Coal/Polymer Coprocessing with Efficient Use of Hydrogen

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Abstract

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. Catalyst-directed coliquefaction of coal and polymeric materials not only has attractive environmental implications but also has the potential to enhance the economic viability of traditional liquefaction processes. By exploiting the higher H/C ratio of the polymeric material and using it as a hydrogen source, the overall process demand for molecular hydrogen and hydrogen donor solvents may be reduced.

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. Work in the past six months has focused on analysis of light gaseous products for neat reactions of tetradecane, resulting in mass balances greater than 94%. The experimental protocol developed in the previous project period was used 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. Mechanistic modeling studies were also initiated in order to support and quantify the mechanistic ideas put forth to explain the experimental observations.

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I. Executive Summary

Model feedstocks were used to identify the underlying reaction pathways, kinetics, and mechanisms controlling coal liquefaction in the presence of plastics and catalysts. This approach permits the investigation of the feasibility of coprocessing coal with waste polymers while facilitating product analyses and obtaining detailed information about the intrinsic reactivities and binary interactions. Experiments in the first year of the project demonstrated that when reacted in binary mixtures, the conversion of tetradecane, a model compound of polyethylene, increased while the selectivities to primary products of 4-(naphthylmethyl) bibenzyl (NBBM) were enhanced. Variation of the relative concentrations of the components revealed that the effect was indeed a chemical one and not simply a result of dilution. Work in the past six months has focused on analysis of light gaseous products for neat reactions of tetradecane, resulting in mass balances greater than 94%. The experimental protocol developed in the previous project period was used 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. Mechanistic modeling studies were also initiated in order to support and quantify the mechanistic ideas put forth to explain the experimental observations.

II. Introduction

Alternatives for the disposal of used plastic products are being sought as public concern for the environment has escalated in recent years. As the number of landfills closing each year exceeds the number being opened, disposal through landfilling is becoming a less viable option.¹ Since approximately 80% of the municipal solid waste stream (MSW) is landfilled, this will have a dramatic impact on the disposal of used products.² These circumstances present an ideal opportunity for a dramatic paradigm shift in waste disposal practices since landfilling is actually an inefficient use of resources.

A significant portion of the MSW, approximately 18% by volume, is comprised of plastic products.² The US alone produces 60 billion pounds of polymers annually, and their production is projected to increase.³ The public has responded to the growing use of plastics by pressuring industry and government to promote recycling as a means of extending the useful lifetime of plastic products. Incineration, i.e., energy recovery through burning, is simple yet viewed adversely by the public. Alternative recycling approaches in which mixed plastics are ground, melted and then reshaped result in a loss of material strength and are therefore not widely applied.⁴

Another strategy for plastics resource recovery is tertiary recycling, a method in which the polymers are broken down into their corresponding monomers or into petrochemicals and fuels. However, variations in the supply and composition of waste plastics and unfavorable economics have restricted the widespread application of this technology. Coprocessing of polymeric waste with other materials may provide potential solutions to the deficiencies of current resource recovery processes, including unfavorable process economics. By incorporating polymeric waste as a minor feed into an existing process, the variations in plastic supply and composition could be mediated and as a result, allow for continuous operation. One option for coprocessing is to react polymeric waste with coal under direct liquefaction conditions.⁵⁻⁷ Coprocessing of polymeric waste with coal provides for simultaneous conversion of both feedstocks into high-valued fuels and chemicals.

Catalyst-directed liquefaction of plastic and coal mixtures can be employed in order to reduce the process hydrogen requirements and convert the feed macrostructures into useful fuels and chemicals. The underlying motivation for catalyst-directed coliquefaction of polymers and coal is to use the polymers as the hydrogen source and exploit their inherently higher H/C ratio. However, this goal requires information about the underlying reaction pathways, kinetics, and mechanisms controlling coal liquefaction in the presence of catalysts and polymeric materials. A series of experiments using model compounds and real feedstocks for both polymeric waste and coal provides the starting point for unraveling the complex, underlying chemistry. Neat pyrolysis and reactions in the presence of hydrogen, in the presence of a hydrogen donor solvent, in the presence of a catalyst, and in a combined atmosphere span the full range of relevant processing environments. Neat and binary mixture pyrolysis reactions both at low and high pressures are the logical starting point in that they provide valuable thermal baseline information from which subsequent experiments may be judged. Results from thermal degradation studies which have been conducted over a broad range of pressures will be discussed in the following sections.

III. Experimental

Although much of the experimental approach was described previously, there have been sufficient refinements and additions that some of the information bears repeating in this report.^{8,9}

In order to obtain information about underlying reaction pathways, kinetics, and mechanisms without the complicating effects of the macrostructure, experiments were performed using model compounds for both coal and polyethylene, a voluminous component of mixed plastic waste. To mimic the structure of coal, 4-(naphthylmethyl) bibenzyl (NBBM) (MW=322) was used. NBBM contains both condensed and isolated aromatic species connected by short alkyl chains. An added feature is that it contains five different aromatic-aliphatic or aliphatic-aliphatic carbon-carbon bonds. Successful predictions of the relevant primary products for real systems using NBBM confirmed the adequacy of this model compound, and thus, it will be employed in this study.¹⁰⁻¹³ The structure of NBBM is depicted in Figure 1.

Figure 1: Structure of coal model compound 4-(naphthylmethyl) bibenzyl.

Although numerous hydrocarbons may serve as appropriate model compounds for high density and low density polyethylene, tetradecane, $C_{14}H_{30}$ (MW=198), was chosen as an appropriate compromise in reactant size.

The model compound experiments have been conducted at both low and high pressures to span the range of relevant processing conditions. Low pressure batch pyrolyses of these model compounds were conducted in 3.1 ml glass cryules (Wheaton). High pressure reactions were conducted in batch reactors constructed from 316 stainless steel. The reactors were fitted with glass sleeves in order to minimize wall interactions, which resulted in an effective reactor volume of 8.25 ml. A two-way ball valve was attached to the reactor in order to trap product gases for analysis by gas chromatography.

For both low and high pressure experiments, reactions were carried out in an isothermal (± 1 °C) fluidized sand bath. For the low pressure pyrolyses, the cryoules were charged with the appropriate amount of reactant, purged with argon, and sealed using an oxygen/propane flame. Pyrolyses were conducted at both 420 and 450°C, and reaction times ranged from 5-150 minutes. Specific reaction conditions are summarized in Table 1. Upon completion of the reaction period, the ampoules were removed from the sand bath and were placed into a room temperature sand bath to cool. Each reaction time was at minimum duplicated and in some cases, three replicates were performed. The reproducibility for each set of experiments is also listed in Table 1.

Gaseous products were collected using a sampling system of a known volume of 18.1 ml, and quantified using an HP 5890 GC equipped with a thermal conductivity detector employing a 6 ft stainless steel Porapak Q column (Supelco). The liquid and solid reaction products were extracted from the ampoules using 5 ml of methylene chloride, and an external standard (biphenyl) was added. Product identification and quantification, which enabled reactant conversions and product selectivities to be determined, were achieved using an HP 6890 GC/MS and HP 6890 GC equipped with a flame ionization detector, respectively, each employing a Hewlett Packard 30 m crosslinked 5% Ph Me Silicone capillary column.

For the high pressure experiments, the reactor was filled with the appropriate amount of reactant, and pressurized to 2500 psig with nitrogen in order to ensure a leak-free seal was obtained. The reactors were then purged with 1000 psig of nitrogen five times prior to reaction in order to completely exclude oxygen. The reactors were pressurized to 1000 psig (cold; 2345 psig at reaction temperature) with nitrogen, and thermal degradation was conducted at 420°C for 20-150 minutes. Specific reaction conditions are summarized in Table 2. Upon completion of the reaction time, the reactor was immersed in a room temperature sand bath to quench the reaction. Gaseous products were collected using a sampling system, and liquid and solid products were extracted with 15 ml of methylene chloride. Product analysis was conducted using the same methods described for the low pressure experiments. A schematic of the pressurizing and coupling system constructed for this project is depicted in Figure 2.

IV. Results and Discussion

A. Low Pressure Reactions

For low pressure pyrolysis of tetradecane and NBBM, analysis and interpretation of liquid products formed were presented in previous DOE reports.^{8,9} Quantification of gaseous products from these sets of reaction conditions, as shown in Table 1, has since been carried out, and the results will be presented in the following section.

A. 1. Neat Tetradecane Pyrolysis

Neat pyrolysis of tetradecane was conducted at loadings ranging from 6.2 to 27.8 mg (1.01×10^{-2} to 4.53×10^{-2} M). A plot of conversion versus time for the different concentrations is provided in Figure 3. Overall, the tetradecane conversion increased as the reactant loading was increased. For the reaction conditions studied, the dependence of the degradation rate on concentration was most pronounced at low loadings, as the rate became relatively insensitive to reactant loading at higher concentrations. This behavior is

Table 1: Reaction conditions for low pressure pyrolysis experiments.

Reaction Set	C14 Loading (mg)	NBBM Loading (mg)	Reaction Temperature (°C)	Reaction Times (min)	Reproducibility (%)
C ₁₄ -6.2(a)	6.2	0.0	420	20-150	±2
C ₁₄ -12.3(a)	12.3	0.0	420	20-150	±2
C ₁₄ -12.3(b)	12.3	0.0	450	20-150	±3
C ₁₄ -20(a)	20.0	0.0	420	20-150	±1
C ₁₄ -20(b)	20.0	0.0	450	20-150	±3
C ₁₄ -27.8(a)	27.8	0.0	420	20-150	±2
C ₁₄ -27.8(b)	27.8	0.0	450	20-150	±3
NBBM-20	0.0	20.0	500	5-60	±2
NBBM-20(a)	0.0	20.0	420	5-150	±2
Bin(1)	6.2	10.0	500	5-60	±1
Bin(1x-1x)	6.2	10.0	420	5-150	±1
Bin(1x-2x)	6.2	20.0	420	5-150	±2
Bin(2x-2x)	12.3	20.0	420	5-150	±2
a = 420°C b = 450°C 1x = molar loading equivalent to 6.2 mg tetradecane 2x = molar loading equivalent to 12.3 mg tetradecane					

Table 2: Reaction conditions for high pressure pyrolysis experiments.

Reaction Set	C14 Loading (mg)	NBBM Loading (mg)	Reaction Temperature (°C)	Reaction Times (min)	Reproducibility (%)
C ₁₄ -16.5	16.5	0.0	420	20-150	±2
C ₁₄ -32.7	32.7	0.0	420	20-150	±2
C ₁₄ -53.2	53.2	0.0	420	20-150	±2
NBBM-53.2	0.0	53.2	420	20-150	±2

A **B**

Figure 2: (A) Flow diagram of pressurizing system.
(B) Schematic of gas sampling apparatus.

Figure 3: Comparison of neat tetradecane conversions as a function of reactant loading.

indicative of an overall reaction order that is a function of concentration and approaches first order kinetics at higher concentrations. At the lowest reactant concentration, the best fit of the overall reaction order was 1.75.

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. The alkene which had the second highest selectivity was ethylene, but its selectivity decreased with increasing conversion and reactant concentration as shown in Figure 4. The selectivity achieved a maximum of 0.45 at the lowest conversion and the lowest reactant loading, and the minimum selectivity of 0.20 was observed at the highest conversion for the highest reactant loading. The selectivities of 1-butene and 1-pentene were lower than that of ethylene but remained relatively constant with both conversion and reactant loading at values of approximately 0.17 and 0.12, respectively.

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. The selectivity to butane is plotted as a function of conversion in Figure 5 and is representative of this behavior. 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. There was a significantly higher alkene to alkane

Figure 4: Comparison of ethylene selectivity as a function of reactant loading.

Figure 5: Comparison of n-butane selectivity as a function of reactant loading.

ratio for the liquid products than for the gaseous products, with longer α -olefins predominating at the higher carbon numbers. The observations for product distributions for species with higher carbon numbers have previously been discussed, and therefore will not be repeated.^{8,9}

Overall, the product distributions were rationalized in terms of the typical free radical Rice-Herzfeld and Rice-Kossiakoff mechanisms for low pressures, which are represented in Figure 6.¹⁴⁻¹⁷ The decomposition is initiated by carbon-carbon bond fission along the main chain to form two primary radicals. These primary radicals form secondary radicals through hydrogen abstraction from a secondary carbon or an intramolecular hydrogen rearrangement. These secondary radicals then undergo β -scission to form α -olefins and primary radicals. Termination occurs by recombination of radicals. Detailed kinetic modeling using these mechanistic ideas is currently being carried out.

The trends observed for the gaseous products can be explained by considering the reaction pathways leading to the formation of these products and the impact of changes in total concentration on the relative rates of these pathways. The most striking trend observed was the decrease in the selectivity to ethylene with increasing reaction time and reactant concentration. This behavior can be rationalized by noting that the formation of ethylene occurs primarily through a unimolecular reaction, a β -scission reaction of a primary radical to form ethylene and a smaller primary radical. As reaction time and the initial reactant concentration increase, bimolecular reactions become more favorable, leading to both a reduction in the formation mechanism and an increase in the degradation pathways for ethylene. These factors can also be used to explain the trends in methane selectivity, though the behavior observed was not as profound.

The relatively constant selectivity values which were observed for the other gaseous α -olefins are a result of the balance of formation and depletion of these products. These products will continue to form from larger hydrocarbons undergoing reaction and will also continue to react themselves. However, the mechanisms involved for these species are not as drastically affected by reaction time or reactant concentration as those for ethylene, since these are formed by both unimolecular and bimolecular reactions, such as intramolecular and intermolecular hydrogen shifts, followed by subsequent β -scission reactions. The balance achieved results in relatively constant values of product selectivities.

The increase in the yields of gaseous n-alkanes at higher concentrations can be explained by noting that hydrogenation of olefins and continued thermal cracking can occur as both the reaction time and number of intermolecular reactions increase. As the proportion of bimolecular reactions increases, there is a higher probability that a primary radical will be capped and become stable rather than undergo further degradation via unimolecular reactions.

A. 2 Neat NBBM Pyrolysis

The low pressure, neat NBBM pyrolysis experiments have been discussed previously.^{8,9} The major and minor products formed during NBBM pyrolysis are either in the liquid or solid phases, and therefore gas analysis was not conducted. However, there remains a question as to whether the low molecular weight products were quantified exactly, due to slight partitioning between the liquid and vapor phases. This possibility is currently being investigated using a simulation package and experiment, and any necessary changes to the previously reported results will be made.

- Initiation

- Propagation

- Termination

Figure 6: Proposed mechanism for pyrolysis of tetradecane.^{14, 15}

A. 3. Binary Mixture Pyrolysis

It has been shown that favorable interactions exist during low pressure coprocessing of NBBM and tetradecane.^{8,9} In binary mixtures, the conversion of tetradecane increased while the selectivity to primary products of NBBM pyrolysis was enhanced. These observations were attributed to the stabilization of NBBM-derived radicals through hydrogen abstraction from tetradecane which in turn, increased the rate of tetradecane conversion. The relative concentrations of each reactant also affected the tetradecane conversion and selectivity towards primary products of NBBM. Increasing both the NBBM to tetradecane ratios and the overall reactant loading resulted in an increase of interactions between NBBM and its derivatives and an enhancement of tetradecane degradation, as shown in Figure 7.

The overall mechanism for degradation of tetradecane was similar for the neat and binary mixture experiments, but some differences in product selectivities were observed as a result of binary interactions. These differences depended upon both the overall reactant concentration and the relative amount of NBBM in the system. The effect of coprocessing NBBM and tetradecane at low concentrations can be observed by comparing the C₁₄-6.2(a) and Bin(1x-1x) experimental results. Although there was a significant increase in the polymer model compound reactivity, there were only small changes in the tetradecane-derived product spectra. The only products which had significantly different selectivities with the addition of NBBM were ethylene and methane. This is consistent with the changes observed as the initial concentration of tetradecane in the neat experiments was raised, as described in the previous section. During binary pyrolysis, tetradecane radicals are initiated through intermolecular hydrogen abstraction reactions with NBBM-derived radicals, forming secondary radicals, thus increasing the total radical population at a given tetradecane conversion. This reduces the relative concentration of precursors for the formation of ethylene and increases the rate of termination of tetradecane-derived radicals, which leads to diminished yields of ethylene. The dependence of the selectivity of ethylene as a function of concentration is shown in Figure 8.

As the loading of NBBM was increased at a constant tetradecane loading, there was a decrease in selectivity towards α -olefins and gaseous hydrocarbons, and an increase towards paraffins of carbon numbers greater than seven. This behavior can be explained by noting that there is an enhancement in the rate of recombination reactions for tetradecane-derived radicals under these reaction conditions. With higher NBBM loadings, there is a relative increase in the rate of initiation of radicals since NBBM initiates more readily than tetradecane. This will lead to an overall increase in termination reactions since the rate of termination of free radicals will be equal to the rate of initiation at steady state. As previously discussed, the NBBM radicals which are formed during coprocessing will initiate tetradecane radicals through intermolecular hydrogen abstractions, resulting in a higher effective tetradecane-radical population. The increased rate of recombination reactions of tetradecane-derived radicals will lead to higher yields of n-alkanes at the expense of α -olefins and light hydrocarbons, which is somewhat similar to the effect of increasing the overall tetradecane concentration during neat pyrolysis.

The Bin(1x-2x) and Bin(2x-2x) reaction sets displayed similar trends in tetradecane-derived product distributions, despite showing differences in the reaction products of NBBM and in the reactivity of the polymer model compound. Higher selectivities for secondary products of NBBM degradation, such as phenyl methyl naphthalene, were observed for the Bin(1x-2x) reaction set. These differences can be explained by noting that at higher relative concentrations of tetradecane, there will be fewer NBBM-NBBM and more NBBM-tetradecane interactions. This also leads to significantly

Figure 7: Comparison of tetradecane conversions as a function of reactant loading during binary reactions.

Figure 8: Comparison of ethylene selectivities as a function of reactant concentrations.

increased yields of primary products of NBBM degradation. The differences in conversion of tetradecane in the Bin(1x-2x) and Bin(2x-2x) reaction sets are similar to those for the C₁₄-6.2(a) and C₁₄-12.3(a) experiments, indicating that the primary role of NBBM is to enhance the rate of initiation but not to alter the subsequent decomposition pathways of tetradecane. The nature of the tetradecane interactions is similar during the binary reactions to those observed during neat reactions as suggested by the comparable product slates

B. High Pressure Reactions

Initial high pressure reactions revealed that the stainless steel reactors possibly exhibited some catalytic behavior.⁹ In order to prevent these interactions, glass sleeves were constructed and have been used in all subsequent reactions. Reactant conversions and product distributions have since been reproducible and consistent with pyrolyses performed at low pressure in the glass ampoules, and thus it is believed that catalytic behavior has been minimized.

Initially, gaseous product analysis from high pressure reactors was conducted employing a sampling system constructed using a miniature pressure regulator as shown in Figure 9. Reactors were attached to the regulator and opened, allowing gaseous species to expand across the diaphragm of the regulator and then be sampled with a gas-tight syringe at a reduced pressure. Based on quantification using gas chromatography of the syringe sample, the molar concentration of each species in the regulator outlet stage could be calculated. Overall gaseous product yields were then obtained by using pressure and volume relationships between the inlet and outlet sides of the regulator.

Although the gas sampling system was believed to be accurate, low mass balances (approximately 75%) were observed during initial experiments using both the glass sleeves and the sampling system. Upon further investigation, it was shown that the inconsistencies were attributed to incomplete quantification of the gaseous species. It was determined that equilibrium of gaseous species was not being achieved in the system, particularly between the inlet and outlet stages of the regulator, and thus the gaseous product yields were considerably underestimated. Therefore, a new gas sampling system was assembled, as shown in Figure 2, with emphasis placed on achieving good mixing during expansion and simplifying the required calculations. Analysis of subsequent experiments using the new sampling system resulted in significantly improved mass balances which were much more consistent with those obtained during low pressure reactions and greater than 95% for most cases.

After refining the product analysis protocol, neat high pressure experiments were conducted using each of the model compounds at the conditions listed in Table 2. In order to compare directly the results of these experiments to those obtained from the low pressure reactions, reactant concentrations equal to the low pressure reactions were employed. The ratio of the volumes of the stainless steel reactors and the pyrex ampoules was 2.66/1, and reactant loadings were increased accordingly. These reaction sets will be used as benchmarks for comparison of future high pressure reactions. Discussion of the results of these experiments is presented in the following sections.

B. 1. Neat Tetradecane Pyrolysis

High pressure pyrolysis experiments of tetradecane were conducted using the methods described in the experimental section of this report with reactant loadings detailed in Table 2. The reaction set C₁₄-16.5 will not be included in this discussion since it was not possible to quantify n-alkanes due to the low reactant loading and the amount of solvent

Figure 9: Schematic of apparatus which was initially employed for gas sampling of high pressure reactions.

required for extraction. Therefore, discussion will focus on the C_{14} -32.7 and C_{14} -53.2 reaction sets and comparison of the results to their low pressure counterparts, C_{14} -12.3(a) and C_{14} -20(a), respectively.

Comparison of tetradecane conversion as a function of reactant concentration and total reaction pressure is shown in Figure 10. 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 similar 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.

Of the light hydrocarbons, ethylene, ethane, and propylene displayed the most notable differences in their product selectivities. The yields of each of these were significantly reduced for the high pressure reactions, with the C_{14} -53.2 reaction set having the lowest values, as shown in Figure 11 for ethylene. For n-alkanes larger than butane, the high pressure reactions resulted in notably higher yields than those observed in the low pressure pyrolyses. The α -olefin selectivities followed similar trends for both sets of reactions, with the olefins of higher carbon numbers (>8) showing higher selectivities during the low pressure experiments.

Although the detailed mechanistic modeling study currently in progress will be used to interpret the differences between the low and high pressure reactions, initial mechanistic speculation can be put forth to explain these trends. At higher total pressures in which a high concentration of inert molecules is present, the rate of recombination reactions can be enhanced substantially due to the ability of a third body to dissipate the energy of the reactants. This would explain the absence of methane and reduced yields of light hydrocarbons for the high pressure reactions. Radical precursors which could potentially lead to their formation are small and mobile and will therefore undergo recombination with higher frequency. The combination of these species with themselves and other radicals would lead to increased yields of n-alkanes of higher carbon numbers and reduced

Figure 10: Comparison of tetradecane conversion as a function of reactant concentration and reaction pressure.

Figure 11: Comparison of ethylene selectivities as a function of reactant concentration and reaction pressure.

selectivities to longer α -olefins. Although the underlying mechanistic explanation is not as broad, these trends are similar to the enhanced production of n-alkanes at the expense of light hydrocarbons and α -olefins with an increasing overall reactant concentration discussed earlier.

For the reactions carried out at high pressure, the dependence of the product spectra on increasing the initial tetradecane loading is the same as that observed at low pressure. As the reactant loading was raised, the selectivity to light hydrocarbons declined, and the yields of α -olefins and n-alkanes increased. These trends can again be rationalized in terms of an increase in the selectivity to bimolecular reactions as the total concentration increases.

B. 2. Neat NBBM Pyrolysis

Neat high pressure pyrolysis of NBBM was performed to provide a comparison to low pressure experiments and to serve as a baseline for subsequent high pressure experiments.⁹ The overall conversion for NBBM was reduced during the high pressure experiments, as shown in Figure 12. Two of the major products formed during high pressure pyrolysis were toluene and 1-methyl-4-(naphthylmethyl) benzene, which were produced from fission of the bibenzyl bond in NBBM, and subsequent hydrogen abstraction. The other major product formed was 1-(2-phenylethenyl)-4-(naphthylmethyl) benzene, which is most likely formed through intermolecular hydrogen abstraction and a subsequent β -scission. Minor selectivities were observed for a number of species, all of which were mentioned in previous reports during discussion of low pressure NBBM pyrolysis.^{8,9}

Although the major and minor reaction products observed during NBBM degradation were the same for both high pressure and low pressure pyrolyses, there were significant differences in product yields between the two sets of experiments. The most notable differences in the observed selectivities were for toluene and its complement, 1-methyl-4-(naphthylmethyl) benzene, which are shown in Figure 13. The yields of this product pair were almost equivalent during the low pressure experiments but are clearly significantly different, and much lower, for the high pressure reactions. The selectivity to 1-(2-phenylethenyl)-4-(naphthylmethyl) benzene was also reduced during the high pressure reactions in comparison to the low pressure runs. The yields of the minor products were essentially unchanged with the exception of 1-(4-(4-methyl)phenylmethyl)benzyl naphthalene, which was formed in higher yield during the high pressure reactions.

The reduction in both NBBM conversion and the formation of 1-(2-phenylethenyl)-4-(naphthylmethyl) benzene can be rationalized by noting that at high pressures, an increase in radical recombination reactions due to partitioning of species into different phases is likely. Simulation of the phase behavior has suggested that molecules such as NBBM and 1-(2-phenylethenyl)-4-(naphthylmethyl) benzene are liquids under reaction conditions, and that smaller molecules formed during the degradation of NBBM, e.g., through dissociation of the bibenzyl bond, preferentially enter the gas phase. Once these species have entered the gaseous phase, they will primarily undergo recombination reactions with other molecules due to the low concentration of possible reaction sites and the stabilization provided by inert nitrogen molecules. A high proportion of these gaseous species will be the toluene radical and the 1-methyl-4-(naphthylmethyl) benzene radical, which upon recombination will form NBBM, resulting in a reduction in NBBM conversion when compared to the low pressure reactions. The rate for the formation of 1-(2-phenylethenyl)-4-(naphthylmethyl) benzene would also be reduced due to partitioning of smaller species into the gaseous phase. As previously stated, the formation of 1-(2-phenylethenyl)-4-(naphthylmethyl) benzene occurs through bimolecular hydrogen abstraction reactions and

Figure 12: Comparison of NBBM conversion for low and high pressure reactions.

Figure 13: Comparison of toluene and 1-methyl-4-(naphthylmethyl) benzene as a function of reaction pressure.

subsequent β -scission. As the concentration of radicals in the liquid phase diminishes, the rate of intermolecular hydrogen transfer reactions will lower, leading to a reduction in formation of 1-(2-phenylethenyl)-4-(naphthylmethyl) benzene.

A satisfactory explanation for the discrepancy between the selectivities of toluene and its complement has not yet been put forth. However, initial results suggest that quantification of toluene in the gas phase will significantly increase the observed selectivity to toluene. There was not a significant enough increase in the yield of other products which would be formed from benzyl radical precursors to account for the differences in yields. Upon further investigation, it was determined that a significant amount of toluene was present in the vapor phase prior to liquid extraction and was not being quantified. This was suggested by a comparison of the mass and phenyl ring balances of the low and high pressure reactions. The balances were much lower for the high pressure reactions, which could possibly be a direct result of incomplete quantification of toluene, since it is formed in significant yield. Preliminary calculations have shown that only observed products which have molecular weights lower than naphthalene have a significant vapor pressure prior to extraction; therefore, the yields of larger reaction products and the NBBM conversion reported for the high pressure experiments are believed to be accurate.

The two options for quantifying the toluene in the vapor phase are gas analysis, as described earlier for the light hydrocarbons from tetradecane pyrolysis, and computational simulations of the reaction system to obtain quantitative information about phase partitioning. Both of these techniques will be attempted, and once accurate overall product yields are obtained, further mechanistic interpretation of the reaction system will be conducted.

V. Conclusions

Recent investigations have demonstrated the feasibility of coprocessing of coal with polymers. In this study, feedstock interactions were observed using model compound mimics of both coal and polyethylene. In binary mixtures, the conversion of tetradecane increased while the selectivity to primary products of NBBM pyrolysis was enhanced. These observations were attributed to the stabilization of NBBM-derived radicals through hydrogen abstraction from tetradecane which in turn, increased the rate of tetradecane conversion.

The initial loading of each reactant and the 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 there were significant changes in product selectivities. NBBM showed increased selectivity towards secondary products, while n-alkanes were formed in higher yields for tetradecane degradation. The higher proportion of NBBM resulted in an increase of self-interactions, which resulted in a larger quantity of retrograde condensation reactions. The higher loadings of NBBM also yielded larger tetradecane-derived radical populations within the system, leading to increased rates of recombination and a shift in the products towards longer paraffins. 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. These effects on conversions and selectivities were attributed to an increase in both tetradecane-NBBM and tetradecane-tetradecane reactions at higher concentrations.

In order to optimize the interaction between reactants, further experimental and theoretical studies will be conducted at high pressures and in the presence of hydrogen donor solvents and catalysts in order to delineate the underlying kinetics, pathways, and mechanism controlling coal/polymer coprocessing.

VI. Path Forward

Work carried out in the next six months will focus on both high pressure pyrolysis experiments and computational modeling of tetradecane degradation. The pyrolysis experiments will provide insight into the reaction pathways and mechanisms which dominate the interactions of these reactants at high pressures. Once this data has been obtained, the effects of adding hydrogen donor solvents and catalysts to the system may be addressed. The computational modeling will provide verification of proposed reaction mechanisms for tetradecane degradation. This will be accomplished by providing estimates of rate parameters, i.e., pre-exponential factors and activation energies for relevant reaction families during tetradecane pyrolysis, and using tools developed for computer-generation of complex reaction mechanisms.

VII. Manuscripts and Publications

Broadbelt, L.J., "Polymer Resource Recovery Through Coprocessing: Thermal and Catalytic Chemistry", Invited Lecture, Department of Chemical Engineering, North Carolina State University, Raleigh, NC, October **1997**.

De Witt, M.J. and Broadbelt, L.J., "Coprocessing of Polymeric Waste with Coal: Reaction of Polyethylene and Coal Model Compounds", Annual Scientific Meeting of the Center for Catalysis and Surface Science, Evanston, IL, September **1997**.

Broadbelt, L.J., "Mechanistic Modeling of Complex Reaction Systems", UOP Workshop on Complex Reaction Kinetics, Des Plaines, IL, March **1998**.

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

De Witt, M.J. and Broadbelt, L.J., "Detailed Kinetic Modeling of the Reactions of Polyethylene and Coal Model Compounds", *in preparation*.

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