



The effect of tetramethylurea and hexamethylphosphoramide on the dissolution of coal
by Christina Ichioka

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in
Chemical Engineering
Montana State University
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Abstract:

Coal liquefaction by tetramethyl urea (TMU) and hex-amethylphosphoramide (HMPA) has potentially significant process advantages over coal-liquefaction systems currently under development. In this investigation, the effects of solvent type, temperature, and time on coal conversion behavior are determined. Experiments were conducted on Kittanning coal in a batch reactor at atmospheric pressure under nitrogen purge and temperatures below the boiling points of the solvents.

Coal conversion to 41% was achieved using a 1:1 mixture of the solvents for 40 minutes at 320 degrees Fahrenheit. The maximum dissolution using pure TMU, 23%, was observed after 12 hours at 320 degrees Fahrenheit. Pure HMPA as the solvent produced a colloidal suspension that blocked separation of residue and liquid product.

Dissolution and initial dissolution rate tended to increase with increasing run temperature. Dissolution rate was fast until condensation reactions dominated. Maximum dissolution was achieved at shorter times with increasing run temperatures.

Solvent retention levels increased with increasing run temperature. Substantial amounts of TMU and HMPA were incorporated into the residue, probably at least in part as solvent fragments.

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A thesis submitted in partial fulfillment
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MONTANA STATE UNIVERSITY
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APPROVAL

of a thesis submitted by

Christina Ichioka

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

May 28, 1985
Date

John T. Sears
Chairperson, Graduate Committee

Approved for the Major Department

May 28, 1985
Date

John T. Sears
Head, Major Department

Approved for the College of Graduate Studies

7-9-85
Date

W. M. Malve
Graduate Dean

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ABSTRACT

Coal liquefaction by tetramethylurea (TMU) and hexamethylphosphoramide (HMPA) has potentially significant process advantages over coal-liquefaction systems currently under development. In this investigation, the effects of solvent type, temperature, and time on coal conversion behavior are determined. Experiments were conducted on Kitting coal in a batch reactor at atmospheric pressure under nitrogen purge and temperatures below the boiling points of the solvents.

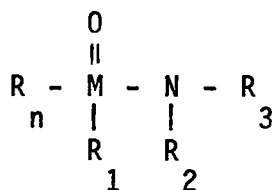
Coal conversion to 41% was achieved using a 1:1 mixture of the solvents for 40 minutes at 320 degrees Fahrenheit. The maximum dissolution using pure TMU, 23%, was observed after 12 hours at 320 degrees Fahrenheit. Pure HMPA as the solvent produced a colloidal suspension that blocked separation of residue and liquid product.

Dissolution and initial dissolution rate tended to increase with increasing run temperature. Dissolution rate was fast until condensation reactions dominated. Maximum dissolution was achieved at shorter times with increasing run temperatures.

Solvent retention levels increased with increasing run temperature. Substantial amounts of TMU and HMPA were incorporated into the residue, probably at least in part as solvent fragments.

INTRODUCTION

Sears [1] has suggested a coal-conversion method on which this investigation is based. This method has potentially significant process advantages over coal-liquefaction systems currently under development. In it, coal is dissolved under mild conditions of temperature and pressure by a class of solvents represented by the formula



where M is a carbon, phosphorus, or sulfur atom. Specifically, tetramethylurea and hexamethylphosphoramide were found to be effective in dissolving bituminous coal.

Tetramethylurea

Tetramethylurea (1,1,3,3-Tetramethylurea, temur, TMU), one of the few ureas that is liquid at room temperature, has a wide liquid-phase temperature range which is uncommon for urea derivatives. Some physical properties of TMU are listed in Table 1.

Table 1. Physical properties of tetramethylurea [2].

Structure	
Molecular formula	C H N O 5 12 2
Molecular weight	116.16
Boiling point (C)	176.5 (1 atm)
Melting point (C)	-1.2
Density (g/ml)	0.9619 (25 C)
Viscosity (poise)	0.01401 (25 C)
Dielectric constant	23.45
Dipole moment (Debye)	3.37
Basicity (aqueous pK _B)	12
Specific conductivity (mho/cm)	< 2 x 10 ⁻⁸ (25 C)

The specific conductivity of TMU, an aprotic solvent, is low, as expected. An aprotic solvent is incapable of donating suitably labile hydrogen atoms to form hydrogen bonds with appropriate species [3]. A coplanar molecule (including the four carbon atoms), TMU exhibits maximum resonance.

The three electronegative hetero-atoms are symmetrically bonded to the more positively-charged carbon atom due to the amide resonance [2]. Increasing the substitution of hydrogen atoms by methyl groups to form linear derivatives of urea results in decreasing both the total electron density at the C=O bond and the C-N bond strength [4]. The absence of the usually strong association of amides (hydrogen bonding involving the hydrogen on the amide nitrogen) makes TMU act only as a hydrogen-bond acceptor [2]. The relatively high boiling point and dipole moment, however, indicate a strong dipole association, despite the expected hindrance by the four methyl groups.

The capacity for ion solvation is determined by the dipole moment and dielectric constant of a species [2]. Since TMU has a lower dielectric constant than other simple carboxamides with approximately the same dipole moment, the dissolving power of TMU for strongly ionic salts is low, approximating that of acetone. As expected, the dissolving power is good for the iodides, moderate for the bromides, and poor for alkali and alkaline earth chlorides and sulfates. The fact that nitrates have good solubilities indicates that anion solvation also affects the dissolving power. Although alkali cyanides, cyanates, thiosulfates, and acetates exhibit low solubilities, many salts of transition metals have good solubilities in TMU. The high pi-electron density in the amide group, especially in the

pi-orbital of the carbonyl oxygen, explains the exceptional solvation of alkali metal ions.

Like pyridine, TMU is completely miscible with water and all common organic solvents. The optimum hydration conditions occur at a water: TMU molar ratio of 6:1, which produce a water/TMU mixture of maximum density [2]. TMU has a high solvent power for aromatic hydrocarbons. Although significant electron delocalization occurs in both species, the interaction is not strong enough to result in charge transfer. Luttringhaus and Dirksen [2] speculate that the dissolving power is probably due to the favorable molecular structure of TMU, the van der Waals forces of the methyl groups, and the interactions between the resonance systems of the solvent and solute. In its dissolving power and miscibility, TMU is most similar to pyridine. However, TMU has the following advantages over pyridine: TMU is not accompanied by homologues, it has a more convenient boiling point, and it can be made almost anhydrous by simple distillation. The good dissolving power of TMU can be explained by considering the ellipsoid form of the polar liquid. An ellipsoid form, under equal conditions of polarity as a spherical form, produces a higher dissolving power. The surface of the molecule is mostly formed by the methyl groups which accounts for the high dissolving power for hydrocarbons [5]. Although the four lipophilic methyl groups shield the carbonyl oxygen to a large extent, the

good solubility of univalent and polyvalent hydroxy compounds and carboxylic acids is due to the only slightly impaired ability of the carbonyl oxygen to hydrogen bond [2]. In the presence of strong acids, TMU is protonated readily. It is assumed that protonation on the oxygen atom occurs with TMU since the mechanism has been demonstrated for both N,N-dialkylamides and urea. The strong shielding of the carbonyl group prevents reaction with Grignard compounds but can not withstand attack from lithium and most organosodium compounds, which are more reactive.

TMU has been found to be useful as a non-aqueous medium for many chemical reactions. It is an exceptional titration solvent since it has a good dissolving power for acids and bases, gives large potential breaks, affords good recoveries, is easily purified, and is commercially available [5]. TMU accelerates base-catalysed prototropic double-bond shifts by combining a solvating power for alkali ions with the ability to hydrogen bond with the interfering free alcohol formed in the reaction [2]. Mixtures of TMU and carbonyl chloride are suitable as acylation media; kinetic data indicate that TMU combines with the hydrogen chloride formed. TMU is used to prepare mono- and difunctional phosphonium salts from tertiary phosphines. In the reduction of diazonium hexafluorophosphates, TMU has been used as a source of hydride hydrogen in an ionic mechanism. TMU is recommended as diluent in the Ullmann synthesis of biaryls

from aryl halides when higher reaction temperatures are needed, since the boiling point of TMU is 23 degrees Centigrade higher than that of dimethylformamide, which is normally used. TMU significantly accelerates the metallation of triphenylmethane with sodamide. Good yields of high purity have been achieved in the alkylation of tertiary heterocyclic amines in TMU. TMU has been used as a component of solvent systems for paper chromatography. A possible use of TMU is in the analysis of proteins, since amino acids and their derivatives have significant differences in solubility.

Hexamethylphosphoramide

Hexamethylphosphoramide (tris(dimethylamino)phosphine oxide, HMPT, HMPA) is the best electron donor and polar aprotic solvent of all the common aprotic solvents, including TMU [6]. Some physical properties of HMPA are listed in Table 2. A pyrimidal molecule, HMPA has a large dipole moment and high basicity (electron-donating ability) which are caused by the symmetrical distribution of positive charge over the N_3P grouping and the high electron density on the oxygen atom.

Table 2. Physical properties of HMPA [6].

Structure	
Molecular formula	C ₆ H ₁₈ N ₃ P O
Molecular weight	179.20
Boiling point (C)	235 (1 atm)
Melting point (C)	7.20
Density, 20 C/4 C	1.0253
Dynamic viscosity	3.5 cS (60 C)
Dielectric constant	30 (20 C)
Dipole moment (Debye)	5.37 (25 C)
Vapor pressure	0.07 mm (30 C)

HMPA is miscible with water in all proportions and with many polar and nonpolar organic solvents, but not with saturated hydrocarbons [6]. Unsaturated hydrocarbons, phenols and diphenols, alcohols and aromatic amines, glycols, and mono- and dicarboxylic acids react with HMPA to form stable crystalline stoichiometric complexes, some with melting points up to 200 degrees Celsius. HMPA also forms complexes

with metal salts and chlorinated solvents. Alkali metal salts have very good solubilities in HMPA. HMPA dissolves alkali metals (Li, Na, K) by accepting an electron to form a paramagnetic solution that contains radical-anions. Bronsted and Lewis acids react with HMPA. An acid, H+A-, causes A to replace one or more N(CH₃)₂ groups. Normant [6] proposed a mechanism involving a 1:1 complex of the acid, HA, hydrogen bonded to the oxygen atom of HMPA.

Since it is one of the most powerful cation-solvators known [7], HMPA has been used as a solvent for electrolysis. Due to the sterically easy accessibility of the negatively-polarized oxygen atom, cations are strongly solvated while the steric hindrance around the positively-polarized phosphorus atom prevents significant anion solvation [6]. However, reactions involving anions, such as bimolecular elimination and bimolecular nucleophilic substitution, are accelerated by HMPA since anion reactivity is increased in the polar aprotic solvent. Good yields of substitutions of bromo-, chloro-, and fluorobenzenes with mercaptans, secondary amines, and phenylacetylenes have been achieved under mild conditions in HMPA. Hydrocarbon derivatives, R'X', in which the halogen atom X' is very firmly bound will react with Grignard compounds RMgX only in HMPA. Metal ketyls are synthesized readily in HMPA. The metallation of acids as weak as toluene with alkali metal occurs in HMPA. Organometallic compounds of cadmium, magnesium, tin, and zinc can be

directly synthesized from the metals and alkyl halides in HMPA. Addition of a small amount of HMPA accelerates the formation of carbodiimides from isocyanates. The rate of substituent exchange between trialkylboranes and 1-alkenes is increased in HMPA. Dismutation of chlorosilanes occurs at low temperatures in the presence of 0.5 to 15% of HMPA. Excellent yields in alkylations and moderate yields in acylation and carboxylation reactions are obtained with HMPA as the solvent. HMPA has been used as a Lewis base with polymerization catalysts. HMPA is used as an electron-transfer agent in the dimerization of styrene and alpha-methylstyrene.

Ouchi et al. [8] reduced eight coals by HMPA-sodium-t-butylalcohol at room temperature and atmospheric pressure. After reduction, more than 70 weight percent of the coal was soluble in pyridine; the maximum solubility (90 weight percent) was exhibited by coals having about 88 weight percent carbon content. The pyridine-soluble material had a higher H/C ratio (the carbon content slightly lower, the oxygen content slightly higher and the hydrogen content almost double that of the original coal), was richer in aliphatic and olefinic structures, and had aromatic ring structures that were extensively saturated after reduction. Ouchi et al. theorized that hydrogenation in coal occurred by the splitting of ether linkages or reduction of quinone and carbonyl groups, where t-BuOH may be source of hydrogen.

Wooton et al. [9] obtained nuclear-magnetic-resonance data indicating that HMPA-soluble solvent-refined coal (86.0% carbon, 5.0% hydrogen, 2.3% nitrogen) is approximately 95% aromatic in character. A heteroatom such as nitrogen or sulphur is believed to be incorporated in some of the aromatic structures.

Sternberg and Donne [10] discovered only 3 percent of Pocahontas (low volatile bituminous) coal was soluble in HMPA while 90 percent was soluble in a solution of lithium in HMPA. HMPA by itself is a poor solvent for coal even though other solvents such as dimethylsulphoxide and N-methyl-2-pyrrolidone belonging to the same class of dipolar aprotic solvents as HMPA are proven to be good coal solvents. The increased solubility with the addition of lithium is believed to be due to the formation of readily solvated aromatic anions produced by the transfer of electrons from lithium to the aromatic nuclei in coal. This "coal anion" intermediate readily reacts with alkylating agents, converting coal into a benzene-soluble material.

Hombach [11] treated coals of different rank with a selection of common solvents, including HMPA. Although the solubilities of the coals in the pure solvents were low, Hombach observed mixtures of the solvents with enhanced dissolving power. Similar results were observed by Reilly as cited by Kiebler [12] and Rybicka [13]. Data [12] indicate that the successive extraction of coal with two or more

solvents of different solvent power will result in the same yield as would be achieved by the better solvent alone. HMPA was found to be relatively ineffective as both a coal solvent and a reducing medium [11]. It was postulated that this behavior is due to "the poor chemical stability of this reagent since the elemental analysis of the reduced coal gives evidence for incorporation of solvent fragments". However, Hombach did not elaborate as to the nature of the evidence.

TMU vs. HMPA

Since TMU and HMPA belong to the same class of polar aprotic solvents, many physical and chemical characteristics of the solvents are comparable. Similar properties of TMU and HMPA include the following [2, 5, 6]:

- (i) $N(CH_3)_2$ groups are symmetrically arranged about a core atom.
- (ii) The oxygen atom bonded to the core atom has a high electron density while a positive charge is distributed over the core atom and the nitrogen atoms.
- (iii) TMU and HMPA are miscible with many polar and nonpolar organic and inorganic solvents.
- (iv) Since the positive charge density is shielded by the methyl groups and the electron density is exposed, the solvents are good electron donors.

(v) Cations are strongly solvated while the steric hindrance around the positive charge density prevents significant anion solvation.

(vi) Reactions involving anions (e.g., bimolecular nucleophilic substitution and bimolecular elimination reactions) are accelerated by the solvents.

(vii) The solvents are hydrogen-bond acceptors and electron acceptors and donors but not hydrogen-bond donors or hydrogen donors.

(viii) In the presence of Bronsted or Lewis acids, protonation of HMPA occurs by the replacement of one or more $N(CH_3)_2$ groups; protonation of TMU occurs either on the nitrogen or oxygen atom.

(ix) Both solvents are inert to organomagnesium compounds and alkali metal amides and hydrides.

The effectiveness of TMU relative to HMPA has been studied [6]. The major differences between the solvents are as follows:

(i) Since the electron density on the oxygen atom of HMPA is higher than that of TMU, HMPA is a more effective electron donor, hydrogen-bond acceptor, cation solvator, and accelerator of reactions involving anions.

(ii) HMPA is not miscible with saturated hydrocarbons.

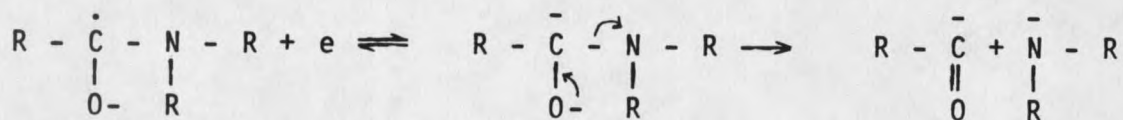
(iii) HMPA is noted to form complexes with both organic and inorganic solvents while relatively little mention in the literature is made of similar behavior with TMU.

(iv) Attack by nucleophiles and bases can fragment TMU while HMPA is rarely disrupted. Nucleophiles, B-, introduced or produced during a reaction attack the positively-polarized carbon atom that can result in the removal of amide ions from TMU. These amide ions then compete with the nucleophile in addition, substitution, and autoxidation reactions. Since phosphoramides are much more stable than amides of carboxylic acids, the presence of nucleophiles rarely disrupts HMPA. The steric hindrance around the positively-polarized phosphorus atom makes HMPA stable to nucleophiles, and HMPA is not hydrolysed in alkaline media unlike TMU, making HMPA an ideal solvent for reactions with nucleophilic or basic reactants. HMPA is superior to other polar aprotic solvents as an autoxidation medium because of its stability to bases, unlike amides and lactams, and its inability to form carbanions, therefore not autoxidizing itself. Although the strongly basic organometallic compounds of alkali metals and KOH attack TMU, HMPA is not affected under typical reaction conditions. HMPA is more effective than TMU as a solvent for the isomerization of olefins. TMU and HMPA lose the hydrogen atoms beta to the polar group to bases only under extreme conditions.

(v) Acting as electron acceptors, TMU forms an unstable radical-anion that rapidly decomposes while the radical-anion of HMPA is considerably more stable. An electron donor, TMU can also act as an electron acceptor to become an

unstable radical-anion. Since the anion of TMU cannot be stabilized by charge delocalization, it rapidly decomposes into two ions (Figure 1). Although HMPA also decomposes when acting as an electron acceptor, the radical-anion of HMPA is much more stable than that of TMU, making HMPA the only known polar aprotic solvent that can be used for syntheses involving dissolved reactive metals.

Figure 1. Decomposition of the radical-anion of TMU.



Process Advantages

Whitehurst et al. [14] presented the following guidelines that should be considered in new or improved coal liquefaction technology:

- (i) The key to success of a process is hydrogen utilization efficiency.
- (ii) Solvents can be overhydrogenated.
- (iii) The optimal conditions and intrinsic selectivities for catalytic and thermal reactions are different.
- (iv) High conversion of coal to soluble products in the initial dissolution step is not necessary when hydrogen-rich liquids are the final product.

(v) Solids separation presents problems in the processes presently under development.

(vi) Temperatures are very high and reaction times are very long in these processes.

(vii) Denitrogenation is the most problematic and least understood reaction.

Based on these guidelines, the process developed by Sears [1] shows potential as a commercial process. Due to the absence of hydrogen overpressure and strong acids, solvent hydrogenation is unlikely in the dissolution step. Hydrogenation of the coal hydrocarbons in a separate hydrogenation reactor could reduce hydrogen requirements and would allow optimization of the dissolution and catalytic hydrogenation steps. The mild conditions of temperature and pressure used in Sears' process should result in easier solids separation than current processes.

Preliminary Experiments

Sears [1] obtained extraction values of 42% for high volatile bituminous Sewickley coal with TMU and 62% for medium volatile bituminous Bakerstown coal with HMPA by Soxhlet extraction. Simple extraction at room temperature on Bakerstown coal using a 1:1 mixture of TMU and HMPA resulted in a 57% loss in weight. Minimum colloidal organic micelle formation occurred when a 1:1 mixture of TMU and HMPA was used as solvent. It is believed [1] that this

behavior could correlate with the tendency of the dissolution products to initially have high oxygen content, as observed by the Union Carbide Corporation and cited by Sears, forming functional groups that are likely to prefer separate phases of oil and solvent. Sears postulated that the solvents "stabilize the products by modification of the solvent cage to accommodate the dissolved molecule in a stable configuration".

Mechanisms of Coal Liquefaction

Although many coal conversion mechanisms have been proposed to describe direct liquefaction processes, most investigators adopt one of three initial coal depolymerization processes. Depolymerization involves breaking bonds in the insoluble coal, destroying the coal macromolecules to produce soluble products. For high-temperature processes, thermal depolymerization is usually the depolymerization mechanism proposed. During thermal depolymerization, the thermal energy exceeds the strengths of some coal bonds, causing the bonds to cleave homolytically to produce a radical pair. The free radicals then abstract hydrogen atoms from either a hydrogen donor present in the solvent or from a donor group which is part of the coal to become stable compounds of lower molecular weight than the original coal. Continuing thermal cleavage of coal bonds produces soluble

fragments which react further. The solvent is a heat-transfer medium and may supply hydrogen to the reactions. However, the depolymerization rate is almost independent of the solvent since homolytic cleavage produces uncharged intermediates which are not affected considerably by the solvent.

Another depolymerization mechanism commonly proposed for high-temperature processes is the thermal cleavage of coal bonds followed by a radical chain mechanism. The depolymerization rate may be dependent on the donor-solvent concentration. Larsen [15] cites Heredy who concluded that the rate-determining step for product formation involved hydrogen by observing a deuterium-isotope effect on the amount of products formed using tetralin, a hydrogen donor. However, a reasonable radical-chain mechanism can not be proposed when the solvent is not a hydrogen donor. Since homolytic processes are not dependent on the concentration of non-hydrogen donor solvents, data indicate that an alternate process occurs involving the non-hydrogen donor solvent in the rate-determining step.

Larsen [15] is currently investigating a competitive depolymerization mechanism which is consistent with observed data: depolymerization by direct solvent attack on covalent bonds in the coal (solvolysis). During solvolysis, a solvent molecule participates in the transition state of the

reaction. A charged intermediate may or may not be involved. Since the transition state is more highly charged than the coal and solvent (assuming that a neutral solvent molecule attacks a bond in the coal), the reaction should be sensitive to the overall polarity of the solvent, in addition to its ability to chemically attack. The belief that depolymerization of coal may be due at least in part to direct solvent attack is based on the following observations: (i) the strong dependence of the extent of depolymerization on the solvent concentration, (ii) the high conversion of coals to soluble products at temperatures too low for thermolytic bond cleavage to be the major depolymerization mechanism, (iii) the decrease in conversion with decreasing solvent basicity and nucleophilicity, and (iv) the probable covalent bonding of solvents to both soluble and insoluble coal products. Details of the cited evidence is presented in the following:

(i) Larsen proposed the solvolysis process after observing the dependence of the conversion of coals to soluble products on the concentration of pyridine or phenol. The extent of solvolytic depolymerization of coals in pyridine or phenol was also found to be strongly dependent on the coal rank; bituminous coals exhibited much higher extraction values than subbituminous coals.

(ii) According to Atherton and Kulik [16], homolytic cleavage should not occur in processes with temperatures at or

below 550 - 700 degrees Fahrenheit. Previous investigators [12, 17, 18, 19, 20, 21] have found significant extents of extraction of coals in a variety of solvents at relatively low temperatures which can not be rationalized by homolytic, thermal bond cleavage.

(iii) Consistent with solvolytic depolymerization principles, coal conversion was found to be enhanced when the solvent used has an available electron pair [15]. Indole, similar to pyridine but having a less accessible electron pair on nitrogen in the pi system, gives much lower coal conversions than pyridine. Chemical bonding between some oxygen-containing group and the unshared electron pair in the solvent is assumed to occur [22]. Kiebler [12] observed that solvents with unshared pairs of electrons, especially amine bases, are often so effective in depolymerizing coal that solvolytic bond cleavage must be occurring. Analysis of coal extracts indicated that the extracts originated as a result of both thermal and solvent depolymerization of the coal. Some solvents (e.g. pyridine) incited a process of peptization or colloidal dispersion of the coal in addition to producing apparently soluble coal products; solvolytic depolymerization of coal was thought to probably occur when an extract contains a mixture of organic compounds including highly complex, high-molecular weight molecules and colloids.

(iv) Treating coals with amines at 73 - 520 degrees Fahrenheit, Collins et al. [23] found amines bonded to both the coal extracts and residues. While bound 14C-labeled pyridine can be exchanged with unlabeled pyridine, 14C-labeled tetrahydroquinoline (THQ) bound to the coal products can not be exchanged with unlabeled THQ. From these observations, Collins et al. speculated that the THQ is covalently incorporated while Atherton and Kulik [16] went further to hypothesize that THQ participates in the chemical reactions in which covalent bonds of coal are broken.

Effect of Physical Properties of Solvents on Liquefaction

Extensive research has been performed to determine which, if any, solvent properties reflect the effectiveness of the solvent in coal extraction. No singular physical property of solvents can adequately account for the interactions between coal and solvent [19, 22]. The physical properties most often considered as a criterion for solvent effectiveness are surface tension [12, 24, 25] and internal pressure [12, 22, 26]. Internal pressure is defined as

$$\text{Internal pressure} = P_i = \frac{(\Delta H_v - RT)\rho}{m} = \frac{\Delta E}{V} \quad (1)$$

where m is the molecular weight of the solvent, ρ is the density, ΔH_v is the latent heat of vaporization, V is the molecular volume, and ΔE is the energy of vaporization per

mole. By comparing coal conversion results obtained by several investigators, Kiebler [12] cites Kreulen et al. who observed a tendency of enhanced yield with solvents having high values of surface tension. However, since the data compiled were obtained by various experimental procedures on dissimilar coals, the theory of yield dependence on surface tension is insufficiently based [12]. Kiebler [27] attempted to determine a relation between the yield of coal extract and the physical and chemical nature of solvents. Statistical analyses were made of yields of extract obtained from 150 to 300 degrees Celsius and various physical properties of the solvent, including surface tension at room temperature and that extrapolated to the extraction temperature, internal pressure, dipole moment, dielectric constant, latent heat of vaporization at the boiling point of the solvent and at the extraction temperature, refractive index, specific refraction, and molecular volume. Based on correlation coefficients, the internal pressure of a solvent has the most significant correlation to yield; this relationship can be expressed as $Y = a + bP_i$ where a and b are constants dependent on temperature. Kiebler noted that although the internal pressure is not the sole factor which determines solvent power, the equations relating yield and internal pressure and temperature do support the theory of yield dependence on the extent of both thermal depolymerization and solvolysis. However, for coal extraction systems

operating at temperatures below the normal boiling point of the solvent, no correlation exists between yield and surface tension and the relationship between yield and internal pressure was determined to be inapplicable [18, 20, 28]. Thus, no single or combination of physical properties of solvents has been found to reflect solvent power in coal conversion systems operating under similar conditions of moderate temperature and pressure as those considered in this investigation.

Effect of Chemical Structure of Solvents on Liquefaction

Investigations on the effect of the chemical structure of solvents on extraction have produced substantial results. Dryden [22] observed that both the yield and nature of the coal extract are affected by the coal composition and extraction conditions, as well as the chemical nature of the solvent. Dryden determined that the best specific solvents for coal have structures containing a nitrogen atom with an available unshared pair of electrons. Solvents of this chemical nature were found to consistently swell the coal. Since solvent power is associated with the accessibility of the unshared electron pair to interact with the coal, interfering influences such as excessive hydrogen bonding [29] and participation of the lone pair in resonance of the molecular nucleus [20] are undesirable. Although many investigators believe that the electron-donor character of a

solvent reflects solvent effectiveness in coal extraction, Marzec et al. [18] compiled data indicating that the electron-acceptor property of the solvent is of the same order of importance as its electron-donor property in influencing coal conversion.

Effect of Coal Rank on Liquefaction

In conjunction with the chemical nature of the solvent, the coal rank dictates solvent effectiveness. Dryden [22] observed that the yield of extract decreases rapidly as the coal rank increases from 85 to 89% carbon and becomes negligible beyond 92 to 93% carbon. However, the trend of soluble coal content with rank also depends on the solvent; some solvents such as pyridine produce a maximum yield in the bituminous range (ca. 80 to 93% carbon [26, 30]) while others such as ethylenediamine exhibit a steadily decreasing yield with increasing rank through this range. As discussed previously, HMPA-sodium-t-butylalcohol produces a maximum yield with coals having about 88 weight percent carbon content [8]. Based on conversion results, Wen and Lee [30] cited Fisher et al. who determined that high volatile bituminous coals appear to be the most desirable rank for coal liquefaction processes. Whitehurst et al. [14] also noted the advantage of low hydrogen requirement for high yields when using bituminous coals. Occasionally, the relative solvent power of two solvents may be reversed by

changing the type of coal treated [31]. However, rank alone does not dictate coal reactivity. Catalytic effects of mineral matter aid coal liquefaction. Specifically, pyrite or pyrrhotite (a nonstoichiometric mineral produced by the reduction of pyrite) is commonly believed to cause catalytic activity although ion-exchangeable iron may have catalytic properties [14].

Influence of Coal Pretreatment on Liquefaction

Coal pretreatment also affects the yield of soluble products. Clark and Wheeler [32] preheated two bituminous coals before extraction with cold solvent for enhanced yields. However, thermal pretreatment of a different bituminous coal by Whitehurst et al. [14] resulted in decreased conversion. Once degradation or retrogression of the coal has occurred, it can not be reversed even with extreme liquefaction conditions [16]. Drying coal in an inert atmosphere to slightly over 212 degrees Fahrenheit may promote reactions, although predominantly with low-ranked coals [14]. Oxidation of coal by exposure to air at temperatures up to 212 degrees Fahrenheit influences the amount of obtainable extract [22]. Although oxidation typically lowers the maximum yield when using benzene or pyridine as solvent, it is unlikely that a single rule applies to all cases since the effect of oxidation depends on the primary oxidation products and the solubility of coal.

Influence of Extraction Conditions on Liquefaction

Extraction conditions can counter efforts to maximize coal conversion. The presence of oxygen in the extraction apparatus tends to decrease the yield obtained [12, 22]. In the absence of catalyst, hydrogen will not appreciably react with high volatile bituminous coal at temperatures below 500 degrees Celsius [30]. During extraction, faster rates of coal conversion are obtained when the coal and solvent system is agitated [22]. However, excessive shaking sometimes reduces yield [21]. Guin et al. [cited in 14, 33] have observed that stirring rate affects the breakage of the coal particles. Due to the quick disintegration of the particles, the internal pore volume becomes insignificant in a rapidly-stirred reactor. Although numerous investigators have examined coal-particle-size effects on coal conversion and the possible importance of mass transport limitations, the results are inconsistent. Based on a literature survey, Whitehurst et al. [14] cited Kloepper et al. who considered particle size to be a variable of secondary importance. Extracting bituminous coals of 72 to 240 mesh B.S.S. with amines at room temperature and near the boiling point of the solvent, Dryden [22] found that yield tended to increase with decreasing particle size. Examining the benzene-pressure extraction of coal at temperatures between 428 and 560 degrees Fahrenheit, Asbury [34] also observed enhanced yields when using coal ground further to micron size. Using

a micro-autoclave, Curran et al. [35] studied the kinetics of coal conversion with hydrogen donor solvents in the temperature range of 715 to 825 degrees Fahrenheit. Yields from runs with 28 to 48 mesh particles were identical to those from corresponding runs using 100 to 200 mesh particles. From short contact time runs (less than two minutes) at 800 to 850 degrees Fahrenheit using hydrogen-donor solvents on coals sized from 45 to 600 microns, Whitehurst et al. [14] observed little, if any, effect of particle size on coal conversion behavior. Intraparticle mass transport limitations were concluded to appear insignificant in coal liquefaction systems using hydrogen-donor solvents. Also, no effect of coal particle size on the chemistry of coal conversion was observed. Within the particle size range generally used, Lee [30] stated that the rate of coal extraction is independent of particle size. Whitehurst et al. [14] cited Anderson et al. who investigated the extraction of a high volatile bituminous coal in tetralin with the influence of ultrasonic energy under mild conditions of temperature (117 - 189 degrees Fahrenheit). Although the ultimate yields were identical, a faster initial extraction rate was observed with 220 to 270 mesh particles than with 40 to 60 mesh particles. Similar results were noted by Kiebler as cited by Hoffman [26]. Using a rocking bomb autoclave, Whitehurst et al. [14] cited Jenny who examined coal conversion in tetralin under

hydrogen overpressure. As particle size decreased from 40 to 100 mesh to -325 mesh, decreasing yields were observed. However, the tendency of increasing wetting resistance with decreasing particle size was noted as a factor, which would produce lower yields than could be observed with a better agitation system. Considering the findings of these investigators, no apparent trend is consistently observed that would imply mass transport limitations on coal conversion. Any particle size effect is probably due to variations in mineral or maceral contents of the size ranges caused by grinding and sizing or to differences in the conversion procedures [14].

Research Objective

The purpose of this thesis is to examine coal conversion behavior through extraction by tetramethylurea and hexamethylphosphoramide under atmospheric pressure and temperatures below the boiling points of the solvents. The results obtained will be used as a basis by co-investigators for additional studies aimed at optimizing the extraction process in order to ultimately assess the process potential.

EXPERIMENTAL

Resources

TMU and HMPA, both 99% pure, were supplied by the Aldrich Chemical Company. Acetone, 98% pure, was supplied by the Aldrich or Bakers Chemical Company. High volatile bituminous Kittanning coal chunks, recently mined, were obtained from Dr. Stiller at West Virginia University; specifications were not available. The choice of coal to be used in this investigation was based on preliminary dissolution experiments using several bituminous coals. Only Kittanning coal significantly dissolved in the solvents. A Kittanning coal chunk, approximately 7" x 5" x 5", was ground, sized to 150 - 200 Tyler mesh, dried at 100 - 105 degrees Celsius overnight, then stored in a dessicator purged with nitrogen. Cylinders of 99.9% pure (commercial grade) nitrogen were filled by Western Welding. Elemental analyses and ash contents of the three grinding batches that were used are listed in Table 3. Although the ash contents are quite different, the elemental contents of the three batches on a moisture- and ash-free basis are similar. Micro ultimate analyses were performed by Mr. Timothy L. Ward with a Carlo Erba Model 1100 Elemental Analyzer, a Carlo Erba DP110 integrator, and an Osborne 1 computer at

