Measuring and Predicting Reaction Kinetics for Clean Use of Biofuels

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Fuels from renewable biomass already make up part of our energy picture, and this must increase.

- Renewable resources are inherently sustainable.
- To make them truly sustainable, we must develop efficient collection, conversion, and usage technologies.
- Producing liquid fuels is especially desirable because of their high energy density, necessary for aircraft and highway vehicles.
- The public has begun to recognize that using food resources to make biofuels is at best a transitional strategy, so...
- Lignocellulosic resources from crops and waste streams are presently the top candidates.
- Relative to petroleum-based fuels, they are thought to generate increased aldehyde and NOx pollutants due to their high content of oxygen and sometimes nitrogen.
- We are working to explore, explain, and help solve these challenges.

We are working on two major aspects.

- Obtaining flame kinetics of biofuel model compounds:
  - Measurements with flame-sampling molecular-beam mass spectrometry (MBMS)
  - Predicting kinetics using theory, computational quantum chemistry.
  - Obtaining pyrolysis products and kinetics for thermal generation of biofuels from cellulose.
  - Pyroprobe flash pyrolysis and GC/MS analysis.
  - Predicting kinetics for thermal generation of biofuels from cellulose using our new Reactive Molecular Dynamics methods.

Morpholine is a useful “model compound.” We proposed a mechanism...

MBMS gives minor-species and free radical concentrations, making it a powerful test of models and aid to data interpretation.

(3) Reactive Molecular Dynamics will give kinetics at an elementary-reaction level.
- The Reactive Molecular Dynamics algorithms and RMDFF force field were developed for my group's polymer-pyrolysis research.
- In classical molecular dynamics, thermal motions are modeled at an atomistic level using classical physics (FFrona) and harmonic force fields.
- In RxMD, algorithms are implemented and force fields are modified to capture bond-breaking and -making.
- This new molecular-simulation method promises to yield powerful, quantitative insights into reactions that convert biomass into fuels, as it has for polymer decomposition.

We are now starting to model cellulose kinetics with our new code.

1. We use molecular-beam mass spectrometry in Amherst and at Lawrence Berkeley National Lab to analyze biofuel flame chemistry.
2. We are using quantum chemistry to compute thermo, predicted flame structure and analyzed the model's reaction fluxes...
3. ...and obtained the data, finding many of these initial predictions to be in very good agreement. Now analyzing/modeling minor species.
4. Milligram-scale flash pyrolysis and TGA/DSC provide key kinetics data.

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