A HETEROGENEOUS BIODIESEL PRODUCTION KINETIC MODEL

UN MODELO CINÉTICO HETERGÉNEO PARA LA PRODUCCIÓN DE BIODIESEL

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Abstract

This work presents a heterogeneous dynamic model for the production of biodiesel using palmitic triglyceride and methanol as raw materials. Triglycerides are the main compounds in vegetable oils and when its total is beyond 97%, it is possible to produce biodiesel by means of a basic transesterification employing sodium hydroxide as a catalyst. The model takes into account that triglycerides are not soluble in alcohol so two liquid phases exist in the batch reactor, causing the reaction to occur in the triglyceride-methanol interphase. Results show that the model successfully calculates the concentration profile of triglyceride, alcohol and biodiesel in time as well as the intermediaries' products in the reactor. It also predicts concentration profiles at different temperatures in accordance to the Arrhenius' Law.

Keywords: biodiesel, kinetic modeling, transesterification, batch reactor, kinetic.

Resumen

Este trabajo presenta el desarrollo de un modelo dinámico para la producción de biodiesel utilizando como materias primas triglicérido palmítico y metanol. Los aceites vegetales se componen principalmente de triglicéridos y cuando la concentración de estos últimos es mayor al 97%, se utiliza un catalizador básico para llevar a cabo la reacción de transesterificación para obtener biodiesel. Este modelo considera que los triglicéridos no son solubles en el metanol, por lo que se forman dos fases al colocar ambos en un reactor por lotes, lo cual provoca que la reacción se lleve a cabo únicamente en la superficie de la gotas, esto es en la interfase metanol-triglicérido. Los resultados obtenidos con el modelo predicen de manera satisfactoria los perfiles de concentración de triglicéridos, alcohol y biodiesel en el tiempo, así como la concentración de los productos intermedios dentro del reactor. Así mismo predice la disminución del tamaño de las gotas y los perfiles de concentración a diferentes temperaturas.

Palabras clave: biodiesel, modelado, transesterificación, reactor por lotes, cinética.

1 Introduction

The usage of vegetable oils as fuel was deeply considered in the early days of the Diesel engine development. In fact, Rudolph Diesel himself demonstrated the performances of his engine using peanut oil. Nonetheless, the high viscosity of vegetable oils makes their use unsuitable for existing engines. It is interesting to note that, even though the viscosity of vegetable oil is ten times higher than diesel's, their corresponding esters' viscosities vary by a factor of two. The means to reduce vegetable oil viscosity has been widely studied and several methods have been developed (Kiss *et al*., 2008). Some of

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the most reported include: 1) direct use and blended with Diesel (Maa y Hanna, 1999), 2) use of micro emulsions with short-chain of alcohols (Maa y Hanna, 1999), 3) thermal cracking (pyrolysis) of vegetable oils (Charusiri y Vitidsant, 2005), 4) transesterification of triglycerides catalyzed by bases, acids or enzymes (Hills, 2003), and 5) esterification of fatty acids with alcohols, using acid (H_2SO_4) or solid acid catalysts (Kiss *et al*., 2006-I), (Kiss *et al*., 2006-II).

Biodiesel, in an ordinary sense, is understood as the fuel obtained from vegetable oils, animal fats or greases. However, in order to be classified as biodiesel, it must meet ASTM D 6751, or 14214:2008 European standards for flash point, water and sediment content, viscosity, sulfated ash, total sulfur, copper strip corrosion, cetane index, cloud point, carbon residue, acid number, free and total glycerin, phosphorus and vacuum distillation end point as indicates in Table 1. (García y García, 2006).

Biodiesel has several distinct advantages when compared to Diesel obtained from petroleum. In addition of being fully competitive to Diesel in most technical aspects it is 98.3% biodegradable within 21 days (García y García, 2006) and its higher flash point makes its handling and storage safer. With the exception of NO_x emissions, it is safe to argue that biodiesel is cleaner than Diesel since its emissions of CO during combustion are 50% lower; biodiesel does not contain sulfur so there are no SO_x emissions; there are no particle emissions either; biodiesel does not hold polycyclic aromatic hydrocarbons (PAH), or their nitro polycyclic aromatic hydrocarbons derivate (nPAH). It should not be overlooked that CO_2 produced by biodiesel combustion is a link in the natural carbon cycle meaning that no additional contribution of carbon is added to biosphere, disregarding the fuels used for harvest raw materials.

The two main disadvantages of biodiesel are its lower calorific power compared to Diesel (9,500 kcal/kg vs. 10,800 kcal/kg) and a gelation temperature near 0°C. The most common uses of biodiesel in compression-ignition engines are in its pure form, B100, or blended with diesel in 5% (B5) or 20% (B20). Minor engine modifications may be required in older diesel engines to avoid seals' dissolution of when pure biodiesel is used; however B5 and B20 blends can be used without any adjustment (Ataya *et al*., 2007).

The chemical structure of biodiesel is of fatty acid alkyl esters and two of the most common means to obtain it by chemical reaction are: transesterification using an alkali catalyst to transform triglycerides in their corresponding fatty acid alky esters (if the content of free fatty acids is lower than 1.5 %), and esterification using an acid catalyst to obtain the alkyl esters of free fatty acids (when concentration of free fatty acids is more than 2%). Strong liquid acid catalysts are less sensitive to free fatty acids concentration and can simultaneously conduct esterification and transesterification; however, this reaction is slower and requires higher reaction temperatures than basic reactions (Lotero *et al*., 2005).

The transesterification is the dominant aspect of the biodiesel production process since vegetable oils and animal greases are mainly triglycerides. Transesterification is the chemical conversion of triglycerides in their corresponding esters and consists in the reaction of a short chain alkyl alcohol with vegetable oils or animal greases in the presence of an alkaline catalyst, like NaOH or KOH. Triglycerides are formed by three molecules of long chain fatty acids linked to a glycerol molecule. The triglycerides molecules have a little polar part and three non polar long chains (C-10 to C-18); they are non-polar substances at low temperatures and are not soluble in polar substances like alcohols, causing two liquid phases in the reaction mixture. The chemical structure of triglycerides produces micelles when they are in a polar medium (Stryer, 2005), therefore when triglycerides molecules are polar alcohol and polar catalyst reaction mixture (alkali or acid), they form drops in a continuous polar phase.

There are several alcohols that can be used in transesterification: methanol, ethanol, 2-propanol and butanol mainly. There are although some important differences due to the alcohol used in the reaction: fatty acid ethyl esters form stable emulsions during transesterification (Van Gerpen, 2004), thus making it more difficult to separate it from glycerin than the fatty acid methyl esters.

Three consecutive and reversible reactions take place during the transesterification process. In the first one, the triglyceride reacts with one molecule of alcohol forming an alkyl ester molecule (biodiesel) and a diglyceride molecule; secondly, the diglyceride molecule obtained reacts with another alcohol molecule producing another alkyl ester and a monoglyceride molecule; finally the monoglyceride molecule formed reacts with a third alcohol molecule producing a new alkyl ester and a glycerin molecule, see Fig. 1.

Table 1. Biodiesel and Diesel specifications according to European and American Std.

Specification	Units	14214:2008	ASTMD 6751-7b	EN 590:1999
Density 15°C	g/cm^3	0.86-0.90		0.82-0.845
Viscosity 40°C	mm^2/s	3.5-5.0	1.9-6.0	2.0-4.5
Distillation	% @ °C		90%, 360°C	85%, 350°C-95%,360°C
Flashpoint (Fp)	°C	101 min	93 min	55 min
CFPP	°C	*country specific		*country specific
Sulphur	mg/kg	10 max	15 max	350 max
CCR 100%	% mass		0.05 max	
Carbon residue (10% dist. residue)	% mass	0.3 max		0.3 max
Sulphated ash	% mass	0.02 max	0.02 max	
Oxid ash	% mass			0.1 max
Water	mg/kg	500 max	500 max	200 max
Total contamination	mg/kg	24 max		24 max
Cu corrosion max	3h/50°C	1	3	1
Oxidation stability	Hrsat 110°C	6	3	N/A (25 g/m^3)
Cetane index		51 min	47 min	51 min
Acid value	mgKOH/g	0.5 max	0.5 max	
Methanol	%mass	0.20 max	0.2 max or Fp<130°C	
Ester content	% mass	96.5 min		
Monoglyceride	% mass	0.8 max		
Diglyceride	% mass	0.2 max		
Triglyceride	% mass	0.2 max		
Free glycerol	% mass	0.02 max	0.02 max	
Total glycerol	% mass	0.25 max	0.24 max	
Iodine value		120 max		
Linolenic acid ME	% mass	12 max		
C(x:4) & greater unsaturated esters	% mass	1 max		
Phosphorus	mg/kg	4 max	10 max	
Alkalinity	mg/kg			
Gp I metals (Na,K)	mg/kg	5 max	5 max	
Gp II metals (Ca,Mg)	mg/kg	5 max	5 max	
PAHs	% mass			11 max
Lubricity/wear	μm at 60°C			460 max

Therefore three alcohol molecules are needed to convert one triglyceride molecule in biodiesel; however, it is necessary to use an excess of alcohol in order to displace the reaction equilibrium toward alkyl ester production. Typically, a molar relation alcohol/triglyceride of 6:1 is needed when virgin vegetable oil is used in the reaction, and 7:1 for residual vegetable oil. However an excess of alcohol causes an increase in the solubility of glycerin in the reaction mixture, causing the separation to be harder (Kargbo, 2010).
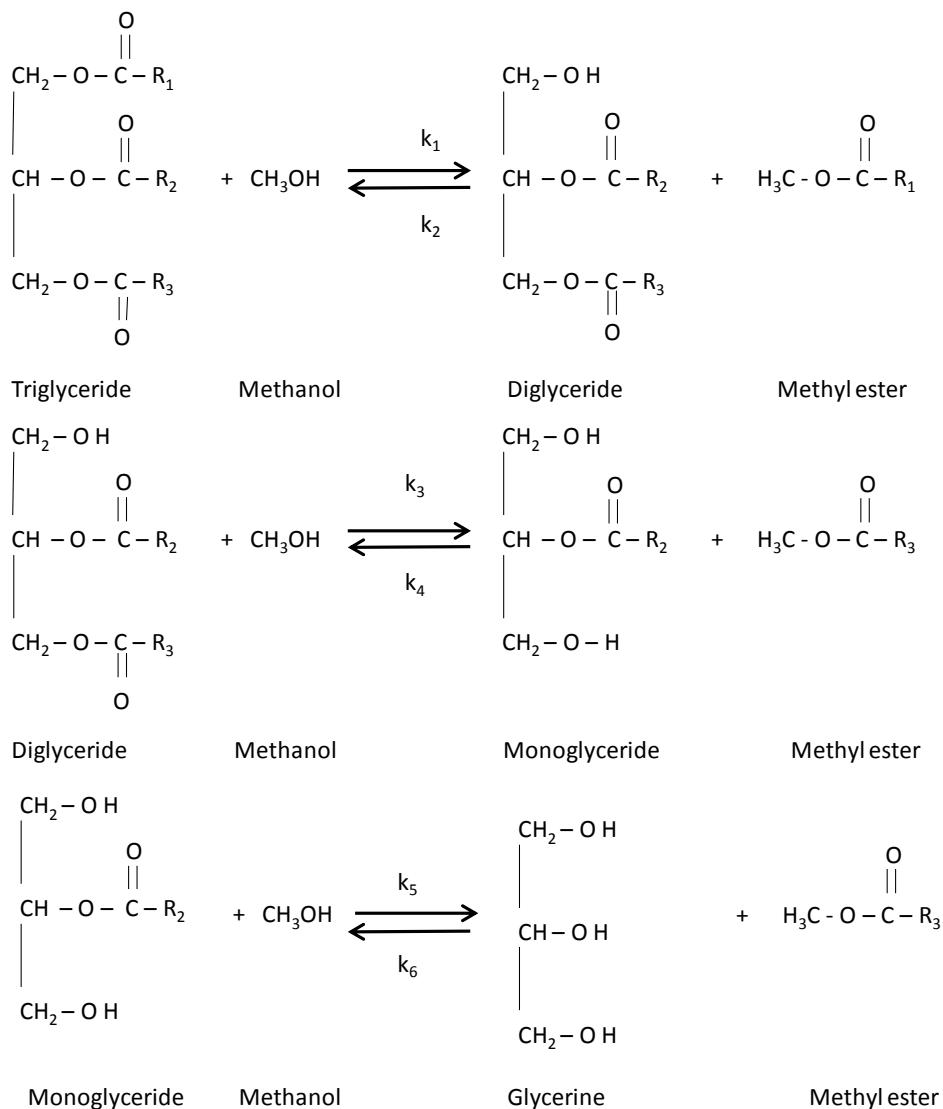
Fig. 1. Transesterification reaction of triglyceride and methanol to biodiesel and glycerin.

Although transesterification is faster than esterification, the presence of a considerable amount of free fatty acids in the reaction mixture (higher than 2%) with alkali catalyst, triggers soap formation as a byproduct, which impedes product separation and reduces the efficiency of biodiesel production:
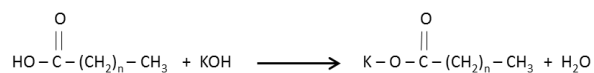
Water also generates problems in the reaction mixture because hydrolyzes triglycerides and create free fatty acids and then producing soap:
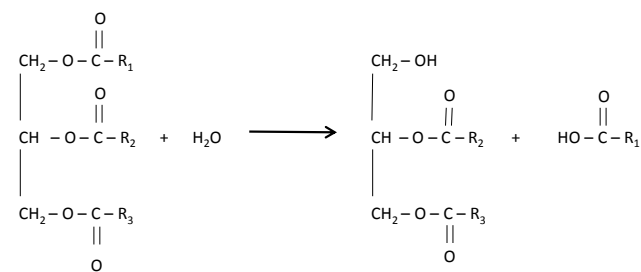
Triglyceride and alcohol phases are not miscible (Lide,

2004) and create two liquid layers upon their initial introduction into the reactor. Mechanical mixing is normally applied to increase the contact between the reactants, facilitating an increase in mass transfer rate (Noureddini y Zhu, 1997). The lipid solubility in the reaction mixture during transesterification can be solved by improving the stirred inside the reactor, or by adding hexane as a solvent. It has been reported that the addition of co solvents enhances the miscibility and results in a faster reaction rate (Boocock *et al.*, 1996). Agitation increases the number of droplets and decreases their dimension; thereby the interfacial surface area available for reaction also increases. Ataya *et al.* (2007) reported an experimental study which proves the importance of mass transfer in the biodiesel acid reaction. They found that different reaction rates exist when there is only one phase in the reaction mixture (by adding a solvent), when there are two liquid phases with agitation, and when there are two liquid phases without agitation. The reaction rates obtained were considerable higher in the case with a homogeneous phase, lower when droplets were formed by agitation; and a very low reaction rate when the two liquid phases were without agitation. They presented the different yields obtained for each case; however they did not develop a model to explain the occurring mass transfer phenomena. In this work, the influence of the mass transfer in the transesterification reaction to obtain biodiesel was investigated by developing a mass transfer-kinetic dynamic model and comparing its calculations with the experimental results reported by Noureddini and Zhu, (1997). The model considers that two different liquid phases are formed in a transesterification batch reactor when triglycerides, methanol and NaOH are stirred in an isothermal reactor. Noureddini and Zhu, (1997) developed a homogeneous model for the transesterification reaction based on the fact that drops are present in the reactor only in the 10 earliest minutes of the reaction. Nonetheless, 80% of the triglycerides reacting those 10 earliest minutes of the transesterification reaction, just when the drops are present in the reaction mixture. By parameter estimation, the model calculates the six reaction kinetic constants in the transesterification reaction, assuming that the kinetic constants are a function of temperature. The activation energy is then obtained by using three different sets of reaction kinetic constants.

2 The model

The reaction system considered in the model is essentially heterogeneous (González-Brambila, López Isunza, 2008; Lizardi-Jiménez, Gutiérrez-Rojas, 2011) because there are two liquid phases: the non polar triglyceride phase and the polar methanol phase. Several variables influence the reaction rate: temperature, solubility of the phases, and stirring velocity; all of them encourage the reaction conversion. The model considers only palmitic triglyceride, which reacts with methanol at 50°C and a Reynolds number of 6200, with NaOH as catalyst in the batch reactor. The palmitic triglyceride is formed by three molecules of palmitic acid bonded by a glycerin molecule, see Fig. 2.
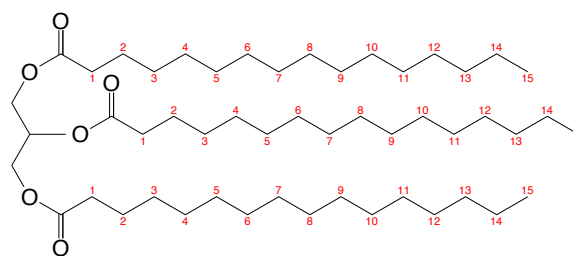

Fig. 2. Chemical structure of palmitic triglyceride.

The three reactions occur at the interphase between the two liquid phases since the triglycerides, methanol and catalyst are present in the drop's surface. Fig. 3 shows the schematic representation of the two phases in the reactor. At the beginning of the reaction the drops are formed by palmitic triglyceride ($C_{51}H_{98}O_{69}$), molecular weight 807.32, density = 0.8752 g/cm^3; its water solubility, reported in 100 ppm is equal to 0.0; alcohol solubility is 0.00423 (Lide, 2004). Table 2 shows the properties of the raw material, products and byproducts of the transesterification reaction considered in the model.

The following assumptions have been made to develop the model:

- Three consecutive reversible reactions take place; see equations 1, 2 and 3 in Fig. 4.

- The reactive used is palmitic triglyceride, this triglyceride has three identical alquil radicals; thus a unique methyl ester of palmitic acid is formed by the three reactions.

Table 2. Properties of raw materials, products and byproducts of transesterification.

Name	Formula	Molecular weight	Density g/cm^3	Solubility (in 100 parts of)			Boiling point $^\circ$C
				Water	Alcohol	Ether	
Palmitic triglyceride	$C_{51}H_{98}O_6$	807.32	0.8757	0	0.00421	v.s.	310-320
Palmitic diglyceride	$C_{35}H_{68}O_5$	568	—	—	—	—	—
Palmitic monoglyceride	$C_{19}H_{38}O_5$	330	—	—	—	—	—
Glycerin	$C_3H_8O_3$	92	1.26	∞	∞	∞	290
Methanol	CH_4O	32	0.792	∞	∞	∞	64.7
Biodiesel	$C_{17}H_{34}O_2$	270.457		—	∞	—	415-418

- The molar relation alcohol/triglyceride used is 6:1. Considering a stoichiometric molar relation of 3:1, all the triglyceride can react; however its concentration is determined by equilibrium at the end of the reaction. It is important to note that there will also be alcohol in reactor at the end of the reaction.

- Since glycerides and glycerin are not soluble in alcohol, they form drops in a continuous phase due to its polar compound.

- The catalyst is soluble only in alcohol.

- The reactions take place only in the interphase surface of the drops.

- The density of the drops remains constant during the reaction despite the fact that at the beginning of the reaction the drops are formed by triglyceride. During the reaction the drops are formed by triglyceride, diglyceride, monoglyceride and glycerin. At the end of the reaction the drops are mainly formed by glycerin.

- The batch time is 60 minutes.

- Interfacial mass transfer coefficients remain constant during the reaction time, even though compositions of both phases change in time.

- The temperature remains constant in the batch reactor, during the reaction.

- The reactor is ideally stirred.
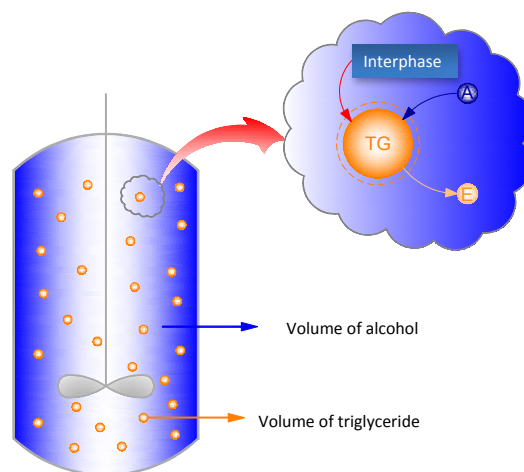
Fig. 3. Scheme of the stirred bioreactor tank.

$$TG + A \;\underset{k_2}{\overset{k_1}{\rightleftharpoons}}\; DG + E \qquad \text{.........} \qquad (1)$$

$$DG + A \;\underset{k_4}{\overset{k_3}{\rightleftharpoons}}\; MG + E \qquad \text{.........} \qquad (2)$$

$$MG + A \;\underset{k_6}{\overset{k_5}{\rightleftharpoons}}\; Gli + E \qquad \text{.........} \qquad (3)$$

Fig. 4. Reaction sequence used in the model.

2.1   The mass balances

The triglyceride volume is equal to the volume of each drop multiplied by the number of drops

$$V_{TG} = (N_g)(V_g) \qquad (1)$$

The volumetric area of the drops is calculated by Eq. (2), and volume of the liquid in the reactor is equal to the alcohol volume plus the triglyceride volume (Eq. 3).
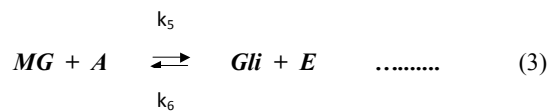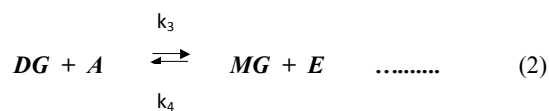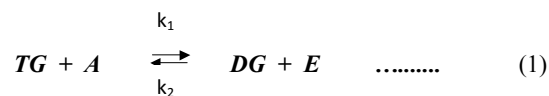
$$a_{vg} = \frac{6}{d_g} \qquad (2)$$

$$V_R = V_A + V_{TG} \qquad (3)$$

Considering ε as the methanol volume, the triglyceride volume can be defined as $V_{TG} = 1 - \varepsilon$, then $V_R = 1$, and $\varepsilon = V_A / V_R$.

2.2   The mass balances in the liquid phase

The evolution of the alcohol (C_A) and ester (C_E) profiles concentration in the liquid phase are given by the interfacial mass transfer between the methanol phase and the drop-liquid interphase, as shown in Eqs. (4) and (5):

$$\frac{dC_A}{dt} = k_m a_{vg}(C_{al} - C_{Ai}) \qquad (4)$$

$$\frac{dC_E}{dt} = k_m a_{vg}(C_{Ei} - C_{El}) \qquad (5)$$

2.3   The mass balances in the drop-liquid interphase

The evolution of the triglyceride concentration in the drop-liquid interphase is given by the consumption and generation of triglyceride as shown in Eq. (6). It is also described in the reaction sequence in Fig. 4:

$$\frac{dC_{TG}}{dt} = -k_1 C_{TG} C_A + k_2 C_{DG} C_E \qquad (6)$$

In the same manner, the evolution in the concentrations of diglyceride, monoglyceride and glycerin in the drop-liquid interphase are given by their generation and consumption, according with the reaction path shown in Fig. 4:

$$\frac{dC_{DG}}{dt} = k_1 C_{TG} C_A - k_2 C_{DG} C_E - k_3 C_{DG} C_A + k_4 C_{MG} C_E \qquad (7)$$

$$\frac{dC_{MG}}{dt} = k_3 C_{DG} C_A - k_4 C_{MG} C_E - k_5 C_{MG} C_A + k_6 C_{Gli} C_E \qquad (8)$$

$$\frac{dC_{Gli}}{dt} = k_5 C_{MG} C_A - k_6 C_{Gli} C_E \qquad (9)$$

The alcohol interfacial mass transfer profile in the drop-liquid interphase is equal to the generation and consumption of alcohol in the three reversible reactions:

$$k_m a_{vg}(C_{Al} - C_{Ai}) = -(k_1 C_{TG} C_A - k_2 C_{DG} C_E)$$
$$- (k_3 C_{DG} C_A - k_4 C_{MG} C_E)$$
$$- (k_5 C_{MG} C_A - k_6 C_{Gli} C_E) \qquad (10)$$

The ester interfacial mass transfer between the drop surface and the alcohol phase is equal to the production and consumption of the ester:

$$k_m a_{vg}(C_{Al} - C_{Ai}) = k_1 C_{TG} C_{Ai} - k_2 C_{DG} C_{Ei}$$
$$+ k_3 C_{DG} C_{Ai} - k_4 C_{MG} C_{Ei}$$
$$+ k_5 C_{MG} C_{Ai} - k_6 C_{Gli} C_{Ei} \qquad (11)$$

2.4   The drops radius

In the beginning of the reaction, the whole drop is formed by triglyceride. During the reaction time the radii of drops is reduced because the ester produced is transferred to the methanol phase and due to the fact that ester is soluble in alcohol. Therefore the rate of change in drop radius is a function of the glycerides consumed (reaction constants k_1, k_3 and k_5), the generation of glycerides (reaction constant rates k_2, k_4 and k_6), and the density and superficial area of the drops. So Eq. (12) takes the form:

$$\frac{dr_g}{dt} = -\frac{1}{\rho_g a_{vg}}(k_1 C_{TG} C_{Ai} - k_2 C_{DG} C_{Ei} + k_3 C_{DG} C_{Ai}$$
$$- k_4 C_{MG} C_{Ei} + k_5 C_{MG} C_{Ai} - k_6 C_{Gli} C_{Ei}) \qquad (12)$$

2.5   The model solution

These equations were held dimensionless and the resulting set of nonlinear ODE was solved with a fourth-order Runge-Kuta method in a FORTRAN program developed by the authors. The transport and kinetic parameters in the model were estimated using

Table 3. Initial parameters of the model.

Parameter	Value
Reactor volume (cm^3)	1000.0
Initial drop diameter (cm)	0.5
Interfacial mass transfer coefficient (cm/s)	0.5×10^{-2}
Triglyceride density (g/cm^3)	0.8969
Alcohol density (g/cm^3)	0.7018
Initial triglyceride concentration (g/cm^3)	0.7
Initial diglyceride concentration	0.0
Initial monglyceride concentration	0.0
Initial glycerine concentration	0.0
Triglyceride molecular mass	807.32
Triglyceride solubility in alcohol (in 100 ppm)	0.00421

a Marquardt non-linear estimation method (Meeter., 1965), (Draper and Smith, 1996), and validated with the experimental results reported by Noureddini and Zhu [13]. The parameters estimated were the six constant reactions and the mass transfer coefficient between drops and alcohol phase. Table 3 shows the initial parameters of the model.

The model was compared with the experimental results at 50°C, while the six reaction rate constants for 40°C and 60°C were estimated. The variation of the rate reaction constants (k_1, k_2, k_3, k_4, k_5 and k_6) with respect to temperature can be described by the Arrhenius relationship (Eq. 13):

$$k = Ae^{-\frac{Ea}{RT}} \tag{13}$$

where A is the Arrhenius constant or frequency factor, Ea is the activation energy for the reaction, R is the ideal gas constant, and T is absolute temperature. Taking natural logarithm of both sides of Eq. 13, a straight line equation is obtained, Eq. (14):

$$\ln k = \ln A - \frac{Ea}{RT} \tag{14}$$

thus, a plot of $\ln k$ versus $1/T$ results in a straight line with slope $-Ea/R$.

3 Results and discussion

The model's equations successfully predicted the evolution on time of triglyceride, diglyceride, monoglyceride, glycerin, methanol and ester (biodiesel) concentrations in the batch reactor. Moreover, it calculates the diminishment in time of the drop radius as a function of the reaction rates and mass transport phenomena. Fig. 5 compares the model results to the experimental results at a reaction temperature of 50°C, experimental results are shown with symbols while model results are presented as continuous lines. It can be observed that the model accurately predicts the experimental results. The triglycerides concentration diminishes continuously in time due to the consumption in reaction 1. It is important to mention that reaction 1 is almost irreversible because the methyl ester palmitic acid concentration in the surface of the drops is negligible, mainly at the beginning of the reaction.

The diglyceride concentration is zero at the beginning of the reaction since the initial raw material considered in the model was only palmitic triglyceride. Between minutes 1 to 7 after the reaction begins, the diglyceride concentration increases since reaction 1 occurs only toward the right side, and reaction 2 takes place at a very low rate since the raw material (diglyceride) concentration is almost zero. After minute 7, the diglyceride concentration starts to decrease due to the fact that reaction 2 also increases its reaction rate toward monoglyceride production. After minute 20, the diglyceride concentration becomes constant because reactions 1 and 2 are in equilibrium.

The monoglyceride concentration is equal to zero at the beginning of the reaction and its concentration increases slowly during the early minutes of the reaction; during this time reaction two produces monoglyceride. However, later on, the monoglyceride concentration decreases due to the production of metil ester of palmitic acid (biodiesel) caused by reaction three.
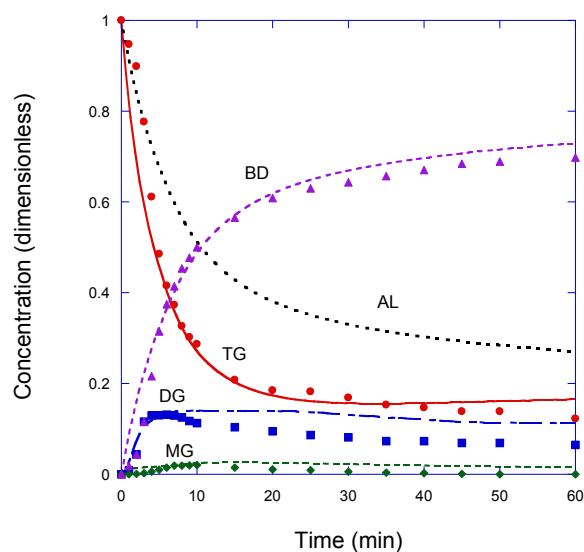
Fig. 5. Comparison between experimental and model results. ● Experimental triglyceride concentration, ──Model triglyceride concentration, ■ Experimental diglyceride concentration, ─·──· Model diglyceride concentration, ◆ Experimental monoglyceride concentration, - - - Model monoglyceride concentration, ▲ Experimental ester concentration, ── Model ester concentration, - - - Model alcohol concentration.

The alcohol concentration decreases continuously during the 60 minutes of where takes place reaction, due to the fact that biodiesel production increases constantly. However the alcohol concentration never reaches a low concentration because it exists in excess stoichiometric relation in the reactor. It must be noted that the alcohol concentrations predicted by the model were greater than the experimental results reported. This deviation maybe explained that some methanol might have been lost during experiments; this assumption is based on the fact that methanol's boiling point is 64°C, as shown in Table 2, and the reaction temperature is 50°C. Even more, the experimental results were developed for soybean oil as raw material, which is a mixture of lauric acid (C-12) (5% w), myristic acid (C-14) (0.1% w), palmitic acid (C-18) (9,8% w), arachidic acid (C-20) (<0.1% w), palmitioleic acid (C-16:1) (0.4% w), oleic acid (C-18:1) (42.5% w), linoleic acid (C-18:2) (34.9% w) and linolenic acid (C-18:3) (2.6% w).

Fig. 6 shows how glycerin concentration increases in time as a function of the biodiesel continuous production. It is also possible to see the evolution

of the drop's radius in time, which diminishes continuously as a function of the triglyceride consumption and biodiesel production. There were no experimental results found about the drop's radius diminishment in literature, so it was not possible to compare these results. The transesterification reaction occurs mainly in the ten minutes after the reaction beginning. After twenty minutes, the conversion to biodiesel is negligible, as it can be seen in Figs. 5 and 6. It can be appreciated that after 10 minutes the amount of palmitic triglyceride converted to biodiesel is 68.5%, and after 20 minutes is close to 82.7%, as shown in Fig. 7.

Temperature has a significant kinetic effect on the reaction rates as proved by both the model predictions and the experimental results, and shown in Fig. 8, where the biodiesel production is plotted for three different temperatures, 40, 50 and 60°C. It can also be seen that as temperature increases, the biodiesel is produced faster and in bigger amounts. The model also was used obtain the six reaction constants for each temperature case (40, 50 and 60°C), as shown in Table 4. These results are consistent with the experimental results proving the stability of the model. Fig. 9 displays the natural logarithm of the reaction constants are plotted versus $1/T$, for the six reactions that take place to produce biodiesel by transesterification.
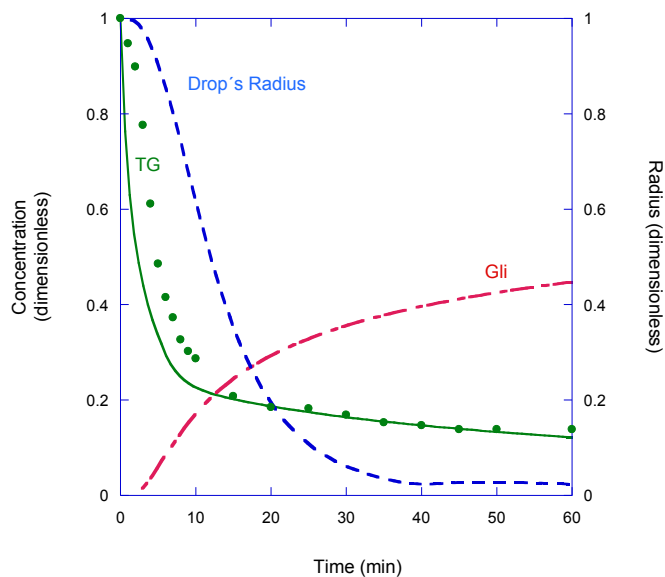

Fig. 6. Evolution of glycerin and triglyceride profile concentration and drop's radius, at 50°C. ● Experimental triglyceride concentration, ── Model triglyceride concentration, ─·── Model glycerin concentration, - - - Model drop's radius evolution.

Table 4. Reaction constants at different temperatures.

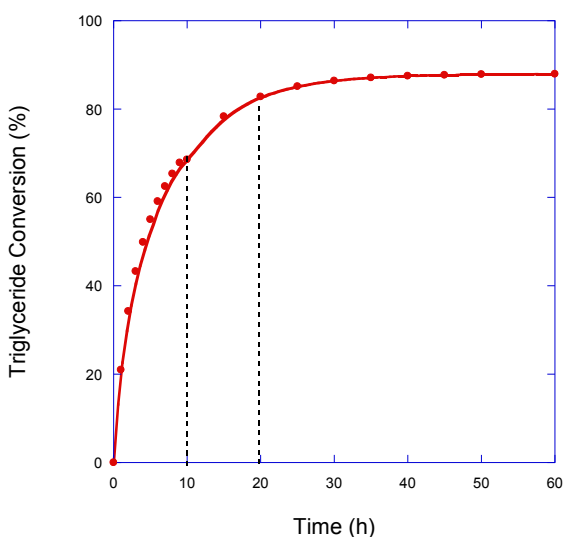| Reaction constant	Temperature		
	40°C	50°C	60°C
k_1	0.0038	0.0042	0.0085
k_2	0.0008	0.00085	0.0015
k_3	0.002	0.0033	0.0062
k_4	0.002	0.0025	0.0042
k_5	0.0015	0.0018	0.0045
k_6	0.00007	0.00008	0.00018

Fig. 7. Conversion of triglyceride in time at 50°C, according with model predictions.
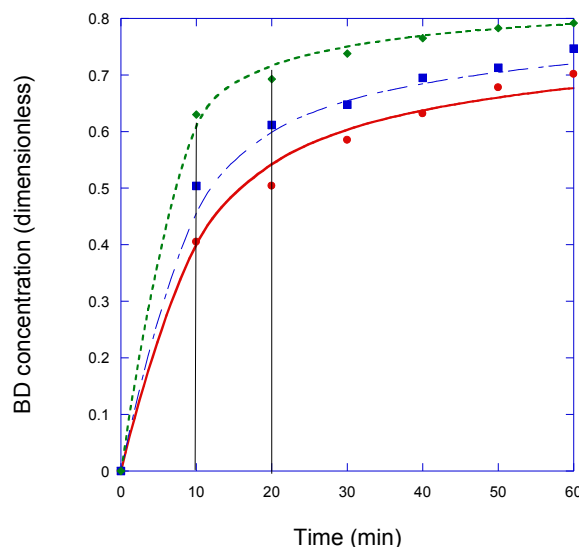

Fig. 8. Experimental data and predicted model biodiesel concentration at three different temperatures. ● Experimental data at 40 °C, — Model prediction at 40 °C, ■ Experimental data at 50°C, - - - Model prediction at 50°C, ◆ Experimental data at 60°C, - - - Model prediction at 60°C.

Table 5 shows the slopes, the interception at the origin, the standard deviation, the activation energy calculated for each one of the six reaction constants for each of the different temperatures (40, 50 and 60 °C). This information was obtained by adjusting the reaction constants using a parameter estimation method. Using these results, it was possible to obtain the equation for each reaction constant, Eqs. (15) to (20):

$$k_1 = 55.994 \times 10^3 e^{\frac{46.266}{RT}} \tag{15}$$

$$k_2 = 62 \times 10^{-6} e^{-\frac{9.6405}{RT}} \tag{16}$$

$$k_3 = 3.877 \times 10^{-14} e^{-\frac{76.1133}{RT}} \tag{17}$$

$$k_4 = 2.8949 \times 10^{-17} e^{-\frac{90.3692}{RT}} \tag{18}$$

$$k_5 = 6.4099 \times 10^{-10} e^{-\frac{46.5482}{RT}} \tag{19}$$

$$k_6 = 15.13598 \times 10^5 e^{\frac{52.1587}{RT}} \tag{20}$$

Conclusions

This study demonstrates that it is possible to calculate, by means of a set nonlinear ODE, the concentration profiles, of raw materials, products and byproducts that occur in the transesterification reaction of biodiesel production. The model, which includes the kinetic sequence, mass transport phenomena and the occurring reactions, is validated successfully with experimental results at different temperatures. The model also estimates the reduction of drops radii during the reaction, which is of great importance since the reaction takes place in the drops surface; it also takes into account that two liquid phases are present in the reactor since triglyceride is not soluble in alcohol.

Table 5. Slope, Interception, Activation Energy and Standard Deviation for Reaction Constants.

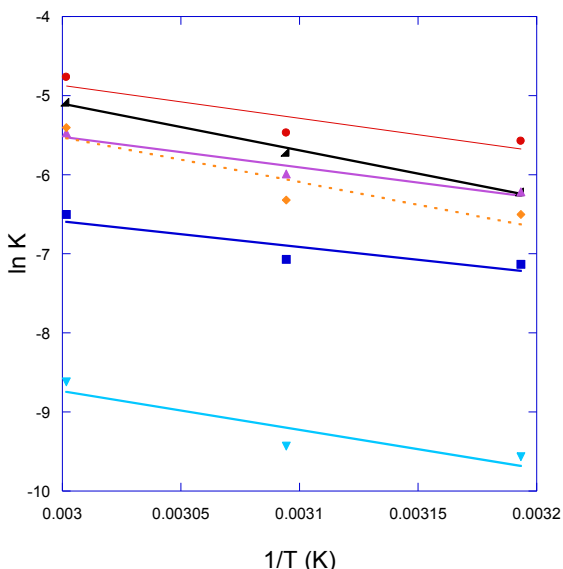| Reaction rate constant	Slope (m)	Intercept (b)	$Ea = (mR)$ (cal/mol)	R
k_1	-4165.6	7.6277	8277.91	0.91014
k_2	-3250.7	3.1646	6459.81	0.89873
k_3	-5892.9	12.577	11710.4	0.99647
k_4	-3853	6.038	7656.71	0.97038
k_5	-5689.4	11.542	11306.01	0.92642
k_6	-4888.6	5.9299	9714.66	0.91694

Fig. 9. Straight lines for the six reaction rate constants in function of temperature. ● Reaction one, ■ Reaction two, ◆ Reaction three, ◆ Reaction four, ▲ Reaction five, ▼ Reaction six.

According to the model's results, the maximum possible biodiesel production that can be obtained, one hour after the reaction started, is 67.7% for a reactor operating at 40°C; 72.0% at 50°C and 79.0% at 60°C. It is impossible to achieve a 100% biodiesel concentration since all three reactions are in equilibrium. It must be stated that it would be highly inefficient to operate a batch reactor for a whole hour since 80% of the biodiesel produced in that hour is obtained during the first 10 minutes and 90% during the first 20 minutes, for an operation temperature of 60°C. Finally, it is proved that the set of reactions that take place in the reactor during the biodiesel production is a function of time and can be expressed by the Arrhenius relationship.

Nomenclature

A	Arrhenius constant
a_{vg}	volumetric area of drop
BD	biodiesel
C	concentration
d_g	diameter of drop
E	activation energy
k	reaction constant
k_m	mass transfer coefficient in drop's interphase
N	number of
R	ideal gas constant
T	temperature
V	volume

Greeks letters
ρ	density
ε	% alcohol volume

Subscripts

1	in reaction 1
2	in reaction 2
3	in reaction 3
4	in reaction 4
5	in reaction 5
6	in reaction 6
A	Methanol
DG	Diglyceride
E	Ester
g	drop
Gli	Glycerin
i	in drop-liquid interphase
l	in alcohol liquid phase
R	reactor
TG	Triglycerides

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