# Development of reactor and analytical systems for the improved study of polyolefin hydroprocessing

by
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## Abstract

Polyolefin hydroprocessing is an emerging field that uses catalytic chemistry to deconstruct the recalcitrant C-C bonds of plastics, generating processable, valuable alkane products. Although advances have been made in catalyst design and reactor engineering, there remains little standardization across the field, and common practices in quantitation and the use of batch reactors restrict or even mislead experimentalists. Here, we evaluate and improve upon existing polyolefin hydroprocessing technologies and techniques to enable improved study of the associated catalysis.

First, we identify how typical workup procedures using small-scale batch reactors can systematically skew measured selectivities and impede carbon balances. For acidic hydrocracking, this is a result of the prevalence of isomeric, highly-volatile alkane liquids, which are difficult to capture by conventional methods, leading to an overestimation of readily captured light gas and liquid products. We propose and trial several alternative capture methods for improving the carbon balance, and find that flow-through vapor capture and solvent solubilization of isomers are the two most effective approaches. Furthermore, the optimal workup method depends on the concentration of isomer intermediates, which is sensitive to the reaction condition. We provide quantitative guidelines for selecting an appropriate workup method, as well as detailed methods of how calibration, quantitation, and product capture were performed to make our methods accessible to all investigators.

Second, inspired by the success of flow-through capture, we synthesize existing literature design elements into a new reactor system for flow chemistry in polyolefin hydroprocessing. This reactor employs reactive separation for the continual removal and online quantification of volatile products at the hydrocracking process condition. We use this reactor in a semi-continuous manner to measure the vapor production rate and product selectivity for acidic hydrocracking at a pseudo-steady state condition. A simple mathematical model of the process is developed which indicates the extraction rate is closely linked to the underlying polymer cracking rate, in agreement with the experimental response of the extraction rate to changes in process conditions.
We show how this semi-continuous reactor can extend the scope of experiments for polyolefin hydroprocessing by demonstrating it utility for catalyst screening, investigating transient phenomena, and comparing polymer substrates of high and low molecular weights. The reactor design is further extended to accommodate continuous processing by means of a polymer melt inlet, which we demonstrate. Construction and operation of the reactor are outlined in detail such that the design may be readily implemented in other laboratories.

Third, we propose a design for high molecular weight polyolefin hydroprocessing in a plug-flow configuration. We briefly assess the practicality of such a reactor, in terms of residence time, pressure losses, and achievable conversion, for acid hydrocracking and hydrogenolysis using packed bed and static catalytic mixer catalysts, respectively. As the static catalytic mixer route appeared most promising, we further develop this concept into the detailed design of an associated reactor system.

The contents of this thesis provide strategies for improving the quality of existing polyolefin hydroprocessing experiments and enable new routes for investigation. We hope that the use of these methods and reactors can help to standardize the field of and lead to better, more quantitative discoveries for tackling the plastics crisis.

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