Reactive-extraction of pongamia seeds for biodiesel production

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Biodiesel (FAME) was produced from *Pongamia* seeds (commonly known as Karanja) by reactive-extraction. Reactive-extraction involves contacting ground seeds directly with alcohol and catalyst i.e. without intervening extraction of the vegetable oil. This process has the potential to reduce cost by removing the need for capital and running cost-intensive steps such as oil extraction of seeds. Reaction parameters such as seed size (>2 mm to <1 mm), seed/solvent ratio (wt/wt) (1:2-1:4), temperature (30-60°C) and rate of mixing (250-550 rpm) were studied. The maximum 98.5% conversion to biodiesel was achieved at: seed size (<1 mm), seed/solvent ratio (wt/wt) (1:4), rate of mixing (550 rpm) at 60 °C for 1 hr with 0.1 M catalyst (KOH) concentration, meeting International (ASTM) as well as National (BIS) specifications

Keywords: Pongamia, Methanol, Reactive Extraction, Biodiesel/ FAME

Introduction

The rising price of petroleum fuels, depletion of oil reserves and stiff regulations on exhaust emissions have necessitated the substitution of fossil fuels with less polluting and easily available renewable fuels for use in internal engines. Development of biodiesel as an alternative and renewable source of energy for the mechanized agricultural and transportation sector has become critical in the national effort towards maximum self-reliance for the corner stone of our energy security strategy[1]. The non-edible oils such as Neem (*Azadirachta indica*), Mahua (*Madhuca indica*), Karanja (*Pongamia glabra /pinnata*), Jatropha curcas and Tobacco (Nicotiana tabacum) seed oil are easily available in many parts of the world including India and are very economical compared to edible oils. *Jatropha curcas* and *Pongamia pinnata* can be cultivated on any type of soil, and have low moisture demand. The cultivation of these plants is easier and plants have high oil content (25-30%)[2].

Conventional method for the production of biodiesel from Pongamia[1] and other seeds involve various stages: oil extraction, purification (degumming, deacidification, dewaxing, dephosphorization, dehydration, etc.) and

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esterification/transesterification. The requirement of these multiple processing stages constitute over 70% of the total production cost of biodiesel if refined oil is used as feedstock. Therefore, process of extraction, esterification and transesterification or simply termed as reactive extraction has the potential to cut down the processing cost. Reactive-extraction differs from the conventional biodiesel production process in which the oil-bearing material contacts with alcohol directly instead of reacting with pre-extracted oil. In other words, extraction and transesterification proceed in one step, with alcohol acting both as an extraction solvent and a transesterification reagent[3]. Since its introduction by Harrington and D'arcy Evans[4], numerous researchers have investigated the performance and feasibility of this process. However, whether it can replace the current transesterification technology remains to be seen. The possibility of producing biodiesel via reactive-extraction can only be materialized once the process as a whole has been fully characterized[5]. The various parameters affect the reactive extraction of oil bearing biomass to produce biodiesel[6-7]. It was also asserted by Haas et al.[8] that biodiesel produced by reactive-extraction is more expensive than biodiesel produced via conventional transesterification, due to the large amounts of methanol required for the process. The application of reactive-extraction not only intensifies the process, but also

removes the need for a specific step to extract these toxic substances in the downstream processing, reducing the exposure of workers to such substances[4]. This approach, however, can be applied to almost any lipid-bearing material[9-10].

Various reports describe the use of incubator shaker in biochemical and biocatalytic reactions[11]. Esterification reactions of 4-methyloctanoic acid (4-MOA) with PEG in an organic monophase and water/organic biphasic system using Novozym435[R] as the catalyst were carried out in a New Brunswick Scientific Innova™ 4080 incubator shaker at 350 rpm at 45°C[12]. Enzymatic transesterification of racemic 4-methyl hexanoic acid methyl ester and 4-methyloctanoic methylester to their butyl esters were carried out in New Brunswick Scientific Innova™ 4080 incubator shaker[13]. Studies have been carried out on extraction of algae oil and its transesterification in an electric shaker at 300rpm for 3 hrs[14]. The present investigation illustrates the effect of various parameters on the reactive extraction of Pongamia seeds for biodiesel production using incubator shaker at authors' laboratory.

Material and methods
Materials and reagents

Pongamia pinnata seeds were procured from Pantnagar Agriculture University (Uttarakhand, India). Potassium Hydroxide (>87%), Methanol was purchased from Merck (India) Ltd.

Characterization of the Pongamia seeds

Moisture content of *Pongamia* seeds was determined using oven method according to ISTA (International Seed Testing Association) rule. The oil content of *Pongamia* seeds was determined using BS EN ISO 659:1999 method. Free fatty acid content in oil (Acid value). The acid value of *Pongamia* oil was determined using ASTM method- D-974/04. Fatty acid composition of pongamia seed oil was determined using gas chromatograph. The oil was saponified with NaOH (1.1 M), followed by extraction with di ethyl ether, washing with water, solvent recovery by distillation to give white semi solid fatty acids. The acid value of the fatty acid mixture is 202 mg KOH/g. About 0.1 ml oil fatty acid was converted to methyl ester using 2 ml diazomethane before being injected into the GC.

Reactive-extraction of Pongamia seeds

Reactive-extraction of *Pongamia* seeds was carried out using whole seeds (with seed coat). The *Pongamia*

seeds were crushed in Retsch Model SM-100 cutting mill (Hann, Germany) with feed rate up to 10kg/h, feed size of <60x80 mm and a output size of 0.25-20 mm. These crushed seeds were separated by sieves to give the three fraction of seeds (>2 mm, 1-2 mm, <1 mm). During entire study period the seeds were kept in amber colored air tight bottles to avoid moisture and photoxidation on seeds. However, the seeds were pre dried at 60°C before use. Each fraction of seed was used in experiments by taking different seed/solvent ratio (w/w) (1:2, 1:3, 1:4), and KOH molar concentrations (0.1 M). The alkali catalyst methanol solution was prepared with the 0.1 M KOH concentration. The solution was distributed into smaller containers with suitable size (250 mL) and was preheated up to 40°C. The dried seeds of desired size were poured in the containers, and the reaction was allowed to proceed inside the incubator shaker (KS 4000i control, IKA-Werke GmbH *and* Co. KG, Staufen, Germany) with the desired temperature and agitation speed. After 1 hr the reaction mixture was filtered and concentrated at atmosphere pressure. The crude product was taken in a separating funnel to allow it to settle. The result was two distinct liquid phases; the first was methyl ester or biodiesel on the top and the second was the densed phase of glycerol. The upper biodiesel phase was washed with warm water (2x5 ml) and the product analysed by GC analysis. The residual seeds were re extracted to ascertain the removal of total oil from the seeds.

Ester (FAME) characterization

The composition of the transesterification products was determined using Agilent 6890 series gas chromatograph (GC) equipped with flame ionization detector and HP-1 methyl siloxane capillary column (30 m x 320 µm x 0.25 µm) (Hewlett Packard, Palo Alto, CA, USA). The detector temperature was programmed at 300°C with flow rate of 0.8 ml/min. The injector temperature was set at 240°C. Nitrogen gas was used as carrier gas. The identification of the peaks was determined by comparing retention time of standard reference samples (from Aldrich) analyzed under the same conditions.

GC - MS of the product was also determined using *BSEN 14105: 2003* method to check for presence of any mono, di and triglyceride using Perkin Elmer (clarus) 600/ 560D GCMS with a ZB-5 Inferno (Phenomenex[R]) capillary column (15 m x 0.25 mm, i.d. 0.10 µm film thickness) and helium as carrier gas. The oven

Table 1—Fatty acid composition of *Pongamia* seeds under present study

Fatty acid composition	wt%	Literature value (wt%)
Palmitic acid (C16:0)	14.3 (0.03)	10.6
Stearic acid (C18:0)	5.0 (0.035)	6.8
Oleic acid (C18:1)	46.7 (0.20)	49.4
Linoleic acid (C18:2)	14.4 (0.15)	19.0
Arachidic acid (C20:0)	8.1 (0.05)	4.1
Behenic acid (C22:0)	8.5 (0.05)	5.3
Lignoceric acid (C24:0)	2.3 (0.01)	2.4

Values are mean±standard deviation of triplicate determination
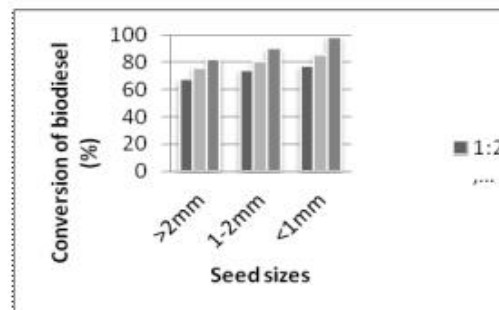

Fig. 1—Biodiesel conversion versus different seed sizes of *Pongamia* (seed/ solvent ratio (wt/wt): 1:2, 1:3, 1:4 and RPM: 250, 400, 550, reaction time 1 hr, reaction temperature 60°C)

temperature /programme was an initial temperature of 50°C for 1 min., a ramp of 15°C/ min. to 180°C (hold for 0 min.), a ramp of 7°C / min. to 230°C (hold for 0 min.) and a ramp of 10°C / min. to 370°C (hold for 10 min.). The esters obtained by transesterification were then tested for estimating their fuel properties according to the ASTM standard test methods of analysis[15].

Results and discussion

In 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 parameters necessary for achieving the maximum conversion to the desired product. The oil content of *Pongamia* seed and the free fatty acid content i.e. acid value are important parameters for designing of the experiments. The moisture content of *Pongamia* seeds was determined as 4.6 % while as the oil content of the seeds and acid value determined as 27.1 % and 2.5 mg KOH/g respectively. However, the seeds were preheated at 60°C before each experiment.

The fatty acid profile of *Pongamia* oil from the seeds under present study was determined by GC and is presented in Table 1. The fatty acid composition values were in the range of the literature values as: palmitic acid (C16:0; 14.3 wt%), oleic acid (C18:1; 46.7 wt%), linoleic acid (C18:2; 9.4 wt %), stearic acid (C18:0; 6.0 wt%), arachidic acid (C20:0; 8.1 wt%), behenic acid (C20:0; 8.5 wt%), lignoceric acid (C24:0; 2.3 wt %)[16]. Acid catalyst could have been used but it takes longer reaction period >10 hrs. Generally alkali catalyst is favoured in reactive-extraction for much the same reasons as in transesterification of vegetable oils[17].

Reactive-extraction of pongamia seeds
Influence of seed size

The seed size has a significant role in reactive extraction. Experiments were designed with three different seed sizes (>2 mm, 1-2mm, <1 mm). The results obtained from seed size >2 mm showed 67.8%, 75.7%, 82.3% conversion at seed/ solvent ratio (wt/wt) of 1:2, 1:3, 1:4 and 250, 400, 550 rpm respectively, whereas seed size 1-2 mm showed 74.1%, 80.89%, 90.1% conversion. A conversion of 77.6%, 85.6% and 98.5% was obtained using seed size <1 mm at seed/ solvent ratio (wt/wt) 1:2, 1:3, 1:4 and 250, 400, 550 rpm respectively (Fig. 1). Conversion of oil (TG) clearly increases with decreasing seed particle size. This is in agreement with Zakaria *et al.*[7] findings for reactive extraction of rapeseed. The smaller the particle size, the greater the proportion of broken surface cell walls releasing more oil at the particle surface. The oil at the surface is not, of course, released to the bulk solvent by internal diffusion, rather it is solubilised or washed off at a much quicker rate. It is postulated that if most of the oil accumulates at the particle surface, less solvent is needed for extraction, since the diffusion process is minimized. The oil content was not observed after reextraction of the residual seeds which showed the whole oil has been used in the reactive extraction process.

Influence of seed/ solvent ratio (wt/wt)

In reactive extraction, methanol acts as an extraction solvent as well as alcoholysis reagent. Therefore, the (stoichiometric) excess solvent used should extract the oil and take part in the transesterification whilst shifting the reaction substantially to the product side[13]. Three seed/solvent ratios (wt/wt) (1:2, 1:3, 1:4) were investigated in the present study. The seed/solvent ratio (wt/wt) 1:2
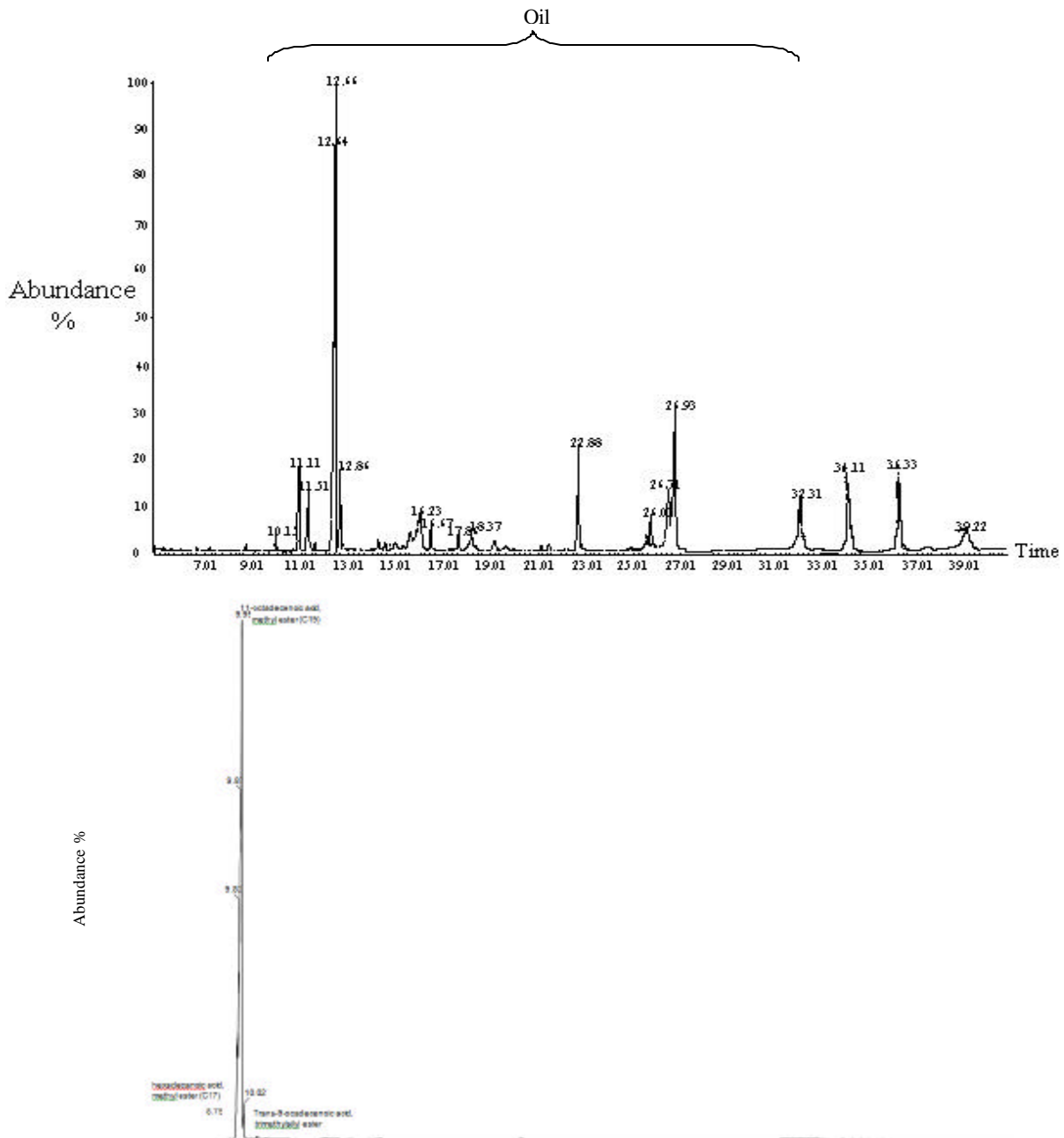
Fig. 2—GC-MS of *Pongamia* Oil and Biodiesel

showed 67.8 to 77.6% conversion using seed size >2 mm to <1 mm at 250 rpm. whereas seed/solvent ratios (wt/wt) 1:3 showed 75.7% to 85.6% conversion using seed size >2 mm to <1 mm at 400 rpm. The maximum conversion of FAME 90.1 and 98.5% were achieved at seed/solvent ratios (wt/wt) 1:4 using seed size 1-2 mm and <1mm at 550 rpm. The results were depicted in Fig 1. The maximum seed to solvent ratio of 1:4 produces the maximum conversion of the three ratios used, with each increase in ratio resulting in a clear increase in conversion. This implies that higher ratios would produce higher conversion, but at 98.5% there isnmm:'t much further to go, so further increases may not be justifiable in practice. Large amount of solvent is needed in reactive extraction to drive the extraction as well as reaction. The results were further supported by GC-MS of product after derivatization and presented in Fig 2. A comparison of GC-MS of oil and biodiesel (FAME) showed no peak in biodiesel spectra after a retention time of 10.02 min that clearly indicative of absence of any triglycerides,
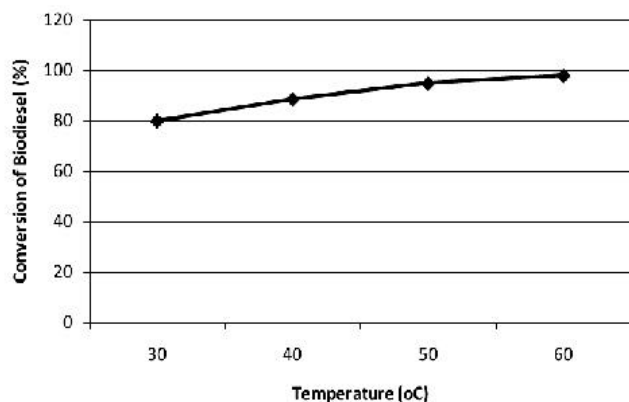
Fig. 3—Conversion of biodiesel as function of temperature (seed size <1 mm, seed/ solvent ratio (wt/wt) 1:4, RPM 550, catalyst (KOH) concentration 0.1 M, reaction time 60 minutes)
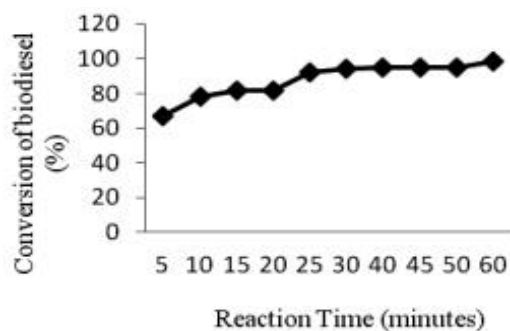

Fig. 4—Biodiesel conversion versus reaction time (seed size <1 mm, seed/solvent ratio (w/w) 1:4, RPM 550, reaction temperature 60ºC, catalyst (KOH) concentration 0.1M)

Table 2—Physico-chemical properties of biodiesel with comparison to standards

Parameters	Units	Values	Methods	Limits
Acid value	mgKOH/gm	0.4 (0.02)	ASTM-D-994	0.5 max.
Viscosity (at 40 ºC)	cSt	4.11 (0.01)	ASTM-D-445	1.9-6.0
Density (at 15 ºC)	g/cc	0.875 (0.002)	ASTM-D-4052	0.860-0.900
Ester content FAME	wt/wt %	98.5 (0.1)	EN 14103	96.5 min.
Phosphorus content	% mass	0.00003	ASTM-D-4951	0.01 max.
Total glycerine	% wt/wt	0.1734(0.001)	ASTM-D-6584	0.240 max.
Free glycerine	% wt/wt	0.0041	ASTM-D-6584	0.020 max
Methanol	% wt/wt	Not detected	EN 14110	0.2 max.
Moisture	% wt/wt	0.180 (0.002)	ASTM-D-2709	0.05 max.
Triglycerides	%wt/wt	Nil	ASTM-D-6584	-
Diglycerides	%wt/wt	Nil	ASTM-D-6584	-

Values are mean±standard deviation of triplicate determination

di and monoglycerides in biodiesel while as in oil (triglycerides) the peaks with retention time of 10.02 min were observed. The spectra are in close resemblance with *BSEN 14105: 2003* method and further the evaluation of biodiesel by ASTM method confirms the above values.

Influence of Mixing Intensity

Mixing is very important in the transesterification reaction, as oils or fats are immiscible with the potassium hydroxide-methanol solution. This is exacerbated in reactive extraction as there is now a third phase (solid) to take into account. Here, reactive extraction was conducted with three different stirring rates of 250, 400 and 550 rpm. The use of 550 rpm resulted in higher conversion. At low agitation speeds, the distribution of seeds was not as uniform as at higher agitation speeds. The seeds settled on the bottom of the reaction vessel and this reduced the biodiesel conversion.

Influence of reaction temperature

In general, temperature affects both the rate of diffusion and reaction. Studies were carried out at 30, 40, 50 and 60ºC with seed size < 1 mm, seed/ solvent ratios (wt/wt) 1:4, catalyst (KOH) concentration 0.1 M for 60 minutes with stirring speed of 550 rpm. The conversion of biodiesel (FAME) versus temperature was plotted in Fig. 3. It was observed from the figure that conversion of FAME increased to 80.0%, 88.6%, 94.8% and 98.5% at reaction temperatures of 30, 40, 50 and 60º C, respectively. Oil extraction, on the other hand, proceeds faster at higher temperature as the viscosity of the oil and solvent is reduced and diffusivity is increased[6].

Influence of reaction time

The experiment was carried out using seed size <1 mm, seed/ solvent ratios (wt/wt) 1:4 at 550 rpm and 60ºC. Reaction time was monitored by taking sample at regular

intervals, processing and analyzing by GC. A conversion of 66.8% and 81.4% were achieved after 5 and 20 minutes. Rate of reaction is fast in the initial 5 minutes, but slow thereafter. It showed an increasing order of reaction and 98.51% conversion was achieved after 60 minutes (Fig 4). Reaction time of 1 hr seems to be an ideal time to get desired conversion of the product meeting the ASTM specifications.

Determination of physical properties of the esters (FAME)

The properties of the produced fatty acid methyl esters were measured using standard methods of analysis[15]. Some properties of biodiesel, which are acid value, viscosity, density, ester content, moisture, phosphorus content, glycerol purity, were determined at optimised reaction conditions and results were tabulated in Table 2.

The acid value of the FAME products can be used as a detection of free fatty acid content of the fuel. It is clear that acid value of FAME products (0.4 mg KOH/gm) meet the standard limit, indicating that the free fatty content will not cause operational problems, such as corrosion and pump plugging, caused by corrosion and deposit formation[18]. Viscosity is a significant fuel property that affects the flow and atomization characteristics of a liquid fuel. This parameter is also useful for evaluating the methyl ester contents of biodiesel samples, since there is a correlation between the contents of esters and the viscosity: the higher the viscosity, the lower the ester content[19]. Thus viscosity and density are found to be 4.11 cSt (at 40 °C) and 0.875 g/cc (at 15°C) respectively also ascertains that final optimized product meet the ASTM specification. The Phosphorus content, glycerine and moisture content are also coherent with the standard limits.

Conclusion

The present study depicts that biodiesel can be made directly from *Pongamia* seeds by reactive-extraction. The conversion of biodiesel was found to be affected by factors investigated. The best result under optimized conditions was 98.51% conversion using seed size (<1 mm), seed/solvent (w/w) ratio 1:4, catalyst (KOH) concentration (0.1 M) at 550 rpm and 60°C. In reactive-extraction, once oil is extracted out from the seed, it is instantaneously converted to FAME. Therefore, reactive-extraction using incubator shaker can actually reduce the time and solvent required for biodiesel production

from various oilseeds as compared to the conventional method, thus will be promising method for biodiesel production.

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