

Quality Improvement of Produced Biodiesel and Glycerol from Jatropha oil Transesterification

S.I.Hawash, N.K.Attia, E.A.Abdel Kader, and G.EIDiwani

Abstract—In the production of biodiesel from vegetable oils, separation and purification of biodiesel and glycerol as a by-product are critical processes. Conventional methods used for this separation are gravitational settling, decantation and filtration. Biodiesel and glycerol were produced through transesterification of jatropha curcas oil (JCO) using; KOH as a liquid base catalyst and CaO as a solid super base catalyst respectively with methanol. Reducing free fatty acids for (JCO) by esterification was studied. Biodiesel purification is performed by washing using water and acids. Fuel properties of produced fatty acids methyl esters (biodiesel) including; density, viscosity, flash point, cetane number, acid value and iodine value were qualified. The results showed that; the produced biodiesel can safely be used as an alternative diesel fuel. The use of solid base catalyst (CaO) showed a great improvement in produced glycerol purity up to 99.46%. A comparison between homogeneous and heterogeneous reaction conditions and products' purity are presented.

Key words— Biodiesel, Jatropha curcas, homogeneous, Vegetable oils pretreatment, Glycerol separation, Decalcification, Glycerol purification.

1 INTRODUCTION

Alkyl esters of long chain fatty acid are called biodiesel. Biodiesel is obtained by transesterification of the triglycerides found in vegetable oils and animals fats with an excess of a primary alcohol (most commonly methanol) in the presence of homogeneous or heterogeneous catalyst [1,2]. Homogeneous catalytic systems have many drawbacks such as removal of these catalysts to purify produced biodiesel and glycerol (as a by-product) which produce a considerable amount of waste water. Transesterification using environmentally benign solid catalysts is a promising route to overcome this problem [3]. Heterogeneous catalysts could be easily separated from the reaction mixture by filtration and then reused. For developing biodiesel production much interest has been focused on solid base catalysts for transesterification of vegetable oils with methanol [4-5]. At the laboratory scale, different heterogeneous catalysts have been used, and the amount of base waste water of purification is decreased leading to downsizing the process equipment. Therefore, the environmental impact has been reduced as well as the process cost [6-7]. Among these heterogeneous base catalysts is calcium oxide, which is one of the important heterogeneous catalysts as it has high basicity, low solubility, low price and is easier to handle [8].

CaO as a catalyst; must be treated with ammonium carbonate solution and calcinated at high temperature, to obtain high conversion of Jatropha curcas oil to biodiesel [9].

Residues and impurities left in the crude biodiesel after the reaction are dangerous to any combustion system and must be removed. Purification of biodiesel from its chemical by products downstream of the esterification and transesterification reactions was studied [10-11].

Many biodiesel purification techniques exist, including methods to clean up feedstock's crude biodiesel, and most recently to polish biodiesel for improved cold temperature performance [12-13]. It is preferable to remove potentially problematic materials from the feedstock prior to process this feedstock into biodiesel [14].

High-purity glycerol is an ingredient or processing aid for healthcare products, fuel additives, lubricants, personal care products, cosmetics and food [15-16]. Researchers have studied several purification steps that can produce high-purity glycerol. Various new techniques for purifying glycerol promise better quality and lower cost and technologies are required [17].

This work aims to produce biodiesel and glycerol; as a by-product from JCO by both homogeneous and heterogeneous transesterification reactions. Then make a comparison between the production and purification for both biodiesel and glycerol produced using homogeneous and heterogeneous transesterifications.

2 MATERIALS AND METHODS

2.1 Materials

Jatropha curcas oil (JCO) extracted at the National Research Centre, Egypt was used for the production of biodiesel for both homogeneous and heterogeneous transesterification. Methanol of 99.8% analytical reagent, El-Nasr, Adwic, Egypt was used for transesterification. Potassium

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hydroxide purified pellets of 95% minimum assay was used as the catalyst for homogeneous transesterification. Calcium oxide (Extra pure) obtained from Oxford Laboratory Reagent; India was used for heterogeneous transesterification. Purified ammonium, citric acid not less than 99%, H₂SO₄Analar (BDH) and phosphoric acid 85% were also used.

2.2 Methods

2.2.1 Jatrophacurcas oil characteristics

It's important to note that many transesterification processes were investigated to produce biodiesel from JCO. The components that support combustion in the oil are the basis in biodiesel which have different properties that can be characterized by the number of hydrogen and carbon atoms bonded together. The physical and chemical properties of JCO and fatty acids composition are summarized in Tables 1 and 2 respectively. The properties of the oil will be a mixture of the properties of fatty acids it contains and the biodiesel will also exhibit a mixture of these properties [18].

TABLE (1) PHYSICAL AND CHEMICAL CHARACTERISTICS OF JATROPHA CURCAS OIL

Parameter	Value
Acid value (mg KOH/g sample)	5.4-6
Saponification value (mg KOH/g oil)	189.7
Kinematic viscosity at 30°C (mm ² /sec)	53.3
Density (g/cm ³)	0.91
Iodine number (gI ₂ /100g sample)	105
Unsaponified (% weight)	0.7

TABLE (2) FATTY ACID COMPOSITION OF USED JCO

Fatty acid	Systemic name	Composition (%wt.)
Palmitic (16 : 0)	Hexadecanoic acid	18 .04
Stearic (18 : 0)	Octadecanoic acid	6.08
Oleic (18 : 1)	Cis -9- octadenoic acid	28 .18
Linoleic (18 : 2)	Cis-9-cis12octadenolic acid	47.70

2.2.2 Average molecular weight of jatropa oil.

Average molecular weight of JCO can be calculated according to two procedures. In the first one, the oil's molecular weight (MM_{oil}) is calculated using the following equation:

$$MM_{oil} = [3MM_{FA} + MM_{glycerol}] - 3MM_{OH,H}$$

where, MM_{FA}, is calculated from the percentage and molecular weight of fatty acids composition.

MM_{glycerol} and MM_{OH, H} represent the molecular masses of glycerol and OH group and a hydrogen atom, respectively [19].

The second method for molecular weight determination is calculated from acid value and saponification value by the following equation [9].

$$M = 56.1 \times 1000 \times 3 / SV - AV$$

where, M is the molecular weight (g), SV is Saponification value (mg KOH/ g oil), and AV is acid value (mg KOH/ g oil) respectively.

2.2.3 Free fatty acid esterification (pretreatment)

Free fatty acids (FFAs) cause two major problems in jatropa oil transesterification. First is soap formation (fatty acid salt) which makes the finished product more difficult in use Eq. (1). Second is water formation which will retard the transesterification reaction and decomposes the formed methyl esters to fatty acids and glycerol Eq. (2).



When FFA is less than 3% those problems are negligible by using single step (transesterification). Two methods are used to treat oil's high FFAs according to their existence proportion.

Oils contain FFAs above 4%, these FFAs are converted to soaps using NaOH and NaCl then remove the formed soaps above and below the oil. High FFAs content was neutralized with NaOH (0.5N) and heated to 70°C (in a water bath for one hour with constant stirring (≈ 500 rpm). NaCl (10% by wt.) was added to help settling of the soap formed, after one hour it is transferred to a separating funnel and allowed to settle out. After soap removal, oil is washed with hot water three times (1:1 by volume) then oil is dried at 110°C till all water was removed. The dried oil was analyzed for FFA content determination.

Oils with FFAs less than 4%; in this case, the most common treatment method is esterification by using H₂SO₄ (1.525% by volume) and methanol then heated to 60°C for 90 minutes. The acid value of the product separated at the bottom of a separating funnel; is measured. The product was catalyzed by KOH with methanol to produce biodiesel in 24 min. reaction time. The main disadvantages of this method are the long reaction time (90 minutes) and dark color regenerated after esterification.

2.2.4 Transesterification processes

Transesterification of triglyceride is affected to reduce viscosity of oil and produce fatty acid methyl esters and glycerol. Transesterification was carried out using both homogeneous and heterogeneous catalyst with methanol. The homogeneous reaction was carried out at 65°C with a 6:1 molar ratio of methanol to oil and 1% of KOH catalyst by weight of JCO [18]. However, the heterogeneous

tranesterification was made using CaO as catalyst (1.5% w/v) with molar ratio 12:1 of methanol to oil at 70 °C [9]. The glycerol layer settles down immediately at the bottom of the separating vessel. Rate of separation is determined by measuring the settled volume with time. After complete separation excess methanol from methyl ester and glycerin is to be evaporated.

2.2.5 Biodiesel purification

In homogeneous transesterification using KOH as catalyst, after separation of glycerol and recovery of excess methanol, biodiesel still has traces of soaps, alkalinity and other impurities that must be removed via a wash process using 1:1 by weight water to biodiesel to produce clean, pure fuel. Biodiesel is washed with acidulated water; then fresh water and permitted to settle for separation from biodiesel and the process is repeated until washing water is neutral [18]. Once all the water is removed, the remaining clean biodiesel is dried and is ready for final quality determination.

While for heterogeneous transesterification using CaO as solid catalyst, super base decalcification of the as-synthesized biodiesel from calcium ions is achieved by washing with water (10:1 by volume). Citric acid was added as complexing agent (mol : mol of Ca⁺⁺: citric acid), the mixture was stirred for 15 minutes at 45°C followed by centrifugation at 3000 rpm for 15 minutes. The upper clean layer obtained is purified biodiesel [20] and the remaining calcium ions in biodiesel were determined by EDTA titration.

The performance of the decalcification process was evaluated by determining the change in concentration of calcium ions in biodiesel before and after decalcification according the following equation:

$$\text{Decalcification efficiency (\%)} = \frac{(\text{Ca}^{++} \text{ in sample} - \text{remained Ca}^{++})}{\text{Ca}^{++} \text{ in sample}} \times 100$$

2.2.6 Purification of produced glycerol

The layer at the bottom of the decanter was contained glycerol, unreacted methanol, soaps and most of the catalyst. Glycerol purification in homogeneous transesterification is achieved by the addition of phosphoric acid [12], after methanol recovery. Phosphoric acid was added to this layer in ratio 1:25 by wt. (i.e. 25 kg of crude glycerol 50% purity, need 1kg of phosphoric acid) to neutralize the catalyst and convert soaps back to free fatty acids. On the other hand, the glycerol produced in heterogeneous transesterification using CaO, has high purity after filtration and excess methanol recovery. Purity of glycerol in both transesterifications was determined using HPLC with 101 column (Shimadzu 7.9mmx 30 cm) and maintained at 40°C. Separation was achieved by pumping water through the column at 1ml/min for 25min. Measurement was performed by measuring changes in the refractive index (RI).

Biodiesel yield was found out by comparing the moles of produced glycerol with the theoretical value; and based on this ratio, percent yield of biodiesel is calculated according to following equation [5].

$$(\%) \text{ biodiesel yield} = \frac{\text{Mol of experimental glycerol}}{\text{Mol of theoretical glycerol}} \times 100\%$$

3 RESULTS AND DISCUSSIONS

3.1 Molecular weight of JCO

Molecular weight of JCO was determined by the two procedures mentioned in experimental part and it is found to be 895 g/mol., in average for both calculations.

3.2 Pretreatment of JCO

Results of pretreatment of JCO for decreasing FFAs content are shown in Table 3. The results show that according to the two methods used, FFAs reduced from 9 % to 0.4 % using NaOH and NaCl and from 3 % to 0.25 % using H₂SO₄ respectively.

TABLE (3) PRETREATMENT RESULTS OF JCO BY ESTERIFICATION

Reagent	FFA% before treatment	Temperature (°C)	Time (min.)	FFA % after treatment
NaOH+NaCl	9	70	60	0.4
H ₂ SO ₄	2.7- 3	60	90	0.25

3.3 Biodiesel processes flow chart

Steps of transesterification processes for homogeneous and heterogeneous reactions are shown in flow chart illustrated in Figure 1. These processes have two different start points, if FFAs content is below 3% the esterification process is not necessary and JCO can go directly to the transesterification processes. The figure shows washing and acidification using phosphoric acid of produced biodiesel and crude glycerol through homogeneous transesterification respectively. Washing and acidification of biodiesel; produced through heterogeneous transesterification is shown in the figure as well as the separation of agglomerated citric acid and calcium ions, in addition to pure glycerol (94.4 %).

3.4 Separation of glycerol from reaction mixture

Rate of separation of glycerol from reaction mixture through homogeneous and heterogeneous transesterification is illustrated in Figure 2. Complete separation of crude glycerol from reaction mixture is achieved in 20 minutes for both transesterification cases; taking in consideration the amount of unreacted methanol to be removed. The crude glycerol in both cases is produced using the same JCO weights. For heterogeneous transesterification separation is achieved after filtration of CaO. Difference in volumes is according to the purity of produced crude glycerol which is 50% in case of homogeneous transesterification while; it is 99.4 % in case of heterogeneous one.

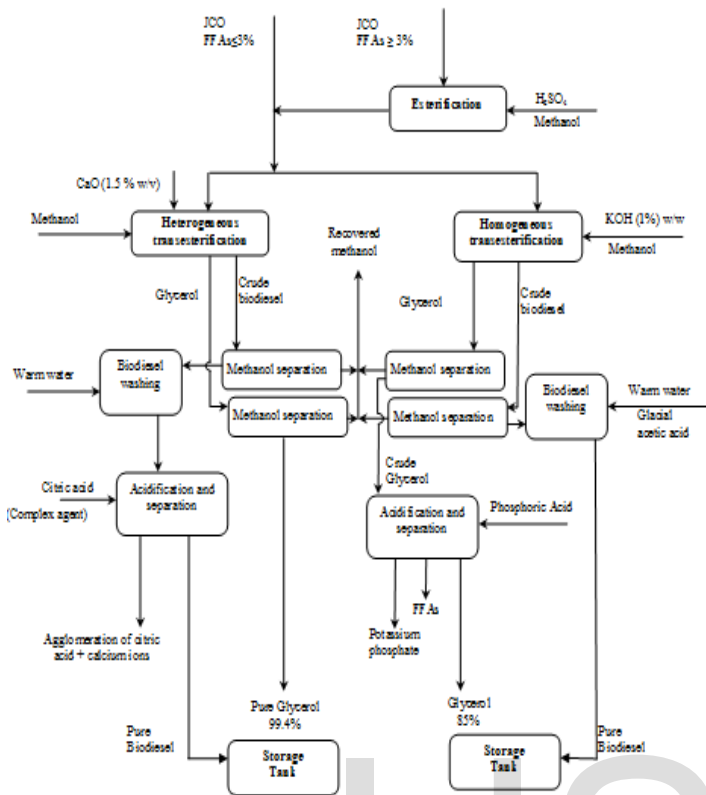


Fig. 1 Comparison between production of biodiesel and glycerol as a byproduct by homogeneous and heterogeneous methods

3.5 Biodiesel properties

The yield of biodiesel reached 96% using KOH in homogeneous transesterification. Washing biodiesel with warm water to get rid of soaps and traces of glycerol and catalyst gave good results concerning biodiesel properties as shown Table 4.

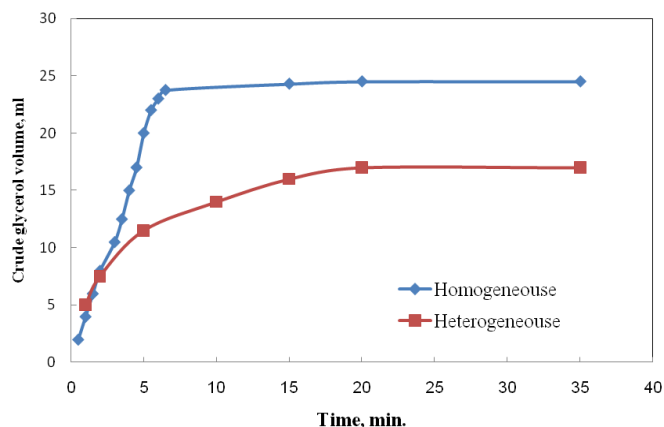


Fig. 2 Comparison between separation rates of produced glycerol from reaction mixtures by homogeneous and heterogeneous transesterification

The decrease in kinematic viscosity to 5.01 mm²/s; is the important fuel property of the transesterified JCO; this

indicates that the flow ability of raw jatropha oil has been increased to a significant extent which indicates complete burning without any ignition delay. Acid value decreased significantly after transesterification reaction and within standard limit (max. 0.8 ASTM). Also, the density of jatropha biodiesel was reduced when compared with density of raw jatropha oil (0.91).

TABLE (4) PROPERTIES OF PRODUCED JATROPHA BIODIESEL COMPARED TO PETROLEUM DIESEL

Property	Jatropha biodiesel	Petroleum diesel
Kinematic viscosity at 20 °C (mm ² /s)	5.01	3-5
Density (g/cm ³)	0.87	0.075 - 0.84
Flash point °C	135	68
Pour point °C	-9	-20
Cloud point °C	6	-15
Cetane number	49	40 - 46
Ash content (%)	0.004	0.008 - 0.010
Sulfur content (%)	0.06	0.35 - 0.55
Carbon residue (%)	Nil	0.17
Water content (%)	0.04	0.02 - 0.05
Calorific value (MJ/kg)	40.56	42
Acid value (mg KOH/g)	0.26	--
(gm I/ Iodine value 100gm)	23 - 29	--

3.6 Efficiency of decalcification process

Using CaO as solid base catalyst, results of decalcification with water and citric acid are illustrated in Table 5. Washing with water only is the less effective removal of calcium ions as 48%. Decalcifying using citric acid separately, increased the efficiency to 92%. The performance of adding citric acid with water as complexing agent raised the efficiency of decalcification process up to 96%. Citric acid does not disperse easily in biodiesel due to agglomeration of citric acid with Ca⁺⁺, then it can be removed easily from biodiesel and also it does not led to emulsion after infusion with water.

3.7 Glycerol purification

Glycerol produced from homogeneous transesterification is 50% purity. Addition of phosphoric acid neutralizes the catalyst and converts soaps back to FFA. Three distinct layers were separated with FFA on the top, glycerol in the middle and sodium phosphate at the bottom. The purified glycerol was 85% purity according to the HPLC analysis. Glycerol produced through heterogeneous transesterification is a colorless transparent liquid with density of 1.263kg/L and its purity is 99.4% which was determined using the HPLC technique.

3.8 Comparison between optimum operating conditions for biodiesel production

Biodiesel was prepared through homogeneous and heterogeneous transesterification using optimum operating condition for both cases. Table 6 shows differences in

optimum operating conditions and products purities between homogeneous and heterogeneous transesterification.

TABLE (5) EFFICIENCY OF DECALCIFICATION PROCESS

Washing conditions	Ca ²⁺ in biodiesel (ppm)		Ca ²⁺ removal efficiency %
	Before treatment	After treatment	
Water (washing)	192	101	48 %
Citric acid (decalcifying agent)	101	8	92%
Water + Citric acid	192	8	96%

4 CONCLUSION

Biodiesel as well as glycerol (which produced as a transesterification byproduct) were produced using both homogeneous and heterogeneous reactions. Biodiesel was purified using acidified and fresh water in case of homogeneous transesterification. Citric acid proved to be the best decalcifying agent for purification of biodiesel from calcium ions since it does not disperse in biodiesel and prevents emulsion formation after infusing with water.

TABLE (6) COMPARISON OF HOMOGENEOUS AND HETEROGENEOUS TRANSESTERIFICATION CONDITIONS

Parameter	Transesterification	
	Homogeneous	Heterogeneous
Catalyst used	Potassium hydroxide	Activated calcium oxide
Catalyst dose	1% (w/w)	1.5% (w/v)
Catalyst reuse	Not possible	Possible for 3 times
Catalyst handling	Not easier to handle	Easier to handle
Molar ratio (methanol : oil)	6 : 1	12 : 1
Reaction time (hr)	1 hr.	1 hr.
Reaction temperature (°C)	65	70
Filtration	---	Filtrate CaO
Settling and separation time	20 minutes	20 minutes
Biodiesel yield (%)	97%	96%
Purification of biodiesel	Washing with water (v / v) then acidification using phosphoric acid	Washing with water 10 : 1 (v / v) and decalcification using citric acid
Crude glycerol purity (%)	50	99.46
Glycerol purity after treatment (%)	85	---

Specifications of the produced biodiesel by both homogeneous and heterogeneous transesterification of jatropha oil are fitting with that required for use as petroleum diesel alternative. Glycerol produced through heterogeneous transesterification is 94.4 % purity which doesn't need further purification. On the other hand, glycerol produced through homogeneous transesterification can reach 85 % purity after acidulation process. A comparison between homogeneous and heterogeneous reaction conditions and products' purity are discussed.

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