



Kinetic Study of Neem Biodiesel Production

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Authors' contributions

This work was carried out in collaboration between all authors. Author ME supervised the synthetic study; author AEP supervised the kinetic study; authors JM, SS and MZK were involved in the analyses and measurements. All authors read and approved the final manuscript.

Research Article

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ABSTRACT

Aims: The kinetic features of neem biodiesel production were studied to establish the conversion parameters that govern optimal product yield in minimum reaction span. The mechanistic features of the dual acid/base catalytic conversion were investigated to gain an insight into the influence of methoxide nucleophilic attack and catalytic restoration on reaction yield in the final stage.

Study Design: The reaction kinetics was investigated by UV-Vis absorption spectrophotometry. Neem biodiesel was extracted from neem oil via a two-stage chemical process. The neem oil feedstock is comparatively high in free fatty acids and its reduction is facilitated by an initial acid-catalysed pre-treatment. The second stage constitutes base-catalyzed transesterification to neem biodiesel and the glycerol by-product at 55°C. The kinetic study focused on the second stage, which is underexplored with neem oil.

Place and Duration of Study: Chemistry Department, Arts and Sciences, The Petroleum Institute, Abu Dhabi, UAE.

Methodology: Suitable time intervals were selected to monitor the transesterification, and the absorbances of the resulting biodiesel were recorded in the far visible region at 700 nm (λ_{max}).

Results: It was found that the base-catalyzed reaction is rapid (<300 s) at the stipulated temperature and reaches completion after significant conversion to the biodiesel product. Absorbances were recorded after 1-minute cooling in an ice-water bath. Graphical delineation of the results revealed that the transesterification step conforms to zero-order kinetics. The difficulty encountered in making measurements was the fluctuating

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absorbances due to the separation of the phases – the rising biodiesel and the sinking glycerol.

Conclusion: The purpose of this study assists in defining the rate determining stage associated with the process. The biodiesel yield is 65% and inhibition of the reaction at lower temperatures or introduction of an inhibitor could be considered to prolong the final stage to acquire improved biodiesel yields.

Keywords: *Neem biodiesel; kinetics; mechanistic features; reaction order; spectrophotometry.*

1. INTRODUCTION

Alternative fuels play a role in contributing to sustainable development. The global search for economical feedstock to generate biodiesel to resemble petro-diesel has been the focus of intensive research [1-5]. The production of biofuel from non-edible crops tends to be cost efficient and the neem plant has been relatively underexplored for this purpose [6]. In this study neem biodiesel is being considered as a potential future biofuel and the primary purpose of investigating the kinetics of the transformation is to establish the reaction span and parameters that influence the rate of chemical conversion [7-9]. Studying the kinetic features of neem biodiesel production will focus on identifying the key factors that could be addressed to improve the process. Unlike most common biofuel processes the mechanistic features of neem biodiesel production are governed by a dual acid-base catalysed treatment, in the presence of methanol. According to the literature [8], both processes take about an hour - thus making the production of neem biodiesel lengthy and arduous. The rate-determining step (slowest step) in the process is associated with the first stage of reduction of free fatty acids (FFA) from neem oil. It lasts about an hour, and entails protonation of the carboxylic acid (FFA) followed by emergence of an oxonium intermediate. The presence of water interferes with the nucleophilic attack and can influence the rate of the process-thus the pre-acid treatment stage emerges as the rate-determining stage. The detailed mechanistic features and kinetics of the second stage have not been previously explored with neem oil and this work, therefore, makes a significant contribution to the development of an emerging alternative fuel.

Extensive studies have been conducted on the extraction of biodiesels from different feedstock and the characteristics of biodiesels of different origins on engine performances and emissions have become topics of increasing importance. Biodiesel can be derived from a variety of animal and vegetable oils [4,13-20]. Neem is made up largely of triglycerides and appreciable amounts of triterpenoid compounds, which give it the bitter taste. It is hydrophobic and emulsification in water, for medicinal purposes, requires formulation with appropriate surfactants. Neem oil also contains steroids (campesterol, beta-sitosterol, stigmasterol) and appreciable levels of triterpenoids of which azadirachtin is the most well-known and studied. The azadirachtin content of neem oil varies from 300 ppm to over 2000 ppm depending on the quality of the neem seeds crushed. The average composition of neem oil fatty acids is: Ω -6 linoleic acid: 6-16%; Ω -9 oleic acid: 25-54%; hexadecanoic acid: 16-33%; octadecanoic acid: 9-24% [5].

2. MATERIALS AND METHODS

2.1 Neem Biodiesel Preparation

Commercial neem oil was purchased from a retail outlet. Due to the high FFA content of neem oil a two-step process was used to produce the biodiesel [6,8]. Initially the neem oil underwent acid-catalyzed esterification followed by base-catalyzed transesterification. The acid esterification stage involved mixing 250 mL neem oil with 1% H₂SO₄ in the presence of methanol at about 55°C to reduce free fatty acids (FFA) [21-23]. The mixture was stirred for about 30 minutes and then separated in a separating funnel to remove the excess alcohol along with the impurities. The ensuing purified neem oil underwent alkaline conversion at the same temperature. For this process 5 g of KOH was dissolved in methanol and mixed with the separated product of the acid esterification process. Under final separation the esterified neem oil (biofuel) along with methanol float to the top. Methanol was evaporated and the residue (biodiesel) was tested for purity and found to conform to the parameters of commercial biodiesel [6].

2.2 Absorption Spectrophotometry

Neem biodiesel displays optimum absorbance in the far visible range, at 700 nm (λ_{max}). Absorbance studies were found to be convenient because no serious interference was encountered with neem oil and the other components in the mixture, all of which absorb at wavelengths remote from 700 nm. After the initial stage of acid treatment to remove excess free fatty acids, 25 mL aliquots of the separated neem oil were placed in round-bottomed flasks and simultaneously subjected to base transesterification under the appropriate experimental conditions. To ensure continuous monitoring of the chemical conversion, 3-5 mL-aliquots were siphoned from successive flasks at suitable time intervals (<1min), cooled to ambient temperature, transferred to glass cuvettes and subjected to digital absorption spectrophotometry. A Thermo Electron (USA) Genesys 20 visible spectrophotometer, Model 4001/4 was used. The analytical performance of the instrument was appropriately validated prior to each measurement. Absorbances relating to the biodiesel fraction were recorded directly from a digital-readout screen.

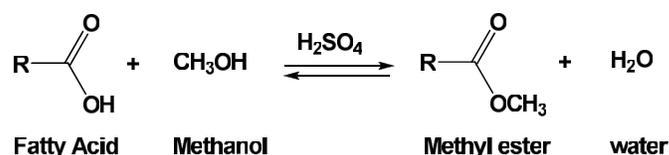
3. RESULTS AND DISCUSSION

3.1 Mechanistic Features

Stage 1 – Acid pretreatment (Fig. 1): free fatty acids (FFA) occur naturally with a high percentage in most inedible oils and in particularly neem oil [8]. Their presence in more than 2% can seriously affect the biodiesel yield by producing soap as a by-product [10]. Consequently, unwanted emulsification and separation problems occur. In order to decrease the FFA content in neem oil, an esterification of the feedstock under mineral acidic conditions should be initially performed to convert the excess of FFA to FAME (fatty acid methyl ester) [10]. According to E. Fisher [23], carboxylic acids can undergo esterification in the presence of an acidic catalyst producing water as by-product (Fig. 1). The first step of the process is the protonation of the carbonyl oxygen of the carboxylic acid leading to the formation of the oxonium ion (1), a strong electrophile, susceptible to a nucleophilic attack by the oxygen atom of the available alcohol (methanol in this case) to produce the oxonium tetrahedral intermediate (2). After multiple proton exchange reactions the neutral tetrahedral intermediate (3) can either eliminate a water molecule to produce the desired methyl ester

(4) or can lose methanol and dissociate back to the starting carboxylic acid (FFA) [11]. The main drawback of the Fischer esterification under acidic conditions is that all the steps are reversible. However, according to Le Chatelier's principle, this problem could be reduced if a large excess of alcohol is used or alternatively, by removing the produced water. Therefore, if the water content of the original sample of neem oil is high, the equilibrium will be shifted towards the hydrolysis of the tetrahedral intermediate (3) to the carboxylic acid formation. In addition to that, if water is present in the reaction vessel a competition between the two nucleophiles (H_2O and CH_3OH) might take place affecting therefore, the yield and rate of the desired product since water is a stronger nucleophile than some aliphatic alcohols [12]. The methyl esters produced could be hydrolyzed to the FFA which could prolong the process and affect the yield of the reaction.

General Reaction: Acid-Catalysed Pretreatment of Fatty Acids



General Mechanism: Acid-Catalysed Pretreatment

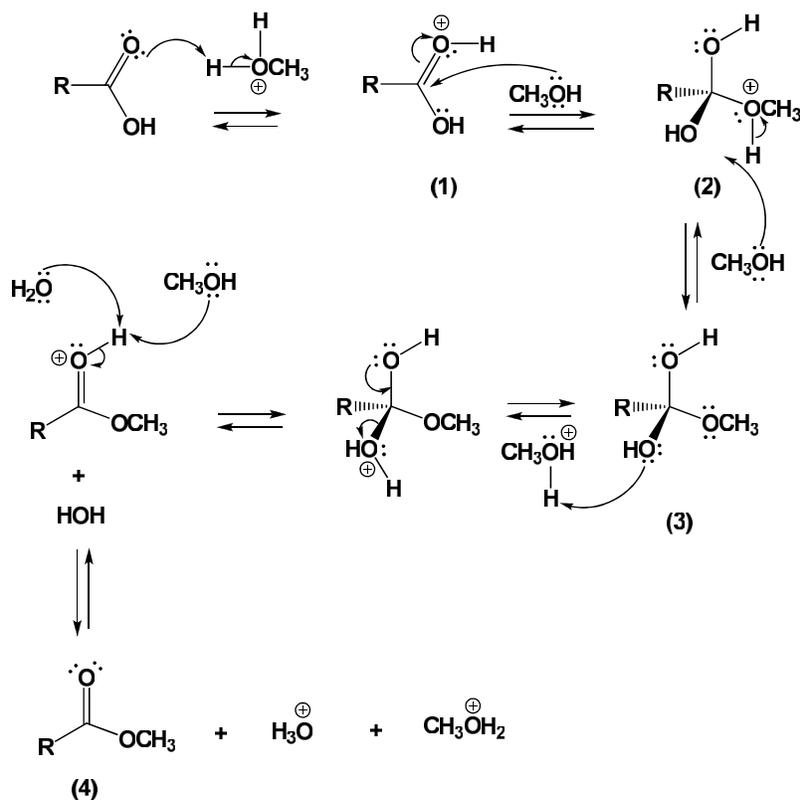


Fig. 1. Acid-catalysed esterification of neem oil into biodiesel

Stage 2 – Base transesterification [24]: the first step in the transesterification process under basic conditions is the nucleophilic attack of the methoxide ion to one carbonyl group of the triglyceride producing the tetrahedral alkoxide intermediate. This intermediate ultimately releases a methyl ester molecule while the corresponding diglyceride alkoxide is formed. The 3rd step of the process is a Brønsted acid-base reaction between the diglyceride alkoxide and methanol. The methanol loses a proton and produces another molecule of methoxide ion along with a diglyceride molecule. The latter is now ready for another cycle in which monoglycerides are formed followed by glycerol, respectively, while a molecule of methyl ester is formed in every stage. Like esterification, the transesterification is a reversible reaction. To get the desired methyl ester, the equilibrium reaction must be shifted in the right direction. Therefore, a large excess of the alcohol is usually employed as solvent. Here again, if the neem oil contains a high percentage of H₂O, a competition reaction between the hydroxide and the alkoxide ion would lead to the hydrolysis of some of the produced ester, with consequent formation of the carboxylate salt (soap). On the other hand, if the reaction is unfinished, there will be triglycerides, diglycerides and monoglycerides left in the reaction mixture in addition to glycerol [10], which leads to a very low biodiesel production yield and difficulties in isolating the methyl esters (biodiesel). Furthermore, even if the alcohol/oil mixture is water free, some water molecules are produced as by-products in both reactions, affecting the overall biodiesel formation yield.

Clearly, the mechanistic features of the dual acid-base conversion reflect areas of transformation that could inhibit the rate—such as the formation of sluggish intermediates or the rivalry between nucleophilic components. Therefore, it was essential to identify steps in the mechanism that could be addressed to improve the production yield and the kinetics. The presence of water affects both stages of the process, but its effect is more pronounced in the first stage, where it tends to strongly inhibit the overall transformation.

3.2 Kinetic Study

The main difficulty encountered in conducting the kinetic study was the problem of recording measurements quickly within the reaction span; and the need to establish accuracy of absorbance while faced with the rising biodiesel fraction, buoyant methanol and sinking glycerol in the cuvette. This created fluctuations in the readings and a lapse of time until the system stabilised. The biodiesel is trapped in the middle of the light-weight methanol and unprocessed neem oil at the top and the heavier glycerol at the bottom.

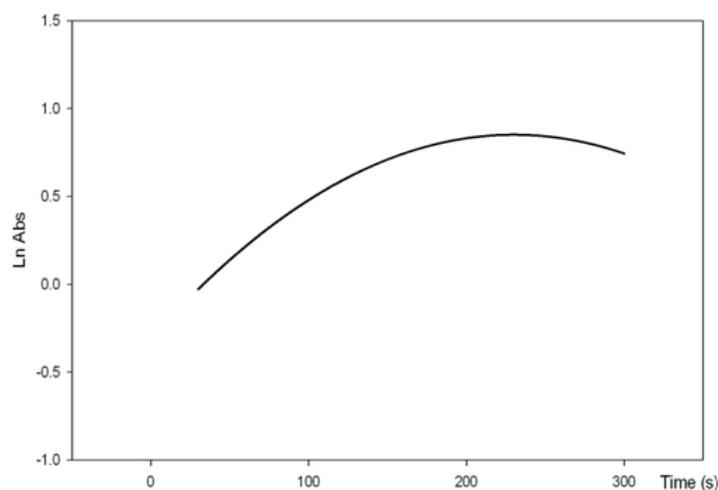
Minor colorimetric differences in the hue of the mixture with refinement of the neem biodiesel fraction could affect the molar absorptivity. However, neither methanol nor neem oil absorb in the region of neem biodiesel ($\lambda_{\text{max}} = 700 \text{ nm}$) and thus, the final digital readout when the spectrophotometer settled down could be considered valid, within experimental limits. Although temperature effects were controlled by cooling the sample, slight temperature gradients could also affect the molar absorptivity. The literature states that the dual acid-base catalysed conversion takes roughly 2 hours, with constant stirring. This constitutes about an hour for stage one (acid-treatment) and another for stage two (base-treatment). Most biodiesel processes from other feedstock [2] omit stage one and employ the base-catalysed conversion, which generally reduces the time taken by almost a factor of two – compared with this process as described in the literature. However, as shown below (under reaction order) the second stage of the process does not really make a difference to the span of the chemical conversion. The initial acid treatment stage to remove appreciable fatty-acid content from neem oil and secure a more refined starting material is the rate determining stage. The study clearly demonstrates that the duration of the second stage is

not appreciable and, thus, the overall time taken for the process is equivalent to the span of conventional biodiesel conversions. Therefore, for bulk preparation of neem biodiesel the order could be significant and could significantly influence the rate. These factors are discussed in detail below.

3.3 Reaction Order

Mathematical treatment of the data to determine reaction order was limited to the second step (base-catalysed conversion) [5,6]. The study focused on the direct relationship between absorbance and concentration (Beer's law), denoted by A, and elapsed time (seconds) to establish if it satisfied either first, second or zero order configuration. From basic kinetic principles it is evident that if any of the plots (best fits to the data) of $\ln A$ vs. time; $1/A$ vs. time; or A vs. time (Figs. 2a, b, c) conforms normally to a linear regression ($y = mx + C$) the reaction order is thus defined. Bearing in mind that the biodiesel product (not reactant) was measured the slope of a linear plot would be converse to that of a measured reactant, as expected.

Referring to Fig. 2a, a plot of $\ln A$ vs. time produced a distinct ascending curve indicating that linearity was absent. Fig. 2b, $1/A$ vs. time, resulted in a smooth descending curve, displaying no indications of linearity. Both curves seemed to gradually decline, from about 200 s, signaling the end of the process. Fig. 2c represents a plot of A vs. time and clearly delineates linearity in the first 200 s and as the chemical reaction reaches the closing stages the graph flattens out at values >200 s. The data (unbroken line) in Fig. 2c suggest that the base-catalysed transesterification process tends to conform to a zero order reaction. The reaction reaches completion in <300 s, indicating that for bulk preparation of neem biodiesel about 4 minutes are adequate to complete the process. Contrary to the literature [8] the second stage (base-catalyzed transesterification) is quick (<5 min) and involves rapid deprotonation of methanol with subsequent nucleophilic attack of the methoxide ion to a viable intermediate that leads to almost immediate formation of the biodiesel product. The rate is constant which is convenient as bulk concentrations will not be affected by the reaction rate (zero order). Clearly, therefore, the rate determining stage is the initial acid-catalysed conversion – and the second stage can be accomplished within a few minutes.



(a)

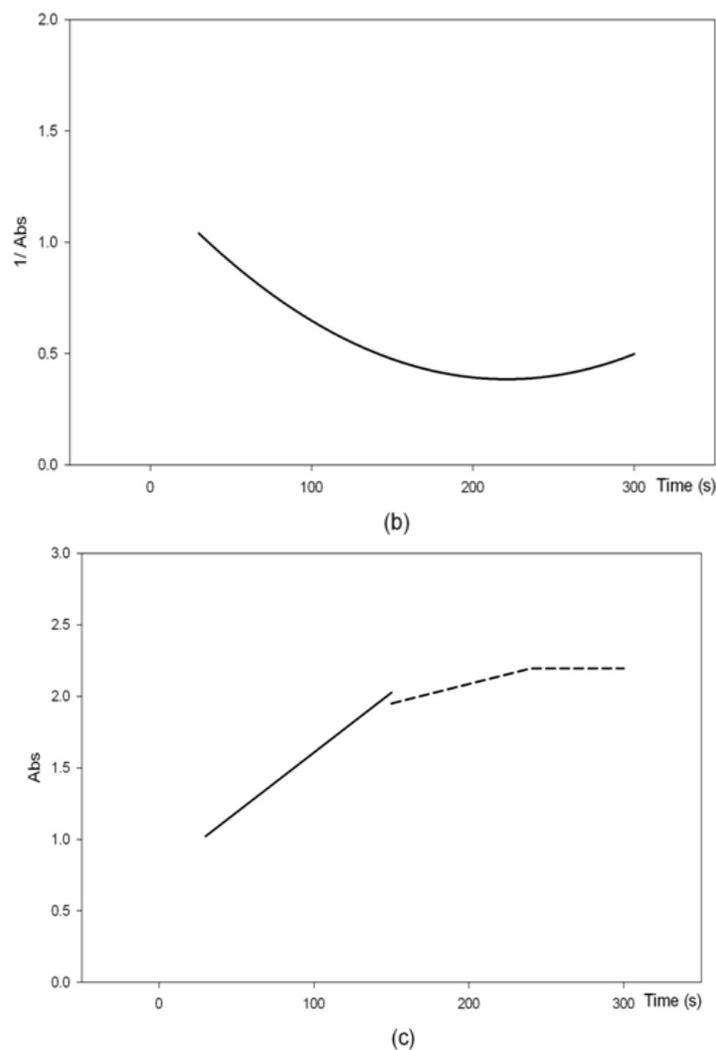


Fig. 2. Plots of: (a) $\ln A$ vs time; (b) $1/A$ vs time; (c) A vs time

4. CONCLUSION

Kinetic study of neem biodiesel (at 55°C) using digital absorption spectrophotometry (700 nm, λ_{\max}) established the reaction span and produced results that corresponded to zero-order configuration with reference to the final base-catalyzed stage of the conversion. Minor colorimetric differences and temperature gradients could affect the molar absorptivity, but the results were accurate within experimental limits. Our research establishes the duration of the final stage, which contrary to the literature, is within 300 s. This brings the dual acid-base process in line with the duration of other similar processes as the final base-catalyzed step does not contribute appreciably to the determination of the reaction rate.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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