The dissolution and swelling of bituminous coal in N-methyl-pyrrolidone

Joseph M. Stoffa
West Virginia University

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The Dissolution and Swelling of Bituminous Coal in N-Methyl-Pyrrolidone

Joseph M. Stoffa

Thesis Submitted to the College of Engineering and Mineral Resources at West Virginia University in partial fulfillment of the requirements for the degree of

Master of Science in Chemical Engineering

Dr. Alfred H. Stiller, Chair
Dr. Peter G. Stansberry
Dr. Richard Turton

Department of Chemical Engineering

West Virginia University

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Abstract

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Joseph M. Stoffa

Research detailed herein examined the extraction and swelling of a bituminous coal in the super solvent n-methyl-pyrrolidone. Correlations were developed to describe the extraction and swelling observed in the coal-solvent system. These correlations describe swelling and extraction based on experimental parameters such as extraction time and extraction temperature. The research concluded that swelling and extraction may be related processes. The most significant result of the research was a proposed relationship between the rapidness of coal swell and the coal’s solubility in the solvent. The research served as support for coal structure models and solvent extraction mechanisms published in peer reviewed literature.
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Chapter 1 – Introduction

Discussion of US energy independence has revitalized interest in coal utilization. Coal is underutilized as a feedstock for liquid fuels and as a base for value added products. This research concerned coal’s use as a base for value added products. Specifically, the work focused on the solvent extraction of bituminous coal using the super solvent n-methyl-pyrrolidone. Solvent extraction separates the desirable carbonaceous portion of coal from the undesirable inorganic portion of coal. Solvent extraction removes virtually all inorganic matter from coal, including sulfur in the form of pyrite. Because many undesirable elements, such as arsenic and mercury, are substitutions in the pyrite matrix, solvent extraction will also remove some heavy metals present in coal\(^1\). The product of solvent extraction, coal extract, is a solid carbonaceous material having almost zero ash. Coal extract have been used as a feedstock for carbon fibers, carbon foams, carbon fuel cell fuel, fuel additives, nuclear grade graphite, pitch additives, and more.

Solvent extraction may also participate in the future of energy production in the United States. New clean coal power plants designed under DOE programs such as Vision 21 and Future Gen will require a purer feed coal to reduce pollution. If progress can be made in lowering the costs of solvent extraction, solvent extraction could compete will less effective conventional coal cleaning methods such as dense medium separation and froth flotation. If solvent extraction is unable to compete economically with conventional coal cleaning technology, it may still play a role in power production. New clean coal power facilities will
be more costly than current power plants. The higher costs of these facilities could be offset by producing a value added feedstock in addition to producing power.

The research detailed herein recorded the swell and extraction of a bituminous coal in the super solvent n-methyl-pyrrolidone. The swell and extraction was described as a function of process parameters, the extraction temperature and extraction time. The relationship between swell and extraction was examined. The porosity of the bituminous coal used in the research was examined using mercury porisimetry. The porosity of the bituminous coal and its relationship to solvent extraction and solvent swelling of coal was examined. To summarize, the research discussed herein accomplished the following.

1) Collected data on the solvent swelling of bituminous coal
2) Collected data on the solvent extraction of bituminous coal
3) Examined the porosity of bituminous coal via mercury porisimetry
4) Correlated the extent of coal swelling to processing parameters
5) Correlate the extent of solvent extraction to processing parameters
6) Determined the relationship between swelling and extraction
Chapter 2 – Background

Section 2.1 – What is Coal

“G.L. Jansen, a geologist and coal petrographer, referred to coal simply as ‘organic sediment’.” Merriam-Webster defines coal as “a black or brownish black solid combustible substance formed by the partial decomposition of vegetable matter without free access of air and under the influence of moisture and often increased pressure and temperature that is widely used as a natural fuel.” “More specifically, it can be said that coal is a combustible solid, usually stratified, which originated from the accumulation, burial, and compaction of partially decomposed vegetation in previous geologic ages.” Coal primarily contains carbon, hydrogen, oxygen, sulfur, and lesser amounts of up to 60 other elements. Coal contains these elements because they were present in the parent material, were incorporated with the coal during coalification, or were mixed with the coal during mining.

The coalification process spans millions of years, and there are many levels of coalification. Coalification is a function of how long the parent organic material is buried, and the temperature and pressure to which the parent organic material is exposed. Coal is classified according to rank, a measure of the degree of coalification. The coal ranks, in order of increasing coalification, are lignite, sub-bituminous, bituminous, and anthracite. The coalification cycle is presented graphically in Figure 2-1.
Some coal properties are correlated with coalification. As coalification increases, the aromaticity of the coal structure increases. Accompanying this increase in aromaticity is a decrease in hydrogen and oxygen content. When anthracite undergoes further coalification, it is no longer classified as coal, it is classified as graphite. Pure graphite is the most aromatic form of carbon, and contains no hydrogen. Other carbonaceous materials may contain the same constituents as coal, but are not defined as coal because they have a proportionally large amount of inorganic matter, or because they have not undergone a metamorphic change. For example, oil shale and peat are elementally similar to coal, but are not considered coals. The American Standards Testing Methods (ASTM) has definitions of various coal ranks, and these definitions are presented as Table 2-1.
While these ranks are useful, they do not describe the non-carbonaceous constituents of coal or the structure of coal. Even though two coals may be of the same rank, High-volatile A bituminous coal for example, they may have varying constituents and structure. Understanding coal requires knowledge of the constituents of coal, how these components are connected, and what chemistry is applicable to coal. For these reasons, the following sections examine the constituents of coal, the structure of coal, and the functional groups of coal.
Section 2.1.1 – Constituents of Coal

Some have described coal as “a very complex heterogenous mixture of organic compounds and minerals, analogous to a fruit cake.” Continuing the analogy, it would be helpful to summarize the ingredients of the fruit cake that is coal. It would be accurate to say that both fruit cake and coal are composed mainly of the elements carbon, oxygen, and hydrogen. With respect to fruit cakes, it would be more specific to say they contain sugar, water, and fruits. With respect to coals, it would be more specific to say they contain various organic groupings. These organic groupings are analyzed and defined by petrographers. Petrography is based on the microscopic examination of materials, and is defined as “the description and systematic classification of rocks.” Although coal does not meet all definitions of a rock, petrography is a useful tool for describing and classifying coal.

When coal is examined under magnification, it appears as a collection of smaller organic groups, known as macerals. Macerals in coal are analogous to minerals in rocks, but macerals, unlike minerals, have no fixed chemical composition or definite crystal structure. Macerals are characterized according to their source material, morphology, nature of formation, similarity in chemical composition, internal structure, level of reflectivity or color, and degree of coalification.

Coal contains three major maceral groups; Vitrinite, Liptinite (also called Exinite), and Inertinite. Vitrinite macerals are the result of coalified woody tissues. These coalified woody tissues are derived from the stems, roots, and vascular tissue of parent leaf material. The next
most common maceral group is Liptinite, also known as Exinite. “The macerals of the Liptinite maceral group are derived from the resinous and waxy materials of plants, including resins, cuticles, spore and pollen exines, and algal remains that constitute resinite, cutinite, sporonite, and alginate, respectively.” Another common maceral group is Inertinite. It is presumed that Inertinite results from the charring of plant tissue. “Inertinite derives its name from the fact that it is inert or semi-inert during normal carbonization processes in a retort.”

The major maceral groups, particular maceral names, origins, and important maceral properties are presented as
Table 2-2⁸. Pictures of Vitrinite (Vitrinite maceral group), Alginite (Liptinite maceral group), and Fusinite (Inertinite maceral groups) are presented below as Figure 2-2⁹.
Table 2-2 – Origin and importance of macerals and maceral groups

<table>
<thead>
<tr>
<th>Maceral Group</th>
<th>Maceral</th>
<th>origin</th>
<th>Group Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vitrinite</td>
<td>Collinite</td>
<td>Wood or bark</td>
<td>Principal constituent of coal, readily hydrogenated, oxidized easily, relatively oxygen rich</td>
</tr>
<tr>
<td></td>
<td>telinite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Liptinite</td>
<td>Resinite</td>
<td>Plant Resins</td>
<td>Yields greatest quantity of by-products when carbonized</td>
</tr>
<tr>
<td>(exinite)</td>
<td>Cutinite</td>
<td>Needles and leaf cuticles</td>
<td></td>
</tr>
<tr>
<td>Sporinite</td>
<td>Spores</td>
<td></td>
<td>Readily hydrogenated in coals with more than 25% volatile</td>
</tr>
<tr>
<td>Alginite</td>
<td>Algae</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Inertinite</td>
<td>Sclerotinite</td>
<td>Fungal Remains</td>
<td></td>
</tr>
<tr>
<td>Micrinite</td>
<td>Granular matter from protoplasm</td>
<td>Relatively inert, not easily hydrogenated or oxidized</td>
<td></td>
</tr>
<tr>
<td>macrinite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Semifusinite</td>
<td>Wood or bark severely oxidized before burial</td>
<td>An important additive in coke</td>
<td></td>
</tr>
</tbody>
</table>

Figure 2-2 – From left to right, Alginite, Vitrinite, and Fusinite
In addition to maceral groups, coal contains inorganic constituents. These inorganics are often incorrectly referred to as ash. Ash is the post-combustion form of inorganic material, but prior to combustion it is proper to refer to these constituent more generally as inorganics. Some examples of inorganic constituents include clay minerals, carbonates, sulfides, oxides, quartz, phosphates, heavy minerals, and accessory minerals\textsuperscript{10}. A listing and description of these inorganic compounds is presented below as Table 2-3\textsuperscript{10}. 
Table 2-3 – Summary of the minerals in coal

<table>
<thead>
<tr>
<th>Mineral Group</th>
<th>First Stage of Coalification: Synergistic Formation, Synsedimentary, Early Diagenetic (intimately intergrown)</th>
<th>Second Stage of Coalification: Epigenetic Formation Deposited in Fissures, Cleats, and Cavities (coarsely intergrown)</th>
<th>Transformation of Synergistic Minerals (intimately intergrown)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clay Minerals</td>
<td>Kaolinite, illite, sericite, clay minerals with mixed-layer structure, montmorillonite, tonstein</td>
<td></td>
<td>Illicite, chlorite</td>
</tr>
<tr>
<td>Carbonates</td>
<td>Siderite-ankerite concretions, dolomite, calcite, ankerite, siderite, calcite</td>
<td>Ankerite, calcite, dolomite, ankerite in fusite</td>
<td></td>
</tr>
<tr>
<td>Sulphides</td>
<td>Pyrite concretions, melnikovite-pyrite, coarse pyrite (marcasite), concretion of FeS₂-CuFeS₂-ZnS</td>
<td>Pyrite, marcasite, zinc sulphide (sphalerite), lead sulphide (galena), copper sulphide (chalcopyrite, pyrite in fusite)</td>
<td>Pyrite from the transformation of syngeneric concretions of FeCO₃</td>
</tr>
<tr>
<td>Oxides</td>
<td>Hematite</td>
<td>Geothite, lepidocrocite (&quot;needle iron ore&quot;)</td>
<td></td>
</tr>
<tr>
<td>Quartz</td>
<td>Quartz Grains</td>
<td>Chalcedony and quartz from the weathering of feldspar and mica</td>
<td>Quartz</td>
</tr>
<tr>
<td>Phosphates</td>
<td>Apatite</td>
<td>Phosphorite, apatite</td>
<td></td>
</tr>
<tr>
<td>Heavy Minerals and accessory minerals</td>
<td>Zircon, rutile, tourmaline, orthoclase, biotite</td>
<td></td>
<td>Chlorides, sulfates, and nitrates</td>
</tr>
</tbody>
</table>
Section 2.1.2 – Structure of Coal

The focus of research was bituminous coal, so it was important to understand bituminous coal structure. The structure of bituminous coal is not as straightforward as diamond or graphite. Coal is a collection of many different molecular units, coal has no definite structure or exact composition. There is near universal agreement that coal can be modeled as a large three-dimensional crosslinked macromolecular network of polynuclear aromatic clusters connected by relatively strong bonds\(^{11,12}\). This description of coal is graphically represented in the Wiser Model of bituminous coal, and has gained wide acceptance\(^{13}\). Figure 2-3 is an example of a large polymer-like carbonaceous molecule that exists in coal according to the Wiser Model\(^{13}\).

![Figure 2-3 – Macromolecular network model of bituminous coals\(^{13}\)]
Some research suggests that coal contains relatively small molecules occluded, or trapped, within a macromolecular network similar to the one in Figure 2-3\textsuperscript{14}. This is known as the guest-host model. The guest host model is applicable to some coals, but does not describe some high volatile bituminous coals\textsuperscript{15}. Nishioka and Gorbaty judged the guest-host model inadequate for describing Illinois No. 6 high volatile bituminous coal\textsuperscript{15}. Nishioka and Gorbaty found no evidence to support the guest-host model, but did create their own model known as the monophase concept.

The monophase concept postulates that

1) large amounts of neutral small molecules are not tightly occluded inside the coal network and

2) the “mobile phase” consists largely of partial constituent of macromolecules\textsuperscript{15}.

The reason to favor the monophase model is recent research showing that soluble molecules in coal are solubilized without breaking covalent bonds\textsuperscript{16}. This agrees with the hypothesis of coal structure proposed by Stiller in a 1981 patent concerning the solvent extraction of bituminous coals\textsuperscript{17}.

**Section 2.1.3 – Functional Groups of Coal**

In addition to carbon, the organic portion of coal contains hydrogen, oxygen, and nitrogen. These are the elements necessary to form the functional groups defined by organic chemistry. Organic chemistry may assist in predicting the behavior of coal in lesser known systems. To determine what functional groups are appended to coal molecules, researchers
use FTIR (Fourier Transform Infrared Analysis), NMR (Nuclear Magnetic Resonance), and XRD (X-ray Diffraction). The relevance of specific functional groups to coal chemistry is summarized below.

R-OH  (Hydroxyl)

Hydroxyl groups in coal are interaction sites that solvents use to form hydrogen bonds. Solvent-coal hydrogen bonds are of interest because many solvents are thought to dissolve coal through a process requiring hydrogen bonding. FTIR studies of various coal ranks suggest that as coal rank increases from lignite to bituminous, there is a decrease in oxygen and hydroxyl content\(^{18}\). This implies that higher rank coals contain fewer interaction sites with which to form hydrogen bonds with solvents\(^{4}\).

\[
\begin{array}{c}
\text{R} \\
\text{H}
\end{array} 
\]  
\(\text{(Aldehyde)}\)

Aldehydes are polar functional groups. The electronegative oxygen pulls the bonding pair of electrons towards itself, creating an electron deficiency at the carbon atom\(^{19}\). Treatment of aldehydes with oxidizing agents, such as nitric acide, transforms the aldehydes to carboxylic acids. Coal researchers transform aldehydes to carboxylic acids using oxidizing chemicals such as hydrogen peroxide. Pretreatment of coal with oxidizing agents often results in increased extraction yields.
Ketones are hydrogen bond acceptors, but not hydrogen bond donators. Therefore, ketones can not form hydrogen bonds with themselves. This makes ketones more volatile than alcohols or carboxylic acids of similar molecular weight. A ketone can combine with an electrophile to form resonance stabilized cation.

\[
\begin{align*}
\text{R-C-R} & \quad \text{(Ketone)} \\
\end{align*}
\]

“Carboxyl groups are characteristic constituents of more complex functional groups such as carboxylic acids and amides.”

\[
\begin{align*}
\text{R-C=O} & \quad \text{(Carboxyl)} \\
\end{align*}
\]

The amino functional group is of interest because the nitrogen can donate its electron pair to the proton of an acid. When the nitrogen donates its electron pair, it becomes positively charged.

\[
\begin{align*}
\text{R-N-H} & \quad \text{(Amino)} \\
\end{align*}
\]

In organic chemistry the sulfhydryl group is a functional group composed of a sulfur and a hydrogen. When the sulfhydryl group is connected to a carbon atom, it is known as a thiol, formerly called by the name mercaptan.
Esters can participate in hydrogen bonds as hydrogen bond acceptors, but cannot act as hydrogen bond donors, unlike their parent alcohols and acids.

Examples of the functional groups mentioned can be found in Figure 2-3, the Wiser Model of bituminous coals.
Section 2.2 – Solvent Extraction

Solvent extraction is a mild coal refining technology. Although solvent extraction uses chemicals to dissolve the coal, it’s analogous to physical cleaning, as the chemical composition of the coal is preserved.

Section 2.2.1 – Coal Solvents

“In 1951, Oele et al. proposed a system for the classification of coal solvents. Oele et al. grouped solvents used in coal extraction into four general types, which are discussed below.

Group 1) Non-specific solvents – Extract a small amount of coal (up to 10%) at temperatures up to 135°C. These solvents extract the resins and wax residues found in coal. The material extracted with Group 1 solvents is typically aliphatic in nature. Examples of Group 1 solvents include acetone, alcohols, benzene, chloroform, and ethers.

Group 2) Specific solvents – Specific solvents dissolve a larger portion of coal (20 to 40%) than non-specific solvents, and are used at temperatures below 230°C. Specific solvents extract coal by a process of physical dissolution. Dryden showed that effective specific solvents are those that contain a nitrogen atom and an oxygen atom with unshared electrons as a
lone pair\textsuperscript{21}. This lone pair of electrons tends to affect the solvent polarity and the coal swelling characteristics of the coal. The nature of the extracted coal is virtually indistinguishable from the original coal.

Group 3) Degrading solvents – Degrading solvents extract the majority of coal (up to 90\%) at temperatures up to 425°C. The solvent can be recovered from the solution substantially unaltered. This action is presumed to depend on the mild thermal degradation of coal which produces smaller, more soluble, coal fragments. Anthracene oil and phenanthrene and examples of degrading solvents.

Group 4) Reactive solvents – Reactive solvents extract coal by chemical interaction. The chemical interaction of the solvent promotes degradation during coal extraction. The structure of both the coal and coal solvent change during this process. Examples of reactive solvents include; low temperature alkali hydrolysis of coal by alkaline-alcoholate resulting in partial depolymerization of the coal matrix.\textsuperscript{22}

There is another class of solvents, not considered by Oele, known as super solvents. Super solvents are unique in that they can dissolve of many substances, both polar and non-polar. In 1981 Stiller showed that super solvents are capable of dissolving large amounts of organic material.
Super solvents are a class of dipolar aprotic solvents that are capable of dissolving a large amount of the organic material in coal\textsuperscript{17}.

“Super Solvents have the general formula.

\[
\begin{array}{c}
\text{O} \\
\hline
\text{R}_n \quad \text{M} \quad \text{N} \\
\text{R}_1 \\
\end{array}
\]

Functional representation of a super solvent

Where:

- M is a carbon, sulfur, or phosphorus atom
- R2 and R3 are either a hydrogen or lower alkyl group
- R1 and Rn are either each a lower alkyl group, another group, a monocyclic group or R1 can be another
group, or $R_1$ and $R_3$ can represent the atoms necessary to close a heterocyclic ring, and $n = 1$ where $M = \text{Phosphorus}$ and is otherwise 0. Where $R_n$ and $R_1$ are either or both lower alkyl groups in this formula alkyl can apparently have a carbon content in the range of C1-C4, or possibly C5, of which C1 and C2 are preferable. Preferred substituents for $R_2$ and $R_3$ are methyl and ethyl groups, although it is produced that homologs up to about C4 or possibly higher would produce more or less useful solvent compounds, and the replacement of such groups with one or more hydrogen atoms also appears to be an acceptable alternative. Monocyclic aromatic groups such as benzyl radical might also prove useful as the substituent $R_n$ and $R_1$, because the structure of this group is favorable to the resonance stabilizing function of the solvent. Either or both of $R_n$ and $R_1$ can be another amino group.\(^{17}\)

Dimethyl-sulfoxide (DMSO), N,N-dimethyl-acetamide (DMAA), N-methyl-2-pyrrolidone (NMP), hexamethyl phsphoramide (HMPA), and tetra-methyl-urea (TMU) are some commonly used super solvents.
Section 2.2.2 – NMP Extraction

NMP extraction has been the subject of study by the carbon products research group at West Virginia University for over a decade. Like all coal refining technologies, solvent extraction aimed to separate some portion of coal deemed desirable from some portion of coal deemed undesirable. Solvent extraction refers to a process where coal has been refined by dissolution in a solvent, usually at elevated temperatures, followed by filtration or centrifugation. The filtration or centrifugation step separated the soluble carbonaceous portions of coal from the insoluble organic portions of coal. It was hypothesized that coal undergoes no chemical change during solvent extraction; therefore, solvent extraction has been viewed more as a cleaning process than a chemical upgrading process.

Solvent extraction has been used when the inorganic portion of coal would be unacceptably detrimental to a process, or when the increased cost of solvent extraction has reduced the operating cost of the process enough to justify its use. Typically, solvent extraction has been employed when coal cannot be utilized in certain processes due to its inorganic material, or ash. Often this has meant that the inorganic material would adversely affect some piece of equipment, or make some part of a process inoperable. Carbon fuel cells for example, have been poisoned by the inorganic material in coal, and required a fuel that is very low in inorganic content. If coal will be used as an additive to liquid fuels, the inorganic content will need to be minimized. For conventional uses of coal, such as coal combustion for electricity generation, inorganic material has been detrimental. However, solvent extraction has been deemed more expensive than coping with a less pure feedstock.
Solvent extraction, like any coal cleaning technology, operates by exploiting differences between the desirable and undesirable portions of coal. The soluble portions of coal are typically carbonaceous aromatic macromolecules trapped within the 3-dimensional cross linked lattice of coal as illustrated in the Wiser Model of bituminous coals. The insoluble inorganic portion of the coal consists mainly of pyrite, quartz, and clays. These inorganic materials become ash after the coal is combusted, and are the major source of particulate emissions from the combustion of coal. The temperature and pressures at which solvent extraction operates occupies a large range. Some studies have used extraction temperatures as low as room temperature, while others have employed temperatures up to 300°C.

NMP is used as an extraction solvent because it is effective, relatively safe, and widely used in research. NMP is a super solvent. Table 2-4 summarizes the physical and chemical properties of NMP.
Table 2-4 – Physical and chemical properties of NMP\textsuperscript{23}

\[
\begin{align*}
\text{Empirical Formula:} & \quad \text{C}_5\text{H}_9\text{NO} \\
\text{Molecular Weight:} & \quad 99.13 \\
\text{Physical form:} & \quad \text{Liquid with mild amine-like odor.} \\
\text{Color (APHA):} & \quad 50 \\
\text{Melting Point:} & \quad -24\degree \text{C} (-11.9\degree \text{F}) \\
\text{Boiling Point:} & \quad 202\degree \text{C (395\degree \text{F}) @ 760 mmHg} \\
& \quad 150\degree \text{C (302\degree \text{F}) @ 162 mmHg} \\
& \quad 100\degree \text{C (212\degree \text{F}) @ 24 mmHg} \\
& \quad \text{T}_{\text{sat}} = \frac{\ln (\text{Psat}) + 0.2349}{0.0156} \\
& \quad (\text{T}_{\text{sat}} \text{[\degree \text{C}]}, \text{Psat} \text{[mmHg]}) \\
\text{Viscosity (25\degree \text{C})} & \quad 1.65 \text{ cp} \\
\text{Specific Gravity:} & \quad 1.027 \text{ @ 25\degree \text{C}} \\
& \quad 0.987 \text{ @ 75\degree \text{C}} \\
& \quad 0.969 \text{ @ 100\degree \text{C}} \\
\text{Specific Heat (Cp):} & \quad 0.40 \text{ Kcal/kg at 20\degree \text{C}} \\
& \quad \text{Cp}_{\text{NMP}} = 8.04 \times 10^{-4} \times (T) + 0.38 \\
& \quad (\text{Cp} \text{[cal/gm*\degree \text{C}]}, \text{T} \text{[\degree \text{C}]}) \\
\text{Thermal Conductivity (kNMP):} & \quad \text{kNMP} \\
& \quad = -1\times10^{-4}(T) + 0.1954 \\
& \quad (T \text{[\degree \text{C}]}, \text{kNMP} \text{[W/M/\degree \text{C}]}) \\
\text{Heat of Vaporization} & \quad 127.3 \text{ K cal/kg at 20\degree \text{C}} \\
\text{Interfacial Surface Tension} & \quad (25\degree \text{C}): 40.7 \text{ dynes/cm} \\
\text{Flash Point (open cup):} & \quad 95\degree \text{C (204\degree \text{F})} \\
\text{Dipole Moment} & \quad 4.09+0.04 \text{ Debye} \\
\text{Dielectric Constant (25\degree \text{C}):} & \quad 32.2 \\
\text{Solubility parameter (\(\delta\)):} & \quad 11.0 \\
\text{Miscibility with Other Solvents:} & \quad \text{completely miscible with water and most organic solvents including alcohols, esters, ketones, aromatic and chlorinated hydrocarbons and vegetable oil.}
\end{align*}
\]
Section 2.2.3 – Models of Coal Dissolution via NMP

As discussed previously, models have treated coal as a large 3-dimensional macromolecular network, with extractable carbonaceous substances occluded in the pores in between the macromolecular network\textsuperscript{14}. Research by Takanohasi differed in that it concluded coal was a large aggregate, and Takaanohashi proposed different mechanisms for describing coal dissolution\textsuperscript{14}. Takanohashi’s research suggested that coal is solubilized without breaking covalent bonds\textsuperscript{16}.

The most common model of solvent extraction treated extraction in terms of the electron donor and acceptor interactions in the solvent coal system\textsuperscript{24}. This model assumed that donor-acceptor bonds in coal were responsible for binding together the macromolecular network and the extractable carbonaceous materials that filled the pores of the network\textsuperscript{24}. According to this model, “Extraction is in principle, a substitution reaction: pore substances are replaced by a solvent molecule in their Donor\textsubscript{network} \rightarrow Acceptor\textsubscript{pore substance} or Donor\textsubscript{pore substance} \rightarrow Acceptor\textsubscript{network} bonds that bind together structural elements of an original coal."\textsuperscript{24,27}

Section 2.3 – Solvent Swelling of Coal

Solvent swelling of coal occurs when the physical dimensions of coal increase due to the presence of a solvent. Researchers have studied coal swelling to elucidate coal structure. Additionally, researchers have correlated or related coal swelling with other coal properties; such as coal extraction yield or coal surface area. The hypothesis of why coal swells in a solvent is adapted from polymer research. For this reason, coal swelling studies have tended
to be more interdisciplinary than other coal studies. This has led to a wealth of coal swelling studies, the main points of which appear in summary below.

The amount of coal swelling was measured by the swelling ratio, represented by the symbol $Q$. The swelling ratio was defined as the volume of the swollen coal divided by the volume of the original coal. Coal began to swell as it imbibed a solvent for which it has an affinity. As the coal absorbed solvent, it grew in size, while maintaining its original shape. When the solvent was removed the coal shrank to near its original size and shape. Some destruction of coal samples occurred after swelling and shrinking, but this destruction seemed due to mechanical stresses rather than chemical changes$^{25}$. It is important that coal retained its original shape after swelling and shrinking, because coal swelling models assumed that swelling was a reversible process$^{26}$. Solvents for which coal has a high affinity are referred to as “good swelling solvents.” Swelling in good swelling solvents was found to be independent of the solvent to coal weight ratio and grinding direction$^{11,27}$. In good swelling solvents such as NMP and pyridine, coal was capable of swelling to over twice of its original volume, while still retaining its original shape$^{14}$.

Good extraction solvents were usually good swelling solvents. A solvent is referred to as a “good extraction solvent” if it was effective at dissolving coal. Good extraction solvents included $n$-methyl pyrrolidone (NMP) and carbondisulfide (CS$_2$) and therefore were expected to be good swelling solvents$^{28}$. The ability of a solvent to swell coal was a strong function of the electron donating ability of the solvents$^{14}$. Painter and Shenoy proposed that the swelling
of coal took place by a process of chain disinterspersion. It was postulated that the covalent bonds in the coal matrix acted as chains that were stretched by solvents. In this model, the solvent dissociated the non-covalent cross-links of the coal matrix, which resulted in a swollen coal sample.

Because of the anisotropic nature of coal, coal swelled preferentially in a direction perpendicular to the bedding plane of the coal seam. This directional swelling was observed because coal appears to have been more highly cross-linked in the bedding plane than perpendicular to it. This directional swelling of coal was not noted in most studies because traditionally only bulk swelling has been measured, not the swelling of individually oriented coal pieces. Measuring the swelling ratio of individual coal pieces yielded clues to the structure of coal not provided by the study of the bulk swelling behavior of coal. “The perpendicular/parallel swelling ratios are highest in pyridine and lowest in chlorobenzene, indicating a highly anisotropic arrangement of covalent bonds.” Also, the time to reach maximum swell parallel to the bedding plane is shorter than the time to reach maximum swell perpendicular to the bedding plane. Cody et al also discovered that swelling measured as a function of time passed through a maximum due to the formation of a metastable state.

Other clues about the structure of coal were obtained by studying the swelling of different ranks of coal in various solvents. Observing the swelling ratios of different ranks in different solvents has provided information about the structural changes across varying ranks. Rincon et al found that swelling ratios were higher for lower ranked coals. Rincon also
found that swelling could be used to improve THF (tetrahydrofuran) soluble materials after liquefaction with H-donor solvents\textsuperscript{30}. The trend of increased THF soluble materials correlated with coals of increased swelling ratios\textsuperscript{30}. Rincon et al postulated that that liquefaction of coal by H-donor solvents is a surface area dependent reaction, and that preswelling the coal was a good method for producing greater penetration and diffusion of reactants, increasing the liquefaction yield\textsuperscript{30}.

How quickly coal swells is controlled by how quickly the solvent diffuses into the coal. This is controlled by solvent properties, the size of the coal particles, and the average molecular weight between the crosslinks of the coal matrix\textsuperscript{12}. The diffusion of solvent into coal is modeled by either Fickian diffusion or anomalous transport\textsuperscript{12}. Coal is a glassy solid at room temperature, but transitions to a flexible state as it absorbs solvent. The flexible nature of the swollen coal suggested lower effective crosslink density, and suggested that the elasticity of the solvent swollen coal may be predominantly rubber-like\textsuperscript{26}. The transition from the glassy to rubbery state is generally very sharp\textsuperscript{12}.

When discussing how swelling affects dissolution, if at all, it was helpful to break coal constituents into soluble and non-soluble materials. Current models for coal dissolution postulate that the soluble portions of coal occupy the pore space of coal and extraction more or less leaves the existing macro molecular network intact\textsuperscript{14}. An aggregated structure of coal would imply a model where the coal structure is irrefragably lost upon dissolution.
Chapter 3 – Experimental Plan

By examining process parameters and coal properties, and their effect on the extraction and swelling of bituminous coal, it was possible to develop a correlation describing the solvent extraction and solvent swelling of high-volatile bituminous coal in the super solvent n-methyl-pyrrolidone. It was hypothesized that the developed correlation is general enough to apply to various bituminous coals in super solvent systems.

Section 3.1 – Experimental Matrix

The experimental matrix was a summary of experiments that were performed during the research. The experimental matrix dictated the values of the independent variables during a particular experiment. These variables were manipulated to determine their effect on solvent extraction and solvent swell. The independent variables studied in the experimental matrix were:

1) System temperature
2) Time at temperature
3) Coal size

The system temperature was varied because it may have determined how quickly solvent extraction proceeded. There temperatures of interest ranged from 50°C to 200°C. The time at temperature was varied because it may have determined how far solvent extraction proceeded and to what extent the coal swelled. The times of interest ranged from 2 minutes to 270 minutes. The coal size was varied because it may have determined the rate of solvent extraction and coal swell, and or the extent of solvent extraction and coal swell. There were
three coal sizes of interest, which ranged from a large size of 40 Tyler Mesh (355 µm) to a small size of sub 150 Tyler Mesh (less than 106 µm). These variables and their ranges are illustrated graphically in the experimental matrix, which appears below as Figure 3-1.

<table>
<thead>
<tr>
<th>Size</th>
<th>Time (minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>s1</td>
<td>t1 5</td>
</tr>
<tr>
<td>s2</td>
<td>t2 15</td>
</tr>
<tr>
<td>s3</td>
<td>t3 30</td>
</tr>
<tr>
<td></td>
<td>t4 60</td>
</tr>
<tr>
<td></td>
<td>t5 90</td>
</tr>
<tr>
<td></td>
<td>t6 120</td>
</tr>
<tr>
<td></td>
<td>t7 150</td>
</tr>
<tr>
<td></td>
<td>t8 180</td>
</tr>
<tr>
<td></td>
<td>t9 210</td>
</tr>
<tr>
<td></td>
<td>t10 240</td>
</tr>
<tr>
<td></td>
<td>t11 270</td>
</tr>
<tr>
<td></td>
<td>t1 2</td>
</tr>
<tr>
<td></td>
<td>t2 4</td>
</tr>
<tr>
<td></td>
<td>t3 6</td>
</tr>
<tr>
<td></td>
<td>t4 8</td>
</tr>
<tr>
<td></td>
<td>t5 10</td>
</tr>
<tr>
<td></td>
<td>t6 12-14</td>
</tr>
<tr>
<td></td>
<td>t7 14-16</td>
</tr>
<tr>
<td></td>
<td>t8 16-18</td>
</tr>
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<td></td>
<td>t9 18-20</td>
</tr>
<tr>
<td></td>
<td>t10 20-22</td>
</tr>
<tr>
<td></td>
<td>t11 22-24</td>
</tr>
<tr>
<td></td>
<td>t12 60</td>
</tr>
</tbody>
</table>

**Figure 3-1 – Experimental matrix**

**Section 3.2 – Analytical Procedure for Quantifying Coal Swell**

Coal swelled when imbibing a solvent. The amount a coal swelled, known as the swelling ratio, was the volume of the swollen coal divided by the volume of the original coal, minus one. The swelling ratio, $Q$, appears below as Equation 3-1.

\[
Q = \frac{h_f}{h_i} - 1
\]  

(3-1)
Section 3.3 – Analytical Procedure for Quantifying Coal Solubility

Following solvent extraction, it was necessary to determine how much coal was dissolved in solution. The amount of coal dissolved in the coal-NMP solution was directly proportional to the absorbance of the coal-NMP solution. The absorbance of the coal-NMP solution was measured using a UV-Vis spectrophotometer. Beer’s Law was used to calculate the amount of coal in solution. Beer’s Law appears below.

\[ A = \varepsilon bc \]  \hspace{1cm} (3-2)

In Equation 3-2, \( A \) represents the absorbance of the solution, \( \varepsilon \) is the molar absorptivity, \( b \) is the path length, and \( c \) is the concentration. A solution exposed to UV-VIS spectroscopy should have been absorbent enough to absorb some light, but not so absorbent that too little light was transmitted. Without the proper absorbance, useful data would not have been obtained. The absorbance equals the logarithm of the ratio of the power of the light source before and after passing through the solution. The equation used to calculate absorbance appears below.

\[ A = \log \frac{P_0}{P} \]  \hspace{1cm} (3-3)
$P_0$ and $P$ are, respectively, the power of a beam of monochromatic radiation before and after passing through the solution. Another variable in Beer’s Law is the path length, represented as term $b$. The path length is the length of solution that the UV-Vis monochromatic beam must pass through. Figure 3-2 is a graphical illustration of these properties.

**Figure 3-2 – Radiation passing through solution of path length $b$**

Beer’s Law (Equation $A = abc$) was a non-linear relationship at higher concentrations. For this reason, it was necessary to keep the absorbance of the coal-NMP solutions at or below three. There are two controllable parameters that determined solution absorbency. The first parameter was the path length of the cell that holds the coal-NMP solution. If cell A is ten times the width of cell B, the solution in cell A appeared to have one tenth of the transmittance ($T = P / P_0$) of the solution in cell B. The second adjustable parameter was the dilution of the solution. A relatively dilute solution absorbed less (had a higher transmittance) than a relatively concentrated solution.

It was necessary to know the molar absorptivity of the coal NMP-solution before the concentration of the coal-NMP solution could be calculated. The molar absorptivity, a
measure of the amount of light absorbed per unit concentration, was calculated as follows. A Soxhlet Extraction was performed on all coal samples, small, medium, and large. Soxhlet extraction was performed for 24 hours at reflux under vacuum, to ensure complete extraction. The product was then filtered and vacuum dried at ambient temperature. The product and residue weights were added and mass closure was achieved. A known amount of extract was dissolved in a known amount of NMP. The extract dissolved fully in the NMP, and was then diluted 100:1. The absorbance was measured and plotted as a function of concentration. A linear regression was performed and the slope is the product of the molar absorptivity and the path length.

Section 3.4 – Analytical Procedure for Quantifying Coal Porosity

Porisimetry included the measurement of pore size, pore volume, pore size distribution, density, and other porosity related characteristics. The adsorption, permeability, strength, and density of a material are often influenced by its pore structure. The porosity of the Lower Powellton coal used in this research was characterized via mercury porisimetry. “Mercury porisimetry is based on the capillary law governing liquid penetration into small pores. This law, in the case of a non-wetting liquid like mercury, is expressed by the Washburn equation:

\[ D = \left( \frac{1}{P} \right) 4 \gamma \cos \phi \]  (3-4)
Where $D$ is the pore diameter, $P$ is the applied pressure, $\gamma$ the surface tension of the mercury, and $\phi$ the contact angle between the mercury and the sample, all in consistent units.

The volume of mercury $V$ penetrating the pores was measured directly as a function of applied pressure. This P-V information served as a unique characterization of pore structure.\textsuperscript{31} Mercury porisimetry was capable of observing pore sizes over five orders of magnitude, from 0.003µm to 360 µm.
Chapter 4 – Experimental Procedure

The experimental procedure consisted of the methods necessary to perform extraction of coal with NMP, measure coal swell, quantify coal solubility, and analyze coal porosity. Each of these four tasks is described separately in the following sections.

Section 4.1 – Experimental Procedure for Performing Solvent Extraction

Solvent extraction experiments were run in batches. Each batch was performed at a temperature of interest. For example, the first batch was run at 50°C, and contained samples of small coal in NMP. In this particular batch, there were eleven samples, one sample for each of the eleven times of interest as illustrated in the experimental matrix, Figure 3-1. Experimental batches at temperatures above 140°C had twelve time levels, as illustrated in Figure 3-1. All extraction runs were performed individually in a set of 10ml graduated test tubes.

To begin an experimental batch, each empty test tube was numbered and weighed to one milligram accuracy. The test tube was then filled with 1ml of Lower Powellton coal of the appropriate size, and again weighed to the nearest milligram. The graduated test tube was then filled to the 6 ml graduated mark with NMP, and again weighed to the nearest milligram. After the above procedure was complete for all samples in an experimental batch, the set of test tubes were placed in a test tube rack, and lowered into a fluidized sand bath preheated to the batch temperature.
Once a time of interest was reached, a test tube was removed from the sand bath and allowed to air cool. Test tubes were continually removed at the experimental times until no more test tubes remained. Once the test tubes were removed and cooled the solvent extraction was complete. With solvent extraction completed, the next tasks were to quantify the amount that coal swelled during extraction, and to quantify the amount of coal dissolved in NMP.

Section 4.2 – Experimental Procedure for Measuring Coal Swell

After the test tubes described in the previous section were air-cooled, the extraction runs were complete. At this time the test tubes were centrifuged. The graduation mark to which the coal had swollen was noted. The swelling ratio was calculated as the ratio of the post-extraction volume of the coal divided by the pre-extraction volume of the coal, minus one, in accordance with Equation 3-1. For example, if the coal had expanded to the 2.5 ml mark (from the original 1.0 ml mark), that would have indicated a swelling ratio of 150%. After all the swelling ratios in a particular experimental batch were measured, the next step was to quantify coal solubility.

Section 4.3 – Experimental Procedure for Measuring Coal Solubility

After the swelling ratio was recorded, one or two milliliters (depending on solution darkness) of the coal-NMP solution were withdrawn from the test tube via a graduated pipette. The one or two milliliters of the coal-NMP solution were placed in a 100 ml Enerylmeyer Flask. NMP was added to the flask until the 100 milliliter mark was reached. This resulted in
either a 50:1 or 100:1 dilution of the coal-NMP solution. A portion of the diluted solution was placed in a small polyethylene bottle, and stored in a refrigerated room until ready for analysis.

Coal solubility was quantified by analyzing the absorbance of the coal-NMP solution, as described in Section 3.3 – Analytical Procedure for Quantifying Coal Solubility. The absorbance of the coal-NMP solution was measured in a UV-Vis spectrophotometer.

Adjustment of both of the coal-NMP solution darkness and cell path length were necessary to obtain solutions with the proper absorbance. A cell width (path length) of 0.1 mm was required, which is small compared to most cells. Dilution of the coal-NMP solution was necessary as well. Some coal-NMP samples were diluted by a factor of 50, while most were diluted by a factor of 100. The dilution factor was chosen depending on the darkness of the coal-NMP solution. Light solutions had a dilution factor of 50:1, while average and dark solutions had a dilution factor of 100:1. These dilution factors placed absorbance readings in an acceptable range.

Section 4.4 – Experimental Procedure for Measuring Coal Porosity

Porosity measurements were made to determine if they could be related to coal extraction and coal swelling. Porosity measurements were made via an AutoPore 9220 Mercury Porisimeter. The mercury porisimeter analyzed samples in a sample holder known as a penetrometer. The penetrometer is cleaned and weighed to the nearest milligram. A small amount of coal, approximately 2 grams, was placed in the penetrometer. The
penetrometer was weighed again to the nearest milligram, and the difference was the sample weight. The penetrometer was placed in the mercury porisimeter for analysis. The mercury porisimeter contained its own dedicated vacuum pump, and the sample penetrometer was evacuated to a pressure of 10 µm Hg, well below the vapor pressure of water at room temperature. Once the evacuation pressure was reached, the porisimeter evacuated the sample for an additional hour to ensure a dry sample. Then the porosimeter filled the penetrometer with mercury under a pressure 0.5 psia and the analysis began. The mercury pressure slowly increased and the intrusion of mercury was measured at various pressures. When the mercury pressure reached 30 psi, the low pressure analysis was complete. The penetrometer, filled with mercury, was removed from the low pressure ports and again weighed to the nearest milligram. From this information the density of the coal sample was calculated. Then the penetrometer was placed in the high-pressure test station of the mercury porisimeter, which varied the mercury pressure from 30 psia to 60,000 psia. After the pressure increased to 60,000 psia, the sample was slowly depressurized from 60,000 psia to atmospheric pressure. Whereas the increasing pressure was used to measure mercury intrusion, the decreasing pressure was used to measure mercury extrusion. The amount of mercury extruded relative to the amount intruded quantified the amount of “ink bottle” type porosity.
Chapter 5 – Experimental Results

Section 5.1 – Porosity

As detailed in Section 3.4 – Analytical Procedure for Quantifying Coal Porosity, mercury porisimetry was used to determine the porosity characteristics of coal. To ensure accurate data, there was one sample and three replicates ran for each coal size, a total of four analyses. The data for the four small coal samples follows as Figure 5-1.

![Figure 5-1 – Porosity of small (sub 106 µm) coal](image)

The cumulative intrusion as measured by the mercury porisimeter, in units of ml of mercury per gram of coal sample, is represented by the y-axis. The pore diameter of the coal sample, which was proportional to the mercury over-pressure exerted on the sample by the
porisimeter, is represented by the x-axis. The mercury porisimeter contained four low-pressure analysis ports and two high-pressure analysis ports. The low-pressure and high-pressure ports which the samples were analyzed in are represented by the key in the upper left hand of Figure 5-1. Mercury porisimetry results suggested that most of the porosity in small coal occurred between approximately 80 µm and 20 µm.

Medium sized coal and large sized coal was also analyzed via mercury porisimetry, and the results are represented as Figure 5-2, and Figure 5-3, respectively.

![Figure 5-2 – Porosity of medium (106 to 212 µm) coal](image)
As with the small coal, porosimetry results suggested that most porosity in medium and large coal occurred between 80 µm and 20 µm. However, medium and large coals exhibited less total porosity than small coals. The discrepancy in coal porosity across the different coal sizes could be explained in two ways. The medium and large coal may have contained closed pores which were not opened until the coal was more finely ground. Additionally, the small coal may have had a different composition than the large and medium coals. Due to differences in the friability of coal macerals, grinding may have caused more porous macerals to be concentrated in the smaller coal sizes. This research suggested no difference in composition between the coal sizes – extraction yields were the same across all three sizes of coal. Furthermore, as will be discussed later, UV-Vis spectroscopy suggested no
difference in composition across extracts from various coal sizes. A graph illustrating the porosity differences between the three different coal sizes is presented below as Figure 5-4.

Figure 5-4 – Pore distribution of the three coal sizes
Section 5.2 – Swelling

The amount of coal swell was measured for every solvent extraction run. The swelling ratio appeared to be a function of the extraction temperature, extraction time, and coal size. Coal swelled much more quickly for the higher temperature extractions (140°C to 200°C) than for the lower temperature extractions (50°C to 120°C). For this reason, there are two graphs for each coal size, one for lower extraction temperatures (longer time scales) and one for higher extraction temperatures (shorter time scales). The swelling ratio of small coals at lower extraction temperatures is presented below as Figure 5-5.

Figure 5-5 – Swell of small coal (sub 106 µm) at low temperatures
Figure 5-5 suggested that appreciable coal swelling occurred at temperatures of 80°C and higher. It was observed that coal swelling increased with increasing extraction time. It was also observed that for lower temperatures, coal swell increased with increasing temperature. This contrasted with the swell of small coal during high temperature extraction runs, which is presented below as Figure 5-6.

Coal swelling passed through a maximum somewhere between 120°C and 140°C. Above 140°C, the coal swelling ratio began to decline with increased temperature. This may be due to dissolution, at higher temperatures more extractable material is removed from the coal matrix. The dissolution of extractable material from the coal matrix may have
counteracted swelling. The next graph, Figure 5-7, illustrated the swelling of medium sized coal as a function of time, at different temperatures.

![Graph showing swelling of medium coal (106 - 212 µm) at low temperatures](image)

**Figure 5-7 – Swell of medium coal (106 - 212 µm) at low temperatures**

As with the smaller coal samples discussed earlier, the swelling ratio increased with increasing temperature. Swelling also occurred more quickly for higher temperatures. The swelling ratio of the medium sized coal during high temperature extraction runs is represented by the next graph, Figure 5-8.
Similar to the swelling of small coal discussed earlier, the swelling ratio reached a maximum somewhere between 120°C and 140°C. Again, the swelling ratio decreased with increasing temperature. As before, swelling occurred more quickly at higher temperatures, but ultimately lower temperatures swelled more. The amount of swell observed during the low temperature extraction of large coal is presented below as Figure 5-9.

**Figure 5-8 – Swell of medium coal (106 - 212 µm) at high temperatures**
Figure 5-9 – Swell of large coal (212 - 355 µm) at low temperatures

The swell of large coal at lower temperatures resembled the swell of small and medium coals at lower temperatures. The unique aspect of the swelling of large coal is the observed lag time between when extraction starts and when the coal began to swell. This suggested that swelling is a diffusion controlled process. As with medium and small coals, the swelling ratio increased with increased temperature. The swelling of large coals during high temperature extraction runs is presented below as Figure 5-10.
The swelling ratios for large coal at high temperatures differed from the swelling ratios for small and medium coals at high temperatures. Unlike small and medium coals, the large coal swelling ratio continued to increase with increasing temperature. This result was somewhat anomalous, as the maximum swelling (about 100% swell) and extraction yield at higher temperatures were similar across all three coal sizes. The result may have been due to a time scale that was too short to collect sufficient swelling data.
Section 5.3 – Coal Solubility

Before coal solubility measurements began, it was questioned whether the extracted material was the same across all samples. There were three coal sizes and eight temperatures of interest, so it was possible that different material could be extracted from different coal samples. If different materials were extracted from different samples, it would have implied a different molar absorbptivity for each sample or set of samples, which would have made absorbance comparisons across samples difficult. This issue was resolved by noting the wavelength at which maximum absorbance occurred during UV-Vis analysis. Because the wavelength at which maximum absorbance occurred was the same for all samples, it was determined that the same material was being extracted from all coals and concentration comparisons were valid.

Coal solubility was measured using a UV-Vis spectrophotometer, as described in Section 3.3 – Analytical Procedure for Quantifying Coal Solubility. The concentration (grams of coal dissolved per liter of NMP) of coal in NMP for the low temperature (50°C to 120°C) extraction of small coal is presented below as Figure 5-11. Notice that the time scale ran from five minutes to four and a half hours. This data suggested that the extraction reached a maximum quickly, and that the temperature determined how much coal was dissolved. Relatively small extraction differences occurred across the temperature range.
The next set of experimental conditions focused on higher temperature extraction runs, from 140°C to 200°C. During the higher temperature runs, extraction was negligible, until the temperature reached approximately 185°C. At 185°C, a spike in concentration appeared. Extraction yield data for the higher temperature runs appears below as Figure 5-12.
Figure 5-12 – Small coal (sub 106 µm) in NMP at high temperatures

Little extraction occurred before 170°C, significant extraction occurred at 185°C, and maximum extraction occurred at 200°C. This contrasted with swelling – appreciable swelling occurred at all temperatures. This data suggested that swelling and extraction may be independent processes. Extraction yield data for the lower temperature extractions of medium sized coal is presented below as Figure 5-13.
Figure 5-13 – Medium coal (106 - 212 µm) in NMP at low temperatures

Similar to the lower temperature runs on small coal samples, little extraction was observed at the lower temperatures. Except for a few spikes in concentration, observed solubility was flat for most low temperature runs. The extraction yield for high temperature extraction of medium coal is presented below as Figure 5-14.
Figure 5-14 – Medium coal (106 - 212 µm) in NMP at high temperatures

The concentration of medium coal at higher temperatures resembled the concentration of small coal at higher temperatures. Little extraction occurred at lower temperatures, 140°C and 170°C. Significant extraction did not occur until 185°C. These parallels between the extraction of small and medium coals extended to the large coal sizes. The extraction of large coals at low and high temperatures is illustrated in the following two graphs, Figure 5-15 and Figure 5-16.
Figure 5-15 – Large coal (212 - 355 µm) in NMP at low temperatures

The data represented in Figure 5-15 illustrated that the same trends observed in the extraction of small and medium coals extended to large coals. Very little extraction occurred at the lower temperatures of 50°C to 120°C. Data for the extraction of larger coal sizes at higher temperatures follows as Figure 5-16.
The dissolution of large coal at higher temperatures resembled the dissolution of smaller and medium coals at lower temperatures. Little extraction occurred at the temperatures of 140°C and 170°C. Significant extraction occurred when the temperature reached 185°C and higher. All swelling and extraction data recorded during research is included in this document as Appendix A.

Examination of the data revealed unusual variability in the amount of coal extraction at 185°C. Preliminary extraction runs, which did not use a sand bath, showed excellent repeatability in concentration measurements. This suggested that the fluidized sand bath may not have had a uniform temperature distribution. This would have been especially obvious around a temperature of 185°C, because the coal-NMP system underwent such drastic
changes around this temperature. The temperature profile of the sand bath was measured using a test tube rack and thermocouple. The holes of the test tube rack served as discrete cells through which the thermocouple was placed and allowed to equilibrate. The resultant temperature profile is presented below as Figure 5-17.

Figure 5-17 – Temperature profile of sand bath used in extraction experiments

Figure 5-17 confirmed that the non-uniformity of the sand bath temperature profile could be responsible for the erratic extraction data observed at a temperature of 185°C.
Chapter 6 – Correlation of Extraction and Swell

Section 6.1 – Developing a correlation for swell and extraction data

It was desired to correlate swell data with process parameters. Several regressions of swelling data were performed. Polynomial, logarithmic, linear, and a reciprocal fits were all applied to swelling data. An example set of swelling data and various fits of the data are presented below as Figure 6-1.

![Figure 6-1 – Various fits of swelling data](image)

The reciprocal fit is a custom correlation that was developed during the course of research. The reciprocal fit was developed after it was observed that both swell and extraction
data seemed to approach some maximum asymptotically. For almost all data, the reciprocal fit was superior. By superior, it is meant that the reciprocal fit most often minimized the sum of squares of the residuals between the actual data and predicted fit. The formula for the reciprocal fit appears below.

$$S_T = S_M \left(1 - \frac{1}{C_S \left(\frac{t - t_l}{l}\right)}\right) \quad (6-1)$$

Where:

- $S_T$ = Swell at time $t$
- $S_M$ = Maximum predicted swell
- $C_S$ = Swelling curve factor
- $t$ = time
- $t_l$ = lag time

$$l = \frac{1}{S_M C_S}$$

The variable $l$ ensured that the lag time, $t_l$, offset the curve by the desired time. The effects of the three adjustable parameters of the reciprocal fit, $S_M$, $C_S$, and $t_l$ are illustrated below in Figure 6-2, Figure 6-3, and Figure 6-4.
Figure 6-2 – Effect of increasing $S_M$ on reciprocal fit

Figure 6-2 was generated with $C_S$ held constant at 0.5 and $t_l$ held constant at 4. $S_M$ was varied from 0.4 to 0.8. $S_M$ is the maximum swell predicted by the correlation. The predicted swell will reach $S_M$ at infinite time. As can be seen in Figure 6-2, $S_M$ is simply a multiplier of the curve, it does not affect the general shape of the curve. The shape of the curve is affected by $C_S$, the swelling curve factor. The effect of $C_S$ on the reciprocal fit is presented below as Figure 6-3.
Figure 6-3 was generated with $S_M$ held constant at 0.8 and $t_l$ held constant at 4. $C_S$ was varied from 0.1 to 0.5. As illustrated in Figure 6-3, $C_S$ represents the curve of the reciprocal fit. It could also be said that $C_S$ determined how quickly the swell approached the maximum predicted swell. Linear data would be best approximated by an extremely small $C_S$, while step-function data would be best represented by an extremely large $C_S$. Note that changing both $C_S$ and $S_M$ has no effect on where the reciprocal fit intercepts the x-axis. This is controlled by the lag time parameter, $t_l$. The effect of various lag times on the reciprocal fit is presented below as Figure 6-4.
Figure 6-4 was generated with $S_M$ held constant at 0.8 and $C_S$ held constant at 0.5. $t_l$ was varied from 4 minutes to 20 minutes. As illustrated in Figure 6-4, varying $t_l$ did not affect the shape of the curve or the maximum swell, but simply the x-axis offset of the curve.

The regression to determine the optimum values of $S_M$, $C_S$, and $t_l$ operated as follows. A series of nested for loops were created, to run several million combinations of $S_M$, $C_S$, and $t_l$. $S_M$ was divided into 200 increments, from 0.01 to 2.00. $C_S$ was divided into 250 increments, from 0.01 to 2.50. $t_l$ was divided into 100 increments, from 0 to 100. These divisions resulted into a total of five million combinations of $S_M$, $C_S$, and $t_l$. SSR (the sum of squares of residuals) between the
actual data and the reciprocal fit was calculated for all five million points. The one combination of parameters out of five million that minimized SSR was designated as the best fit. The visual basic computer code used to fit the swelling correlation to the data is included in this document as Appendix B.

The extraction data was also best described by a reciprocal fit, fundamentally the same equation as Equation 6-1, but with different terms for the sake of clarity. The equation used to describe extraction data is presented below.

\[
E_T = E_M \left(1 - \frac{1}{C_E \left(t - \frac{t_l}{t}\right)}\right) 
\]

(6-2)

Where:

\(E_T\) = Extraction at time \(t\)

\(E_M\) = Maximum predicted extraction

\(C_E\) = Extraction curve factor

\(t\) = time

\(t_l\) = lag time

\[l = \frac{1}{1 - \frac{1}{E_M C_E}}\]

Because the adjustable parameters \(E_M\) and \(C_E\) occupied different ranges than their counterparts \(S_M\) and \(C_S\), the regression was similar but not exactly the same. \(E_M\) was divided into 800 increments, from 0.0 to 80.0. \(C_E\) was divided into 250 increments, from 0.00 to 2.50. \(t_l\) divided into 10 increments, from 0 to 10. This
resulted in a total of two millions combinations. As before, the best fit was defined as the combination of parameters that minimized SSR.

Section 6.2 – Correlation of swell data

Data for the swell of small coal at low temperatures, along with reciprocal fits laid over the data, are presented below as Figure 6-5. Data for the high temperature swell of small coal follows as Figure 6-6.

Figure 6-5 – Fitting small coal (sub 106 µm) swell at low temperature
The reciprocal fits correlated well with the data. The reciprocal fit suggested maximum swell occurred at 140°C to 170°C, which is consistent with earlier conclusions. Swelling data and reciprocal fits for the low and high temperature runs of medium sized coal follows as Figure 6-6 and Figure 6-7, respectively.
Figure 6-7 – Fitting medium coal (106 - 212 µm) swell at low temperature
As before, swell increased with temperature, until it maximized around 170°C. Swelling data and reciprocal fits for the low and high temperature runs of large sized coal follows as Figure 6-9 and Figure 6-10, respectively.
Figure 6-9 – Fitting large coal (212 - 355 µm) swell at low temperature
Figure 6-10 – Fitting large coal (212 - 355 µm) swell at high temperature

The large coal followed the same trends as the small and medium coals. The difference was an increased lag time, large coals took longer to begin swelling, especially at lower temperatures. Once swelling began, large coals swelled a similar amount to small and medium coals. Interestingly, the correlation predicted the highest maximum swell at 170°C, which was not observed in the raw data. This supported the idea that maximum swell occurred around 170°C regardless of coal size, but this was not observed in the high temperature swelling of large coals because the time scale was not sufficiently long.
With all six sets of swelling data fit, it was desired to graph the correlation’s adjustable parameters, $S_M$, $C_S$, and $t_l$, as a function of temperature. $S_M$, $C_S$, and $t_l$ graphed as a function of temperature are presented as Figure 6-11, Figure 6-12, and Figure 6-13, respectively.

![Graph of maximum swell as a function of temperature](image)

**Figure 6-11 – Predicted maximum swell as a function of temperature**

As observed, maximum swell increased with temperature until it peaked at 170°C, after which point the maximum swell decreased. The anomalous data point at 80°C is attributed to the somewhat linear looking data of medium coal at that temperature. Linear data is best fit by a reciprocal fit with large $S_M$ and small $C_S$. The swelling curve factor, $C_S$, was also graphed as a function of temperature, and follows as Figure 6-12.
The swelling curve factor remained relatively flat until it spiked dramatically at a temperature of 185°C. This sudden spike was reminiscent of the sudden spike in extraction yield, which was also observed at 185°C (see Chapter 5 – Experimental Results). The swelling curve factor for small coals was greater than the swelling curve factor for medium coals, which was greater than the swelling curve for large coals. This suggested that small coals approached their maximum swell more quickly, which suggested swelling was at least somewhat diffusion dependent. Next, the swelling lag time was graphed as a function of coal size and temperature, and appears as Figure 6-13.
As expected, larger coals had the highest lag times, and swelling lagged until a temperature of 185°C. Medium coal initially had a larger lag time than small coal, but both quickly approached no lag time at 80°C and higher. This data further supported the conclusion that swelling is at least somewhat diffusion controlled. Smaller coals began swelling sooner, and when they began to swell, swelled faster.
Section 6.3 – Correlation of extraction data

The extraction data for low temperature and high temperature runs are presented below as Figure 6-14 and Figure 6-15, respectively.

Note that for the low temperature runs graphed in Figure 6-14, extraction was temperature dependent, but the total observed extraction was relatively small. This contrasted with the extraction of small coal at high temperature, which is presented below as Figure 6-15.
Little extraction occurred at 140°C and 170°C. When the extraction temperature reached 185°C, significant extraction occurred. The maximum extraction predicted at 200°C was higher than the maximum extraction predicted at 185°C – this was consistent with observed data. This trend was repeated with medium and large sized coal samples. Data for the low temperature and high temperature extraction of medium sized coal are presented below as Figure 6-16 and Figure 6-17.
Figure 6-16 – Fitting medium coal (106 - 212 µm) extraction at low temperature
Figure 6-17 – Fitting medium coal (106 - 212 µm) extraction at high temperature

Similar to the small coal samples, little extraction occurred at temperatures up to 170°C. At temperatures of 185°C and higher, the extraction yield immediately spiked. The extraction yield at 200°C was greater than the extraction yield at 185°C. The same trend was observed for the large coal samples. Data for the low temperature and high temperature extraction of large coal are presented below as Figure 6-18 and Figure 6-19.
Figure 6-18 – Fitting large coal (212 - 355 µm) extraction at low temperature
After the reciprocal fit was applied to all sets of extraction data, the adjustable parameters $E_M$ and $C_E$ were graphed as a function of temperature. The extraction lag time was not graphed because it was small, less than four minutes, for all extraction runs. The graphs of $E_M$ and $C_E$ are presented below as Figure 6-20 and Figure 6-21.
The maximum extraction predicted based on temperature was consistent with observed data. Extraction was relatively flat, until it spiked at a temperature of 185°C. As the data suggested, the maximum extraction was predicted at 200°C, which is near the boiling point of NMP, 202°C. Extraction data contrasted greatly with swelling data. The maximum predicted swell changed relatively smoothly with respect to temperature, where the maximum predicted extraction changed abruptly.

Figure 6-20 – Predicted maximum extraction as a function of temperature
The extraction curve factor, $E_M$, appeared erratic across the extraction runs. The extraction lag time, $t_l$, was small for all runs. This suggested that, generally, extraction runs approached their maximum quickly. This contrasted sharply with swelling data, which suggested that lower temperature extractions (less than 185°C) swelled much more slowly than higher temperature extraction runs.
Section 6.4 – Correlation Validation

With the correlation of swell and extraction complete, it was necessary to validate the correlations. The validity of the correlation was qualified by plotting $S_M$ as predicted by the correlation verse $S_M$ as read by eye. This plot is presented below as Figure 6-22.

A good correlation would fall along the line $x = y$, verifying that the correlation does not favor certain trends. From Figure 6-22 it is observed that the swelling correlation generally bracketed the $x = y$ line, although there seemed to be a slight preference for the prediction of higher swelling values. The validity of the extraction correlation was qualified in the same
manner. The validity of the correlation was qualified by plotting $E_M$ as predicted by the correlation verse $E_M$ as read by eye. This plot is presented below as Figure 6-23.

![Figure 6-23 – Scatter plot showing predicted $E_M$ vs. $E_M$ read from data](image)

It is observed from Figure 6-23 that the correlation bracketed the $x = y$ line. It is concluded from the above two graphs that the developed correlations were valid in correlating process parameters with swelling and extraction data.
Chapter 7 – Conclusions

The research collected data on the swelling, extraction, and porosity of high volatile bituminous coal (Lower Powellton seam). Swelling and extraction data were collected for over 300 extraction runs. These extraction runs varied temperature, which ranged from 50°C to 200°C, extraction time, which ranged from 2 minutes to 270 minutes, and coal size, which ranged from 355 µm to less than 106 µm. The swell of the bituminous coal post dissolution was measured via optical methods, while the extraction yield was measured via UV-Vis spectroscopy. The porosity of the coal was measured via mercury porisimetry. Swelling, extraction, and porosity data were examined independently, and a novel correlation was developed between swelling and process parameters, and between extraction and process parameters. Concurrent examination of swelling and extraction correlations suggested a relationship between swelling and extraction.

Data collected during researched showed that the maximum swell observed increased with increasing temperature, until 170°C, after which maximum observed swell decreased. It is hypothesized that swell decreased after 170°C due to the sharp increase in extraction yield that occurred at temperatures higher than 170°C. Increased extraction resulted in significant material being removed from the coal matrix, which may have counteracted swelling. At higher temperatures, temperature weakly affected the maximum observed swell. However, the speed with which the coal swelled increased sharply with increasing temperature. The speed with which the coal swelled maximized at the highest extraction temperature, 200°C.
Data collected during research showed that extraction was relatively negligible with respect to temperature, until a temperature of 185°C, at which point extraction increased dramatically. It was not determined whether this sharp increase in solubility is due to the nature of the extractable material, the nature of the solvent extracting the material, or a combination of the two. All extraction runs showed very little lag time irrespective of coal size, which suggested that the onset of dissolution occurred quickly.

The relationship observed between swelling and extraction is the most significant research result. The research suggested that the maximum observed extraction, $E_M$, was proportional to the swelling curve factor, $C_S$. Both of these parameters were fairly flat, until they spiked dramatically at a temperature of 185°C. This suggested that if material was not extracted from the coal matrix, swelling was a relatively slow process. However, when the extractable material was significantly soluble in the solvent, the coal swelled quickly. This result supported the “extraction is a substitution” mechanism proposed by Marzec. It is hypothesized that, as the extractable material in the coal matrix became soluble (at and above 185°C), extractable coal material was replaced with solvent. This sudden introduction of solvent into a coal matrix, which is hypothesized to now be more porous due to the removal of extractable material, may have caused the coal to swell much more quickly.

One novel contribution of this research was the proposed proportionality between the rapidness with which a coal swells and the maximum observed extraction. The other result of this research is a new correlation, a reciprocal fit, used to relate coal swelling and extraction to
processing time and temperature. The optimum parameters for these correlations were found through a “brute force” method, which found the combination of parameters that minimized the sum of squares of the residuals between the correlation and actual data. This research was also significant in that it supported existing literature. It appeared that the dissolution of bituminous coal in a super solvent does take place through a substitution mechanism\textsuperscript{24}. 
Chapter 8 – Recommendations for Future Work

There is an opportunity for further research into super solvent and bituminous coal systems. Research could be performed on other coals, to determine whether the previously developed correlation is general enough to apply to other bituminous coals, other solvents, and even perhaps other ranks of coal. Further research could be performed on the mechanism of the substitution process that is solvent extraction. Does the extractable material dissolve out of the coal matrix, leaving the matrix intact? Or, does the coal matrix cease to exist upon dissolution? The small lag time observed during extraction suggested the latter, but more extraction experiments employing larger coal sizes may be necessary to elucidate the extraction mechanism.

A large area of work remains for anyone willing to investigate why coal swelling and extraction change so dramatically at 185°C, and furthermore, why swelling and extraction are best fit by a reciprocal correlation. Starting from first principles, it should be possible to develop a model describing coal extraction. This model would yield understanding of extraction phenomena observed during this research. Additionally, research could be performed to investigate the relationship between other coal properties and swelling and extraction. In addition to processing time, processing temperature, and coal size, it would be desirous to relate the maceral content of coal to its swelling and extraction behavior.
In summary, many research opportunities still exist concerning the solvent extraction of bituminous coal via super solvents. The research completed herein has raised questions that could serve as the basis of further research.
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## Appendix A – Solvent Extraction Data and UV-Vis Data

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Appendix B – Visual Basic Code used to Fit Correlation to Data

Sub regression()
'
' regression Macro
' Macro recorded 3/26/2006 by Joe Stoffa
',
' These variables will determine the resolution of the optimization
Dim nSwellLevels
Dim nConstantLevels
Dim nTimeLevels

' These variables represent the correlation's adjustable parameters
Dim nSwell
Dim nConstant
Dim nTime

' These variables are the optimum values found during optimization
Dim nOptimumSwell
Dim nOptimumConstant
Dim nOptimumTime
Dim lnOptimumSSR

' Initialize the optimum SSR to something high
lnOptimumSSR = 999

' Turn off screen updating before we start
Application.ScreenUpdating = False

' There are three loops here, two nested and parent
' These loops examine all combinations of adjustable parameters
For nLoop1 = 1 To 200
    For nLoop2 = 1 To 250
        For nLoop3 = 1 To 100
            ' First, we set the current swell, constant, and time

            ' Set the maximum swell
            nSwell = 0.1 * nLoop1

            ' Set the constant
            nConstant = 0.01 * nLoop2

            ' Set the lag time

            ' Compute the correlation
            ' Do some calculations...

            ' Add the calculations here
            ' Do some more calculations...

            ' Compute the SSR
            lnSSR = some_function(nSwell, nConstant, nTime)

            ' Update the optimum SSR if necessary
            If lnSSR < lnOptimumSSR Then
                lnOptimumSSR = lnSSR
                nOptimumSwell = nSwell
                nOptimumConstant = nConstant
                nOptimumTime = nTime
            End If
        Next nLoop3
    Next nLoop2
Next nLoop1
End Sub
nTime = nLoop3

' adjust the spreadsheet
Range("swellMaximum").Value = nSwell
Range("curveFactor").Value = nConstant
Range("lagTime").Value = nTime

' Check to make sure we don't divide by zero
' If we're going to, we'll simply skip that combination
If Range("SSR").Text <> "#DIV/0!" And Range("SSR").Text <> "#VALUE!" Then
  If Range("SSR").Value < lnOptimumSSR Then
    lnOptimumSSR = Range("SSR").Value
    nOptimumSwell = Range("swellMaximum").Value
    nOptimumConstant = Range("curveFactor").Value
    nOptimumTime = Range("lagTime").Value
  End If
End If

Next ' For nLoop3 = 0 To nTimeLevels
Next ' For nLoop2 = 0 To nConstantLevels
Next ' For nLoop = 0 To nSwellLevels

' Turn on screen updating before we end
Application.ScreenUpdating = True

Range("swellMaximum").Value = nOptimumSwell
Range("curveFactor").Value = nOptimumConstant
Range("lagTime").Value = nOptimumTime

End Sub