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TECHNOLOGICAL FEATURES OF PROCESSING VEGETABLE OILS INTO FUEL

A mathematical model describing the transformation of technical animal fats under the influence of alcohol and a catalyst in the biodiesel.

Key words: *mathematical modeling, methyl ester, transesterification, animal fat.*

Introduction. Biodiesel is a clean burning fuel derived from a renewable feedstock such as vegetable oil or animal fat. It is biodegradable, non-inflammable, non-toxic and produces lesser CO₂, sulfur dioxide and unburned hydrocarbons than petroleum-based fuel. Biodiesel is a fuel made from fat. Either virgin vegetable oil or waste vegetable oil can be used to make quality fuel. Fats are converted to biodiesel through a chemical reaction involving alcohol and catalyst. Nowadays, due to the price of virgin oil such as canola, soybean oil, the use of low-cost feedstock, such as waste frying oils in an acid-catalyzed process, should help make biodiesel competitive in price with petroleum diesel, beyond being a suitable way to reuse waste materials. Alternatively, it is a good strategy to find out some vegetable oils that is not used in the food chain so that they tend to be a cheaper feedstock, as is the case for castor oil. Bioethanol (ethanol from biomass) is an alternative to methanol, because it allows production of entirely renewable fuel [1]. For both feedstocks, the transesterification reaction takes place in the biodiesel process production. This reaction can be carried out in the presence of alkaline, acid, and enzyme catalysts or using supercritical alcohol [2].

Bearing this in mind, in this work the modeling of transesterification process of vegetable oils is studied with focus on developing a systematic method that can be used whenever an estimation of reaction rate constants is necessary.

Materials. The castor oil was obtained and the frying vegetable oil was collected from a local restaurant. The castor oil had 1.2 % of free fatty acid (FFA) and the frying oil had 3.2% of free fatty acids (determined according to the AOCS official method Ca 5a-40 as oleic acid).

Equipment. The experiments were carried out in a batch stirred tank reaction (BSTR) of a 1 liter reactor, equipped with a reflux condenser, a mechanical stirred, and a stopper to remove samples.

Method of analysis. Gel-permeation chromatography (Waters, USA) also called high-performance size-exclusion chromatography (HPSEC) was used for the triglycerides, diglycerides, monoglycerides, ethyl esters and glycerol analysis according to Shoenfelder [6]. The mobile phase was HPLC-grade tetrahydrofuran (JT Baker, USA). The relative percentage of each component (x_i) was give by HPSEC and it was determined by Eq. 1, where x_i was calculated dividing the peak area of the ester by sum of the peak area of all components.

$$x_i = \left(\frac{A_{EE}}{A_{TG} + A_{DG} + A_{MG} + A_{EE} + A_{GL}} \right). \quad (1)$$

The molar concentration was calculated using Eq. 2. M_i was determined by dividing the product of the density (d_i) by the relative percentage x_i by the molecular weight of each component (Mw_i).

$$M_i \text{ (mol/L)} = \left(\frac{x_i \times d_i \times 1000}{Mw_i} \right). \quad (2)$$

Experimental conditions. The system was maintained at atmospheric pressure and the experiments were carried out at constant temperature. The agitation was kept constant at 400 rpm. The reaction time was about 25 minutes. The experiments were carried out with 1% wt of sodium hydroxide, molar ratio ethanol: vegetable oil of 6:1. To examine the temperature dependency of the reaction rate constants, reactions at 30, 40 and 50°C were studied.

CAPE tool for Biodiesel Production (Transesterification)

Specifically, a step-by-step optimization procedure for the calculation of the reaction rate constants as a function of temperature used in this work is described below:

Determining the appropriate forms of rate expressions. A system of differential equations based on kinetic model presented by Nouredini and Zhu [1] and Bambase et al. [2], shown in Eqs. 3-8, were used to model the stepwise transesterification reaction.

$$\frac{d[\text{TG}]}{dt} = -k_1[\text{TG}][\text{A}] + k_2[\text{DG}][\text{EE}] - k_7[\text{TG}][\text{A}]^3 + k_8[\text{GL}][\text{EE}]^3, \quad (3)$$

$$\frac{d[\text{DG}]}{dt} = k_1[\text{TG}][\text{A}] - k_2[\text{DG}][\text{EE}] - k_3[\text{DG}][\text{A}] + k_4[\text{MG}][\text{EE}], \quad (4)$$

$$\frac{d[\text{MG}]}{dt} = k_3[\text{DG}][\text{A}] - k_4[\text{MG}][\text{EE}] - k_5[\text{MG}][\text{A}] + k_6[\text{GL}][\text{EE}], \quad (5)$$

$$\frac{d[\text{GL}]}{dt} = k_5[\text{MG}][\text{A}] - k_6[\text{GL}][\text{EE}] + k_7[\text{TG}][\text{A}]^3 - k_8[\text{GL}][\text{EE}]^3, \quad (6)$$

$$\frac{d[\text{EE}]}{dt} = k_1[\text{TG}][\text{A}] - k_2[\text{DG}][\text{EE}] + k_3[\text{DG}][\text{A}] - k_4[\text{MG}][\text{EE}] + k_5[\text{MG}][\text{A}] - k_6[\text{GL}][\text{EE}] + k_7[\text{TG}][\text{A}] - k_8[\text{GL}][\text{EE}]^3, \quad (7)$$

$$\frac{d[\text{A}]}{dt} = -\frac{d[\text{EE}]}{dt}, \quad (8)$$

where [TG], [DG], [MG], [EE], [A] and [GL] are the respective concentrations of triglyceride, diglyceride, monoglyceride, ethyl ester, alcohol, and glycerol expressed in mol/L. Kinetic rate constants have units L/mol·min.

Estimating a set of temperature dependent kinetic rate constants for each temperature considered in the experiments. Temperature dependent kinetic rate constants of the three consecutive and reversible reactions were established based upon the kinetic scheme presented in Eqs. 3-8. Let θ specify the parameters vector, which contains all the kinetic rate constants. The objective of the mathematical estimation of model parameters is to find out θ by minimizing the objective function, $\min E(\theta)$:

$$E(\theta) = \sum_{n=1}^{np} \left[\frac{([\text{TG}]_n - [\text{TG}]e_n)^2}{[\text{TG}]e_{\max}^2} + \frac{([\text{DG}]_n - [\text{DG}]e_n)^2}{[\text{DG}]e_{\max}^2} + \frac{([\text{MG}]_n - [\text{MG}]e_n)^2}{[\text{MG}]e_{\max}^2} + \frac{([\text{GL}]_n - [\text{GL}]e_n)^2}{[\text{GL}]e_{\max}^2} + \frac{([\text{EE}]_n - [\text{EE}]e_n)^2}{[\text{EE}]e_{\max}^2} \right] = \sum_{n=1}^{np} \varepsilon_n^2(\theta), \quad (9)$$

where [TG] e_n , [DG] e_n , [MG] e_n , [GL] e_n and [EE] e_n are the molar concentrations of triglyceride, diglyceride, monoglyceride, glycerol and ethyl ester at the sampling time n . [TG] $_n$, [DG] $_n$, [MG] $_n$,

$[GL]_n$ and $[EE]_n$ are the concentrations computed by the model at the sampling time n . $[TG]_{e_{max}}$, $[DG]_{e_{max}}$, $[MG]_{e_{max}}$, $[GL]_{e_{max}}$ and $[EE]_{e_{max}}$ are the maximum measured concentrations and the term np is the number of sampling points. Here, $\varepsilon_n(\theta)$ is the error in the output due to the n th sample.

Applying an equation based on Arrhenius form to describe the influence of temperature and fit it to the optimized values obtained for each temperature. From the k -values obtained at different temperatures, the activation energy for each ethanolysis step was estimated using the integrated form of the Arrhenius equation:

$$k = Ae^{-\frac{E_a}{RT}}, \quad (10)$$

where k is the reaction rate constant, L/mol·min; A is the frequency factor; E_a is the activation energy, cal/mol; R is the universal gas constant, $R=1.9872$ cal/mol·K and T is the absolute temperature, K. Results and Discussion. The frying oil had a free fat acid (FFA) content higher than 1%; then the alkaline catalyst would be destroyed because the FFA reacted with the sodium hydroxide to produce soaps and water, hence, reducing the ester conversion. Fig. 1 (A and B) show the effect of the time on the frying oil and on the castor oil transesterifications. The castor oil transesterification is very rapid because the ethyl ester concentration is 2 mol/L, (conversion of 72%) after 2 minutes, while that the higher conversion for frying oil (72%) is achieved after 20 minutes, at the same temperature (50°C).

In the transesterification reaction, the reactants initially form a two-phase liquid system, because the TG and alcohol phases are not miscible [3]. This fact decreases the contact between the reactants and consequently, the reaction conversion.

The castor oil and its derivatives are completely soluble in alcohols [7]. This fact leads to increase the mass transfer in the first stage of the reaction, and hence the ester conversion. Thus, the kinetic constant of the castor oil reaction (TG → DG) is higher than of other vegetable oils, for the same process temperature.

Summary. The performances of a reliable systematic procedure to describe the reaction kinetic of the transesterification process were assessed.

The kinetic model presented acceptable fits, in comparison to experimental observations, using the proposed methodology. Values of activation energy for ethanolysis reaction indicated that higher temperatures favor the formation of DG (for the reaction $TG \leftrightarrow DG$ values of E_a for the forward reaction has a magnitude higher than the corresponding backward step), but also favor the consumption of MG and GL (for $DG \leftrightarrow MG$ and $MG \leftrightarrow GL$ values of E_a for the forward reaction has a magnitude lower than the E_a of the inverse reaction)

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ТЕХНОЛОГІЧНІ ОСОБЛИВОСТІ ПЕРЕРОБКИ РОСЛИННИХ ЖИРІВ У ПАЛИВО

Наведені математичні моделі, що описують процес перетворення технічних тваринних жирів під дією спирту і каталізатора у дизельне біопаливо.

Ключові слова: математичне моделювання, метиловий ефір, переестерифікація, тваринний жир.

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ТЕХНОЛОГИЧЕСКИЕ ОСОБЕННОСТИ ПЕРЕРАБОТКИ РАСТИТЕЛЬНЫХ ЖИРОВ В ТОПЛИВО

Приведены математические модели, описывающие процесс преобразования технических животных жиров под действием спирта и катализатора в дизельное биотопливо.

Ключевые слова: математическое моделирование, метиловый эфир, переэстерификация, животный жир.

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УДК 621.396.96.095.4

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ФУНКЦІЯ НЕВИЗНАЧЕНОСТІ ДВОАНТЕННИХ РАДІОМЕТРИЧНИХ КОМПЛЕКСІВ

Проведено ґрунтовне дослідження функції невизначеності двоантенного радіометричного комплексу. Виявлено зміну форми функції невизначеності при переході від обробки вузькосмугових до надширокосмугових просторово-часових сигналів та надано фізичну інтерпретацію цій зміні. Доведено, що традиційні для активної радіолокації критерії широкосмуговості та надширокосмуговості не можуть бути використані у пасивній радіолокації. Отримані у статті результати можуть скласти основу розроблюваних відповідних критеріїв, які врахують класичне відношення ширини смуги до центральної частоти настройки приймача та геометрію антенної системи радіометричних комплексів.

Ключові слова: функція невизначеності, радіометричний комплекс, критерії, радіолокація.

Вступ. На сьогодні один з основних критеріїв за яким активні радіолокаційні системи розділяють на вузькосмугові, широкосмугові та надширокосмугові (НШС) є порівняння з порогом відношення ширини смуги ΔF робочих частот до центральної частоти f_0 високочастотної частини приймача. Зокрема, вважається [1, 2], що радіолокаційні системи, які задовольняють умові $\frac{\Delta F}{f_0} \leq 0,01$ – є вузькосмуговими, умові $0,01 < \frac{\Delta F}{f_0} < 0,2$ – є широкосмуговими і умові $0,02 < \frac{\Delta F}{f_0} < 2$ – є надширокосмуговими. Таке розподілення, як показано нижче, не може бути перенесено на класифікацію радіометричних комплексів (РМК).

У статті не уточнюються відомі критерії, а розробляються нові критерії класифікації РМК, засновані на аналізі форми функції невизначеності (ФН) РМК.