Biodiesel Production from Olive Cake Oil

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Abstract

Olive cake is thought to be a green source of oil that can be used for biodiesel manufacturing. Jordan produces a large amount of olive cake as a by-product from olive oil production process. The objective of this paper is to investigate the potential of using Jordanian olive cake as a source of oil for biodiesel manufacturing.

In this work, olive cake oil is extracted from olive cake samples, collected from modern olive pressing plants, using hexane as an extraction solvent. The oil is converted to biodiesel (methyl ester) in two-steps process: acid-catalyzed esterification followed by alkalicatalyzed transesterification. It is found that the oil content in olive cake represents approximately 13.75 % by mass. The results of the two step transesterification process shows that maximum yield is 74.29 and obtained at 30%v/v of methanol/oil ratio, 65^{o}C temperature with 1.0 % by weight KOH catalyst. The produced biodiesel contributes only to about 0.057% of the total Primary energy consumption.

Keywords: Olive Cake, Olive Cake Oil, Biomass, Biodiesel, Transesterification, Jordan

Contents

1 Introduction

The needs for energy has continuously increased due to the human activities, development (industrialization) and population increase [1-5]. Traditional world's energy sources (oil and coal) are limited and will not last very long. Besides, the extensive fossil fuel utilization causes serious pollution problems throughout the world and results in many undesirable phenomena represented by climate change, global warming and acid rain. This increased research and development studies for new alternative energy sources.

Renewable energy sources such as solar, wind, geothermal, hydropower and biomass energy can be a supplementary or alternative resource for energy production. Moreover, these sources have limited local and much lower impacts on environment than conventional energy sources.

However, biofuels is now believed to be as a major factor for the explosion in grains and oilseeds prices worldwide. Biofuel production programs have several social and environmental impacts and affected food markets through diverting grain away from food for fuel, encouraging farmers to remove land from agriculture in order to grow crops for bio-fuel production and increasing financial speculation in grains and pushing up food prices [6]. The World Bank secret report confirms that biofuels have forced "food prices up by 75% in the period between 2002 and February 2008 [6]. The incentive to biofuel production is expected to rise with increasing energy and crude oil prices and thus food prices.

Therefore, utilizing biomass residues for biodiesel or bioethanol production will reduce the contribution of biofuels production to food price. Biomass energy is one of the defined as the biological material such as agricultural residues, animal wastes, forestry and wood processing residues, municipal and industrial wastes. Biomass is seen as one of the few renewable indigenous, widely dispersed energy sources and one of the most promising, renewable energy sources. It is, among the renewable forms of energy, the major source of the primary energy supply [7].

Biomass can be converted, at lower cost and with higher conversion efficiency, to other usable forms of energy like biofuels [8]. Upon conversion, biomass emits approximately the same amount of carbon as is taken up during photosynthesis in the course of plant growth. Therefore, the use of biomass does not contribute to a buildup of CO_2 in the atmosphere and hence the energy obtained from biomass can be considered as "CO_2 – neutral".

Jordan is an energy importing country that depends on energy and oil producing countries to meet its energy demands. The imported energy cost averaged more than 10% of the gross national product (million JD 1916 for the year 2009 [9]) and consumed 40–45% of the foreign exchange earned by exports of all Jordanian commodities in the last three decades [10].

Figure 1 depicted the local primary energy consumption and the contribution of the produced energy to the overall energy consumption (%) during the period 2005-2009. In 2009, the overall demand for the primary energy was nearly 7739 thousands TOE (Tone Oil Equivalent) with a growth rate of 5.5% in comparison with that of the year 2008. The contribution of the locally produced crude oil and natural gas to the overall energy consumption is very small. It is only 3.2 % for the year 2008 and 3.3 % for the year 2009. Generally, it can be said that Jordan's energy consumption has been increasing year by year.

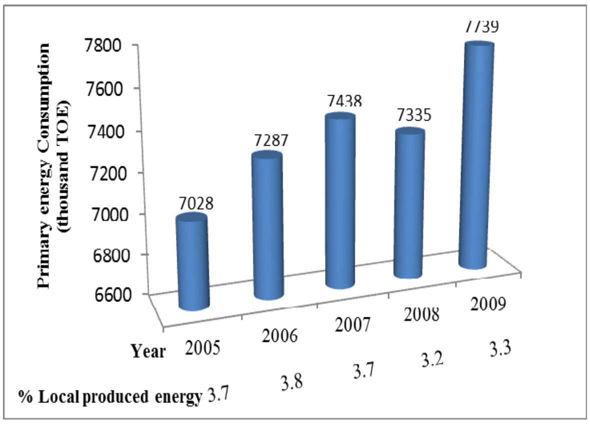

Figure 1: Primary energy consumption and the contribution of the produced energy to the overall Energy consumption (%) during the period 2005-2009 (source data [9])

For long-term security, it is necessary to move towards the use of renewable energy sources and develop new technologies to increase the energy production efficiency. Successful progress in this field helps sustainable development through economic growth and pollution control. Moreover, the diversification of energy sources and increasing the renewable energy share to the energy mix helps sustainable development through economic growth, social security and pollution control.

The government efforts in this field targeted to increase the new and renewable energy share to the energy mix to reach 7% by 2015 and 10% by 2020 [9]. Most of these efforts concentrated on utilizing wind and solar resources. Biomass received only minor attention in spite of the fact that when low cost biomass residues are used, the cost of electricity is often competitive with fossil fuel-based power generation [7].

Biomass residues are relatively cheap energy resource to provide the initial feedstock in bio-energy industry. This would mean the elimination of a waste stream and gives biofuel producer a chance to reduce costs. This is because more than 60–85% of the biofuel fuel cost comes from the feedstock [11].

2 Olive Cake As a biomass Source in Jordan

In Jordan, there is no real investment or consideration for biomass in the energy sector. In a very limited manner, conventional biomass in the form of wood and animal waste is used to produce energy by direct combustion. However, olive cake is in the discussion of being a renewable alternative biomass energy source to be utilized in Jordan.

In Jordan, the olive tree is one main natural resource with an estimated 17 million olive trees farmed in about 107,000 hectares (about 36% of the total cultivated area) with a growth rate of 1 million olive trees per year [12]. The produced olive fruit represent about one third of the total amount of fruit produced [13]. Pressing olive fruits for oil extraction produces annually a large amount olive cake, the solid by-product of olive fruit after pressing for extraction of oil. It comprises a significant fraction, 13-30%, of the olive fruit [14, 15].

The amount of dried olive cake produced as a by-product in olive extraction plants in Jordan in the period from 2005 to 2009 were shown in Figure 2. This amount of olive cake makes it the single most important agricultural byproduct in the country. However, accumulation of such large amounts of olive cake in its raw form imposes a disposal and pollution burden causes serious environmental concerns [16, 17].

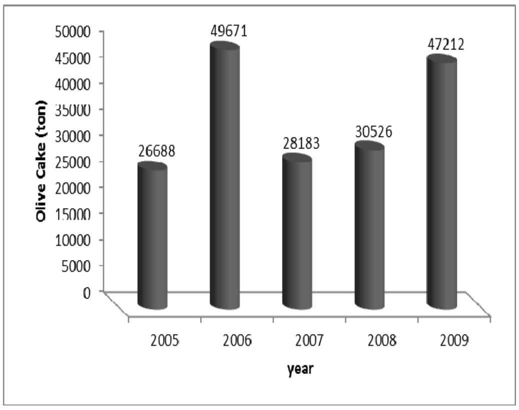

Figure 2: Dried olive cake produced from olive seeds in olive extraction plants in Jordan [13].

The olive cake contains a small oil fraction (10 to 15 %). This amount of oil is extracted and consumed only in soap industry. Olive cake rest (remaining solid after oil extraction) has a little economic value and most of them are dumped in the environment, where they may be contaminated by fungi or release toxic compounds [15]. On the other hand, some are used to feed animals and combusted, without any control, in boilers or used to heat homes. At the end of this un-controlled combustion process, CO, particulate matters and hydrocarbons are formed at considerable amounts in the flue gas.

Therefore, utilization of this source for energy production through a systematic method of raw material management could be significant in terms of energy cost savings and in terms of pollution control. Moreover, utilizing olive cake as solid fuel or as a source for biodiesel production will not affect the supply of food and hence food prices.

3 Previous Work

Several research is available about how to utilize olive cake as energy source. Most of these research focus on the combustion of olive cake as solid fuel using different combustion technologies such as bubbling fluidized bed combustor [18-21] and circulating fluidized bed [22]. In these studies the hydrodynamics and combustion processes in a bench-scale fluidized-bed combustor with OC as a fuel was investigated. The combustion efficiency was found to be ranged from 83 to 95% and increased with air-flow rate, the particle size used and decreases with the bed temperature, fluidization velocity, and the feed rate.

However, only little work has been conducted to investigate the possibility of manufacturing biodiesel from the oil extracted from olive cake (olive cake oil). Yasin [27] used immobilized lipase to produce biodiesel with pomace oil and a three-step addition of methanol. The maximum biodiesel yield was 93% at 25°C in 24 h reaction. The stability test showed that a small enzyme deactivation occurred after being used repeatedly for 10 consecutive batches. Sinem et al., [28] used a single step esterification reaction, with different catalysis, and found that the maximum biodiesel yield was 80% obtained at 30% of methanol/oil ratio, 60°C temperature for 60 min with NaOH catalyst. An organic based manganese additive was used to improve the biodiesel properties and the performance in a direct injection diesel engine.

Although lipases are generally effective catalysts and are non-polluting [29], they are expensive [30-33] and can be denatured in the presence of FFAs and short chain alcohols (such as methanol and ethanol). They are also subjected to significant negative effect by the formation of glycerol [30-32].

The use of alkaline catalysts for transesterification of oil with FFA content more than 1 % (corresponds to an acid value of 2 mg KOH/g) is problematic due to the formation of unwanted soap which inhibits separation of the alkyl esters and glycerol, reduce the ester conversion rate and ultimately lower the yield [34-40]

However, other research showed that the FFA limit for alkaline–catalyzed transesterification should be 1 mg KOH/g (0.5% FFA) [41-43]. The work presented here is based on the initial assumption that the acid catalysis must decrease the acid value of olive cake oil to less than 1 mg KOH/g (0.5% FFA).

On the other hand, acid catalysis is more efficient when the amount of free fatty acids in the oil exceeds 1% [36, 44–46]. However, the reaction requires a longer reaction time (about 4 the times needed by alkalicatalyzed reaction [38]) and run at higher reaction temperature. Moreover, the water formation during the acid–catalyzed reaction of the FFAs with the methanol can stop the esterification reaction of FFAs before it could be completed. Also, biodiesel contaminated with water can cause engine corrosion or reaction with glycerides to produce soaps and glycerol. Additionally, acid catalysts are difficult to recycle and operate at high temperatures, and give rise to serious environmental and corrosion problems [38, 47].

The objective of this work was to apply two-step trans-esterification approach for converting olive cake oil to methyl ester (biodiesel).

4 Experimental Section

4.1 Samples collection

Fifty raw olive cake samples were obtained as a by-product from 30 modern olive extraction plants located in different areas in Jordan: In Irbid, Ajloun and Jerash in the north and Madaba in the south. The olive cake material was collected fresh during the olive production months (November and December/2010). The samples were then irregularly numbered.

4.2 Samples preparation

Initially, the olive cake was not suitable for processing because of its high moisture content, and initial drying was required. An olive cake sample was taken and dried in an oven for 1 h at 105oC. This time and temperature were found to be sufficient for further processing (sufficient to achieve constant weight).

4.3 Oil extraction

About 10g of dried olive cake samples were prepared and placed into a thimble in the Soxhlet extractor fitted to conical flask. 100 ml Hexane is used as an extracting solvent. At the end of the extraction process, when the recycled solvent becomes clear, the extraction solvent is recovered. The oil sample, which was cooled to the room temperature, was then weighed. The amount of oil was determined from the original sample. The amount of oil was determined from the original sample weight and the weights of the extraction cup before and after the extraction, i.e. by directly weighing the extracted oil [48].

$$\%\ oil\ recovered = \frac{(W_2 - W_1)}{W_3} \times 100$$

Where W_1 = weight of the extraction cup

W_2 = weight of the extraction cup + extract

W_3 = weight of the dry olive cake sample

4.4 Acidity and peroxide value of the extracted oil

Acid value and peroxide value of olive cake oil was determined according to IUPAC Standard Methods II.D.1 and II. D.13, respectively [49].

4.5 Biodiesel Production

Olive cake represents a valuable low cost biomass source for biodiesel manufacturing. Such low price raw material is of special interest since it will significantly reduce the production costs of biodiesel. In this way, the price of biodiesel will be in competition with petroleum based diesel [50, 51].

For biodiesel production, two-steps process, acid-catalyzed esterification followed by alkalicatalyzed transesterification was used. The effect of reaction temperature, KOH concentration and methanol ratio on the biodiesel yield was investigated.

4.5.1 Materials and experimental methods

The extracted oil from olive cake was used for biodiesel production. All chemicals used in the experiments such as methanol (99.5%) and sulfuric acid (99% pure) were of analytical grade. Potassium Hydroxide in pellet form was used as a base catalyst for transesterification reaction. And Sodium Bicarbonate particles were used for acid neutralization. The chemicals were obtained all from Merck.

4.5.2 Acid-catalyzed pre-treatment

The pretreatment of olive cake oil was carried out in 250 mL three necked round bottom reactor equipped with magnetic stirrer, a reflux condenser, thermometer and stopper to remove samples. The reactor was placed in water bath, the water bath sets on heating and mixing plate. A known amount of oil cake oil was poured into the reaction flask and heated to 60^{o}C. The methanol was added to the heated oil (40 v%) and stirred for a few minutes. Sulfuric acid was then added to the mixture. Two different H_2SO_4 volumes were used: 1 ml and 5 ml. The mixture was agitated under reflux for 4 hr. After the reaction completed, the mixture was allowed to settle in a 500 ml separation funnel for 3 hr. The bottom layer which contains methanol-water-H_2SO_4 fractions was removed. The upper layer consisted of olive cake oil having lower content of FFA and impurities were purified by washing with hot sodium bicarbonate solution (5% w/v), to neutralize excess H_2SO_4 and reduce the acidity, and allowed to settle for 3 hr for complete phase separation. Again the bottom layer was drained. The acidity of the bottom layer was detected with phenolphthalein indicator. The procedure was repeated until the drained layer becomes basic.

The treated oil was then washed with distilled water and the mixture was allowed to still for 3 hr for complete separation between the two layers. The procedure was repeated until the washing water had a pH value that was similar to that of distilled water. The treated oil was then dried by gentle heating for complete water removal. Finally, the acid value of the oil product was determined.

The pretreatment test was performed at different methanol-oil ratios (20 and 40% v/v) and different catalyst-oil ratios (2, 5 and 10 % v/v)

4.5.3 Alkali-catalyzed transesterification

The transesterification reaction was carried out by using the same experiment setup of pretreatment step. The reactor was initially charged with treated oil (oil with low FFA content) then heated to the required temperature. The potassium hydroxide pellets was dissolve in methanol and the mixture was heated to the oil temperature then fed to the flask. Stirring velocity was kept at 800 rpm. The reaction was timed as soon as the potassium hydroxide – methanol solution was fed to the reactor. The reaction was kept at a desired temperature for 4 hr. After the reaction; the mixture was poured into a separating funnel and allowed to settle for 3 hr. The ester layer was separated by gravity and located in the upper layer. The glycerol, extra methanol and undesired products were in the lower layer and were decanted. The biodiesel layer was washed with distilled water for complete removal of excess methanol and any catalyst traces. The washing step was repeated until the washings were neutral. The ester layer was then dried by gentle heating to obtain the refined biodiesel. The degree of oil conversion and the biodiesel yield were recorded.

The transesterification step was repeated for different reaction temperature, namely 40, 50, 60°C, different methanol ratios (10, 20 and 50 v%) and with different KOH concentrations (1, 1.5 and 2 wt % of the olive oil).

5 Results and discussion

5.1 Acidity and peroxide value

For olive oil extracted from olive cake, the measured acid value as % of oleic acid was 49 mg KOH/g oil. The peroxide value of the oil was measured as 205.36 mEq O_2/kg oil. Such values were higher than those required by Regulation EC/1989/2003 [56] (Acidity < 0.8%; peroxide value <20 mequiv. O_2 kg^{-1}). Thus, such oil is said to be Virgin Lampante Olive Oil and do not fit for human consumption.

5.2 Oil content

The oil content in the samples lies between 11.2 to 15.6 %, on average 13.74 %, on dry matter basis. For the year 2009, the amount of olive cake collected was 47212 ton. This means that the total amount of extracted oil can be as high as 6487 ton/year. However, the peroxide value and acidity of the oil were 205.36 mEq O_2/kg oil and 24.5 % oleic acid, respectively and thus this oil cannot be used as fat source of the diet.

However, olive cake oil might be of interest to be used for biodiesel manufacturing. Such feedstock effectively reduces the manufacturing cost of biodiesel because the feedstock accounts approximately for 70–95% of the total biodiesel production costs [46, 38, 54-59].

5.3 Utilizing olive cake for biodiesel production

For high FFA content oil, an acidic catalyst can be used initially to convert FFA to the esters and to decrease the FFA level to 0.5% then the transesterification of oil can be performed using an alkaline catalyst.

5.3.1 Pre-treatment with acidic catalyst

H_2SO_4 was used to esterify and reduce FFA content of olive cake oil from 24.5% to less than 1% (acid value of 2 mg KOH/g oil).

The pretreatment step was carried with different catalyst concentrations: 2% and 10% v/v of oil, and methanol ratios (20 and 40% v/v). All tests were performed at constant reaction temperature of 60°C. A Summary of the experimental conditions and results were shown in Table 1.

The results (run 1 and 2) indicated that with catalyst concentrations 2% v/v and methanol to oil ratio of 20%, it was possible to reduce the FFA content from 24.5 % (acid value of 49 mg KOH/g oil) to 1.51 %. The FFA content of the treated oil was lower when the methanol to oil ratio was increased to 40 % v/v. Increasing the acid concentration (Run 2, 3 and 4) reduced the FFA content of the oil. In order to reduce the FFA to FFA level to 0.5%, an H_2SO_4 concentration of 10% v/v of oil was required. It represented the lowest ratio which provided acid value of oil less than 1 mg KOH/g oil within the reaction time (4 hr), so it was selected as the optimum catalyst-to-oil ratio.

Table 1: Influence of operating variables on the oil to methyl ester (biodiesel) conversion in acidic catalyst pretreatment of olive cake oil

	Olive Oil		Pretreatment					
Run #	OC oil (g)	Acid Value % FFA	Methanol (v%)	H_2SO_4 (v%)	Time (hr)	Temp. (^oC)	Treated oil (g)	Acid Value % FFA
1	42.753	24.5	20	2	4	60	38.5572	1.51
2	42.504	24.5	40	2	4	60	37.6761	0.93
3	42.441	24.5	40	5	4	60	36.7152	0.78
4	42.884	24.5	40	10	4	60	35.4196	0.52

5.3.1 Alkali-catalyzed transesterification

The pretreated olive cake oil obtained in the pretreatment step, with the reduced acid number, was transesterified with methanol by using potassium hydroxide as the catalyst to convert the triglycerides to methyl esters.

In order to investigate the different operating parameters on the conversion of olive cake oil to biodiesel, the reaction was carried out with different methanol-to-oil ratios (20, 30, 50 % v/v), different catalyst concentration (1, 1.5 and 2 wt %) and reaction temperature (40, 50 and 60^{o}C). In all experiments, the reaction time was set constant (4 hr). The experimental conditions were presented in Table 2 together with the calculated conversion of olive cake oil to biodiesel or methyl esters.

Runs 1, 2 and 3 were performed for treated oil but with different FFA content: 1.51, 0.93 and 0.52 %FFA (acid value of 3.02, 1.86 and 1.04 mg KOH/g oil, respectively). The results indicated that the conversion of oil to biodiesel was higher for oil with the lower acid value. With 0.52 %FFA feedstock, the conversion to methyl ester (49.58 %) was higher than that for the case of 1.51 %FFA by a factor of 1.24. Moreover, it was also observed that those methyl ester layers could be more easily separated from the glycerol-rich phases than the ones produced using the more acidic olive cake oil.

Table 2: Influence of operating variables on the oil to methyl ester (biodiesel) conversion in alkali-

catalyzed transesterification of olive cake oil

	Transesterfication								
Run #	Treated Olive oil (g)	% FFA	Methanol (v%)	KOH (wt%)	Time (hr)	Temp. (^{o}C)	Biodiesel (g)	Unreacted oil (g)	Yield %
1	38.557	1.51	20%	1%	4	60	15.447	10.051	40.063
2	37.676	0.93	20%	1%	4	60	17.212	9.132	45.680
3	35.420	0.52	20%	1%	4	60	17.561	3.7138	49.580
4	39.221	0.63	20%	1.5%	4	50	25.510	2.387	65.040
5	38.257	0.55	20%	1.0%	4	50	19.030	3.138	49.740
6	33.144	0.58	20%	1.5%	4	40	18.039	2.6	54.420
7	36.456	0.56	50%	1.5%	4	50	**Failed due to emulsion formation**		
8	32.775	0.54	20 %	2%	4	50	15.280	1.170	46.620
9	39.04	0.55	30 %	1.5 %	4	50	17.39	1.082	44.54
10	37.58	0.53	10 %	1.5 %	4	50	17.87	2.131	47.54
11	38.16	0.57	20 %	1.5 %	4	60	20.34	2.814	53.31
12	37.851	0.52	50%	1.5%	4	60	**Failed due to emulsion formation**		

The methanol/oil ratio is one of the most important factors affecting the yield of biodiesel. The transesterification is usually carried out with an extra amount of methanol in order to shift the equilibrium to the direction of methyl ester formation.

The methanol/oil ratio is one of the most important factors affecting the yield of biodiesel. The transesterification is usually carried out with an extra amount of methanol in order to shift the equilibrium to the direction of methyl ester formation.

The effect of methanol to oil ratio was investigated in runs 4, 7, 9 and 10. Increasing the ratio from 10 % in run 10 to 20 % in run 4 resulted in an increase in the degree of oil conversion from 47.54% to 65.04%. When the ratio was increased further to 30 % (run 9) and 50 % (run 7), the degree of conversion reduced to 44.54 in run 8 and an emulsion formed (run 9). In the lateral, it was not possible to make any purification and separation for the mixture and thus the test was assumed to be failed. Similar result was found also when the esterification reaction carried out at 60^{o}C (run 12)

The reduction in the conversion and the formation of emulsion with increasing the methanol/oil ratio could be because excess methanol could drive the combination of ester product and glycerol into mon-glycerides [60]. It could also increase the solubility of glycerol which remained in the ester phase and hence leading to foam formation and interfere the separation of ester product and by-products [61]. To investigate the effect of the catalyst concentration on the degree of olive cake oil conversion, the reaction was carried out at three different catalyst concentrations (1, 1.5 and 2 wt/v % of oil: runs 5, 4 and 8, respectively). For a catalyst concentration of 1.5 wt % of oil (run 4), the conversion to methyl ester content was achieved 65.04% within 4 hr. At 2 wt% of oil (run 8), however, the conversion (46.620) was lower than those of 1.0 wt% (49.740 achieved in run 5). This behavior was similar to that reported by Encinar Jose et al., [62] and Meher et al., [63]. This could be due to the formation of soap during transesterification in the presence of high concentration of KOH and resulted in the increasing of viscosity of the reactants [10] and hence hindered the separation of the methyl ester phase during the washing step. Thus, the lower conversions were obtained at high catalyst concentration. Therefore, 1.5 wt% was selected as the optimum catalyst concentration.

The temperature effects on the alkali-catalyzed transesterification of pretreated olive cake oil was investigated at three different reaction temperatures (40, 50, and 60^{o}C; runs 6, 4, 11, respectively). Increasing the temperatures from 40^{o}C to 50^{o}C, the conversion increased by a factor of 1.2. However, if the temperature increased up to 60^{o}C, there was a slight reduction in the conversion (by the same factor, i.e. 1.2). This was due to the fact that high temperature enhances both transesterification and saponification reactions.

The conditions in run 5 were considered as the optimum conditions. Hence, the maximum yield thus estimated was 74.29 %. For 6487 ton/year olive cake oil produced, the calculate amount of biodiesel that can be produced was 4219.1 ton/yr biodiesel (corresponds to 4. 872 M. L/yr). This contribution of this to the total imported conventional diesel will be only 1.02 % (corresponds to 0.26% of the total consumed diesel and 0.055% of the total Primary energy consumption).

6 Conclusion

Olive cake is produced in significant amount in Jordan (about 47212 ton for the year 2009) as by-product from olive oil production process. The heating value of this material was measured as 24.5 MJ/kg. This was equivalent to 28212 TOE.

Moreover, the oil content in olive cake was found to be 13.74 %. With combine process of acid-catalyzed esterification followed by alkalicatalyzed transesterification, the maximum biodiesel yield was 74.29 and obtained at 30%v/v of methanol/oil ratio, 65°C temperature with 1.0 % by weight KOH catalyst. The produced biodiesel contributes only to about 0.057% of the total Primary energy consumption. As a biomass source, the potential of olive cake in the energy saving program is not promising. It contributes only to 0.055% when olive cake oil would be converted to biodiesel.

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