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Coal/Polymer Coprocessing with Efficient Use of Hydrogen

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Principal Author(s): Dr. Linda J. Broadbelt and Matthew J. De Witt	
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Submitting Organization(s) Northwestern University
2145 Sheridan Road
Name & Address Department of Chemical Engineering (1)
Evanston, IL 60208

(2)

(3)

(4)

(5)

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Abstract

Low- and high-pressure pyrolysis experiments employing tetradecane and 4-(1-naphthylmethyl)-bibenzyl (NBBM) as model compounds for polyethylene and coal, respectively, were conducted at 420°C at different reactant loadings both neat and in binary mixtures. These reaction sets demonstrated that when reacted in binary mixtures, the conversion of tetradecane increased while the selectivities to primary products of NBBM were enhanced in the gas phase. Variation of the relative concentrations of the components revealed that the effect was indeed a chemical one and not simply a result of dilution. As the polymer mimic to coal model compound ratio increased, there was a decrease in self-interactions of NBBM with minimal changes in the degradation products of tetradecane. Increasing the overall reaction pressure in the system through addition of an inert gas from atmospheric pressure to 2360 psig resulted in small decreases in reactant conversions and altered product distributions only slightly. Overall, the experiments carried out demonstrated that favorable interactions exist in the gas phase during coprocessing, and the primary reaction pathways and mechanism governing the interactions between the feedstocks were elucidated.

Low pressure pyrolysis experiments employing a high molecular weight polymer and a model compound for coal were conducted to address the effect of phase behavior on the overall degradation mechanism and reaction pathways during coprocessing. Thermal degradation of high density polyethylene (HDPE) and 4-(1-naphthylmethyl)bibenzyl was conducted at 420°C at different reactant loadings, both neat and in binary mixtures. During binary mixture experiments, there was an enhancement in the selectivities to primary products of NBBM at longer reaction times, with a significant reduction in the formation of secondary and tertiary products. These favorable interactions occurred because the polymer induced diffusion limitations in the system compared to neat NBBM pyrolysis, which minimized NBBM self-interactions and promoted reactions with the surrounding polymer. The degradation pathways of HDPE during binary mixture experiments were similar to those during neat reactions, with slight changes to the product yields that were consistent with increasing the overall reactant loading during neat pyrolysis. Variation of the relative reactant loadings indicated that the favorable feedstock interactions were still realized with only slight alterations in the product slate for NBBM and increased yields of saturated species derived from HDPE. Overall, the experiments carried out demonstrated that favorable interactions exist in both the liquid and gas phases during coprocessing, and primary reaction pathways and the mechanism governing the interactions between the feedstocks were elucidated.

To aid in interpretation of the experimental results, detailed mechanistic modeling was carried out. In recent years, the use of mechanistic modeling to identify the underlying kinetics of complex systems has increased greatly. One of the challenges to kinetic

modeling is constructing a model which can capture the essential chemistry of a system while maintaining a manageable model size. The rate-based generation of mechanistic models is an attractive approach since kinetically significant species can be determined and selectively included in the final mechanism. In previous work, an algorithm for the effective rate-based generation of reaction mechanisms was developed. In work carried out in the last year, novel modifications were made to the core components of the algorithm, which included introducing thermodynamic constraints into the estimation of the controlling rate parameters and using an alternative approach for determining the species included in the final model. Once implemented, the adapted rate-based building criterion was successfully employed to build a compact mechanistic model for tetradecane pyrolysis. Though thousands of species and reactions were generated, only a small portion of these was deemed necessary and incorporated into the final model. Experimental data were used to determine frequency factors for a subset of the reaction families, while all other kinetic parameters were set based on literature values. The final optimized values for the frequency factors were consistent with literature, and the model was able to accurately predict reactant conversions and product yields for varying reaction conditions. Both relative trends and the actual values were predicted correctly over a wide range of reactant conversions and initial reactant loadings. It was also observed that increasing the quantity of species initially seeded resulted in a mechanism which was smaller in size but had comparable fitting and predicting capabilities as models seeding only the reactant. Subsequent regeneration of the reaction mechanisms using the optimized values for the frequency factors resulted in smaller models with comparable capabilities.

Work in the final, extended project period will complete mechanistic modeling of neat NBBM pyrolysis and binary mixtures of tetradecane and NBBM. Novel changes will be made to the core algorithms for model generation and solution to allow the multiphase behavior of the binary system to be captured. This will be a substantial advance in automated modeling capabilities, while also serving to consolidate all of the experimental data collected during the grant period within a quantitative framework.

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I. Executive Summary

Work during the entirety of this grant has focused on four main areas: (1) identifying the reaction pathways and mechanism underlying binary reactions between coal and polyethylene using model compounds; (2) reaction of the coal model compound, 4-(1-naphthylmethyl)bibenzyl (NBBM), with high density polyethylene (3) detailed kinetic modeling of the decomposition of the polyethylene model compound, tetradecane, and (4) detailed kinetic modeling of NBBM neat and in binary mixtures with tetradecane. The first item is detailed in a manuscript that has been accepted for publication in Energy & Fuels and is attached as Appendix A to this report. The second item is described in a manuscript that has been submitted for publication in Energy & Fuels and is attached as Appendix B to this report. The third item is summarized in a manuscript that has been submitted for publication in Industrial & Engineering Chemistry Research and is attached as Appendix C. These manuscripts will also form the nucleus of the Ph.D. thesis of Matthew De Witt, the graduate student who has been dedicated to this project. These three manuscripts document and summarize work for the entire project period. The original hypotheses of the project and the investigative approaches used are described in detail. The body of this report focuses on our current work to develop neat and binary mixture models of NBBM and tetradecane.

II. Introduction

Recently, concerns over the inadequacy of current treatment and disposal methods for mixed plastic wastes have driven the exploration of new strategies for viable plastics resource recovery. The emphasis of the recovery is to obtain high-valued, useful products from the waste polymers. Post-consumer waste plastics are a major contributor to the municipal solid waste (MSW) stream, constituting approximately 11% by weight and 21% by volume of waste in landfills [1]. Over 40% of the landfills in the United States were closed in the past decade, and it is estimated that over half of the remaining ones will be full by the end of the century [2]. This poses a significant dilemma since there appears to be no immediate decrease in the usage of plastic products; in fact, due to their versatility, the usage will most likely increase.

The current motivation for the recovery of plastics is due to government mandates, rather than to industrial initiatives. Some states, such as California, Oregon, and Wisconsin, have passed laws which specify that plastic bottles must be manufactured from a minimum of 25% recycled plastics. Germany dictated that over 80% of all plastic packaging must be recycled by methods other than combustion by 1996 [3-5]. Conventional plastics recycling technologies encounter a number of difficulties which range from costly separation to removal of impurities and contaminants. A consequence of these problems is that products manufactured from recycled polymers are of lower quality and higher cost (approximately 10% higher for high-density polyethylene (HDPE)) than those from the corresponding virgin polymer [4]. As a result, in the United States, only about 4% of 30 million tons of the total plastics produced are recycled each year [6].

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, 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 [2,7,8]. Coprocessing of polymeric waste with coal provides for simultaneous conversion of both feedstocks into high-valued fuels and chemicals. To develop this strategy, an approach combining experiment and modeling

was used to unravel the complex chemistry underlying the binary interactions of polymeric feedstocks and coal.

III. Modeling Methodology

The capability to generate reaction mechanisms via the computer was exploited to model NBBM and NBBM/tetradecane pyrolysis chemistry at the mechanistic level. The same approach employed to model neat tetradecane pyrolysis chemistry as described in Appendix C was used. Required input consisted of the structure of the reactant and the rules by species react. Although the number of reactions comprising a detailed description of the chemistry is potentially large, the number of different types of chemical transformations is small. In addition to the five pairs of forward and reverse reaction types used to describe the conversion of tetradecane (bond fission and recombination, hydrogen abstraction, β -scission and radical addition, disproportionation and molecular addition and (1,4), (1,5) and (1,6) hydrogen shift reactions), ipso substitution reactions were included. These reaction types were repetitively applied to the reactants and their progeny to build the reaction mechanism. To prevent the explosive growth that would be observed if all species were allowed to undergo all possible transformations, a rate-based constraint was applied. The characteristic rate was systematically varied to assess its impact on the mechanism generated.

In order to apply the rate-based algorithm and to allow solution of the reaction mechanism, rate constants were specified as the reactions were revealed. The rate constants were obtained through a hierarchical approach. For a small subset of important reactions among low molecular weight species, experimental values were accessed from a lookup table. For all other reactions, typical values of frequency factors, one for each reaction type, were used, and activation energies were specified using linear free energy relationships employing heat of reaction as the reactivity index. In order to specify the heat of formation values required, the NIST Structures and Properties Database was accessed on-the-fly. Furthermore, incorporating entropy and heat capacity information allowed equilibrium constants to be calculated to constrain the reverse reaction pairs thermodynamically.

Because of the two-phase nature of NBBM and NBBM/tetradecane reactions, new capabilities had to be developed for model solution. A parsing algorithm was developed that automatically duplicates all reactions in the mechanism, writing one instance of the reaction for the gas phase and one for the liquid phase. The parser also adds transport reactions, allowing for communication between the gas phase and the liquid phase. Equilibrium between the phases for each species was enforced by determining the value of the distribution coefficient. HYSIS was used to develop correlations for K_{eq} values of different compound classes as a function of molecular weight. Furthermore, values for the mass transfer coefficients from the vapor to the liquid phase were identified that ensured that equilibrium would be maintained.

IV. Results and Discussion

Unique correlations to define $K_{eq} = C_{i,liquid}/C_{i,vapor}$ as a function of molecular weight were developed for species containing no rings, species with isolated aromatic rings and species containing naphthenic rings from phase behavior simulations using HYSYS. These correlations are specified as equations 1-3.

No rings
$$K_{eq} = -0.1424 + 0.03972 * M_w - 2.935 \times 10^{-4} * M_w^2 + 1.438 \times 10^{-6} * M_w^3 \quad (1)$$

$$\begin{aligned} \text{Isolated aromatic rings} \quad K_{eq} = & -131.8 + 6.177 * M_w - 1.124 \times 10^{-1} * M_w^2 + 2.935 \times 10^{-3} * M_w^3 \\ & - 4.326 \times 10^{-6} * M_w^4 + 7.375 \times 10^{-9} * M_w^5 \end{aligned} \quad (2)$$

$$\text{Naphthenic rings} \quad K_{eq} = -624.3 + 13.37 * M_w - 9.424 \times 10^{-2} * M_w^2 + 2.233 \times 10^{-4} * M_w^3 \quad (3)$$

The reaction mechanism in this study was generated using estimates of the Arrhenius frequency factors, E_o , and α for each reaction family from the literature. The literature values used for each of these parameters are shown in Table 1 of Appendix C. The model was constructed using an initial NBBM concentration of 2.0×10^{-2} mol/L (20.0 mg) and a reaction temperature of 420°C.

During model construction, the primary user-specified parameter which was varied was the threshold, ϵ . Varying this parameter significantly influenced both the types of *reactive* species and the total quantities of reactions and species included in the *reactive* model. The different models generated were evaluated based on three main criteria: 1) the inclusion of major reaction products as observed during experiment, 2) the ability to reproduce the temporal variations of the major products, and 3) the ability to obtain physically reasonable values for the subset of frequency factors which were optimized using experimental data.

Because it was not possible to obtain a mechanism of reasonable size for NBBM and NBBM/tetradecane that met these modeling goals, additional strategies were used to reduce the model size further. First, using the initial mechanism constructed as a guide, key reactive intermediates of high rank were identified and "seeded" into the initial reactant pool. Because these species no longer had to be formed at a rate greater than R_{min} to be included in the model, the threshold could be raised, targeting a smaller mechanism that achieved the modeling targets. In NBBM pyrolysis, it was necessary to seed the product of ipso substitution and subsequent β -scission of a benzyl radical at the internal phenyl position of NBBM. For binary mixture modeling, it was necessary to seed all of the allylic radicals from C_3 - C_{13} and another secondary radical for each olefin from C_5 - C_{13} . With these initial species pools, model building is currently in progress to identify the appropriate threshold that allows the modeling goals to be met.

V. Conclusions

In addition to the conclusions put forth in the individual manuscripts of Appendices A, B and C, we can draw some preliminary conclusions about the mechanistic modeling of neat NBBM and binary mixtures of NBBM and tetradecane. Phase behavior plays an important role in directing the chemistry of NBBM neat and in mixtures and therefore must be accounted for in modeling. By using automated model construction techniques that duplicated all reactions in the mechanism to describe chemistry in both the liquid and gas phases, allowing for transport between the phases and specifying distinct parameters for the reactions in the different phases, we were able to create a general framework for modeling two phase systems. Correlations were developed to specify the distribution coefficient of different compound classes as a function of molecular weight, and values for the mass transfer coefficients for transport from the vapor to the liquid phase were identified. Seeding was shown to be an important strategy for maintaining a manageable model size, particularly for the binary system in which the number of species was much larger even for a model describing primary products only.

VI. Path Forward

The extended project period will be devoted to completing the NBBM and NBBM/tetradecane modeling work. The user-defined threshold will be lowered until all products of interest are included in the model. Frequency factors for the gas phase reactions will be fixed at the values optimized from neat tetradecane modeling, and a small set of frequency factors for reactions in the liquid phase will be determined from neat NBBM modeling. The binary mixture reactions will therefore provide the opportunity to test the predictive capabilities of the binary model, as all parameters will be fixed based on the single component values. Furthermore, the ability to describe two phase systems during mechanism generation will be developed, allowing the assembly of mechanisms that are more tailored for the actual system under study.

VII. Manuscripts, Presentations and Publications

Broadbelt, L.J., De Witt, M.J. and Dooling, D.J., "Application of Computer Generation of Reaction Mechanisms Using Quantitative Rate Information to Hydrocarbon Pyrolysis", Symposium on Chemistry of Reactive Intermediates and Modeling in Hydrocarbon Conversion, American Chemical Society National Meeting, August, 1999.

De Witt, M.J., Dooling, D.J. and Broadbelt, L.J., "Computer Generation of Reaction Mechanisms Using Quantitative Rate Information", AIChE Chicago Local Section Annual University Night, April, 1999.

Broadbelt, L.J., De Witt, M.J., and Woo, O.S., "Understanding Degradation of Polymers Through Experiment and Mechanistic Modeling", SC Johnson Polymer, April, 1999.

Broadbelt, L.J., De Witt, M.J. and Dooling, D.J., "Computer Generation of Reaction Mechanisms Using Quantitative Rate Information", AIChE Spring Meeting, Houston, TX, March, 1999.

De Witt, M.J. and Broadbelt, L.J., "Binary Interactions Between Tetradecane and 4-(1-Naphthylmethyl) Bibenzyl During Low and High Pressure Pyrolysis", *in press Energy & Fuels*, 1999.

De Witt, M.J. and Broadbelt, L.J., "Binary Interactions Between High Density Polyethylene and 4-(1-Naphthylmethyl) Bibenzyl During Low Pressure Pyrolysis", *submitted to Energy & Fuels*, 1999.

De Witt, M.J., Dooling, D.J. and Broadbelt, L.J., "Computer Generation of Reaction Mechanisms Using Quantitative Rate Information: Application to Long-Chain Hydrocarbon Pyrolysis", *submitted to Ind. Eng. Chem. Res.*, 1999.

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IX. Appendices

Binary Interactions Between Tetradecane and 4-(1-Naphthylmethyl) Bibenzyl During Low and High Pressure Pyrolysis

Matthew J. De Witt and Linda J. Broadbelt*
Department of Chemical Engineering
Northwestern University
Evanston, Illinois 60208-3120

Abstract

Low and high pressure pyrolysis experiments employing tetradecane and 4-(1-naphthylmethyl)bibenzyl (NBBM) as model compounds for polyethylene and coal, respectively, were conducted at 420°C at different reactant loadings both neat and in binary mixtures. These reaction sets demonstrated that when reacted in binary mixtures, the conversion of tetradecane increased while the selectivities to primary products of NBBM were enhanced in the gas phase. Variation of the relative concentrations of the components revealed that the effect was indeed a chemical one and not simply a result of dilution. As

the polymer mimic to coal model compound ratio increased, there was a decrease in self-interactions of NBBM with minimal changes in the degradation products of tetradecane. Increasing the overall reaction pressure in the system through addition of an inert gas from atmospheric pressure to 2360 psig resulted in small decreases in reactant conversions and altered product distributions only slightly. Overall, the experiments carried out demonstrated that favorable interactions exist in the gas phase during coprocessing, and primary reaction pathways and mechanisms governing the interactions between the feedstocks were elucidated.

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 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. Tertiary recycling strategies include coprocessing of polymeric waste with other materials to potentially enhance reactivity and product selectivities through synergistic effects. One option for coprocessing is to react polymeric waste with coal under direct liquefaction conditions.⁵⁻⁷ Coprocessing of polymeric waste with coal may provide for simultaneous conversion of both feedstocks into high-valued fuels and chemicals.

Although the viability of coprocessing of polymeric waste with coal has been demonstrated,⁵⁻⁷ the complexity of real feedstocks obscures the nature of the interactions among them and makes it difficult to unravel the underlying reaction pathways, kinetics, and mechanism. The development of processes for coprocessing would benefit from greater fundamental understanding of constituent interactions. In order to begin to obtain this information which can aid in process optimization, a series of experiments using model compounds for coal and polyethylene, a voluminous component of polymeric waste, has been carried out. Neat and binary mixture pyrolysis reactions both at low and high pressures were a logical starting point since they provide valuable thermal baseline information to which experiments with additional components may be compared. Results from thermal degradation studies which have been conducted over a broad range of pressures and reactant loadings will be discussed.

Experimental

In order to obtain information about underlying reaction pathways, kinetics, and mechanism without the complicating effects of the macrostructure, experiments were performed using model compounds for both coal and high density polyethylene, a

voluminous component of mixed plastic waste. To mimic the structure of coal, 4-(1-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 was employed in this study.⁸⁻¹¹ The structure of NBBM with the main chain carbon-carbon bonds labeled A-E is depicted in Figure 1. Although numerous hydrocarbons may serve as appropriate model compounds for high density polyethylene, tetradecane, $C_{14}H_{30}$ (MW=198), was chosen as an appropriate compromise in reactant size.

The model compound experiments were 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 pyrex ampoules (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 ampoules were charged with the appropriate amount of reactant, purged with argon, and flame sealed. Pyrolyses were conducted at 420°C with reaction times ranging from 5-150 minutes. 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.

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 (TCD) 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 yields to be determined, were achieved using an HP 6890 GC/MS and HP 6890 GC equipped with a flame ionization detector (FID), respectively, each employing a Hewlett Packard 30 m crosslinked 5%-diphenyl-95%-dimethylsiloxane capillary column. The yield values were then used to calculate selectivity values for each product, which were defined as the ratio of the moles of the species formed to the moles of reactant converted.

For quantification of gaseous products, response factors for toluene and α -olefins and paraffins of carbon numbers of one to six were determined by using gaseous standards for each species. For liquid and solid products, response factors based on the external standard, biphenyl, were measured for representative species, while those for the remaining species were estimated using interpolation between these values. For linear hydrocarbons, calibration was performed using hexane, octane, and tetradecane. For species derived from the coal model compound, response factors were calculated for benzene, toluene, 1-naphthylphenylmethane, and NBBM.

At low reaction times, mass balances greater than 99% were obtained for all reaction sets. However, the mass balances diminished with increased reactant loading and extent of reaction, depending upon the reactants employed. For neat tetradecane pyrolysis, mass balances were greater than 94% for all data sets. The yields of n-pentane and 1-pentene are low since masking by the solvent caused difficulty in quantifying the liquid fraction of these species. The overall mass balance for neat NBBM pyrolysis reached a

minimum of 91% at the highest conversion. Mass balances for binary mixture reactions at varying reaction times were consistent with the trends observed during the neat reactions. The reproducibility for the majority of reaction sets in this study was better than $\pm 1\%$ and at maximum $\pm 3\%$. Therefore, the error bars for all figures presented in this paper are on the order of the symbol size used.

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) with nitrogen, and thermal degradation was conducted at 420°C for 20-150 minutes. 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 of known volume of 345 ml. Liquid and solid products were extracted by washing the glass liner and reactor with a total of 15 ml of methylene chloride. Product analysis was conducted using the same methods described for the low pressure experiments. Mass balances observed during high pressure reactions were slightly higher than those obtained at low pressures.

Results and Discussion

Low Pressure Reactions. Neat and binary mixture batch pyrolysis reactions of tetradecane and NBBM were conducted at low pressures. Neat reactions were conducted to identify the controlling degradation mechanism for each reactant and to provide baseline information for subsequent binary mixture reactions. Comparison of these reaction sets permitted the identification of the underlying feedstock interactions during coprocessing. The effects of altering both the initial reactant ratio and the overall reactant loading on the

conversions and product selectivities were also addressed for binary mixture reactions.

Representative experimental data from the various reaction sets are summarized in Tables 1-

3. Results and discussion of these reaction sets are reported in the following sections.

Neat Tetradecane Pyrolysis. Low pressure neat pyrolysis of tetradecane was conducted with initial loadings ranging from 6.2 to 27.8 mg (1.01×10^{-2} to 4.53×10^{-2} M). Simulation of the phase behavior for the reaction conditions in these studies was performed using the software package HYSIS employing the Peng-Robinson equation of state. These results indicated that at low pressures, all species were in the gas phase during tetradecane pyrolysis. A plot of conversion versus time for the different concentrations is provided in Figure 2. 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 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 using the integral method was 1.75.

Detailed product 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 ± 0.05 . The alkene which had the second highest selectivity was ethylene, and its yield as a function of conversion is plotted in Figure 3. As revealed in Figure 3, its yield was a decreasing function of initial reactant concentration, and its selectivity also decreased with increasing conversion and reactant

concentration. The selectivity achieved a maximum of 0.45 ± 0.02 at the lowest conversion and the lowest reactant loading, and the minimum selectivity of 0.20 ± 0.02 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 ± 0.02 and 0.12 ± 0.02 , respectively.

Paraffins in the C_3 - C_5 range were all formed with lower selectivities than their corresponding alkene. Propane, butane, and pentane all showed increases in yield and selectivity with increasing initial concentration. The yield of butane is plotted as a function of conversion in Figure 4 and is representative of this behavior. Methane displayed the opposite trend, decreasing with increasing reactant loadings. The trends for C_4 and C_5 paraffins as a function of carbon number were similar to those observed for the corresponding 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 ratio for the liquid products than for the gaseous products, with α -olefins predominating at the higher carbon numbers. The selectivity of α -olefins for the higher carbon numbers was relatively independent of reactant concentration. The yields of the corresponding paraffins, however, showed significant increases with increasing conversion and reactant loading, and the selectivities increased as the initial reactant loading was raised. These trends are shown for 1-undecene and n-undecane in Figure 5.

Overall, the product distributions were consistent with those reported previously for long-chain paraffin pyrolysis conducted at moderate temperatures and low pressures.¹²⁻¹⁶

As discussed in detail in these studies, thermolysis of long n-alkanes under mild conditions leads to high yields of gaseous products and α -olefins, with minor yields of n-alkanes smaller than the parent species. The pyrolytic degradation occurs through a combination of unimolecular and bimolecular free-radical reactions, with the relative rates depending upon the reaction temperature and substrate pressure. In particular, the controlling reaction mechanism can be rationalized by using a combination of the Rice-Herzfeld and Rice-Kossiakoff mechanisms, which are represented in Figure 6.¹²⁻¹⁴ The decomposition is initiated by carbon-carbon bond fission along the main chain to form two primary radicals. These primary radicals can then propagate through three main types of reactions: β -scission, intermolecular hydrogen abstraction, and intramolecular hydrogen abstraction. Isomerization through intramolecular hydrogen abstraction forms secondary radicals, which can undergo the same types of propagation reactions. If the secondary radical undergoes a β -scission, an α -olefin and a smaller primary radical are formed, and the primary radical can then undergo similar reactions until the resulting species is too small to further decompose. The high yields of terminal olefins and gaseous species, with smaller proportions of n-alkanes, observed in our work and the literature suggest that the dominant mode of propagation is isomerization of primary radicals followed by β -scission of secondary radicals. For the experimental studies presented in this paper, preliminary detailed kinetic modeling has been carried out and reveals that these mechanistic ideas are able to capture the experimental trends observed.¹⁷

The trends observed as a function of the initial reactant loading for the gaseous species 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 competitive with unimolecular reactions due to the increase in substrate concentrations. These bimolecular reactions lead to a reduction in the rate of formation of ethylene since there is a corresponding decrease in the relative population of primary radicals in the system. In addition, ethylene degradation rates are higher due to increased addition reactions. The increase in bimolecular reactions also results in a reduction in the number of sequential isomerization/ β -scission steps higher molecular weight radicals undergo. Consequently, there is an increase in the yields of long-chain alkanes at the expense of smaller species. This idea will be discussed further when the n-paraffin product trends with increasing reactant loadings are discussed.

The increase in the selectivities of gaseous n-alkanes at higher initial reactant concentrations can be explained by noting that secondary thermal cracking can occur as the number of intermolecular reactions increases, which would lead to an increase in the quantity of precursors for the formation of the gaseous species. In addition, 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.

The observed decrease in selectivity of α -olefins for carbon numbers greater than seven as reaction time increases can be rationalized by noting that these species undergo secondary reactions at longer reaction times. Reactions including initiation (primarily at the allylic position which ultimately results in the formation of propylene), intermolecular hydrogen abstraction, and radical addition reactions will lead to the disappearance of the longer alkenes. The formation rate of the olefins will also be reduced with increasing conversion, since there will be fewer precursors available for their formation.

As mentioned above, the increase in long paraffin yields with increasing conversion and loading can be explained using mechanistic arguments. By employing mechanistic modeling, it has been possible to estimate the effect of reactant concentration and conversion on the concentration of radicals in the system.¹⁷ It has been shown that although the total radical concentration increases with increasing reactant loading, the relative radical yields (the ratio of the total sum of radicals to the initial reactant loading) show the opposite trend. The reduction in the total normalized radical population as reactant concentration increases is predominantly due to reduction in yields of low molecular weight radical species. This suggests that the ability of higher molecular weight radicals to undergo sequential isomerization/ β -scission steps is diminished when hydrogen abstraction is a competing pathway with an enhanced rate. The increase in the alkane to alkene ratio and the reduction in small molecule yields, e.g., ethylene, are both consistent with this idea.

Neat NBBM Pyrolysis. Neat pyrolysis of NBBM provided the baseline to which subsequent binary experiments were compared. Although NBBM is primarily in the liquid phase at the reaction conditions employed, rudimentary experiments with a U-tube reactor configuration revealed non-negligible amounts of NBBM in the vapor phase. Accordingly, predictions of the phase behavior for the system using the same methodology described in the previous section indicated that approximately 98.4% of NBBM was in the liquid phase under reaction conditions. The major and minor products that were identified and quantified during NBBM pyrolysis are shown in Figure 7. Two of the major products from pyrolysis of NBBM were toluene and 1-methyl-4-(1-naphthylmethyl)benzene, each observed with a selectivity of greater than 0.28 at all reaction times studied. The other major product was 1-(2-phenylethenyl)-4-(1-naphthylmethyl)benzene, with an initial

selectivity of approximately 0.37 ± 0.01 , which decreased linearly with reaction time to 0.12 ± 0.01 at 150 minutes.

Minor selectivities were observed for a number of products from NBBM pyrolysis, the selectivity of which either increased or decreased with increasing reaction time. Two minor products, 4-methylbibenzyl and 1-(4-methylbenzyl)-4-(1-naphthylmethyl)benzene, were observed with initial selectivities of 0.055 ± 0.001 and 0.070 ± 0.001 , respectively. Each of these showed a reduction in selectivity as reaction time progressed, which is one possible indicator of subsequent decomposition reactions. Other minor products included 1,4-(bi-1-naphthylmethyl)benzene, 1-naphthylphenylmethane, naphthalene, 1-methylnaphthalene, 1-benzyl-4-(1-naphthylmethyl)benzene, 1-methyl-4-(2-phenylethenyl)benzene, p-xylene and bibenzyl which showed increased selectivities with reaction time. The selectivities to these species, which accounted for 7-10% of the total product spectra at low conversions, are depicted in Figure 8.

Mechanistic interpretation using the ideas put forth by Walter et al.¹¹ for pyrolysis of NBBM in the presence of high pressure of an inert gas successfully accounted for the observed product spectra from neat pyrolysis at low pressures in our study. The major exception, though, was the appearance of 1-(2-phenylethenyl)-4-(1-naphthylmethyl)benzene in our study, which was not observed by Walter et al.¹¹ As Walter et al.¹¹ reported, the formation of high yields of toluene and 1-methyl-4-(1-naphthylmethyl)benzene is consistent with the proposed mechanism involving fission of the bibenzyl linkage (bond D) in NBBM. This is the weakest bond in the molecule, since the radicals which are formed can be stabilized by the adjacent phenyl rings and will thus undergo homolysis most readily.¹⁸⁻²⁰ Initially, these radicals are stabilized through hydrogen abstraction from the bibenzyl linkage or the $-CH_2-$ unit linking the naphthyl and

center phenyl moieties of other NBBM molecules. Although the carbon-hydrogen bond strengths for these two sites are comparable (88 kcal/mol versus 84 kcal/mol)²¹, the majority of the chemistry controlling product formation occurs at the bibenzyl linkage. The radical which is formed through hydrogen abstraction at the $-CH_2-$ unit would not likely undergo β -scission or disproportionation and therefore predominantly acts as a site for hydrogen shuttling. Furthermore, products resulting from recombination of this radical were not observed, suggesting that steric hindrance precludes it or cleavage is likely.

Once a radical is formed on the bibenzyl linkage of NBBM, it can undergo various reaction pathways to form 1-(2-phenylethenyl)-4-(1-naphthylmethyl)benzene, a product not reported by Walter et al.¹¹ The formation of the unsaturated species in this study can be explained through analogy to explanations for the formation of stilbene during pyrolysis of 1,2-diphenylethane (1,2-DPE).^{18-20,22} During 1,2-DPE pyrolysis, Miller and Stein¹⁸ showed that once a radical is formed on the bibenzyl linkage, stilbene can be formed through two major and one minor pathway. Disproportionation of 1,2-DPE radicals directly forms stilbene, and recombination of two 1,2-DPE radicals, when followed by a hydrogen abstraction to form a radical which decomposes rapidly by β -scission, indirectly forms stilbene. The minor stilbene formation pathway is through β -scission of a hydrogen atom from a 1,2-DPE radical. It is likely that the formation of 1-(2-phenylethenyl)-4-(1-naphthylmethyl)benzene in our study occurs through analogous reaction pathways. However, it is assumed that the disproportionation and recombination reactions can occur with any radical in the system.

In addition to the aforementioned reaction pathways, free radical ipso-substitution reactions were also important routes for NBBM conversion and the formation of several minor products. Our observations were consistent with the free radical ipso-substitution

scheme as proposed by Walter et al.¹¹ An example of this type of reaction pathway is the addition of a benzyl radical to the 1-naphthyl position of a NBBM molecule followed by a β -scission of this intermediate to form 1-naphthylphenylmethane. This was shown to be a relevant minor reaction pathway in this study. Likewise, various radical attacks at the phenyl ring at bond C can explain the appearance of 1-(4-methylbenzyl)-4-(1-naphthylmethyl)benzene, 1,4-(bi-1-naphthylmethyl)benzene, and 1-benzyl-4-(1-naphthylmethyl)benzene. Overall, the main reaction families for NBBM pyrolysis are bond homolysis, hydrogen abstraction, radical ipso-substitution, β -scission, and radical disproportionation and recombination reactions.¹¹

Binary Mixture Pyrolysis. Reactions of binary mixtures of tetradecane and NBBM at low pressures revealed interactions between the reactants and synergistic effects. Reactions were conducted varying both the initial reactant ratio and the overall reactant loading. As observed in Figure 9, the conversion of tetradecane was significantly enhanced for all of the reactions which were conducted in the presence of NBBM. The pseudo-first order rate constants for tetradecane degradation increased from $3.6 \times 10^{-5} \text{ s}^{-1}$ for the 6.2 mg loading to $6.3 \times 10^{-5} \text{ s}^{-1}$ and $6.9 \times 10^{-5} \text{ s}^{-1}$ in the presence of 10.0 and 20.0 mg of NBBM, respectively, and from $5.2 \times 10^{-5} \text{ s}^{-1}$ to $8.6 \times 10^{-5} \text{ s}^{-1}$ for the 12.3 mg loading with the addition of 20.0 mg of NBBM. These increases were rationalized in terms of kinetic coupling.²³ 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}).²⁰ 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 competitively 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 decomposition reactions similar to those observed during neat pyrolysis.

Although analogous rate constants measured in the gas phase and reaction path degeneracy suggest that hydrogen abstraction at benzylic sites is slightly faster than aliphatic sites,²² phase behavior favors hydrogen abstraction from tetradecane. During coprocessing, there are reactions occurring in both the gas and the liquid phases. Phase behavior predictions indicated that during binary mixture reactions at the highest reactant loadings, approximately 97.4% of NBBM and 4.1% of tetradecane were in the liquid phase. When NBBM homolytically cleaves, the smaller (primarily benzyl) radicals are able to partition into the gas phase; during neat reactions, there are few viable reaction pathways in the gas phase due to the low vapor fraction of NBBM. When these species enter the gas phase during binary mixture reactions, though, they will encounter high relative concentrations of tetradecane, which will favor NBBM-tetradecane interactions. Once a tetradecane radical is formed, it will follow a degradation mechanism very similar to that observed during neat pyrolysis due to the relative high concentrations of tetradecane in the gas phase. Overall, this will result in an increase in tetradecane reactivity since initiation to form tetradecane radicals through hydrogen abstraction will occur more readily than carbon-carbon bond fission.

Both the initial charge of each reactant and the overall reactant loading strongly influenced reactant conversions and product selectivities during coprocessing. The conversion of tetradecane was most dramatically affected by both of these factors during the binary experiments. In order to quantify the effect of increasing the initial NBBM to tetradecane ratio, the Bin(1:1) and Bin(1:2) reactions were compared. As the loading of NBBM was increased, the rate of conversion of tetradecane was enhanced. This result is consistent with an increase in the effective radical concentration in the system with a higher loading of NBBM, which in turn increases the conversion of the polymer mimic. The rate enhancement observed during neat pyrolysis for tetradecane as the loading was increased is

also observed when NBBM is present. The rate of conversion of tetradecane was enhanced at a constant NBBM loading, as the rate was higher for the Bin(2:2) than for Bin(1:2). However, a reduction in conversion was observed at long reaction times. The highest rate of conversion was obtained when both factors contributed to the disappearance of tetradecane, as the Bin(2:2) showed the largest rate of conversion. As the total reactant concentration increases, the rate of bimolecular reactions increases. The rate of hydrogen abstraction from tetradecane by NBBM-derived radicals increases with increasing concentrations, thus increasing the rate of tetradecane degradation further. Therefore, increasing both the molar ratio of NBBM to tetradecane and the total molar concentration results in an enhancement of the polymer model compound reactivity.

Although changes in concentration influenced the major products of NBBM, the conversion of NBBM was not strongly affected as shown in Figure 10. As discussed previously, the degradation of the coal model compound primarily occurs through the thermolysis of bond D. As described above, the radicals afforded will react selectively with tetradecane rather than with other NBBM molecules if they diffuse into the gas phase, and therefore, the consumption of NBBM associated with self-interactions through hydrogen abstraction will be diminished. During the neat NBBM studies, the gas phase radicals, which primarily consist of benzyl and to a lesser extent the complimentary radical formed during homolytic fission of bond D, can undergo recombination reactions to reform NBBM. During coprocessing, however, the radicals evolved from bond D scission that interact with tetradecane will not have the opportunity to recombine to form NBBM. The data suggest that a balance is achieved between these two effects and consequently, the conversion of NBBM is essentially unchanged.

The overall mechanisms for degradation of tetradecane and NBBM were similar for the neat and binary mixture experiments, but some differences in product selectivities were

observed as a result of binary interactions. As with the variations in tetradecane conversions, these differences also 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 on tetradecane-derived products can be observed by comparing the C₁₄-6.2 and Bin(1:1) 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 ethylene and methane selectivities displayed the most significant differences with the addition of NBBM. The dependence of the selectivity of ethylene as a function of concentration and the addition of the NBBM co-reactant is shown in Figure 11. In addition to the reduced formation of ethylene and methane, the yields of α -olefins also decreased while the selectivities of longer paraffins increased. As previously described, these trends are consistent with those observed as the initial concentration of tetradecane in the neat experiments was raised, and the changes are consistent with a reduction in repeated unimolecular degradation steps of higher molecular weight radicals.

With the addition of tetradecane, the selectivity to NBBM-derived primary products significantly increased. Since abstraction of hydrogen from tetradecane is favored due to phase behavior, NBBM radicals are capped and stable before undergoing secondary reactions. This effect on the overall product yields can be discerned from Figures 12 and 13. The radicals which are formed from cleavage of the bibenzyl bond in NBBM will abstract hydrogen from tetradecane with higher selectivity and afford higher yields of toluene and its complement. This behavior is also illustrated by the trends observed for the selectivity of 1-(2-phenylethenyl)-4-(1-naphthylmethyl)benzene, the species produced as NBBM-derived radicals are capped during neat pyrolysis, which is shown in Figure 14. The selectivity to this species decreases with the addition of tetradecane at longer reaction times. This observation, coupled with the increased selectivities for primary products of

NBBM, indicates that NBBM-derived radicals are abstracting hydrogen from tetradecane rather than from NBBM. These favorable interactions between feedstocks are even more apparent in the selectivity trends of other NBBM-derived products, such as 1-naphthylphenylmethane, a product formed through secondary reactions. Since the benzyl radicals that would lead to formation of 1-naphthylphenylmethane via ipso-substitution are shuttled away from NBBM with the addition of tetradecane, its selectivity decreases.

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. As stated above, this behavior can be explained by noting that there is reduction in the ability of tetradecane-derived radicals to undergo repeated unimolecular transformations under these reaction conditions.

Increasing the molar loading of tetradecane while keeping the coal model compound loading constant resulted in little change in the tetradecane-derived product distributions. The differences in conversion of tetradecane in the Bin(1:2) and Bin(2:2) reaction sets are similar to those for the C₁₄-6.2 and C₁₄-12.3 experiments, indicating that the primary role of NBBM under such conditions is to enhance the rate of initiation but not to alter the subsequent decomposition pathways of tetradecane. Therefore, 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.

It has been shown that during low pressure co-reaction of coal and polymer model compounds, favorable interactions between reactants exist. 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, increases 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.

High Pressure Reactions. A series of high pressure reactions was conducted to determine the influence of overall system pressure on the reaction mechanism and kinetics. The same total reactant molar concentrations used during the low pressure sets were employed when possible, but it was necessary to perform some reactions with increased concentrations due to analytical limitations. Representative experimental data from the various reaction sets are shown in Tables 1-3. Results and discussion of the neat and binary mixture experiments in the presence of an inert gas at high pressure are reported in the following sections.

Neat Tetradecane Pyrolysis. High pressure pyrolysis experiments of tetradecane were conducted using the methods described in the experimental section with reactant loadings varying between 16.5 and 53.2 mg. The reaction set C₁₄-16.5 will not be included in this discussion since it was not possible to fully quantify n-alkanes due to the low reactant loading and the amount of solvent required for extraction. Therefore, discussion will focus on the C₁₄-32.7 and C₁₄-53.2 reaction sets and comparison of the results to their low pressure counterparts, C₁₄-12.3 and C₁₄-20, respectively. It should be noted that the high pressures for the reactions discussed in the following sections are due to the inert gas, not an increase in the quantity of substrate charged to the system. Furthermore, simulation of the phase behavior for the reaction conditions employed indicated that tetradecane was exclusively in the gas phase during reaction. Therefore, the reaction sets that will be discussed are not analogous to the high pressure liquid phase pyrolysis of long-chain

paraffins described to some extent in the literature.²⁴⁻²⁷ Few studies on the effects of increasing inert pressure on gas phase long-chain hydrocarbon pyrolysis have been carried out; thus there is little information available in the literature from which to draw comparisons.^{28,29}

Comparison of tetradecane conversion as a function of reactant concentration and total reaction pressure is shown in Figure 15. 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 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 selectivities of each of these were significantly reduced for the high pressure reactions, with the C₁₄-53.2 reaction set having the lowest values. 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 bimolecular reactions can be enhanced substantially due to two effects: the ability of third bodies to dissipate the energy

of the reactants and the effect of increasing pressure to promote "cage" effects.³⁰ Third bodies can substantially improve rates of exothermic reactions, particularly recombination reactions, by dissipating the energy of the reactants that is released during reaction.³⁰ In addition to dissipating the energy evolved during reaction, high concentrations of inert gas lead to an enhancement in bimolecular reactions due to the ability to increase the frequency of collisions of reacting species by reducing their ability to migrate away from each other.^{30,31} The observations in our studies at high pressures are similar to the "cage" effects described during liquid phase reactions, which would be the limiting case at extremely high pressures.^{19,31} The combination of the two effects would explain the absence of methane and reduced yields of light hydrocarbons for the high pressure reactions. Radical precursors which could potentially lead to the formation of light hydrocarbons will undergo bimolecular reactions with higher frequency. The combination of these species with themselves, other radicals, and molecular species would lead to increased yields of n-alkanes of higher carbon numbers and reduced selectivities to longer α -olefins. The observation that the reactant conversion is not significantly affected by reaction pressure can be explained by noting that although recombination rates would be enhanced, bimolecular propagation reactions, which lead to the conversion of tetradecane, increase.

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 and long α -olefins declined, while the yields of n-alkanes increased. It should be noted, though, that the magnitude of the selectivity differences was larger for the high pressure reaction. These trends can again be rationalized in terms of a relative decrease in repeated unimolecular radical transformations with increasing reactant loadings, in addition to the contributions of inert molecules to bimolecular reaction rates at high pressure.

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 with binary mixtures. Phase simulations revealed that the percent of NBBM in the vapor phase increased at higher total pressures to a value of approximately 12% for these reaction conditions. The phase behavior with respect to increasing system pressure goes against intuition, in which one would expect high molecular weight species to more selectively partition into the liquid phase. However, the increase in system pressure is due to the addition of an inert gas, not the addition of reactant. Therefore, even though the vapor pressure of NBBM is quite low and thus its partial pressure in the vapor phase is also low, the total number of moles of NBBM in the gas phase to establish thermodynamic equilibrium is not insignificant and increases as the total pressure increases.

The overall conversion for NBBM, which is consistent with values reported by Walter et al.¹¹ for similar reaction conditions, was reduced during the high pressure experiments compared to the low pressure reaction sets, as shown in Figure 16. Two of the major products formed during high pressure pyrolysis were toluene and 1-methyl-4-(1-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-(1-naphthylmethyl)benzene. Minor selectivities were observed for a number of species, all of which were reported above for low pressure NBBM pyrolysis.

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 yields were for the three major products. The yields of the bond D product pair were almost equivalent during the low pressure experiments but

were clearly significantly different for the high pressure reactions, as shown in Figure 17. Toluene showed an increase in yield for the high pressure reactions, while 1-methyl-4-(1-naphthylmethyl)benzene showed diminishing yields. The selectivity to 1-(2-phenylethenyl)-4-(1-naphthylmethyl)benzene was also reduced during the high pressure reactions compared to the low pressure runs. The yields of the minor products were essentially unchanged with the exception of 1-(4-methylbenzyl)-4-(1-naphthylmethyl)benzene, 4-methylbibenzyl, and naphthalene, which showed slightly higher yields during the high pressure reactions.

The reduction of NBBM conversion can be rationalized by taking into account the phase behavior at high pressures and the ability of inert molecules to facilitate bimolecular reactions. Since the vapor fraction of NBBM increases at high pressure, this also implies that the majority of the NBBM-derived radicals, which have higher vapor pressures than the parent compound, will also be in even higher proportion in the gas phase. Accordingly, the concentration of 1-methyl-4-(1-naphthylmethyl)benzene radicals in the gas phase will be significantly enhanced with high concentrations of inert gas. Without the availability of high concentrations of NBBM as in the low pressure reactions, hydrogen abstraction reaction rates will diminish and recombination rates, mediated by inert molecules, will become more likely. This scenario, along with increased recombination of benzyl and 1-methyl-4-(1-naphthylmethyl)benzene radicals, explains the decreased conversion of NBBM, which is consumed to a lesser extent by hydrogen abstraction. This also explains the decrease in the selectivities to 1-methyl-4-(1-naphthylmethyl)benzene and 1-(2-phenylethenyl)-4-(1-naphthylmethyl)benzene, since both of which rely on a hydrogen abstraction step for their formation.

Although the same logic would imply that the selectivity to toluene should also decrease, postulating an additional reaction pathway for its formation helps to resolve this

conflict. Initially, in order to explain the increase in toluene yields, an overall phenyl ring balance was calculated. The balances for the low and high pressure reaction sets were essentially equivalent, indicating that toluene was being formed at the expense of 1-methyl-4-(1-naphthylmethyl)benzene and 1-(2-phenylethenyl)-4-(1-naphthylmethyl)benzene. Under the scenario presented in the previous paragraph, two reaction types in the gas phase that would be enhanced at high pressures are radical recombination and radical addition. As stated above, the higher overall inert pressures result in both increased rates of bimolecular reactions and higher proportions of larger molecular weight species in the gas phase. One particular reaction pathway which will be enhanced at high pressures is the recombination of a 1-methyl-4-(1-naphthylmethyl)benzene radical and a radical on the ethyl linkage of NBBM. The product of this recombination reaction possesses a tertiary carbon, providing a center for facile bond fission, and a benzyl radical which would ultimately result in the formation of toluene could be easily released. These ideas are captured in Figure 18 and comprise a viable reaction pathway for the increased selectivity to toluene with a concomitant reduction in the yields of 1-methyl-4-(1-naphthylmethyl)benzene and 1-(2-phenylethenyl)-4-(1-naphthylmethyl)benzene. In addition to recombination reactions, radical addition is also enhanced. Addition of a 1-methyl-4-(1-naphthylmethyl)benzene radical to the alkene present in the highest yield, 1-(2-phenylethenyl)-4-(1-naphthylmethyl)benzene, can ultimately form the intermediate species shown in Figure 18, and a benzyl radical may be released as discussed above. This type of radical addition would lead to a further enhancement in the selectivity of toluene at the expense of the other major products.

Additional experimental evidence supported the hypothesis that recombination reactions of NBBM-derived species were favored as a result of vapor-liquid partitioning at high pressure. Comparison between high and low pressure reaction sets revealed that there was a decrease in the sum of the naphthyl moieties for the high pressure reactions. In

addition, there was a larger quantity of higher molecular species as evidenced by an increase in products with longer chromatographic retention times. It was not possible to identify all of these high molecular weight compounds that eluted at times greater than NBBM, but through mass spectrometry it was possible to identify 4,4'-(bi-1-naphthylmethyl)bibenzyl, a product formed through either radical recombination or the radical addition pathway presented in the previous paragraph. The difference in naphthyl ring balances is attributed to the increase in the yields of high molecular weight products which were not quantified, which result from reaction mechanisms similar to the one presented in Figure 18. The selectivity of bibenzyl, a minor product formed during NBBM pyrolysis, remained relatively constant during the high pressure experiments. This can be rationalized by noting that although the rate of recombination is enhanced at high pressures, the concentration of radicals other than benzyl radicals in the gas phase significantly increases. These effects result in minimal changes in the observed bibenzyl yields.

With the exceptions discussed above, the reaction pathways and mechanism for the neat pyrolysis of NBBM are similar for both high and low pressure reaction conditions, as evidenced by the similar product yields. Overall, the only significant difference is that higher molecular weight species are more selectively partitioned into the vapor phase at high pressures, which leads to an increase in recombination and radical addition reactions. These reactions result in increased yields of toluene at the expense of 1-methyl-4-(1-naphthylmethyl)benzene and 1-(2-phenylethenyl)-4-(1-naphthylmethyl)benzene primarily.

Binary Mixture Pyrolysis. Pyrolysis of binary mixtures of tetradecane and NBBM at high pressures showed interactions between the reactants and synergistic effects similar to those observed during the low pressure experiments. Phase behavior predictions indicated that during binary mixture reactions at the highest reactant loadings, approximately 87.5% of NBBM and 1.2% of tetradecane were in the liquid phase. As observed in Figure 19, the

conversion of tetradecane was once again significantly enhanced for all of the reactions which were conducted in the presence of NBBM. For the high pressure reactions, the pseudo-first order rate constant for tetradecane degradation increased from $4.2 \times 10^{-5} \text{ s}^{-1}$ to $1.0 \times 10^{-4} \text{ s}^{-1}$ for the 32.7 mg loadings, which corresponded to the same molar concentration as 12.3 mg loadings for the low pressure reactions. The reactivity of NBBM was relatively unaffected during coprocessing, which is consistent with observations from low pressure experiments, indicating that the primary degradation mechanism for NBBM remained unchanged.

The changes in the trends for tetradecane-derived products during binary mixture reactions at high pressures were similar to those observed during the low pressure reaction sets. During coprocessing, the yields of light hydrocarbons and α -olefins diminished while the selectivity to longer paraffins increased. As was the case at low pressures, upon initiation of an NBBM molecule, the radicals which are formed will selectively abstract hydrogen from a tetradecane molecule, initiating a tetradecane radical. Once initiated, these species will undergo degradation mechanisms similar to those observed during neat reactions.

The effect of increasing the overall tetradecane loading at a constant NBBM loading was investigated by comparing the Bin(2:2) HP and Bin(3.2:2) HP reaction sets. The product selectivities for the α -olefins were relatively unaffected as the reactant ratio changed. However, there was a more significant increase in paraffin selectivities with increased loadings of the polymer mimic at high pressures than there was at low pressures. This increase was a result of both the increase in the relative amount of tetradecane radicals and the facilitation of bimolecular reactions at high inert pressures.

The alterations to the degradation mechanism for NBBM during coprocessing at high pressures were similar to those observed for reactions at reduced pressures. As tetradecane was introduced, there was a decrease in secondary and tertiary reactions, with an increase in the yield of 1-methyl-4-(1-naphthylmethyl)benzene. The relative selectivity of toluene, however, remained nearly constant. The former observations were attributed to the stabilization of NBBM-derived radicals through abstraction of readily available hydrogen from tetradecane molecules, which also resulted in enhanced tetradecane reactivities. The relatively constant value of toluene selectivity during coprocessing can be explained by considering how the relative reaction rates of competing mechanistic steps change during coprocessing. The rate of recombination of NBBM-derived intermediates diminishes as evidenced by the reduced yields of NBBM-derived secondary and tertiary products. In particular, the increased yields of 1-methyl-4-(1-naphthylmethyl)benzene indicate that the recombination mechanism between an NBBM radical and 1-methyl-4-(1-naphthylmethyl)benzene radicals discussed above for neat NBBM pyrolysis at high pressure is lowered. Therefore, there will be a decrease in the formation of toluene from this pathway. However, the yield of toluene through favorable interactions with the polymer mimic is increased due to stabilization of benzyl radicals by tetradecane before they can undergo further reactions. It is suggested that these two effects balance each other for binary mixtures at high pressures, resulting in relatively constant yields of toluene.

The result of increasing the ratio of the polymer mimic to the coal model compound on NBBM-derived products was the same as that observed at low pressures. As the tetradecane loading increased at a constant NBBM concentration, the selectivity to products formed through self-interactions of NBBM decreased. With a higher concentration of tetradecane, there is an increased proportion of reactions between NBBM and tetradecane-derived molecules and intermediates, which leads to the altered distributions of NBBM-derived products. This is consistent with the behavior at low pressures and is illustrated

for 1-(2-phenylethenyl)-4-(1-naphthylmethyl)benzene in Figure 20 as a representative example at high pressure, indicating that NBBM-derived radicals selectively react with tetradecane.

Coprocessing of tetradecane and NBBM at high pressures resulted in favorable interactions similar to those observed for reactions conducted at low pressures. The reactivity of tetradecane was significantly enhanced, while the degradation pathways for NBBM remained relatively unaffected. The only significant differences in the trends of the product spectra were that increased yields of longer paraffins were observed and a relatively constant selectivity to toluene was obtained during coprocessing at high pressures. Overall, comparison of the experiments conducted at low and high pressures demonstrated that coprocessing provides similar and favorable interactions in both pressure regimes.

Conclusions

Recent investigations have demonstrated the feasibility of coprocessing of coal with polymers. In this study, feedstock interactions were observed using model compounds 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 in the gas phase, which in turn increased the rate of tetradecane conversion.

At low pressures, the initial loading of each reactant and the overall loadings 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 a shift in the products towards longer paraffins. The increase in high molecular weight paraffin yields was attributed to a relative reduction of repeated unimolecular radical transformations with increasing reactant loadings. Increasing the initial charge of both reactants resulted in a significant enhancement of tetradecane reactivity. The primary product yields from NBBM were essentially identical 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 conducted 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.

As the overall system pressure was increased, small changes in the relative rates of competing reaction pathways for NBBM and tetradecane decomposition were observed. For neat pyrolysis of tetradecane at high pressures of an inert gas, the yield of normal paraffins was increased at the expense of lighter hydrocarbons and α -olefins. These observations were attributed to enhancement in the rate of bimolecular reactions for tetradecane-derived radicals due to the ability of high concentrations of inert molecules to facilitate energy transfer and to promote "cage" effects. With respect to neat NBBM-derived products, there was an increase in toluene formation at high pressures. It is likely that this occurred mainly through recombination of radical species of NBBM and 1-methyl-4-(1-naphthylmethyl)benzene, or radical addition of a 1-methyl-4-(1-naphthylmethyl)benzene radical to 1-(2-phenylethenyl)-4-(1-naphthylmethyl)benzene, and

subsequent cleavage of a benzyl radical. The rates for these reactions were enhanced at high pressures due to the phase behavior of the system. For binary mixture reactions at high pressures, the favorable interactions observed at low pressures were still realized, with only slight enhancement of paraffin yields and constant yields of toluene being observed.

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Table 1: Representative Experimental Data for Neat Tetradecane Pyrolysis Conducted at Low and High Pressure

Reaction Set	6.2	6.2	12.3	12.3	20	20	27.8	27.8	32.7-HP	32.7-HP	53.2-HP	53.2-HP
Reaction Time (min)	40	120	40	120	40	120	40	120	HP	HP	HP	HP
Pressure ^a	LP	LP	LP	LP	LP	LP	LP	LP	HP	HP	HP	HP
C ₁₄ H ₃₀ Loading (mg)	6.4	6.2	12.3	12.2	19.7	20.2	27.6	27.7	32.5	32.8	53.0	52.8
C ₁₄ H ₃₀ Conversion	0.10	0.24	0.11	0.32	0.11	0.32	0.14	0.35	0.11	0.29	0.12	0.30
Product Yield (x10 ³) ^b												
methane	2.55	6.98	2.46	6.98	2.23	6.60	1.97	5.78	0.00	0.00	0.00	4.28
ethylene	4.04	9.77	3.92	9.33	3.58	8.00	3.05	6.35	1.73	4.95	1.41	7.55
ethane	4.05	10.27	4.61	12.14	4.89	12.64	4.61	11.69	2.71	7.09	2.44	8.92
propylene	3.43	10.00	4.21	12.60	4.75	13.32	4.56	12.30	2.79	8.14	2.64	6.26
propane	1.49	4.36	2.47	7.10	3.33	8.87	3.54	9.22	1.98	5.10	2.25	4.70
1-butene	1.71	4.59	2.04	5.66	2.35	6.03	2.24	5.77	1.71	4.39	1.53	3.71
n-butane	0.18	1.34	0.73	2.58	1.17	3.68	1.34	4.22	1.13	2.67	1.17	3.91
1-pentene	1.22	3.18	1.45	3.92	1.66	4.04	1.50	3.80	1.28	3.89	1.30	2.10
n-pentane	0.05	0.45	0.11	0.95	0.42	1.45	0.49	1.71	0.29	1.54	0.68	5.26
1-hexene	1.43	3.12	1.73	4.13	2.43	5.21	2.53	5.39	2.08	4.80	1.98	1.45
n-hexane	0.00	0.00	0.00	0.18	0.16	0.42	0.28	0.71	0.29	0.74	0.28	3.39
1-heptene	0.82	1.80	1.18	2.68	1.78	3.62	1.67	3.35	1.48	2.94	1.42	1.13
n-heptane	0.00	0.00	0.00	0.26	0.20	0.57	0.25	0.69	0.39	0.71	0.52	2.60
1-octene	0.93	2.16	1.22	2.84	1.51	2.99	1.54	3.02	1.23	2.02	1.11	0.76
n-octane	0.00	0.00	0.00	0.25	0.08	0.42	0.19	0.57	0.19	0.47	0.35	1.86
1-nonene	0.96	2.07	1.08	2.49	1.30	2.51	1.38	2.60	0.87	1.43	0.95	0.54
n-nonane	0.00	0.00	0.00	0.21	0.00	0.34	0.15	0.47	0.20	0.27	0.27	1.74
1-decene	0.94	1.91	1.03	2.29	1.22	2.27	1.28	2.31	0.88	1.43	0.95	0.48
n-decane	0.00	0.04	0.00	0.07	0.11	0.28	0.15	0.38	0.15	0.24	0.27	1.55
1-undecene	0.82	1.65	0.90	1.93	1.04	1.93	1.08	1.93	0.79	1.31	0.85	0.46
n-undecane	0.00	0.09	0.00	0.15	0.09	0.25	0.14	0.33	0.17	0.25	0.26	1.45
1-dodecene	0.79	1.54	0.86	1.75	0.97	1.78	1.00	1.75	0.75	1.25	0.81	0.10
n-dodecane	0.00	0.00	0.00	0.00	0.00	0.05	0.04	0.08	0.00	0.05	0.04	0.34
1-tridecene	0.18	0.36	0.19	0.40	0.21	0.40	0.22	0.40	0.18	0.29	0.19	0.05
n-tridecane	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.04	0.00	0.00	0.02	0.05

(a) LP: Low pressure, HP: High pressure. (b) Product yield defined as: (moles species i formed)/(initial moles tetradecane).

Table 2: Representative Experimental Data for Tetradecane-Derived Products During Binary Mixture Pyrolysis

Reaction Set	(1:1) ^a	(1:1)	(1:2)	(1:2)	(2:2)	(2:2)	(2:2)-HP	(2:2)-HP	(3:2:2)-HP	(3:2:2)-HP
Reaction Time (min)	40	120	40	120	40	120	40	120	40	120
Pressure ^a	LP	LP	LP	LP	LP	LP	HP	HP	HP	HP
C ₁₄ H ₃₀ Loading (mg)	6.1	6.4	6.4	6.3	12.2	12.2	32.5	32.7	53.0	53.0
C ₁₄ H ₃₀ Conversion	0.19	0.38	0.22	0.42	0.26	0.48	0.23	0.44	0.24	0.47
NBBM Loading (mg)	10.1	9.9	19.9	19.9	20.0	20.0	53.0	53.1	53.0	53.1
Product Yield (x10 ²) ^b										
methane	3.95	9.86	3.99	9.88	3.92	9.99	0.00	0.00	0.00	0.00
ethylene	6.01	11.48	5.83	9.89	5.39	9.09	2.86	6.61	2.52	5.34
ethane	7.65	17.40	7.72	17.35	8.17	18.67	5.08	12.53	5.07	12.59
propylene	6.99	16.49	6.67	14.90	7.76	16.60	4.95	11.26	4.97	11.78
propane	4.32	10.38	4.31	10.67	5.63	13.28	4.05	9.14	4.42	10.96
1-butene	3.49	7.17	3.40	6.49	3.75	7.14	2.84	5.80	2.86	5.81
n-butane	1.51	4.31	1.61	4.81	2.21	6.39	2.45	5.72	2.78	7.02
1-pentene	2.48	4.82	2.40	4.28	2.51	4.72	2.41	4.75	2.40	4.71
n-pentane	0.84	1.79	0.71	2.18	0.89	2.89	1.54	3.64	1.77	4.54
1-hexene	2.69	5.53	3.27	5.23	3.58	6.09	3.33	5.53	3.52	5.64
n-hexane	0.00	0.84	0.43	1.13	0.57	1.80	1.20	2.67	1.54	3.53
1-heptene	1.64	3.36	1.85	2.85	2.22	3.41	1.94	2.94	2.16	3.31
n-heptane	0.00	0.56	0.28	0.79	0.35	1.18	0.92	1.84	1.18	2.67
1-octene	1.73	3.15	1.75	2.58	1.92	2.90	1.61	2.18	1.84	2.40
n-octane	0.00	0.53	0.25	0.92	0.35	1.13	0.82	1.59	1.04	2.09
1-nonene	1.65	2.72	1.52	2.15	1.81	2.33	1.22	1.38	1.38	1.56
n-nonane	0.00	0.00	0.23	0.70	0.32	0.93	0.61	0.99	0.83	1.48
1-decene	1.56	2.48	1.35	1.89	1.56	1.98	1.17	1.32	1.30	1.45
n-decane	0.00	0.40	0.19	0.63	0.26	0.80	0.57	0.88	0.75	1.31
1-undecene	1.29	1.97	1.12	1.42	1.31	1.49	1.02	1.12	1.11	1.20
n-undecane	0.00	0.37	0.19	0.50	0.24	0.65	0.56	0.76	0.71	1.15
1-dodecene	1.22	1.77	1.03	1.22	1.19	1.29	0.96	1.03	1.03	1.10
n-dodecane	0.00	0.00	0.05	0.19	0.06	0.24	0.13	0.29	0.13	0.28
1-tridecene	0.26	0.39	0.24	0.28	0.27	0.26	0.21	0.25	0.24	0.28
n-tridecane	0.00	0.00	0.00	0.10	0.00	0.12	0.06	0.17	0.08	0.22

(a) LP : Low pressure, HP : High pressure. (b) Product yield defined as: (moles species i formed)/(initial moles tetradecane).
(c) (a:b) denotes ratio of a moles of tetradecane to b moles of NBBM loaded, referenced to 1.0E-2 M of NBBM corresponding to a value of b = 1.

Table 3: Representative Experimental Data for NBBM-Derived Products During Low and High Pressure Pyrolysis

Reaction Set	N-20	N-20	N-53.2	N-53.2	(1:1) ^a	(1:1)	(1:2)	(1:2)	(2:2)	(2:2)	(2:2)-HP	(2:2)-HP	(3:2:2)-HP	(3:2:2)-HP
Reaction Time (min)	40	120	40	120	40	120	40	120	40	120	40	120	40	120
Pressure ^a	LP	LP	HP	HP	LP	LP	LP	LP	LP	LP	HP	HP	HP	HP
NBBM Loading (mg)	20.3	20.3	53.0	52.9	10.1	9.9	19.9	19.9	20.0	20.0	53.0	53.1	53.0	53.1
NBBM Conversion	0.23	0.65	0.16	0.51	0.26	0.61	0.23	0.61	0.24	0.61	0.15	0.50	0.21	0.51
C ₁₄ H ₃₀ Loading (mg)	0.0	0.0	0.0	0.0	6.1	6.4	6.4	6.3	12.2	12.2	32.5	32.7	53.0	53.0
Product Yield (x10 ³) ^b														
toluene	7.58	23.14	6.51	23.80	10.16	27.50	8.95	25.29	9.07	26.73	6.28	22.76	7.86	23.91
ethylbenzene	0.00	0.41	0.00	0.23	0.00	0.65	0.05	0.77	0.17	1.16	0.14	0.84	0.25	1.15
p-xylene	0.00	1.12	0.00	0.51	0.00	1.21	0.07	1.33	0.18	1.63	0.11	1.09	0.17	1.38
naphthalene	0.23	1.18	0.17	0.95	0.20	1.21	0.25	1.59	0.33	2.25	0.26	1.99	0.29	2.13
1-methylnaphthalene	0.26	1.52	0.17	0.89	0.31	1.42	0.31	1.48	0.34	1.57	0.26	1.08	0.33	1.19
bibenzyl	0.09	0.41	0.06	0.31	0.00	0.27	0.08	0.32	0.08	0.28	0.04	0.23	0.04	0.21
4-methylbibenzyl	1.10	3.22	0.82	2.85	1.15	2.82	1.25	3.57	1.34	4.05	1.16	3.82	1.37	3.99
1-methyl-4-(2-phenylethenyl)-benzene	0.09	0.98	0.06	0.53	0.00	0.73	0.10	0.68	0.10	0.51	0.07	0.35	0.09	0.30
1-naphthylphenyl	0.81	4.24	0.52	2.79	0.72	2.55	0.78	3.15	0.71	2.54	0.46	1.90	0.50	1.57
methane														
1-methyl-4-(1-A)benzene ^c	7.63	19.75	4.70	12.55	9.76	25.06	8.78	22.02	9.01	23.34	5.43	15.09	6.34	16.27
1-benzyl-4-(1-A)benzene	0.33	2.74	0.17	1.78	0.26	1.37	0.28	1.91	0.29	1.55	0.17	1.27	0.18	0.94
1-(4-methylbenzyl)-4-(1-A)benzene	1.37	2.95	1.28	3.18	0.89	1.79	1.33	2.77	1.25	2.58	1.23	2.85	1.21	2.41
1-(2-phenylethenyl)-4-(1-A)benzene	7.18	11.17	4.26	9.47	7.67	7.73	6.86	7.12	6.34	4.63	4.31	4.88	4.24	3.63
1,4-(bi-1-A)benzene	0.83	4.11	0.34	3.15	0.70	2.14	0.76	2.84	0.68	2.16	0.36	2.01	0.35	1.44

(a) LP: Low pressure, HP: High pressure. (b) Product yield defined as: (moles species i formed)/(initial moles NBBM). (c) Symbol A denotes (naphthylmethyl).

(d) (a,b) denotes ratio of a moles of tetradecane to b moles of NBBM loaded, referenced to 1.0E-2 M of NBBM corresponding to a value of b = 1.

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

Figure 2: Comparison of neat tetradecane conversion as a function of reactant loading for low pressure pyrolysis experiments.

Figure 3: Comparison of ethylene yield as a function of reactant loading and conversion for neat pyrolysis of tetradecane at low pressures.

Figure 4: Comparison of n-butane yield as a function of reactant loading and conversion for neat pyrolysis of tetradecane at low pressures.

Figure 5: Comparison of 1-undecene and n-undecane selectivities as a function of reactant loading and conversion for neat pyrolysis of tetradecane at low pressures.

Initiation

Propagation

Termination

} Termination Products

Figure 6: Proposed mechanism for pyrolysis of tetradecane.¹²⁻¹⁴

Figure 7: Major and minor products observed during NBBM pyrolysis at 420°C.

Figure 8: Comparison of selectivities for 1-naphthylphenylmethane (O), 1,4-(bi-1-naphthylmethyl)benzene (X), 1-benzyl-4-(1-naphthylmethyl)benzene (Δ), 1-methylnaphthalene (+), naphthalene (∇), p-xylene (□), 1-methyl-4-(2-phenylethenyl)benzene (l), and bibenzyl (♦) as a function of conversion for neat NBBM pyrolysis.

Figure 9: Comparison of tetradecane conversions as a function of reactant loading during binary reactions for low pressure reaction sets.

Figure 10: Comparison of conversion of NBBM as a function of reactant loading during binary reactions for low pressure reaction sets.

Figure 11: Comparison of ethylene selectivity as a function of conversion and reactant loadings for low pressure reaction sets.

Figure 12: Comparison of toluene selectivity as a function of reactant loading and conversion for low pressure reaction sets.

Figure 13: Comparison of 1-methyl-4-(1-naphthylmethyl)benzene as a function of reactant loading and conversion for low pressure reaction sets.

Figure 14: Comparison of selectivities of 1-(2-phenylethenyl)-4-(1-naphthylmethyl)benzene as a function of reactant loading and conversion for low pressure reaction sets.

Figure 15: Comparison of conversions for neat tetradecane pyrolyses as a function of reactant concentration and reaction pressure.

Figure 16: Comparison of NBBM conversion for low and high pressure neat pyrolysis reactions.

Figure 17: Comparison of toluene and 1-methyl-4-(1-naphthylmethyl)benzene selectivities for neat NBBM pyrolysis as a function of reaction pressure and conversion.

Figure 18: Proposed mechanistic scheme for the formation of toluene at the expense of 1-methyl-4-(1-naphthylmethyl)benzene and 1-(2-phenylethenyl)-4-(1-naphthylmethyl)benzene at high pressures.

Figure 19: Comparison of tetradecane conversions for binary mixture reactions conducted at low and high pressures.

Figure 20: Comparison of 1-(2-phenylethenyl)-4-(1-naphthylmethyl)benzene selectivities as a function of reactant loadings and conversion at high pressures.

Binary Interactions Between High Density Polyethylene and 4-(1-Naphthylmethyl)Bibenzyl During Low Pressure Pyrolysis

Matthew J. De Witt and Linda J. Broadbelt*
Department of Chemical Engineering
Northwestern University
Evanston, Illinois 60208-3120

Abstract

Low pressure pyrolysis experiments employing a high molecular weight polymer and a model compound for coal were conducted to address the effect of phase behavior on the overall degradation mechanism and reaction pathways during coprocessing. Thermal degradation of high density polyethylene (HDPE) and 4-(1-naphthylmethyl)bibenzyl (NBBM) was conducted at 420°C at different reactant loadings, both neat and in binary mixtures. During binary mixture experiments, there was an enhancement in the selectivities to primary products of NBBM at longer reaction times, with a significant reduction in the formation of secondary and tertiary products. These favorable interactions occurred because the polymer induced diffusion limitations in the system compared to neat NBBM pyrolysis, which minimized NBBM self-interactions and promoted reactions with the surrounding polymer. The degradation pathways of HDPE during binary mixture experiments were similar to those during neat reactions, with slight changes to the product yields that were consistent with increasing the overall reactant loading during neat pyrolysis. Variation of the relative reactant loadings indicated that the favorable feedstock interactions were still realized with only slight alterations in the product slate for NBBM and increased yields of saturated species derived from HDPE. Overall, the experiments carried out demonstrated that favorable interactions exist in both the liquid and gas phases during coprocessing, and primary reaction pathways and the mechanism governing the interactions between the feedstocks were elucidated.

Introduction

The growing abundance of mixed plastic waste and diminishing landfill space in the United States are driving the exploration of new strategies for viable plastics resource recovery. Post-consumer plastic is a major contributor to the municipal solid waste stream, comprising approximately 18% by volume.¹ Disposal through landfilling is becoming a less viable option, however, as the number of landfills closing each year exceeds the number being opened.² This poses a significant dilemma because there appears to be no immediate decrease in the usage of plastic products; in fact, due to their versatility, their usage will most likely increase. Current recovery methods suffer from a number of inadequacies, which range from costly separation to the removal of impurities and contaminants. As a result, products manufactured from recycled polymers are of lower quality and higher cost than those produced from the corresponding virgin resins.³ Therefore, new methods for the recovery of spent plastics must be developed.

A strategy for plastics resource recovery that is currently gaining momentum 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 the waste plastics and unfavorable economics have restricted the widespread application of this technology. These problems can be minimized, though, by coprocessing polymeric waste with other materials for which a process has already been developed. By incorporating plastics as a co-feed to an existing process, variations in supply and composition can be mediated, allowing for continuous operation. One option is to coprocess plastic waste with coal under direct liquefaction conditions,⁴⁻⁶ which may provide for simultaneous conversion of both feedstocks into high-valued fuels and chemicals. Although the viability of coprocessing of plastic waste with coal has been demonstrated,⁴⁻⁶ the nature of the interactions between the feedstocks is unclear. Process

development for these technologies would benefit from a greater understanding of the underlying reaction pathways, kinetics, and mechanism during coprocessing. In order to begin to obtain this information, studies have been conducted in our laboratory using a combination of both model compounds and real feedstocks.

Previous studies employing model compounds for coal and polyethylene demonstrated that favorable interactions exist during binary reactions.⁷ It was shown that the selectivities to primary products of the coal model compound were significantly enhanced in the presence of the polymer mimic (tetradecane), which also resulted in increased reactivity of the polymer model compound. These experiments provided substantial insight into the reaction pathways and mechanism controlling the degradation of these species, both neat and in binary mixtures. In the work described here, we have conducted reactions of a high molecular weight reactant, high density polyethylene (HDPE) with M_w 125,000, neat and in the presence of the coal model compound, 4-(1-naphthylmethyl)biphenyl (NBBM). The fundamental information obtained from the previous study using model compounds for both reactants was used to help deconvolute the complicated interactions when a real feedstock is used and to understand the effect of phase behavior on the overall degradation mechanism and reaction pathways. The following sections will describe the experimental protocol that was employed and the results obtained for the HDPE/NBBM studies, and these results will be discussed and compared to the experiments with model compounds.

Experimental

Neat and binary mixture experiments were conducted employing high density polyethylene (HDPE) and 4-(1-naphthylmethyl)biphenyl (NBBM). The reactions were conducted at 420°C in 3.1 mL pyrex ampules for 30-240 minutes. The HDPE was obtained from Aldrich Chemical (M_w 125,000) in pellet form. It was necessary to melt and cut the HDPE pellets at 120±5°C to obtain samples of appropriate weight; however, the

melting conditions are mild enough that no degradation is observed. NBBM has been used repeatedly as a model compound for coal and has successfully predicted the relevant primary products for real systems.⁸⁻¹¹ It contains both condensed and isolated aromatic ring structures joined by short alkyl chains, as well as five different aromatic-aliphatic or aliphatic-aliphatic carbon-carbon bonds. The structure of NBBM is depicted in Figure 1. The ampules were initially charged with the appropriate amount of reactant(s), purged with argon, and then sealed using a propane/oxygen torch. Three sets of neat HDPE experiments, using loadings of 12.3, 20.0 and 27.8 mg, respectively, were conducted. For binary mixture reactions, both the total initial reactant loading and overall reactant ratio were varied. Specific reactant loadings are shown in Tables 1-3. Upon completion of sample preparation, the ampules were placed in an isothermal ($\pm 1^\circ\text{C}$) fluidized sandbath at the specified reaction temperature for a predetermined amount of time. At the end of the reaction period, the ampules were cooled in a room temperature fluidized sandbath. Each reaction time was at minimum duplicated, and in some cases, up to five replicates were performed.

Overall gaseous product yields were obtained employing the same methodology as used for the low pressure model compound studies described previously.⁷ Once gas analysis was performed, extraction was carried out by placing the ampules in 14 mL vials, adding approximately 7 mL of cyclohexane (HPLC-grade) and 20 mg of an external standard (biphenyl), and capping the vials. Cyclohexane was chosen as the solvent since a large range of products could be extracted, but the highest molecular weight compound solubilized could still be analyzed using gas chromatography. Extraction was conducted for a minimum of 12 hours, with occasional manual agitation of the vials. Quantitative analysis through a series of extractions using different solvent volumes for different lengths of time revealed that this protocol was sufficient to completely extract products of carbon numbers less than 24 and partially extract up to carbon number 35. The extracted liquid and solid products were identified and quantified using gas chromatography and mass

spectrometry as described for the model compound experiments.⁷ The percent conversion of HDPE for this study, X_{HDPE} , was determined using the equation:

$$X_{\text{HDPE}} = \frac{(W_i - W_{\text{g+e}})}{W_i} \times 100 \quad (1)$$

where W_i is the initial weight loading of HDPE, and $W_{\text{g+e}}$ is the weight of the gaseous and extracted liquid and solid products which were quantified. It should be noted that there were extracted liquid and solid products that could not be identified due to low relative yields, and these species were not included in the calculation of X_{HDPE} . In addition, products for carbon numbers C_6 and C_7 could not be fully quantified due to the presence of these species as an impurity in the extraction solvent, and *n*-pentane and 1-pentene yields are believed to be low since there was difficulty in quantifying the liquid fraction of these species. For binary mixture reactions, products of carbon number C_{21} could not be fully quantified because chromatographic peaks for these species were merged with a peak of a species derived from the coal mimic.

Results and Discussion

Neat Pyrolysis of High Density Polyethylene (HDPE)

The three sets of pyrolysis experiments, using loadings of 12.3, 20.0, and 27.8 mg, respectively, were conducted to provide comparison to reactions using tetradecane and to provide baseline information to which subsequent binary mixture reactions could be compared. Because it was only possible to track the evolution of low molecular weight products from HDPE in detail, a true measure of the polymer conversion was not obtained, and therefore, selectivity values were not used for interpreting the experiments with the polymer. Instead, comparison of reaction products at different reactant loadings was conducted using normalized molar yields, which were defined as the number of moles of product *i* divided by the corresponding moles of reactant charge. Representative product yields for neat HDPE pyrolysis are summarized in Table 1. The reproducibility of

calculated yield values for the shortest reaction times was $\pm 7\%$, which decreased with increasing reaction time to $\pm 2\%$ at 240 minutes.

The primary products observed during HDPE pyrolysis were linear hydrocarbons, consisting of α -olefins, *n*-alkanes, and minor yields of internal olefins, which is consistent with results from the literature.¹² These products are similar to those found during tetradecane pyrolysis conducted in our laboratory,⁷ indicating that the feedstocks decompose via similar free-radical mechanisms. Light gaseous hydrocarbons and high molecular weight α -olefins were initially found in the highest yields for all reaction sets, and their yields increased with reaction time. The yields of paraffins for carbon numbers greater than C_{10} increased at a faster rate than the corresponding α -olefins, while internal olefin yields increased much more slowly. The two products formed in the highest yields for all of the reaction times and reactant loadings studied were ethane and propylene. The trends observed for the *n*-alkanes and α -olefins with respect to reaction time were similar to those observed during our previous studies employing tetradecane.⁷

During the pyrolytic degradation of HDPE, initiation occurs through the fission of a main chain carbon-carbon bond to form two primary radicals. These radicals then propagate through three main types of reactions: intermolecular hydrogen abstraction, intramolecular hydrogen abstraction, and β -scission. Termination occurs through either recombination or disproportionation. These reaction types are consistent with those postulated to occur during low pressure hydrocarbon pyrolysis.¹³⁻¹⁵ However, the pyrolysis of HDPE is complicated by the fact that reactions are occurring in both the liquid and the gas phase. The liquid phase is primarily composed of high molecular weight hydrocarbons, while the gas phase consists of low molecular weight species which have diffused from the liquid phase. In the liquid phase, bimolecular reactions involving the polymer, such as intermolecular hydrogen abstraction, will be favored over unimolecular decomposition due to the high concentrations of substrate.^{16,17} Unimolecular pathways

will initially predominate in the gas phase, but as reaction time proceeds and the concentration of hydrocarbons increases, bimolecular reactions will become more competitive. During HDPE pyrolysis, the two phase system leads to higher relative ratios of *n*-alkanes to α -olefins than observed during gas-phase tetradecane pyrolysis since saturated hydrocarbons are primarily formed through intermolecular hydrogen abstraction.

The normalized yields of both *n*-alkanes and α -olefins for carbon numbers greater than C₈ were initially found to be very similar. However, there were significant changes in the respective yields as reaction time increased. The yields of lower molecular weight α -olefins of carbon numbers C₈-C₂₄ increased more significantly at longer reaction times. Representative trends are shown in Figures 2 and 3 as a function of reaction time and carbon number for the 20 mg reactions. The increased yields of shorter hydrocarbons are observed because these species are more stable than longer compounds due to the lower number of possible sites for main chain cleavage or hydrogen abstraction. In addition, smaller α -olefins can be produced as longer species undergo further degradation.

The *n*-alkanes also showed an increased selectivity towards smaller products as reaction time increased, due to the same reasons discussed in the previous paragraph for α -olefins. However, there was also a marked increase in yields of high molecular weight paraffins. In particular, the yields of *n*-alkanes of carbon numbers C₂₀-C₂₄ showed significant growth with reaction time, which is contrary to the behavior for the α -olefins of the same carbon numbers. The α -olefins of these carbon numbers formed at a slightly slower rate than the paraffins and had relatively constant yields for reaction times greater than 90 minutes. The trends for the saturated product yields are presented in Figures 4 and 5 for the 20 mg experiments. The increase in the yields of the full range of *n*-alkanes occurs because the saturated species are primarily formed through hydrogen abstraction reactions, which predominate in the liquid phase and also in the gaseous phase at longer reaction times. As a result, the α -olefin to *n*-alkane ratio became smaller with increasing

reaction time since the paraffins continue to form at increased rates as the olefins undergo further degradation.

Though not shown in Tables 1 or 2, internal olefins, in addition to α -olefins, were also observed during neat pyrolysis of HDPE. These species were most likely formed through an intermolecular hydrogen abstraction from a secondary carbon followed by either disproportionation or β -scission of an adjacent C-H bond.¹⁸ However, the yields of these species were much lower than those observed for the α -olefins and the *n*-alkanes, which is expected due to the low rates of the reactions leading to internal olefins at the reaction conditions employed in this study. Since the internal olefins were not produced in significant yield as compared to the other primary products, the remaining discussion will focus on the *n*-alkanes and α -olefins.

As was observed during tetradecane pyrolysis, the initial reactant loading affected the final product distributions obtained during thermal degradation of HDPE. For low molecular weight hydrocarbons (C_1 - C_5), the trends observed as a function of initial reactant loading were similar to those observed during studies employing tetradecane in our laboratory.⁷ There was a significant reduction in the formation of methane and ethylene with increasing reactant loading. The normalized yields of propylene, 1-butene, and 1-pentene, though, were relatively constant through 150 minutes of reaction time, but began to deviate at longer times with the yield of each decreasing with increasing reactant loading. The selectivities to the other gaseous hydrocarbons were independent of initial reactant loading.

The trends observed for the gaseous species can be explained by considering how the changes in total substrate charged affect the relative rates of the formation pathways for the low molecular weight species. Similar to tetradecane pyrolysis,⁷ the most striking trend observed was the decrease in the yield of ethylene with increasing reaction time and reactant loading. This behavior can again be rationalized by noting that ethylene primarily forms through a unimolecular reaction, i.e., a β -scission reaction of a primary radical to form

ethylene and a smaller primary radical. As substrate concentrations in the gas phase increase with increasing reaction time and initial reactant loading, bimolecular reactions become more competitive with unimolecular reactions. Therefore, there is a reduction in the rate of formation of ethylene since the bimolecular reactions lead to a decrease in the relative population of primary radicals in the system. In addition, ethylene degradation rates are higher due to increased consumption through addition reactions. The decrease in the formation of methane occurs because the corresponding precursors (methyl radicals) are primarily formed through repeated unimolecular degradation steps, which are diminished with increasing substrate concentrations. The reduction in the yields of the other gaseous unsaturated hydrocarbons at the longest reaction times can be explained by noting these species can undergo degradation through addition reactions as the concentration of gas phase species increases, which occurs as reaction time proceeds.

Although the yields of low carbon number α -olefins ($< C_6$) were similar for the three reactant loadings at low reaction times, the yields of longer terminal olefins showed deviation over the full range of reaction times studied. An example of this trend is shown in Figure 6 where the yield of 1-eicosene ($C_{20}H_{40}$) is plotted as a function of reaction time and reactant loading. The highest yields for 1-eicosene were observed for the 12.3 loading experiments, with decreasing yields for increased loadings. The yields of high molecular weight n -alkanes, however, followed the opposite trend than that for the α -olefins, increasing with increased reactant loadings. These observations are attributed to an increase in bimolecular reactions in the gas phase due to higher relative hydrocarbon concentrations as reaction evolves, which is the same effect observed during neat tetradecane pyrolysis.⁷ For thermal degradation of both tetradecane and HDPE, the α -olefin to n -alkane ratio was found to decrease with increasing reactant loading for all carbon numbers. This trend is shown for the degradation of HDPE in Figure 7 using the ratio of 1-octadecene to n -octadecane as a representative example.

Overall, the pyrolysis of HDPE resulted in the same major types of product types as those observed during tetradecane pyrolysis, and the relative primary product yields and trends are similar during tetradecane and HDPE pyrolysis. This indicated that these species degrade via similar reaction mechanisms and that tetradecane is an adequate model compound for identifying the dominant reaction families and in particular, helping to understand the gas phase transformations of HDPE degradation products.

Coprocessing of NBBM with HDPE

Binary mixture reactions using HDPE and NBBM were conducted to probe binary interactions between the reactants, and the results were compared to the model compound studies to determine the effects of phase behavior on reactant conversions and product yields. Both the initial reactant ratio and the overall reactant loading were varied as summarized in Tables 2-3. The same experimental procedure used during neat HDPE pyrolysis was employed. Product trends for species derived from HDPE are reported in normalized yields as used for the neat reactions, while selectivity values are used for NBBM-derived products. The use of selectivity values is possible because the conversion of NBBM was directly measured, and selectivities permit for direct comparison of these results to studies previously conducted employing NBBM.⁷ The selectivity value of a product was defined as the ratio of the moles of the species formed to the moles of NBBM converted. The reproducibility of yields for HDPE-derived species was the same as for the neat reactions. The error for the selectivities of NBBM-derived species was $\pm 5\%$ at the lowest reaction time and decreased to $\pm 2\%$ for the 240 minute reactions.

The products observed during binary mixture reactions of HDPE and NBBM were similar to those observed during previous studies in our laboratory for the co-reaction of tetradecane and NBBM. The HDPE-derived products were primarily composed of α -olefins and *n*-alkanes, while NBBM-derived species were identical to those previously reported.⁷ Trends in product yields revealed that synergistic effects similar to those

observed during model compound studies existed. During binary mixture reactions with HDPE, there was an increase in the selectivity to primary products of the coal model compound at higher conversions and also a significant reduction in the formation of unsaturated NBBM species. Though these beneficial interactions were similar to those observed during model compound studies, there were some differences in the underlying feedstock interactions due to the phase behavior of the system. In contrast to the tetradecane/NBBM reactions, aliphatic hydrocarbons were present in significant quantities in the liquid phase during HDPE/NBBM coprocessing.

The conversion of NBBM during neat pyrolysis and binary mixture reactions with tetradecane and HDPE is shown in Figure 8. The data set Bin(2:2) corresponds to binary reactions between 12.3 mg of tetradecane and 20.0 mg NBBM at the same reaction conditions, which were previously reported.⁷ It can be seen that the conversion of the coal model compound was slightly reduced during coprocessing with HDPE as compared to the previous studies. This can be explained by noting that during reactions with the polymer, the conversion of NBBM will be reduced due to two main factors. First, the recombination of NBBM-derived radicals in the liquid phase following homolysis of the bibenzyl linkage is enhanced compared to the neat reactions due to "cage" effects which are promoted by the polymer,^{19,20} which inhibits NBBM degradation. This explanation is consistent with the observation that the conversion of the coal model compound was independent of the initial reactant ratio or overall reactant loading during coprocessing since the polymer comprises a significant enough portion of the liquid phase to impart "cage" effects for all reaction sets studied. In addition to the effects of diffusion limitations, there is also a reduction in the overall degradation rate of NBBM since there are fewer NBBM self-interactions as compared to neat pyrolysis or coprocessing with tetradecane due to the increased fraction of aliphatic hydrocarbons in the liquid phase. The combination of these effects results in a slight inhibition in the conversion of the coal model compound when reacted with the polymer.

The calculated conversion values for HDPE, X_{HDPE} , were similar during both the neat and the binary mixture reactions. This is contrary to the significant enhancement of tetradecane reactivity that was observed during previous coprocessing studies.⁷ These discrepancies can be explained in part by considering that the overall molecular weight distribution was not characterized during the HDPE studies. During reactions employing tetradecane, the reactant is well defined and it is straightforward to calculate a value for reactant conversion, i.e., the total moles of tetradecane converted during the reaction period normalized by the initial moles charged. For reactions with HDPE, however, the reported conversion values are based on the total extracted products that were quantified and do not reflect other changes in the overall molecular weight distribution of the sample indicative of reaction. Molecular weight distributions for the reacted polyethylene samples could not be obtained in our laboratory due to the specialized solvents and high temperature apparatus needed for this analysis. Although the calculated conversions of HDPE are approximately equal as a function of reaction time during coprocessing, the changes in the NBBM-derived product selectivities which will be discussed below indicate that favorable interactions between NBBM and the polymer do exist.

For NBBM-derived products, 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 and reactant loading in Figure 9. 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. The selectivity to toluene during binary mixture reactions with HDPE was initially similar or lower, depending on the reactant loadings, than that observed during neat NBBM pyrolysis. At conversions greater than about 40%, though, the selectivity was significantly enhanced for

all reactions with the polymer. This behavior is opposite of that observed during binary reactions with tetradecane, where the selectivity of primary products was enhanced over the entire range of conversions studied.⁷ To probe this discrepancy, product yields for other species were compared to determine if competing reaction pathways were favored over stabilization of the radicals formed from fission of the bibenzyl linkage. However, it was found that the yields of other NBBM-derived species which were quantified were not significantly enhanced at low reactant conversions. This indicated that new reaction pathways must exist which initially consume the radicals evolved during homolysis of NBBM and lead to products which are not quantified by gas chromatography. This hypothesis was supported when phenyl and naphthyl ring balances were calculated for the various reactions products quantified. Though the ring balances were very similar for neat and binary mixture reactions conducted with model compounds, balances obtained for binary mixture reactions with HDPE were initially significantly lower. As conversion increased, though, the ring balances for reactions with the polymer approached those obtained during the model compound studies. This indicates that products are initially formed which are not, or can not be, quantified because either they are not solubilized during extraction or do not elute on the column. However, these species must undergo degradation as reaction time increases, ultimately releasing the ring moieties. A plausible explanation for these observations is that the NBBM-derived radicals are undergoing liquid phase, bimolecular reactions with the polymer.

When NBBM radicals are evolved during bond fission, these species have a high probability of reacting with aliphatic hydrocarbons in the liquid phase. A representative reaction would be the addition of a benzyl radical to α -olefins derived from the polymer, which the product distribution measured during neat HDPE pyrolysis indicates are in high concentration in the liquid phase. Initially, reactions such as this would result in the formation of long-chain alkyl benzenes rather than stabilization of the benzyl radical to form toluene. Other radicals formed during NBBM homolysis would likely undergo similar

reactions, and these NBBM-HDPE interactions in the liquid phase result in a reduction in the selectivity to primary products at low conversions. However, the respective products formed could undergo facile degradation at longer times due to the weak bond that is formed. As a result, the NBBM-derived radicals which initially interacted with HDPE will ultimately be released. As reaction time progresses, the quantity of high molecular weight polymer decreases, making it easier for species to diffuse through the liquid phase and migrate into the gas phase. In addition, once an NBBM-derived radical is stabilized through hydrogen abstraction from the polymer, the reduction in diffusion limitations at longer reaction times permits the stabilized species to move away from the reactive site (radical formed on the polymer during hydrogen abstraction) and reduces the frequency of hydrogen shuttling induced by "cage" effects. When smaller species enter the gas phase, they either will have already been stabilized through interactions with the polymer or will have an increased probability of abstracting hydrogen from the high relative concentrations of HDPE-derived hydrocarbon species. It can be seen in Figure 9 that the selectivity trends for toluene are consistent with this explanation.

In addition to the increase of the selectivity to primary products at higher conversions, there was a significant reduction in the selectivity of products formed through NBBM-NBBM ipso-substitution reaction pathways during coprocessing with HDPE. These observations are consistent with those observed during coprocessing of the model compounds;⁷ however, the reduction was much more pronounced for NBBM-HDPE coprocessing. The selectivities for 1-naphthylphenylmethane, a product formed primarily through ipso-substitution pathways at the 1-naphthyl position,^{7,11} are shown in Figure 10. The trends for this species are representative of those observed for all other products formed directly through NBBM-NBBM ipso-substitution pathways, and these indicate that HDPE is more effective than tetradecane at preventing retrograde reactions.

During the model compound studies, it was shown that NBBM was primarily in the liquid phase while tetradecane was selectively partitioned into the gas phase.⁷ This phase

behavior resulted in favorable interactions when NBBM-derived species entered the gas phase. The same benefits are also realized in the present study since low molecular weight species which form as HDPE decomposes partition into the gas phase, particularly at higher conversions. However, the interactions of NBBM-derived species with the polymer as described above result in reduced NBBM self-interactions throughout the full range of reaction times studies.

The increased interactions between NBBM-derived radicals and the polymer is even more apparent when the selectivities for 1-(2-phenylethenyl)-4-(1-naphthylmethyl)benzene are compared for different reaction conditions, as shown in Figure 11. Although the C-H bond dissociation energy is lower for a carbon on the bibenzyl linkage of NBBM ($\approx 85 \text{ kcal mol}^{-1}$) than on a secondary carbon on HDPE ($\approx 95 \text{ kcal mol}^{-1}$)²¹ and thus abstraction is energetically favored at the benzylic sites, reaction path degeneracy and diffusion limitations favor interactions with the polymer. The reduction in selectivities to 1-(2-phenylethenyl)-4-(1-naphthylmethyl)benzene indicates that NBBM- and HDPE-derived radicals are primarily stabilized by interacting with polymeric chains rather than with NBBM.

As described above, the yields of products formed through NBBM-NBBM ipso-substitution reactions diminished during coprocessing with both tetradecane and HDPE. Accordingly, there was an increase in the selectivities of NBBM-derived species which are formed through competing pathways. The trends for these products were similar during binary mixture reactions with both tetradecane and HDPE; however, there were some products which had higher overall selectivities when NBBM was coprocessed with the polymer as compared to tetradecane. In particular, there were four minor NBBM-derived species, 1-methylnaphthalene, ethylbenzene, p-xylene, and 4-methylbibenzyl, which showed enhanced selectivities during coprocessing with the polymer. These observations were explained by considering the increased interactions with the polymer in the liquid phase contrary to reactions with tetradecane. Concurrent with the increased yields of 1-

methylnaphthalene, a decrease in the selectivity to 1,4-bi-(1-naphthylmethyl)benzene, a species formed through an ipso-substitution reaction of a 1-methylnaphthalene radical at the internal phenyl ring of NBBM, was observed. Since NBBM self-interactions are more effectively reduced during reactions with the polymer, there is an increase in selectivities to species whose precursors would be consumed through such pathways, which is the case for 1-methylnaphthalene. In addition to stabilization effects, substitution reactions involving HDPE-derived radicals and NBBM in the liquid phase can lead to the enhanced formation of other minor NBBM products contrary to reaction with tetradecane. For instance, substitution reactions at the 1-naphthyl position of NBBM or 1-methyl-4-(1-naphthylmethyl)benzene by an HDPE-derived radical would result in the release of radicals that could ultimately form 4-methylbibenzyl or p-xylene. This would allow for the increased yields of these low molecular weight species and also would support the explanation for the diminished ring balances at short reaction times. Analogously, the formation of ethylbenzene can occur through similar substitution reactions at the internal phenyl ring on NBBM.

The effects of coprocessing on the HDPE-derived product slate were very similar to those observed during binary mixture reactions employing tetradecane.⁷ During reactions with model compounds, it was observed that the selectivity to high molecular weight *n*-alkanes increased at the expense of longer α -olefins, ethylene and methane. These trends were also apparent for products of all carbon numbers during coprocessing of HDPE and NBBM. These product trends are shown for 1-pentadecene and *n*-pentadecane as representative members of the product classes in Figures 12 and 13, respectively. As a result, the α -olefin to *n*-alkane ratio, which is presented as a function of carbon number in Figure 14 for reactions conducted for 180 minutes, was significantly reduced during the binary mixture reactions. Overall, the trends of adding NBBM to the system followed those observed as the initial loading of HDPE was increased during neat pyrolysis.

With the addition of NBBM, there is a relative increase in the initiation of HDPE-derived radicals in the system due to favorable feedstock interactions. This results in an increase in the rate of termination for these radicals and also a reduction in the repeated unimolecular degradation steps of high molecular weight radicals. Consequently, the formation of saturated hydrocarbons is favored over unsaturated species. Therefore, the yields of *n*-alkanes increase at the expense of the corresponding α -olefins and gaseous hydrocarbons.

Both the initial reactant ratio and the overall reactant loading strongly influenced the trends for higher molecular weight HDPE-derived product yields during coprocessing. Representative trends are shown for 1-pentadecene and *n*-pentadecane in Figures 12 and 13, respectively. In order to quantify the effect of increasing the initial NBBM to HDPE ratio, the HDPE(12.3:12.3) and HDPE(12.3:20) reaction sets were compared. As the loading of NBBM was increased, there was a significant decrease in the yields of high molecular weight α -olefins with a concurrent increase in the yields of the corresponding paraffins. This is consistent with the explanation for increased yields of saturated species presented in the preceding paragraph since the total radical population increases with increased NBBM loading. The effect of increasing the HDPE reactant loading on product trends for the aliphatic hydrocarbons was also observed during coprocessing with NBBM, which can be discerned by comparing the HDPE(12.3:20) and HDPE(20:20) reaction sets. The paraffin yields once again increased at the expense of the α -olefins, which is consistent with the trends observed during neat HDPE pyrolysis. Overall the lowest α -olefin and highest paraffin yields for high molecular weight species were observed for the HDPE(20:20) reactions, where both increasing the polymer loading and adding NBBM influenced the degradation pathways of the polymer.

In addition to the changes in the product yields for higher molecular weight species, coprocessing was found to affect the product trends for some of the gaseous hydrocarbons. The resulting alterations to the product yields were similar to those observed during

coprocessing studies employing tetradecane.⁷ For the gaseous species derived from HDPE, the yields of olefins of carbon numbers C₂-C₅ and methane were most notably affected during coprocessing. The yields for ethylene during binary mixture reactions are shown in Figure 15 and are representative of those observed for the other unsaturated species. The changes in the trends for these species are similar to those observed as the initial concentration of HDPE in the neat experiments was raised, and are consistent with a reduction in repeated unimolecular degradation steps of higher molecular weight radicals. In addition to the reduction in the rates of formation, the unsaturated species are also consumed through bimolecular pathways, such as radical addition reactions, as reaction time proceeds.

Conclusions

Binary mixture reactions employing HDPE and NBBM have shown that the feedstock synergism that was observed during reactions with tetradecane and NBBM was still obtained.⁷ In this study, there was an increase in selectivity to primary products of the coal model compound with a significant reduction in the formation of secondary and tertiary products. The major difference in the product trends for reactions with the polymer, though, is that there was initially a minimal enhancement or inhibition in the formation of primary products of NBBM, depending upon reactant loadings, followed by subsequent enhancement. This observation, in addition to the reduced selectivity to secondary and tertiary products of NBBM as compared to the model compound studies, was primarily due to the differences in the phase behavior in the reaction system during coprocessing with HDPE. In this study, the high proportion of HDPE in the liquid phase induced diffusion limitations in the system which resulted in a slight reduction in the rate of NBBM degradation, but also minimized NBBM-retrograde reactions by promoting reactions with the surrounding polymer. However, the HDPE-NBBM interactions initially led to alternative reaction pathways for the coal-derived radicals to form products which

could not be identified and quantified. These products eventually underwent degradation themselves, though, resulting in significantly enhanced selectivities for primary products at longer reaction times. Therefore, the increase in selectivity to primary NBBM products observed during previous studies was still realized, but as an added benefit, there was a significant reduction in the formation of NBBM retrograde products.

The effects of coprocessing on the HDPE-derived product yields were similar to those observed during studies employing tetradecane, where a significant increase in the yields of high molecular weight paraffins at the expense of the full range of α -olefins was observed. The changes were more marked for reactions with the polymer, though, which were attributed to the occurrence of additional bimolecular reactions in the liquid phase which resulted in the formation of *n*-alkanes and consumption of α -olefins. Increasing the relative loadings of the components only slightly altered the product selectivities for NBBM, but resulted in enhanced yields of longer alkanes at the expense of α -olefins. These observations were consistent with increasing the overall polymer loading during neat pyrolysis.

Overall, the degradation mechanisms of HDPE and tetradecane are similar for both neat pyrolysis and reaction in the presence of NBBM. By employing the information obtained from previous model compound studies,⁷ it was possible to deconvolute the complicated feedstock interactions and identify the relevant reaction pathways during reactions employing the polymer. Therefore, the model compound reactions that were previously carried out provided valuable insight and guidance when reactions with a more complicated feedstock were performed.

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

Figure 2: Comparison of normalized yields of selected α -olefins for 20 mg reactant loading of HDPE.

Figure 3: Comparison of normalized yields of α -olefins as a function of reaction time and carbon number for 20 mg reactant loading of HDPE.

Figure 4: Comparison of normalized yields of selected n -alkanes for 20 mg reactant loading of HDPE.

Figure 5: Comparison of normalized yields of *n*-alkanes as a function of reaction time and carbon number for 20 mg reactant loading of HDPE.

Figure 6: Comparison of normalized yields of 1-eicosene as a function of reaction time and reactant loading for neat pyrolysis of HDPE.

Figure 7: Comparison of α -olefin to n -alkane ratio for C_{18} as a function of reaction time and reactant loading for neat pyrolysis of HDPE.

Figure 8: Comparison of the conversion of NBBM during neat pyrolysis and binary mixture reactions with tetradecane and HDPE.

Figure 9: Comparison of toluene selectivities during neat pyrolysis of NBBM and binary mixture reactions with tetradecane and HDPE.

Figure 10: Comparison of 1-naphthylphenylmethane selectivities during neat pyrolysis of NBBM and binary mixture reactions with tetradecane and HDPE.

Figure 11: Comparison of 1-(2-phenylethenyl)-4-(1-naphthylmethyl)benzene selectivities during neat pyrolysis of NBBM and binary mixture reactions with tetradecane and HDPE.

Figure 12: Comparison of normalized yields of 1-pentadecene during neat pyrolysis of HDPE and binary mixture reactions with NBBM.

Figure 13: Comparison of normalized yields of *n*-pentadecane during neat pyrolysis of HDPE and binary mixture reactions with NBBM.

Figure 14: Comparison of the α -olefin to *n*-alkane ratio at a reaction time of 180 minutes for various carbon numbers for neat pyrolysis of HDPE and binary mixture reactions with NBBM.

Figure 15: Comparison of normalized yields of ethylene during neat pyrolysis of HDPE and binary mixture reactions with NBBM.

Computer Generation of Reaction Mechanisms Using Quantitative Rate Information: Application to Long-Chain Hydrocarbon Pyrolysis

Matthew J. De Witt, David J. Dooling, and Linda J. Broadbelt*
Department of Chemical Engineering
Northwestern University
Evanston, Illinois 60208-3120

Abstract

In recent years, the use of mechanistic modeling to identify the underlying kinetics of complex systems has increased greatly. One of the challenges to kinetic modeling is constructing a model which can capture the essential chemistry of a system while retaining a manageable size. The rate-based generation of mechanistic models is an attractive approach since kinetically significant species can be determined and selectively included in the final mechanism. In previous work, an algorithm for the effective rate-based generation of reaction mechanisms was developed.¹ Novel modifications were made to the core components of the algorithm in our study, which included introducing thermodynamic constraints into the estimation of the controlling rate parameters and using an alternative approach for determining the species included in the final mechanism. Once implemented, the adapted rate-based building criterion was successfully employed to construct a compact mechanistic model for low pressure tetradecane pyrolysis. Though thousands of species and reactions were generated, only a small portion of these were deemed necessary and incorporated into the final model. Experimental data were used to determine frequency factors for a subset of the reaction families, while all other kinetic parameters were set based on literature values. The final optimized values for the frequency factors were consistent with literature, and the model was able to accurately fit experimental data from different reaction conditions. With no adjustment to the optimized frequency factors, the mechanistic model for tetradecane pyrolysis was able to accurately predict reactant conversions and product yields for varying reaction conditions. Both relative trends and

the actual values were predicted correctly over a wide range of reactant conversions and initial reactant loadings. It was also observed that increasing the quantity of species initially seeded resulted in a mechanism which was smaller in size but had comparable fitting and predicting capabilities as models seeding only the reactant. Subsequent regeneration of the reaction mechanisms using the optimized values for the frequency factors resulted in smaller models with comparable capabilities.

Introduction. The use of kinetic modeling has significantly increased in recent years due to both economical and environmental driving forces. Kinetic modeling allows for the facile and rapid investigation of various processing conditions while at the same time allowing the modeler to evaluate proposed reaction mechanisms, quantify the underlying reaction kinetics, and interpret complex experimental data. Furthermore, the information obtained from mechanistic modeling can be subsequently used for overall process improvement and optimization.

The major challenge to constructing mechanistic models is the extreme complexity that accounting for all possible reactions, products, and reactive intermediates creates. It is certainly possible to manually construct a reaction mechanism for very simple systems with limited reaction pathways. However, as system complexity increases, the model size grows significantly, and the construction becomes extremely time-consuming and tedious. The pyrolysis of hydrocarbons, for example, can generate thousands of reactive intermediates and products, making tabulation and tracking of all the species very difficult. Manual construction of models for such systems is daunting, and therefore employing computers to automatically generate these large mechanisms is attractive. As computer technology improves, the time required for model construction and solution decreases, permitting the generation of more complicated mechanistic models. Although models of significant size can be developed using typical workstations today, there is still a limit to the overall mechanism size which can be solved in a reasonable amount of time. Therefore,

there is a driving force to create the smallest mechanism possible which still contains all kinetically significant species and reactions. Hence, the ability to determine necessary and important species with the exclusion of "unreactive" ones is a vital aspect of the automated construction of reaction mechanisms.

The program for automatic mechanism generation of Broadbelt et al., NetGen,²⁻⁴ has been successfully used to generate reaction mechanisms for several distinct reaction chemistries. The original version of NetGen generated reaction mechanisms using a rank-based generation criterion, which limited the addition of a species to the growing network based upon the number of successive reactions necessary to produce it starting from the initial reactant pool. For example, a rank one model would contain all species which could be directly formed from the reactants, while a rank two model would contain all the species in a rank one model plus all species that could be formed directly from the products of rank one. Although adequate models were produced using this approach, many insignificant species of low rank could be included, while truly important "reactive" species of higher rank were omitted. Therefore, recent work has been carried out to improve the ability of the program to consider a larger number of species while retaining only those which influence the kinetics.^{1,5} The basic approach is to estimate reaction rate constants during generation and solve the model as it is being constructed, allowing for the determination of important species in the growing mechanism. These studies have considered a significantly higher number of total species than the rank-based generation criterion, while distilling these species into a more manageable reaction mechanism. The work which will be discussed in this paper expands on the previous studies of Susnow et al.¹ by introducing thermodynamic constraints into the estimation of the controlling rate parameters and a modified approach for determining the species included in the final mechanism. Furthermore, several different models were built by varying the parameters controlling the rate-based generation and each model's utility was assessed through its ability to capture

experimental data for tetradecane pyrolysis collected in our laboratory.⁶ The methodology employed and its application to long-chain hydrocarbon pyrolysis are discussed below.

Details of the Rate-Based Building Algorithm. To generate a reaction mechanism for long-chain hydrocarbon pyrolysis which would be valid over wide ranges of temperature, concentration, and reaction time yet still maintain a manageable size, necessary *reactive* species were determined employing a rate-based generation criterion. The algorithm employed was similar to that of Susnow et al.¹; however, some key modifications enhanced its capabilities. As in the previous studies, the rate-based generation algorithm exploits the capability of NetGen to estimate rate constants as the mechanism is generated, thereby allowing the growing mechanism to be solved during construction, affording species' concentration versus time profiles.¹ This quantitative information is then used to determine which species that have not yet been permitted to undergo further reaction are most significant in the growing mechanism by comparing each species' rate of formation to a minimum specified rate. Species whose rates of formation exceed this minimum rate are next allowed to react. This rate-based construction permits the model to efficiently consider a large quantity of species during construction, while including only those species which are found to be kinetically significant. This results in a model of a much more manageable size as compared to rank-based construction, while still retaining the essential species which influence the overall kinetics.

Initially, the reactant or reactants for which the mechanism is being generated are specified by the user. These are treated as reactive species and are added to the reactive species list. The temperature, pressure, and reactor type which are to be employed are also specified. The input values for the temperature and pressure should be reasonable for the conditions for which the final model will ultimately be used. However, because the reactions are described at the mechanistic level and the rate constants are temperature dependent, the model is valid beyond the conditions used for its construction. Only when

significant changes in the underlying mechanistic chemistry occur would the model become invalid. The user then specifies the total reaction time and the particular types of reactions which the reactive species may undergo, e.g., hydrogen abstraction, bond fission, and β -scission reactions are each likely during hydrocarbon pyrolysis. To provide additional handles for maintaining a manageable model size, the user may also dictate the feasible and dominant reaction pathways which would occur for the specified reaction conditions by invoking specific reaction rules, or constraints, on the reaction types. For example, one reasonable constraint for *n*-alkane thermolysis is that for initiation, only carbon-carbon single bonds would be permitted to undergo homolytic bond fission.⁷

Once the user-specified parameters have been set, the reactive species are allowed to react to form intermediates and products dictated by the specified reaction families and constraints using algorithms discussed in detail in the literature.¹⁻⁵ Some reactions will result in the formation of species which are currently not in the mechanism, and these species are not permitted to immediately undergo further reactions. These species are labeled *unreactive* in the growing model. The rate of formation of a particular *unreactive* species, and hence its kinetic significance, is solely dependent upon *reactive* species. It should be noted that although there is distinction between *reactive* and *unreactive* species, all species and reactions which are generated are tracked throughout the entire model construction process.

To quantify the rates of formation of the *unreactive* species and therefore determine which species will be allowed to react next, the species balance equations must be combined with the appropriate reactor design equations and the model must be solved. Clearly, rate constants are necessary to accomplish this; the methodology used to calculate the reaction rate constants for each reaction in the growing mechanism will be discussed in the following section. It is likely that the rates of formation of *unreactive* species will change dramatically as reaction proceeds. Therefore, an approach that iterates over the independent variable of the reactor of interest has been adopted. The following discussion

will focus on a batch reactor in which the independent variable is time. The logic diagram for this approach is shown in Figure 1. First, the user-specified total reaction time is divided into smaller subintervals. The total reaction time is not divided evenly; rather, fine increments are used at early times when species concentrations and rates of formation change rapidly. As time increases, the generated mechanism undergoes fewer changes, allowing larger intervals to be taken. This uneven discretization of time helps to reduce the time for model generation while allowing short- and long-time behavior to be examined. Choice of reaction time as the controlling iteration variable differs from the approach in previous work,¹ where intervals of reactant conversion were used. The current approach is more general in that it can easily be applied to systems with many reactants and, hence, many different reactant conversions, without ambiguity. Furthermore, it more accurately reflects the dynamics of systems in which reactants quickly reach equilibrium or have a very slow rate of conversion.⁸

Once the total reaction time has been discretized, the model equations are integrated using a standard differential equation solver⁹ to the end of the first subinterval. Upon completion of integration for the subinterval, a characteristic rate of change for the system, R_{char} , is calculated. In previous work, R_{char} was based upon the amount of the reactant converted over the time required to achieve that conversion, i.e., the rate of disappearance of the reactant.¹ However, this approach does not necessarily capture the rate of change of the most dynamic species in the system and, again, is not easily applied to systems with more than one reactant. In this work, the characteristic rate of the system was defined as:

$$R_{char} = \max(|r_i|)$$

where r_i is the net rate of formation of species i , and the function $\max$ selects the largest absolute value of r_i from the set of all r_i for reactive species over the interval of integration. After generation has surpassed the first subinterval, an r_i value is calculated for all subintervals included in the current interval. Therefore, R_{char} is defined as the largest

absolute instantaneous rate of change of any *reactive* species in the system over the full interval.

Once R_{char} has been determined, the minimum rate of formation for a species to be considered *reactive*, R_{min} , is calculated:

$$R_{min} = \varepsilon \cdot R_{char} \quad , \quad \varepsilon > 0$$

where ε is a user-defined threshold. The list of *unreactive* species is then inspected, and the species with the largest rate of formation, $r_{j,max}$, is selected. If $r_{j,max}$ is greater than R_{min} , species j is added to the *reactive* species list. The new *reactive* species is then subjected to the reaction rules, and all of the possible reactions for the new species are generated. The new model, with one more *reactive* species and (possibly) several more *unreactive* species than the previous model, is then solved for the same time subinterval. The R_{char} , R_{min} , and $r_{j,max}$ values are recalculated, and the new $r_{j,max}$ and R_{min} are compared. This iterative procedure continues until $r_{j,max}$ is less than R_{min} . At this point, the algorithm proceeds to the next time subinterval and the entire process is repeated. The process terminates after the last subinterval has been traversed.

The user can tailor the model size through the ε parameter and the total reaction time. Decreasing ε will result in larger reaction mechanisms since *unreactive* species will need to be formed at a smaller fraction of the characteristic rate of the system to be considered as *reactive*. Varying the length of the total reaction time allows for the investigation of a wide range of reactant conversions. It is beneficial if the user is able to estimate the relative magnitude of the total reaction time based on the type of chemistry which is being studied. For example, it is reasonable that hydrocarbon pyrolysis at moderate temperatures (400-500°C) will proceed on the order of minutes rather than milliseconds. However, exact time values are not essential, as one can quickly observe whether a model will be appropriate based upon the quantity and types of species which have been deemed *reactive*.

As noted above, this procedure is similar to that employed by Susnow et al.,¹ with two major differences: 1) time, rather than reactant conversion, is used to control model building and 2) the characteristic rate of change in the system, R_{char} , is defined more broadly. The discretization of time is a more generally applicable approach. Furthermore, basing R_{char} on the most dynamic species in the system rather than on the rate of disappearance of a single reactant has the potential to reduce the quantity of species which are deemed *reactive*, and thus the overall size of the mechanism can be more easily controlled. This can be very effective when considering systems in which the reactant quickly equilibrates. For these systems the discretized net rate of disappearance for the reactant (R_{char} in this case), as used previously¹, decreases rapidly. Since R_{min} is proportional to R_{char} , a low R_{char} will result in species with low rates of formation becoming *reactive*, increasing the model size.

Rate Constant and Thermochemical Property Estimation. To employ the rate-based generation criterion during model construction, it is essential to have reliable estimates of the reaction rates in the mechanism. Inaccurate estimates can result in either the exclusion of necessary species or the addition of unreactive ones. The exclusion of necessary species can result in mechanisms which are unable to capture the chemistry of a reaction system, while larger mechanisms with superfluous species will require longer generation and solution times. In this work, a hierarchical approach was employed to calculate rate parameters for all reactions generated during the construction of the rate-based mechanism. During model generation, all reactions created are first compared to a user-defined rate constant library containing specific reactions and their respective Arrhenius frequency factors and activation energies. If a generated reaction exists in this library, the appropriate rate constant parameters from the library are assigned within the model. For this investigation, available experimental rate constants for *n*-alkane pyrolysis¹⁰⁻¹² were used.

If experimental data for particular reactions are not available, a combination of literature values, linear free energy relationships (LFERs), and thermodynamic data is used to estimate the rate parameters. Specifically, typical literature values or optimized values of frequency factors and the Evans-Polanyi relationship are used to estimate rate constants for forward reactions, k_f , while the reverse rate constants were constrained by reaction thermodynamics. The Evans-Polanyi relationship¹³ relates the activation energy, E_A , to the heat of reaction, ΔH_{rxn} , through the equation:

$$E_A = E_0 + \alpha \Delta H_{rxn} \quad (1)$$

where E_0 is termed the intrinsic barrier to reaction, and α is the reaction transfer coefficient. E_0 , α , and the Arrhenius frequency factor are assumed to be constant within a particular reaction family. The overall rate constant as a function of temperature for the forward reaction is calculated assuming the Arrhenius relationship is valid.

Once rate constants for forward reactions are calculated, equilibrium constants, K_p , are used to calculate the rate constants for the corresponding reverse reactions, k_r . Also, since the rate constants are on a per event basis, the ratio of the reaction path degeneracy of the forward to the reverse reaction, $rpdratio$, must also be included, yielding equation 2:

$$k_r = rpdratio \cdot k_f / K_p \quad (2)$$

This approach differs from previous implementations of NetGen in which thermodynamic consistency was not strictly enforced. K_p as a function of temperature can be calculated from the change in Gibbs free energy upon reaction, ΔG_{rxn} , using the definition of the equilibrium constant:

$$K_p(T) = \exp(-\Delta G_{rxn}(T) / RT) \quad (3)$$

and the dependency of ΔG_{rxn} on temperature through the corresponding enthalpy, entropy, and heat capacity values:

$$\Delta G_{rxn}(T) = \sum_i \nu_i \mu_i(T) \quad (4)$$

where

$$\mu_i(T) = \Delta h_i(T_0) + \int_{T_0}^T c_{p,i}(T') dT' - T \left[s_i(T_0) + \int_{T_0}^T \frac{c_{p,i}(T')}{T'} dT' \right]$$

where ν_i is the stoichiometric coefficient, μ_i is the chemical potential, and T_0 is the temperature at which the enthalpy, h_i , and entropy, s_i , are reported. The functional form chosen for the temperature dependence of $c_{p,i}(T)$ values in this study was a third order polynomial.

As a new species is generated within the reaction mechanism, the NIST Structures and Properties thermochemical database¹⁴ is searched to determine if experimentally-derived properties are tabulated. Quantities such as enthalpy and entropy are typically given at a particular reference state, while heat capacities are tabulated at several different temperatures. If experimental values are unavailable, a group additivity method is applied to estimate the species' thermochemical properties.¹⁵ If this approach fails, properties are calculated using MOPAC, a semi-empirical computational chemistry package.^{16,17} This approach is consistent with that previously taken.¹⁻⁵

Using thermodynamic data and equations 3 and 4, K_p can be calculated for each respective reaction in the overall mechanism and the reverse rate constant, k_r , is calculated from equation 2. By adding the capability to estimate entropies and heat capacities and calculate equilibrium constants to the mechanism generation algorithms, thermodynamic consistency is strictly enforced. This was a critical addition to the routines for rate-based mechanism generation, as the approach relies heavily on accurate quantification of reaction rates.

Application of the Rate-Based Generation Algorithm. A mechanism for low pressure tetradecane pyrolysis was generated to determine the effectiveness of the adapted rate-based generation algorithm. This reaction system was chosen since it would compliment experimental work which has been conducted in our laboratory.⁶ Low pressure batch pyrolysis studies of tetradecane were conducted at 420 and 450°C in 3.1 mL pyrex ampules. Reactant loadings ranged from 6.2 to 27.8 mg (1.01×10^{-2} to 4.53×10^{-2} mol/L) with reaction times varying between 10-150 minutes.

The pyrolysis of tetradecane was observed to follow the typical free radical Rice-Herzfeld and Rice-Kossiakoff mechanisms for low pressure hydrocarbon pyrolysis, and product distributions were consistent with those reported in the literature.¹⁸⁻²² Light gaseous hydrocarbons were formed in the highest yields, with the highest selectivities observed for ethane and propylene. For higher molecular weight species, α -olefins were the major products with minor yields of the corresponding *n*-alkanes. This reaction system would serve as an adequate test for the rate-based generation criterion since thermolysis of a long chain paraffin can lead to thousands of intermediates and stable products. However, only a small fraction of these are kinetically significant. By determining these influential species, a mechanism of reasonable size can be generated. This final mechanism can then be used to determine optimized values of a small subset of the controlling kinetic rate parameters, and these can subsequently be used for model predictions of reactant conversions and product yields for varying reactant loadings.

For gas-phase hydrocarbon pyrolysis at moderate temperatures, six important reaction families were identified. Homolytic bond fission, radical recombination and disproportionation, β -scission, radical addition, and hydrogen abstraction reactions, both intramolecular and intermolecular, were incorporated. The reaction mechanism in this study was generated using estimates of the Arrhenius frequency factors, E_0 , and α for each reaction family from the literature. The literature values used for each of these parameters

are shown in Table 1. The model was constructed using an initial tetradecane concentration of 3.22×10^{-2} mol/L (20.0 mg) and a reaction temperature of 420°C.

During model construction, the primary user-specified parameter which was varied was the threshold, ϵ . Varying this parameter significantly influenced both the types of *reactive* species and the total quantities of reactions and species included in the *reactive* model. The different models generated were evaluated based on three main criteria: 1) the inclusion of major reaction products as observed during experiment, 2) the ability to reproduce the temporal variations of the major products, and 3) the ability to obtain physically reasonable values for the subset of frequency factors which were optimized using experimental data.

Once a mechanism was obtained that met these modeling goals, additional strategies were examined for reducing the model size further. First, using the initial mechanism constructed as a guide, key reactive intermediates of high rank were identified and "seeded" into the initial reactant pool. Because these species no longer had to be formed at a rate greater than R_{min} to be included in the model, the threshold could be raised, resulting in a smaller mechanism that still achieved the modeling targets. Second, the impact of the kinetic parameters on model generation was explored by regenerating the models using the parameters obtained from optimization against experimental data.

Variation of Threshold, ϵ .

Model Characteristics. The model characteristics as the threshold, ϵ , was varied are summarized in Table 2. Quantities monitored were the numbers of total and *reactive* species, the numbers of total and *reactive* reactions, and the inclusion of major products and key intermediates. The user-specified threshold was initially set equal to 1.0, which resulted in a model that was generated very quickly, but only included a portion of the species observed during the experimental studies. Therefore, the threshold was slowly reduced to obtain an adequate model while preventing excessive growth. In addition, as

the threshold was reduced and the number of *reactive* species in the model increased, the generation time significantly increased, providing impetus to proceed cautiously. As Table 2 shows, all of the species that were observed experimentally were not deemed *reactive* until the threshold was reduced to a value of 5.0×10^{-5} . However, the generated mechanism was unable to capture the underlying chemistry, which was attributed to the absence of other necessary species, which were primarily reactive intermediates. Reducing the threshold to a value of 1.0×10^{-5} resulted in a mechanism that overestimated the yields of long-chain α -olefins at higher reaction times, and the frequency factor for initiation was significantly too high. This was attributed to the inability of the α -olefins to undergo subsequent degradation at longer reaction times due to the absence of their corresponding allylic and secondary radicals in the mechanism. In particular, 2-propenyl radical was not a *reactive* species. This is one of the products formed during fission of the weakest bond in an α -olefin (allylic bond), and it ultimately results in the formation of high yields of propylene. Since it was believed the olefinic radicals were necessary to generate an adequate model for a wide range of conversions, the threshold was further reduced.

As the threshold was reduced below a value of 1.0×10^{-5} , the number of *reactive* species and overall model construction time became very sensitive to the incremental change of the threshold value, with both quantities increasing significantly with only slight reductions ($\pm 1.0 \times 10^{-6}$) in the specified threshold. Therefore, the threshold was reduced at fine increments until 2-propenyl radical was included as a *reactive* species in the final generated model. This occurred when the threshold was set at a value of 7.0×10^{-6} , which resulted in a manageable model size with essential chemical detail. The overall mechanism, which will be referred to as Mechanism I, included a total of 19,052 species and 479,206 reactions, but the rate-based criterion reduced this to only 289 *reactive* species and 102,257 reactions. It should be noted, however, that the actual number of unique reactions is much lower than the reported quantities imply. The listed values count the forward and reverse of a particular reaction separately, and reaction path degeneracy is accounted for by

specifically writing each equivalent site as a unique reaction. For example, a total of 16 reactions are written for the abstraction of a secondary hydrogen on *n*-hexane by a particular radical: the forward and reverse of the abstraction of the eight distinct secondary hydrogens on the molecule. Although this final model took a considerable amount of time to construct because of the burden imposed by "on-the-fly" solution, a rank-based model with products of comparable rank had over 6,000 *reactive* species. Solution of a model of this size would not be feasible due to hardware limitations.

Determination of Rate Parameters and Predictive Capabilities. Experimental data from pyrolysis reactions of tetradecane at a loading of 20.0 mg conducted at 420°C and 450°C were used to optimize a subset of the controlling rate parameters. The different parameters which *could* be varied in the mechanism are shown in Table 1. However, only the parameters shown in Table 3 were optimized using experimental data, while all others were constrained at their literature values. As shown in the table, only frequency factors were permitted to vary, while all activation energies and transfer coefficients were set. It can be observed that the final optimized values for the frequency factors were reasonably consistent with literature values for the respective reaction families.

A parity plot comparing the fitted model yields to the experimentally observed yields for major and minor products employing the frequency factors in Table 3 is shown in Figure 2. The yield of a particular product was defined as the moles of the species formed normalized by the initial moles of tetradecane charged to the system. The model did an excellent job of fitting the experimental data from the pyrolysis reactions over several orders of magnitude. The majority of the variance was attributed to differences between fitted and experimental values for long chain *n*-alkanes, which were only minor products. It is not easily discernible in Figure 2, but reactant conversions for both temperatures were fit extremely well using Mechanism I. Also, major products which were formed in higher yields, including gaseous hydrocarbons and α -olefins, were fit very well. A comparison

between the experimental and fitted yields for 1-butene, *n*-octane, and 1-decene for tetradecane pyrolysis conducted at 420°C is shown in Figure 3 and is representative of the agreement for most other species. It should be reiterated that although the optimized frequency factors were fit using data from two temperatures, there were no adjustments made to the activation energies.

Once appropriate rate parameters were obtained, the predictive capabilities of Mechanism I were assessed. In particular, the ability of the model to predict reactant conversions and product yields for varying reactant loadings was investigated. The results which follow are truly predictions, i.e., no adjustments were made to the six frequency factors fitted to the 20.0 mg pyrolysis data. A comparison of predicted and experimental conversion values for tetradecane pyrolysis for different initial reactant loadings is shown in Figure 4. The experimental conversions for initial reactant loadings of 6.2 and 27.8 mg of tetradecane are shown as symbols, with each respective model prediction shown as lines. The mechanistic model was able to accurately predict the trends in the experimental conversions as a function of reactant loading and the actual conversion values very well.

As a representative example of the ability to predict product yields, a comparison of the predicted and experimental evolution of propylene as a function of reactant conversion and reactant loading is shown in Figure 5. The comparison for propylene is shown since it was one of the major products formed during tetradecane pyrolysis. Also, the data are plotted in terms of moles rather than yields to make the different data sets more discernible. The model was able to accurately predict both the trends in the data as well as the actual values over a wide range of conversions and reactant loadings. These observations were consistent with those for other gaseous hydrocarbons and long-chain α -olefins. A comparison of the predicted and experimental evolution of 1-decene is shown in Figure 6. The predictions for *n*-alkanes were also good, but there was more variance for these predictions than for the major products. It should be noted that Mechanism I was able to accurately predict product yields and trends for species regardless of whether their rates of

formation were increasing, decreasing, or went through a maximum as the reaction proceeded.

Overall, a mechanistic model for low pressure tetradecane pyrolysis was constructed using a rate-based generation algorithm with only a small number of user-specified variables. The model was able to accurately fit experimental yields for various products over several orders of magnitude at two different reaction temperatures with no adjustments to the corresponding activation energies. The mechanistic model was then able to accurately predict reactant conversions and product yields for varying reactant loadings employing the rate parameters optimized for independent reaction sets. In addition, although it was not discussed in the previous sections, the model was able to predict the correct behavior for product trends for different reaction conditions such as changes in the relative α -olefin/paraffin ratio for varying reactant loadings.

Effect of Varying Initial Reactant Pool. It was observed that the user-specified threshold strongly impacted the resulting mechanistic model for the low pressure pyrolysis of tetradecane. The threshold had to be incrementally reduced until certain intermediates, necessary to accurately capture the underlying chemistry over a wide range of conversions, were included in the mechanism. However, care had to be taken to vary the threshold at small increments to prevent explosive growth since the rate-based construction became very sensitive to the input threshold. As observed, though, it was possible to generate a robust model, provided caution was exercised during the construction process. An alternative approach to varying the threshold until certain species are included in the mechanism is to specify these species in the initial reactant pool, thus deeming them *reactive* from the onset. Placing a particular species in the initial reactant pool can be very helpful, especially if it is known to be an important and necessary species to the mechanism *a priori*. A similar approach used by Joshi²³ for rank-based construction was shown to reduce the overall model size significantly.

During the initial rate-based generation of tetradecane pyrolysis, only tetradecane, the reactant, was specified in the initial reactant pool. As discussed above, Mechanism I could not adequately fit the experimental data until olefinic radicals were included in the model. This only occurred at very low threshold values, potentially resulting in other less important species being included in the mechanism as well. To investigate whether a smaller mechanism could be constructed by selectively placing important reactive intermediates in the initial reactant pool, Mechanism II was generated in a manner identical to Mechanism I, with the exception of the initial reactant pool. In addition to tetradecane, allylic radicals of all α -olefins of carbon numbers 3 to 13 (e.g. 1-penten-3-yl) and one additional non-allylic radical for α -olefins of carbon numbers 5 to 13 were placed in the initial reactant pool. During model construction, the user-specified threshold was reduced until all species observed experimentally were included in the reaction mechanism. This was achieved when the threshold was set at a value of 3.5×10^{-5} . The overall mechanism included a total of 11,530 species and 310,008 reactions, while the rate-based criterion reduced this to a *reactive* mechanism of only 221 species and 64,762 reactions, respectively. Mechanism II took approximately half as long to generate as Mechanism I, and because it was smaller, shorter model solution and optimization times were realized. In addition, it should be noted that the user-specified threshold necessary to meet the modeling targets was higher than that used in the previous section, and also the model generation was not as sensitive to incremental changes to the threshold.

Frequency factors for selected reaction families in Mechanism II were determined by fitting experimental data in the same manner as for Mechanism I. Final optimized values of the frequency factors for the model with the larger initial species pool are shown in Table 3. It should be noted that these values are consistent with those obtained during optimization of Mechanism I and are comparable with those found in the literature for each reaction family. The different product yields obtained for Mechanism II using the optimized parameters in Table 3 were very similar to those obtained for Mechanism I. A

representative comparison of the experimental and fitted yields of 1-octene using Mechanism I and Mechanism II is shown in Figure 7. Overall, the fitted yields for Mechanism I were in slightly better agreement with the experimental values. This observation can be rationalized by noting that when only seeding tetradecane, the mechanism truly grows directly from the reactant. Therefore, if all species of interest are included in the model, then other components which are necessary for their formation must also be present in the model. When seeding reactive intermediates in addition to the reactant, though, it is possible to generate a mechanism which may include the majority, but not all, of the kinetically significant species. However, the differences in the fitted yields and optimized parameters between Mechanisms I and II are very subtle, indicating that both mechanisms can perform effectively.

The prediction of the reactant conversions and product yields for different initial reactant loadings were very similar for the two mechanisms, with Mechanism I predicting the experimental values slightly better. This is consistent with the observations made during the fitting of experimental data as discussed above.

Overall, seeding reaction intermediates in addition to the reactant resulted in the generation of a smaller reaction mechanism, which reduced the time required for model construction, solution, and parameter optimization. The optimized frequency factors for the mechanism were consistent with those for Mechanism I, and the model fit and predicted experimental data very well. Therefore, this study demonstrates that if kinetically important species are known *a priori*, the efficiency of the construction of a mechanistic model using the rate-based generation algorithm can be improved, resulting in a smaller, more easily solvable model.

Regeneration of Reaction Mechanisms Using Optimized Parameters Obtained During Initial Model Construction. As discussed in the previous sections, compact mechanistic models for low pressure tetradecane pyrolysis were generated using a rate-based generation

criterion. These models were able to both accurately fit experimental data from different reaction temperatures, as well as predict reactant conversions and product yields for different initial conditions. During model construction, several controls had to be specified by the user: the relevant reaction families, estimates of the kinetic parameters, the specified threshold for determination of *reactive* species, and the initial species pool. The effects of varying the user-specified threshold and initial species pool were discussed, and it was observed that both significantly affected the construction process and the final *reactive* mechanism obtained. The estimates provided for the controlling kinetic parameters may also have a significant influence on the generated model. In particular, the values used for the LFER parameters and the Arrhenius frequency factors are very important since the majority of forward reaction rate constants are calculated using this method, while the reverse rate constants are calculated using these forward rate constants and equilibrium information. It is very important to have accurate estimates for these parameters since inaccurate ones will result in the construction of either mechanisms that are unable to capture the underlying chemistry or models that include superfluous species and require longer generation and solution times.

For the construction of Mechanisms I and II, parameters for the frequency factors were set based upon reported literature values. However, these values are usually reported over a range, forcing the user to decide upon the particular values that will be employed. Thus, the ultimate choices may impact the model construction and may alter the list of species in the final mechanism. As discussed in the previous sections, a subset of the frequency factors were adjusted from the literature values selected for construction to optimized values obtained by fitting to experimental data. These optimized parameters had therefore been "tailored" to the reaction mechanism and chemistry under investigation. Therefore, it seems logical to employ these parameters to regenerate the reaction mechanisms to determine if improvements can be made to the final *reactive* models. Two possible benefits of regenerating a reaction mechanism with the new parameters are 1) a

reduction in the overall size of the mechanism since species that are kinetically insignificant for the particular experimental system being studied can be removed from the model and 2) the model may fit experimental data more accurately and provide better predictive capabilities because it becomes more focused on the particular experimental system of interest rather than the generic construction for which it is initially employed. To explore the effects of the rate parameters on model construction, the mechanisms for the low pressure pyrolysis of tetradecane described in the previous sections were regenerated using optimized parameters. It is also possible to vary the initial species pool during regeneration, but this would not permit for the direct comparison of using optimized rather than literature parameters. Therefore, the same initial reactant pools used to construct the two reaction mechanisms discussed in the previous sections were employed. The user-specified threshold, ϵ , was once again used to guide mechanism generation toward the established modeling goals.

Regeneration Seeding Only Tetradecane. The optimized parameters of Mechanism I were used to regenerate a model seeding only tetradecane at a concentration of 3.22×10^{-2} M and a reaction temperature of 420°C , as used for the initial construction of Mechanism I. All requisite species were included in the model when a threshold of 1.2×10^{-5} was employed. This regenerated model (Mechanism III) consisted of 253 *reactive* species and 71,707 reactions, and a total of 13,074 species and 378,506 reactions. This model was smaller than Mechanism I and took approximately half the total time to generate, indicating that model reduction could occur during regeneration employing optimized kinetic parameters. Mechanism III was then used to fit the experimental data while permitting the same subset of kinetic parameters to be optimized as for the previous mechanisms. Mechanism III fit the experimental data from both reaction temperatures very well, and the final optimized values for this model are shown in Table 3. It can be seen that the majority of the optimized parameters were very close to those obtained for Mechanism I with the exception

of the frequency factor for bond fission; the value for Mechanism III was more consistent with typical literature values. The fitted product yields for Mechanism I and Mechanism III were almost identical over the full range of conversions studied, indicating that the new mechanism was as effective as the original model. A comparison of the fitted yields of ethylene for the two mechanisms is shown in Figure 8 as a representative example. The predictive capabilities for the two models were also very similar, with almost identical estimates for the product yields for different initial reactant loading.

Regeneration of the model for tetradecane pyrolysis seeding only the reactant and using previously optimized values resulted in a mechanism that was more compact than the original model, while retaining comparable fitting and predicting capabilities. However, the new mechanism did not require as stringent of a threshold value to meet the desired modeling goals. This was a result of the mechanistic generation being more "focused" on the particular system of interest.

Regeneration Varying the Initial Species Pool. The effect of varying the initial reactant pool during regeneration was addressed using the same methodology presented previously. The initial pool was identical to that used to construct Mechanism II and consisted of tetradecane, allylic radicals of all α -olefins of carbon numbers 3 to 13, and one additional non-allylic radical for α -olefins of carbon numbers 5 to 13. The mechanism was generated using the optimized parameters for Mechanism I and a threshold of 3.5×10^{-5} , which was the final threshold employed to construct Mechanism II. The regenerated *reactive* mechanism consisted of 166 species and 48,265 reactions, with a total of 7,469 species and 206,946 reactions. This new model (Mechanism IV) was significantly smaller than Mechanism II, which was generated using approximate values from the literature. Similar to the approach for previous models, Mechanism IV was then used to fit the experimental data while permitting the small subset of kinetic parameters to be optimized. The final optimized values for this model are shown in Table 3. It can be seen that the majority of

the optimized parameters were very close to those for Mechanism II, while the frequency factor for initiation was reduced, which was also observed during the regeneration while seeding only tetradecane. The ability of the two models with the larger initial species pools to fit and predict reactant conversion and product yields were equivalent, with only slight differences for a few of the minor products. A comparison for the fitted yields of propylene for the two mechanisms is shown in Figure 9 as a representative example. Overall, the models had comparable performance, with Mechanism IV being more compact and providing a better estimate for the frequency factor for initiation.

The reduction in the number of *reactive* species from 221 for Mechanism II to 166 for Mechanism IV is primarily due to the absence of methylalkyl radicals in the latter. For instance, 2-ethylhexyl radical, which is primarily formed through radical addition reactions such as those of a 1-butyl radical to 1-butene or an ethyl radical to 1-hexene, was excluded from Mechanism IV because of the smaller radical addition rate constant used during regeneration. The majority of the other species that were not deemed *reactive* are formed through similar reaction pathways. The reduction in the addition rate constant and the absence of these unnecessary species indicate that the mechanistic generation has been more focused on the particular system of interest.

Overall, regeneration with optimized parameters resulted in more compact reaction mechanisms that still captured the experimental data very well. The new models provided estimates for the frequency factor for bond homolysis that were in better agreement with the literature values, with no sacrifice in the fitting or predictive capabilities of the mechanisms. This occurred since the mechanisms had become "tailored" to the particular system of interest, and truly insignificant species were removed. In addition, a higher value for the user-specified threshold could be used when seeding only tetradecane for the same reasons. When also seeding reactive intermediates during regeneration, the rate-based algorithm resulted in the construction of the most compact reaction mechanism which still contained essential chemical information.

Conclusions. A robust mechanistic model of low pressure tetradecane pyrolysis was constructed using algorithms for automated model construction and a rate-based generation criterion. Novel modifications were made to the core algorithmic components in this work to improve and broaden the rate-based approach. The major alterations were the use of time rather than conversion as the controlling iteration and termination variable, the new definition for the characteristic rate of change in the system, and the use of thermodynamic data to impose thermodynamic consistency between forward and reverse reactions.

For the investigation of low pressure tetradecane pyrolysis, the rate-based model construction was successfully employed to produce a compact model with essential chemical detail. Once constructed, the model was able to accurately fit experimental data from two different reaction temperatures with no adjustment to the activation energies for any reactions. Only frequency factors were permitted to vary, and the final optimized values were consistent with literature values for each respective reaction family. Once rate parameters were determined, the mechanistic model was able to accurately predict reactant conversions and product yields for varying reaction conditions with no adjustments to the optimized rate parameters. Both relative trends and the actual values were predicted correctly over a wide range of reactant conversions and initial reactant loadings.

When kinetically significant species were placed in the mechanism at the onset of generation, the final reactive mechanism became more compact, and comparable fitting and predictive capabilities were obtained. Subsequent regeneration using optimized parameters reduced the model size without compromising the capabilities of the model. The most compact reaction mechanism for tetradecane pyrolysis was obtained when kinetically significant species were "seeded" and optimized rate parameters were used to construct the model. It should be noted, however, it is possible to reduce the mechanism too severely such that the optimized parameters would no longer have physical meaning.

The adapted rate-based generation methodology developed in this work can be used to generate manageable reaction mechanisms for different reactant pools and reaction rules. The user need only specify reactant(s), allowed reaction families, the threshold, and the final reaction time, and the mechanism is generated automatically. This approach allows the user to expend less energy on generating and tracking the species in the reaction mechanism and instead to focus on analyzing model characteristics and performance. Once an adequate model has been generated, the user can predict reactant conversions and product yields for other reaction conditions, facilitating the study of various sets of reaction conditions, thereby reducing the experimental burden.

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Table 1: Parameters used for initial rate-based generation of mechanism for low pressure tetradecane pyrolysis.

Reaction Family	A^a	E_0^b	α
Bond Fission	1.0×10^{15}	0.0	1.0
β -Scission	1.0×10^{14}	14.24	0.5
Radical Addition	1.0×10^8	14.24	0.5
Radical Recombination	1.0×10^8	0.0	0.0
Intermolecular H-Abstraction			
R•	1.0×10^8	13.3	0.7/0.3
H•	1.0×10^{11}	13.3	endo/exo
Intramolecular H-Abstraction			
1,4-shift	2.0×10^{11}	21.0	0.5
1,5 or 1,6-shift	2.0×10^{10}	12.0	0.5
Disproportionation	1.0×10^9	0.0	0.0

(a) The units of the frequency factor, A , are 1/s for unimolecular reactions and L/(mol•s) for bimolecular reactions.

(b) The units of the intrinsic barrier to reaction, E_0 , are kcal/mol.

Table 2: Effect of variation of user-specified threshold on characteristics of constructed reaction mechanisms for tetradecane pyrolysis using the rate-based generation algorithm.

User-specified Threshold	Number of		Number of		Comments
	Total Species	Reactive Species	Total Reactions	Reactive Reactions	
1.0×10^0	1,174	73	31,610	5,150	only alkanes C ₁ -C ₇
1.0×10^{-1}	1,387	76	36,094	5,981	only alkanes C ₁ -C ₈
1.0×10^{-2}	1,991	87	56,086	10,849	only alkanes C ₁ -C ₁₁
1.0×10^{-3}	2,894	97	77,686	13,214	no <i>n</i> -tridecane
1.0×10^{-4}	3,005	98	80,298	13,230	no <i>n</i> -tridecane
7.0×10^{-5}	3,113	99	82,910	13,236	no <i>n</i> -tridecane
5.0×10^{-5}	3,180	101	87,652	16,638	no allylic radical
1.0×10^{-5}	4,842	128	131,506	30,250	no allylic radical
8.0×10^{-6}	6,692	153	178,950	36,289	no allylic radical
7.0×10^{-6}	19,052	289	479,206	102,257	all species of interest

Table 3: Optimized Arrhenius frequency factors^a for low pressure tetradecane pyrolysis mechanisms constructed using rate-based generation algorithm.

Reaction Family	Mechanism I	Mechanism II	Mechanism III	Mechanism IV
Bond Fission	1.5×10^{17}	1.3×10^{17}	5.9×10^{16}	6.9×10^{16}
β -Scission	3.6×10^{12}	1.9×10^{12}	1.9×10^{12}	2.0×10^{12}
Radical Recombination	3.9×10^7	1.0×10^7	1.8×10^7	1.0×10^7
Intermolecular H-Abstraction: R•	5.2×10^7	3.9×10^7	4.5×10^7	4.9×10^7
Intramolecular H-Abstraction 1,5 or 1,6-shift ^b	5.0×10^9	3.3×10^9	4.7×10^9	5.8×10^9
Disproportionation	1.0×10^7	5.6×10^7	1.0×10^7	3.8×10^7

(a) The units of the frequency factors, A, are 1/s for unimolecular reactions, and L/(mole·s) for bimolecular reactions.

(b) The frequency factor for 1,4-intramolecular hydrogen abstraction is optimized as $(10 \cdot A_{1,5\text{-shift}})$.

Figure 1: Flow diagram illustrating the iterative algorithm for rate-based mechanism generation (adapted from Susnow and co-workers, 1997).

Figure 2: Comparison of fitted model yields using Mechanism I and experimentally observed yields for major and minor products of tetradecane pyrolysis employing the Arrhenius frequency factors listed in Table 3.

Figure 3: Comparison of fitted model yields (lines) using Mechanism I and experimentally observed yields (symbols) of various species for tetradecane pyrolysis conducted at 420°C.

Figure 4: Comparison of experimental (symbols) and predicted (lines) conversion of tetradecane for initial tetradecane loadings of 6.2 and 27.8 mg using Mechanism I.

Figure 5: Comparison of the experimental (symbols) and predicted (lines) evolution of propylene for initial tetradecane loadings of 6.2, 12.3, and 27.8 mg using Mechanism I.

Figure 6: Comparison of the experimental (symbols) and predicted (lines) evolution of 1-decene for initial tetradecane loadings of 6.2, 12.3, and 27.8 mg using Mechanism I.

Figure 7: Comparison of the experimental (symbols) and fitted (lines) yields of 1-octene for tetradecane pyrolysis conducted at 420°C using Mechanisms I and II.

Figure 8: Comparison of the experimental (symbols) and fitted (lines) yields of ethylene for tetradecane pyrolysis conducted at 420°C using Mechanisms I and III.

Figure 9: Comparison of the experimental (symbols) and fitted (lines) yields of propylene for tetradecane pyrolysis conducted at 420°C using Mechanisms II and IV.