J Am Oil Chem Soc (2010) 87:903–908
DOI 10.1007/s11746-010-1566-1

ORIGINAL PAPER

Parametric Study of Jatropha Seeds for Biodiesel Production by Reactive Extraction

Savita Kaul · Jyoti Porwal · M. O. Garg

Received: 9 July 2009 / Revised: 25 February 2010 / Accepted: 1 March 2010 / Published online: 23 March 2010

Abstract The purpose of the present study was to reduce the cost and increase the efficiency of biodiesel production by reactive extraction (in situ) of Jatropha seeds. Oil from the seeds was extracted and reacted in a single step. Experimental studies have been carried out to maximize the yield of biodiesel by varying the reaction parameters viz. seed size (<0.85 mm to >2.46 mm), seed/solvent ratio (w/w) (1:2.6–1:7.8) and catalyst concentration (0.05–0.1 M). Under the optimized conditions: seed size (>2.46 mm), seed/solvent ratio (w/w) (1:7.8), catalyst concentration (0.1 M) and reaction time 1 h, approximately 98% conversion to biodiesel was achieved meeting International (ASTM) as well as National (BIS) specifications. The results were supported by HPLC analysis.

Keywords Jatropha seed · Methanol · Extraction · Reactive extraction · Transesterification · Biodiesel

Introduction

India is looking at alternative fuel sources to reduce its dependence on imported oil as it currently imports about 60–70% of its petroleum requirements [1]. 'Biodiesel', a renewable, low-emissions diesel fuel derived from fats and oils, consisting of the simple alkyl esters of fatty acids (FA) is presently making a global transition from a research and demonstration concept to commercial production. One of the challenges to widespread adoption of biodiesel is its cost, compared with petroleum diesel fuel. The relative high price of biodiesel arises from the high cost of the refined edible oils that are predominant feed-stocks for fuel production [2]. Edible oil such as soybean oil in the USA, rapeseed oil in Europe and palm oil in countries with a tropical climate, such as Malaysia, are being used for the production of biodiesel. However, in India, there are several non-edible oil seed species which could be utilized as a source for biodiesel production. Among these, *Jatropha curcas* is a multipurpose species with many attributes and considerable potential. The oil from the seeds is potentially the most valuable end product, with properties, such as, good oxidation stability as compared to soybean oil [3], low viscosity as compared to castor oil and better cold properties as compared to palm oil. In addition, viscosity, free fatty acids, density of the oil and the biodiesel are stable within the period of storage [4].

Contemporary industrial technology for the synthesis of fatty acyl esters of vegetable oil involves the isolation of oilseed triglycerides by extrusion [5] or solvent extraction, degumming, refining of the oil and its alkali-catalyzed transesterification. Hexane extraction is the main technology for oil recovery [6, 7], it contributes to the production of atmospheric smog, global warming, and is classified as a hazardous air pollutant [8]. Also, the replacement of lost solvent represents a significant cost to the extraction facility, and therefore interest exists in further reducing or eliminating the use of hexane in oilseed extraction.

The conventional method for the production of biodiesel from Jatropha and other seeds involve various stages; oil extraction, purification (degumming, deacidification, dewaxing, dephosphorization, dehydration, etc.) and esterification/transesterification. The requirement of these multiple processing stages constitute over 70% of the total production costs of biodiesel if refined oil is used as the feedstock [9]. Therefore, development of in-situ extraction,

S. Kaul (✉) · J. Porwal · M. O. Garg
Chemical Sciences Division, Indian Institute of Petroleum, Dehradun, India
e-mail: skaul@iip.res.in

Table 1 Physico-chemical properties of biodiesel with comparison to standards

No.	Parameter	Units	Values	Methods	Limits
1	Acid value	mg KOH/gm	0.4	ASTM-D-994	0.5 max.
2	Viscosity (at 40 °C)	cSt	4.25	ASTM-D-445	1.9–6.0
3	Density (at 15 °C)	g/cc	0.875	ASTM-D-4052	0.860–0.900
4	Phosphorus content	%mass	0.00003	ASTM-D-4951	0.001 max.
5	Total glycerine	%wt/wt	0.1734	ASTM-D-6584	0.240 max.
6	Free glycerine	%wt/wt	0.00322	ASTM-D-6584	0.020 max.
7	Ester content FAME	%wt/wt	98.8	EN 14103	96.5 min.
8	Methanol	%wt/wt	Nil	EN 14110	0.2 max.
9	Moisture	%wt/wt	0.04	ASTM-D-2709	0.05 max.
10	Glycerol purity	%	93.25	ASTM-D-6584	–

esterification and transesterification or simply termed as reactive extraction has the potential to cut down the processing costs. Reactive extraction differs from the conventional biodiesel production process in that the oil-bearing material is brought into contact with the alcohol directly instead of reacting with pre-extracted oil. In another words, extraction and transesterification proceed in one single step, with alcohol acting both, as an extraction solvent and a transesterification reagent [10].

The present investigation illustrates the effectiveness of parametric study on the reactive extraction of Jatropha seeds in biodiesel production at the authors' laboratory.

Experimental Section

Reagents and Materials

Jatropha curcas seeds were procured from the Pantnagar Agriculture University (Uttarakhand, India). Sodium hydroxide (>96%), methanol, and carbon tetrachloride were purchased from Merck (India) Ltd.

Procedure

Characterization of the Jatropha seeds

Moisture content of Jatropha seeds

The moisture content of the Jatropha seeds was determined using the oven method according to ISTA (International Seed Testing Association) rules.

Oil Content of Jatropha Seeds

The oil content of the Jatropha seeds was determined using the BS EN ISO 659:1999 method.

Free Fatty Acid Content in Oil (Acid Value)

The acid value of the Jatropha oil was determined using the ASTM method-D-974/04.

Fatty Acid Profile by GC

The fatty acid composition of the seed oil was determined using an Agilent 6890 series gas chromatograph (GC) equipped with a flame ionization detector and HP-1 methyl siloxane capillary column (30 m × 320 μm × 0.25 μm) (Hewlett Packard, Palo Alto, CA, USA). Jatropha oil was saponified with NaOH (1.1 M), followed by extraction with ether, washing with water, solvent recovery by vacuum distillation to give white semi solid fatty acids. About 0.1 ml oil fatty acid was converted to methyl ester using 2 ml diazomethane before being injected into the GC. The detector temperature was programmed at 300 °C with a flow rate of 0.8 ml/min. The injector temperature was set at 240 °C. Nitrogen gas was used as the carrier gas. The identification of the peaks was determined by comparing the retention time of standard reference samples (from Aldrich) analyzed under the same conditions.

Phosphorus Content of Oil

Jatropha oil was analyzed by an Atomic Emission Spectrometer (AES), Model: DPE, PS (3000 UV), AES Instrument (LEEMAN LABS, INC., NEW HAMPSHIRE, USA).

Moisture Content of Jatropha Oil

The moisture content of the Jatropha oil was analyzed using a Karl Fischer Titrator (Metrohm 798 MPT Titrino, Metrohm Ion Analysis, Metrohm Ltd. CH-910, Herisau/Switzerland) following the ASTM-D-874 method.

Reactive Extraction of Jatropha Seeds

Reactive extraction of Jatropha seeds was carried out using whole seeds (with seed coat). The Jatropha seeds were crushed in a Retsch Model SM-100 cutting mill (Haan, Germany) with a feed rate up to 10 kg/h, feed size of <60 × 80 mm and an output size of 0.25–20 mm. These crushed seeds were separated by sieves to give the three fractions of seeds (<0.85 mm, >0.85 to <2.46 mm, >2.46 mm). During the entire study period, the seeds were kept in amber-colored air-tight bottles to eliminate moisture and to prevent photooxidation of the seeds. Each fraction of seeds was used in the experiments by taking different seed/solvent ratios (w/w) (1:2.6, 1:5.2, 1:7.8), and NaOH molar concentrations (0.05 M, 0.075 M, 0.1 M). The solvent, i.e., MeOH was placed in a three-necked round-bottom flask. The catalyst was dissolved in the solvent at 40 °C with mechanical stirring. The seeds (14.0 g) were poured into the flask and the reaction was carried out for 1 h at 65 °C with mechanical stirring. After 1 h, the reaction mixture was cooled and filtered. The solvent was recovered from the filtrate by vacuum distillation. A brown-colored crude product was obtained. The crude product was washed with hot water (30 mL) and extracted with CCl_4 (30 mL × 3). The solvent was removed to give a light yellow product subsequently analyzed by HPLC. In the optimized experiment, the transesterification of >2.46 mm seeds (100 gm.) at a seed/solvent ratio (wt/wt) (1:7.8) and catalyst concentration (0.1 M), In which the yellow colored crude product was obtained that gave two separate layers when allowed to separate in a separating funnel. The upper biodiesel phase and the lower glycerol phase was separated out, purified, and analysed by HPLC (Fig. 1). The biodiesel and glycerol phase showed approximately 98 and 93% purity. The biodiesel was finally analysed by ASTM methods and results were presented in Table 1.

HPLC Analysis of the Product

The chromatographic apparatus consisted of HPLC, a Model 600 pump with a quaternary gradient system, a model 2996 UV detector at 215 nm and a 600 controller model code 6CE all from Waters, Milford, MA, USA. The HPLC method for quantification of mono, di, triglycerides and esters (biodiesel) formed during the production of biodiesel were reported using a combined gradient with aqueous, organic and non-polar mobile phases on a nova pack C_{18}, 4-μm column. The oil (triglycerides), fatty acids and biodiesel (FAME) were characterized using methyl oleate, methyl linoleate, methyl palmitate, methyl stearate, 1,2-diolein, 1,3-diolein, trilinoleate, and tripalmitate as standard reference samples.

All the samples were filtered through a 0.2-μm millipore filter paper, an injection volume of 10 μL and a flow rate of 1 mL/min were used in the experiments. The column temperature was held constant at 45 °C, all the samples were dissolved in hexane using a UV detector at 215 nm. Channel A contained water, channel B methanol, channel C Hexane and channel D contained IPA with 0–10 min, 10% A + 90% B, 10–20 min 100% B, 20–30 min, 40% B + 25% C + 35% D, 30–40 min, 40% B + 35% C + 25% D and for the last 5 min back to an initial flow of 10% A + 90% D [11].

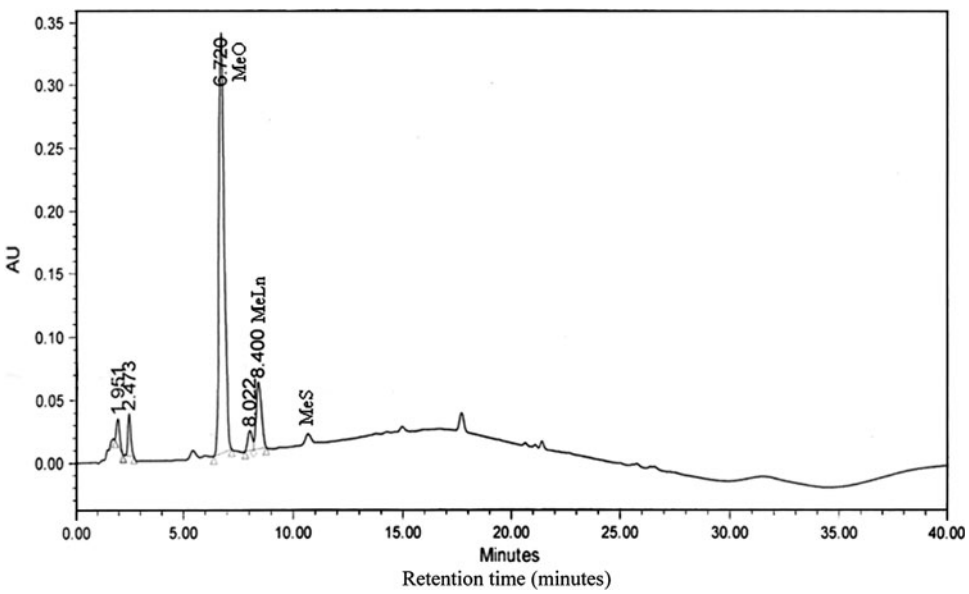

Fig. 1 HPLC analysis of Biodiesel (1:750, >2.46 mm, 0.1 M catalyst concentration) (where *MeO* methyl oleate, *MeLn* methyl linoleate, *MeS* methyl stearate)

Result and Discussion

The fatty acid profile of *Jatropha curcas* oil has been reported previously [12]. Typically, 1% of the vegetable oils are unsaponifiable compounds (carotenoids, phospholipids, tocopherols, or tocotrienols and oxidation products).

The moisture content of Jatropha seeds was determined as 4.05%. The oil content of the seeds was determined as 33.40% with an acid value of 3.8 mg KOH/g. The phosphorus content and moisture content of the oil analyzed was 101 mg/L and 0.0455%. The fatty acid profile of Jatropha oil was determined by GC as palmitic acid (C16:0; 17.4 wt%), Oleic acid (C18:1; 50.3 wt%), linoleic acid (C18:2; 23.2 wt%), stearic acid (C18:0; 6.0 wt%) (Fig. 2).

In the reactive extraction, the extraction and transesterification occurs in situ, therefore, the study of physicochemical characteristics of seeds are necessary for the transesterification process for ascertaining the reaction conditions necessary for achieving the maximum conversion to the desired product. The oil content of Jatropha seeds and the free fatty acid content i.e. acid value are important parameters in the designing of experiments.

Parametric Study of Reactive Extraction of Jatropha

Effect of Seed Sizes

The seed size has a great role in reactive extraction. Experiments were designed with three different sizes of seeds (<0.85 mm, >0.85 to <2.46 mm, >2.46 mm). The results obtained from seed size <0.85 mm were not encouraging. No conversion was observed at 0.05 and 0.075 M catalyst concentrations using a 1:2.6 seed/solvent ratio (w/w). The conversion increased to 94.36% while using a 0.1 M catalyst concentration, and a 1:7.8 seed/solvent ratio (w/w) as shown in (Fig. 3). The medium seed size (>0.85 to <2.46 mm) showed better results than <0.85 mm seed size. A conversions of 7.02, 6.73, 18.11% were observed at 0.05, 0.075, 0.1 M catalyst concentrations using a 1:2.6 seed/solvent ratio and a conversion of 28.58, 81.1, 96.03% was observed at 0.05, 0.075, 0.1 M catalyst concentrations using a 1:7.8 seed/solvent ratio (Fig. 4). In the parametric study, seed size >2.46 mm seems to be better in comparison to the other two seed sizes. A conversion of 32.06–68.88% was observed at a 1:2.6–1:5.2 seed/solvent ratio (w/w) and a catalyst concentration of 0.05–0.1 M.

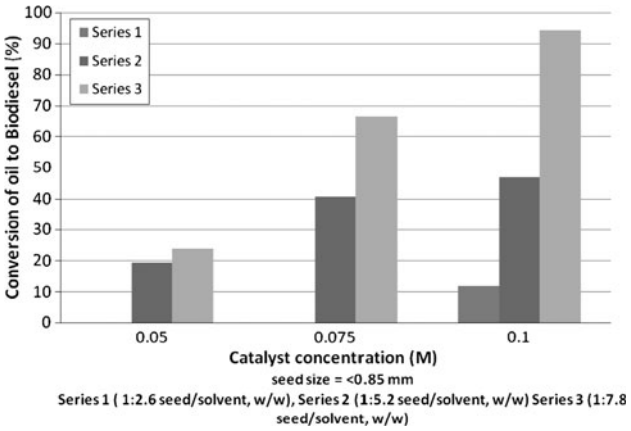

Fig. 3 Biodiesel conversion versus catalyst concentration with small seed size (<0.085 mm)

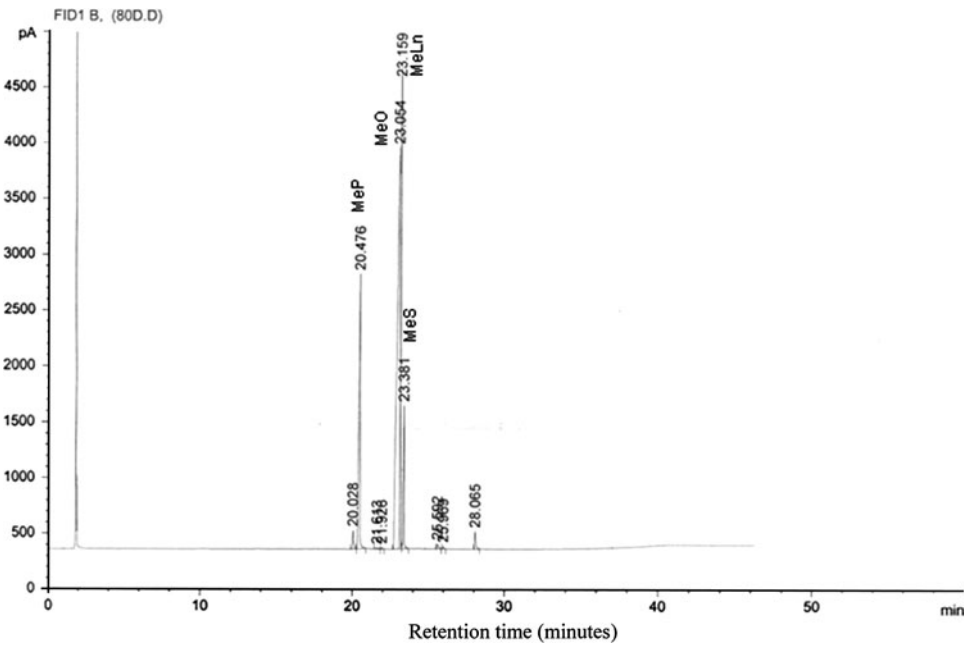

Fig. 2 GC chromatogram of fatty acid profile of Jatropha oil (where *MeP* methyl palmitate, *MeO* methyl oleate, *MeLn* methyl linoleate, *MeS* methyl stearate)

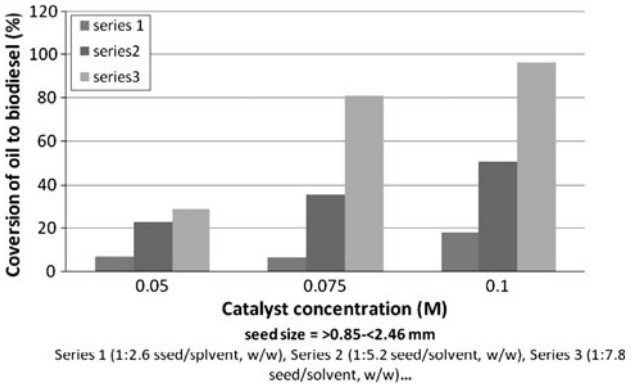

Fig. 4 Biodiesel conversion versus catalyst concentration with medium seed size (>0.085 to <2.46 mm)

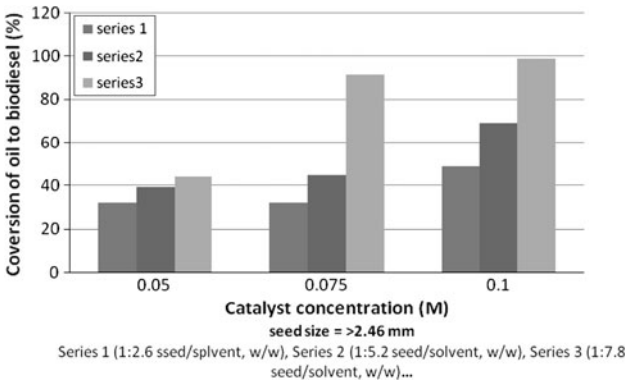

Fig. 5 Biodiesel conversion versus catalyst concentration with larger seed size (>2.46 mm)

While using a seed/solvent ratio of 1:7.8, this seed size showed 91.58 and 98.82% conversions at 0.075 and 0.1 M catalyst concentrations as shown in (Fig. 5). Thus, moisture content effects in situ transesterification [13] with small seed size (<0.85 mm) showed variation during consecutive repetitions of experiments.

Effect of Seed/Solvent Ratios (w/w)

In the reactive extraction, methanol acts not only as an extraction solvent but also as an alcoholysis reagent [14]. Therefore, a suitable amount of solvent should be able to extract the oil and shift the reaction in a forward direction effectively. Three seed/solvent ratios (w/w) (1:2.6, 1:5.2, 1:7.8) were investigated in the present study. A seed/solvent ratio of 1:2.6 showed 0–48.76% conversion at 0.05–0.1 M catalyst concentration using all three seed sizes (<0.85 to >2.46 mm). The reason may be because the solvent was not enough to extract the oilseeds when a low ratio was used. While a 1:5.2 seed/solvent ratio (w/w) and a catalyst concentration of 0.1 M showed 50.91 and 68.88% conversions using seed size >0.85 to <2.46 and >2.46 mm, respectively, which was better than seed/solvent ratio (w/w) 1:2.6. Using 1:7.8 ratio a minimum conversion of 23.8% with seed size <0.85 mm and 0.05 M catalyst concentration was observed and maximum 98.82% conversion was observed using a >2.46 mm seed size, at a catalyst concentration of 0.1 M. The results are given as graphical presentations (Figs. 3, 4, 5), in which seed/solvent ratio of 1:7.8 seems to be best at all catalyst concentrations and seed sizes.

Effect of Catalyst Concentration

Alkaline catalysis is known to achieve the transesterification of acyl glycerol with high speed and efficiency, and to be more effective than acid catalysis [15]. In the present study, sodium hydroxide was used and all the experiments were carried out at three different catalyst concentrations (0.05, 0.075, 0.1 M). It was observed that using 0.05 M catalyst concentration, 0–44.06% conversion was achieved. The reason for a lower conversion rate at a lower catalyst concentration is also due to fact that the acid value of oil is on the high side $\simeq$3.8 mg KOH/g. The catalyst concentration 0.075 M showed 66.41, 81.1, 91.5% conversion at seed/solvent ratio of 1:7.8, seed size of <0.85 mm, >0.85 to <2.46 mm, >2.46 mm, respectively. While at 0.1 M catalyst concentration, using all three seed sizes (<0.85mm, >0.85 to <2.46 mm, >2.46 mm), biodiesel conversion was observed as 94.36, 96.03, and 98.82%, respectively. However, In the whole study (Fig. 3, 4, 5) 0.1 M catalyst concentration was found to be best as it showed $\simeq$98% conversion with >2.46 mm seed size and 1:7.8 seed/solvent ratio (w/w). From HPLC analysis (Fig. 1) it is clear that biodiesel prepared under these conditions shows absence of triglycerides [11].

Effect of Reaction Time

The reaction time was monitored by taking samples at regular intervals, processing and analyzing them by HPLC. Comparable data shown in Fig. 6, reveals that the rate of reaction is fast in seed size <0.85 mm as compared to >2.46 mm from 0 to 15 min. A conversion of 53.79–92.33% and 57.94–66.99% is observed, respectively, using these seed sizes. Almost up to 30 min, all the three sizes showed a conversion of 93.97, 95.73, and 96.72%, respectively, and beyond this time a constant conversion rate was observed with each seed size. Again the best conversion (98.82%) was observed with seed size >2.46 mm. The results were also supported by HPLC analysis (Fig. 1).

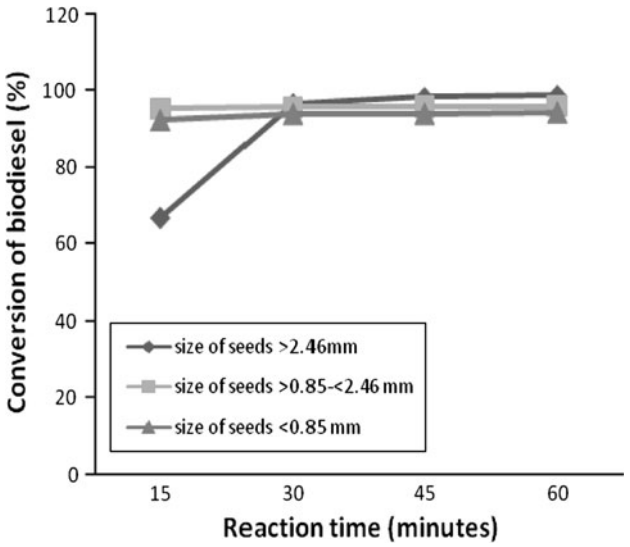

Fig. 6 Biodiesel conversion versus reaction time in reactive extraction (seed/solvent ratio (w/w) 1:7.8, catalyst (NaOH) concentration 0.1 M)

Conclusion

It has been demonstrated that biodiesel can be produced satisfactorily by the reactive extraction of oilseeds. The yield of biodiesel was found to be significantly affected by three factors investigated. The best result under optimized conditions were approximately 98% conversion by HPLC method using seed size (>2.46 mm), at seed/solvent (w/w) ratio (1:7.8) and catalyst concentration (0.1 M). In comparison with the conventional transesterification, reactive extraction of non-edible oilseeds is a very promising method for biodiesel production. Harrington and Catherine [16] studied in situ transesterification of a series of sunflower seeds under catalysis using methanol and compared the data to conventional transesterification. Comparing the results obtained in this work with other studies reported in the literature [17, 18], it was found that the maximum FAME yield obtained was much higher at almost 98% and can be achieved within 1 h of the reaction period. This is a very convenient method because the extraction and reaction occurs in a single step, which eliminates the high cost associated with solvent extraction and oil cleanup.

Acknowledgments This work was carried out supported by UKIERI Collaborative Research Awards and UKIERI DST Science and Technology Awards 2007.

References

1. Sharma RP (2004) Prospects and current status of biodiesel as an alternative fuel in India. Proceedings of Indo-Swedish workshops on Biofuel conversion II pp 19–34
2. Zhang Y, Dube MA, McLean DD, Kates M (2003) Biodiesel production from waste cooking oil: 2 Economic assessment and sensitivity analysis. Bioresour Technol 90:229–240
3. Emil A, Zahira Y, Kartom KS, Manal I, Jumat S (2009) Characteristic and composition of Jatropha curcas oil seed from Malaysia and its potential as biodiesel Feedstock. Euro J Sci Res 29:396–403
4. Augustus GS, Jayabalan M, Seiler GJ (2002) Biomass Bioenergy 23:161–164
5. Rittner H (1984) Conditioning of oil bearing materials for solvent extraction by extrusion. JAOCS 61(7):1200–1203
6. Kemper TG (1997) Solvent recovery and loss management in technology and solvents for extracting oilseeds and non-petroleum oils. AOCS Press, Champaign, pp 148–152
7. Kaul S, Goyal HB, Bhatnagar AK, Gupta AK (2009) Effect of aging on quality of jojoba oil from Indian locations. Ind Crops Prod 29(1):102–107
8. National Emission Standards for Hazardous Air Pollutants, Part A, Section 112, US Public Law 101–549, The clean Air Act Amendment of 1990, 1990, available at http://www.epa.gov/oar/caa/caa112.txt
9. Zeng J, Wang X, Zhao B, Sun I, Wang y (2009) Rapid in situ transesterification of sunflower oil. Ind Eng Chem Res 48(2): 850–856
10. Georgogiannia KG, Kontominasa MG, Pomonisa PJ, Avlonitisb D, Gerisc V (2008) Conventional and in situ transesterification of sunflower seed oil for the production of biodiesel. Fuel Process Technol 89:503–509
11. Holcapek M, Jandera P, Fischer Jan F, Prokes B (1999) Analytical monitoring of the production of biodiesel by high performance liquid chromatography with various detection methods. J Chromatogr A 858:13–31
12. Kaul S, Saxena RC, Kumar A, Negi MS, Bhatnagar AK, Goyal HB, Gupta AK (2007) Corrosion behavior of biodiesel from seed oils of Indian origin on diesel engine parts. Fuel Process Technol 88:303–307
13. Qian J, Fei Wan, Sen Liu, Zhi Yun (2008) In situ alkaline transesterification of cottonseed oil for production of biodiesel and nontoxic cottonseed meal. Bioresour Technol 99:9009–9012
14. Ozgul S, Turkay S (2002) Variables affecting the yields of methyl esters derived from in situ esterification of Rice Bran Oil. JAOCS 79:611–614
15. Freedman B, Pyrde EH, Mounts TL (1984) Variables affecting the yields of fatty esters from Transesterified vegetable oils. JAOCS 61:1638–1643
16. Harrington KJ, Catherine DV (1985) A comparison of conventional and in situ methods of transesterification of seed oil from a series of sunflower cultivars. 73:25–228
17. Mondala A, Ling K, Toghiani H, Hernandez R, French T (2008) Biodiesel production by in situ transesterification of municipal primary and secondary sludges. Bioresour Technol 100: 1203–1210
18. Su E, Xu W, Gao K, Zheng Y, Wei D (2007) Lipase catalysed in situ reactive extraction of oilseeds with short chained alkyl acetates for fatty acid ester production. J Mol Cat B Enzyme 48:28–32