Numerical Simulation of Transesterification and Sensitivity Study

Isam Janajreh
Masdar Institute
ijanajreh@masdar.ac.ae

Mohamed Almusharrekh
Masdar Institute
malmusharrekh@masdar.ac.ae

Abstract

Transesterification is mainly achieved through a batch or semi-continuous reactors of the two immiscible reactants (methanol or ethanol and lipid or trigleceride) in the presence of a catalyst. The latter reactor has the advantage of high throughput, modularity, and is characterized with least labor that renders a highly efficient process and a better quality product. This work explains the development of a transesterification numerical simulation model. It is based on the three dimensions Navier-Stokes, reactive, multiple fluid species in a semi-continuous modular reactor. The model reaction is based on six reversible reactions with kinetics data that are inferred from the work of Noureddini et al. [1] and reproduced in our lab [2]. In particular, this work entails a sensitivity study of the methanol/lipid ratio, inlet velocity, temperature, pressure, and tube length in an attempt to find the optimal design and operation conditions. Results demonstrated that higher conversion and product yield is achieved at higher temperatures and higher methanol to triglyceride molar ratios. This work also provides detailed and valuable information on the molar and mass fractions of the main and intermediate species (diglycerids and monoglycerids), as well as the progression of each of the six reactions.

Introduction

Biodiesel is considered a sustainable alternative to diesel fuel as it can be utilized in current internal combustion diesel engine without any modification. It is transesterified from the combination of methanol or ethanol and triglycerides/lipid to form mono-alkyl Easter with the presence of a catalyst. Trapped grease, waste cooking oil, and animal fat can all be used as a substitute for the feedstock. Triglyceride and alcohol are immiscible and the onset of the reaction is mass-transfer limited. At a later reaction stage, and due to the generation of the product, immiscibility is reduced and the reaction moves to become kinetically limited [1, 3, 4]. Boer and Bahri [5] investigated the state of mixing of oil and alcohol and observed the two-phase mass transfer limitation in the form of a slugged flow of dispersed biphasic mixture. Mixing or induced turbulence, a higher temperature reaction, and an increase in the alcohol amount enhance the preferable forward reaction. At the same time, a catalyst can reduce the activation energy for the elementary reactions to proceed. The stoichiometric molar ratio is three moles of alcohols to one mole triglyceride, but this ratio rarely achieves satisfactory conversion. Our latest results and elsewhere [1, 3, 4] showed a sigmoidal reaction progressing for the transesterification. Hence, significant agitation is required to increase the reaction rate as indicated by Boocock et al. [6]. The main reaction followed a

slow stage, followed by a sharp increase and finally reaching slow asymptotic values. It is attributed to the reduction in droplet sizes, consequent surfactant action of the intermediates, and the effect of solvability properties of the product biodiesel as also observed by Boocock et al. [6], Ma et al. [7], and Zhou et al. [8]. They all described the reaction mixture during this stage as a pseudo-single-phase emulsion. The final reaction stage is attributed to the two-phase reversion, as glycerol concentration increases, ineffectiveness of the catalyst that dissolves in the polar phase, and the depletion of the glyceride reactants.

The main assumption of the simulation is homogenization of the two reactants at the reactor inlet, assuming that the two reactants are pumped/injected together via peristaltic or diaphragm type pump at a reasonable head. This assumption makes it possible to proceed with single-phase flow of multiple reacting species. Hence, introducing the turbulence to the flow through operating conditions and reactor configuration is the key behind the validity of this assumption. The simulation is carried out for an upright dual cylindrical reactor in which the flow is injected tangentially at values much higher than the laminar regime (Reynolds number $\cong$ 6000). Results of the kinetic studies done elsewhere by the authors [9] compare favorably with the literature. The values of the rate constant and activation energy for the eight elementary and reversible reactions used in this work are reported in Table 1. It should be noted that the kinetic model of these inferred values is pseudo first-order that combined with shunt-reaction scheme, as was also stated by Freedman et al. [10]. This work is intended to show the feasibility of carrying high-fidelity reactive flow simulation to the transesterification considering the main assumption above. Different operation conditions are considered in attempt to validity of the model as a conceptual design tool at an early stage of reactor design.

Table 1. Reaction measured rate constant and activation energy compared
to those obtained in the literature [9]

Reaction rate constant	K1	K2	K3	K4	K5	K6	K7	K8
WCO at 50°C	0.0356	0.1718	0.0688	0.2786	0.0866	0.0025	4.3E-9	0.0031
WCO at 60°C	0.0414	0.1579	0.0846	0.3054	0.1126	0.005	1.9E-8	0.0014
Noureddini and Zhu [2]	**0.049**	**0.102**	**0.218**	**1.280**	**0.239**	**0.007**	**7.84E-5**	**1.5E-5**
Activation Energy kJ/kmol	**E1**	**E2**	**E3**	**E4**	**E5**	**E6**	**E7**	**E8**
WCO at 50-60°C	0.1319	0.0737	0.1823	0.0807	0.2304	0.6342	3.0544	0.6825
Noureddini and Zhu [2]	0.0632	0.0477	0.0955	0.0704	0.0308	0.0461	-	-

Governing Equations and Model Development

System of Equations

Modeling reactive flow requires the application of flow continuity, momentum, energy equations, and species transport additional to the turbulence scalars. The transesterification starts as soon as the reactant components are brought into the reactor and under favorable reaction conditions. The flow is governed by the Navier-Stokes equations associated with temporal, convective, viscous, and source terms and is described as

$$\underbrace{\frac{\partial}{\partial t}(\phi)}_{Time\ rate} + \underbrace{\frac{\partial}{\partial x_i}(u_i\phi)}_{advective} = \underbrace{-\frac{\partial}{\partial x_i}\left(\Gamma_\phi \frac{\partial\phi}{\partial x_i}\right)}_{diffusion} + \underbrace{S_\phi}_{source}$$

(1)

where u_i is the ith (x, y, and z) velocity component and S^ϕ is the source term due to the dispersed phase interaction. ϕ is the dependent variable corresponding to density (ρ) constituting the continuity, the velocity density multiple (ρu_i) constituting the momentum, and the temperature (T) to govern the energy. ϕ can also represent turbulent scalars, i.e., turbulent kinetic energy (k) and the turbulent dissipation rate (k). These two equations in steady state flow regime are written as

$$\rho u_i \frac{\partial k}{\partial x_i} = \mu_t\left(\frac{\partial u_j}{\partial x_i} + \frac{\partial u_i}{\partial x_j}\right)\frac{\partial u_j}{\partial x_i} + -\frac{\partial}{\partial x_i}\left(\frac{\mu_t}{\sigma_k}\frac{\partial k}{\partial x_i}\right) - \rho\varepsilon$$

$$\rho u_i \frac{\partial\varepsilon}{\partial x_i} = C_{1\varepsilon}\frac{\mu_t\varepsilon}{k}\left(\frac{\partial u_j}{\partial x_i} + \frac{\partial u_i}{\partial x_j}\right)\frac{\partial u_j}{\partial x_i} + \frac{\partial}{\partial x_i}\left(\frac{\mu_t}{\sigma_\varepsilon}\frac{\partial\varepsilon}{\partial x_i}\right) - C_{2\varepsilon}\frac{\rho\varepsilon^2}{k}$$

(2)

The right hand terms are representing the diffusion, the generation, and destruction/ dissipation of the turbulent quantities, respectively. In these equations, μ_t is the eddy viscosity, which is an order of magnitude higher than the laminar viscosity, and is written as

$$\mu_t = f_\mu C_\mu \rho\, k^2/\varepsilon$$

(3)

where f and C are user defined constants and $C_{1\varepsilon}$, $C_{2\varepsilon}$, σ_k and σ_ε are empirical constants. The species m_i transport equation:

$$\frac{\partial}{\partial t}(\rho m_i) + \frac{\partial}{\partial x_i}(\rho u_i m_i) = \frac{\partial}{\partial x_i}\left(\rho D_{i,m} + \mu_t/Sc_t\right)\frac{\partial m_i}{\partial x_i} + R_i + S_i$$

(4)

where $D_{i,m}$ is the diffusion coefficient of m_i specie, Sc_t is the turbulent Schmidt number and is defined as the ratio of the eddy viscosity μ_t to the eddy diffusivity $D_{i,m}$. These transport equations incorporate an additional reaction source term R_i that accounts for species reaction and are governed by the stoichiometric reaction below:

$$\sum_{i=1}^{N} v'_{i,r} S_i \quad \overset{k_{f,r}}{\underset{k_{b,r}}{\Leftrightarrow}} \quad \sum_{i=1}^{N} v''_{i,r} S_i \tag{5}$$

The reaction rate is proportional to the concentration of the reaction products raised to specified power coefficients. That is, the ith species production/destruction due to the reaction r is written as

$$R_{i,r} = M_{i,r}(v''_{i,r} - v'_{i,r})\left(k_f \prod_{j=1}^{N} C_{j,r}^{\eta'_{j,r}} - k_b \prod_{j=1}^{N} C_{j,r}^{v''_{j,r}}\right) \tag{6}$$

where k_f and k_b are the forward and backward reaction constants based on Arrhenius equation 5, C_j is the molar concentration of jth specie raised to stoichiometric coefficients v and reaction order η, and M_i is the molecular weight of species i [11].

Initially, the CFD analysis is pursued as a non-reactive flow to investigate the flow field throughout the tabular reactor, evaluate pressure loss and pressure head/mass flow needed. The reactive flow at different flow settings of stoichiometric and over stoichiometric of the methanol lipid (WCO) and temperatures were carried out. These analyses and reactions are developed within the framework of the Fluent code [12].

Reactor Configuration and CFD Setup

An illustration of the transesterification reactor is depicted in Figure 1. For detailed drawings of the chambers and their exact dimensions, see Rabu's thesis work. The tubular reactor consists of two coincided and separated chambers and with many features, including compactness, low-pressure drop, ease of temperature control, isothermal reaction condition, and modular configuration for easy scaling up/down. The modularity can be achieved through multiple reactor stacks or simply by using longer tubing fitted on the same end-caps. The reactants are introduced circumferentially and hence minimize the pressure drop and increase the residence flow time while following a swirling trajectory.
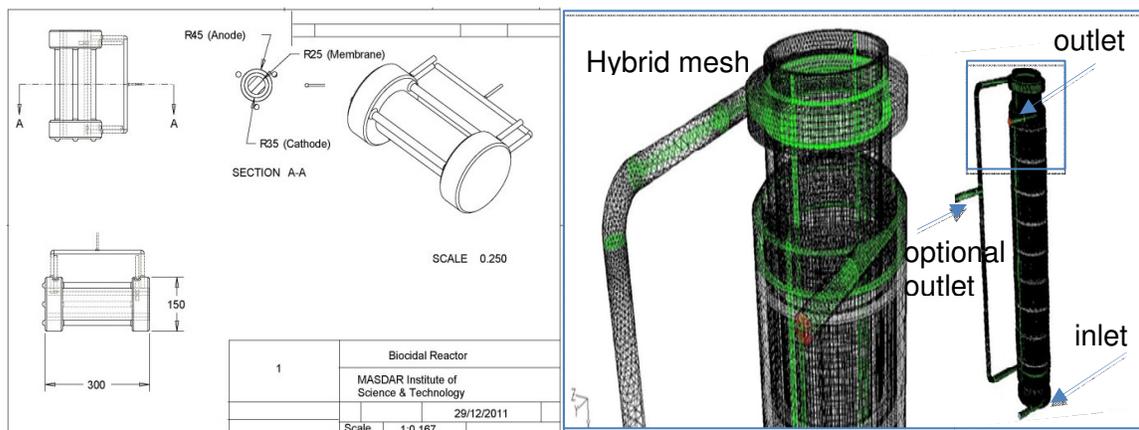
Figure 1. Reactor tube configuration (dimensions are mm) and the discretized mesh

A hybrid hexagonal and trigonal mesh is generated; it captures the near wall steep flow transition and consists of 275,00 cells for the two chambers in addition to the connecting tubing as shown in Figure 1. The two reactants species are interring the inner then the outer chambers of the upright reactor at an inlet Reynolds number (Re) near 6000 (based on the bottom inlet diameter of 4mm) and 1 to 3 triglyceride-methanol molar ratio. Atmospheric pressure outlet boundary condition is assigned at the outer tubular chamber located at the top. The no-slip wall velocities are imposed on all the surfaces of the reactor. Description of the six species is summarized in Table 2 following the work of Narvaez et al. [3]. The ideal mixture is used to determine the overall properties of the mix where it is needed, as written below:

$$\varphi_m = \sum_{i=1}^{n} m_{f,i} \varphi_i$$

(8)

where φ is the property and the subscripts i and m signify the ith species and mixture; $m_{f,i}$ is the mass fraction of the ith specie.

Table 2. Summary of species properties and MW

Species	Chemical formula	Molecular weight	Viscosity (kg/m.s)	Cp (J/kg.^{o}C)	Density Kg/m^3
Methanol	CH_4O	32	3.96e-4	1.470e3	791.8 [20]
Waste oil or Triglyceride	$C_{54}H_{105}O_6$	849	1.61e-2	2.2e3	883.3
Diglyceride	$C_{37}H_{72}O_5$	596	-	-	880
Monoglyceride	$C_{20}H_{40}O_4$	344	-	-	875
Biodiesel	$C_{18}H_{36}O_6$	284	1.12e-3	1.187e3	870
Glycerol	$C_3H_9O_3$	93	1.412e0	0238.6	1261

In experimental work of the author, virgin oil and WCO were used as feedstock that had been collected from the institute canteen and generated at a substantial rate of nearly 60 liters/week. Palm oil and sunflower oil are the most common types of oil used locally. The molecular formula $C_{54}H_{105}O_6$ is very representative of these types of oil carried out and at both 50 and 60º C (333K). These operating temperatures values are lower than the boiling point of the methanol when the reactor operates at near atmospheric pressure. A steady state solution is sought for the flow, which enters the reactor by means of an external low head pump (peristaltic or diaphragm) at an adjustable flow rate of 50 to 1,000 ml/min.

In this work, transesterification is attempted at two different temperatures, 50° C and 60° C, at a Reynolds number beyond the laminar regime to induce the homogeneity of the reactants. Therefore, the mass transfer limiting stage is avoided, suggesting a single-phase flow of multiple species as indicated by Boer.

Simulation Results

Baseline Study

The flows simulate an ideal mixture of the two reacting species (methanol and biodiesel). Figure 1 shows the pathlines of the mixture for none reactive flow trajectory colored by the residence time and its velocity contours. For the given reactor, the total particle transfer time at relatively 15 m/s (Re=4000) is about 0.9 seconds. It should be noted that this is over an order of magnitude higher than if the flow were introduced axially along the reactor axis.
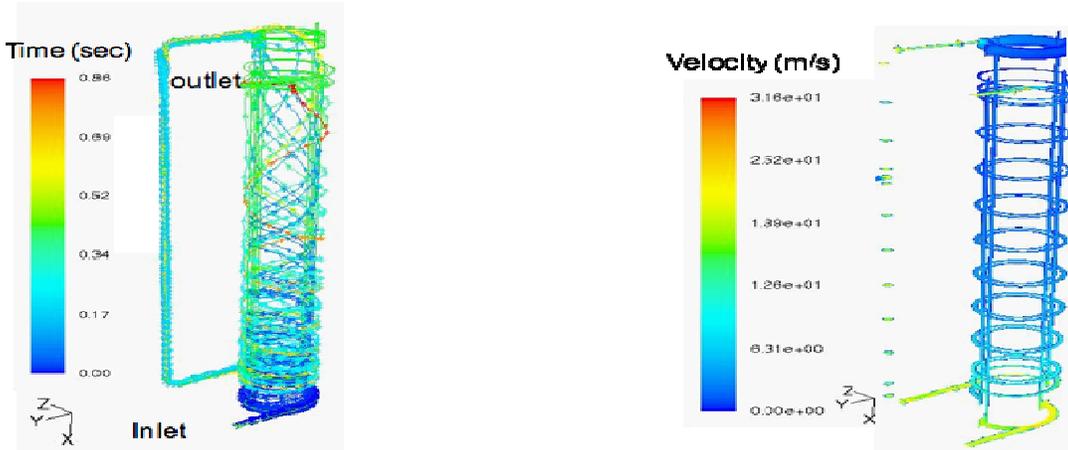
Figure 2. Flow trajectory colored by the resident time (right) and its velocty (left)

The flow is injected at relatively high velocity that enhances the required homogenized mixing state of the reactants and avoidance of mass transfer limitation. The mixture, however, is entrained in a swirl trajectory that enhances the reactivity because of the long residence time. Stoichiometry reactive flow is simulated at corresponding three moles of methanol to one mole of WCO (mass ratio of 1:8.745). The model is tested initially at low mass flow conditions within the laminar regime (Re=1, based on the smallest tube diameter of 1cm). The resulting molar fraction of the species through the reactor are shown in Figure 3 and summarized in Table 3.

Table 3. Species molar fraction at idealistic conditions

Port & ratio/Species	$C_{54}H_{106}O_6$ (WCO)	CH_4O	$C_{18}H_{36}O_2$ (FAME)	$C_3H_9O_2$	Conversion*
inlet	0.25	0.75	0	0	28%
outlet	0.18	0.54	0.21	0.07	

*Conversion=(0.25-0.18)/0.25
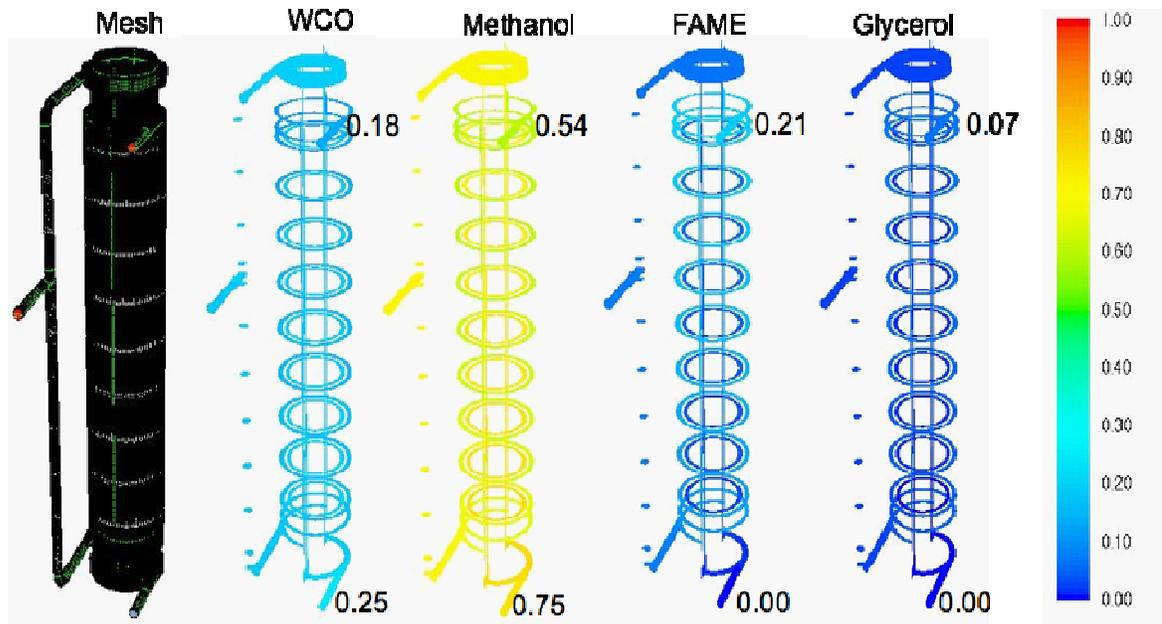
Figure 3. Molar fraction of species across the reactor (global scale)

At this velocity, a conversion of 28% is achieved, and the low conversion is attributed to the relatively shorter residence time and low kinetics of the reacting species. Batch transesterification processes typically take several hours of processing time, and from the Noureddinni batch reactor work, the reaction took several minutes to reach nearly 30% conversion [1] and at higher molar ratio (1:6).

Results of the species concentration at a more practical flow rate conditions 600 ml/min (Re=1,000) are summarized in Table 4. This clearly shows the effectiveness of continuous reactor as a higher conversion of 66% is attained in only fraction of a minute. This may sound counterintuitive due to the reduction in residence time; however, the kinetics of the reactants are more pronounced in activation of the reaction, even with the absence of the mass transfer limitation by the stipulated perfect homogeneous assumption of the incoming flow. However, excess methanol also provides more availability for other reactions to proceed and hence will definitely simulate the experimental observation. It demonstrates the influence of the excess methanol and the interplay with the presence of the reversible reactions as the flow surpasses the initial two-phase flow mass transfer limitation.
The simulation results emphasize the advantage of efficient mixing of the flow, which can definitely reduce the additional methanol concentration, relax the downstream method of their separation to improve process economy to some extent.

Table 4. Species molar fraction at practical conditions

Port & ratio/species	$C_{54}H_{106}O_6$ (WCO)	CH_4O	$C_{18}H_{36}O_2$ (FAME)	$C_3H_9O_2$	Conversion
9:1 methanol-WCO molar ratio					
inlet	0.10	0.90	0	0	66%
outlet	0.034	0.702	0.198	0.066	

Sensitivity Study

Modularity of the reactor makes it possible and easy to carryout sensitivity studies for the configuration as well as the inlet flow conditions. This includes the effect of reactor size, the molar ratio, the inlet velocity, and temperature. Results for the influence of the increase in the methanol-triglyceride ratio and increase in the inlet flow velocity are shown in Figure 4. As the molar ratio is increased, the rate of the forward reaction dominates the reverse reaction according to Le Chatelier's principle to consume the additional reactant by proceeding with the forward reaction faster towards the equilibrium; therefore, more lipid conversion takes place. The velocity trend, however, is the opposite: as higher velocity reduces the residence time and consequently lower conversion occurs.
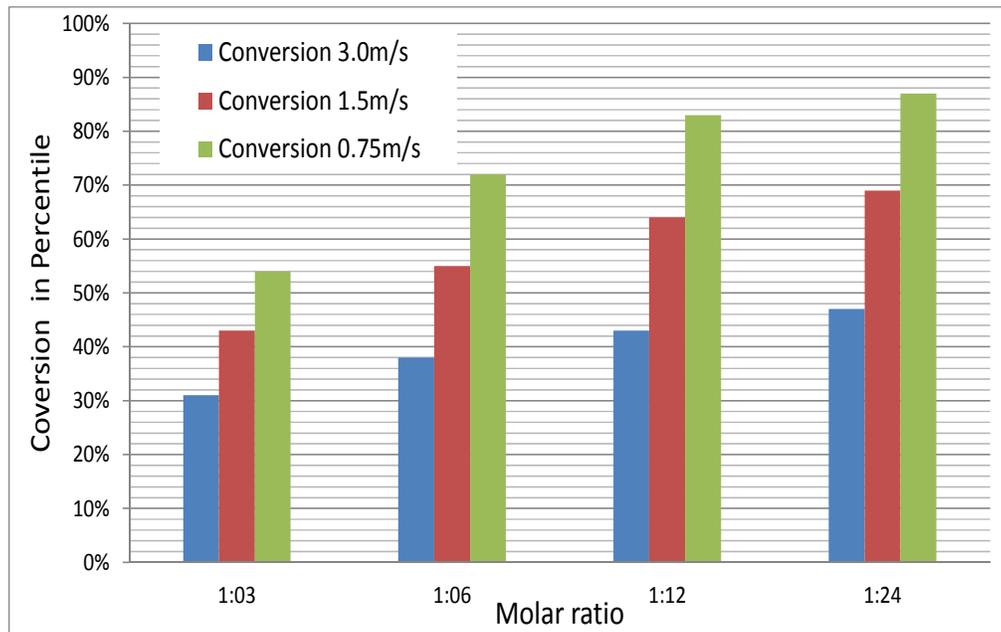
Figure 4. Influence of molar ratio and velocity

Results of the effect of the inlet reactant temperature are depicted in Figure 5. As the reaction is neither exothermic nor endothermic, the temperature effect does not reflect a unified trend and is also less pronounced. It again may appear counterintuitive, as the increase of the temperature resulted in a slightly lower conversion. It is, however, due to the revisable

reaction that also feeds both ways on the temperature according to their activation energy. In general, irreversible reaction rate increases with the increase of the temperature, while reversible reactions require an optimal value for the conversion and the desired yield.
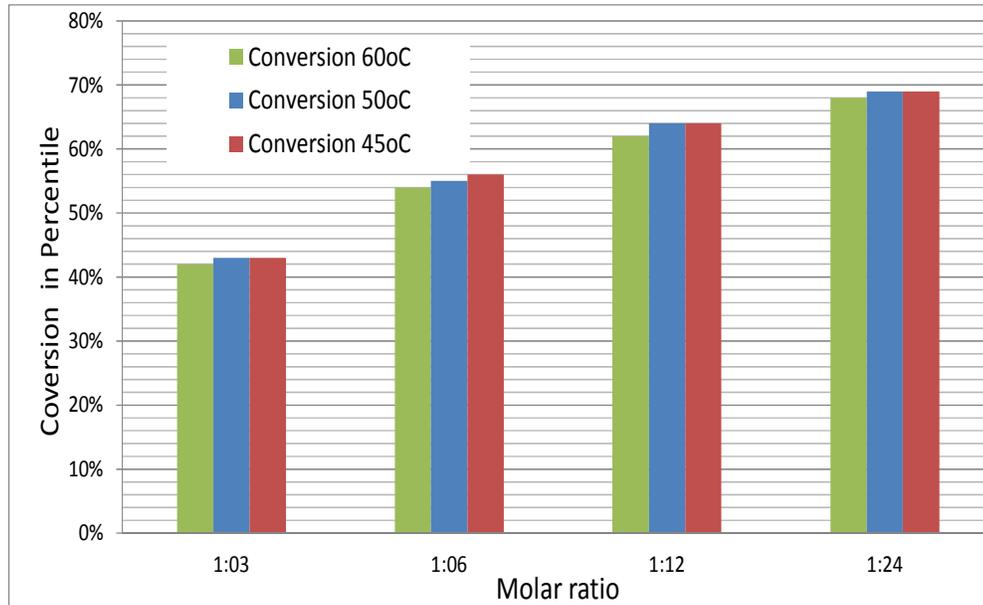
Figure 5. Influence of the temperature on the conversion

Results of the influence of the reactor size are depicted in Figure 6. It clearly shows the pronounced effect of the reactor length that dominates the increase in the diameter or width. This is due to the swirling momentum that is maintained for the longer reactor, while it fades out for the wider diameter reactor.
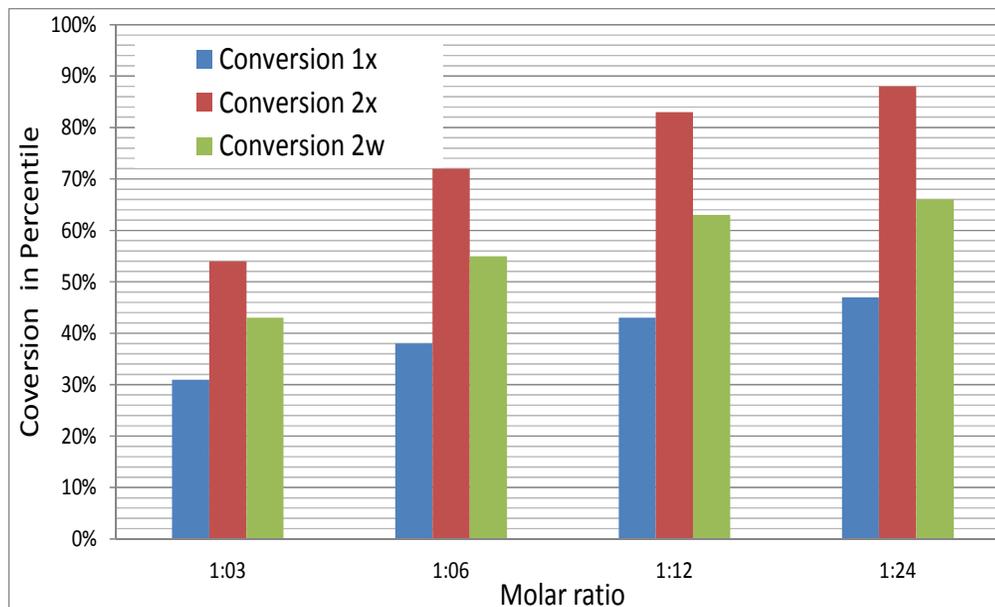
Fig. 6. Influence of the reactor length and width on the conversion at fixed inlet conditions (velocity and temperature)

Conclusion

The high-fidelity reactive flow model that is based on CFD for transesterification was developed in this work. It simulates the flow within a continuous upright tubular reactor configuration. Chemical kinetics of eight elementary reactions were used, and the flow is assumed to be a single homogenous phase of multiple species representing the two reactants (methanol and triglyceride/lipid), the intermediates (dioglyceride and monoglyceride), and products (biodiesel/FAME and glycerol). As the flow injected tangentially along the circumference of the reactor, it follows a swirling trajectory, and hence it resulted in an order of magnitude increase in residence time, compared to the tube length transfer time. Reactive flow at laminar Reynolds number results in low conversion of the WCO, while turbulent flow significantly increases the conversion rate. A sensitivity study shows that the conversion is also in the favor of the excess amount methanol, as well as lower inlet velocity value while maintained within the turbulent regime. The latter is attributed to the longer reaction time during the fluid trajectory.

Temperature influence seems counterintuitive due to the inclusion of the reversible reactions; however, the influence is also less significant than other parameters, i.e., molar ratio and reactor size. The influence of reactor length is significant as it also attributes to the increase in the reaction time. It is, however, more dominant than the increase in the reactor diameter/width. This work emphasizes efficient mixing of the flow interplaying as a parameter to the excess methanol molar amount, which can increase the economy of the process by avoiding the added consumable expense, as well as avoiding the downstream separation being thermal or using additional washing water.

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Biographies

ISAM JANAJREH is currently an associate Mechanical Engineering professor and the director of the waste to energy lab at the Masdar Institute. He is an internationally recognized expert in the area of waste to energy, particularly in the feedstock characterization thermochemical pathways, including gasification and pyrolysis. He has authored more than 80 publication in the subject and participated in over 80 conferences. Dr. Janajreh may be reached at ijanajreh@masdar.ac.ae.

MOHAMED ALMUSHARREKH is currently a Ph.D. candidate at Masdar Institute. He earned his M.S in Mechanical Engineering, 2014, from Masdar Institute; Mohamed is part of the waste management group of Dr. Janajreh; he is well versed in both the experimental and the simulation of feedstock transesterification. Mr. Almusharrekh can be reached at malmusharrekh@masdar.ac.ae.