Fundamental Kinetics of Supercritical Coal Liquefaction:
Effect of Catalysts and Hydrogen-Donor Solvents

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Abstract:
The overall objective of this research project is to investigate experimentally and theoretically the chemical kinetics of thermolytic reactions with the ultimate goal of improving coal liquefaction conversion. The theoretical work involves distribution-kinetics concepts to develop chemical reaction models for macromolecular conversion into individual components. Experiments with polymeric model compounds provide a well-characterized simulation of thermolytic chemical-bond scissions under various conditions, including in presence of catalysts, hydrogen donors, and peroxides. In addition to coal processing, the work has significance for plastics recycling.

Model macromolecular compounds provide a means to study reaction kinetics of complex materials undergoing molecular cracking for fuel and feedstock processing. Molecular-weight distributions (MWDs) and their moments are measured by HPLC gel permeation chromatography (GPC). The experimental data are interpreted with a population-balance equation based on continuous-distribution kinetics, and rate coefficients are determined for chain-end and random degradation processes. Accompanied by this mathematical analysis, the studies have revealed essential features of macromolecular chain scission kinetics.

Over the past year we constructed and tested a new reactor that allows thermolysis of macromolecular solids at high temperatures in a molten-salt bath. Polyethylene pyrolysis experiments provided gas-, liquid-, and solid-phase products that were analyzed with GC and HPLC-GPC. For polyethylene melt stirred by bubbles of flowing nitrogen gas at atmospheric pressure, the novel reactor permits uniform-temperature depolymerization. Sweep-gas experiments at temperatures 370-410 °C allowed pyrolysis products to be collected separately as reactor residue (solidified polyethylene melt), condensed vapor, and uncondensed gas products. Molecular-weight distributions (MWDs) determined by HPLC-GPC indicated that random scission and repolymerization (cross-linking) broadened the polymer-melt MWD. Observing the repolymerization reaction is difficult if the condensate and melt are not recovered separately as in the described experiments. The C_1 - C_5 uncondensed gas products were formed by chain-end scission, according to the continuous-distribution theory proposed to interpret the experimental data. The mathematical model accounts for the mass transfer of vaporized products from the polymer melt to gas bubbles. The driving force for mass transfer is the interphase difference of MWDs based on equilibrium at the vapor-liquid interface. The chain-end scission activation energy and preexponential were determined to be 35 kcal/mol and $1.14\times10^{8} s^{-1}$, respectively.

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