Development of Computational Models for Polymer Scission

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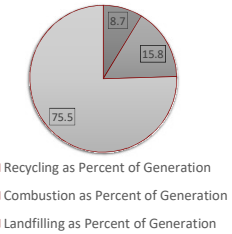
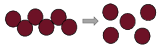
Background

Plastic Waste in 2018[1]



- In 2018, the United States produced 35.68 million tons of plastic waste.[1]
- Plastics pose a significant risk to the environment and a waste management issue due to their durability.[2]
- One method for reducing plastic waste is chemical recycling.
- Chemical recycling involves the breakdown of hydrocarbon polymers into monomers.
- Selective depolymerization utilizes catalysts in order to breakdown the initial plastic.
- Hydrogenolysis is when a molecular bond is cleaved by hydrogen.



- Random scission models for hydrocarbon polymers have been made but neglect the atomistic details of the system. These models also do not account for a moving boundary.
- One issue with modelling polymers is, as the number of carbon in the hydrocarbon chain increases, the number of possible reactions and complexity of the system increases.

Research Question

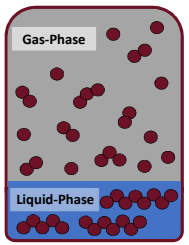
- How, and to what extent, can we realistically model the scission of a polymer through hydrogenolysis in a batch reactor so that it is useful in the design of improved catalysts for polymer scission?

Objectives

- Develop computational models for the scission of hydrocarbons which account for the physics of the system
- Utilize the models alongside experimental data to find reaction rate constants

Research Methods

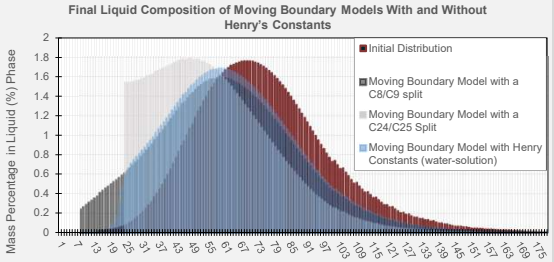
- Four computational models were created in MATLAB.
  - Computational Models with Henry Constants
    - These models assigned Henry constants to each molecule within the system in order to account for the molecules presence in the gas and liquid phase.
  - Computational Models without Henry Constants
    - These models assumed that all hydrocarbons were either completely in the liquid-phase or the gas-phase, which simplified the model equations.
  - Computational Models with a Moving Boundary
    - These models account for the change in volume of the liquid and gas phases due to the scission of liquid-phase hydrocarbons into gas-phase hydrocarbons, which decreases the liquid volume fraction.
  - Computational Models without a Moving Boundary
    - These models assume the volume of the liquid phase does not change, allowing for a simple approximation of the moving boundary model.
- Once the equations for the separate cases were derived, a simple system of decane (C10) splitting into pentane (C5) was modelled.
- Building from the C10 system, the computational models were built utilizing an algorithm to write the rate equations for each reaction.
- Then, each of the models were analyzed for consistency with each other in order to find the extent to which each simplification changed the overall results. In analyzing the effect of Henry constants, two sets of Henry's constants were used. The water-solution set are based on the published Henrys constants for hydrocarbons in water and the estimated set are values with various magnitudes based on the likelihood of the hydrocarbons presence in the liquid and gas phase.

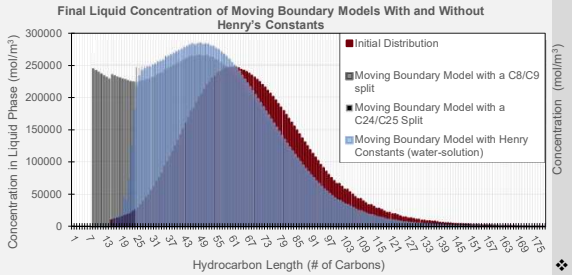


Constant Volume Reactor

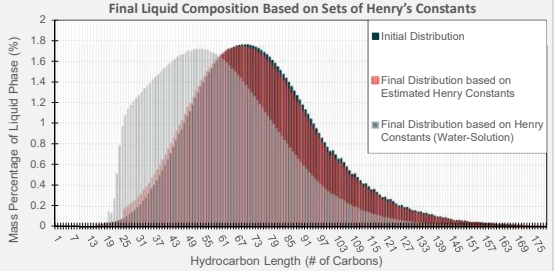
Results of Computational Models

Effect of Henry's Law Constant



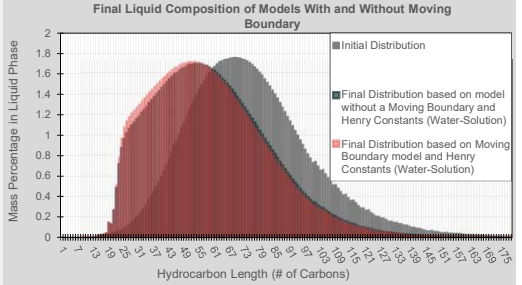


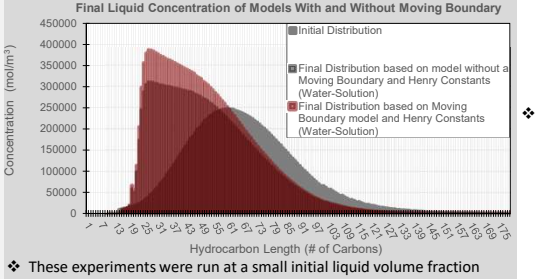
- In these graphs, the results of the moving boundary models with and without Henry constants are shown. The two models without Henry constants both partially agree with the model with Henry constants. The C8/C9 split calculated a similar liquid composition for C25-C179 while the C24/C25 split has a similar drop in liquid concentration of C1-C8 to the model with Henry constants. The moving boundary model with C24/C25 provides a good approximation of the final concentration of the model with Henry's constants for C30 – C179 while the model with a C8/C9 split does not. Therefore, the moving boundary models without Henry's constants can provide limited insight into the concentration and liquid composition into the final product of the model with Henry's constants.



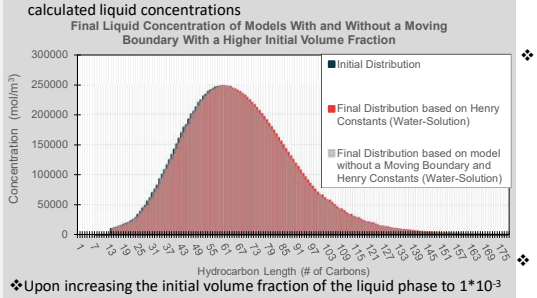
- In these experiments, the moving boundary model was run with different Henry's Law constants. Based on the different final liquid compositions, the results of the model appears to be significantly impacted by the Henry's constants used.

Effect of Moving Boundary





- These experiments were run at a small initial liquid volume fraction ($1*10^{-5}$). The estimation used in the model without a moving boundary does appear to have a small affect on the resulting liquid composition at a lower initial volume fraction while causing a notable change in the calculated liquid concentrations



- Upon increasing the initial volume fraction of the liquid phase to $1*10^{-3}$ in the experiments shown on this graph, the accuracy of the approximation increased. Thus, the increase in initial liquid volume fraction mitigates the difference in the two models, allowing for the model with out a moving boundary better approximate the model with a moving boundary without additional computational expense.

Variables Used in Computational Models

Variable	Value	Variable	Value
Pressure[β]	11.859 bar	Rate Order for Hydrogen	-3
Density of Liquid	700 kg/m³	Temperature[β]	573 Kelvins
Rate Constant	1.25 *10⁶ Pa³/(mol/m³)/s	Initial Liquid Volume Fraction*	1*10⁻⁵
Time Span	23.5 hours	Time Span[β]	24 hours

*Unless otherwise specified β = Values from Argonne National Lab Experimental Data

Effect of Henry Constants and Moving Boundary on the Final Pressure of the System

Model	Final Pressure (bar)
Moving Boundary w/ Henry Constants (water –solution)	42.1
Constant Liquid Volume Fraction w/ Henry Constants (water –solution)	42.2
Moving Boundary w/ Henry Constants (estimated)	1.12*10⁶
Constant Liquid Volume Fraction w/ Henry Constants (estimated)	1.12 *10⁶

- This table depicts the results from computational models with Henry constants when the moving boundary is accounted for and is not accounted for. Based on these values, the estimation of a constant liquid volume fraction does not significantly change the final pressure of the system computed by the model but the Henry constant values used appear to have a significant impact on the final calculated pressure.

Conclusions

- The models without Henry's constants do appear to provide some insight to the system with Henry's constants but does not offer a usable approximation of the liquid phase concentration or composition. Therefore, the use of Henry's constants is preferred for assessing a system but the models without Henry's constants can be used to draw some general conclusions about the system without the extra computational expense necessary for the equations in the model with Henry's constants.
- The Henry's constants have a significant impact on the output of the computational model. Therefore, Henry's constants which account for the intermolecular interactions in the liquid and gas phase are preferable.
- The model that assumes a constant liquid volume fraction appears to approximate the liquid composition and final pressure of the model with a moving boundary. Differences in the calculated concentration between the two models appear at lower initial liquid volume fractions. Therefore, at a high liquid volume fraction, the model without a moving boundary approximates the same values as the moving boundary model with less computational expense.

Acknowledgements

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