

Modelling of a Hydrotreating Reactor to Produce Renewable Diesel from Non-Edible Vegetable Oils

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This research is focused on modelling of a large-scale trickle-bed reactor to produce renewable diesel via hydrotreating of non-edible vegetable oil with NiMoP/Al₂O₃ catalyst. The two-dimensional axisymmetry of a non-isothermal vertical cylindrical trickle-bed reactor with a diameter of 1.5 m and a length of 8 m was modelled using computational fluid dynamics concept by considering mass and momentum transfer in gas, liquid and solid phases. The reactor is packed with spherical catalyst particles of 1.5875 mm in diameter under the pressure of 3.45 MPa and the inlet temperature of 325 °C. Triglyceride of 5 wt% in dodecane is fed as liquid phase, and hydrogen of 188 mol hydrogen/triglyceride is fed as gas phase. The inlet gas velocity is 0.05 m/s. Simulation results show that the vegetable oil (triglyceride) conversion is 53.2 %, the product yield is 13.4 wt%, the product purity is 95.8 wt%, and the production rate is 2.45 t/d. To obtain higher conversion and production rate, further simulation was conducted by varying the inlet gas velocity and the inlet temperature. The optimum condition is reached at the inlet gas velocity of 0.01545 m/s and the inlet temperature of 375 °C with the triglyceride conversion being 88.3 %, the product yield being 58.5 wt%, and the product purity being 97.8 wt%, while the production rate being 4 t/d.

1. Introduction

Biodiesel is one of the most promising alternative fuel which is expected to replace petroleum diesel fuel in the future. Due to its high oxygen content, the use of biodiesel in existing diesel engines is very limited. In several countries, including the United States, biodiesel is blended with conventional petroleum diesel at only up to 20 % in volume (U.S. Department of Energy, 2015). Biodiesel has low oxidative stability and very high water content, which can shorten the life of fuel filters and promote corrosion (Bezergianni and Dimistriadis, 2013). A new oxygen-free biofuel called renewable diesel is developed.

Similar to biodiesel, renewable diesel is a substitute for diesel oil which is mainly made from vegetable oils. The main difference between renewable diesel and biodiesel is the chemical structures. While biodiesel is basically an ester, renewable diesel consists of straight-chain alkanes with 15 - 18 carbon atoms. It is chemically the same as petroleum diesel and can be used directly in unmodified diesel engines at any level of blends. Pure renewable diesel can even be used without blending. Renewable diesel shows superior properties compared to biodiesel such as higher cetane number, oxidative stability, and heating value (Bezergianni and Dimistriadis, 2013).

Renewable diesel can be produced via various processes. One of the most favourable and common method is catalytic hydroprocessing or hydrotreating. In catalytic hydrotreating, vegetable oil as the liquid feed is reacted with hydrogen as the gas feed in the presence of metal catalyst to produce renewable diesel. Gaseous hydrogen is used to remove oxygen atoms from triglyceride molecules in vegetable oil. The process is called hydrodeoxygenation. The process involves three phases: vegetable oil (triglycerides) as the liquid phase, hydrogen as the gas phase, and metal catalyst as the solid phase. Multiphase (three-phase) catalytic reactors are used. The most frequently used three-phase reactors are trickle-bed reactors and slurry reactors. Trickle-bed reactor is a type of fixed bed reactor, while slurry reactor is a type of bubble column or stirred reactor. Trickle-bed reactors have many advantages compared to slurry reactors, such as higher reaction conversion, lower operation or maintenance costs, lower catalyst loss, and lower separation cost (Ranade et al., 2011). A trickle bed reactor was selected in the present study.

The kinetic studies of hydrodeoxygenation have been investigated by Zhang et al. (2014) using waste cooking oil over a dispersed nano-catalyst, Kumar et al. (2014) using stearic acid over supported nickel catalysts, and Attanatho (2012) using oleic acid and triolein over supported nickel catalysts. The studies on the modelling and simulation of hydrodeoxygenation reactors are very scarce, even though modelling is very useful and far more superior than experimental works in terms of time and cost efficiency. Models based on computational fluid dynamics (CFD) may give results which agree with experimental data. So far, limited number of researches were carried out using CFD to model different small-scale reactors: micro-channel reactor for kinetic study (Attanatho, 2012), ebullated (fluidized)-bed reactor (Gollakota et al., 2015), and cocurrent upflow fixed-bed reactor (Subramanyam et al., 2015) with different reactants: triglyceride (Attanatho, 2012) and pyrolysis bio-oil (Gollakota et al., 2015). The present study focuses on hydrotreating of vegetable oils (represented by triglyceride) in large-scale trickle-bed reactor using NiMoP/Al₂O₃ spherical catalysts. The reactants, the kinetic model, and the catalyst used in this study is the same as those in Attanatho (2012) while the reactor is similar to the one used in Subramanyam et al. (2015) but is a large-scale one. The objective of this research is to obtain a reactor model with optimum condition to produce 4 t/d renewable diesel via hydrotreating of non-edible vegetable oils.

2. Modelling

Figure 1 illustrates our strategy in the modelling. The two-dimensional axisymmetry of a non-isothermal vertical cylindrical trickle-bed reactor with a diameter of 1.5 m and a length of 8 m was modelled using computational fluid dynamics (CFD) concept by considering mass, momentum and heat transfers in the gas and liquid phases. The reactor is packed with spherical catalyst particles of 1.5875 mm in diameter. The model of the solid phase considers the radial mass and heat transfers. The models for all phases were simulated simultaneously under the pressure of 3.45 MPa and the inlet temperature of 325 °C. The kinetic model was adopted from Attanatho (2012), where the reactants are hydrogen and triglyceride and the main products are heptadecane (C₁₇) and octadecane (C₁₈).

2.1 Momentum transfer

The momentum transfer was modelled using the two-phase Darcy's law approach. The model is basically the continuity equation combined with the Darcy's law as described Eqs(1) – (3):

$$\frac{1}{r} \frac{\partial (rc_1 U_r)}{\partial r} + \frac{\partial (c_1 U_z)}{\partial z} = \frac{1}{r} \frac{\partial}{\partial r} \left(r D_c \frac{\partial c_1}{\partial r} \right) + \frac{\partial}{\partial z} \left(D_c \frac{\partial c_1}{\partial z} \right) \quad (1)$$

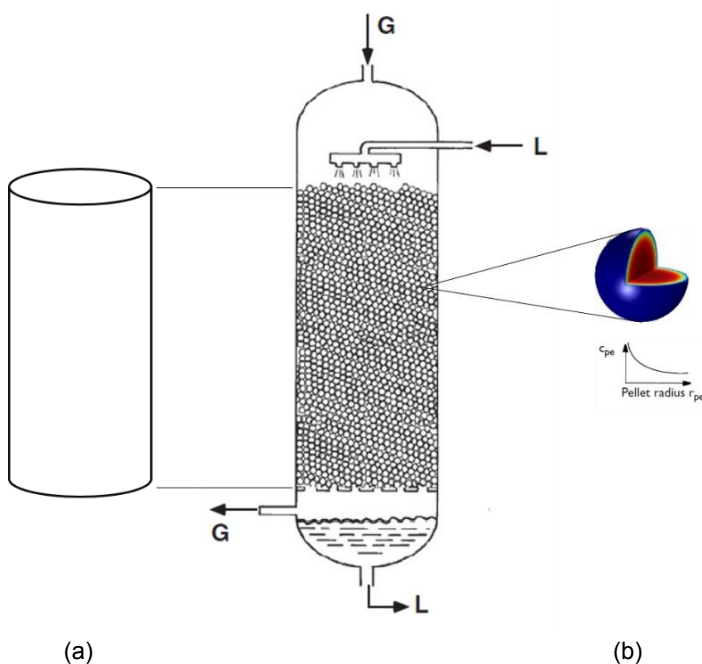


Figure 1: Strategy in modelling: (a) Macroscale (gas and liquid phase), (b) microscale (solid phase)

$$U_r = -\frac{\kappa}{\mu} \frac{\partial p}{\partial r} \quad (2)$$

$$U_z = -\frac{\kappa}{\mu} \frac{\partial p}{\partial z} \quad (3)$$

2.2 Mass transfer

The convection-diffusion equation for gas-phase mass transfer is as Eq(4):

$$-\left(\frac{1}{r} \frac{\partial}{\partial r} \left(r D_{Gr} \frac{\partial C_{G,i}}{\partial r} \right) + \frac{\partial}{\partial z} \left(D_{Gz} \frac{\partial C_{G,i}}{\partial z} \right) \right) + \left(u_{Gr} \frac{\partial C_{G,i}}{\partial r} + u_{Gz} \frac{\partial C_{G,i}}{\partial z} \right) = -R_{GL,i} \quad (4)$$

The governing equation for liquid phase mass transfer is a diffusion-convection equation as Eq(5):

$$-\left(\frac{1}{r} \frac{\partial}{\partial r} \left(r D_{Lr} \frac{\partial C_{L,i}}{\partial r} \right) + \frac{\partial}{\partial z} \left(D_{Lz} \frac{\partial C_{L,i}}{\partial z} \right) \right) + \left(u_{Lr} \frac{\partial C_{L,i}}{\partial r} + u_{Lz} \frac{\partial C_{L,i}}{\partial z} \right) = R_{GL,i} - R_{LS,i} \quad (5)$$

For mass transport in the catalyst pellet (solid phase), a diffusion-reaction equation (Eq(6)) is used:

$$\frac{1}{r^2 r_{pe}^2} \frac{\partial}{\partial r} \left(-r^2 D_{pe,i} \frac{\partial C_{pe,i}}{\partial r} \right) = R_{pe,i} \quad (6)$$

2.3 Heat transfer

Heat transport is considered only in the macroscale model. For the microscale model, the temperature in the catalyst pellet is assumed to be uniform. Thermal equilibrium is assumed to happen, such that the temperature difference between the phases can be neglected. There is only one equation for heat transfer as Eq(7):

$$(\rho C_p)_{eff} \left(u_r \frac{\partial T}{\partial r} + u_z \frac{\partial T}{\partial z} \right) - \left(\frac{1}{r} \frac{\partial}{\partial r} \left(r k_{er} \frac{\partial T}{\partial r} \right) + \frac{\partial}{\partial z} \left(k_{ez} \frac{\partial T}{\partial z} \right) \right) = Q_{bed} \quad (7)$$

2.4 Boundary conditions

For momentum transfer at the reactor outlet, the outlet pressure is specified; while at the reactor inlet, the inlet velocity is specified. For mass and heat transfers in macroscale model, the boundary conditions at the reactor inlet is the flux, and at the reactor outlet is the zero first derivate. At the reactor wall, all boundary conditions are no flux, except for the heat transfer where the boundary condition is the heat flux because there is heat transfer from the catalyst bed to the reactor jacket. The boundary conditions in the solid model are as Eqs(8) and (9):

$$\text{at } r = 0: \quad \frac{\partial C_{pe,i}}{\partial r} = 0 \quad (8)$$

$$\text{at } r = R: \quad -D_{pe,i} \frac{\partial C_{pe,i}}{\partial r} = R_{LS,i} \quad (9)$$

3. Simulation

The process parameters used for the base case are shown in Table 1. Triglyceride (TG) is a limiting reactant, while hydrogen is in excess. TG is diluted in dodecane with the concentration being 5 wt%. The TG concentration is kept at a low level to prevent the catalyst deactivation.

3.1 Concentration profiles

The profiles of the TG, C_{17} and C_{18} concentrations are shown in Figure 2 to Figure 5. Figure 2 (a) exhibits that the TG concentration in the liquid phase decreases in the axial direction. The average concentration of TG in the solid phase of the catalyst also decreases from the inlet to the outlet of the reactor though the decrease is

not as significant as in the liquid phase (Figure 2 (b)). When the TG concentration in the liquid phase decreases in the axial direction, the number of TG molecules moving from the liquid phase to the catalyst surface also decreases. The average concentration of TG in the catalyst pellet gradually decreases in the axial direction. The average concentration of TG in the catalyst is always less than that in the liquid phase. It can be seen that the TG concentration in the liquid phase near the inlet is 1.32 mol/m^3 , while the average concentration of TG in the catalyst is 1.24 mol/m^3 . This occurs because there is the liquid-solid mass transfer resistance around the catalyst pellets.

Table 1: Process parameters of the reactor for base case simulation

Parameter	Value
Reactor diameter	1.5 m
Reactor length	8 m
Catalyst particle diameter	1.5875 mm
Reactor outlet pressure	3.45 MPa
Inlet temperature	325 °C
H ₂ /TG molar ratio in feed	188 mol/mol
Inlet gas velocity	0.05 m/s
TG concentration in liquid feed	5 wt%
FFA/TG mass ratio in liquid feed	1.5 wt%
Cooling fluid temperature	30 °C

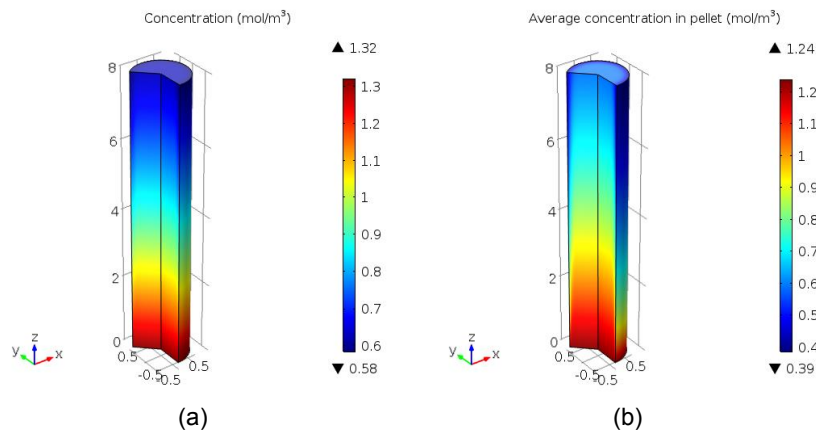


Figure 2: The TG concentration in (a) liquid phase, (b) in solid phase (average)

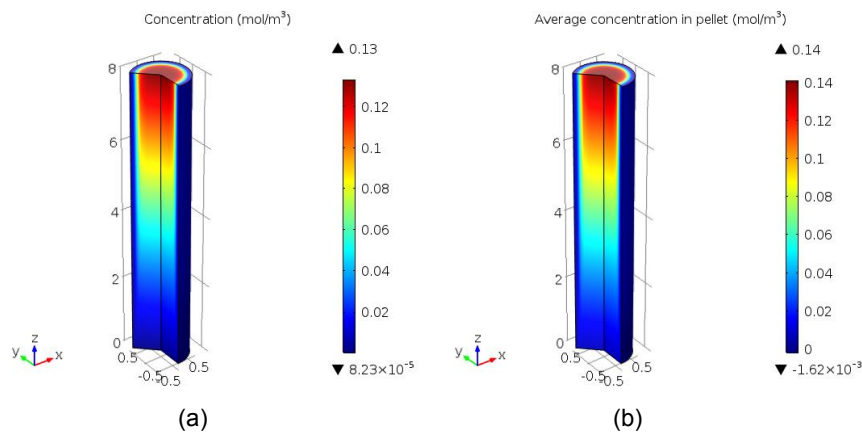


Figure 3: The C₁₇ concentration in (a) liquid phase, (b) in solid phase (average)

The difference between the C₁₇ concentration in the liquid phase and in the solid phase is not significant. The C₁₈ concentration can be seen in Figure 3 and Figure 4. This happens because the liquid-solid mass transfer

resistances for both C_{17} and C_{18} are very low. As the products, the average concentrations of C_{17} and C_{18} in the solid phase are always greater than those in the liquid phase. The C_{18} concentration is greater than the C_{17} concentration in both the liquid phase and the solid phase. This is because the production rate of C_{18} is greater than that of C_{17} . When the reaction rates are averaged over the whole volume of the reactor, the average production rate of C_{17} and C_{18} are $2.852 \times 10^{-4} \text{ mol/ (m}^3 \cdot \text{s)}$ and $1.385 \times 10^{-3} \text{ mol/ (m}^3 \cdot \text{s)}$.

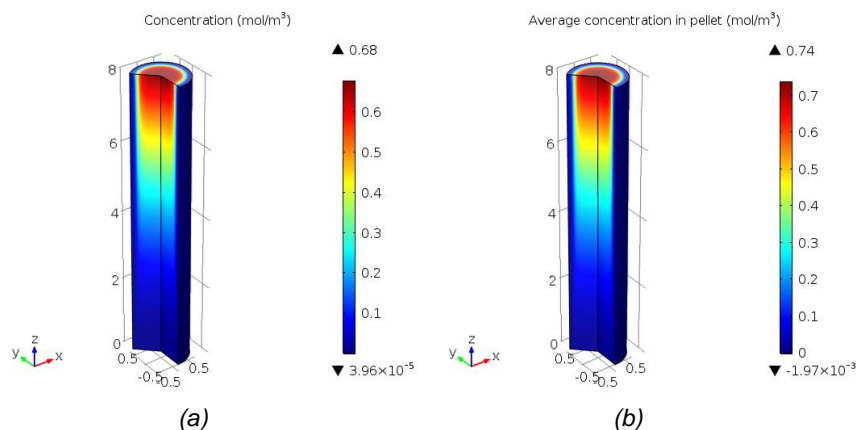


Figure 4: The C_{18} concentration in (a) liquid phase, (b) in solid phase (average)

3.2 Reactor performance

The reactor performance is represented by the TG conversion, the product yield, the product purity, and the production rate. The simulation results depict that under the parameter setting above the TG conversion is 53.2 %, the product yield is 13.4 %, the product purity is 95.8 %, and the production rate is 2.45 t/d. This indicates that the reactor performance is still low. The production rate is still under the target, 4 t/d and the TG conversion is under 90 %. Further simulation with the variation of key parameters is required.

3.3 Effect of the inlet temperature

The inlet temperature was varied from 300 °C to 400 °C. The results are shown in Figure 5 (a). It can be observed that the increase in the inlet temperature results in the increase in the product yield and the product purity. The trend proves that higher product selectivity can be achieved in higher temperature. However, as the inlet temperature increases, the TG conversion decreases. There exists a trade-off between the TG conversion and the product yield or purity. The optimum temperature can then be determined from the production rate profile. It is the temperature at which the production rate curve reaches its peak, which is 375 °C and the corresponding production rate is 4.61 t/d. The TG conversion, the product yield, and the product purity under this condition are 50.6 %, 21.4 %, and 96.2 %.

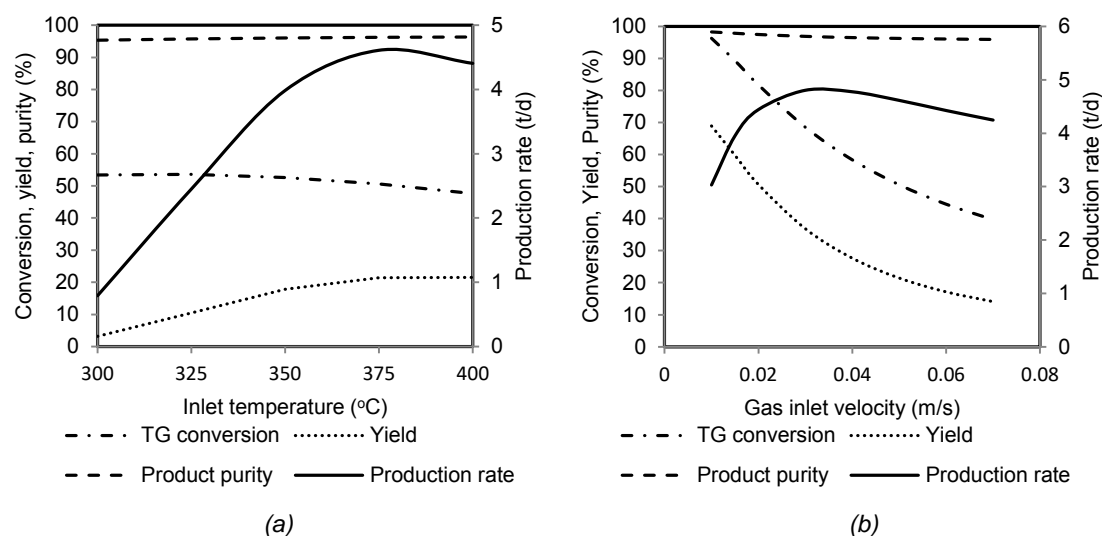


Figure 5: The effects of (a) the inlet temperature at $U_{G0}=0.05 \text{ m/s}$, and (b) the inlet gas velocity at $T_0 = 375$ °C.

3.4 Effect of the inlet gas velocity

The results obtained from the variation of the inlet temperature show that while the production target (4 t/d) is achieved, other key parameters i.e. the TG conversion, the product yield, and the product purity are still low. Further simulations are conducted by varying the inlet superficial gas velocity (U_{G0}) from 0.01 m/s to 0.07 m/s at 375 °C. The results are shown in Figure 5 (b). The TG conversion, the product yield, and the product purity are all inversely proportional to the inlet gas velocity. This phenomenon happens because the higher the inlet gas velocity, the shorter the residence time of the reactants. Although the higher inlet gas velocity results in the lower reactor performances in terms of the conversion, the yield, and the purity, it also means that the larger number of reactant molecules enters the reactor so that the production rate could be higher. There is a trade-off between the production rate and other performance parameters. As shown in Figure 5 (b), the maximum production rate is 4.80 t/d and achieved at the inlet gas velocity of 0.03 m/s. However, under this condition, the TG conversion is still low (68.5 %). This induces higher separation costs. By using non-linear regression results of the simulation data, the inlet gas velocity was decided at the level of 0.01545 m/s for the optimum condition. At this level, the TG conversion, the product yield, the product purity, and the production rate are 88.3 %, 58.5 %, 97.8 %, and 4 t/d.

4. Conclusions

The model of a large-scale trickle bed reactor for renewable diesel production via hydrotreating of triglyceride has been developed. The research may be considered the first one focusing on the aspect. The optimum condition to produce 4 t/d renewable diesel and high product purity is as follows: the inlet temperature is 375 °C and the inlet gas velocity is 0.01545 m/s, with the TG conversion, the product yield, the product purity, and the production rate being 88.3 %, 58.5 %, 97.8 %, and 4 t/d.

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