



Extraction of Colstrip coal using supersolvents in conjunction with the water-gas shift reaction
by Sylvester John Losinski

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 extraction using supersolvents, tetramethylurea (TMU) and hexamethylphosphoramide (HMPA), in the presence of the water-gas shift reaction may be a viable method for hydrogenating and extracting coal products in one operation. In this investigation the effects of solvent mixture, solvent pH, temperature, and carbon monoxide pressure on coal extraction were evaluated. Experiments were conducted on Colstrip sub-bituminous coal and other coals in a magnetically stirred batch autoclave with carbon monoxide pressures ranging from 250 to 1000 psig.

Extraction of Colstrip coal to 35 percent was observed at 1607deg;C using a solvent mixture of TMU/HMPA/Tetralin/H₂O with a pH of 13.12 and a carbon monoxide pressure of 500 psig.

It was found that extraction decreased with increasing carbon monoxide pressure in the range of 250 to 1000 psig, but the extraction value for any pressure was greater than when carbon monoxide was not used.

Extraction by the present procedure was not found to be temperature dependent over the range of 25 to 200°C. Possible explanations for this unexpected result have been presented.

Solvent was retained in the extraction residue in the amount of 6 to 17 percent by weight. The total extraction must be dramatically increased, or the amount of solvent retention decreased, for the process to be viable as a coal extraction method.

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Bozeman, Montana

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Approval

of a thesis submitted by

Sylvester John Losinski

This thesis has been read by each member of the author's graduate 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.

March 5, 1986
Date

John T. Sears
Chairperson, Graduate Committee

Approved for the Major Department

March 5, 1986
Date

John T. Sears
Head, Major Department

Approved for the College of Graduate Studies

March 10, 1986
Date

Henry L. Parsons
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ABSTRACT

Coal extraction using supersolvents, tetramethylurea (TMU) and hexamethylphosphoramide (HMPA), in the presence of the water-gas shift reaction may be a viable method for hydrogenating and extracting coal products in one operation. In this investigation the effects of solvent mixture, solvent pH, temperature, and carbon monoxide pressure on coal extraction were evaluated. Experiments were conducted on Colstrip sub-bituminous coal and other coals in a magnetically stirred batch autoclave with carbon monoxide pressures ranging from 250 to 1000 psig.

Extraction of Colstrip coal to 35 percent was observed at 160°C using a solvent mixture of TMU/HMPA/Tetralin/H₂O with a pH of 13.12 and a carbon monoxide pressure of 500 psig.

It was found that extraction decreased with increasing carbon monoxide pressure in the range of 250 to 1000 psig, but the extraction value for any pressure was greater than when carbon monoxide was not used.

Extraction by the present procedure was not found to be temperature dependent over the range of 25 to 200°C. Possible explanations for this unexpected result have been presented.

Solvent was retained in the extraction residue in the amount of 6 to 17 percent by weight. The total extraction must be dramatically increased, or the amount of solvent retention decreased, for the process to be viable as a coal extraction method.

INTRODUCTION

Sears (1) has suggested a novel approach to the liquefaction of coal using a specific group of chemicals that he called supersolvents. In preliminary experiments, at room temperature and pressure, he was able to show that solvents of the general formula



exhibit unusually high extraction characteristics for certain types of coal. Based upon this evidence he submitted a proposal to the Department of Energy to investigate the feasibility of using a supersolvent extraction process for the liquefaction of coal. The ensuing research grant has provided the funding for this investigation and other related work.

Co-investigators T. Ward (2) and C. Ichioka (3) examined the effectiveness of tetramethylurea, hexamethylphosphoramide, and other supersolvents on the extraction of coal. Their efforts revealed that the blending of supersolvents resulted in better extraction of coal than could be obtained by any one supersolvent alone. They were also able to document that relatively large amounts of solvent were retained in the coal residue.

T. Sahin, another co-investigator, performed several experiments in a packed bed reactor with hydrogen overpressure in an effort to determine if enhanced extraction of coal could be achieved by hydrogenation of coal in the presence of supersolvents. His efforts were thwarted by materials handling and coal swelling problems, but he was able to tentatively conclude that hydrogen overpressure was ineffective in enhancing the extraction of coal.

Other investigators have documented the high reactivity of the nascent hydrogen formed in the water-gas shift reaction (4,5,6). Sears (7) postulated that enhanced extraction of coal may be possible by using the water-gas shift reaction in conjunction with supersolvent extraction. This process would have a distinct advantage over other extraction processes in that both the extraction and hydrogenation of the coal could be accomplished in one operation.

Whitehurst et al. (8) identified several factors that should be considered when evaluating a new or improved coal-liquefaction technology. The most important of these factors are:

- △ hydrogen utilization efficiency
- △ solvent overhydrogenation
- △ generation of hydrogen-rich final products
- △ ease of solids separations
- △ reduction of reaction time
- △ reduction of process temperature

Preliminary experimental work performed by Sears (1) indicates that the supersolvent coal-liquefaction process may have significant advantages

over existing coal-liquefaction processes based on the factors identified by Whitehurst.

The purpose of this investigation was to examine the extraction of coal using supersolvents in conjunction with the water-gas shift reaction. The effects of reaction parameters such as temperature, pressure, solvent, and pH of the solvent were to be characterized.

Coal Structure

Coal deposits were formed by the action of pressure and heat on plant matter over long periods of time. During the coalification process progressive elimination of oxygen, primarily in the form of carbon dioxide and water, leads to coals of higher rank (9). On a geologic timescale plant matter is first converted to peat and then to lignite, sub-bituminous, bituminous, and finally anthracite coal. Several excellent references are available on the origin and formation of coal (9,10,11).

It has been found that the morphological nature of coal is very complex. Microscopic examination of coal reveals that it is not homogeneous, but instead is a mixture of several different identifiable macerals or lithotypes. Each lithotype exhibits different physical and chemical properties. Some of the lithotypes are primarily inert mineral matter, while others contain high quantities of extractable material.

The chemical makeup of coal has been studied by many scientists (12,13,14). Several persons have proposed structures, incorporating experimentally observed functional groups, that portray an "average" coal molecule. The structure for a bituminous coal proposed by Shinn

(15) is shown in Figure 1. As can be seen from the model structure, coal is a highly crosslinked aromatic compound with a large number of oxygen-containing functional groups. Most of the nitrogen in the coal molecule is tied up in the aromatic rings and as such is probably immune to low severity liquefaction reactions. There are several relatively weak bonds in the coal structure, primarily ester and ether bonds, and it is thought that liquefaction reactions are initiated at these sites (16).

Solvent Theory

Several approaches have been presented to explain the correlation between solvent characteristics and their extractive properties on coal. Most solvent theory approaches have originated from one of two dissolution models: those of Dryden and van Krevelen (17,18).

Dryden (17) asserts that coal consists of 'micelles' that can be assumed to be rigid and relatively indestructible. Coal extraction solvents act by swelling the micelle network so that smaller molecular units contained within the micelle may diffuse through the newly enlarged pores. A suitable solvent must therefore swell the coal structure and stabilize the coal fragments that are transported to the surface via osmotic diffusion.

Van Krevelen (18) contends that coal can be viewed as a cross-linked polymer and hence the principles of polymer theory apply. He believes that the amount of extractable material dissolved by a solvent is determined by that solvent's solubility parameter, $\delta^2_0 = \delta^2_D + \delta^2_P + \delta^2_H$, a thermodynamic property, and the solubility

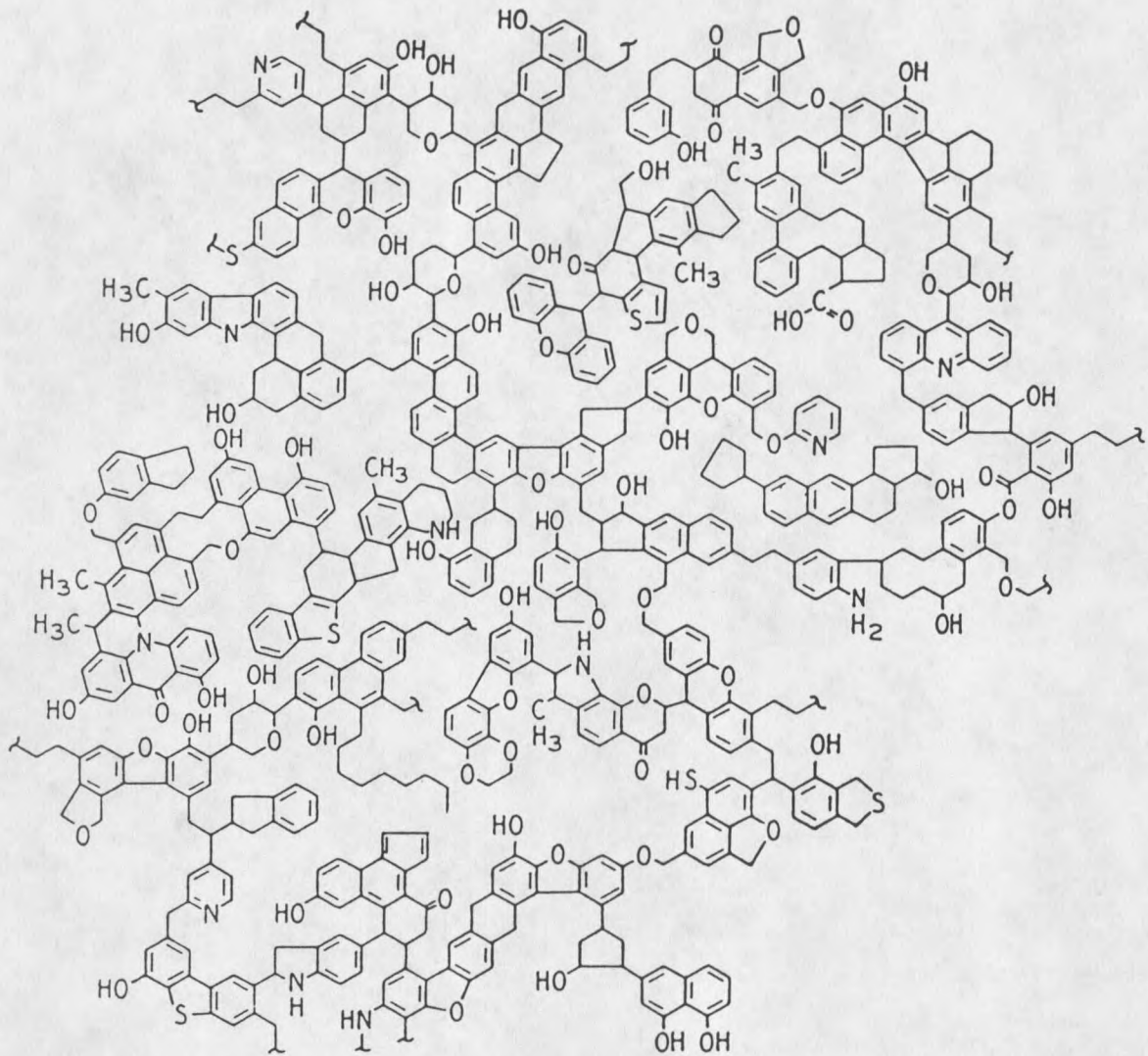


Figure 1. Shinn's Model of Bituminous Coal Structure

parameter of the coal. The overall solubility parameter is comprised of a dispersion component, a polar component, and a hydrogen bonding component. Maximum solubility of the coal is obtained when the solubility parameters of the coal and solvent are equal.

It is possible that Hombach (19) has made a significant contribution to the work of van Krevelin by suggesting that the overall solubility parameter may be adjusted by using a mixture of solvents. By using a mixture of solvents it would then be possible to tailor the solubility parameter of the solvent to that of the target coal.

Ward (2) has suggested that the overall solubility parameter may not be the ideal criteria for selection of an extraction solvent. He has presented evidence that individual solubility parameters, functions of the overall solubility parameter, should be tailored so that they match the individual solubility parameters of the target coal.

TMU and HMPA

Hexamethylphosphoramide, HMPA, and tetramethylurea, TMU, are the solvents of interest in this investigation. HMPA and TMU are members of a class of solvents called dipolar aprotic solvents. The structures of each are shown in Figure 2 and some of their physical properties are listed in Table 1.

HMPA is a colorless mobile liquid, which is miscible with water in all proportions. It is also miscible with many polar and nonpolar organic solvents, but not with saturated hydrocarbons (20). HMPA is prepared by reacting phosphorous oxide trichloride with an excess of

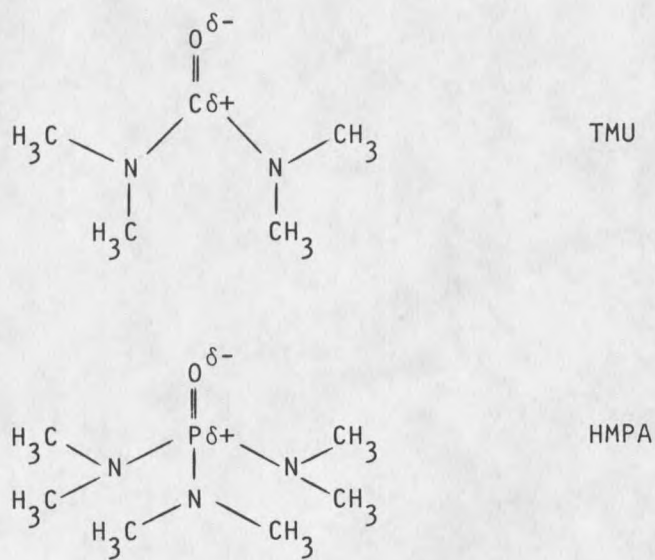
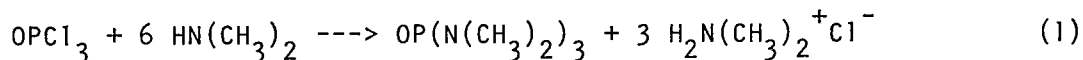


Figure 2. Structure of TMU and HMPA

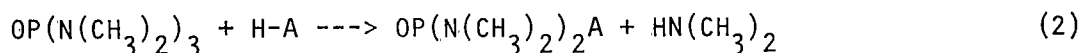
Table 1. Physical Properties of TMU and HMPA

Physical Properties	TMU	HMPA
Molecular Weight	116.16	179.20
Boiling Point ($^{\circ}\text{C}$)(1 atm)	176.5	235
Melting Point ($^{\circ}\text{C}$)	-1.2	7.20
Density (g/ml)(25 $^{\circ}\text{C}$)	0.9619	1.0253
Dielectric Constant	23.45	30.00
Dipole Moment (debye)	3.37	5.37

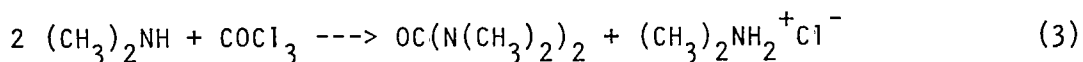
dimethylamine. The stoichiometry of the reaction is shown in Equation (1).



The chemical properties of HMPA are primarily due to the partial ionic character and polarity of the molecule. A high electron density, partial negative charge, is located around the oxygen atom, and a partial positive charge is distributed over the nitrogen and phosphorous atoms. The charge separation and unhindered electron cloud about the oxygen atom make HMPA an excellent hydrogen bond acceptor and a poor hydrogen bond donor. HMPA is very stable at temperatures below its normal boiling under basic conditions, but can readily be attacked by Lewis or Bronstead acids. The products of acidic attack are shown in Equation (2).



TMU is also a colorless liquid that is miscible with all common organic solvents as well as with water. TMU is prepared by reacting phosgene and dimethylamine as illustrated in Equation (3).



TMU is stable at temperatures below its normal boiling point under most conditions. Luttringhaus (21) has documented the protonation of TMU under severe acidic conditions, but contends that TMU is an excellent reaction medium for many conditions and is very unreactive while being an excellent solvent.

The author refers the reader to the works of Normant (20) for exhaustive information concerning the chemical properties of HMPA and to Luttringhaus (21) for the properties of TMU.

The physical and chemical properties of HMPA and TMU are similar in many ways. Some of the most notable similarities are:

- ▲ Both are miscible with water in all proportions.
- ▲ Both solubilize a wide range of organic compounds, particularly aromatic compounds.
- ▲ Both molecules have an oxygen atom that carries a negative charge and a positive charge that is delocalized by resonance over a central atom and nitrogen atoms.
- ▲ Both have high dielectric constants and large dipole moments.
- ▲ Both are liquid at room temperature and have a wide liquid-state temperature range.

A word of caution is probably in order concerning the handling of TMU and HMPA. The pathologic consequences of exposure to these chemicals have not been very well documented. It is speculated that HMPA in particular may be a skin-contact carcinogen.

Water-Gas Shift Reaction

Several scientists have documented the enhanced reactivity of the nascent hydrogen formed from the water-gas shift reaction over elemental hydrogen in the hydrogenation of coal and coal derived products (22,23, 24). This process has since been named 'Costeam.' The water-gas shift reaction involves the reaction of carbon monoxide and steam to produce hydrogen and carbon dioxide and derived its name from its industrial use

to increase the hydrogen content of water gas produced from the reaction of steam with hot coke or coal. The stoichiometry of the reaction is shown in Equation (4).



For the conditions involved in this experimentation, low temperature and low to moderate pressure, the thermodynamic equilibrium of this reaction lies far to the right as written in Equation (4). The reader is referred to Smith and Van Ness (25) for additional information regarding the thermodynamics of the water-gas shift reaction.

The mechanism of the water-gas shift is not very well delineated and there is some controversy over this matter. There are several catalysts, homogeneous and nonhomogeneous, that are known to catalyze the reaction. The alkali catalyzed water-gas shift mechanism proposed by Elliot (26) is shown in Figure (3). Because almost all of the experimentation of this investigation was conducted under alkaline conditions, it is believed that this mechanism may be of importance to the present investigation.

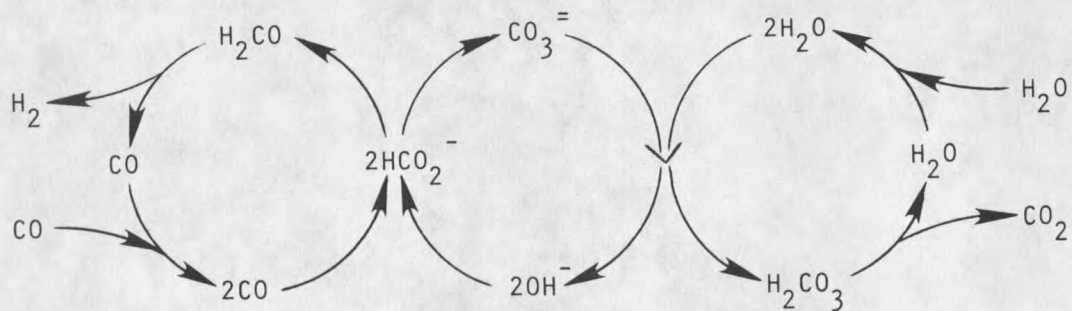


Figure 3. Proposed Mechanism of Aqueous Alkali Catalyzed Water-Gas Shift Conversion.

Related Work

To the author's knowledge, prior to this work no one has attempted to extract coal with a strongly reactive solvent in conjunction with the water-gas shift reaction. The solubility of water in TMU and HMPA makes possible the contact of coal with both water and a good coal solvent in a single phase. A great deal of work has been performed on the solvent extraction of coal and a good deal of work has been performed on the hydrogenation of coal using the water-gas shift reaction, but the combined effects of using both at one time have not been investigated.

As discussed earlier in this thesis, Dryden (17) and van Krevelen (18) have formulated many of the currently accepted theories regarding the solvent extraction of coal. The reader is referred to their works for a detailed study of solvent extraction of coal.

Work performed by scientists subsequent to that of Dryden and van Krevelen have contributed significantly to the understanding of the solvent extraction of coal. Hombach (19) was able to demonstrate that a correlation existed for the dissolution of coal between the solubility parameter of the coal and the solubility parameter of the solvent. Using solubility parameter theory, he was able to explain the long-standing observation that bituminous coals generally exhibited the largest degree of dissolution for most of the good coal extraction solvents. Good coal extraction solvents have solubility parameters close to those of bituminous coals. Hombach was also the first person to demonstrate that a mixture of poor solvents for coal can act as a better solvent when chosen with respect to the solubility parameter.

The work of Ward (2) and Ichioka (3) substantiate that of Hombach in that they, too, were able to observe enhanced dissolution of coal by using a mixture of appropriately chosen solvents. Ward suggests that individual solubility parameters instead of the overall solubility parameter should be the criteria for engineering the ideal coal extraction solvent. He contends that individual solubility parameters of the solvent mixture should match the individual solubility parameters of the target coal.

T. Sahin, a co-worker, unsuccessfully tried to hydrogenate coal in the presence of TMU and HMPA using a packed bed reactor and hydrogen overpressure. He was thwarted by materials handling problems. Coal swelling, which Dryden (17) identified as the first step of the extraction process, caused the packed bed reactor to plug up and virtually no solvent could permeate the coal plug. Sahin determined that some other coal-solvent contact method must be incorporated if these materials-handling problems were to be eliminated.

Many scientists have studied hydrogenation of coal using the water-gas shift reaction. Fischer (27) is credited with first documenting the use of carbon monoxide and water for the hydrogenation of coal. Later, Appell (28) initiated a substantial research effort to study the solubilization of low rank coal with carbon monoxide and water. The work of Appell is often quoted in current water-gas shift reaction literature on coal hydrogenation.

The work of Appell et al. on coal hydrogenation is far too extensive to be covered in any detail in this thesis, but some observations he has made should be presented. For coal hydrogenation

using the water-gas shift reaction with carbon monoxide overpressures of 4500 psi and reaction temperatures in the range of 375-400°C, Appell has documented the following facts:

- △ Conversion of coal to solvent-soluble products is greatest for low rank coals.
- △ Conversion increases with carbon monoxide overpressure up to 1000 psi and then increases only slightly with additional pressure.
- △ Conversion increases with increasing temperature.
- △ Conversion is twice as great with carbon monoxide overpressure as with hydrogen overpressure.
- △ Exposure of coal to air causes conversion to drop.

From Appell's observations he has concluded that the water-gas shift reaction may inhibit condensation reactions that lead to insoluble products. He has also concluded that the most significant contribution to the solubilization of low rank coals is probably due to the activated hydrogen species formed by the water-gas shift reaction.

Ross et al. (23) have also performed experimentation on the hydrogenation of coal using the water-gas shift reaction. Ross's investigations have revealed some important facts not documented by Appell. The most pertinent of these facts relative to this investigation are:

- △ There is a dramatic increase in the solvent-soluble fraction of coal when the pH of the water for the water-gas shift reaction is greater than 12.6.
- △ Basic water solutions alone do not enhance solubility.

- △ The use of hydrogen instead of carbon monoxide under basic conditions does not promote increased solubility.

Ross has suggested that the formate ion may act as a catalyst for the hydrogenation of coal under water-gas shift conditions.

Takemura and Ouchi (24) have investigated the catalytic liquefaction of coal using carbon monoxide and water in the presence of a cobalt-molybdenum catalyst. The results of their study roughly parallel those of Appell and Ross. Takemura and Ouchi have proposed that hydrogenolysis of the coal occurs by three routes: hydrogenolysis by the nascent hydrogen, solvolytic reaction with water, and stabilization of coal fragments in a vehicle oil.

Hydrogen can be formed in-situ by methods other than the water-gas shift reaction. Mondragon et al. (27) have studied the hydrogenation of coal using the zinc-water-coal reaction. Mondragon has documented that this method works best with low rank coals and works better at higher temperatures. These results are consistent with observations made by previously mentioned investigators working with the water-gas shift reaction and lend credible evidence to the speculation that the nascent hydrogen species is the key to enhanced coal dissolution.

Several studies have been made that attempt to characterize the reactivity of the nascent hydrogen formed in the water-gas shift reaction on coal by using model compounds (27,28,29,30). The reader is referred to these studies for information regarding the model compounds and the reaction products identified.

Research Objective

The objective of this research was to evaluate the action of the dipolar aprotic solvents TMU and HMPA under water-gas shift conditions on the extraction of coal. The total extraction of the coal observed was to be correlated with the experimental reaction variables of temperature, carbon monoxide overpressure, solvent blend, and pH of the initial solvent. Additionally, the quantity of solvent retained in the residue after extraction was to be evaluated. Designed to be a preliminary study, this research was not intended to be exhaustive in characterizing each reaction variable, but to determine the general extraction trends associated with each variable. The viability of this process and identification of promising research-work directions were to be evaluated.

EXPERIMENTAL

Raw Materials and Chemical Reagents

Colstrip sub-bituminous coal was used almost exclusively in the work performed in this investigation. The coal sample was obtained from the crushing mill of Western Energy Corporation located in Colstrip, Montana. As received, the coal consisted of particles ranging in diameter from about one inch to approximately 60 mesh. While in transit, the coal was stored under atmospheric conditions. When received at Montana State University, the sample was placed under nitrogen to prevent any further oxidation. The time that the coal sample was exposed to the atmosphere is estimated to be about one week.

Savage lignite and Bakerstown coal were used on a limited basis in this investigation. The Savage lignite sample was obtained from a fellow student at Montana State University. It was stored under atmospheric conditions, and it is not known how much time had elapsed since the sample was mined. The Bakerstown coal was obtained directly from the mine in Preston County, West Virginia, and was stored under atmospheric conditions while in transit.

All of the coal samples were sized for experimental use using the same method. Each sample was loaded into a two-liter porcelain ball mill while under a nitrogen atmosphere. After the ball mill had operated for about 24 hours the sample was removed, while under a nitrogen atmosphere, and sized using standard Tyler screens. Only sample material

ranging in size from 60 to 100 mesh was retained. The sized sample material was stored under a nitrogen atmosphere until used for experimentation.

The manufacturer and purity of the solvents, reagents, and gases used in this investigation are shown in Table 2. No additional testing was performed to confirm the purity of these chemicals.

Table 2. Chemical Reagents Used

Chemical	Source	Purity
TMU	Aldrich Chemical	99%
HMPA	Aldrich Chemical	99%
Tetraline	Aldrich Chemical	99%
Sodium Hydroxide	Chemical Stockroom	Unknown
Hydrochloric Acid	Chemical Stockroom	Unknown
Acetone	VanWaters & Rogers	99.5%
Carbon Monoxide	Airco	99.9%
Nitrogen	Liquid Air Corp.	98.6%

Experimental Apparatus

The apparatus used in this experimentation was a modified magnetically stirred catalytic reactor manufactured by Autoclave Engineers. A detailed drawing of the reactor vessel is shown in Figure 4, and the pertinent mechanical characteristics are listed in Table 3. An additional agitation vane was added to the reactor to enhance the turbulence of mixing within the reactor. A flow scheme for the reactants in the apparatus is shown in Figure 5.

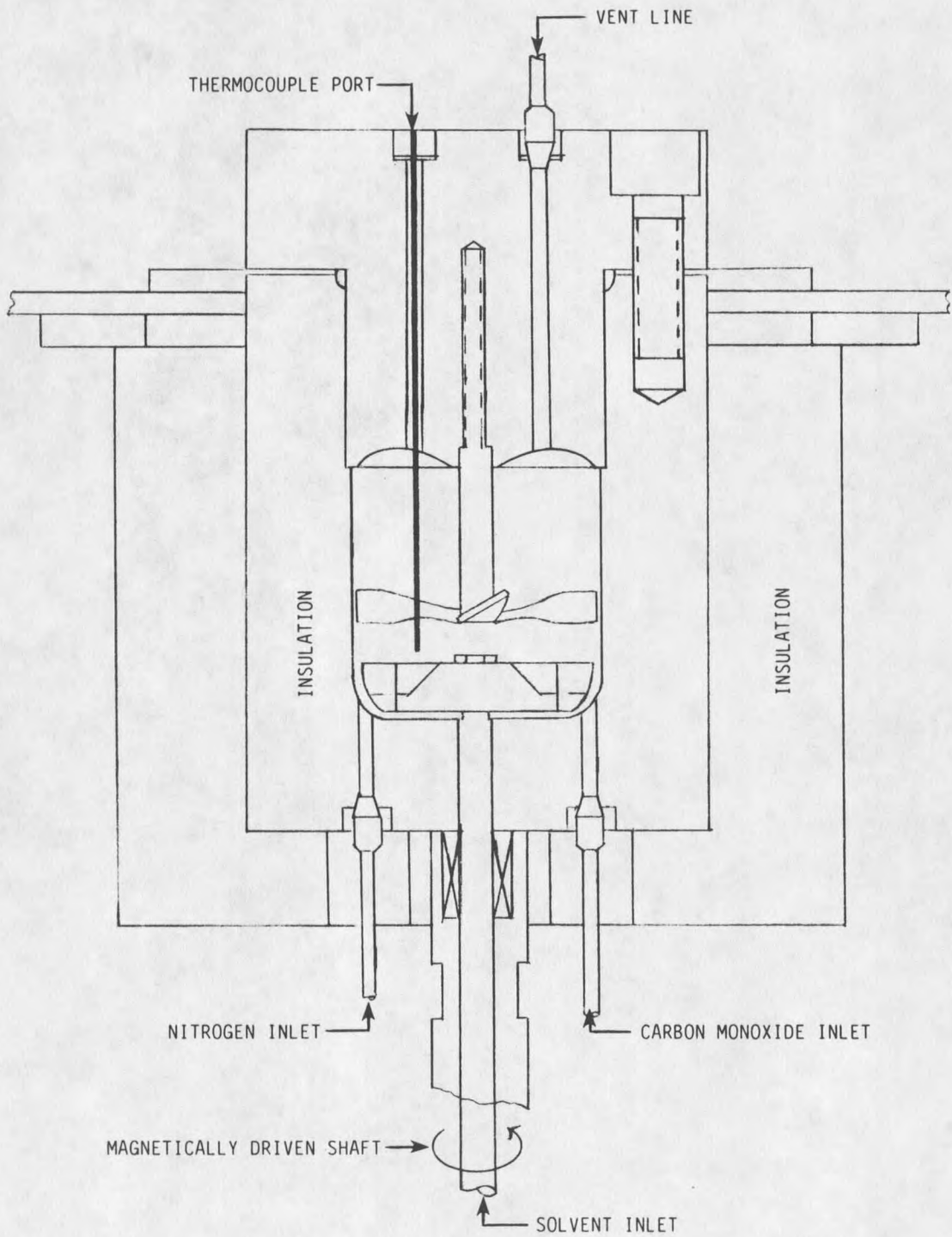


Figure 4. Magnetically Stirred Reactor.

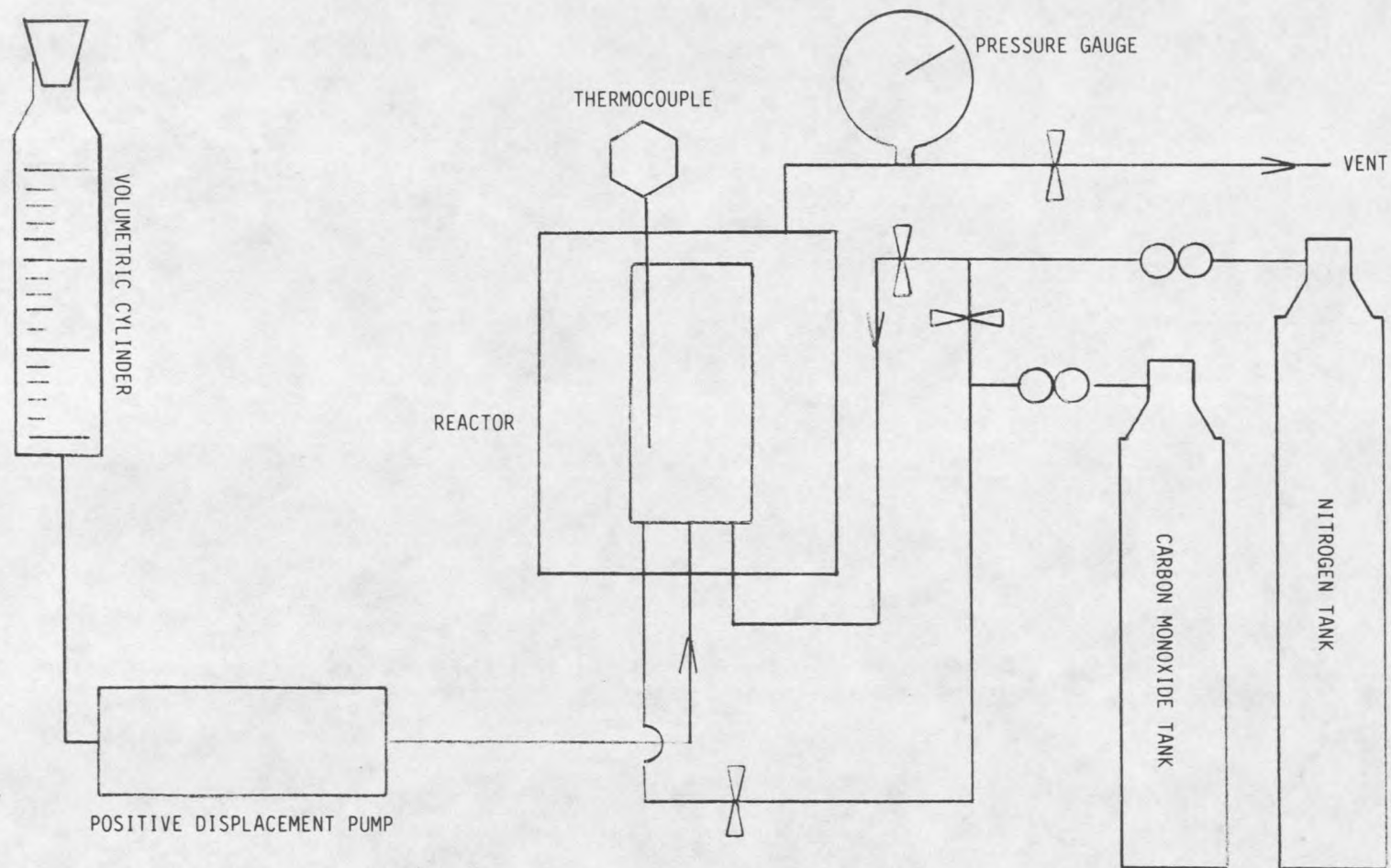


Figure 5. Flow Diagram for Experimental Reactor.

Table 3. Specifications of Magnetically Stirred Reactor.

Item	Specification
Reactor Material	Stainless Steel SA-182-F316
Reactor Volume	19.4 cubic inches
Working Pressure	0-3600 pounds per square inch
Working Temperature	72-1000 degrees Fahrenheit
Agitator Speed	0-2500 revolutions per minute

An adjustable positive displacement pump manufactured by Milroyal capable of delivering 70.0 cc/hr was used to introduce solvent to the reaction vessel.

Coal residues were separated from the extraction solvents using a vacuum filtration flask fitted with a conical funnel and Whatman #1 filter paper. The in-house vacuum was used as the vacuum source.

The pH measurements of the solvent mixtures and extraction products were made using an Orion Model 901 microprocessor ionalyzer fitted with a research grade pH electrode and a double junction reference electrode. A two solution buffer system was used to calibrate the apparatus.

The preparation, storage, and handling of the coal samples were carried out under nitrogen in a DriLab HE-43-2 glove box manufactured by Vacuum/Atmospheres Corporation. The samples were also weighed in the glove box.

Ash analyses were performed using a high temperature oven capable of at least 750°C. The weights of the samples were measured using a Mettler H80 analytical balance.

Elemental analyses (C,H,N) of the coal and coal residues were performed using a Carlo Erba Elemental Analyzer fitted with a DP 110 integrator and interfaced with an Osborne 1 microcomputer. The samples were weighed for the elemental analyses using a Cahn 29 electrobalance.

Experimental Procedure

A pre-weighed coal sample weighing approximately five grams was introduced to a reactor vessel at room temperature. The reactor was immediately sealed and purged with nitrogen. After a nitrogen purge of approximately five minutes, the power to the heating mantle of the reactor was turned on. Because of the large thermal mass of the system, approximately 12 to 15 hours were required after applying power to the reactor for the internal temperature to approach steady state.

During the time that the reactor was heating up, the solvent was prepared by adding 143 ml of TMU, or TMU-HMPA mixture, to 7 ml of water. Sodium hydroxide or hydrochloric acid was then added to the solvent mixture to adjust the pH. The pH of the solvent was measured at room temperature, just prior to its introduction to the reactor.

After the reactor warm-up period, 150 ml of solvent was introduced to the reactor at a volumetric flow rate of about 15 ml/min, using the positive displacement pump. The magnetic stirrer was activated and the speed adjusted to 1000 rpm. Carbon monoxide was introduced to the system and the pressure in the reactor was generally adjusted to 500 psig. The reactor was allowed to operate for one hour.

After the reactor had operated for one hour, the magnetic stirrer was turned off and the power to the heating mantle was also turned off. The reactor was allowed to cool for approximately ten hours.

The gases in the reactor were vented and the reactor was purged with nitrogen for 10-15 minutes. The reactor was opened and the contents removed using a vacuum-suction device. The reactor was washed with acetone to remove and recover small amounts of remaining residue.

The solvent coal-extract residue mixture was then filtered in a vacuum filtration flask fitted with preweighed Watman #1 filter paper. The acetone wash used to clean the reactor was filtered to recover the small amount of coal residue it contained. The coal residue filter-cake was then washed with acetone until the effluent appeared clear and the filter-cake appeared dry.

The filter-cake was placed in a vacuum desiccator that was attached to a vacuum pump capable of approximately 0.1 torr. The residue was weighed periodically and deemed dry when no significant weight change was detected between weighings at daily intervals. Most of the coal residue filter-cakes were considered dry after approximately one week in the desiccator.

Analytical Procedure

Water analyses on the coal samples were carried out in an air-available oven operating at 103°C. The coal samples were placed in porcelain crucibles and weighed on a Mettler H80 analytical balance. The samples were placed in the drying oven for 24 hours. The samples were then removed from the oven, allowed to cool to room temperature,

and weighed. The loss in weight of the samples was attributed to water loss. The assumption of water loss will be addressed later in this thesis.

Ash analyses on coal samples were performed by placing preweighed samples in porcelain crucibles and inserting them in an air-available ashing oven operating at 750°C. The samples were allowed to remain in the oven for 24 hours.

Elemental analyses (C,H,N) of the coal and coal residues were performed by the author using standard quantitative procedures associated with the operation of a Carlo Erba elemental analysis machine.

RESULTS AND DISCUSSION

Total extraction on a mineral-matter and water-free basis for Colstrip sub-bituminous coal and other coals used in this investigation ranged from 10 to 35 percent. The range of reaction conditions used to achieve these results are listed below:

- △ Temperature -- 25-205°C
- △ CO overpressure -- 250-1000 psig
- △ Reaction time -- 1 hour
- △ Solvent blends -- TMU-H₂O, TMU-HMPA-H₂O, TMU-HMPA-Tetralin-H₂O
- △ Solvent pH -- 7-14

Because of high nitrogen concentrations in the residue, it was apparent that significant amounts of solvent were retained in the coal residue and somewhat complicated the interpretation of the extraction results. Assumptions regarding the concentration of nitrogen in the residue had to be made in order to calculate the extraction in the coal.

It was also discovered that at temperatures of 100-103°C, conditions normally associated with the drying of coal, compounds other than water must be volatilized from the coal. The specifics of this discovery and documentation will be presented later in this section.

Calculations and Assumptions

Absolute extraction of the organic matter of coal samples was calculated using Equation (5).

$$AE = \frac{WC * CWA - WR * RWA * RS}{WC * CWA} \quad (5)$$

where:

AE = absolute extraction

WC = weight of coal on an ash- and water-contained basis

CWA = correction factor to correct for water and ash in the coal

WR = weight of solid residue

RWA = correction factor for water and ash in the residue

RS = correction factor for solvent in the residue

The value of CWA, the correction factor for the water and ash in the coal, was calculated using Equation (6). It was assumed that only matter conventionally described as "moisture" was volatilized from the coal when left in an air-available oven at 103°C for 24 hours. It was also assumed that combustion of the coal was complete after 24 hours in an air-available ashing oven operating at 750°C.

$$CWA = 1 - MW - MA \quad (6)$$

where:

MW = mass fraction of water in the coal on a wet-coal basis

MA = mass fraction of ash on a wet-coal basis

The value of RWA, the correction factor for the water and ash in the residue, was calculated using Equation (7). Again it was assumed that only water was volatilized from the residue when left in an

air-available oven at 103°C for 24 hours. Ashing was assumed complete after combustion in an air-available oven for 24 hours at 750°C.

$$RWA = 1 - MWR - MAR \quad (7)$$

where:

MWR = mass fraction of water in the residue

MAR = mass fraction of ash in the residue

Because of the excessively high nitrogen content of the residue, it became evident that solvent and/or solvent fragments were retained in the residue. Incorporation of solvent in the coal residue manifests itself as a lowering of the observed degree of extraction. The use of the solvent correction factor, RS, was an attempt to quantify the amount of solvent retained in the coal residue matrix so that the total amount of material extracted from the coal could be estimated.

Several assumptions were required so that the solvent retention correction factor could be calculated. The first assumption was that the residue on a solvent-free basis would have the same mass fraction nitrogen as the original coal. This assumption is probably valid because most of the nitrogen in the coal is tied up in aromatic rings. Model compound studies performed by Lynch (30) have demonstrated that aromatic rings containing nitrogen are hydrogenated under water-gas shift conditions, but hydrolysis of the ring does not occur. It is thought that nitrogen will be neither concentrated in the products nor in the residue because of its distribution within the coal matrix. The reader is referred to the proposed coal structure shown in Figure 1 to verify the expected position of nitrogen in the coal matrix.

The second assumption made in the calculation of the solvent retention factor was that the solvent does not fragment under the reaction conditions encountered in this investigation and was retained in the residue as a complete molecule. As reported by Luttringhaus and Normant (20,21), the reaction conditions encountered in this experimentation should not be severe enough to fragment TMU and HMPA, but the author was unable to verify this in his experimentation.

It was further assumed that when mixtures of solvents were used, the solvents were retained in the same molar ratio in the residue as were available in the bulk solvent. This assumption is dubious at best. A more thorough discussion of the possible errors associated with each assumption used in the calculations is presented in the errors and reliability section of this thesis.

The solvent correction factor has the units of grams of solvent-free residue per gram of solvent-containing residue. The simultaneous solution of four elemental balance equations and a constraint equation are required to generate the solvent correction factor. The reader wishing additional information on the solvent retention factor calculations is referred to Appendix B, where a sample calculation is illustrated.

All of the raw data generated during the course of this investigation are presented to the reader in Appendix A. A sample calculation that details the entire calculation sequence for one experimental run is shown in Appendix B. The results of all of the extraction runs as calculated are shown in Appendix C.

Error and Reliability of Measurements

This investigation was designed to be cursory in nature, and as such, more emphasis has been placed on detecting trends in extraction characteristics for specified reaction parameters than in documenting the exact magnitude of extraction.

Great care was taken during the experimental procedure and analytical methods used in this experimentation to obtain accurate data. In spite of the fact that caution was taken, several assumptions that were subjective in nature were used in the course of calculating the coal extraction value. Each term used in the absolute extraction equation, Equation (5), has an inherent relative error and those are shown in Table 4. The reader is referred to Appendix D for information on how the relative error values were established.

Table 4. Relative Error of Measurements.

Variable	Relative Error
WC	±0.1%
WR	±2.0%
CWA	±0.5%
RWA	±0.2%
RS	±1.9%

Using the error propagation method outlined by Mickley et al. (31), it has been calculated that the extraction value for run 17, which is considered average, may be high or low by as much as 4.0 percentage

points. The error bar for all illustrations showing run 17 should extend 4.0 percentage points above and below the calculated value. The length of the error bars is a weak function of the extraction, but the author has chosen to consider the error constant over the range of extraction values in this investigation.

The Coal Drying Anomaly

It has long been known that low rank coals contain a significant amount of moisture. The amount of moisture in a coal sample has traditionally been characterized by drying a freshly ground sample of coal in an oven at 100-103°C for 24 hours and attributing the weight loss to that of water loss. Elemental analysis of a Colstrip coal before and after the standard drying procedure has revealed that compounds other than water must be volatilized. The elemental analyses for the wet and dry coal samples are shown in Table 5.

Table 5. Elemental Analysis for Wet and Dry Coal.

Colstrip Coal	Weight Percent			Ash Content
	Elemental Analysis			
	N	C	H	
Wet	0.92	56.67	4.48	8.04
Dry	1.13	67.55	4.58	(9.78)*

*Calculated

Using a 100-gram, wet-coal basis and a measured "moisture" content of 17.8 percent, the gram-mole loss of each element can be calculated. It was assumed that no ash was lost during drying and the oxygen content

of the coal could be calculated by difference. The results of that calculation are shown in Table 6.

Table 6. Gram-Mole Elemental Loss (gmole/100g wet coal).

	N	C	H	O
Gram-Mole	0.000	0.095	0.720	0.997

As can be seen from Table 6, there is insufficient hydrogen liberated to account for all of the oxygen if the off-gas products are assumed to be water. In reality, a complex mixture of gases are probably given off during the drying process. Although not verified, it is suspected that methane, water, carbon dioxide, and small amounts of other compounds are driven off of the coal during the drying procedure. See Appendix E for the derivation of a combination of compounds which will satisfy the elemental loss values shown in Table 6.

Research directed at identifying exactly what materials are volatilized in the drying procedure is recommended by the author. It is conceivable that products of value may be identified in the off-gas and recovered at minimal expense.

Temperature Effects

A series of experiments was run to assess the effect of temperature on the extraction of Colstrip coal under water-gas shift conditions. The solvent consisted of 143 ml of TMU and 7 ml of water. The pH of the solvent was adjusted with sodium hydroxide and in all cases was greater than 12. In all runs the carbon monoxide overpressure was maintained at

500 psig. A plot of the results is shown in Figure 6. As can be seen, there is little or no observed temperature effect. This result appears contrary to that observed by Appell (22). Under water-gas shift conditions, he observed an increase in the extraction of coal with increasing temperature for temperatures in the range of 400°C. Van Bodegom (16) has documented cases of no temperature dependence for some solvents under pure solvent extraction conditions.

Several factors have been identified that may account for the fact that no temperature effect was observed. In the cases where a temperature effect has been documented (22), the reaction temperature was at or above the softening point of coal. Temperatures encountered in this experimentation were well below the softening point of coal, and it is suspected that a different extraction mechanism may be involved.

There is also the possibility that solubility limits of the coal extract in the solvent have been reached and a temperature effect would not be observed. The experimental apparatus used in this investigation has a very large thermal mass, and it is not possible to isolate the reaction products immediately after the reaction. The reactor vessel was cooled for approximately 12 hours before the reaction products were removed. The solvent-coal-residue mixture in all cases was filtered at room temperature. It is possible that some of the extracted material may have precipitated because of a limited solubility capacity of the solvent, in which case the solvent could be saturated with coal extract. The observed extraction would then be only a measure of the solubility of the various coal extract molecules in the solvent at room temperature and not a measure of total extraction occurring during the reaction.

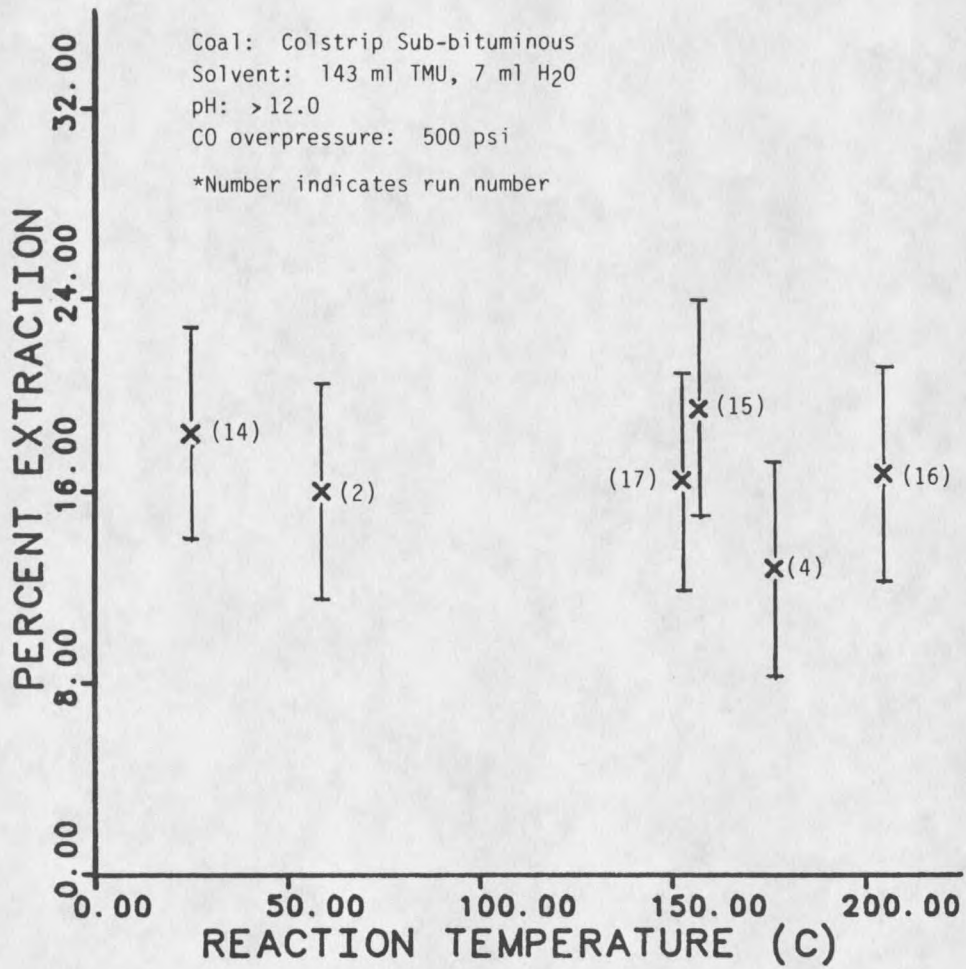


Figure 6. Temperature Dependence of Extraction.

Additional research should be performed to evaluate the solubility limit of the coal extract products in the solvent. The author recommends that a soxhlet extraction using solvent heated to the reaction temperature be used to remove all coal-extract material from the residue. The apparatus would need to be operated under partial vacuum to achieve these conditions. Using this system, a true measure of the effectiveness of the water-gas shift reaction can be determined.

Pressure Effects

A series of experiments was run to assess the effects of carbon monoxide overpressure on the extraction of Colstrip coal under water-gas shift conditions. In each run the temperature was maintained at 160°C and the pH of the solvent was greater than 12. The solvent again was 143 ml of TMU and 7 ml water. A plot of the results is shown in Figure 7. To the surprise of the author, there is a pronounced negative pressure effect. This result is contrary to results documented by Appell (22). He observed a positive effect for pressures up to about 1000 psig, but his reaction temperatures were near 400°C.

It was originally thought that increasing the carbon monoxide overpressure would increase the concentration of the nascent hydrogen available to the coal and hence lead to greater extraction. Due to the physical limitations of the reactor system, it was not possible to measure the extent or the rate of just the water-gas shift reaction; therefore, it was not possible to determine if the nascent hydrogen concentration increases with pressure.

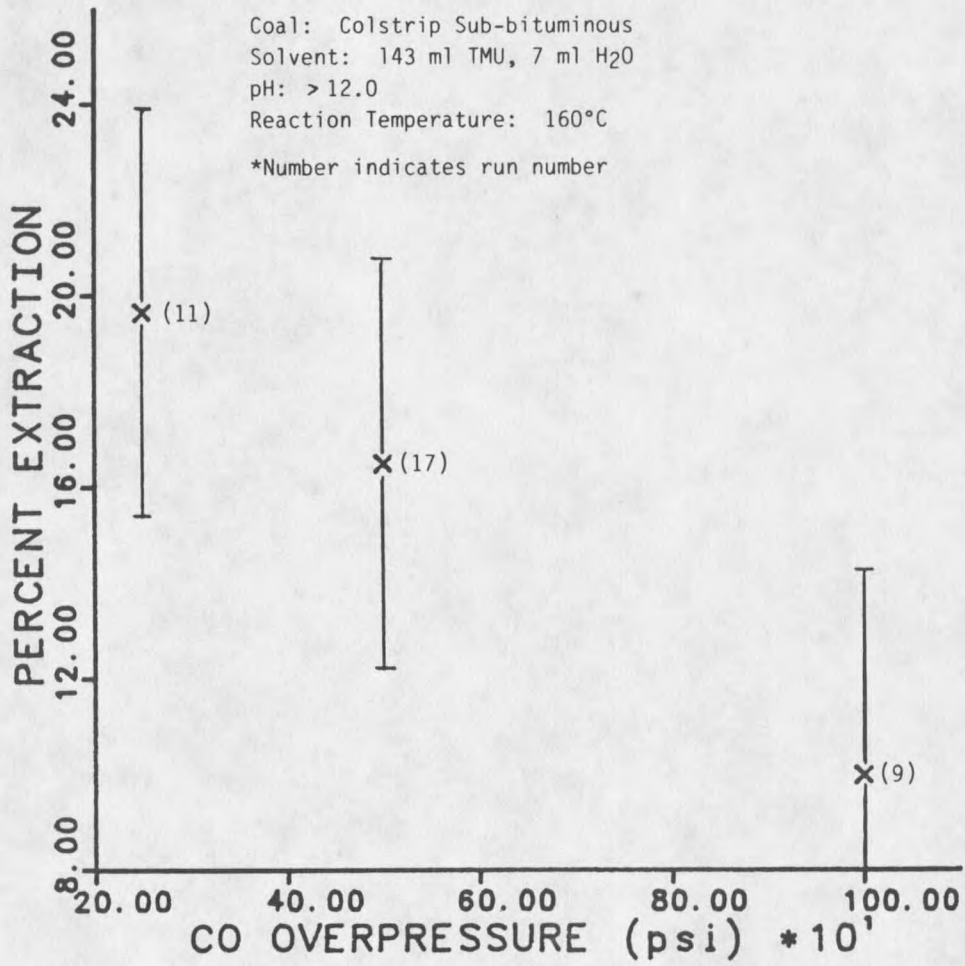


Figure 7. Pressure Dependence of Extraction.

Additional research should be performed to evaluate the extent and rate of the water-gas shift reaction. Carbon monoxide and carbon dioxide can easily be separated by gas chromatography methods. By periodically determining the relative amounts of carbon dioxide and carbon monoxide in the vapor phase, both the rate and extent of reaction could be measured.

The negative pressure effect observed may be due to a chemical species which alters the extraction characteristics of the solvent. It is possible that increased concentrations of formate ion in the solvent will decrease the solubility of the coal extract in the solvent. Formate ion is generated in a reaction between carbon monoxide and water. An increase in the carbon monoxide overpressure would produce a corresponding increase in the concentration of the formate ion in the solvent mixture. Because the TMU molecule is so highly polar, it may be possible that its effectiveness as a coal solvent would be decreased in the presence of the formate ion.

Appell (22) may not have encountered the negative pressure effect due to the fact that his reaction conditions were different than those of this investigation. He performed the water-gas shift hydrogenation of coal in the presence of a vehicle oil which did not dissolve coal to any appreciable degree. Appell then extracted the coal residue with pyridine and benzene. His results were primarily by pyridine and benzene extractions and not that of a one-step hydrogenation and extraction method.

It is also possible that a change in the character of the extraction products due to a change of reaction conditions is responsible for

the negative pressure effect. If the coal hydrogenation products are solubility limited, then reaction conditions that promote the most soluble products will show the greatest observed extraction.

The observed extraction for carbon monoxide overpressure over the range of 250-1000 psig is greater than the observed extraction when there is no carbon monoxide overpressure. Therefore, a maximum extraction value for the coal sample should exist for a carbon monoxide overpressure in the range of 0-250 psig. The author recommends that future research be directed so that the optimum carbon monoxide overpressure is identified.

pH Effects

It has been reported by other researchers that at low temperatures proper reaction pH is essential for the water-gas shift reaction to proceed at any appreciable rate (30). Basic conditions are generally reported to be superior with the best results obtained when the pH is greater than 12.6. For this reason, the pH of the reaction solvent before and after the reaction was closely monitored. A plot of original solvent pH versus percent extraction is shown in Figure 8, and a plot of final solvent pH versus percent extraction is shown in Figure 9. In all runs Colstrip coal was used, carbon monoxide overpressure was 500 psi, and the solvent was TMU and water. The runs encompassed a range of reaction temperatures, but this is not thought to be significant since extraction is a weak function of temperature.

As can be seen from Figure 8, most of the experimental runs were performed at high pH. One run was performed under acidic conditions and

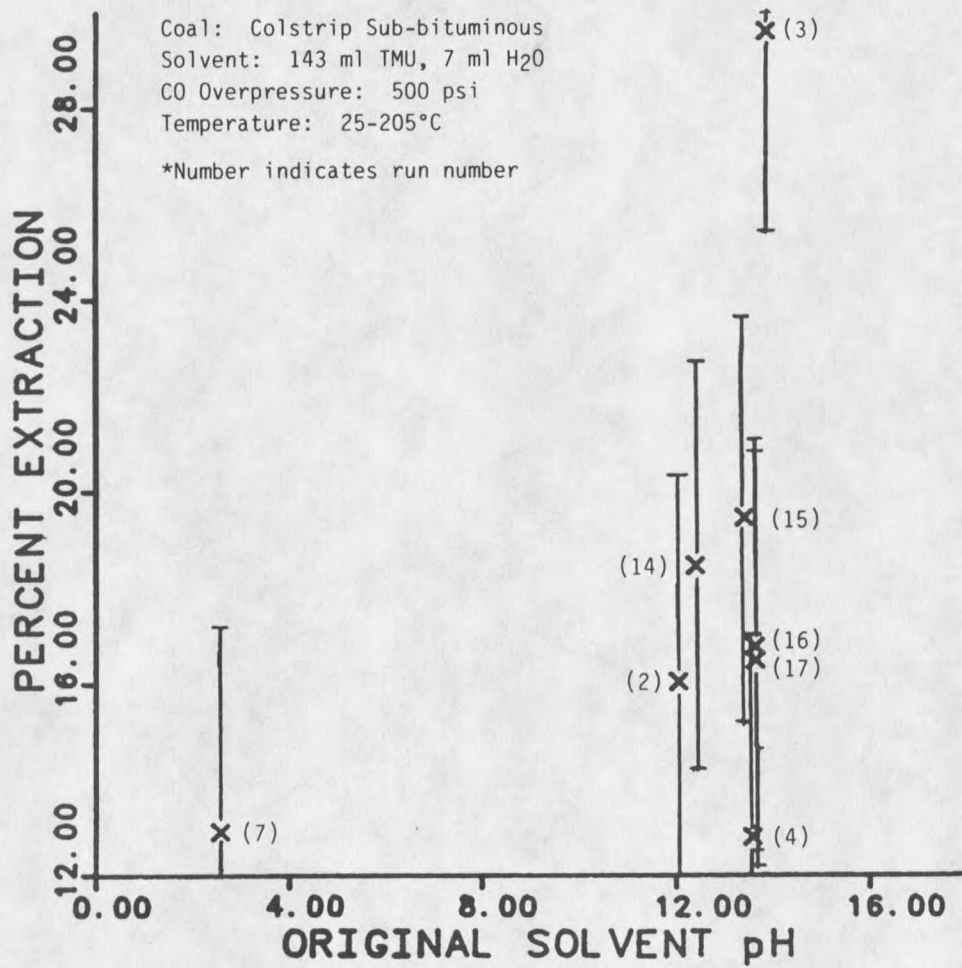


Figure 8. pH of Solvent Before Reaction Versus Observed Extraction.

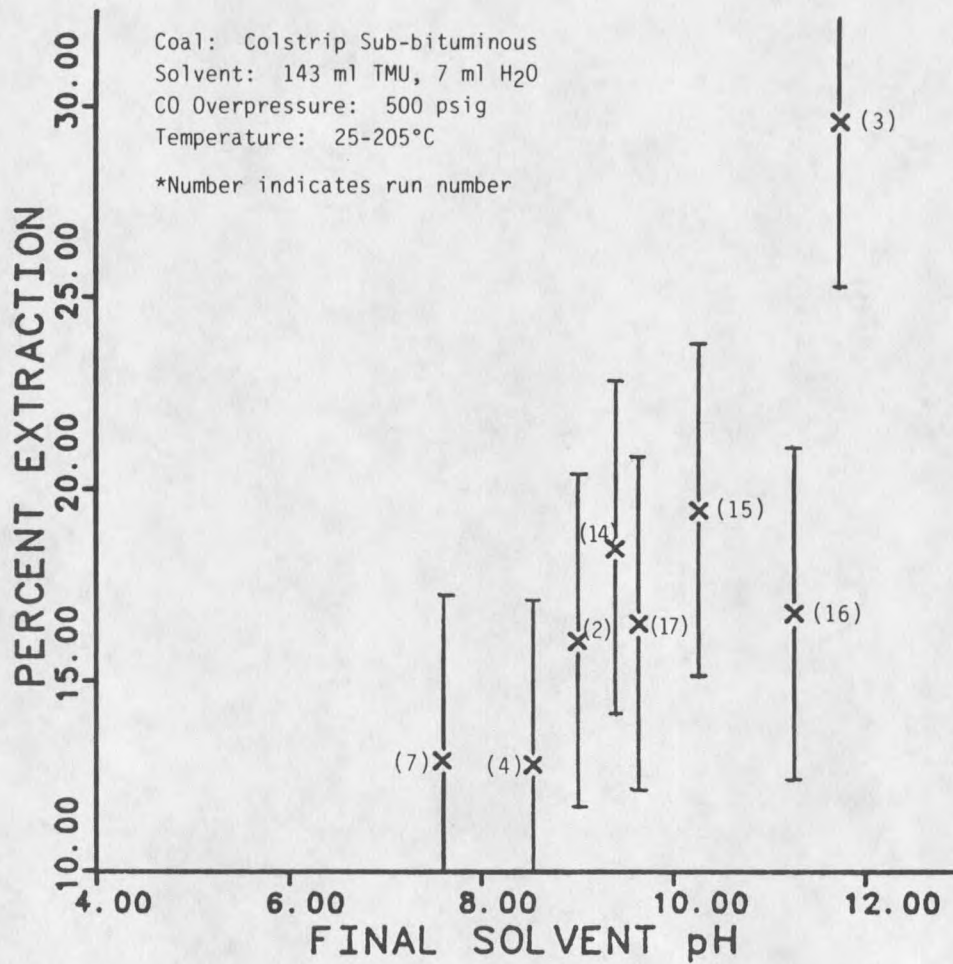


Figure 9. pH of Solvent After Extraction Versus Observed Extraction.

was only marginally successful. Although speculative, it appears that extraction may rise dramatically when the pH of the solvent is greater than 12.6 to 13.0. Ross (23) documented that a pronounced increase in extraction was observed when the solvent pH for the water-gas shift reaction was greater than 12.6.

Based upon examination of Figure 9, it appears that a rough correlation exists between the final pH of the solvent and the extraction of the coal. In general, it appears that extraction increases with increasing final solvent pH. The author finds this observation interesting in light of the fact that there was only a weak correlation between original solvent pH and extraction.

It is possible that the pH effect and the negative pressure effect may be related. As postulated in the pressure effects section of this thesis, the formate ion concentration may dictate the coal extract solubility in the solvent. Increasing the formate ion concentration will lower the pH of the solvent and hence could possibly lower the solubility of coal extract in the residue.

Because of the apparent buffering effect of the coal in the reaction, one run was performed where solid sodium hydroxide was added to the coal. It was believed that if enough sodium hydroxide were present, then the solvent pH would remain high during the reaction. This run, run number 3, is represented by the highest observed extraction value shown in Figure 9. The result of this run would indicate to future researchers that methods of running the reaction should be analyzed whereby the reaction pH is maintained at a high level throughout the reaction.

One run, run number 20, was also performed where sodium carbonate instead of sodium hydroxide was used to adjust the pH of the solvent. Observed extraction with the sodium carbonate was only 13 percent, which was significantly lower than for sodium hydroxide under the same conditions. This result is interesting in light of the fact that the final pH of 10.2 is relatively high. One would predict, based upon Figure 9, that this high pH value should correspond to a relatively high extraction rate. It is uncertain whether this result is due to differences in the solubility of sodium carbonate in the solvent or its chemical character. Additional research should be performed to identify which bases work best using the water-gas shift solvent extraction method.

Coal Rank Effects

A series of three experimental runs was performed to evaluate the effect of coal rank on extraction results under water-gas shift conditions. Savage lignite, Colstrip sub-bituminous, and Bakerstown high-volatile bituminous coals were used; the solvent was 143 ml TMU and 7 ml water for each run. All experiments were run at 160°C, 500 psi carbon monoxide overpressure, and with a solvent pH greater than 12.6. The results are shown in Figure 10.

As can be seen from Figure 10, there appears to be a significant correlation between the rank of coal and the total dissolution. Low rank coals appear to be solubilized to a greater degree than higher rank coals. Appell (22) and Takemura (24) have also documented that low rank coals are more reactive under water-gas shift conditions.

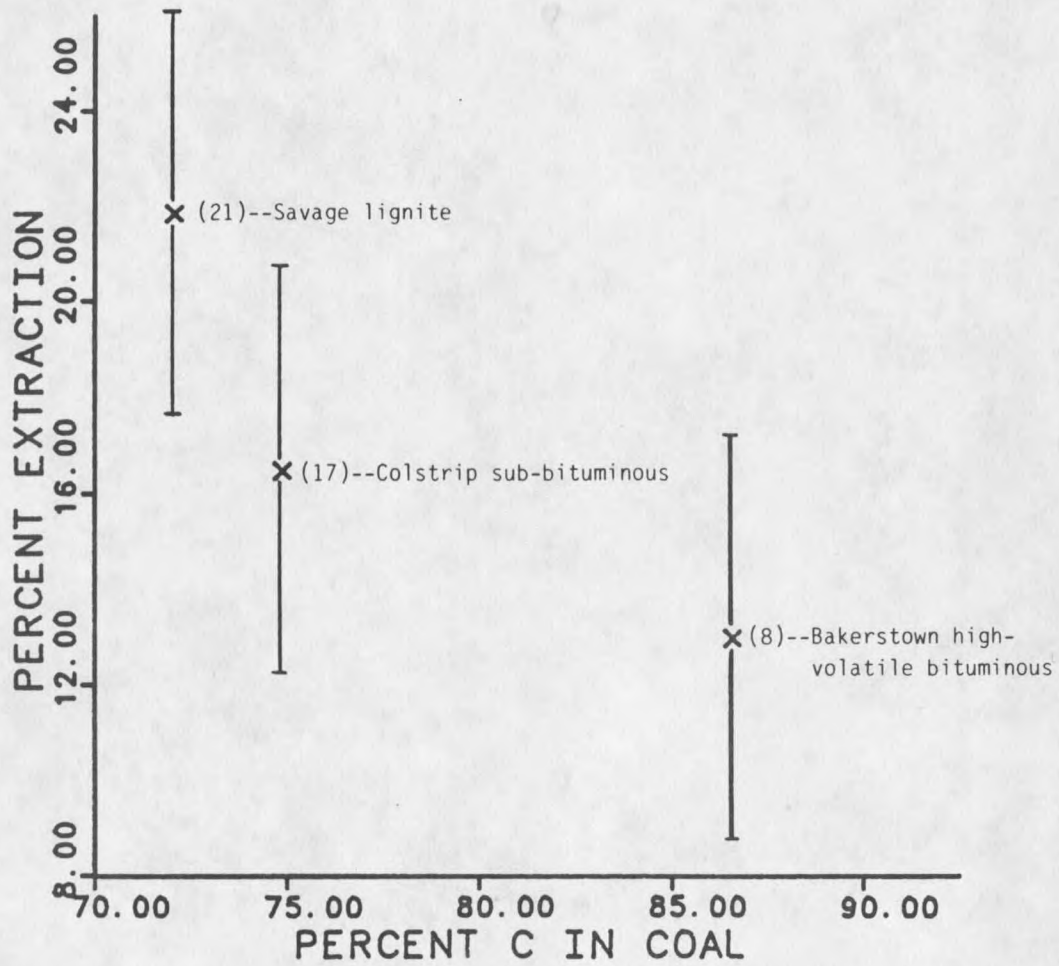


Figure 10. Initial Carbon Content Versus Observed Extraction.

Researchers working on coal extraction using solvents alone generally report that the best results are observed with bituminous coal (17).

Coals of low rank are apparently more readily attacked by nascent hydrogen than coals of higher rank. This no doubt is due to a difference in attack sites or functional groups within the coal matrix, ester and ether linkages being the prime candidates. The correlation between coal rank and observed extraction lends credible evidence to the presence of nascent hydrogen attack under the conditions used in this experiment.

Solvent Retention

When it was observed that a significant amount of solvent was retained in the residue, it was postulated that a correlation may exist between the observed extraction and the amount of solvent retained in the coal residue. In Figure 11, the amount of extraction is plotted versus solvent retention for Colstrip coal. In each case the solvent was TMU and water, and the carbon monoxide overpressure was 500 psi. The reaction temperature and solvent pH varied considerably.

Dryden (17) states that for specific solvents, and TMU is considered a specific solvent, a certain amount of the solvent is chemisorbed on the coal at room temperature. Apparently the chemical nature of the surface of the coal residue does not change appreciably with increased extraction. A change in the solvent retention would be expected if the surface characteristics of the coal changed.

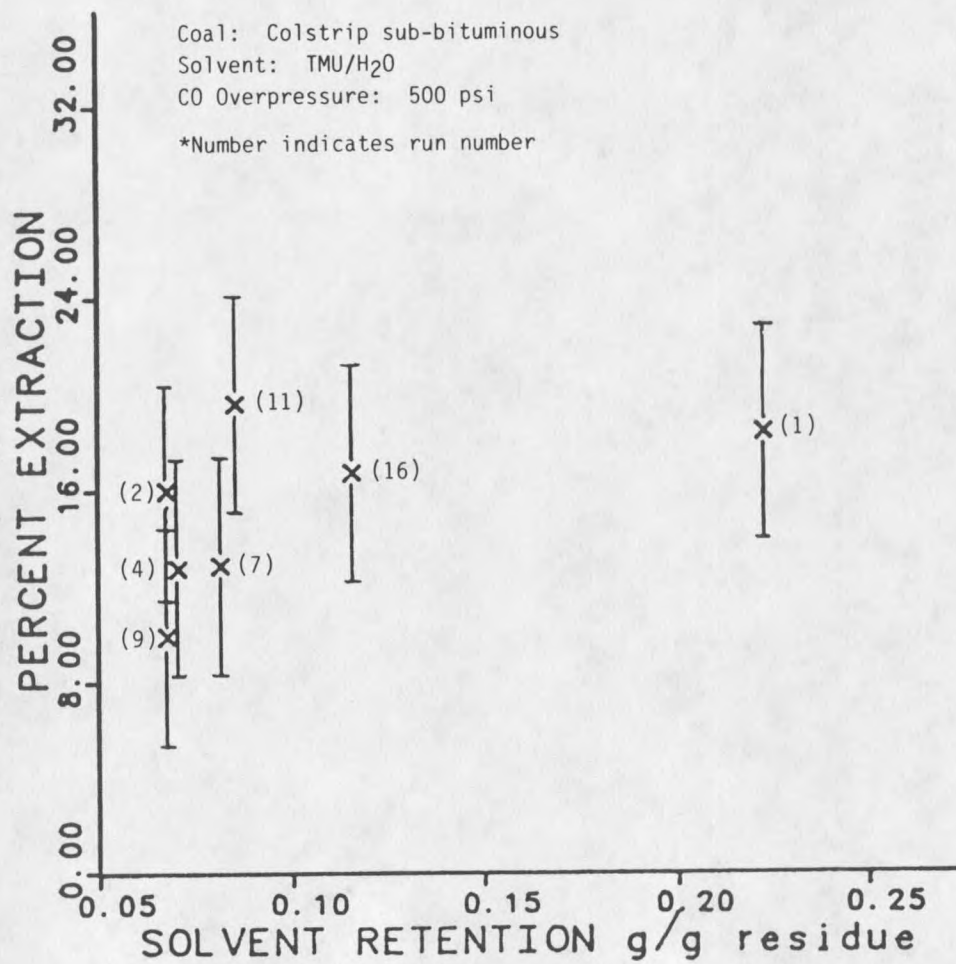


Figure 11. Solvent Retention Versus Extraction.

The reader should note that a certain amount of variation in the solvent retention can probably be attributed to experimental technique. Each residue was washed with acetone until the effluent from the residue filter-cake appeared colorless. The colorless endpoint was subjective, and it is known that some residues were washed with considerably more acetone than others.

The viability of the water-gas shift solvent extraction process is in grave jeopardy unless methods can be devised to remove the solvent from the residue or dramatically increase the extraction. Because of the cost associated with these solvents, virtually all of the solvent must be recovered from the coal residue for the process to be economically feasible. Researchers must solve this significant problem if the water-gas shift solvent extraction method is to become commercially feasible. The author feels that the chances for complete recovery of the solvent are very slim.

Additional Experimentation

Some experiments were performed that were designed to test a hypothesis or substantiate data that other researchers have presented. These experiments were performed for two reasons. The first was to ensure that the reaction parameters and conditions used in this experimentation had a reasonable chance for success and the second was to identify subject areas with adequate potential to justify additional research work. The results of these experimental runs and the pertinent reaction conditions are shown in Table 7, with specific conditions given in Appendix A.

Table 7. Extraction Results for Individualized Experiments.

Run No.	Solvent	Weight % Extraction
12	TMU/Tetralin/HMPA/H ₂ O	35
13	TMU/HMPA/H ₂ O	23
19	TMU/Tetralin/H ₂ O	20
15	TMU/H ₂ O/additional H ₂ O	19
17	TMU/H ₂ O (normal run)	17
18	TMU/H ₂ O/H ₂ overpressure	11

To help determine if the water-gas shift reaction plays an important role in the extraction of Colstrip coal, one experiment was performed where hydrogen overpressure was used in place of carbon monoxide overpressure. As shown in Table 7 for run 18, substantially less extraction was observed under hydrogen overpressure than for any run where carbon monoxide was used. While not conclusive, the results of run 18 are evidence that the nascent hydrogen formed via the water-gas shift reaction is more reactive in hydrogenation of Colstrip sub-bituminous coal than elemental hydrogen.

Ward (2) presented substantial evidence that enhanced coal extraction could be observed when a mixture of solvents was used. He documented his greatest extraction value for a run using a solvent mixture of TMU, HMPA, and tetralin. The author surmised that this mixture of solvents may also work under water-gas shift conditions. As shown in Table 7 for run 12, the observed extraction was quite high. In fact,

this was the highest extraction value documented during the course of this investigation.

Runs 13 and 19 were also performed using a mixture of solvents. In run 13, a mixture of TMU and HMPA was used, and the observed extraction was significantly better than if just TMU, run 17, were used as a solvent. In run 19, a mixture of TMU and tetralin was used and the observed extraction was only slightly greater than if just TMU were used as a solvent. It appears that, if chosen properly, a mixture of solvents may be more effective in the extraction of coal under water-gas shift conditions than any one solvent alone.

One run was also performed to determine if adequate water was present in the solvent mixture to satisfy the requirements for the water-gas shift reaction. In all other runs, 7.5 ml of water was used with the solvent. In run 15, an additional 7.5 ml of water was added to the solvent. It was thought that if water was a limiting reactant under normal experimental conditions, then an increase in the extraction would be observed when additional water was added. The additional 7.5 ml of water present in the solvent for run 15 had no significant effect on the extraction value.

SUMMARY AND CONCLUSIONS

1. The largest extraction observed for Colstrip sub-bituminous coal was 35 percent. To achieve this result, water-gas shift hydrogenation was used in conjunction with a solvent mixture of 50 ml TMU, 50 ml HMPA, 50 ml tetralin, and 5 ml water on 4.92 g of coal.
2. Solvent extraction under water-gas shift conditions is greater than solvent extraction alone or solvent extraction in the presence of hydrogen overpressure.
3. There appears to be no temperature effect for the water-gas shift reaction solvent extraction in the range of 25 to 200°C. Some evidence exists that solubility limits of coal extract in the solvent may have masked a temperature effect.
4. There appears to be a negative pressure effect for extraction relative to carbon monoxide overpressure in the range of 250 to 1000 psig. However, this may be an artifact from chemical formation for the conditions in these experiments.
5. A correlation exists between the final solvent pH and the observed extraction. As the final solvent pH increases, the observed extraction also increases. It appears that initial solvent pH must be greater than about 12.6 for significant extraction to occur.
6. Solvent is retained in the coal residue. For the conditions encountered in this experimentation, 6 to 17 percent of the weight of the residue could be attributed to incorporated solvent.

7. Lower rank coals are more easily extracted under water-gas shift solvent extraction conditions than higher rank coals.
8. Compounds other than water are volatilized under conditions normally associated with the drying of coal.

RECOMMENDATIONS FOR FUTURE RESEARCH

1. Tests should be run to determine the extent and rate of the water-gas shift reaction for the conditions employed in this experimentation.
2. An effort should be made to isolate the extraction products from the solvent and characterize their chemical nature. This would help to clarify if the solvent retention assumptions used in this study are valid. It is recognized that this is experimentally very difficult.
3. The relative effectiveness of different bases used to control the pH of the reaction should be evaluated.
4. Multiple extraction experiments should be run to determine if solvent solubility limitations control the extent of the reaction.
5. Tests should be run to evaluate the carbon monoxide overpressure conditions that maximize coal extraction.
6. Tests should be run to characterize the off-gas products from the drying of coal.

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APPENDICES

APPENDIX A

RAW DATA FROM EXTRACTION EXPERIMENTS

Table 8. Experimental Conditions for Each Extraction Run.

Run No.	Coal	Solvent	Pressure (psig)	Temperature (°C)	pH Before	pH After
1	Colstrip	TMU/H ₂ O	600	167.5	13.30	7.72
2	Colstrip	TMU/H ₂ O	480	59.0	12.02	9.00
3	Colstrip	TMU/H ₂ O ad. NaOH	500	169.5	~14	11.74
4	Colstrip	TMU/H ₂ O	490	177.0	13.62	8.54
6	Colstrip	TMU/H ₂ O	550	161.5	6.89	8.70
7	Colstrip	TMU/H ₂ O/HCl	500	158.0	N/A	7.60
8	Bakerstown	TMU/H ₂ O	500	157.0	12.78	7.75
9	Colstrip	TMU/H ₂ O	1000	150.0	12.78	9.05
11	Colstrip	TMU/H ₂ O	250	158.5	12.92	9.64
12	Colstrip	TMU/HMPA/TET/H ₂ O	500	162.0	13.12	10.67
13	Colstrip	TMU/HMPA/H ₂ O	500	160.0	~14	11.01
14	Colstrip	TMU/H ₂ O	500	25.0	12.44	9.40
15	Colstrip	TMU/H ₂ O/ad. H ₂ O	500	157.5	13.46	10.27

Table 8--continued.

Run No.	Coal	Solvent	Pressure (psig)	Temperature (°C)	pH Before	pH After
16	Colstrip	TMU/H ₂ O	500	205.5	13.68	11.27
17	Colstrip	TMU/H ₂ O	500	153.0	13.69	9.65
18	Colstrip	TMU/H ₂ O	500(H ₂)	158.0	12.53	9.98
19	Colstrip	TMU/TET/H ₂ O	500	158.5	12.46	9.22
20	Colstrip	TMU/H ₂ O/NaCO ₃	500	157.5	12.89	10.21
21	Sav. Lig.	TMU/H ₂ O	500	152.5	13.43	11.00

Table 9. Raw Data for Experimental Extraction Runs.

Run No.	Initial Wt. Coal (g)	Final Wt. Residue (g)	Elemental Analysis Residue			% Ash Residue
			Nitrogen	Carbon	Hydrogen	
1	4.8848	2.8216	1.88	66.07	4.80	10.55
2	5.0654	3.8890	1.82	66.90	4.92	9.54
3	5.0680	3.2118	1.26	64.60	4.51	11.26
4	5.0219	4.0324	1.85	67.21	4.65	10.22
6	4.9910	3.8205	4.27	66.86	5.40	10.42
7	4.9051	3.9721	1.97	63.02	4.64	10.17
8	5.2574	4.8928	1.75	75.05	4.76	10.21
9	5.0043	4.1049	1.83	65.12	4.69	9.59
11	4.9893	3.7349	2.02	64.88	4.80	9.87
12	4.9190	3.4738	3.63	64.60	5.27	12.04
13	4.7062	3.8941	4.27	62.18	5.27	13.93
14	5.5857	4.9807	3.53	64.97	5.29	10.26
15	5.7302	4.2123	1.93	66.66	4.82	10.06

Table 9--continued.

Run No.	Initial Wt. Coal (g)	Final Wt. Residue (g)	Elemental Analysis Residue			% Ash Residue
			Nitrogen	Carbon	Hydrogen	
16	5.8376	4.6545	2.36	65.51	4.63	9.97
17	5.3344	4.0886	1.85	66.22	4.76	10.61
18	5.2971	4.2758	1.86	67.83	4.92	9.60
19	5.2327	3.6494	1.54	67.16	4.92	9.68
20	4.9143	3.8501	1.94	67.23	5.06	9.75
21	4.8204	3.4953	3.70	64.18	4.57	8.65

Table 10. Chemical Analysis of Coal Used in Experimentation.

Coal	Elemental Analysis (%)			% Ash Content	% Water Content
	Nitrogen	Carbon	Hydrogen		
Colstrip (wet)	0.92	56.67	4.48	8.04	17.80
Colstrip (dry)	1.13	67.55	4.58	N/A	0.0
Savage Lignite (wet)	1.07	52.01	3.35	6.50	27.96
Savage Lignite (dry)	1.35	65.58	3.85	N/A	0.0
Bakerstown (wet)	1.62	77.49	4.86	10.25	0.27

APPENDIX B

SAMPLE CALCULATION

SAMPLE CALCULATION

This appendix shows the calculation sequence for run 13.

Needed experimental data:

Solvent: 68 ml TMU, 75 ml HMPA

Colstrip coal: initial wt 4.7062 g
 mass fr H₂O 0.178
 mass fr ash 0.0804
 elemental analysis (dry, ash containing)
 N 1.13% C 67.55% H 4.58%

Residue: weight 3.8941 g
 mass fr H₂O .0242
 mass fr ash .1393
 elemental analysis (wet, ash containing)
 N 4.28% C 62.18% H 5.27%

Calculate elemental analysis of coal organic matter on an ash and water-free basis.

Element	Water-Free Weight	Ash Correction	Corrected Weight	% Organic Ash & Water-Free
Nitrogen	0.0093		0.0093	1.25
Carbon	0.5553		0.5553	74.88
Hydrogen	0.0377		0.0377	5.08
Ash	0.0804	-0.0804	-0.0-	-0.0-
Oxygen	0.1393		0.1393	18.78
Total	0.8220		0.7416	99.99

Next the residue analysis is calculated on a dry, ash-free basis. Assume that material volatilized at 103°C is water.

$$\text{Hydrogen loss due to water} = .0242 \times (2\text{gH}/18\text{gH}_2\text{O}) = .0027\text{g}$$

$$\text{Oxygen loss due to water} = .0215\text{g}$$

Element	Wet Analysis	Correction Weight	Corrected Weight	% Ash & Water-Free
Nitrogen	0.0428		0.0428	5.12
Carbon	0.6218		0.6218	74.33
Hydrogen	0.0527	-0.0027	0.0500	5.98
Ash	0.1393	-0.1393	-0.0-	-0.0-
Oxygen	0.1434	-0.0215	0.1219	14.57
Total	1.0000		0.8365	100.00

Adjust elemental analysis by removing solvent molecules until the nitrogen concentration is the same as the original coal (1.25).

Assume that solvent is retained in the residue in the same molar ratio as in the bulk solvent.

Assume that solvent molecules do not fragment.

$$68 \text{ ml TMU} * .9687 \text{g TMU/ml} = 65.87 \text{g TMU}$$

$$78 \text{ ml HMPA} * 1.0253 \text{g HMPA/ml} = 76.90 \text{g HMPA}$$

Calculate elemental mass fraction for solvent.

	H	C	N	O	
TMU	6.86	34.06	15.91	9.07	
HMPA	7.73	30.93	18.04	20.19	
Total	14.59	64.99	33.95	29.26	142.79g total
MF	0.1022	0.4551	0.2378	0.2049	1.000 total

Set up four mass balance equations and a constraint equation so that the final nitrogen concentration is equal to 1.25%.

- H = total weight of hydrogen in corrected residue
- C = total weight of carbon in corrected residue
- O = total weight of oxygen in corrected residue
- N = total weight of nitrogen in corrected residue
- S = total weight of solvent

The equations are:

$$H = .0512 - S(.1022)$$

$$C = .7433 - S(.4551)$$

$$O = .1457 - S(.2049)$$

$$N = .0512 - S(.2378)$$

$$N/(H+C+O+N) = .0125$$

Simultaneous solution of the above equations yields:

$$H = .0422$$

$$C = .6651$$

$$O = .1105$$

$$N = \underline{.0104}$$

$$.8282 \text{ (solvent ret factor)}$$

The above results yield a corrected residue elemental analysis:

$$H = 5.10\%$$

$$C = 80.31\%$$

$$O = 13.34\%$$

$$N = 1.25\% \text{ (the value expected)}$$

All of the information for calculating the absolute extraction as per Equation (5) of the thesis is now available.

$$WC = 4.7062$$

$$CWA = .7416$$

$$WR = 3.8941$$

$$RWA = .8365$$

$$RS = .8282$$

Based on the above data, $AE = 22.5\%$

APPENDIX C

RESULTS OF EXTRACTION RUNS

Table 11. Absolute Extraction Values and Solvent Retention for Each Experiment Run.

Run No.	Absolute Extraction (%)	Solvent Retention (g/g res)	Run No.	Absolute Extraction (%)	Solvent Retention (g/g res)
1	35.87	0.0412	13	22.50	0.1718
2	16.05	0.0681	14	18.46	0.2237
3	29.62	0.0201	15	19.46	0.0758
4	12.81	0.0712	16	16.78	0.1159
6	35.57*	0.2893	17	16.50	0.0702
7	12.92	0.0816	18	11.04	0.0696
8	13.00	0.0201	19	19.78	0.0435
9	9.99	0.0679	20	12.74	0.0742
11	19.66	0.0862	21	21.85	0.2142
12	34.84	0.2028			

APPENDIX D

ERROR ANALYSIS

ERROR ANALYSIS

This error analysis uses the procedure presented by H. Mickley (31) in the Applied Mathematics in Chemical Engineering textbook.

The equation used to compute the absolute extraction of coal used in this thesis is:

$$AE = \frac{WC \cdot CWA - WR \cdot RWA \cdot RS}{WC \cdot CWA}$$

where:

WC = weight of the coal
 CWA = correction factor for water and ash in the coal
 WR = weight of the residue
 RWA = correction factor for water and ash in the residue
 RS = correction factor for solvent retained in the residue

The correction factor for water and ash in the coal, CWA, is given by the following equation:

$$CWA = 1 - MW - MA$$

where:

MW = mass fraction water in the coal
 MA = mass fraction ash in the coal

The correction factor for water and ash in the residue, RWA, is given by the following equation:

$$RWA = 1 - MWR - MAR$$

where:

MWR = mass fraction water in the residue
 MAR = mass fraction ash in the residue

Identification of Relative Error of Experimental Variables

Because the results obtained from run 17 appear to be average, the error analysis calculation will be based upon that run. The following experimental data were obtained:

Original Colstrip Coal: weight = 5.3344 g
 mass fraction water = 0.178
 mass fraction ash = 0.0804

Extraction Residue: weight = 4.0886 g
 mass fraction water = 0.0272
 mass fraction ash = 0.1061
 solvent retention factor (as calculated
 using procedure found in Appendix B) =
 0.9298

The weight of the coal introduced to the reactor was measured on a Mettler H80 analytical balance with sensitivity at the 0.1 mg level. Assuming that no coal was lost upon introduction to the reactor, the author feels confident that the true weight of the coal sample is within 5 mg of the measured value.

The relative error therefore is:

$$\text{relative error WC} = \frac{0.005}{5.3344} * 100 = \pm 0.09\%$$

The weight of the residue was measured using the same analytical balance as used to measure the coal samples. Although the weight of the residue recovered is likely accurate to $\pm 0.1\%$, mass loss in filtering and handling is suspected. The author feels confident that no more than 2% was lost and therefore sets the confidence limit at $\pm 2\%$.

$$\text{relative error WR} = \pm 2.0\%$$

Several water analyses were performed on the coal sample and the author has determined that all measured water content values lie within $\pm 1.4\%$ of the average value.

Several ash analyses were also performed on the coal sample and the author has determined that all measured ash content values lie within $\pm 1.0\%$ of the average value.

Using the accuracy limits specified above, the relative error of the water and ash correction factor for the coal is:

$$\begin{aligned} \text{r.e. CWA} &= \frac{((1-.1780-.0804) - (1-.1780*1.014-.0804*1.01))}{(1-.1780-.0804)} * 100 \\ &= \pm 0.5\% \end{aligned}$$

Although only one ash and water determination was performed for each coal-residue, it was assumed that the confidence limits of each measurement would be the same as for the coal. The relative error of the coal residue water and ash correction factor is:

$$\begin{aligned} \text{r.e. RWA} &= \frac{((1-.0272-.1061) - (1-.0272*1.014-.1061*1.01))}{(1-.0272-.1061)} * 100 \\ &= \pm 0.2\% \end{aligned}$$

The factor used to correct for solvent retained in the coal residue is based upon several assumptions for which no verifiable proof exists. A confidence limit was estimated using logical constraints for the system. If no solvent were retained, then the correction factor would be 1.0. If solvent were retained as whole molecules, then the calculated solvent correction factor should be very accurate. For run 17, the solvent correction factor was calculated to be 0.9298. It should be reasonably certain that the solvent correction factor for run 17 will be located between 1.0 and 0.9298. If it is assumed that the solvent correction factor is accurate to 25% over the range in which it must logically be limited, then it can be calculated as follows:

$$\text{relative error RS} = (1-.9298) * .25 * 100 = \pm 1.9\%$$

Approximate values of the data and the estimated maximum errors are then the following:

Variable	Approximate Value	Measured To
WC	5.3344	± 0.005 g
WR	4.0886	± 0.082 g
RWA	0.8667	± 0.002
CWA	0.7416	± 0.004
RS	0.9298	± 0.018

The absolute values of the partial derivatives for AE with respect to each variable are:

$$\frac{\partial \text{AE}}{\partial \text{WR}} = \frac{\text{RWA} * \text{RS}}{\text{WC} * \text{CWA}} = 0.2037$$

$$\frac{\partial \text{AE}}{\partial \text{RWA}} = \frac{\text{WR} * \text{RS}}{\text{WC} * \text{CWA}} = 0.9610$$

$$\frac{\partial \text{AE}}{\partial \text{RS}} = \frac{\text{WR} * \text{RWA}}{\text{WC} * \text{CWA}} = 0.8958$$

$$\frac{\partial \text{AE}}{\partial \text{CWA}} = \frac{\text{WR} * \text{RWA} * \text{RS}}{\text{WC} * \text{CWA}^2} = 1.123$$

The maximum deviation from the calculated value for the absolute extraction is then:

$$\begin{aligned}\delta AE &= 100 * (.2037*.082+.9610*.002+.8958*.018+1.123*.004) \\ &= \pm 3.9\%\end{aligned}$$

Therefore, the error bar for the extraction for run 17 should extend 3.9% above and below the calculated value. Although it is obvious that the error bar is a function of each of the experimental variables, it works out that they are of approximately the same length for each run. The author has chosen to use error bars of 4% on all graphs.

APPENDIX E

"WATER" LOSS JUSTIFICATION

'WATER' LOSS JUSTIFICATION

The elemental loss in gmoles per 100g wet coal is:

C 0.095 H 0.720 O 0.997

Will any combination of compounds suspected of being volatilized from the coal account for the observed mass loss?

If it is assumed that H_2O , CO_2 , and CH_4 are volatilized, then:

Let: W = moles of water
 C = moles of carbon dioxide
 M = moles of methane

Elemental Balance Equations:

C balance: $C + M = 0.095$
 H balance: $2W + 4M = 0.720$
 O balance: $W + 2C = 0.997$

Simultaneous solution yields: impossible solution negative value for methane.

It is assumed that H_2O , CO_2 , and O_2 are volatilized, then:

Let: W = moles of water
 C = moles of carbon dioxide
 O = moles of oxygen

Elemental Balance Equations:

C balance: $C = 0.095$
 H balance: $2W = 0.720$
 O balance: $W + 2C + 2O = 0.997$

Simultaneous solution yields:

C = 0.095 W = 0.36 O = 0.22

This appears to be a plausible solution.

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