Numerical Simulation of Transesterification

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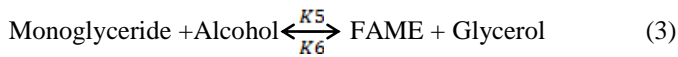Masdar City, Abu Dhabi, UAE
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Abstract— Transesterificatoin is a chemical reaction process in which two immiscible liquids react in the presence of a catalyst to form biodiesel, and the less desired glycerol. The efficiency of the process depends on numerous variables, including reactants molar ratio, flow and agitation speed, temperature and pressure, residence time, reactor configuration as well as the amount of the catalyst. Investigating these parameters experimentally is a fairly involved job that requires a highly skilled analyst with direct access to high fidelity analytical tools to assess product purity including GCMS, HPLC and FTIR additional to the ability to carry multiple set of ASTM standards for the heating value, T90 distillation, Flash and Cloud points, lubricity, Viscosity, Density, Vapor Pressure etc. Although numerical simulation can't replace the true essence of production and assessment of the biodiesel product, it can be used at the conceptual level to investigate the trend, parametric dependency and offset numerous experimentation hassles and their associated capital and cost. This work details the development of numerical reactive flow model applied to transesterification following a coupled thermo-chemical flow. It consists of several reactions with known rate constants and activation energies. The model has been used to carry parametric study of the process parameters. Special attention here is given to the rate of reactions and their behavior in a semi-continuous tubular reactor.

Keywords—transesterification; reactive flow; rate of reaction

I. INTRODUCTION

Modeling of a reactive flow process such as transesterification requires understanding of the main flow reactions, side reactions and radicals. These reactions are given elsewhere [1]. The following reactions describe the transesterification reaction.

$$\text{Triglyceride + Alcohol} \underset{K2}{\overset{K1}{\rightleftarrows}} \text{FAME + Diglyceride} \qquad (1)$$

$$\text{Diglyceride + Alcohol} \underset{K4}{\overset{K3}{\rightleftarrows}} \text{FAME + Monoglyceride} \qquad (2)$$

$$\text{Monoglyceride + Alcohol} \underset{K6}{\overset{K5}{\rightleftarrows}} \text{FAME + Glycerol} \qquad (3)$$

Theoretically, one mole of oil consumes three moles of alcohol to produce three moles of Fatty Acid Methyl Ester (FAME) and one mole of glycerol. Although, the reactions tends to follow an equilibrium [2], above stoichiometric such as excess methanol additional to presence of catalyst and higher temperature are used to steer the forward reactions and

production of FAME. Their integration of these reaction to the flow is carried out through additional source terms to each of the fundamental laws which are governed by the Navier-Stokes equations. These equations are associated with temporal, advective, viscous, and source terms and are written as:

$$\frac{\partial}{\partial t}(\phi) \;+\; \frac{\partial}{\partial x_i}(u_i \phi) = -\frac{\partial}{\partial x_i}\left(\Gamma_\phi \frac{\partial \phi}{\partial x_i}\right) + S_\phi$$

Time rate   advective   diffusion   source (4)

Where u is the velocity and $S\phi$ is the source term due to the interaction, destruction or creation of other species. Φ is the dependent variable which is density (ρ), the velocity density multiple (ρu), or the temperature (T) to constitute the continuity, momentum, and the energy respectively. It can also represent turbulent kinetic energy and its dissipation rate. Additionally, there are equal numbers of transportation species as many of the flow species and incorporating the reaction source term/rates as [3]:

$$\frac{\partial}{\partial t}(\rho m_i) + \frac{\partial}{\partial x_i}(\rho u_i m_i) = \frac{\partial}{\partial x_i}\left(\rho D_{i,m} + \mu_t / Sc_t\right)\frac{\partial m_i}{\partial x_i} + R_i + S_i \quad (5)$$

$$\sum_{i=1}^{N} v'_{i,r} S_i \underset{k_{b,r}}{\overset{k_{f,r}}{\Longleftrightarrow}} \sum_{i=1}^{N} v''_{i,r} S_i \qquad (6)$$

$$R_{i,r} = M_{i,r}(v''_{i,r} - v'_{i,r})\left(k_f \prod_{j=1}^{N} C_{j,r}^{n^*_{rj}} - k_b \prod_{j=1}^{N} C_{j,r}^{v'^*_{j,r}}\right) \qquad (7)$$

The where m, D spiecie analyses and reaction are achieved within the framework of Fluent code [4]. Using reactive CFD in the analysis of transesterifcation still appears in a few work. Janajreh and Alshrah [5] have carried out both non-reactive and reactive flow for tubular reactor to model the transesterification of the two reactants and their products. Their work however only demonstrated the feasibility of CFD in obtaining the concentration of the species and their products. Less emphasis was given to the details of reaction activity and their rate distribution. Another work by the same author shows the evaluation of the reaction kinetics of the waste cooking oil transesterification followed by implementing these values in a reactive flow model. A sensitivity study was carried out considering molar ratio, flow condition, and different geometrical configuration. Nevertheless, the importance of the reaction kinetics and its vital role that plays in influencing the yield did not grasp the author attention. In this work, the details of transesterification process inside a 3D cylindrical single cavity reactor is studied. The influence of the velocity and molar ratio on chemical kinetics will be demonstrated and

discussed. The results aim to gain more insight to the distribution of the flow kinetics and their correlation to the classical flow fields including velocity, temperature and turbulence kinetic energy.

II. SYSTEM SETUP

The model setup and flow properties is similar to the author's previous work. It consists of a single tubular reactor (30cm length) with circumferential inlet at the bottom and an exit at the top. The properties of the species are found elsewhere and the activation energies of each reaction used are shown in Table I [1].

TABLE I.   CHEMICAL KINETIC CONSTANTS OF REACTIONS

Reaction	K at 50 oC and Reynold's Number=6200	Activation Energy (J/mol)	Pre-exponential factor (A)-calculated
1. Triglyceride → Diglyceride	0.05	54,998	$3.925*10^7$
2. Digleceride → Triglyceride	0.11	41,555	$5.78*10^5$
3. Diglyceride → Monoglyceride	0.215	83,094	$5.91*10^{22}$
4. Monoglyceride → Diglyceride	1.228	61,249	$9.88*10^9$
5. Monoglyceride → Glycerol	0.242	26,685	5,355
6. Glycerol → Monoglyceride	0.007	40,116	21,533

III. RESULTS OF SIMULATION AND DISCUSSION

A. Yield of Biodiesel

TABLE 1 shows the yield of biodiesel based on the actual mass fraction at the outlet over the maximum theoretical mass fraction for a stoichiometric reaction.

TABLE II.   YIELD OF BIODIESEL

Velocity (m/s)	V_1 (0.33)		V_2 (0.60)	
Molar Ratio	3:1 Case 1	9:1 Case 2	3:1 Case 3	9:1 Case 4
Yield (%)	36.06	36.28	32.70	32.69
Mass flow rate (l/h)	73.80	73.62	134.75	134.88
Turbulent Kinetic Energy $(m^2/s^2) *10^{-6}$	1.128	1.283	5.062	5.319

The main assumption that was imposed in the numerical simulation is that the two immiscible liquids, oil and methanol, are well mixed at the inlet. Comparing the yield of FAME when the alcohol:oil molar ratio was increased, under the same velocity, there was no major change. Although it is proved experimentally that increasing the molar ratio would push the reaction forward [7], numerically this cannot be shown since the reaction occurs at the facial interface and the simulations were based on a homogeneous, Eulerian flow of multiple species rather than two-phase flow. In this sense, the physics behind this setup should be further enhanced to take into account the immiscibility of the reactants. Looking at the yields for the two different velocities, it is noticed that the yield favors the lower velocity due to the longer residence time inside the reactor. Although the observed Turbulent kinetic energy is larger at higher velocity, residence time plays more role in the overall forward reactions.

B. Kinetic Rate of Reactions

There is no certain trend for the kinetic rates of the reactions when the alcohol molar ratio was raised. However, a slightly higher kinetic rate is observed in the case of a higher velocity. Fig. 1 shows the contours of R1 and R5 rate of reactions and they are non-localized, taking place all over the volume. Their kinetic rates are summarized in TABLE 2.
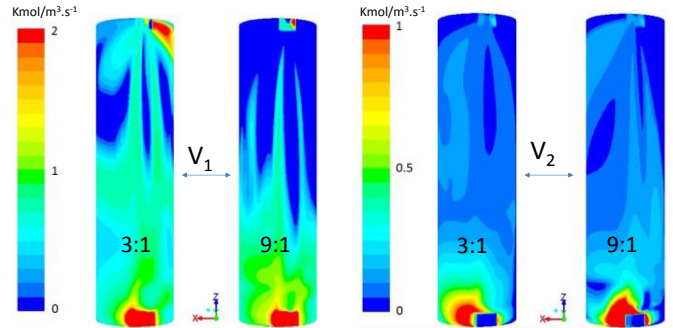

Fig. 1.   *Kinetic rate of some reactions for the three cases.*

TABLE III.   KINETIC RATE OF REACTIONS

Kinetic Rate $(kmol/m^3 s)$	Case 1	Case 2	Case 3	Case 4
Reaction 1	0.6212	0.6916	0.7290	0.7143
Reaction 2	0.4357	1.2733	1.3470	1.3357
Reaction 3	5.9052	20.1951	21.5121	21.7219
Reaction 4	8.9857	7.9511	7.7013	8.0000
Reaction 5	0.1073	0.1179	0.1351	0.1463
Reaction 6	0.0317	0.0294	0.0307	0.0325

IV. CONCLUSION

Numerical simulations of the transesterfication following 3D reactive flow of six elementary reactions was carried out. The yield and the behavior of the reactions within a semi-continuous bio-reactor are also investigated in which 36% conversion is achieved. The assumption of a well-mixed flow needs to be reconsidered when analyzing the methanol to oil molar ratio. Larger velocity results in a lower yield due to a shorter residence time even though the additional TKE.

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