

Biodiesel Production in Stirred Tank Chemical Reactors: A Numerical Simulation

Alejandro Regalado-Méndez, Rubí Romero Romero, Reyna Natividad Rangel, and Sigurd Skogestad

Abstract

The biodiesel production was performed in stirred tank chemical reactor by numerical simulation. The main results are that the percentage of conversion from triglyceride to biodiesel is approximately of 82 % when the molar flow ratio between triglyceride/alcohol is 1:5. This system displays only one equilibrium point. Since there are imaginary eigenvalues in the Jacobian matrix analysis, the equilibrium point is unstable. The biodiesel production in stirred tank chemical reactor is good because the settling time is short, and has higher conversion.

Keywords

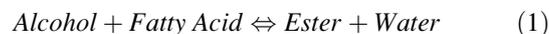
Biodiesel • Equilibrium point • Numerical simulation • CSTR • Phase map

Introduction

Among the preoccupations that concern the world are the reduction of petroleum reserves due to the increased use of diesel fuel, and the environmental issues that caused by the climate change [1]. This situation brings significant attention to new alternatives that secure the future energy supplies. For instance, researchers have focused their investigations to explore plant-based fuels, plant oils, and fats as promising bio-

fuel sources [2]. As a result, biodiesel derived from vegetable oils, can be an option to replace diesel. Biodiesel, consisting of methyl esters of fatty acids [3], is commonly obtained by transesterification of vegetable oils that compromise triglycerides with methanol in the presence of a catalyst [4]. This clean renewable fuel is superior to diesel oil in terms of sulfur and aromatic content. Also, it is environmentally safe, non-toxic, and biodegradable.

The esterification reaction to generate biodiesel can be conceptually represented by the following in (1):



The transesterification reaction can be carried out in a continuous stirred tank chemical reactor (CSTR). CSTR are the most common process unit in chemical industries process [5]. Since CSTR are the central part of a whole chemical process the stability study is a relevant topic [6, 7].

The purpose of this work is to investigate the dynamic behavior of CSTR in biodiesel production. We consider the case where vegetable oil reacts with methanol to form methyl esters (biodiesel) and glycerol in the presence of a homogeneous alkaline catalyst (NaOH). This case is investigated because alkali-catalyzed transesterification is the most often used in industry. First, the simulations are performed at different feed ratios of alcohol to oil. Second,

A. Regalado-Méndez (✉)
Centro Conjunto de Investigación en Química Sustentable
UAEMex-UNAM, Unidad San Cayetano, Km 14.5 Carretera
Toluca-Atlacomulco, Toluca 50200, México

Universidad del Mar, Ciudad Universitaria SIN, Puerto Ángel,
Oaxaca 70902, México
e-mail: alejandromendez33@gmail.com

R.R. Romero • R.N. Rangel
Centro Conjunto de Investigación en Química Sustentable
UAEMex-UNAM, Unidad San Cayetano, Km 14.5 Carretera
Toluca-Atlacomulco, Toluca 50200, México
e-mail: romeror@uaemex.mx; matividadr@uaemex.mx

S. Skogestad
Department of Chemical Engineering, Norwegian
University of Science and Technology, Trondheim 7034, Norway
e-mail: skoge@nt.ntnu.no

the equilibrium points will be computed. Finally, the bifurcation and stability analysis is also explored.

The present article is arranged in the following order. In section “Theory”, shows theoretical background to develop this investigation. Section “Case Study”, the continuous stirred tank chemical reactor model is explained for the case of biodiesel production. Section “Results” shows the results and discussion based on the case study.

Theory

Dynamic Model for CSTR

The dynamics of **CSTR** in which m reactions take place involving n ($n > m$) chemicals species can be described by (2):

$$\begin{aligned} \dot{C} &= \theta(C_{in} - C) + Er(C, T) \\ \dot{T} &= \theta(T_{in} - T) + Hr(C, T) + \gamma(u - T) \end{aligned} \quad (2)$$

where:

- $C \in \mathbb{R}^n$ is the vector of concentrations of chemical species.
- $C_{in} \in \mathbb{R}^n$ is the vector non-negative and constant feed concentrations.
- $T \in \mathbb{R}$ is the vector temperature.
- $T_{in} \in \mathbb{R}$ is the vector feed temperature.
- $r(C, T) \in \mathbb{R}^m$ is the smooth, non-negative, bounded vector of reaction kinetics, with $r(C, T) = 0 \forall t \leq 0$.
- $E \in \mathbb{R}^n \times \mathbb{R}^m$ is the stoichiometric matrix.
- $H(C, T) \in \mathbb{R}^m$ is the smooth, bounded row vector of reaction enthalpies, with $H(C, T) = 0 \forall t \leq 0$.
- θ is the reactor dilution rate (i.e. flow rate/volume).
- γ is the heat transfer parameter.
- u is the jacket or wall temperature, which is taken as the *control input*.

Non-linearity in models of equations (2) are introduced by the reaction kinetics $r(C, T)$. Commonly, $r(C, T)$ has a polynomial or rational dependency on C and has an Arrhenius dependency on T . Due to this kinetics, CSTRs can display a great variety of dynamic behaviors from multiplicity of steady states to sustained oscillations, including odd attractors [8]. Figure 1 sketched a CSTR.

Bifurcation and Stability Analysis

Bifurcation theory provides tools for a system stability analysis under its parametric changes [10]. As the parameters undergo changes, the existence of multiple steady states, sustained oscillations and traveling waves might occur for highly nonlinear processes [11].

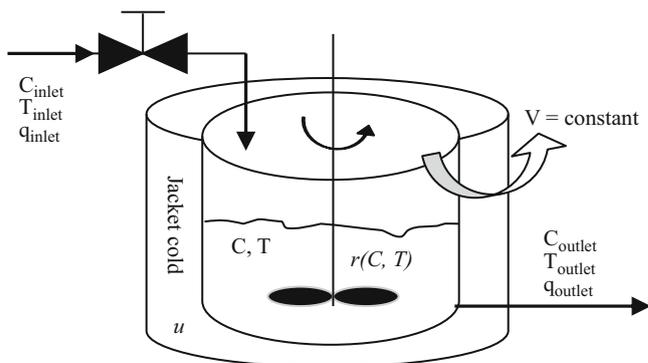


Fig. 1 Continuous stirred tank chemical reactors (based on [9])

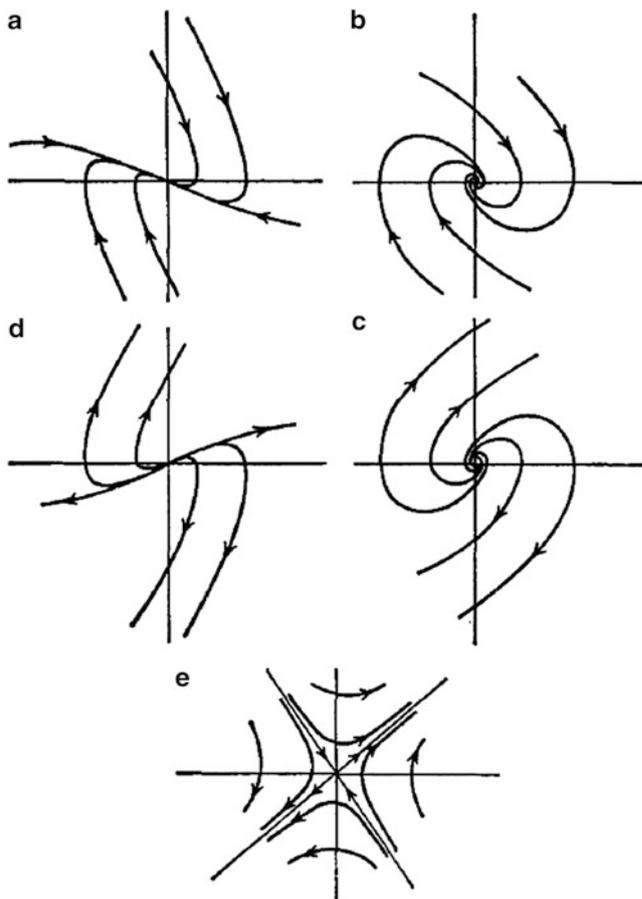


Fig. 2 (a) Stable node, (b) stable focus, (c) unstable focus, (d) unstable node, (e) saddle point [15]

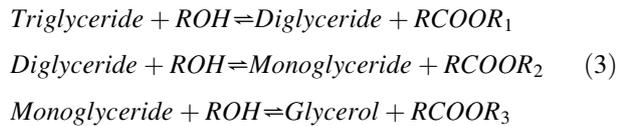
Nonlinear system theory states that if all eigenvalues of the Jacobian matrix lie in the open left half of the complex plane, the system is stable [12]. Conversely, the steady state is unstable if the Jacobian matrix has at least one eigenvalue in the open right half of the complex plane [13, 14].

Figure 2 shows the distinction between stable and unstable nodes or foci is made to indicate that the trajectories move toward the stable type of critical point and away from

the unstable point. The saddle point arises when the roots of the characteristic equation are real and have opposite sign. In this case there are only two trajectories that enter the critical point, and after entering, the trajectories may leave the critical point (permanently) on either of two other trajectories. No other trajectory can enter the critical point, although some approach it very closely [14, 15].

Case Study

Triglyceride (oils/fats) reacts with alcohol in the presence of the catalyst to give fatty acid alkyl esters and glycerol. The reaction proceeds in three steps as shown below [16]:



where r_1 , r_2 , and r_3 are the fatty acid chains associated with glycerol in triglyceride. K_1 , K_2 , K_3 are equilibrium constants, $K_1 = k_1/k_2$, $K_2 = k_3/k_4$, and $K_3 = k_5/k_6$ where k_1, k_2, \dots, k_6 are forward and backward rate constants. The reaction rates of each reaction are as follows:

$$\begin{aligned} r_1 &= k_1 C_{TG} C_{ROH} - k_2 C_{DG} C_{AE_1} \\ r_2 &= k_3 C_{DG} C_{ROH} - k_4 C_{MG} C_{AE_2} \\ r_3 &= k_5 C_{MG} C_{ROH} - k_6 C_G C_{AE_3} \end{aligned} \quad (4)$$

where C_{TG} , C_{DG} , C_{MG} , C_G , C_{AE} and C_{ROH} represent the concentration of triglyceride, diglyceride, monoglyceride, glycerol, alkyl esters (biodiesel), and alcohol respectively. The temperature dependency of the rate constant (k_i) is expressed by Arrhenius' law [17]:

$$k_i = k_i^0 \exp(-E_{A,i}/RT) \quad (5)$$

The kinetic parameters are shown in Table 1. The heat of the reaction is $\Delta H_R = -5.07 \times 10^3 \text{ J/mol}$ for each reaction, calculated from the heat of the formation data [16].

Table 1 Kinetic parameters [18]

Component	Symbol	Units	Symbol	Units
	K°	L/mol min	E_A	J/mol
TG	1.469×10^8		58,782.6720	
ROH	105,100		44,962.0452	
DG	1.19×10^{10}		67,193.9532	
AE	1.725×10^8		58,225.8276	
MG	24,940		30,031.9164	
G	1.469×10^8		46,042.2396	

Results

The numerical simulation of biodiesel production in a CSTR has been performed in MATLAB[®] version 2012b.

Figure 3 shows the concentration profile for the five molar flow ratios between triglyceride/alcohol in the case of $\theta = 0.06 \text{ min}^{-1}$, $u = 5$, $T_c = 400 \text{ K}$, the set of ODEs are integrated using the explicit Runge-Kutta method. All shapes are asymptotic. The settling time diminish when the molar flow ratio between triglyceride/alcohol increase. The relationship between settling time and the molar flow ratio is the form $\tau_A^{1:5} < \tau_A^{1:4} < \tau_A^{1:3} < \tau_A^{1:2} < \tau_A^{1:1}$. In addition, we can see that concentration of biodiesel ($C_{Biodiesel}$) in steady state increase when molar flow ratios between triglyceride/alcohol increase.

Hence, the molar flow ratio between triglyceride/alcohol is too sensitive for biodiesel production.

Figure 4 shows reactor temperature profile for the five molar flow ratios between triglyceride/alcohol. In addition, be seen that reactor temperature (T) in steady state diminish when the ratios of triglyceride/alcohol increase.

In order to find the equilibrium points of CSTR, the model of CSTR in steady state was solved by Newton method for nonlinear system equation. The vector of equilibrium points for five molar flow ratios between triglyceride/alcohol are given in Table 2. Notice that the maximum production of biodiesel is given when the molar flow ratio between triglyceride/alcohol is 1:5. It is in agreement with [19] since there is excess of alcohol. Notice that, there is only one equilibrium point for each molar flow ratio of triglyceride/alcohol. Many studies about characterization and stabilization of equilibrium points show that when

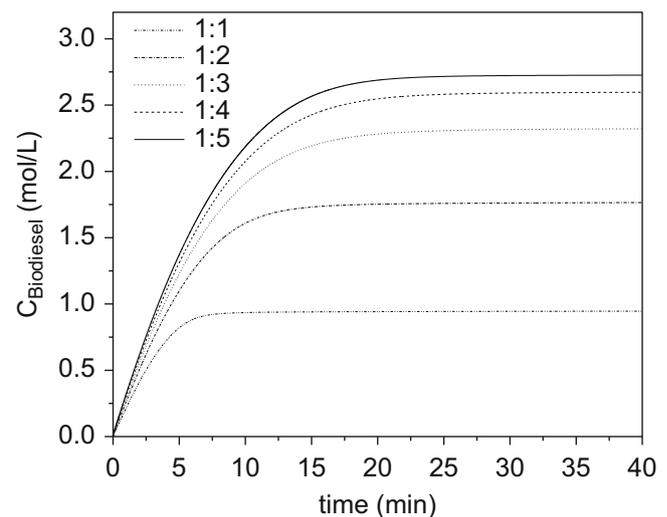


Fig. 3 Concentration profiles at different molar flow ratios of triglyceride/alcohol

there is only one equilibrium point in the dynamic system it should be an unstable point. Aforementioned is in agreement with [6, 8, 20].

Figure 5 illustrates the bifurcation map for 5 M flow ratios between triglyceride/alcohol. All shapes diminish asymptotically and the shape with more pronounced slope is when the molar flow ratio between triglyceride/alcohol is 1:5. In addition, the biodiesel concentrations increase when the dilution rates diminish because at less value of dilution rate the behavior of CSTR is like a batch reactor. This is not desirable because there are not advantages of continuous process.

Hence, the molar flow ratio 1:5 of triglyceride/alcohol is chosen to perform the phase maps, concentration behavior and temperature behavior because this relationship leads to the maximum biodiesel concentration.

Figure 6 shows phase maps in steady state without control in the case of molar flow ratio between triglyceride/alcohol is 1:5. These maps give an idea of the maximum reference point that could be fed in some control law. Also, in Fig. 6 we observe that the maximum biodiesel composition approximately is 2.72 mol/L. It is important know that because the

conversion could not be reached for higher value in the input. In addition, the maximum conversion is reached when cooling jacket temperature is 435 K.

Figure 7 presents concentration profiles for the most important components in the case of molar flow ratio between triglyceride/alcohol is 1:5, $\theta = 0.06 \text{ min}^{-1}$, $u = 5$, $T_c = 400 \text{ K}$. The purpose of this figure is to show that as the reaction precedes, the concentration of the desired product, biodiesel, increases asymptotically. However, after 26 min there is no significant change in these values. This situation also happens with the rest of the components which no further change occurs after reaching this time. In addition, triglyceride concentration in steady state ($\tau_A \approx 26 \text{ min}$) is around of 0.18 mol/L, and the conversion of triglyceride is compute by $(1 - 0.18)/1 \times 100 = 82 \%$.

Figure 8 depicts the dynamic behavior of reactor temperature. Also, the settling time of the reactor (τ_A) and the steady state reactor temperature are 26.3 min and 350.52 K respectively. In addition, there is the relationship between settling time and dilute rate as follows $\tau_A \approx 4\theta^{-1}$ because $4\theta^{-1} = 4(0.15 \text{ min}^{-1})^{-1} = 26.67 \text{ min} \approx \tau_A$, this is according with [20, 21].

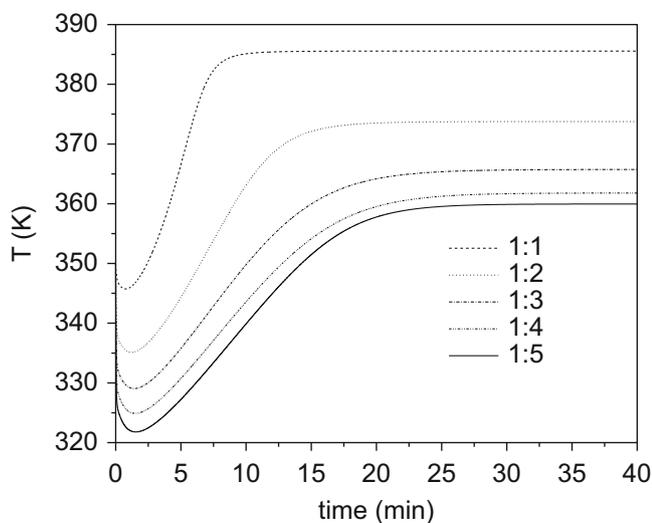


Fig. 4 Temperature profiles at different molar flow ratios of triglyceride/alcohol in the case of $\theta = 0.06 \text{ min}^{-1}$, $u = 5$ and $T_c = 400 \text{ K}$

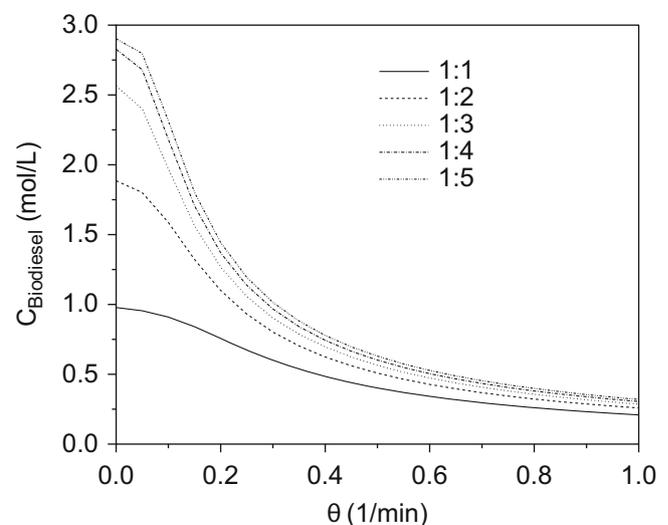


Fig. 5 Bifurcation map at different molar flow ratios between triglyceride/alcohol in the case of $u = 5$ and $T_c = 400 \text{ K}$

Table 2 Equilibrium points with $\theta = 0.06 \text{ min}^{-1}$, $u = 5$ and $T_c = 400 \text{ K}$

Variable	1:1	1:2	1:3	1:4	1:5
C_{TG}	0.485757	0.354256	0.204793	0.118279	0.060609
C_{ROH}	0.052477	0.375401	0.820382	1.491553	2.278931
C_{DG}	0.225128	0.108635	0.055797	0.030556	0.018673
C_{MG}	0.144949	0.156599	0.108546	0.076785	0.059503
C_G	0.144166	0.421412	0.640027	0.775062	0.861034
C_{AE}	0.947523	1.627004	2.179937	2.508459	2.721064
T	385.5553	363.0733	360.0601	358.7252	359.6604

C_i concentration of component i , mol/L; T temperature, K

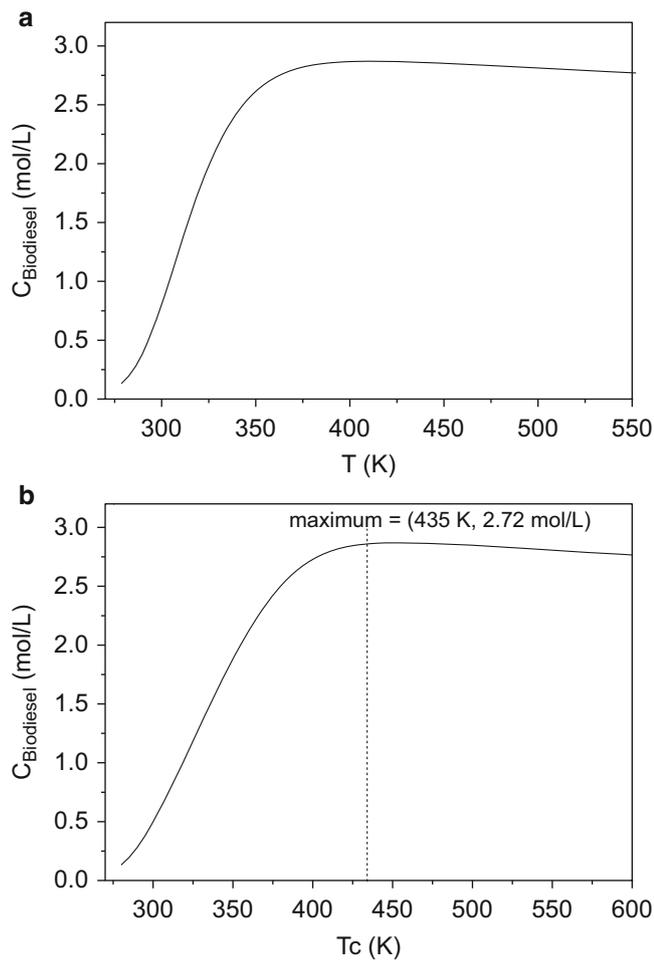


Fig. 6 (a) Phase map in steady state for $C_{Biodiesel}$ versus reactor temperature. (b) Phase map in steady state for $C_{Biodiesel}$ versus cooling jacket temperature. Both cases with $\theta = 0.06 \text{ min}^{-1}$, $u = 5$ and $T_c = 400 \text{ K}$

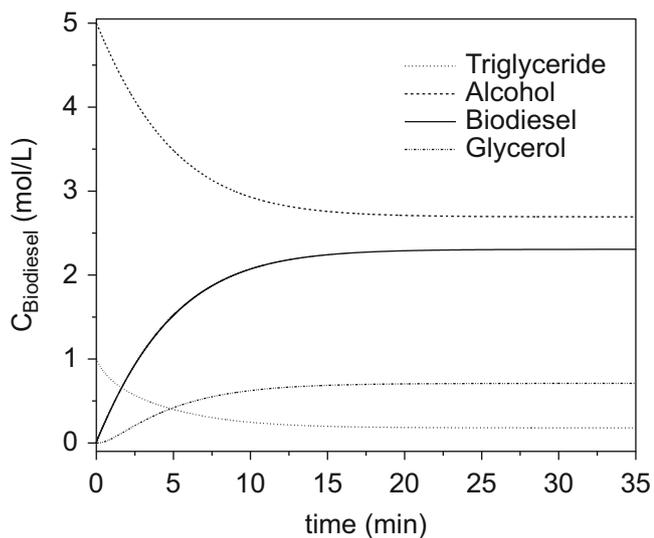


Fig. 7 Concentration behavior of principal components carryout in CSTR for biodiesel production

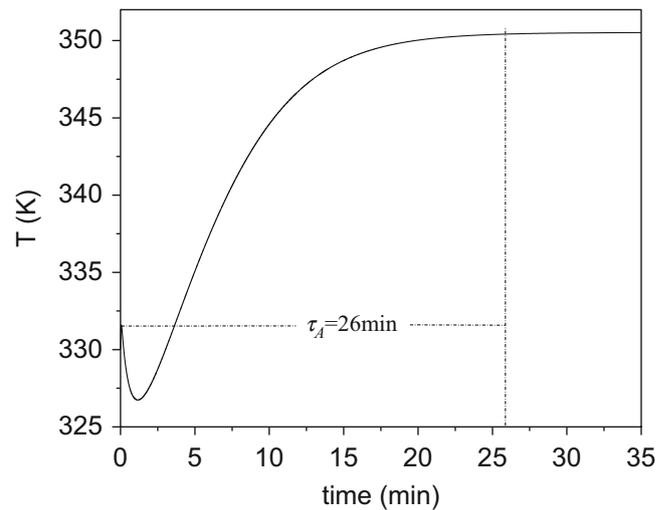


Fig. 8 Temperature behavior in the case of $\theta = 0.15 \text{ min}^{-1}$, $u = 5$ and $T_c = 435 \text{ K}$

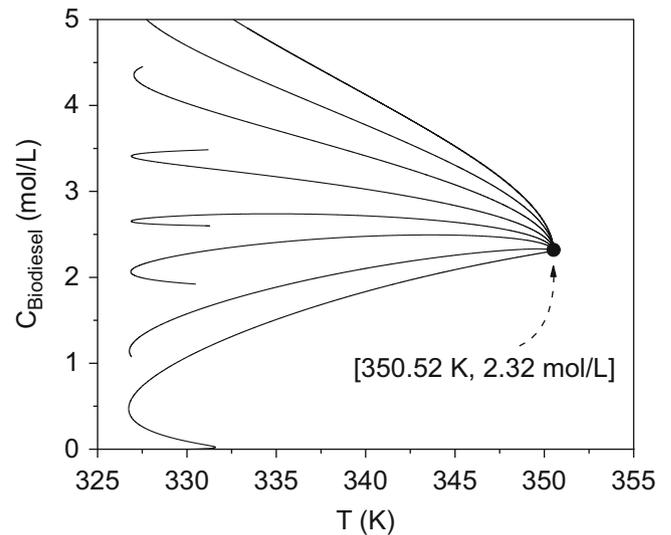


Fig. 9 Phase diagram in the case of $\theta = 0.15 \text{ min}^{-1}$, $u = 5$ and $T_c = 435 \text{ K}$

The phase-plane plot has been constructed by performing simulations for a large number of initial conditions when the molar flow ratio between triglyceride/alcohol is 1:5. Figure 9 sketches the phase portrait in steady state without control. One steady state value is clearly shown. Also, all shapes converge to equilibrium point (350.52 K, 2.32 mol/L). In addition, the phase map is similar to Fig. 2c, thus the equilibrium point can be characterized as an unstable focus. To confirm the characterization of equilibrium point was performed an eigenvalue analysis for the Jacobian matrix at steady state. Therefore, there are two complex root there the equilibrium point is an unstable point. Detail about this stability analysis is available in the appendix.

Conclusion

The CSTR is a good continuous process to carry out biodiesel production because the settling time is short, and acceptable conversion of triglycerides to biodiesel is achieved. However, this process is expensive because is needed excess of alcohol.

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Appendix

The particular model for the case study is governed by the next set of ordinary differential equations.

$$\begin{aligned}
 \frac{dx_1}{dt} &= \gamma_1 - \theta x_1 - \beta_1 x_1 x_2 + \beta_2 x_3 x_4 \\
 \frac{dx_2}{dt} &= \gamma_2 - \theta x_2 - \beta_1 x_1 x_2 + \beta_2 x_3 x_4 \\
 &\quad - \beta_3 x_3 x_2 + \beta_4 x_5 x_6 - \beta_5 x_5 x_2 + \beta_6 x_7 x_8 \\
 \frac{dx_3}{dt} &= \gamma_3 - \theta x_3 + \beta_1 x_1 x_2 - \beta_2 x_3 x_4 \\
 &\quad + \beta_3 x_3 x_2 - \beta_4 x_5 x_6 \\
 \frac{dx_4}{dt} &= \gamma_4 - \theta x_4 + \beta_1 x_1 x_2 - \beta_2 x_3 x_4 \\
 \frac{dx_5}{dt} &= \gamma_5 - \theta x_5 + \beta_3 x_3 x_2 - \beta_4 x_5 x_6 \\
 &\quad + \beta_5 x_5 x_2 - \beta_6 x_7 x_8 \\
 \frac{dx_6}{dt} &= \gamma_6 - \theta x_6 + \beta_3 x_3 x_2 - \beta_4 x_5 x_6 \\
 \frac{dx_7}{dt} &= \gamma_7 - \theta x_7 + \beta_5 x_5 x_2 - \beta_6 x_7 x_8 \\
 \frac{dx_8}{dt} &= \gamma_8 - \theta x_8 + \beta_5 x_5 x_2 - \beta_6 x_7 x_8 \\
 \frac{dx_9}{dt} &= \gamma_9 - \theta x_9 + \Delta H_{rxn} [\beta_1 x_1 x_2 - \beta_2 x_3 x_4 \\
 &\quad + \beta_3 x_3 x_2 - \beta_4 x_5 x_6 + \beta_5 x_5 x_2 - \beta_6 x_7 x_8] + u(T_c - x_9)
 \end{aligned} \tag{6}$$

Where: $\beta_i = k_i^0 \exp(-E_{A_i}/R x_9)$ and $\gamma_i = \theta x_{i,0}$

Using the expansion Taylor series the dynamic system governing by (6) can be represented by (7).

$$\begin{aligned}
 \frac{d\bar{x}}{dt} &= \bar{f} \\
 \bar{f} &= \bar{f}_{\bar{x}_e} + A|_{\bar{x}_e} [\bar{x} - \bar{x}_e]
 \end{aligned}$$

Reordering the before equation

$$\frac{d\bar{x}}{dt} = \underbrace{\begin{bmatrix} \frac{\partial f_1}{\partial x_1} & \cdots & \frac{\partial f_1}{\partial x_9} \\ \vdots & \ddots & \vdots \\ \frac{\partial f_9}{\partial x_1} & \cdots & \frac{\partial f_9}{\partial x_9} \end{bmatrix}}_A \underbrace{\begin{bmatrix} x_1 \\ \vdots \\ x_9 \end{bmatrix}}_{\bar{x}} + \bar{f}_{\bar{x}_e} + \underbrace{A|_{\bar{x}_e}}_B \underbrace{\begin{bmatrix} x_{1,e} \\ \vdots \\ x_{9,e} \end{bmatrix}}_{\bar{x}_e} \tag{7}$$

In deviation variables $\xi = \bar{x} - \bar{x}_e$ (7) have the next form:

$$\frac{d\xi}{dt} = A|_{\bar{x}_e} \xi + \bar{f}_{\bar{x}_e} \tag{8}$$

For the case study the function *Jacobian* matrix values are:

$$\bar{f}_{\bar{x}_e} = \begin{bmatrix} -19.43 \\ -166.33 \\ -27.48 \\ 19.44 \\ -68.06 \\ 46.93 \\ 99.97 \\ 99.97 \\ -194461.33 \end{bmatrix} \times 10^{-15} \cong 0 \tag{9}$$

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