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Full Length Article

Kinetics of amidation of free fatty acids in jatropha oil as a prerequisite for biodiesel production

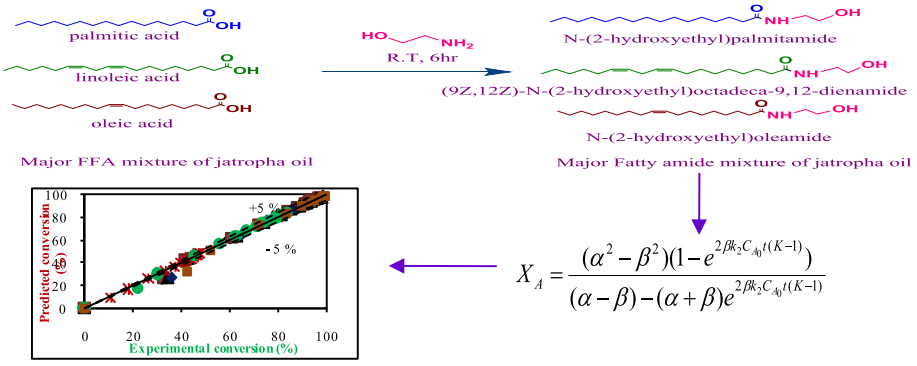
Hari Priya Das [a], T.S.V.R. Neeharika [b], Chintha Sailu [a], V. Srikanth [b], T. Prathap Kumar [c], K.N. Prasanna Rani [b,*]

[a] University College of Technology, Osmania University, Hyderabad 500007, India
[b] Centre for Lipid Research, CSIR-Indian Institute of Chemical Technology, Hyderabad 500007, India
[c] Chemical Engineering Division, CSIR-Indian Institute of Chemical Technology, Hyderabad 500007, India

HIGHLIGHTS

- It is a comprehensive study on amidation of FFA present in jatropha oil using monoethanolamine.
- Fatty acid amide obtained as by-product was established by with analytical tools such as IR, ^{1}H NMR and ESI-MS.
- Optimization of amidation process parameters.
- Development of a kinetic model for amidation of FFA Present in jatropha oil.

GRAPHICAL ABSTRACT



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ABSTRACT

Owing to the growing demand for transportation fuel, enormous efforts are being carried on development of alternate fuels mainly biodiesel from various renewable sources. Different pretreatment methods are adopted for the preparation of biodiesel, major one of the them is the removal of free fatty acids (FFA). Literature reveals esterification as an essential unit process for the reduction of FFA by conversion into its respective esters. In this study, FFA present in jatropha oil were reduced by amidation reaction using monoethanolamine for use in biodiesel. The by-product obtained is fatty acid amide. The fatty acid amide obtained was separated from the feedstock by filtration or centrifugation. This pre-treated oil can be directly transesterified for the preparation of biodiesel without undergoing any process step for removal of unreacted amine. Also, the reaction kinetics of jatropha oil with monoethanolamine was studied with batch experiments at 34–64 °C and at molar ratios of FFA-monoethanolamine varying from 1:0.5 to 1:2 with different speeds of agitation. Based on the experimental results, 1:1.5 FFA-monoethanolamine molar ratio at 34 °C and 550 rpm gave maximum reduction in free fatty acids. The effect of reaction conditions such as temperature and molar ratio on the kinetics has been studied. Observed reaction rate data was fitted to the regression technique. Estimated kinetic model reaction rate constants and equilibrium constant were fitted to the Arrhenius and van't Hoff equations respectively. The deacidified jatropha oil was transesterified by conventional method and was characterized for its physico-chemical properties.

* Corresponding author at: Centre for Lipid Research, CSIR-Indian Institute of Chemical Technology, Tarnaka, Uppal Road, Hyderabad 500007, India.
E-mail address: knpr@iict.res.in (K.N.P. Rani).

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1. Introduction

The transportation sector heavily relies on petroleum and petroleum derived fuels and there is a growing demand for transportation fuel [1]. Different alternatives are being explored in order to bridge the gap between supply and demand in the sustainable way. Biodiesel derived from plant oils is one of the most potential and promising options. Plant oils have the potential to provide functionally equivalent, renewable and environmentally friendly replacements for these finite fossil-based raw materials, provided that their composition can be matched to end-use requirements, and that they can be produced on sufficient scale to meet current and growing industrial demands.

Biodiesel produced from edible sources has the limitations of food security issues and hence not considered as a sustainable approach in Indian scenario [2]. Therefore, non-edible tree borne oils are promising candidates for biodiesel. Jatropha oil is one such oil.

Fatty acid amides are amides formed from a fatty acid and an amine. Fatty acid amides contain a saturated or unsaturated alkyl chain derived from a fatty acid and can be divided into these categories monoamides, secondary amides, tertiary amides and alkanolamides. Amides are formed by direct reaction of the fatty acid and ammonia at 180–200 °C and 0.3–0.7 MPa (3–7 bar) [3]. The most widely used synthetic route for primary amides is the reaction of a fatty acid with anhydrous ammonia. Alkanolamides are made from triglycerides, fatty acids, fatty acid methyl esters by reaction with monoethanolamine or diethanolamine using base catalysts.

They are widely used as lubricating or slip agents and polythene film additives. Hoong et al. [4] disclosed a rapid method of production for fatty acid amide from fatty acid and urea. Piazza et al. [5] prepared butyl amide of ricinoleic acid from a neat mixture of castor oil and n-butylamine without using catalyst.

Kumar et al. carried out aminolysis of oils such as used cotton seed oil, karanja oil and jatropha oil in the presence of a heterogeneous catalyst to obtain fatty acid alkanolamides for use in improvement of lubricity for diesel fuel. They have reported higher conversion of used cotton seed oil to fatty alkanolamides with 5 wt % of catalyst, 6:1 molar ratio of diethanolamine/oil and in 45 min [6]. Wang et al. synthesized oleoyl ethanolamide, where native oil was used as an acyl donor and a mixed solvent was used as the reaction media. The study reports more than 90% fatty acid ethanolamide after 3 h of reaction time [7]. Kolancılar prepared laurel oil alkanolamides from laurel oil and ethanolamine using ethanolamine/laurel oil molar ratio of 10:1 and claimed complete conversion in 9 h at room temperature [8].

A detailed discussion on chemistry, properties and applications of fatty acid alkylolamides is described by Sanders [9]. Karaulov synthesized fatty acid ethanolamides from *Linum catharticum* oils and *Cololabis saira* fats by aminolysis at 140 °C for 2 h. The researchers claimed yields of ~70% [10]. Another study by Wang showed 97.2% conversion of linoleoyl ethanolamide using methyl linoleate, ethanolamine and sodium methoxide at 30 °C [11].

Though an attempt was made earlier by some researchers using mono and diethanolamine as a free fatty acid removal agent present in vegetable oils [12], no literature exists on the application of amidation of free fatty acids present in oil as a pretreatment step for the preparation of biodiesel.

The main objective of this study was to reduce the free fatty acids present in jatropha oil by amidation using monoethanolamine. The advantage of the process is the added value generated by amidating the free fatty acids, thus lowering oil loss than conventional neutralization, and utilization of fatty acid amides obtained for further applications. This unit process best handles feed stocks with high FFA. The oil or fat used in alkaline transesterification reactions should contain no more than 1% FFA. If the free fatty acids level exceeds this threshold, saponification hinders the separation of the ester from glycerol and reduces the yield and the formation of fatty acid methyl esters. Hence, in an attempt to adopt a novel technique for the reduction of FFA, we have used amidation of free fatty acids as a pre-treatment in order to reduce the FFAs. The by-product obtained is fatty acid amide. This can be separated from the feedstock by filtration or centrifugation. This pre-treated oil can be directly transesterified for the preparation of biodiesel without any water washing step since the amidation reaction performed in this study does not require any catalyst unlike conventional esterification methods where mineral acids are adopted as catalyst. To the best of our knowledge, this method used here is the first of its kind employed for the removal of FFA In addition, kinetics of the amidation reaction also were determined and reported for the first time.

2. Materials and methods

2.1. Materials

Jatropha oil was purchased from the local market and used as such for our study. Monoethanolamine, methanol, potassium hydroxide and all other reagents were purchased from M/s. Sd. Fine Chem. Pvt. Ltd., Mumbai. The reagents were of 99% purity and used without any purification.

2.2. Analytical methods

The acid value was determined for the quantitative measure of the content of free fatty acids in the reaction mixture using AOCS method [13]. The extent of reaction conversion was based on the titrimetric analysis of the FFA in the samples and in the final product. Infrared (IR) analysis of the fatty acid amide obtained was carried out using Perkin Elmer Fourier-transform Infrared spectrophotometer (Model 1765, Perkin Elmer). ^{1}H NMR spectra were recorded on Bruker UXNMR spectrometer using $CDCl_3$ operating at 400 MHz at 25 °C. Chemical shifts δ are reported relative to tetramethylsilane (TMS) ($\delta = 0.0$) as an internal standard. Mass spectra were recorded using electron spray ionization-mass spectrometry (ESI-MS) using Waters e2695 separators module (Waters, Milford, MA) mass spectrometer. The fatty acid composition of jatropha oil was determined by converting them to fatty acid methyl esters followed by GC. The analysis of methyl esters was carried out using Gas Chromatograph Agilent 6890 series equipped with flame ionization detector [14]. The stationary phase used was a capillary column, DB-225 MS (i.d. 0.25 mm, length 30 m). The oven temperature was programmed from 180 to 220 °C at 5 °C per minute and nitrogen with a flow rate of 35 mL/min was used as carrier. The injector and detector temperatures were maintained at 250 and 300 °C respectively. The area percentage was recorded using HP Chem Station Data System.

2.3. Experimental procedure

Experiments for the kinetic study were carried out by reacting jatropha oil (150 g) containing 15.75 g of FFA and monoethanolamine (5 g) in a 250 mL stirred vessel equipped with a mechanical stirrer and provision for sampling. The reactor was then allowed to attain a constant temperature of 34 °C using a thermal bath with a speed of agitation of 550 rpm. Samples (1gm) were drawn at periodic intervals of 15–360 min to determine the disappearance of the FFA and conversion of the said reaction. The product (amide) formed during the reaction was separated from the reaction