

Biodiesel production from Jatropha seeds using heterogeneous integrated extraction reaction process

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Producción de biodiesel a partir de semillas de jatropha usando un proceso heterogéneo a base de una reacción de extracción integrada

Producció de biodièsel a partir de llavors de Jatropha fent servir un procés heterogeni a base d'una reacció de extracció integrada

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RESUMEN

En este artículo se informa sobre los procesos de extracción y transesterificación integrados para la producción de biodiesel a partir de semillas de Jatropha Curcas (JCL) utilizando hexano y metanol por medio de una transesterificación catalizada por bases.

Se han investigado los efectos del tiempo de reacción, de la dosis de catalizador, de la proporción líquido sólido, del tipo de disolvente y del tamaño del grano de las semillas de JCL en la producción de biodiesel. Se ha observado que el hexano tenía tanto el papel de solvente como de sustancia extractiva, lo que incrementaba la eficacia de la extracción del aceite y facilitaba la transferencia de masa. El máximo rendimiento del biodiesel (90,8%) se obtenía con una proporción de hexano-semilla de 5:1 (vol. /p), metanol-semilla de 1:1 (vol. /p), Ca O activado del 1% por peso de semillas, velocidad de agitación de 700 rpm, temperatura de 70°C para un tiempo de reacción de 6 horas.

Palabras clave: Biodiesel; transesterificación – disolvente; in situ; semillas de Jatropha.

SUMMARY

Integrated extraction and transesterification process for biodiesel production from Jatropha Curcas (JCL) seeds using hexane and methanol via base catalyzed transesterification is reported in this paper.

The effects of reaction time, catalyst dose, liquid to solid ratio, type of solvent and grain size of JCL seeds on biodiesel production were investigated. It was found that hexane played the role of both co – solvent and co – ex-

tractant which enhanced the efficiency of oil extraction and facilitated mass transfer. The highest biodiesel yield (90.8%) was obtained at hexane to seed ratio of 5:1 (vol / wt), methanol to seed ratio 1:1 (vol /wt), activated Ca O of 1% by wt of seeds, stirring speed 700 rpm, temperature of 70°C at reaction time 6 hours.

Key words: Biodiesel; Transesterification – Co – Solvent; in-situ; Jatropha seeds.

RESUM

En aquest article s'informa sobre els processos d'extracció i transesterificació integrats per la producció de biodièsel a partir de llavors de Jatropha Curcas (JCL) utilitzant hexà i metanol fent servir una transferència catalitzada per bases.

S'han investigat els efectes del temps de reacció, de la dosi de catalitzador, de la proporció líquid-sòlid, del tipus de dissolvent i de la mida del gra de les llavors de JCL en la producció de biodièsel. S'ha observat que el hexà tenia el paper de solvent i de substància extractant, i això incrementava l'eficàcia de l'extracció del oli i facilitava la transferència de massa. El màxim rendiment del biodièsel (90,8%) s'obtenia amb una proporció de hexà-llavor de 5:1 (vol. /p), metà-llavor de 1:1 (vol. /p), CaO activat del 1% per pes de llavors, velocitat d'agitació de 700 rpm, temperatura de 70°C per un temps de reacció de 6 hores.

Paraules clau: Biodièsel; transesterificació – dissolvent; in situ; llavors de Jatropha.

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1. INTRODUCTION

Biodiesel fuel is one example of biomass energy and it is generally made of methyl esters of fatty acids produced by the transesterification reaction of triglycerides with methanol with the help of catalyst.^(1,2,3)

Recently, non-edible oils obtained from plant species such as *Jatropha curcas* L. have been considered as a promising biomass feedstock with great potential for biodiesel production because it does not conflict with the food crisis: since it is not main food source.^(4, 5)

Alcoholysis of vegetable oils produces fatty acids alkyl esters that are excellent substitutes for conventional fossil diesel fuels^(6, 7). The viscosity of net vegetable oil is about 10 -20 times that of the diesel⁽⁶⁾, that's why transesterification is necessary to approach to that of diesel fuel.

One of the alternatives to produce biodiesel from vegetable oils is in-situ transesterification or "reactive extraction" process. This process combines the steps of lipid extraction and transesterification to produce biodiesel.^(9, 10)

The simultaneous solvent extraction and in situ transesterification on biodiesel processing from *Jatropha* seeds affected positively both biodiesel production yield and biodiesel quality⁽¹¹⁾. The main advantage of this combined process is that it allows solvent extraction to be applied to oil seeds and then in situ transesterification to extracted oils. Methanol is a not very efficient solvent for oil extraction due its immiscibility⁽¹¹⁾. Quantity of a co-solvent such n-hexane into the reaction mixture can improve significantly the mass transfer of oil into alcohol (methanol or ethanol) and also intensify the transesterification reaction between oil and alcohol^(4,5,12,13). In the case of *Jatropha* seeds, n-hexane is an efficient solvent for oil extraction and its non-polarity can also limit the removal of free fatty acids and water from the seeds.⁽⁷⁾

Integration of these stages could minimize biodiesel production cost⁽¹¹⁾. Since the use of reagents and solvents are reduced and the analysis is easier and not expensive.^(14, 15)

In this present study, the main objective is to apply the biodiesel production technology using a solid catalyst (CaO as super base catalyst) to the in-situ transesterification of *Jatropha curcas* L, where the main reaction variables that strongly affect the cost of this process were studied.

2. METHODOLOGY

Materials.

Stored *Jatropha* seeds, supplied from Ministry of Agriculture which oil content was 20%, were used in the experimental work. Methanol (99% purity) and n-hexane (>98% purity) were supplied from Adwic company, Egypt. Calcium oxide (Ex. Pure) was obtained from Oxford Laboratory Reagent, India. Ammonium carbonate purified LR was obtained from S.d. fine-chem. Ltd., India. Calcium oxide is activated according to previous studies^(16,17), by immersing in $(\text{NH}_4)_2\text{CO}_3$ and calcined at 900° C for 1.5 hrs.

Experimental work

Preparation of calcium oxide as heterogeneous super base catalyst.

Calcium oxide (24g) was dipped in 200 ml ammonium car-

bonate solutions (12% by wt) then the mixture was stirred for 30 minutes at room temperature.

After filtration and drying the precipitate was dried at 110°C till constant weight, the dried solid was milled and sieved (48 mesh) then calcined at 900°C for 1.5 hours. After cooling in a desiccator to room temperature the base CaO catalyst is ready to use.

Characterization of the CaO catalyst.

The basic strength of the catalyst was tested using Hammett's indicators. Also the prepared CaO was characterized by X-ray diffraction (XRD) and XRD patterns were analyzed to find out the crystalline phase. Scanning electron microscope (SEM) and Brunauer-Emmer-Teller (BET) method for surface area determination.

Extraction and transesterification of lipid in crushed *Jatropha* seeds.

All experiments were conducted using two mesh sizes of *Jatropha* seeds, 12 mesh and 28 mesh or 1.7 mm and 0.6mm respectively. In all trials the moisture content of crushed *Jatropha* seeds was less than 1% by weight after drying crushed *Jatropha* seeds at about 100°C for 24 hours.

The experimental set-up is depicted in Fig.1. Both extraction and transesterification of lipids were processed in integrated reactor. In a typical run certain weight of crushed *Jatropha* seeds were fixed in the extraction chamber. The predetermined volume of hexane, methanol and weight of catalyst were remixed in the transesterification chamber (glass reactor with magnetic stirrer). The reaction was carried out in single neck 1000ml glass flask equipped with a soxhlet, a magnetic stirrer and water bath mounted on a heater. The apparatus was heated to a constant temperature for certain reaction time. As shown in Fig 1.

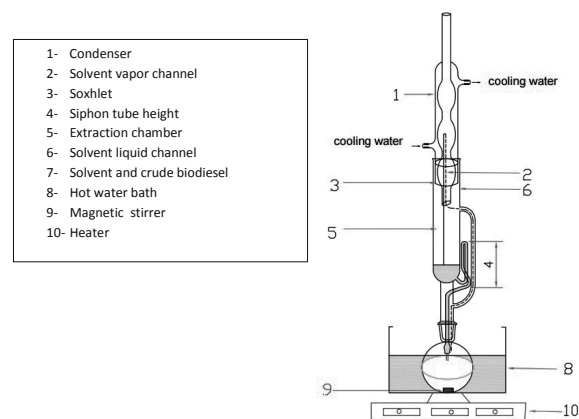


Fig.(1). The experimental set-up for in-situ transesterification from *Jatropha* seeds.

The mixed solvent in the glass reactor (7) evaporated, passed through the solvent vapor channel (2), and then collected in extraction chamber (5) to extract the oil. The mixed solvent with extracted oil flowed into the transesterification chamber (7) through solvent liquid channel (6), where the transesterification reaction occurred.

In the whole reaction, the mixed solvent was used repeatedly. After the reaction completed, the residue of *Jatropha* seeds could be taken out separately from the extraction chamber. The reaction mixture was obtained, filtered and

evaporated to remove excess solvent by using a rotary evaporator, then products are placed in a separating funnel, let overnight which results in generation of two layers: hydrophobic layer (hexane, FAME and glycerides) and hydrophilic layer (water, glycerol and excess methanol).

3. RESULTS AND DISCUSSION

Characterization of the catalyst (CaO)

Specifications of CaO used as base catalyst are shown in table 1.

Table (1) Characterization of CaO.

Basicity	BET	SEM morphology	CaCO ₃ content
Over 18.5*	8.9 m ² /g	1- Particles similar to each other	Nil
		2- Grains sintered	

* Basicity means the basic strength of the catalyst (i.e. the basic sites on catalyst surface).

Jatropha curcas oil characterization

The oil content of jatropha seeds in the actual study was determined quantitatively to be 20% based oil dry seed weight. Such amount of oil in jatropha seeds was in agreement with the results reported in previous work⁽¹⁸⁾ (20 – 28.3%) which is less than the average in jatropha curcas seeds (JCS) cited in the literature which is about 35%⁽¹⁹⁾ this may be due to the long storage of seeds. Jatropha oil used in this study was rich in linoleic acid (48.18%), oleic acid (28.46%) and palmitic acid (18.22%)⁽¹⁸⁾. The kinematic viscosity of the crude jatropha oil is 53.3 mm²/sec. The variation dependence of chemical composition of crude oil and its physical properties is due to change in climatic agricultural conditions.⁽¹⁶⁾

Effect of Experimental Conditions on the in-situ transesterification process

Effect of reaction time on percent oil conversion to fatty acid methyl ester (FAME).

The variation of reaction time had great effect on the yield of FAME as shown in Fig.2. The yield of FAME remarkably increased with increasing the reaction time within 6 hours, but no significant increase was observed by increasing reaction time. So the optimal reaction time was 6 hours in this study.

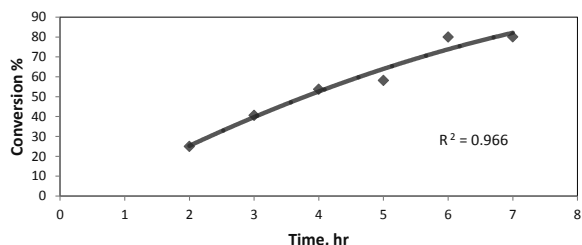


Fig.(2). Effect of the reaction time on biodiesel yield at 70°C, 700rpm, 1% by wt of oil catalyst with 3:1 volume ratio of hexane to methanol and 28 mesh size of seeds.

Effect of n-hexane to methanol volume ratio.

Fig.3. illustrates the effect of n-hexane to methanol volume ratio on percent FAME yield. From the results it can be seen that increasing volume of n-hexane to volume of methanol from 1 to 10 increased conversion from 35% to 64.5% at 70°C after 4 hours reaction time.

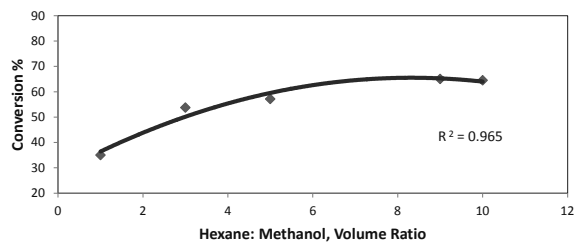


Fig. (3). Effect of volume of n-hexane to methanol at 70°C at 700 rpm, 1% by wt of oil catalyst for 4hrs.

Effect of hexane to oil molar ratio on percent FAME yield.

The results of varying hexane to oil molar ratio indicate that above molar ratio 103:1 hexane to oil, there is no significant increase in FAME yield percent.

Effect of methanol to oil molar ratio.

The results of in-situ transesterification on percent FAME yield from JCL seeds using different methanol: oil molar ratio are shown in Fig.4. From the results it is clear that increasing molar ratio of methanol: oil from about 112 to 865 increases oil conversion to FAME from 47.6% to 80.54% at 70°C after 4 hours reaction time. Increasing molar ratio to 950 no significant increase in FAME percent was observed.

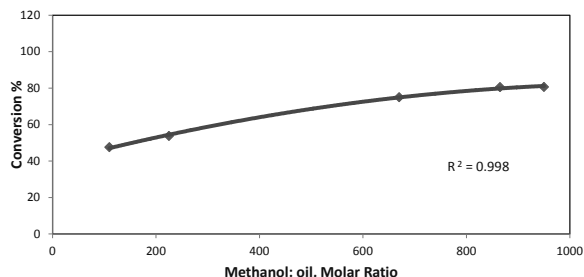


Fig.(4). Effect of methanol to oil molar ratio at 70°C, 700 rpm, 1wt of oil catalyst, 28 mesh size of seeds for 4 hrs.

Effect of catalyst dose on percent oil conversion to FAME.

The effect of activated calcium oxide amount on the FAME yield was investigated. The results revealed that the conversion reached its maximum at catalyst dose 5% by weight of oil (1% by weight of seeds) as shown in Fig.5. Above this dose (7% by wt of oil) the percent FAME yield decreases because more products were absorbed, and the yield of FAME decreased as shown in Fig.6 which is in good agreement with previous work. (20)

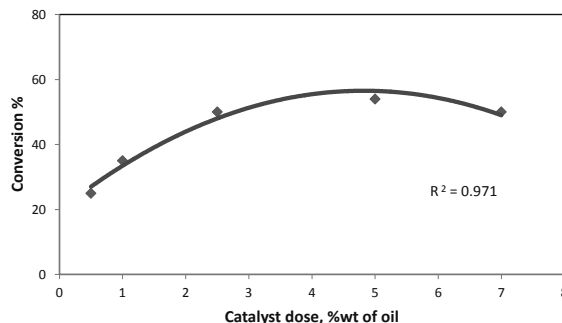


Fig.(5). Effect of catalyst dose on biodiesel yield at 70°C, 700 rpm with 3:1 volume ratio of n-hexane to methanol for 4 hrs.

The relationship between transesterification reaction and grain size of JCL seeds.

Two grain sizes of JCL seeds were studied in in – situ transesterification at 70°C with 5 :1 volume ratio of n-hexane to methanol, 1% by weight of seeds catalyst at different reaction times (3 to 6 hours).

Results shown in table 2 illustrated the two grain sizes were 12 and 28 mesh (1.7 mm and 0.6mm) and it is clear that differences in percent FAME yield ranged from 1.2% to 3%, which show significant change in conversion while when the reaction time reached 6 hours there are no any influence by the change in seeds particle size.

Table (2) Effect of grain size of jatropha seeds at 70oC, 700 rpm with 5:1 to methanol, 1% volume ratio of n-hexane by wt of oil catalyst at different reaction times.

Time h	Conversion%	
	12 mesh	28 mesh
3	45	47
4	51	54
5	75	79
6	80	80

Best results obtained at the experimental operating conditions applied in a final experiment from which the dependence of the conversion of jatropha seeds at these best reaction conditions reached about 91%.

4. CONCLUSIONS

Production process of biodiesel by combining extraction and transesterification with heterogeneous activated CaO catalyst proved to be successful and more advantageous than the conventional process. The process is simpler being in one step, so that only one reactor is required, avoiding the repeated heating and cooling processes.

Reproducibility of experimental results is within 2%.

Hexane played the role of both co – solvent and co – extractant, which enhanced the efficiency of liquid extraction and the formation of a single phase containing both methanol and lipid which facilitated the mass transfer.

Fatty acid methyl ester produced reached 1.82 % by weight of seeds (91%oil conversion) by applying the best operating conditions for transesterification of JCL seeds at 70°C, 700 rpm, 1% by weight of seeds catalyst, 5 : 1 by volume hexane to methanol after 6 hours reaction time ,1.9% by weight of seeds applying extraction with solvent followed by heterogeneous esterification which is insignificant difference regarding the advantages previously mentioned. Smaller seed particle size increases rate of reaction (from 1.2% to 3%) which indicated that the rate is controlled by internal mass transfer.

Methanol is a not very efficient solvent for oil extraction so it is mixed with n-hexane and optimum volume of n-hexane to methanol was found to be 1:5.

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