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Binary Interaction Parameters from Reacting Mixture Data. Supercritical Biodiesel Process with CO₂ as Cosolvent

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Abstract

A method is presented for the calculation of binary interaction parameters from reacting mixture data. The process studied is the supercritical methanol transesterification of triolein with CO₂ as cosolvent. The reaction precedes through 3 reversible reactions in series, on solid a solid catalyst (Nafion[®] SAC-13), for which kinetics is known. To describe reactor performance, kinetic constants and the binary interaction parameters for the Peng-Robinson equation of state, are necessary. These were included in the reactor model. Previously published view-cell observations and thermodynamic calculations indicate that no condensation occurs in the reactor. Kinetic and thermodynamic parameters were determined by a global optimisation procedure. From the rate constants obtained, the process exhibits some reversibility, despite the excess methanol used. Our methodology allows obtaining the binary interaction coefficients for the intermediate reaction species (dioleins and monooleins) that were unavailable so far. The method is sensitive to the errors in the measured concentrations.

1. Introduction

For the design of the process equipment, it is necessary to know the thermodynamics of the fluid phases. For high-pressure processes, the thermodynamics are best represented by a suitable equation of state (EoS). In this approach, the use of binary systems data for the thermodynamics of mixtures is usually made. Therefore, the knowledge of the pertinent binary interaction parameters (BIPs), appearing in the mixing rules, is essential. For reactions proceeding in several steps in series, often intermediate species cannot be synthesised for performing specific phase equilibrium studies. This is the case, for example, the high-pressure transesterification of triglycerides with methanol.

In supercritical (SC) processes, cubic equations of state of the Van der Waals type (with appropriate mixing rules) are extensively used today to calculate component fugacities or concentrations in the reacting phases. They are mostly used for the prediction of vapour-liquid (VL) and liquid-liquid (LL) distribution of reactants and products in multiphase reactors. An example of a process with growing industrial interest is the SC transesterification of vegetable triglycerides with methanol to produce biodiesel, in the presence of an excess of CO₂. In this process, conversions close to 99% are possible at very small reaction times [1-3]. In connection to this process, we have recently shown [4] that the density of the reacting mixture directly affects the concentration of the species within the reactor, as the density depends on the BIPs of the different species. Since mixture thermodynamics affects the kinetic model through gas-phase concentrations, the total number of parameters involved becomes generally large because many components are present.

The overall stoichiometry of biodiesel production, is as follows:

Where 3 moles of fatty acid methyl ester (FAME or biodiesel) are formed by transesterification (ester interchange) of triglyceride oil with 3 mols of methanol. Process (1) takes place stepwise through three reversible reactions in series, each one liberating an ester molecule, with the glycerol molecule generated in the last step, as illustrated by the following reactions:

Where A = triglyceride, and B = methanol, D = diglycerides, M = monoglycerides, E = fatty acid methyl ester (FAME, methyl oleate in our case), and G = glycerol. In our process [5], inert carbon dioxide, CO₂, is added to the feed in order to lower its critical point. Integral reaction runs were made at 200 bar and temperatures of 150°C to 205°C on Nafion SAC13, a superacid ion-exchange solid catalyst [5], in a continuous reactor. Historically, the biodiesel processes were carried out at various conditions, mostly in liquid-phase batch reactors [6]. Operating in gas phase conditions, a continuous process in a tubular reactor becomes possible, in contrast with the liquid-phase, low tonnage, where batch operation is usually employed. Other ester interchange reagents (i.e., methyl acetate) have been also used in SC processing for biodiesel production [7,8], which offers certain advantages, as it is free from glycerol formation. Simulation studies on biodiesel manufacturing using methanol, in SC CO₂ have been made [9,10]. Homogeneous or heterogeneous catalysis, or even no catalyst, can be used depending on the type of reactor. However, using a solid catalyst provides obvious advantages compared with a homogeneously catalysed process conducted in CSTRs as in the case of the Henkel process [6], provided that catalyst deactivation is tolerable. The advantage of heterogeneous catalysis on the energy usage for SC process conditions has been pointed out as well.

In our previous articles [5, 11] we used the solid catalyst Nafion® SAC -13, in a bench-scale, packed-bed reactor, since a continuous plug-flow reactor process would be the preferred industrial choice. Manufacturer's data for the SAC catalyst show its superior activity compared to the standard ion-exchange catalysts (Amberlyst-15, Dowex 50) in a number of liquid-phase organic reaction types. An ASPEN simulation study of a SC process was presented by Glisic and Skala [10], where they compare the energy input for different processes alternatives (sub-critical vs. super-critical processing, homogeneous vs. heterogeneous catalysis, long-time catalyst activity vs. catalyst costs, etc.). They concluded that heterogeneous catalyst could be a good choice in view of reduced methanol excess. Recently, Kolb and co-workers [3] presented a demonstration plant for SC continuous biodiesel production using La_2O_3 on $\gamma\text{-Al}_2\text{O}_3$ as catalyst placed in a specially designed micro reactor assembly. Very large space-velocities were possible with an otherwise stable catalyst. However, for their extreme process conditions (about 400°C, 400 bar), free-fatty acids are formed. Recently, we proposed a novel idea based on a two-reactor SC process, which we modelled on the basis of the experimental kinetics available on Nafion SAC-13 [11]. In our two-reactor process [5], an inter-stage selective glycerol removal (effected by partial expansion and recompression of the fluid) was found to increase reaction rate and triglyceride conversion by shifting chemical equilibrium to the formation of products, resulting in reduced space-time values. Our work shows that much work can yet be done to improve the SC biodiesel process, including the kinetic modelling to account for free-fatty acid formation [3].

The use of cubic EoS of the van der Waals type has been found most successfully employed in SC fluid processes [14-18]. The Peng-Robinson [19] modification of the Redlich-Kwong EoS [20] is used extensively today, as summarized by Reid [21]. The EoS for a pure fluid can be extended to mixtures via the mixing rules, containing one BIP, k_{12} , for a binary mixture,

with the quadratic mixing rules for the a -value [22]. The application of the EoS to multicomponent mixtures involves the consideration of all possible i - j pairs present. Brunner and co-workers [23], have developed a software (PE 2000), which considers more than fifty EoS, with several mixing rules for the most popular ones. In general, despite several attempts to correlate BIP have been made [14, 24-27], the BIPs are still measured in phase equilibrium experiments. In the predictive method of Jaubert et al. [27], the database is available today for up to 40 chemical groups and gases related mostly to petroleum fluids using the predictive PR-EoS [28]. Other GC-EOS methods have been found appropriate for non-reactive and reactive SC fluid engineering studies [28, 29].

In this work, we present in a simulation model for the SC biodiesel production process. For high-pressure process simulation, the approach used by the most common simulators (ASPEN, CHEMCAD, ProSim, PROII, etc.) to predict VL phase equilibria is based on the EoS method (i.e., the ϕ - ϕ approach). In this case, two parameters are calculated, that is, the a_i (T , T_c , P_c , ω) and the b_i (T , P_c , T_c), where i are the pure species, T_c is the critical temperature, P_c is the critical pressure, and ω is the acentric factor. In the case of the reactions of eq. (2), there are 6 reactants and products, plus inert CO_2 added on purpose. Thus, 7 species are present in total. Then, the mixing rules are applied to each binary system. So in principle, the number of possible BIPs for 7 components becomes quite large. Furthermore, to model the reactor, the rate constants for the different reactions are necessary. In a high-pressure vapour-phase process, component fugacities, activities or molar concentrations are required to express the reaction rates. So, the kinetics of the above reactions, eqs. (2), requires 6 more kinetic constants, k_i (T), and their activation energies. Then, the conservation equations for the reactor can be written. On the other hand, if the reacting fluid composition is available from experiment in a given reactor at different

space-time and temperature, the BIPs k_{ij} and the rate coefficients, k_i , must be obtained simultaneously by fitting the measured concentrations in the fluid of the reactor. This is the case studied in the present work.

To the best of our knowledge, only two research groups have attempted to determine the BIPs using data on a SC reacting mixture. The first group was that of Bertuccio et al. [30]. Their process was the SC hydrogenation of a pharmaceutical organic intermediate carried out in a trickle-bed reactor. The authors directly calculated the k_{ij} values (using PR-EoS) to fit the observed phase distribution of reactants in the gas and liquid phases. A second research group [31], used a rather indirect calculation to obtain the k_{ij} (reaction was the production of the synthesis gas). In their approach, they first used UNIFAC, and then they combined the UNIFAC results with the Redlich-Kwong-Soave-EoS to obtain by regression the binary parameters of the multicomponent mixture. In the present work, we have used a direct approach similar to that of Bertuccio et al. Thus, our method is based on BIPs optimisation to fit the observed concentrations of reactants, products, and inerts, at the exit of a gas-phase reactor.

Our purpose in this work was first to propose a novel methodology for the joint determination of binary parameters, k_{ij} , and rate constants, k_i , for the case where fluid properties are described with the PR-EoS. Secondly, we applied this method to develop our key tool, i.e., a model for a continuous, integral catalytic, packed-bed reactor for the production of biodiesel from triolein and methanol with CO_2 as cosolvent. To this end, the measured concentrations of reactants, intermediate species, and products for a bench-scale reactor, were analysed with our reactor model that uses available catalytic rate equations from a previous work. As will be shown, a large number of different BIPs are required for the thermodynamic description of the vapour-phase of the reacting mixture containing 7 different components. Some of the BIPs were available from existing phase-equilibrium studies, but most of the BIPs for the reaction

intermediates (monoglycerides, diglycerides, glycerol) are not available. Thus, the unknown parameters have been calculated by a global optimisation method.

2. Experimental Section

2.1 Background

The experimental study behind this work was presented elsewhere [11]. Here we report only the most significant features. The detailed process flow diagram, showing feed system, instruments and controls is shown on Fig. 1. A summary of the experimental reactor and the catalyst used is given in Tables 1 and 2.

Fig 1. Experimental setup. 1-Oil reservoir; 2-Pump; 3,6,9,13,16,28-Ball valves; 4,7,10-Check valves; 5-CO₂ Cylinder; 8-CO₂/Me OH mixture cylinder; 11-Air-driven compressor; 12-Pressure regulator; 14- Cooler; 19-Relief valve; 20-Static mixer; 21-Pre-heater; 22-Rupture disk; 23- Reactor; 24-Backpressure valve; 25- High temperature bath; 26- Low temperature bath; 27-Rotameter; 29-Gas-meter

The plant was operated at steady state conditions. Note that in our set-up a continuous fractionation of exit the reactor outlet stream was carried out in two exchangers in series (constant-temperature baths) operated at atmospheric pressure. The 1st bath was operated at 70°C where the heavier components (triolein, FAME, and glycerol) were condensed. The remaining effluent gas (CO₂ and methanol vapours) was cooled in a 2nd bath kept at -10°C where methanol was condensed. Finally, the remaining gas stream (only CO₂) was measured in a dry-gas meter. For detailed operating procedures and chromatographic methods we refer to our previous publication [11].

Table 1. Properties of reactor and catalyst

	Reactor	
Type		Tubular type (Titanium) ^a
Cylinder inside dimensions		152 mm x 15.5 mm
Volume		26.8 cm ³
Cross section		188.69 mm ²
Heating resistance		2.5 kW
	Catalyst ^b	
Designation ^b		Nafion® SAC-13
Catalyst loading. W		9 g
Type		SAC/amorf. SiO ₂ composite
Nafion content		13%
Extrudates		1x9.4 mm
Pore volume. V _g		>0.6 cm ³ /g
Surface area. S _g		>200 m ² /g
Acidity type		Brönsted only
Active sites conc.		0.13 meq/g
Active groups		-CF ₂ -CF ₂ -SO ₃ H
Nafion clusters size		20-60 nm
Moisture		1-3%
	Other catalyst properties	
Internal porosity. ε _p		0.57
Pore diameter, calculated ^d		12 nm (micropor.)
Particle diameter. d _p		2.416 mm
Bulk density, measured		0.314 g/cm ³
SAC-13 vs. pure Nafion activity ^c		118.7 times larger
Hammet value		-14 to -10

^a Eurotechnica (Germany). ^b DuPont-Engelhard (USA) [12].

^c Dodecene-1 liquid phase isomerization rate at 70°C

^d Farrauto and Bartholomew [34]

Table 2. Scope of the measurements

Temperature		150°, 180°, 205 °C
Pressure		250 bar
Space-time, τ		0.5-4 min
Vegetable oil type		Sunflower
Oil mass flow rates		0.2-1.4 g/min
Solvent mass flow rate		16.2 to 2.3 g/min
Feed composition, mass %		CO ₂ /Me OH/Oil, 69.4/23/7.6

2.2 Insuring Gas-phase Conditions in Experimental Reactor

Two types of checks were made to make sure that the reactor was operated under gas phase conditions. The first check is based on thermodynamic calculations [5]. The second check is based on direct experimental observations using a view-cell [13].

2.2.1 Thermodynamic Calculations

The first check was based on the calculations [5] using the RK-Aspen EoS. Specifically, pure component properties (molecular weight (MW), boiling point (T_b), T_c, P_c and ω), were taken from the ASPEN database. For the critical constants, the recommended values were used [9]. In cases where it was necessary, recognised methods of estimation [22, 31] were employed. The values taken from the ASPEN database are given in Table 3. As discussed in the Introduction, we proposed [5] a two-step process with expansion and recompression of the flowing stream in between the two reactors. In our process [5], the use of the PT diagram was necessary for avoiding condensation in the reactor. The PT diagram is shown on Fig 2 [5]. The bubble-point line (BPL) and dew-point line (DPL) were calculated using the ASPEN Plus process simulator. The critical point and the operating P and T for the fluid in the first reactor are marked on the figure. As seen on Fig 2, condensation can be safely ruled out.

Table 3. Physical Properties, Critical Constants and Acentric Factors of Components (ASPEN database)

	Triolein	Dirolein	Monoolein	Methyl oleate
Molecular weight (kg/kmol)	885	621	356	296
Normal Boiling, Tb (K)	827	765.03	674.82	596
Liq. volume at Tb (m ³ /kmol)	2.71	1.11	0.53	0.49
Critical temp., Tc (K)	977	920	835	721
Critical pressure (MPa), Pc	0.334	0.505	1.056	1.103
Critical volume (m ³ /kmol), Vc	3.25	2.83	1.254	1.108
Pitzer's acentric factor, ω	1.97	1.76	1.53	1.04

Fig 2. PT diagram for the feed mixture to the reactor [5]. Composition is in mole %

2.2.2 View-cell Observations

Recent authors [13] made view-cell observations that lent credibility to the previously described predictions [5]. These authors performed isothermal compression of the reacting mixture to different final pressures in a view-cell, and their PT data were then plotted as experimental data

points on a PT diagram. These points, located on both sides of the critical point of the mixture, fell between the BPL and DPL. The observations were done on a mixture corresponding to the reactor inlet conditions. In the reactions of eq (2), it is evident that the products are more volatile than the reactants. Therefore, if the reactant mixture is seen in the view-cell to be a homogeneous gas-phase [13], with more reason the mixture of reactor outlet will remain homogeneous. Other authors for a similar SC process have published view-cell observations. The method of Tavlarides and co-workers [33] is recommended if future researchers perform view-cell observations.

Fig 3. Recesson of the DPL for increasing space-times [5]. The multicomponent mixture is that prevailing at reactor exit. (The white and black dots indicate a possible PT progress to avoid condensation)

3. Theory

First, it is important to have a reliable reactor model that can be used to predict performance for changes in feed composition, operating temperature and space-time. In this

section we present the reactor model, analysis of plug-flow behaviour, reaction kinetics, and a simulation model for the reactor. Our second purpose here is to define the equation of state used to calculate the thermodynamic features of fluids.

3.1 Reactor Feed and Output Streams.

The bench-scale plant (Fig. 1) was operated continuously at steady-state conditions. As seen on Table 2, four different flow rates and three temperatures were tried in the reactor. After changes in process settings (flow rate and temperature) new steady-state conditions were ensured by waiting sufficient time before analysing reactor effluent. Analytical procedures to measure the reactor feed reactants and output product concentrations, were described in detail elsewhere [11].

3.2 Reactor Considerations

We first justify that plug-flow conditions prevailed in the reactor (see Fig. 1 and Table 1), as this is a key assumption for the model. Note that volume-equivalent particle diameter for the catalyst was given in Table 1. Moreover, the bed void fraction was around 0.75. To assess axial dispersion in the experiments, we need to calculate the Reynolds and Péclet numbers for flow in the packed bed. These are defined as:

$$\text{Re} = \frac{ud_p}{\nu} \quad \text{Pé} = \frac{uL}{D_{ax}} \quad (3)$$

Very few authors have studied dispersion for flow of SC fluids [35, 36]. We presented axial mass dispersion information for flow of SC fluids [36] and represented their data on the Levenspiel and Bischoff graph [37]. The dispersion data of Abaroudi et al. [36] are for neat and modified SC carbon dioxide. In our reaction runs, Reynolds number was 7-80, so the values of the dispersion number can be taken as 0.6-0.7 from the dispersion graph [36]. From the values of bed void

fraction and reactor length, the Péclet values are 152-180, hence large enough for plug flow conditions to be assumed ($Pé > 100$).

3.3 Kinetics

For the reactions of eqn. (2), the following empirical catalytic rate equations given by eqs. (4) have been used. The kinetic model was successfully used in recent articles for the transesterification process [5, 11, 13, 33]. This is:

$$\begin{aligned} r_1 &= k_1 C_A C_B - k_2 C_D C_E \\ r_2 &= k_3 C_D C_B - k_4 C_M C_E \\ r_3 &= k_5 C_M C_B - k_6 C_G C_E \end{aligned} \quad (4)$$

Mechanistic catalytic rate equations of the Langmuir-Hinshelwood, Eley-Rideal and other types [38], have been proposed [39] for this process for low-pressure, liquid-phase conditions on a different catalyst and feed composition. Unfortunately, similar kinetic information is not available for the high-pressure gas-phase process on our SAC-13 catalyst. In this paper, we assume that the kinetics of the 3 reactions of eq. (2) is given by eq. (4).

The relationship between molar concentrations and mole fractions for a high-pressure gas is as follows:

$$C_i = \frac{Py_i}{ZRT} \quad i = A, B, M, D, E, G, CO_2 \quad (5)$$

Where, Z , is the compressibility factor of the gas mixture, calculated from the PR-EoS (see section 3.5). The dependence of k_i on temperature is given by the following Arrhenius equation:

$$k_i(T) = k_{i0} \exp\left(\frac{-E_i}{RT}\right) \quad (6)$$

1 For the kinetic constants appearing in eqs. (4), for $i=1-6$.

2

3 *3.4 Catalytic Reactor Model*

4 In this section we develop a simulation model in terms of the space-time (the reciprocal of space-
5 velocity), a customary industrial measure of contact time in catalyst terminology. We will
6 consider a one-dimensional, isothermal packed-bed reactor, where a slice of catalyst mass dW ,
7 occupies a differential volume, dV , of length dL . In view of the small bed length, pressure drop is
8 assumed to be negligible. A steady-state mass balance for components in terms of the catalyst
9 mass and reaction rates in the fluid phase, can be written as:

$$10 \quad \frac{dF_i}{dW} = \sum_{j=1}^3 v_{ij} r_{ij} \quad i = A, B, M, D, E, G, CO_2 \quad (7)$$

11 Where F_i are the molar flow rates of species i ; r_{ij} is the net formation rate for species i in reaction
12 j (see eqns. 4) and v_{ij} are the stoichiometric coefficients (all equal to ± 1 in our case). For inert
13 CO_2 ,

$$14 \quad \frac{dF_{CO_2}}{dW} = 0 \quad (8)$$

15 The initial conditions for eqns. 7 and 8, for $W = 0$ ($L = 0$) are given in Table 4 expressed in moles.
16 In the above equations the catalyst mass is expressed in terms of catalyst bed volume using the
17 bed density, ρ_B , (see Table 1). The above mass balance system can be written, as:

$$18 \quad \frac{dF_i}{\rho_B S dL} = \frac{F dy_i}{\rho_B S dL} = \sum_{j=1}^3 v_{ij} r_{ij} \quad (9)$$

19 Where F is the total molar flow rate in the reactor cross-section, S ; and L is the reactor length
20 coordinate. F is the sum of all reacting species including inerts. Pressure is assumed to be
21 constant as reasoned before. As derived from the overall reaction stoichiometry, see eqn. (1),
22 fluid density is constant for constant P and T within the reactor. Thus, in a given run, the

- 1 parameter F is constant. Introducing the rates given by eqs. (4), as a function of concentrations,
 2 into the mass balance eqs. (9), and using mole fractions, y_i , by use of eq. (5), the isothermal
 3 reactor model consists in the following set of initial-value ordinary differential equations:

$$\begin{aligned}
 \frac{dy_A}{dL} &= -\Psi r_1' \\
 \frac{dy_B}{dL} &= -\Psi(r_1' + r_2' + r_3') \\
 \frac{dy_D}{dL} &= \Psi(r_1' - r_2') \\
 \frac{dy_M}{dL} &= \Psi(r_2' - r_3') \\
 \frac{dy_G}{dL} &= \Psi(r_3') \\
 \frac{dy_E}{dL} &= \Psi(r_1' + r_2' + r_3') \\
 \frac{dy_{CO_2}}{dL} &= 0
 \end{aligned} \tag{10}$$

- 4
 5 Where the following symbols are defined in the Nomenclature section:

$$\begin{aligned}
 r_1' &= k_1 y_A y_B - k_2 y_D y_E \\
 r_2' &= k_3 y_D y_B - k_4 y_M y_E \\
 r_3' &= k_5 y_M y_B - k_6 y_G y_E \\
 \Psi &= \frac{\rho_B S P^2}{F(ZRT)^2}
 \end{aligned} \tag{11}$$

- 6
 7 The initial conditions for the system of equations eqs. (9) to (11) are given in Table 4.

- 8 **Table 4. Initial Mole Fractions for Reactor Model, L= 0 (P = 250 bar)**

Temperature	Me OH y_{B0}	Triglyceride y_{A0}	Carbon dioxide $y_{(CO_2)0}$
150°C	0,3129	0,0041	0,6831
180°C	0,3129	0,0036	0,6835
205°C	0,3129	0,0037	0,6834

All product mole fractions at bed inlet are zero.

- 9
 10
 11

3.4.1 Reactor simulation

The integration of the reactor equations for a catalyst mass in the reactor, W , provides the mole fractions, y_i , at any length coordinate, L , including the reactor exit ($L_{\max} = 152$ mm). For the integration of the model, a 4th-order Runge-Kutta algorithm was used. Two important points regarding the model equations deserve comment.

First, in order to calculate the gas-phase concentrations, a value of Z for the gas mixture at a location, L , in the bed is needed. The value of Z is calculated from the PREoS, using the VdW mixing rules. A value of Z involves the following calculations: the current mole fractions y_i , the values for critical constants (T_c, P_c), the acentric factor for the pure species, and the BIP for each binary pair in the mixture. The critical properties are taken mainly from the literature or estimated (see Table 3). In this way, for the 3 component pairs present at reactor inlet (i.e., Me OH-triolein, MeOH-CO₂, triolein-CO₂), a value of an initial Z can always be calculated. As will be discussed, in the first iteration the other BIPs are set to zero.

Second, note that the above mass balance equations constitute a useful simulation tool for a reactor holding a given amount of catalyst ($W = 9$ g in our case). Recall that a simulation model is not the same as a design model, although the conservation equations look the same. In the simulation model, the variable parameter for simulating the reactor is the molar flow rate, F , which changes from run to run for the various flow rates (of Table 1) with fixed W . The relationship between molar flow rate and space-time is as follows:

$$\tau = \frac{W}{w} = \frac{W}{FM_0} \quad (12)$$

Where w is the total mass flow rate, that it is indeed constant along reactor length, L ; M_0 is the average molecular mass of the inlet fluid gas mixture, and τ is the space-time (i.e., reciprocal of the space-velocity). In this way, the mole fractions y_i are solved for each molar flow rate F . In

summary, since F is inversely proportional to the space-time, the simulation model allows the prediction of mole fractions y_i as a function of τ , by running the program at different flow rates, F . As it is common in continuous catalytic reactors, a single parameter is used that defines reactor contact time. This is the space-time, τ (or the space-velocity, SV). For a given reactor temperature T , by changing τ , the composition of the fluid at reactor output is changed, since contact time with the catalyst is changed.

3.5 The Peng-Robinson EoS

The pressure-explicit Peng-Robinson EoS is utilized in this work [19]. For a pure substance, the equation is:

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)+b(v-b)} \quad (13)$$

Where v is the molar volume, b is the excluded volume, and a is the attractive pressure constant. For the case of mixtures, a and b depend on temperature and composition. Assuming the one-fluid Van der Waals mixing rules for a and b , the following expressions for a , and b , of the mixture, were employed:

$$a = \sum_i \sum_j y_i y_j a_{ij} \quad (14)$$

$$b = \sum_i y_i b_i \quad (15)$$

The a_{ij} is related to the geometric mean, $\sqrt{a_i a_j}$ and the binary interaction coefficients, k_{ij} , as follows:

$$\begin{aligned}
 a_{ij} &= \sqrt{a_i a_j} (1 - k_{ij}) \\
 k_{ij} &= k_{ji} \\
 k_{ii} &= 0
 \end{aligned}
 \tag{16}$$

The a_i , b_i for pure components are:

$$a_i = 0.45724 \frac{R^2 T_{ci}^2}{P_{ci}} \left[1 + \chi_i (1 - T_{ri}^{0.5}) \right]^2 \tag{17}$$

$$b_i = 0.07780 \frac{R T_{ci}}{P_{ci}} \tag{18}$$

$$\chi_i = 0.37464 + 1.54226 \omega_i - 0.2699 \omega_i^2 \tag{19}$$

It should be recalled that the mixture coefficient a is temperature-dependent; while b is not. In most cases, but not always [40], k_{ij} change slowly with T . For the PR EoS used here, we corrected k_{ij} for T when necessary (see eq. 22). Once the mixture's a and b are calculated and the critical constants and acentric factors are known, the compressibility factor Z , necessary in the reactor model, is found by solving the cubic equation:

$$Z^3 - (1 - B)Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - B^3) = 0 \tag{20}$$

Where, Z , A and B , are:

$$Z = \frac{Pv}{RT} \quad A = \frac{aP}{R^2 T^2} \quad B = \frac{bP}{RT} \tag{21}$$

A numerical method for solving eqs. (20)-(21), is available [42]. However, in the MATLAB[®] code used here, the cubic equation in Z is solved with the Cardano (trigonometric) method [41]. The method gives 3 roots. For a gaseous mixture, the largest root is chosen [22]. Two additional points deserve comment.

The first comment refers to the reactor model. To calculate the component molar concentrations at a certain location in the reactor, a value for Z is required, see eqn (5). This is calculated by solving the eqs.(10)-(21), for the current values of y_i . The pure fluid critical

constants necessary for a_i and b_i , were taken from the literature or estimated (see Table 3). T_c and P_c and ω are known for methanol, triolein, diolein, monoolein, glycerol, methyl oleate, and carbon dioxide. The second comment is that for certain component pairs of the mixture, the BIPs were available in the literature but for temperatures that seldom coincided with the reactor temperature. In these cases, we used the following regression expression, available in the process simulator, to reduce the k_{ij} to temperature T :

$$k_{ij} = k_{ij}^1 + k_{ij}^2 T + \frac{k_{ij}^3}{T} \quad (22)$$

The superscripted coefficients k_{ij}^n for use in eqn. (22), have been obtained for all the cases, so that the resulting k_{ij} can be calculated at any temperature. The use of eqn. (22) gave excellent results in our work. Other expressions are available [44].

3.6.1 Number of Parameters and Optimisation Strategy

The number of BIPs for our reacting mixture, has a total number of $n = 7$ components interacting in pairs. Thus, in principle there would be a total number of 49 binary interaction parameters to be used in eq. (16). The restrictions imposed on the values of k_{ij} , given in eq. (16) imply that the number of different parameters is restricted to $n(n-1)/2 = 21$ elements. Therefore there are only 21 different elements in the 7×7 BIP matrix. This is quite a large number of parameters to calculate in an optimisation problem, unless some shortcut or specific condition can be invoked. The simplifying conditions we used consisted in taking the BIP values from phase-equilibrium studies available in the literature, and update them to the temperature of interest.

The BIPs found in the literature correspond to the following pairs: methanol-triolein, methanol-glycerol, methanol-CO₂, triolein-CO₂, methyl oleate-CO₂, methyl oleate-methanol, and

glycerol-CO₂. Thus, for our problem, $m = 7$ parameters are known in advance and the optimisation problem involves only $n-m = 14$ unknown parameters. Additionally, there are 6 more rate parameters for each temperature. For these parameters, however, previous data have been already published, that were used as guess values in the optimisation. In summary, the strategy to solve the optimisation problem is shown on Fig. 4.

This strategy considers the joint optimisation of the PREoS parameters, k_{ij} , and the rate constants, k_i . For a given reaction temperature, T , our algorithm works as follows. Refer to Fig 4. The initial values for the k_{ij} set to zero, while the values for the kinetic constants, k_i , are taken from our previous publications or given values with curves adjusted manually. In the first step of the algorithm (3rd block from top of Fig 4), the k_{ij} values are those from the first step (that is, all $k_{ij} = 0$) while the set of kinetic constants is now found by optimisation. Then, the m values of k_{ij} available from the literature, updated to temperature T , are used, and the global optimisation program is run to find the $n-m$ unknown parameters with the kinetic coefficients kept constant. The procedure is re-iterated until a satisfactory change in the value of the objective function, FO , is obtained. The values of the objective function after running the optimisation of k_i , and after running the optimisation of k_{ij} , are called FO_0 and FO_1 , respectively in Fig 4 (see FO_0 and FO_1 in Fig 4).

Fig 4. Optimisation methodology for calculating the rate constants (k_i) and the binary interaction parameters (k_{ij}) for a run at temperature T

1 The objective function used is based on the squared relative molar concentration deviations [45].
 2 This is:

$$FO = \sum_{i=1}^7 \sum_{j=1}^4 \left(\frac{C_{ij}^{\text{exp}} - C_{ij}^{\text{model}}}{C_{i,\text{max}}^{\text{exp}}} \right)^2 \quad (23)$$

3
 4 Where, i is the component number, and j refers to runs at different flow rate. In this equation the
 5 values of $C_{i,\text{max}}$ in the denominators are introduced to equalise the contributions of the minor
 6 species (triolein, diolein, monoolein) and those of the major species (methanol and CO_2) in the
 7 summations.

8 In summary: for a given temperature, 4 experimental data sets are available with 7
 9 balance equations to be satisfied for each set, that leads to 28 equations, while 6 kinetic
 10 parameters and 14 binary interaction parameters must be determined. This means a total number
 11 of 20 parameters. Since 84 equations must be satisfied to determine 60 parameters, the use of an
 12 optimisation method such as that described above makes sense. We want to point out that the
 13 BIPs are not constant with temperature; therefore different values for k_{ij} are determined for every
 14 temperature. As described later, when the values of k_{ij} are taken from the literature, they are
 15 updated to the temperature of interest. When the results on the k_{ij} are discussed, only those for
 16 205 °C are given, for the reasons commented in the Results and Discussion section.

17

18 3.6.2 Optimisation Algorithms Employed

19 If we seek a global minimum, the alternative methods available in the MATLAB library
 20 are: *Globalsearch*, *Multistart* and *Genetic algorithm (GA)*. Many researchers agree today that GA
 21 is a successful method because it is very efficient and it supports any type of constraints. Its main
 22 drawback is the very large number of iterations. For the same biodiesel process (without

catalyst), some authors [45,46] showed that the global GA and the local Levenberg-Marquardt algorithm performed quite similarly for fitting the rate constants for the batch reactor case. In the present work, we used the *Globalsearch* function because of its lower computing cost than GA. It has a reasonable speed, and it yields similarly low values for the objective function minima [47], discussed next.

Table 5. Minima of the objective function* with Genetic algorithm and Globalsearch

T, °C	FO ₁ with GA	FO ₁ with Globalsearch
150	1.2248	1.2253
180	0.2339	0.2339
205	0.2417	0.2549

*OF₁ after 3 iterations, see Fig 4

Nevertheless, we wanted to investigate how GA performed in comparison. So we implemented GA and compared its results with the Globalsearch results for solving the parameters. We found that the two methods yielded about the same minima for FO, as shown in Table 5. Therefore, we continued with *Globalsearch* hereinafter.

4. Results and discussion

Table 6 and Table 7 summarise the initial mass flow rates of methanol, triolein, intermediates and final products present at reactor outlet. We want to note here that Tables 6 and 7 supersede Table 5 of our previous paper [11], that is now amended after checking the mass balance calculations.

Table 6. Inlet mass flow-rates to reactor [11]

Temperature (°C)	CO ₂ (g/min)	Methanol (g/min)	Triolein (g/min)	Total mass flow (g/min)
------------------	-------------------------	------------------	------------------	-------------------------

150	11.71	3.90	1.42	17.03
	5.90	1.97	0.72	8.59
	3.08	1.03	0.37	4.49
	1.71	0.57	0.21	2.48
180	13.43	4.48	1.42	19.33
	7.14	2.38	0.76	10.28
	3.53	1.18	0.37	5.08
	2.20	0.73	0.23	3.16
205	12.91	4.30	1.42	18.64
	6.90	2.30	0.76	9.96
	3.39	1.13	0.37	4.89
	2.11	0.70	0.23	3.05

Table 7. Mass flow-rates measured at reactor outlet [11]

T (°C)	Methanol (g/min)	Triolein (g/min)	Dirolein (g/min)	Monoolein (g/min)	Glycerol (g/min)	FAME (g/min)	CO₂ (g/min)
150	3.8926	1.2107	0.0958	0.0029	0.0043	0.1072	11.7126
	1.9594	0.5557	0.0616	0.0043	0.0029	0.0812	5.9045
	1.0180	0.2054	0.0372	0.0023	0.0035	0.0924	3.0838
	0.5502	0.0162	0.0065	0.0000	0.0063	0.1740	1.7069
180	4.4277	0.7500	0.1277	0.0250	0.0954	0.4638	13.4336
	2.3296	0.2948	0.0469	0.0097	0.0566	0.4707	7.1414
	1.1465	0.0680	0.0190	0.0052	0.0319	0.2798	3.5301
	0.7092	0.0128	0.0059	0.0031	0.0232	0.2076	2.1950
205	4.1828	0.1574	0.0647	0.0308	0.1170	1.1302	12.9149
	2.2293	0.0553	0.0257	0.0133	0.0688	0.6610	6.9022
	1.0908	0.0026	0.0041	0.0045	0.0380	0.3632	3.3901
	0.6791	0.0023	0.0021	0.0023	0.0234	0.2268	2.1110

We proceed now to discuss here the results for the kinetic parameters and for the BIPs in separate sections. Special emphasis has been put on the plausibility of the parameter values obtained.

4.1 Results for Kinetic Parameters

Table 8 summarizes our results for the kinetic constants for the 3 temperatures of the study. The rate constants are expressed in the same units as those obtained before [5] for comparison (see Table 9). The confidence intervals are also given in Table 8. This shows, the precision for rate constants is only $\pm 30\%$, usually larger.

The values given in Table 8 must be interpreted correctly. First, the rate constants k_i must be positive. Secondly, a zero, or close to zero, value for a reverse reaction rate constant, (for example, k_2, k_4 or k_6) means that some reactions given by eqns. (4) tend to be irreversible.

The most relevant feature from the kinetic constants obtained is that they are similar in magnitude to those obtained previously [5], a fact that lends confidence to the values calculated in this work. Table 9 shows a comparison of the central values of Table 8 with those previously obtained [5]. In general, the central values found for the direct reaction rate constants (k_1, k_3, k_5) are, in many cases, of the same order of magnitude as those previously published. Table 8 reports the confidence intervals for all the constants. It is evident that, for the 3 temperatures, the direct rate constants (k_1, k_3, k_5) are relatively well determined, whereas the inverse rate constants are not so well defined. This is because the reverse rate constants (k_2, k_4, k_6) had a smaller effect on the objective function used in the optimisation program. In the optimisation procedure used to obtain the central values for k_i , the restriction of positive values for the constants was indeed introduced, as noted above. However, that restriction could not be implemented in the calculation of the confidence intervals, because of the structure of the Matlab function used. Obviously, the kinetic constants must be positive. Therefore, the intervals of confidence of Table 8 are given *only to reflect* the relative precision for the constants.

1 **Table 8. SC Biodiesel Process: Final Values of Kinetic Constants with their Confidence Intervals**

T (°C)	k ₁	k ₂	k ₃	k ₄	k ₅	k ₆
150	0.145±0.07	39.57±68.95	0.523±0.46	5.326±574.14	5.465±3.1	0±11.28
180	1.228±0.3	60.650±71.48	5.914±1.8	250.508±205.12	17.069±4.3	20.981±8.8
205	6.955±22.26	282.83±1238.0	13.996±11.3	243.301±172.3	19.476±9.5	17.548±10.4

2 Values are expressed in L²/(mol·kg_{cat}·min). Multiply by 17 x 10⁻⁹ to obtain m⁶/(mol.kg_{cat}.s)

3

4 **Table 9. Final values of kinetics constants vs. those found previously**

T (°C)	k ₁	k ₂	k ₃	k ₄	k ₅	k ₆
150	0.145 (0.16)	39.57 (0.78)	0.523 (0.62)	5.32 (25.4)	5.465 (4.0)	0 (6.0)
180	1.23 (2.9)	60.650 (9.5)	5.914 (3.9)	250.50 (48.4)	17.07 (93.6)	20.98 (45.2)
205	6.95 (4.8)	282.8 (66.)	13.99 (10.0)	243.30 (50.0)	19.47 (792.)	17.54 (287.)

5 Values in parentheses are those obtained by Osmieri et al. [5]

6

7

8 As will be discussed later, the Arrhenius expressions for the kinetic constants of Table 8,
 9 and particularly their activation energies, provide sufficient basis to assure the plausibility of the
 10 values of the kinetic constant obtained. This is because only the central values were considered.
 11 Some of the reverse rate constants, for example k₆, are zero (see Table 8) for specific
 12 temperatures. This is just because the reactions written in eqs (2) tend to be irreversible, as we
 13 will reason in the next paragraph. The tendency of k₄, k₅, k₆ in going from 180°C to 205°C,
 14 anticipates smaller activation energies for these constants. In general, the confidence intervals are
 15 very large for the reverse constants.

16 From the values of Table 8, the equilibrium constants K₁, K₂, K₃, for the reactions of eqn.
 17 (2), can be figured out (K being = direct rate constant/ reverse rate constant). For example at
 18 205°C, the series of values K₁, K₂, K₃ is 0.03, 0.06, 1.0 as can be seen from the central values. In
 19 our previous publication [5] the series of values K₁, K₂, K₃ are 0.07; 0.07; 3.0, hence, with good
 20 agreement with the values obtained here, and showing the same tendency towards irreversibility.
 21 This same feature is observed for the other reverse constants for the other temperatures. So it

seems that the consecutive reactions of eqs (2) will progressively turn from reversible to irreversible. The same feature is observed from the experimental points of C_A vs. τ , to be presented later on Fig. 6, where triolein concentrations vs. τ are represented. From the plots of C_A at large τ , the equilibrium conversion of triglyceride was found to increase from 91% (at 180°C) to 97% (at 205°C). This would indicate that the conversion increased slightly with increasing temperature. This is the expected feature for a reversible endothermic reaction. However, here we must be very cautious when drawing conclusions because of the experimental errors associated with the measured concentrations, particularly at the lowest temperature of 150 °C.

In summary, based on the kinetic constants fitted, the three reaction steps, written as in eq. (2), are still a little reversible. However, as the ester interchange progresses along the 3 carbons of the triglyceride molecule, the process becomes more irreversible. As temperature is increased, the equilibrium conversion would seem to increase, but more data would be needed on that. In conclusion, the values of k_i at the three temperatures allow calculation of their activation energies. The results are given in Table 9, and the regression lines are represented in the Arrhenius plots of Fig 5.

4.1.1 Activation energies of kinetic constants

The activation energies for k_1 , k_3 , and k_4 show higher values than the others. Moreover, k_2 and k_5 show a lower value compared to our previous results. However, the energies obtained are typical activation energies for catalytic processes according to the literature. A range of 60-120 kJ/mol has been given for solid-catalysed reactions by Smith [48]. Catalyst scientists [34] consider activation energies generally within a narrower range, say, about 60-80 kJ/mol, that is, at the lower end of the Smith range. For high-tonnage catalytic processes (steam-reforming,

1 water-gas shift reaction), activation energies are in the upper end of the range (110-125 kJ/mol
2 for industrial catalysts).

3 **Table 10. Pre-exponential factors and activation energies for kinetic parameters.**

	k_0 $L^2/(\text{mol} \cdot \text{kg}_{\text{cat}} \cdot \text{min})^*$	E kJ/mol
k_1	$5.31 \times 10^{13} (9.04 \times 10^6)$	118.07
k_2	$9.83 \times 10^7 (1.5496)$	52.39
k_3	$2.47 \times 10^{12} (4.199 \times 10^4)$	102.13
k_4	$9.56 \times 10^{15} (1.625 \times 10^8)$	121.94
k_5	$5.49 \times 10^5 (9.33 \times 10^{-3})$	40.12

*Values in parentheses in $\text{m}^6/\text{mol} \cdot \text{kg} \cdot \text{s}$

4
5
6 As noted above, lower activation energies of k_2 and k_5 , were anticipated from their values at
7 180°C and 205°C on Table 7. In summary, the activation energies obtained are typical of solid
8 catalysts.

9 A possible explanation for the larger energies of Table 10 and Fig 5, is that the
10 uncatalysed reactions could contribute to the observed rates. Still another explanation for the low
11 energies of Table 10, is that decomposition of FAME to free fatty acid might take place for the
12 high temperatures of the process. In such case, less FAME than predicted by kinetics would
13 appear, because some of the product would be lost. In a SC process with a supported catalyst,
14 Kolb and co-workers [3], observed a substantial formation of free fatty acid at the high
15 temperature of their process. In our experiments, free fatty acid was not examined, but our
16 previous data indicate that this is not formed to an appreciable amount [10].

Fig. 5. Arrhenius plot for kinetic constants determined in this work ($L^2/mol\ kg_{cat}\ min$)

4.1.2 How Good are Kinetic Constants

We ask ourselves how good are the estimates of the kinetic constants obtained with our non-linear optimisation method. As far as the constant k_1 is concerned, however, a clear response can be given, because a linear estimate can be obtained as follows. Initial reaction rate of triolein provides an independent estimate of k_1 using the differential method of kinetic analysis [38, 48]. This value is written as k_{1fit} in Fig 5. Repeating this procedure for the other temperatures, the activation energy of k_1 is obtained. At $\tau = 0$, no product is present, therefore the values of k_1 can be calculated from the initial rate of reaction of A, as follows:

$$r_{\tau \rightarrow 0} \equiv r_0 = k_1 C_{A0} C_{B0}$$

$$k_1 = \frac{r_0}{C_{A0} C_{B0}}$$

(24)

The initial rate, r_0 , can be measured and the mole concentrations C_{A0} and C_{B0} , can be evaluated exactly from the inlet compositions. A value for r_0 is obtained from the initial slope of the integrated plots of y_A or C_A vs. τ , from integral reactor data, as follows:

$$r_0 = \frac{1}{M_0} \left(\frac{dy_A}{d\tau} \right)_{\tau=0} \quad (25)$$

The values of k_1 from the non-linear optimisation and those from the initial rates differ less than 18-28%, indicating that the optimization method is acceptable.

Table 11. Pre-exponential factor and activation energy of k_1 as calculated from initial rates and from optimisation

Method	$k_0, \text{m}^6/(\text{mol.kg}_{\text{cat.}}.\text{s})$	E, kJ/mol
Initial rates	4.76×10^3	98.51
Optimisation	9.03×10^5	118.07

Considering the three temperatures allows calculation of the Arrhenius equation for k_1 fit. The Arrhenius parameter values obtained with the methods are compared in Table 11 and shown in Fig 5.

4.2 Results on Binary Interaction Parameters

The values of the Peng-Robinson interaction parameters k_{ij} are given as a matrix in Table 12, where the boldface values are the parameters taken from the literature (reduced to actual temperature). All the k_{ij} values are within the usual range for these parameters. Note however, that some parameters are negative. These correspond to the following binary systems:

-Methanol with triolein, diolein, and monoolein

-Triolein, diolein and monoolein with all the other components except CO_2 .

-FAME with monoolein, diolein, and triolein.

-Methanol with CO_2 .

A negative k_{ij} value, indicates a strong interaction between the i and j molecules in the mixture. Negative k_{ij} are usually found in mixtures of unlike molecules, i.e., polar and nonpolar molecules, showing non-ideality. In a previous article [49], we found negative BIPs in the thermodynamics of solubility of solids in neat and SC CO_2 modified with cosolvents. As it is known, this corresponds to cases of solubility of solids in a nonpolar gas. Obviously, we still do not have means to judge this interaction for mono- and di-olein with certain components, but we do have information about some k_{ij} for pairs involving triolein, that would be similar with the type of interaction found. For temperatures ranging from 200°C to 230°C , Romanielo and co-workers [50] report also negative k_{ij} values for the interaction between triolein and methanol.

For 180°C up to 205°C , the methanol-triolein binary system has negative values for all the three k_{ij} ; with a value of $k_{ij} = -0.1180$ found at 205°C . It is reasonable to think that diolein and monoolein in the presence of methanol will behave similarly as triolein with methanol, in view of their similar molecular structure. This is also the case of the polar nature vs. the non-polar nature of oleins (diolein and monoolein) when mixed with glycerol (a highly polar polyol), giving negative k_{ij} . The reasoning presented above would provide some basis for the negative k_{ij} of Table 12, in particular for the pairs of the first column (or first row) and for polar/non-polar systems. Similarly, the values of the FAME-glycerides, and CO_2 with either diolein or monoolein should also be acceptable.

1 **Table 12. Matrix of BIPs for the components of the reacting mixture containing CO₂ (T = 205°C)**

	Methanol	Triolein	Diolein	Monoolein	Glycerol	FAME	CO₂
Methanol	0	-0.1180	-0.1751	-0.1759	0.0371	0.0485	0.2768
Triolein	-0.1180	0	-0.1859	-0.1912	0.1456	-0.1864	0.0985
Diolein	-0.1751	-0.1859	0	-0.1865	-0.1751	-0.0862	-0.1894
Monoolein	-0.1759	-0.1912	-0.1865	0	-0.1901	-0.1931	-0.0513
Glycerol	0.0371	0.1456	-0.1751	-0.1901	0	-0.1886	0.3093
FAME	0.0485	-0.1864	-0.0862	-0.1931	-0.1886	0	0.0109
CO₂	0.2768	0.0985	-0.1894	-0.0513	0.3093	0.0109	0

2 Boldface k_{ij} are from the literature [50-52], and reduced to 205°C.
3
4
5

6 We want to make a final remark about the limit bounds imposed to k_{ij} values in the
7 optimisation programs. Although the bounds were taken rather wide, in some cases the fitted
8 parameters took values just onto one of the bounds, suggesting that larger (or smaller) values
9 could be better. This behaviour is more frequent for the temperatures of 150°C and 180°C, as the
10 higher experimental error or lack of accuracy of data leads the optimal parameters to fall on the
11 bounds. Since experimental data from 205°C fits much better to the model, best results have been
12 found for this temperature, while the values for the other temperatures are not so good. In
13 general, the methodology followed in this work to obtain binary interaction parameters has
14 proved to be very sensitive to the accuracy and error of data, so a word of caution is necessary
15 when using the present method. The k_{ij} for 205 °C are well within expected limits, as can be
16 noticed in Table 12.

17 Finally, represented on Fig 6 are the integrated reactor model equations and the
18 corresponding experimental data points for component concentrations, plotted vs. space-time,
 τ . The values shown correspond to concentrations prevailing at reactor exit.

Fig 6. Simulated and experimental concentration profiles measured at reactor exit vs. space-time, τ . Runs at $T = 150^\circ, 180^\circ$ and 205°C , $P = 250$ bar.

5. Conclusions

Using the experimental data for the operation of a bench-scale, integral catalytic packed-bed reactor, the analysis and simulation of a SC biodiesel production process was done. To this

end, a reactor simulation model was developed to simulate a biodiesel production process via triglyceride transesterification with methanol in the presence of CO₂ as cosolvent.

Previous studies show that transesterification takes place as three reversible reactions in series. For a high-pressure process, reactor simulation at a given pressure and T involves the use of the rate coefficients as well as the thermodynamic parameters for the fluid phase. To this purpose, the Peng-Robinson EoS, with the one-fluid Van der Waals rules for mixtures, was used. The global optimization procedure used in this work allows to simultaneously calculate the kinetic parameters, k_i , and the PR-EoS k_{ij} parameters. Based on the values of the rate constants, and on the chemical equilibrium constants calculated from them, we can conclude that the three reaction steps are still somewhat reversible, despite the excess of methanol used. As temperature is increased from 180 °C to 205 °C, the equilibrium conversion of triglyceride increases from 91 to 98%. This would suggest a reversible endothermic reaction. However, because of the experimental errors in the measured concentrations, further insight into the thermal character of the reaction is needed.

The method presented in this work allowed calculating the values of the BIPs for the intermediate reaction species (diolein, monolein) that were not available so far. The PR-EoS k_{ij} values for the component pairs obtained are reasonable on the basis of their chemical nature, but further research is needed for the full verification of the methodology. The values of k_{ij} obtained are better for 205 °C than for the lower temperatures (150 °C and 180 °C), because the method proposed in this work is very sensitive to the accuracy of the experimental data.

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Nomenclature

a	Attractive constant, $\text{Pa}\cdot\text{m}^6/\text{mol}^2$
A, B	Coefficients defined by eqns (21)
a_i	PR EoS, pure i coefficient, eq (17)
a_{ij}	Binary interaction coefficient, $= (1 - k_{ij})(a_i \cdot a_j)^{0.5}$
b	Co-volume, m^3/mol
b_i	b coefficient for pure i , eq (18)
C_i	Concentration component i , mol/m^3
D_{ax}	Axial dispersion coefficient, m^2/s
d_p	Particle diameter, m
E_i	Activation energy for k_i , kJ/mol
F	Total molar flowrate, mols/s
F_i	Molar flowrate, mols/s
FO	Objective function, eq (23)
k_i	Rate constant, $i = 1-6$, $\text{m}^6/(\text{mol}\cdot\text{kg}\cdot\text{s})$
k_{ij}	Binary interaction parameter,
k_{ij}^n	Regression coefficients, eqn (22)
L	Reactor length, m
M_0	Average molecular mass, kg/mol
P	Pressure, Pa
$Pé$	Péclet number for mass, eq. (6)
R	Ideal-gas constant, $= 8.314 \text{ J}/\text{mol}\cdot\text{K}$
Re	Reynolds number, eq. (6)
r_0	Initial rate, eqn(25), $\text{mol}/\text{kg}\cdot\text{s}$
r_i	Reaction rate of i , $\text{mol}/(\text{kg}\cdot\text{s})$
r	Modified rates, eqn (11), $\text{m}^3/(\text{mol}\cdot\text{kg}\cdot\text{s})$

r_{ij}	Reaction rate of i in reaction j, mol/kg.s
S	Reactor cross section, m ²
SV	Space velocity, 1/s
T	Absolute temperature, K
u	Superficial velocity, m/s
W	Catalyst mass, kg
w	Total mass flowrate, kg/s
y_i	Mole fraction component i,
Z	Compressibility factor,

Greek symbols

v_{ij}	Stoichiometric coefficients, eqn (7)
Ψ	Mass transfer group, eq (11), mol.kg.s/m ⁷
τ	Space-time, s
χ	Peng-Robinson coeff. Eqn (19)
ω	Acentric factor,
ϵ	Porosity,
ν	Dynamic viscosity, m ² /s

Acronyms and subscripts

BIP	Binary interaction parameter
BPL	Bubble-point line
CP	Critical point
DPL	Dew-point line
EoS	Equation of state
SC	Supercritical
FAME	Fatty acid methyl ester
SV	Space velocity

c
rCritical
Reduced

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