of its environmentally beneficial attributes and its renewable nature. There are obstacles to production biodiesel the first one is the high price of biodiesel [1]. One of the means to address the higher priced is research and develops methods to reduce the cost of biodiesel. A reduced cost option is to produce biodiesel from waste fats and oils [2.3]. The second obstacle is using raw vegetable oils for diesel engines can cause numerous engine related problems [4.5.6].

The increased viscosity and low volatility of vegetable oils lead to severe engine deposits, injector coking, and piston ring sticking [6.7]. However, these effects can be reduced or eliminated through transesterification of vegetable oil to form fatty acid methyl esters (FAME) commonly known as biodiesel, since the implementation of the European standard specification EN 14214 in 2004, a standardized definition for biodiesel has been agreed a from any kind of feedstock, under fulfilling the given quality specifications

[8.9.10]. There are some factors affecting changes of the oils and fats, similar to oxidation transformations. as a result of that, It is necessary to identification of some key parameters (acid value and free fatty acids (FFA) content, moisture content, viscosity and fatty acid profile of the used oil) is a prerequisite for

determining the viability of the oil or fat transesterification process and is essential to identify the right processes that can be performed to achieve best results with the yield and purity of the produced biodiesel.

A number of researchers have worked with feedstocks that have elevated FFA levels, alkaline catalysts have been used and the FFAs were removed from the process stream as soap and considered waste. As FFA levels increase this becomes undesirable because of the loss of feedstock as well as the deleterious effect of soap on glycerin separation. The soaps promote the formation of stable emulsions that prevent separation of the biodiesel from the glycerin during processing. Waste greases typically contain from 10% to 25% FFAs. This is far beyond the level that can be converted to biodiesel using an alkaline catalyst. An alternative process is to use acid catalysts that some researchers have claimed are more tolerant of free fatty acids [11.12.13]. On the other hand some researchers showed that acid catalysts are too slow to be practical for converting triglycerides to biodiesel [14].

However, acid catalysts appear to be quite effective at converting FFAs to esters and this reaction is fast enough to be practical [15.16]. Thus, an acid catalyzed pretreatment

step to convert the FFAs to esters followed by an alkali catalyzed step to convert the triglycerides should provide an effective and efficient method to convert high FFA feedstocks to biodiesel. A search of the patent literature showed that others had taken advantage of this approach [17.18.19]. Researchers have mentioned that the oil should not contain more than 1% FFA for alkaline-catalyzed transesterification reactions. This corresponds to an acid value of 2 mg KOH/g. If the FFA level exceeds this amount, the formation of soap will inhibit the separation of the ester from the glycerin and also reduce the ester conversion rate [13.20.21]. The work presented here is based on the initial assumption that the acid catalysis must decrease the acid value of the mixture to less than 2 mg KOH/g [22.23]. The another study provided a process for the preparation of oils containing over 50% free fatty acids (palm oil) was mixed with methanol (77% of the weight of the oil) and sulfuric acid (0.75% of the weight of the oil) and stirred at 69°C for 1 h. The reaction products were distilled under vacuum and the yield obtained was 97.0%. The acid value of the distillate was equivalent to about 5% palmitic acid [24].

This acid level is approximately equal to an acid value of 10 mg KOH/g which is much higher than the value of 0.8 mg KOH/g specified in ASTM specification PS121 for biodiesel [25]. Wherein the work presented here is based on the initial assumption that the acid catalysis must decrease the acid value of the mixture to 2 mg KOH/g. The other major obstacle to acid catalyzed esterification for FFAs is water formation. Water can prevent the conversion reaction of FFAs to esters from going to completion.

In a further study, experimental research methods showed there's a possibility to reach the level of acid value to 2 mg KOH/g, the researcher have developed a technique to reduce the FFA level of high FFA feedstocks with an acid catalyzed pretreatment by using a multi-step process [16]. This process system has been followed in the current study.

Experimental

The purpose of this study was to develop a technique for producing biodiesel from low cost feedstocks by developing a process to reduce the FFA level of high FFA feedstocks to 1% FFA with an acid catalyzed pretreatment.

To investigate the effects of molar ratio, reaction temperature, reaction time, and catalyst amount on the acid catalyzed conversion of free fatty acids to butyl esters, a

Laboratory scale reactor was used. The reactor consisted of a 1000 ml round bottom glass flask and a water cooled condenser that returned any vaporized butanol to the reacting mixture and Dean Stark. Unless otherwise noted, the reaction temperature was maintained at 113°C using a hot plate magnetic stirrer. This

temperature was below the boiling point of butanol so the reaction vessel did not need to be pressurized.

Results and discussion

Preparation of butyl ester from material with high FFA

In this section was studied a series of tests that were conducted to develop the acid catalyzed pretreatment process. The initial acid value of the recycled vegetable oil before the reaction was measured 149 mg KOH/g. Published results suggested that the acid catalysis must decrease the acid value of the mixture to less than 2 mg KOH/g before the alkaline catalysis will give satisfactory results, and this was the initial target for the pretreatment [13.14.20.21].

The titration is made dissolving the raw material in a mixture of hexane/ethanol, using KOH and phenolphthaleine as indicator. The amount of water of the raw material is also determined by the method of Dean Stark (ASTM D95). Acid catalyzed reaction stops in many cases at an acid value that is well above the 2 mg KOH/g target, this is due to the effect of the water produced when the FFAs react with the alcohol to form esters.

To investigate the influence of different catalysts and their amounts, reaction time on the acid value of the recycled vegetable oil, three different acid catalysts were studied. The first one was obtained during the research, as shown by previous studies using aluminum phosphate as acidic heterogeneous catalyst in obtaining esters of fatty acids does not work. Therefore, in laboratory conditions was obtained by another catalyst $\text{Al}_2(\text{HPO}_4)_3$, which proved to be effective.

The second catalyst is AMBERLYST₁₅TM, and the last one is $\text{Fe}_2(\text{SO}_4)_3$, four different amounts of catalysts (0, 2.5, 5, and 10 wt%) and a 7-h reaction time were selected. After the initial mixing of the reactants, samples were extracted at 1 min, 15 min, 30 min, and 60 min, 120 min, 240 min and the acid value was measured. The acid values were also recorded of the recycled vegetable oil and butanol before the catalyst was added. The test results are shown in table 1.

The influence of the catalyst amount on the acid value during the 7-h test is shown in table 2 for a 9:1 molar ratio of butanol to FFA. As can be seen, with zero catalyst the acid value reached only 127 mg KOH/g at the end of the test.

Table 1

Effect of catalyst amount and reaction time on the acid value of recycled vegetable oil by 9:1 molar ratio of butanol to FFA

Run time Min	Acid value (mg KOH/g)											
	$\text{Fe}_2(\text{SO}_4)_3$				AMBERLYST ₁₅				$\text{Al}_2(\text{HPO}_4)_3$			
	Catalyst amount				Catalyst amount				Catalyst amount			
	0 %	2.5 %	5 %	10 %	0 %	2.5 %	5 %	10 %	0 %	2.5 %	5 %	10 %
1	149	148,7	148,5	148,2	149	148,8	148,6	148,3	149	148,9	148,7	148,4
15	148,7	146,6	142,4	138,3	148,7	147,7	143,4	140,3	148,7	147,8	146,4	143,2
30	147,3	138,4	131,5	117,9	147,3	140,3	134,5	121,9	147,3	143,4	136,5	124,9
60	140,1	125,2	103,9	88,6	140,1	127,4	112,9	91,3	140,1	129,1	109,9	94,3
120	135,2	91,6	71,5	48,7	135,2	96,6	80,1	51,1	135,2	103,3	83,5	53,1
240	127,6	49,2	30,2	9,6	127,6	63,8	39,2	12,2	127,6	75,2	42,7	13,5

However, with the catalyst present, there was a very rapid reduction in acid value that occurred immediately after addition of the acid catalyst to the mixture of high FFA and butanol. The acid value of the recycled oil was reduced from 148.7 to 49.2 mg KOH/g when 2.5% $\text{Fe}_2(\text{SO}_4)_3$ catalyst was used. When the catalyst level was increased to 5%, the acid value decreased to 30.2 mg KOH/g. When used 10% for the recycled vegetable oil, the acid value decreased to as low as 9.6 mg KOH/g. the Iron (III) sulfate catalyst showed the best results compared with the other catalysts that used in study. However, even when 10% $\text{Fe}_2(\text{SO}_4)_3$ was used, the acid value did not reach the 2 mg KOH/g target.

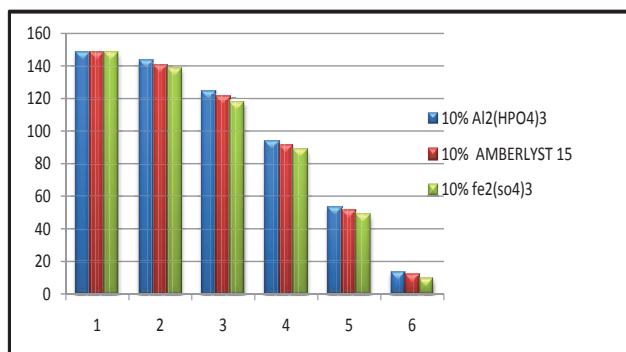


Fig. 1. Influences of the three different acid catalysts types amounts 10 wt%, on the acid value of butyl esters, molar ratio of the mixtures butanol and recycled oil high FFA 9:1

A method that would be sufficiently robust to process high FFA while using reasonable amounts of butanol and acid catalyst was needed. Since water formation when the FFAs are converted to esters inhibits the reaction, the water must be removed to complete the reaction. Hammond (1998) suggested that this could be accomplished using a multi step process.

The first step would be conducted as previously described. When the reaction has reached equilibrium after 15 min to 7 h, the mixture would be allowed to settle and the butanol water fraction that separates would be removed.

Then, additional butanol and acid catalyst can be added and the reaction continued for another step. Although experience has shown that only two steps are usually needed, this sequence can be repeated as many times as necessary to reduce the acid level below 1%.

This two step acid catalysis process offers the potential to reach lower FFA levels while using less alcohol and catalyst. The effect of molar ratio, reaction time, and acid catalyst amount on the acid value of the mixture was determined for a 2–step reaction at 113°C. Initially, a two step pretreatment process was investigated with each reaction. 60 minutes were allowed so that the total reaction time would be addition to single step pretreatment. It was clear that the amount of catalysts and butanol could be substantially reduced if the time for each step were extended to 90 minutes.

With a 7hours reaction time for the first step and a 9:1 molar ratio of butanol, the acid value of the recycled

vegetable oil decreased to 9.2 mg KOH/g. Using the product from this first step, and a reaction time of 90 min , the molar ratio for the second step was varied from 6:1 to 20:1, by adding 1%wt amounts of Iron (III) sulfate at each molar ratio between butanol : recycled oil high FFA .The acid value of the mixture decreased to 2.2 mg KOH/g even with the lowest molar ratio used in the second step as can be seen in fig. 2.

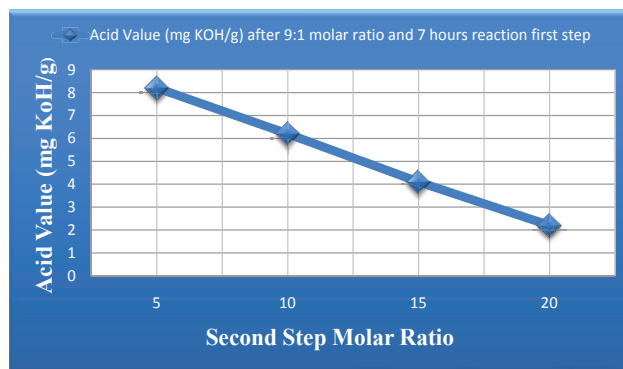


Fig. 2. Effect of molar ratio on the acid value of the mixture in 2nd step for 90 min reaction time

This approach appeared to provide a robust process that could achieve the targeted acid value with sufficient margin to allow for property variations in the feedstock.

Conclusions

The objective of this study was to investigate the use of low–cost, high FFA feedstocks to producing fuel good quality biodiesel. It was determined that feedstocks with high FFAs could not be transesterified with the traditional alkaline catalysts that have been used with good success for vegetable oils. Alkaline catalysts form soap when they react with the FFAs. A process was developed to use acid catalysts to pretreat the high FFA feedstocks until their FFA level was below 1% allowing the subsequent use of alkaline catalysts to convert the triglycerides. The following specific conclusions are based on the process development portion of this project.

- Increasing the acid catalyst amount is very effective in decreasing the acid value of the mixture in the first pretreatment step, using a 9:1 molar ratio and 7hours of reaction time.
- The acid catalyzed pretreatment reaction decreased the acid value of the synthetic mixture to 2 mg KOH/g with using the 2–step acid catalyzed, the best results in 20:1 molar ratio.
- The use of butanol cost effective and environmentally justified in the production of biofuels from waste oil and fat industry.

Literature list

1. F. Ma, M.A. Hanna., (1999.) 1. Biodiesel production: a review. Bioresour. Techno, 70(1)
2. Chhetri, A. B.; Watts, K. C.; Islam, M. R., (2008). Waste cooking oil as an alternate feedstock for biodiesel production. Energies, 1 (1), 3-18

3. Refaat, A. A.; Attia, N. K.; Sibak, H. A.; El Sheltawy, S. T.; El Diwani, G. I., (2008a). Production optimization and quality assessment of biodiesel from waste vegetable oil. *Int. J. Environ. Sci. Tech.*, 5 (1), 75-82
4. Vellguth, G. 1983. Performance of vegetable oils and their monoesters as fuels for diesel engines. SAE Paper No. 83-1358. Warrendale, Pa.: SAE
5. Clark, S. J., L. Wagner, M. D. Schrock, and P. G. Piennaar. 1984. Methyl and ethyl soybean esters as renewable fuels for diesel engines. *JAOCS* 61(10): 1632-1638.
6. Perkins, L. A., and C. L. Peterson. 1991. Durability testing of transesterified winter rape oil (*Brassica napus* L.) as fuel in small bore, multi-cylinder, DI, CI engines. SAE Paper No. 91-1764. Warrendale, Pa.: SAE.
7. Zhang, Q., M. Feldman, and C. Peterson. 1988. Diesel engine durability when fueled with methyl ester of winter rapeseed oil. ASAE Paper No. 88-1562. St. Joseph, Mich.: ASAE.
8. Freedman, B., E. H. Pryde, and T. L. Mounts. 1984. Variables affecting the yields of fatty esters from transesterified vegetable oils. *JAOCS* 61(10): 1638-1643.
9. Mittelbach, M., and P. Tritthart. 1988. Diesel fuels derived from vegetable oils: III. Emission tests using methyl esters of used frying oil. *JAOCS* 65(7): 1185-1187.]
10. Wimmer, T. 1995. Process for the production of fatty acid esters of lower alcohols. U.S. Patent No. 5399731.
11. Freedman, B., E. H. Pryde, and T. L. Mounts. 1984. Variables affecting the yields of fatty esters from transesterified vegetable oils. *JAOCS* 61(10): 1638-1643.
12. Aksoy, H. A., I. Kahraman, F. Karaosmanoglu, and H. Civelekoglu. 1988. Evaluation of Turkish sulphur olive oil as an alternative diesel fuel. *JAOCS* 65(6): 936-938.
13. Liu, K. 1994. Preparation of fatty acid methyl esters for gas-chromatographic analysis of lipids in biological materials. *JAOCS* 71(11): 1179-1187.
14. Canakci, M., and J. Van Gerpen. 1999. Biodiesel production via acid catalysis. *Trans. ASAE* 42(5): 1203-1210.
15. Jeromin, L., E. Peukert, and G. Wollmann. 1987. Process for the pre-esterification of free fatty acids in fats and oils. U.S. Patent No. 4698186.
16. Hammond, E. G. Personal communication. Dept. of Food Science, Iowa State Univ., Ames, Iowa, 16 September 1998.
17. Kawahara, Y., and T. Ono. 1979. Process for producing lower alcohol esters of fatty acids. U.S. Patent No. 4164506.
18. Lepper, H., and L. Friesenhagen. 1986. Process for the production of fatty acid esters of short-chain aliphatic alcohols from fats and/or oils containing free fatty acids. U.S. Patent No. 4608202.
19. Stern, R., G. Hillion, P. Gateau, and J. C. Guibet. 1987. Process for manufacturing a composition of fatty acid esters useful as gas oil substitute motor fuel with hydrated ethyl alcohol and the resultant esters composition. U.S. Patent No. 4695411.
20. Freedman, B., and E. H. Pryde. 1982. Fatty esters from vegetable oils for use as a diesel fuel. In *Vegetable Oils Fuels: Proc. of the Intl. Conf. on Plant and Vegetable Oils as Fuels*, 117-122. St. Joseph, Mich.: ASAE.
21. Mittelbach, M., B. Pokits, and A. Silberholz. 1992. Production and fuel properties of fatty acid methyl esters from used frying oil. In *Liquid Fuels from Renewable Resources: Proc. of an Alternative Energy Conference*, 74-78. St. Joseph, Mich.: ASAE.
22. Feuge, R. O., E. A. Kraemer, and A. E. Bailey. 1945. Modification of vegetable oils: IV. Reesterification of fatty acids with glycerol. *Oil and Soap* 22(8): 202-207.
23. Nye, M. J., and P. H. Southwell. 1984. Conversion of rapeseed oil to esters for use as diesel fuel. Fifth Canadian Bioenergy R and D. Seminar, 487-490. London, U.K.: Elsevier Applied Science.
24. Keim, G. I., and N. J. Newark. 1945. Treating fats and fatty oils. U.S. Patent No. 2383601.
25. Howell, S. 1997. U.S. biodiesel standards: An update of current activities. SAE Paper No. 971687. Warrendale, Pa.: SAE.