



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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ON THE DISSOLUTION OF COAL

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A thesis submitted in partial fulfillment
of the requirements for the degree

of
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in
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APPROVAL

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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.

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TABLE OF CONTENTS

| | Page |
|--|------|
| 1. LIST OF TABLES | vii |
| 2. LIST OF FIGURES | viii |
| 3. ABSTRACT | ix |
| 4. INTRODUCTION | 1 |
| Tetramethylurea | 1 |
| Hexamethylphosphoramide | 6 |
| TMU vs. HMPA | 11 |
| Process Advantages | 14 |
| Preliminary Experiments | 15 |
| Mechanisms of Coal Liquefaction | 16 |
| Effect of Physical Properties of Solvents on Liquefaction | 20 |
| Effect of Chemical Structure of Solvents on Liquefaction | 22 |
| Effect of Coal Rank on Liquefaction | 23 |
| Influence of Coal Pretreatment on Liquefaction | 24 |
| Influence of Extraction Conditions on Liquefaction | 25 |
| Research Objective | 27 |
| 5. EXPERIMENTAL | 28 |
| Resources | 28 |
| Procedure | 29 |
| 6. RESULTS | 32 |
| Extraction Results | 32 |
| Retention Results | 47 |
| H/C and O/C Results | 66 |
| 7. DISCUSSION | 68 |
| 8. SUMMARY | 83 |
| 9. REFERENCES CITED | 85 |

TABLE OF CONTENTS -- Continued

| | Page |
|---|------|
| APPENDICES | 89 |
| Appendix A - Raw data | 90 |
| Appendix B - Raw results | 93 |
| Appendix C - Equation derivations | 97 |
| Derivation of Equation (4) | 98 |
| Derivation of Equation (5) | 100 |

LIST OF TABLES

| | Page |
|---|------|
| 1. Physical properties of TMU | 2 |
| 2. Physical properties of HMPA | 7 |
| 3. Kittanning coal chunk analyses | 29 |
| 4. Effect of startup procedure on dissolution | 33 |
| 5. Coal dissolution results | 36 |
| 6. Residue ashing results | 38 |
| 7. TMU retention results | 49 |
| 8. Total solvent retention assuming 1:1 solvent incorporation | 53 |
| 9. HMPA retention assuming 1:1 solvent incorporation | 54 |
| 10. TMU retention assuming 1:1 solvent incorporation | 55 |
| 11. Total solvent retention based on phosphorus data | 56 |
| 12. HMPA retention based on phosphorus data | 57 |
| 13. TMU retention based on phosphorus data | 57 |
| 14. Raw data for TMU runs | 91 |
| 15. Raw data for TMU+HMPA runs | 92 |
| 16. Raw results for TMU runs | 94 |
| 17. Raw results for TMU+HMPA runs assuming 1:1 solvent incorporation | 95 |
| 18. Raw results for TMU+HMPA runs based on phosphorus data | 96 |

LIST OF FIGURES

| | Page |
|---|------|
| 1. Decomposition of the radical-anion of TMU | 14 |
| 2. Dissolution apparatus | 30 |
| 3. Apparent dissolution vs. time | 40 |
| 4. Apparent dissolution vs. short-contact time | 41 |
| 5. Actual dissolution vs. time | 42 |
| 6. Actual dissolution vs. short-contact time | 43 |
| 7. Dissolution based on ash tests vs. time | 45 |
| 8. TMU retention vs. time for TMU runs | 50 |
| 9. TMU retention vs. dissolution for TMU runs | 52 |
| 10. Total retention vs. time | 58 |
| 11. Total retention vs. dissolution | 59 |
| 12. HMPA retention vs. time | 61 |
| 13. HMPA retention vs. dissolution | 62 |
| 14. TMU retention vs. time | 63 |
| 15. TMU retention vs. dissolution | 64 |
| 16. Ionic mechanism of coal reduction | 79 |
| 17. TMU as a hydride transfer agent | 79 |

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.

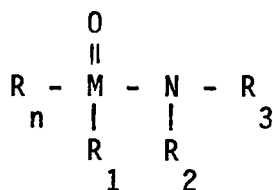
Coal conversion to 41% was achieved using a 1:1 mixture of the solvents for 40 minutes at 320 degrees Fahrenheit. The maximum dissolution using pure TMU, 23%, was observed after 12 hours at 320 degrees Fahrenheit. Pure HMPA as the solvent produced a colloidal suspension that blocked separation of residue 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 ₅ H ₁₂ N ₂ O |
| 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.

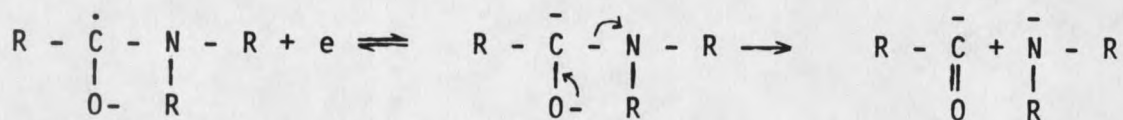
(iii) HMPA is noted to form complexes with both organic and inorganic solvents while relatively little mention in the literature is made of similar behavior with TMU.

(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

Montana State University. Phosphorus analyses were performed by Guelph Chemical Laboratories Ltd. at Guelph, Ontario. The dissolution apparatus consisted of a 500 milliliter Erlenmeyer flask, a Cenco hotplate/magnetic stirrer, a condenser, and a 20 - 680 degrees Fahrenheit thermometer (Figure 2).

Table 3. Kittanning coal chunk analyses. *

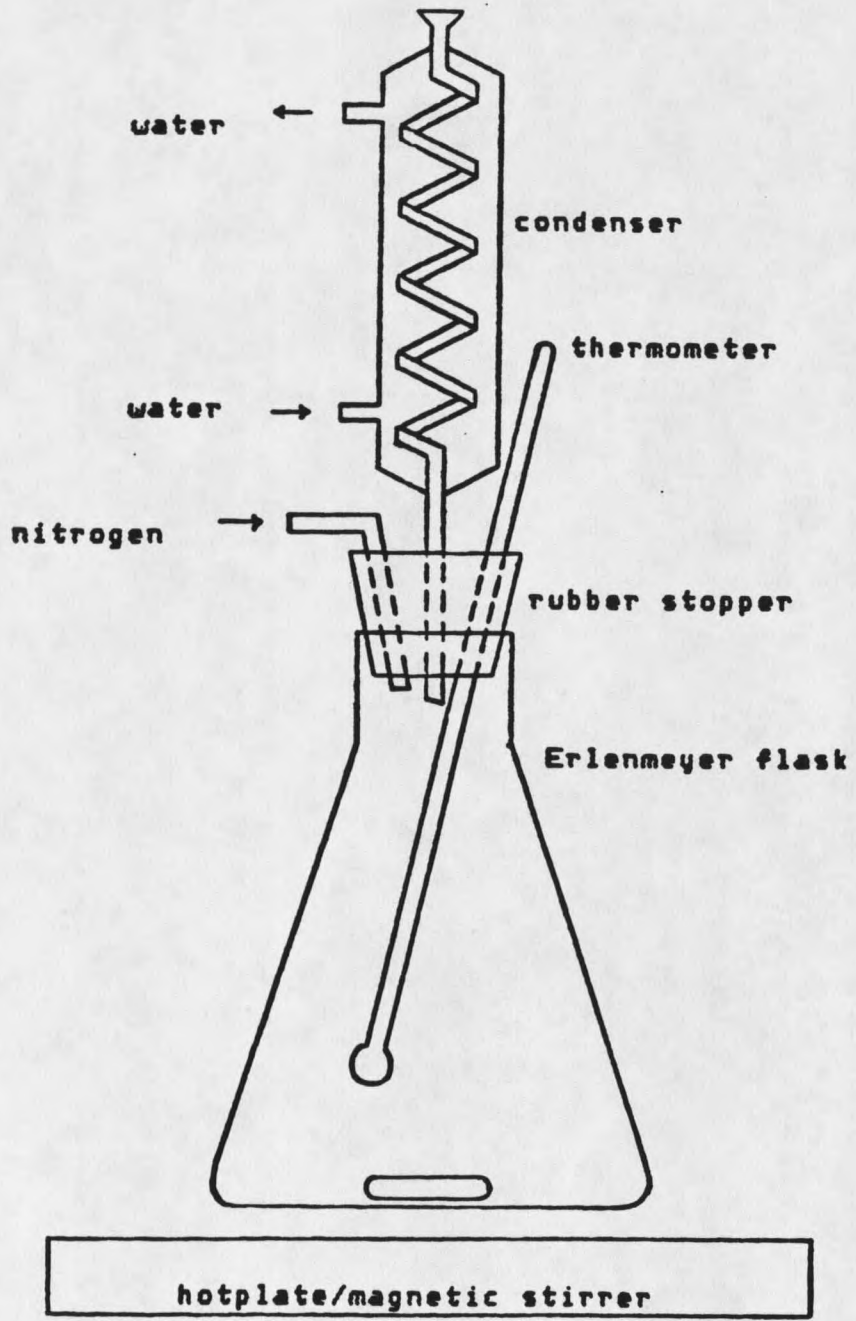
| Batch | % Ash | % N | % C | % H | % O | % P | Run numbers |
|-------|-------|----------------|------------------|----------------|----------------|----------------|-------------|
| 1 | 9.5 | 1.45 (1.31) | 84.13 (76.14) | 5.61 (5.08) | - | 0.06 (0.05) | 14 - 29 |
| 2 | 8.9 | 1.44 (1.31) | 85.47 (77.86) | 5.69 (5.18) | 6.30 (5.74) | 0.18 (0.16) | 30 - 35 |
| 3 | 13.9 | 1.45 (1.25) | 85.01 (73.19) | 5.68 (4.89) | - | - | 36 - 39 |

* Values in parentheses have a moisture-free (mf) basis; other values have a moisture- and ash-free (maf) basis.

Procedure

The batch reactor, purged with nitrogen and constantly agitated, contained 200 milliliters of solvent and three to four grams of coal. The solvent was TMU, HMPA, or a 1:1 (by volume) mixture of TMU and HMPA. Two startup procedures were attempted: (1) combining coal and solvent before heating the system to run temperature and (2) adding coal after preheating the system with solvent to run temperature. The

Figure 2 Dissolution apparatus.



temperature of the system was maintained to within +/- 5 degrees Fahrenheit of the desired run temperature, which was either 79, 200, or 320 degrees Fahrenheit. Higher run temperatures were not considered to avoid significant TMU loss by vaporization. Time and temperature were recorded at frequent intervals. Immediately after each run was over, the slurry was quenched and vacuum filtered, the liquid product was collected, and the residue was washed with acetone until the filtrate was clear. The residues were vacuum dried under about 0.1 torr in a dessicator attached to a mechanical pump for approximately one week until daily weighings indicated maximum weight loss had been attained. The residue was quickly weighed (due to the significant weight gain observed of the vacuumed residue on exposure to air) before being sampled for carbon, hydrogen, nitrogen, oxygen, phosphorus, and ash analyses. In the ash analyses, coals and residues were weighed in crucibles at room temperature before and after being ashed in a 700 degree Celsius oven for at least 24 hours.

RESULTS

Extraction Results

HMPA as the solvent produced with all of the coals tested an undesirable colloidal suspension or gel that greatly impeded filtration. Of the two startup procedures, the solvent-preheating method is preferred to the method of simultaneous heating of solvent and coal because in the latter method a lower dissolution was typically attained and an unpredictable time was needed for the system to reach the run temperature. Exemplary runs are given in Table 4 for comparison. For a run time of 20 minutes, considerably higher dissolution was obtained with preheated solvent than with simultaneous heating of solvent and coal, despite the additional 12 minutes of contact between solvent and coal in the latter run. Although actual dissolution values became similar after a run time of one hour, solvent preheating is still the preferred method because of the lower amount of solvent retained. The disadvantages of high solvent retention are discussed in the Retention Results section. Only after 12 hours did the method of simultaneous heating produce similar apparent dissolution and higher actual dissolution (but with almost twice the solvent retention) than corresponding values produced by the method of solvent

Table 4. Effect of startup procedure on dissolution.

| Solvent | Temp (F) | Heating Procedure | Run Time (min) | Heating time(min) | Apparent Diss (%) | Actual Diss (%) | Solvent Retention* | Run number |
|----------|----------|-------------------|----------------|-------------------|-------------------|-----------------|--------------------|------------|
| TMU+HMPA | 200 | solvent | 20 | + 0 | 7.4% | 11.6% | 0.069 | 19 |
| TMU+HMPA | 200 | solvent+coal | 20 | + 12 | 1.5% | 6.1% | 0.046 | 14 |
| TMU+HMPA | 200 | solvent | 60 | + 0 | 8.0% | 13.5% | 0.068 | 27 |
| TMU+HMPA | 200 | solvent+coal | 60 | + 10 | 4.7% | 12.6% | 0.079 | 12 |
| TMU+HMPA | 200 | solvent | 720 | + 0 | 20.5% | 27.9% | 0.074 | 34 |
| TMU+HMPA | 200 | solvent+coal | 720 | + 15 | 20.8% | 34.2% | 0.134 | 15 |

* Units of solvent retention are (g solvent/g maf coal).

preheating. Dissolution data were accumulated, therefore, using preheated TMU and a 1:1 preheated mixture of TMU and HMPA as solvent.

Apparent dissolution (ie., dissolution of coal accounting for moisture and ash but not solvent incorporation) was calculated from

$$\text{Apparent Diss. (\%)} = \frac{(\text{g coal-g wet residue})}{\left(1 - \frac{\text{g ash}}{\text{g coal}}\right) (\text{g coal})} \times 100 \quad (2)$$

assuming that i) drying the coal at 100 - 105 degrees Celsius removed all of the moisture without altering chemical bonds in the coal, ii) the actual ash content of the coal can be determined from the ashing method performed, and iii) acetone has no effect except to remove excess solvent from the residue. Wet residue refers to residue that is wet because of solvent incorporation. From the elemental analyses (Appendix A), the actual dissolution can be determined if these additional assumptions are valid: iv) whole solvent molecules are incorporated into the residue and v) the weight percents of nitrogen and phosphorus in the coal remain constant through the dissolution process so that any change in nitrogen and phosphorus content is due to incorporation of TMU and/or HMPA. Based on these assumptions, the elemental contents of dry (solvent-free) residues can be determined and are listed in Appendix B. For runs using TMU as solvent, the actual dissolution was calculated from

$$\text{Actual Diss. (\%)} = \frac{(\text{g coal} - \text{g dry residue})}{\left(1 - \frac{\text{g ash}}{\text{g coal}}\right) (\text{g coal})} \times 100 \quad (3)$$

where

$$\text{g dry residue} = \text{g wet residue}$$

$$x \left(\frac{\frac{\text{g N}}{\text{g solvent}}}{\frac{\text{g N}}{\text{g solvent}}} - \frac{\frac{\text{g N}}{\text{g wet residue}}}{\frac{\text{g N}}{\text{g coal}}} \right) \quad (4)$$

For runs using a 1:1 mixture of TMU and HMPA as solvent, the actual dissolution was calculated from Equation (3) where

$$\begin{aligned} \text{g dry residue} &= \text{g wet residue} \times \\ & \left[1 - \frac{(\text{g N/g wet res})}{(\text{g N/g TMU})} + \left(\frac{(\text{g N/g HMPA})}{(\text{g N/g TMU})} - 1 \right) \left(\frac{(\text{g P/g wet res})}{(\text{g P/g HMPA})} \right) \right] / \\ & \left[1 - \frac{(\text{g N/g coal})}{(\text{g N/g TMU})} + \left(\frac{(\text{g N/g HMPA})}{(\text{g N/g TMU})} - 1 \right) \left(\frac{(\text{g P/g coal})}{(\text{g P/g HMPA})} \right) \right] \end{aligned} \quad (5).$$

Apparent and actual dissolution results are listed in Table 5; Equations (4) and (5) are derived in Appendix C. Observing the expense of phosphorus analyses, only half of the runs using a 1:1 mixture of TMU and HMPA were analyzed for phosphorus content. All of the actual dissolution results from Equations (3) and (5) are similar to those based on a

Table 5. Coal dissolution results.

| Solvent | Temp (F) | Run time (min) | Apparent Diss (%) | Actual Diss (%) | Run number |
|---------|----------|----------------|-------------------|-----------------|------------|
| TMU | 79 | 60 | 5.3% | 5.4% | 21 |
| TMU | 79 | 60 | 2.9% | 3.1% | 35 |
| TMU | 79 | 720 | 2.4% | 5.2% | 22 |
| TMU | 79 | 2880 | 4.7% | 5.7% | 31 |
| TMU | 200 | 20 | 8.4% | 13.1% | 39 |
| TMU | 200 | 40 | 12.4% | 18.3% | 38 |
| TMU | 200 | 60 | 3.7% | 9.9% | 23 |
| TMU | 200 | 720 | 9.1% | 15.2% | 24 |
| TMU | 200 | 2880 | 15.5% | 21.2% | 30 |
| TMU | 320 | 20 | 10.5% | 16.9% | 25 |
| TMU | 320 | 720 | 16.2% | 22.8% | 26 |
| TMU | 320 | 2880 | 10.1% | 19.3% | 32 |

| Solvent | Temp (F) | Run time (min) | Apparent Diss (%) | Actual Diss(%)# | Actual Diss(%)+ | Run number |
|----------|----------|----------------|-------------------|-----------------|-----------------|------------|
| TMU+HMPA | 79 | 75 | 0% | - | 2.1% | 16 |
| TMU+HMPA | 79 | 735 | 2.6% | - | 4.2% | 17 |
| TMU+HMPA | 79 | 2880 | 6.7% | 8.0%* | 8.0% | 33 |
| TMU+HMPA | 200 | 20 | 7.4% | - | 11.6% | 19 |
| TMU+HMPA | 200 | 60 | 8.0% | 13.6%* | 13.5% | 27 |
| TMU+HMPA | 200 | 720 | 20.5% | 27.8% | 27.9% | 34 |
| TMU+HMPA | 200 | 2880 | 1.4% | 23.9% | 23.7% | 29 |
| TMU+HMPA | 320 | 10 | 21.5% | - | 40.2% | 37 |
| TMU+HMPA | 320 | 20 | 18.2% | 33.9% | 33.7% | 20 |
| TMU+HMPA | 320 | 40 | 20.6% | - | 41.2% | 36 |
| TMU+HMPA | 320 | 720 | 15.2% | 30.0%* | 29.4% | 28 |

Based on nitrogen and phosphorus analyses.

+ Based on nitrogen analyses and assuming 1:1 solvent incorporation.

* Data indicate negative TMU incorporation into the residue.

1:1 (by volume) solvent-incorporation assumption, which will now be adopted for those runs using both solvents.

Dissolution values based on ashing results as well as elemental analyses were calculated from Equation (3) where

$$\begin{aligned} \text{g dry residue} = & \text{g coal} \times \left(\frac{\text{g dry residue}}{\text{g wet residue}} \right) \\ & \times \left(\frac{(\text{g ash})/(\text{g coal})}{(\text{g ash})/(\text{g wet residue})} \right) \end{aligned} \quad (6)$$

and are listed in Table 6. Runs using pure TMU as solvent consistently produced ashes of a lavender hue very similar to that of the coal. However, phosphorus analyses and the unique colors of the ashes from the higher-temperature runs using a 1:1 mixture of the solvents indicated that the HMPA incorporated into the residues did not completely combust (up to 21 weight percent phosphorus was present in the ashed residue). Also, duplicate runs ashing approximately one gram of residue did not consistently have similar dissolution results. Therefore, there is doubt that the ashing technique used adequately represents the true ash content of the residues. These complications force the dissolution results based on ash tests to be considered secondary to the dissolution results based on weighing the coal and residue and back-calculating the net weight loss.

Table 6. Residue ashing results.

| Solvent | Temp (F) | Run time (min) | Dissolution (sample 1,2) | Ash color (major/minor) | Run number |
|---------|----------|----------------|--------------------------|-------------------------|------------|
| TMU | 79 | 60 | 0%, 6% | Lavender/grey | 21 |
| TMU | 79 | 60 | 0%, 0% | Lavender | 35 |
| TMU | 79 | 720 | 0%, 0% | Lavender | 22 |
| TMU | 79 | 2880 | 0%, 3% | Lavender/orange | 31 |
| TMU | 200 | 20 | - | - | 39 |
| TMU | 200 | 40 | - | - | 38 |
| TMU | 200 | 60 | 0%, 0% | Lavender/grey | 23 |
| TMU | 200 | 720 | 0%, 4% | Lavender | 24 |
| TMU | 200 | 2880 | 7%, 16% | Lavender/orange | 30 |
| TMU | 320 | 20 | 8%, 20% | Lavender | 25 |
| TMU | 320 | 720 | 15%, 16% | Lavender | 26 |
| TMU | 320 | 2880 | 12%, 18% | Lavender/grey | 32 |

| Solvent | Temp (F) | Run time (min) | Dissolution (sample 1,2) | Ash color (major/minor) | Run number |
|----------|----------|----------------|--------------------------|-------------------------|------------|
| TMU+HMPA | 79 | 75 | 0%, 0% | Lavender | 16 |
| TMU+HMPA | 79 | 735 | 0%, 4% | Lavender | 17 |
| TMU+HMPA | 79 | 2880 | 3%, 7% | Lavender/orange | 33 |
| TMU+HMPA | 200 | 20 | 9%, 11% | Lavender/grey | 19 |
| TMU+HMPA | 200 | 60 | 13%, 20% | White/purple | 27 |
| TMU+HMPA | 200 | 720 | 26%, 38% | White/purple | 34 |
| TMU+HMPA | 200 | 2880 | 44%, 45% | White/purple | 29 |
| TMU+HMPA | 320 | 10 | - | - | 37 |
| TMU+HMPA | 320 | 20 | 44%, 45% | White | 20 |
| TMU+HMPA | 320 | 40 | - | - | 36 |
| TMU+HMPA | 320 | 720 | 62%, 63% | Blue-green | 28 |

Apparent dissolution results are illustrated in Figures 3 and 4. The maximum apparent extraction, 21.5%, is achieved with a 1:1 ratio of the solvents at the highest temperature considered (320 degrees Fahrenheit) in ten minutes. The maximum apparent dissolution for runs using TMU as solvent, 16.2%, is observed at the same temperature but after 12 hours. Actual dissolution results assuming a 1:1 ratio of solvent incorporation for runs using a mixture of TMU and HMPA are illustrated in Figures 5 and 6. As expected, dissolution and initial dissolution rate tend to increase with increasing temperature. At room temperature, dissolution proceeds similarly for both sets of solvent runs. However, at 200 and 320 degrees Fahrenheit, dissolution is significantly increased by the presence of HMPA. The maximum dissolution attained, 41.2%, is achieved using a 1:1 ratio of the solvents for 40 minutes at 320 degrees Fahrenheit; the run exhibiting the maximum apparent dissolution of 21.5% has an actual dissolution of 40.2%. Using TMU as solvent, the maximum dissolution attained, 22.8%, is observed at 320 degrees Fahrenheit after 12 hours. Both apparent and actual dissolution appear to reach a maximum within 12 hours at 320 degrees Fahrenheit using pure TMU as solvent and at 200 and 320 degrees Fahrenheit using a 1:1 mixture of the solvents. Maximum dissolution is achieved at shorter times with increasing temperatures. The 1:1 mixture of TMU and HMPA as solvent is more effective than pure TMU in dissolving coal.

Figure 3. Apparent dissolution vs. time

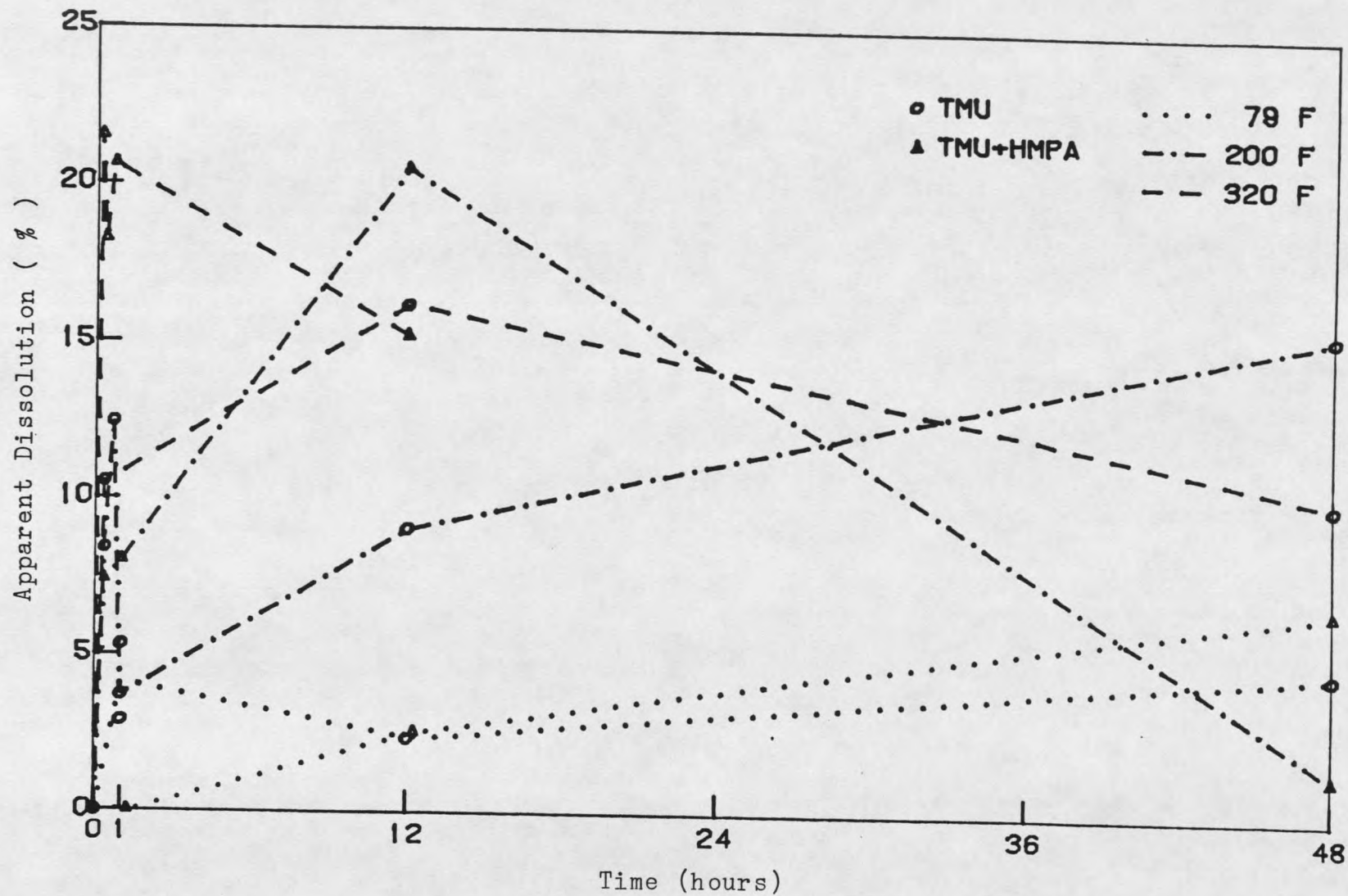


Figure 4. Apparent dissolution vs. short-contact time

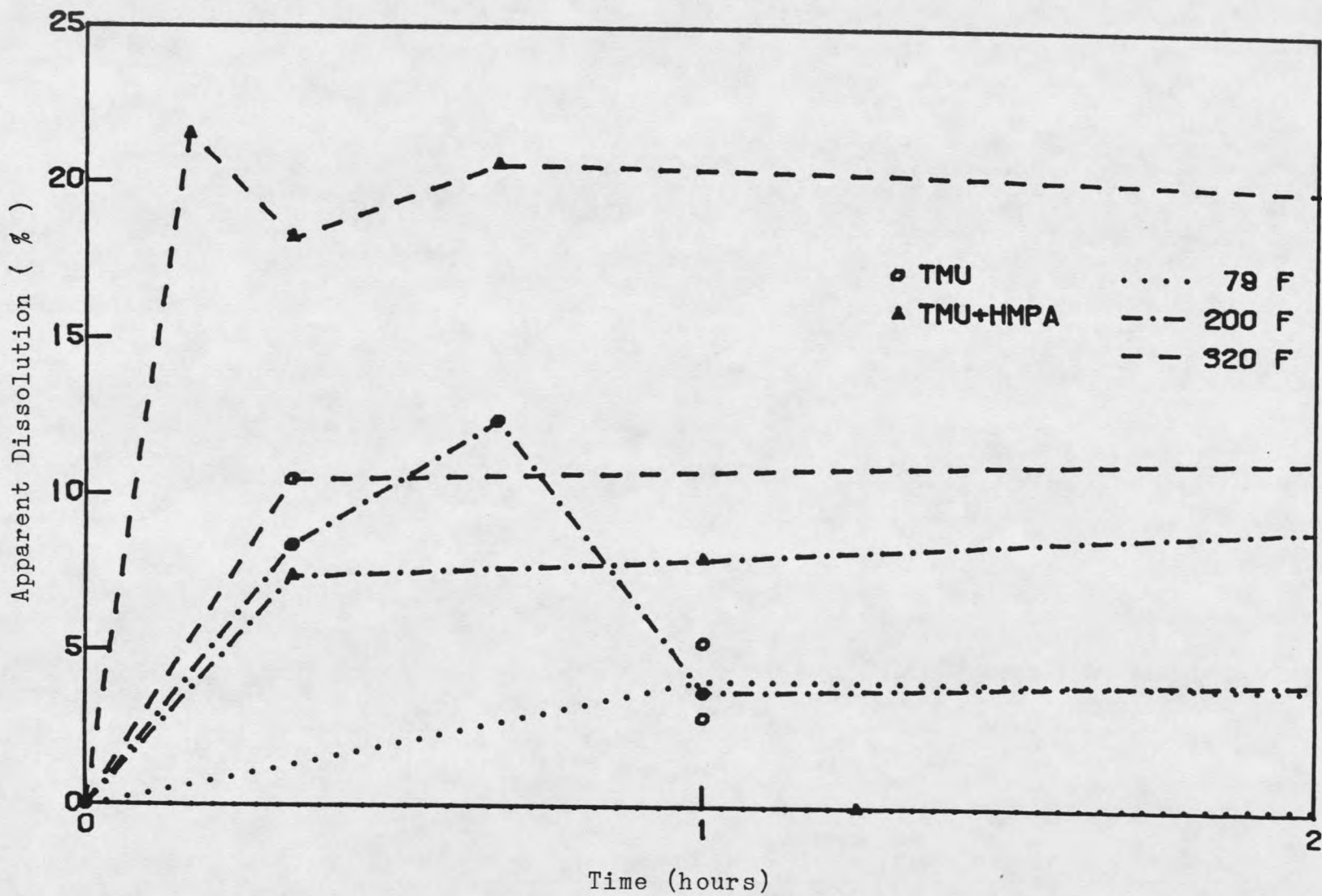


Figure 5. Actual dissolution vs. time

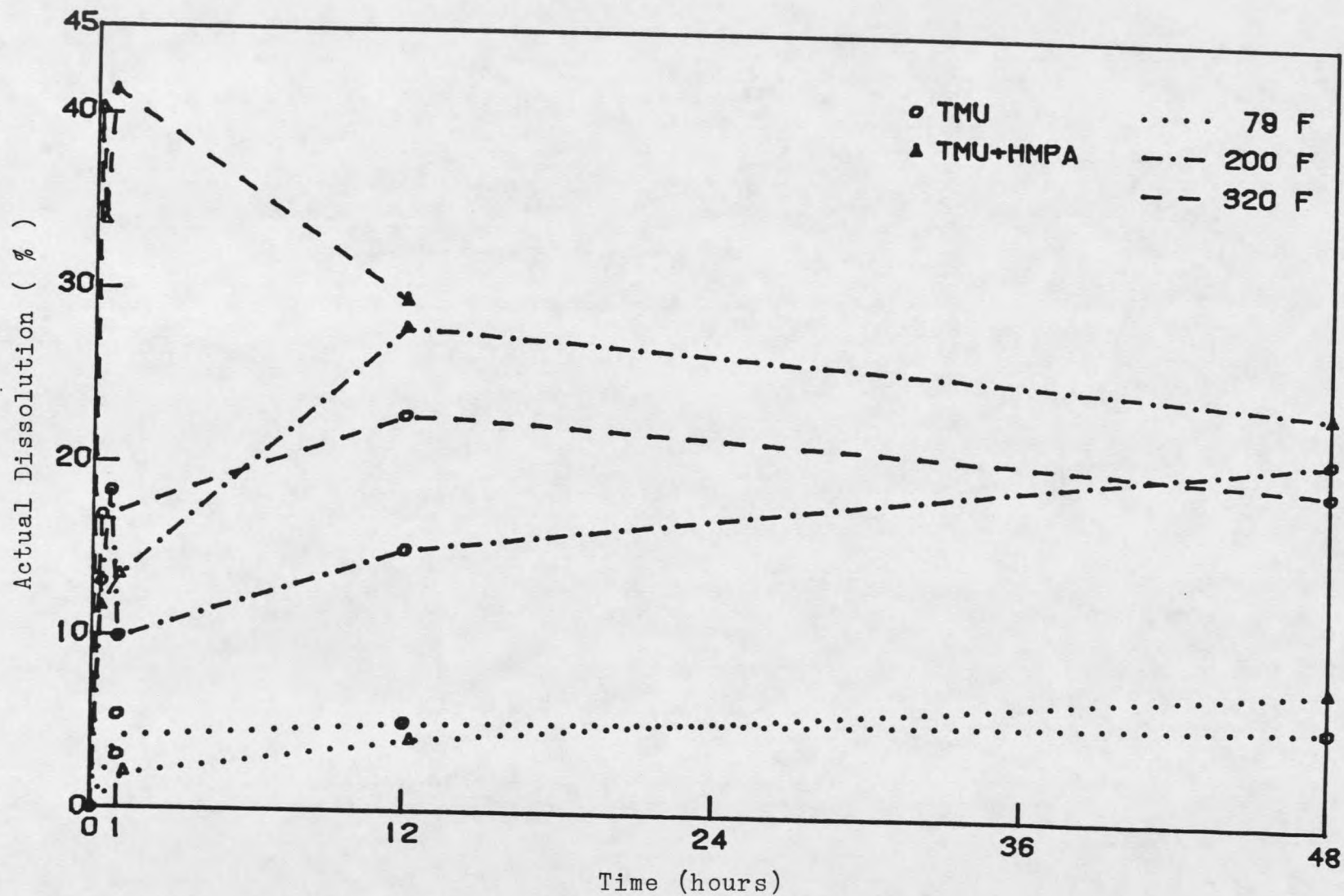
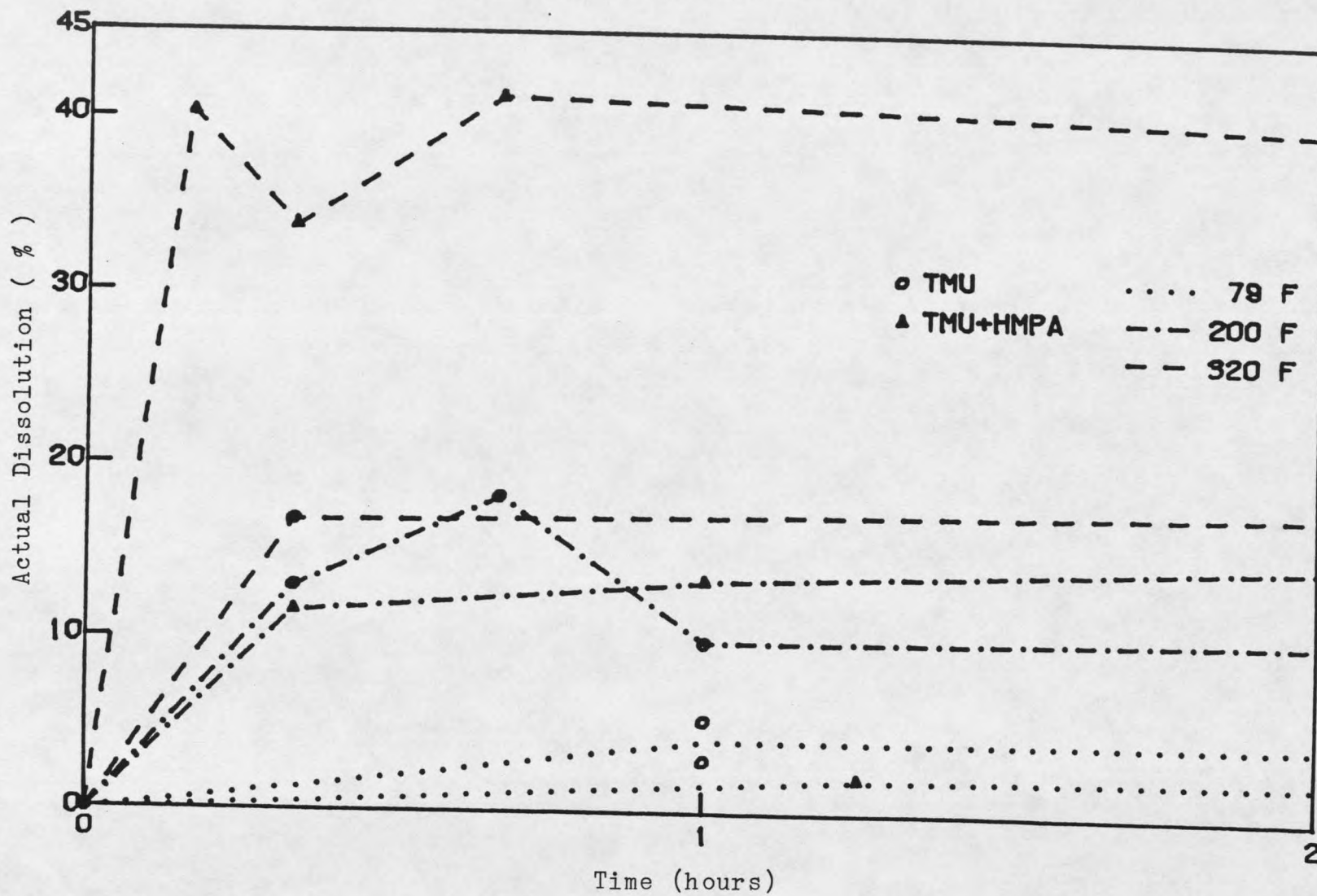
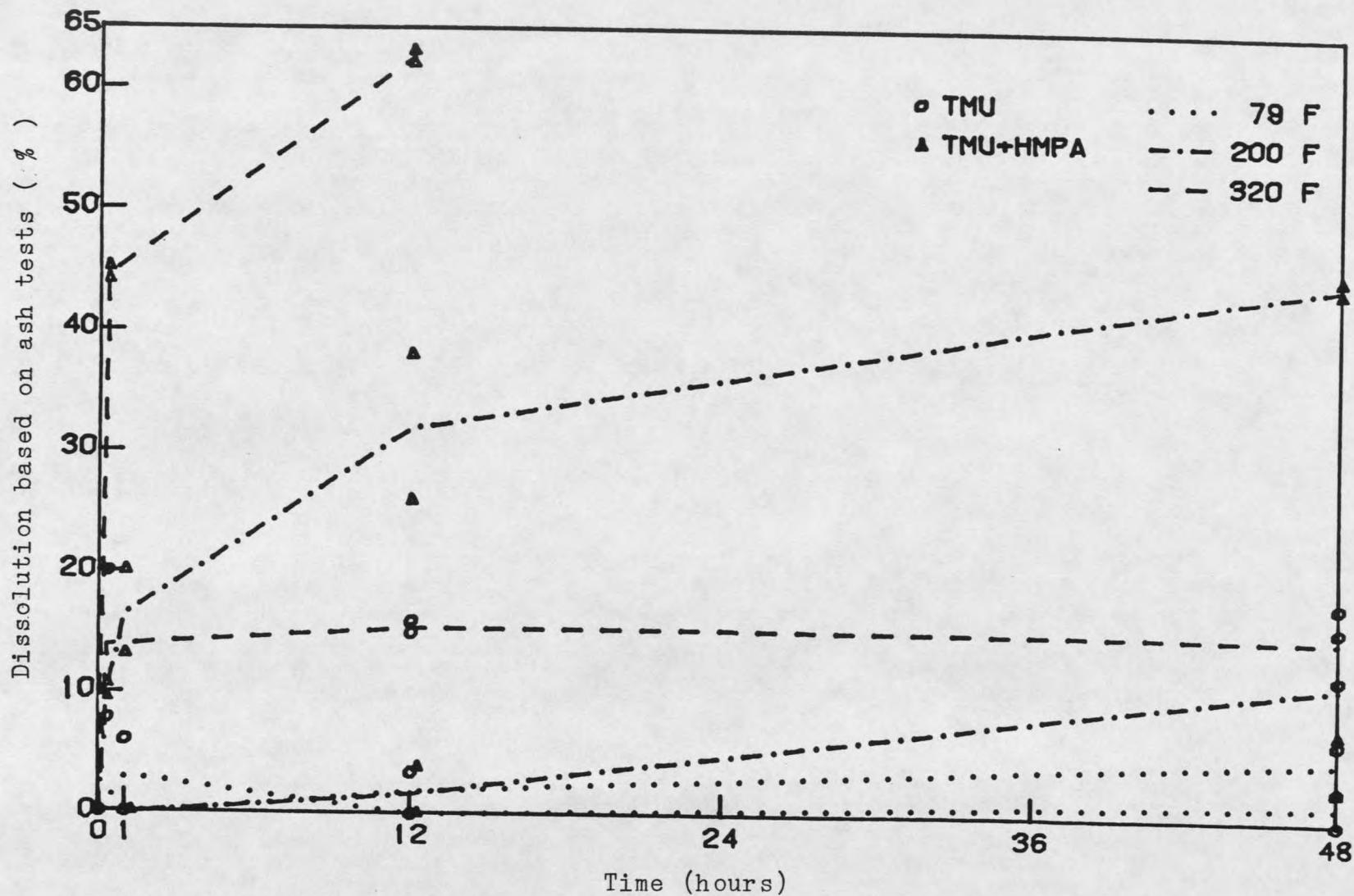


Figure 6. Actual dissolution vs. short-contact time



Dissolution calculations based on ash tests are illustrated in Figure 7. The tendency of enhanced actual dissolution with increased temperature is corroborated by the ashing results. While little difference in dissolution versus time trends with solvent type are observed at room temperature, the 1:1 mixture of TMU and HMPA used as solvent again produces higher dissolution than TMU at elevated temperatures. The attainment of maximum dissolution, however, is not apparent in the ashing results as it is in the previous actual dissolution calculations based on solvent retention. Dissolution based on ash tests is markedly lower for runs using TMU at room temperature and 200 degrees Fahrenheit than corresponding dissolution calculations based on nitrogen data. At 320 degrees Fahrenheit, the correlation between the two sets of dissolution calculations for TMU is improved. For runs using a 1:1 ratio of TMU and HMPA as solvent, dissolution at room temperature based on ash tests is slightly lower but comparable to that based on nitrogen and phosphorus data. As temperature and run time are increased, dissolution based on ash tests becomes increasingly higher than corresponding dissolution calculations based on elemental analyses. Maximum dissolution, 63%, is observed using a 1:1 mixture of the solvents at 320 degrees Fahrenheit for 12 hours. However, as previously stated, dissolution calculations based on ash tests are not

Figure 7. Dissolution based on ash tests vs. time



as accurate in describing the true dissolution behavior as those based solely on elemental analyses since (i) phosphorus analyses of the uniquely colored ashes from the higher-temperature runs using a 1:1 mixture of the solvents indicated that the HMPA incorporated into the residues did not completely combust, incorrectly elevating the dissolution values based on ash tests, (ii) reproducible dissolution results could not be consistently attained, and (iii) error in the elemental analyses is transmitted through both methods of calculating actual dissolution.

Considerable dissolution of coal can be achieved with TMU and HMPA at temperatures below the boiling points of the solvents. Based on elemental analyses, 22.8% dissolution was observed using TMU at 320 degrees Fahrenheit for 12 hours. Dissolution to 41.2% was observed using a 1:1 mixture of TMU and HMPA for 40 minutes at 320 degrees Fahrenheit. Although the presence of HMPA in the 1:1 solvent mixture enhanced dissolution at the higher temperatures, using pure HMPA in the dissolution process is not feasible until a method is developed to separate the colloidal material produced. Solvent preheating to run temperature before adding coal was preferred over simultaneous heating of solvent and coal because in the latter procedure a lower dissolution was attained for run times under 12 hours and additional and variable solvent/coal contact time was unavoidable while heating the system to run temperature.

Dissolution and initial dissolution rate tended to increase with increasing run temperature. Maximum yields were attained within 12 hours at 320 degrees Fahrenheit using TMU as solvent and at 200 and 320 degrees Fahrenheit using a 1:1 mixture of the solvents. Higher run temperatures allow maximum dissolution to be achieved at shorter times. Since all of the runs analyzed for phosphorus content had dissolution values similar to those assuming 1:1 (by volume) solvent incorporation, the assumption was adopted for those runs using a 1:1 mixture of TMU and HMPA to limit expenses. The purpose of the phosphorus analyses now becomes to substantiate the assumptions made to determine dissolution.

Retention Results

Coupled with dissolution analyses, solvent retention is another important factor in assessing the potential of coal conversion through extraction by TMU and HMPA. If significant retention occurs, the expensive solvents produce a high cost penalty either from solvent loss through irrevocable incorporation into the residue or from additional processing requirements to recover the solvents, or both. In this investigation, high solvent retention is also undesirable because the assumption made of whole solvent molecules being incorporated into the residue was not substantiated. The error caused by this assumption can not be adequately estimated, but data indicate that solvent fragments are

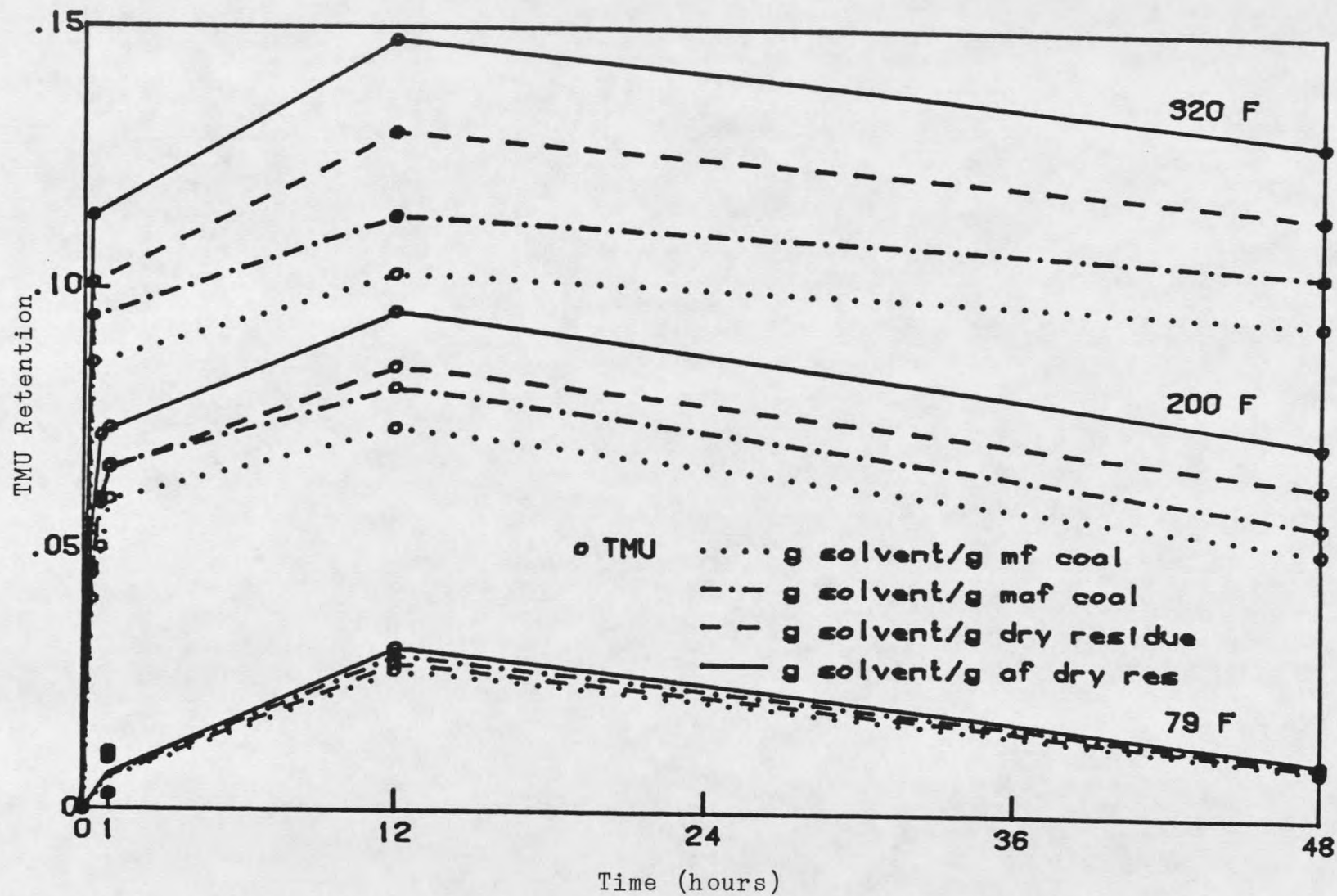
incorporated. Sears [1] observed that after extraction with HMPA followed by washing with alcohol, a fluorescence scan measurement of a residue showed only approximately 0.4% by weight HMPA retention, indicating encouraging process potential. Based on the same assumption used to determine actual dissolution, solvent retention is calculated by subtracting the weight of dry residue from the weight of wet residue and then dividing the difference, the weight of incorporated solvent, by a normalizing weight, such as the initial weight of the coal. Four normalizing weights are considered: dry coal weight, ash-free dry coal weight, dry residue weight, and ash-free dry residue weight. Both dry and ash-free dry bases are used to observe the effect of the different ash contents (8.9%, 9.5%, and 13.9%) of the three Kittanning coal grinds used.

Retention results for runs using pure TMU as solvent are listed in Table 7. The maximum TMU retention (with the weight of moisture-free coal as the basis) of 10.3% is observed after 12 hours at the highest temperature examined. TMU retention is plotted as a function of time in Figure 8. As with dissolution, solvent retention increases with increasing temperature and exhibits maximums with time. However, while actual dissolution-versus-time plots (Figure 5) indicated the attainment of maximum dissolution only at 320 degrees Fahrenheit using pure TMU, Figure 8 indicates maximum TMU retention is achieved in less than 48 hours at

Table 7. TMU retention results.

| Solvent | Temp (F) | Run time (min) | $\frac{\text{g solvent}}{\text{g mf coal}}$ | $\frac{\text{g solvent}}{\text{g maf coal}}$ | $\frac{\text{g solvent}}{\text{g dry residue}}$ | $\frac{\text{g solvent}}{\text{g af dry res}}$ | Run number |
|---------|-------------|-------------------|---|--|---|--|---------------|
| TMU | 79 | 60 | 0.010 | 0.011 | 0.010 | 0.011 | 21 |
| TMU | 79 | 60 | 0.003 | 0.003 | 0.003 | 0.003 | 35 |
| TMU | 79 | 720 | 0.027 | 0.030 | 0.028 | 0.032 | 22 |
| TMU | 79 | 2880 | 0.009 | 0.010 | 0.010 | 0.011 | 31 |
| TMU | 200 | 20 | 0.040 | 0.047 | 0.045 | 0.054 | 39 |
| TMU | 200 | 40 | 0.050 | 0.059 | 0.060 | 0.072 | 38 |
| TMU | 200 | 60 | 0.060 | 0.066 | 0.065 | 0.073 | 23 |
| TMU | 200 | 720 | 0.074 | 0.081 | 0.085 | 0.096 | 24 |
| TMU | 200 | 2880 | 0.051 | 0.056 | 0.064 | 0.072 | 30 |
| TMU | 320 | 20 | 0.086 | 0.094 | 0.101 | 0.114 | 25 |
| TMU | 320 | 720 | 0.103 | 0.114 | 0.130 | 0.147 | 26 |
| TMU | 320 | 2880 | 0.095 | 0.104 | 0.115 | 0.129 | 32 |

Figure 8. TMU retention vs. time for TMU runs



all temperatures considered. TMU retention is plotted as a function of actual dissolution in Figure 9. TMU retention tends to increase with increasing dissolution, with maximums attained possibly at 79 and 200 degrees Fahrenheit. Maximum TMU retention is observed for the run exhibiting the highest dissolution.

To assess the assumptions made to determine actual dissolution, solvent retention results assuming a 1:1 ratio of solvent incorporation (Tables 8-10) are compared to those using phosphorus data (Tables 11-13) for runs using a mixture of TMU and HMPA as solvent. As with actual dissolution results, total retention results appear essentially identical (Tables 8 and 11, Figures 10 and 11). Total retention is again observed to increase with increasing temperature. However, further analysis uncovers a complication for half of the runs (starred in Table 5) analyzed for phosphorus content. Due to the fixed sequence of calculations, TMU retention can be calculated only after HMPA retention is determined. To satisfy both the nitrogen and phosphorus mass balances with the stated assumptions, three of the runs listed in Table 13 indicate negative TMU incorporation into the residue (i.e., molecules of TMU are produced from the coal-solvent interaction) which is improbable considering the relatively high nitrogen content and symmetry of TMU compared to proposed coal structures and isolated coal fragments. The negative retention values do not correlate with

Figure 9. TMU retention vs. dissolution for TMU runs

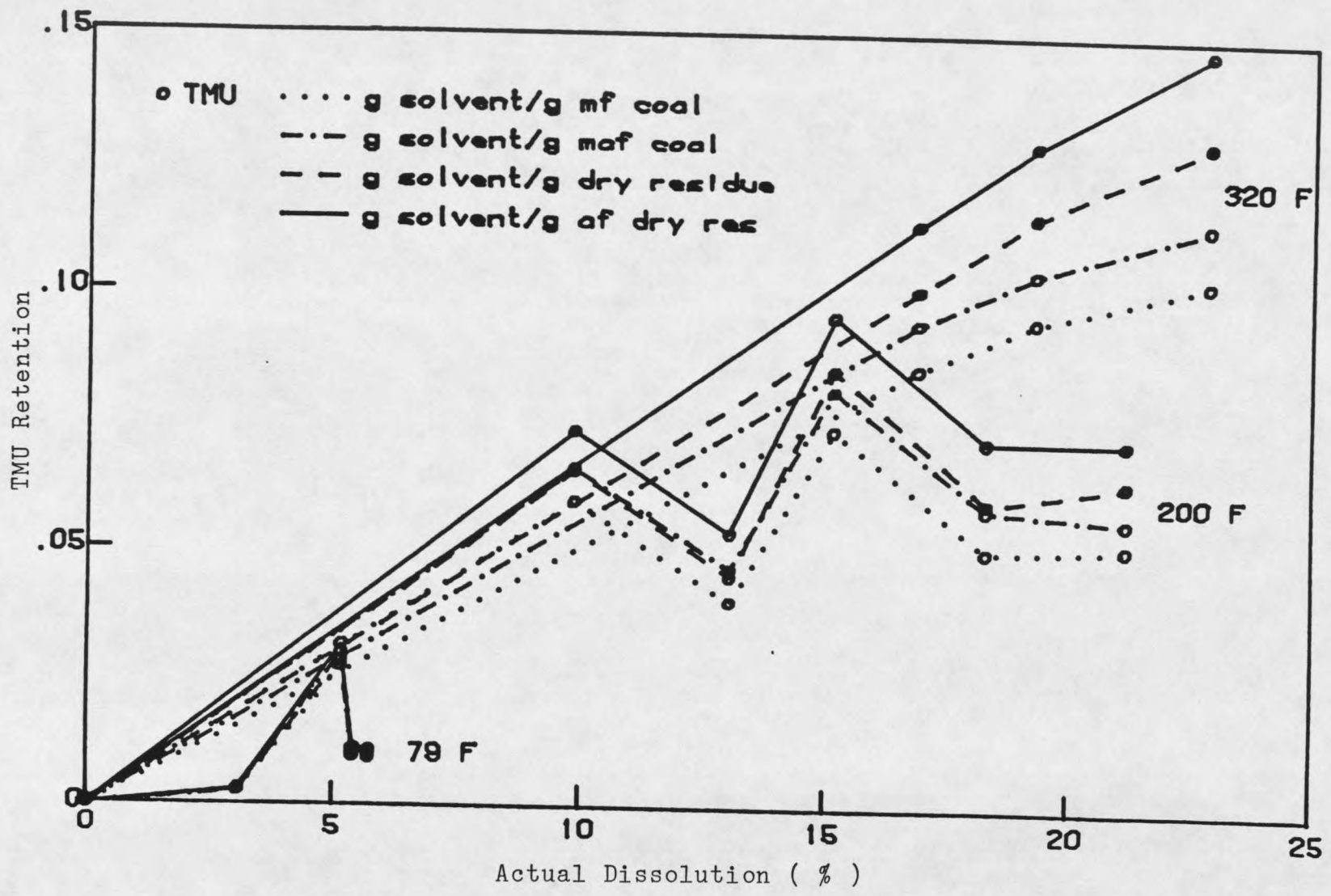


Table 8. Total solvent retention assuming 1:1 solvent incorporation.

| Solvent | Temp (F) | Run time (min) | $\frac{\text{g solvent}}{\text{g mf coal}}$ | $\frac{\text{g solvent}}{\text{g maf coal}}$ | $\frac{\text{g solvent}}{\text{g dry residue}}$ | $\frac{\text{g solvent}}{\text{g af dry res}}$ | Run number |
|----------|----------|----------------|---|--|---|--|------------|
| TMU+HMPA | 79 | 75 | 0.022 | 0.024 | 0.022 | 0.025 | 16 |
| TMU+HMPA | 79 | 735 | 0.015 | 0.016 | 0.015 | 0.017 | 17 |
| TMU+HMPA | 79 | 2880 | 0.011 | 0.012 | 0.012 | 0.013 | 33 |
| TMU+HMPA | 200 | 20 | 0.063 | 0.069 | 0.070 | 0.078 | 19 |
| TMU+HMPA | 200 | 60 | 0.062 | 0.068 | 0.071 | 0.079 | 27 |
| TMU+HMPA | 200 | 720 | 0.067 | 0.074 | 0.090 | 0.102 | 34 |
| TMU+HMPA | 200 | 2880 | 0.202 | 0.223 | 0.257 | 0.292 | 29 |
| TMU+HMPA | 320 | 10 | 0.161 | 0.187 | 0.246 | 0.312 | 37 |
| TMU+HMPA | 320 | 20 | 0.142 | 0.157 | 0.204 | 0.237 | 20 |
| TMU+HMPA | 320 | 40 | 0.177 | 0.206 | 0.275 | 0.350 | 36 |
| TMU+HMPA | 320 | 720 | 0.130 | 0.143 | 0.176 | 0.203 | 28 |

Table 9. HMPA retention assuming 1:1 solvent incorporation.

| Run number | $\frac{\text{g HMPA}}{\text{g mf coal}}$ | $\frac{\text{g HMPA}}{\text{g maf coal}}$ | $\frac{\text{g HMPA}}{\text{g dry residue}}$ | $\frac{\text{g HMPA}}{\text{g af dry res}}$ |
|------------|--|---|--|---|
| 16 | 0.011 | 0.012 | 0.011 | 0.013 |
| 17 | 0.008 | 0.008 | 0.008 | 0.009 |
| 33 | 0.006 | 0.006 | 0.006 | 0.007 |
| 19 | 0.032 | 0.035 | 0.036 | 0.040 |
| 27 | 0.032 | 0.035 | 0.036 | 0.041 |
| 34 | 0.034 | 0.038 | 0.046 | 0.052 |
| 29 | 0.104 | 0.115 | 0.132 | 0.150 |
| 37 | 0.083 | 0.096 | 0.126 | 0.160 |
| 20 | 0.073 | 0.081 | 0.105 | 0.122 |
| 36 | 0.091 | 0.106 | 0.141 | 0.180 |
| 28 | 0.067 | 0.073 | 0.090 | 0.104 |

Table 10. TMU retention assuming 1:1 solvent incorporation.

| Run number | <u>g TMU</u> <u>g mf coal</u> | <u>g TMU</u> <u>g maf coal</u> | <u>g TMU</u> <u>g dry residue</u> | <u>g TMU</u> <u>g af dry res</u> |
|---------------|----------------------------------|-----------------------------------|--------------------------------------|-------------------------------------|
| 16 | 0.011 | 0.012 | 0.011 | 0.012 |
| 17 | 0.007 | 0.008 | 0.007 | 0.008 |
| 33 | 0.005 | 0.006 | 0.006 | 0.006 |
| 19 | 0.031 | 0.034 | 0.034 | 0.038 |
| 27 | 0.030 | 0.033 | 0.035 | 0.038 |
| 34 | 0.033 | 0.036 | 0.044 | 0.050 |
| 29 | 0.098 | 0.108 | 0.125 | 0.142 |
| 37 | 0.078 | 0.091 | 0.120 | 0.152 |
| 20 | 0.069 | 0.076 | 0.099 | 0.115 |
| 36 | 0.086 | 0.100 | 0.134 | 0.170 |
| 28 | 0.063 | 0.070 | 0.086 | 0.099 |

Table 11. Total solvent retention based on phosphorus data.

| Solvent | Temp (F) | Run time (min) | $\frac{\text{g solvent}}{\text{g mf coal}}$ | $\frac{\text{g solvent}}{\text{g maf coal}}$ | $\frac{\text{g solvent}}{\text{g dry residue}}$ | $\frac{\text{g solvent}}{\text{g at dry res}}$ | Run number |
|----------|-------------|-------------------|---|--|---|--|---------------|
| TMU+HMPA | 79 | 2880 | 0.012 | 0.013 | 0.013 | 0.014 | 33 |
| TMU+HMPA | 200 | 60 | 0.063 | 0.070 | 0.072 | 0.081 | 27 |
| TMU+HMPA | 200 | 720 | 0.067 | 0.074 | 0.090 | 0.102 | 34 |
| TMU+HMPA | 200 | 2880 | 0.204 | 0.225 | 0.260 | 0.296 | 29 |
| TMU+HMPA | 320 | 20 | 0.144 | 0.159 | 0.207 | 0.240 | 20 |
| TMU+HMPA | 320 | 720 | 0.135 | 0.149 | 0.185 | 0.212 | 28 |

Table 12. HMPA retention based on phosphorus data.

| Run number | <u>g HMPA</u> <u>g mf coal</u> | <u>g HMPA</u> <u>g maf coal</u> | <u>g HMPA</u> <u>g dry residue</u> | <u>g HMPA</u> <u>g af dry res</u> |
|------------|-----------------------------------|------------------------------------|---------------------------------------|--------------------------------------|
| 33 | 0.028 | 0.031 | 0.030 | 0.033 |
| 27 | 0.071 | 0.079 | 0.081 | 0.091 |
| 34 | 0.029 | 0.032 | 0.039 | 0.045 |
| 29 | 0.174 | 0.192 | 0.222 | 0.252 |
| 20 | 0.131 | 0.144 | 0.189 | 0.219 |
| 28 | 0.237 | 0.262 | 0.325 | 0.373 |

Table 13. TMU retention based on phosphorus data.

| Run number | <u>g TMU</u> <u>g mf coal</u> | <u>g TMU</u> <u>g maf coal</u> | <u>g TMU</u> <u>g dry residue</u> | <u>g TMU</u> <u>g af dry res</u> |
|------------|----------------------------------|-----------------------------------|--------------------------------------|-------------------------------------|
| 33 | -0.016 | -0.018 | -0.017 | -0.019 |
| 27 | -0.008 | -0.009 | -0.010 | -0.011 |
| 34 | 0.038 | 0.041 | 0.051 | 0.057 |
| 29 | 0.030 | 0.033 | 0.038 | 0.044 |
| 20 | 0.013 | 0.014 | 0.019 | 0.022 |
| 28 | -0.102 | -0.113 | -0.140 | -0.161 |

Figure 10. Total retention vs. time

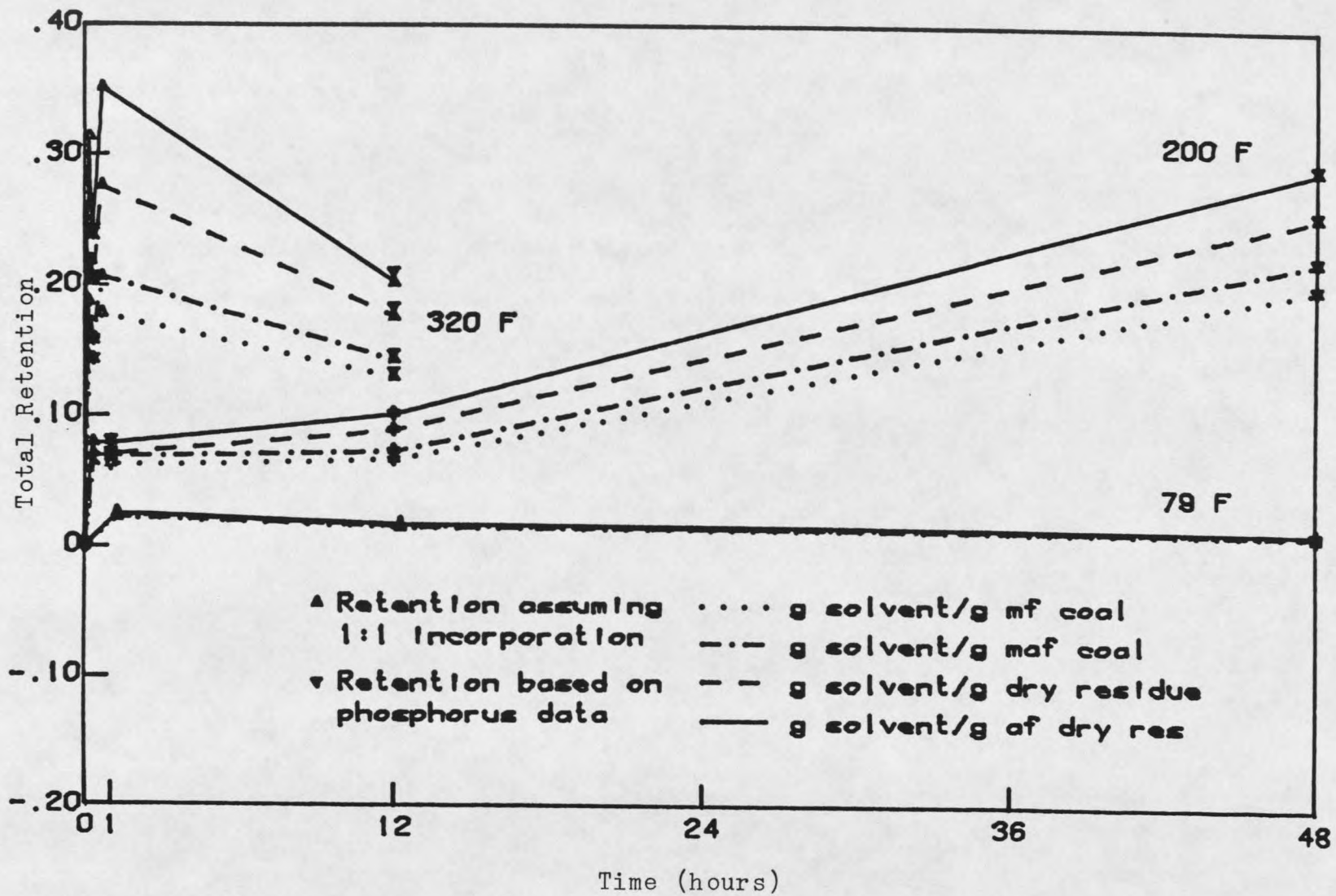
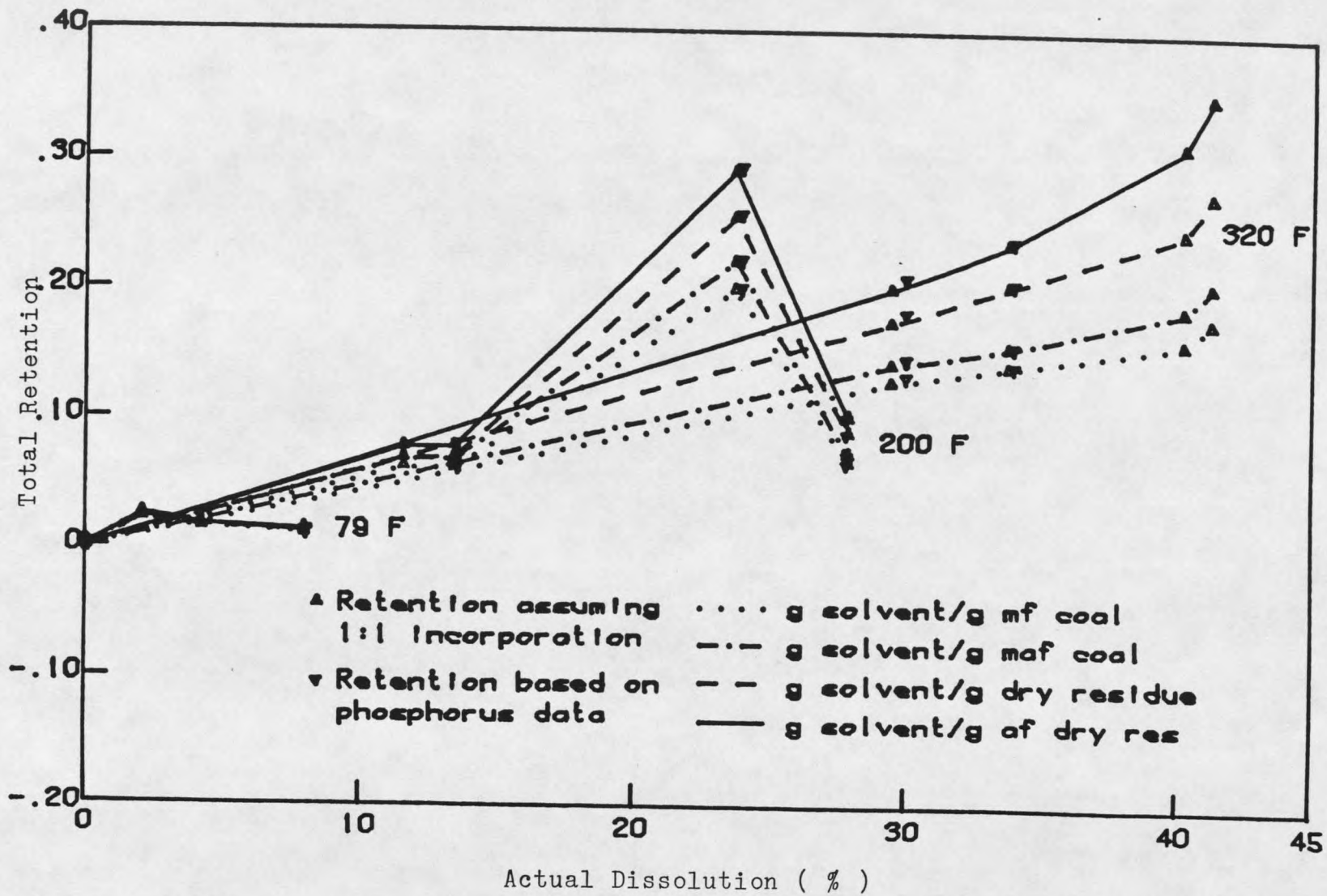


Figure 11. Total retention vs. dissolution



temperature, time, or dissolution. Only one of the runs analyzed for phosphorus content has TMU retention high enough to be comparable to the corresponding values assuming 1:1 solvent incorporation. To compensate, HMPA retention results based on phosphorus analyses tend to be higher than those based on a 1:1 solvent incorporation assumption, since total retention results calculated by the two methods are similar. TMU and HMPA retention trends with time and dissolution are illustrated in Figures 12 through 15. As expected, the disparity between the two sets of HMPA retention results and the two sets of TMU retention results increases with increasing run temperature, since solvent retention follows the same trend. However, no correlation is evident between the two sets of HMPA retention results or the two sets of TMU retention results.

The trends of solvent retention based on the four normalizing coal and residue weights are shown in all of the tables and graphs. As expected, the basis chosen makes the difference in retention values most pronounced in high retention runs. However, solvent retention trends with time and dissolution are found to be independent of the normalizing weight chosen. Total retention increases to undesired levels in runs with moderate to high dissolution. Except for the thorough washing of the residue with acetone, procedures to minimize this tendency were not attempted.

Figure 12. HMPA retention vs. time

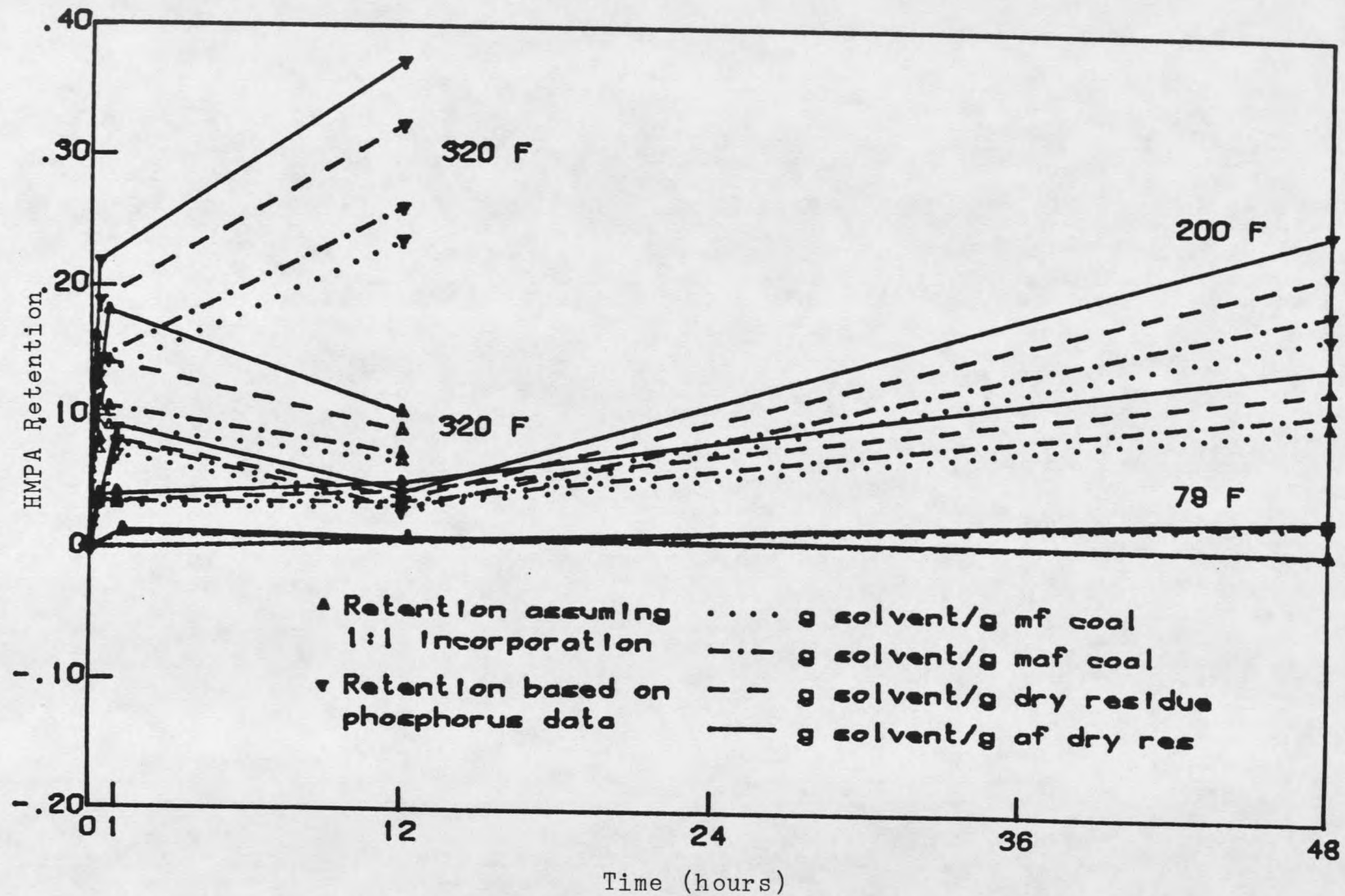


Figure 13. HMPA retention vs. dissolution

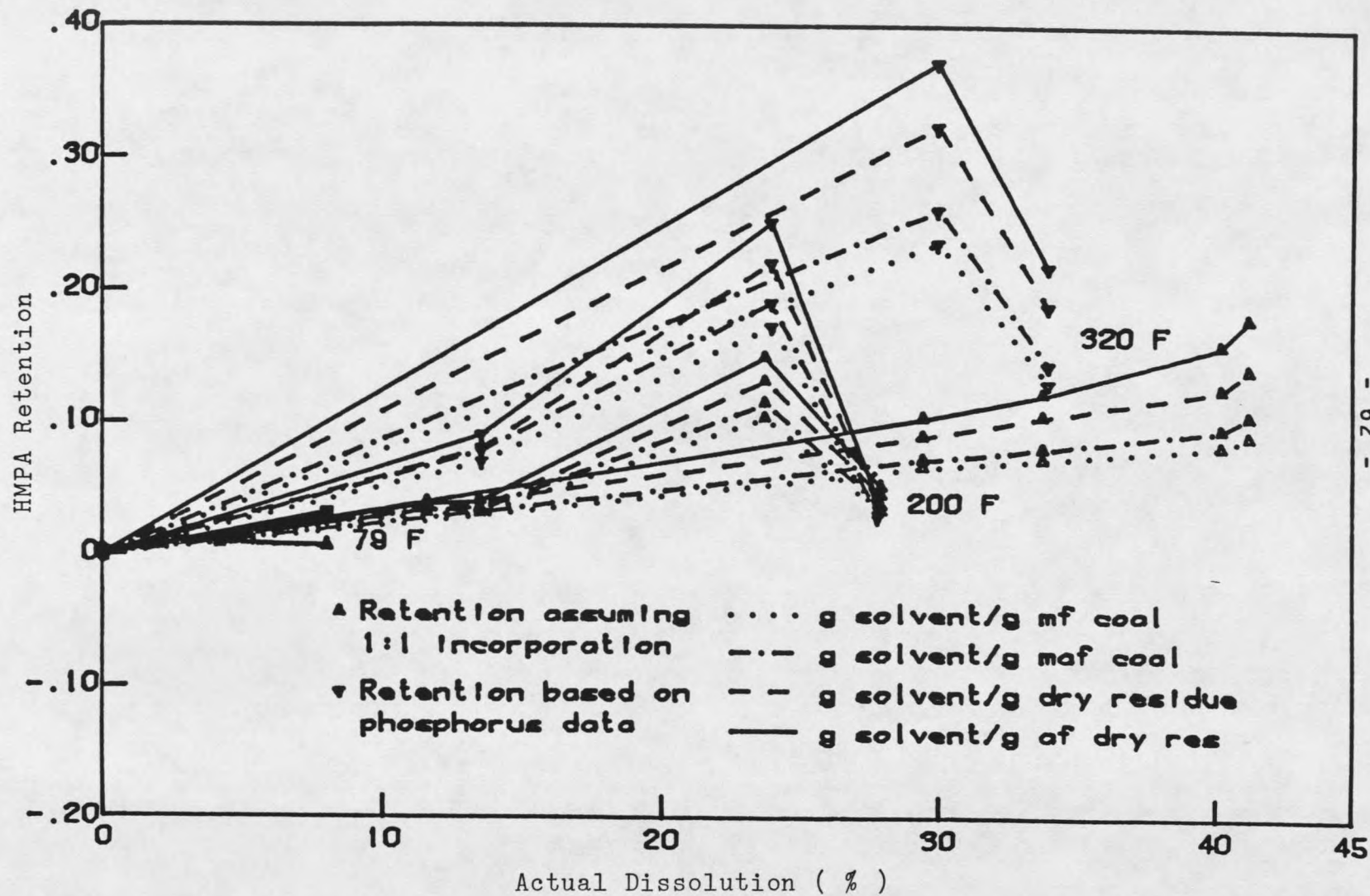


Figure 14. TMU retention vs. time

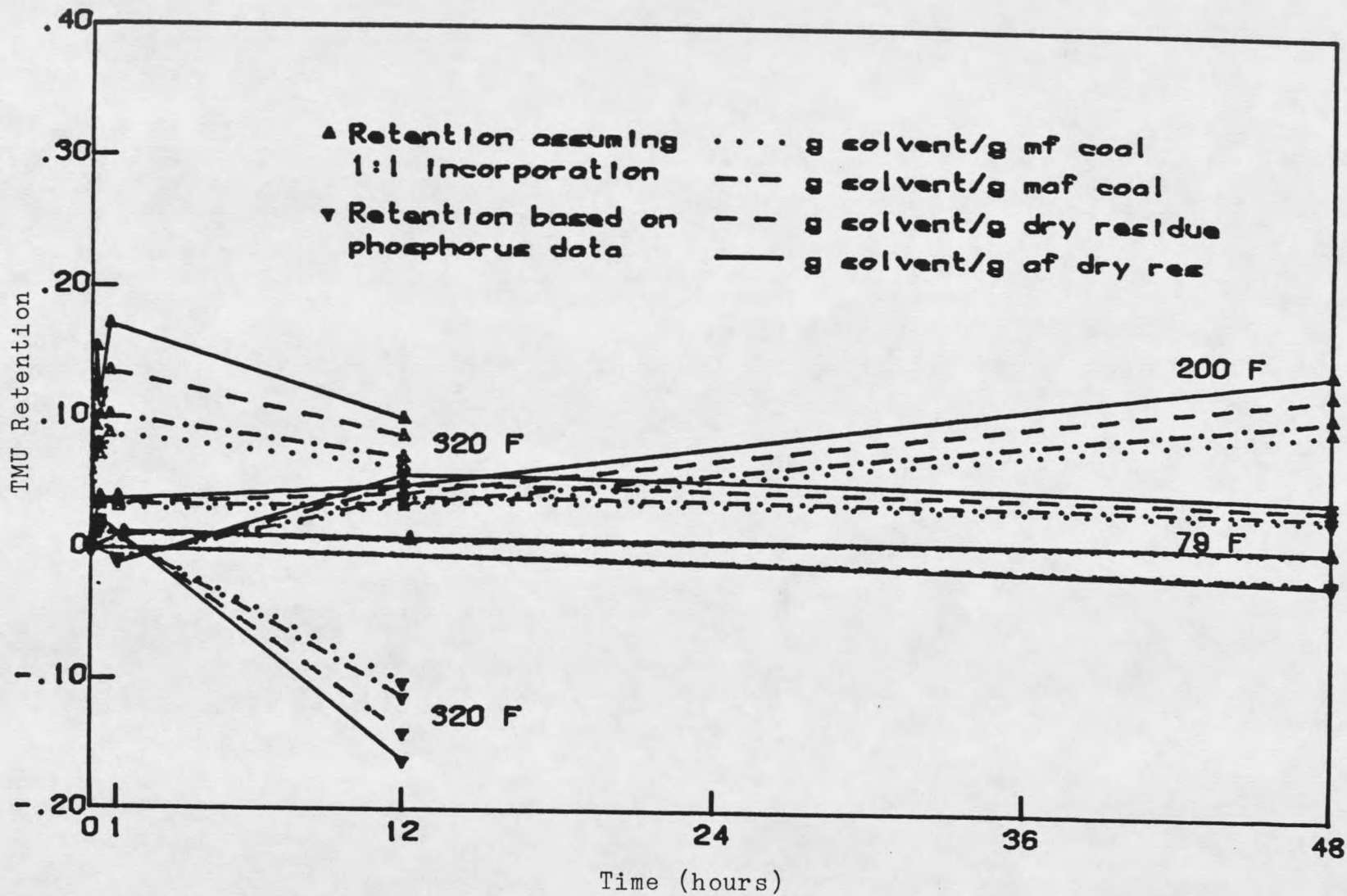
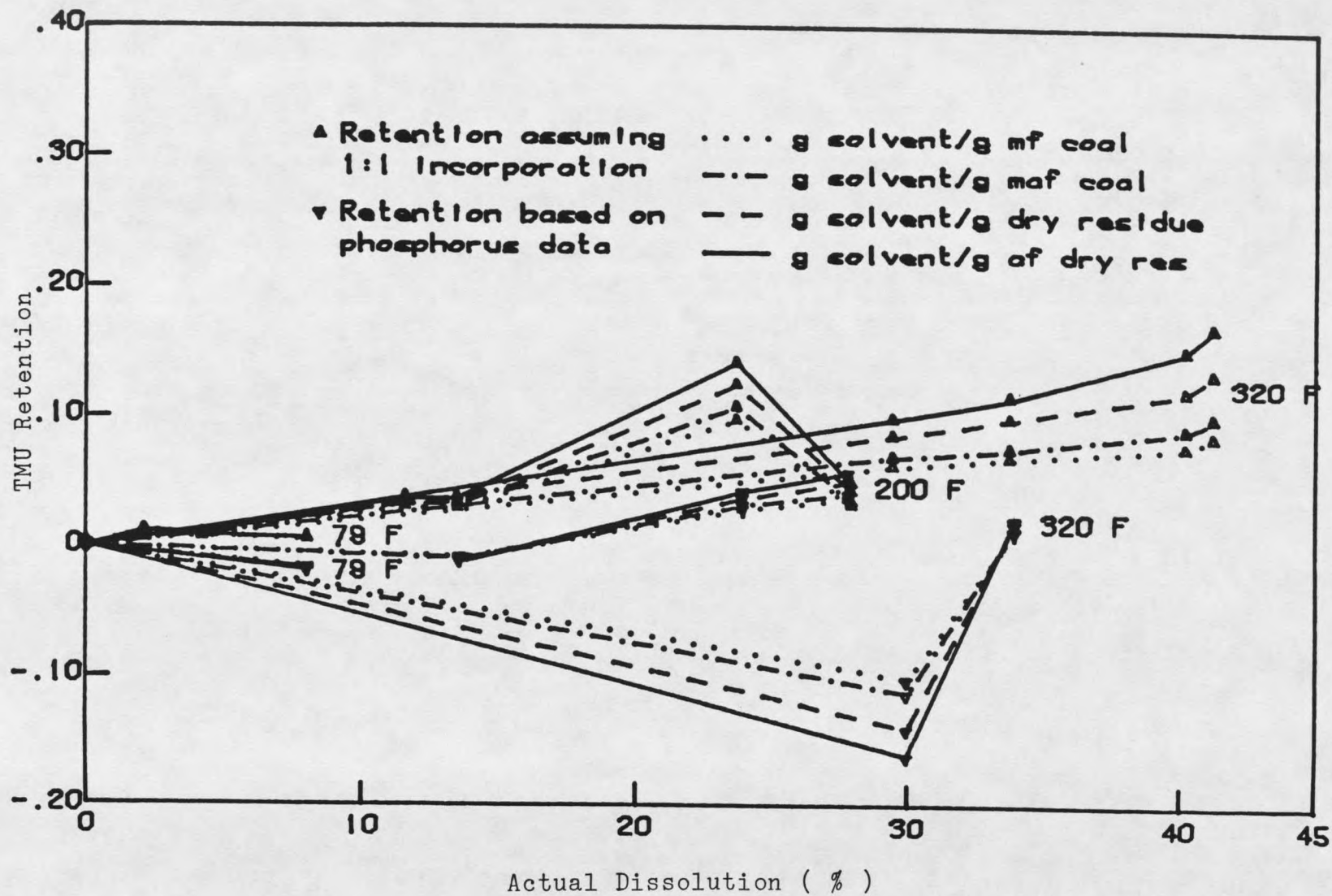


Figure 15. TMU retention vs. dissolution



Low solvent retention values could not be attained in this investigation for runs with significant dissolution. Retention to 10.3% with a moisture-free coal basis was observed using TMU as solvent for 12 hours at 320 degrees Fahrenheit. The maximum dissolution using TMU was also attained at these conditions. TMU retention increases with increasing temperature and exhibits maximums with time within 48 hours at all three temperatures. Consideration of run times greater than 48 hours at 79 and 200 degrees Fahrenheit to determine maximum dissolution values is encouraged when noting that TMU retention possibly passes through a maximum with increasing dissolution, indicating that low retention may be attained with maximum dissolution. However, run times greater than 48 hours were not investigated because extraction time must be short for commercial feasibility [14]. For runs using a mixture of TMU and HMPA as solvent, retention calculations assuming a 1:1 ratio of solvent incorporation compared to those using phosphorus data produced conflicting results. As with actual dissolution results, total retention results are essentially identical. Retention is again observed to increase with increasing temperature. However, for three runs negative solvent retention values are calculated based on phosphorus content, which can not be modeled by any assumption of solvent-incorporation ratio. No correlation is apparent between the two

sets of HMPA retention results or the two sets of TMU retention results.

H/C and O/C Ratios in Residue

Although the dissolution mechanism is not known, an indication of what is occurring during the process may be given by micro ultimate analysis data corrected for solvent retention (Tables 16 and 18 in Appendix B). However, these results must be considered questionable because they are based on the same assumptions made that produced negative solvent retention values. Also, error in the elemental analyses may contribute to produce anomalous H/C and O/C ratios [36]. Calculated carbon, hydrogen, and molar H/C contents of the dry residues assuming 1:1 solvent incorporation (Table 17 in Appendix B) are within 4% of those based on phosphorus data (Table 18) while the two sets of oxygen and molar O/C contents differ by less than 18%. Hydrogen/carbon ratios tend to decrease as a function of time from the average initial value of 0.793 for coal (the H/C values for the three grinds range from 0.790 to 0.794) for runs at 320 degrees Fahrenheit. For runs using pure TMU at 200 degrees Fahrenheit, H/C values oscillate between 0.767 and 0.792, the range being below the initial H/C value for Kittanning coal. However, the remaining runs using TMU at room temperature or a 1:1 mixture of the solvents at room temperature or 200 degrees Fahrenheit produce H/C values ranging from

0.737 to 0.840, neither consistently lower nor higher than that of coal. Similar behavior is noted for H/C as a function of actual dissolution. Oxygen/carbon ratios exhibit no apparent trend with temperature, time, or dissolution. No conclusion can be made as to whether or not the soluble products initially have high oxygen contents as proposed by the Union Carbide Corporation and cited by Sears [1].

DISCUSSION

Based on the resources available to the author, the following assumptions are made in order to calculate dissolution and retention values: i) drying the coal at 100 - 105 degrees Celsius overnight removed all of the water without altering chemical bonds in the coal, ii) the true ash content of the coal can be determined from the ashing method performed, iii) acetone has no effect other than to remove excess solvent from the residue, iv) whole solvent molecules are incorporated into the residue, and v) the weight percents of nitrogen and phosphorus in the coal remain constant through the dissolution process so that any change in nitrogen and phosphorus content is due to incorporation of TMU and/or HMPA. For runs using a mixture of TMU and HMPA, the additional assumption of a 1:1 ratio of solvent incorporation into the residue was adopted after noting similar dissolution trends to those based on elemental analyses. However, the results based on these assumptions were found to be inaccurate in describing the coal dissolution process.

Although the dissolution results appear satisfactory, the solvent retention results indicate that the error caused by one or more of the five initial assumptions is large enough to produce negative solvent retention values. Since the weight percents of nitrogen in TMU and HMPA are similar

(24.12% vs. 23.45%, respectively), dissolution calculations are virtually independent of the ratio of solvents incorporated into the residue and can be modelled by any assumption of retention ratio. Although the phosphorus analyses do not significantly affect dissolution results, they are essential in determining solvent retention. Contrary to the fifth assumption, Tsao and Losinski [37] have recently observed that the weight percent of nitrogen in the coal fluctuates during extraction by TMU and HMPA. However, the maximum error caused by this assumption will reverse only two of the three negative retention values: if all of the nitrogen initially in the coal is assumed to be extracted before the run time is over, TMU retention is -0.063 grams solvent per gram of moisture-free coal for run 28 which had the most negative retention value of the three runs. Making the first three assumptions and the fifth assumption with respect to the phosphorus content probably contributes little to the error that produced the negative retention values. Although experimental technique and the inaccuracy of the elemental analyses could account for some of the error, previous research of HMPA as a coal solvent [11] indicates that making the fourth assumption produces considerable uncertainty. If fragments of HMPA with higher phosphorus/nitrogen ratios than the whole solvent molecule are also incorporated, TMU retention (as whole and/or

fragment solvent molecules) could be calculated as non-negative for all runs. Examples of HMPA fragments satisfying this condition have one, two, or all three amide groups cleaved (which can occur in the presence of an acid [6]) before incorporation of the remaining fragment into the residue. TMU retention would increase, HMPA loss would be unchanged (assuming fragments are formed only with incorporation) or increased (if the fragmentation steps are independent of the incorporation steps), and total retention would increase or decrease, depending on the characteristics and amounts of incorporated TMU and/or HMPA fragments. Actual dissolution may be higher or lower than the calculated values based on incorporation of whole solvent molecules, the lowest limit being the apparent dissolution values. However, the elemental analyses indicate considerable retention of solvent as whole and/or fragmented molecules which would make actual dissolution higher than apparent dissolution, whatever the constitution of the incorporated molecules.

For runs using pure TMU as solvent, adopting the fourth and fifth assumptions is again expected to account for a major part of the error. Dissolution and retention values would vary depending on (i) the fluctuation of the nitrogen content of the residue during liquefaction and (ii) the functionality of TMU fragmentation and retention in the residue on temperature, time, and dissolution. For example,

if TMU acts as an electron acceptor during liquefaction, ionic fragments formed from the decomposition of the radical-anion of TMU could be incorporated into the residue. Providing an alternate source of solvent fragments, nucleophiles produced during extraction could remove amide ions from TMU [6]. However, since analytical techniques to determine the presence of incorporated solvent fragments were not available, the stated actual dissolution values are taken to be the best representations of the true values.

Rigorous mass balances can not be applied until the constitutions and amounts of dissolved product and incorporated solvent have been established. To obtain results that accurately describe the liquefaction process, the error caused by making each assumption needs to be assessed so modifications of the assumptions can be made which better model the process. Since negative solvent retention values do not correlate with temperature, time, or dissolution, any trends of the magnitude of error with these variables can not be determined. Although commonly adopted in coal conversion studies, the first assumption made in the analysis probably is not true. The error in making the first assumption can be estimated by analyzing by gas chromatography the vapor released during drying and performing an extensive analysis of the coal using nuclear magnetic resonance (nmr), electron paramagnetic resonance (epr), and other spectroscopic techniques during the drying process to

determine (i) the types of bonds between water and coal, (ii) if the water is completely removed during the drying process, and (iii) if any bonds other than those involving water removal are altered.

Error in the second assumption can be determined with less difficulty than that in the other assumptions by securing a responsive oven capable of ashing samples according to ASTM D3174 (1973) standards [38]: moisture-free coal is heated in a cold muffle furnace to 500 degrees Celsius in one hour and 750 degrees Celsius in two hours, followed by heating to constant weight at 750 degrees Celsius. At this heating rate, pyrite is completely oxidized and sulfur is expelled before the calcite is decomposed. Discussions promoting the standardization of the ashing temperature at 700 - 750 degrees Celsius for coal have been underway since 1978. Although higher ash contents may be recorded and the ashing time would be increased, the loss of the volatile mineral constituents would be reduced. Low-temperature ashing to determine yields on a mineral-matter-free (mmf) basis was not attempted due to the larger error anticipated in using an oven rather than an oxygen-plasma asher. If the appropriate equipment for low-temperature ashing were available, dissolution values on a mmf basis would be higher than corresponding values on an ash-free basis and the theoretical maximum conversion of 100% could be achieved.

Since acetone has been observed to be an inactive coal solvent [28], error caused by adopting the third assumption is expected to be small. However, it is possible that acetone with the residual TMU and/or HMPA further extracts products during the washing step, since mixtures of solvents can have enhanced dissolving power [11, 12, 13]. Error in the third assumption can be assessed by determining the components extracted by various wash liquids, analyzing the residue for retention of wash liquid, and comparing the yields obtained using the various wash liquids (including none at all). Before the error can be estimated, however, knowledge of the coal-solvent interactions is required to modify the fourth and fifth assumptions, so accurate yields and retention values can be calculated for comparison. Roy et al. [19] also assumed whole solvent molecules to be incorporated into the residue (the fourth assumption) when studying coal liquefaction using DMSO, a polar aprotic solvent in the same class of solvents as TMU and HMPA. The fifth assumption was adopted by Kiebler [12] in order to calculate yields. However, Pullen [39] cited Whitehurst and Mitchell who found that nitrogen in coal was not significantly reduced during solvent extraction; in contrast, Atherton and Kulik [16] cited researchers at the Mobil Research and Development Corporation who found that nitrogen-rich compounds were concentrated in the coal during the early stages of solvent extraction with the trend reversing at

extended liquefaction times. Error in the fourth and fifth assumptions can be determined after performing an extensive analysis using spectroscopic techniques on the coal, residues, liquid products, and model compounds. Since error in the fourth assumption also propagates through the fifth assumption, special emphasis should be placed on understanding the mode of solvent retention.

Condensation of the coal products due to competing reactions is indicated by the maximum dissolution limits of the high temperature runs and by the lower dissolution results obtained when coal and solvent are heated together to run temperature rather than when the solvent is preheated before adding coal. Dryden [22] cited Tebbett et al. who stated that the extraction yield may pass through a maximum during the heating of solvent and coal together to run temperature due to aggregation or resorption of the extract. Whether or not this occurs, optimization of heating conditions is important because differences in preheater products can affect all subsequent reactions [39]. Solvolytic cleavage is probably occurring in the preheaters of present-day direct conversion plants [15]. Since extract resorption alters the coal structure and can involve solvent molecules [14], condensation reactions affect solvent retention. Since degregation/retrogression of coal is an irreversible process [16], solvent preheating proves to be the preferred procedure both theoretically and experimentally. Other

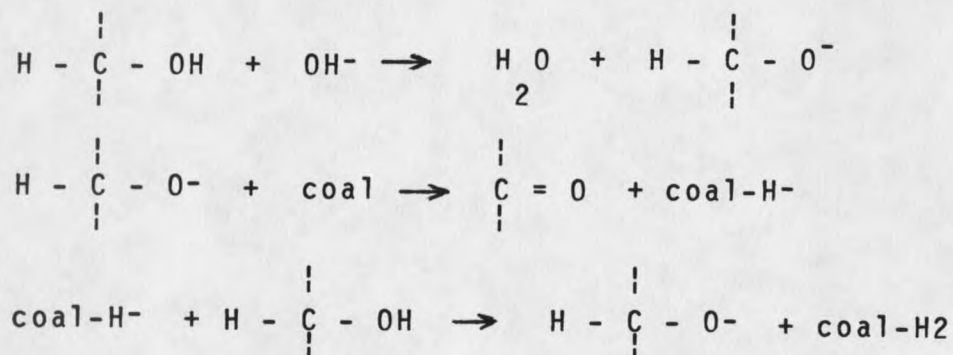
investigators have also noted the occurrence of repolymerization reactions. Kiebler [12] cited Jostes who observed the tendency of coal extracts to repolymerize when exposed to light. Although not experimentally confirmed, Jostes proposed that repolymerization of coal extracts upon cooling does occur; later, Clarke et al. [40] supported the theory experimentally. Yields are then dependent on the temperature at which the extracts are separated from the residues. Pullen [39] noted that initial conversion reactions proceed equally well in hydrogen- and nonhydrogen-donor solvents, indicating that an external source of hydrogen is not initially required. After observing decreased yields with extended reaction times in non-donor solvents, Neavel [41] concluded that recombination of coal products into insoluble high molecular weight substances was occurring. Based on Neavel's findings, Whitehurst [40] proposed that the condensation reactions involved hydrogen abstraction from the hydroaromatic coal structure. Hoffman [26] believed coal conversion involved a series of depolymerization steps followed by repolymerization steps. At a given temperature, equilibrium was believed to exist between depolymerization and repolymerization processes. In this investigation of coal conversion by TMU and HMPA, equilibrium does not appear to be attained within 48 hours at any of the temperatures considered.

The considerable yields obtained at temperatures too low for extensive thermolytic bond cleavage and the dependence of yield on solvent type indicate that solvolysis is the major depolymerization mechanism. However, a dissolution mechanism based on the given data and stated assumptions can not be derived. Initial activation energies were not evaluated due to the large error that would be introduced by assuming that the true initial reaction rate is that based on a 10 - 60 minute run. Shorter run times were not attempted due to the uncertainty in dissolution caused by the filtration time. The differences in ability of TMU and HMPA to dissolve coal are exemplified by the dissolution and retention results. Pure HMPA appears to solvate coal but the apparent formation of colloidal material prevents the determination of the magnitude of solvent effectiveness. Although no mention was made of colloid formation, previous investigators [10, 11] have noted that HMPA by itself is a poor coal solvent. It is possible that saturated hydrocarbons, immiscible in HMPA, are produced which prevent solid-liquid separation by filtration, although HMPA may also be complexing with other coal products. The colloidal material is apparently dispersed by the presence of TMU, which is miscible with saturated hydrocarbons. TMU by itself is not as effective as a mixture of TMU and HMPA in dissolving coal. Because of colloid formation when using pure HMPA as solvent, it was not determined if the extraction yield using

the solvent mixture is greater than or equal to the sum of the yields using the pure solvents, which would indicate whether or not TMU and HMPA act independently in solvating coal. Other investigators have proposed coal dissolution mechanisms which may be applicable to this process. Roy et al. [19] believed solvation is an electrostatic phenomenon with "the coulombic forces (ion-dipole, dipole-dipole) and hydrogen bond providing a major contribution to the solvation process. Solvation proceeds through donor and acceptor properties in one extreme through the intermediate dipole association and formation of unstable coordination compounds to van der Waal's interaction". Although Atherton and Kulik [16] noted that some coal radicals probably react with the solvent (the free radical concentration is about 2×10^{19} free radicals per gram of coal in a high volatile bituminous coal [42]), heterolysis, not homolysis, is most likely the primary means by which coal is decomposed in processes with temperatures at or below 550 - 700 degrees Fahrenheit. Since TMU and HMPA strongly solvate and then shield cations to accelerate reactions involving anions, heterolysis would be encouraged in the solvents. After obtaining data from strongly basic systems at 635 degrees Fahrenheit using a hydrogen-donor solvent that could not be explained by the radical chain mechanism, Ross and Blessing [17] suggested that the operative mechanism of coal conversion was ionic in nature, involving hydride donation by the solvent followed

by proton transfer. Hydrogen could be supplied by the coal itself [43]. The reduction mechanism and net reaction are illustrated in Figure 16 where coal-H⁻ and coal-H₂ are an anionic intermediate and reduced coal, respectively. They hypothesize that the major role of hydride donors in coal liquefaction processes is the reduction of quinones and other oxidants in coal to unreactive compounds; the coal then liquefies thermally with no hydrogen addition. In the reduction of aryldiazonium hexafluorophosphates, TMU was used as a source of hydride hydrogen [44]. Formed from the ionic decomposition of aryldiazonium hexafluorophosphate in TMU, highly-reactive aryl cations, Ar⁺, abstract hydride from the solvent according to Figure 17. The resultant urea carbonium ion is believed to react with a PF₆⁻ ion to yield PF₅ and fluorinated TMU. Although it is possible that hydride transfer occurs between TMU and coal, no documented evidence was found regarding HMPA as a hydride transfer agent or supporting the hydride transfer mechanism with the solvents and coal.

Figure 16. Ionic mechanism of coal reduction.



Net reaction:

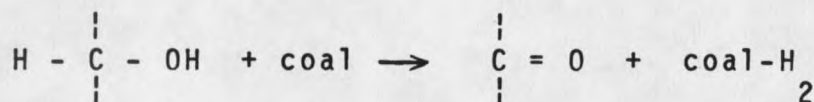
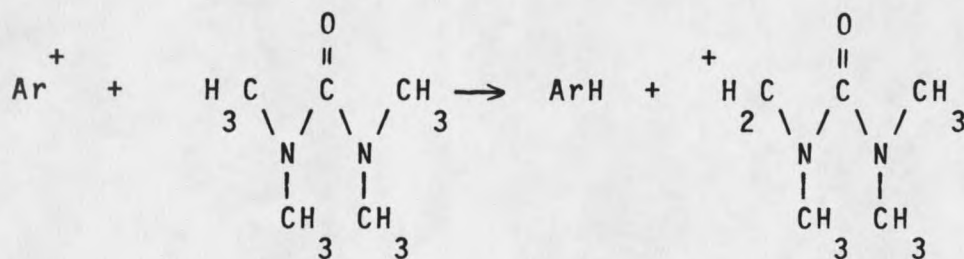


Figure 17. TMU as a hydride transfer agent.



Since dissolution and initial dissolution rate tend to increase with increasing temperature, higher dissolution values and rates are expected at temperatures above those examined in this investigation. Kiebler [12] cited Pott et al. who found that maximum yields are obtained when the extraction temperature is slightly below the decomposition temperature (defined as that temperature where a rapid evolution of gas occurs) of the residue, approximately 700 to

750 degrees Fahrenheit. However, higher reaction temperatures can promote undesirable side reactions (e.g., excess gas and coke production), make yields much more sensitive to other reaction variables such as hydrogen overpressure, and pose equipment problems. Whitehurst et al. [14] and Pott et al., as cited by Kiebler [12], found little advantage in using reaction temperatures above 800 degrees Fahrenheit on bituminous coals. Also, retention results indicate a large amount of interaction between coal and solvent: retention levels increase with increasing temperatures and the incorporation of solvent fragments into the residue is indicated. Unable to remove incorporated solvent from coal residues, other investigators [12, 16, 23] have also noted large quantities of solvent retention. Dryden [28] hypothesized that the unpaired electrons of nitrogen or oxygen in specific solvents form complexes with coal molecules, causing solvent incorporation. The swelling of coal has been postulated [16] as a result of the formation of these complexes. Although basic nitrogen solvents have been found to be outstanding in dissolving coal, most of the investigators have also noted that the considerable solvent loss via incorporation makes their use impractical in a commercial process [16]. Unless measures can be taken to reduce irreversible solvent incorporation to acceptable levels, economic trade-offs will dictate the optimum dissolution, which may be much less than the maximum dissolution that can be obtained.

Therefore, the retention results indicate the need for: (i) additional process modification to minimize solvent retention and (ii) access to analytical instruments not available to the author to evaluate the error in each assumption made to calculate actual dissolution and retention.

To maximize the process potential, the following procedures should be considered:

(i) The assumptions made to calculate yields should be modified to better model the liquefaction process. In particular, the coal-solvent interaction needs to be determined so accurate yields and retention values can be calculated.

(ii) Maximum yields should be determined. The number of extraction stages should be maximized since complete extraction can never be obtained in a single stage. To prevent the extraction yield from passing through a maximum due to condensation reactions during coal and solvent preheating, Dryden [22] cited Tebbett et al. who recommended that a Soxhlet or countercurrent method be used when possible.

(iii) Solvent recovery should be maximized. Conditions promoting solvent loss by fragmentation or incorporation into the residue should be avoided when possible. Solvent/residue separation and residue washing techniques should be thorough and standardized. Different wash liquids should be considered.

(iv) Results using other bituminous coals should be compared. If various particle sizes are considered to

observe possible mass-transfer restrictions, attention should be given to minimize attrition.

(v) Inexpensive solvents blended with TMU and HMPA have been used and should be further explored. Ward has prepared less costly solvent combinations and obtained encouraging dissolution results [37]. A maximum dissolution of 55% was observed for Bakerstown coal using 80% tetralin, 10% TMU, and 10% HMPA in 10 minutes at 320 degrees Fahrenheit. Atherton and Kulik [16] noted that whenever basic nitrogen solvents are used in conjunction with other solvents in dissolving coal, they disproportionately control the chemistry of the process. Unfortunately, coals have been found to selectively absorb the nitrogen bases [14]. Ward et al. [45] proposed that "TMU and HMPA act most importantly as swelling/attacking agents and that solvation/stabilization of product species can be done with aromatic/hydroaromatic solvents which, by themselves, are relatively inactive towards coal at these conditions".

SUMMARY

1. A 1:1 mixture of TMU and HMPA is more effective than pure TMU in dissolving Kittanning coal. Coal conversion to 41% can be achieved using a 1:1 mixture of the solvents for 40 minutes at 320 degrees Fahrenheit. The maximum dissolution using TMU as solvent, 23%, was observed after 12 hours at 320 degrees Fahrenheit. HMPA as the solvent apparently produced a colloidal suspension that could not be isolated.
2. Dissolution and initial dissolution rate tend to increase with increasing run temperature.
3. Dissolution rate is fast initially but tapers off when condensation reactions begin to dominate.
4. Maximum dissolution is achieved at shorter times with increasing run temperatures.
5. Solvent retention levels increase with increasing run temperature.
6. Substantial amounts of TMU and HMPA are incorporated into the residue, probably at least in part as solvent fragments.

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APPENDICES

APPENDIX A

RAW DATA

Table 14. Raw data for TMU runs.

| Solvent | Temp (F) | Run time (min) | Coal wt (g) | Residue wt (g) | %N | Wet Residue %C | %H | %O | Run number |
|---------|----------|----------------|-------------|----------------|------|----------------|------|------|------------|
| TMU | 79 | 60 | 3.9925 | 3.8361 | 1.54 | 77.16 | 5.12 | 6.14 | 21 |
| TMU | 79 | 60 | 4.0029 | 3.9016 | 1.38 | 76.65 | 5.42 | 5.82 | 35 |
| TMU | 79 | 720 | 3.9850 | 3.9068 | 1.94 | 77.14 | 5.20 | 6.09 | 22 |
| TMU | 79 | 2880 | 3.9937 | 3.8233 | 1.54 | 76.57 | 5.08 | 5.73 | 31 |
| TMU | 200 | 20 | 4.0033 | 3.7142 | 2.24 | 72.14 | 4.95 | | 39 |
| TMU | 200 | 40 | 3.9310 | 3.5105 | 2.54 | 71.55 | 5.01 | | 38 |
| TMU | 200 | 60 | 3.8833 | 3.7674 | 2.71 | 75.54 | 5.31 | 6.42 | 23 |
| TMU | 200 | 720 | 3.9705 | 3.7172 | 3.10 | 70.16 | 5.21 | 6.23 | 24 |
| TMU | 200 | 2880 | 4.0085 | 3.4417 | 2.68 | 71.15 | 5.06 | 6.51 | 30 |
| TMU | 320 | 20 | 3.9884 | 3.7205 | 3.40 | 68.04 | 5.01 | 6.57 | 25 |
| TMU | 320 | 720 | 4.0397 | 3.6207 | 3.93 | 69.40 | 5.16 | 6.66 | 26 |
| TMU | 320 | 2880 | 4.0099 | 3.6863 | 3.67 | 70.75 | 5.15 | 6.52 | 32 |

Table 15. Raw data for TMU+HMPA runs.

| Solvent | Temp (F) | Run time (min) | Coal wt (g) | Residue wt (g) | %N | Wet Residue | | | | Run number |
|----------|----------|----------------|-------------|----------------|------|-------------|------|------|------|------------|
| | | | | | | %C | %H | %O | %P | |
| TMU+HMPA | 79 | 75 | 4.0060 | 4.0187 | 1.80 | 77.82 | 5.23 | 6.04 | | 16 |
| TMU+HMPA | 79 | 735 | 4.0015 | 3.9079 | 1.65 | 75.75 | 5.08 | 6.14 | | 17 |
| TMU+HMPA | 79 | 2880 | 3.9970 | 3.7521 | 1.58 | 76.33 | 5.44 | 5.72 | 0.67 | 33 |
| TMU+HMPA | 200 | 20 | 2.9538 | 2.8289 | 2.78 | 74.43 | 5.26 | 6.37 | | 19 |
| TMU+HMPA | 200 | 60 | 4.0077 | 3.7679 | 2.79 | 72.15 | 5.36 | 5.88 | 1.36 | 27 |
| TMU+HMPA | 200 | 720 | 3.9959 | 3.2505 | 3.17 | 73.66 | 5.67 | 6.13 | 0.77 | 34 |
| TMU+HMPA | 200 | 2880 | 3.9979 | 3.9461 | 5.90 | 67.40 | 5.93 | 6.48 | 3.08 | 29 |
| TMU+HMPA | 320 | 10 | 3.9784 | 3.2407 | 5.70 | 64.53 | 5.62 | | | 37 |
| TMU+HMPA | 320 | 20 | 3.0139 | 2.5219 | 5.12 | 63.19 | 5.43 | 6.75 | 2.74 | 20 |
| TMU+HMPA | 320 | 40 | 3.9881 | 3.2797 | 6.11 | 62.03 | 5.62 | | | 36 |
| TMU+HMPA | 320 | 720 | 3.9869 | 3.4422 | 4.68 | 60.82 | 5.00 | 6.94 | 4.78 | 28 |

APPENDIX B

RAW RESULTS

