

**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.

RESULTS TO DATE: To probe the complex chemistry underlying coprocessing of coal and polymeric waste, experiments using the model compounds 4-(1-naphthylmethyl)bibenzyl (NBBM) and tetradecane, respectively, were carried out. Reactions were performed at 420°C and at both atmospheric pressure and 1000 psig (cold) to mimic coal liquefaction conditions. The reactant concentration was varied for the neat reactions, and a range of relative concentrations was used for binary mixture reactions. The reactions conducted at low and high pressure showed similar trends for both neat and binary mixture reactions. The selectivity to primary products of NBBM was enhanced in the presence of tetradecane, and the conversion of tetradecane was also increased. Although the majority of the results can be rationalized in terms of coupled free radical reactions, a significant contribution to the enhancements observed is due to phase behavior, i.e., partitioning of the tetradecane, tetradecane-derived radicals and low molecular weight NBBM-derived radicals into the vapor phase. Experiments were therefore carried out with NBBM and high density polyethylene to probe the effect of the phase behavior on the enhancements observed.

High density polyethylene was reacted neat and in the presence of NBBM at low pressure and employing 20 mg of each reactant at 420°C for 30-180 minutes. The results were compared to neat experiments of both high density polyethylene and NBBM carried out at various reactant loadings. Synergistic interactions were observed in this binary system as well, and significant changes in the product selectivities of NBBM-derived products resulted. In particular, an enhancement in the selectivities of primary products was observed at higher reactant conversions, while yields of secondary and tertiary products were significantly reduced over the full range of reaction times studied. The selectivity to toluene, one of the primary products of NBBM, is shown for various reaction sets as a function of reactant conversion in Figure 1. The trends shown for toluene are similar to those observed for 1-methyl-4-(1-naphthylmethyl) benzene, the complimentary product formed from fission of the bibenzyl linkage in NBBM, followed by subsequent hydrogen abstraction. It can be seen that the selectivity to toluene during binary reactions with HDPE was initially significantly lower than that observed during neat reactions and was only enhanced compared to neat reactions for reactant conversions greater than about 40%.

This behavior is opposite to that observed during binary reactions with tetradecane, where the selectivity of primary products was enhanced over the entire range of conversions studied.

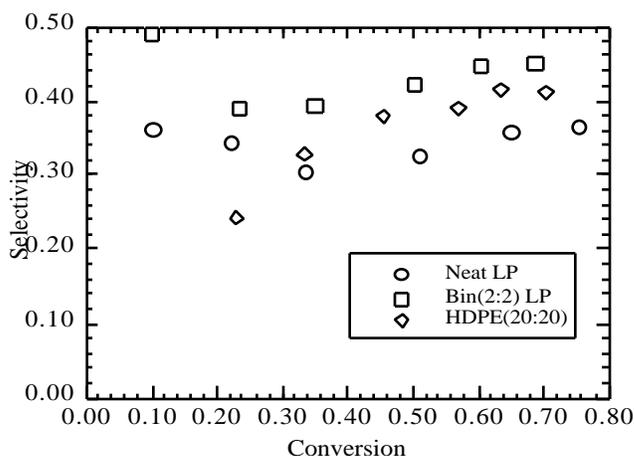


Figure 1. Comparison of toluene selectivities during neat pyrolysis of NBBM and binary mixture reactions with tetradecane and HDPE.

As a complement to the experimental work, detailed kinetic modeling was used to provide insight into the fundamental underlying chemistry. Using tools for automated model construction, a detailed kinetic model of tetradecane pyrolysis was formulated. Rate constants included in the model were specified using a hierarchy of techniques, including calculation of equilibrium constants to ensure that thermodynamic consistency was maintained for

reverse reaction pairs. The threshold for rate-based building was systematically varied until the major products observed experimentally were included as species in the model

built and the model was capable of capturing the secondary decomposition of olefins observed at longer reaction times. Model tuning was performed to capture the experimental data at one set of experimental conditions by adjusting the frequency factors for only four reaction families. A parity plot of experimental yields and model yields for this reaction set is shown in Figure 2a, demonstrating that the model was able to capture minor product yields and reactant conversion alike. The model also had predictive capability. As shown in Figure 2b, the model was able to capture the yield of propylene as a function of different reactant loadings over all reactant conversions studied without any further adjustment to the parameters of the model.

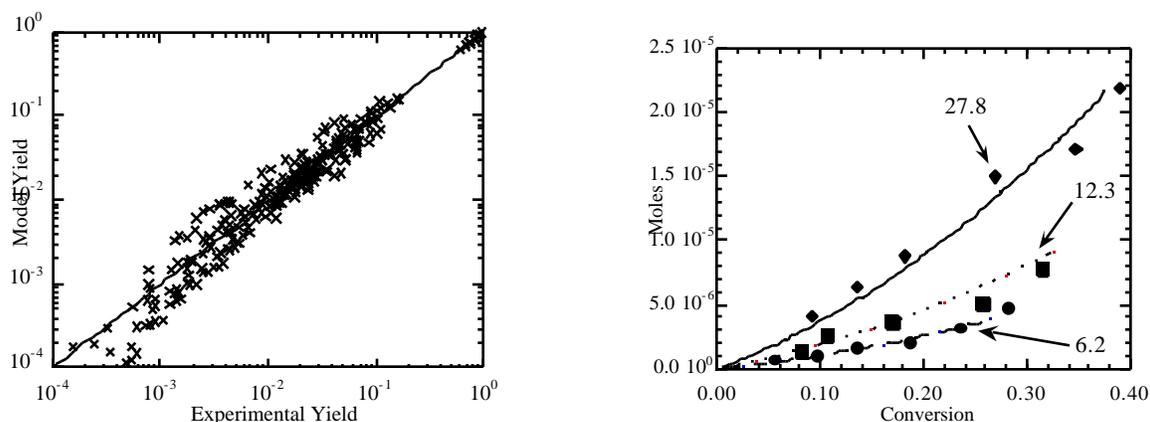


Figure 2. (a) Comparison of fitted model yields and experimentally observed yields for major and minor products of tetradecane pyrolysis. (b) Comparison of experimental (symbols) and predicted (lines) conversions of tetradecane for initial tetradecane loadings of 6.2 and 27.8 mg.