ADVANCED THERMALLY STABLE JET FUELS

Technical Progress Report April 1993 – June 1993

H.H. Schobert, S. Eser, C. Song, P.G. Hatcher, P.M. Walsh, M.M. Coleman

Contributions from:

R. Arumugam, C. Burgess, K. Gergova, W-C. Lai, X. Liang, P. Sanghani,
J. Stallman, K. Wenzel, J. Yu

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OBJECTIVES

The Penn State program in advanced thermally stable coal-based jet fuels has five broad objectives: 1) development of mechanisms of degradation and solids formation; 2) quantitative measurement of growth of sub-micrometer and micrometer-sized particles suspended in fuels during thermal stressing; 3) characterization of carboaceous 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 production of high yields of cycloalkanes by direct liquefaction of coal.

SUMMARY

The product distribution and reaction mechanisms for pyrolysis of alkylcyclohexanes at 450°C have been investigated in detail. In this report we present results of pyrolysis of cyclohexane and a variety of alkylcyclohexanes in nitrogen atmospheres, along with pseudo-first order rate constants, and possible reaction mechanisms for the origin of major pyrolysis products.

Measurements and preliminary calculations of incipient deposition, presented in earlier reports, suggested that the growth of deposit on the bottom of a microautoclave could be explained by gravitational settling of particles formed in suspension. In the present period, settling velocities were calculated by equating the difference between gravitational and buoyant forces to Stokes' Law for viscous drag. The calculated particle settling rate at 8 hours is in satisfactory agreement with experimental measurements, but at longest measurement times the calculated rates are too high by a factor of 100. One possible explanation for this discrepancy is that, upon opening and emptying the reactor, re-suspension of large particles loosely attached to the deposit could cause an overestimate of the size of suspended particles, in turn leading to a high value for the calculated deposition rate.

Addition of PX-21 activated carbon effectively stops the formation of carbonaceous solids on reactor walls during thermal stressing of JPTS. It appears that 50 mg of PX-21 per 10 mL of fuel is sufficient to prevent carbon deposition, and stabilizes JPTS at 425°C. At least 100 mg. of PX-21 is necessary for preventing solid deposition at 450°C for 5 h. The reactions during thermal stressing of JPTS with high surface area activated carbon are quite different from those taking place in the absence of added carbon.

A review of physical and chemical interactions in supercritical fluids has been completed. There are still a number of unanswered questions in this area, including the nature of solubility enhancement by added co-solvent, the effect of solvent-solute or solute-solute clustering on reactions, the change of phase behavior as reaction proceeds, and the effects of participation of a supercritical fluid on reaction kinetics and mechanisms.

Work has begun on thermal stability studies of a second generation of fuel additives. These compounds include 1,2,3,4-tetrahydro-1-naphthol, 9,10-phenanthrene-diol, phthalan, and 1,2-benzenedimethanol. We have shown previously that benzyl alcohol can retard the degradation of jet fuel for at least six hours at elevated temperatures. To push this work further, it is important to understand the phase behavior of a mixture of benzyl alcohol and fuel (for which dodecane is taken as a model) and whether the system is a one- or two-phase system under conditions of interest. Current work involves a comparison of the Flory and Sanchez and Lacombe liquid fluid models, and an evaluation of their adequacy to apply to the jet fuel system.

With careful selection of the feedstock, it is possible to achieve 85–95% conversion of coal to liquids, with 40–50% of the dichloromethane-soluble products being naphthalenes. (Further hydrogenation of the naphthalenes should produce the desired highly stable decalins.) Pyrolysis-gas chromatography-mass spectrometry has been shown to be a very useful predictive tool in relating the composition of the lighter liquefaction products to the structural features of the feedstock coals.

TECHNICAL PROGRESS

Task 1. Investigation of the Quantitative Degradation Chemistry of Fuels

Pyrolysis of Alkylcyclohexanes at 450°C and Elevated Pressure. Product Distribution and Reaction Mechanisms (Contributed by Wei-Chuan Lai and Chunshan Song)

Introduction

The current petroleum-derived jet fuels are limited to maximum operating temperatures of below 300°C (Hazlett, 1991; Roquemore et al., 1989). Fuel in the new hypersonic aircraft may reach temperatures in the range of 400–500°C (Hazlett, 1991; Moler, 1989; Walkins and Krukoni, 1992). Apparently, the temperatures experienced are much higher than the current maximum operating temperature for the conventional aviation jet fuels. The future high-performance aircraft requires advanced jet fuels which are thermally stable even under severe thermal conditions (Lee and Niedzwiecki, 1989). The thermal stability of jet fuels is governed mainly by their chemical composition (Song et al., 1993; Lai et al., 1992). Knowledge of the thermal stability of the fuels' components is important for predicting the performance of such fuels under various operating conditions.

The future fuels may derive from hydrocarbon resources such as coal, oil shale, and tar sands, as well as from petroleum. The fuels derived from different hydrocarbon resources tend to have quite different compositions. For instance, Lai and Song (1993) characterized two JP-8 jet fuel samples, including a coal-derived JP-8C and a petroleum-derived JP-8P. They found that the coal-derived JP-8C fuel is significantly different from petroleum-based JP-8P in the molecular composition. JP-8P, a conventional petroleum-derived fuel, is rich in long-chain alkanes ($\approx 61\%$) ranging from C_8 to C_{17} with major components in the range of C_{10} to C_{15} , and contains alkylcyclohexanes account for about 14%. In contrast, JP-8C, a test jet fuel derived from hydrotreating of coal liquids produced as by-products from coal gasification, is composed mainly of monocyclic and bicyclic alkanes, and hydroaromatic compounds. The dominant compounds in JP-8C are alkyl-substituted cyclohexanes ($\approx 40\%$) and decalins, and long-chain alkanes only account for about 10% of JP-8C. Unlike JP-8P, the low-boiling components are abundant in JP-8C. For example, cyclohexane and C_1 - to C_2 -substituted cyclohexanes are the dominant components in JP-8C and they account for about 22% of JP-8C. Most of the cyclohexanes in JP-8P are C_3 - to C_6 -substituted cyclohexanes.

The study of model compounds facilitates clarifying the chemistry of pyrolytic degradation and mechanisms of solid formation, and allows enhancing the intrinsic stability of jet fuels by optimizing fuel composition. This section will focus on the pyrolytic thermal stability study of alkylcyclohexanes. The results concerning the pyrolysis of model long chain compounds (tetradecane) and the effects of hydrogen-donors on the fuel stability have been described in Song et al. (1993b,c).

Pyrolysis of alkylcyclohexanes has received much less attention than alkanes and alkylbenzenes, although cyclohexane has been studied extensively under high temperatures above 600°C (Billaud et al., 1991; and references cited therein). Fabuss et al. (1964a,b) studied the thermal decomposition rates of several saturated hydrocarbons including cyclohexane and C₁- to C₄-cyclohexanes in a static test apparatus, and the activation energies of cyclohexane and its derivatives were found to range from 61 to 63 kcal/mol. They also developed an empirical equation to correlate molecular structure and the first-order rate constant for decomposition at 427°C and elevated pressures. Zychlinski et al. (1983) pyrolyzed cyclohexane and six n-alkylcyclohexanes (C₁-, C₂-, C₃-, C₄-, C₆-, and C₈-cyclohexane) in a tubular reactor at high temperatures (650 to 850°C) and 1 atm pressure. They found that the decomposition is initiated by C-C scission in the alkyl chain followed by radical attacks to all C-H bonds of the reactant. Mushrush and Hazlett (1984) pyrolyzed tridecylcyclohexane for 15–180 min at 723 K (450°C) and about 600 kPa (6 atm) in a batch reactor made of 316 stainless steel tube. The major reaction products they observed are n-alkanes, 1-alkenes, methylcyclohexene, cyclohexanes, benzene, and toluene (the only substituted benzene formed). Little information regarding the reaction mechanisms was presented except that the aromatic compounds are the secondary products from the dehydrogenation of the substituted cyclohexenes. Savage and Klein (1988) studied the pyrolysis of tridecylcyclohexane at 375–450°C for 10–180 min. They showed that dealkylation near or at the ring is the major reaction and the ring opening being minor; the two major product pairs are cyclohexane plus 1-tridecene and methylenecyclohexane plus n-dodecane with initial selectivities of about 0.08. The activation energy of tridecylcyclohexane decomposition was 59.4 kcal/mole over the temperature range 400–450°C.

Experimental

1. Reagents and pyrolysis procedures. The chemicals used in pyrolysis experiments were obtained from Aldrich Chemical Company or TCI America, and were used as received. Prior to pyrolysis experiments, the purities of the chemicals were analyzed in our laboratory using gas chromatography (GC) and gas chromatography-mass

spectrometry (GC-MS). The chemicals from Aldrich are cyclohexane (CH, purity: 99.9+%), methylcyclohexane (MCH, purity: 99.5%), ethylcyclohexane (ECH, purity: 99.5%), n-propylcyclohexane (PCH, purity: 99.7%) and n-butylcyclohexane (BCH, purity: 99.4%). Those from TCI America include n-hexylcyclohexane (HCH, purity: 98.2%), n-octylcyclohexane (OCH, purity: 99.5%), and n-decylcyclohexane (DCH, purity: 99.5%).

Pyrolyses were performed in 25 mL tubing bomb reactors at 450°C for a heating period of 12–480 min under an initial pressure of 0.69 MPa UHP-N₂ (cold). The details of the tubing bomb reactors were described elsewhere (Song et al., 1993a,b). The reactor was loaded with 5 mL sample and leak-tested. To provide an inert pyrolysis environment and minimize oxidation reaction, the sealed reactor was purged repetitively (6 times) with 6.9 MPa UHP-N₂ to remove oxygen/air in the reactor or dissolved in the sample. The reactor was then pressurized to the desired starting pressure of 0.69 MPa with UHP-N₂ before being immersed into a preheated, isothermal at 450°C, fluidized sand bath. The reaction pressure and temperature was closely monitored immediately after the experiment was started. The sample reached 420°C in 3 min and the desired pyrolysis temperature of 450±4°C in about 4–6 min. The reactor was removed from the fluidized sand bath after the desired stressing time, and immediately quenched in a cool water bath. The products were collected and separated into gas, liquid, and solid deposits immediately after the reactor was cool enough. The fresh gaseous and liquid products were then analyzed by GC and GC-MS.

2. Product chemical analysis. The gaseous products were analyzed for their compositions and quantities by using a Perkin-Elmer Autosystem GC equipped with two detectors, a thermal conductivity detector (TCD) and a flame ionization detector (FID). The TCD was used to determine H₂, CO, CO₂, CH₄, C₂H₂, C₂H₄, and C₂H₆ via a 10-foot long, 1/8-inch diameter stainless steel column packed with 100/120 Carbosieve SII (from Supelco). Hydrocarbon gases from C₁ to C₆ were separated via a 6-foot long, 1/8-inch diameter stainless steel column packed with 80/100 Chemipack C18 by the FID. The gaseous products were identified by retention time comparison with known standard gases, and were quantified by external standard method.

Two liquid samples were collected from each experiment: one was the liquid residue directly collected from the reactor and the other was washed from the reactor wall with pentane. The compounds in the liquid products were analyzed on an HP 5890 Series II GC coupled with an HP 5971A Mass Selective Detector (MSD) and quantified by a Perkin-Elmer GC 8500. The column used was a 30 m, 0.25 mm i.d., 0.25 µm film thickness, fused silica capillary column (J&W DB-17 or Restek Rtx-50, coated with 100% phenylmethylpolysiloxane). More analytical details may be found elsewhere (Lai

et al., 1992; Song et al., 1993b; Lai and Song, 1993). The solid deposits are operationally defined as the materials which are not soluble in the resulting liquid co-products and pentane (washing solvent). The solid deposits are to be analyzed by Fourier transform infrared spectroscopy and NMR spectroscopy and will not be discussed in this report.

Results and Discussion

1. Decomposition rate constant. Figure 1 gives representative system time-pressure profiles during pyrolysis of three model compounds, cyclohexane, ethylcyclohexane, and n-butylcyclohexane at 450°C under initial N₂ pressure (cold) of 0.69 MPa. Recall that the pyrolysis was conducted in a static apparatus (25 mL tubing bomb) using a 5 mL sample. The volume ratio of sample to reactor is kept constant (about 1/5); this implies that the initial reactant concentrations in the reactor are different for the hydrocarbon reactants studied. For example, the initial reactant concentrations are about 1.81×10^{-3} mol/mL, 1.41×10^{-3} mol/mL, and 1.15×10^{-3} mol/mL, for CH, ECH, and BCH, respectively. The different initial concentrations are reflected in the early-stage time-pressure profiles. Figure 1 shows that the system pressure quickly increases to 4.5 MPa, 3.9 MPa, and 3.2 MPa, for CH, ECH, and BCH, respectively, in 5 min when the hydrocarbon liquids reach an equilibrium boiling state. The system pressure then increases with increasing residence time under different pressure increasing rate depending on the sample stressed. The system pressure for the pyrolysis of CH remained nearly constant after the initial increase; on the other hand, the pressure increases steadily for ECH and BCH. The monotonic pressure increase indicates the continuous hydrocarbon decomposition to smaller compounds.

The results of detailed product analysis for the pyrolysis of CH, MCH, and ECH were reported in Table 1, where only major individual reaction products and product groups were presented. The hydrocarbon products were expressed as molar percentage of the initial amounts of reactants (cyclohexane, methylcyclohexane, or ethylcyclohexane). Similarly, Tables 2 and 3 provide the molar yields of products from the pyrolysis of other alkylcyclohexanes (PCH, BCH, HCH, OCH, and DCH). The products include C₁-C₄ gaseous yields and liquid yields such as alkanes, alkenes, cycloalkanes, cycloalkenes, benzenes, and naphthalenes.

Hydrocarbon pyrolysis at elevated pressure is very complex kinetically. The thermal decomposition in general can be approximated by a first-order relation though self-acceleration and self-inhibition are not uncommon (Fabuss et al., 1964a). The first-order rate equation can be expressed as shown in Equation (1).

$$-\frac{dC}{dt} = k C \quad (1)$$

where C is the reactant concentration, t is the reaction time, and k is the first-order rate constant. The rate equation can be solved for the rate constant, and expressed as a function of the reactant conversion (α , the fraction of reactant reacted) as shown in Equation (2).

$$k = \frac{1}{t} \ln \frac{1}{1 - \alpha} \quad (2)$$

As mentioned earlier, the preheat (from room temperature to the reaction temperature, 450°C) time is about 4–6 min, and has to be accounted for in calculating an adjusted (effective) reaction time. Table 4 presented the calculated pseudo-first-order rate constants using least-squares regression (Draper and Smith, 1981). Figures 2 and 3 compare the experimental reactant conversions to the values predicted from the rate constants in Table 4 for 2 compounds, PCH and OCH. The line corresponding to exact agreement is drawn as a diagonal. We can see that the predicted and experimental conversions are generally in good agreement.

Fabuss et al. (1964a) used an empirical group contribution method to develop an empirical equation to correlate molecular structure and the first-order rate constant for cyclic saturated hydrocarbons decomposed at 427°C and elevated pressures. They used characterization number, n , to represent the molecular structure. The characterization number depends on the basic ring structure and the type of side chains. Their correlation is shown as Equation (3)

$$k = 0.044 - 0.0114 n + 0.00008 n^2 \quad (3)$$

Note that the value -0.0114 was misprinted as -0.114 in Fabuss et al. (1964a,b). They cautioned that Equation 3 was probably less reliable for alkyl side chains longer than C_4 .

We also used a similar approach and developed a correlation for alkylcyclohexanes (up to DCH). The characterization numbers of cyclohexanes studied in our work were also shown in Table 4. Figure 4 presents the experimental rate constants of

alkylcyclohexanes at 450°C as a function of characterization number (n) of molecular structure. The data were fitted to a second-order polynomial as shown in Equation 4.

$$k = -0.151 + 0.00875 n + 0.000426 n^2 \quad (4)$$

The statistical measures are as follows. R^2 equals 0.993, which means that 99.3% of the total variation about the response mean has been explained by Equation 4 (Draper and Smith, 1981). The internal F statistic is used to test the adequacy and is 346.2 with 2 and 5 degrees of freedom. The value 346.2, which is much larger than $F(2, 5, 0.99) = 13.27$ (the value from F-distribution table with 2 and 5 degrees of freedom under 99% confidence level), indicates that the adequacy is very significant. In other words, this is a good fit and far exceeds that expected for an adequate model. The standard error of the residuals for the model prediction, which is a measure of prediction uncertainty, is 0.047. The satisfactory statistical measures imply that Equation 4 would be useful for estimating decomposition rate constants for cyclohexane and C_1 - to about C_{10} -cyclohexanes stressed at 450°C in a batch reactor with volume ratio of sample to reactor about 1/5.

2. Pyrolysis products and Reaction Mechanisms. Examining the data in Tables 1–3, we can find several trends regarding the relative product distribution for alkylcyclohexanes with various side-chain length. First, the yields of isomerization products (cyclopentanes) from cyclohexanes decrease with increasing side-chain length. Second, for the pyrolysis of alkylcyclohexanes with alkyl $\geq C_4$ -, at early decomposition stage, i.e., at low conversion level, the major 6-membered ring products are cyclohexane, methylenecyclohexane, and cyclohexene. The primary reaction pathway seems to result in major product pairs; for example, for the pyrolysis of OCH, cyclohexane plus 1-octene, methylenecyclohexane plus n-heptane, cyclohexene plus n-octane, and methylcyclohexane plus 1-heptene. Besides, other product pairs (n-alkanes plus cyclohexylalkenes, and 1-alkenes plus alkylcyclohexanes) were also produced, but in lower yields. Third, the yields of unsaturate compounds such as cyclohexene tend to increase to a maximum then decrease with time. Fourth, there is an induction period for the formation of aromatic compounds such as benzenes and naphthalenes. These results will be further discussed in more detail (see below).

The results in Tables 1–3 will be discussed first and be followed by the mechanisms deduced from the detailed product distribution. Figure 5 presents the cyclohexane selectivity to major products at 450°C for 4 hr, which has a cyclohexane conversion of 5.0%. The product selectivity was defined as the ratio of a product's molar yield to the conversion of reactant. At the conversion level of 5.0 mol%, the major

products are methylcyclopentane (4.2 mol%), hydrogen (1.1 mol%), and cyclohexene (0.35 mol%). Apparently, methylcyclopentane, an isomerization product, is the most abundant product and accounts for 83% (selectivity) of the pyrolysis molar yields. The pyrolysis of cyclohexane has been studied extensively under high temperatures (above 600°C). Billaud et al. (1991) compiled cyclohexane pyrolysis literature after 1960. It was shown that the thermal decomposition of cyclohexane under high temperatures led to 1-hexene, cyclohexene, and the lighter cracking products such as hydrogen, methane, acetylene, ethylene, ethane, propene, 1,3-butadiene, and 1-butene. Few studies have shown such a significant selectivity (83%) to methylcyclopentane as in our study. Based on the identified product distribution, the possible reaction mechanisms for major pyrolysis products of cyclohexane were proposed as shown in Scheme I.

The pyrolysis of cyclohexane proceeds by radical reaction pathways. The reaction mechanisms consist of initiation (paths 1 and 2), propagation (paths 2–7), and termination (path 8). The mechanisms in Scheme I are for major products and thus are just a part of more complete mechanisms. The main initiation process is believed to proceed through ring-opening with the formation of n-hexyl diradical (path 1), and path 2 is the minor initiation process. This can be reasoned from the bond dissociation energies; the breaking of the the C-H bonds requires an energy of 95.5 kcal/mole (March, 1985), whereas breaking the C-C bonds only requires 77 kcal/mole. The n-hexyl diradical then abstract hydrogen from cyclohexane, and form cyclohexyl radical and 1-hexyl radical (path 3). The cyclohexyl radical then proceeds to form cyclohexene through decomposition (path 4) Hydrogen and more cyclohexyl radical were formed through hydrogen transfer reaction (path 5). The 5-hexenyl radical was formed from cyclohexyl radical through path 6; the intramolecular hydrogen transfer (ring closure) of the former results in the formation of methylcyclopentyl radical (path 7). The rate constant for the ring closure process (path 7) is $k=1.0 \times 10^5 \text{ s}^{-1}$ at 25°C with $E_a=6.1 \text{ kcal/mole}$ (Franz et al., 1984). Methylcyclopentane was formed in path 8 through hydrogen transfer. The formation of methylcyclopentane from intermediate 5-hexenyl radical has been reported in the literature (Lamb et al., 1963; Lal et al., 1974; March, 1985). The rules for ring closure were reported by Baldwin and co-workers (1976, 1977a,b, 1982). It was reported that both five- and six-membered rings may be formed from radicals containing a 5,6 double bond, but in general the five-membered rings (exo addition) are much more favored due to more favorable entropy and stereoelectronic factors than the larger six-membered rings (endo addition).

Figure 6 presents the methylcyclohexane selectivity to major products at 450°C for 4 hr, which has a conversion of 12%. The major products are methane (7.5 mol%),

dimethylcyclopentanes (5.1 mol%), hydrogen (3.2 mol%), ethylcyclopentane (1.2 mol%), cyclohexene (0.95 mol%), and methylcyclopentene (0.74 mol%). Similar to the pyrolysis of cyclohexane, isomerization products (now dimethylcyclopentane and ethylcyclopentane) are still the major products; however, methane becomes the most abundant product. The pyrolysis of methylcyclohexane also proceeds by radical reaction pathways, and its mechanisms are similar to that of cyclohexane. However, for methylcyclohexane, the initiation process now proceeds through more paths. Two of them are believed to be the major paths and have comparable rates, i.e., ring-opening with the formation of methylhexyl diradical (path 1), and the homolytic cleavage of the C-C bond between the ring and the side-chain to form methyl and cyclohexyl radicals (path 2). The formation of methyl radical may partly account for the abundant CH_4 yield. Other initiation processes include abstraction of the single hydrogen atom attached to the cyclohexyl carbon bearing the methyl group (path 3), and abstraction of the hydrogen atom on the methyl side chain (path 4). The former abstraction step produces a relatively more stable tertiary MCH radical and the latter leads to less stable primary MCH radical.

Figure 7 shows the product distribution from ECH pyrolysis at 450°C as a function of conversion. Methane and ethane are the most abundant products through the entire pyrolysis period; the ECH selectivities to methane and ethane range from about 0.4 to 0.6. The selectivity of ECH to 5-membered ring isomerization product, C₃-cyclopentane, is about 0.14–0.19 for the first 4 hr and drop to 0.1 at 8 hr stressing. It is clear from Tables 1 and 2 that the selectivity of cyclohexanes to corresponding 5-membered ring isomerization product, cyclopentanes, decreases with increasing side-chain length. Another point to notice among the alkylcyclohexanes (C₂- to about C₁₀-cyclohexane) is that in general alkylcyclohexane with longer side-chain seems to have higher molar yields of methylcyclopentane as shown in Figure 8, which presents the temporal methylcyclopentane product for the pyrolysis of ECH, PCH, BCH, and OCH, at 450°C . The exception is that PCH and BCH have similar methylcyclopentane. Figure 8 also shows that the methylcyclopentane yield increase with time; this implies that methylcyclopentane is mainly a primary product from ring-closure process of 5-hexenyl radical as shown in Scheme I.

Figure 9 shows the n-butylcyclohexane selectivity to major products at 450°C for 0.2 hr, which has a conversion of 4.0%. The primary reaction pathway for the pyrolysis of n-butylcyclohexane seems to result in 5 major product pairs at early decomposition stage; the preference of certain product pairs formation allows proposing the possible reaction mechanisms. The possible reaction mechanisms based on the identified products

were presented as shown in Scheme II. The mechanisms were based on the discussion of BCH pyrolysis and can be generalized and applied to other alkylcyclohexanes.

The pyrolysis of n-butylcyclohexane starts with initiation reaction and followed by propagation and termination pathways. The initiation processes likely include 1) the cleavage of the C-C bonds on the side chain especially the β and γ bonds (and δ bonds for longer side-chain); however, the homolytic cleavage of the C-C bond between the ring and the side-chain (α bond) to form cyclohexyl and 1-butyl radicals is less favorable because of higher bond energy; and 2) the cleavage of the C-H bonds on the side chain. The propagation pathways involving β -scission and H-transfer were given in Scheme II. The formation of the five-pair major initial products can be rationalized by the radical reaction pathways I-V. Note that ring-opening process was also included as pathway VI in Scheme II to account for the formation of 5-membered ring compounds. Pathway VI in Scheme II is similar to paths 6-8 of Scheme I for cyclohexane. We can see from Figure 10, which presents product distribution for BCH pyrolysis, that after 1 h at 450°C, the yields of methylenecyclohexane and ethenylcyclohexane begin to decrease with increasing residence time, presumably due to hydrogenation to form methylcyclohexane and ethylcyclohexane, respectively. Cyclohexane and methylcyclohexane become the two most predominant liquid products after 2.5 h stressing. These results suggest that pathways I and IV dominate in long-duration BCH pyrolysis. In Figure 7, we can find that cyclohexene is the most abundant liquid yield followed by cyclohexane and methylcyclohexane, and methylenecyclohexane is only a minor product in this case. The preference of cyclohexene formation indicates that the reaction via cyclohexyl radical is a major path, similar to path III in Scheme II, and the low methylenecyclohexane indicates that one of the major pathways for n-BCH becomes a minor one for ECH.

Figure 11 presents product distribution for PCH pyrolysis. At low conversion level (3.4%), PCH has high selectivity to cyclohexane (0.22), methylenecyclohexane (0.14), and cyclohexene (0.12). The molar yields of methylenecyclohexane and cyclohexene reach a maximum at the conversion level of about 0.39 (after 2.5 hr stressing). On the other hand, the molar yield and selectivity of cyclohexane and methylcyclohexane increase monotonically with heating time; After 4 hr stressing (PCH conversion = 0.65), the yield and selectivity of cyclohexane are 19.5 mol% and 0.30, respectively. Examining the results of ECH, PCH, and BCH at low conversion level, we can make the following observations. First, for ECH pyrolysis, the pathway to cyclohexene is favored followed by cyclohexane and MCH, and the yield of methylenecyclohexane is low. Second, for BCH pyrolysis, the pathways to cyclohexane and methylenecyclohexane are favored (selectivity about 0.2) followed by cyclohexene,

MCH, and ethenylcyclohexane (selectivity about 0.12, 0.08, and 0.07, respectively). Third, for PCH pyrolysis, the reaction mechanisms are more similar to that of BCH than to that of ECH. For example, at the PCH conversion level of 7.1%, the pathway to cyclohexane is highly favored (selectivity about 0.29) followed by methylenecyclohexane and cyclohexene (selectivity about 0.16). The high selectivity of methylenecyclohexane is a characteristic of alkylcyclohexane with long side-chain such as BCH. The early selectivity to MCH is low (about 0.02). Fourth, the yields of 5-membered ring isomerization products (alkylcyclopentanes) from cyclohexanes decrease significantly with increasing side-chain length. For example, unlike the pyrolysis of cyclohexane and methylcyclohexane, which has very high selectivity to alkylcyclopentanes, the selectivity to isomerization products from ECH and PCH is low, 0.14 and 0.08, respectively.

Figure 12 presents the OCH selectivity to major products at 450°C for 0.2 hr, which has a OCH conversion of 9%. Like the pyrolysis of BCH, methylenecyclohexane and cyclohexane have the highest selectivity (about 0.17 and 0.14, respectively) followed by cyclohexene (selectivity about 0.09) and other minor products such as MCH, ethenylcyclohexane, and 3-butenylcyclohexane (selectivity about 0.04–0.05). The pathways to produce cyclohexylalkenes such as 3-butenylcyclohexane and 4-pentenylcyclohexane are similar to and can be generalized from pathway V in Scheme II. Figure 13 presents the DCH selectivity to major products at 450°C for 0.2 hr, which has a DCH conversion of 17%. The product selectivity distribution is quite similar to that of BCH and OCH. For pyrolysis of alkylcyclohexanes with long side-chain such as OCH and DCH, the selectivity to individual products was all reduced. This can be rationalized from the production of more minor products through pathway V in Scheme II.

References

1. Baldwin, J. E. *J. Chem. Soc., Chem. Commun.* 1976, 734-736.
2. Baldwin, J. E.; Kruse, L. *J. Chem. Soc., Chem. Commun.* 1977a, 233-235.
3. Baldwin, J. E.; Thomas, R. C.; Kruse, L. I.; Silberman, L. *J. Org. Chem.* 1977b, 42 (24), 3846-3852.
4. Baldwin, J. E.; Lusch, M. J. *Tetrahedron* 1982, 38 (19), 2939-2947.
5. Billaud, F.; Duret, M.; Elyahyaoui, K.; Baronnet, F. *Ind. Eng. Chem. Res.* 1991, 30, 1469-1478.
6. Draper, N. R.; Smith, H. *Applied Regression Analysis* 1981, John Wiley & Sons: New York.

7. Fabuss, B. M.; Kafesjian, R.; Smith, J. O.; Satterfield, C. N. *Ind. Eng. Chem. Proc. Des. Dev.* 1964a, 3(3), 248-254.
8. Fabuss, B. M.; Smith, J. O.; Satterfield, C. N. In *Advances in Petroleum Chemistry and Refining*; McKetta, John J., Ed.; 1964b, Volume 9, pp.156-201. Interscience Publishers: New York.
9. Franz, J. A.; Barrows, R. D.; Camaioni, D. M. *J. Am. Chem. Soc.* 1984, 106, 3964.
10. Hazlett, R. N. *Thermal Oxidation Stability of Aviation Turbine Fuels*. ASTM Monograph 1, American Society for Testing and Materials: Philadelphia, PA, 1991; 163 pp.
11. Lai, W.-C.; Song, C.; Schobert, H. H.; Arumugam, R. *Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem.* 1992, 37(4), 1671-1680.
12. Lai, W.-C.; Song, C. *Fuel* 1993, submitted.
13. Lal, D.; Griller, D.; Husband, S.; Ingold, K. U. *J. Am. Chem. Soc.* 1974, 96, 6355-6377.
14. Lamb, R. C.; Ayers, P. W.; Toney, M. K. *J. Am. Chem. Soc.* 1963, 85, 3483-3486.
15. Lee, C. M.; Niedzwiecki, R. W. *Prepr. Pap.-Am. Chem. Soc., Div. Pet. Chem.* 1989, 34, 911-919.
16. March, J. *Advanced Organic Chemistry*, 3rd edition. 1985, Wiley: New York.
17. Moler, J. L.; Steward, E. M. *Prepr. Pap.-Am. Chem. Soc., Div. Pet. Chem.* 1989, 34, 837-840.
18. Mushrush, G. W.; Hazlett, R. N. *Ind. Eng. Chem. Fundam.* 1984, 23, 288.
19. Roquermore, W. M.; Pearce, J. A.; Harrison III, W. E.; Krazinski, J. L.; Vanka, S. P. *Prepr. Pap.-Am. Chem. Soc., Div. Pet. Chem.* 1989, 34, 841-849.
20. Savage, P. E.; Klein, M. T. *Ind. Eng. Chem. Res.* 1988, 27 (8), 1348-1356.
21. Song, C.; Eser, S.; Schobert, H. H.; Hatcher, P. G. *Energy & Fuels* 1993a, 7, 234-243.
22. Song, C.; Lai, W.-C.; Schobert, H. H. *Ind. Eng. Chem. Res.* 1993b, submitted.
23. Watkins, J. J.; Krukoni, V. J. *Supercritical Fluid Fractionation of JP-8*, Final Report, U.S. Air Force Aero Propulsion and Power Laboratory, WL-TR-91-2083, 1992; 159 pp (Available from NTIS).
24. Zychlinski, W.; Bach, G.; Glauch, B.; Zimmermann, G. *J. Fur Praktische Chemie* 1983, 325, 66-74.

Task 2. Investigation of Incipient Deposition

Growth and Deposition of Particles During Heating of Coal-Derived Aviation Gas Turbine Fuels (Contributed by Prashant C. Sanghani and Peter M. Walsh)

Introduction

Measurements and preliminary calculations described in the previous report of work under the research program suggested that the growth of deposit on the bottom of a tubing bomb reactor during stressing of coal-derived jet fuel could be explained by gravitational settling of particles formed in suspension. Work during the period under review was intended to further test this idea and refine both the measurements and the calculations.

Measurements

Mixtures containing 81.5 wt% JP-8C and 18.5 wt% tetradecane were used for all of the experiments described below. The sizes of suspended particles and the masses of deposits on the side walls and bottom of the reactor were measured as a function of time, from 2 to 18 hours at 450°C under nitrogen. The measurements consisted of:

1. Deposit on the bottom of the reactor.
2. Deposit on the side walls of the reactor.
3. Size distribution of suspended particles.
4. Concentration of suspended particles at some of the longer times.

A new particle sizing instrument (Horiba LA-900) capable of measurement over the size range from 0.04 to 1000 μm range was received, set up, and used to determine the size distributions of suspended particles. Having the sizing instrument in the jet fuels lab made it possible to make the measurements within an hour or so after the end of the stressing period, in contrast with the time of several days which was typical of earlier runs.

The growth of deposits on the sides and bottom, per unit of projected area, is shown in Figure 14. The value of observing the time dependence rather than making the measurements at a single time is apparent from the shape of the curve. For example, the instantaneous deposition rate at six hours is approximately twice the average rate over the period from 0 to 6 hours.

Our immediate interest is in the rate of deposit growth on the bottom of the reactor, and the contribution to this deposit from particle settling. The ultimate objective is to use the settling rate and size measurements to determine the rate of addition of

material to particles in suspension, and to compare this rate with the direct addition of material from the vapor to the vertical wall. Before doing this we need to determine whether or not settling is an important mechanism of transport of material to the lower part of the reactor. To discriminate settling from direct addition, the deposit mass per unit area on the vertical wall was subtracted from the observed deposit mass per unit area on the bottom, to correct for the contribution of direct deposition at the bottom. These data were then differentiated, by dividing the mass/area increments by the time increments, to determine the time dependence of the deposition rate. The result of these calculations is shown in Figure 15. The points are scattered, but suggest a period of formation of reactive species from precursors in the initial mixture, followed a period of rapid deposit growth, and finally a period of declining deposition rate due to depletion of the precursors.

The development of the particle size distribution is shown in Figure 16. The distribution reported by the instrument is a function of the ratio of the refractive indices of the particles and suspending liquid (cyclohexane). We are using an estimate of 1.19 for this ratio. The sizes may change when more information about the refractive index of the particles has been gathered. Except for the size distribution at 6 hours, which appears to be anomalous, there is little change in the distribution during the first 8 hours. A period of rapid growth follows, causing an increase in size from 1 to 4 μm during the period from 8 to 12 hours. There little further increase in size during the period from 12 to 16 hours. The volume-based mean particle size is shown as a function of time in Figure 17.

Discussion

Settling velocities were calculated by equating the difference between gravitational and buoyant forces to Stokes' law for viscous drag, assuming that fuel vapor completely and uniformly filled the enclosure. Specific-surface-area-weighted mean particle sizes were used for these calculations. The product of particle concentration and settling velocity is the average rate of deposit growth per unit area on the bottom, assuming that particle concentration and mean size are uniform throughout the reactor. The vapor viscosity was estimated using the Lucas method (Reid, Prausnitz, and Poling, 1987) and the particle density was assumed to be 1300 kg/m^3 . The calculated settling rates are compared with the measured deposition rates in Figure 18. The measurements, shown by the circles, are the same as in Figure 15. The calculated rate at 8 hours is in satisfactory agreement with the measurements, but at the longest times the calculated rates are a factor of 100 too high. A possible explanation is that many of the large, 4 μm , particles which were suspended in the liquid product had actually settled to the bottom of

the reactor during stressing, but were not strongly attached to the deposit. Re-suspension of these particles on opening and emptying the tubing bomb would cause an overestimate of the size of suspended particles and an overestimate of the suspended particle concentration, leading to a high value for the calculated deposition rate. In the next phase of work we will concentrate on the shorter times, during which the particles are still growing. The mechanism and rate of attachment of particles to a deposit are also of interest, so we will return to that problem when the growth stage is better understood.

Reference

1. R. C. Reid, J. M. Prausnitz, and B. E. Poling, *The Properties of Gases & Liquids*, McGraw-Hill, New York, Fourth Edition, Chapter 9, 1987.

Task 3. Characterization of Solid Gums, Sediment, and Carbonaceous Deposits.

*Effects of Adding High Surface Area Activated Carbon PX-21 to JPTS Jet Fuel
(Contributed by Katia Gergova, Rathnamala Arumugam, and Semih Eser)*

Introduction

Our previous studies showed that activated carbon addition causes considerable changes on degradation reactions during thermal stressing of jet fuels at high temperatures and prevents solid deposition on reactor surfaces [1]. Addition of the high surface area activated carbon PX-21 is effective in suppressing thermal degradation reactions of jet fuel heated to a high temperature (450°C) [2]. The increased stability provided by the activated carbon can be explained by the termination of free radical chain reactions on active carbon surfaces. A 100 mg PX-21 addition to 10 mL of jet fuel significantly enhanced its thermal stability and prevented solid deposition on reactor surfaces in both nitrogen and air atmospheres. At a lower temperature (at 425°C for 5 h), 50 mg of carbon per 10 mL of jet fuel was sufficient to keep the color of the starting jet fuel virtually the same without any visible change [3]. Higher concentrations of alkanes and lower concentrations of alkylated aromatics are found in the liquid products upon adding activated carbons. It also appears that the apparent N₂ surface area of the activated carbons used as additives is an important parameter which determines their effectiveness in suppressing solid deposition [2]. The higher the surface area, the more effective is the added carbon.

The present work provides data on the composition of the liquid, gaseous and solid products obtained after thermal stressing of JPTS jet fuel at 450°C and 425°C for 5h.

Experimental

Two sets of experiments were performed on JPTS at two different temperatures, 425°C and at 450°C. Experiments were carried out on 10 mL JPTS alone and mixed with 50 mg high surface area activated carbon PX-21 at 425°C for 5h in stainless steel microautoclaves under 100 psi of nitrogen or air and at 450°C for 5h.

GC analyses were conducted using a Perkin-Elmer 8500 with a fused silica capillary column. The quantitative analysis of the liquid products was performed based on calibration curves obtained from external standards. The compounds in the liquid products were identified by capillary gas chromatography-mass spectrometry (GC-MS) using a Hewlett-Packard 5890 II GC coupled with HP 5971A mass selective detector.

The gaseous products were analyzed using a Perkin Elmer AutoSystem gas chromatograph equipped with two different columns and detectors for quantifying gaseous components. The hydrocarbon gases ranging from C₁ to C₆ were analyzed with a flame ionization detector (FID). The gaseous products were identified by comparing their retention time with those of standard gases from Supelco, and quantified by external standard method.

The apparent surface area of activated carbon PX-21 was determined before and after stressing with JPTS by N₂ adsorption at 77K using a Quantachrome automated adsorption apparatus, Autosorb-1, model ASIT. From the adsorption data, the BET surface areas were calculated [4]. The activated carbons after stressing with JPTS jet fuel samples were examined using a polarized-light microscope, Nikon Microphot FXA-II. The samples were embedded in epoxy resin and polished using alumina before microscopic examination.

Results and Discussion

1. Analysis of liquid products obtained after thermal stressing of JPTS mixed with activated carbon PX-21. 10 mL of JPTS jet fuel were stressed with 50 mg of PX-21 activated carbon at 425°C for 5 h in nitrogen and air atmosphere. Table 5 summarizes the results obtained from these experiments. It is apparent from Table 5 that the liquid yield obtained after thermal stressing of JPTS mixed with activated carbon is higher than the liquid yield of stressed JPTS alone in nitrogen and in air atmosphere. The final gas pressure build up after thermal stressing experiments is also different. We can assume

from the difference in pressure that JPTS jet fuel stressed alone produces more gases than JPTS stressed with PX-21 activated carbon. Based on these results we can conclude that the cracking processes for the liquids stressed with PX-21 were inhibited, contributing to the enhanced stability of the long-chain alkanes. The presence of activated carbon PX-21 during thermal stressing of JPTS leads to the prevention of solid deposition on the metal reactor surfaces as seen from Table 5. It should be also noted that the weight of the activated carbon increases (about 30%wt) after thermal stressing with JPTS due to adsorption of stressed products on active surfaces and/or deposition of carbonaceous solids on the activated carbon surfaces. The data in Table 5 are also a good example for the influence of oxygen during thermal stressing of jet fuel. As can be seen, the solid mass recovered from the reactor walls tends to increase and the liquid yield decreases for the samples stressed in an air atmosphere compared to those stressed in nitrogen.

The results for thermal stressing experiments of JPTS with and without PX-21 at 450°C for 5 h in nitrogen and air atmosphere were presented in our previous report. At higher temperature the liquid yields are lower, the final pressure build up is higher and more solid is deposited on the reactor walls after stressing of JPTS alone. The trends observed for the liquid obtained at 450°C are the same as those for the liquid obtained at 425°C. The liquid yields are higher, the final pressure is lower and no deposit formation can be seen on the reactor walls after the experiments with activated carbon PX-21. There are more distinct differences between the compositions of the liquids obtained at 450°C. The presence of oxygen during thermal stressing at this high temperature contributes to degradation of jet fuel to a higher degree.

Figure 19 shows the gas chromatograms of the unstressed JPTS and the liquid products from thermal stressing of JPTS alone and with 100 mg PX-21 at 450°C for 5h in nitrogen. From Figure 19 one can see that the concentration of short-chain alkanes at the beginning of the chromatogram is considerably higher for the liquid stressed alone. It should be noted also that the concentrations of toluene and methyl naphthalenes are much higher for the sample stressed alone than those of JPTS stressed with PX-21. The long-chain alkanes are, however, are still the major constituents of the liquid obtained in the presence of PX-21. In all GC analyses, care was taken to inject the same volume of the samples. The relatively low overall intensities of the peaks seen in the stressed products suggest that the portions of the liquid products may not be GC amenable. The stressed liquids will be analyzed by HPLC for identification of heavier compounds.

Figure 20 shows the gas chromatograms of unstressed JPTS compared to JPTS stressed alone and with 100 mg PX-21 at 450°C for 5h in air. As different from stressing in nitrogen, the presence of PX-21 is not as effective in preserving the long-chain alkanes.

Higher extents of cracking (e.g, relatively high concentrations of short-chain alkanes) are, however, evident in the liquid stressed alone. The comparison of the chromatograms in Figures 19 and 20 show that the presence of oxygen limits the stabilizing effect of the added carbon upon stressing the fuel under the same conditions.

Table 6 gives the GC and GC/MS results for the liquids obtained after stressing of JPTS alone and with PX-21 at 425°C in nitrogen and air atmosphere. For comparison the identified compounds and their concentrations for unstressed JPTS are also listed in Table 6. Table 6 illustrates the higher concentration of long-chain alkanes in the liquids obtained after stressing with activated carbon. The same trends can be observed for the branched-chain alkanes. No consistent change was observed for the alkenes, while the concentration of cycloalkanes is generally higher for the liquid stressed in the presence of activated carbon. As far as the aromatics are concerned, the concentration of C₁ and C₂ alkyl aromatics do not show any correlation while the concentration of C₃-, C₄- and C₅-alkyl aromatics is higher for the unstressed liquid as well as the liquid obtained after thermal stressing of JPTS mixed with PX-21.

A series of plots was prepared to observe the differences in the yields of selected compounds (compared to the concentrations in the unstressed JPTS) in the stressed liquids, including the total yields of resulting liquid products after stressing with and without PX-21 at 425°C and 450°C in nitrogen and air atmosphere. Figures 21 and 22 show percent weight plotted versus alkane carbon number for the unstressed and stressed JPTS jet fuel at 425°C in nitrogen and air, respectively. The C₈ and C₁₄ are coeluted with other compounds and are not listed in Figure 21 and 22. Short-chain alkanes C₅-C₇ are present in considerably higher concentrations in the liquids obtained after stressing of JPTS alone than in the liquids obtained after thermal stressing of JPTS mixed with PX-21. The yield of long-chain alkanes C₉-C₁₅ is significantly higher in the liquids obtained after stressing of JPTS with PX-21 than in the JPTS stressed alone and almost equal to the concentration of long-chain alkanes in the unstressed JPTS. It should be noted that the yield of long-chain alkanes in the liquids stressed in air atmosphere is lower than the yield of same compounds in the liquids stressed in nitrogen.

In Figures 23 and 24 the percent weight is plotted versus branched alkane carbon number for the unstressed JPTS and stressed JPTS jet fuel at 425°C in nitrogen and air atmospheres, respectively. From Figures 23 and 24 one can see the same trends are valid for branched alkanes as for normal alkanes. While the C₉-C₁₅ alkanes are in higher concentration in the liquids obtained from JPTS mixed with activated carbon, C₅-C₈ alkanes are in higher concentration in the liquids obtained from the JPTS stressed alone, for the experiments which were carried out in nitrogen as well as in air atmosphere.

Figure 25 shows the percent weight plotted versus number of alkyl groups on benzene for the unstressed and stressed JPTS jet fuel at 425°C in nitrogen and air. From Figure 25 it can be clearly seen that the concentration of C₄ and especially C₃ benzenes is considerably higher than the concentration of C₁ and C₂ benzenes for all the liquids. The concentration of C₁, C₂ and C₃ alkylbenzenes is higher for the liquids obtained from stressing of JPTS alone than with PX-21, while the concentration of C₄ benzenes is higher for the liquids stressed with PX-21. However, the concentration of C₄ alkylbenzenes is also relatively high for the unstressed JPTS. There is not a clear predominance in the concentration of alkylbenzenes in the liquids obtained in air than in nitrogen atmosphere.

The next four figures (Figures 26–29) show percent weight (in the liquid product) plotted versus alkane carbon number and branched alkane carbon number for the unstressed and stressed JPTS alone and mixed with 100 mg PX-21 at 450°C in nitrogen and air atmospheres, respectively. From Figures 26 and 27 some noticeable differences can be observed between the concentration of alkanes in the liquids obtained in nitrogen and air. At high temperatures (450°C), pyrolysis reactions of certain compounds in the fuel become significant and result in the cracking of long-chain alkanes and formation of more gases and short-chain alkanes. The oxygen which is present in a high concentration when thermal stressing is conducted in air atmosphere enhanced pyrolysis reactions. Figure 26 clearly shows that these processes lead to formation of more C₅-C₉ alkanes and less C₁₀-C₁₅ alkanes.

Figures 28 and 29, where the percent weight is plotted versus branched alkanes carbon number, show that the concentration of long-chain branched alkanes C₁₀-C₁₂ is lower in the liquids obtained after thermal stressing of JPTS mixed with PX-21 in air than in nitrogen. Exactly the opposite trends can be observed for the short-chain alkanes.

In summary, from the quantitative analysis of unstressed JPTS jet fuel, JPTS stressed with and without PX-21 we can conclude that the concentration of short-chain paraffins in the liquids stressed with PX-21 as well as the concentration of C₁, C₂ and C₃ benzenes is considerably lower than the concentration of the same compounds in the liquids stressed without PX-21. The processes of thermal degradation of JPTS jet fuel when PX-21 is added are delayed to a higher extent in nitrogen than in air especially at a higher temperature (450°C).

2. Analysis of gaseous products obtained after thermal stressing of JPTS mixed with high surface area activated carbon PX-21 at 425°C. There are substantial differences in the head space gas yield and composition obtained after thermal stressing of JPTS with and without PX-21 activated carbon in nitrogen. Table 7 shows the head

space gas composition in percent by volume of gases obtained from stressing of JPTS alone and mixed with 50 mg PX-21 at 425°C in nitrogen and in air atmosphere. The data for the headspace gas obtained in air with PX-21 is very different from the other gas analyses. The extremely low CH₄ concentration of this gas sample may be due to a leak from the gas sampling bag. It is unlikely that such low methane contents result from thermal degradation reactions even in the presence of active surfaces. This column of data will not be included in discussions, which will be restricted to reactions in nitrogen atmosphere.

One can see that major compounds of gas sample obtained after thermal stressing of JPTS with PX-21 in nitrogen are methane, ethane coeluted with ethylene, and propane. Except for butene, propylene and, C₄-C₆ gas species are in negligible concentrations. These species, especially propylene, are present in higher concentrations in the gas sample obtained after thermal stressing of JPTS alone in nitrogen. Lower methane and propylene and higher propane and butene yields in the presence of PX-21 point out significantly different reaction mechanisms of thermal degradation upon carbon addition.

3. Analysis of solid products before and after thermal stressing of JPTS mixed with high surface area activated carbon PX-21. In our previous report we analyzed the microstructure of deposits obtained after thermal stressing with JPTS. Figure 30a shows the microstructure of activated carbon PX-21 before stressing with JPTS. PX-21 activated carbon has 2090 m²/g BET N₂ surface area and shows anisotropic microstructure which is not a usual characteristic of activated carbons. Most important effect of adding activated carbons during thermal stressing of jet fuel is prevention of solid deposition on metal reactor surfaces even after thermal stressing at 450°C. Figure 30b shows polarized-light micrograph of PX-21 after thermal stressing of JPTS at 425°C in air atmosphere. From Figure 30b one can see very long but isolated single particle of carbonaceous solid. The solid deposit in Figure 30b appears to be fine pyrolytic carbon and is a result of gas-phase reactions. Most probably, this deposit was loosely formed on an active section of the reactor walls and mixed with activated carbon particles. It should be noted that the amount of activated carbon PX-21 added to jet fuel is significantly lower than the amount of other activated carbons used in our previous studies.

In addition, surface area measurements have been used to observe the changes in the surface of added PX-21 activated carbon as a function of temperature and gas atmosphere during thermal stressing. Table 4 shows the BET N₂ surface area of PX-21 activated carbon after thermal stressing at 425°C and 450°C in nitrogen and air atmosphere. From Table 4 one can see that the initial surface area of PX-21 activated carbon decreases substantially (initial surface area 2090 m²/g). The surface areas of PX-

21 after thermal stressing at 450°C decrease more than at 425°C. Most probably, the higher temperature contributes to more intensive interaction of carbon surface with jet fuel sample. It should be also noted that the surface areas of PX-21 after thermal stressing in air is lower than in nitrogen. These results lead to the conclusion that oxygen also contributes to the adsorption processes. The lower the surface area of activated carbon, the less effective the carbon will be for preventing carbon deposition and stabilize jet fuel during thermal stressing.

Conclusions

The analysis of liquid, gaseous and solid products obtained after thermal stressing of JPTS with high surface area activated carbon PX-21 show that PX-21 addition effectively stops the formation of carbonaceous solids on the reactor walls. PX-21 also increases stability and suppress the thermal degradation of jet fuel after stressing at 425°C and 450°C for 5 h. It appears that 50 mg PX-21 is sufficient to prevent carbon deposition and stabilizes JPTS jet fuel during thermal stressing at 425°C. The experimental data suggest that at least 100 mg PX-21 is necessary for preventing solid deposition at 450°C for 5h. The processes of thermal degradation of JPTS were delayed more in the nitrogen atmosphere compared to the air atmosphere. However, the results obtained for JPTS stressed in air even at 450°C showed that no carbonaceous solid was observed on the reactor walls.

The data for the gaseous products obtained after thermal stressing of JPTS with and without PX-21 at 425°C for 5h show that the reactions during thermal stressing of JPTS with high surface area activated carbon are quite different from those taking place in the absence of added carbon.

References

1. Eser, S., Gergova, K., Arumugam, R. and Schobert, H. H. Formation of Solid Deposits from Jet Fuels in the Presence of Different Solid Carbons, Extended abstract, International Conference Carbon 92, p. 241, 1992.
2. Schobert, H. H., Eser, S., Song, C., Hatcher, P., Walsh, P., Coleman, M. Advanced Thermally Stable Jet Fuels, Technical Progress Report, November 1992-January 1993.
3. Schobert, H. H., Eser, S., Song, C., Hatcher, P., Walsh, P., Coleman, M. Advanced Thermally Stable Jet Fuels, Technical Progress Report, February 1993-March 1993.
4. Gregg, S. and Sing, K. S. W. Adsorption, Surface Area and Porosity, Academic Press, London 1982, 285.

Task 4. Coal-based Fuel Stabilization studies

1. Thermal stability of a second generation of fuel additives (Contributed by John B. Stallman, Michael M. Coleman)

Introduction

In an effort to further probe and improve upon the nature of benzyl alcohol stabilization of jet fuel, a second generation of antioxidants has begun to be investigated.

Several examples of the new stabilizers are shown in Scheme III. Compound 1, 1,2,3,4-tetrahydro-1-naphthol, hopefully will have several additional benefits above those of benzyl alcohol. As with benzyl alcohol, compound 1 has the benzylic proton we believe is responsible for antioxidant properties. Moreover, it also possesses two tetralynic protons that may further enhance its ability to scavenge radicals thereby increasing the antioxidant potential.

Compound 2, 9,10-phenanthrenediol, should also possess excellent antioxidant properties. Again, it contains two benzylic protons, but after the initial radical abstraction, the newly formed benzylic radical should have an attenuated stability as a result of resonance throughout the phenanthrene ring system. This added stability should thermodynamically permit a more facile regeneration of the intact hydrocarbon jet fuel.

Compound 3, phthalan, again, should have additional antioxidant properties above those of benzyl alcohol. The molecule contains, instead of the two benzylic protons present in benzyl alcohol, four benzylic protons. This would hopefully permit one molecule of phthalan to prevent the decomposition of twice the amount of jet fuel that is possible with benzyl alcohol. Additionally, the polar hydroxyl substituent of benzyl alcohol has now been replaced with a relatively nonpolar furan ring. This should give an increase of solubility in the rather nonpolar jet fuel.

The compound 4, 1,2-benzenedimethanol, should also possess superior antioxidant properties. As with phthalan, there are now four benzylic protons. Moreover, after an initial oxidation of one of the benzene methanol substituents of compound 4 to an aldehyde (the transformation demonstrated to occur for benzyl alcohol), the remaining benzyl alcohol like protons should induce an intramolecular self-reduction to provide the starting benzenedimethanol.

Experimental

Compounds 3 and 4 are commercially available. The synthesis of the remaining antioxidants mentioned above is depicted in Scheme IV. 1,2,3,4-Tetrahydro-1-naphthol was synthesized by the reduction of commercially available α -tetralone with sodium borohydride in methanol in the presence of cerium(III) chloride heptahydrate. 9,10-Phenanthrenediol was synthesized from commercially available 9,10-phenanthrene-9,10-dione via a simple reduction with diisobutylaluminum hydride. The thermal stressing of these new generation antioxidants is currently in progress.

2. Theoretical Models To Study The Phase Behavior of Jet Fuel (Contributed By Xinglong Liang, Michael M. Coleman)

Introduction

From the fuel stabilization studies in our group, we know that benzyl alcohol can retard the degradation of jet fuel for at least six hours at elevated temperature.[1] In the thermal stability study the thermal stressing was performed at 425°C in 25ml type 316 stainless steel microreactors under 1.0 MPa of UHP-grade N₂. It is very interesting to study the phase behavior of jet fuel, which is a matter of considerable practical importance. Questions we are asking now are: What is the phase behavior of mixture of benzyl alcohol and dodecane? Are they one phase or two phase under these conditions? To answer these questions we try to predict the phase behavior in the first step.

Among the various theories of solutions, two most widely used ones are Flory's and Sanchez and Lacombe's liquid fluid models.[2-6] In this report, these two theories are compared and their adequacy to apply to the jet fuel system is discussed.

Flory's Theory

(A) Equation of State. The Flory theory use a partition function which requires a separation of internal and external degrees of freedom. It is assumed that the configurational partition function of a system of N r-mers, each with 3cr degrees of freedom, is given by [7]:

$$Z(T,V) = Z_{int}(T)[Z_{ext}(T,V)]^{3crN} \exp(-E_0/kT) \quad (1)$$

Flory and co-workers[2-4] suggested the following partition function for a system of N r-mers:

$$Z(T,V) = \text{const} (v^{1/3} - v^{*1/3})^{3crN} \exp(-E_0/kT) \quad (2a)$$

$$= \text{const } v^{*crN} (\tilde{v}^{1/3} - 1)^{3crN} \exp(crN\tilde{\rho}/\tilde{T}) \quad (2b)$$

where V is total volume; $v=V/rN$, volume per mer; v^* is close-packed or hard core mer volume; $\tilde{v} \equiv V/rNv^* \equiv v/v^*$ reduced volume; $\tilde{\rho} \equiv 1/\tilde{v}$, reduced density; and E_0 is the mean intermolecular energy. Flory assumed a van der Waals form for E_0 , that is, an energy that is inversely proportional to volume:

$$-E_0 = (rN) \frac{(s\eta/2)}{v} = \left(\frac{rNs}{2}\right) \frac{\eta/v^*}{\tilde{v}} \quad (3a)$$

or

$$-E_0/kT = crN\tilde{\rho}/\tilde{T} \quad (3b)$$

where s is number of intermolecular contact sites per mer; $rNs/2$ total number of pair interaction; η/v^* energy characteristic of a mer-mer interaction (η has units of energy $\times$ volume); $\epsilon^* = s\eta/2v^*$, the interaction energy per mer in the close-packed configuration ($\tilde{v} = 1$); $\tilde{T} = T/T^*$, reduced temperature; and $T^* = \epsilon^*/ck$.

The equation of state is obtained in the usual way from the partition function:

$$P = kT \left(\frac{\partial \ln(Z(T,V))}{\partial V} \right)_T \quad (4)$$

which yields

$$\tilde{P}\tilde{v}/\tilde{T} = \frac{\tilde{v}^{1/3}}{\tilde{v}^{1/3} - 1} - \frac{1}{\tilde{v}\tilde{T}} \quad (5a)$$

or

$$\tilde{\rho}^2 + \tilde{P} - \tilde{T}\tilde{\rho}(1 - \tilde{\rho}^{1/3})^{-1} = 0 \quad (5b)$$

where $\tilde{P} = P/P^*$, reduced pressure, and $P^* = \epsilon^*/v^* = ckT^*/v^*$. The reduced density and volume can be more conveniently expressed in terms of the mass density ρ or the specific volume v_{sp} ($\rho = 1/v_{sp}$):

$$\tilde{\rho} \equiv \rho/\rho^* \equiv v_{sp}^*/v_{sp} \equiv 1/\tilde{v} \quad (6)$$

where v_{sp}^* is the close-packed volume per unit mass and

$$\rho^* = 1/v_{sp}^* \quad (7)$$

Differentiation of the equation of state with respect to temperature at constant pressure yields at zero pressure:

$$v_{sp}^* = v_{sp} \left[\frac{1 + T\alpha}{1 + 4T\alpha/3} \right]^3 \quad (8)$$

where $\alpha = \partial \ln v / \partial T|_p$ is the thermal expansion coefficient.

Differentiation of equation of state with respect to temperature at constant volume yield at zero pressure:

$$P^* = \tilde{v}^2 T \gamma = \tilde{v}^2 \alpha / \beta \quad (9)$$

where $\gamma = \partial P / \partial T|_v$ is the thermal pressure coefficient and $\beta = -\partial \ln V / \partial P|_T$ is the isothermal compressibility.

From the equation of state itself there obtains at zero pressure

$$\begin{aligned} T^* &= \frac{T \tilde{v}^{4/3}}{(\tilde{v}^{1/3} - 1)} \\ &= \frac{T}{\tilde{\rho}(1 - \tilde{\rho}^{1/3})} \end{aligned} \quad (10)$$

Equations (8)-(10) will give the value of v_{sp}^* , P^* , T^* and not all of the four fundamental molecular parameters but the products of them, rv^* , $r\epsilon^*$ and rc , can be determined by:

$$rv^* = M v_{sp}^* \quad (11)$$

$$r\epsilon^* = M P^* v_{sp}^* \quad (12)$$

$$rc = M P^* v_{sp}^* / k T^* \quad (13)$$

where M is the molecular weight of the r-mer.

The Gibbs free energy per mole g° is given by

$$g^\circ \equiv \frac{(-kT \ln Z + PV)}{N} \quad (14a)$$

$$= r\epsilon^* \left[-\tilde{\rho} + \tilde{P}\tilde{v} - 3\tilde{T} \ln(\tilde{v}^{1/3} - 1) \right] \quad (14b)$$

(B) Mixtures. Application of the theory to a mixture requires the adoption of set of combining rules:

1. The mer volumes v_1^* and v_2^* are chosen so that

$$v_1^* = v_2^* = v^*$$

2. The closed-packed volume of the mixture V^* is equal to the sum of the pure component closed-packed volumes:

$$\begin{aligned} V^* &= r_1 N_1 v_1^* + r_2 N_2 v_2^* = r N v^* \\ &= N [x_1 M_1 v_{sp;1}^* + x_2 M_2 v_{sp;2}^*] \end{aligned}$$

where

$$N = N_1 + N_2$$

$$x_1 = 1 - x_2 = N_1 / N \quad (\text{mole fraction})$$

$$r = x_1 r_1 + x_2 r_2$$

3. The total number of pair interactions in the mixture is equal to the sum of the pure component pair interactions:

$$\begin{aligned} \frac{1}{2}(r_1 N_1 s_1 + r_2 N_2 s_2) &= srN/2 \\ &= N_{11} + N_{22} + N_{12} \end{aligned}$$

where

$$s \equiv \phi_1 s_1 + \phi_2 s_2$$

$$\phi_1 = r_1 N_1 / rN = 1 - \phi_2$$

$$N_{ij} = \text{number of } i,j \text{ pairs}$$

The partition function of the mixture is then given by

$$Z(T, V) = \text{const } Z_{\text{comb}} (v^{1/3} - v^{*1/3})^{3(c_1 r_1 N_1 + c_2 r_2 N_2)} \exp(-E_o/kT) \quad (15a)$$

and $k \ln(Z_{\text{comb}})$ is the usual Flory-Huggins combinatorial entropy:

$$k \ln Z_{\text{comb}} = -k(N_1 \ln \phi_1 + N_2 \ln \phi_2) \quad (16)$$

$$-E_o = (N_{11} \eta_{11} + N_{12} \eta_{12} + N_{22} \eta_{22}) / v \quad (17a)$$

It is assumed that among the $srN/2$ pair interactions, the interactions are random; thus

$$N_{11} = \frac{1}{2}(s_1 r_1 N_1 \theta_1)$$

$$N_{22} = \frac{1}{2}(s_2 r_2 N_2 \theta_2)$$

$$N_{12} = s_1 r_1 N_1 \theta_2 = s_2 r_2 N_2 \theta_1 \quad (18)$$

$$\theta_1 = 1 - \theta_2 = s_1 r_1 N_1 / srN \quad (19)$$

$$-E_o/rN = s(\theta_1^2 \eta_{11} + 2\theta_1 \theta_2 \eta_{12} + \theta_2^2 \eta_{22})/2v \quad (17b)$$

$$= s(\theta_1 \eta_{11} - \theta_1 \theta_2 \Delta\eta + \theta_2 \eta_{22})/2v \quad (17c)$$

$$\Delta\eta \equiv \eta_{11} - 2\eta_{12} + \eta_{22} \quad (20)$$

Now let

$$x_{12} \equiv s_1 \Delta\eta / 2v^{*2} \neq x_{21} \quad (21)$$

then

$$-E_o/rN = (\phi_1 P^*_1 + \phi_2 P^*_2 - \phi_1 \theta_2 x_{12})(v^*/\tilde{v}) \quad (17d)$$

$$-E_o/rN = p^* v^*/\tilde{v} = ckT^*/\tilde{v} \quad (17e)$$

where

$$c \equiv \phi_1 c_1 + \phi_2 c_2 \quad (22)$$

$$P^* \equiv \phi_1 P^*_1 + \phi_2 P^*_2 - \phi_1 \theta_2 x_{12} \quad (23)$$

$$T^* \equiv P^* v^*/ck = P^*/(\phi_1 P^*_1/T^*_1 + \phi_2 P^*_2/T^*_2) \quad (24)$$

The partition function (15a) for the mixture can now be expressed in terms of reduced variables:

$$Z(T, V) = \text{const } v^{*crN} Z_{\text{comb}} (v^{1/3} - 1)^{3crN} \exp(crN/\tilde{v}T) \quad (15b)$$

which is identical that of the pure component (2b), the mixture satisfies the same equation of state (5) with p^* and T^* defined by Eqs (23) and (24).

The chemical potential is

$$\mu_1 = \left(\frac{\partial A}{\partial N_1} \right)_{T, V, N_2} = -kT \left(\frac{\partial \ln Z}{\partial N_1} \right)_{T, V, N_2} \quad (25)$$

$$\mu_1 - \mu_0 = kT \left[\ln \phi_1 + \left(1 - \frac{r_1}{r_2} \right) \phi_1 \right] + r_1 v^*_1 \tilde{\rho} x_{12} \theta_2^2$$

$$+ r_1 \epsilon^*_1 \left\{ \tilde{\rho}_1 - \tilde{\rho} + \tilde{P}_1 (\tilde{v} - \tilde{v}_1) + 3\tilde{T}_1 \ln \left[\frac{\tilde{v}_1^{1/3} - 1}{\tilde{v}^{1/3} - 1} \right] \right\} \quad (26)$$

Lattice Fluid Model

(A) Equation of State. The Gibbs free energy G is

$$G = -kT \ln Z(T, P) \quad (28)$$

$$Z(T, P) = \sum_{V, E} \Omega(E, V, N) \exp \{-(E + PV)/kT\} \quad (29)$$

where $\Omega(E, V, N)$ is the number of configurations available to a system of N molecules whose configurational energy and volume are E and V respectively. The summations extend over all values of E and V .

A lattice is used to approximate Ω . For a system of N r -mers and N_0 vacant sites, Ω is [8]

$$\Omega = \left(\frac{1}{f_0}\right)^{N_0} \left(\frac{\omega}{f}\right)^N \quad (30)$$

where ω is the number of configurations available to a r -mer in the close-packed state; $f_0 = N_0/(N_0 + rN)$, fraction of empty sites; and $f = rN/(N_0 + rN)$, fraction of occupied sites. The derivation of Eq (30) assumes that the coordination number Z of the lattice is large and that all configuration of the N r -mers and N_0 empty sites are energetically equivalent.

The reduced volume $\tilde{v}$ and density $\tilde{\rho}$ are defined as

$$\tilde{v} = v_{sp}/v_{sp}^* \quad (31)$$

$$\tilde{\rho} = 1/\tilde{v} = \rho/\rho^* = \frac{rN}{rN + N_0} = f \quad (32)$$

where v_{sp} is specific volume and $\rho = 1/v_{sp}$ is the mass density.

The total volume is given by

$$V = (N_0 + rN)v^* \quad (33)$$

or

$$\tilde{v} \equiv V/V^* \equiv v/v^*; \quad V^* = rNv^* \quad (34)$$

The total number of pair interactions is $\frac{Z}{2}(N_0 + rN)$. If random mixing of mers and vacant sites is assuming, then the probability that two sites are occupied by mers is equal to f^2 . Denoting the mer-mer interaction energy by ϵ , the mean intermolecular energy is

$$E = \frac{Z\epsilon(N_0 + rN)f^2}{2} \quad (35a)$$

or

$$E/rN = -\tilde{\rho}\epsilon^* \quad (35b)$$

where $\epsilon^* = Z\epsilon/2$ is the total interaction energy per mer. Since E and Ω are functions of a single parameter, the number of empty sites in the lattice, the double sum over E and V required in the evaluation of the partition function can be replaced by a single sum over N_0 :

$$Z(T,P) = \sum_{N_0=0}^{\infty} \Omega \exp\{-(E+PV)/kT\} \quad (36)$$

The Gibbs free energy is

$$G = E + PV - kT \ln \Omega \quad (37)$$

or in reduced variables

$$G/(Nr\epsilon^*) \equiv \tilde{G} = -\tilde{\rho} + \tilde{P}\tilde{v} + \tilde{T} \left[(\tilde{v}-1) \ln(1-\tilde{\rho}) + \frac{1}{\tilde{r}} \ln \left(\frac{\tilde{\rho}}{\omega} \right) \right] \quad (38)$$

where $\tilde{T}$ and $\tilde{P}$ are reduced temperature and pressure:

$$\tilde{T} \equiv T/T^*; \quad T^* \equiv \epsilon^*/k \quad (39)$$

$$\tilde{P} \equiv P/P^*; \quad P^* \equiv \epsilon^*/v^* \quad (40)$$

The minimum value of the free energy is found in the usual way:

$$\left(\frac{\partial \tilde{G}}{\partial \tilde{v}} \right)_{\tilde{T}, \tilde{P}} = 0 \quad (41)$$

which yields

$$\tilde{\rho}^2 + \tilde{P} + \tilde{T} \left[\ln(1-\tilde{\rho}) + \left(1 - \frac{1}{\tilde{r}} \right) \tilde{\rho} \right] = 0 \quad (42)$$

Equation (42) is the equation of state for the lattice fluid. $\tilde{\rho}$ is the dependent variable and $\tilde{P}$ and $\tilde{T}$ are the independent variables. Equation (42) defines the value of $\tilde{\rho}$ at given $(\tilde{T}, \tilde{P})$ that minimize the free energy. Equation (38) and (42) completely describe the thermodynamics of the model fluid. The thermal expansion coefficient α , the isothermal compressibility β , and the thermal pressure coefficient γ are given by

$$T\alpha = \frac{1 + \tilde{P}\tilde{v}^2}{\tilde{T}\tilde{v}[1/(\tilde{v}-1) + 1/r] - 2} \quad (43)$$

$$P\beta = \frac{\tilde{P}\tilde{v}^2}{\tilde{T}\tilde{v}[1/(\tilde{v}-1) + 1/r] - 2} \quad (44)$$

$$T\gamma = P^*(\tilde{\rho}^2 + \tilde{P}) \quad (45)$$

A fluid is completely characterized by three molecular parameters ϵ^* , v^* and r , or equivalently, the three equations of state parameters T^* , P^* , and ρ^* , which can be defined experimentally [8]. Flory theory, the molecular parameter can be obtained from the equation of state parameters:

$$\epsilon^* = kT^* \quad (46)$$

$$v^* = kT^*/P^* \quad (47)$$

$$r = MP^*/kT^*\rho^* = M/\rho^*v^* \quad (48)$$

(B) Mixtures. The combined rules are as follows:

1. The close-packed molecular volume of each component is conserved. If an i molecule occupies r_i^0 sites in the pure state and has a close-packed molecular volume of $r_i^0 v_i^*$, then it will occupy r_i sites in the mixture, where

$$r_i = r_i^0 (v_i^*/v^*)$$

This rule guarantees additivity of the close-packed volumes:

$$\begin{aligned} V^* &= r_1^0 N_1 v_i^* + r_2^0 N_2 v^* \\ &= (r_1 N_1 + r_2 N_2) v^* \end{aligned}$$

2. The total number of pair interaction in the close-packed mixture is equal to the sum of the pair interaction of the components in their close-packed pure state, that is

$$\frac{Z}{2}(r_1^0 N_1 + r_2^0 N_2) = \frac{Z}{2}(r_1 N_1 + r_2 N_2) = \frac{Z}{2} r N$$

where

$$r \equiv r_1^0 x_1 + r_2^0 x_2$$

$$\equiv r_1 x_1 + r_2 x_2$$

$$N = N_1 + N_2$$

and

$$v^* = \phi_1^0 v^*_1 + \phi_2^0 v^*_2 \quad (49)$$

where

$$\phi_1^0 = r_1^0 N_1 / (r_1^0 N_1 + r_2^0 N_2) = r_1^0 N_1 / r N = 1 - \phi_2^0 \quad (50)$$

The volume of the mixture is

$$\begin{aligned} V &= (N_o + r_1 N_1 + r_2 N_2) v^* \\ &= (N_o + rN) v^* \end{aligned} \quad (51)$$

and the reduced volume is

$$\tilde{V} \equiv V/rNv^* \equiv (N_o + rN)/rN = 1/\tilde{\rho} \quad (52)$$

The number of configurations available to a system N_1 r_1 -mers, and N_2 r_2 -mers and N_o empty sites is approximately given by

$$\Omega = \left(\frac{1}{f_o}\right)^{N_o} \left(\frac{\omega_1}{f_1}\right)^{N_1} \left(\frac{\omega_2}{f_2}\right)^{N_2} \quad (53)$$

where

$$f_o = N_o / (N_o + rN) = 1 - \tilde{\rho}; \quad f_1 = \phi_1 \tilde{\rho}; \quad f_2 = \phi_2 \tilde{\rho} \quad (54)$$

$$\phi_1 = r_1 N_1 / rN = 1 - \phi_2 \quad (55)$$

and ω_1 is the number of configurations available to a r_1 -mer in the close-packed pure state.

If random mixing of the mer and vacant sites is assumed, the intermolecular energy can be written as

$$E/rN = -\tilde{\rho} \epsilon^* \quad (56)$$

where

$$\epsilon^* = \phi_1 \epsilon_{11}^* + \phi_2 \epsilon_{22}^* - \phi_1 \phi_2 kT \chi \quad (57)$$

$$\chi = (\epsilon_{11}^* + \epsilon_{22}^* - 2\epsilon_{12}^*)/kT \quad (58)$$

The Gibbs free energy is

$$\begin{aligned} \tilde{G} &\equiv G/rN\epsilon^* \\ &= -\tilde{\rho} + \tilde{P}\tilde{V} + \tilde{T} \left[(\tilde{V}-1) \ln(1-\tilde{\rho}) + \frac{1}{\tilde{T}} \ln \tilde{\rho} + \frac{\phi_1}{r_1} \ln \left(\frac{\phi_1}{\omega_1} \right) + \frac{\phi_2}{r_2} \ln \left(\frac{\phi_2}{\omega_2} \right) \right] \end{aligned} \quad (59)$$

$$\tilde{T} = T/T^*; \quad T^* = \epsilon^*/k \quad (60)$$

$$\tilde{P} = P/P^*; \quad P^* = \epsilon^*/v^* \quad (61)$$

The equation of state is

$$\tilde{\rho}^2 + \tilde{P} + \tilde{T}[\ln(1-\tilde{\rho}) + (1 - \frac{1}{r})\tilde{\rho}] = 0 \quad (62)$$

which is identical as equation (42)

The chemical potential μ_1 is given by

$$\begin{aligned} \mu_1 &= \left(\frac{\partial G}{\partial N_1} \right)_{T,V,N_2} \\ &= kT \left\{ \ln \phi_1 + \left(1 - \frac{r_1}{r_2} \right) \phi_2 + r_1^0 \tilde{\rho} \left[\chi + \left(1 - \frac{v^*_1}{v^*_2} \right) \lambda_{12} \right] \phi_2^2 \right\} \\ &\quad + r_1^0 kT^* \left\{ -\tilde{\rho} + \tilde{P}\tilde{v} + \tilde{T} \left[(\tilde{v}-1) \ln(1-\tilde{\rho}) + \frac{1}{r_1^0} \ln \left(\frac{\tilde{\rho}}{\omega_1} \right) \right] \right\} \end{aligned} \quad (63)$$

where

$$\begin{aligned} \lambda_{12} &\equiv \partial(\epsilon^*/kT)/\partial\phi_1 \\ &= \frac{1}{\tilde{T}_1} - \frac{1}{\tilde{T}_2} + (\phi_1 - \phi_2)\chi = -\lambda_{21} \end{aligned} \quad (64)$$

$$\tilde{T}_i = T/T_i^*; \quad \tilde{P}_i = P/P_i^* \quad (65)$$

The chemical potentials have the following properties:

1. They reduce correctly to their appropriate molar pure state values; for example,

$$\lim_{\phi_1 \rightarrow 1} \mu_1 \equiv \mu_1^0 = r_1^0 \epsilon^*_{11} \tilde{G}(\phi_1=1) = r_1^0 \epsilon^*_{11} \tilde{G}_1 \quad (66)$$

2. At low temperature or high pressure, the reduced densities approach their maximum value of unity. In this limit with $v^*_1 = v^*_2$, the Flory-Huggins chemical potentials are recovered:

$$\lim_{\phi_1, \rho_1 \rightarrow 1} (\mu_1 - \mu_1^0) = kT \left[\ln \phi_1 + \left(1 - \frac{r_1}{r_2} \right) \phi_2 + r_1 \chi \phi_2^2 \right] \quad (67)$$

3. This is only one parameter, ϵ^*_{12} or χ , that characterizes a binary mixture. All other parameters are known from the pure components. Knowledge of ω_i is not required since it is absent in the difference $\mu_1 - \mu_1^0$.

Discussion

Both Flory and Liquid Fluid theories use a van der Waals type of potential energy for the fluid mixture, but differ in their representation of the volume dependent part of the entropy of the mixture. The Flory treatment essentially assumes that the system's free volume is distributed among each of the systems lattice sites or cells, as shown in Figure 43, whereas the Sanchez-Lacombe lattice fluid model allows for empty lattice sites or holes, as in Figure 44.

Both theories require three equation-of state parameters for each pure component. Therefore, it is very important that these parameters for a given system be evaluated from experimental values of ρ , α , and β (or γ) determined at the same temperature and pressure.

Both the LF theory and Flory's theory can qualitatively explain the feature of the upper and lower critical phase phenomena in nonpolar systems.

However, the LF model has an initial advantage over the Flory's model because it converges to the ideal gas law at low densities. The Flory model assumes a certain amount of order to exist and is therefore limited to densities found in the solid state and in liquids far below their critical temperatures.

The LF model also has advantages over the Flory model in that it does not introduce the reduced degrees of freedom parameter, c , and the molecular surface contact parameter, s , which are both difficult to measure and estimate.

Our next step for the work on the phase behavior of jet fuel will be applying the LF model to the benzene alcohol - dodecane system and the ethanol - dodecane system.

Reference

1. Coleman, M. M., Selvaraj, L., Sobbowiak, M., Yong, E., *Energy & Fuels*, 1992, **6**, 535-539.
2. Flory, P. J., Orwoll, R. A., and Vrij, A., *J. Ame. Chem. Soc.*, 1964, **86**, 3515.
3. Flory, P. J., Amer, J., *Chem. Soc.* 1965, **87**, 1833.
4. Eichinger, B. E. and Flory, P. J., *Trans. Faraday Soc.*, 1968, **64**, 2035.
5. Flory, P. J., *Discuss. Faraday Soc.* 1965, **87**, 1833.
6. Lacombe, R. H. and Sanchez, I. C., *J. Phys. Chem.*, 1976, **80**, 2568.
7. Prigogine, I., "The Molecular Theory of Solutions," Chapter XVI. North-Holland Publ., Amsterdam, 1957.
8. Sanchez, I. C. and Lacombe, R. H., *J. Phys. Chem.*, 1976, **80**, 2352.

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

1. Direct Coal Liquefaction: a Potential Route to Thermally Stable Jet Fuel (Contributed by Caroline E. Burgess).

Introduction

The principal mechanism of fuel degradation at temperatures above 300°C is pyrolytic decomposition. Cycloalkanes are much more resistant to thermal degradation than are *n*-alkanes or alkylaromatics [1]. Indeed, decalin shows remarkable thermal stability even at 450° [1, 2]. Hydroaromatics, such as tetralin, are also quite stable at these temperatures when reacted neat [1, 2] and can suppress the thermal degradation of other compound classes, such as *n*-alkanes, in a process termed hydrogen-transferring pyrolysis [3, 4]. Thus high concentrations of cycloalkanes and hydroaromatics in a real fuel (which of course may contain dozens of components) could provide significant thermal stability.

Direct liquefaction of coal could potentially provide a facile route to liquids boiling in the jet range and containing the desired cycloalkanes and hydroaromatics. The key chemical steps in this process would be the liberation of the aromatic units by cleavage of whatever crosslinks or other interactions hold them in the coal structure, and the hydrogenation of the aromatics to cycloalkanes or hydroaromatics. Clearly, coals showing good reactivity during liquefaction are desirable. To facilitate liberation of the aromatic ring systems, it would be helpful to select coals containing a relatively low population of crosslinks. To minimize downstream processing, it would also be useful to select coals in which a preponderance of the aromatic structures are naphthalene derivatives, to allow direct hydrogenation to decalins and tetralins. Similarly, it would be desirable to have a low content of heteroatoms, also to minimize downstream treatment of the liquids. Not all of these features are available in coals of a given rank. High reactivity and small aromatic units are characteristics of coals at the low end of the rank range. Low crosslink density and relatively low heteroatom content are more likely to be found in the bituminous rank range. Thus the selection of potential feedstocks may involve a compromise to achieve a reasonable balance among these desired characteristics.

We are conducting an exploratory study to test the hypothesis that it is possible to form high yields of cycloalkanes and hydroaromatics boiling in the jet range by selection of feedstocks to contain a high proportion of small aromatic units and relatively few

crosslinks; and by choosing catalyst and reaction conditions to liberate the desirable structural features of the coal. In this section we report results of reactions of two bituminous coals subjected to temperature-programmed liquefaction, particularly, the effects of coal, solvent, and catalyst on conversion, product slate, and product quality.

Experimental

The coals were obtained from the Penn State Coal Sample Bank and Data Base. The provenance and characteristics of the coals are shown in Table 11. The solvents, catalysts, and reagents used in this work were purchased from commercial vendors and used without further purification.

Liquefaction reactions were conducted in stainless steel microautoclave reactors of nominal 30 mL capacity. Pyrene and 9,10-dihydrophenanthrene (DHP) were used as liquefaction solvents. The reactors were charged with 4 g coal and 4g of the desired solvent. For those reactions in which a catalyst was used, coal was dried and impregnated with ammonium tetrathiomolybdate (ATTM) or NiCl_2 as described in previous work [5]. The reactors were pressurized to 7 MPa with H_2 at ambient temperature. The concept of temperature-programmed liquefaction has been discussed elsewhere [5, 6]. Briefly, the reactor is immersed in a sandbath preheated to 200°C and held for 15 min. The temperature is then ramped to 425° at 7°/min, and is held at 425° for 30 or 60 min. At the end of a reaction, the reactor is quenched by immersion in cold water.

Products were emptied from the tubing bomb into a dry tared thimble using dichloromethane (DCM) and extracted with DCM for about 36-48 h until the extracted solvent appeared clear. The products were then extracted with tetrahydrofuran (THF) for about 24-36 h until the extracted solvent appeared clear. The DCM was rotoevaporated from the DCM-solubles, and then the sample was extracted with hexane. The THF-insoluble portion was rinsed with acetone and pentane and dried at 100°C for 12 h. The THF-soluble fractions were dried for 1 h at 60°C. The hexane-soluble fractions were analyzed by GC/FID and GC/MS. The conditions of the GC used were a rate of 4 °C/min from 40 to 280 °C.

Results and Discussion

The principal experimental results are summarized in Table 12. The DCM-solubles include gas yields, and gas yields were $\leq 5\%$ for all reactions. The principal compound classes identified in the hexane-soluble portions of the DCM-soluble products are summarized in Table 13. For convenience, we will occasionally refer to three ratios:

a) THF-solubles to the sum of the DCM-solubles expressed as THF/DCM; b) aromatic compounds of one ring to those with two rings or more, (i.e., benzenes + phenols to naphthalenes + phenanthrenes + polynuclear aromatics) expressed as B+P/ ≥ 2 -ring; and c) the total aromatic compounds to alkanes, expressed as $\Sigma\text{Aro}/\Sigma\text{Ali}$.

For reactions without catalyst, conversions to DCM-solubles depend mainly on solvent. For a given solvent, conversions of the two coals are similar. However, DHP is clearly superior to pyrene for increasing conversions. Even though pyrene is well known as a hydrogen shuttler [7], DHP is a potent hydrogen donor [8]. Furthermore, in non-catalytic reactions, most of the hydrogen consumption comes from the solvent rather than gas-phase H_2 [8], so it is not surprising that substantially higher conversions are achieved in DHP. Although the conversions of the two coals in a given solvent are comparable, and the comparative effects of pyrene versus DHP are comparable, the change in product slates with increased conversion is quite different between the two coals. With DECS-6, the increased conversion effected by DHP comes largely via formation of THF-solubles. THF/DCM increases from 0.23 for reaction in pyrene to 0.64 for reaction in DHP. In contrast, THF/DCM is essentially unchanged (and in fact slightly decreases from 0.37 to 0.33) for reactions of DECS-12 in these solvents. DHP reduces the proportion of aromatics with ≥ 2 rings in the DCP-solubles, and increases the proportion of total aromatics relative to alkanes, relative to results obtained using pyrene. For DECS-6, the B+P/ ≥ 2 -ring ratio is 0.98 for reaction in pyrene, and 0.73 for reaction in DHP. $\Sigma\text{Aro}/\Sigma\text{Ali}$ increases from 1.46 to 1.80 for reaction in pyrene and DHP, respectively. The effect of solvent on the B+P/ ≥ 2 -ring ratio for DECS-12 is quite similar, 1.19 for reaction in pyrene decreasing to 0.83 when DHP is used. A remarkable difference is seen in the $\Sigma\text{Aro}/\Sigma\text{Ali}$ ratio for DECS-12 relative to DECS-6. For both coals, reaction in DHP increases this ratio relative to reaction in pyrene, but the products from reaction of DECS-12 have so fewer *n*-alkanes that there is an order-of-magnitude difference in the $\Sigma\text{Aro}/\Sigma\text{Ali}$ ratios. Characterization of these two coals by flash pyrolysis GC/MS has shown the preponderance of *n*-alkanes in DECS-6 relative to DECS-12 [9].

For reactions in pyrene, the addition of catalyst not unexpectedly enhances conversion of both coals. Using either MoS_2 or NiCl_2 , the conversion of DECS-6 increases by about 30 percentage points (Table 12). Both catalysts increase the conversion in the hydrogen-shuttling solvent pyrene to the same level as obtained by using the strong hydrogen donor solvent DHP without catalyst. However, the two catalysts have quite different effects on the product slate. MoS_2 , which could be considered to be a hydrogenation catalyst [10-12], provides a very high yield of light products, THF/DCM being only 0.06. In comparison, NiCl_2 , a cracking catalyst [12-13]

provides almost the same conversion, but a higher yield of preasphaltenes than attained with MoS₂. Using NiCl₂ catalyst, the THF/DCM ratio is about the same as obtained in pyrene but without catalyst, i.e., 0.19 vs. 0.23, respectively. Thus NiCl₂ appears to increase the depolymerization of DECS-6, but not to alter the relative proportion of products; in comparison, MoS₂ seems both to increase the depolymerization and shift the product slate toward lighter products.

However, when deductions are drawn based on conversion data, it is important not to lose sight of the fact that these product classifications are based on solubility behavior, which potentially could mask differences in molecular composition. For NiCl₂/pyrene reaction of DECS-6, there is a substantial increase in the amount of naphthalenes in the DCM-solubles relative to the MoS₂-catalyzed reaction, which actually decreases the B+P/≥2-ring ratio, from 1.87 for MoS₂ catalysis to 1.32 with NiCl₂. With DECS-12, catalytic reaction in pyrene also increases conversion to about the same value as obtained in non-catalytic reaction in DHP. Use of MoS₂ shifts the product slate to lighter products, as occurred with DECS-6, although the effect is not quite so pronounced for DECS-12, THF/DCM decreasing from 0.37 to 0.23. With NiCl₂, however, the proportion of preasphaltenes in the product is actually enhanced relative to reaction without catalyst. In this case the effect of NiCl₂ catalysis is quite different for the two coals. However, when product composition is examined, a reduction of the B+P/≥2-ring ratio is observed for NiCl₂-catalyzed reaction of DECS-12 in pyrene relative to MoS₂, which can, as in the similar case of DECS-6, be attributed to a large increase in naphthalenes and a loss of phenols in the DCM-solubles. It is possible that the reduction of phenols and the concurrent increase in THF/DCM ratio could mean that retrogressive reactions are promoted by the NiCl₂ cracking without the stabilization of hydrogen from an H-donor or hydrogenation catalyst.

The effect of reaction time was evaluated only for DECS-6, by comparing reactions with high-temperature holding times of 30 and 60 min for both MoS₂ and NiCl₂ in pyrene. Little change was observed in either conversion or product slate. It is unlikely that the slight changes in conversion or product slate observed after 60 min would repay the additional processing costs associated with a doubling of the residence time at 425°.

The combination of the MoS₂ hydrogenation catalyst and DHP donor solvent in reaction of DECS-6 provided the highest conversion observed in the present work, 95%. The product slate was about the same as that obtained for MoS₂ and pyrene, with THF/DCM of 0.06. Liquefaction of DECS-6 in DHP without catalyst actually increased the THF/DCM ratio relative to non-catalytic reaction in pyrene. The catalytic effect of the added MoS₂ thus seems important for shifting the product slate to lighter—on the

basis of solubility classifications—products, regardless of whether a hydrogen donor or hydrogen shuttler is used as solvent. Using DHP with NiCl_2 produced no increase in conversion relative to that of NiCl_2 and pyrene. There is, though, a shifting of the THF/DCM ratio to 0.15, compared with 0.19 for NiCl_2 /pyrene, and 0.23 for non-catalytic reaction in pyrene. It is noteworthy that the combination of catalyst and donor solvent produces the lowest values of the B+P/ ≥ 2 -ring ratio observed for this coal, 0.46 for MoS_2 -catalysis and 0.53 for NiCl_2 . Thus 40–43% of the DCM-solubles from DECS-6 for catalytic reaction in DHP are naphthalene derivatives.

For liquefaction of DECS-12 in pyrene, NiCl_2 provided higher conversions than MoS_2 , 84 vs 77%, respectively. The same superiority of NiCl_2 is observed when DHP is used as the solvent, the conversions being 89 and 85%, respectively. For both coals, a change of solvent from pyrene to DHP when MoS_2 is used as the catalyst produces essentially the same effect: an additional 6-8 percentage points of conversion, and a reduction of THF/DCM to 0.06. On the other hand, the change of solvent has different effects for the coals when NiCl_2 is used as the catalyst. We discussed the DECS-6 case above; for DECS-12, an increase in conversion and significant shift of THF/DCM is observed when DHP is used instead of pyrene. The combination of a catalyst and donor solvent causes significant reductions in the B+P/ ≥ 2 -ring ratio, as was seen for DECS-6. Indeed, nearly 50% of the DCM-solubles from MoS_2 /DHP reaction of DECS-12 are naphthalene derivatives.

An additional aspect of NiCl_2 catalysis is its ability to reduce yields of phenols relative to similar reactions in the presence of MoS_2 . For all but one coal/solvent combination, the concentration of phenols in the DCM-solubles is lower for the NiCl_2 -catalyzed reaction relative to MoS_2 , the single exception being DECS-6/DHP. But if there is a reduction in phenols when using NiCl_2 , and a concurrent increase in THF/DCM, it could be the lost phenols are participating in retrogressive reactions by crosslinking to THF-solubles. Solomon et al. [14] have suggested that functional groups containing oxygen participate in retrogressive reactions. It is also apparent these crosslinking reactions are repressed when a donor solvent or a good hydrogenation catalyst is used.

Attaining the highest conversion with either coal under these reaction conditions clearly requires the presence of the donor solvent in addition to a catalyst. For DECS-6, 95% conversion is achieved for MoS_2 /DHP reaction. Any other combination of solvent, catalyst, or both provides conversions in the range 83–89%. For DECS-12, the highest conversion, 89%, was obtained in NiCl_2 /DHP reaction; the other combinations of solvent and catalyst gave conversions of 77–85%. For either coal and either solvent, the lowest

values of THF/DCM are invariably obtained with MoS₂ catalysis. THF/DCM ratios of 0.06 can be achieved for either coal with this catalyst, along with conversions in the 85–95% range. Furthermore, MoS₂/DHP liquefaction produces DCM-solubles that are 40–50% naphthalene derivatives. The subsequent hydrogenation of this product could, in principle, provide a liquid that contains ≈50% of the desirable, high-thermal-stability decalins and tetralins.

Summary and conclusions

This section reports preliminary results of work still in progress. We have so far shown that, with careful selection of the feedstock, it is possible to achieve 85–95% conversions, with THF/DCM ratios <0.1 and 40–50% of the DCM-solubles being naphthalenes. We have not yet attempted to improve these results by optimizing reaction conditions. The DCM-solubles are highly aromatic, with $\Sigma\text{Aro}/\Sigma\text{Ali}$ approaching 30 for some reactions of DECS-12. It is clear that both a hydrogenation of the product and a hydrodeoxygenation to remove phenols, neither of which is an insignificant operation, still must be investigated. Nevertheless, if these two further transformations can be effected, either by some alteration of reaction strategy such as "reverse temperature staging" [15] or by separate subsequent reactions, the prospect exists for direct conversion of bituminous coals to high yields of liquids containing high concentrations of desirable decalins and tetralins. Such a product could be the foundation of a jet fuel with excellent high-temperature stability characteristics.

References

1. Eser, E., Song, C., Schobert, H., Hatcher, P., Copenhaver, R., Jiang, H., Li, R., Parzynski, M., and Peng, Y. *Advanced Thermally Stable Jet Fuels Development Program Annual Report, Vol. II*, WRDC-TR-90-2079, July 1989 - June 1990.
2. Song, C., Eser, S., Schobert, H.H., Hatcher, P.G., Coleman, M.M., and Walsh, P. *Advanced Thermally Stable Coal-Derived Jet Fuels*, Progress Report, 18-1124-TPR-1, July 1991 - November 1991,
3. Lai, W.C., Song, C., and Schobert, H.H. *Ind. Eng. Chem.* 1993 (submitted).
4. Song, C., Lai, W-C., and Schobert, H.H. *American Chemical Society, Division of Fuel Chemistry, Preprints*, **37** (4), 1655, 1992.
5. Huang, L., Song, C., and Schobert, H.H. *American Chemical Society, Division of Fuel Chemistry, Preprints*, **37** (1), 223, 1992.
6. Song, C., Schobert, H.H., and Hatcher, P.G. *Energy & Fuels*, **6**, 326, 1992.
7. Derbyshire, F.J. and Whitehurst, D.D. *Fuel*, **60**, 655, 1981.

8. Artok, L. and Schobert, H.H. *Fuel Proc. Tech.*, 1993, accepted.
9. Burgess, C., Wenzel, K., Song, C., Hatcher, P., and Schobert, H.H. Proceedings of the 7th International Conference on Coal Science, September, 1993.
10. Weller, S.W. in *Proceedings of the Fourth International Conference on the Chemistry and Uses of Molybdenum*, Eds. H.F. Barry and P.C.H. Mitchell, Climax Molybdenum Co., Ann Arbor, MI, 179, 1982.
11. Naumann, A.W., Behan, A.S., and Thorsteinson, E.M. in *Proceedings of the Fourth International Conference on the Chemistry and Uses of Molybdenum*, Eds. H.F. Barry and P.C.H. Mitchell, Climax Molybdenum Co., Ann Arbor, MI, 313 1982.
12. Derbyshire, F.J. "Catalysis in Coal Liquefaction," IEA CR/08, IEA Coal Research, London, 1988.
13. March, J. *Advanced Organic Chemistry: Reactions, Mechanisms, and Structure, 2nd Edition*, McGraw-Hill, Inc. New York, 1977.
14. Dutta, R. and Schobert, H.H. *American Chemical Society, Division of Fuel Chemistry, Preprints*, this volume, 1993.
15. Solomon, P.R., Serio, M.A., Deshpande, G.V., Kroo, E., Schobert, H.H., and Burgess, C. in *Coal Science II*. Eds. H.H. Schobert, K.D. Bartle, and L.J. Lynch. ACS Symposium Series No. 461, American Chemical Society, Washington, D.C., 1991, p 193.

2. Structural Correlation of Coal Liquefaction Oils with Flash Pyrolysis Products (Contributed by Caroline E. Burgess and Kurt Wenzel)

Introduction

Much work has been done to elucidate the average structure of different ranks of coal [1-5]. These models provide some idea of the typical functional groups and the size of the aromatic ring clusters for different ranks of coal. There has also been much work done on analysis of coal liquids, mainly the light oil fractions [6-9]. However, there is limited data on the comparison of liquefaction products to structural features of different coals. The most well-known work to date is by Given and coworkers [9-11]. Anderson et al. [12] and Calkins et al. [13] used NMR to correlate coal characteristics to coal liquefaction or pyrolysis products. Flash pyrolysis GC/MS has been used as a technique for coal analysis, specifically, to monitor the transformation of certain maceral groups through coalification [5, 14-16]. We felt that flash pyrolysis GC/MS could be useful for providing specific information that may be related to the lighter liquefaction products.

The focus of the work in this section is the comparison of structural features of coals (rank that ranges between subbituminous C to hvA bituminous) to the structural features of the light liquids obtained from coal liquefaction.

Experimental

Five coals were provided by the Penn State Coal Data Bank along with rank and elemental and maceral compositions. These coals and related structural information are listed in Table 14. The coals were then characterized by several methods. ^{13}C -NMR CPMAS parameters were a contact time of 1000 μs , a 90° pulse of 5-7 μs , and a pulse delay of 1 s. For dipolar dephasing, the parameters used were the same, and t was varied from 2.5 μs to 2 ms. The equipment used for flash pyrolysis GC/MS was a DuPont GC/MS with the pyroprobe connected to the injection port of the GC/MS. The sample was pyrolyzed for 10 s at 610°C . The conditions of the GC used were a rate of $4^\circ\text{C}/\text{min}$ from 30 to 280°C .

The liquefaction conditions were 425°C for 1 h in a 75 ml microautoclave, with pyrene as a solvent (10g:10g coal-to-solvent-ratio) and cold H_2 pressure 7MPa. The reactors were heated in a fluidized sandbath, and the time required to heat the reactors to the reaction temperature was about 10 minutes. The reactors were quenched in cold water at the end of reaction. Products were emptied from the tubing bomb into a dry tared thimble using dichloromethane (DCM) and extracted with DCM for about 36-48 h until the extracted solvent appeared clear. The products were then extracted with tetrahydrofuran (THF) for about 24-36 h until the extracted solvent appeared clear. The DCM was rotoevaporated from the DCM-solubles, and then the sample was extracted with hexane. The residue was rinsed with acetone and pentane and dried at 100°C for 12 h. The THF-soluble fractions were dried for 1 h at 60°C .

The hexane-soluble fractions were analyzed by GC/FID and GC/MS. The conditions of the GC used were a rate of $4^\circ\text{C}/\text{min}$ from 40 to 280°C . The residues were analyzed by CPMAS ^{13}C -NMR and flash pyrolysis GC/MS under the same conditions as described previously.

Results and Discussion

The discussion will focus on two coals (DECS-6 and -12); the others follow a similar pattern of behavior. ^{13}C -NMR of DECS-6 (Figure 45, top spectrum) indicates $f_a = 0.65$, with the aliphatic peak being sharp at ≈ 30 ppm. The $f_{ha} = 0.412$ indicates a fairly high proportion of the aromatic compounds are protonated. This could mean that the aromatic clusters are not highly condensed, or that the functional groups on the aromatic

rings contain long chains of aliphatic groups instead of the aliphatics being attached at several spots on the rings. The small peak at ≈ 180 ppm indicates the presence of carboxylic acid groups, and the shoulder at ≈ 150 ppm indicates a presence of phenols/ether groups. The pyrogram for DECS-6 is shown in Figure 46. The dominant feature of the flash pyrolysis products is the series of n-alkanes/alkenes and the biomarkers prist-1-ene and cadalene. Phenols make up the bulk of the remaining products. The dominance of the alkanes/alkenes also suggests the aliphatic portion of the coal could be long-chain aliphatics.

^{13}C -NMR of DECS-12 indicates $f_a = 0.70$. The aliphatic peak at ≈ 30 ppm is shorter and more blunt than for DECS-6. From dipolar dephasing data, the $f_{\text{ha}} = 0.290$. There are no carboxyl groups, and the phenolic area is slightly less (Table 15). This could mean the aromatic rings are more condensed, and that most of the attached functional groups will be oxygen or shorter alkyl groups. The dominant features of the pyrolysis products are naphthalenes, benzenes, and phenols. The presence of alkanes/alkenes is less in DECS-12 than in DECS-6 (Table 16).

Conversion data are presented in Table 17. The highest conversions were obtained with DECS-6 and -12 at 425°C for 1 h with pyrene. For DECS-6, the dominant products in the hexane-soluble fraction are alkanes with some contribution from phenols and naphthalenes (Table 16). For DECS-12, the dominant products are phenols and naphthalenes. The ^{13}C -NMR of both residues indicate loss of aliphatics and oxygen compounds.

For coals DECS-9, PSOC-831, and PSOC-1379, the conversion and DCM-solubles are less than the other two coals. DECS-9 and PSOC-1379 are coals with a higher oxygen content. At 425°C , the loss of oxygen functional groups, e.g. by thermal cleavage of bonds, creates nascent reactive sites, which, if not capped by $\text{H}^\bullet$, can be sites for retrogressive crosslinking reactions [17-18]. Alkanes and phenols were dominant components for the hexane-solubles from DECS-9. PSOC-1379 behaves in a similar manner to DECS-6. For PSOC-1379, the hexane-solubles contain alkanes, naphthalenes, and phenols. For PSOC-831, alkanes and phenols dominate the hexane-solubles. ^{13}C -NMR of the residues from these reactions indicates the loss during liquefaction of those structures or functional groups that were identified in the unreacted coal by flash pyrolysis GC/MS.

The flash pyrolysis GC/MS pyrograms for each coal show compositional features very similar to GC/MS chromatograms of the light fractions, the exception being PSOC-831. If the pyrograms of unreacted coal indicate an abundance of alkanes/alkenes, the oils produced during liquefaction are found to have abundant alkanes, and the residue has

14. Hatcher, P.G., Lerch, H.E., III, Kotra, R.K., and Verheyen, T.V. *Fuel*, 1988, **67**, 1069.
15. Anderson, K.B., Winans, R.E., and Botto, R.E. *Org. Geochem.*, 1992, **18**, 829.
16. van Aarssen, B.K.G., de Leeuw, J.W., and Horsfield, B. *J. Anal. Appl. Pyrol.*, 1990, **20**, 125.
17. Solomon, P.R., Serio, M.A., Deshpande, G.V., Kroo, E., Schobert, H.H., and Burgess, C. in *Coal Science II*. Eds. H.H. Schobert, K.D. Bartle, and L.J. Lynch. **ACS Symposium Series No. 461**, American Chemical Society, Washington, D.C., 1991, p 193.
18. Tomic, J. *PhD Dissertation*, The Pennsylvania State University, 1993.

APPENDIX 1
TABLES

Table 1. Molar Yields of Products from the Pyrolysis of Cyclohexane, Methylcyclohexane, and Ethylcyclohexane at 450°C under initial 0.69 MPa N₂.

Reactant Name	CH	MCH	ECH	ECH	ECH	ECH	ECH	ECH	ECH
Reactant (mmole)	45.37	39.06	35.29	35.17	35.21	35.24	35.29	35.57	35.52
Reactant (g)	3.811	3.828	3.952	3.939	3.944	3.947	3.952	3.984	3.978
Experimental No.	TS91	TS92	AS1	AS2	AS3	TS43	TS60	TS65	TS73
Residence time ^a	4 hr	4 hr	0.2 hr	0.5 hr	1 hr	1 hr	2.5 hr	4 hr	8 hr
Product	molar yield (%) ^b								
Hydrogen	1.07	3.20		0.68	1.29	1.08	2.40	3.58	8.89
Methane	0.21	7.46	1.83	2.93	5.05	4.09	8.67	14.16	37.88
Ethylene	0.04	0.14	0.30	0.40	0.54	0.40	0.79	0.67	0.53
Ethane	0.09	0.65	1.20	1.88	3.29	3.57	6.97	11.88	32.97
Propene	0.05	0.32	0.03	0.04	0.10	0.15	0.28	0.48	0.69
Propane	0.03	0.31	0.05	0.08	0.18	0.24	0.62	1.78	5.17
1-Butene	0.08	0.47	0.00	0.01	0.05	0.05	0.17	0.49	0.46
n-Butane	0.00	0.10		0.00	0.07	0.05	0.15	1.05	1.74
Pentenenes (mainly 2- and 3-)		0.11	0.03	0.06	0.14	0.15	0.22	0.58	0.77
n-Pentane		0.03				0.00	0.08	0.42	1.08
1-Hexene	0.04	0.03							
n-Hexane	0.01		0.05	0.05	0.05	0.07	0.08	0.18	0.47
Cyclohexene	0.35	0.95	0.56	1.12	2.01	1.83	3.75	4.43	1.53
Cyclohexane	94.97	0.28	0.18	0.39	0.76	0.72	2.04	3.89	8.91
Methylcyclohexene		0.35		0.06	0.12	0.07	0.14	0.60	0.40
Methylenecyclohexane		0.08	0.19	0.17	0.24	0.17	0.27	1.18	1.49
1-Methylcyclohexene		0.59	0.27	0.66	1.21	0.85	1.64	2.81	0.93
Methylcyclohexane		88.12	0.42	0.43	0.46	0.48	1.07	1.89	5.08
C ₂ -cyclohexene			0.10	0.19	0.31	0.28	0.77	1.01	0.79
Ethylcyclohexane	0.03		97.10	94.81	91.23	92.39	82.64	66.26	37.00
C ₃ -cyclohexane		0.08	0.05	0.05	0.05	0.03	0.03	0.05	0.06
n-Propylcyclohexane	0.02						0.08	0.10	0.22
C ₄ -cyclohexane				0.02	0.02	0.02	0.33	0.34	0.62
C ₅ -cyclohexane							0.04	0.09	0.16
Cyclopentene	0.04	0.11							
Methylcyclopentene		0.74							
Methylcyclopentane	4.18	0.08	0.08	0.13	0.23	0.25	0.57	1.32	4.16
Dimethylcyclopentane		5.05							
Ethylcyclopentane		1.18							
C ₃ -cyclopentane			0.41	0.93	1.64	1.07	2.46	6.27	6.22
Benzene		0.12			0.04	0.04	0.40	1.11	4.21
Toluene		0.09			0.13	0.13	0.54	2.06	5.73
C ₂ -benzene							0.19	0.47	3.00
C ₃ -benzene							0.07	0.28	1.27
C ₄ -benzene								0.05	0.31
Indan							0.01	0.04	0.29
Methylindan								0.06	0.60
C ₂ -indan								0.04	0.18
Naphthalene							0.02	0.03	0.37
Methylnaphthalene							0.02	0.05	0.46
C ₂ -naphthalene								0.02	0.12
(Alkyl-)bicyclohexyl							0.15	0.19	0.15

a) Pyrolysis of 5 ml reactant in 25 ml reactors plunged into the sandbath preheated to 450°C.

b) The molar yield based on initial reactants (cyclohexane, methylcyclohexane, or ethylcyclohexane).

Table 2. Molar Yields of Products from the Pyrolysis of n-Propylcyclohexane, and n-Butylcyclohexane at 450°C under initial 0.69 MPa N₂ (Cold).

Reactant Name	PCH	PCH	PCH	PCH	PCH	BCH	BCH	BCH	BCH	BCH	BCH
Reactant (mmole)	31.40	31.47	31.52	31.46	31.13	29.21	28.55	29.21	28.70	28.88	28.54
Reactant (g)	3.957	3.965	3.972	3.964	3.922	4.090	3.997	4.090	4.018	4.043	3.996
Experimental No.	AS4	AS5	AS6	AS7	TS93	AS8	TS81	AS36	TS61	TS66	TS74
Residence time ^a	0.2 hr	0.5 hr	1 hr	2.5 hr	4 hr	0.2 hr	0.5 hr	1 hr	2.5 hr	4 hr	8 hr
Product	molar yield (%) ^b										
Hydrogen		0.54	0.93	3.03	6.07		0.73	1.25	4.23	6.45	12.08
Methane	0.81	1.03	2.49	6.12	14.67	0.24	1.29	3.23	8.28	16.01	49.73
Ethylene	0.13	0.17	0.29	0.39	0.58	0.12	0.23	0.71	0.78	0.92	0.69
Ethane	1.65	2.19	4.97	12.34	25.13	0.42	2.10	2.98	9.73	17.09	36.44
Propene	1.41	2.05	3.67	4.35	5.02	0.34	0.91	1.34	2.67	3.05	2.99
Propane	0.70	1.15	2.90	7.06	14.87	0.74	2.30	5.28	12.14	20.76	31.04
1-Butene		0.01	0.08	0.25	0.60	0.72	1.35	3.29	3.06	2.72	1.81
n-Butane		0.03	0.13	0.63	2.04	0.37	1.10	2.15	7.31	11.40	12.17
1-Pentene		0.02	0.07	0.21	0.30		0.04	0.05	0.41	1.41	0.72
n-Pentane		0.07	0.24	0.83	1.60		0.06	0.09	0.80	2.06	2.80
n-Hexane		0.03	0.11	0.40	0.57		0.07	0.16	0.84	1.46	1.36
Heptene								0.07	0.13	0.23	0.39
Heptane								0.10	0.50	0.80	0.98
Cyclohexene	0.40	1.14	2.62	4.16	3.73	0.49	1.02	2.14	2.33	3.21	0.35
Cyclohexane	0.76	2.04	4.93	10.98	19.51	0.81	2.80	3.67	9.53	20.14	16.91
Methylcyclohexene		0.04	0.14	0.59	1.00			0.08	0.92	1.26	0.31
Methylenecyclohexane	0.47	1.08	1.93	1.98	1.39	0.90	2.23	2.64	2.20	1.90	0.62
1-Methylcyclohexene	0.06	0.31	0.96	2.59	2.56	0.07	0.61	0.98	2.93	3.19	1.09
Methylcyclohexane	0.05	0.13	0.43	1.52	4.40	0.33	1.76	1.55	6.56	12.68	11.77
Ethenylcyclohexane	0.12	0.24	0.35	0.30	0.20	0.30	0.83	0.95	0.46	0.11	
1-Ethylcyclohexene+Ethylidenecyclohexane							0.15	0.16	0.70	0.43	
Ethylcyclohexane	0.26	0.28	0.36	0.72	1.17	0.04	0.13	0.21	1.09	2.27	1.97
2-Propenylcyclohexane				0.09		0.07	0.19	0.20	0.10		
C ₃ -cyclohexane			0.05	0.12	0.12				0.29	0.62	0.78
n-Propylcyclohexane	96.58	92.86	82.96	61.41	35.22	0.02	0.09	0.10	0.68	0.91	0.90
C ₄ -cyclohexane			0.03	0.07	0.08	0.41	0.57	0.61	1.16	0.64	0.57
C ₄ -cyclohexene	0.07	0.09	0.12	0.18	0.38	0.24	0.58	0.81	2.34	1.94	1.15
n-Butylcyclohexane	0.01	0.03	0.08	0.15	0.30	95.95	88.08	81.79	57.47	25.56	6.35
C ₅ -cyclohexane			0.05	0.17	0.21					0.21	0.11
n-Pentylcyclohexane				0.05	0.07		0.04	0.05	0.32	0.18	0.18
C ₆ -cyclohexane		0.09	0.27	0.79	0.71		0.02		0.11	0.08	0.05
n-Hexylcyclohexane				0.09	0.10						
Methylcyclopentane	0.13	0.38	0.99	2.45	5.43	0.11	0.48	0.64	2.07	5.71	7.41
Ethylcyclopentane		0.04	0.04	0.12	0.31			0.04	0.13	0.47	0.80
C ₃ -cyclopentane				0.17	0.26					0.55	1.25
C ₄ -cyclopentane	0.28	0.62	1.50	2.80	3.24						
Benzene			0.16	0.64	2.43		0.02	0.05	0.71	2.51	4.71
Toluene			0.08	0.76	3.22				1.36	5.20	8.93
C ₂ -benzene				0.24	1.22				0.60	0.70	4.68
C ₃ -benzene				0.22	0.77				0.20	0.89	2.18
C ₄ -benzene				0.03	0.26		0.04		0.09	0.54	1.03
C ₅ -benzene					0.04				0.09	0.15	0.25
Indan					0.14				0.06	0.18	0.64
Methylindan					0.29					0.44	1.27
C ₂ -indan					0.17					0.23	0.75
Naphthalene					0.13		0.02		0.13	0.28	1.18
Methylnaphthalene					0.25				0.05	0.34	1.18
C ₂ -naphthalene					0.06					0.22	0.75
(Alkyl-)bicyclohexyl			0.07	0.37	0.44		0.03	0.04	0.27	0.19	0.17

a) Pyrolysis of 5 ml reactant in 25 ml reactors plunged into the sandbath preheated to 450°C.

b) The molar yield based on initial reactants (n-propylcyclohexane or n-butylcyclohexane).

Table 3. Molar Yields of Products from the Pyrolysis of n-Hexylcyclohexane, n-Octylcyclohexane, and n-Decylcyclohexane at 450°C under initial 0.69 MPa N₂ (Cold).

Reactant Name	HCH	HCH	OCH	OCH	OCH	OCH	DCH	DCH	DCH
Reactant (mmole)	23.74	23.68	20.78	20.77	20.81	20.82	18.12	18.18	18.21
Reactant (g)	3.989	3.978	4.073	4.071	4.079	4.080	4.058	4.072	4.078
Experimental No.	AS9	AS10	AS11	AS32	AS12	AS35	AS13	AS34	AS14
Residence time ^a	0.2 hr	0.5 hr	0.2 hr	0.35 hr	0.5 hr	1.0 hr	0.2 hr	0.35 hr	0.5 hr
Product	molar yield (%) ^b								
Hydrogen	1.01	1.68		0.40	1.41	5.41	2.01	0.88	2.35
Methane	0.62	1.30	0.89	0.94	1.96	10.99	0.77	1.43	2.22
Ethylene	0.39	0.48	0.53	0.47	0.53	1.11	0.42	0.44	0.62
Ethane	1.00	1.84	1.46	1.71	2.57	8.79	1.35	1.63	3.16
Propene	0.89	1.39	1.00	2.02	2.13	3.09	1.48	1.87	2.98
Propane	1.04	1.91	1.22	2.48	3.28	10.72	2.00	3.38	5.19
1-Butene	0.52	0.67	0.62	1.31	1.90	3.07	1.02	1.32	1.82
n-Butane	0.73	1.91	0.81	1.97	3.02	8.20	1.44	2.46	4.71
1-Pentene	0.40	0.67	0.63	1.24	1.32	2.38	1.08	1.35	1.96
Pentenenes (2- and 3-)		0.13				0.54		0.21	0.27
n-Pentane	1.92	4.55	0.49	1.40	2.66	6.89	1.03	1.63	3.20
1-Hexene	1.16	2.05	0.55	1.12	1.49	2.00	1.22	1.70	2.25
Hexenes (2- and 3-)	0.13	0.38		0.12	0.22	0.84	0.07	0.22	0.43
n-Hexane (n-C ₆)	0.72	1.69	0.46	1.07	1.86	4.63	0.93	1.42	2.60
1-Heptene			0.43	0.84	1.12	1.07	0.81	1.11	1.53
2-Heptene		0.05		0.07	0.14	0.45	0.06	0.08	0.22
n-Heptane (n-C ₇)			1.29	2.77	4.64	9.03	0.81	1.22	2.20
1-Octene			1.05	1.82	2.31	2.27	0.64	0.71	1.24
n-Octane (n-C ₈)		0.18	0.44	1.09	1.80	4.06	0.64	1.03	1.88
1-Nonene					0.06		0.50	0.60	0.79
n-Nonane (n-C ₉)			0.03	0.06	0.18	0.56	1.98	2.97	4.96
1-Decene					0.03		1.18	1.51	1.77
n-Decane (n-C ₁₀)	0.01	0.03		0.05	0.12	0.35	0.81	1.22	2.14
n-Undecane (n-C ₁₁)	0.02	0.06	0.02	0.06	0.12	0.39	0.03	0.13	0.23
n-Dodecane (n-C ₁₂)	0.02	0.05	0.02	0.11	0.09	0.26	0.06	0.11	0.21
n-Tridecane (n-C ₁₃)						0.08		0.05	0.16
n-Tetradecane (n-C ₁₄)				0.08		0.04		0.03	0.08
n-Pentadecane (n-C ₁₅)									0.11
n-Hexadecane (n-C ₁₆)								0.10	0.11
Cyclohexene	0.88	2.04	0.79	1.85	2.83	4.74	1.36	2.03	3.22
Cyclohexane	1.43	3.43	1.29	3.11	5.07	11.81	2.43	3.84	6.49
Methylcyclohexene	0.13	0.51		0.05	0.20	0.79	0.08	0.18	0.61
Methylenecyclohexane	0.48	0.48	1.52	2.72	3.20	3.23	1.75	2.23	2.17
1-Methylcyclohexene	1.42	3.38	0.23	0.90	2.32	4.18	1.18	2.13	4.41
Methylcyclohexane	0.56	1.41	0.52	1.30	2.27	5.78	0.94	1.52	2.93
Ethenylcyclohexane	0.44	0.66	0.44	0.80	1.00	0.73	0.60	0.96	0.90
1-Ethylcyclohexene+Ethylidenecyclohexane	0.07	0.26	0.05	0.06	0.31	0.76	0.16	0.19	0.47
Ethylcyclohexane	0.43	1.08	0.45	1.06	1.83	4.25	0.79	1.29	2.40
2-Propenylcyclohexane	0.40	0.67	0.41	0.71	0.90	0.69	0.57	0.72	0.95
Cyclohexylpropene	0.03	0.06		0.04	0.10	0.21	0.03	0.08	0.15
C ₃ -cyclohexene					0.04	0.12			0.13
n-Propylcyclohexane	0.35	0.82	0.34	0.74	1.26	2.73	0.76	1.10	1.96
3-Butenylcyclohexane	0.34	0.51	0.34	0.55	0.65	0.43	0.46	0.60	0.68
Cyclohexylbutene				0.04	0.13	0.39	0.03	0.16	0.24
n-Butylcyclohexane	0.06	0.14	0.24	0.53	0.86	1.71	0.48	0.76	1.35
4-Pentenylcyclohexane	0.08	0.12	0.29	0.48	0.51	0.35	0.41	0.58	0.56
n-Pentylcyclohexane	0.02	0.06	0.27	0.61	0.98	1.82	0.49	0.80	1.39
5-Hexenylcyclohexane			0.29	0.50	0.50	0.37	0.40	0.54	0.55
Cyclohexylhexene						0.14		0.05	0.09
1-Hexylcyclohexene	0.14	0.12				0.08			
C ₆ -cyclohexane	0.67	0.96				0.07			
n-Hexylcyclohexane	89.21	79.48	0.07	0.17	0.23	0.72	0.44	0.72	1.12

Table 3 (Continued)

6-Heptenylcyclohexane			0.06	0.11	0.11	0.08	0.34	0.41	0.44
Cyclohexylheptene				0.08	0.09	0.15	0.04	0.05	0.07
C ₇ -cyclohexane	0.14	0.12							
n-Heptylcyclohexane	0.03	0.04	0.03	0.07	0.11	0.32	0.46	0.68	1.10
7-Octenylcyclohexane			0.02	0.02	0.04	0.09	0.37	0.46	0.38
C ₈ -cyclohexane			0.26	0.65	0.85	1.19			
n-Octylcyclohexane			90.93	79.90	69.35	38.67	0.11	0.19	0.29
8-Nonenylcyclohexane							0.09	0.11	0.10
C ₉ -cyclohexane			0.08	0.06	0.05	0.03			
n-Nonylcyclohexane	0.01	0.02	0.05	0.09	0.09	0.15	0.06	0.11	0.15
C ₁₀ -cyclohexane							0.47	0.63	0.88
n-Decylcyclohexane			0.05	0.06	0.07	0.10	83.21	75.13	56.81
C ₁₁ -cyclohexane			0.13	0.04			0.06	0.06	0.06
n-Undecylcyclohexane				0.04	0.05	0.08	0.07	0.08	0.10
C ₁₂ -cyclohexane	0.03	0.08		0.04	0.12	0.19		0.05	0.15
n-Dodecylcyclohexane					0.02	0.04	0.06	0.07	0.10
C ₁₃ -cyclohexane			0.02	0.06	0.06	0.13	0.03	0.07	0.28
n-Tridecylcyclohexane							0.05		0.07
C ₁₄ -cyclohexane					0.02	0.02		0.06	0.10
n-Tetradecylcyclohexane					0.02	0.03	0.02	0.03	0.04
C ₁₅ -cyclohexane				0.04	0.08	0.11	0.03	0.03	0.15
n-Pentadecylcyclohexane					0.02	0.04	0.02	0.03	0.03
C ₁₆ -cyclohexane				0.05	0.07	0.14	0.03	0.06	0.10
n-Hexadecylcyclohexane					0.01		0.02	0.04	0.02
n-Heptadecylcyclohexane							0.02	0.07	0.02
Methylcyclopentane	0.20	0.50	0.12	0.40	0.67	2.17	0.26	0.45	0.91
Dimethylcyclopentene				0.05	0.13	0.38	0.04	0.06	0.20
Ethenylcyclopentane	0.02	0.03		0.04	0.05	0.05			0.04
Ethylcyclopentane		0.03			0.05	0.27			0.12
Benzene	0.02	0.09		0.04	0.11	0.85			0.24
Toluene	0.09	0.41		0.05	0.21	1.26	0.08		0.70
C ₂ -benzene		0.04				0.27			0.14
C ₃ -benzene						0.06			0.05
(Alkyl-)bicyclohexyl	0.61	0.60		0.03	0.11	0.40	0.02	0.08	0.12

a) Pyrolysis of 5 ml reactant in 25 ml reactors plunged into the sandbath preheated to 450°C.

b) The molar yield based on initial reactants (n-hexylcyclohexane, n-octylcyclohexane, or n-decylcyclohexane).

Table 4. Pseudo-First-Order Rate Constants of Alkylcyclohexanes at 450°C.

Compound	Conversion range	Rate constant, hr ⁻¹	Characterization #, n
Cyclohexane	0.05	0.013	12
Methylcyclohexane	0.11	0.030	13
Ethylcyclohexane	0.024-0.63	0.12	17
n-Propylcyclohexane	0.032-0.65	0.25	21
n-Butylcyclohexane	0.034-0.94	0.34	25
n-Hexylcyclohexane	0.092-0.19	0.53	33
n-Octylcyclohexane	0.087-0.61	0.99	41
n-Decylcyclohexane	0.163-0.43	1.28	49

Table 5. Yields of Liquids and Solids Products and Pressure Build Up from Thermal Stressing Experiments at 425°C on JPTS Jet Fuel Alone and Mixed with PX 21.

Sample Liquid 10 ml Solid 50 mg	Solid on reactor walls, mg ± 10 mg	Liquid yield, ml ± 0.3 ml	Final gas pressure (cold), psi ± 100 psi	Increase of weight of solid, %
JPTS in N ₂	20	9.0	200	-
JPTS+PX-21 in N ₂	-	9.5	100	32
JPTS in air	30	8.2	200	-
JPTS+PX-21 in air	-	8.8	100	34

Table 6. Compounds Identified and Weight Percent of the Liquids Obtained after Thermal Stressing of JPTS Alone and in the Presence of Activated Carbon PX-21 at 425°C in Air and Nitrogen Atmosphere.

Compounds	JPTS, neat, wt %	JPTS (air), wt %	JPTS+ PX-21 (air), wt %	JPTS (N ₂), wt %	JPTS+ PX-21 (N ₂), wt %
n-Propane+Propene	0.00	0.92	0.43	0.19	0.20
Butane+Butene	0.00	2.00	2.01	1.11	1.37
2-Methyl Butane+Cyclobutane	0.00	0.77	1.39	0.65	1.08
n Pentane+Pentene	0.00	1.02	1.46	0.83	1.15
Pentane	0.00	0.37	0.31	0.29	0.53
Pentene	0.00	0.30	0.43	0.24	0.00
Pentene	0.00	0.52	0.52	0.44	0.37
2-Methyl Pentane	0.00	0.39	1.05	0.55	0.83
3-Methyl Pentane+Methyl Pentene	0.00	0.37	0.56	0.40	0.46
n-Hexane	0.04	0.94	1.08	0.70	1.29
Hexene	0.03	0.46	0.58	0.47	0.32
2-Hexene	0.00	0.14	0.16	0.17	0.11
Methyl Cyclopentane	0.01	0.63	0.88	0.74	0.87
3-Methyl Hexane	0.02	0.27	0.51	0.39	0.45
n-Heptane	0.03	0.64	1.02	0.79	0.87
Cyclohexane+Methyl Cyclopentane	0.00	0.29	0.48	0.34	0.35
C ₂ -Cyclopentane	0.00	0.52	0.61	0.60	0.42
Br. Alkane	0.00	0.07	0.16	0.11	0.12
Heptene	0.00	0.13	0.18	0.19	0.11
Dimethyl Cyclopentene	0.00	0.13	0.14	0.13	0.08
Cyclohexene	0.00	0.06	0.04	0.03	0.03
Methyl Cyclohexane	0.07	0.34	0.49	0.39	0.41
2-Methyl Heptane	0.11	0.35	0.70	0.46	0.54
Ethyl Cyclopentane	0.14	0.28	0.52	0.36	0.41
3-Methyl Heptane	0.09	0.34	0.43	0.38	0.35
Methyl Cyclohexane	0.00	0.07	0.09	0.13	0.06

Compounds	JPTS, neat wt %	JPTS (air), wt %	JPTS+ PX-21 (air), wt %	JPTS (N ₂), wt %	JPTS+ PX-21 (N ₂), wt %
C ₄ -Cyclohexane	0.42	0.32	0.33	0.35	0.38
n-Decane	4.62	3.30	3.53	3.43	3.82
Dimethyl Decane	2.16	1.16	1.15	1.23	1.32
C ₄ -Cyclohexane	0.00	0.00	0.00	0.00	0.00
C ₄ -Cyclohexane	1.76	1.15	1.20	1.30	1.35
m-Xylene	0.00	0.62	0.61	0.66	0.72
Br. Alkane	2.19	1.47	1.61	1.65	1.81
2,6 DimethylNonane	2.44	1.28	1.22	1.36	1.56
3,7-Dimethyl Nonane	3.16	2.45	2.25	2.45	2.49
C ₄ -Cyclohexane+Br. Alkane	1.56	0.91	0.75	0.96	1.03
C ₄ -Cyclohexane	0.00	0.32	0.34	0.36	0.36
C ₃ -Benzene	0.00	0.35	0.34	0.40	0.30
Br. Alkane	0.00	0.44	0.44	0.47	0.37
Trimethyl Decane	2.70	1.66	1.62	1.68	1.38
Br. Alkane	0.77	0.51	0.53	0.54	0.27
Trimethyl Decane	3.09	1.87	1.84	1.89	1.72
5-Methyl Decane	1.17	0.66	0.66	0.65	0.53
4-Methyl Decane	1.60	0.99	0.94	0.96	0.88
2-Methyl Decane	1.17	0.73	0.79	0.76	0.69
n-Propyl Benzene+ n-Butyl Cyclohexane	1.70	1.12	1.19	1.14	1.03
Trimethyl Nonane	2.38	1.48	1.44	1.44	1.43
3-Methyl Decane	1.19	0.72	0.74	0.69	0.67
C ₃ -Benzene (Isomers)	1.84	1.50	1.89	1.66	1.76
C ₃ -Benzene	0.81	0.55	0.70	0.75	0.69
C ₃ -Benzene	0.00	0.19	0.18	0.08	0.21
n-Undecane	5.36	3.50	3.89	3.88	4.29
C ₅ -Cyclohexane	0.37	0.22	0.26	0.35	0.31
C ₃ -Benzene	2.03	1.68	2.22	2.32	2.31
C ₄ -Benzene+Decalin	1.19	0.96	0.95	1.01	1.10

Compounds	JPTS, wt %	JPTS (air), wt %	JPTS+ PX-21 (air), wt %	JPTS (N ₂), wt %	JPTS+ PX-21 (N ₂), wt %
Br. Alkane+C ₅ -Cyclohexane	0.00	0.38	0.37	0.39	0.44
C ₄ -Benzene	7.36	0.66	0.82	0.75	0.83
6,5-Methyl Undecane+ C ₃ -Benzene	1.41	0.96	1.10	1.02	1.16
4-Methyl Undecane	0.69	0.39	0.39	0.40	0.43
2-Methyl Undecane	0.93	0.56	0.56	0.55	0.61
C ₄ -Benzene	0.76	0.57	0.71	0.61	0.71
Methyl Decalin+C ₄ -Benzene	0.73	0.95	1.05	0.70	1.12
n-Pentyl Cyclohexane+ n-Butyl Benzene	2.08	1.28	1.35	1.30	1.50
C ₄ -Benzene	0.00	0.00	0.00	0.00	0.00
C ₄ -Benzene	0.63	0.52	0.65	0.58	0.66
C ₄ -Benzene+Dihydro Indene	0.47	0.57	0.65	0.55	0.70
Methyl Decalin	0.33	0.38	0.29	0.32	0.35
C ₄ -Benzene	0.43	0.37	0.40	0.39	0.44
C ₄ -Benzene	0.00	0.00	0.00	0.00	0.00
n-Dodecane	3.11	2.01	2.05	2.05	2.38
Dimethyl Undecane	1.01	0.52	0.42	0.50	0.63
C ₄ -Benzene	1.14	0.81	0.76	0.86	1.01
C ₅ -Benzene+C ₆ -Cyclohexane	0.00	0.00	0.00	0.00	0.00
C ₄ -Benzene	0.37	0.32	0.36	0.30	0.39
6,5-Methyl Dodecane+C ₄ -Benzene	1.21	0.87	0.80	0.75	0.93
Trimethyl Dodecane	0.94	0.50	0.41	0.43	0.57
C ₅ -Benzene+2-Methyl Dodecane	0.50	0.35	0.34	0.33	0.42
3-Methyl Dodecane	0.60	0.36	0.33	0.35	0.44
n-Hexyl Cyclohexane	0.35	0.23	0.18	0.23	0.26
C ₄ -Benzene	0.16	0.41	0.46	0.53	0.17
C ₅ -Benzene	0.00	0.00	0.08	0.00	0.10
n-Tridecane	2.25	1.37	1.39	1.37	1.68
Dimethyl Dodecane+Methyl Indan	0.64	0.40	0.43	0.43	0.52

Compounds	JPTS, wt %	JPTS (air), wt %	JPTS+ PX-21 (air), wt %	JPTS (N ₂), wt %	JPTS+ PX-21 (N ₂), wt %
C ₅ -Benzene+Methyl Indene	0.00	0.04	0.03	0.05	0.07
Tetralin+Br. Alkane+ Alkyl Benzene	0.36	0.26	0.20	0.31	0.33
6-Methyl Tridecane	0.55	0.29	0.19	0.21	0.27
5-Methyl Tridecane+C ₂ -Indan	0.33	0.16	0.19	0.25	0.35
4-Methyl Tridecane	0.42	0.18	0.18	0.20	0.25
2-Methyl Tridecane	0.46	0.21	0.22	0.24	0.28
Trimethyl Dodecane	0.73	0.29	0.29	0.30	0.41
3-Methyl Tridecane	0.35	0.19	0.19	0.21	0.25
C ₅ -Benzene+n-Heptyl Cyclohexane	0.35	0.22	0.20	0.26	0.26
Naphthalene+n-Tetradecane	1.76	0.95	1.13	0.95	1.31
Br. Alkane	0.61	0.28	0.26	0.23	0.26
5-Methyl Tetradecane	0.12	0.07	0.08	0.07	0.09
4-Methyl Tetradecane	0.18	0.09	0.06	0.07	0.09
2-Methyl Tetradecane	0.18	0.11	0.10	0.09	0.12
3-Methyl Tetradecane	0.21	0.09	0.07	0.08	0.11
n-Octyl Cyclohexane	0.09	0.04	0.04	0.06	0.07
n-Pentadecane	0.61	0.33	0.30	0.31	0.40
2-Methyl Naphthalene	0.00	0.04	0.16	0.07	0.16
1-Methyl Naphthalene	0.00	0.01	0.12	0.04	0.11
Dimethyl Naphthalene	0.00	0.00	0.00	0.03	0.03
1-Ethyl Naphthalene	0.00	0.00	0.00	0.00	0.03
Dimethyl Naphthalene (Isomers)	0.00	0.00	0.00	0.00	0.05
2-Ethyl Naphthalene	0.00	0.00	0.00	0.00	0.00
Dimethyl Naphthalene	0.00	0.00	0.00	0.00	0.03
Dimethyl Naphthalene	0.00	0.00	0.00	0.02	0.07

Compounds	JPTS neat, wt %	JPTS (air), wt %	JPTS+ PX-21 (air), wt %	JPTS (N ₂), wt %	JPTS+ PX-21 (N ₂), wt %
n-Octane+C ₂ -Cyclohexane	0.44	0.81	1.29	1.09	1.11
C ₃ -Cyclopentane	0.00	0.19	0.23	0.26	0.22
C ₃ -Cyclopentane	0.30	0.20	0.18	0.25	0.15
Br. Alkane	0.15	0.26	0.26	0.43	0.26
Dimethyl Cyclohexane	0.00	0.18	0.20	0.30	0.32
Methyl Cyclohexene	0.00	0.19	0.14	0.27	0.13
Dimethyl Cyclohexane	0.07	0.12	0.17	0.20	0.19
C ₃ -Cyclohexane	0.54	0.49	0.57	0.57	0.60
4-2-Methyl Octane	0.58	0.61	0.80	0.71	0.80
Ethyl Cyclohexane+3-Methyl Octane	0.63	0.92	1.02	1.02	1.01
Toluene	0.03	0.40	0.51	0.54	0.53
n-Nonane	1.62	1.58	1.90	1.76	1.87
Nonene	0.33	0.26	0.29	0.28	0.35
C ₃ -Cyclohexane	0.88	0.82	0.87	0.88	0.89
Dimethyl Octane	0.00	0.26	0.40	0.28	0.30
C ₃ -Cyclohexane	1.42	0.88	0.97	0.91	1.04
Br. Alkane	1.33	0.89	1.04	0.93	1.03
Br. Alkane	0.77	0.53	0.59	0.56	0.58
C ₃ -Cyclohexane	0.78	0.50	0.26	0.51	0.55
4-Methyl Nonane	2.08	1.33	1.00	1.39	1.60
n-Propyl Cyclohexane	1.39	1.01	0.84	1.07	1.17
Oxtahydro Indene	0.83	0.59	0.54	0.73	0.78
3-Methyl Nonane	1.02	0.72	0.68	0.75	0.81
Ethyl Benzene	0.06	0.14	0.11	0.20	0.37
p-Xylene	0.20	0.30	0.12	0.38	0.40
m-Xylene	0.22	0.34	0.60	0.50	0.63
Dimethyl Ethyl Cyclohexane	0.50	0.37	0.35	0.40	0.41
Tetramethyl Cyclohexane	1.07	0.74	0.78	0.81	0.86
Br. Alkane	0.74	0.56	0.59	0.60	0.63
C ₄ -Cyclohexane	0.41	0.36	0.38	0.38	0.42

Table 7. Composition of the Headspace Gases Obtained after Thermal Stressing of JPTS Alone and in the Presence of Activated Carbon PX-21 at 425°C in Air and in Nitrogen.

Compounds	JPTS (air), vol %	JPTS+PX-21 (air), vol %	JPTS (N ₂), vol %	JPTS+PX-21 (N ₂), vol %
Methane	49.72	2.73	37.58	34.55
Ethane+Ethylene	29.73	12.22	34.06	34.73
Propane	12.03	15.60	14.20	20.99
Propylene	3.02	3.20	9.67	0.00
i-Butane	1.01	0.99	0.94	1.07
Butane	0.94	0.80	0.56	0.00
Butene	1.73	26.53	1.67	8.66
Pentane	1.37	7.03	1.14	0.00
Pentene	0.42	30.90	0.10	0.00
Hexane	0.02	0.00	0.08	0.00

Table 8. Surface Area of PX-21 Activated Carbon after Thermal Stressing at 425°C and 450°C in Nitrogen and Air Atmosphere.

Process condition	BET surface area, m ² /g
425°C, 5h, nitrogen	785
425°C, 5h, air	630
450°C, 5h, nitrogen	550
425°C, 5h, air	320

Table 9. Isomer Distribution for the Diels-Adler Reaction between Isoprene and Methyl Acrylate.³⁵

press., MPa	temp. K	distribution, %	
		A	B
atmospheric	308	99.5	0.5
atmospheric	313	99.5	0.5
atmospheric	320	99.6	0.5
atmospheric	333	98.3	1.7
atmospheric	423	99.6	0.4
4.90	323	67.1	32.9
7.45	323	38.9	61.1
11.77	323	71.3	28.7
15.69	323	55.5	24.5
19.12	323	31.0	19.0
20.60	323	35.9	14.1

Table 10. Experimental Results for Pyrolysis of Coal Model Compounds in Supercritical Water.⁴³

reactant	products	
	pyrolysis	hydrolysis
A.
Dibenzyl Ether

Phenethyl Phenyl Ether

1,3-Diphenylpropane		XXXX
B.
Guaiacol

Benzyl Phenyl Ether

Benzyl Phenyl Amine

1,2-Diphenylethane		XXXX
C.
Phenyl Ether	XXXX	XXXX
Diphenylmethane	XXXX	XXXX
Diphenylsulfone	XXXX	XXXX
Diphenyl	XXXX	XXXX
Diphenylmethane		XXXX

XXXX No Reaction

Table 11. Properties of Coals.

Coal Number	DECS-6	DECS-12
Seam, State	Blind Canyon	Pittsburgh #8, PA
Rank	h _v A b	h _v A b
%C	81.72	84.75
%O	10.10	7.37
%H	6.22	5.66
%S	0.40	0.83
%N	1.56	1.40
%Mineral Matter	6.67	11.88
H/C	0.905	0.794

Table 12. Liquefaction Conversion Data for DECS-6 and DECS-12.

Expt #	Temp	Catalyst	Solvent	TC	THF-Sol	DCM-Sol	THF/DCM
tb 6-8	TPL, 425-30	none	pyrene	55.2	10.5	44.7	0.235
tb 6-9	TPL, 425-30	none	DHP	83.0	32.5	50.5	0.644
tb 6-3	TPL, 425-30	MoS ₂	pyrene	89.3	5.1	84.2	0.061
tb 6-4a	TPL, 425-30	NiCl ₂	pyrene	83.0	13.1	69.9	0.187
tb 6-10	TPL, 425-30	MoS ₂	DHP	95.0	5.7	89.3	0.064
tb 6-11	TPL, 425-30	NiCl ₂	DHP	83.2	11.0	72.2	0.152
tb 6-6	TPL, 425-60	MoS ₂	pyrene	88.2	3.6	84.6	0.043
tb 6-7	TPL, 425-60	NiCl ₂	pyrene	87.3	12.7	74.6	0.170
tb 12-5	TPL, 425-30	none	pyrene	51.9	14.0	37.9	0.369
tb 12-6	TPL, 425-30	none	DHP	81.7	20.1	61.6	0.326
tb 12-3	TPL, 425-30	MoS ₂	pyrene	76.8	14.5	62.3	0.233
tb 12-4	TPL, 425-30	NiCl ₂	pyrene	84.2	28.3	55.9	0.506
tb 12-7	TPL, 425-30	MoS ₂	DHP	85.4	5.1	80.3	0.064
tb 12-8	TPL, 425-30	NiCl ₂	DHP	88.7	13.1	75.6	0.173

TC = total conversion

DCM-Sol = DCM-Solubles + Gas Yield

THF/DCM = ratio of THF-Solubles to DCM-Solubles

Table 13. Percent Area of Major Compounds in GC of Hexane-Solubles.

Expts	Benzenes	Phenols	2-Ring	3-Ring	4-Ring +	Alkanes	B+P/2-Ring	$\Sigma\text{Aro}/\Sigma\text{Ali}$
tb 6-8	3.7	25.6	27.7	2.3	0.0	40.6	0.98	1.46
tb 6-9	8.9	18.2	35.4	n.d.	1.8	35.8	0.73	1.80
tb 6-3	14.6	30.6	21.0	3.2	0.0	30.5	1.87	2.28
tb 6-4	19.2	25.8	29.4	3.8	0.9	21.0	1.32	3.77
tb 6-10	0.5	19.4	40.5	n.d.	3.1	36.6	0.46	1.73
tb 6-11	2.6	20.5	43.4	n.d.	0.0	33.4	0.53	1.99
tb 6-6	2.7	44.7	22.8	3.9	2.9	23.0	1.60	3.35
tb 6-7	8.6	29.5	34.5	3.9	0.0	23.5	0.99	3.26
tb 12-5	8.3	41.8	20.7	20.8	0.6	7.8	1.19	11.8
tb 12-6	15.4	28.3	46.7	n.d.	6.2	3.3	0.83	29.3
tb 12-3	5.0	46.4	29.2	2.2	4.5	12.8	1.43	6.82
tb 12-4	6.3	32.2	38.6	6.6	4.4	11.9	0.78	7.40
tb 12-7	2.4	30.1	48.1	n.d.	10.4	9.1	0.56	10.0
tb 12-8	2.6	23.4	39.5	n.d.	31.1	3.4	0.37	28.4

2-Ring = alkylated aromatics and hydroaromatics composed of two rings

3-Ring = alkylated aromatics and hydroaromatics composed of three rings

4-Ring = alkylated aromatics and hydroaromatics composed of four rings and other polynuclear aromatics

n.d. = not determined

B+P/ $\geq$ 2-Ring = Benzenes + Phenols/2-Ring + 3-Ring + 4-Ring +

$\Sigma\text{Aro}/\Sigma\text{Ali}$ = Total Aromatics/ Total Alkanes

Table 14. Properties of Coals.

Coal Number	DECS-9	PSOC-1379	DECS-6	DECS-12	PSOC-831
Seam, State	Deitz, MT	Colorado F, CO	Blind Canyon	Pittsburgh #8, PA	Brazil Block
Rank	sub C	h _v C b	h _v A b	h _v A b	h _v C b
%C	76.11	76.74	81.72	84.75	83.85
%O	17.50	15.96	10.10	7.37	8.64
%H	5.14	4.97	6.22	5.66	4.97
%S	0.33	0.63	0.40	0.83	0.94
%N	0.91	1.69	1.56	1.40	1.61
%Mineral Matter	7.28	5.09	6.67	11.88	4.16
H/C	0.803	0.770	0.905	0.794	0.704
%Vitrinite		92.2	69.1	83.0	79.2
%Liptinite (Resinite)		0.6 (0.1)	17.0 (5.0)	8.1 (2.6)	4.9
%Inertinite		7.2	13.6	8.9	15.9

Table 15. ¹³C-NMR and H/C Ratio Data for Coals and Liquefaction Residues.

Experiment	Coal	Reaction Cond	<i>f_a</i>	<i>f_{CO}</i>	<i>f_{OH}</i>	<i>f_{ha}</i>	H/C Res
Raw Coal	Pittsburgh #8	None	0.70	0.00	0.03	0.29	0.794
TB12-2		425°C, 1h, pyrene	0.81	0.00	0.11		0.584
Raw Coal	Blind Canyon	None	0.65	0.01	0.05	0.41	0.905
TB6-2		425°C, 1h, pyrene	0.84	0.03	0.02		0.58
Raw Coal	Deitz, Mt	None	0.57	0.08	0.05	0.21	0.803
TB9-2		425°C, 1h, pyrene	0.81	0.07	0.09		0.546
Raw Coal	Colorado F	None	0.67	0.11	0.08	0.16	0.770
TB1379-2		425°C, 1h, pyrene	0.82	0.04	0.11		0.542
Raw Coal	Brazil Block	None	0.72	0.01	0.06	0.22	0.704
TB831-2		425°C, 1h, pyrene	0.86	0.02	0.03		0.526

f_{CO} - fraction carboxyls, *f_{OH}* - fraction phenols/ethers

Table 16. Relative Area Percents Calculated from GC Data.

Expt	Benzenes	Phenols	Naphthalenes	Alkanes	Phenanthrenes
FP 6	2.3	9.7	15.9	72.0	0.0
TB 6-2	4.7	11.9	19.9	63.5	0.0
FP 12	11.3	31.3	39.9	18.1	0.0
TB 12-2	11.7	54.1	21.2	12.9	0.0
FP 9	4.5	39.9	0.0	55.6	0.0
TB 9-1	0.0	50.2	13.8	35.9	0.0
FP 1379	12.1	26.3	0.5	60.4	0.7
TB 1379-2	0.0	30.8	18.6	50.6	0.0
FP 831	10.5	32.9	4.2	52.0	0.2
TB 831-2	10.1	53.8	33.5	2.7	0.0

FP - flash pyrolysis experiments, TB - coal liquefaction hexane-soluble reaction

Table 17. Coal Liquefaction Data Conversion Data.

Experiment	Coal	Reaction Cond	Conversion	THF Solubles	DCM Solubles
TB12-2	Pittsburgh #8	425°C, 1h, pyrene	60.0	11.7	48.4
TB6-2	Blind Canyon	425°C, 1h, pyrene	66.9	11.3	55.6
TB9-2	Deitz	425°C, 1h, pyrene	51.6	8.9	42.6
TB1379-2	Colorado F	425°C, 1h, pyrene	41.8	8.0	33.8
TB831-2	Brazil Block	425°C, 1h, pyrene	45.4	11.9	33.5

APPENDIX 2
FIGURES

Figure 1. System Time-Pressure Profiles during pyrolysis of Cyclohexane, Ethylcyclohexane, and n-Butylcyclohexane at 450°C under Initial N₂ Pressure (Cold) of 0.69 MPa.

Figure 2. Predicted versus Measured Values of n-Propylcyclohexane Conversion at 450°C.

Figure 3. Predicted versus Measured Values of n-Octylcyclohexane Conversion at 450°C.

Figure 4. Experimental Rate Constants of Alkylcyclohexanes at 450°C as a Function of Characterization Number (n) of Molecular Structure.

Figure 5. Cyclohexane Selectivity to Major Products at 450°C for 4 hr (Conversion = 0.05) under Initial N₂ Pressure (Cold) of 0.69 MPa.

Figure 6. Methylcyclohexane Selectivity to Major Products at 450°C for 4 hr (Conversion = 0.12) under Initial N₂ Pressure (Cold) of 0.69 MPa.

Figure 7. Product Distribution for Ethylcyclohexane Pyrolysis at 450°C under Initial N₂ Pressure (Cold) of 0.69 MPa.

Figure 8. Temporal methylcyclopentane product for Alkylcyclohexanes Pyrolysis at 450°C under Initial N₂ Pressure (Cold) of 0.69 MPa.

Figure 9. n-Butylcyclohexane Selectivity to Major Products at 450°C for 0.2 hr (Conversion = 0.04) under Initial N₂ Pressure (Cold) of 0.69 MPa.

Figure 10. Product Distribution for n-Butylcyclohexane Pyrolysis at 450°C under Initial N₂ Pressure (Cold) of 0.69 MPa.

Figure 11. Product Distribution for n-Propylcyclohexane Pyrolysis at 450°C under Initial N₂ Pressure (Cold) of 0.69 MPa.

Figure 12. n-Octylcyclohexane Selectivity to Major Products at 450°C for 0.2 hr (Conversion = 0.09) under Initial N₂ Pressure (Cold) of 0.69 MPa.

Figure 13. n-Decylcyclohexane Selectivity to Major Products at 450°C for 0.2 hr (Conversion = 0.17) under Initial N₂ Pressure (Cold) of 0.69 MPa.

Figure 14. Growth of Deposits from Mixtures of 81.5 wt% JP-8C and 18.5 wt% Tetradecane at 450°C under Nitrogen.

Circles: Mass of deposit per unit area on the bottom of the reactor.

Triangles: Mass of deposit per unit area on the vertical wall of the reactor

Figure 15. Experimental Rates of Deposit Growth by Settling on the Bottom of the Reactor, as a Function of Time.

These rates were determined by subtracting the measurements shown by the triangles in Figure 14, from the measurements shown by circles, then dividing the changes in mass/area by the corresponding time increments. The subtraction was intended to remove the contribution from direct reaction of vapor species with the bottom surface.

Figure 16. Size Distributions of Suspended Particles as Functions of Time, Determined by Light Scattering (Horiba LA-900).

On the vertical axis is the percent of total particle volume in each size bin. The stressing time is shown at the upper right in each figure.

Figure 17. Mean Particle Size (volume basis) as a Function of Time, Determined from the Distributions shown in Figure 16.

Figure 18. Comparison of Measured and Calculated Deposition Rates by Settling of Particles to the Bottom of the Reactor.

Circles: Measurements, from Figure 2, with scale change.

Triangles: Calculated flux of particles to the bottom by gravitational settling.

Figure. 19. Gas Chromatograms of Unstressed JPTS, JPTS Stressed Alone and JPTS Stressed with PX-21 at 450°C for 5 h in Nitrogen.

Figure. 20. Gas Chromatograms of Unstressed JPTS, JPTS Stressed Alone and JPTS Stressed with PX-21 at 450°C for 5 h in Air.

Figure 21. Percent Weight Plotted versus Alkane Carbon Number for the Unstressed and Stressed JPTS Jet Fuel at 425°C for 5 h in Nitrogen.

Figure 22. Percent Weight Plotted versus Alkane Carbon Number for the Unstressed and Stressed JPTS Jet Fuel at 425°C for 5 h in Air.

Figure 23. Percent Weight Plotted versus Branched Alkane Carbon Number for the Unstressed and Stressed JPTS Jet Fuel at 425°C for 5 h in Nitrogen.

Figure 24. Percent Weight Plotted versus Branched Alkane Carbon Number for the Unstressed and Stressed JPTS Jet Fuel at 425°C for 5 h in Air.

Figure 25. Percent Weight Plotted versus Number of Alkyl Groups for Benzene for the Unstressed and Stressed JPTS Jet Fuel at 425°C for 5 h in Nitrogen and Air.

Figure 26. Percent Weight Plotted versus Alkane Carbon Number for the Unstressed and Stressed JPTS Jet Fuel at 450°C for 5 h in Nitrogen.

Figure 27. Percent Weight Plotted versus Alkane Carbon Number for the Unstressed and Stressed JPTS Jet Fuel at 450°C for 5 h in Air.

Figure 28. Percent Weight Plotted versus Branched Alkane Carbon Number for the Unstressed and Stressed JPTS Jet Fuel at 450°C for 5 h in Nitrogen.

Figure 29. Percent Weight Plotted versus Branched Alkane Carbon Number for the Unstressed and Stressed JPTS Jet Fuel at 450°C for 5 h in Air.

400 μ m

Figure 12a

400 μ m

Figure 12b

Figure 30. Polarized-Light Micrographs of PX-2¹ and PX-21 after Thermal Stressing with JPTS at 425°C for 5 h in Air Atmosphere.

Figure 31. Pressure-Temperature Diagram for a Pure Component.³

Figure 32. Reduced Density-Reduced Pressure Diagram for a Pure Component in the Vicinity of its Critical Point.³

Figure 33. The Six General Categories of PT Projections for Binary Mixtures.⁴

Figure 34. Solubilities of Naphthalene in Supercritical Ethylene at 298 K and 318K.^{17,18}

Figure 35. Solubilities of Naphthalene in Supercritical Ethylene as a Function of Ethylene Density.^{17,18}

Figure 36. Solubility Increase of Acridine at 50°C with a Cosolvent-doped Solvent.⁸

Figure 37. $\bar{v}_2^\infty$ vs. Density for Naphthalene in Ethylene at 12 °C.⁽²⁵⁾

Figure 38 Ratio of Observed Biomolecular Rate Constant for Spin Exchange in Ethane to the Rate Constant Predicted from the Stokes-Einstein Relationship as a Function of Pressure. Temperatures are 308 K (Circles), 313 K (Diamonds), and 331 K (Squares).³⁴

Figure 39. Equilibrium Constant for Tautomerization of 2-Hydroxypyridine/2-Pyridone in Supercritical 1,1-Difluoroethane at 402 K.⁵⁸

Figure 40. Equilibrium Constant for Tautomerization of 2-Hydroxypyridine/2-Pyridone in Supercritical Propane at 393 K.⁵⁸

Figure 41. Deactivation (DA) by Coking under Gaseous Phase and Reactivation (RA) in the Supercritical Region for the Isomerization of 1-Hexane on γ - Al_2O_3 Catalyst under CSTR Conditions.⁶²

Figure 42. Model of Overall Diffusion of the Products in Three Reaction Phases.⁶³

Figure 43. The Flory's Model. Each Lattice Site holds a Cell that Contains the Free Volume for the Site's Particle.

Figure 44. The Sanchez-Lacombe Model. The Vacant Lattice Sites, or Holes, Represent the Free Volume of the System.

^{13}C NMR for Blind Canyon

Figure 45. ^{13}C -NMR for DECS-6 for Raw Coal (top) and for Reacted (425°C) Coal Residue (bottom).

Figure 46. Flash Pyrolysis Pyrogram for DECS-6.

APPENDIX 3
SCHEMES

Scheme I. Possible Mechanisms for Major Pyrolysis Products of Cyclohexane

Scheme II. Possible Mechanisms for Major Products of n-Butylcyclohexane

Scheme III

Scheme IV

The chemical structure of the proposed stabilizers and the method of synthesis of 1,2,3,4-Tetrahydro-1-naphthol and Phenanthrenediol.

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Dear Sir:

The attached text was inadvertently omitted from our Technical Progress Report 92-PC92104-TPR-4, entitled "Advanced Thermally Stable Jet Fuels" (It should follow immediately after page 22.). This report covers the time frame of April 1993 through June 1993 under Contract No. DE-FG22-92PC92104. The tables and figures discussed in this text have been included in the appropriate appendices. Please consider this as an addendum to this report.

Sincerely,

Harold H. Schobert
Chairman

HHS:kc

cc: S.Lavan
D. Storch

Enclosure (3)

Physical and Chemical Interactions in Supercritical Fluids-A Review
(Contributed by Jian Yu)

Introduction

Supercritical phenomena near the critical point, such as large activation volume, local anisotropy, and high compressibility, are expected to have a significant influence on physicochemical processes which govern fuel degradation. This general review is on physical and chemical interactions in supercritical fluids which may be of interest in studying thermal decomposition of jet fuels under supercritical conditions.

The unique solvent properties of a supercritical fluid (SCF) have been known for more than a century [1], but it is only in the past fifteen years or so that SCF solvents have received considerable attention, mainly due to interest in extraction and separation processes [2]. The appeal of SCF solvents derives from their unusual physicochemical properties. For example, these fluids have liquid-like densities and thus solvent power, gas-like diffusivities and viscosities, high heat transfer coefficients, and zero surface tension [3]. Moreover, these properties can be easily manipulated by pressure and/or temperature. The unique properties of SCFs have led to widespread industrial applications as extraction solvents [3,4]. Recently, the use of SCF solvents as reaction media has received growing interest mainly because of applications such as oxidation of hazardous wastes in supercritical water [5]. The current state of SCF science and technology can be found in several recently published review papers [4-9] and books [3, 10-14].

The objective of this section is to review basic physical and chemical interactions underlying many uses of SCF solvents with particular emphasis on the fields related to reactions in SCFs. Since the phase behavior of mixtures in their critical region has significant influence on the chemical reaction in the SCF solvent, the phase behavior of SCF-solute mixtures is discussed. Unusual behavior of chemical reactions in SCFs seems to be related to unusual interactions between the reactants and the SCF solvent. Therefore, a discussion of intermolecular interactions in SCF solutions will precede the description of reactions in SCFs.

Phase Behavior of SCF-Solute Systems

An understanding of the phase behavior of SCF systems is necessary to capitalize fully on the unique solvent characteristics of SCFs. Although practical SCF processes always involve multicomponent mixtures, many unusual properties of SCFs can be found by considering the phase behavior of a pure SCF solvent.

Figure 31 shows a schematic pressure-temperature diagram for a pure substance [3]. The critical point is defined as the point where the two fluid phases, liquid and gas, become

indistinguishable. The supercritical region for a pure component refers to the region of temperature and pressure above the critical temperature (T_c) and the critical pressure (P_c), as shown in the hatched region of Figure 31. In this region, the fluid is highly compressible and slight changes in pressure and/or temperature result in extremely large variations in the physicochemical properties. These unusual properties can be further illustrated with the help of Figure 32, a density-pressure plot of a typical SCF solvent [3]. The SCF region of interest falls in the range of reduced pressure $P_r = P/P_c = 1.01-1.5$ and reduced temperature $T_r = T/T_c = 1.01-1.1$ [8]. In this region, the fluid density can be very close to that of the normal liquid, and this gives the fluid a high capacity for solutes. At the same time, the compressibility (the slope of the isotherm) is very high, going to infinite at the critical point. This means that very small pressure changes give large density variations. The distinguishing feature of an SCF is the fact that, while it has liquid-like density, it possesses a very high compressibility. This makes it possible to use pressure as a very sensitive means of manipulating and controlling the solvent characteristics, spanning the continuum range from gas-like to liquid-like. These features make the SCF attractive for both solubility-based separation processes and systems undergoing chemical reactions.

Since SCF processes always involve multicomponent mixtures, it is important to understand the phase behavior of SCF mixtures. The phase behavior data for SCF mixtures can be quite complex even for simple binary mixtures. Figure 33 shows the six general categories of PT projections for binary mixtures [4]. The discussion of these phase diagrams is beyond the scope of this section. The detailed description can be found in recent several review papers [4, 15, 16] and book [3]. We will place our attention on the phenomena of solubility in SCFs, the use of cosolvents to enhance solubility and improve selectivity and the interactions between solutes.

1. SCF Solubility. The simplest type of phase behavior of SCF mixtures is the solubility of a solid solute, such as naphthalene, in an SCF solvent. Figure 34 shows the solubility of solid naphthalene in supercritical ethylene ($T_c = 282$ K, $P_c = 50$ bar) at 298 and 318 K [17, 18]. At pressure below 50 bar, naphthalene solubility is very low for both temperatures, as can be expected for the solubility of a solid in a gas. As the pressure is increased and the critical pressure is approached, the solubility begins to increase rapidly. The solubility enhancement of several orders of magnitude can be obtained with an increase in pressure in the vicinity of 50 bar at the constant temperature. Besides, it can be found that while isobarically increasing temperature in the high pressure region increases naphthalene solubility, increasing temperature at constant pressure just above 50 bar results in the solubility decrease of about one order of magnitude. This opposing temperature effects are due to two

competing influences of temperature on SCF solvent density and solid sublimation pressure which affect the solubility of the solid in the SCF solvent. From Figure 32 one can find that the density is much more sensitive to temperature near the critical pressure than in the high pressures. At near-critical pressures, the effect of temperature on the SCF density dominates the effect on solid sublimation pressure and increasing temperature results in the decrease of SCF density and thus solubility. At the higher pressures the effect of temperature on solid sublimation pressure is dominant and the temperature increase results in corresponding solubility increase. This solubility behavior can be further illustrated by Figure 35, which shows the effect of SCF solvent density on naphthalene solubilities by plotting naphthalene solubilities versus ethylene densities at 298 and 318 K [17, 18]. The solubilities increase with increasing ethylene densities along each isotherm due to increasing solvent power, and with increasing temperature at constant density due to increasing naphthalene sublimation pressure.

The solubility behavior discussed above is general and is exhibited by any liquid or solid material that dissolves in an SCF. This general solubility behavior can be exploited in separation processes. In particular, the ability to vary continuously solvent density and thus control solvent power can enhance the selectivity of the solvent. Also, the solvent and extract can be easily separated, and fractionation of multiple solutes can be achieved by stepwise reductions in solvent density. These solvent properties can also be exploited in certain chemical reaction processes. With modest change in the temperature or pressure, reaction rates can be altered significantly by adjusting the solubilities and thus the concentrations of reacting species over a wide range. At the same time, the rate constant itself and thus the rates of certain reactions can potentially be adjusted over several orders of magnitude using a modest change in pressure because of thermodynamic solvent effects on rate constants, as discussed later. In addition, the products can be easily separated from the reaction mixtures by adjusting pressure or temperature if the products exhibit different solubility behavior from the reactants.

2. Effects of Cosolvents on Solubilities of Heavy Organic Solutes. The solubilities of heavy organic solutes in SCFs can be greatly enhanced by adding nonpolar cosolvents [19] or polar cosolvents [20] to the SCF solvents. Figure 36 shows an example of solubility enhancement by a polar cosolvent [8]. A cosolvent, also called entrainer, modifier or moderator, which is a small amount (1–5%) of an additional component and usually of medium volatility between the solute and the SCF solvent, does not change significantly the critical properties or density of the solvent mixture [8]. A suitable cosolvent can not only greatly enhance solubility but also increase selectivity [21].

Dobbs et al. undertook a series studies which probed the effects of various cosolvents on solubilities [19–21]. When small amounts of nonpolar alkane cosolvents are added to

supercritical CO₂, the solubilities of nonpolar aromatic hydrocarbon increase significantly [19]. For three n-alkane cosolvents used in their studies it is found that the solubility enhancements increase with the size or the polarizability of the cosolvent. Also, the solubility enhancements increase as the cosolvent concentrations increase. In most cases, the solubility is increased more by the presence of only 3.5 mol% cosolvent than by the increase in the pressure of several hundred bar. For nonpolar solutes and cosolvents, however, there is no indication of increased selectivity. The ratio of the solute solubilities in the cosolvent system to in the pure solvent system is relatively constant over a wide range of pressure or density, so no real improvement in selectivity could be anticipated by temperature and pressure manipulation.

Similar results have also been observed for polar cosolvents with polar solutes [20]. As compared to the pure solvent system, the polarity effect in the polar cosolvent system shifts the solubility isotherms upward by a relatively constant factor. The solubility enhancements for systems that form strong hydrogen bonds, however, are frequently greater than those found for the nonpolar solutes. For 2-aminobenzoic acid, the addition of only 3.5 mol% methanol increases the solubility 620%. These findings suggest that cosolvents may enhance selectively the solubility of certain compounds in terms of specific types of intermolecular interactions.

In subsequent work, the authors demonstrated the effect of a cosolvent on the selectivity of supercritical CO₂ for a pair of solids in terms of the chemical functionality of the components [21]. For the 2-aminobenzoic acid-anthracene pair the addition of only 3.5 mol% methanol increases selectivity of 2-aminobenzoic acid vs. anthracene from 2 to 10 at 120 bar, while increasing the yield by a factor of 4.5. This large increase in the selectivity can be attributed to the stronger molecular interaction between 2-aminobenzoic acid and methanol.

3. Interactions between Solutes. There is considerable experimental evidence to suggest that the presence of secondary solutes can significantly affect the solubility of a primary solute [21-23]. In general it is found that the solubility of a given solid in the ternary (two solutes plus solvent) system increases relative to that in the binary system in proportion to the solubility of the other solid in the SCF solvent [21]. For example, naphthalene is of much higher solubility in supercritical CO₂ than phenanthrene. Consequently, the phenanthrene solubility in the ternary system is increased by 75% while the corresponding increase in naphthalene solubility is only 20% [22]. Additional information is provided by Kwiatkowski et al. [23] for the phenanthrene/anthracene/CO₂ system. The solubility of anthracene in the ternary system is higher than in the binary system, whereas the solubility of phenanthrene is slightly lower than in the binary system. This suggests that phenanthrene (about 10⁻³ mol fraction) raises the solubility of anthracene (about 10⁻⁵ mol fraction) but that anthracene does not affect the phenanthrene because of its sufficiently low concentration.

Unusual solubility behavior in SCFs, including enhanced solubilities, cosolvent effects, and synergistic effect of mixed solutes, as discussed above, may be related to unusual intermolecular interactions present in SCFs. In addition, unusual behavior of chemical reactions in SCFs can also be explained by this unusual molecular interactions. Before discussing reactions in SCFs, let us first discuss the molecular structure of SCF solutions.

Molecular Structure of SCF Solutions

The understanding of the molecular interactions and structure in SCF solutions has grown considerably in the recent years. This information is useful for understanding both macroscopic properties (for example, solubilities and selectivities in SCF solutions) and the thermodynamic solvent effect on rate constants of homogeneous reactions. The molecular interactions in SCF solutions are significantly different from those in normal liquids. A unique feature of SCFs is that solvent molecules condense around solutes in the highly compressible near-critical region. This physical condensation is often called clustering, which was first suggested by Eckert et al. [24] to explain the large negative partial molar volumes that were observed in SCFs. Evidence for solvent clustering is quite broad. Solubility enhancements in solute/cosolvent/solvent system and solute/solute/solvent system, discussed in the last section, suggest that increased molecular interactions occur between components and are the first strong indication of this unusual behavior. The measurement of the infinite dilution partial molar volumes of several solutes in SCFs provides further evidence of solvent clustering [24, 25]. In the dense, far-supercritical regions where the fluids are relatively incompressible, the infinite dilution partial molar volumes (PMVs) of several organic solids in SCF ethylene and CO₂ are slightly positive. However, very large negative values in PMVs are observed for these dilute organic solids in the highly compressible region of the solvent, which is near the solvent critical point. The magnitude of these negative values can be as large as $-20000 \text{ cm}^3/\text{mol}$ and is the largest in the region where the solvent is most compressible. See, for example, the PMV of naphthalene in SCF ethylene, just 3°C from the critical temperature, in Figure 37 [25]. These data suggest that the clustering of many solvent molecules occurs when a solute molecule is added to solution. This condensation or contraction is the cause of the highly negative partial molar volumes.

While the solubility and the partial molar volume data provide evidence of clustering, more detailed information has been obtained recently using spectroscopic techniques which measure directly intermolecular interactions in dilute SCF solutions. Spectroscopic methods used at present include UV-visible, fluorescence, and IR spectroscopy.

Based on solvatochromic shifts in the UV absorption spectrum of phenol blue in SCFs, Kim and Johnston first suggested the link between the local density and the isothermal

compressibility [26], showing that the difference between the local density and the bulk density increased as the isothermal compressibility increased. This idea is used to interpret and obtain local densities from absorption data of phenol blue in SCFs. Morita and Kajimoto [27] have measured UV absorption spectra of 4-(dimethylamino)benzonitrile (DMABN) in supercritical ethane. The bathochromic shifts observed at various densities are found to be much larger than those expected from Onsager's theory. This indicates that solvent molecules aggregate around solute molecules and form cluster even in a nonpolar supercritical fluid like ethane.

Additional work has been done by using UV absorption measurements to quantify the clustering around solutes in solute/cosolvent/solvent systems [28, 29]. The local compositions of an SCF and a cosolvent around a solute are estimated using spectral shift data. It is found that in the highly compressible near-critical region the local concentration of a cosolvent around a solute is much higher than that in the bulk, showing that strong interaction occurs between the solute and the cosolvent.

Another spectroscopic approach is fluorescence spectroscopy. Brennecke et al. [30] used fluorescence spectroscopy to study directly the intermolecular interactions in dilute SCF solutions. Fluorescence intensity ratios in the fluorescence spectra of pyrene and naphthalene in SCF CO_2 , C_2H_4 , and CF_3H indicate much stronger solute/solvent interactions near the critical point and yield liquid-like local densities in the highly compressible region even when the bulk density is quite low. These results demonstrate that high local densities in SCFs are not limited to solute/solvent systems of strong specific hydrogen-bonding, acid-base, charge-transfer, dipole-dipole, or induced dipole-dipole interactions.

Theoretical calculations also support the concept of clustering. Petsche and DeBenedetti [31] have performed molecular dynamics simulations of supercritical mixtures which distinctly show the clustering of solvents around the solute in the attractive mixture and a negative cluster or hole in the repulsive mixture. Lee and co-workers [32, 33] have calculated pair correlation functions for model SCF systems using integral equation theories. Their results are also consistent with the theory of local density augmentation.

Studies of chemical reactions in SCF solvents have also suggested solvent clustering around a reactant molecule near the solvent critical point. Randolph and Carlier [34] have studied the Heisenberg spin-exchange reaction between nitroxide free radicals in supercritical ethane to probe the nature of solvent structure near the critical point. They compared observed values of bimolecular spin-exchange rate constant with values predicted from the Stokes-Einstein relationship that assumes a "structureless" fluid. While the Stokes-Einstein theory accurately predicts the rate constants at high pressures, deviations are seen closer to the critical point. Observed rate constants are larger than those predicted in the vicinity of the critical point with the largest deviation at temperature nearest to the critical temperature (Figure 38). A

possible explanation is solvent cage effects or clustering which results in a longer radical-radical collision time. In a low-viscosity fluid like ethane, an increased collision time results in stronger spin exchange and thus a higher rate of reaction. A comparison of reaction collision time between observed and predicted from Stokes-Einstein theory showed that an average reaction contact time is about 3 times as large as the Stokes-Einstein prediction. These observation is consistent with local density augmentation of solvent molecules around the radicals in the vicinity of the critical point.

Ikushima and coworkers [35] have used IR spectroscopy to explore the solvent effects of supercritical CO₂ on the Diels-Alder reaction between isoprene and methyl acrylate. Their results indicate that the activation volume of the reaction attains greatest negative value and the excess number of solvent molecules around the reacting species is greatly increased in the near-critical region. These results also strongly support the concept of clustering.

This unusual local behavior involving increased molecular interaction in asymmetric SCF solutions seems to be the cause of unusual solubility behavior, as stated in the last section, and of unusual behavior of chemical reactions which will be discussed in the next section.

Reactions in Supercritical Fluids

While the unique properties of SCF solvents have been widely used in extraction processes and other separation processes, little use has been made of them as media for reactions mainly because not much is known about the mechanisms of chemical reactions in these solvents. Many of the desirable properties of SCFs which are used in separation processes can, however, also be exploited in systems undergoing chemical reactions. These properties include high component diffusivities and low viscosities relative to liquids which can result in enhanced mass transfer rates and extremely pressure-tunable solvent properties which can be used to adjust and control certain chemical reactions. Using SCFs as reaction media, it is in principle possible to: (1) enhance reaction rates due to both increased reactant solubilities and favorable thermodynamic pressure effects on reaction rate constants; (2) increase the selectivity of a reaction while maintaining high conversion; (3) dissolve reactants in a single phase to eliminate the need for heterogeneous reactions; (4) separate the reaction products by utilizing the phase behavior exhibited by the mixture in its critical region; and (5) regenerate catalysts by SCF extraction of the deactivating agents. These findings have stimulated interest in reactions using SCF media. Related subjects have been reviewed recently by several authors [5-7, 36-38].

The SCF solvent can affect the reaction by either participating as a reactant or functioning only as a reaction medium or both. The participation of the SCF solvent in the

reaction can be evidenced by incorporating the solvent molecules into reaction products. Hydrolysis reactions in supercritical water [39-44], which will be discussed later, provide good examples of the participation of the SCF solvent in reactions. As reaction media, SCF solvents can influence reactions through mechanical pressure effect, diffusional limitations, electrostatic interactions, and phase behavior. These SCF solvent effects will be discussed in the following. Then, some interesting examples about reactions in SCF solvents will be presented.

1. SCF Solvent Effects. The appeal of SCF solvents as reaction media derives from their unique pressure-adjustable solvent properties. It is well-known that chemical reactions are influenced by solvent effects. In the highly compressible SCF region, the SCF solvent properties are extremely pressure sensitive. The influence of solvent effects on the chemical reactions can be achieved by using pressure as the processing lever. This effect of pressure on reactions in SCF solvents appears to be unique and consequently pressure can be used as an effective means of manipulating and controlling reactions in SCF solvents. The effects of pressure on reaction rate can be obtained through the pressure dependence of the reactant concentrations or through the pressure dependence of the rate constants. The latter can be substantial in the highly compressible near-critical region of the solvent. By means of transition state theory [45, 46], the effects of pressure on the reaction rate constants can be explained.

For a bimolecular reaction the reactants A and B are assumed to be in chemical equilibrium with the transition state $M^\ddagger$.

The variation of the reaction rate constant k with pressure is given by

$$\left(\frac{\partial \ln k}{\partial P} \right)_T = -\frac{\Delta V^\ddagger}{RT} \quad (2)$$

where $\Delta V^\ddagger$, the volume of activation, is the difference in the partial molar volumes of the transition state species M , and the reactants A and B and is given by

$$\Delta V^\ddagger = \bar{V}_M - \bar{V}_A - \bar{V}_B \quad (3)$$

It is noteworthy that Equation 2 is valid only if the rate constant is expressed in pressure-independent units, such as mole fraction or molality. If the rate constant is expressed in pressure-dependent concentration units, such as mole/liter, Equation 2 must be corrected by a term including the isothermal compressibility of the solution, as given by [47]

$$\left(\frac{\partial \ln k}{\partial P} \right)_T = -\frac{\Delta V^\ddagger}{RT} + (1-n)k_T \quad (4)$$

where n is the sum of the stoichiometric coefficients of the reactants (when the coefficient is one for the transition state species).

The form of Equation 2 can be compared with the temperature dependence of the rate constant which defines the activation energy E_a .

$$\left(\frac{\partial \ln k}{\partial T}\right)_P = \frac{E_a}{RT^2} \quad (5)$$

However, contrary to activation energies of normal reactions which are always positive, volumes of activation $\Delta V^\ddagger$ can be either positive or negative. If $\Delta V^\ddagger$ is positive, then reaction will be retarded by pressure. Otherwise, the reaction rate will be enhanced by pressure.

In conventional liquid solutions, pressure changes in kilobars are required to affect the rate constant significantly because $\Delta V^\ddagger$ is usually in the range of -50 to $+20$ cm^3/mol [46]. However, in the highly compressible SCF solutions, small pressure changes can produce substantial variations in the rate constant because the magnitude of $\Delta V^\ddagger$ is much larger. For example, Simmons and Mason [48] found activation volumes lower than -3000 cm^3/mol for the dimerization of chlorotrifluoroethylene near its critical point. Johnston and Haynes [49] reported activation volumes as low as -6000 cm^3/mol for the unimolecular decomposition of α -chlorobenzyl methyl ether using supercritical 1,1-difluoroethane as a reaction medium, demonstrating the ability of SCFs to adjust reaction rate.

Since many SCF solvent properties change with changes in the pressure, and each can affect chemical reactions dramatically, one can conclude that unusual large activation volumes for reactions in SCF solvents account not only for the direct pressure effect, but also for the variation of solvent properties with pressure. Along these lines, Wu et al. [50] defined an apparent activation volume in terms of transition state theory to interpret the effect of pressure on the overall reaction rate. The apparent activation volume is divided into various contributions as given by

$$\Delta V_{\text{app}} = -RT \left(\frac{d \ln r}{dP} \right) = \Delta V_{\text{int}}^k + \Delta V_{\text{comp}}^k + \Delta V_{\text{diff}}^k + \Delta V_{\text{elec}}^k + \Delta V_{\text{p}}^\pi \quad (6)$$

The first two terms of right hand side in Equation 6, which account for mechanical pressure effects (intrinsic) and solvent compressibility, are the same as those in Equation 4. The third term comes from the contribution of diffusional limitations which is dominant for the diffusion controlled reaction. The effect of electrostatic interactions is considered in the fourth term. The last term represents phase behavior effects which can be important for reactions taking place in more than one phase. The weight of each contribution in Equation 6 is related to reaction types.

Diffusional limitations may influence reaction rates significantly at high SCF solvent densities where the mobilities of individual molecules become restricted because of the increased viscosity of the medium. Abraham and Klein [51] carried out the reaction of benzylphenylamine in supercritical water and supercritical methanol and found that the reactant conversion passed through a minimum as the solvent loading increased. They explain observed kinetics using solvent cage effects which suppress pyrolysis kinetics such that at increasing

solvent loading, the pyrolysis reaction become diffusion limited. Lawson and Klein [41] thermolyzed guaiacol in supercritical water and found similar phenomena. Helling and Tester [52] found that the direct oxidation of CO in supercritical water is much slower than predicted by existing models, either global expression or a system of elementary reactions while the water gas shift reaction is much faster than predicted. They suggest that water forms a cage around the CO, acting as a diffusional barrier which retards the direct oxidation reactions and promotes the water gas shift reaction between solvent and solute. These results are consistent with the concept of local density enhancement or clustering because clustering of solvent molecules around solute molecules is necessary to form a solvent cage.

It should be indicated here that the formation of solvent cages does not always affect reactions in SCF solvent. As proposed by Brennecke [38], the key factor determining whether the solvent cage will influence the reaction in any way is the relative time scales of the solvent cage and the reaction. If the reaction occurs within the period in which the solvent cage has its integrity, one will expect some effect of the cage on the reaction. Otherwise, one might not find any effect of the solvent cage.

Electrostatic interactions affect the reaction rate constant by shifting the equilibrium between the reactants and transition state. That is, a change in the polarity of SCF solvent will increase or decrease the reaction rate depending on whether the transition state is more or less polar than the initial reactants. Solvent properties such as the solubility parameter or dielectric constant have been used to correlate the electrostatic interaction in an SCF solution to the rate constant. Johnston and Haynes [49] correlated the rate constant of the unimolecular decomposition of α -chlorobenzyl methyl ether with the dielectric constant, ϵ , of supercritical 1,1-difluoroethane using classic Kirkwood analysis [45, 53]. Townsend et al. [43] followed the development of Kirkwood and correlated the hydrolysis rate constants of dibenzyl ether, phenylethyl phenyl ether, and guaiacol with ϵ of supercritical water. Klein and his colleagues [54, 55] found that the addition of salts increased the hydrolysis rate constants. This is due to the increase in ϵ brought about by the ionization of the salt. In all of these examples the transition states are more polar than the initial reactants because the rate constants increase with ϵ .

The phase behavior of SCF systems could affect the overall reaction rate by the partitioning of the reactant between phases. This can be manipulated by the pressure. Wu et al. [56] described the effects of phase behavior on dibenzyl ether (DBE) pyrolysis kinetics in supercritical toluene. The pyrolysis conversion of DBE is suppressed from 90% under neat conditions to 50% with a toluene loading of 0.21 g/cm³. The suppression of the overall reaction rate is explained by the existence of both vapor and liquid phases. The addition of supercritical toluene dilutes and reduces the amount of DBE in the faster reacting liquid phase.

Torry et al. [55] found that with the increase of salt concentrations in the reaction mixture the overall hydrolysis rate first increased and reached a maximum and then decreased. This is interpreted in terms of the solution phase behavior. The initial increase in overall rate with the addition of salt results from an increase in the hydrolysis rate constant since the transition state of hydrolysis reaction is more polar than the reactants and the salt addition increases solvent polarity and thus increases the rate constant. Subsequent salt addition would still increase the rate constant but cause noticeable phase separation of supercritical solution into a liquid-like phase containing salt and a gas-like phase containing organic. This would lead to a decrease in the availability (effective concentration) of water for hydrolysis, thereby offsetting the ever-increasing rate constant and decreasing the overall reaction rate.

In summary, the unique solvent properties exhibited by the SCF solvent makes it attractive as the reaction medium. In addition to temperature, pressure as an additional and effective means can be used to manipulate and control chemical reactions in SCF solvents. The effects of pressure on the reaction rates can be realized by adjusting the solubilities and thus the concentrations of the reactants and by adjusting the rate constants. A remarkable characteristic of reactions in SCF solvents is the fact that the influence of pressure on the rate constants may be quite large especially in the highly compressible near-critical region. This large dependence of the rate constants on pressure can, in terms of transition state theory, be explained by large activation volumes which account not only for direct pressure effect but also for the variations in solvent properties with pressure. The potential ability of SCF solvents to control or manipulate chemical reactions can be exploited in a variety of ways. This is described as follows.

2. Adjustment of Reaction Rates and Selectivities. As discussed above, in the highly compressible SCF region pressure and/or temperature can be used as sensitive means to manipulate and control reaction rates due to unusual solubility behavior and remarkable thermodynamic solvent effect on the reaction rate constant. Also, for certain parallel reactions with obviously different activation volumes reaction selectivities can be adjusted or enhanced by operating at suitable pressure and temperature because of different thermodynamic pressure effect on individual rate constant. A few studies have shown that the use of SCFs as reaction media leads to significant variations in the reaction rates and product selectivity.

Johnston and Haynes [49] observed that the reaction rate constant for the unimolecular decomposition of α -chlorobenzyl methyl ether in supercritical 1,1-difluoroethane ($T_c=386.6$ K, $P_c=45.0$ bar) can be increased by one order of magnitude with a change in pressure of only 15 bar at conditions near the critical point of 1,1-difluoroethane. The increase in the rate constant is attributed to the large negative volume of activation (as low as $-6,000$ cm³/mol) which

occurs in the vicinity of the critical point of 1,1-difluoroethane where the solution exhibits very large compressibility and relatively strong solute-solvent interactions.

Ikushima et al. [35, 57] reported that significant changes in rate constants and product distribution with pressure occurred in the vicinity of the critical point for the Diels-Alder reaction between isoprene and methyl acrylate in supercritical CO₂. The activation volume is the most negative near the critical point (as low as -750 cm³/mol) [35]. In this Diels-Alder reaction, the two cyclohexene isomers, methyl 4-methyl-3-cyclohexene-1-carboxylate (A) and methyl 3-methyl-3-cyclohexene-1-carboxylate (B) are produced. Table 9 gives isomer distribution for this reaction. The chief product is (A) at atmospheric pressure. However, in supercritical CO₂ medium, the isomer distribution varies with pressure. The distribution ratio of (B) to (A) is the greatest in the critical region where supercritical CO₂ medium favors the production of (B). This change in the isomer distribution in the critical region could be attributed to the aggregation of the solvent molecules leading to the steric constraints to the reacting species. Probably such steric constraints hinder the motion of isoprene species leading to the formation of the sterically stable para product (A), and consequently the ratio meta/para product would significantly increase.

Pyrolysis reactions in supercritical water provide further examples that demonstrate the ability of SCF to control chemical reaction rates and selectivities. Klein and his coworkers have studied decomposition in supercritical water of a series of coal model compounds [39-43, 51]. Their experimental results are summarized in Table 10 in terms of the structures of the reactants, pyrolysis products, and hydrolysis products. These results suggest that hydrolysis reaction always involves a saturated carbon with a heteroatom-containing leaving group (LG) and proceeds in parallel with a free-radical pyrolysis pathway. In addition, they found that the selectivity to hydrolysis products increases with water density, with no discontinuity at the critical point. The hydrolysis rate constant also increases with water density. The above observations have been concisely summarized in terms of mechanistic hypothesis of Equation 7.

This single step summarizes each hydrolysis reaction of Table 10 and depicts the nucleophilic attack of the solvent on a saturated carbon atom with a heteroatom-containing leaving group. This mechanism thus would not allow for hydrolysis of either a diaryl alkane or a heterocycle devoid of a saturated carbon. The above mechanism suggests that hydrolysis reaction proceeds

through a polar transition state. The evidence for this interpretation includes increased hydrolysis rate constant with increased dielectric constant according to the Kirkwood formalism [43]. Additional evidence of the polar nature of hydrolysis is that the addition of salts increases the hydrolysis rate constant [54, 55].

The chemical reaction equilibria can also be adjusted with SCFs. Peck et al. [58] studied SCF solvent effects on the tautomeric equilibria of 2-hydroxypyridine and 2-pyridone at infinite dilution. Solvents are 1,1-difluoroethane ($T_c=386.6$ K, $P_c=45$ bar) and propane ($T_c=369.8$ K, $P_c=42.5$ bar). The measured equilibrium constant increases by a factor of 7 in 1,1-difluoroethane for a pressure range 21–207 bar at 403 K, while it more than doubles in propane over the same pressure range at 393 K, as shown in Figures 39 and 40 respectively. One can note that in the highly compressible near-critical region, K_c is extremely strongly dependent on pressure for both solvents, demonstrating enormous adjustability of SCFs.

3. SCF as a Medium for Homogeneous Reactions. The unique solvent properties of an SCF make it possible to dissolve reactants that otherwise have very limited solubilities in a single fluid phase and run the reactions homogeneously. Oxidation of organic materials in supercritical water provides an example for this application.

The properties of supercritical water ($T_c=374^\circ\text{C}$, $P_c=218$ atm) are much different from those of normal liquid water. Under supercritical conditions, water behaves like a dense gas and can completely dissolve organic substances and gases such as oxygen, nitrogen and carbon dioxide. On the other hand, inorganic salts are almost insoluble and exhibit low dissociation in supercritical water [59]. These reverse solubility properties relative to normal liquid water make supercritical water an excellent medium for oxidation of organic wastes, since organics and oxygen can be brought together in a single, homogeneous phase and inorganics can be readily removed from solutions by precipitation.

Modell and his coworkers [59-61] demonstrated that many toxic organic wastes can be almost completely destroyed by supercritical water oxidation. At 250 atm, when hazardous organic wastes are subjected to supercritical water oxidation, complex organics break down to low molecular weight organics which are completely miscible with supercritical water and then are rapidly oxidized to carbon dioxide and water. Heteroatoms are converted to their acid forms which can be neutralized and recovered as salts or a brine and metals are oxidized to oxides which can be recovered as solids. It is found that the destruction efficiency for total organic carbon exceeds 99.999% in the temperature range of 600-650°C and at residence time of only 5 seconds. It is interesting to note the fact that no hazardous NO_x is formed when several nitrogen-containing compounds are oxidized in supercritical water [61]. This means that supercritical water oxidation of nitrogen-containing organic wastes is of much less deleterious

effect on the environment than high temperature incineration.

4. Heterogeneous Catalytic Reactions in SCFs. The unique physicochemical properties of SCFs can also be exploited in heterogeneous catalytic reactions. It is well-known that all organic reactions on solid catalysts are accompanied by simultaneous formation of undesirable carbonaceous residues (or "coke") which form a deposit on the internal and/or external surface of catalysts, plug access to active sites and thus result in catalyst deactivation. Industrially coke removal or catalyst regeneration is carried out by burn-off in air. High temperatures occurring during this regeneration inevitably cause decays in catalyst structure and thus reduce its lifetime. Recently, several authors have demonstrated that coked catalyst can be regenerated by removing coke compounds with SCFs, based on their high ability to desorb heavy hydrocarbons.

Tiltscher et al. [62] demonstrated how SCF reaction media can be used to extract heavy hydrocarbon by-products from coked catalysts for two heterogeneous catalytic reactions: cis-/trans- isomerization of 1-hexene ($T_c=504$ K, $P_c=31.1$ bar) on a low active shell catalyst (γ - Al_2O_3 /Al-metal; specific surface area about $5\text{ m}^2/\text{g}$) and disproportionation of 1,4-diisopropylbenzene in the presence of benzene and n-pentane as a diluent ($T_c=528$ K, $P_c=43$ bar for the mixture) on a highly active zeolite catalyst (type 13 NaHX; specific surface area about $500\text{ m}^2/\text{g}$). Figure 41 shows conversion-time plot for the isomerization of 1-hexene on γ - Al_2O_3 catalyst. If the isomerization reaction is carried out in the gaseous phase ($T=523.3$, $P=15$ bar) under CSTR conditions, the resulting conversion versus time curve shows a typical deactivation course. The deactivation of catalyst results from side reactions which produce low volatile oligomeric compounds (C_{12} to C_{30}) which remain on the catalyst surface and finally cause coking. If the pressure of reaction mixture is isothermally increased to 500 bar, the oligomers are stripped from the catalyst surface. After readjustment of stationary conditions the expected degree of conversion is reached. In spite of the higher reactivity at high pressure no catalytic decay occurs even after extremely long reaction time.

While the activity of the shell catalyst which has been deactivated by forming heavy hydrocarbon by-products under subcritical conditions can be recovered and maintained under supercritical conditions, some different results are observed for the zeolite catalyst [62]. Although catalyst lifetime can be markedly increased under supercritical reaction conditions, reactivity is lowered. This different performance in reactivity for two catalysts seems to be related to their different porous structure. Although the authors did not mention porous structure of two catalysts, it can be inferred from specific surface area data that the shell catalyst is macroporous in nature while the zeolite catalyst is mainly microporous. Restricted diffusion of reactants in the macroporous shell catalyst is not a major problem. Coke formed on such

catalysts can be easily extracted and removed. In contrary, for the highly microporous zeolite catalyst restricted diffusion may be significant especially under high supercritical pressures. Probably restricted diffusion results in a decrease in coke extraction rate relative to coke formation rate which is high at the higher pressures and thus results in a decrease in catalyst activity.

In a study of the possible coke removal from zeolite catalysts by supercritical ethyl benzene and benzene, Manos and Hofmann [63] found that a complete reactivation of a zeolite catalyst by SCFs is impossible. Only coke precursors can be redissolved since the larger coke molecules are less soluble. However, under supercritical conditions, less coke is deposited on the catalyst since coke precursor is simultaneously extracted by the supercritical solvent and thus catalyst deactivation is slowed down.

Yokota et al. [64-66] demonstrated that supercritical reaction conditions may offer some merit to the Fischer-Tropsch (FT) synthesis reaction. The conventional FT synthesis reaction is a solid-catalyzed gas phase reaction with a large heat of reaction, which results in the local superheating of the catalyst bed. At the same time, the reaction produces high molecular weight hydrocarbons (wax) which do not vaporize under the reaction conditions, cover the catalyst surface, and plug the micropores of the catalyst. Although a slurry phase FT synthesis process can promote the heat transfer and the wax removal from the catalyst, the diffusion of synthesis gas in micropores is so slow that the overall reaction rate is lower than that in the gas phase reaction condition [67]. When FT synthesis is carried out using supercritical n-hexane as the reaction medium, it is found that the SCF transports heat more effectively than the gas phase medium, transports materials faster than the liquid medium, and desorbs the products in situ as effectively as the liquid medium [64-66]. Since the desorption of product from the catalyst surface and its transfer in the catalyst pores are consecutive processes, this well-balanced rates of desorption and transfer in the supercritical phase result in the most effective overall transfer of products and enhanced activity maintenance as compared to either gas phase or liquid phase reaction media (Figure 42).

Conclusions

Supercritical fluids possess physicochemical properties intermediate between those of liquids and gases. Moreover, these properties can be easily manipulated by pressure. The phase behavior of SCF solutions can be quite complex. The solubilities of heavy organic solutes in SCFs can be controlled and manipulated with moderated changes in pressure or temperature. In addition, SCF solubility behavior can be greatly affected by adding cosolvents to the SCF solvent, which can be used to improve selectivities. The chemical reactions in SCF solvents can be quite different from those in normal liquid solutions. Because of the extreme

pressure dependence of SCF solvent properties and the unusual thermodynamic pressure effect on the reaction rate constant, the chemical reactions in the SCF solvent can be controlled using pressure as the processing lever. These unusual solubility behavior and unusual chemical reaction behavior in SCF solvents seem to be related to their unusual solvent properties and their unique interactions with solutes or reactants. Spectroscopic experiment studies and theoretical calculations and modeling have suggested that there is local density augmentation or solvent clustering around the solute near the critical point of the solvent. In addition, it has been suggested that there is enhanced solute-solute interactions near the critical point.

Because of these unique characteristics, SCFs have received considerable attention in a number of important fields such as extraction, chromatography, and chemical reaction processes. Although much progress in SCF technology has occurred in the past decade, there are still a number of unanswered questions in this area: What is relationship between the extraordinary solubility enhancements brought about by adding small amounts of cosolvent and local cosolvent composition enhancements around the solute? How does the solvent-solute and/or solute-solute clustering influence chemical reaction? How does the phase behavior of the reaction mixtures change with the degree of reactions? What effects does the participation of an SCF in reactions have on the reaction kinetics and mechanism? These questions submit considerable experimental and theoretical challenges. The recent advances in the molecular understanding of SCF solutions have provide a pathway to address these questions [13, 14]. It can be anticipated that as fundamental processes that govern SCF solvents are understood, these fascinating fluids will find more extensive applications.

References

1. Hannay, J. B. and Hogarth, J., "On the solubility of solids in gases," *Proc. R. Soc. London*, **29**, 324 (1879).
2. Johnston, K. P., "Supercritical fluids," In *Encyclopedia of Chemical Technology*, 3rd ed., Suppl. Vol., John Wiley & Sons, New York, 1984, p. 872.
3. McHugh, M. A. and Krukonis, V. J., *Supercritical Fluid Extraction: Principles and Practice*, Butterworths, Boston, 1986.
4. Paulaitis, M. E., Krukonis, V. J., Kurnik, R. T., and Reid, R. C., "Supercritical fluid extraction," *Rev. Chem. Eng.*, **1**, 179 (1983).
5. Shaw, R. W., Brill, T. B., Clifford, A. A., Eckert, C. A., and Franck, E. E., "Supercritical water: A medium for chemistry," *C&N*, December 23, 1991, p. 26.
6. Subramaniam, B. and McHugh, M. A., "Reactions in supercritical fluids-A review," *Ind. Eng. Chem. Process Des. Dev.*, **25**, 1 (1986).
7. Tiltscher, H. and Hofmann, H., "Trends in high pressure chemical reaction

- engineering," *Chem. Eng. Sci.*, **42**, 959 (1987).
8. Brennecke, J. F. and Eckert, C. A., "Phase equilibria for supercritical fluid process design," *AIChE J.*, **35**, 1409, (1989).
 9. Johnston, K. P., Peck, D. G., and Kim, S., "Modeling supercritical mixtures: How predictive is it?" *Ind. Eng. Chem. Res.*, **28**, 1115 (1989).
 10. Squires, T. G. and Paulaitis, M. E., Eds., *Supercritical Fluids: Chemical and Engineering Principles and Applications*, ACS Symposium Series 329, ACS, Washington, DC, 1987.
 11. Johnston, K. P. and Penninger, J. M. L., Eds., *Supercritical Fluid Science and Technology*, ACS Symposium Series 406, ACS, Washington, DC, 1989.
 12. Bruno, T. J. and Ely, J. F., Eds., *Supercritical Fluid Technology: Reviews in Modern Theory and Applications*, CRC Press, Boca Raton, 1991.
 13. Bright, F. V. and McNally, M. E. P., Eds., *Supercritical Fluid Technology: Theoretical and Applied Approaches in Analytical Chemistry*, ACS Symposium Series 488, ACS, Washington, DC, 1992.
 14. Kiran, E. and Brennecke, J. F., Eds., *Supercritical Fluid Engineering Science: Fundamentals and Applications*, ACS Symposium Series 514, ACS, Washington, DC, 1993.
 15. McGlashan, M. L., "Phase equilibria in fluid mixtures," *J. Chem. Thermodynamics*, **17**, 301 (1985).
 16. Street, W. B., "Phase equilibria in fluid and solid mixtures at high pressure," In *Chemical Engineering at Supercritical Fluid Conditions*, Paulaitis, M. E., Penninger, J. M. L., Gray, R. D., and Davidson, P., Eds., Ann Arbor Science, Ann Arbor, Michigan, 1983, p. 3.
 17. Diepen, G. A. M. and Scheffer, F. E. C., "The solubility of naphthalene in supercritical ethylene, 2," *J. Phys. Chem.*, **57**, 575 (1953).
 18. Tsekhanskaya, Y. V., Iomtev, M. B., and Mushkina, E. V., "Solubility of naphthalene in ethylene and carbon dioxide under pressure," *Russ. J. Phys. Chem. (Engl. Transl.)*, **38**, 1173 (1964).
 19. Dobbs, J. M., Wong, J. M., and Johnston, K. P., "Nonpolar co-solvent for solubility enhancement in supercritical fluid carbon dioxide," *J. Chem. Eng. Data*, **31**, 303 (1986).
 20. Dobbs, J. M., Wong, J. M., Lahiere, R. J., and Johnston, K. P., "Modification of supercritical fluid phase behavior using polar cosolvents," *Ind. Eng. Chem. Res.*, **26**, 56 (1987).
 21. Dobbs, J. M. and Johnston, K. P., "Selectivities in pure and mixed supercritical fluid

- solvent," *Ind. Eng. Chem. Res.*, **26**, 1476 (1987).
22. Kurnik, R. T. and Reid, R. C., "Solubility of solid mixtures in supercritical fluids," *Fluid Phase Equil.*, **8**, 93 (1982).
 23. Kwiatkowski, J., Lisicki, Z., and Majewski, W., "An experimental method for measuring solubilities of solids in supercritical fluids," *Ber. Bunsenges. Phys. Chem.*, **88**, 865 (1984).
 24. Eckert, C. A., Ziger, D. H., Johnston, K. P., and Ellison, T. K., "The use of partial molar volume data to evaluate equations of state for supercritical fluid mixtures," *Fluid Phase Equil.*, **14**, 167 (1983).
 25. Eckert, C. A., Ziger, D. H., Johnston, K. P., and Kim, S., "Solute partial molar volumes in supercritical fluids," *J. Phys. Chem.*, **90**, 2738 (1986).
 26. Kim, S. and Johnston, K. P., "Molecular interactions in dilute supercritical fluid solutions," *Ind. Eng. Chem. Res.*, **26**, 1206 (1987).
 27. Morita, A. and Kajimoto, O., "Solute-solvent interaction in nonpolar supercritical fluid: A clustering modal and size distribution," *J. Phys. Chem.*, **94**, 6420 (1990).
 28. Yonker, C. R. and Smith, R. D., "Retention in supercritical fluid chromatography: Influence of the partial molar volume of the solute in the stationary phase," *J. Phys. Chem.*, **92**, 1664 (1988).
 29. Kim, S. and Johnston, K. P., "Clustering in supercritical fluid mixtures," *AIChE J.*, **33**, 1603 (1987).
 30. Brennecke, J. F., Tomasko, D. L., Peshkin, J. and Eckert, C. A., "Fluorescence spectroscopy studies of dilute supercritical solutions," *Ind. Eng. Chem. Res.*, **29**, 1682 (1990).
 31. Petsche, I. and Debenedetti, P. G., "Solute-solvent interactions in infinitely dilute supercritical mixtures: A molecular dynamics investigation," *J. Chem. Phys.*, **91**, 7075 (1989).
 32. Cochran, H. D. and Lee, L. L., "Solvation structure in supercritical fluid mixtures based on molecular distribution functions," In Ref. 11, p. 27.
 33. Wu, R.-S., Lee, L. L., and Cochran, H. D., "Structure of dilute supercritical solutions: Clustering of solvent and solute molecules and the thermodynamic effects," *Ind. Eng. Chem. Res.*, **29**, 977 (1990).
 34. Randolph, T. W. and Carlier, C., "Free-radical reactions in supercritical ethane: A probe of supercritical fluid structure," *J. Phys. Chem.*, **96**, 5146 (1992).
 35. Ikushima, Y., Saito, N., and Arai, M., "Supercritical carbon dioxide as reaction medium: Examination of its solvent effects in the near-critical region," *J. Phys. Chem.*, **96**, 2293 (1992).

36. Wu, B. C., Paspek, S. C., Klein, M. T., and LaMarca, C., "Reactions in and with supercritical fluids-A review," In Ref.12, p. 511.
37. Boock, L., Wu, B. C., LaMarca, C., Klein, M. T., and Paspek, S. C., "Reactions in supercritical fluids," *CHEMTECH*, December, 1992, p. 719.
38. Brennecke, J. F., "Spectroscopic investigations of reactions in supercritical fluids: A review," In Ref. 14, p. 201.
39. Abraham, M. A. and Klein, M. T., "Pyrolysis of benzylphenylamine neat and with tetralin, methanol, and water solvents," *Ind. Eng. Chem. Prod. Res. Dev.*, **24**, 300 (1985).
40. Abraham, M. A., Wu, B. C., Paspek, S. C., and Klein, M. T., "Reactions of dibenzylamine neat and in supercritical fluid solvents," *Fuel Sci. Technol. Int.*, **6**, 557 (1988).
41. Lawson, J. R. and Klein, M. T., "Influence of water on guaiacol pyrolysis," *Ind. Eng. Chem. Fundam.*, **24**, 203 (1985).
42. Townsend, S. H. and Klein, M. T., "Dibenzyl ether as a probe into supercritical fluid solvent extraction of volatiles from coal with water," *Fuel*, **64**, 635 (1985).
43. Townsend, S. H., Abraham, M. A., Huppert, G. L., Klein, M. T., and Paspek, S. C., "Solvent effects during reactions in supercritical water," *Ind. Eng. Chem. Res.*, **27**, 143 (1988).
44. Houser, T. J., Tiffany, D. M., Li, Z., McCarville, M. E., and Houghton, M. E., "Reactivity of some organic compounds with supercritical water," *Fuel*, **65**, 827 (1986).
45. Laidler, K. J., *Chemical Kinetics*, McGraw-Hill, New York, 1965, Chap. 5.
46. Eckert, C. A., "High pressure kinetics in solution," *Annu. Rev. Phys. Chem.*, **23**, 239 (1972).
47. Hamann, S. D. and Bradley, R. S., *High-Pressure Physics and Chemistry*, V. 2, Academic Press, London, 1963, p. 163.
48. Simmons, G. M. and Mason, D. M., "Pressure dependency of gas phase reaction rate coefficients," *Chem. Eng. Sci.*, **27**, 89 (1972).
49. Johnston, K. P. and Haynes, C., "Extreme solvent effects on reaction rate constants at supercritical fluid conditions," *AIChE J.*, **33**, 2017 (1987).
50. Wu, B. C., Klein, M. T., and Sandler, S. I., "Solvent effects on reactions in supercritical fluids," *Ind. Eng. Chem. Res.*, **30**, 822 (1991).
51. Abraham, M. A. and Klein, M. T., "Solvent effects during the reaction of coal model compounds," In Ref. 10, p. 67.

52. Helling, R. K. and Tester, J. W., "Oxidation kinetics of carbon monoxide in supercritical water," *Energy & Fuels*, **1**, 417 (1987).
53. Kirkwood, J. G., "Theory of solutions of molecules containing widely separated charges with special application to Zwitterions," *J. Chem. Phys.*, **2**, 351 (1934).
54. Huppert, G. L., Wu, B. C., Townsend, S. H., Klein, M. T., and Paspek, S. C., "Hydrolysis in supercritical water: Identification and implications of a polar transition state," *Ind. Eng. Chem. Res.*, **28**, 161 (1989).
55. Torry, L. A., Kaminsky, R., Klein, M. T., and Klotz, M. R., "The effect of salts on hydrolysis in supercritical and near-critical water: Reactivity and availability," *J. Supercrit. Fluids*, **5**, 163 (1992).
56. Wu, B. C., Klein, M. T., and Sandler, S. I., "Reactions in and with supercritical fluids: Effect of phase behavior on dibenzyl ether pyrolysis kinetics," *Ind. Eng. Chem. Res.*, **28**, 255 (1989).
57. Ikushima, Y., Ito, S., Asano, T., Yokoyama, T., Saito, N., Hatakeda, K., and Goto, T., "A Diels-Alder reaction in supercritical carbon dioxide medium," *J. Chem. Eng. Japan*, **23**, 96 (1990).
58. Peck, D. G., Mehta, A. J., and Johnston, K. P., "Pressure tuning of chemical reaction equilibrium in supercritical fluids," *J. Phys. Chem.*, **93**, 4297 (1989).
59. Modell, M., Gaudet, G. G., Simson, M., Hong, G. T., and Biemann, K., "Supercritical water: Testing reveals new process holds promise," *Solid Wastes Management*, August 1982, p. 26.
60. Modell, M., "Supercritical water oxidation," In *Standard Handbook of Hazardous Waste Treatment and Disposal*, Freeman, H., Ed., McGraw Hill, New York, 1989.
61. Thomason, T. B. and Modell, M., "Supercritical water destruction of aqueous wastes," *Hazardous Waste*, **1**, 453 (1984).
62. Tiltscher, H., Wolf, H., and Schelchshorn, J., "Utilization of supercritical fluid solvent-effects in heterogeneous catalysis," *Ber. Bunsenges. Phys. Chem.*, **88**, 897 (1984).
63. Manos, G. and Hofmann, H., "Coke removal from a zeolite catalyst by supercritical fluids," *Chem. Eng. Technol.*, **14**, 73 (1991).
64. Yokota, K. and Fujimoto, K., "Supercritical phase Fischer-Tropsch synthesis reaction," *Fuel*, **68**, 255 (1989).
65. Yokota, K. and Fujimoto, K., "Supercritical phase Fischer-Tropsch synthesis reaction: 2. The effective diffusion of reactant and products in the supercritical phase reaction," *Ind. Eng. Chem. Res.*, **30**, 95 (1991).

66. Yokota, K., Hanakata, Y., and Fujimoto, K., "Supercritical phase Fischer-Tropsch synthesis reaction: 3. Extraction capability of supercritical fluids," *Fuel*, **70**, 989 (1991).
67. Huang, S. H., Lin, H. M., Tsai, F. N., and Chao, K. L., "Solubility of synthesis gases in heavy n-paraffins and Fischer-Tropsch wax," *Ind. Eng. Chem. Res.*, **27**, 162 (1988).

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