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Numerical Modeling Of Palm Oil Transesterification In Stirred Tank Reactor

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Abstract:

This paper presents mathematical model describing the transesterification of palm oil for biodiesel production in a batch continuously stirred tank reactors (CSTR). The model describes the chemical kinetics of transesterification reactions and describes the transient and spatial concentration of triglycerides, diglycerides, monoglycerides, glycerol and biodiesel production in CSTR reactors. Reaction rate constants were written in the Arrhenius form. The reactor hydrodynamics is modeled using computational fluid dynamics (CFD) technique. The transesterification kinetics was coupled to the reactor hydrodynamics, therefore providing better understanding of a three-dimensional complex processes occurring in the reactor.

An analysis of key process variables; the reactor temperature and impeller speed were varied to achieve the maximum palm oil conversion rate to biodiesel while maintaining the molar concentration of alcohol and triglycerides at ratio 6:1. The effect of varying operating temperature and impeller speed ranging 50^0 to 100^0 C and 150 RPM to 750 RPM were respectively investigated. Variation of mixing intensity and reactor temperature appear to have similar to the reaction rate. Zones of higher reaction rates were observed near the impeller tip diameter. The model results were validated against published literature data and good correlation between model simulations and experimental data was observed. Thus, the computer model can potentially assist for better understanding of the reactor kinetics as well as the complex flow. The model can therefore be used as a design and optimization tool for stirred reactors in biodiesel production.

Keywords: Biodiesel**,** Transesterification, Triglycerides, Methyl Esters, Palm Oil, Kinetics.

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1. Introduction

Presently, biodiesel as a clean-burning fuel is being produced from vegetable oils or animal fats. Its chemical structure is that of fatty acid alkyl esters. Biodiesel is produced by transesterification of oils with short-chain alcohols or by the esterification of fatty acids. Transesterification of vegetable oils and fats to methyl and ethyl esters using different reactants, reaction conditions and catalysts have been reported (Freedman et al., 1984). The transesterification reaction consists of transforming triglycerides into fatty acid alkyl ester, in the presence of an alcohol, such as methanol or ethanol, and a catalyst, such as an alkali or acid, with glycerol as a byproduct (Hoydoncx, 2004). Three reversible reactions are believed to occur consecutively (Freedman, 1986).

Due to the increasing industrial use of esters, the variables that influence the process of ester transesterification have received extensively investigation, (Sankaran, V, 1990) and Kusy, 1882). Among the main variables studied were the type of catalyst, molar ratio of alcohol to vegetable oil and temperature. Additionally, the significance of research has been reported on the transesterification of esters with alcohol. However, only limited studies reported in the detailed process on the stirred reactors for the production of esters from vegetable oils.

The transesterification of vegetable oils has been reported, for example, the review paper by (Sridharam, 1974). Dufek, *et al* (1972) studied the esesterification and transesterification of carboxystearic acid using acid catalyst. Freedman, *et al* (1986) investigated the alkaline based catalyst on the transesterification of soybean oil with methanol. They varied the operational parameters such as temperature and molar ratio of alcohol to soybean oil. They reported that a pseudo first-order kinetics provided a satisfactory mechanism with experimental results, At large molar excess of alcohol a second-order kinetics provided a satisfactory mechanism with experimental results at 6:1 molar ratio of alcohol to oil, assuming reversible reactions.

Darnoko, *et al* (2000 studied the kinetics of base-catalyzed transesterification of palm oil with methanol at 6:1 molar ratio of alcohol to oil. They reported that the best kinetics mechanism appeared to be a pseudo second-order. However, a second-order mechanism is more convenient and more suitable than a pseudo second-order mechanism for predicting a conversion yield. Using a second-order mechanism, the initial concentrations of all reactants are needed; generally, these concentrations are known depend on the given condition. In contrast, using a pseudo second-order mechanism, a couple of an initial concentration of triglycerides (TG) and initial highest concentrations of diglycerides (DG) and monoglycerides (MG) are needed.

Of particular importance during the transesterification process in the degree of mixing between the catalyst and the triglyceride (TG) phases, usually, TG and alcohol are not miscible. Mechanical agitation is usually used to increase the contract between the reacting phases, therefore, enhancing mass transfer rate. Thus, the mixing intensity is expected to influence the kinetic reactions of transesterification process (Theerayut *et. al* 2004). Detailed understanding of the mixing effect on the transesterification process is a valuable tool for process optimization and scale-up.

The objective of this work is to develop a predictive tool for process optimization and reactor scale-up during transesterification of palm oil with methanol as catalyst. This tool is based on the reactor hydrodynamics and the kinetics of transesterification and takes the advantage of the power of computational fluid dynamics (CFD) for detailed investigation of CSTR reactor operating conditions. The reaction condition focused on the reported optimum condition for transesterification of palm oil at atmospheric pressure: 6:1 molar ratio of alcohol to oil, reactor temperature 60 °C, and catalyst concentration 1% wt of oil (Darnoko and Cheryan, 2000).

2. Kinetic Modeling

Srivastava, and Prasad (2000) reported that typically, vegetable oils consist of triglyceride (TG) from 90 to 98 % by weight of oil and small quantities of diglycerides (DG) and monoglycerides (MG). In this work, the initial composition of palm oil is similar to that of Theerayut *et. al* (2004), that is, consisting of TG 95.7%, DG 3.7%, and MG 0.6%. Following the approach of Freedman, *et. al.* (1986), first the TG is converted stepwise to DG, MG and finally into glycerol (GL) as shown below (Equations 1a through 1c).

$$TG + A \underset{k_2}{\overset{k_1}{\leftrightarrow}} DG + E \tag{1a}$$

$$DG + A \underset{k_4}{\overset{k_3}{\leftrightarrow}} MG + E \tag{1b}$$

$$MG + A \underset{k_5}{\overset{k_5}{\leftrightarrow}} GL + E \tag{1c}$$

where *A* and *E* represents the alcohol and ester, respectively.

The molecular weights of TG, DG, and MG of palm oil and molecular weight of ME are those of Theerayut *et. al* (2004), and are 849.5, 597.0, 344.5, and 284.5 kg/kmol, respectively. A molecular weight of GL was 92.1 kg/kmol (Perry, R.H., *et. al*, 1997).

The general form of second-order rate equations governing the step-wise reactions for the transesterification of TG in is shown below (Equations 2a through 2f) without shunt reactions, Freedman (1986) and Noureddini and Zhu (1997):

$$\frac{d[TG]}{dt} = -k_1[TG][A] + k_2[DG][ME] \qquad \text{(2a)}$$

$$\frac{d[DG]}{dt} = k_1[TG][A] - k_2[DG][E] \qquad \text{(2b)}$$
$$- k_3[DG][A] + k_4[MG][ME]$$

$$\frac{d[MG]}{dt} = k_3[DG][A] - k_4[MG][ME] \qquad \text{(2c)}$$
$$- k_5[MG][A] + k_6[GL][ME]$$

$$\frac{d[GL]}{dt} = k_5[MG][A] - k_6[GL][ME] \qquad \text{(2d)}$$

$$\frac{d[E]}{dt} = k_1[TG][A] - k_2[DG][ME] + k_3[DG][A]$$
$$- k_4[MG][ME] + k_5[MG][A] - k_6[GL][ME] \qquad \text{(2e)}$$

$$\frac{d[A]}{dt} = \frac{-d[ME]}{dt} \qquad \text{(2f)}$$

where k_1 to k_6 are reaction rate constants (L/mol.s) and are those of Theerayut *et. al* (2004). The [TG], [DG] [MG], [GL], [A], and [ME] are respectively the mole concentrations (mol/L) of TG, DG, MG, GL, alcohol, and esters in a reaction mixture are evaluated by simultaneously solving Equation 2 above. The kinetic data for palm oil transesterification were those by Darnoko and Cheryan (2000). The reaction kinetics is coupled with the reactor hydrodynamics through the use of CFD technique to shed more light on the complexity of CSTR reactive flow. The CFD reactor modeling is briefly discussed below.

3. Model Governing Equations

CFD models of the thermochemical processes such as the reactive flow is governed by the continuity and momentum equations and include description of fluid flow, heat and mass transfer, and chemical reactions. The process fundamental governing equations are the conservation laws of mass, momentum, energy and species, namely the following equations (3a) through (3d), respectively.

$$\frac{\partial \rho}{\partial t} + \nabla.(\rho \vec{u}) = S_p \qquad \text{(3a)}$$

$$\frac{\partial (\rho \vec{u})}{\partial t} + \nabla.(\rho \vec{u}\vec{u}) = -\nabla p + \nabla.(\mu \nabla \vec{u}) + S_u \qquad \text{(3b)}$$

$$\frac{\partial (\rho H)}{\partial t} + \nabla.(\rho \vec{u} H) = \nabla.(\lambda \nabla T) + S_H \qquad \text{(3c)}$$

$$\frac{\partial (\rho Y_i)}{\partial t} + \nabla.(\rho \vec{u} Y_i) = \nabla.(D \nabla (\rho Y_i)) + S_H \qquad \text{(3d)}$$

where S_s is the mass source in the system

CFD enforces these conservation laws over a discretized flow domain in order to compute the systematic changes in mass, momentum and energy as fluid crosses the boundaries of each discrete region (FLUENT 12 User's Guide, 2009).

The reactor flow pattern is calculated from conservation equations for mass and momentum (Eqns. 3a and 3b). Once the flow pattern is known, then the temperature and the transport of chemical species are calculated from equations 3c and 3d, respectively.

4. Process Overview and Model Description

The reactor design specifications and operating conditions are similar to the experimental set up Theerayut *et. al* (2004).

Thus, the computational domain represents a 2-Liter reactor equipped with Lightin 210 type mechanical stirrer so that the speed was varied from 150, 300 and 750 rpm, respectively. The reactor temperature was varied between 50, 60 and 100 ^{o}C, respectively. The model initial condition was such that the palm oil consists of TG 95.7%, DG 3.7%, and MG 0.6%. The reactor walls were assumed adiabatic while the batch process time was about 2 minutes. The scope of this simulation is to model is limited to the hydrodynamics of CSTR reactor coupled with the chemical reactions during transesterification of palm oil.

5. Computational Procedure

The partial differential equations (3a – 3d) are finite-differenced resulting into a set of linear algebraic equations which are solved iteratively. At each time step, the algebraic equations are solved simultaneously for all computational cells. Initial conditions are required, these are the mass fractions of TG, DG, and MG and the reactor temperature. The boundary conditions pertain to the impeller speed and stationary reactor wall. The open top reactor was modeled as symmetry boundary. Figure 1 shows the computational domain used in the present study which was descritized for the iterative solution.

6. Results and Discussion

The CSTR reactor geometry is illustrated in Figure 1 depicting major sections of the reactor. Figures 3 through 12 depict transient concentration (volume averaged) during the transesterification of palm oil in the CSTR reactor.

Figures 2 and 3 show the concentration of esters and TG in which the model results compare well with the published data by Theerayut *et. al* (2004).

The effect of impeller speed on the rate of transesterification is depicted on Figures 4 through 6. Results indicate that the rate of production of ester is highest at 350 rpm impeller speed. That is, at 350 rpm the mass transfer rate is highest during transesterification in CSTR.

The effects of reactor temperature are shown in Figures 7 through 9. For the range of temperature investigated, the results indicate the higher temperature, the higher the transesterification rate. Further, Figure 10 shows that for all the investigated impeller speed, the transesterification is nearly complete within 60 seconds.

The spatial concentrations of ester and triglycerides were investigated. Figure 11 shows that highest concentration of ester is near the impeller where the maximum concentration is about 91.7%. On the other hand, Figure 12 depicts higher concentration near the impeller zones. It is observed that nearly all the TG has been consumed leaving only 0.44%.

Figure 13 shows the turbulence intensity is highest in the impeller zones. High intensity facilitates the transesterification rate as discussed earlier. The observed mixing intensity corresponds with the reactor flow patter as shown by the velocity vectors in Figure 14 which is responsible for enhancing the mixing intensity.

7. Conclusion

The mathematical model for predicting the transesterification of palm oil to biodiesel has been devised. The model reproduces the rates of ME production which starts with a sudden increase followed by a lower production rate as the reaction approaches equilibrium. Variation of agitation speed and reactor temperature appear to have similar effect to the reaction rate. Zones of higher reaction rates were observed near the impeller tip diameter where turbulent intensity was highest. The model results were validated against published literature data. Good correlation between model simulations and experimental data was observed. The computer model can potentially assist for better understanding of the reactor kinetics as well as the complex three-dimensional flow. The model can therefore be used as a design and tool for stirred reactors in biodiesel production.

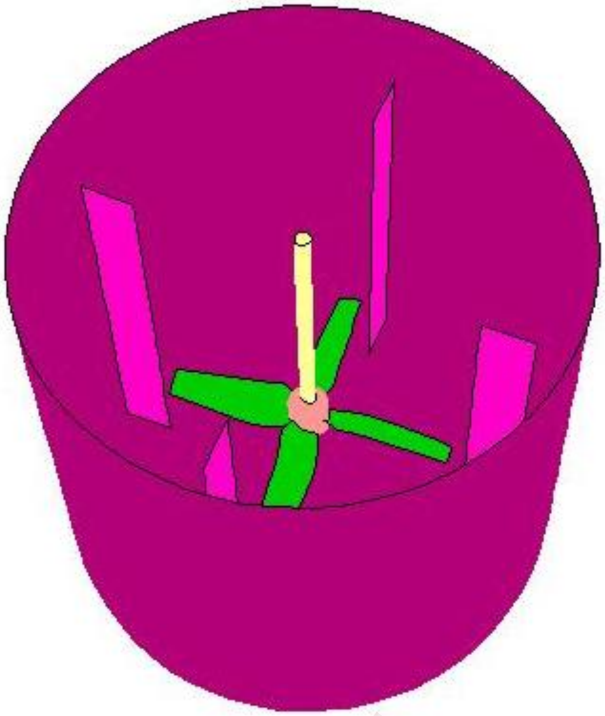

Figure 1: CSTR reactor with four baffles and agitated with a four-blade Lightin 210

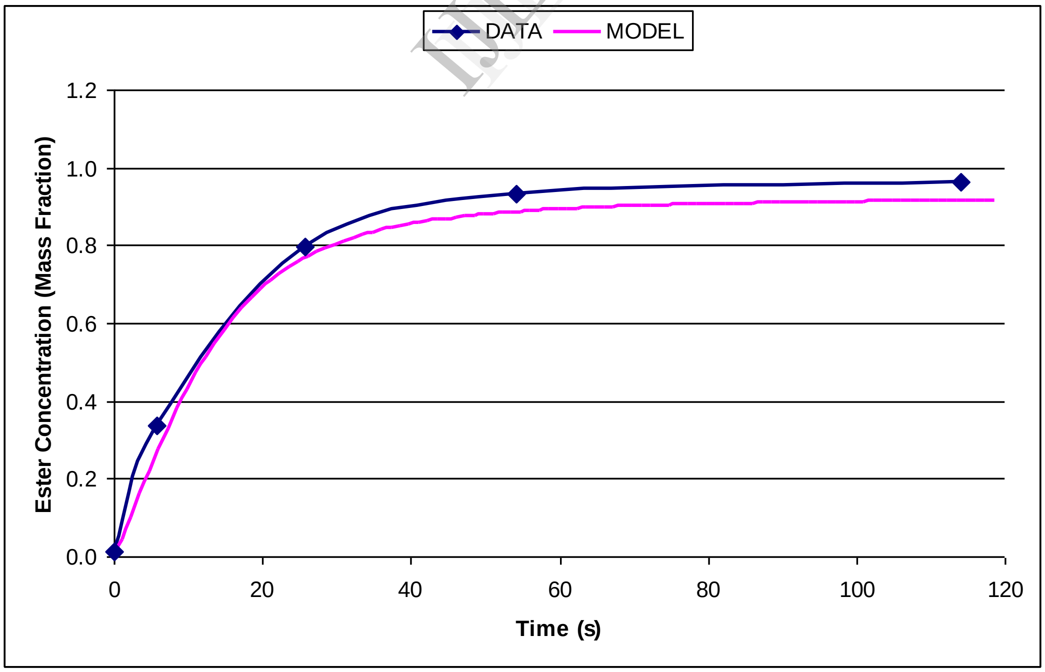

Figure 2: Rate of formation of ester (biodiesel) during the first two minutes

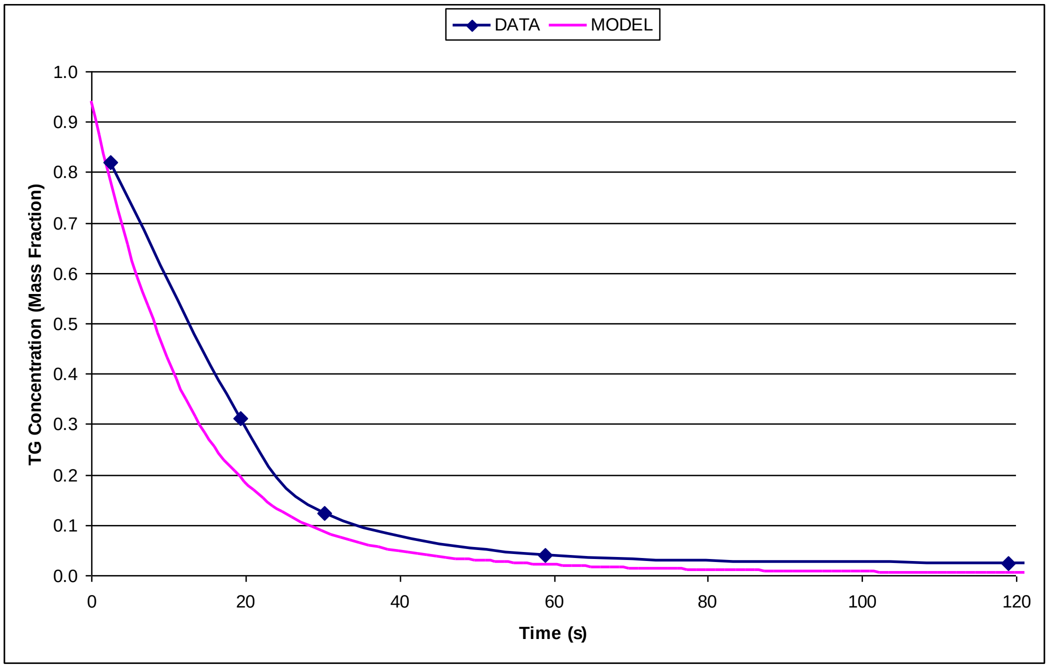

Figure 3: Rate of decomposition of TG during the first two minutes.

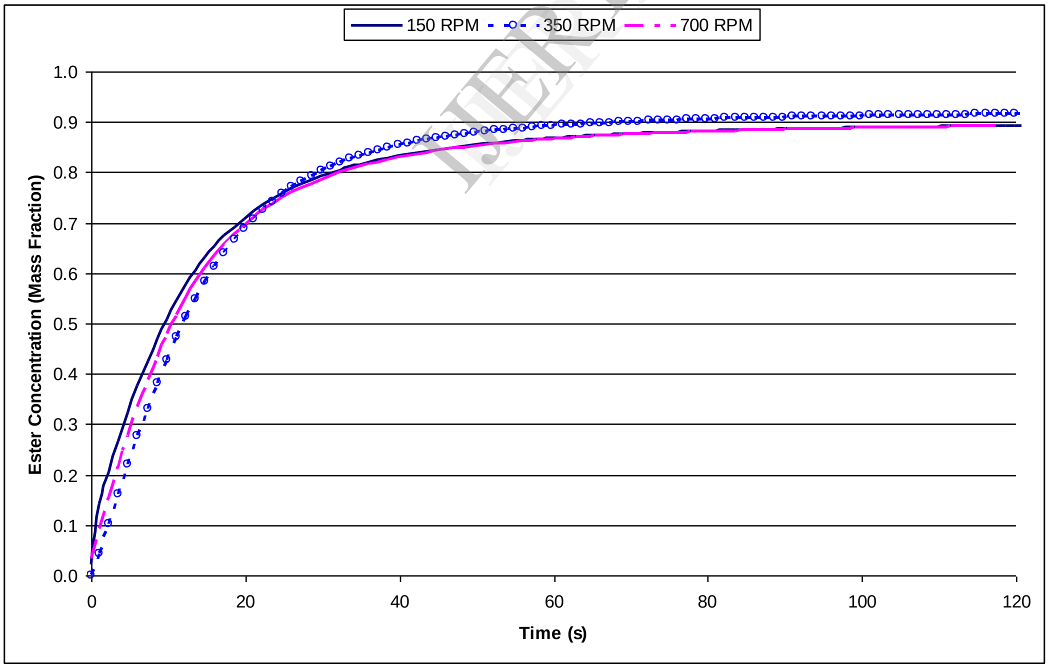

Figure 4: Model prediction of ester concentration with varying impeller speed

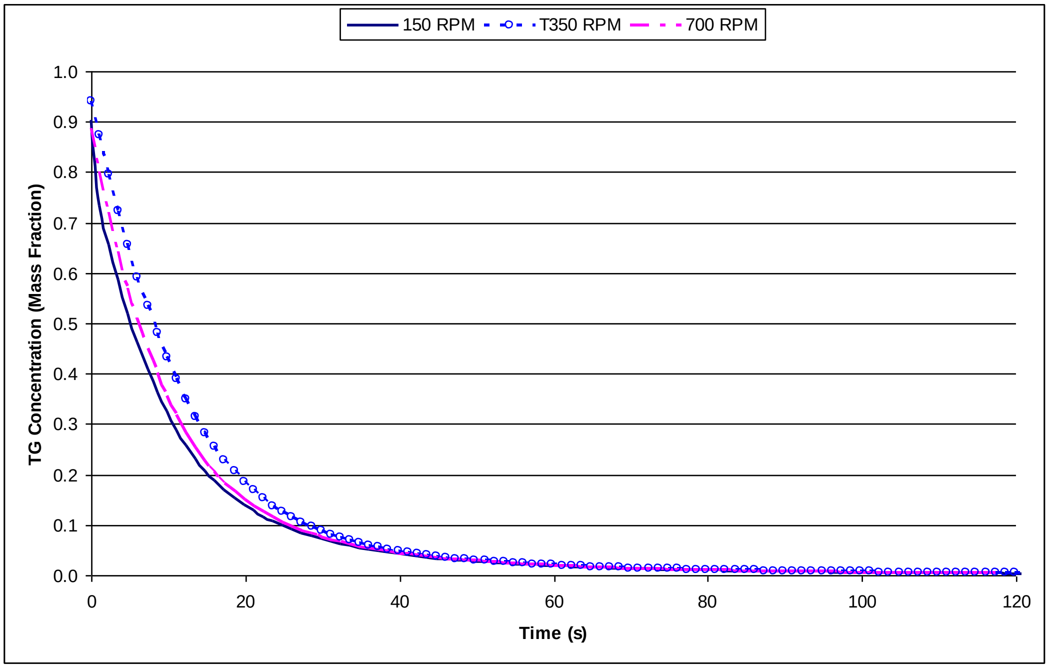

Figure 5: Model prediction of TG decomposition as the impeller sped is varied

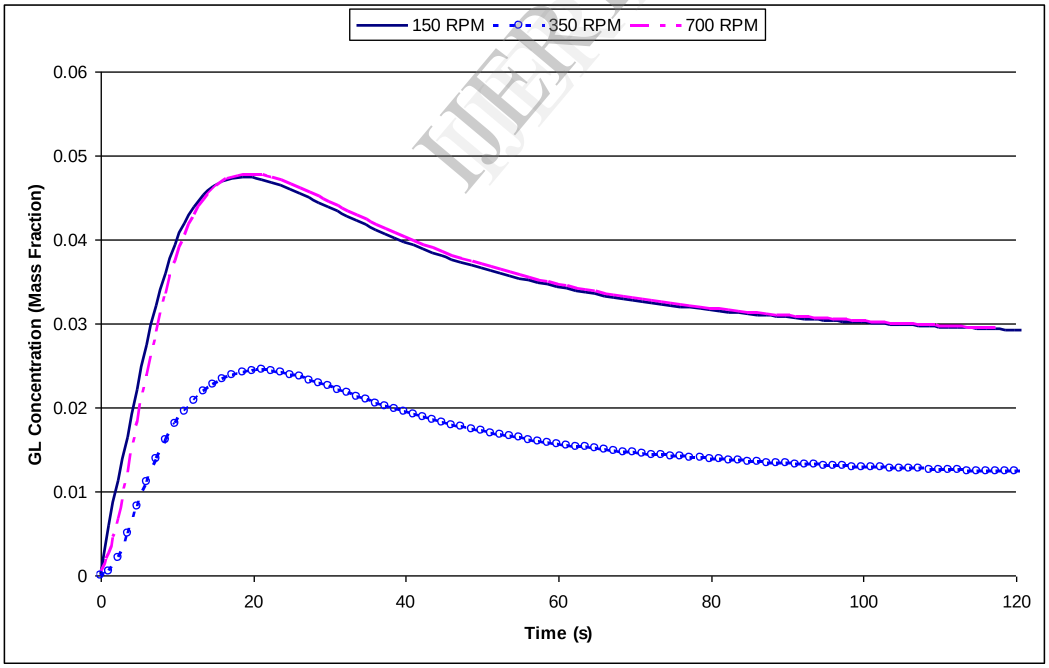

Figure 6: Model prediction of GL concentration with varying impeller speed

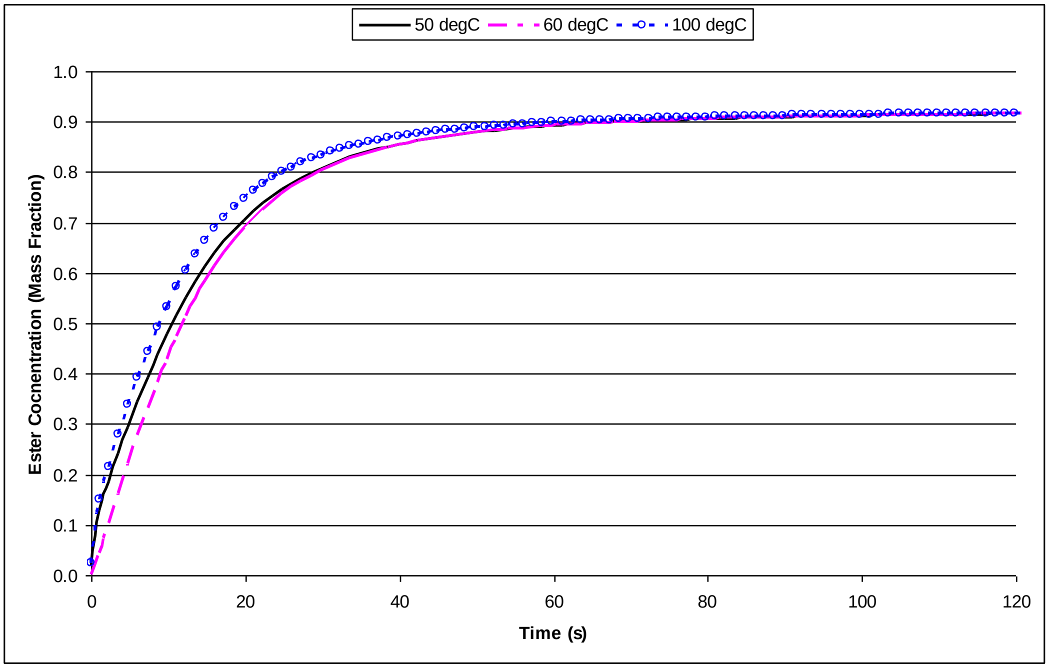

Figure 7: Model prediction of ester concentration as the reactor temperature is varied

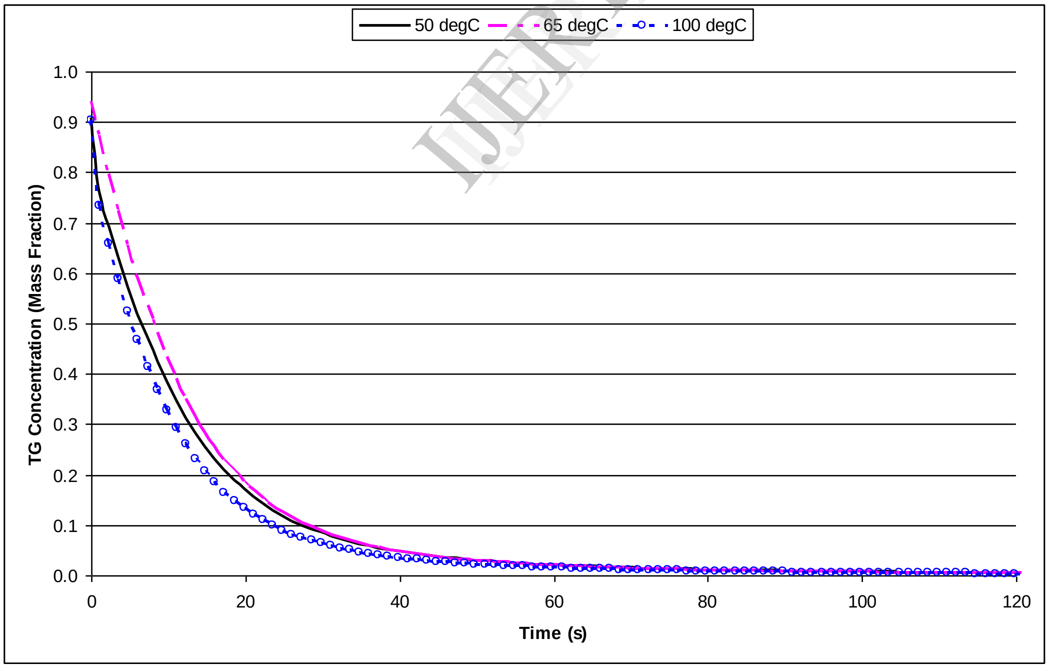

Figure 8: Model prediction of TG decomposition as the reactor temperature is varied

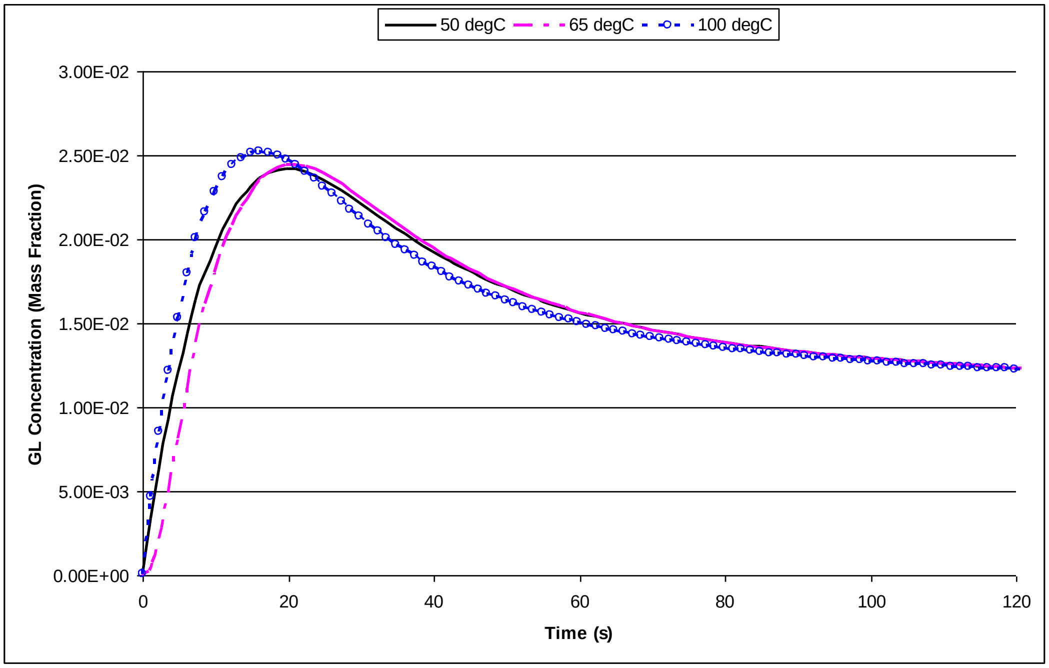

Figure 9: Model prediction of GL concentration as the reactor temperature is varied

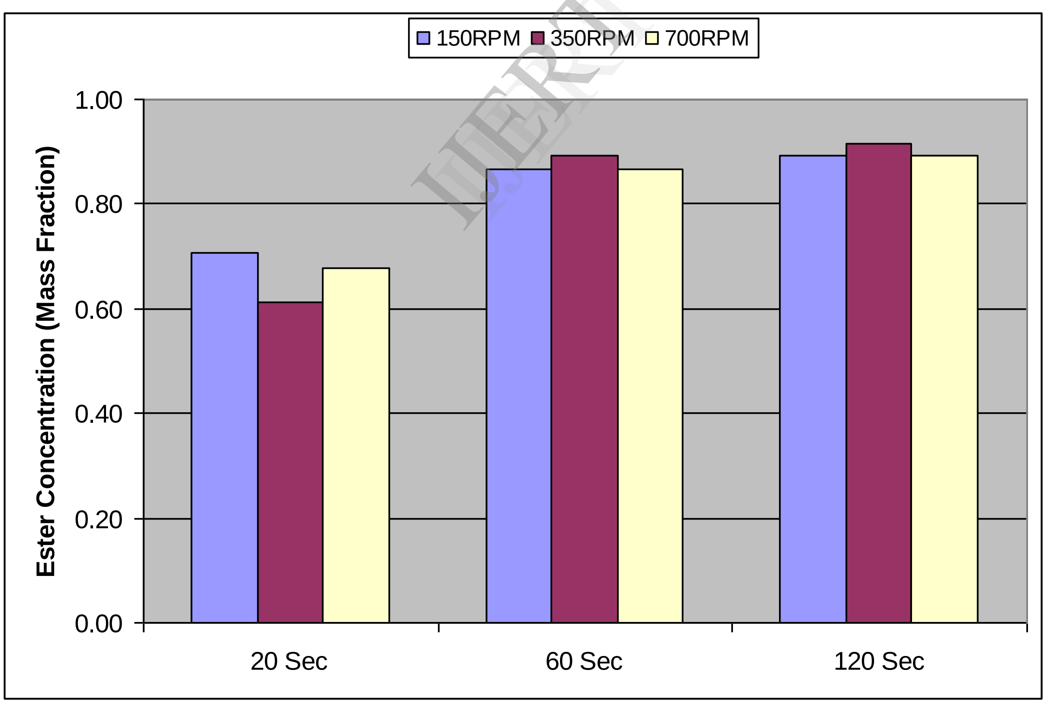

Figure 10: Model prediction of ester concentration as impeller speed is varied

The results depicting contour plots and vector flow pattern are discussed in the next Section. In these results, the blue and red colors represent the minimum and maximum values, respectively.

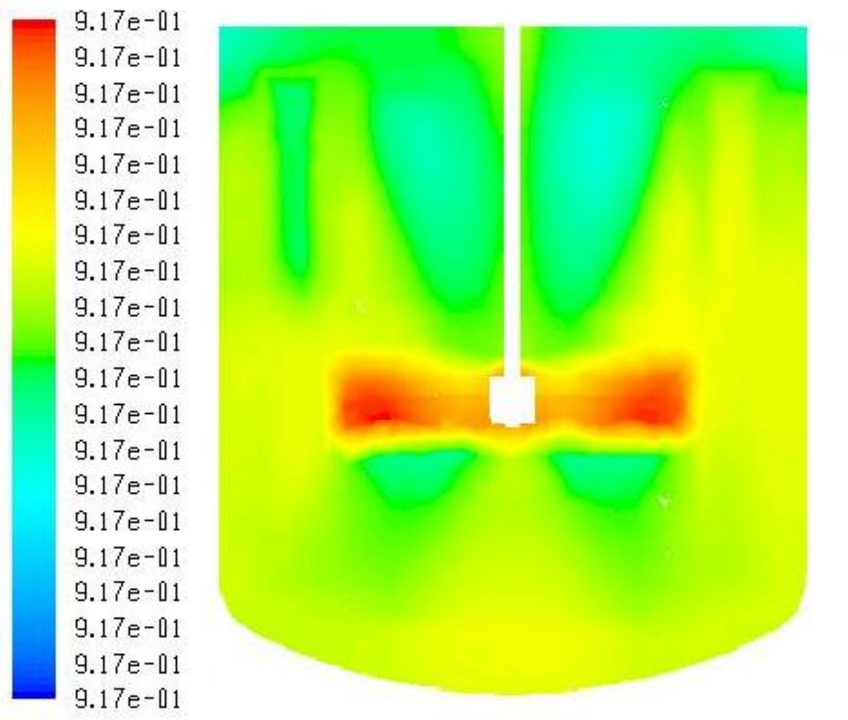

Figure 11: Ester concentration (mass fraction) in the reactor mid-plane

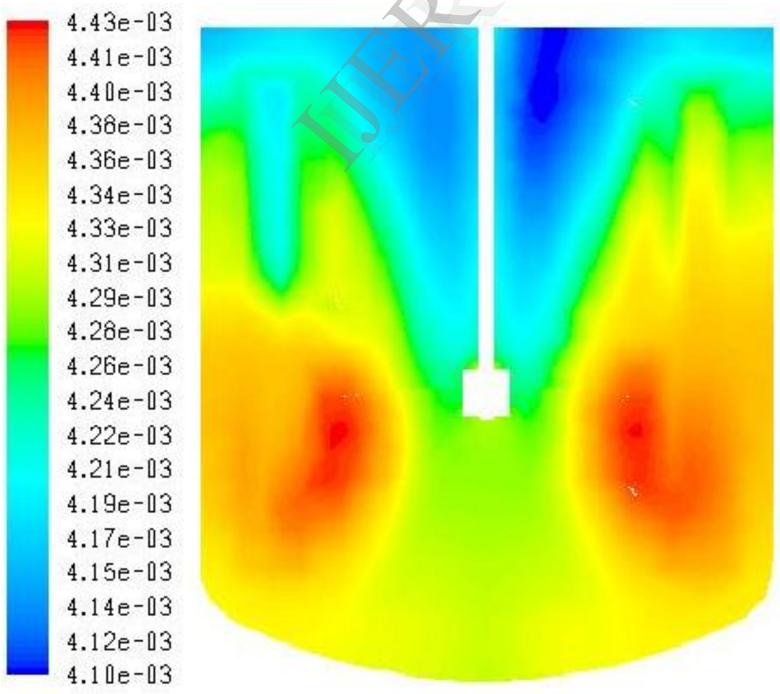

Figure 12: TG concentration (mass fraction) in the reactor mid-plane

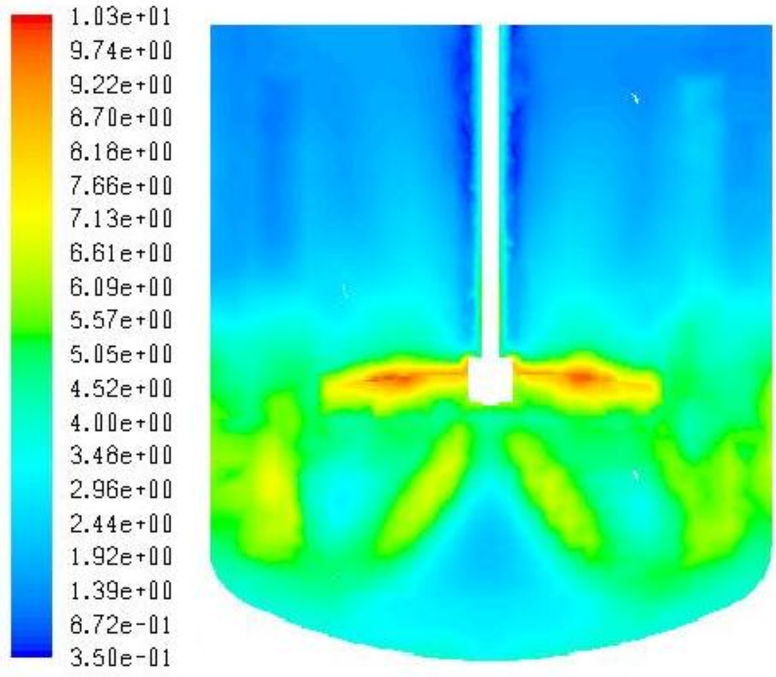

Figure 13: Turbulence intensity across the vertical reactor mid-plane

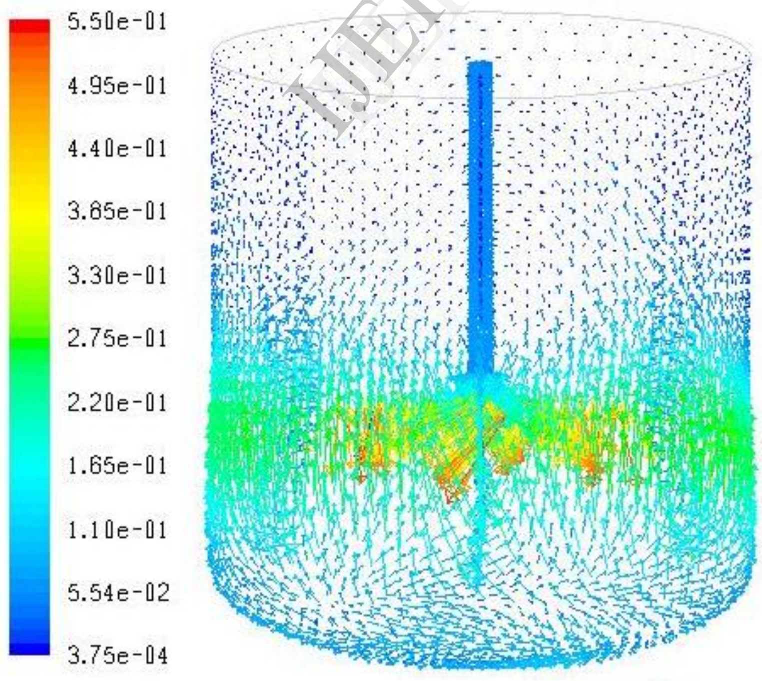

Figure 14: Velocity flow pattern across the vertical reactor mid-plane

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