

Biodiesel from Restaurant Cooking Oils Using Trans-esterification Process

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Abstract

The biodiesel prepared from Restaurant Cooking Oils (RCO) using trans-esterification process as well as the influence of major operating parameters on the reaction including catalyst amount, temperature, and alcohol/oil ratio have been studied in the present paper. Experimental results showed a good effectiveness of biodiesel yield 93% based on optimum conditions catalyst 1%, alcohol/oil mass ratio 2/5 under 40°C.

Keywords: Biodiesel, trans-esterification, restaurant cooking oils (RCO), fuel characterization.

NOMENCLATURE

KOH	Potassium Hydroxide	CI	Cetane Index
FTIR	Fourier Transform Infra-Red Spectrometer	RI	Refractive Index
TLC	Thin Layer Chromatography	R	Alcohol/Oil ratio (W/W)
η	Efficiency (%)	FCC	Fluid Catalytic Cracking
W/W	Weight /Weight	RCO	Restaurant Cooking Oils
EIA	Energy Information Administration		
USA	United State of America		
EU	Europe Union		
UK	United Kingdom		

INTRODUCTION

Today, the biodiesel production has received mainly attention international owing to the world energy crisis and ecological issues. Biodiesel is a mixture of methyl esters of long-chain fatty acids lauric, palmitic, stearic, etc. this biofuel is prepared typically from vegetables oils, including soybean oils, palm oil, rapeseed, sunflower oil and their derivatives as well as beef and sheep tallow and poultry oil from animal sources and Restaurant Cooking Oils (RCO). Oil or fat reacts with alcohol in the presence of sodium/potassium hydroxide catalyst to form biodiesel, methyl-esters, and glycerin [1-2].

Huge quantities of RCO and animal fats are available throughout the world, especially in the developed countries. Management of such waste materials poses an important challenge due to their removal difficulties and possible pollution of water, air and land resources. Even though some of these waste cooking oils are utilized for soap manufacture, a

large quantity of it is discharged into rivers causing environment pollution. The Energy Information Administration (EIA) estimates that 100,000,000 gallons of RCO is produced per day in USA, 135,000 tons/year in Canada, 1,000,000 tons/year in EU, 200,000 tons/year in UK [3-4].

The RCO is characterized by their nutritional value and some other constituents containing fatty acids. The sunflower oil is one example of these oils and its lower content of saturated fatty acids exceeded 12%, and it contains a large number of mono or polyunsaturated fatty acids such as oleic acid especially linoleic acid. This oil can lose its nutritional quality by fritting, and increase levels of free fatty acids created. Therefore, the society thought to avoid its rejection to the sink and to reuse this residue as feedstock especially to produce biodiesel to sustain the economic sector of energy [5]. On the other hand, the great problem of shortening fossil energy resources can be partially solved by finding an alternative that can meet our future needs as a biofuel which is biodiesel. This novel renewable energy resource is different to the classic diesel in many important aspects such as the percentage of oxygen, the number of unsaturated component present in the biodiesel [6], and relatively the cost which is estimated with a factor of 2.5% in the case of biodiesel produced from the algae oils [7,8], taking into account that the feedstock oil costs constitute approximately more than 80% of the overall cost of biodiesel production [9]. Above all, biodiesel is considered as an ecofriendly product [10,11], and it is seen as the best candidate for substituting diesel fuels in diesel engines. It burns like petroleum diesel as it involves regulated pollutants. In addition, biodiesel has better efficiency than gasoline and exhibits great potential for compression-ignition in engines. Diesel fuel can be also replaced by biodiesel made from vegetable oils [12]. The biodiesel contributes to reduce the negative impact of certain pollutants emission and deteriorates many others. For quantifying the effect of biodiesel it is important to consider the raw material used, driving cycle, vehicle technology..etc. The use of biodiesel will allow a balance to be sought between agriculture, economic development, and the environment [13].

At the beginning of diesel engines uses we utilized vegetable oils as fuels. The inconvenient of this biofuel is its high viscosity for use in most existing diesel engines as a straight replacement fuel oil. There are many ways to reduce vegetable oils' viscosity like dilution, micro-emulsification, pyrolysis, and trans-esterification. The latest process is one of the most common methods used to reduce oil viscosity in biodiesel industry [14].

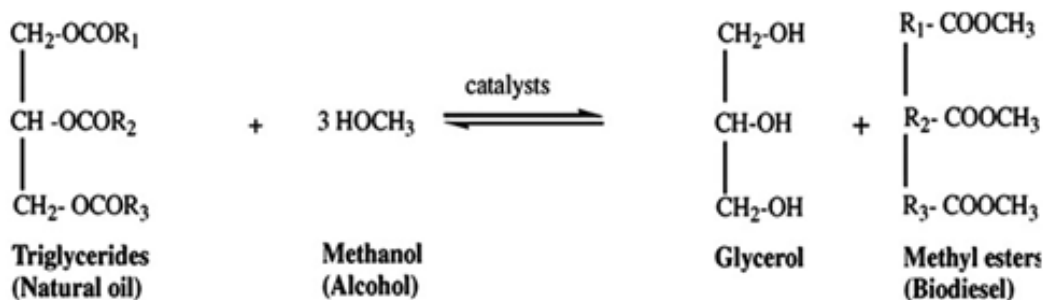


Figure 1. Trans-esterification of oil to biodiesel using an alkali catalyst [8,16]

The trans-esterification (Fig. 1) is a method wherein vegetable oils, animal fats or microalgae oils are mixed with an alcohol (ethanol or methanol) in the presence of a homogeneous catalyst (acid or basic) [15], or heterogeneous (catalysts based on alumina, metal oxides of group IIA) mixed oxides and transition metal oxides supported on various porous supports. This operation may be performed cold or hot depending to the operator conditions.

The present work presents the biodiesel synthesis by trans-esterification of RCO, coming mainly from fritting potatoes using the methanol in presence of the potassium hydroxide (KOH) under various operating conditions controlling the biodiesel synthesis process. The characterization of the biodiesel produced is performed by Fourier Transform Infra-Red Spectrometer (FTIR) and by Thin the Layer Chromatography (TLC).

EXPERIMENTAL SETUP

The experimental device of the trans-esterification process of biodiesel from RCO used is composed of two necked-flasks containing one unit of fritting waste oil 1% of KOH, alcohol/oil mass ratio 2/5 under continuous agitation during 1h at 40°C. The simplified reaction of the biodiesel synthesis is shown in Figure 1. Washing and evaporation are the last steps practiced on the biodiesel produced to remove glycerine and reactive excess present in the reaction medium. The characterization of the biodiesel produced is carrying out by TLC and FTIR testing using solvent mixture of hexane 40%, oil-ether 10% and acetic-acid 0.5, spectrophotometer IR Cary 660.

RESULTS AND DISCUSSIONS

Trans-esterification (biodiesel synthesis) could be explained as a reaction between acid and alcohol to produce ester and water. In the present case, the acid and the ester are oil (triglyceride) and biodiesel respectively. The yield of this reaction is calculated by the ratio between the weight of the two component biodiesel and oil by the following equation [17].

$$\eta(\%) = \frac{\text{Weight of biodiesel}}{\text{Weight of oil}} * 100 \quad (1)$$

Parameters Influencing the Trans-esterification Process

The bioethanol production by trans-esterification process was affected by various parameters [18,19], the most important taken in account are:

Catalyst amount. The effect of this parameter has been showed by varying the weight ratio of the catalyst from 0.5 to 1.5% under operating conditions cited previously. The bioethanol produced showed a good inflammability (see Fig. 2). A slight increase in bioethanol yield η to reach its limit value of 93% for a catalyst/oil ratio 1%. Up to this value the increase of KOH weight ratio is unfavorable (Table 1). The density and the refractive index indicated negligible variations estimated at 1.62% and 0.14% respectively (Table 1).

Temperature. The influence of the temperature on the trans-esterification process is very important; it can be the principal cause of the soap formation in the reaction medium. Hence, the control of its values is necessary to optimize the biodiesel produced. It is obvious that the maximum bioethanol yield is obtained at high temperature 40°C. Above this value any increase in temperature decreases the biodiesel production (Table 1). This is due to the direct influence of the temperature on the viscosity of reacted oil and formation of the biodiesel.



Figure 2. Inflammability test of the biodiesel synthesis

Table 1. Parameters influencing the biodiesel production

Parameter		Biodiesel yield (%)	Density (20°C)	Refractive Index	W biodiesel (g)
Catalyst concentration KOH (%)	0.5	92.81	0.879	1.453	
	1.0	93.10	0.865	1.455	
	1.5	85.57	0.865	1.453	
Temp.(°C)	40	93.10	0.865	1.455	
	50	92.10	0.868	1.456	
	60	90.20	0.866	1.456	
R=Alcohol/Oil ratio(W/W)	2/5	93.02	0.865	1.453	85.21
	5/2	24.45	-	1.456	11.20
	1/1	00.00	-	0.000	00.00

Table 2. Characterization of biodiesel synthesis compared with different diesel-fuels

Characteristics	Bio	Weak	Heavy	Kerosene	Diesel
Density (g/cm ³)	0.89	0.83-0.84	0.86-0.89	0.780	0.90
Viscosity at 20°C (mm ² /s)	6.86	-	-	-	-
Flash point (°C)	130	-	-	32-45	60-70
Cetane Index (CI)	46	47-50	50-60	40-50	20-30

Methanol/oil ratio. In Table 1, an alcohol/oil ratio=2/5 produce 85.21g of biodiesel, subsequently any change in the ratio value decreases the trans-esterification yield. Last results may be due to the insufficient amount of ethanol and the presence of a high content of potassium hydroxide. After the trans-esterification of RCO and decantation of the reaction mixture to remove the aqueous phase and the glycerol, the biodiesel produced must be washed using distilled water or acid which served to remove the glycerol and neutralize the alkaline medium.

B. Characterization of the Biodiesel Produced

The quality of the biodiesel produced must be conform to the International European biodiesel standard (EN14214) fixing the limits for glycerol, glycerides, alcohol, moisture and free fatty acid. These products residue can lead to engine deposits and fuel deterioration during storage [14,20]. To verify the

quality of the biodiesel synthesis, a comparative study was performed with the conventional diesel fuel produced by the Sbaâ-refinery laboratory (SORALCHIN) located in Adrar province in south Algeria. The biodiesel synthesized present a density value similar to that given by the heavy-diesel and a cetane index with larger range 46-82 which indicate a good characteristic of the biofuel produced (see Table 2).

The purity and the effectiveness of the biodiesel produced using TLC testing during an hour are shown in Figure 3. We observe a good purity of the biodiesel produced. Only one spot has been observed after six washing operations with different percentage of catalyst amount and fixed alcohol/oil ratio of 2/5. Washing six times the final product of biodiesel by water allowed to remove glycerin, alcohol and impurities trace [21].

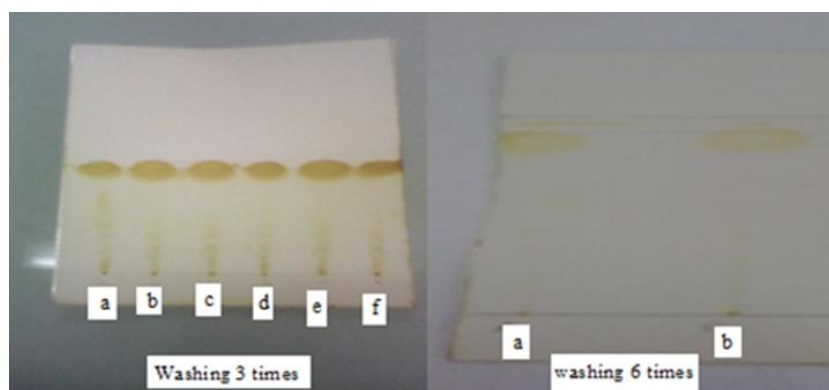


Figure 3. TLC analysis of the biodiesel versus KOH, a. biodiesel (0.5%, 40°C), b. biodiesel (1%, 40°C), c. biodiesel before washing, d. (1.5%, 40°C), e.(1%, 50°C), f. (1%, 60°C).

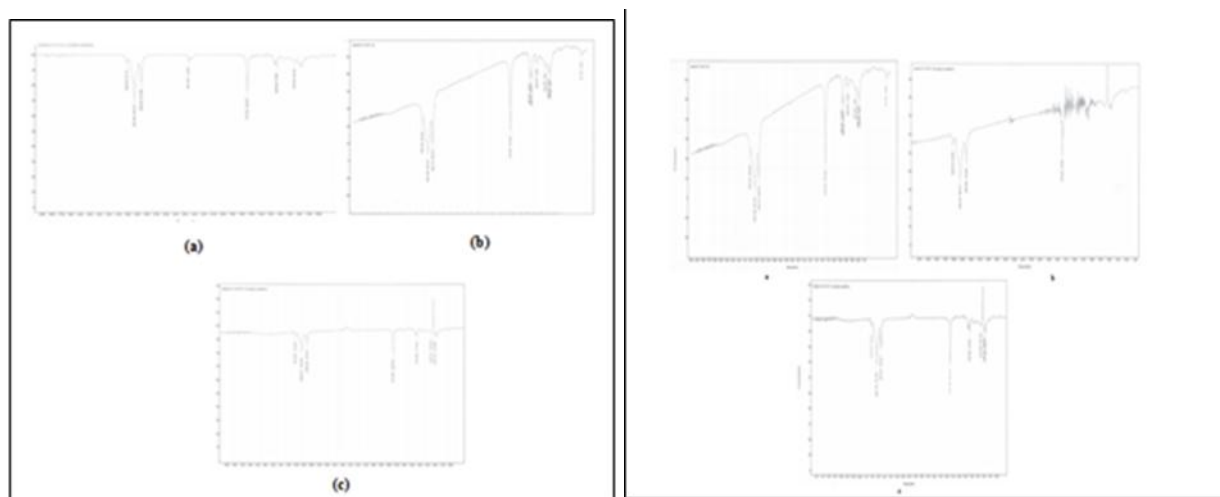
The distillation of the biodiesel produced from RCO indicated its evaporation point at 100°C. It has a low temperature compared with different fuels due to the presence of water trace. The variation of the biodiesel percentage present in the fuel to distillate from 10 to 90% increased the evaporation temperature and reached its high value 343°C. These biodiesel evaporation temperatures remained the highest value (Table 3).

Table 3. Distillation temperature versus biodiesel ratio (°C)

Distillate volume (%)	Diesel (FCC)	Biodiesel
IP	160-170	100
10%	220	330
50%	250	337
65%	270	340
90%	310-320	343

The FTIR spectra presented in Figure 4 shown the appearance of characteristic peaks in the different case; at 1741-1743 cm⁻¹ matching to the molecule group C=O ester band, another band has been showed at 2850-2910 cm⁻¹ corresponding to the C-H band. The signal appeared between 2100-2250 cm⁻¹ it can be owed to the C≡C, with some impurities. This signal is very intense using 1% of oil/ KOH ratio which prove the good trans-esterification process efficiency under these operation conditions.

This analysis method has been also used to verify the constitution and the nature of the final product of the trans-esterification reaction varying the temperature from 40 to 60°C (Figure 4). Their results showing the appearance of same peaks indicating the same constitutions with different intensities; the use of 1% of KOH and alcohol/oil ratio 2/5 less than 40°C involved the obtaining of optimum yield of methyl ester.



A. KOH (a. 0.5%, b. 1%, c. 1.5%), 40°C, R=2/5 B. KOH(1%), R=2/5,(a. 40°C, b. 50°C, c. 60°C)

Figure 4. FTIR spectra of the methyl-ester (biodiesel) under operation conditions

CONCLUSION

The RCO coming from fritting vegetables of local restaurant in Adrar province in south Algeria constitutes an important biomass and a favorable medium for biodiesel preparation by trans-esterification process.

In the present experimental work, the biodiesel was characterized by its physical and fuel proprieties using EU standard. From tests, the flash point found is 130°C. Compared to the conventional diesel-fuels, the quality and the effectiveness of the biodiesel production by trans-esterification process is acceptable and encourages its development in the future. It is necessary to prospect novel techniques, catalysts and operation conditions to enhance the biodiesel yield, to shorten the development process, and to reduce the energy consumed as well as the cost of the product.

Globally, the quantity of RCO available seemed favorable for developing an industry of biodiesel in Algeria. Though, initially it is essential to build many pilot trans-esterification system at various locations for settling results obtained in laboratories before transposing the process in an industrial scaling.

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