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Modelling and Simulation of Transesterification Reaction in a Batch Reactor

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ABSTRACT

A dynamic model for the transesterification reaction in a batch reactor was developed for the triglyceride, methanol, intermediates and products (alkyl ester and glycerol) concentrations. The model took into account of mass transfer and kinetic on the reaction process. In this present study, the effect of methanol to triglyceride molar ratio on conversion of triglyceride was investigated at fixed temperature and catalyst concentration. The model consists of system of ordinary differential equations, and the differential equations representing the rates of disappearance and production of species involved were solved using the fourth-order Runge-Kutta method. Simulated results obtained herein agree exceedingly well with the general observations in the literature.

Keywords: Biodiesel, Mathematical model, Kinetics, Mass transfer, Batch Reactor.

INTRODUCTION

Biodiesel (FAME) is a clean- burning fuel derived from vegetable oils or animal fat and is an advantageous alternative to fossil diesel fuel because of its biodegradability, bio-renewable nature, very low sulphur content and toxicity, low volatility or flammability, good transport and storage properties, higher cetane number, and its salutary atmospheric CO_2 balance for production [1].

Biodiesel is usually produced by the trans-esterification of large branched triglycerides (TG) (vegetable oils) into smaller, generally straight- chain molecules of alkyl (most often methyl) esters in the presence of catalyst [2]. Di – and mono glycerides (DG and MG) are intermediates and glycerol (G) is the side product.

The reaction system in a batch reactor may be considered as a pseudo- homogeneous one with no mass transfer limitation [3]. Nonetheless, a reaction mechanism consisting of an initial mass transfer- controlled region followed by kinetically controlled region is generally proposed [4]. The convectional base catalyzed trans-esterification is characterized by slow reaction rates at both initial and final reaction stages limited by mass transfer between polar methanol/glycerol phase and non- polar oil phase [5]. Determination of rate constants for the triglycerides transesterification reaction at different operating conditions were previously considered [6-8].

The use of a feasible and comprehensive dynamic model allows the study of batch reactor performance under different operational conditions such as reaction temperature, catalyst concentration, and impeller speed. Such a model can be a valuable tool in the development of new control strategies in order to avoid process failure and to optimize reactor performance. The solution to the new system model acknowledging mass transfer and kinetic was presented [9].

In the model presented by Klofutar et al, the influence of mass transfer was neglected but the influence of both mass transfer and kinetic was considered in this study in order to determine favourable operating conditions.

Three main reaction steps are usually identified in transesterification of oil as follows:
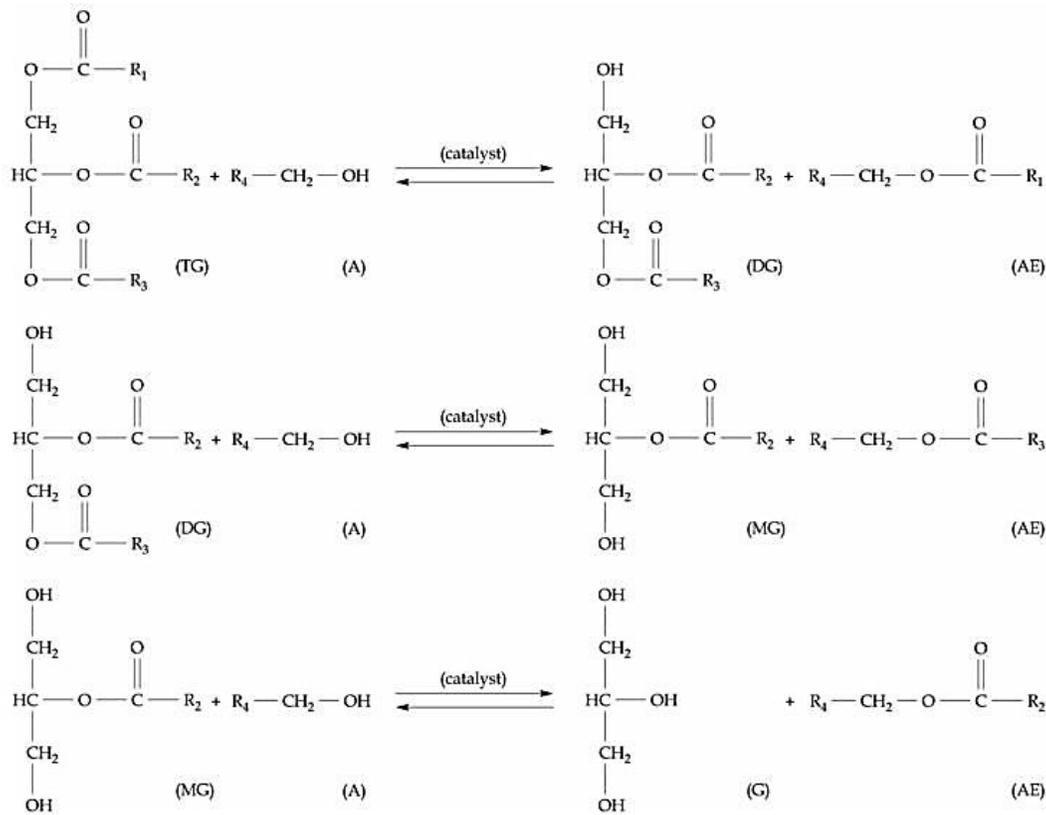

Figure 1: Reaction Scheme of Triglyceride Transesterification to Glycerol and Alkyl ester.

MATHEMATICAL MODEL

In order to develop a model able to represent both chemical kinetics and the mass transfer phenomena, the following assumptions were made:

1. First order for all compounds involved in the reaction.
2. The transfer of oil (TG) as well as reaction intermediates (DG and MG) from the oil phase towards the methanol phase is assumed [10].
3. The process model indicates that trans-esterification is controlled by both mass transfer and reaction kinetic steps.
4. It is also assumed that TG, DG and MG are present at chemical equilibrium.

EQUATION OF REACTION

In this process model, besides the three consecutive reaction, a shunt reaction, in which three methanol molecules react simultaneously with a triglyceride [8], is included.

$$TG + CH_3OH(A) \underset{k_4}{\overset{k_1}{\rightleftharpoons}} DG + ME \tag{1}$$

$$DG + CH_3OH(A) \underset{k_5}{\overset{k_2}{\rightleftharpoons}} MG + ME \tag{2}$$

$$MG + CH_3OH(A) \underset{k_6}{\overset{k_3}{\rightleftharpoons}} G + ME \tag{3}$$

$$TG + 3CH_3OH(A) \underset{k_8}{\overset{k_7}{\rightleftharpoons}} G + 3ME \tag{4}$$

Subject to those aforementioned assumptions, the following equations represent mass transfer and first order reaction kinetics for all the compounds.

$$\frac{dC_{TG}}{dt} = k_{L(TG)}a\left(C_{TGi} - C_{TG}\right) - k_1 C_{TG} C_A + k_4 C_{DG} C_{ME} - k_7 C_{TG} C_A^3 + k_8 C_G C_{ME}^3 \tag{5}$$

$$\frac{dC_{DG}}{dt} = k_{L(DG)}a\left(C_{DGi} - C_{DG}\right) + k_1 C_{TG} C_A - k_2 C_{DG} C_A - k_4 C_{DG} C_{ME} + k_5 C_{MG} C_{ME} \tag{6}$$

$$\frac{dC_{DG}}{dt} = k_{L(DG)}a\left(C_{DGi} - C_{DG}\right) + k_1 C_{TG} C_A - k_2 C_{DG} C_A - k_4 C_{DG} C_{ME} + k_5 C_{MG} C_{ME} \tag{7}$$

$$\frac{dC_G}{dt} = k_3 C_{MG} C_A - k_6 C_G C_{ME} + k_7 C_{TG} C_A^3 - k_8 C_G C_{ME}^3 \tag{8}$$

$$\frac{dC_A}{dt} = -k_1 C_{TG} C_A - k_2 C_{DG} C_A - k_3 C_{MG} C_A + k_4 C_{DG} C_{ME} + k_5 C_{MG} C_{ME} + k_6 C_G C_{MG} \tag{9}$$

$$\frac{dC_{ME}}{dt} = k_1 C_{TG} C_A + k_2 C_{DG} C_A + k_3 C_{MG} C_A - k_4 C_{DG} C_{ME} - k_5 C_{MG} C_{ME} - k_6 C_G C_{MG} + 3k_7 C_{TG} C_A^3 - 3k_8 C_G C_{ME}^3 \tag{10}$$

The associated initial and conditions are as follows,

$$C_{TG} = C_{TGi} \ @ \ t=0, \ C_{DG} = 0 \ @ \ t=0, \ C_A = C_{Ai} \ @ \ t=0$$

$$C_{MG} = 0 \ @ \ t=0, \ C_G = 0 \ @ \ t=0, \ C_{ME} = 0 \ @ \ t=0$$

METHOD OF NUMERICAL SOLUTION

The method adopted for the solution of the system of ordinary differential equations (5) to (10) for the model of transesterification reaction in a batch reactor is the fourth order Runge-Kutta method. A mathematical algorithm to solve these systems of equations was developed and implemented into computer program using MATLAB software. The parameters reported by [4] and [9] were used for simulation in this study, which are given below:

The mass transfer parameters for the trans-esterification reaction [9]:
$K_{L(TG)}$ = 1.47 * 10^{-6} m/s

$K_{L(DG)}$ = 1.80 * 10^{-5} m/s

$K_{L(MG)}$ = 1.31 * 10^{-6} m/s

a = 0.35 m^2/m^3 (*)

Table 1: The reaction rate constants [8] used in the simulations

Rate Constants	Temperature (40^0C)
k_1	0.0225
k_2	0.0447
k_3	0.0627
k_4	0.0011
k_5	0.0067
k_6	0.0012
k_7	$1.2 * 10^{-4}$
k_8	$1.4 * 10^{-7}$

The physical properties of compounds involved in the reaction are as follows (Literature):

ρ_{TG} = 945 kg/m^3

ρ_{DG} = 1697 kg/m^3

ρ_{MG} = 980 kg/m^3
M_{TG} = 871.55 kg/kmol
M_{DG} = 611.73 kg/kmol
M_{MG} = 351.91 kg/kmol

SIMULATION RESULTS AND DISCUSSION

The simulation of the model gives a solution for the concentration of compounds involved in the reaction against time at different operating conditions and the obtained results are compared with the previous models reported in the literature, which agrees reasonably well with it. This present model is studied by considering the effect of triglyceride to methanol molar ratio at constant temperature and for a constant catalyst concentration.

Concentration continuously decreases and at the end of the process, equilibrium was approached. The DG concentration increases rapidly during an initial period of reaction , reaching a peak concentration of about 5%, 3%, 0.5% and 0.1% for triglyceride- methanol molar ratio of 1:6, 1:9, 1:16.2 and 1:22.7 respectively at 400C and after that slowly decreases. During the transesterification process, the formation of MG was not that visible, indicating that it formed as an intermediate and also disappeared before the end of the reaction.
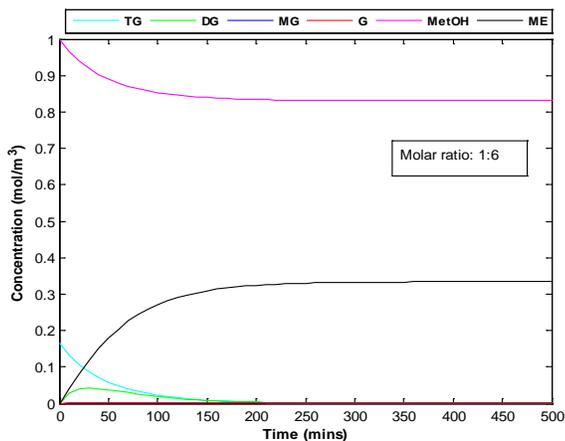
Figure 1: Concentration of species with time at molar ratio of 1:6
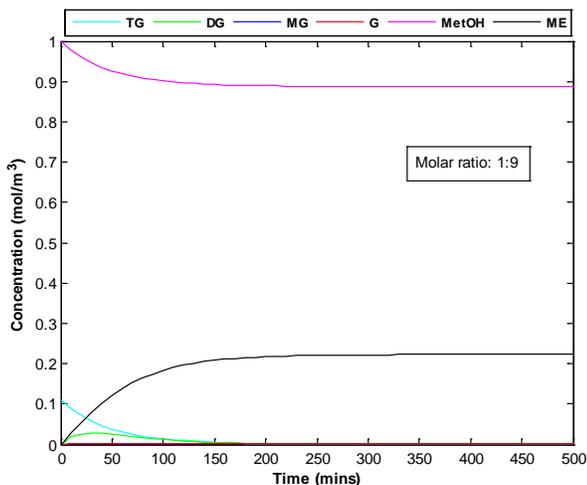

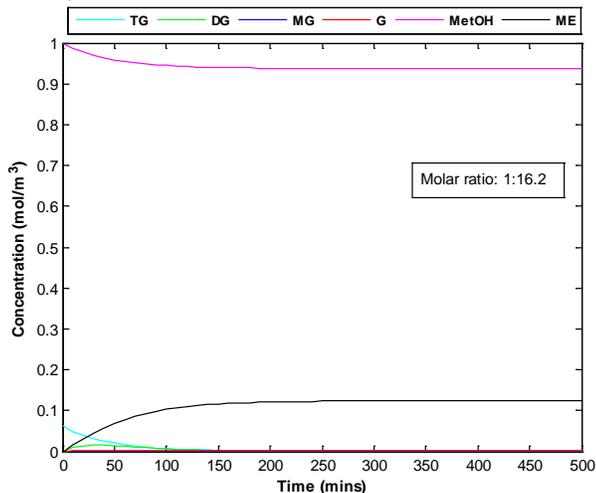Figure 2: Concentration of species with time at molar ratio of 1:9

Figure 3: Concentration of species with time at molar ratio of 1:16.2
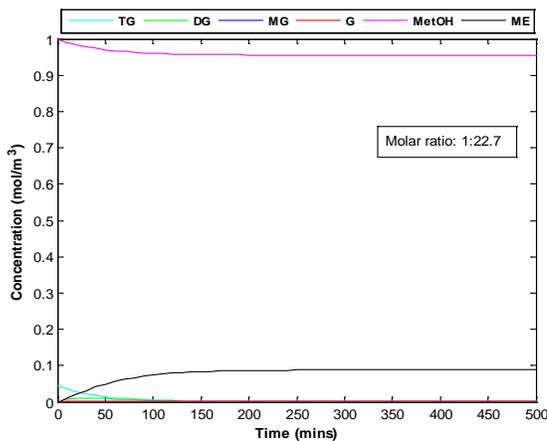

Figure 4: Concentration of species with time at molar ratio of 1:22.7

Figure 1-4 also revealed the curves for the production of methyl ester (Biodiesel). From these figures, triglyceride conversions were very low during the beginning of reactions, which involved a low methyl ester production rate at this stage. The conversion then increased slowly during the transesterification process and at the end remained approximately constant as equilibrium was approached. Nevertheless, the existence of three regions of different rate behaviour (mass transfer, kinetic and final controlled regions) was assumed [4]. In this present study, only mass transfer and kinetic controlled regions were acknowledged. It was also found that triglyceride conversion to methyl ester (Biodiesel) was higher at 1:6 molar ratio of TG to methanol (metOH). Further increase in TG to methanol molar ratio conversion does not increase. The optimum molar ratio of TG to methanol was 1:6.

CONCLUSION

In this present study, a mathematical model able to represent both mass transfer phenomenon and reaction kinetics at a given temperature (40^0C) for the transesterification reaction between vegetable oil and methanol in a batch reactor was developed and solved numerically by Runge- Kutta method. It was simulated by using MATLAB software. Parametric study carried out on the model shown that the triglyceride conversion to methyl ester (biodiesel) was higher at 6:1 molar ratio of methanol to triglyceride. Further increase in methanol to triglyceride molar ratio conversion does not increase. The optimum molar ratio of methanol to triglyceride was 6:1.

NOTATION

a	Dispersion coefficient, m^{-1}.
C_A	Concentration of methanol, mol/dm^3
C_{DG}	Concentration of di-glyceride, mol/dm^3
C_G	Concentration of glyceride, mol/dm^3
C_{ME}	Concentration of methyl ester, mol/dm^3
C_{MG}	Concentration of mono-glyceride, mol/dm^3
C_{TG}	Concentration of triglyceride, mol/dm^3
K	Rate constant, s^{-1}
$K_{L(DG)}$	Mass transfer coefficient of di-glyceride, m/s
$K_{L(MG)}$	Mass transfer coefficient of mono-glyceride, m/s
$K_{L(TG)}$	Mass transfer coefficient of triglyceride, m/s
M_{DG}	Molecular mass of di-glyceride, kg/kmol
M_{MG}	Molecular mass of mono-glyceride, kg/kmol

M_{TG} Molecular mass of triglyceride, kg/kmol
Greek letters
ρ Density, kg/m^3
Subscripts
A   Methanol
I   Initial condition
DG   di-glyceride
ME   methyl ester
MG   mono-glyceride
TG   triglyceride

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