U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

Kinetic Modeling of Lignin Flash Pyrolysis

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Background and Introduction

The conversion of biomass (cellulose, hemicellulose, and lignin) into transportation fuels by pyrolysis, gasification, and liquefaction processes involves pyrolysis as either the single or a component cause of fragmentation. The work to be performed herein focuses on the flash pyrolysis of lignin and on addressing the problems associated with lignin conversion.

The pyrolysis of biomass generates three different energy products in varying quantities: coke, light gases, and oils. Flash pyrolysis gives high oil yields, but the oil produced is generally of poor quality. Such bio-oils are problematic in that they:

- are reactive, acidic, and viscous (rendering them unsuitable for transportation to a refinery via pipeline)
- require substantial additional processing to make them suitable for introduction into a refinery.

These limitations speak to the need to improve the pyrolysis process towards a higher quality bio-oil. To this end, a number of problems associated with lignin pyrolysis have been identified and will be addressed in order to improve the quality of bio-oil produced from biomass conversion.

➢ Problems:
- Little information exists regarding reactions that occur during rapid pyrolysis or during the subsequent condensation process
- Reactive products and radical formation leads to cross-linking – char formation
- Lignin pyrolyzes at higher temperature and over a broader range of temperatures

➢ Solutions:
- Elucidate pyrolysis reaction mechanisms via complementary quantum mechanic calculations and experiments
- Discover mechanisms for depolymerizing lignin to form stable products
- Disassemble lignin at lower temperatures
- Design catalysts that lower reaction barriers

To date, models used to describe the pyrolysis of lignin have been overly simplistic and have been based almost entirely on bond homolysis type reactions (Figure 1). However, recent theoretical work performed at NREL suggests that concerted reactions (Figure 2) leading to stable closed shell species may play a role in the fragmentation of lignin. This is expressed in Figure 3 as a plot of estimated kinetic rate constants versus temperature.

Figure 1. Bond homolysis reactions. A) C-O homolysis; B) C-C homolysis

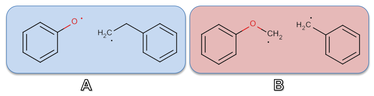
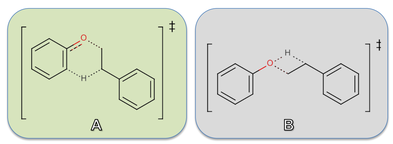


Figure 2. Concerted Reactions. A) retro-ene; B) Maccoll



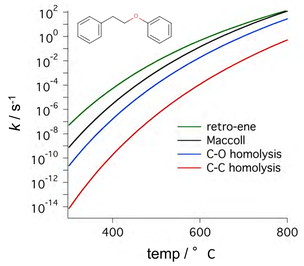


Figure 3. CBS-QB3 calculated rate constants show concerted reactions are 100 to 1,000 times faster than bond homolysis for PPE.

Approach

➢ The objectives of this project are:
1) develop a molecular-level understanding of the kinetics of biomass pyrolysis, with an emphasis on the gas-phase kinetics of lignin
2) ascertain the correlation between the theoretical understanding gained from 1) and experimental flash pyrolysis data obtained experimentally.

➢ Theoretical methods will be used to:
- investigate of the thermochemistry of lignin linkage units
- develop kinetic models that can accurately predict the lignin product slate
- design catalysts that can lower reaction barriers that lead to more desirable products

Lignin is a large biopolymer with a heterogeneous composition and no defined primary structure. As a result of lignin's inherent complexity and size, model compounds (linkage units) will be studied.

➢ Model Compound: 2-phenylethyl phenyl ether (PPE), Figure 4A.
- β-ether linkage (50% of inter-unit linkages)
- Simple structure can be studied with reasonable time and resource constraints.
- Readily modified to study realistic substituent effects, Figure 4B

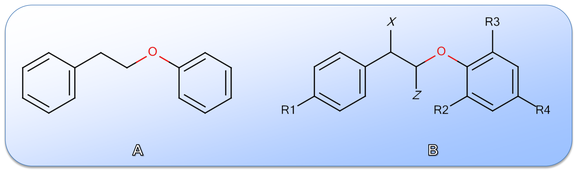


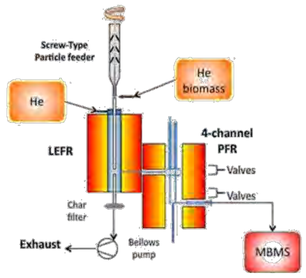
Figure 4. A) PPE; B) Possible PPE functionalization schemes. X = H or OH; Z = H or CH_2OH ; $R_1 = R_2 = R_3 = R4$ = H, OH, or OCH3.

➢ Quantum Mechanical (QM) methods:
- Geometry optimization and electronic energy calculations
- Transition state identification and optimization
- QM estimation of reaction rate constants
- Kinetic modeling of lignin linkage unit pyrolysis

Experimental methods will be used to measure the kinetics and product slate of the pyrolysis of the lignin linkage units studied theoretically. Two reaction schemes are proposed for the pyrolysis of lignin linkage units:

1) laminar entrained flow reactor (LEFR), Figure 5
   - reaction kinetic studies
2) hyper-thermal nozzle, Figure 6
   - mechanism studies

Figure 5. Laminar entrained flow reactor (LEFR)



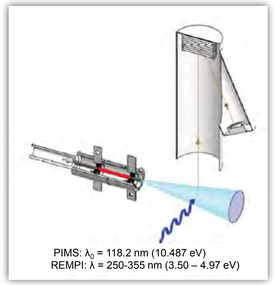


Figure 6. Hyper-thermal nozzle reactor

Impact

The results of this project will lead to a better understanding of the thermochemical decomposition routes of lignin in biomass. Such a detailed understanding can facilitate the development of targeted catalysts that can lower pyrolysis temperatures, improve product slates, and generate an overall better bio-oil product. A sensitivity study detailed in Technical Report (NREL/TP-6A20-46589, 2010) indicates that even slight improvements in the quality of the bio-oil used in fuel production can reduce the cost of the fuel product significantly. By improving the quality of bio-oil produced from the pyrolysis of biomass, the work described herein has the potential to reduce the cost of transportation fuels derived from biomass.

Acknowledgments

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Understanding the significance of concerted reactions in lignin pyrolysis.