92PC92104-TPR-20

ADVANCED THERMALLY STABLE JET FUELS

Technical Progress Report
April - June 1997

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January 1998

Prepared for U.S. Department of Energy
under
Contract No. DE-FG22-92PC92104 --04

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OBJECTIVES

The Penn State program in advanced thermally stable jet fuels has five components: 1) development of mechanisms of degradation and solids formation; 2) quantitative measurement of growth of sub-micrometer and micrometer-sized particles during thermal stressing; 3) characterization of carbonaceous deposits by various instrumental and microscopic methods; 4) elucidation of the role of additives in retarding the formation of carbonaceous solids; and 5) assessment of the potential of producing high yields of cycloalkanes and hydroaromatics from coal.

SUMMARY

The thermal decomposition of a binary mixture of *n*-butylbenzene and *n*-butylcyclohexane was studied under supercritical conditions. The experiments were conducted at 425 °C for 15 to 60 minutes. The pyrolysis showed that there is some interaction between the individual components as evidenced by the changes in the decomposition rates of these compounds relative to those obtained from the corresponding neat pyrolysis experiments. In addition to observed changes in decomposition rates, the pyrolysis products from the binary mixture were found to contain hybrid compounds, such as cyclohexylethylbenzene, which were produced by cross-reactions between *n*-butylbenzene and *n*-butylcyclohexane species. These results suggest that the solid deposition from the binary mixture can have different characteristics with possible non-additive effects which cannot be predicted from the behavior of the individual compounds.

Substantial differences were observed between the composition of the pyrolysis products obtained from the binary mixtures under a starting supercritical or gas phase. Starting supercritical conditions favor the formation of toluene, C_6-diphenyls, and cyclohexyl-C_6-benzenes, and suppress the formation of styrene, cyclohexylbenzene, and other light products. Depending on the effective solid formation or deposition mechanisms, these differences in pyrolysis product composition as a function of pressure can also influence the deposit formation.

An investigation aimed at establishing the minimum necessary volumetric concentrations of hydrogen donors, i.e., tetralin, benzyl alcohol, and THQ, for significantly inhibiting the

degradation of *n*-tetradecane at 450 °C, for a residence time of 30 minutes, was performed. In this work, we have also compared the efficacy of each donor under identical conditions. Moreover, we have investigated the stability of THQ in the binary mixture at low temperature (250 °C) and long residence time (up to 6 hours).

Although we identified several novel additives as important leads in the development of practical high temperature thermal stabilizers; they are susceptible to autoxidation at lower temperatures and thus limit their application. Consequently, a series of studies was undertaken aimed at developing novel “hybrid” stabilizers, based on the combination of two or more of our existing candidate additives, which will have complementary antioxidant abilities for the full temperature range of stabilization. For example, “crossing” BzOH with tetralin leads to three new compounds, each containing the necessary features of their “parents”, i.e., a benzylic alcohol moiety and a partially reduced naphthalene.

A series of coals and petroleum resids were reacted under conditions simulating delayed coking to determine if the delayed coking route is viable for producing an advanced aviation feedstock. From the limited experimental work conducted to date, it appears that it may yet prove to be viable. Indeed, the fact that product distributions do not vary significantly from industry values is favorable. However, work must continue to enhance the selectivity of the pyrolysis reactions to favor the desired coal-derived aromatics.

Task 1. Investigation of the Quantitative Degradation Chemistry of Jet Fuels.

1. Supercritical-Phase Thermal Decomposition of a Mixture of n-Butylbenzene and n-Butylcyclohexane (Contributed by Jian Yu and Semih Eser)

Introduction

In the last quarterly report, we presented the results from the supercritical-phase thermal decomposition of a binary mixture of *n*-dodecane and *n*-butylbenzene [1]. In this work, the mixture thermal decomposition studies were extended to another binary mixture, which consists of 50.49 wt % of *n*-butylbenzene (*n*-BBZ), 49.44 wt % of *n*-butylcyclohexane (*n*-BCH), and small amounts of impurities. Table 1 presents the critical properties of the mixture, which were estimated using the methods recommended in API Technical Data Book [2], and those of pure compounds [3]. Thermal stressing experiments were carried out in a Pyrex glass tube reactor at 425 °C for 15–60 min.

Results and Discussion

1. Reaction Rate. Figure 1 shows the conversions of individual model compounds as a function of reaction time from the thermal decomposition of pure *n*-BBZ, pure *n*-BCH, and *n*-BBZ/*n*-BCH mixture at 425 °C for 15–60 min with a loading ratio of 0.36. The loading ratio was defined as the ratio of the initial sample volume at room temperature to the reactor volume. For the mixture, the initial reaction conditions correspond to a reduced temperature ($T_r = T/T_c$) of 1.05 and a reduced pressure ($P_r = P/P_c$) of 1.80, which was calculated using the Soave–Redlich–Kwong equation of state [4]. It can be seen that the conversions for the decomposition of *n*-BCH in the mixture are significantly higher than those for the decomposition of pure *n*-BCH while the conversions for the decomposition of *n*-BBZ in the mixture are significantly lower than those for the decomposition of pure *n*-BBZ. This means that the presence of *n*-BCH inhibits the decomposition of *n*-BBZ and the presence of *n*-BBZ accelerates the decomposition of *n*-BCH.

Figure 2 shows a comparison of *n*-BBZ conversions from the thermal decomposition of pure *n*-BBZ, in *n*-BBZ/*n*-C_{12} mixture, and in *n*-BBZ/*n*-BCH mixture, under similar conditions. It seems that *n*-C_{12} and *n*-BCH exhibit very similar inhibiting effect on the decomposition of *n*-BBZ. This is probably due to comparable hydrogen abstraction rates from *n*-C_{12} and *n*-BCH by free radicals, as discussed later.

2. Product Distributions. Figure 3 shows the GC chromatogram of the liquid products from the thermal decomposition of *n*-BBZ/*n*-BCH mixture at 425 °C for 60 min with a P_r of 1.80. Most of the liquid products produced from the mixture reactions derive from either the

decomposition of *n*-BBZ component or the decomposition of *n*-BCH component. There are, however, some products which are unique to the reaction of the mixture. Among these are cyclohexylethylbenzene, cyclohexylpropylbenzene, eight cyclohexyl-C_6-benzenes, and several C_7-cyclohexanes.

Figures 4 and 5 show the molar yields of some light and heavy products, respectively, as a function of reaction time from the thermal decomposition of the binary mixture at 425 °C with a P_r of 1.80. The product yield was expressed as the number of moles per 100 moles of the feed initially charged. The cyclohexyl-C_6-benzenes include eight isomers and the C_6-diphenyls include four isomers. The yields of most of the light products increase with reaction time. The yield of styrene decreases and the yield of methylenecyclohexane remains unchanged as reaction time increases. The yields of cyclohexylethylbenzene, cyclohexylpropylbenzene, and 1,3-diphenylpropane increase while the yields of cyclohexyl-C_6-benzenes and C_6-diphenyls first increase and then remain unchanged or decrease with the increasing reaction time.

Table 2 shows a comparison of product distribution between supercritical (i.e., initial supercritical phase) and subcritical (i.e., initial gas phase; temperature is above critical temperature, but pressure is below critical pressure) conditions from the thermal decomposition of *n*-BBZ/*n*-BCH mixture at 425 °C for 60 min. Two loading ratios were used: 0.36 for supercritical (P_r = 1.80) and 0.08 for subcritical (P_r = 0.77). One can see that supercritical conditions favor the formation of toluene, C_6-diphenyls, and cyclohexyl-C_6-benzenes, and suppress the formation of styrene, cyclohexylethylbenzene, and other light products. It seems that there are no significant differences between supercritical and subcritical conditions in the yields of cyclohexylpropylbenzene and 1,3-diphenylpropane.

3. Reaction Mechanisms. The formation of the products from the thermal decomposition of *n*-BBZ/*n*-BCH mixture can be explained by free radical mechanisms. For the thermal reactions of *n*-BBZ/*n*-BCH mixture, the initiation occurs mainly by homolytic cleavage of C_α–C_β bond in *n*-BBZ because the cleavage of this bond, which produces a resonance-stabilized benzyl radical, is much easier than breaking any other bond in both compounds. The radicals produced by the initiation reactions can abstract hydrogen atoms from *n*-BBZ and *n*-BCH molecules to form various parent radicals, including four phenylbutyl radicals and eight *n*-butylcyclohexane radicals (four cyclohexylbutyl radicals and four butylcyclohexyl radicals). Figure 6 shows the structures of these parent radicals.

The formation of the products from the decomposition of *n*-BBZ component can be explained by the decomposition of four phenylbutyl radicals, including α, β, γ, and δ-phenylbutyl radicals, and a series of subsequent hydrogen abstraction and radical addition reactions, as shown in Figures 7 and 8 [1]. Tetralin could be formed by the cyclization of a δ-phenylbutyl radical and benzene could be produced by "ipso" attack of a hydrogen atom on *n*-butylbenzene, ejecting butyl radical and forming benzene, as suggested by Freund and Olmstead [5].

The formation of the products from the decomposition of *n*-BCH component can be rationalized by the reactions shown in Figures 9 and 10. Some C_{10} olefins (with different double bond positions) were also observed. These C_{10} olefins could be produced by the decomposition of four butylcyclohexyl radicals or cyclohexyl-1-butyl radical on the ring, followed by hydrogen abstraction. It seems that the decomposition of *n*-butylcyclohexane radicals on the ring is not significant as compared to the decomposition at the side chain, as evidenced by the relatively low yields of C_{10} olefins.

Cyclohexylethylbenzene can be produced from the addition reactions between cyclohexyl radical and styrene, while cyclohexylpropylbenzene could be formed from the addition reactions between cyclohexylmethyl radical and styrene, or between vinylcyclohexane and benzyl radical. The formation of eight cyclohexyl-C_6-benzenes can be attributed to the addition reactions between eight *n*-butylcyclohexane radicals and styrene. The addition reactions between *n*-butylcyclohexane radicals and propylene could lead to the formation of C_7-cyclohexanes. Figure 11 shows some examples of the addition reactions unique to the reaction of the *n*-BBZ/*n*-BCH mixture.

The decomposition of pure *n*-BCH is relatively slow because of low initiation rates. The addition of *n*-BBZ to *n*-BCH increases the radical concentration for the decomposition of *n*-BCH because of high initiation rates of *n*-BBZ, which leads to an increase in the rates of hydrogen abstraction from *n*-BCH, and, thus, an increase in *n*-BCH decomposition rates, as shown in Figure 1. On the other hand, the fraction of radicals which participate in hydrogen abstraction from *n*-BBZ decreases because of the presence of *n*-BCH, leading to a decrease in *n*-BBZ decomposition rates.

The decomposition of *n*-BBZ is inhibited by the addition of *n*-C_{12} or *n*-BCH because some of the radicals, which would abstract hydrogen atoms from *n*-BBZ in the absence of *n*-C_{12} or *n*-BCH, abstract hydrogen atoms from *n*-C_{12} or *n*-BCH. Since the rates of hydrogen abstraction from *n*-C_{12} and *n*-BCH are comparable, both compounds should exhibit similar inhibiting effect on the decomposition of *n*-BBZ, as shown in Figure 2.

Styrene is very reactive while cyclohexene and methylcyclohexenes are not reactive in radical addition reactions, as indicated by Figure 4. The high-molecular-weight compounds formed in mixture reactions are not stable and their formation rates decrease with reaction time (Figure 5). It seems that cyclohexyl radical is more reactive than benzyl radical in radical addition reactions with styrene, as evidenced by Figure 5 which shows that the yield of cyclohexylethylbenzene is higher than that of 1,3-diphenylpropane. If both radicals had exhibited comparable reactivity in radical additions, the yield of cyclohexylethylbenzene would have been lower than that of 1,3-diphenylpropane because of the lower concentration of cyclohexyl radical than benzyl radical.

The radical addition reactions between parent radicals (phenylbutyl radicals and *n*-butylcyclohexane radicals) and styrene are favored under supercritical conditions because of the higher concentrations of parent radicals, leading to higher yields of C_6-diphenyls and cyclohexyl-C_6-benzenes and low styrene yield (Table 2). Correspondingly, the formation of decomposition products (light products) is suppressed under supercritical conditions because fewer parent radicals decompose. More toluene is formed under supercritical conditions because more high-molecular-weight compounds which undergo further decomposition to form toluene and other compounds.

Conclusions

There is some interaction between the individual components during pyrolysis of a binary mixture of n-butylbenzene and n-butylcyclohexane, as evidenced by the changes in the decomposition rates of these compounds relative to those obtained from the corresponding neat pyrolysis experiments. In addition to observed changes in decomposition rates, the pyrolysis products from the binary mixture were found to contain hybrid compounds, such as cyclohexylethylbenzene, which were produced by cross-reactions between n-butylbenzene and n-butylcyclohexane species. These results suggest that the solid deposition from the binary mixture can have different characteristics with possible non-additive effects which cannot be predicted from the behavior of the individual compounds.

Substantial differences were observed between the composition of the pyrolysis products obtained from the binary mixtures under a starting supercritical or gas phase. Starting supercritical conditions favor the formation of toluene, C_6-diphenyls, and cyclohexyl-C_6-benzenes, and suppress the formation of styrene, cyclohexylethylbenzene, and other light products. Depending on the effective solid formation or deposition mechanisms (i.e., catalytic or non-catalytic), these differences in pyrolysis product composition as a function of pressure can also influence the deposit formation.

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Table 1. Critical Properties of Model Compounds and Their Mixture

	T_c, °C	P_c, MPa
n-BBZ	387	2.89
n-BCH	394	2.57
n-BBZ + *n*-BCH	391	2.74

Table 2. Comparison of Product Distributions between Supercritical and Subcritical Conditions from *n*-BBZ/*n*-BCH Mixture at 425 °C for 60 min.

	product yield, mol/100 mol feed charged	
	supercritical, P_r = 1.80	subcritical, P_r = 0.77
cyclohexane	1.53	2.07
cyclohexene	0.74	1.15
methylcyclohexane	0.71	0.92
methylenecyclohexane	0.10	0.56
toluene	7.61	5.55
ethylbenzene	0.96	1.07
styrene	0.54	1.99
cyclohexylethylbenzene	0.12	0.20
cyclohexylpropylbenzene	0.06	0.07
1,3-diphenylpropane	0.10	0.09
C_6-diphenyls (4)	0.26	0.14
cyclohexyl-C_6-benzenes (8)	1.06	0.67

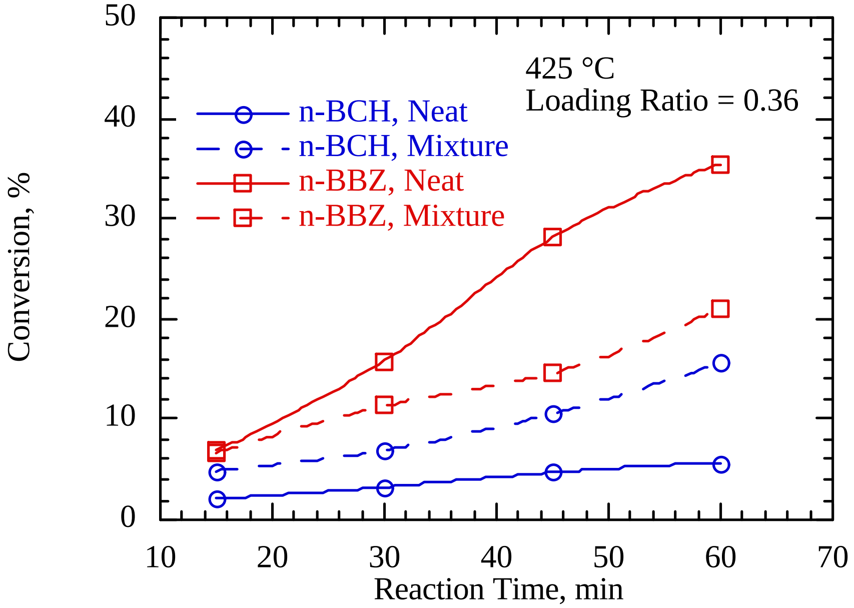


Figure 1. Conversions of *n*-BBZ and *n*-BCH Versus Reaction Time from Thermal Decomposition of Pure Compounds and Mixture at 425 °C.

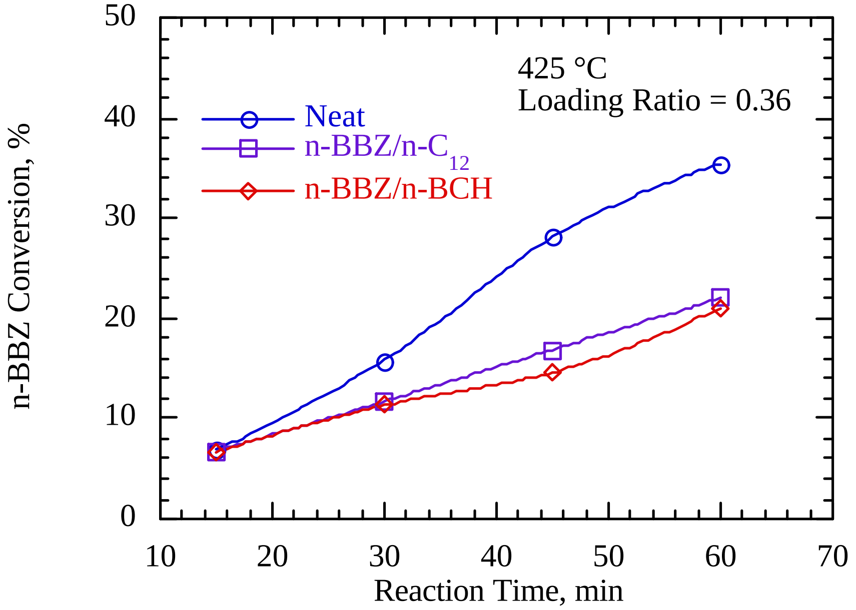


Figure 2. Comparison of *n*-BBZ Conversions from Thermal Decomposition of Pure *n*-BBZ, in *n*-BBZ/*n*-C_{12} Mixture, and in *n*-BBZ/*n*-BCH Mixture.

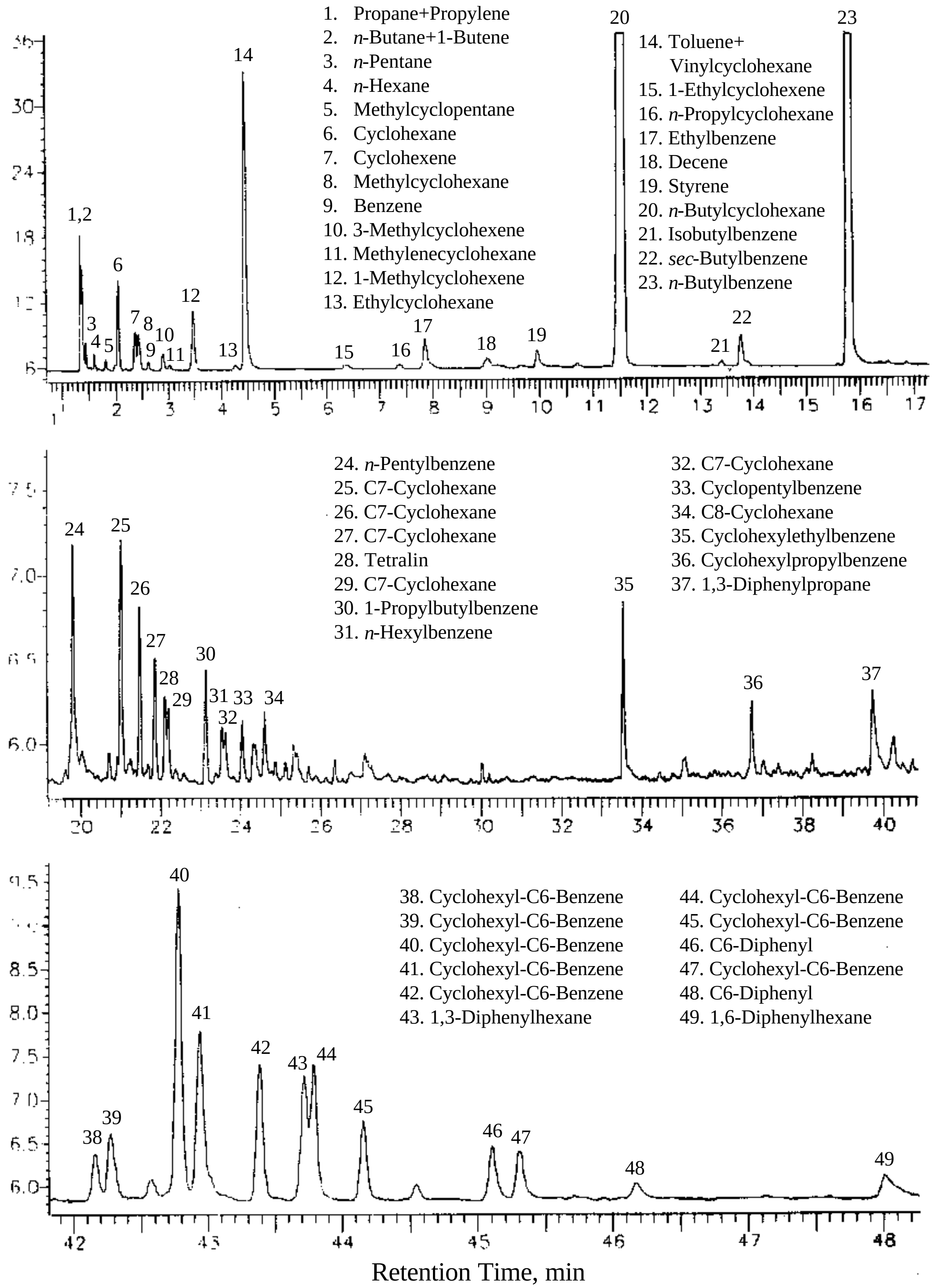


Figure 3. GC Chromatogram of Liquid Products from Thermal Decomposition of Mixture of n-BBZ and n-BCH at 425 °C for 60 min with a P_r of 1.80.

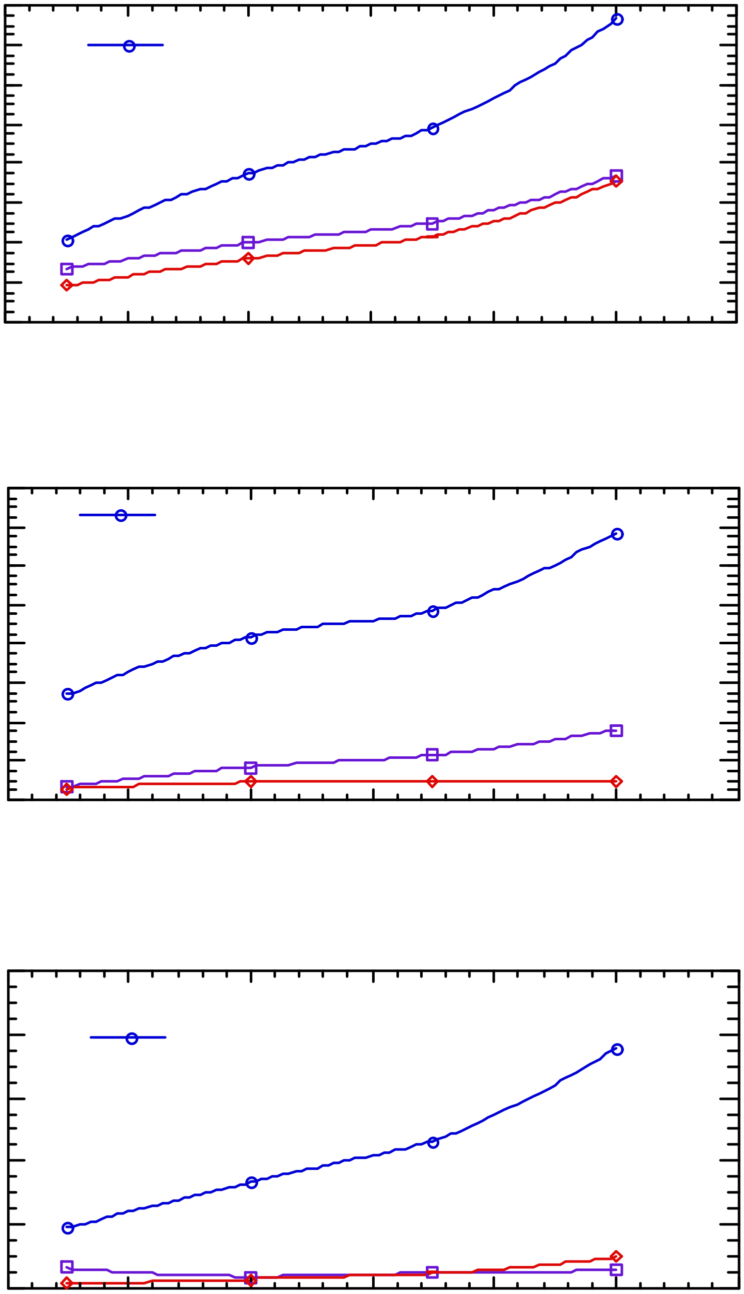


Figure 4. Yields of Low-Molecular-Weight Products as a Function of Reaction Time from Thermal Decomposition of *n*-BBZ/*n*-BCH Mixture at 425 °C.

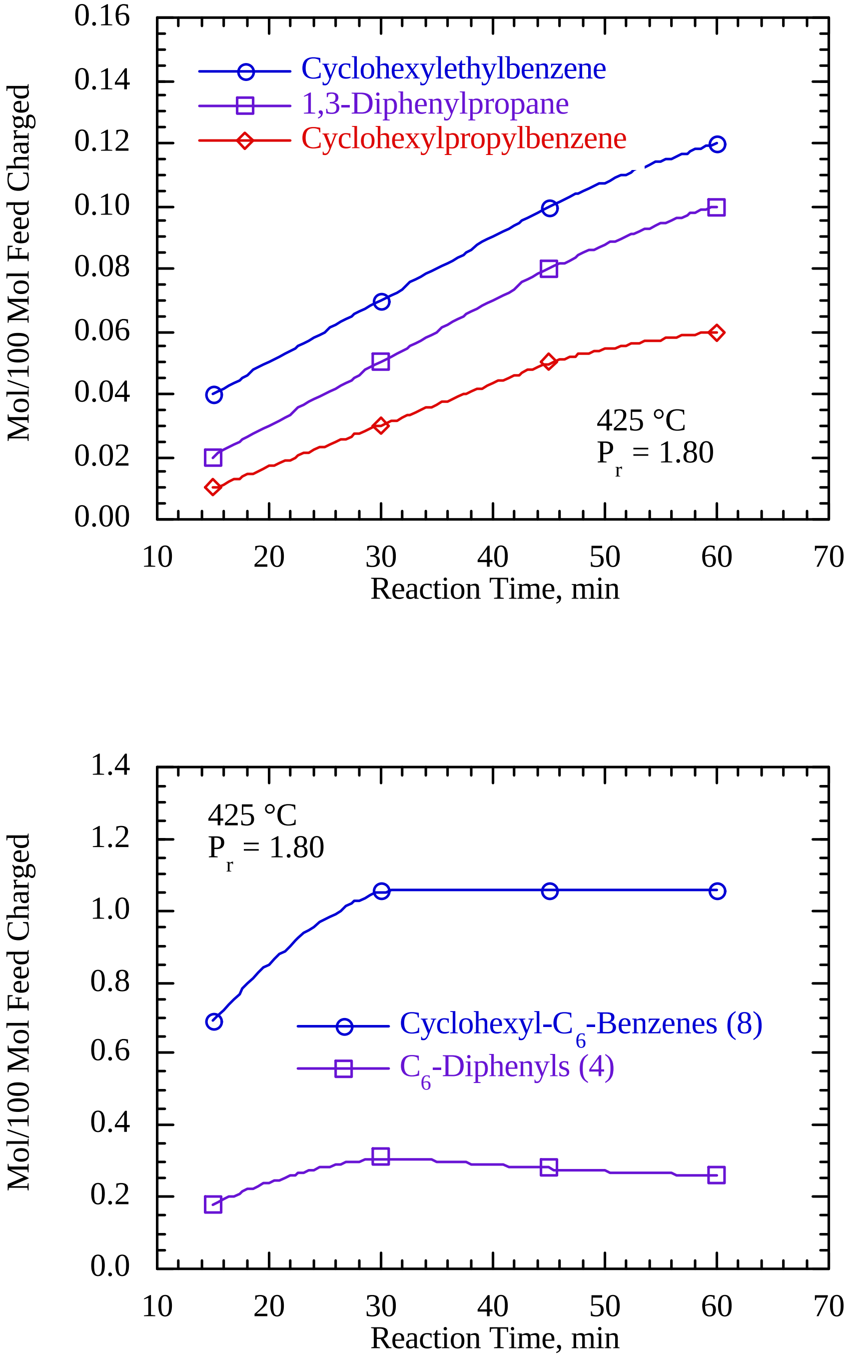
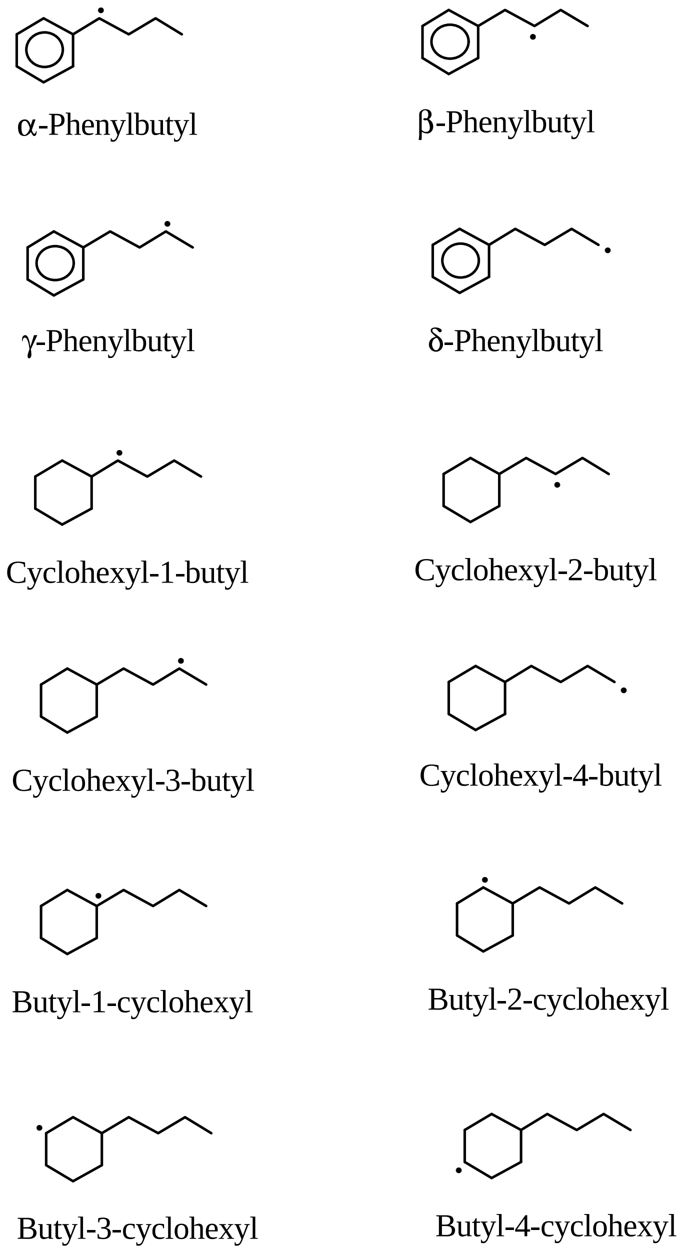


Figure 5. Yields of High-Molecular-Weight Products as a Function of Reaction Time from Thermal Decomposition of *n*-BBZ/*n*-BCH Mixture at 425 °C.



α-Phenylbutyl

β-Phenylbutyl

γ-Phenylbutyl

δ-Phenylbutyl

Cyclohexyl-1-butyl

Cyclohexyl-2-butyl

Cyclohexyl-3-butyl

Cyclohexyl-4-butyl

Butyl-1-cyclohexyl

Butyl-2-cyclohexyl

Butyl-3-cyclohexyl

Butyl-4-cyclohexyl

Figure 6. Structures of Parent Radicals from Thermal Decomposition of *n*-BBZ/*n*-BCH Mixture.

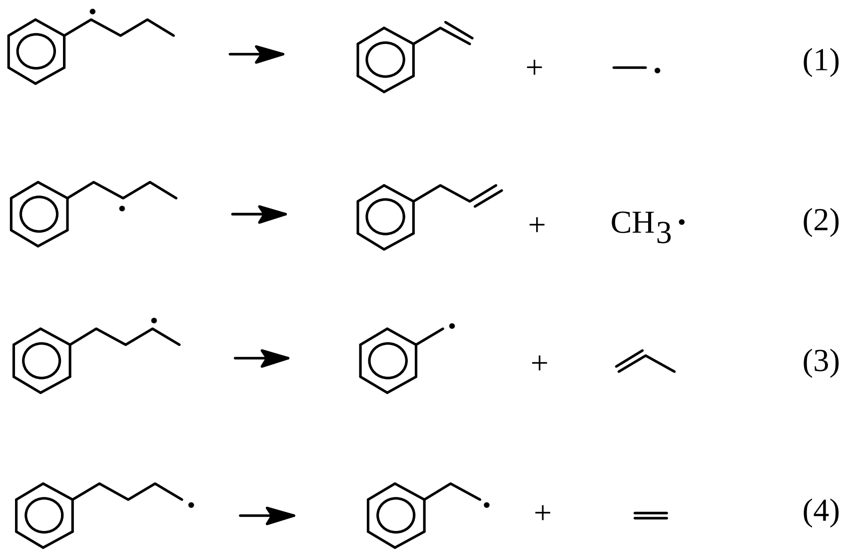


Figure 7. Primary Reactions from Thermal Decomposition of *n*-BBZ Component in *n*-BBZ/*n*-BCH Mixture [1].

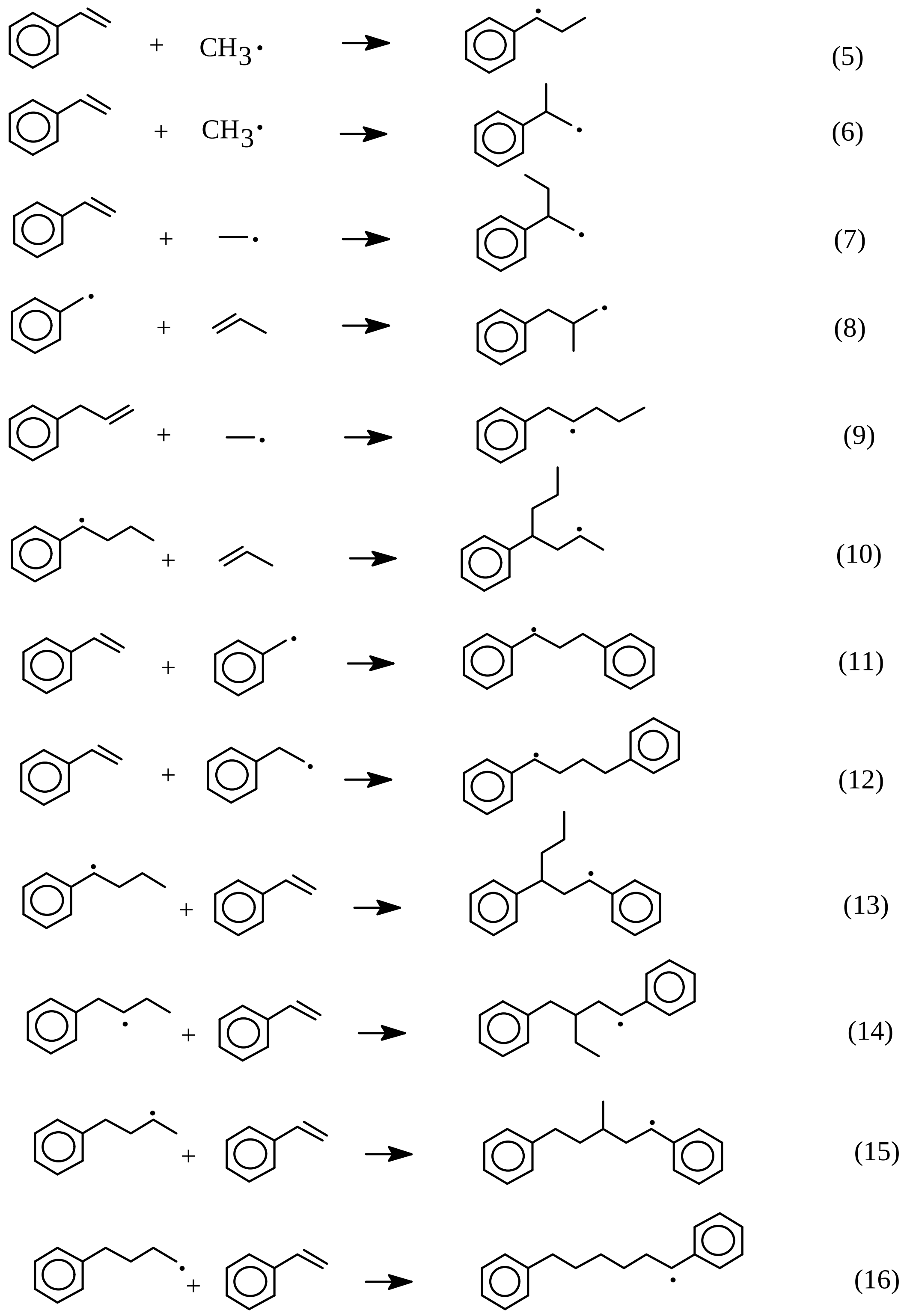


Figure 8. Addition Reactions from Thermal Decomposition of *n*-BBZ Component in *n*-BBZ/*n*-BCH Mixture [1].

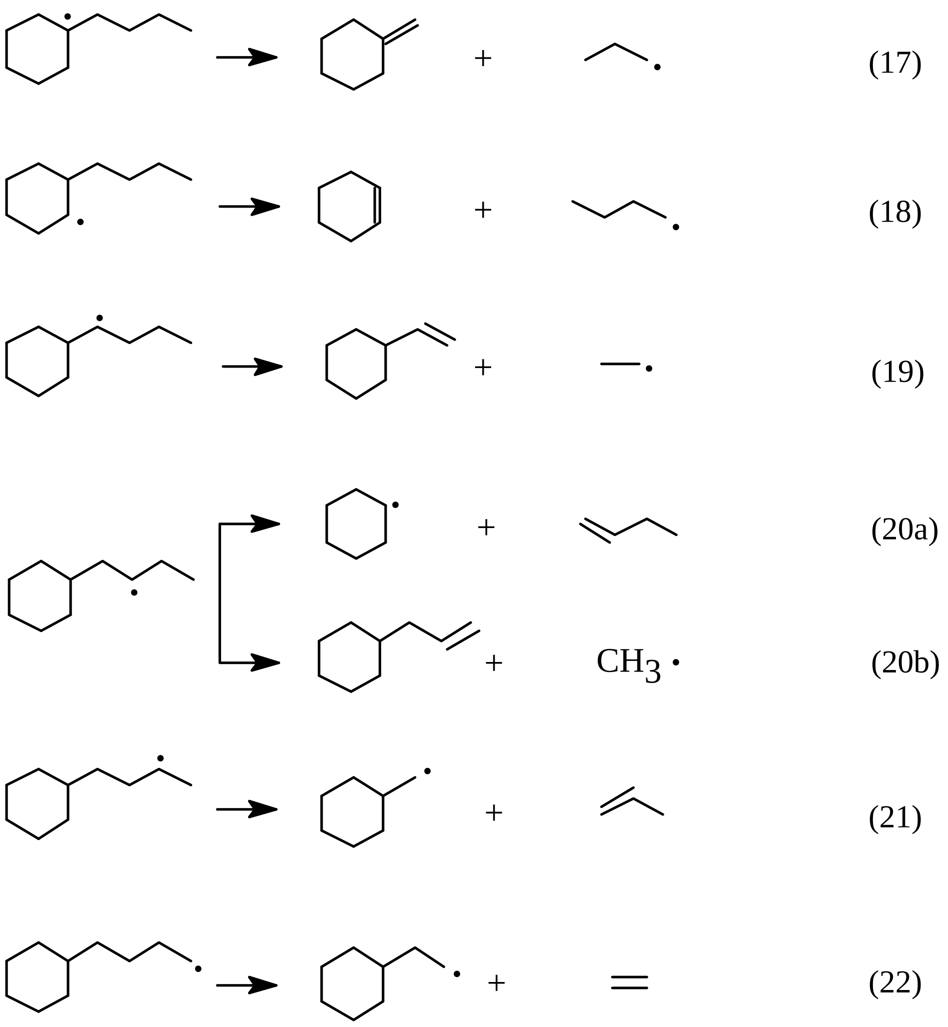


Figure 9. Primary Reactions from Thermal Decomposition of *n*-BCH Component in *n*-BBZ/*n*-BCH Mixture.

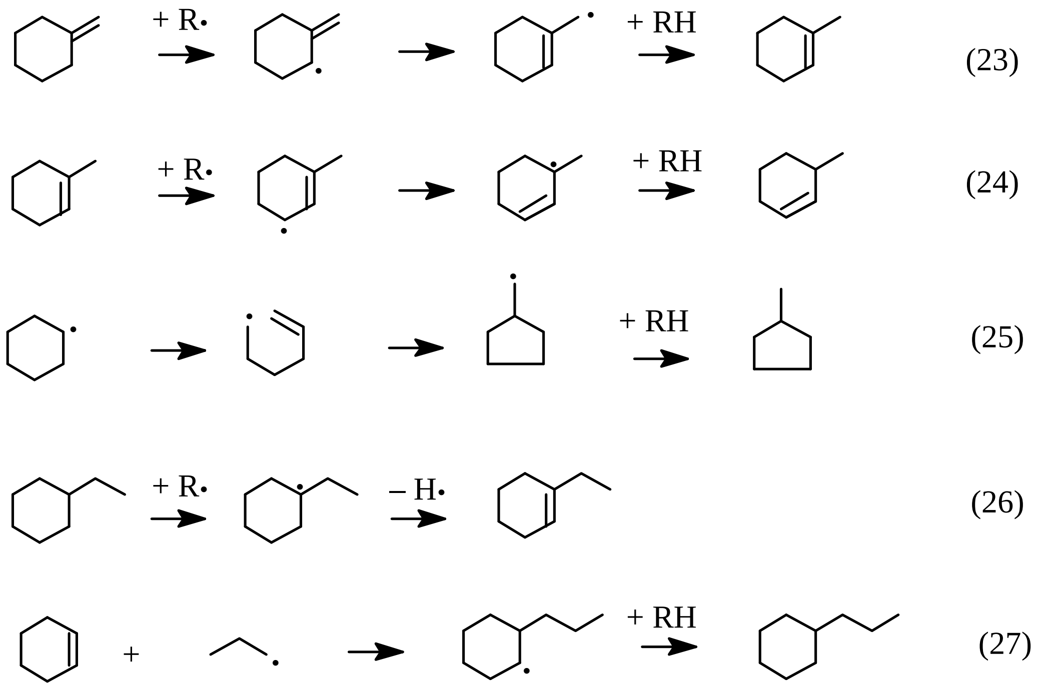
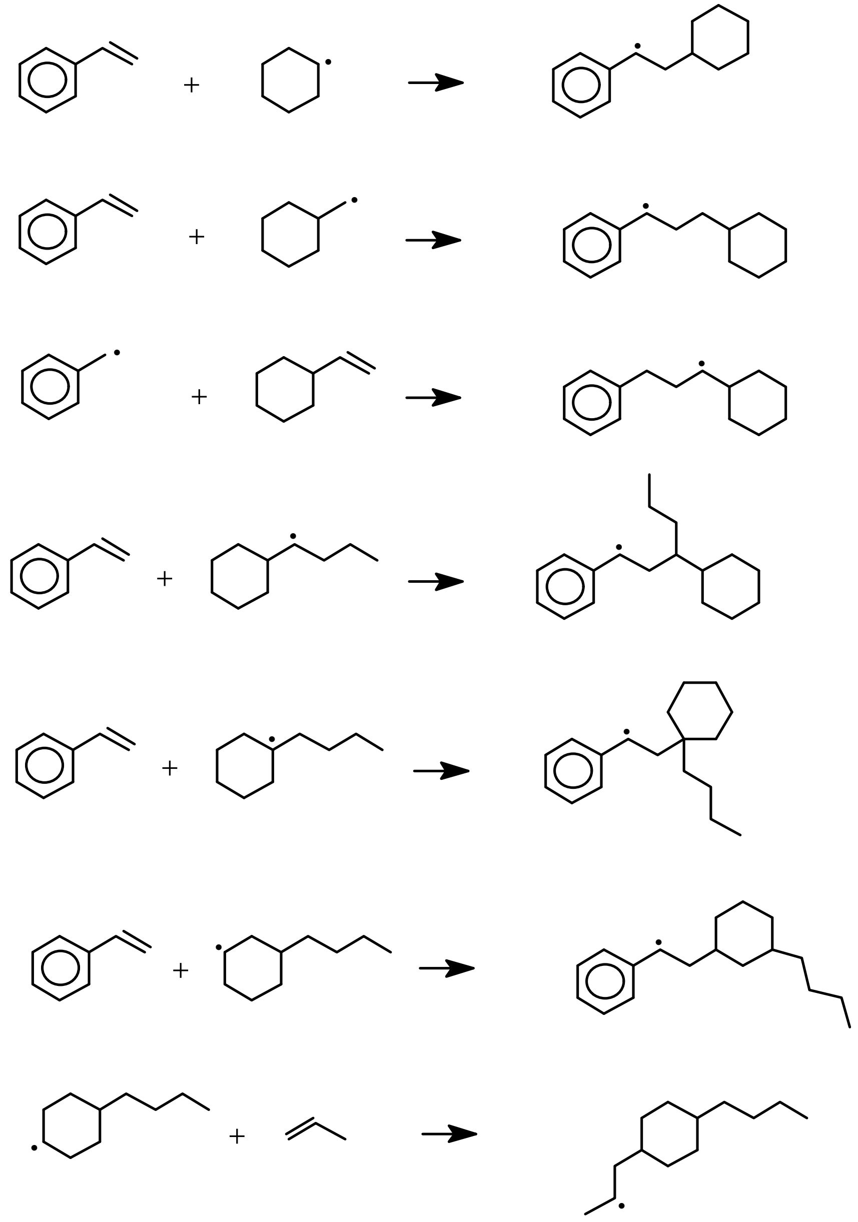


Figure 10. Secondary Reactions from Thermal Decomposition of *n*-BCH Component in *n*-BBZ/*n*-BCH Mixture.



(28)

(29)

(30)

(31)

(32)

(33)

(34)

Figure 11. Examples of Addition Reactions Unique to the Reaction of *n*-BBZ/*n*-BCH Mixture.

2. Studies on the Effects of the Concentration of Hydrogen Donors on the Pyrolysis of n-Tetradecane at 450 °C in a Batch Reactor (Contributed by A. Venkataraman, C. Song, and M. Coleman)

Introduction

In a previous report we discussed the results of our study aimed at evaluating the efficacy of various hydrogen donors, and investigated the role of the phase conditions, i.e., subcritical or supercritical regime, in influencing the pyrolytic decomposition of n-tetradecane in a binary mixture of n-tetradecane and a hydrogen donor at 450 °C in a batch reactor [Venkataraman et al., 1997]. The hydrogen donors selected for the study were 1,2, 3,4-tetrahydronaphthalene (tetralin), benzyl alcohol, and 1,2,3,4-tetrahydroquinoline (THQ); the sample (reactant) volumes were varied from 1 mL to 11 mL to generate different phase conditions during pyrolysis. It was determined that THQ was by far the most effective hydrogen donor both in terms of its radical scavenging ability as well as its own stability at 450 °C. Furthermore, it was inferred that interactions between the hydrogen donors and n-tetradecane are not affected significantly by the phase conditions during pyrolysis.

In this report, we present the results of our investigation aimed at establishing the minimum necessary volumetric concentration of each hydrogen donor for significantly inhibiting the degradation of n-tetradecane at 450 °C, for a residence time of 30 minutes and a sample volume of 5 mL, in a 23.2 mL batch reactor under an initial nitrogen (UHP) pressure of. approximately one atmosphere. In this work, we have also compared the efficacy of each donor under identical conditions. Moreover, we have investigated the stability of THQ in the binary mixture at a low temperature (250 °C) and long residence times (up to 6 hours) in the batch reactor under UHP nitrogen atmosphere.

Experimental

A detailed description for the experimental setup, analytical procedure for determining the product distributions and extent of degradation of reactants, and methodology for analysis has been reported elsewhere [Song and Lai, 1994 a,b]. The volumetric concentration of the three hydrogen donors was varied from 0.5 to 10 vol %, in a sequence comprising 0.5, 1.0, 3, 5 and 10 vol % runs at 450 °C. In these runs, the residence time was kept constant at 30 mins for a sample volume of 5 mL and an initial nitrogen pressure of one atmosphere. The low temperature runs involving THQ were carried out at residence times from 2 to 6 hours, in increments of 2 hours. The purity of THQ, tetralin, and Benzyl alcohol as determined from GC and GC/MS analyses were approximately 98%, 97%, and 99%, respectively.

Results and Discussion

The product distributions obtained from the pyrolysis of binary mixtures of THQ and tetradecane at 450 °C at various volumetric concentrations and constant residence time of 30 minutes in the 23.2 mL batch reactor are tabulated in Tables 1 and 2. The weights of product gas and liquid recovered from the reactor after pyrolysis are also presented at the bottom of the tables. It is evident from the table that the extent of degradation of n-tetradecane is small and does not change appreciably as the volumetric concentration of THQ is decreased from 10 to 3%. The same is true for the molar concentrations of paraffins and olefins with carbon numbers in the range from 8 to 13. It is known that the observed inhibition in the decomposition of n-tetradecane is attributable to the highly efficient radical scavenging ability of THQ, its excellent resonance stabilization properties, and the donation of 4 hydrogen atoms for every THQ molecule converted to the stable final product, quinoline [Emily et al., 1996]. Note the increase in the concentration of quinoline as the volumetric concentration of THQ is decreased from 10 to 5%, and finally to 3%.

However, when the THQ volumetric concentration is decreased further from 3 to 1% and finally to 0.5%, the molar percent of n-tetradecane that decomposes into products (parafins and olefins) increases sharply as observed from the data in Table 2. At a volumetric concentration of 0.5%, the molar amount of THQ remaining unconverted is only 73.5% with considerable formation of quinoline (25.91%). It is to be expected that with a further decrease in THQ concentration, the mole percent of n-tetradecane remaining unconverted will rapidly approach that for infinite dilution, i.e., pyrolysis of neat n-tetradecane. Thus, from the above data, one may conclude that the minimum necessary volumetric concentration of THQ that results in a significant (acceptable) inhibition of n-tetradecane decomposition is approximately 1 vol %.

The product distributions for binary mixtures of n-tetradecane and tetralin, as well as that for n-tetradecane and benzyl alcohol at identical conditions and volumetric concentration levels (as for THQ), are displayed in Tables 3 and 4, and Tables 5 and 6, respectively. Trends similar to those for THQ are observable when the volumetric concentration of each hydrogen donor is decreased from 10 to 3, and finally to 0.5%. It is evident that when the volumetric concentration of the donor is less than approximately 1%, the decomposition of n-tetradecane increases significantly, and the scavenging power of each donor is greatly diminished. Note that for tetralin, it may seem from Table 4 that the volumetric concentration of 0.5% results in a product distribution that is not significantly different from that for 1%. This observation, however, is likely to be an artifact due to uncertainties in experiment. The data presented in Tables 1 through 6 are summarized in Figure 1, which plots the molar concentration of n-tetradecane remaining unconverted in the reactor against the volumetric concentration of the hydrogen donor in the binary mixture. It is obvious from the figure that THQ is clearly the best and most effective stabilizer at all concentrations investigated; it is intriguing that a 1 vol% strength of THQ is more effective in inhibiting n-tetradecane decomposition than 10 vol% strengths of either tetralin or benzyl alcohol. It is also seen that the efficacy of 0.5 vol% THQ is comparable to that of 10 vol% benzyl alcohol, although the molar amount of latter donor remaining unconverted is higher (compare Tables 2 and 5). This remarkable scavenging power of THQ is yet to be fully understood given the fact that tetralin also donates 4 hydrogen atoms per parent molecule, and its product, naphthalene, is equally if not more stable than quinoline.

Experiments involving low-temperature (250 °C) stressing of a nitrogen purged 10 vol% THQ and 90 vol% n-tetradecane binary mixture for various residence times from 2 hours up to 6 hours under nitrogen atmosphere did not generate any measurable quantities of product gas or C3 to C13 alkanes / alkenes in the product liquid. Neither could measurable quantities of any THQ reaction products be detected in the liquid product even after 6 hours of stressing. It will be of interest to ascertain whether both tetralin and benzyl alcohol also exhibit the same behaviour as THQ at these low-temperature conditions.

Nonetheless, the overall implication of the above results especially from a practical applications viewpoint is that the minimum necessary concentration of each donor for significantly inhibiting n-tetradecane decomposition is approximately 1 vol%. THQ emerges as the favorite choice on account of its intrinsically superior thermal stabilizing properties. Further studies are anticipated on confirming the radical scavenging abilities of THQ and other donors at this concentration during pyrolysis of actual mixtures of jet fuel and the hydrogen donor.

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TABLE 1. PYROLYSIS OF N-TETRADECANE AT VARIOUS			
VOLUMETRIC CONCENTRATIONS OF THQ AT 450 C			
SAMPLE VOLUME = 5 ML			
RESIDENCE TIME = 30 MINS			
INITIAL N2 PRESSURE = ATMOSPHERIC			
VOL. CONC. OF THQ (%)	10	5	3
EXPT. NUMBER	79	89	87
COMPONENT	MOL (%)	MOL (%)	MOL(%)
HYDROGEN	0.00	0.00	0.00
METHANE	0.96	1.09	0.97
ETHANE	1.58	1.59	1.52
ETHYLENE	1.27	1.63	1.60
PROPANE	1.15	1.61	1.58
PROPYLENE	1.18	1.83	1.72
ISOBUTANE			
N-BUTANE	0.38	0.51	0.54
1-BUTENE	0.39	0.72	0.79
N-PENTANE	0.16	0.28	0.32
1-PENTENE	0.19	0.51	0.56
N-HEXANE	0.17	0.23	0.25
1-HEXENE	0.3	0.48	0.54
N-HEPTANE	0.13	0.20	0.23
1-HEPTENE	0.22	0.40	0.44
N-OCTANE	0.09	0.15	0.16
1-OCTENE	0.18	0.25	0.28
N-NONANE	0.1	0.12	0.13
1-NONENE	0.17	0.12	0.16
N-DECANE	0.09	0.08	0.07
1-DECENE	0.16	0.07	0.10
N-UNDECANE	0.08	0.05	0.08
1-UNDECENE	0.15	0.09	0.11
N-DODECANE	0.01	0.01	0.01
1-DODECENE	0.13	0.18	0.15
N-TRIDECANE	0.04	0.02	0.03
1-TRIDECENE	0.04	0.03	0.11
N-TETRADECANE	97.4	95.0	94.3
1-TETRADECENE	0.02	0.10	0.15
N-PENTADECANE	0.01	0.11	0.13
N-HEXADECANE	0	0.07	0.09
N-HEPTADECANE	0	0.00	0.02
N-OCTADECANE	0	0.00	0.00
QUINOLINE*	4.32	5.5	7.63
THQ*	93.1	92.6	89.7
Product Gas wt. (g)	0.04	0.05	0.04
Product Liquid wt. (g)	3.86	3.78	3.66
Initial wt. of reactants (g)	3.93	3.882	3.85
Recovery (%)	98.09	98.66	96.10
*Yield is based on the initial molar charge of THQ			

TABLE 2. PYROLYSIS OF N-TETRADECANE AT VARIOUS THQ VOLUMETRIC CONCENTRATIONS AT 450 C		
SAMPLE VOLUME = 5 ML		
RESIDENCE TIME = 30 MINS		
INITIAL N2 PRESSURE = ATMOSPHERIC		
VOL. CONC. OF THQ (%)	1	0.50
EXPT. NUMBER	90	86
COMPONENT	MOL (%)	MOL(%)
HYDROGEN	0.00	0.00
METHANE	1.56	2.71
ETHANE	2.02	2.97
ETHYLENE	2.46	3.67
PROPANE	2.61	3.43
PROPYLENE	3.44	4.86
ISOBUTANE		
N-BUTANE	1.13	1.92
1-BUTENE	1.31	2.11
N-PENTANE	1.90	1.58
1-PENTENE	0.89	3.33
N-HEXANE	1.60	1.54
1-HEXENE	0.72	2.21
N-HEPTANE	1.05	1.17
1-HEPTENE	0.51	1.55
N-OCTANE	0.85	0.92
1-OCTENE	0.43	1.19
N-NONANE	0.67	0.75
1-NONENE	0.34	1.01
N-DECANE	0.56	0.72
1-DECENE	0.30	0.84
N-UNDECANE	0.46	0.11
1-UNDECENE	0.04	0.75
N-DODECANE	0.47	0.06
1-DODECENE	0.02	0.19
N-TRIDECANE	0.12	0.00
1-TRIDECENE	0.12	0.00
N-TETRADECANE	88.8	84.90
1-TETRADECENE	0.09	0.17
N-PENTADECANE	0.03	0.19
N-HEXADECANE	0.04	0.14
N-HEPTADECANE	0.02	0.07
N-OCTADECANE	0.01	0.02
QUINOLINE*	10.3	25.91
THQ*	87.6	73.50
Product Gas wt. (g)	0.07	0.10
Product Liquid wt. (g)	3.67	3.69
Initial wt. of reactants (g)	3.838	3.81
Recovery (%)	97.45	99.53
*Yield is based on the initial molar charge of THQ		

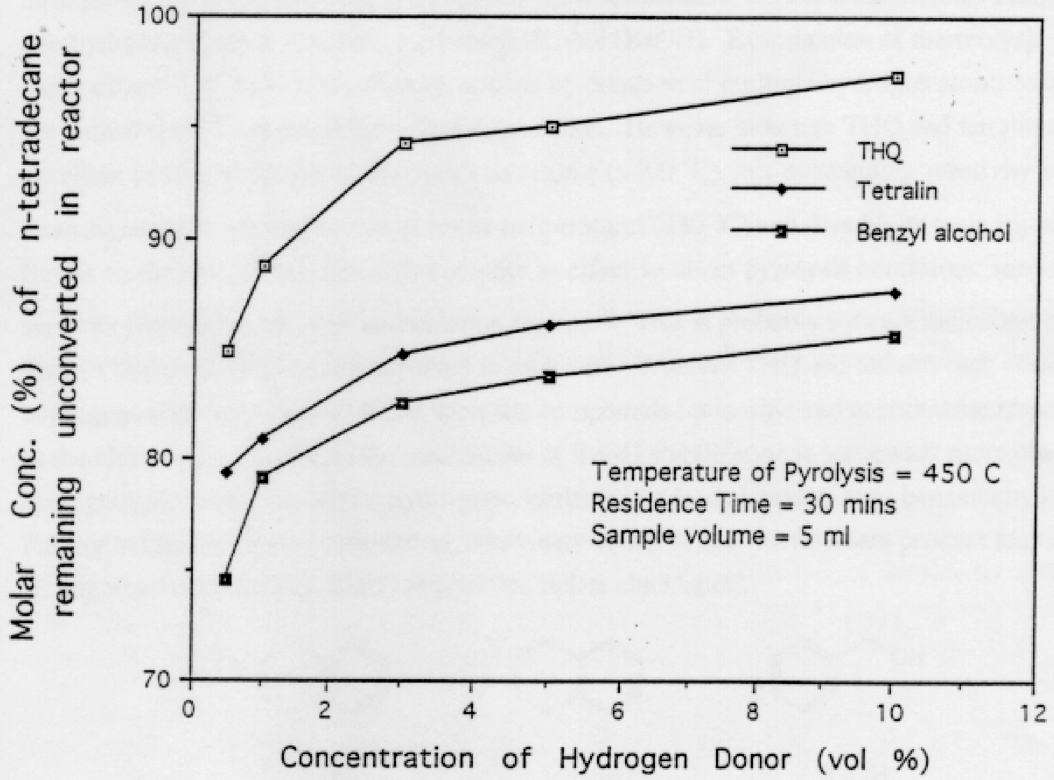
TABLE 3. PYROLYSIS OF N-TETRADECANE AT VARIOUS VOLUMETRIC CONCENTRATIONS OF TETRALIN AT 450 C			
SAMPLE VOLUME. = 5 ML			
RESIDENCE TIME = 30 MINS			
INITIAL N2 PRESSURE = ATMOSPHERIC			
VOL. CONC. OF TETRALIN (%)	10	5	3
EXPT. NUMBER	14 - 14	92	96
COMPONENT	MOL (%)	MOL (%)	MOL(%)
HYDROGEN	0.00	0.00	0.00
METHANE	1.07	1.29	1.40
ETHANE	1.77	2.21	2.49
ETHYLENE	1.98	2.33	2.77
PROPANE	1.83	1.94	2.32
PROPYLENE	2.14	2.04	2.20
ISOBUTANE			
N-BUTANE	1.39	1.76	2.07
1-BUTENE	1.73	2.03	2.88
N-PENTANE	1.04	1.20	1.43
1-PENTENE	1.61	1.98	2.67
N-HEXANE	0.67	0.83	1.14
1-HEXENE	1.44	2.06	2.60
N-HEPTANE	0.54	0.84	1.06
1-HEPTENE	0.95	1.13	1.50
N-OCTANE	0.61	0.55	0.79
1-OCTENE	0.89	0.88	1.09
N-NONANE	0.33	0.38	0.61
1-NONENE	0.6	0.69	0.70
N-DECANE	0.3	0.34	0.51
1-DECENE	0.52	0.63	0.61
N-UNDECANE	0.34	0.32	0.43
1-UNDECENE	0.37	0.47	0.54
N-DODECANE	0.06	0.09	0.06
1-DODECENE	0.35	0.46	0.49
N-TRIDECANE	0.04	0.05	0.08
1-TRIDECENE	0.07	0.11	0.28
N-TETRADECANE	87.7	86.1	84.8
1-TETRADECENE	0.05	0.09	0.10
N-PENTADECANE	0.04	0.07	0.13
N-HEXADECANE	0.04	0.08	0.09
N-HEPTADECANE	0.03	0.03	0.03
N-OCTADECANE	0.01	0.02	0.02
1-METHYL INDAN*	3.87	4.65	5.34
NAPHTHALENE*	3.66	4.98	5.68
TETRALIN*	89.6	88.4	87.3
Product Gas wt. (g)	0.04	0.04	0.05
Product Liquid wt. (g)	3.86	3.76	3.93
Initial wt. of reactants (g)	3.93	3.882	4.11
Recovery (%)	98.09	97.89	96.64
*Yield is based on the initial molar charge of tetralin			

TABLE 4. PYROLYSIS OF N-TETRADECANE AT VARIOUS VOLUMETRIC CONCENTRATIONS OF TETRALIN AT 450 C		
SAMPLE VOLUME = 5 ML		
RESIDENCE TIME = 30 MINS		
INITIAL N2 PRESSURE = ATMOSPHERIC		
VOL. CONC. OF TETRALIN (%)	1	0.50
EXPT. NUMBER	94	95
COMPONENT	MOL (%)	MOL(%)
HYDROGEN	0.01	0.00
METHANE	2.66	2.19
ETHANE	2.34	2.98
ETHYLENE	3.23	3.45
PROPANE	3.26	4.14
PROPYLENE	5.03	5.37
ISOBUTANE		
N-BUTANE	1.57	2.20
1-BUTENE	4.61	5.10
N-PENTANE	1.31	1.87
1-PENTENE	3.34	3.98
N-HEXANE	1.24	1.62
1-HEXENE	2.71	3.00
N-HEPTANE	1.21	1.51
1-HEPTENE	1.75	1.91
N-OCTANE	0.94	1.15
1-OCTENE	1.24	1.35
N-NONANE	0.71	0.84
1-NONENE	0.80	0.86
N-DECANE	0.59	0.71
1-DECENE	0.65	0.72
N-UNDECANE	0.60	0.73
1-UNDECENE	0.77	0.83
N-DODECANE	0.12	0.18
1-DODECENE	0.63	0.77
N-TRIDECANE	0.09	0.10
1-TRIDECENE	0.19	0.24
N-TETRADECANE	80.9	79.4
1-TETRADECENE	0.19	0.23
N-PENTADECANE	0.13	0.15
N-HEXADECANE	0.11	0.11
N-HEPTADECANE	0.06	0.08
N-OCTADECANE	0.03	0.06
1-METHYL INDAN*	6.77	8.83
NAPHTHALENE*	10.50	11.97
TETRALIN*	80.4	77.5
Product Gas wt. (g)	0.08	0.06
Product Liquid wt. (g)	3.651	3.71
Initial wt. of reactants (g)	3.82	3.82
Recovery (%)	98.09	98.77
*Yield is based on the initial molar charge of tetralin		

TABLE 5. PYROLYSIS OF N-TETRADECANE AT VARIOUS VOLUMETRIC CONCENTRATIONS OF BENZYL ALCOHOL AT 450 C			
SAMPLE VOLUME. = 5 ML			
RESIDENCE TIME = 30 MINS			
INITIAL N2 PRESSURE = ATMOSPHERIC			
VOL. CONC. OF BENZYL ALCOHOL (%	10	5	3
EXPT. NUMBER	28	97	98
COMPONENT	MOL (%)	MOL (%)	MOL(%)
HYDROGEN	0.02	0.00	0.02
METHANE	1.48	2.16	1.88
ETHANE	4.07	1.95	2.54
ETHYLENE	0.48	2.29	3.93
PROPANE	3.56	1.89	2.28
PROPYLENE	2.08	2.11	3.51
ISOBUTANE			
N-BUTANE	3.3	1.44	1.52
1-BUTENE	2.5	2.27	4.33
N-PENTANE	0.69	1.11	1.20
1-PENTENE	0.55	2.27	3.20
N-HEXANE	0.9	0.99	1.07
1-HEXENE	1.1	2.26	2.54
N-HEPTANE	0.6	0.89	1.08
1-HEPTENE	0.61	1.46	1.62
N-OCTANE	0.43	0.64	0.82
1-OCTENE	0.47	1.00	1.21
N-NONANE	0.4	0.44	0.63
1-NONENE	0.42	0.63	0.83
N-DECANE	0.38	0.43	0.60
1-DECENE	0.43	0.64	0.92
N-UNDECANE	0.37	0.40	0.56
1-UNDECENE	0.39	0.59	0.77
N-DODECANE	0.07	0.08	0.12
1-DODECENE	0.36	0.49	0.69
N-TRIDECANE	0.02	0.11	0.06
1-TRIDECENE	0.1	0.24	0.16
N-TETRADECANE	85.7	83.8	82.6
1-TETRADECENE	0.01	0.10	0.16
N-PENTADECANE	0.01	0.08	0.07
N-HEXADECANE	0.01	0.06	0.06
N-HEPTADECANE	0	0.03	0.04
N-OCTADECANE	0	0.02	0.02
BENZALDEHYDE*	4.32	5.96	7.19
TOULENE*	3.26	4.70	6.50
BENZENE*	2.48	2.66	3.88
BENZYL ALCOHOL*	88.6	84.6	80.8
Product Gas wt. (g)	0.04	0.05	0.05
Product Liquid wt. (g)	3.86	3.69	3.72
Initial wt. of reactants (g)	3.93	3.894	3.86
Recovery (%)	98.09	98.09	97.82
*Yield is based on the initial molar charge of benzyl alcohol			

TABLE 6. PYROLYSIS OF N-TETRADECANE AT VARIOUS VOLUMETRIC CONCENTRATIONS OF BENZYL ALCOHOL AT 450 C			
SAMPLE VOLUME = 5 ML			
RESIDENCE TIME = 30 MINS			
INITIAL N2 PRESSURE = ATMOSPHERIC			
VOL. CONC. OF BENZYL ALCOHOL (%	1		0.50
EXPT. NUMBER	99		100
COMPONENT	MOL (%)		MOL(%)
HYDROGEN	0.02		0.03
METHANE	2.94		3.97
ETHANE	3.05		4.23
ETHYLENE	3.16		5.21
PROPANE	3.86		3.95
PROPYLENE	4.57		5.12
ISOBUTANE			
N-BUTANE	3.27		5.11
1-BUTENE	4.88		6.33
N-PENTANE	2.45		3.67
1-PENTENE	4.17		4.56
N-HEXANE	1.98		3.12
1-HEXENE	3.39		4.67
N-HEPTANE	1.83		2.45
1-HEPTENE	2.11		3.42
N-OCTANE	1.38		1.95
1-OCTENE	1.62		2.21
N-NONANE	1.14		2.63
1-NONENE	1.21		2.80
N-DECANE	0.94		1.64
1-DECENE	0.94		1.54
N-UNDECANE	0.82		1.56
1-UNDECENE	0.79		1.46
N-DODECANE	0.20		0.55
1-DODECENE	0.73		1.34
N-TRIDECANE	0.12		0.49
1-TRIDECENE	0.23		0.16
N-TETRADECANE	7979.2		74.5
1-TETRADECENE	0.21		0.21
N-PENTADECANE	0.15		0.11
N-HEXADECANE	0.10		0.08
N-HEPTADECANE	0.06		0.05
N-OCTADECANE	0.02		0.02
BENZALDEHYDE*	8.45		13.57
TOULENE*	7.34		10.78
BENZENE*	3.88		6.77
BENZYL ALCOHOL*	78.2		68.1
Product Gas wt. (g)	0.08		0.10
Product Liquid wt. (g)	3.703		3.69
Initial wt. of reactants (g)	3.836		3.84
Recovery (%)	98.09		98.62
*Yield is based on the initial molar charge of benzyl alcohol			

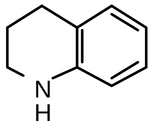
Figure 1. Effect of Hydrogen Donor Concentration (vol %) on Conversion of n-Tetradecane in a Batch Reactor



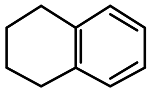
Task 4. Coal-based Fuel Stabilization Studies

Design and Synthesis of Second Generation Jet Fuel Stabilizers (contributed by Stephen Philip Fearnley and Michael M. Coleman)

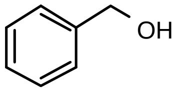
In recent years we have identified several novel additives as important leads in the development of a practical high temperature thermal stabilizer for jet fuels.[1] Three in particular have proved effective in model studies at elevated temperature: tetrahydroquinoline (THQ), tetrahydronaphthalene (tetralin) and benzyl alcohol (BzOH). Examination of thermolysis products has confirmed our belief that all three operate by donation of multiple hydrogen atoms to quench the radical species responsible for fuel degradation. However although THQ and tetralin are excellent hydrogen donors in the pyrolysis regime (>400 C), this outstanding reactivity yields them susceptible to autoxidation at lower temperatures (250 C) and thus limits their application.[2a] BzOH on the other hand, although not quite as effective under pyrolysis conditions, readily survives passage through the autoxidation regime.[2b] This is probably a direct indication of the distinct chemical mechanisms involved in each case. Whereas THQ and tetralin each donate four hydrogens with formation of stable aromatic compounds (quinoline and naphthalene respectively) as the ultimate driving force, the mechanism of BzOH stabilization is somewhat more obscure, an analogous stepwise loss of two hydrogens resulting in a formal oxidation to benzaldehyde. Further oxidation, disproportionation, combination, etc, of this intermediate product may all play an important role and this clearly requires complete elucidation.



THQ



tetralin

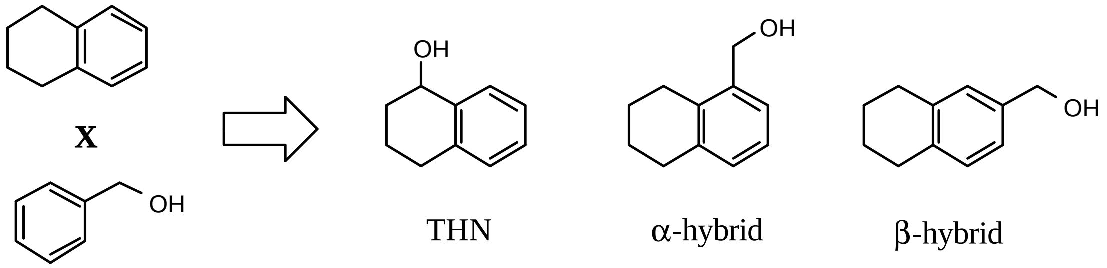


BzOH

This contrasting efficiency over a range of temperatures has led us to consider the following questions:

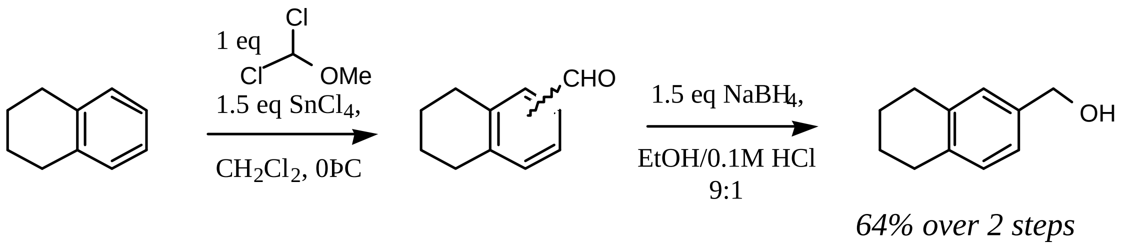
What if the crucial structural elements neccessary for stabilisation in both autoxidative and pyrolysis regimes are combined within the same molecule? Will complementary antioxidant abilities allow access to the full range of stabilization? In addition will synergistic effects now come into play, whereby enhanced capabilities are observed? What of the effects of substitution pattern? How will all this differ from direct use of admixtures? Finally, can relative efficiency be predicted with the aid of molecular modeling as opposed to exhaustive exploratory testing?

With these questions in mind, we have undertaken a series of studies aimed at the development of novel "hybrid" stabilizers based on combination of two or more of our existing candidate additives. For example, "crossing" BzOH with tetralin leads to three new compounds as shown, each containing the neccessary features of their "parents", *i.e.* a benzylic alcohol moiety and a partially reduced naphthalene. Indeed, some precedent for this approach already exists within our own studies,[1b] as we have previously shown that 1,2,3,4-tetrahydro-1-naphthol (THN) proves marginally more effective in prevention of dodecane degradation at high temperatures (450 C under 1 MPa of N_2).

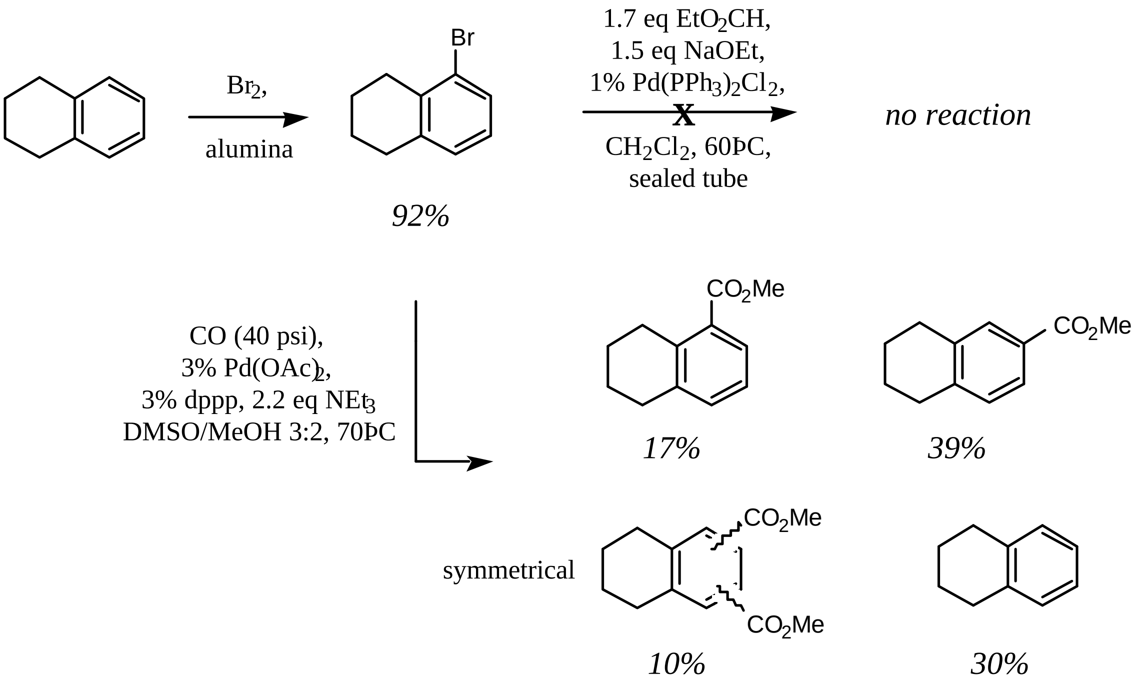


THN α-hybrid β-hybrid

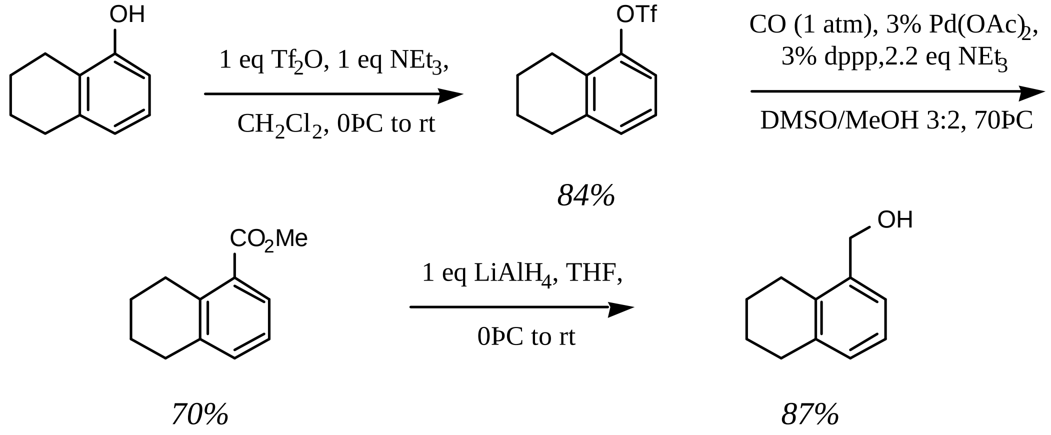
Although THN is commercially available, provision of the other hybrids in the quantities required for preliminary degradation studies required an expedient synthetic route. Thorough examination of the literature[3] revealed both to be known compounds, though no direct synthesis was available. Reduction of the corresponding carbonyl compounds proved a viable alternative. In the case of the β-hybrid, a modified Friedel-Crafts type formylation of tetralin[4] unexpectedly yielded a mixture of the 2 aldehydes. Sodium borohydride reduction[5] (under slightly acidic conditions to preclude competing acetal formation) followed by distillation (110-120 C @ 300-400 miliTorr) yielded the required alcohol in 64% yield overall.



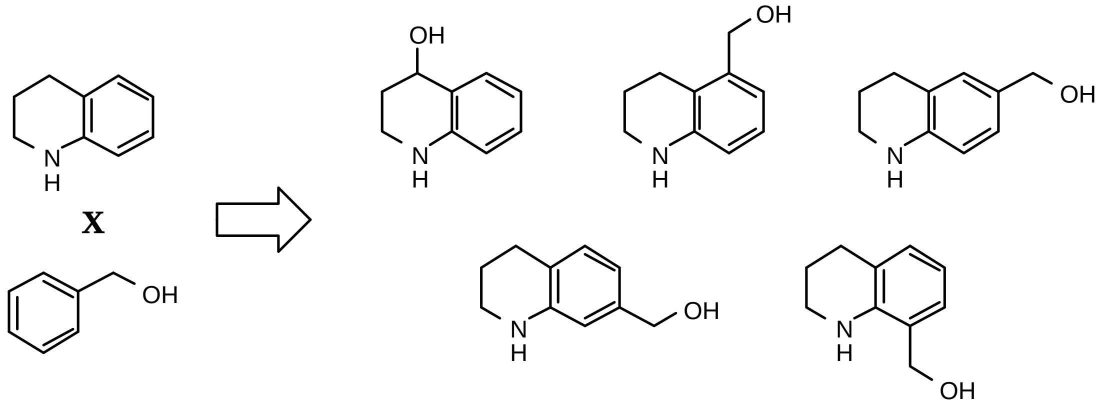
For the α-hybrid a less direct approach was required, as Friedel-Crafts chemistry was known to sterically favour the β-position. However the corresponding bromide had been reported with remarkable and exclusive regioselectivity.[6] An ensuing carbonylation, either of the Grignard-type or palladium mediated, would yield the neccessary substrates for reduction. Bromination proceded as described and carbon monoxide insertion to produce the ester was investigated. Although an *in situ* generation technique failed,[7] use of higher pressures[8] revealed some interesting features. As well as some simple over-reduction to tetralin, a mixture of three carbonylation products was produced: both the α- and β-hybrids, and a symmetrical diester, of as yet unconfirmed regiochemistry. Either the bromination is not as selective as at first claimed, or some unusual mechanism is at work in the palladium mediated carbonylation.



One solution to the question of regioselectivity is to start with the commercially available reduced α-naphthol and proceed *via* its triflate,[9] similar in reactivity to the corresponding halide. A standard triflation,[10] followed by palladium mediated carbonylation[11] yielded the α-ester in moderate yield. Simple lithium aluminium hydride reduction afforded the required benzylic alcohol. This process is currently being scaled up.



With sufficient quantities of the tetralin-BzOH hybrids in hand, we shall turn our attention to the complementary THQ-BzOH species, of which there are 5 possibilities, although this chemistry is expected to be of a little more complex nature due to neccessary use of N-protecting groups.



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Task 5. Exploratory Studies on the Direct Conversion of Coal to High-Quality Jet Fuels

Development of Coal-Based Jet Fuel Feedstock via Coprocessing of Coal and Resid
(contributed by Shona Martin)

Introduction

In the development of superior jet fuels for the next century, there are many factors that must be taken into consideration. Coal-derived jet fuels are inherently more stable than their petroleum counterparts. The presence of 2- and 3-ring coal derived aromatics and hydroaromatics impart a thermal stability not present in the paraffinic petroleum analogues. The most promising way of producing liquid fuels from coal under current market conditions and process economics is the incorporation of coal in an appropriate refinery stream.

In the search for an attractive alternative to conventional coprocessing, delayed coking appears to be a suitable candidate. This "bottom-of-the-barrel" petroleum process utilizes long reaction times to produce gases, distillates and coke from relatively low value feedstocks such as vacuum resid [1-3]. Further, it does not suffer from many of the inherent disadvantages associated with direct liquefaction, i.e. high pressure operation in hydrogen atmospheres, and hence is an attractive alternative to conventional coprocessing methods. In practice [1-3], the feed is rapidly heated to *ca* 500 ^{o}C in the coke drum. The vapor products (gases, naphtha and gas oil) are stripped off and sent to a fractionator tower while the coke remains in the drum, reacting to produce a high quality coke. The distillates can be subsequently catalytically upgraded to produce synthetic fuels. Typical product distributions from industrial coking operations are: 10-15% gas; 50-60% liquids; and 30-35% coke [1-3].

The application of a delayed coking type process to generate coal derived liquids is not new. Speight reports on a such a modified process termed *extractive coking* [4]. Coal and an appropriate H-donor solvent are coked in a two stage process at 400 and 450 ^{o}C, with continual removal of lighter overhead product (typically fractionated into recycle solvent, gases, light oil and middle distillates). Similarly, the Exxon Donor Solvent process has been reported to utilize a secondary coking step to produce addition liquids from the vacuum bottoms slurry [4]. Utilizing this two-stage method liquid yields increase in the order of *ca* 10 wt% (Table 1).

Work conducted during this reporting period has comprised simulated delayed coking experiments with an expanded experimental matrix. In addition to those employed previously [5], feedstocks examined include a commercial coker feed together with an additional coal sample. Similarly, three aspects are of concern in this study; the quantitative aspect of incorporation of coal into this process on the yield of light ends, the qualitative aspect of soluble products and the physical and optical properties of the resultant coke.

Experimental

Samples Five coal samples were utilized in this study from the Penn State Coal Sample Bank and Data Base. Analyses are summarized in Table 2. Samples were ground to -60 mesh and dried under vacuum at 110 ^{o}C for 2 hours prior to use.

Procedures The reactions were carried out in vertical 25 ml microautoclave reactors with *ca* 8g feed (resid:coal ratio of 2:1 w/w) at 500 ^{o}C for 120 min. Tests were conducted under an N_2 environment at atmospheric pressure. Products were recovered as reported previously [4]. In this report, a new term will be introduced. Distillate will describe the “liquid” obtained upon completion of the reaction, independent from that recovered from soxhlet extraction. Conversion of feed into soluble products and gases was calculated on the basis of recovered THF-insoluble residue (coke) and reported on total feed basis.

GC/GC-MS n-Hexane soluble products were qualitatively analyzed by GC and GC-MS using a Hewlett Packard 5890 II GC coupled with an HP 5971 A mass spectrometer operating at electron impact mode (EI, 70 eV). The column was a DB-17 column; 30m x 0.25mm, coated with 50% phenyl 50% methylpolysiloxane with a film thickness of 0.25μm. A temperature program of 40 to 280 ^{o}C at heating rate of 6 ^{o}C/min and a final holding time of 15 min were used. Samples were solubilized in methylene chloride at a concentration of 100 mg/ml.

Results and Discussion

Figure 1 gives the mass of coke formed under the experimental regime employed above. As anticipated, for the reaction conducted at the moderately higher temperature of 500 ^{o}C with the coker feed, coke concentration is moderately higher in the presence of coals, in the region of *ca* 4 g, corresponding to ~30-45 wt% of the product distribution. Feed has been listed in order of decreasing rank; DECS 29, 12, 6, 24 and 8. However, these figures are only moderately increased over those reported previously by Tomic, which are of the order 3-4 g [5,6]. This is more adequately presented in Figure 2 , which demonstrates the product distribution of concern to this study, namely solid coke (THF-insoluble residue) and light hydrocarbon species (gas, distillates and oils). It should be noted that concentrations of asphaltenes and preasphaltenes were negligible (0.05 wt%) and are hence not included in Figure 2. Again, it can be noted that for these reactions product distribution does not deviate significantly from the commercial yields discussed above [1-3].

It can be generally stated that coke concentration increases commensurate with addition of coal. This is most apparent for the higher rank coals examined, in particular Upper Banner. Pittsburgh #8, Blind Canyon and Illinois #6 demonstrate comparable coke concentrations with Wyodak appearing to be the poorest. From Figure 2 , it can be seen however that light product yield decreases parallel with the increase in coke yield. To this end, the run with Upper Banner would therefore at first appear to be the worst case scenario and Wyodak the best, when considering liquid yield. Again, other coals, within experimental error, are the same.

However the concern of this work lies not only in quantitative aspects of simulated delayed coking of coals and resid but also in the qualitative aspect of the products. Gas composition identified three main components which were C_1-C_3 hydrocarbons, as anticipated. Under this experimental regime, only the run with CF produced appreciable quantities of “distillate”. The relevant GCMS chromatogram of the distillate is given in Figure 3. It is characterized by 2-, 3- and 4-ring polyaromatics as the heaviest species; e.g., naphthalene, anthracene/phenanthrene and pyrene and their alkylated derivatives. Examination of the oils from the suite of feedstocks considered here indicated that all oils analyzed displayed similar compositions as that for CF with the exception of the feed comprising CF and DECS 29. Figures 4 and 5 provide the chromatograms of oils from coking of CF and that from CF and DECS 29, respectively. CF oils appear to have a similar composition to that of the distillate with the notable exception that the oils contain smaller alkylated monocyclic species such as ethyl and dimethyl benzene.

Conclusions and Future Work

From the limited experimental work conducted to date, it appears that delayed coking route for advanced aviation feedstock production may yet prove to be viable. Indeed, the fact that product distributions do not vary significantly from industry values is favorable. However, work must continue to enhance the selectivity of the pyrolysis reactions to favor the desired coal-derived aromatics. Work scheduled for the next quarter will include; further analysis of the solid coke to determine its suitability as a fuel coke (e.g., elemental CHNS analysis, NMR, and optical microscopy) together with further delayed coking tests to examine effects of temperature, time (4hr), coal concentration (< 5 wt%) and perhaps a more fluid coal sample.

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Table 1. Comparative Yields in One and Two-Stage Exxon Donor Solvent Process [4]

Product	Liquefaction	Liquefaction plus Coking
H_2O, CO_2, CO	10	10
H_2S, NH_3	4	4
C_1-C_3	6	9
C_4, C_5	3	4
Naphtha	15	16
Fuel oil	17	25
Liquefaction bottoms	48	-
Coke and ash	-	35
Liquid yield (%w/w dry coal)	35	45
H_2 consumption (scf/bbl liquid)	5600	4100

Table 2. Analysis of Project Coals

	Upper Banner	Pittsburgh #8	Blind Canyon	Illinois #6	Wyodak
Rank	hVAb	hVAb	hVAb	hvCb	sub C
Moisture [a]	2.44	2.40	4.73	13.20	28.42
Ash [a]	6.2	10.0	5.56	11.62	9.90
%C [b]	86.6	83.3	81.28	76.3	74.4
%H	5.5	5.7	6.24	5.3	5.2
%N	1.6	1.4	1.55	1.3	1.0
%S	0.6	1.3	0.42	6.4	0.9
%O	5.7	8.4	10.5	10.7	18.5

Fluidity (dppm)	8942	20002	3	49	-

a As received; *b* daf

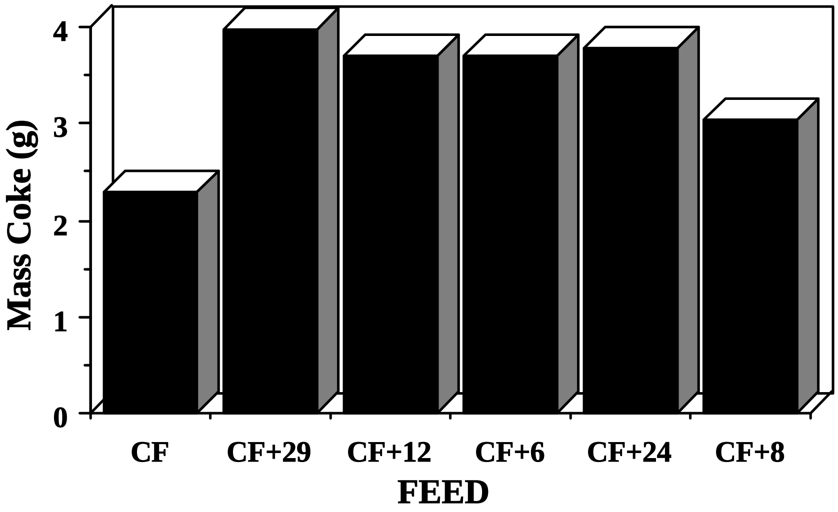

Figure 1. THF-Insoluble Concentration from Coking Experiments at 500 ^{o}C, 120 min, N_2 atmosphere

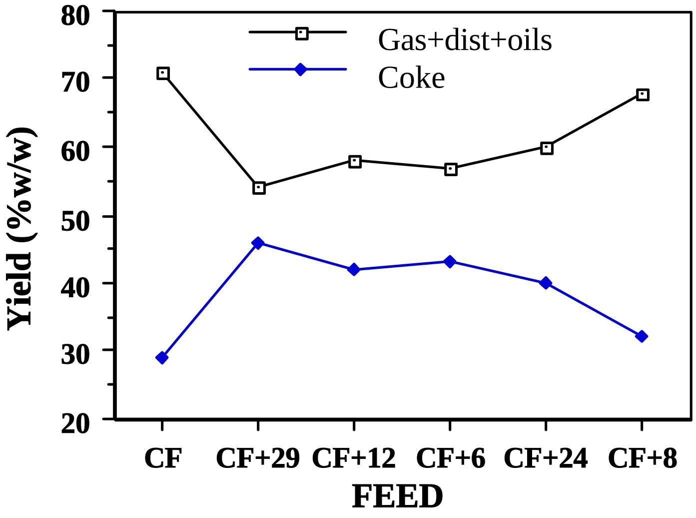

Figure 2. Yield of Sols and Solids from Co-coking of BP Coker Feed and Selected Coals at 500 °C, 2 hours, N_2 atmosphere.

KEY:

CF	Coker feed
CF+29	Coker feed and DECS 29
CF+12	Coker feed and DECS 12
CF+6	Coker feed and DECS 6
CF+24	Coker feed and DECS 24
CF+8	Coker feed and DECS 8

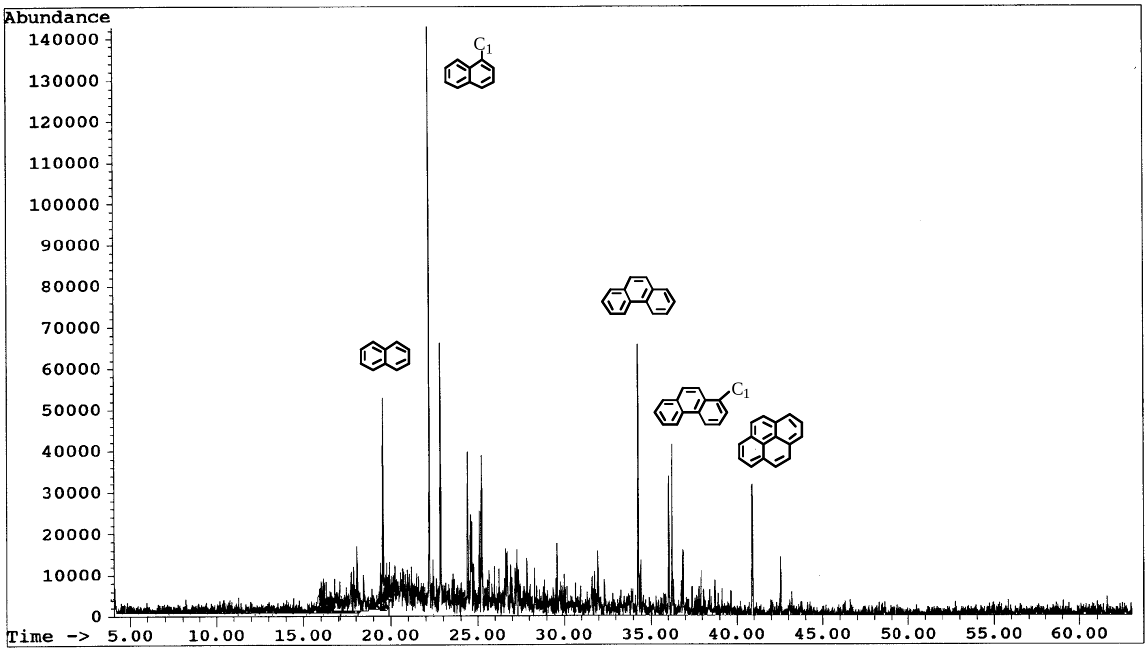

Figure 3. GCMS Chromatogram of Distillate from Coking Coker Feed at 500 ^{o}C, 2 hr, N_2 atmosphere.

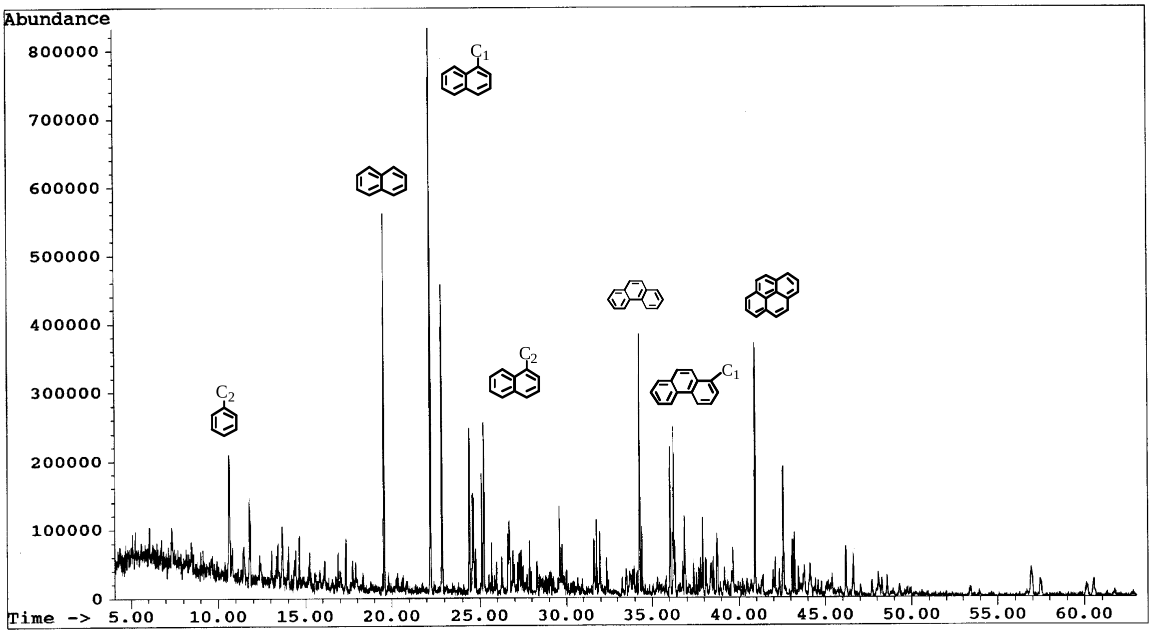

Figure 4. GCMS Chromatogram of Oils from Coking of Coker Feed, 500 °C, 2 hr, N_2 environment.

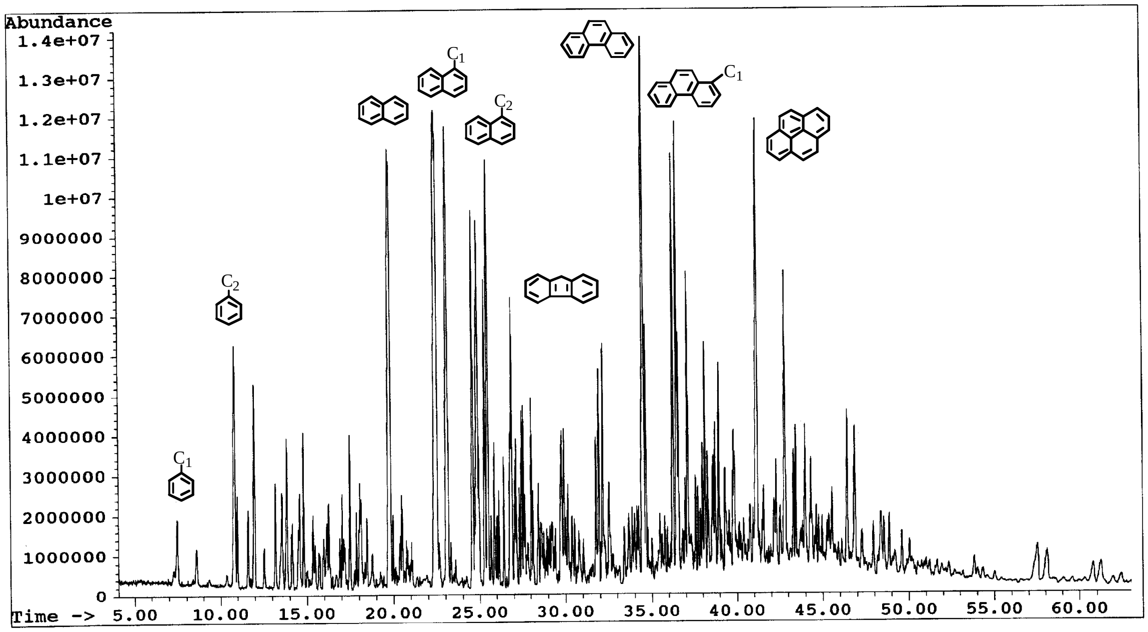

Figure 5. GCMS Chromatogram of Oils from Co-coking of Coker Feed and Upper Banner, 500 °C, 2hr, N_2 environment.