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Kinetic modeling of catalytic esterification of non-edible macauba pulp oil using macroporous cation exchange resin

Keila L.T. Rodrigues[a], Vânya M.D. Pasa[b], Érika C. Cren[a,*]

[a] Department of Chemical Engineering, School of Engineering, Federal University of Minas Gerais, Belo Horizonte, Minas Gerais. 31270-90, Brazil
[b] Laboratory of Fuel Testing, Department of Chemistry, Institute of Exact Sciences, Federal University of Minas Gerais, Belo Horizonte, Minas Gerais, 31270-901, Brazil

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ABSTRACT

Conversion of non-edible oils through heterogeneous catalysis and their kinetic aspects are essential in order to produce economically viable biodiesel. Especially for oils containing high Free Fatty Acids (FFA) content since those cannot be viably converted through homogenous catalysis. Herein, the heterogeneous catalytic esterification kinetics of macauba pulp acid oil was exploited. The reaction tests were conducted in a stirred batch reactor with ethanol, and a cation exchange resin (Purolite® CT275)as a catalyst. The reaction kinetics was modeled based on a pseudo-homogeneous (PH) model of second order, showing good agreement with the experimental data acquired under different reaction conditions. The reaction progress was monitored by validated HPLC and GC methods. The internal and external mass transfer resistances were evaluated, and show that the rate limiting step is the surface reaction. To assess the catalyst stability, scanning electron microscopy was performed on both fresh and spent (after 10 reaction cycles) catalysts; reuse of catalyst was conducted without further treatment. The catalyst recycling demonstrates good performance where 85% of its performance was retained, and the SEM images show that the materials were structurally stable. Because the Pseudo-Homogeneous model properly described the kinetic aspects of the esterification process it was possible to estimate thermodynamic parameters by using the Arrhenius plot. The activation energy of the forward reaction was determined as 44.0 kJ/mol, while for the reverse reaction was 11.7 kJ/mol. Therefore, the kinetic and thermodynamic descriptions along with the catalyst stability upon several cycles without any further treatment reflect the viability of these resins for industrial application in the energy sector. Furthermore, combining these features with the low cost of macauba pulp acid oil, we conclude that the process is suitable for scaling up studies.

1. Introduction

Biodiesel is a well-recognized alternative biofuel with properties similar to petrodiesel [1]. It has potential to satiate energy demand and lessen green house gases, which consequently decreases global warming [2].Industrially, the main production process for biodiesel is the transesterification of vegetable oils via alkaline homogeneous catalysis to produce alkyl esters [3].The homogenous route has many advantages such as high selectivity, low reaction time, and obviates the use of high temperatures or pressures [4]. However, it inconveniently produces a large quantity of effluents originated from washing and neutralization steps, which are crucial to obtain the products [5]. Further, these effluents must be properly treated before disposal, which considerably increases production costs [6,7].

Importantly, for adequate catalytic performance in an alkaline homogenous system certain characteristics of the oil must be met. Its free fatty acids (FFA) proportion must not exceed 0.5% wt. and the water content must be less than 0.3%wt. [8]. These conditions are hindrance when working with oils with high FFA content, which induces soap formation as an unwanted by-product, hence requiring an additional separation process [9]. Thus, the homogeneous process has some restrictions and need high-quality raw materials, which implies high production costs, and in turn is not economically competitive with petrodiesel [10]. Therefore, alternative processes have been of extensive research in order to reduce the production cost of biodiesel.

The global cost for the biodiesel production can be considerably reduced by using bio-waste materials, such as used cooking oils, inedible oils, and animal fats [9,11]. Conversion of edible oils to biodiesel causes a negative impact on society because the reduction of food supply lead to an economic imbalance [1]. Thus, non-edible oils area promising alternate for traditional edible food crops for having low cost and is an eco-friendly source [12].Hence non-edible oils, such as

* Corresponding author.
E-mail address: erikacren@ufmg.br (É.C. Cren).

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macauba palm (*Acrocomia aculeata*)are suitable to be used as an alternative raw material for biodiesel production. Macauba palm is an important tree that grows in semi-arid tropical regions [13,14]. It has an oil production capacity of approximately 6.2 ton/year per acre [15], which is larger than that of soybean oil (~0.5 ton/year per acre),the main oleaginous raw material used for biodiesel production in Brazil [13]. Furthermore, the cost of macauba commercial crops is around US $ 78.19/ton, which is very competitive when compared to other crops, like *Jatroph acurcas* (US$ 810.00/ton), soybean (US$ 1360.00/ton), and palm (US$ 115.77/ton) [14].

The full use of its fruits can generate different products and co-products [6]. Other important characteristic of macauba palm is its perennial crop that has high resistance to pests, temperature variations, and the ability to grow in low-rain fall areas. Thereby, making it large-scale production sustainable, as required by the bioenergy sector [6,13,14]. However, the macauba pulp oil has high acidity, reaching FFA content above 65 wt.%, turning it unsuitable for homogenous catalysis [16]. The high FFA content in the pulp oil is formed mainly during the macauba fruit harvest and post-harvest period [17].

Alternatively, high-FFA oils can be processed by heterogeneous catalysts. The heterogeneous catalysis is advantageous when compared to its counterpart because the catalyst is easily recovered, reused, and allows one to convert high-FFA oils without soap formation; thus not requiring the neutralization and washing steps [3,18]. Recently, cation exchange resins have attracted considerable attention because of their easy catalyst separation, mild reaction conditions, no equipment corrosion, high concentration of acid sites, and lower wastewater production. They are porous polymeric solid catalysts that contain numerous active acid sites which can catalyze esterification reactions [19,20]. Furthermore, resins are suitable for long-time operations, commercially available [19], they show good catalytic stability and potential to industrial applications [17,19–24].There are few cation exchange resins especially designed for the esterification of high-FFA oils, namely, the Amberlyst™ and Dowex™ HCR-W2 series; both series of resins contain $–SO_3H$ as their active acid sites [20].

Moreover, raw materials for biodiesel production commonly contain bulky molecules such as glycerides and esters, which may occlude pores and prevent reactants to reach the catalytic active sites [20]. Thus, catalysts with lower porosity are undesirable to prevent catalyst deactivation. Additionally, the pore size must be large enough so reactants can diffuse into the internal area of the catalyst to assess the active sites. The opposite phenomena is observed in microporous materials where mass transfer allow results with an insufficient performance [12].

Owing to the complexity between chemical and physical properties of resins as catalysts, the kinetics of biodiesel production via esterification by macroporous cation resins is essential to bring this process to practical applications. Thus, it is essential to determine the production rate, energy consumption, and process optimization, since those are important parameters to determine the industrial applicability of these resins [21].One of the most used kinetic models in heterogeneous catalytic systems is the pseudo-homogeneous (PH) model. The pH model represents the rate-determining step as being the reaction of both reactants (e.g., carboxylic acid and alcohol in the esterification reaction) adsorbed on the catalyst surface [25].

Herein, the esterification kinetics of a bath process to produce ethyl esters by using a cation exchange resin (Purolite® CT275) as catalyst, and macauba pulp acid oil as raw material was investigated to show the applicability of this process. The pseudo-homogeneous kinetic model (PH) was applied to study the esterification kinetics under controlled reaction conditions. Additionally, the reusability of the catalyst and thermodynamic studies are also presented.

Table 1
Datasheet of Purolite® CT275 resin.

Property	CH-A
Structure	Macroreticular structure
Matrix	Polystyrene crosslinked with divinylbenzene
Appearance	Spherical Beads
Functional Group	Sulfonic Acid
Form	Acid form
Ion exchange capacity (meq/g)	5.2 (Dry)
Particle Size Range (μm)	650-900
Surface area (m^2/g)	20-40
Average pore diameter (Å)	400-700
Pore Volume (mL/g)	0.4-0.6
Specific Gravity (g/mL)	1.2
Moisture Retention	51-59 % (H^+form)
Maximum working temperature (°C)	120

2. Materials and methods

2.1. Materials

Macauba pulp oil was extracted from the pulp (mesocarp) of the macauba fruit (*Acrocomia aculeate)* using a screw press expeller. The oil was obtained from the Cooperative Riachão, an association of small rural co-workers in Montes Claros city(Minas Gerais State, Brazil). Macroporous cation exchange resin (Purolite®CT275) was supplied by Kurita Do Brasil LTDA (São Paulo State, Brazil) and used as a heterogeneous catalyst. Its properties summarized in Table 1 are reported by the company.

Anhydrous ethanol (99.8%) was obtained from Dinamycs® (São Paulo State, Brazil). Chromatography grade methanol (99.8%) and isopropanol (99.5%) were purchased from J. T. Backer (USA), and n-hexano (95%) from Mallinckrodt Chemicals (USA).Ionized water was obtained by purification using a Millipore Direct-Q® system (Darmstadt, Germany).

2.2. Macauba pulp oil characterization

The physical-chemical characterization of the macauba oil started by removing solid particle residues from the crude oil using a filter paper with an average pore size of 28 μm. Chemical composition of major fatty acids was determined by converting fatty acids to methyl esters, and further analyzing the products by gas chromatograph (Shimadzu). The GC system was equipped with a flame ionization detector, and the analysis condition was performed according to AOCS Official Method Ce 1-62 [26]. The water content was quantified by Karl-Fischer titration, according to ASTM D4176 Official method [27], while the FFA content was determined by titration according to AOCS Ca 5a-40 Official Method [28].

2.3. Esterification process

The esterification reaction was carried out in a batch system using a jacketed glass reactor vessel of 110 cm^3, connected to a thermostatic bath to control the temperature of the reactor heating fluid. A thermocouple to measure the reaction temperature, and a reflux condenser was attached to the reactor, which was operated under Purolite CT275 stirring conditions using and magnetic stirrer bar and constant temperature. All the experiments were carried out with 30 g of macauba pulp oil, 30.4 wt.% of catalyst loading (Purolite CT275 resin), molar ratio of ethanol to oil at 8.6:1, and evaluated of during 9 h of reaction. Aliquots of 500 μL were withdrawn by syringes and the FFA conversion was determined by High Performance Liquid Chromatography (HPLC) according to methodology described in section 2.4.