

Journal of Scientific & Industrial Research Vol. 79, December 2020, pp. 1080-1086



Transesterification of *Jatropha curcas* Oil by using K Impregnated CaO Heterogeneous Catalyst

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Received 24 August 2020; revised 22 September 2020; accepted 09 November 2020

Growing environmental concern and fast depletion of conventional fossil fuel resources have induced an urgent search for alternative energy sources. In this regard, biodiesel obtained from *Jatropha* oil (a non-food oil), seems to be a very promising alternative. Though a lot of research is already done in catalytic transesterification, in the present work, conversion of high FFA (5.5%) bearing Jatropha oil to methyl ester was studied using synthesized KF/CaO solid catalyst. The novelty of this heterogeneous catalyst is the omission of two major steps — neutralization step in which acid is used followed by transesterification using the basic homogeneous catalyst. The catalyst KF/CaO is easily prepared from cheap chemicals and is safe for the environment. The catalyst was characterized by mean of TPD of CO₂, X-ray diffraction, BET surface area (SA) analyzer. Catalytic transesterification of this oil was studied with different reaction parameters to achieve a 97% conversion. Optimization of conditions (molar ratio of methanol/oil, time, temperature and catalyst dosage) was also established. The present work makes the process not only safer to the environment but also shows the gateway for greener alternatives to the energy of high FFA oils.

Keywords: Biodiesel, CaO supported KF catalyst, FFA, Non-edible oil, Optimization

Introduction

Skyrocketing crude oil prices and environmental pollution have initiated the research towards alternative fuel resources.¹ Biodiesel is one such promising alternate fuel source. Biodiesels are mainly combination of fatty acid alkyl ester formed through the trans-esterification of vegetable oils and alcohol.² Transesterification being a reversible reaction requires 1.6 times higher methanol quantity to alter the equilibrium towards product.³ The process is generally assisted either by homogeneous acid-base catalysts or by heterogeneous catalysts.⁴ Biodiesel is non-toxic, biodegradable, renewable, free of sulphur, with low emission profile, and high flash point.⁵ It may be blended with petro-diesel and used in compression-ignition engines.

Out of the various raw materials, non-food oils are the selected ones for biodiesel formation, in view of food versus fuel conflict. However, most of such oils bear a higher percent of free fatty acid (FFA %) that interferes with the process of transesterification. In the commonly used process, the homogeneous catalysis, the higher content of FFAs is first neutralized by acid treatment and then alcoholysed with the help of base. Use of homogeneous catalysts (KOH, NaOH, etc.) has numerous disadvantages like complexity in transesterified product separation, requirement of a large amount of water for removal of the impurities, and presence of residual glycerol and catalyst in the organic phase. To overcome this problem, more environmental-friendly heterogeneous catalysts have been investigated.⁶ Solis base catalysts have benefits for instance easy isolation from the reaction product, reduced product cost, high activity, selectivity, reusability and longer catalytic life.^{7,8}

The transesterification of oil and alcohol has been established through different types of heterogeneous catalysts by earlier researchers. Corro *et al.* examined transesterification process for Jatropha oil and methanol using SiO₂'HF catalyst.⁹ Xie *et al.* reported 87% of methyl ester for transesterification of soybean oil using KNO₃/Al₂O₃ catalyst under the optimized condition of 15:1 methanol/ soybean oil molar ratio, 6.5% of catalyst in reflux condition for 7 h.¹⁰ Biodiesel obtained from sunflower oil by means of

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activated calcium oxide had been reported by Granados *et al.*¹¹ and more than 99% of methyl ester was produced using Sr^{2+} -CaO/MgO as a catalyst. The higher was attained due to high SA as well as the basic nature of the catalyst. The transesterification conditions were studied to decide the optimal conditions by Sr^{2+} -CaO/MgO.¹² Li *et al.* observed stable and magnetic CaO derived from MIL–100 (Fe) impregnated with Ca(CH₃COO)₂ is assumed to be a promising active solid catalyst for biodiesel synthesis¹³, while Vujicic *et al.* studied the CaO catalyst and obtained the maximum conversion (91%), synthesized from sunflower oils.¹⁴

Despite many successful approaches shown for the generation of biodiesel from bio-oil using CaO based catalysts, it suffers low stability under reaction conditions. Therefore modified CaO based catalyst need to have acid-base character and more stability to ensure successful processing of high FFA containing *J. curcas* oil. In the present work, KF/CaO catalyst was prepared to transesterify high FFA *J. curcas* oil. The catalyst performance was measured under mild experimental conditions. BET SA, XRD, CO₂-TPD were used for catalyst characterization. Further, its transesterification parameters have been optimized.

Experimental Details

Materials and Physico-Chemical Properties of the Stock Oil

J. curcas oil with slightly higher FFA (5.5%) was purchased from Churu, Rajasthan, India. All chemicals are reagent grade and used without further purification. Methanol (HPLC grade), CaO, and KF were procured from Sigma Aldrich, Bengaluru. The properties of Jatropha oil like acid value, saponification value, iodine value, unsaponifiable matters were determined through titration methods.¹⁵

Catalyst Preparation

The KF/CaO was synthesized using the wet impregnation technique. In this process, 10 gm of CaO was grinded to powder form and adsorbed in a 15–20 ml of KF solution (2.5 gm of KF) for 1 h. The prepared slurry was kept in a desiccator, connected to the vacuum pump to open pores of the support. Then the slurry was warmed in a water bath to remove the water content after that drying in air oven at 105°C for 5 h. After crushing, calcination was done at 600°C for a period of 4 h with the temperature program 105–600°C at the rate of 5°C/min.

Basic Characterization of the Catalyst

Basic characterization of the KF/CaO is very significant to identify the active positions of the catalyst towards transesterification reaction. These are BET SA, XRD and Basicity. Tristar 3000 surface area analyzer (Micromeritics, USA) was used to calculate catalyst SA. The catalysts SA were determined by BET method using N₂ as adsorbate gas at -196° C (liquid nitrogen Temp.). Phases of the catalyst were identified by XRD study using D-8 advanced (M/S Bruker AXS, Germany) X-ray defractometer. The prepared catalyst basicity was measured by CO₂-TPD technique using Auto Chem 2910 (Micromeritics, USA).

Transesterification Reaction

Jatropha oil (50 ml) and a certain quantity of developed catalyst were put in a 200 ml one-necked flat bottom flask coupled with a temperaturecontrolled magnetic stirrer and reflux condenser using water as coolant. The desired quantity of methanol was then added into the reaction vessel. The mixture has been stimulated and refluxed for 3 h at 65°C. When the reaction was finished, the reaction product was centrifuged and preserved for 24 hours without interference from catalyst particles. The product got separated into two layers, the top most layer is biodiesel and the bottom one is glycerol. The biodiesel was then distilled out under 4 mg of pressure at 170 to 190°C to obtain pure biodiesel. The progress of the transesterification reaction was periodically observed by Thin Layer Chromatography (TLC). C₆H₁₄, (C₂H₅)₂O and CH₃COOH were used as a solvent for TLC in the proportion of 85:15:1 respectively. Finally, for further analysis, pure biodiesel was used.

Quantification of ME in Biodiesel by Analytical Techniques

The ¹H-NMR analysis method was applied for the quantification of Jatropha oil conversion into the transesterified product. The ¹H-NMR study was executed using Bruker 300 MHz spectrometer using CDCl₃ solvent and tetramethyl silane (TMS) as the internal standard. The signal appears at 2.30 ppm due to methylene protons of all fatty acids products and the methoxyprotons of the methyl esters appear at 3.68 ppm were considered for quantification.

In addition, the Jatropha oil fatty acid composition and its biodiesel were determined by GC (Hewlett-Packard 5880) having DB-23 column coupled with FID (flame ionization detector). The GC condition was as follows: FID temperature and injector temperature, 250° C; running temperature programmed to 180° C for 1 min, then increased at 4° C/min up to 240° C and kept at this temperature for 15 min. The FAME was procured from Sigma-Aldrich and used as standards for GC analysis. The Jatropha oil's fatty acid composition found from chromatogram are shown in Table 1.

Results and Discussion

Catalyst Characterization

Based on nitrogen adsorption isotherms of CaO and KF/CaO catalyst, the SA of CaO and KF/CaO are found to be 3.48 and 5.99 m²/g respectively. The SA of CaO is lower as compared to CaO supported KF catalyst. The increase in SA might be because of the increased concentration of surface hydroxyl group on the surface of KF/CaO catalyst or open up of the closed pores over the catalyst at the time of calcination.

The main phases such as porlandite, lime, calcite, KCaF₃ are identified from the XRD spectra of KF/CaO. The accumulation of KF over CaO ends up with the creation of KCaF₃, mainly responsible for improved activity and stability of catalyst.¹⁶ The active constituent KCaF₃ may be formed during the calcinations process of the KF/CaO catalyst which is responsible to increase the biodiesel production.

CO₂-TPD was mainly studied to understand the catalyst basicity. Catalyst basicity was determined based on temperature of CO_2 peak appearance, the peak area and peak height. Considering the peak area of blank run and peak area of catalyst, the amount of catalyst basicity was calculated. Consequently, the catalyst basicity order has been identified on the basis of total amount of catalyst basicity. The total amount of basicity in CaO (201.64 µmol/g) is higher than the KF/CaO catalyst (117.17 µmol/g). Alternatively, the activity of KF/CaO was higher than the CaO in terms of catalytic performance. Low SA of CaO is considered as one of the causes those are responsible towards the lowering of catalytic activity. This might be due to the resistance involved during dispersion of the reactants to reach the basic active sites located inner layer of the catalyst.

Jatropha Oil and its Transesterification for Biodiesel using KF/CaO

Jatropha Oil's Physicochemical Properties

The Jatropha oil's physicochemical properties were estimated as per IS 3492 specification, which are

Table 1 — J. curcas oil's fatty acid composition					
Fatty acid	Percent (w/w)				
Stearic acid (C18:0)	10.9				
Linoleic acid (C18:2)	9.0				
Palmitic acid (C16:0)	23.2				
Arachidic acid (C20:0)	0.4				
Palmitoleic acid (C16:1)	0.8				
Oleic acid (C18:1)	52.0				

Та	ble 2 —	Physico-	chemi	cal p	properties of	of $J. \alpha$	<i>curcas</i> oil	
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Chemical properties	Experimental results	Specification IS 3492
Acid value (mg KOH/g)	2–14	Maximum 20
Saponification value (mg KOH/g)	188	185–195
Iodine value (g/100g)	94	93–107
Unsaponifiable matter (w/w percent)	1.1	Max 3.0

listed in Table 2. Most importantly, the crucial parameter such as acid number was 11 mg KOH/g (apprx. 5.5% FFA).

Determination of Methyl Ester in Biodiesel by ¹H-NMR

The spectrum of ¹H-NMR for Jatropha oil and Jatropha ME using KF/CaO catalysts are illustrated in Fig. 1a & 1b respectively. The ME obtained from Jatropha oil's conversionwas determined by the equation¹⁷:

$$C (Conversion) = 100 \times \frac{2A_{ME}}{3A_{\alpha-CH_2}}$$

C represents the conversion of TG to ME; A_{ME} represents summation of the integration methoxyprotons present in the ME; $A_{\alpha-CH2}$ represents total number of the methylene protons in the system. The digits 2 and 3 imply that two and three numbers of protons are present in methylene carbon and methoxide carbon respectively.

The appearance of the ¹H-NMR peaks around 4.2-4.4 ppm for Jatropha oil confirms the presence of glyceridic protons. The peak detected at 5.4 ppm corresponds to unsaturated protons in all the ME products and Jatropha oil. In ¹H-NMR band of biodiesel, the disappearing of glycedic protons (4.2–4.4 ppm) and presence of a fresh peak at 3.68 ppm reflects the –OCH₃ protons confirms the Jatropha oil conversion to biodiesel. GC profiles of Jatropha ME using KF/CaO are illustrated in Fig. 2, which gave the existence of different esters such as methyl



Fig. 2 — GC-FID chromatogram of Jatropha biodiesel

stearate (MeS), methyl linolenate (MeLn), methyl palmitate (MeP) and methyl oleate (MeO). Every element was estimated by relating the peak ranges with their available standards. The quality of the biodiesel has been assessed by using this method.

Catalytic Activity of CaO, KF and KF/CaO

Before catalyst preparation, the individual pure substrate was tried for Jatropha oil transesterification, which produced 22% and 82% of conversion using pure CaO and KF, respectively under optimized reaction conditions such as residence time 3 h; methanol/ oil molar ratio 10:1; catalyst dosage, 3 wt.% and temp. 65°C. Poor conversion with CaO resulted from soap generation. Endalew et al. stated almost 18 percent ME during the reaction between rich FFA containing Jatropha oil and methanol under identical condition in presence of CaO.¹⁸ Nevertheless, CaO was an active solid catalyst for the trans-esterification of slight FFA containing oils. But in high FFA oil, Ca²⁺ was leached from CaO in presence of alcoholic solvents and it reacted with FFA to form soap as a major drawback. This soap formation has reduced catalytic activity by reducing the probability of adsorption of CH₃OH on the catalyst surface and subsequently reducing the higher reaction rate. The conversion for high FFA oil was therefore very low. Soap formation was totally avoided during the trans-esterification reaction performed with KF/CaO catalyst under the same

experimental environments. The conversion was achieved by more than 97%.

Influence of Reaction Parameters on the Trans-Esterification of Jatropha Oil

Effect of Methanol/ Oil Molar Ratio on Conversion

The methanol/Jatropha oil molar ratio versus conversion is described in Fig. 3a. The reaction rate has rapidly rised with the methanol to oil molar proportion. The conversion increased more than 97% by using KF/CaO with a rise of molar proportion from 6:1 to 10:1. Nevertheless, once the molar fraction of alcohol-oil was over 10:1, the conversion remains unchanged. This result concluded the optimized methanol-oil molar ratio is 10:1. This is in-line with the previous experiment in which soybean oil was altered to biodiesel with a 10:1 methanol-oil molar ratio, using KF/ZnO as a solid base catalyst.¹⁹

Effect of Reaction Time on Conversion

The impact of time period on conversion was observed using a 3wt.% catalyst dosage at 65°C. The plot of time duration against conversion is presented in Fig. 3b. A steady rise in conversion upto 3 h of the reaction was observed after that it remained constant. The reaction took place fast and the conversion altered slightly after 3 h. So, the optimum conversion was found to be above 97% in 3 h. Biodiesel yield over 95% was obtained with 4% KF/CaO-Fe₃O₄ in 3 h at 65°C having molar ratio of 12:1.²⁰



Fig. 3 — Effect of reaction parameters on transesterification of Jatropha oil (conversion %): (a) methanol/oil molar ratio; (b) reaction time (h); (c) reaction temperature ($^{\circ}$ C); (d) catalyst amount (%)

Effect of Reaction Temperature on Conversion

The graph of temperature versus conversion is illustrated in Fig. 3c. Methanol/ oil molar ratio of 10:1 and 3% catalyst for transesterification reaction was studied in a variety of reaction temperatures, such as 60°C, 65°C, 70°C and 80°C. The conversion reached more than 97% at 65°C. However, the conversion decreased with further increase in temperature. At a temperature higher than 65°C, methanol can vaporize and converted to the gaseous methanol this could be a reason for the decreased oil's conversion. Conversion of oil to methylester is a temperature-dependent reaction.^{21,22} At higher temperatures, the conversion decreased. Wen et al. reported 96.8% biodiesel yield of Chinese tallow seed oil having acid value (2.4 mg KOH/gm) using KF/CaO catalyst at 65°C in 2.5 h with 12:1 molar proportion and 4 wt% catalyst amount.16

Effect of Catalyst Amount on Conversion

The influence of the KF/CaO catalyst quantity on conversion is shown in Fig 3d. It has been observed that the Jatropha oil conversion increases slowly when the catalytic amount is increased from 1 to 3 wt.%. The gradual increase in product yield was due to an upsurge in active positions in the reaction solution. Furthermore, analysis of several solid base catalysts in triolein and palm kernel oil transesterification shows that catalyst activity is narrated to the total basic sites.^{23,24} Though, the biodiesel product has improved only slightly with additional rise in the KF / CaO catalyst dosage. Thus, it was clear that higher catalyst loading did not have much influence to improve the conversion. The maximum conversion of 97% was attained in 3 h at 3 wt.% KF/CaO catalyst amount with a 10:1 molar ratio. Liu et al. reported, the best results in 3% SrO catalyst amount, 12:1 molar fraction of methanol to oil at 65°C while using soybean oil for transesterification reaction.²⁵ Li-CaO catalyst (5 wt%) was used for the Jatropha oil transesterification to attain maximum conversion.²⁶

Conclusions

Generally, non-traditional oils or waste cooking and industrial oils are available and recommended for non-food applications such as biofuel production. But these oils content high FFA, which needs special catalyst/process for economic conversion to biodiesel. The present modified catalyst KF/CaO overcomes the limitations & provided a conversion of more than 97%. The enhanced KF/CaO catalytic activity was found over CaO for the trans-esterification of 5.5% FFA Jatropha oil to ME. KF/CaO catalyst preparation demonstrated a vital part in achieving high catalytic recital. The catalyst activity observed in transesterification depended on the new active crystal present in the catalyst. XRD result also confirmed that the catalyst has fresh crystal KCaF₃ which increased catalytic stability and activity. Finally, 97% conversion has been achieved with catalyst calcined at 600°C for 4 h under the optimum state of methanol/Jatropha oil molar ratio of 10:1, 3 wt.% catalyst dosage, 65°C reaction temperature in 3 h.

Acknowledgment

The authors are thankful to the Director, CSIR-Central Institute of Mining and Fuel Research (CIMFR), Dhanbad, India for allowing to publish the paper.

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