TITLE Coal/Polymer Coprocessing with Efficient Use of Hydrogen

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ABSTRACT

OBJECTIVE: Inadequacies of current recovery and disposal methods for mixed plastic wastes drive the exploration of viable strategies for plastics resource recovery. The combination of diminishing landfill space and increasing usage of plastic products poses a significant dilemma, since current recovery methods are costly and ill-suited to handle contaminants. Coprocessing of polymeric waste with other materials may provide potential solutions to the deficiencies of current resource recovery methods, including unfavorable process economics. By incorporating plastic waste as a minor feed into an existing process, variations in supply and composition could be mediated, permitting continuous operation. One attractive option is the coprocessing of polymeric waste with coal under direct liquefaction conditions, allowing for simultaneous conversion of both feedstocks into high-valued products.

A series of model compound experiments has been conducted, providing a starting point for unraveling the complex chemistry underlying coliquefaction of coal and polymeric materials. Tetradecane ($C_{14}H_{30}$) was used as a polyethylene mimic, and 4-(naphthylmethyl)bibenzyl (NBBM) was used as a coal model compound. Neat and binary mixture reactions of tetradecane and NBBM were carried out in an inert atmosphere at both low and high pressures to establish a thermal baseline for subsequent catalytic experiments. Preliminary experiments with real feedstocks allowed the extrinsic factors (i.e., diffusion limitations, solvent effects) to be identified. The combination of these two sets of experiments will ultimately be used to carry out process optimization and formulate strategies for catalyst development.

RESULTS TO DATE: Experiments in the last year in which the relative concentrations of NBBM and tetradecane were varied revealed that the effect reported previously was indeed a chemical one and not simply a result of dilution. The initial loading of each reactant and overall loading were found to affect both the conversion of tetradecane and the overall product distribution during coprocessing. As the NBBM to tetradecane ratio was raised, only a slight difference in reactant conversions was observed, but a significant change in the selectivity towards primary products from NBBM occurred. The higher proportion of NBBM resulted in an increase of self-interactions, which resulted in a larger quantity of retrograde condensation products. Increasing the initial charge of both reactants resulted in a significant enhancement of tetradecane reactivity. The primary product yields from the coal model compound showed a slight decrease when compared to the reactions conducted with the same reactant ratio but lower total loading. However, the values were higher than those observed for the reactions carried out with a larger ratio of NBBM to tetradecane.

Work in the past year has also focused on analysis of light gaseous products for neat reactions of tetradecane, resulting in mass balances greater than 94%. Gas analysis revealed that α-olefins and paraffins with carbon numbers from 1 to 5 were major products of tetradecane pyrolysis at all concentrations studied. The highest molar product selectivities at all initial concentrations were observed for propylene and ethane, which had approximately equal values. These remained relatively constant throughout the range of reaction times studied and were independent of the initial reactant loading, with an average value of approximately 0.38. Paraffins in the C_2-C_5 range were all formed with lower selectivities than their corresponding alkene. Propane, butane, and pentane all showed increases in selectivity with

increasing concentration. Methane displayed the opposite trend, decreasing with increasing reactant loadings. The trends for the paraffins as a function of carbon number were similar to those observed for α-olefins, i.e., a decrease in yield with increasing carbon number. However, the reduction in yield as carbon number increased was much more marked for the paraffins than for α-olefins. These trends were even more evident when alkanes and alkenes in the range of carbon numbers from 7 to 12 were examined.

An experimental protocol was developed to conduct experiments at elevated pressures more representative of coal liquefaction conditions and both neat and binary mixture reactions of tetradecane and NBBM were examined. Initial high pressure reactions revealed that the stainless steel reactors possibly exhibited some catalytic behavior. In order to prevent these interactions, glass sleeves were constructed and were used in all subsequent reactions. Reactant conversions and product distributions are reproducible and consistent with pyrolyses performed at low pressure in the glass ampoules, and thus it is believed that catalytic behavior has been minimized. Comparison of tetradecane conversion as a function of reactant concentration and total reaction pressure is shown in Figure 1. The conversion is relatively insensitive to the reaction conditions for low reaction times, but the conversion for the reactions at high pressure diminished at longer times. The high pressure experiments yielded products similar to the low pressure neat pyrolysis reactions, with α-olefins and n-alkanes as the primary products. However, the observed selectivities for products from the two different pressure regimes were different, particularly for the n-alkanes and light hydrocarbons. In addition, methane was not observed during the high pressure reactions.

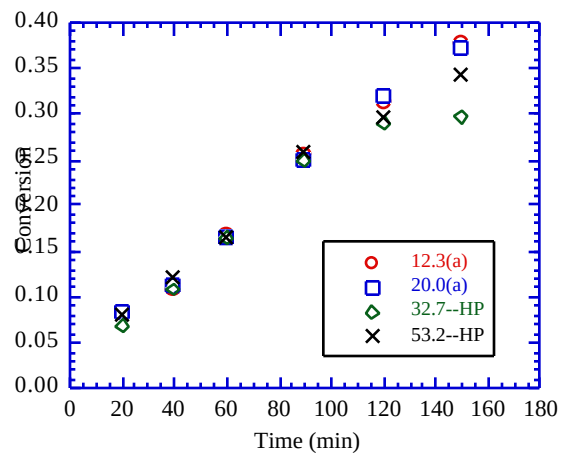

Figure 1: Comparison of tetradecane conversion as a function of reactant concentration and reaction pressure.

Three sets of pyrolysis experiments, using loadings of 12.3, 20.0, and 27.8 mg respectively, were performed in 2 ml glass ampoules with high density polyethylene (HDPE) at 420°C for 30-180 minutes. The primary products observed during HDPE pyrolysis were linear hydrocarbons, consisting of α-olefins, n-alkanes, and internal olefins, which is consistent with results from the literature. These products are similar to those found during tetradecane pyrolysis, indicating that both feedstocks decompose by the same basic mechanisms. The α-olefins were initially found in the highest yield for all reaction sets, and increased with higher conversions. Initially, the overall yields of α-olefins for carbon numbers C_8-C_{24} were very similar. At longer reaction times, however, there was an increased selectivity towards products of smaller carbon numbers. These trends are shown in Figure 2.

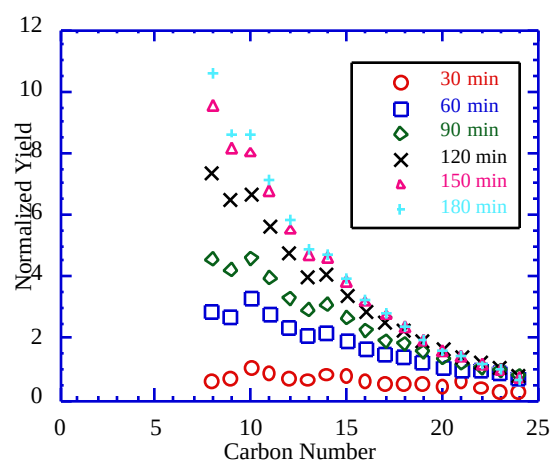

Figure 2: Comparison of normalized yields of α-olefins as a function of time and carbon number for HDPE pyrolysis.

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MANUSCRIPTS

De Witt, M.J. , Dooling, D.J. and Broadbelt, L.J., "Decomposition of Polyethylene Model Compounds: Modeling of Tetradecane Pyrolysis", in preparation, **1998**.

De Witt, M.J. and Broadbelt, L.J., "Coprocessing of Polymeric Waste with Coal: Reaction of Polyethylene and Coal Model Compounds", in preparation, **1998**.

De Witt, M.J. and Broadbelt, L.J., "Coprocessing of Polymeric Waste with Coal: Reaction of Polyethylene and Coal Model Compounds", Preprints of the American Chemical Society, Division of Fuel Chemistry, San Francisco, CA, April **1997**.

PRESENTATIONS

De Witt, M.J. , Dooling, D.J. and Broadbelt, L.J., "Coprocessing of Polymeric Waste with Coal: Reaction of Polyethylene and Coal Model Compounds", submitted to the Annual Meeting of the American Institute of Chemical Engineers, Miami Beach, FL, November **1998**.

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STUDENT SUPPORT

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