

TITLE Coal/Polymer Coprocessing with Efficient Use of Hydrogen

AUTHORS Linda J. Broadbelt* and Matthew J. De Witt
email: broadbelt@nwu.edu
phone: 847/491-5351
fax: 847/491-3728
Northwestern University
2145 Sheridan Road
Department of Chemical Engineering
Evanston, IL 60208

ABSTRACT

OBJECTIVE: Environmental and economical concerns over diminishing landfill space and the growing abundance of mixed plastic waste mandate development of viable strategies for recovering high-valued resources from waste polymers. Coprocessing of waste polymer mixtures with coal allows for the simultaneous conversion of coal and plastics into high-valued fuels. However, there is limited information about the underlying reaction pathways, kinetics, and mechanisms controlling coal liquefaction in the presence of polymeric materials.

A series of model compound experiments has been conducted, providing a starting point for unraveling the complex, underlying chemistry. Thermolysis studies of model compounds of polyethylene and coal were conducted in batch reactors. Tetradecane ($C_{14}H_{30}$) was used as a polyethylene mimic, and 4-(naphthylmethyl)bibenzyl (NBBM) was used as a coal model compound. Reaction temperatures were 420 and 500°C, and batch reaction times ranged from 5-150 minutes. Detailed product analysis using gas chromatography and mass spectrometry enabled the reactant conversion and product selectivities to be determined. Reaction of single components and binary mixtures allowed the kinetic coupling between feedstocks to be examined.

RESULTS TO DATE: The major products observed from the pyrolysis of tetradecane were α -olefins, with minor selectivity to n-alkanes. The highest selectivity, 0.13, was obtained for 1-heptene, and α -olefins with carbon numbers of 6 to 11 were also observed in significant quantities. The product distribution was rationalized in terms of typical free radical Rice-Herzfeld and Rice-Kossiakoff mechanisms [1-2]. The mechanism is initiated by carbon-carbon bond fission to form two primary radicals. These primary radicals form secondary radicals through hydrogen abstraction from a secondary carbon or through an intramolecular hydrogen rearrangement. These secondary radicals then undergo β -scission to form α -olefins and primary radicals. Termination occurs by recombination or disproportionation of radicals.

Two of the major products formed during pyrolysis of NBBM, which are afforded by carbon-carbon bond fission and subsequent hydrogen abstraction, were toluene and 1-methyl-4-(naphthylmethyl) benzene, each observed with a selectivity greater than 0.28 at all reaction times studied. The other major product was 1-(2-phenylethenyl)-4-(naphthylmethyl) benzene, with an initial selectivity of approximately 0.35 which decreased linearly with reaction time to 0.11 at 150 minutes. Minor selectivities were observed for a number of products from NBBM pyrolysis, including methyl bibenzyl and phenyl methyl naphthalene.

Mechanistic interpretation using the ideas put forth by Walter et al. [3] successfully accounted for the majority of the products observed in significant yield. The formation of high yields of toluene and 1-methyl-4-(naphthylmethyl) benzene was consistent with a mechanism involving fission of the weak bibenzyl bond and subsequent hydrogen abstraction. The quantitative yield of phenyl methyl naphthalene was consistent with a free radical ipso-substitution scheme also put forth by Walter et al. [3]. Attack by a benzyl radical of the NBBM molecule at the 1-naphthyl position with subsequent β -scission of the NBBM

backbone affords phenyl methyl naphthalene. In order to account for the formation of 1-(2-phenylethenyl)-4-(naphthylmethyl) benzene, an additional set of reaction steps was put forth in this work involving hydrogen abstraction from the carbon atoms of the bibenzyl bond of NBBM followed by β -scission of a carbon-hydrogen bond. Overall, the main reaction families for NBBM pyrolysis of bond thermolysis, hydrogen abstraction, radical ipso-substitution, β -scission, and radical recombination accounted for all major products observed.

Reactions of binary mixtures of tetradecane and NBBM revealed interactions between the reactants and synergistic effects. Tetradecane conversion was increased in the presence of NBBM, which was rationalized in terms of kinetic coupling. The internal carbon-carbon bonds of tetradecane have a higher bond dissociation energy (90 kcal mol^{-1}) than that of the bibenzyl bond in NBBM (60 kcal mol^{-1}) [4]. This has the potential to increase the quantity of radicals in the system with respect to the neat tetradecane experiments at a particular reaction time. The NBBM-derived radicals can easily abstract hydrogen from the secondary carbons of tetradecane, forming a tetradecane-derived radical and converting a tetradecane molecule, enhancing its conversion. Once formed, these tetradecane-derived radicals undergo their own decomposition reactions as observed for neat pyrolysis, and similar product yields and selectivities were observed.

The interactions between NBBM and tetradecane were further interpreted by examining the products derived from NBBM. Since abstraction of hydrogen from tetradecane is facile and has a high reaction path degeneracy of 24, NBBM radicals are capped and stabilized through this abstraction step before undergoing secondary reactions. This effect on the overall product yields can be discerned from Figure 1a. The radicals formed from bibenzyl bond thermolysis abstract hydrogen with higher selectivity and afford higher yields of toluene and 1-methyl-4-(naphthylmethyl) benzene. Correspondingly, the selectivity to the radical ipso-substitution pathway and formation of phenyl methyl naphthalene are diminished with the addition of tetradecane as shown in Figure 1b. Therefore, it can be seen that during low pressure pyrolysis, favorable interactions between the two reactants exist. The effective tetradecane conversion was increased, and primary product selectivities were enhanced.

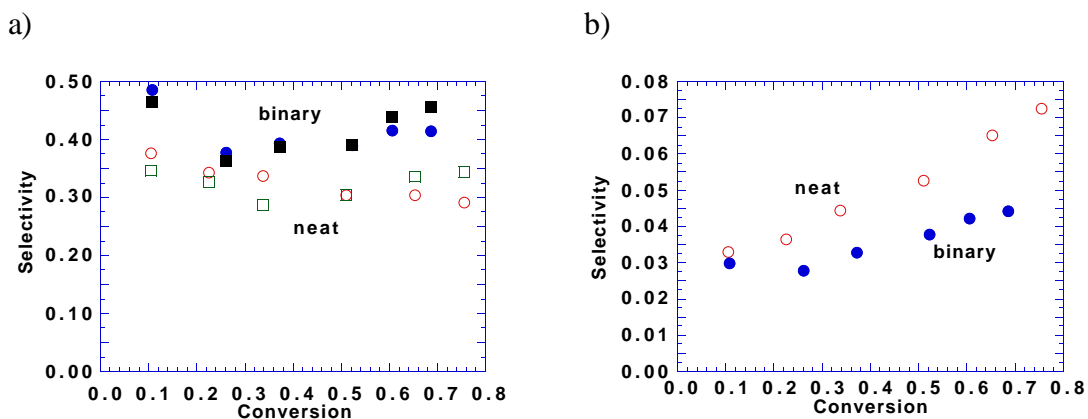


Figure 1. Presence of tetradecane a) increases the selectivity to the primary products, toluene (squares) and 1-methyl-4-(naphthylmethyl) benzene (circles), and b) decreases the selectivity to the addition product, phenyl methyl naphthalene, during reaction of NBBM.

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- [4] Poutsma, M.L., *Energy & Fuels*, 1990, **4**, 113-131.