

Biodiesel Transesterification Reaction Simulation Module Documentation

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Abstract

Transesterification is the traditional process for converting triglyceride materials into biodiesel, a renewable fuel suitable for combustion within diesel engines. In this reaction, triglycerides (TG) are esterified with methanol (MeOH) in the presence of a sodium hydroxide (NaOH) catalyst. Because this reaction is reversible and sensitive to temperature, reaction outcome is highly dependent on variations in starting materials and other parameters. This interactive webpage implements a computational strategy to predict reaction outcomes for any starting conditions with a high degree of accuracy, permitting *in silico* research and optimization of reaction conditions. The following documentation details key parameters utilized within the reaction simulation, as well as the body of experimental and theoretical work used to generate this simulation procedure. The computational methods and proper usage of the webpage are also detailed here.

1. Webpage Usage Overview

Conditions Entry: Upon generating the webpage, the user will be prompted on the left hand side of the screen with a panel titled “Initial Conditions Entry”. Here, the initial amounts of the three reactants involved in the transesterification reaction - triglyceride, methanol, and sodium hydroxide can be entered using either mass or volume values. Temperature must also be selected. Finally, the length of simulation time required and simulation precision must be selected. A smaller input will increase the precision of the simulation but consequently increase the time required to generate results, and vice-versa. When all conditions are entered, the “Generate Reaction Simulation” button will initiate the simulation procedure. This process may be repeated for additional simulations.

Results Main Panel: Once the simulation procedure has concluded, results will be displayed adjacent to the conditions entry. Underneath the title “Simulation Results” a one line summary displays the initial reactant amounts and reaction temperature. The main results panel also contains six graphing procedures, some with interactive tools to give more information on specific timepoints. Below this main results panel, a drop down menu can be accessed on the bottom left hand side to switch between the six available graphs.

Yield Panel: Below the graphing panel, more information is curated regarding yield, concentration, and mass data for reactive species at any simulated timepoint, which may be selected with the accompanying slider. Simulation data at ALL timepoints may be downloaded as a .csv document here, either as mass or concentration data.

2. Model Assumptions

Engineering approximations were necessary during the design of the reaction simulation procedure, of which most concerned the homogeneity of the reaction mixture through time. Mass and heat transfer limitations may arise when mixing is not sufficiently turbulent^[10], which may invalidate isothermal and homogeneous concentration assumptions and lower the observed rate of reaction from simulated values.

The most important approximations are the following:

1. Negligible temperature and concentration gradients throughout the reaction vessel
2. Negligible volumetric changes through the course of reaction
3. Negligible loss of volatile reactants by vaporization (primarily methanol)
4. All water and free fatty acids present in reactants have been removed during pretreatment

Previous experimental work has shown that hysteresis effects can cause a latency period in reaction, where mixing is insufficient to fully homogenize the reaction mixture. With strong mixing, with a Reynolds number greater than approximately 6000^[10], this latency period may be avoided.

As a rule of thumb, if the reaction vessel is a well-mixed closed-system, and all reactants are properly pretreated to remove unfavorable contaminants, simulated results may be expected to be highly accurate for the system being studied. Plug flow or batch reactors are well-approximated by this simulation procedure.

3. Material Parameters

The masses of triglyceride, sodium hydroxide, and methanol were approximated to be 885.4 g/mol, 39.997 g/mol, and 32.04 g/mol. The densities of triglyceride and methanol were approximated to be 0.930 g/mL and 0.791 g/mL, respectively^[9].

Table 3.1 | Density and Molar Mass Values

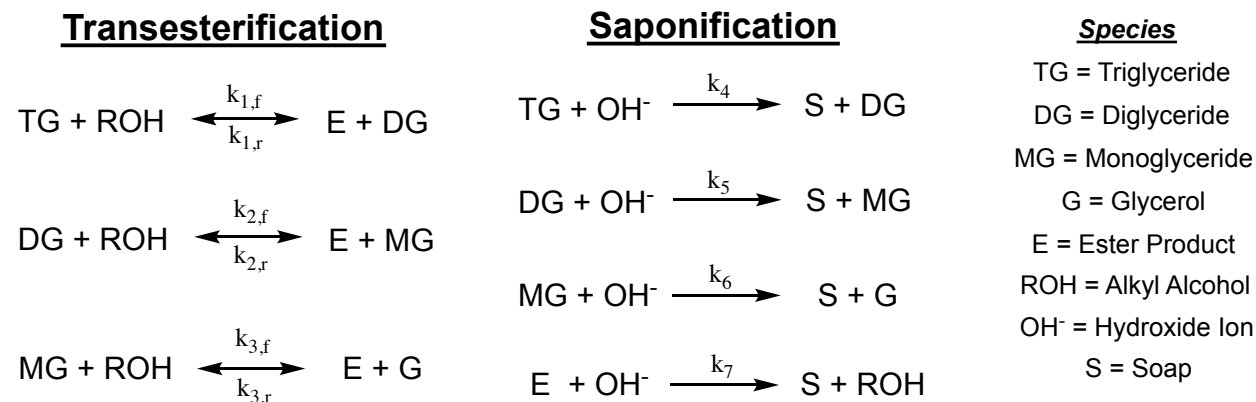
Material	Molar Mass (g/mol)	Density (g/mL)
<i>Triglyceride</i>	885.4	0.93
<i>Sodium Hydroxide</i>	39.997	--
<i>Methanol</i>	32.04	0.791

4. Reaction Constants

Reaction rate constants were approximated using temperature dependent Arrhenius equations. Pre-exponential factors and activation energies were obtained through experimental studies conducted on rapeseed oil^[5]. In these studies, rate constants were determined by fitting numerical integration models to experimental concentration values as a function of isothermal reaction temperature.

5. Integration Method

The procedure utilized in this webpage uses Runge-Kutta 4 (RK4) integration, a higher order numerical integration method held as the industry standard in reaction kinetics estimations. The experimental rate constants can be used in conjunction with quasi steady state assumptions to yield a simplified reaction network^[15] that yields easily to numerical integration, shown below:



Numerical integration is dependent on user input regarding the timestep used, where users may select a more or less precise timestep depending on the requirements of their specific reaction conditions. RK4 integration is also performed on nondimensionalized concentration values, where all concentrations are normalized by the initial concentration of triglyceride molecules.

6. Quantified Error Estimates

Error was estimated in the simulation procedure using a collection of experimental data gathered on transesterification yields at various timepoints, with various catalyst and alcohol concentrations, and at various temperatures.^[1, 2, 3, 4, 6, 8, 10, 12, 13, 14, 16] Reactions were simulated using identical parameters to those used in experimental studies, and their results compared. Seventy-seven reactions were catalogued and aggregate statistics for simulation accuracy were determined.

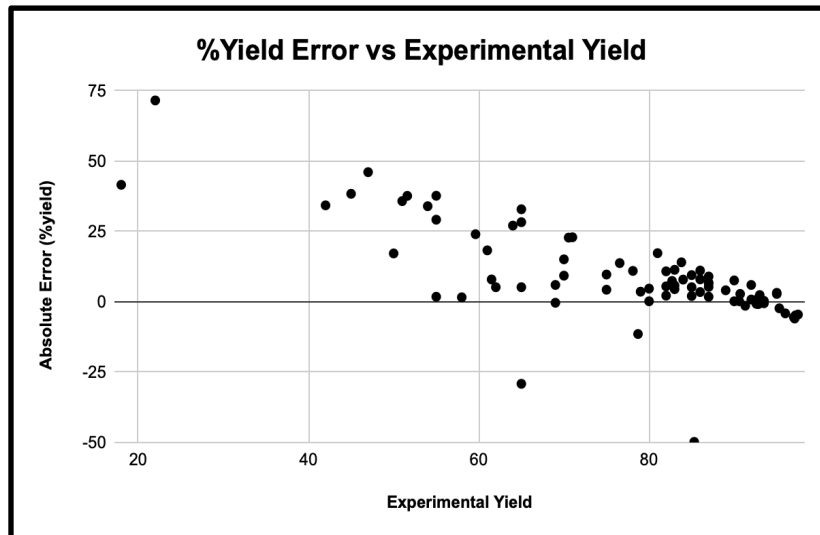


Figure 6.1 | Error in estimated yield vs experimental concentration value

Variability can largely be explained by a combination of experimental error, mass and heat transfer approximations, and the use of suboptimal feedstock by experimental researchers. This includes feedstock high in water and/or free fatty acid molecules. From all experimental reaction values, the **average absolute error was determined to be 9.32%**, and the **standard deviation of error was 14.22%**. However, since the simulation is nearly universally an overestimate, this fact may simply be taken into consideration when drawing conclusions from simulated yield estimates.

7. About the Authors

Henry Dikeman is an incoming senior chemical engineering student at the University of Minnesota. His passion is the development of renewable feedstocks and biochemical processes in the field of energy production.

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Patrick Gibbons-Peterson is an incoming senior chemical engineering student at the University of Minnesota. He is interested in the intersection between chemical engineering and computer science and finds purpose in taking on sustainability oriented engineering projects.

8. References

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