



Valorization of diverse low-value wastes into biodiesel

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Abstract

This study investigates the potential of various types of wastes as feedstocks in the transesterification of triglycerides into fatty acid methyl esters, commonly referred to as biodiesel. These wastes include waste olive oil, waste chicken fat and waste coffee oil. These types of virtually free and readily available materials are drawing growing attention in light of the global trend to develop sustainable energy and lessen the impact of fossil fuels on the environment. Furthermore, turning these wastes into a biofuel offers a more appealing alternative to ordinary low-value processings such as landfilling, composting and incineration. Optimization of the feedstock extraction was performed and extraction yields of 8.3%, 9.0%, 75.2% and 10.9% were obtained for olive pomace, olive mill wastewater (OMW), chicken fat and coffee oil respectively. The highest yields obtained in the conversion of these feedstocks - in their refined form - into biodiesel were 71%, 86% and 56% for olive oil, chicken fat and coffee oil respectively. The biodiesel produced was characterized for its FFA content, density, Gross Calorific Value and TLC profile. Results were compared with literature as well as European specifications EN14214. Finally a conclusion concerning the economic viability of the process was drawn.

Keywords: biodiesel, fatty acid methyl esters, biofuel, waste valorization, waste management, animal fats, coffee grounds

1. Introduction

Due to the finite supplies of fossil fuels and growing concerns of global warming, the energy sector is nowadays called upon to develop fuel substitutes that are renewable and sustainable. Biomass-derived fuels such as biodiesel are well accepted alternatives to petroleum-based diesel fuel as they are economically feasible and environmentally-friendly. The numerous advantages of biodiesel over diesel fuel are its portability, ready availability, renewability, higher combustion efficiency, lower sulfur and aromatic content, higher cetane number, higher biodegradability, better emission profile and safer handling, besides being non-toxic [1-6]. Biodiesel is defined by ASTM (American Society for Testing and Materials) as a mixture of long-chain monoalkylic esters from fatty acids derived from vegetable oils and fats [7]. Alkali-catalyzed transesterification is the most preferred method employed in biodiesel production. This chemical process is a reaction between a triglyceride and an alcohol with low molecular weight, usually methanol or ethanol (**Figure 1**).

Prevalent feedstocks for this fuel are virgin edible vegetable oils such as canola, soybean, palm and sunflower [8]; however it is important to prospect new sources which are more economically competitive and which do not compete with the food chain [9]. In this regard, waste vegetable oils and animal fats are given a special attention because of their low market value, relative abundance and underexploitation [10,11]. The feedstocks selected in this study pertain to this category; they include: waste olive oil, waste chicken fat and waste coffee oil. Their refining and subsequent conversion into biodiesel was carried out and conclusions were drawn as to their potential.

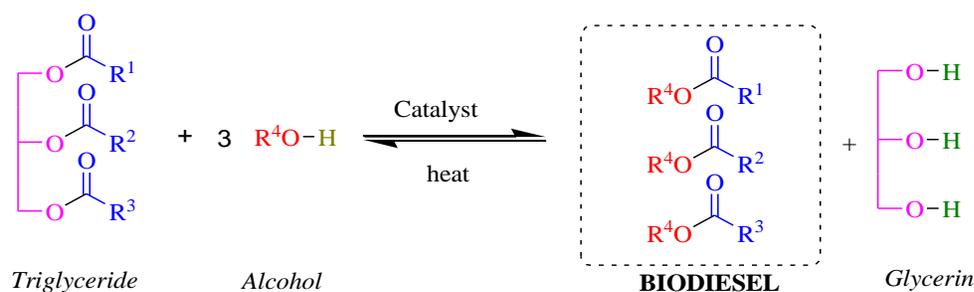


Figure 1: Transesterification reaction leading to the formation of biodiesel.
 Typical conditions: R¹, R², R³ = long alkyl chains (C₁₄-C₂₂); R⁴ = CH₃;
 catalyst = KOH, NaOH, MeONa; heat = 60°C.

2. Experimental

2.1 Chemicals and equipment

Methanol was 99.5% pure and supplied by VWR. n-Hexane was 99% pure and supplied by Sigma Aldrich. Potassium hydroxide, 86% pure, was supplied by Fluka, Switzerland. Sodium sulfate was supplied by J.T.Baker, USA. Sodium methoxide as a 5.4 M (30 wt%) solution in methanol was supplied by Acros Organics, USA. Ethyl acetate was supplied by Sigma Aldrich. Silica gel was supplied by Fluka, Switzerland. Phosphoric acid used in the washings of biodiesel was made from 85% phosphoric acid supplied by Fluka, Switzerland. Medical grade oxygen used in bomb calorimetry measurements was supplied by Maghreb Oxygen, Morocco. Phenolphthalein was supplied by Sargent-Welch, USA, and was used as a 1% solution in ethanol. Potassium permanganate was supplied by Sargent-Welch, USA. Thin Layer Chromatography (TLC) was operated with 5x10 cm plates with an eluant ethyl acetate/hexane 85:15 and a 1% KMnO₄ in 4% NaOH staining bath. TLC plates made of a silica gel matrix supported on polyethylene terephthalate were supplied by Fluka, Germany.

Oil and biodiesel samples were centrifuged in a 5500 rpm Hettich centrifuge, model EBA 30 or in a 2700 rpm Clay Adams/Becton Dickinson centrifuge, model 420227. Vacuum distillations and vacuum filtrations were performed by means of piston-powered vacuum pump (0.85 atm, 38 L/min). Water content in waste coffee grounds was determined accurately with a VWR oven, model 1300U. Occasionally, samples were mixed with hexane by means of a VELP scientifica vortex shaker, model Zx3. Ultrasonication was performed with a Branson ultrasonic cleaner, model 1210-EMT (50W, 47 kHz). Gross Calorific Values were measured by means of a Parr 1344EE oxygen bomb calorimeter.

2.2 Preparation of feedstocks

2.2.1 Waste olive oil from pomace

Pomace was collected from a local olive mill. This mill employs a traditional batch press process and is located in *Ain Taoujdate* (33° 56' North 5° 13' West). Since pomace oil cannot be removed physically, even with a mill's powerful hydraulic press, it was extracted chemically with hexane. This solvent was chosen because of its non-polarity, its low normal boiling point (69°C) and its affordability. The extraction yield was calculated according to the formula shown in **Equation 1**.

$$\text{extraction yield} = \frac{\text{mass (oil extracted)}}{\text{mass (pomace sample)}} \times 100 \quad \text{Equ. 1}$$

The typical experimental procedure used to extract olive oil from pomace is as follows. In a 100mL round-bottom flask fitted with a water condenser, 20g of ground and dried pomace was introduced; then, 50mL of hexane was added and the suspension was refluxed at 70°C for the desired extraction time, without stirring. Afterwards, the mixture was filtered over cotton and washed with another portion of 50 mL of hexane to extract as much oil as

possible, before proceeding to evaporation under vacuum to afford a solvent-free olive oil. A scale-up of this reaction by a factor of 10 was also done by performing it in a two-neck 1L round-bottom flask.

2.2.2 Waste olive oil from OMW

Two samples of OMW were collected from the same olive mill mentioned previously. The first sample was collected indoors, freshly after oil extraction, during the olive pressing season in November; the second one was collected outdoors 3 months later (February) after the pressing season was over. The samples were stored at room temperature (18°C) in several opaque 30L plastic drums and allowed to settle for one week prior to use.

30.25 kg of OMW stored in an opaque plastic drum was allowed to settle at room temperature (18°C) for one week, time upon which the distinct top layer of the drum was gently removed. This layer was then transferred into test tubes to be centrifuged at 2700 rpm for 5 min to enable isolation of the oil from water and mud. The resulting clear oil was subjected to a final vacuum filtration followed by a flash distillation at 100°C to remove any residual water. This procedure afforded a total of 2723 g of oil, which corresponds to an extraction yield of 9.0%.

2.2.3 Waste chicken fat

Waste chicken fat was collected from a local chicken shop to be refined. The refining process consisted in chopping the fat manually, melting it at 120°C and finally filtering it to isolate it from various solids (gums, protein residues and suspended particles). The residual amount of water was removed by flash distillation at 100°C under stirring. This sequence afforded a white, opaque, creamy and faintly odorous solid with an overall yield of 79.6%.

2.2.4 Waste coffee oil

A 1L round-bottom flask was charged with 150g of coffee grounds and 750mL of hexane. The flask was then placed in a sonicating bath and irradiated at room temperature for 10 min. Next, it was fitted with a water condenser and the mixture was heated at 70°C by means of an oil bath for 30 min, time upon which the suspension was allowed to cool down to c.a. 40°C. The mixture was then filtered under mild vacuum to afford a brown solution of oil. This solution was subjected to a flash distillation at 100°C to evaporate hexane to finally give a dark fragrant oil.

2.3 Conversion of feedstocks into biodiesel

The typical experimental procedure used to convert oil or fat into biodiesel is as follows. In a 100mL round-bottom flask fitted with a magnetic stir bar and a water condenser, 40g of dried oil or fat was introduced and pre-heated at 60°C under stirring to reduce its viscosity; then, a solution of catalyst dissolved in methanol was added and the mixture was left under vigorous stirring at 60°C for the desired reaction time. Finally, the reaction mixture was transferred to a 125mL separatory funnel where it was allowed to settle for 15 min, time upon which a glycerin layer was observed at the bottom and a biodiesel layer was observed at the top. The biodiesel layer was isolated and washed first twice with a 10% H₃PO₄ solution, next multiple times with warm tap water until clear washings and a neutral pH were attained. The resulting biodiesel layer was dried over sodium sulfate, filtered and finally subjected to a flash distillation at 100°C to evaporate the excess methanol and any residual water to afford pure biodiesel. The yield was calculated according to the formula shown in **Equation 2**.

$$\text{yield} = \frac{\text{mass}(\text{biodiesel produced})}{\text{mass}(\text{oil / fat used})} \times 100 \quad \text{Equ. 2}$$

Quality of the finished product was assessed by determination of the Free Fatty Acid (FFA) content, density at 15°C, Gross Calorific Value and by running a Thin Layer Chromatography according to a literature method [12].

2.4 Free Fatty Acid (FFA) content

A modified literature procedure was employed to determine the FFA content [13]. In a 250 mL Erlenmeyer flask fitted with a magnetic stir bar was introduced 20.00g of analyte (oil, melted fat or biodiesel), 50.00 mL of ethanol and 7.5 mL of phenolphthalein. The flask was stoppered, stirred and heated at 70°C by means of a bain-marie to ensure a complete dissolution; thereafter the mixture was titrated with a freshly made 0.0815M KOH solution in ethanol. Once the volumes of titrant used to neutralize the sample, V_1 , and to neutralize a blank, V_2 , recorded, the Free Fatty Acid content could be calculated according to the formula shown in **Equation 3**.

$$\% \text{FFA (as oleic acid)} = \frac{C_{\text{KOH}} \times (V_1 - V_0) \text{ mL} \times 10^{-3} \times M_{\text{oleic acid}}}{m_{\text{sample}}} \times 100 \quad \text{Equ. 3}$$

3. Results and discussion

3.1 Oil extraction

3.1.1 Waste olive oil from pomace

In the framework of the optimization of olive oil extraction from pomace, different extraction times were tested; results are reported in **Figure 2**.

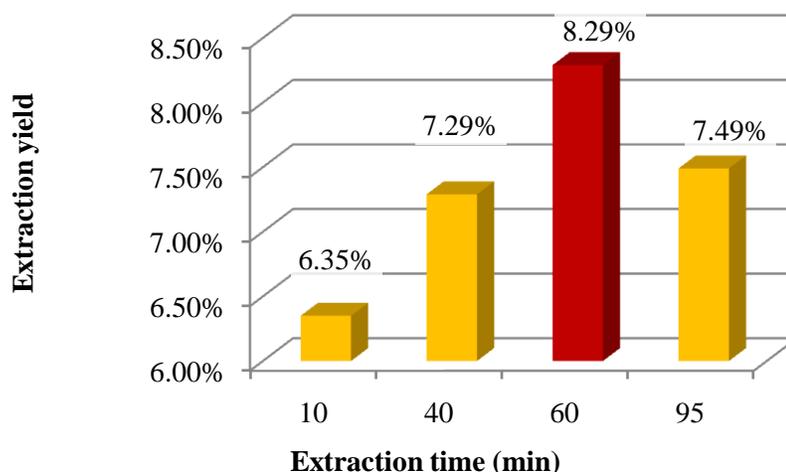


Figure 2: Oil extraction yields from pomace obtained for different extraction times.

Figure 2 indicates that the best extraction time under the conditions tested (20g scale, 2x50mL hexane, 70°C) is 60 min, an optimized time which allows to extract 8.29 g of oil per 100g of pomace. As expected, the extraction yield increases progressively from 10 min to 60 min since the extraction time increases; however this trend is no longer valid at 95 min where the yield drops at 7.49%. The latter can be explained by the irregular composition of the pomace samples used, especially in the content of particles such as crushed pits which are totally oil-free. This problem can be easily solved though by performing the experiment with a sieved sample that is perfectly homogeneous.

3.1.2 Waste olive oil from OMW

OMW is a mixture of vegetation water and soft tissues of the olive fruit and the water used in the various stages of the oil extraction process. It contains olive pulp, mucilage, pectin, oil, etc., suspended in a relatively stable emulsion [14]. The composition of OMW is very variable and depends on olive variety, the ripeness of the fruit, and the extraction process (press or centrifuge) [15]. Physical properties and composition of two OMW samples were determined and compared. Results are shown in **Table 1**.

Table 1: Characterization of OMW samples.

	Sample A : collected during the olive pressing season ^(a)	Sample B : collected after the olive pressing season ^(b)	Literature
pH ^(c)	4.70	4.85	4.5-5 [16,17]
Conductivity (mS/cm) ^(c)	7.0	7.0	12-42 [18]
wt% H₂O	80.3 %	91.9 %	83-94% [19]
wt% Oil	9.0 %	0.1 %	0.03-10% [16]
wt% Total solids	10.7 %	7.7 %	12% [16]
wt% Total dissolved solids	5.0 %	6.3 %	-
wt% Large sediments	4.4 %	0.3 %	-
wt% Mud	1.3 %	1.4 %	-

(a) November 2015.

(b) February 2016.

(c) Determined on a filtered sample.

First of all, **Table 1** shows that the pH of the two OMW samples is nearly the same while their electrical conductivity is identical. The acidic pH found explains the detrimental effect of OMW on the vegetation through soil acidification. The conductivity recorded was found to be much lower than values reported in the literature for other OMW generated by using the traditional pressing method (7.0 vs 12-42). This can be explained by the low usage of sodium chloride, usually used as a natural preservative, in the particular mill studied here. Next, both of these samples are essentially made of water (80.3-91.9%), the remaining being made of a mixture of dissolved solids (e.g. polyphenols, organic acids, nitrogen compounds, sugars [20,21]), large sediments, mud and oil. One can see that the two samples differ greatly in their content of large sediments (4.4% vs 0.3%); this difference is attributed to the different sampling methods used for sample A and sample B. In the case of sample A the sample was taken indoors from a narrow OMW canal whereas in the case of sample B the sample was taken outdoors from the surface of a large OMW pool. Since large sediments have a density which is greater than water, they concentrate at the bottom of the pool; and this explains why only a few of them were found in sample B. In the case of the mud content, no major difference was observed between the two samples (1.3-1.4%); this result is not surprising since the density of this mud was found to be between the densities of water and oil, thus being at their interface. Consequently, since this mud is found on the surface of the effluents, the sampling methods used in A and B make no difference in this case.

Last but not least, the oil content was found to vary substantially between samples A and B (9.0% vs 0.1%). The low value found in sample B is most likely due to the accelerated chemical, photochemical and biological degradations of triglycerides when left exposed in an outdoor pool over a prolonged period of time. In conclusion, since only sample A was found to contain an appreciable amount of oil (9.0%), its oil was isolated and subsequently used for biodiesel production.

3.1.3 Oil extraction from waste coffee grounds

The extraction of coffee oil from waste coffee grounds was first optimized before investigating its potential for biodiesel production. Therefore, parameters such as water content, solvent, sonication time, temperature and time were all tested in order to identify the most adequate extraction conditions. Results are reported in **Table 2**.

Two solvents, acetone and n-hexane, were compared in their efficiency to extract coffee oil from coffee grounds (**entries 1-2**). Hexane was found to be able to extract more coffee oil than acetone, by more than 17%; therefore it was selected as the solvent of choice in the following stages of the optimization. The next parameter to be tested was the reaction temperature. **Entries 2-3** show that increasing the temperature from 60°C to 70°C causes a dramatic increase in the extraction yield (+68%). The effect of the sonication was assessed in **entries 3-4** and **entries 6, 9**. Performing the extraction without the use of sonication as a preliminary step causes a yield loss from

14.8 to 10.5 g/100g of coffee, i.e. a loss of 29%; this illustrates the importance of employing sonication as a means to promote and accelerate the diffusion of coffee oil into the solvent.

Table 2: Optimization of the coffee oil extraction procedure by using unused coffee grounds and waste coffee grounds.

Entry	Coffee used	Solvent ^(a)	Sonication time (min)	Temp. (°C)	Extraction time (min)	Amount of oil extracted (g/100g coffee)
1	Unused coffee grounds ^(b)	Acetone	5	60	160	7.5
2		Hexane	5	60	160	8.8
3		Hexane	5	70	30	14.8
4		Hexane	0	70	30	10.5
5	Waste coffee grounds, wet ^{(b)(c)}	Hexane	5	70	30	4.4 ^(d)
6	Waste coffee grounds, dry ^(b)	Hexane	10	70	30	10.9 ^(e)
7		Hexane	10	70	60	7.5 ^(f)
8		Hexane	10	70	90	7.9 ^(f)
9	Waste coffee grounds, dry ^{(g)(h)}	Hexane	0	70	30	10.3

- (a) Amount: 5 mL/g coffee.
 (b) Supplied by a local supermarket. Type: Arabica.
 (c) Water content : 64 wt%.
 (d) Calculated on a dry weight basis.
 (e) Drying method: 100°C, 4h.
 (f) Drying method: 100°C, 24h.
 (g) Drying method: 150°C, 2h.
 (h) Supplied by a local café. Water content : 63 wt%.

The presence of a large amount of water in coffee grounds was found to be detrimental to the extraction as shown in **entry 5**. This observation can be explained by the reduction of solvation of the non-polar solute by the non-polar solvent; reduction presumably caused by the hindrance of the highly polar water molecules. Consequently under optimized conditions waste coffee grounds should be dried prior to use. Effect of the coffee grounds drying conditions was also tested in **entries 6-7**. When prolonging the drying time from 4h to 24h, the yield dropped from 10.9% to 7.5%, thus indicating that the best drying conditions should be not be too harsh since it could result in a partial vaporisation of the oil. **Entries 7-8** tested the effect of the extraction time. As expected, when increasing the extraction time from 60 to 90 min, a slight increase of the yield was equally observed (+5%).

3.2 Conversion of feedstocks into biodiesel

3.2.1 Biodiesel from waste olive oil

Two different catalysts were tested in the conversion of waste olive oil into biodiesel: potassium hydroxide, KOH, and sodium methoxide, MeONa. Results are reported in **Table 3**.

Table 3: Conversion of olive oil into biodiesel.

Entry	Catalyst	MeOH	T (°C)	Time	Yield (%)
1	KOH, 2.5 wt%	6 equ.	60	1h	47.0
2	MeONa, 2.5 wt%	6 equ.	60	1h	71.0

The difference observed in the yields obtained between KOH and MeONa (47% vs 71%) can be explained first by the poor solubility of KOH in methanol, even when vigorous stirring and heat are applied. Secondly, the active catalyst formed when KOH is used is actually MeOK which results from the reaction of KOH and MeOH to form MeOK and H₂O. The water formed is detrimental to the reaction since it hydrolyzes triglycerides by converting them to free fatty acids and soaps. This side reaction inevitably causes a yield loss, as shown in **Table 3**. On the other hand, the advantage of using a commercial solution of MeONa is that it is perfectly miscible with methanol and water-free. This is because this catalyst is prepared commercially by reacting excess MeOH with sodium metal to produce water-free MeONa and hydrogen gas.

3.2.2 Biodiesel from waste animal fat

Attempts to convert chicken fat into biodiesel were made. Results are reported in **Table 4**.

Table 4: Conversion of chicken fat into biodiesel.

Entry	Type of fat	Catalyst	MeOH	T (°C)	Time	Yield (%)
1	Chicken, refined, not dry ^(a)	MeONa, 2.34 wt%	6 equ.	60	1h	73.0
2	Chicken, refined, dry ^(a)	MeONa, 2.34 wt%	6 equ.	60	1h	86.0
3		1) KOH, 9.93 wt% (1h) 2) MeONa, 2.34 wt% (1h)	6 equ.	60	2h	<10 ^(b)

(a) FFA= 0.57%.

(b) Estimated.

Chicken fat biodiesel was successfully made with a yield of 86.0% (**entry 2**). This result is in line with results reported by Bhatti *et al.* [22]. Adequate reaction conditions to reach this good yield are to use a chicken fat that is refined and dry, MeONa as a catalyst and a reaction time of one hour. As expected, it was found that the presence of water in the reaction medium, even in trace amounts, was detrimental to its success (**entry 1**); a fact that is translated in a yield loss by 15%. Interestingly, when the reaction is performed in a two-step sequence (**entry 3**), by employing KOH in the first step followed by MeONa in the second one, the reaction affords a poor yield. This finding is most likely attributed to the high catalyst loading of KOH used here (9.93%) which acts a factor that enables the saponification reaction to prevail over the transesterification reaction.

3.2.3 Biodiesel from waste coffee grounds

Conversion of coffee oil into biodiesel was carried out with two different catalysts. Results are shown in **Table 5**.

Table 5: Conversion of coffee oil into biodiesel.

Entry	Catalyst	MeOH	T (°C)	Time	Yield (%)
1	KOH, 8.6 wt%	18 equ.	60	1h	< 10
2	MeONa, 2.5 wt%	30 equ.	60	1h	58.0

The best result was obtained with MeONa which afforded a reaction yield of 58.0%. This result is comparable with results reported by Caetano *et al.* [23]. The latter attributed this low yield to an incomplete reaction. The author based this conclusion on a moderate methyl ester content of 69.3%. However, it should be noted that coffee oil is not exclusively made of triglycerides; it is rather made of a complex mixture of compounds in which triglycerides account for only 75% [24,25]. Consequently, unless a laborious isolation of these triglycerides is

performed, the conversion of coffee oil into methyl esters cannot be quantitative. In this regard, separation techniques such as gel permeation chromatography [26] and use of a florisil column [27] have been suggested in the literature.

3.2.4 Physical characterization

Biodiesel samples made from the different feedstocks employed were characterized by their FFA content, density, Gross Calorific value and TLC profile. Results are shown in **Table 6**.

Table 6: Characterization of oil, fat, biodiesel and diesel samples.

Feedstock / Fuel	FFA (%)	Density at 15°C (kg/m ³)	Gross Calorific Value (kJ/g)	TLC profile ^(a)
Olive oil	0.67	882	31.97	<i>Very good. Mostly composed of triglycerides</i>
Chicken fat	0.57	901	40.70	
Coffee oil	2.01	842	39.62	<i>Acceptable. Mainly composed of triglycerides</i>
Olive oil biodiesel	0.45	860	36.66	<i>Very good. Mostly composed of fatty acid methyl esters</i>
Chicken fat biodiesel	0.36	868	38.02	
Coffee oil biodiesel	0.23	832	38.78	
EN 14214 limits for biodiesel	≤ 1 %	860-900	-	-
Diesel ^(b)	-	841	44.77	-

(a) **Qualitative test. TLC: Thin Layer Chromatography.**

(b) **Ultra-Low Sulfur Diesel.**

All the biodiesel samples were found to have FFA contents well below the limit set by the European specification for biodiesel EN14214 (1% max.). Concerning the densities, olive oil biodiesel and chicken fat biodiesel have densities which comply with the specification; however the density of the coffee oil was found to be lower than the specification. It should be noted that as expected the densities of the biodiesel samples determined are always lower than the oil or fat used as a starting material. Gross Calorific Values of all samples were found to be relatively high and suitable for usage in direct combustion. Finally, diesel was also characterized for comparison; its density was found to be lower than biodiesel and feedstock samples. The Gross Calorific Values of biodiesel samples were measured to be lower than diesel's by 15-22%, a result which is higher than the typical 8-11% commonly reported in the literature [28].

Conclusions

This work investigated the potential of unconventional inexpensive feedstocks for biodiesel production, namely olive oil, chicken fat and coffee oil in the form of wastes. Yields of their extraction and conversion into methyl esters were found to be 9.0%/71%, 75.2%/86% and 10.9%/56% for olive oil, chicken fat and coffee oil respectively. Physical characterization of the reaction products indicated that biodiesel samples meet specifications with the exception of coffee oil biodiesel. Concerning the economic viability of the overall biodiesel production process, the attractiveness of the abovementioned feedstocks is in the present case offset by the experimental catalyst loadings (2.34-9.93 wt%) and alcohol molar ratios (6-30 equ.) employed. Preliminary work presented here shall therefore serve as sound grounds for further optimization and development to ensure a greater profitability.

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