

MECHANISMS OF CONSUMPTION OF ALKENES IN SUPERCRITICAL WATER TREATMENT AND PYROLYSIS OF HEXYL BENZENE

Lawrence Lai, Soumya Gudiyella, and William H. Green
Massachusetts Institute of Technology
Cambridge, MA 02139

Abstract

This work studies the chemistry of hexylbenzene treated with supercritical water under conditions of 450°C, 300atm, and <1h residence time through kinetic modeling using Reaction Mechanism Generator (RMG) and experimentation with the underlying motivation of using similar conditions for upgrading of crude oil. Upon comparing the model and experimental product distribution, the model's overprediction of unsaturated species was made manifest, and reasons regarding this overprediction were further investigated in this work. It was found that (I) the hydrogen atoms released during the formation of two ring aromatic compounds may have contributed to the consumption of alkenes, (II) formation of alkyl benzenes through addition between alkenes and smaller aromatics may have decreased yields on unsaturated components, (III) formation of water soluble components in the aqueous phase due to consumption of alkenes is unlikely to have affected the alkene balance.

Keywords

Kinetic Modeling, Alkyl Aromatics, Supercritical Water, Alkenes

Introduction

Supercritical water (SCW) upgrading of crude oil is investigated as a means as an upgrading medium for heavy crude oil due to its unique solvent properties such as its low dielectric constant, high ion product, and high diffusivity (*Caniaz & Erkey, 2014*), as well as its industrial interest (*Choi, 2009*).

This work focuses on the aspects of upgrading chemistry pertaining to unsaturated products through the treatment of hexylbenzene. Through this work, a selectivity of saturated species over unsaturated species was found, contrary to model predictions.

In the past, works in pyrolysis have demonstrated that the cracking of n-hexadecane usually yields more olefins than paraffins (*Rebick, 1981*) (*Wu et al., 1997*), but some works observe higher yields of paraffins than olefins. (*Mushrush & Hazlett, 1984*) (*Gray & McCaffrey, 2002*). The selectivity can be manipulated by its environment, e.g. by varying sulfur content (*Patwardhan et al., 2013*).

In the presence of aromatics (*Carr et al., 2015*) (*Savage et al., 1985*), higher selectivity of paraffins over olefins was observed due to the effects of coking, where compounds of low H:C ratio (*Savage et al., 1985*) are formed, providing a source of the hydrogen atoms needed to form saturates (*Ancheyta, 2011*). However, the details of the chemistry remain somewhat speculative. This present work discusses the possible reasons for the selectivity of alkanes over alkenes when alkylbenzenes are treated with supercritical water, and compares experimental data with the predictions of the Reaction Mechanism Generator (*Green et al. 2015*).

Methods

The details of the methods associated with this work have been published (*Carr et al., 2015*). In short, the organic reactant of interest was spiked with 10 mol% naphthalene as an internal standard, and placed in a 316L stainless steel reactor. This reactor was purged and initially pressurized by 330 psig of helium. This pressure increased to 300bar (75bar in absence of water) when heated to 450°C by a sand bath. Pressure was monitored throughout the residence time of interest. Upon cooling, contents of the reactor were analyzed by GC-MS, GCxGC-FID, GC-FID, and NMR. Kinetic modeling was performed parallel to experiments by the Reaction Mechanism Generator (RMG), where a kinetic model was generated using a flux based algorithm based on thermodynamic and kinetic parameters obtained from the literature and in-house quantum calculations (*Green et al., 2015*).

Results

While the kinetic model fairly accurately predicts the hexylbenzene conversion and the yields of species with saturated alkane chains, it systematically overpredicts alkenes and styrene, as shown in Figure 1.

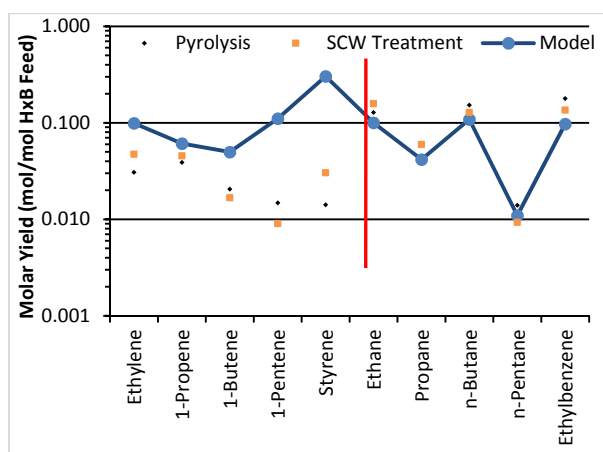


Figure 1. Hexylbenzene treatment at 40 minutes shows overprediction of alkenes by kinetic model. All data points to the left side of the red dividing line are for unsaturated species, and are all over predicted.

As a result of this systematic overprediction, the following hypotheses were tested to explain the discrepancy in the yield of unsaturated compounds unforeseen by the kinetic model. They are as follows:

1. Formation of aromatic compounds containing two or more rings supplies hydrogen atoms to convert alkene chains in alkane chains.
2. Alkenes react with other aromatic compounds, yielding longer chain alkyl benzenes.
3. Alkenes react with water to form water soluble organics.

The formation of multi ring aromatic compounds were observed in experiments, but not predicted by the model. Compounds produced were 1 and 2-methylnaphthalene, 1 and 2-ethylnaphthalene, biphenyl, biphenylmethane, 4-phenyltoluene, bibenzyl, and 1,3-biphenylpropene. By comparing hexylbenzene's H/C ratio of 1.5 to these components with H/C ratio between 0.8 – 1, the production of these components is a plausible source of hydrogen atoms which may potentially saturate double bonds in the reaction environment.

Heptylbenzene was observed as part of the reaction products, indicating the possibility of addition between alkenes and aromatics and/or alkanes and styrene to form longer chain alkyl benzenes, another plausible sink accounting for the missing unsaturated components.

Parallel to the above, the possibility of formation of alcohols through the reaction between alkenes and water was investigated. While measurable amounts of alcohols were found in SCW water experiments, the quantity is much too small to account for the large amount of 'missing' alkenes, and of course this cannot explain the discrepancies related to pyrolysis experiments, where there was no water. Thus, this hypothesis was disproved.

Conclusions

The SCW treatment and pyrolysis of hexylbenzene produces many short chain alkyl benzenes, paraffins and olefins. By observing this product distribution, it can be found that unsaturated species are systematically overpredicted by the kinetic model generated by RMG. Three possible aspects of chemistry were observed through experiments and were absent in the mechanism were (I) the formation of two ring aromatics, (II) formation of longer chain alkyl benzenes, and (III) formation of water soluble products. Out of the three hypothesis, the combination of the first two were shown to be as the most likely cause for the overprediction of unsaturated species by the kinetic mechanism, while the third was shown to be insufficient to explain the observations.

Acknowledgments

Our group would like to acknowledge Saudi Aramco, a founding member of the MIT Energy Initiative, as well as being the sponsor behind this work. We gratefully acknowledge helpful interactions with the Saudi Aramco Supercritical Water technical team.

References

- Ancheyta, J. (2011). Modeling and Simulation of Catalytic Reactors for Petroleum Refining. Wiley. Hoboken, NJ.
- Caniaz, R., Erkey, C. (2014). Process intensification for heavy oil upgrading using supercritical water. *Chemical Engineering Research and Design*. Izmit, Turkey.
- Carr et al. (2015). Supercritical Water Treatment of Crude Oil and Hexylbenzene: An Experimental and Mechanistic Study on Alkylbenzene Decomposition. *Energy and Fuels*. Billerica, MA.
- Choi, K. (2009). Process to upgrade whole crude oil by hot pressurized water and recovery fluid. *US7,740,065*. Saudi Arabia.
- Gray, M., McCaffrey, W. (2002). Role of Chain Reactions and Olefin Formation in Cracking, Hydroconversion, and Coking of Petroleum and Bitumen Fractions. *Energy & Fuels*. Edmonton, Canada.
- Green et al. (2015). Reaction Mechanism Generator (RMG). <http://rmg.mit.edu/>
- Mushrush, G., and Hazlett, R. (1984). Pyrolysis of Organic Compounds Containing Long Unbranched Alkyl Groups. *Ind. Eng. Chem. Fundam.* Washington, D.C.
- Patwardhan et al. (2013). Supercritical Water Desulfurization of Organic Sulfides is Consistent with Free-Radical Kinetics. *Energy & Fuels*. Cambridge, MA.
- Rebick, C. (1981). H₂S Catalysis of n-Hexadecane Pyrolysis. *Ind. Eng. Chem. Fundam.* Linden, NJ.
- Savage, P., Klein, M., and Kukes S. (1985). Petroleum Asphaltene Thermal Reaction Pathways. *Preprints-American Chemical Society. Division of Petroleum Chemistry*. Newark, DE.
- Wu et al. (1997). Radiation Effect on the Thermal Cracking of n-Hexadecane. 1. Products from Radiation-Thermal Cracking. *IND. Eng. Chem. Res.* Tokyo, Japan.