

Biodiesel production through transesterification of soybean oil: A kinetic Monte Carlo study



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ABSTRACT

In the present study, biodiesel production was investigated through transesterification of soybean oil with methanol in presence of NaOH by kinetic Monte Carlo simulation. In this research the kinetic Monte Carlo simulation results qualitatively agree with the existing experimental data. The kinetic parameters for each step of mechanism have been confirmed by simulation. By using the mechanism and kinetics data, the system was studied at different methanol/oil feed ratios and a comparison between kinetic data was provided. The effects of reaction temperature and percentage of catalyst on the rate of reaction were studied.

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1. Introduction

Consuming the diesel fuel has been continuously increasing over the past few years. Emissions of harmful gases such as CO₂, CO, SO_x, NO_x and particulates generated by diesel fuel combustion have led to a serious greenhouse effects, acid rain and the deterioration of human health. Therefore, the identification of environmentally friendly and renewable sources of alternative energy is becoming an urgent mission for researchers [1]. Biodiesel is considered to be an alternative fuel with properties similar to petroleum diesel [2,3]. First, it is made of renewable biological sources, such as herbal oils and animal fats, which react with an alcohol in presence of a catalyst. As further advantages of biodiesel, this fuel is non-toxic, biodegradable and with low emission profiles in comparison to petroleum diesel [4].

Biodiesel fuel is defined as the mono-alkyl esters of long-chain fatty acids synthesized by transesterification of triglyceride in herbal oils or animal fats with alcohol, and is therefore a renewable energy resource [5,6]. It is a process similar to hydrolysis except that water is replaced by alcohol. The resulting extracts are mainly biodiesel and glycerol. The short chain alcohols such as methanol, ethanol, and butanol are frequently used. For practical purposes, methanol is commonly used in biodiesel processes. Methanol is convenient, because of its insensitivity to water. It is used most frequently because of its suitable physical and chemical properties and low cost.

The methanolysis reaction requires presence of a catalyst. Conventionally, biodiesel is produced by chemical alkali- or acid-catalyzed transesterification with short chain alcohols such as methanol and ethanol in presence of inorganic basic or acid catalysts (KOH, NaOH and H₂SO₄) with homogeneous method [7]. In recent years, both the methanolysis of vegetable oils with homogeneous basic catalysts have been widely investigated [8,9]. The most important variables that influence the methanolysis reaction are the type and concentration of the catalyst, the molar ratio of methanol to herbal oil, the reaction temperature, the agitation intensity and purity of reactants.

Reaction kinetics is essential for reactor and process analysis, design, simulation and control. Several authors have investigated the kinetics of homogeneously catalyzed methanolysis [10–13]. Bambase et al. [14] investigated the effect of agitation speed, temperature, catalyst loading and methanol to oil ratio on hydroxide-catalyzed methanolysis of crude sunflower oil. Freedman and coworkers [15] investigated both acid- and alkaline-catalyzed transesterification of soybean oil with butanol and methanol. They proposed pseudo first order kinetics at large molar excess of alcohol and second-order kinetics combined with a shunt reaction scheme at the lower alcohol excess level. Nouredini and Zhu [16] studied transesterification of soybean oil with methanol. In this study, a second-order reaction mechanism was evaluated by mathematical modeling. The reaction rate constants and the activation energies were determined for all the forward and reverse reaction. Diasakov et al. [17] reported kinetics on non-catalytic transesterification reaction of soybean oil processed at 220–235 °C. Wenzel et al. [18] developed a mathematical model describing chemical kinetics of transesterification of soybean oil. They used this model to study the

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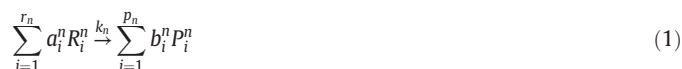
transesterification without catalyst and in presence of NaOCH_3 as a catalyst.

Kinetic Monte Carlo simulation was chosen as a powerful tool in simulating chemical reaction systems [19–21]. In the present study, kinetic Monte Carlo simulation has been utilized to study the rate of transesterification of soybean oil with methanol in presence of NaOH . According to the obtained kinetic data by simulation, the effect of alcohol/oil feed ratio, reaction temperature and percentage of catalyst on the rate of reaction will be studied. These tests could provide a simple screen for developing catalytic systems of methanolysis of soybean oil in presence of NaOH . These data reveal the optimum reaction temperature, alcohol to oil feed ratio and percentage of catalyst.

2. Simulation method

In 1976, Gillespie developed the stochastic simulation algorithm via Monte Carlo methods, in a way that correctly samples the dynamic probability distribution of possible reactions [22]. Stochastic simulations of reaction processes are a powerful and accurate tool for development of quantitative, microscopic models from experimental data, particularly when the kinetics are quite complex. In this study, the Kinetic Monte Carlo (KMC) has been used for simulation of experimental data. Kinetic Monte Carlo simulation was carried out with the help of Chemical Kinetic Simulator (CKS) software, version 1.01 (from IBM, Almaden Research Center, <http://www.Almaden.ibm.com/st/msim/>) [23].

A collection of molecules of different chemical species is considered. The initial concentration of molecules of each species i is C_i . The species interact via a set of M chemical reactions. The n th reaction can be written in familiar form as follows:



where k_n is a reaction rate constant, R_i^n is a reactant molecule of a particular chemical species, and similarly for product molecules P_i^n . The number of reactants is r_n and the number of products is p_n . a_i^n and b_i^n are stoichiometric coefficients.

In the stochastic simulation algorithm, the system evolves one reaction at a time, changing the counts of reactant and product molecules, and thus the associated species concentrations. Which reaction occurs next and the time at which it occurs are chosen using random numbers and probabilistic rules that ensure accurate sampling. In this algorithm, transition rate (a_i) is computed for each reaction, which is proportional to its probability of occurrence relative to other reactions. The propensity for a first-order is $a_i = k_i C_i$ and for a second-order reaction is $a_i = k_i C_i C_j$. Each of the pathways has its own transition rate a_i , and the total transition rate must be the summation of them:

$$a = \sum_i^M a_i \quad (2)$$

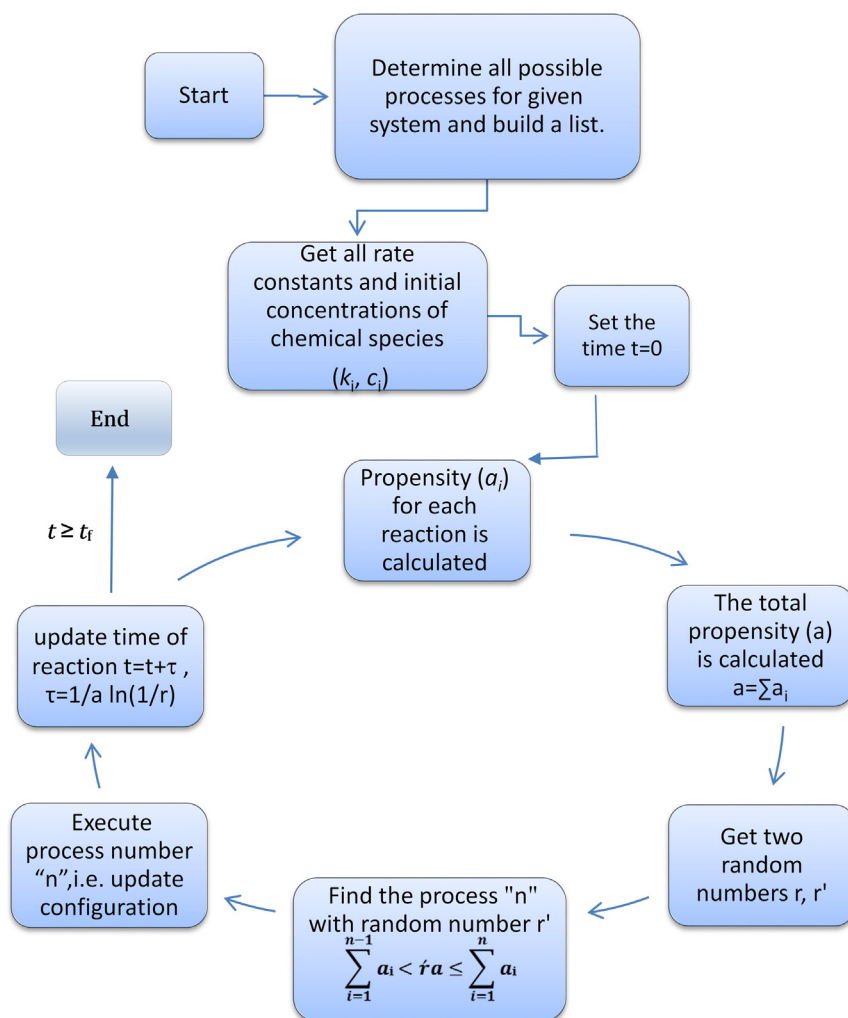


Fig. 1. Flow chart for the process-type list algorithm.

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