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Biodiesel production in a counter-current reactive extraction column: Modelling, parametric identification and optimisation

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HIGHLIGHTS

- A novel biodiesel process in a counter-current reactive extraction column.
- A stepwise reaction–separation model for counter-current reactive extraction.
- Model parameters and process optimisation using an evolutionary algorithm.
- Optimum conditions provide for conversion of 97.7% and yield of 99.5%.
- Counter-current productivity is higher than co-current and batch processes.

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ABSTRACT

Reactive extraction is a potential alternative for biodiesel production, in which reaction and glycerol separation are simultaneous, increasing conversion, yield and process productivity. This paper presents a stepwise reaction–separation model for a counter-current reactive extraction column, used in homogeneous-base-catalyzed palm oil methanolysis, and the models' parameters are identified from the results of a set of experimental tests. In addition, multi-criteria optimisation of the process conditions was performed using an evolutionary algorithm. The optimum conditions provide for palm oil conversion of 97.7%, a yield to FAME of 99.5% and a process productivity of 1.4 m^3 FAME h^{-1} m^{-3} in a single reaction step. Finally, a comparison of the process productivity with co-current and batch processes was made. As the counter-current reactive extraction process does not require the intermediate separation stages required in co-current and batch processes, its productivity is 1.5 and 6.9 times higher than those processes, respectively.

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1. Introduction

Biodiesel is a mixture of fatty acid methyl esters (FAMEs), mainly obtained through the transesterification of fats and oils. The physical properties of biodiesel, which are similar to those of diesel [1,2], the fact that it is produced from renewable raw materials and the environmental advantages resulting from its use [3–5], have transformed biodiesel into the main alternative to replace diesel. Most commercial biodiesel processes use batch stirred tank reactors (STRs) [6] and alkaline homogeneous catalysts [7]. However, these processes have disadvantages in the reaction step, associated with mass transfer and chemical equilibrium limitations, as well as problems in the separation stages, especially when poor quality oils are used as raw materials. Chemical equilibrium, mass transfer limitations and the maximum total glycerol content of the final product, which can be as low as 0.240% w/w [8], in addition to other quality requirements set forth in biodiesel standards, necessitate the search for process strategies to increase oil conversion and yield to FAME.

One of the strategies implemented is the removal of glycerol from the reaction mixture to drive reaction to completion [9]. Batch processes usually have two or more reaction steps, separating the glycerol-rich phase between them and feeding fresh methanol into the next reactor [10,11]. However, recent investigations report the use of process intensification to perform reaction and glycerol separation simultaneously. For example, Dubé et al. [12], Baroutian et al. [13], Cheng et al. [14], among others, evaluated the use of membrane reactors; He et al. [15] and Kiss et al. [16] studied reactive distillation processes, although the latter produces biodiesel by means of the esterification of fatty acids; Kiss [17], presents simulations embedding the experimental results of a reactive absorption process; Kraai et al. [18], investigated biodiesel production in a centrifugal contactor separator; Boucher et al. [9]

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reported pilot plant results of the transesterification of pre-treated canola oil in a laminar flow reactor separator; Narváez et al. [19] evaluated the use of a liquid film reactor (LFR) for palm oil methanolysis by means of reactive extraction in a co-current flow pattern.

A LFR is a custom-made packed column in which the interfacial area for partially miscible phases, methanol-rich and oil-rich, is created in a non-dispersive way, allowing a residence time of less than 5 min in the two-phase separator downstream of the reactor. Residence times in gravity separators downstream of tubular reactors usually range between 15 min and 2 h [20]. Atadashi et al. [21] reported a separation time of 20 min in a centrifugal separator to improve phase separation in homogeneous base catalyzed methanolysis. Despite the advantages of LFR, results suggest that co-current operation is still limited by chemical equilibrium. Conversion of palm oil and yield to methyl esters of 97.5% and 92.2%, respectively, were obtained using this equipment. However, biodiesel standards require conversions and yields higher than 99%.

An alternative approach using LFR to overcome chemical equilibrium and mass transfer limitations is to change the flow pattern from co-current to counter-current. Counter-current reactive extraction allows glycerol separation from the ester-rich phase, where most of the reaction takes place, simultaneously with the transesterification reaction, which increases conversion and yield. Furthermore, as two streams are obtained, one rich in biodiesel and practically free from glycerol, and other rich in glycerol and almost without methanol and biodiesel, the two-phase separator downstream of the reactor can be eliminated and the process time reduced.

This paper presents a stepwise reaction–separation model for counter-current reactive extraction for palm oil methanolysis using sodium hydroxide as a catalyst. The parameters of the model were identified using the maximum likelihood method [22], implemented in an evolutionary algorithm. Model parameters were determined using a set of 168 data, obtained from six experimental tests developed in a reactive extraction pilot plant. Indeed, the model was validated using the Fisher–Snedecor test [22] using further 84 validation data and 56 replication data, obtained from another set of five experimental tests. Identification, validation and replication tests were performed to study the effect of the palm oil mass flow rate, methanol to palm oil molar ratio and feeding point of methanol, while maintaining a constant temperature and catalyst concentration.

In addition, multi-criteria optimisation of the process conditions was performed using an evolutionary algorithm. The optimisation of multiple conflicting criteria leads to trade-off solutions which form the so-called Pareto set or the non-dominated solutions set [23]. The Pareto's domination concept implies that the values of all objective criteria of a potential solution are better than the values of another [24]. A final analysis was made comparing the productivity between counter-current, co-current and batch processes. For the co-current process, a plug flow model was validated using a set of experimental tests performed in the same pilot plant designed for counter-current operation [25], but those results are not however presented in this work. For the batch process, simulations were performed using the kinetics constants reported by Narváez [26] and information about the process presented by Assmann [20].

2. Model description

Fig. 1 is a schematic representation of the counter-current reactive extraction system used in this research. The reactor is a packed column in which the interfacial area for mass transfer between partially miscible phases is created in a non-dispersive way.

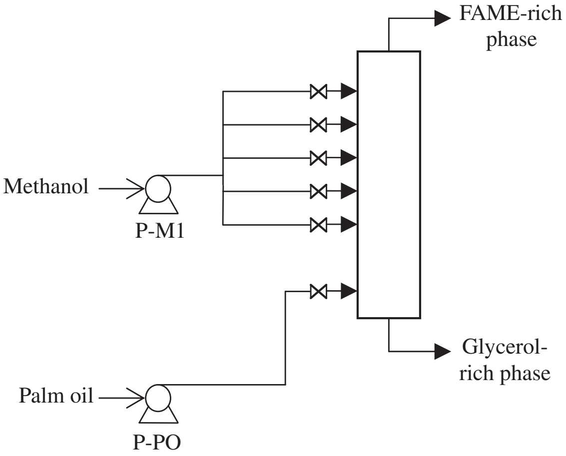

Fig. 1. Schematic representation of the reactive extraction system used in this research.

Considering the relative densities of the raw materials and products, as well as their solubility, palm oil is fed in at the bottom, where glycerol concentration is high, and methanol at the top or at any intermediate point.

For modelling and simulation, the reactive extraction column is represented by a series of identical sets of a perfectly mixed reactor coupled to an ideal liquid–liquid separator, as shown in Fig. 2. The model is based on material balances for every reactor and on material balances and equilibrium phase relations for every separator. Minotti et al. [27] presented a general model for reaction–separation operations, similar to the model presented in this work.

In Fig. 2, N is the number of stages, R_j is the reactor j, S_j is the separator j, F_j is the flow rate leaving the reactor j, L_j is the flow rate of light phase leaving the separator j, P_j is the flow rate of heavy phase leaving the separator j, A_j is the flow rate fed to intermediate stages and A_{N+1} is the flow rate fed to stage N.

Eq. (1) shows the material balance for component i in the jth reactor.

$$L_{i,j+1} + P_{i,j-1} + A_{i,j} - F_{i,j} + r_{i,j}\Delta V = 0 \quad i = 1, 2, \ldots, 6 \tag{1}$$

In Eq. (1), $L_{i,j+1}$ is the flow rate of component i coming from light phase of separator $j + 1$, $P_{i,j-1}$ is the flow rate of component i coming from heavy phase of separator $j - 1$, $F_{i,j}$ is the flow rate of component i leaving reactor j, $r_{i,j}$ is the net rate of formation of component i at reactor j and ΔV is the volume of reactor j. The term $A_{i,j}$ takes into account the flow rate of component i fed to the system at stage j: methanol for the first or intermediate stages and palm oil for the last one.The classical mechanism of three stepwise reactions presented in Fig. 3, with a pseudo-homogeneous second order kinetic model [26,28–30], are used in this work to evaluate the net rate of component formation.The pseudo-homogeneous assumption implies the use of global concentrations in order to evaluate the consumption or generation of different chemical species, regardless of the heterogeneous nature of the reactive system. Fig. 4 shows the rates of formation for the chemical components involved in the reaction and the kinetic model. The pseudo-kinetic constants k_1, k_{-1}, k_2, k_{-2}, k_3 and k_{-3} are parameters that include kinetic and mass transfer effects on reaction rate.Eqs. (2)–(6) show the general material balances and equilibrium relations for the jth phase separator:

$$F_j = L_j + P_j \tag{2}$$

$$F_{i,j} = L_{i,j} + P_{i,j} \quad i = 1, 2, \ldots, 6 \tag{3}$$

$$\gamma_i^L x_i^L = \gamma_i^P x_i^P \quad i = 1, 2, \ldots, 6 \tag{4}$$

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