Phenomenological model for the prediction of the performance of a slurry bubble column reactor for green diesel production

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Abstract. The performance of vegetable oil hydrotreating to produce green diesel in a slurry bubble column reactor was predicted in this study using a phenomenological model. A two-dimensional axisymmetric model of the reactor of 2.68 m in diameter and 7.14 m in height was used. The model consists of species mass transfer equations, an energy transfer equation and a pressure drop equation. Fluid mixing in the reactor was explained by dispersion coefficients. Catalyst distribution along the reactor was also considered. The chemical kinetics developed by Attanatho was used in the model. The effects of the gas and liquid superficial velocities on the triglyceride conversion as well as the green diesel yield and purity were predicted and evaluated. The effect of the superficial gas velocity on the reactor performance is insignificant since the range of superficial velocities in this simulation is in homogeneous flow area. The effect of the liquid superficial velocity is quite significant.

1. Introduction

Green diesel, which is an alternative energy, is a second-generation biofuel. Its constituents have C_{15}-C_{18} paraffin structure that is identical to conventional diesel structure [1]. Therefore, green diesel can be purely used in unmodified car engines [2]. In contrast to biodiesel, green diesel does not have oxygen molecules. This characteristic makes the heating value and density of green diesel are higher than biodiesel. Other advantages of green diesel over biodiesel are higher cetane number and better oxidation stability [2].

Vegetable oil hydrotreating is an alternative method for green diesel production. This mature process has been industrially applied in large scale. The hydrotreating mechanism includes hydrogenation, decarbonation, decarboxylation and hydrodeoxygenation. Hydrodeoxygenation is an oxygen elimination in which triglycerides and free fatty acids containing in vegetable oils react with hydrogen to form water and paraffinic compounds. Decarboxylation and decarbonation are oxygen eliminations to form carbon dioxide or carbon monoxide and paraffinic compounds.

Hydrotreating is a process involving three phases: gas phase (hydrogen), liquid phase (vegetable oil) and solid phase (catalyst). Therefore, reactors used for hydrotreating process are three phase reactors. Two types of three phase reactors used for green diesel production are fixed bed reactors and slurry bubble column reactors. In slurry bubble column reactors, rising gas bubbles agitate slurry so that catalyst particles are suspended in a liquid. Slurry bubble column reactors have some advantages over fixed-bed reactors. They have better temperature control, lower pressure drop, finer catalysts (particle diameter <100 μm), higher yield and batch or continue catalysts release [3].
The experimental researches on green diesel production through hydrotreating process have been carried out by many people. Raw materials used include rapeseed oil [1], jatropha [4], waste cooking oil [5], palm oil [6] and stearic acid [7, 8].

Numerical modelling and simulation researches are useful substitutes for experimental ones. The advantages of modelling and simulation researches are lower cost and faster time. Results predicted by models have various degrees of accuracy depending on the types of models. The best type of models is phenomenological (theoretical) models. This model is based on physical principles (transport phenomena) and chemistry principle (reaction kinetics). Nevertheless, the model still requires empirical correlations. Therefore, in order to preserve high accuracy of a phenomenological model, empirical correlations coupled to the model must be accurate.

Numerical modelling and simulation researches on green diesel production through hydrotreating process are infrequently carried out. Attanatho simulated the process in a microchannel reactor [9], Muharam et al. in a trickle bed reactor [10, 11] and Muharam et al. in a slurry bubble column reactor [12].

This research is to predict and evaluate the performance of a slurry bubble column reactor for vegetable oil hydrotreating, which has not been investigated by the researchers above. The reactor performance was predicted through the simulation of a phenomenological model consisting of species mass transfer equations, an energy transfer equation and a pressure drop equation. The effects of gas and liquid superficial velocities on the reactor performance were then evaluated.

2. Modelling
The kinetic model used in this research was developed by Attanatho [9]. Triglycerides represented vegetable oils. Figure 1 shows the reaction mechanism of hydrotreating reaction proposed by Attanatho [9].

![Figure 1. Mechanism of triglyceride hydrotreating [9].](image)

The reaction mechanism involving 13 chemical components: triglycerides (TG), diglycerides (DG), monoglyceride (MG), free fatty acid (FFA), fatty alcohol (FA), long chain esters (ET), C17 hydrocarbons (C17HC), C18 hydrocarbons (C18HC), carbon monoxide (CO), carbon dioxide (CO2), hydrogen (H2), water (H2O) and C3 hydrocarbons (C3HC). Table 1 shows the rate expressions for each reaction.

Figure 2 illustrates the geometry of the slurry bubble column reactor for modelling. A two-dimensional axisymmetry model of a vertical cylindrical slurry bubble column reactor of 2.68 m in diameter and 7.14 m in length developed by Muharam et al. [12] was used. The model consists of mass transfer equations in the gas and liquid phases, a heat transfer equation and a pressure drop equation.

Triglycerides in dodecane as a solvent and gaseous hydrogen enter the bottom of the reactor. The solid phase (catalyst particles) are suspended in the liquid phase by rising gas bubbles. These gas bubbles play a role in dispersing the slurry in the reactor. The green diesel product exits the reactor from the side, and gas product comes out of the top of the reactor.
Table 1. Reactions and reaction rate expressions for triglyceride hydrotreating [9].

| Reaction | Stoichiometry | Reaction rate |
|----------|---------------|---------------|
| r1       | TG + H₂ → FFA + DG | \( r_1 = k_1 C_{TG} \) |
| r2       | DG + H₂ → FFA + MG | \( r_2 = k_2 C_{DG} \) |
| r3       | MG + H₂ → FFA + C₃H₆ | \( r_3 = k_3 C_{MG} \) |
| r4       | FFA + 2H₂ → FA + H₂O | \( r_4 = k_4 C_{FFA} \) |
| r5       | FA + H₂ → C₃H₆C + H₂O | \( r_5 = k_5 C_{FA} \) |
| r6       | FFA → C₁₇HC + CO₂ | \( r_6 = k_6 C_{FFA} \) |
| r7       | FFA + H₂ → C₁₇HC + CO + H₂O | \( r_7 = k_7 C_{FFA} \) |
| r8       | FA + FFA ↔ ET + H₂O | \( r_8 = k_8 C_{FFA}C_{FA} - k_9 C_{ET}C_{H₂O} \) |

Figure 2. The geometry of the slurry bubble column reactor [12].

2.1. Mass transfer

Gaseous hydrogen enters the reactor from the bottom. In the reactor, the hydrogen molecules exist in the form of raising bubbles. Together with the propane molecules entering from the liquid phase, the hydrogen molecules transport in the gas phase through two mechanisms: dispersion and convection. Some hydrogen molecules then transport to the liquid phase crossing the gas-liquid boundary layers. The gas phase mass transfer is expressed by equation (1):

\[
\frac{D_G \varepsilon_G \partial}{r} \left( \partial \frac{C_{G,i}}{\partial r} \right) + D_G \varepsilon_G \frac{\partial^2 C_{G,i}}{\partial z^2} - u_G \varepsilon_G \frac{\partial C_{G,i}}{\partial z} - k_{GL,i} \alpha \left( \frac{p_{G,i}}{H_{G,i}} - C_{L,i} \right) = 0 \tag{1}
\]

where \( C_{G,i} \) is the gas-phase i-component (hydrogen and propane) concentration, \( D_{G,z} \) and \( D_{G,r} \) are the axial and radial gas-phase dispersion coefficients, \( \varepsilon_G \) is the gas-phase hold up, \( u_G \) is the gas superficial velocity, \( k_{GL,i} \) is the gas-liquid mass transfer coefficient of i-component, \( \alpha \) is the specific interphase area, \( p_{G,i} \) is the partial pressure of i-component and \( H_{G,i} \) is the Henry’s constant of i-component.

In the liquid phase, the hydrogen molecules dissolve and transport with the triglyceride molecules and the other product molecules through two mechanisms: dispersion and convection. All species presenting in the liquid phase are involved in chemical reactions. The liquid phase mass transfer is expressed by equation (2):
\[
\frac{D_{Lr} \varepsilon_L}{r} \frac{\partial}{\partial r} \left( r \frac{\partial C_{L,i}}{\partial r} \right) + D_{Lz} \varepsilon_L \frac{\partial^2 C_{L,i}}{\partial z^2} - u_{Lz} \frac{\partial C_{L,i}}{\partial z} + k_{gl,i} a \left( \frac{p_{g,i}}{H_{L,i}} - C_{L,i} \right) - R_i = 0
\]

(2)

where \( C_{L,i} \) is the liquid-phase \( i \)-component concentration, \( D_{Lz} \) and \( D_{Lr} \) are the axial and radial liquid-phase dispersion coefficients, \( \varepsilon_L \) is the liquid-phase hold up, \( u_{Lz} \) is the liquid-phase superficial velocity and \( R_i \) is the reaction rates.

2.2. Heat transfer

Energy balance in the reactor involves the heat convection and conduction as well as the reaction heat. The gas phase temperature is in a thermal equilibrium with the liquid and solid phases so that the energy balance is expressed as follows:

\[
k_{\text{eff}} \left( \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial T}{\partial r} \right) + \frac{\partial^2 T}{\partial z^2} \right) - \rho C_p u_z \frac{\partial T}{\partial z} - Q = 0
\]

(3)

where \( k_{\text{eff}} \) is the slurry effective heat conduction, \( \rho \) is the slurry density, \( C_p \) is the slurry heat capacity, \( u_z \) is the average superficial velocity and \( Q \) is the reaction heat.

2.3. Pressure drop

The pressure drop due to the friction can be neglected compare to the static height. The pressure drop along the reactor was proposed by Schweitzer and Viguié [13] and expressed by equation (4):

\[
\frac{\partial P}{\partial z} = -(1 - \varepsilon_G) g \rho
\]

(4)

where \( \varepsilon_G \) is the gas holdup.

2.4. Catalyst distribution

The catalyst distribution along the reactor was proposed by Deckwer and Serpemen [14]:

\[
w(\xi) = \bar{w} B_{oc} \exp(-B_{oc} \xi) [1 - \exp(-B_{oc})]^{-1}
\]

(5)

where \( \bar{w} \) is the average catalyst loading, \( \xi \) is the dimensionless axial coordinate and \( B_{oc} \) is the Bodenstein number of the catalyst particles.

The Bodenstein number and Froude number of the catalyst particles are defined as follows [15]:

\[
B_{oc} = \frac{13 Fr}{1 + Fr^{0.85}}
\]

(6)

\[
Fr = \frac{u_g}{\sqrt{g d_R}}
\]

(7)

where \( d_R \) is the reactor diameter.

3. Results and discussion

The above model was then solved numerically using COMSOL. The calculation results were verified by looking at the order of magnitude of the concentration and temperature values as well as their trend to find out its reasonableness.

The process and geometry parameters for simulation can be seen in table 2. The simulation results were in the form of one-dimensional (1D) and three-dimensional (3D) profiles, i.e. for the triglyceride conversion, the green diesel yield and the green diesel purity.
**Table 2.** The process and geometry parameters for the simulation.

| Parameters                                      | Value              |
|------------------------------------------------|--------------------|
| Reactor diameter                               | 2.68 m             |
| Reactor length                                 | 7.14 m             |
| Inlet pressure                                 | 34.47 bar          |
| Inlet temperature                              | 325 °C             |
| Ratio of hydrogen/triglyceride in the feed     | 188 mol/mol        |
| Gas superficial velocity                       | 0.02 m/s           |
| Liquid superficial velocity                    | 0.00025 m/s        |
| Triglyceride concentration in the feed         | 5% w/w             |
| Ratio of FFA/triglyceride in the feed          | 5% w/w             |
| Wall temperature                               | 325 °C             |

Figure 3 shows the profiles of the triglyceride conversion, the green diesel yield and the green diesel purity calculated by the model with the parameter values mentioned in table 2. It can be seen that the liquid superficial velocity of 0.00025 m/s and the gas superficial velocity of 0.02 m/s give a homogeneous slurry. This happens because the fluid flow inside the reactor is in a homogeneous flow regime, which is formed by fulfilling two circumstances: the same distance between two adjacent sparger holes and the same size of the sparger holes. The triglyceride conversion is 0.98. The green diesel yield, which is combined C\textsubscript{17} and C\textsubscript{18} hydrocarbons, is 0.83. The green diesel purity is only 0.77. The performance in the slurry bubble column in this research is better than that in a trickle-bed reactor of 1.5 m in diameter and 8 m in length [11]. This happens because in the slurry bubble column reactor the resident time of the molecules of the reacting components in the liquid phase is longer and the radial heat transfer is better.

![Figure 3](image)

**Figure 3.** The profiles of (a) the triglyceride conversion, (b) the product yield, (c) the product selectivity.
Since the green diesel purity is still low, the gas and liquid superficial velocities need to be evaluated to determine their effects on the green diesel purity. Therefore, the gas superficial velocity was varied in the range of 0.008 m/s - 0.03 m/s, and the liquid superficial velocity was varied from 0.0002 m/s to 0.0004 m/s. The simulation results can be seen in figure 4 and figure 5.

From figure 4, it can be seen that the change in the gas superficial velocity has no significant effect on the triglyceride conversion, the green diesel yield and the green diesel purity. The changes in the gas superficial velocity from 0.008 m/s to 0.03 m/s reduce the triglyceride conversion by only 0.005% and the green diesel yield by 0.007%. However, the green diesel purity drops by 4%. That means that when the gas superficial velocity decreases from 0.02 m/s to 0.008 m/s, the green diesel purity rises from 0.77 to 0.79. The insensitivity of the reactor performance to the change in the gas superficial velocity is caused by the very high pressure of gas bubbles, i.e. 34.47 bar. At very high pressures the hydrogen solubility in the liquid is also very high so that hydrogen act as the excess reactant.

From the point of view of mass transfer, the change in the gas superficial velocity influences the thickness of the gas-liquid boundary layer and the gaseous hydrogen residence time. The simulation results show that the mass transfer rate of hydrogen through the boundary layer is dominant over the convective mass transfer rate of gaseous hydrogen, leading to higher concentration of hydrogen in the liquid phase at higher gas superficial velocity. Although the production rates of C_{17} and C_{18} hydrocarbons are higher at higher gas superficial velocity, the green diesel concentration is lower. This is because the production rates of by-products are also higher.

![Figure 4](image-url)

**Figure 4.** The effects of the gas superficial velocity on: (a) the triglyceride conversion, (b) the product yield, (c) the product purity.

A quite significant change occurs when the liquid superficial velocity varies, as exhibited by figure 5. The triglyceride conversion increases from 0.96 to 0.98 when the liquid superficial velocity decreases from 0.0004 m/s to 0.0002 m/s. With the same increase of the liquid superficial velocity, the green diesel yield increases 3.8% from 0.81 to 0.84, and the green diesel purity rise up from 0.76 to 0.77.
This happens because the longer residence time gives enough time for chemical species molecules in the liquid phase to react. The less responses of the reactor performances against the change in the liquid superficial velocity occurs because the values of the liquid superficial velocity in this research are very low, as if the liquid phase is in a batch operation.

![Graphs](a) (b) (c)

**Figure 5.** The effects of the liquid superficial velocity on: (a) the triglyceride conversion, (b) the product yield, (c) the product purity.

### 4. Conclusions
The effect of the superficial gas velocity on the reactor performance is not significant since the range of superficial velocities in this simulation is in a homogeneous flow regime. The effect of the liquid superficial velocity is quite significant. In order to achieve a certain level of the performance, one must adjust the value of the liquid superficial velocity, rather than the gas superficial velocity.

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