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INFLUENCE OF FREE FATTY ACID CONTENT IN BIODIESEL PRODUCTION ON NON-EDIBLE OILS

A. Ribeiro[1], F. Castro[2] and J. Carvalho[3]
1 CVR – Centre for Waste Valorization, aribeiro@cvresiduos.pt.
2 University of Minho/CT2M, fcastro@ dem.uminho.pt.
3 CVR – Centre for Waste Valorization/CT2M, jcarvalho@cvresiduos.pt

ABSTRACT

The use of alternative feedstock as waste cooking oils (WCO) and bovine tallow for biodiesel production has some advantages. It is cheaper than edible vegetable oils and it is a way to valorize a sub-product. Nevertheless, these oils possess some contaminants, specially free fatty acid (FFA) content, which can reduce the quality and yield of biodiesel production. This problem was solved by testing different operating conditions and different transesterification procedure and equipments for each stage of processing. Technological assessment of process was carried out to evaluate their technical benefits, limitations and quality of final product. In this work biodiesel was produced by an alkali-catalyzed transesterification and by a two step esterification/alkali-catalysed transesterification in cases which FFA content has above 3%. Evaluation of quality from raw materials and final biodiesel was performed according to standard EN 14214. Results show that all parameters analyzed meet the standard and legislation requirements. This evidence proves that in those operational conditions the biodiesel produced from WCO and bovine tallow can substitute petroleum-based diesel.

Keywords: Biodiesel; Free Fatty acid (FFA); Waste Cooking Oil (WCO); Bovine tallow

INTRODUCTION

Energy is the most fundamental requirement for human existence and activities. As an effective fuel, petroleum has been serving the world to meet its need of energy consumption. But the dependence of mankind entirely on the fossil fuels could cause a major deficit in future. Furthermore, the threat of supply instabilities and the increased public awareness on the impacts of fossil fuel emissions on the environment and their potential health hazards triggered governments around the world to impose restrictions on fossil fuel combustion emissions. Hence, the discovery of an alternative source of energy was of immense importance to meet its energy requirements. The application of biodiesel to our diesel engines for daily activities is advantageous for its environmental friendliness over petro-diesel [1,2].

Biodiesel (Fatty Acid Methyl Esters) have become one of the most promising alternative biofuels in the world [2]. Biodiesel has a higher cetane number, no aromatics, and contains 10%–11% oxygen by weight [3,4] These properties reduce the emissions of carbon monoxide (CO), hydrocarbons (HC), and particulate matter (PM) in the exhaust gas [5, 6, 7]. According to Utlu and Kokac [8], there was an average decrease of 14% for CO_2, 17.1% for CO and 22.5% for smoke density when using biodiesel. Puppan [9] have discussed the advantages of biofuels over fossil fuels to be: (a) availability of renewable sources; (b) representing CO2 cycle in combustion; (c) environmentally friendly; and (d) biodegradable and sustainable. Biodiesel, which is considered as a possible substitute of conventional diesel fuel is commonly, composed of fatty acid methyl esters that can be prepared from triglycerides in vegetable oils by transesterification with methanol [10]. The resulting biodiesel is quite similar to conventional diesel fuel in its main characteristics [11].

Transesterification (fig. 1) is the process by which the glycerides present in fats or oils react with an alcohol in the presence of a catalyst to form esters and glycerol [12,13,14]. Catalyst increases the rate of the reaction and also the yield. This reaction proceeds well in the presence of some homogeneous catalysts such as potassium hydroxide (KOH)/sodium hydroxide (NaOH) and sulfuric acid, or heterogeneous catalysts such as metal oxides or carbonates [15]. Depending on the undesirable compounds (especially FFA and water), each catalyst has its advantages and disadvantages. Sodium hydroxide is very well accepted and widely used because of its low cost and high product yield [1]. The most common alcohols widely used are methyl alcohol and ethyl alcohol. Among these two, methanol found frequent application in the commercial uses because of its low cost [13].

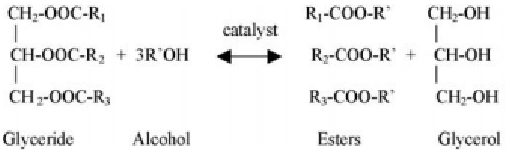

Figure 1 - Transesterification of triglycerides with alcohols.

Vegetable oils are promising feedstocks for biodiesel production since they are renewable in nature, and can be produced on a large scale [16]. However, it may cause some problems such as the competition with the edible oil market, which increases both the cost of edible oils and biodiesel [17,18,19]. For instance, the mass plantation of monoculture plants could benefit the economy of rural population while negatively affecting the water resources and the biodiversity [8]. In order to overcome these disadvantages, many researchers are interested in others feedstocks as waste cooking oils [13,20] and grease and animal fats [21,22], which are not suitable for human consumption and world economy [23]. Currently, chemical methanolysis using alkali-catalyst is the most popular commercialized process that gives high yield in short reaction time. According to many previous studies, a large percentage of biodiesel production cost was accounted for by the feedstock price [24]. However, cheap low grade feedstock often contains large amount of FFA. The interference of free fatty acid (FFA) and water to the alkali-catalyzed process for producing biodiesel has limited the use of those recycled, inexpensive, retrograde feedstock, or whatever may significantly reduce the costs of biodiesel. It was suggested that an acid catalyst be necessarily used to perform transesterification while feeding the low grade oil components [25]. However, the reaction rate of transesterification catalyzed by the acid catalysis is much slower than that catalyzed by alkali catalysis and more methanol is required [26]. Canakci and Gerpen [27] developed a two-stage process where the level of FFA could immediately be reduced to less than 1% using an acid catalyst (H_2SO_4) at the first stage.

The aim of this study was evaluate the influence of FFA in biodiesel production on waste cooking oils (WCO) and bovine tallow and analyze the best operational conditions for each feedstock. It was tested different processes for biodiesel production by a one step alkali-catalyzed transesterification and by an acid and alkali-catalyzed two-step transesterification. The final products of each process were analyzed according to standard EN 14214:2003 related to biodiesel quality.

BIODIESEL PRODUCTION WITH CATALYZED TRANSESTERIFICATION

Alkali-catalyzed transesterification

The use of alkali catalysts in transesterification reaction of waste cooking oil and animal fats is somewhat limited, because FFA content in this feedstock oil reacts with the most common alkaline catalysts (NaOH, KOH, and CH_3ONa) to forms soaps [12]. This reaction is undesirable because soap lowers the yield of the biodiesel and inhibits the separation of the esters from the glycerol. Feedstocks with high free fatty acid will react undesirably with the alkali catalyst thereby forming soap. The maximum amount of free fatty acids acceptable in an alkali- catalyzed system is below 3 wt.% of FFA. If the oil or fat feedstock has a FFA content over 3 wt. %, a pretreatment step is necessary before the transesterification process [18].

Acid- and alkali-catalyzed two-step transesterification

Alkaline and acidic catalysts have their own advantages and disadvantages in transesterification of waste cooking oil or animal fats. Hence, to avoid the problems associated with the use of these catalysts separately, especially the problems of saponification and slow reaction time, many researchers have developed the two-stage acid-and- alkali-catalyzed transesterification. In the first stage, esterification of FFA present in feedstocks is carried out using acid to decrease the FFA level to less than 1%. In the second stage, transesterification of the neutral feedstocks is performed using an alkaline catalyst [12, 13].

Process design

Fig. 2 shows a simplified flow chart of the alkali-catalyst process tested in this study for the transesterification of WCO and bovine tallow.

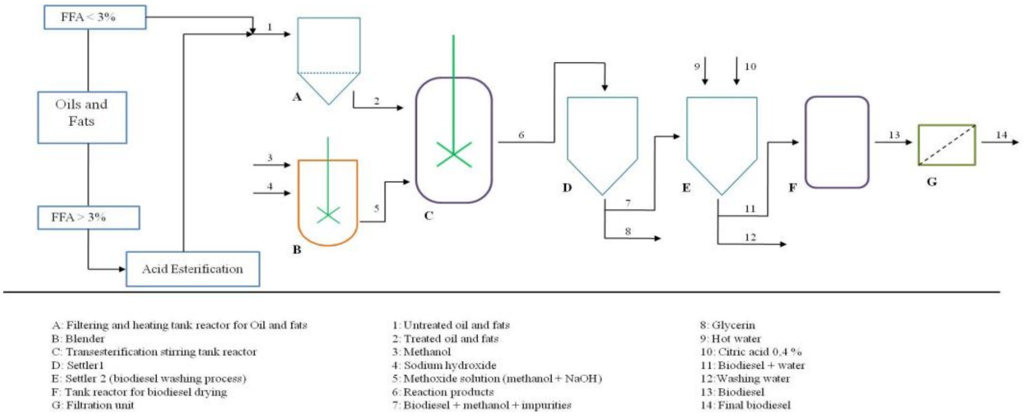

Figure 2 - Simplified process flow chart of alkali-catalyzed biodiesel production

EXPERIMENTAL PROCEDURE

Bovine tallow

Fatty acid methyl ester of bovine tallow as biodiesel fuel was prepared by base-catalyzed transesterification of tallow with methanol in the presence of NaOH as catalyst and a process combining acid esterification and alkali-based transesterification. Before transesterification, tallow was heated among 105–110 ºC for 4 h and then strained the sediment out of the tallow with filter. After this process, the yield of oil recovery from bovine tallow was 43%. Tallow was heated to 63 ºC slowly. In another flask, methanol (9:1 molar ratio methanol/tallow) was mixed with sodium hydroxide (0.5% w/w), until all of the NaOH was dissolved in methanol. This mixture was then added to the melted tallow, and further heated to 63 ºC, for 2 h. Ester was purified by washing with distilled water and citric acid and drying to room temperature.

In the two steps esterification/transesterification tallow was heated to 63 ºC slowly. Methanol (6:1 molar ratio) was mixed with acid sulfuric (0.08% w/w). This mixture was then added to the melted tallow, and further heated to 63 ºC, for 2 h. Ester was purified by washing with distilled water and drying to room temperature. Transesterification reaction was realized by adding a sodium hydroxide solution (0.01 w/w) and methanol (6:1 molar ratio methanol/tallow) to the esters from esterification reaction at 63 ªC for 2 h. Ester was purified by washing with distilled water and citric acid and drying to room temperature.

Waste cooking oils (WCO)

Fatty acid methyl ester WCO as biodiesel fuel was prepared by base-catalyzed transesterification of WCO with methanol in the presence of NaOH as catalyst. Before transesterification, WCO was filtered and heated among 65 - 70 ºC for 30 min. Methanol (5:1 molar ratio methanol/WCO) was mixed with sodium hydroxide (0.01% w/w), until all of the NaOH was dissolved in methanol. This mixture was then added to the WCO, stirred rigorously, and further heated to 60 ºC, for 2 h. Ester was purified by washing with distilled water and citric acid and drying at 100 ºC for 4 h. The final polishing process was realized by filtering the methyl ester in a filtering unit system.

RESULTS AND DISCUSSION

Influence of FFA content

The non edible oils used in biodiesel production have very contaminants, which can increase the FFA content and reduce the efficiency of the process. To determine the proportion and the maximum FFA concentration allowable to alkali-catalyzed transesterification experiments were realized with bovine tallow, varying the initial FFA content and the sodium hydroxide concentration (table 1). These experiments were performed on bovine tallow because WCO has FFA content less than 1%.

Table 1 – Effect of initial FFA content in biodiesel production

Initial FFA content (%)	Methanol molar ratio (methanol/tallow)	Sodium Hydroxide concentration (w/w)	Mass conversion (%)
2,2	9:1	0,5	89
3,5		0,75	74
5,1		1	56 (and soap formation)
7,5		1,25	(Soap formation)

These results shows that initial FFA content have a preponderant influence in alkali transesterification because when its concentration was higher, biodiesel production expressed by mass conversion was reduced and formed soaps. Maximum mass conversion was taken with a lower FFA content of 2,2%. This evidence confirmed that alkali-catalyzed transesterification only can be performed when FFA content was less than 3%.

Mass conversion

One of the most important dependent variables in this experiment is the mass conversion, which is given by the mass ratio of biodiesel (product) to the total initial mass of the raw material and the additives [1].

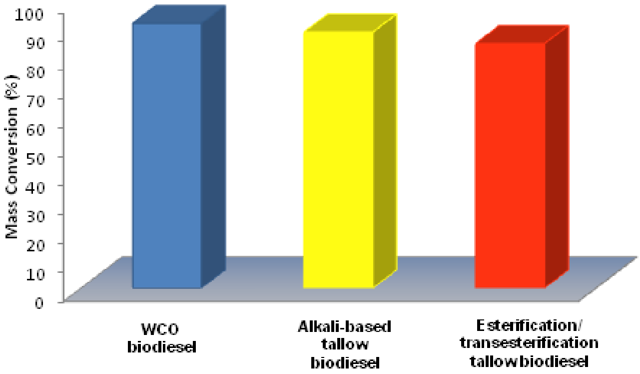

Figure 2 – Mass conversion (%) of biodiesel from the different feedstocks tested

Results demonstrated that WCO biodiesel was the maximum mass conversion of 92%, alkali-based tallow biodiesel was 89% and esterification/transesterification tallow biodiesel was 85% of conversion (Fig.2). Mass conversion depends on several parameters like, reaction temperature and pressure, reaction time, rate of agitation, type of alcohol used and molar ratio of alcohol to oil, type and concentration of catalyst used and principle concentration of free fatty acids (FFA) in the feed oil [12,13,23]. Through these results it is possible to verify that FFA was high influence in the mass conversion because the less FFA content feedstock achieves the highest conversion.

Quality of Biodiesel

The major focal point for biodiesel high quality is the adherence to biodiesel standard specifications. These standard specifications in European Union are established by EN 14214 for biodiesel fuel [1,12,28]. The results of the analyses in the different types of biodiesel produced (Table 2) showed that in generally the quality parameters of standard EN 14214 was accomplished.

Table 2 – Results of biodiesel produced from the different feedstocks tested according to standard EN 14214

Property	Unit	WCO biodiesel result	Alkali-based biodiesel from bovine tallow result	Esterification/ transesterification biodiesel from bovine tallow result	Limits		Test Method
					Minimum	Maximum	
Ester content	% (m/m)	96,8 ± 0,1	94,5 ± 0,2	92,0 ± 0,5	96,5		EN 14103
Density at 15 °C	kg/m^3	881 ± 5	883 ± 0,85	875 ± 1	860	900	EN ISO 3675
Viscosity at 40 °C	mm^2/s	4,75 ± 0,01	5,07 ± 0,02	5,01 ± 0,02	3,00	5,00	EN ISO 3104
Flash point	ºC	174 ± 2	164,0 ± 0,5	150 ± 2	120	-	EN ISO 3679
Carbon residue	% (m/m)	0,20 ± 0,05	-	-	-	0,30	EN ISO 10370
Water content	mg/kg	142 ± 2	492 ± 1	420 ± 2	-	500	EN ISO 3679
Acid value	mg KOH/g	0,25 ± 0,05	0,46 ± 0,02	0,48 ± 0,02	-	0,50	EN 14104
Iodine value	g iodine100 g	62,82 ± 1,50	81,22 ± 0,02	78,22 ± 0,01	-	120	EN 14111
Linolenic acid methyl ester	% (m/m)	8,4 ± 0,5	-	-	-	12,0	EN 14103
Methanol content	% (m/m)	0,12 ± 0,01	0,1 ± 0,01	0,1 ± 0,01	-	0,20	EN 14110
Group I metals (Na + K)	mg/kg	4,71 ± 0,03	-	-	-	5	EN14108 EN 14109

CONCLUSIONS

Biodiesel is gradually gaining acceptance in the market as an environmentally friendly alternative diesel fuel. However, for biodiesel to establish and continue to mature in the market, various aspects must be examined and overcome. Some of the key issues such as improving efficiency of the production process, using low cost feedstock have been reviewed and analyzed. As with any new technology or products, biodiesel will require continuous improvement especially in producing cleaner emissions and having less impact on the environment.

On this study it was used different feedstock oils to produce biodiesel, and it was demonstrated that the effect of various operating and processing parameters on transesterification depends on quality and source of the feedstock oil. According to FFA content, different technological approaches can be used. It was used the alkali-catalyzed process because FFA content in collect frying oil was less than 1%, but when FFA content as a higher value, like on bovine tallow, it was necessary doing a two step process: esterification and transesterification. From the technical assessment in laboratory and a pilot plant, all of these processes proved to be feasible for producing a high quality biodiesel product. Process using waste cooking oils and bovine tallow oil had a high yield of conversion and the analyses on the final biodiesel showed that all quality parameters of the standard 14214 have been respected for witch feedstock oil.

According to these results, it is possible to conclude that the biodiesel produced with tested feedstock was liable to be used in diesel car engines, in a unique way (B100) or blending with fuel diesel (B20, B30 and B50), without decrease of engine efficiency.

REFERENCES

[1] I.M. Atadashi, M.K. Aroua, A. A. Aziz, High quality biodiesel and its diesel engine application: A review, Renewable and Sustainable Energy Reviews 14 (2010) 1999–2008.

[2] N. Chand, Plant oils—Fuel of the future, J. Sci. Ind. Res. 61(2002) 7–16.

[3] Yun-Huin Lin, Jheng-Jin Luo, Sz-Chwun John Hwangb,, Pei-Ru Liau, Weng-Jang Lu, Hom-Ti Lee, 2011. The influence of free fatty acid intermediate on biodiesel production from soybean oil by whole cell biocatalyst. Biomass and bionergy, 35, 2217 – 2223.

[4] M.C. Math, Sudheer Prem Kumar, Soma V. Chetty, M.C. Math, Sudheer Prem Kumar, Soma V. Chetty. Technologies for biodiesel production from used cooking oil — A review. Energy for Sustainable Development 14 (2010) 339–345.

[5] Chang DYZ, Van Gerpen JH. Fuel properties and engine performance for biodiesel prepared from modified feedstocks. Warrendale, PA: Society for Automotive Engineering; 1997. Paper No. 971684.

[6] Chang DYZ, Van Gerpen JH, Lee I, Johnson LA, Hammond EG, Marley SJ. Fuel properties and emissions of soybean oil esters as diesel fuel. J Am Oil Chem Soc 1996;73(11): 1549–55.

[7] Graboski MS, McCormick RL. Combustion of fat and vegetable oil derived fuels in diesel engines. Prog Energy Combust Sci 1998;24:125–64.

[8] Utlu Z, Kokac MS. The effect of biodiesel fuel obtained from waste cooking oil on direct injection diesel engine performance and exhaust emissions. Renew Energy 2008, 33, 1936-1941.

[9] D. Puppan. Environmental evaluation of biofuels, Periodica Polytechnica Series Social and Management Sciences 10 (2002) 95–116.

[10] J.V. Gerpen, Biodiesel processing and production, Fuel Processing Technology 86 (2005) 1097–107.

[11] L.C. Meher, D.V. Sagar, S.N. Naik, Technical aspects of biodiesel production by transesterification—a review, Renewable and Sustainable Energy Reviews 10 (2006) 248–268.

[12] A. Banerjee, R. Chakraborty, Parametric sensitivity in transesterification of waste cooking oil for biodiesel production—A review, Resources, Conservation and Recycling 53 (2009) 490–497

[13] C.C. Enweremadu, M.M. Mbarawa, Technical aspects of production and analysis of biodiesel from used cooking oil—A review, Renewable and Sustainable Energy Reviews 13 (2009) 2205–2224.

[14] M. Zabeti, W.M. Daud, M.K. Aroua, Activity of solid catalysts for biodiesel production: A review, Fuel Processing Technology 90 (2009) 770–777.

[15] J.V. Gerpen, Biodiesel processing and production, Fuel Processing Technology 86 (2005) 1097–107.

[16] Patil PD, Deng S. Optimization of biodiesel production from edible and nonedible vegetable oils. Fuel 2009;88:1302–6.

[17] J. Janaun, N. Ellis, Perspectives on biodiesel as a sustainable fuel, Renewable and Sustainable Energy Reviews 14 (2010) 1312–1320.

[18] FAO, The State of Food and Agriculture, Biofuels: prospects, risks and opportunities. Rome: Food and Agriculture Organization of the United Nations (2008).

[19] J. Kansedo, K.T. Lee, S. Bhatia, Cerbera odollam (sea mango) oil as a promising non-edible feedstock for biodiesel production, Fuel 88 (2009) 1148–50.

[20] F. Pedro, J.N. Correia, R. Idalina, M. João, R. Berkemeier, J.M. Bordado, Production of biodiesel from waste frying oils, Waste Management 26 (2006) 487–94.

[21] L.S.G. Teixeira, J.C.R. Assis, D.R. Mendonça, I.T.V. Santos, P.R.B. Guimarães, L.A.M. Pontes, J.S.R. Teixeira, Comparison between conventional and ultrasonic preparation of beef tallow biodiesel, Fuel Processing Technology 90 (2009) 1164–1166.

[22] S. Saraf, B. Thomas, Influence of feedstock and process chemistry on biodiesel quality, Process Saf. Environ. Prot. 85 (2007) 360–4.

[23] D.Y.C. Leung, X. Wu, M.K.H. Leung, A review on biodiesel production using catalyzed transesterification, Applied Energy 87 (2010) 1083–1095.

[24] A.V.L Pizarro, E.Y. Park. Lipase-catalyzed production of biodiesel fuel from vegetable oils contained in waste activated bleaching earth. Process Biochem. (2003);38:1077-1082.

[25] K.J. Harrington, C. D'Arcy-Evans. A comparison of conventional and in situ methods of transesterification of seed oil from a series of sunflower cultivars. J.Am. Oil Chem. Soc (1985);62: 1009-1013.

[26] F. Ma, M.A. Hanna. Biodiesel production: a review. Bioresour Technol (1990) 70: 1-15.

[27] M. Canakci, J.V. Gerpen. Biodiesel production from oils and fats with high free fatty acid. Trans ASME (2001);44:1429-1436.

[28] L.C. Meher, D.V. Sagar, S.N. Naik, Technical aspects of biodiesel production by transesterification—a review, Renewable and Sustainable Energy Reviews 10 (2006) 248–268.