**Low-Rank Coal Thermal Properties
and Diffusivity**

Final Report

W.F. Ramirez

June 1987

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For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Grand Forks Projects Office
Grand Forks, North Dakota

By
University of Colorado
Department of Chemical Engineering
Boulder, Colorado

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MASTER

EXECUTIVE SUMMARY

This project developed techniques for measuring thermal properties and mass diffusivities of low-rank coals and coal powders. Using the concept of volume averaging, predictive models have been developed for these porous media properties.

We used the Hot Wire Method for simultaneously measuring the thermal conductivity and thermal diffusivity of both consolidated and unconsolidated low-rank coals. A new computer-interfaced experiment is presented and sample container designs developed for both coal powders and consolidated coals. A new mathematical model, based upon volume averaging, is presented for the prediction of these porous media properties. Experimental values were accurately modeled over several orders of magnitude as a function of the gas-phase pressure.

Velocity and temperature effects on liquid-phase dispersion through unconsolidated coal were determined. Radioactive tracer data were used to determine mass diffusivities. A new predictive mathematical model is presented based upon volume averaging. The effective axial dispersion coefficient model presented includes the effects of temperature on molecular diffusion and viscosity, the effects of flow rate on mixing, and the effects of the differences in the coals themselves. Based upon the excellent agreement with experimental results, we believe that this model accounts for most of the major contributions to the effective dispersion coefficient in porous media and provides a consistent means of extending data over a wide range of flows and temperatures.

Vapor-phase diffusivity measurements of organic solvents in consolidated lignite coal are reported. An unsteady-state pressure response experiment with microcomputer-based data acquisition was developed to estimate dispersion coefficients through consolidated lignite coals. The mathematical analysis of the pressure response data provides the dispersion coefficient and the adsorption coefficient.

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1 INTRODUCTION

This project developed techniques for measuring thermal properties and mass diffusivities of low-rank coals and coal powders. These data are of a special nature because of the high moisture, volatile matter, and oxygen content of low-rank coals relative to bituminous coals. Using the concept of volume averaging, predictive models have also been developed for these porous media properties.

The work entailed the development of techniques for high temperature measurements and careful sample preparation. The data obtained and the predictive models developed have utility in the processing and utilization of coals. Process description of liquefaction, gasification, and combustion of low-rank coals requires information on heat capacity, conductivity, and gas diffusivity. The utilization of low-rank coal directly as a fuel requires an energy balance for engineering conceptualization and economic planning and justification.

2 EXPERIMENTAL METHOD AND APPARATUS FOR THERMAL PROPERTY MEASUREMENTS

2.1 Theory of the Hot Wire Method

The mathematical basis for the hot wire method is that of an infinite line heat source immersed in an infinite medium and is summarized by Carslaw and Jaeger (1959) as follows. The time dependent conduction equation in cylindrical coordinates with temperature varying only in the radial direction is:

$$\frac{\partial T}{\partial t} = \alpha \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r} \right) \quad (2.1)$$

where α is the thermal diffusivity of the sample. The sample is initially at constant temperature, $T_{initial}$, and is heated at a constant rate, q , by the line source for $t > 0$. The solution of this problem is given as:

$$T - T_{initial} = -\frac{q}{4\pi k} Ei \left(\frac{-r^2}{4\alpha t} \right) \quad (2.2)$$

where t is the time after the start of heating, r is the radial distance from the line source where the temperature is measured, k is the thermal conductivity of the sample, and q is the heating rate per length of line source. $Ei(-x)$ is defined by:

$$-Ei(-x) = \int_x^\infty \frac{e^{-u}}{u} du \quad (2.3)$$

$$Ei(-x) = y + \ln x - x + O(x^2) \quad (2.4)$$

$$y = 0.5772 \text{ (Euler's constant)} \quad (2.5)$$

For small values of x , namely $r^2/4\alpha t \ll 1$, equation 2.2 can be expressed as:

$$\Delta T = T - T_{\text{initial}} = \frac{q}{4\pi k} \ln \left(\frac{4\alpha t}{r_w^2 C} \right) \quad (2.6)$$

where:

- T = temperature of the wire
- T_{initial} = initial temperature of the wire
- q = heat input per unit length of wire
- r_w = radius of wire
- α = thermal diffusivity of sample
- k = thermal conductivity of sample
- C = $\exp y$ where y = Euler's constant
- t = time after start of heating

This equation is valid only when the dimensionless expression $r_w^2/4\alpha t \ll 1$. Differentiating equation 2.6 with respect to $\ln(t)$ and solving for k yields:

$$k = \frac{q/4\pi}{d\Delta T/d\ln t} \quad (2.7)$$

Substituting equation 2.7 into equation 2.6 yields:

$$\alpha = \frac{r_w^2 C}{4t} \exp \left(\frac{\Delta T d\ln t}{d\Delta T} \right) \quad (2.8)$$

To obtain the values of k and α from experimental data, the temperature rise is recorded as a function of $\ln t$ and is fit using a linear least squares regression. If a

is the slope and b is the y -intercept of the fit, then the equations for k and α are given by:

$$k = q/4\pi a \quad (2.9)$$

$$\alpha = \frac{Cr_w^2}{4} \exp(b/a) \quad (2.10)$$

2.2 The Hot Wire

The wire is 99.9% platinum and has a diameter of 25.4μ . It is desired to have a wire with as small a diameter as possible because the theory assumes a true line heat source. Preliminary tests showed that a wire having a diameter of 25.4μ was the smallest which would not break when the material was being loaded.

2.3 Sample Containers

Two sample containers were used in this study. The first was used for gas, liquid, and powdered samples. The second was used for solid samples. A detailed description of the containers and the procedure for loading samples is given in appendix B. Figure 2.1 shows a schematic of the sample containers. Both containers were machined from stainless steel and have a number of ports. Two are provided for radial and axial thermocouples. The thermocouples are used in the feedback temperature control loop. A port is provided for a calibrated thermometer. Two ports are located on the bottom of the containers. One is for vacuum and pressure gauges and the other leads to vacuum and nitrogen. All ports seal with swagelok fittings. The containers also have an annular space which contains two 600 watt nichrome ceramic beaded heaters. These heaters are used for temperature control of the initial temperature of the sample.

The vacuum gauge operates on a thermal conductivity principle and has a range from 133.3 kPa down to 0.133 Pa ($1000 - 0.001 \text{ torr}$). A bourdon pressure gauge is also used to measure pressures in the sample containers from atmospheric pressure up to 810 kPa (8 atm).

The pump is direct drive and oil sealing capable of pumping the system down to 1.33 Pa (0.010 torr). The sample containers can also be pressurized with nitrogen from a high pressure cylinder. This enables thermal properties to be measured at pressures from 810 kPa (8 atm) down to 1.33 Pa (0.010 torr).

Figure 2.1: Schematic of samples containers.

2.4 Wheatstone Bridge

The basic data collected in this method are temperature of the line source versus time. To do this, the platinum wire which acts as the line source is incorporated as one arm in a Wheatstone bridge. As current is passed through the wire, electrical power dissipation causes its temperature to rise. Since temperature and resistivity are uniquely related for platinum (Riddle et al., 1973), the temperature of the wire is given as a function of resistivity by the expression:

$$T = T_0 + T_1\rho_w + T_2\rho_w^2 + T_3\rho_w^3 + T_4\rho_w^4 \quad (2.11)$$

where ρ_w is the resistivity of the wire. The coefficients were obtained by performing a least squares fit on temperature versus resistivity data for platinum between 0 and 500 °C. The resistivity is determined from the resistance of the wire by the expression:

$$\rho_w = \frac{R_w r_w^2 \pi}{l_w} \quad (2.12)$$

R_w , r_w , and l_w are the resistance, radius, and length of the wire respectively. The resistance of the wire is obtained by reading the power supply voltage, V_t , and the bridge imbalance voltage, V_b , and is given as a function of R_1 , R_2 , R_3 , V_t , V_b by the following derivation (see Figure 2.2). V_b is given by the following relations:

$$V_b = R_2 i_2 - R_1 i_1 \quad (2.13)$$

$$V_b = R_w i_1 - R_3 i_2 \quad (2.14)$$

where i_1 and i_2 are currents in the bridge. Solving equation 2.14 for R_w yields:

$$R_w = \frac{V_b + R_3 i_2}{i_1} \quad (2.15)$$

Solving equation 2.13 for i_1 and substituting into equation 2.15 gives:

$$R_{wire} = \frac{(V_b + R_3 i_2) R_1}{(R_2 i_2 - V_b)} \quad (2.16)$$

Since:

$$i_2 = \frac{V_t}{(R_2 + R_3)} \quad (2.17)$$

Figure 2.2: Wheatstone bridge.

then:

$$R_w = \frac{V_b R_1 (R_2 + R_3) + V_t R_1 R_3}{V_t R_2 - V_b (R_2 + R_3)} \quad (2.18)$$

The resistance of the platinum wire and therefore its temperature is given at any time by equation 2.18. Once the temperature versus time data are collected, ΔT and $\ln t$ are determined for each data point. A least squares fit is done on the data and the thermal conductivity and diffusivity can then be calculated from the slope, y-intercept, and heat input (q) as given in equations 2.9 and 2.10.

The theory of this method assumes the power input q (*power/length*) is constant. In the case of heating by electrical power dissipation, q is given by:

$$q = \frac{V_w^2}{R_w l_w} \quad (2.19)$$

where V_w is the voltage drop across the wire. This assumption is very good if the voltage across the bridge voltage, V_t , is constant. For a 10 K rise in temperature of the wire, the change in q is less than 0.03%. If the current, i , through the bridge is constant, then the change in q is approximately 3% for the same rise in temperature. The wire was therefore heated by placing a constant voltage across the bridge.

The Wheatstone bridge consists of four arms (*see Figure 2.3*). Arms (3) and (4) are both 100 Ω resistors. Arm (1) is a potentiometer which has a variable resistance from 0 to 100 Ω . This arm is used to balance the bridge. The resistors and potentiometer have a temperature coefficient of ± 30 ppm. The exact resistances of the resistors and the potentiometer including leads were measured with a electrometer having a precision of 0.05%. The resistance in arm (2) is made up solely of the thin platinum wire.

2.5 Amplifier, Power Supply, and Switches

Figure 2.3 shows an overall schematic of the electronics for the system. The voltage signal that is produced by the unbalanced bridge, V_b is sent to an amplifier before it is read by the computer. The voltage is amplified by a factor of 16. Signal amplification is necessary because external electromagnetic radiation can produce interference on low level signals (25 millivolts) if the cable transmitting them is longer than a few inches.

Power to the bridge is supplied by a constant voltage mode supply which has a output range of 0-25 volts and 0-4 amperes. In constant voltage mode, the output is stable to within ± 10 μ volts.

Figure 2.3: Schematic of electronics.

The start of any measurement occurs when the power is switched from the dummy resistor ($100\ \Omega$) in Figure 2.3 to the bridge. This is accomplished with a mercury relay switch. A 5 volt signal from the computer digital to analog converter to a transistor allows current to flow through the relay inductor. This causes the switch to close. The mercury relay switch was chosen because its transition from open to close is very smooth with no mechanical rebounding.

2.6 Computer

The computer used in this study is a *Labtech 70* produced by Laboratory Technologies. Its features include a 10 megabyte Winchester fixed disk drive for data storage and a floppy disk drive for file backup. Each diskette is capable of storing 280 kilobytes of information. The central processing unit is a 16 bit 8088/8087 coprocessor which accesses 384 kilobytes of random access memory. The 8088 processor is the core processor while the 8087 handles hardware arithmetic functions. An 8 channel, 12 bit analog to digital converter is also included. The a/d converter is a successive approximation type which allows for sampling rates up to 20,000 per second. The computer is also equipped with an 8 channel, 12 bit digital to analog converter.

The Labtech 70 runs on the Intel *iRMX-86* operating system (*iRMX 86 Operator's Manual*, 1982). This system includes an assembler, *FORTRAN-86* which is a modified version of *FORTRAN 77* (*FORTRAN-86 User's Guide*, 1981), and a vast library of programmable system calls which allow for real-time programming as well as multitasking capabilities.

The computer is an essential part of this experimental apparatus and has been programmed to basically run the experiment. It performs the following tasks with respect to the experiment:

1. A temperature control routine was written to control the initial temperature of the sample. This allows the thermal properties to be measured over a temperature range of 295 to 773 K (22 – 500 °C). The routine is based on a discrete sampling proportional/integral controller.
2. A bridge balancing routine was written to balance the bridge before temperature sampling begins. The routine continuously reads the bridge imbalance voltage and prints it to the console. The bridge is balanced by manually adjusting the resistance of the potentiometer.

3. The data acquisition task performs data acquisition, reduction, and storage. When executed, it first switches power from the dummy circuit to the bridge circuit via the d/a converter and the mercury relay switch. This event marks the start of the wire heating. The routine reads the voltage across the bridge (V_t) and then begins to sample temperature data at a rate of 100 samples per second for 0.5–3 s. This is done via the a/d converter. It then switches power back to the dummy circuit and calculates ΔT and $\ln t$ for each data point. The heat input per length of wire q is also calculated. A least squares fit is done on the ΔT vs $\ln t$ data and the conductivity and diffusivity are determined. The values from both determinations are then written to a permanent file on the fixed disk for storage.

2.7 Temperature Control

Feedback temperature control was incorporated into this apparatus so the initial temperature of the sample could be varied. This allows the thermal properties to be measured over a temperature range of 295 to 773 K (22 to 500 °C). The computer implements temperature control by first reading the temperature of the sample via the two thermocouples and the a/d converter. The duty cycles of the heaters are then calculated based on a discrete sampling proportional/integral controller. Solid state relay switches are used to turn the container heaters on and off. The relays are normally open and are closed by 5 volt signals from the computer d/a. Closing the switches allows 110 volts ac to pass through the heaters. The heaters are 600 watt nichrome ceramic beaded heating wires and are located in the annular space of the sample container.

2.8 Overview

Thermal property measurements were made on gases, liquids, solids, and powders. Measurements were first made on glycerin (99.5%) to establish the accuracy and precision of the instrument. Measurements were made on teflon and nitrogen to verify the accuracy and precision of the apparatus for solid and gas samples. Glass beads were the first material in which the hot wire method was used for thermal property measurements of two-phase samples. Measurements were made on 50 μ glass beads because of their uniform particle size and because they are chemically and physically inert under the conditions in which the properties were measured.

Table 2.1: Measured values of thermal conductivity and diffusivity for glycerin, teflon, and nitrogen.

	Conductivity (W/mK)	Diffusivity (m^2/s)
Glycerin (295 K)	0.292 (0.288)	9.59×10^{-8} (9.67×10^{-8})
Glycerin (347 K)	0.294 (0.291)	7.55×10^{-8}
Teflon (296 K)	0.241 (0.24)	1.19×10^{-7} (1.1×10^{-7})
N ₂ (296 K , 101.3 kPa)	0.026 (0.026)	2.27×10^{-5} (2.2×10^{-5})

Thermal property measurements were also made on spent oil shales and lignite coals.

Figures 2.4 and 2.5 show a typical temperature versus time response for a measurement performed on a sample of powdered shale. Figure 2.4 is a plot of temperature rise versus time. The resolution on the temperature readings is 0.01 K . In Figure 2.5, these same data points are plotted as a function of $\ln t$. The correlation coefficient for the linear least squares fit for these data was 0.9997.

2.9 Glycerin Results

Measurements were made on glycerin (99.5% purity) to establish the accuracy and precision of apparatus. The results of measurements made at two temperatures are presented in Table 2.1. Values in parenthesis were obtained from the literature (Venart and Krishnamurthy, 1968; Andersson and Backstrom, 1977). From this work the accuracy was established to be approximately 1% for the thermal conductivity and 4% for the thermal diffusivity. The precision (95% confidence) is 0.4% for the conductivity and 4.5% for the diffusivity. The accuracy and precision of the diffusivity measurement are typically worse than those of the conductivity measurement for this method. This is due to the fact that in the determination of the diffusivity, the constant $e(2.718...)$ is raised to the power of the ratio of the y -intercept to the slope of the linear least squares fit (see equation 2.10). Therefore small errors in the ratio of y -intercept to slope results in significant errors in the diffusivity.

Figure 2.4: Temperature rise versus time for powdered oil shale, particle diameter 150–495 μ .

Figure 2.5: Temperature rise versus ln (time) for powdered oil shale, particle diameter 150–495 μ .

2.10 Teflon Results

Measurements were made on teflon at 296 K to verify the accuracy and precision of the apparatus when solid samples were used. The value obtained for the conductivity was 0.241 W/mK with a precision of 1.6%. The values in parenthesis were obtained from the literature (Perry and Chilton, 1973). The diffusivity had a precision of 11%.

2.11 Glass Beads Results

Glass beads were the first material in which the hot wire method was used for thermal property measurements of two-phase samples. Glass beads were chosen because they have a uniform particle shape and size and because they are chemically and physically inert under the conditions in which the properties were measured.

Heat transfer mechanisms through two-phase samples are more complicated than those through single-phase solids. Heat transfer through single-phase solids is due to conduction through a single phase while heat transfer through powdered materials is due to conduction through the solid phase, conduction through the fluid phase, and heat transfer between phases at any point in the sample. Conduction in the solid and fluid phases follows a tortuous pathway which adds another degree of complexity to the mechanism. The thermal properties of particulate samples are not true physical properties like those of a single-phase samples but are effective properties which combine the effects of all these contributions.

Measurements were made on a glass bead sample having a particle diameter of 50μ and a bulk density of 1.32 g/cm^3 . Results obtained for the conductivity and diffusivity for glass beads as functions of temperature and pressure are presented in Figures 2.6, 2.7, 2.8 and 2.9. As can be seen in Figures 2.6 and 2.7, both the conductivity and the diffusivity are approximately linear functions of temperature in the range of 293 to 423 K (20 to 150 $^{\circ}C$). The dependence of conductivity and diffusivity on pressure is much more dramatic as seen in Figures 2.8 and 2.9. Both properties vary by orders of magnitude over the range of 82.6 kPa (620 torr) to 1.33 Pa (0.01 torr). These effects are consistent with results of similar studies which are reported in the literature (Wechsler, 1968).

When the pressure in the sample is lowered to 1.33 kPa (0.010 torr), heat transfer through the gas phase by means of conduction is essentially eliminated. Measurement of the thermal conductivity under these conditions gives the contri-

Figure 2.6: Thermal conductivity versus temperature for 50 μ glass beads.

Figure 2.7: Thermal diffusivity versus temperature for 50 μ glass beads.

Figure 2.8: Thermal conductivity versus pressure for 50 μ glass beads.

Figure 2.9: Thermal diffusivity versus pressure for 50 μ glass beads.

bution of conduction through the solid phase to the overall heat transfer mechanism. As the pressure is gradually increased, the contribution of conduction and through the gas phase along with interfacial heat transfer is measured. Measurements under these types of conditions gives information as to which modes of heat transfer dominate the overall mechanism.

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3 LIGNITE COAL THERMAL DIFFUSIVITY AND CONDUCTIVITY PROPERTIES

Lignite coals are composite materials made up of carbon, aromatic and aliphatic hydrocarbons, water, and inorganic oxides (Speight, 1983). A typical composition for a lignite coal is given in Table 3.1. The thermal properties of powdered and consolidated lignite coal samples were measured under a variety of conditions of temperature and pressure. In addition, measurements were done on dried and undried coal samples to determine the effect of moisture content on the thermal properties. To determine the temperature dependence of the thermal properties, measurements were made on undried powdered coal samples from 298 to 333 K (25 – 60 °C) and on dried powdered coal samples from 298 to 773 K (25 – 500 °C). Thermal properties of undried solid coal samples were measured as a function of temperature from 298 to 373 K (25 – 100 °C). Measurements on dried solid samples were made from 298 to 573 K (25 – 300 °C). Measurements were also made as a function of the orientation of the heat transfer to the bedding plane. Coal samples are typically anisotropic so their thermal properties are a function of how the measurement is made with respect to the bedding plane (*either parallel or perpendicular*). Because the thermal properties are a strong functions of pressure for powdered coals, measurements were made at a variety of pressures from above atmospheric down into the millitorr range. Because coal contains a number of volatile components (*especially undried samples*), the lower limit of pressure under which measurements can be made is determined by the vapor pressure of the coal sample. For undried samples, the lower limit is typically around 1.33 kPa (10 torr) and for dried samples, the lower limit is in the millitorr range.

Table 3.1: Typical composition of low-rank lignite coal.

Component	Mass percentage
Moisture	7–25
Volatile matter	27–38
Fixed carbon	40–55
Inorganic oxides	4–7

Basic thermal property data of consolidated and powdered coals are necessary for the solution of relevant heat transfer problems such as coal gasification modeling. The measurement of these properties as functions of temperature, pressure, etc. provides a basic understanding of heat transfer mechanisms through solid and powdered materials.

3.1 Thermal Properties of Undried Powdered Coals

Thermal property data were collected on Indian Head, Martin Lakes, and Wyodak low rank lignite powdered coal samples. Indian Head, Martin Lakes, and Wyodak refer to names of the mines from which the coal samples were taken. The Indian Head mine is located in North Dakota; the Martin Lakes mine is located in Texas; and the Wyodak mine is located in Wyoming. All of the samples had a particle size of not more than $74\ \mu$ (*200 mesh*) and none of the samples were dried. Two sets of measurements were performed on each sample. The thermal properties were first measured as a function of pressure at a constant temperature of $298\ K$ ($25\ ^\circ C$). The pressure varied from 101.3 down to $1.33\ kPa$ ($760 - 10\ torr$) which is the vapor pressure of these undried coal samples. The thermal properties were then measured as a function of temperature at a constant pressure of $101.3\ kPa$ ($760\ torr$). The temperature of the sample was varied from 298 to $333\ K$ ($25 - 60\ ^\circ C$). At temperatures above $333\ K$ ($60\ ^\circ C$), the undried samples begin to produce significant quantities of water in the vapor and liquid phase making the measurements irreproducible. Results for these three coals are given in Figures 3.1-3.4.

3.2 Thermal Properties of Dried Powdered Coals

Thermal property data were collected on powdered samples of Indian Head and Martin Lakes coals after drying. In each case, the raw samples were sifted through 74 and $38\ \mu$ screens. The fraction containing the particle size distribution from 38 to $74\ \mu$ was then placed in an oven at $373\ K$ ($100\ ^\circ C$) and dried by passing dry nitrogen over the coal until its weight became constant. Table 3.2 gives the percentage weight loss for each coal that resulted from the drying process. The weight losses for these samples (25%) are typical for low rank lignite coals. After drying, each sample was resifted to insure a particle size distribution of 38 to $74\ \mu$. The samples were then loaded into the sample container and the thermal properties

Figure 3.1: Thermal conductivity versus temperature for undried powdered coals.

Figure 3.2: Thermal diffusivity versus temperature for undried powdered coals.

Figure 3.3: Thermal conductivity versus pressure for undried powdered coals.

Figure 3.4: Thermal diffusivity versus pressure for undried powdered coals.

Table 3.2: Percentage weight loss due to drying at 373 K.

Coal	% Weight loss
Indian Head	26
Martin Lakes	28

were measured.

Thermal properties of the dried powdered coals were first measured as a function of pressure from 0.107 to 810 *kPa* (0.80 *torr* to 8 *atm*) at room temperature. Properties were then measured as a function of temperature from 293 to 573 *K* (20 to 300 °C). During these measurements, the sample container was sealed and the pressure was allowed to come to its equilibrium value for a given temperature. Values for the thermal properties are given in Figures 3.5–3.8.

3.3 Thermal Properties of Charred Powdered Coals

Thermal property data were collected on a charred powdered sample of Indian Head coal. Raw coal samples were prepared by first sifting through 74 and 38 μ screens. The fraction containing the particle size distribution from 38 to 74 μ was then placed in an oven at 373 *K* (100 °C) and dried by passing dry nitrogen over the sample. The sample was then transferred to a second oven at 673 *K* (400 °C) and dried by passing dry nitrogen over the sample for three hours. The percentage weight losses of the coal sample for the two drying temperatures are given in Table 3.3. The weight loss which results from drying at 373 *K* (100 °C) is mainly due to water while that which results from drying at 673 *K* (400 °C) is mainly due to organic volatiles. The sample was then loaded into the sample container and the thermal properties were measured.

Thermal properties of the powdered coal chars were first measured as a function of pressure from 0.2 *kPa* (1.5 *torr*) to 810 *kPa* (8 *atm*) at ambient temperature. Properties were then measured as a function of temperature from 293 to 773 *K* (20 – 500 °C). During these measurements, the sample container was sealed and the pressure was allowed to come to its equilibrium value for a given temperature. Values for the thermal properties are given in Figures 3.9–3.12

Figure 3.5: Thermal conductivity versus temperature for dried powdered coals.

Figure 3.6: Thermal diffusivity versus temperature for dried powdered coals.

Figure 3.7: Thermal conductivity versus pressure for dried powdered coals.

Figure 3.8: Thermal diffusivity versus pressure for dried powdered coals.

Figure 3.9: Thermal conductivity versus temperature for dried powdered Indian Head char.

Figure 3.10: Thermal diffusivity versus temperature for dried powdered Indian Head char.

Figure 3.11: Thermal conductivity versus pressure for dried powdered Indian Head char.

Figure 3.12: Thermal diffusivity versus pressure for dried powdered Indian Head char.

Table 3.3: Percentage weight loss due to drying at 373 and 673 K.

Temperature °C	% Weight loss
100	26
400	44

3.4 Thermal Properties of Consolidated Coals

Thermal conductivity and diffusivity measurements were made on Usibelli/Alaska solid consolidated coal samples (*specific gravity* = 1.27). Measurements were made both parallel and perpendicular to the bedding plane. In both cases the coal samples were saturated with water at the start of the experiment. Measurements were first taken at room temperature and then the sample was heated at a constant rate of 0.4 K per minute from 293 to 423 K (20 – 150 °C). Measurements were made roughly at 25 K intervals. Values obtained from 293 to 423 K (20 to 150 °C) agree with reported values (Speight, 1983) for coal and are presented in the Figures 3.13 and 3.14. Diffusivity values were not reported for temperatures around 373 K (100 °C) because at these temperatures, water is undergoing a phase transition from liquid to gas making these measurements irreproducible. Figures 3.13 and 3.14 indicate that the thermal properties do not vary significantly depending on the orientation of the measurement to the bedding plane. Thermal conductivity and diffusivity measurements were made on a sample of Freedom solid coal saturated with water for temperatures from 293 to 403 K (20 to 130 °C). Freedom coal is a North Dakota coal which is the coal used by the Great Plains Gasification Plant. Measurements were first taken at room temperature and then the sample was heated at a rate of 0.4 K per minute with measurements being taken at 25 K intervals. The results are presented in Figures 3.15 and 3.16. Values for the conductivity of this saturated sample are slightly higher than the range given by Speight (1983) (0.17-0.38 W/mK). This is due to the high water content of these coals (*typically* 25%). Since the conductivity of water is 0.59 W/mK, it is expected that these coals have a higher conductivity than other coals when they are saturated with water. The heat capacities fall in the range given by Speight (1983) (800-1550 J/kgK).

Thermal property data were collected on samples of dried Freedom and dried Usibelli (*specific gravity* = 0.98) for temperatures from 293 to 573 K (20 to 300

Figure 3.13: Thermal conductivity versus temperature for Usibelli/Alaska saturated solid coal, parallel and perpendicular to bedding plane.

Figure 3.14: Thermal diffusivity versus temperature for Usibelli/Alaska saturated solid coal, parallel and perpendicular to bedding plane.

Figure 3.15: Thermal conductivity versus temperature for Freedom North Dakota Lignite saturated solid coal, perpendicular to bedding plane.

Figure 3.16: Thermal diffusivity versus temperature for Freedom North Dakota Lignite saturated solid coal, perpendicular to bedding plane.

$^{\circ}\text{C}$). Samples of Freedom and Usibelli/Alaska coals were heated to 383 K (110 $^{\circ}\text{C}$) and maintained at that temperature with a nitrogen purge for 3 h. The samples were then cooled to room temperature and heated at a rate of 0.4 K per minute from 293 to 573 K (20 to 300 K). Results are given in Figures 3.17 and 3.18. Values for conductivity of both samples are slightly lower than the values reported by Berkowitz (1979) for dried coals (0.1-0.3 W/mK). This effect is due mainly to numerous small cracks which appeared in the coal samples after they were dried at 383 K (110 $^{\circ}\text{C}$). Drying at 383 K (110 $^{\circ}\text{C}$) typically results in a weight loss of 25% for these samples. Heat capacity values for the Usibelli coal sample fall in the range given by Speight (1983) (800-1550 J/kgK). The values for the Freedom sample were lower than expected. Solid samples of Freedom coal did not remain homogeneous upon drying but tended to disintegrate making the measurement process very difficult and possibly inaccurate especially for the heat capacity measurement.

Figure 3.17: Thermal conductivity versus temperature for dried solid coal, perpendicular to bedding plane.

Figure 3.18: Thermal diffusivity versus temperature for dried solid coal, perpendicular to bedding plane.

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4 THERMAL PROPERTIES OF NITROGEN

The thermal conductivity and thermal diffusivity of nitrogen gas were measured as a function of pressure from 101.3 kPa (760 *torr*) down to 1.33 Pa (0.010 *torr*). Measurement of the thermal properties of gases with the Hot Wire Method is more complex than that of solids, liquids, and powders because of errors which may be introduced from convection, radiation, and the finite dimensions and heat capacity of the hot wire. An analysis of these effects was done first to determine the conditions under which they may cause an error in the thermal properties measurement.

The transient hot wire method normally assumes that the wire (25 μ in diameter) acts as a true line heat source having no radius and no heat capacity. With this assumption, the temperature rise of the wire is linear with the natural logarithm of time and the conductivity and diffusivity of the sample can be determined from the slope and intercept. Healy (1976) presents an analysis whereby the error due to the finite dimensions and heat capacity of the wire can be determined quantitatively. For a true line heat source, the temperature rise as a function of time is given by:

$$\Delta T = T - T_{\text{initial}} = \frac{q}{4\pi k} \ln \left(\frac{4\alpha t}{r_w^2 C} \right) \quad (4.1)$$

For a wire heat source with finite radius and heat capacity, the temperature rise as a function of time is given by:

$$\Delta T = T - T_{\text{initial}} = \frac{q}{4\pi k} \left(\left[1 - \frac{r_w^2 ((\rho C_p)_w - \rho C_p)}{2kt} \right] \ln \left(\frac{4\alpha t}{r_w^2 C} \right) + \frac{r_w^2}{2\alpha t} - \frac{r_w^2}{4\alpha_w t} + \frac{k}{2k_w} \right) \quad (4.2)$$

where $(\rho C_p)_w$ is heat capacity of the wire in $J/m^3 K$, ρC_p is the heat capacity of the sample, α_w is the diffusivity of the wire, and k_w is the conductivity of the wire. Both of these solutions are only valid for large values of $\alpha t/r_w^2$, typically, $t > 0.3s$. The term containing the difference in heat capacities of the wire and the sample contributes the major correction due to the finite radius and heat capacity of the wire. Figure 4.1 shows a plot of ΔT versus $\ln t$ for glycerin ($k = 0.3 W/mK$, $\alpha = 10^{-7} m^2/s$) for both the line source and the finite wire source. This correction is small for glycerin because the heat capacity of the wire and sample are typically very close. For gases, the difference in heat capacities between the wire and sample

Figure 4.1: Temperature versus time response for the finite wire and true line source for a single phase sample.

is typically three orders of magnitude. Under these conditions, the finite radius and heat capacity of the wire must be taken into account by fitting the experimental data to equation 4.2. If data are collected for long times (*more than one second*), the heating of the gas surrounding the wire will induce heat transfer by a convective instability which causes the temperature rise of the wire to be less than that which results from pure conduction. Figure 4.2 shows a plot of ΔT of the wire versus $\ln t$ for nitrogen. For $t < 1s$ ($\ln t < 0$), the data match the finite wire solution. For $t > 1s$, the actual temperature of the wire is less than that predicted by the finite wire solution indicating that a convective instability has been induced. Because the temperature rise of the wire is typically 4 K, the heat transfer due to radiation is less than 0.5 % of that due to conduction and can therefore be neglected. In order to accurately determine the thermal properties of nitrogen at various pressures, the data used must be collected before convection is induced ($t < 1s$) and it must be matched to the finite wire solution rather than the true line source solution.

The thermal properties of nitrogen gas were measured at 296 K (23 °C) from 101.3 kPa (760 torr) down to 1.33 Pa (0.010 torr). Results are presented in Table 2.1 for atmospheric pressures. Values in parenthesis were obtained from the literature (Weast, 1977). Figures 4.3 and 4.4 show these properties as a function of pressure. The thermal properties of nitrogen are not readily available at low pressures. A value of 0.026 W/mK was obtained for the pressure range of 101.3 to 2.66 kPa (760 – 20 torr) which Reid et al. (1977) describe as the low pressure region. The conductivity varies approximately 1% per 101.3 kPa (760 torr) in this region. From 2.66 to 0.067 kPa (20 to 0.5 torr), the conductivity varies dramatically with pressure as the mode of heat transfer changes from pure molecular conduction to Knudsen conduction in which the mean free path of the molecules is on the order of the container dimensions. Reid et al. (1977) describe the pressure range from 66.7 to 1.33 Pa (0.5 – 0.010 torr) as the Knudsen region. In this region the conductivity varies with pressure but not as dramatically as the transition region. In the Knudsen region, the flux, q , is linear with the temperature gradient so the heat transfer can be described in terms of a conductivity. Diffusivity measurements in this region however are not accurate because the gas molecules are not in thermal equilibrium with the wire. This results in a temperature discontinuity at the interface between the wire and the sample. The temperature response of the wire under these conditions has a slope that gives an accurate value for the conductivity but the intercept is incorrect which results in an inaccurate diffusivity measurement. Diffusivities were therefore not measured at pressures below 26.6 Pa (0.20 torr). The diffusivi-

Figure 4.2: Temperature versus time response of nitrogen, finite wire solution and experimental data.

ties increase in the pressure range from 101.3 down to 0.133 kPa (760 – 1.0 $torr$) because the conductivity is essentially constant in this region and the heat capacity (ρC_p) decreases linearly with pressure (Tipler, 1976). In the pressure range from 133.3 to 26.6 Pa (1.0 – 0.2 $torr$), the conductivity decreases more rapidly than the heat capacity resulting in a decrease in the diffusivity. The precision of both the conductivity and the diffusivity measurements decreased as pressures approached the Knudsen region. The precision of the conductivity measurement decreased from 1% to approximately 5%. The precision of the diffusivity measurement decreased from 5% to approximately 20%.

Figure 4.3: Thermal conductivity vs pressure for nitrogen at 23°C.

Figure 4.4: Thermal diffusivity vs pressure for nitrogen at 23°C.

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5 MODELING OF TWO-PHASE THERMAL PROPERTIES

5.1 Overview of Two-Phase Measurements and Modeling

The purpose of modeling is to develop a mathematical description which will fit and predict the effective thermal properties (k , ρC_p) of two-phase samples based upon the thermal properties of the phases (*gas*, *solid*) which make up the sample. The model is developed to predict the effective thermal conductivity and diffusivity of the sample as a function of the conductivity and diffusivity of the gas and solid phases at each of the conditions for pressure in which the measurements were made. This can be done formally by developing a set of differential equations, one for each phase, and applying them to the physical situation in which the measurements were actually made. The mathematical formulation which is presented at the beginning of section 2 (equations 2.1–2.10) will not account for these effects because it assumes the medium surrounding the hot wire is a single phase with a single value of conductivity and diffusivity. These effects can only be accounted for with a formulation which recognizes the presence of two distinct phases, each with their own thermal properties. The development of this formulation involves the use of the technique of volume averaging as defined in the following section.

5.2 Development of Volume Averaged Equations

The technique of volume averaging is described by Slattery (1972) and has been used by a number of people in recent years to describe heat and mass transfer in two-phase media (Ryan et al., 1981; Whitaker, 1981; Carbonnel and Whitaker, 1983; Nozad, 1983; Friedman and Ramirez, 1977). In this technique, the dependent variable associated with the physical situation (*temperature in this case*) is averaged over a representative localized volume (*Figure 5.1*). There is a representative localized volume associated with each point in the medium and there are two volume averaged temperatures (*one for each phase*) associated with each point regardless of whether that point is located in the solid phase, gas phase, or on the interface. The volume averaged temperatures are defined as:

$$T_s^v = \frac{1}{V_s} \int_{V_s} T dV \quad (5.1)$$

Figure 5.1: Averaging volume associated with any point r, θ, z in medium.

$$T_g^\nu = \frac{1}{V_g} \int_{V_g} T dV \quad (5.2)$$

The subscripts s and g refer to the solid and gas phases respectively. V_s is the volume of solid phase within the averaging volume and V_g is the volume of the gas phase within the averaging volume such that:

$$V = V_s + V_g \quad (5.3)$$

where V is the total averaging volume. The volume fractions are defined here as:

$$\epsilon_s = V_s/V \quad (5.4)$$

$$\epsilon_g = V_g/V \quad (5.5)$$

The size of the averaging volume V is subject to the restrictions:

1. It must be large enough so that it contains a representative volume of each phase, ie., it cannot contain only solid or gas.
2. It must be small enough so that the dependent variable temperature does not vary significantly over the characteristic length (*diameter*) of the volume.

The solid phase volume average of a gradient is given by Slattery (1972) as:

$$(\nabla T_s)^\nu = \nabla T_s^\nu + \frac{1}{V_s} \int_{A_{s,g}} \mathbf{n}_{s,g} T dA \quad (5.6)$$

The unit normal vector $\mathbf{n}_{s,g}$ is taken as pointing into the solid phase. The integral is over the interfacial area that is contained within the averaging volume. The gas phase volume average of a gradient is defined in a similar manner. The volume average of a divergence is defined in the same manner as the volume average of a gradient. Using these definitions, the volume averaged differential equations can now be developed. Starting with the point temperature conduction equations for each phase, we have:

$$(\rho C_p)_s \frac{\partial T_s}{\partial t} = \nabla(k_s \nabla T_s) \quad (5.7)$$

$$(\rho C_p)_g \frac{\partial T_g}{\partial t} = \nabla(k_g \nabla T_g) \quad (5.8)$$

Assuming the thermal properties for each phase are constant over the averaging volume, we obtain the volume averaged equations for equations 5.7 and 5.8:

$$\epsilon_s(\rho C_p)_s \frac{\partial T_s^\nu}{\partial t} = \epsilon_s k_s \nabla \left(\nabla T_s^\nu + \frac{1}{V_s} \int_{A_{s,g}} \mathbf{n}_{s,g} T dA \right) + \frac{1}{V} \int_{A_{s,g}} \mathbf{n}_{s,g} k_s \nabla T dA \quad (5.9)$$

$$\epsilon_g(\rho C_p)_g \frac{\partial T_g^\nu}{\partial t} = \epsilon_g k_g \nabla \left(\nabla T_g^\nu + \frac{1}{V_g} \int_{A_{s,g}} \mathbf{n}_{g,s} T dA \right) + \frac{1}{V} \int_{A_{s,g}} \mathbf{n}_{g,s} k_g \nabla T dA \quad (5.10)$$

In order to solve these differential equations, the terms containing integrals must be expressed in terms of volume averaged temperatures. The integral terms involving temperature gradients represent the interfacial heat transfer within the averaging volume (Gray, 1975) and can be expressed as:

$$h\mathcal{A} (T_g^\nu - T_s^\nu) \quad (5.11)$$

for the solid phase and:

$$h\mathcal{A} (T_s^\nu - T_g^\nu) \quad (5.12)$$

for the gas phase. $\mathcal{A}$ is the interfacial area per unit volume and h is the heat transfer coefficient. Since the heat transfer coefficient for a gas/solid interface is generally proportional to the conductivity of the gas phase (Bird et al., 1960), h may be expressed as:

$$h = c_h k_g \quad (5.13)$$

where c_h is a constant.

$\mathcal{A}$ can be determined from the density of the solid phase, ρ_s , the bulk density of the powder, ρ_p , and the particle diameter, $d_{particle}$ as follows. The total mass of a powdered sample can be expressed in terms of the bulk density of the powder or the density of the solid phase (*neglecting the mass of the gas phase*) to give the expression:

$$\rho_p v_p = \rho_s v_{particle} n_{particle} \quad (5.14)$$

where v_p is the volume of the powder, $v_{particle}$ is the volume of a single particle, and $n_{particle}$ is the number of particles in v_p . The number of particles per unit volume

of powder is then:

$$\frac{n_{particle}}{v_p} = \frac{6\rho_p}{\rho_s \pi d_{particle}^3} \quad (5.15)$$

The surface area per unit volume of powder is then given as:

$$\mathcal{A} = \frac{\pi d_{particle}^2 n_{particle}}{v_p} = \frac{6\rho_p}{\rho_s d_{particle}} \quad (5.16)$$

The integral terms involving temperature represent the reduction in conduction due to the tortuosity of the phases. Slattery (1972) made the assumption that these terms are zero when the temperature gradient is zero:

$$\Gamma_s = \frac{1}{V_s} \int_{A_{s,g}} \mathbf{n}_{s,g} T dA = 0 \quad \text{when} \quad \nabla T_s^\nu = 0 \quad (5.17)$$

$$\Gamma_g = \frac{1}{V_g} \int_{A_{s,g}} \mathbf{n}_{s,g} T dA = 0 \quad \text{when} \quad \nabla T_g^\nu = 0 \quad (5.18)$$

Using a Taylor's series to expand Γ about $\nabla T^\nu = 0$ and retaining only the linear terms, we have:

$$\Gamma_s = -\tau_s \nabla T_s^\nu \quad (5.19)$$

$$\Gamma_g = -\tau_g \nabla T_g^\nu \quad (5.20)$$

Here τ_s and τ_g are functions of particle diameter and possibly other geometric factors such as the volume fractions. The final form of the volume averaged equations are now:

$$\frac{\partial}{\partial t} T_s^\nu = \phi_s \nabla^2 T_s^\nu + \psi_s [T_g^\nu - T_s^\nu] \quad (5.21)$$

$$\frac{\partial}{\partial t} T_g^\nu = \phi_g \nabla^2 T_g^\nu + \psi_g [T_s^\nu - T_g^\nu] \quad (5.22)$$

where:

$$\phi_s = \frac{k_s(1 - \tau_s)}{(\rho C_p)_s} \quad (5.23)$$

$$\phi_g = \frac{k_g(1 - \tau_g)}{(\rho C_p)_g} \quad (5.24)$$

$$\psi_s = \frac{c_h k_g \mathcal{A}}{\epsilon_s (\rho C_p)_s} \quad (5.25)$$

$$\psi_g = \frac{c_h k_g \mathcal{A}}{\epsilon_g (\rho C_p)_g} \quad (5.26)$$

Applying these equations to the physical situation, conduction in cylindrical coordinates with temperature varying only in the radial direction, we have:

$$\frac{\partial}{\partial t} T_s^\nu = \phi_s \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial}{\partial r} T_s^\nu \right) + \psi_s (T_g^\nu - T_s^\nu) \quad (5.27)$$

$$\frac{\partial}{\partial t} T_g^\nu = \phi_g \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial}{\partial r} T_g^\nu \right) + \psi_g (T_s^\nu - T_g^\nu) \quad (5.28)$$

Analysis of the terms in these equations by order of magnitude scaling (Krantz, 1970) determines which if any of the terms may be set to 0. To scale the equations, the variables are defined as:

$$T_s^\nu = T_\sigma T_s^* \quad (5.29)$$

$$T_g^\nu = T_\sigma T_g^* \quad (5.30)$$

$$r = r_\sigma r^* \quad (5.31)$$

$$t = t_\sigma t^* \quad (5.32)$$

where T_σ , r_σ , t_σ are scale constants and T_s^* , T_g^* , r^* , t^* are dimensionless variables. Substituting these definitions into equations 5.27 and 5.28 gives:

$$\frac{1}{t_\sigma} \frac{\partial}{\partial t^*} T_s^* = \frac{\phi_s}{r_\sigma^2} \frac{1}{r^*} \frac{\partial}{\partial r^*} \left(r^* \frac{\partial}{\partial r^*} T_s^* \right) + \psi_s (T_g^* - T_s^*) \quad (5.33)$$

$$\frac{1}{t_\sigma} \frac{\partial}{\partial t^*} T_g^* = \frac{\phi_g}{r_\sigma^2} \frac{1}{r^*} \frac{\partial}{\partial r^*} \left(r^* \frac{\partial}{\partial r^*} T_g^* \right) + \psi_g (T_s^* - T_g^*) \quad (5.34)$$

Making the conduction term coefficients one yields:

$$\frac{r_\sigma^2}{t_\sigma \phi_s} \frac{\partial}{\partial t^*} T_s^* = \frac{1}{r^*} \frac{\partial}{\partial r^*} \left(r^* \frac{\partial}{\partial r^*} T_s^* \right) + \frac{r_\sigma^2 \psi_s}{\phi_s} (T_g^* - T_s^*) \quad (5.35)$$

$$\frac{r_\sigma^2}{t_\sigma \phi_g} \frac{\partial}{\partial t^*} T_g^* = \frac{1}{r^*} \frac{\partial}{\partial r^*} \left(r^* \frac{\partial}{\partial r^*} T_g^* \right) + \frac{r_\sigma^2 \psi_g}{\phi_g} (T_s^* - T_g^*) \quad (5.36)$$

Since the time of the simulations and the actual experiments was both 1 s:

$$t_\sigma = 1s \quad (5.37)$$

The temperature response of the samples is assumed to be dominated by the solid phase. Therefore the solid phase time derivative coefficient is taken to be 1. Solving for the length scale, r_σ , yields:

$$r_\sigma = \sqrt{\phi_s} \quad (5.38)$$

Substituting values for t_s and r_s into equations 5.35 and 5.36 gives:

$$\frac{\partial}{\partial t^*} T_s^* = \frac{1}{r^*} \frac{\partial}{\partial r^*} \left(r^* \frac{\partial}{\partial r^*} T_s^* \right) + \psi_s (T_g^* - T_s^*) \quad (5.39)$$

$$\frac{\phi_s}{\phi_g} \frac{\partial}{\partial t^*} T_g^* = \frac{1}{r^*} \frac{\partial}{\partial r^*} \left(r^* \frac{\partial}{\partial r^*} T_g^* \right) + \frac{\phi_s \psi_g}{\phi_g} (T_g^* - T_s^*) \quad (5.40)$$

Values of the ratio ϕ_s/ϕ_g are of order 10^{-4} to 10^{-6} indicating that the time constant of the gas phase is much less than that of the solid phase and the measurement itself. Therefore the time derivative of the gas phase can be set to 0. Values of ψ_g are of order 10^3 to 10^6 ; values of ψ_s are of order 1 indicating that the interfacial heat transfer terms cannot be neglected. With these assumptions, equations 5.27 and 5.28 are now:

$$\frac{\partial}{\partial t} T_s^\nu = \phi_s \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial}{\partial r} T_s^\nu \right) + \psi_s (T_g^\nu - T_s^\nu) \quad (5.41)$$

$$0 = \phi_g \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial}{\partial r} T_g^\nu \right) + \psi_g (T_s^\nu - T_g^\nu) \quad (5.42)$$

The initial condition is given as:

$$T_s^\nu = T_g^\nu = 0, \quad r_w \leq r < \infty, \quad t = 0 \quad (5.43)$$

The boundary conditions are given as:

$$T_s^\nu = T_g^\nu = 0, \quad r \rightarrow \infty, \quad t > 0 \quad (5.44)$$

$$T_s^\nu = T_g^\nu = T_w, \quad r = r_w, \quad t > 0 \quad (5.45)$$

$$q = -\mathcal{A}_w k_s \frac{\partial}{\partial r} T_s^\nu - (1 - \mathcal{A}_w) k_g \frac{\partial}{\partial r} T_g^\nu, \quad r = r_w, \quad t > 0 \quad (5.46)$$

where $\mathcal{A}_w$ is the fraction of the surface area of the wire that is in contact with the solid phase. These equations were solved numerically to obtain values of T_s^ν and T_g^ν as functions of time and radius. A linear least squares fit was then done on T_w versus $\ln t$ data to obtain values of the thermal properties as predicted by this model.

5.3 Overview of Numerical Solution

The spacial (*radial*) dependence of temperature was solved using the weighted residuals method of orthogonal collocation (Finlayson, 1972). This method assumes a

solution which is a linear combination of N orthogonal polynomials ($P_0(x), \dots, P_n(x)$). The temperature is determined only at discrete points (*the collocation points*) which correspond to the roots of the highest order polynomial. Since the highest order term in the solution is of order N , the solution can be expressed as:

$$y(x) = \sum_{i=1}^{N+1} d_i x^{i-1} \quad (5.47)$$

The solution along with its first and second derivatives can be evaluated at the collocation points to give:

$$y(x_i) = \sum_{i=1}^{N+1} x_j^{i-1} d_i \quad (5.48)$$

$$\left. \frac{dy}{dx} \right|_{x_j} = \sum_{i=1}^{N+1} \left. \frac{dx^{i-1}}{dx} \right|_{x_j} d_i \quad (5.49)$$

$$\left. \frac{d^2 y}{dx^2} \right|_{x_i} = \sum_{i=1}^{N+1} \left. \frac{d^2 x^{i-1}}{dx^2} \right|_{x_j} d_i \quad (5.50)$$

These expressions can be written in matrix form to give:

$$\mathbf{y} = \mathbf{Qd} \quad (5.51)$$

$$\mathbf{y}' = \mathbf{Cd} \quad (5.52)$$

$$\mathbf{y}'' = \mathbf{Dd} \quad (5.53)$$

where:

$$Q_{ji} = x_j^{i-1} \quad (5.54)$$

$$C_{ji} = (i-1)x_j^{i-2} \quad (5.55)$$

$$D_{ji} = (i-1)(i-2)x_j^{i-3} \quad (5.56)$$

Solving for $\mathbf{d}$, the first and second derivatives can be written as:

$$\mathbf{y}' = \mathbf{CQ}^{-1}\mathbf{y} = \mathbf{Ay} \quad (5.57)$$

$$\mathbf{y}'' = \mathbf{DQ}^{-1}\mathbf{y} = \mathbf{By} \quad (5.58)$$

These expressions are then substituted for the spacial derivatives in the partial differential equation(s). This step converts the partial differential equation to N coupled ordinary differential equations. The time dependence of temperature is then solved numerically using a variable step size predictor/corrector Gear algorithm (IMSL Library Reference Manual, 1982).

5.4 Single Phase Simulation Using Orthogonal Collocation

Orthogonal collocation was first used to solve the case for single phase samples because the solution could be compared to the analytical solution. This simulation describes a cylindrical medium heated radially by a wire placed at the axial center of the medium. The solution is derived by starting with the conduction equation in cylindrical coordinates with temperature varying in time and in the radial direction only.

$$\frac{\partial T}{\partial t} = \alpha \left(\frac{1}{r} \frac{\partial T}{\partial r} + \frac{\partial^2 T}{\partial r^2} \right) \quad (5.59)$$

The initial and boundary conditions are given as:

$$T = 0, \quad t = 0, \quad r_w \leq r \leq r_o \quad (5.60)$$

$$T = 0, \quad r = r_o, \quad t > 0 \quad (5.61)$$

$$q = -k \frac{\partial T}{\partial r}, \quad r = r_w, \quad t > 0 \quad (5.62)$$

To use orthogonal collocation, the independent variable r must vary from 0 to 1. Therefore a dimensionless r' was defined as:

$$r' = \frac{r - r_w}{r_o - r_w} = \frac{r - r_w}{\delta r} \quad (5.63)$$

Substituting into equations 4.59-4.62 yields:

$$\frac{\partial T}{\partial t} = \alpha \left(\frac{1}{(r' \delta r + r_o) \delta r} \frac{\partial T}{\partial r'} + \frac{1}{\delta r^2} \frac{\partial^2 T}{\partial r'^2} \right) \quad (5.64)$$

$$T = 0, \quad t = 0, \quad 0 \leq r' \leq 1 \quad (5.65)$$

$$T = 0, \quad r' = 1, \quad t > 0 \quad (5.66)$$

$$q = -\frac{k}{\delta r} \frac{\partial T}{\partial r'}, \quad r' = 0, \quad t > 0 \quad (5.67)$$

Applying orthogonal collocation, the equations become:

$$\frac{dT_i}{dt} = \alpha \left(\frac{1}{(r'_i \delta r + r_o) \delta r} \sum_{j=1}^{N+2} A_{ij} T_j + \delta r^2 \sum_{j=1}^{N+2} B_{ij} T_j \right) \quad i = 2, \dots, N+1 \quad (5.68)$$

Table 5.1: Comparison of numerical and analytical solutions for single phase sample.

	Analytical Solution	Numerical solution
Slope	0.161	0.465
Intercept	0.294	0.295
Conductivity	0.300	0.299
Diffusivity	1.00×10^{-7}	1.00×10^{-7}

$$T_i(0) = 0 \quad i = 2, \dots, N + 1 \quad (5.69)$$

$$T_{N+2} = 0 \quad (5.70)$$

$$q = -\frac{k}{\delta r} \sum_{j=1}^{N+2} A_{1j} T_j \quad (5.71)$$

The simulation was done using a conductivity and diffusivity that correspond to those of glycerin. The results are presented in Table 5.1.

A plot of δT of the wire versus $\ln t$ for both the analytical and numerical solutions is presented in Figure 5.2. These results show excellent agreement between the analytical and numerical solutions. The accuracy of the numerical simulation depends somewhat on the position of the outside collocation point, r_0 . The best results were obtained when r_0 was positioned such that the temperature wave would approach but not reach r_0 . For best results, r_0/r_w ranged in value from 10 to 50.

5.5 Two Phase Simulation Using Orthogonal Collocation

Orthogonal collocation was applied to the two-phase problem (*equations 5.41 through 5.46 to give*):

$$\begin{aligned} \frac{dT_{s,i}^\nu}{dt} &= \frac{\phi_s}{(r_i' \delta r + r_o) \delta r} \sum_{j=1}^{N+2} A_{ij} T_{s,j}^\nu + \frac{\phi_s}{\delta r^2} \sum_{j=1}^{N+2} B_{ij} T_{s,j}^\nu + \\ &\quad \psi_s (T_{g,i}^\nu - T_{s,i}^\nu) \quad i = 2, \dots, N + 1 \end{aligned} \quad (5.72)$$

$$\begin{aligned} \frac{dT_{g,i}^\nu}{dt} &= \frac{\phi_g}{(r_i' \delta r + r_o) \delta r} \sum_{j=1}^{N+2} A_{ij} T_{g,j}^\nu + \frac{\phi_g}{\delta r^2} \sum_{j=1}^{N+2} B_{ij} T_{g,j}^\nu + \\ &\quad \psi_g (T_{s,i}^\nu - T_{g,i}^\nu) \quad i = 2, \dots, N + 1 \end{aligned} \quad (5.73)$$

Figure 5.2: Temperature vs time response, analytical and numerical solution for a single phase sample.

The initial and boundary conditions are given by:

$$T_{s,i}^{\nu}(0) = T_{g,i}^{\nu}(0) = 0 \quad i = 2, \dots, N + 1 \quad (5.74)$$

$$T_{s,N+2}^{\nu} = T_{g,N+2}^{\nu} = 0 \quad (5.75)$$

$$q = -A_w \frac{k_s}{\delta r} \sum_{j=1}^{N+2} A_{1j} T_{s,j}^{\nu} - (1 - A_w) \frac{k_g}{\delta r} \sum_{j=1}^{N+2} A_{1j} T_{g,j}^{\nu} \quad (5.76)$$

These equations form a set of coupled ordinary differential equations. The time dependence of temperature was solved using the Gear algorithm.

5.6 Modeling Results of Two-Phase Sample Measurements

Thermal property measurements for 50 μ glass beads were modeled as a function of pressure from 101.3 *kPa* (760 *torr*) down to 2.66 *Pa* (0.020 *torr*). Measurements were made on this sample because of its uniform particle size and shape and because it is chemically and physically inert under the conditions in which the properties were measured. Thermal property measurements for three powdered samples of spent oil shales with different mean particle diameters were also modeled along with thermal property measurements of two samples of powdered coal. One coal sample retained its natural moisture content while the other was dried at 373 *K* (100 $^{\circ}\text{C}$).

In order to model glass bead data, values for the thermal properties of glass were obtained from the literature (Weast, 1977). Values for the thermal properties of nitrogen as a function of pressure were obtained from measurements made with this instrument. Values for the thermal properties of the coal phase were obtained from measurements which were made on wet and dry solid coal samples. Thermal property measurements were not made on solid char samples so the powdered char samples were not modeled. Values for thermal properties of the shale phase were obtained from the literature (Tihen et al., 1968). Thermal properties of the solid phases along with their volume fractions and interfacial area per unit volume are listed in Table 5.2. The thermal properties of the shale samples were the same but the volume fractions and interfacial areas did vary as a function of particle size. The thermal properties, volume fractions, and interfacial areas varied for the coal samples because of the difference in moisture content of the samples.

For each sample, simulations were run using the thermal properties of the appropriate solid phase and those of nitrogen at the pressures where measurements

Table 5.2: Thermal properties, volume fractions, and interfacial area for two-phase samples.

	k_s (W/mK)	$(\rho C_p)_s$ (J/m ³ K)	ϵ_s	$\mathcal{A}$ (m ⁻¹)
Glass Beads, 50 μ	0.96	1.6×10^6	0.60	7.2×10^4
Shale, 125–150 μ	0.50	1.7×10^6	0.44	2.0×10^4
Shale, 150–495 μ	0.50	1.7×10^6	0.39	7.8×10^3
Shale, 495–991 μ	0.50	1.7×10^6	0.38	3.3×10^3
Coal (wet), 50 μ	0.40	2.0×10^6	0.54	6.5×10^4
Coal (dry), 50 μ	0.10	5.0×10^5	0.61	7.3×10^4

were made. Values for the four parameters ($1 - \tau_s, 1 - \tau_g, c_h, \mathcal{A}_w$) were determined in order to minimize the sum of the squares of the errors between the measured and predicted values of the thermal properties at the various pressures. A trial and error search was performed first to obtain approximate values of the parameters that give the best fit for each sample. The search indicated that only a narrow range of values of the parameters produced results that were close to the experimental data. A systematic search for the parameter values was then performed using the Levenberg–Marquardt algorithm (IMSL Library Reference Manual, 1982). For each sample, several sets of initial guesses of the parameters were used including the values obtained from the trial and error search. In all cases, the values which minimized the sum of the squares of the errors were very close to those obtained from the trial and error search.

Himmelblau (1970) presents an analysis by which confidence intervals of the parameters can be estimated from the Jacobian matrix of the Marquardt algorithm. The confidence interval (95%) for the i^{th} parameter, p_i , is given by:

$$C.I. = p_i \pm t_{.975} \sqrt{\frac{s_e C_{ii}}{\eta}} \quad (5.77)$$

where $t_{.975}$ is the t -distribution factor, s_e is the sum of the squares of the errors, and η is the number of degrees of freedom. The matrix $\mathbf{C}$ is defined by:

$$\mathbf{C} = (\mathbf{J}^T \mathbf{J})^{-1} \quad (5.78)$$

where $\mathbf{J}$ is the Jacobian matrix of the Marquardt algorithm.

Table 5.3: Modeling parameter $1 - \tau_s$ for each of the powdered samples.

	$1 - \tau_s$
Glass Beads 50 μ	$8.00 \times 10^{-5} \pm 2.8 \times 10^{-6}$ ($\pm 3.5\%$)
Shale 125-150 μ	$1.00 \times 10^{-4} \pm 6.6 \times 10^{-7}$ ($+ 0.7\%$)
Shale 150-495 μ	$1.00 \times 10^{-4} \pm 8.9 \times 10^{-7}$ ($\pm 0.9\%$)
Shale 495-991 μ	$9.00 \times 10^{-5} \pm 3.9 \times 10^{-7}$ ($\pm 0.4\%$)
Coal (wet) 50 μ	$2.00 \times 10^{-4} \pm 9.4 \times 10^{-8}$ ($\pm 0.1\%$)
Coal (dry) 50 μ	$2.00 \times 10^{-4} \pm 1.1 \times 10^{-6}$ ($\pm 0.6\%$)

Table 5.4: Modeling parameter $1 - \tau_g$ for each of the powdered samples.

	$1 - \tau_g$
Glass Beads 50 μ	$3.00 \times 10^{-2} \pm 4.8 \times 10^{-3}$ ($\pm 16\%$)
Shale 125-150 μ	$9.00 \times 10^{-2} \pm 1.9 \times 10^{-3}$ ($\pm 2.1\%$)
Shale 150-495 μ	$2.63 \times 10^{-2} \pm 9.2 \times 10^{-5}$ ($\pm 0.4\%$)
Shale 495-991 μ	$1.10 \times 10^{-2} \pm 3.6 \times 10^{-5}$ ($\pm 0.4\%$)
Coal (wet) 50 μ	$9.00 \times 10^{-2} \pm 4.1 \times 10^{-3}$ ($\pm 4.6\%$)
Coal (dry) 50 μ	$5.00 \times 10^{-2} \pm 7.3 \times 10^{-3}$ ($\pm 15\%$)

Values for the four parameters for each sample along with the appropriate confidence intervals are given in Tables 5.3, 5.4, and 5.5. Values for the tortuosities ($1 - \tau_s, 1 - \tau_g$) may vary from 0 to 1. A value of 1 indicates that there is no reduction in conductivity in that phase due to tortuosity. A value of 0 indicates that the tortuosity has completely eliminated conduction in that phase. Values for the tortuosities of the solid phases ($1 - \tau_s$) are very small indicating that conduction through the solid phases is greatly reduced by the tortuosity of the sample. This is due to the fact that the contact area between particles in the sample is very small. The fraction of the surface area of the wire that is contacted by the solid phase is also very small as indicated by the small values for $\mathcal{A}_w$. Values for the gas phase tortuosities ($1 - \tau_g$) are not as small as those of the solid phases which indicates that the gas phase has a greater degree of continuity in the sample.

Table 5.5: Modeling parameters $\mathcal{A}_w$ and c_h for each of the powdered samples.

	$\mathcal{A}_w$	c_h (m^{-1})
Glass Beads 50 μ	$2.00 \times 10^{-4} \pm 9.1 \times 10^{-6}$ ($\pm 4.6\%$)	1500 ± 330 ($\pm 22\%$)
Shale 125–150 μ	$4.00 \times 10^{-4} \pm 8.2 \times 10^{-5}$ ($\pm 21\%$)	2500 ± 58 ($\pm 2.3\%$)
Shale 150–495 μ	$4.80 \times 10^{-4} \pm 1.5 \times 10^{-8}$ ($\pm 0.1\%$)	1520 ± 1.0 ($\pm 0.1\%$)
Shale 495–991 μ	$5.00 \times 10^{-4} \pm 4.1 \times 10^{-6}$ ($\pm 1.0\%$)	1500 ± 1.0 ($\pm 0.1\%$)
Coal (wet) 50 μ	$4.00 \times 10^{-4} \pm 1.9 \times 10^{-4}$ ($\pm 47\%$)	900 ± 16 ($\pm 2.6\%$)
Coal (dry) 50 μ	$6.00 \times 10^{-3} \pm 1.2 \times 10^{-3}$ ($\pm 20\%$)	250 ± 39 ($\pm 16\%$)

Confidence intervals for $1 - \tau_s$ were 3% or less of the parameter value indicating that only a narrow range of values produced results that agree with experimental data. Confidence intervals for $1 - \tau_g$, $\mathcal{A}_w$, and c_h all ranged from 0.1 to 47% of the respective parameter value indicating that changes in these parameters had less effect on the simulation results than changes in $1 - \tau_s$.

Values of the coefficients of the scaled equations for glass beads as a function of pressure are given in Table 5.6. Values for ψ_s and $\frac{\phi_s \psi_s}{\phi_g}$ are roughly order 1 indicating that the interfacial heat transfer terms should have been retained. This also indicates that conduction and interfacial heat transfer both contribute to the overall heat transfer mechanism. Values for $\frac{\phi_s}{\phi_g}$ are of order 10^{-4} to 10^{-6} indicating that the time derivative of the gas phase can be neglected as it was.

5.7 Summary of Results

Figures 5.3 and 5.4 give the experimental and modeling results for the conductivity and diffusivity of glass beads. Experimental values for the properties were accurately modeled over a range of 3 to 4 orders of magnitude for this sample. The parameters $1 - \tau_s$ and $\mathcal{A}_w$ were smaller for this sample than those of the other samples. This is most likely due to the uniform particle size and spherical shape which makes the particle to particle contact area and the particle to wire contact area very small.

Figures 5.5 and 5.6 give the experimental and modeling results for the thermal properties of oil shale samples of three different particle sizes. Conductivities for the three samples show similar trends as a function of pressure. It is interesting to

Figure 5.3: Thermal conductivity vs pressure for 50 μ glass beads.

Figure 5.4: Thermal diffusivity vs pressure for 50 μ glass beads.

Figure 5.5: Thermal conductivity vs pressure for oil shale powders at 296 K; points—experimental data, lines—modeled predictions.

Figure 5.6: Thermal diffusivity vs pressure for oil shale powders at 296 K; points—experimental data, lines—modeled predictions.

Table 5.6: Volume averaged coefficients for glass beads.

Pressure (torr)	$\frac{\phi_s}{\phi_g}$	ψ_s	$\frac{\phi_s \psi_g}{\phi_g}$
620	3.1×10^{-5}	5.1	0.43
100	5.3×10^{-6}	4.5	0.43
20	1.8×10^{-6}	3.1	0.43
2.0	1.1×10^{-6}	0.53	0.43
0.8	1.3×10^{-6}	0.18	0.43
0.2	1.3×10^{-6}	0.045	0.43
0.1	1.2×10^{-6}	0.025	0.43
0.02	3.7×10^{-7}	0.02	0.43

note that the diffusivity as a function of pressure behaves differently for the various particle sizes. The solid phase thermal properties for these samples are the same but the volume fraction and particle diameter vary. The particle diameter, $d_{particle}$, and volume fraction, ϵ_s , determine the interfacial area, $\mathcal{A}$. These parameters also affect the gas phase tortuosity, $(1 - \tau_g)$ and the heat transfer constant, c_h . Bird (1960) reported that the heat transfer coefficient for a particle in the absence of free convection decreases with increasing particle size. The heat transfer constants, c_h , for the three shale samples follow this trend.

Figures 5.7 and 5.8 give the experimental and modeling results for the thermal properties of wet and dry coal. The chemical nature of the lignite coal samples varies greatly from those of the shale and glass bead samples. These samples have a high carbon content while the shale and glass bead samples have no carbon content at all. The carbon on the surface of the coal particles adsorbs nitrogen gas resulting in a decrease in the heat transfer coefficient. The dry sample has a higher percentage of carbon which results in an even lower value for c_h . The dry coal has a higher solid phase volume fraction, ϵ_s , which indicates that this sample was more densely compacted when it was loaded into the container. This higher degree of compaction resulted in a higher value of $\mathcal{A}_w$.

Some of the powdered samples exhibited an increase in diffusivity when the pressure decreased from 101.3 kPa (760 torr) down to 1.33 kPa (10 torr). This trend is similar to the increase in diffusivity for pure nitrogen in the same pressure range (Figure 2.9) and indicates that the gas phase dominates heat transfer to a

Figure 5.7: Thermal conductivity vs pressure at 296 K for wet and dry coals; points—experimental data, lines—modeled predictions.

Figure 5.8: Thermal diffusivity vs pressure at 296 *K* for wet and dry coals; points—experimental data, lines—modeled predictions.

Table 5.7: Volume averaged coefficients for powdered samples.

Sample	$\frac{\phi_s}{\phi_g}$	ψ_s (101.3–1.33 <i>kPa</i>)	$\frac{\phi_s \psi_s}{\phi_g}$
Glass Beads, 50 μ	10^{-5} - 10^{-7}	4.5 - 0.53	0.43
Shale, 125-150 μ	10^{-5} - 10^{-7}	1.6 - 0.7	0.030
Wet Coal, 50 μ	10^{-5} - 10^{-7}	1.5 - 1.0	0.057
Shale*, 150-495 μ	10^{-5} - 10^{-6}	0.41 - 0.15	0.021
Shale*, 495-991 μ	10^{-5} - 10^{-6}	0.14 - 0.11	0.019
Dry Coal*, 50 μ	10^{-5} - 10^{-6}	0.63 - 0.30	0.018

greater extent in these samples than the other samples. Table 5.7 lists values of the dimensionless coefficients for the scaled equations for all the powdered samples. Samples with an asterisk exhibited an increase in diffusivity as the pressure was lowered from 101.3 down to 1.33 *kPa* (760 – 10 *torr*). These samples have lower values for the coefficients ψ_s and $\frac{\phi_s \psi_s}{\phi_g}$ which indicates that interfacial heat transfer is less important in these samples. The small values for $\mathcal{A}_w$ indicate that the most of the thermal energy that is generated in the wire initially flows into the gas phase. If interfacial heat transfer does not dominate the overall heat transfer mechanism, the diffusivity will be biased towards that of the gas phase. In samples where interfacial heat transfer is important, thermal energy is transferred from the gas phase to the solid phase and the resulting diffusivity is biased towards the solid phase. In general, the model very accurately described thermal conductivity and thermal diffusivity measurements which varied over several orders of magnitude as a function of the gas phase pressure.

Nomenclature for Sections 1-5

a slope of linear least squares regression ($^{\circ}C$)

A collocation matrix $(N + 2) \times (N + 2)$

A interfacial area per unit volume of two-phase sample (m^{-1})

A_w solid phase fractional contact area to wire (*dimensionless*)

A_{sg} interfacial area within averaging volume (m^2)

b intercept of linear least squares regression ($^{\circ}C$)

B collocation matrix $(N + 2) \times (N + 2)$

$C \exp y$

c_h heat transfer constant (m^{-1})

C_p single phase sample heat capacity (J/kgK)

$(\rho C_p)_s$ solid phase heat capacity (J/m^3K)

$(\rho C_p)_g$ gas phase heat capacity (J/m^3K)

$(\rho C_p)_w$ wire heat capacity (J/m^3K)

h heat transfer coefficient (W/m^2K)

k single phase sample conductivity (W/mK)

k_s solid phase conductivity (W/mK)

k_g gas phase conductivity (W/mK)

k_w wire conductivity (W/mK)

n_{sg} unit normal vector pointing into solid phase

n_{gs} unit normal vector pointing into gas phase

q power input (W/m)

r radial distance (m)
 r_w radius of wire (m)
 r_o radius of exterior collocation point (m)
 r' normalized radius ($\frac{r-r_w}{r_o-r_w}$)
 δr $r_o - r_w$ (m)
 r'_i i^{th} collocation point
 t time (s)
 T single phase temperature ($^{\circ}C$)
 $T_{initial}$ initial single phase sample temperature ($^{\circ}C$)
 ΔT single phase sample temperature rise, $T - T_{initial}$, ($^{\circ}C$)
 T_s solid phase temperature ($^{\circ}C$)
 T_g gas phase temperature ($^{\circ}C$)
 T_i temperature at the i^{th} collocation point ($^{\circ}C$)
 T_s^{ν} solid phase volume averaged temperature ($^{\circ}C$)
 T_g^{ν} gas phase volume averaged temperature ($^{\circ}C$)
 V total averaging volume (m^3)
 V_s volume of solid phase within averaging volume (m^3)
 V_g volume of gas phase within averaging volume (m^3)
 y Euler's constant (.5772)

Greek symbols

α single phase sample diffusivity (m^2/s)

α_w wire diffusivity (m^2/s)

Γ_s solid phase tortuosity integral ($^{\circ}C/m$)

Γ_g gas phase tortuosity integral ($^{\circ}C/m$)

ϵ_s solid phase volume fraction (*dimensionless*)

ϵ_g gas phase volume fraction (*dimensionless*)

π 3.14159...

ρ single phase density (kg/m^3)

τ_s solid phase tortuosity factor (*dimensionless*)

τ_g gas phase tortuosity factor (*dimensionless*)

ϕ_s solid phase parameter, $\frac{k_s(1-\tau_s)}{(\rho C_p)_s}$, (m^2/s)

ϕ_g gas phase parameter, $\frac{k_g(1-\tau_g)}{(\rho C_p)_g}$, (m^2/s)

ψ_s solid phase parameter, $\frac{hA}{\epsilon_s(\rho C_p)_s}$, (s^{-1})

ψ_g gas phase parameter, $\frac{hA}{\epsilon_g(\rho C_p)_g}$, (s^{-1})

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6 VELOCITY AND TEMPERATURE EFFECTS ON LIQUID PHASE DISPERSION IN POROUS MEDIA

6.1 Introduction

The purpose of this study is to determine the dispersion coefficient of water through three types of low-rank coals. These coals are Usibelli (Alaska), South Hallsville (Texas), and Indian Head (North Dakota). The dispersion coefficient was measured as a function of fluid temperature and velocity through unconsolidated samples. The objective of these studies is to improve our knowledge of the transport of liquids through porous media such as coal powders.

6.2 Effective Axial Dispersion Coefficient Model

Friedman and Ramirez¹ proposed the following model for the effective dispersion coefficient (D_z) in porous media as a function of superficial velocity (v), molecular diffusion coefficient (D_{AB}), and mass tortuosity (τ_m).

$$D_z = D_{AB}(1 + \tau_m) + av^\alpha \quad (6.1)$$

where a and α are experimentally determined parameters. Most of the models presented in the literature dwell on the effects of flow rate,²⁻⁵ but there is little or no mention of the effects of temperature. Various papers^{3,6,7} have shown that the value of α may range between 1.0 and 2.0. For unconsolidated packed beds, Perkins³ states that the value of α most reported in the literature is 1.2. This is the value used in this work. The mass tortuosity is a measure of the fact that mass diffusion does not occur in straight tubes, but through a tortuous path in porous media. Friedman and Ramirez¹ indicate that τ_m is primarily a function of the geometry of the porous media. Thus, in an unconsolidated core, it is a measure of the tortuous path due to the packing of different size and shaped particles that make up the core. In this work, we have assumed that the particle sizes are uniformly distributed around the mean particle size. Therefore, for a particular grind of coal, the mass tortuosity is constant throughout a core.

Aris² derived the following model for the effective axial dispersion coefficient in

an open tube of arbitrary cross section.

$$D_z = D_{AB} + \frac{\kappa S}{D_{AB}} v^\alpha \quad (6.2)$$

where α is shown to be 2; κ is a number dependent on the geometry of the cross-section, the variations of the velocity around its mean and the variation of the molecular diffusion coefficient around its mean; and S is a dimensionless constant characteristic of the cross-section.

Assuming that we can extend equation 6.2 to porous media, we can combine it with equation 6.1 to obtain:

$$D_z = D_{AB}(1 + \tau_m) + \frac{E}{D_{AB}} v^\alpha \quad (6.3)$$

where E is a constant that combines κ , a , and S .

Wilke and Chang⁸ propose the following correlation for the molecular diffusion coefficient at low concentrations:

$$D_{AB} = 7.4 \times 10^{-8} \frac{(\psi_B M_B)^{1/2} T}{\mu (\bar{V}_A)^{0.6}} \quad (6.4)$$

where $\bar{V}_A$ is the molar volume of the solute A in cm³/gmole as liquid at its normal boiling point (18.9 for water), μ is the viscosity of the solution in centipoise, ψ_B is an association parameter for the solvent B (2.6 for water), T is absolute temperature in K and M_B is the molecular weight of the solvent.

For a given solvent-solute system, equation 6.4 can be written as:

$$D_{AB} = \text{constant} \left(\frac{T}{\mu} \right) \quad (6.5)$$

Substituting equation 6.5 into equation 6.3 and collecting terms into constants (A and B) that are to be determined experimentally, we obtain:

$$D_z = A(1 + \tau_m) \left(\frac{T}{\mu} \right) + B \left(\frac{\mu}{T} \right) v^\alpha \quad (6.6)$$

$$A = 7.4 \times 10^{-8} \frac{(\psi_B M_B)^{1/2}}{(\bar{V}_A)^{0.6}} \quad (6.7)$$

$$B = \frac{\kappa a S (\bar{V}_A)^{0.6}}{7.4 \times 10^{-8} (\psi_B M_B)^{1/2}} \quad (6.8)$$

In order to determine the coefficients of equation 6.6 from the experimental data, we can rearrange the equation to the following form:

$$\frac{D_x \mu}{T} = A(1 + \tau_m) + B \left(\frac{\mu}{T} \right)^2 v^\alpha \quad (6.9)$$

This equation suggests that if we plot $D_x \mu / T$ versus $(\frac{\mu}{T})^2 v^\alpha$, we should obtain a straight line of slope B and intercept $A(1 + \tau_m)$.

6.3 Experimental Work

6.3.1 Coal Description: We chose three unconsolidated lignite coals for this work: South Hallsville from Texas, Usibelli from Alaska, and Indian Head from North Dakota. The coal properties are presented in Table 6.1. Sieve analyses were performed using standard ASTM sieves ranging from 110 mm down to a fines pan. The particle diameter in Table 6.1 is a mass mean diameter as defined by McCabe and Smith.⁹ The Indian Head coal eluted significant amounts of water soluble material during the experiments as evidenced by extreme discoloration of the waste water. The effluent from the South Hallsville and Usibelli coals showed little discoloration, indicating that very little water soluble material was present.

6.3.2 Experimental Apparatus and Procedure: The experimental apparatus is illustrated in Figure 6.1. The core holder was 27.0 cm in length and 2.54 cm inside diameter. Water was added to the powdered coal until the coal was moist before the core was packed. Small amounts of this mixture were placed in the core holder and tamped down using a packing rod to ensure uniform packing. This was repeated until the core holder was almost full. The core cap was then screwed down tight against the top of the core. The average core length was 26 cm. Small diameter tubing (0.28 mm id.) was used from the pulse injection valve to the bottom of the core and from the top of the core to the fraction collector to ensure minimum dead volume (0.3 cm³ total).

Once the core was installed in the heated environmental chamber, distilled and deionized water was pumped through the core for 24 hours at the lowest flow rate (0.2 ml/min; approx. 3.5 pore volumes) to allow the system to achieve equilibrium temperature, wash out as much water soluble material as possible and make sure the coal was completely saturated. The tracer (10 μ l of 0.25 mCi/g tritiated water)

Figure 6.1: Experimental apparatus for liquid-phase dispersion measurements.

was then placed in the injection valve. The injection valve was activated by a pneumatic switch.

We ran experiments on each coal at 3 temperatures (23°C, 43°C, and 61°C) and 4 flow rates (0.2, 0.4, 0.6 and 0.8 ml/min) for each temperature. A new core was used for each temperature setting (i.e. 4 experiments per core).

The samples from the fraction collector were mixed with liquid scintillation fluor (Aquassure) and analyzed using a Beckman LS 8000 liquid scintillation counter (Analyzer Settings: Preset Error=1.0 Maximum Count Time=20 min). Using the calibration curve for the instrument, the concentration of tritiated water for each sample was determined, and a plot of tracer concentration versus time was generated. A typical concentration versus time curve is shown in Figure 6.2.

6.3.3 Experimental Data Analysis: The effective axial dispersion coefficient is calculated from the concentration versus time curve. The standard techniques used for this purpose are the method of moments or weighted moments.¹⁰ The drawback to these methods is that the porosity of the core is required *a-priori*. Initially, we ran several tracer pulses through each core turning the pump off between experiments. Our data indicated that the experimental cores had a fluctuating porosity due to the reordering of the coal particles when system flow pressure was relieved. While we were able to virtually eliminate the problem by running the pump continuously, the porosity can also shift over a period of time if the coal contains significant quantities of water soluble material. Thus, the assumption of constant porosity may not be valid. We have developed a technique for calculating the effective axial dispersion coefficient and porosity simultaneously for unconsolidated porous media from pulse response curves.

Simple diffusion models predict symmetrical response curves whereas capacitance models are characterized by significant tailing of the response curve.¹¹ A typical impulse response curve from our experiments is presented in Figure 6.2. Based on results such as this, we used the noncapacitance model derived by Carberry and Bretton:¹²

$$C(t) = \frac{Q}{2A_c\phi\sqrt{\pi D_x t}} e^{-\frac{(X-\phi t)^2}{4D_x t}} \quad (6.10)$$

where C is the tracer concentration as a function of time (t) at the end of the core, X is the core length, Q is the quantity of tracer injected and ϕ is the core porosity (void fraction). We assume that if there is a change in the porosity, it is sufficiently slow that it remains essentially constant over the time period of a single experiment.

Each response curve and equation 6.10 were used in conjunction with a nonlinear

Figure 6.2: Impulse tracer response curve—South Hallsville, Temp = 43°C; Flow=0.2 ml/min.

parameter estimation routine to obtain both the porosity and axial dispersion coefficient. The parameter estimation algorithm used was first presented by Marquardt.¹³ The estimator calculates the "best" model coefficients, in this instance ϕ and D_x , based on minimizing the sum of the squares of the differences between the model estimates and the experimental data:

$$\Phi = \min |\hat{Y} - Y|^2 \quad (6.11)$$

where $\hat{Y}$ is the experimental data vector of tracer concentration taken at discrete times and Y is the corresponding vector of tracer concentrations predicted by the model at the same sampling instants. The particular implementation of Marquardt's algorithm used for this work is due to Kuester and Mize.¹⁴ The code was written in single precision FORTRAN 77 and run on an IBM PC-XT.

Table 6.2 presents a series of comparisons of this method, the method of moments, and the method of weighted moments. Case 1 consists of a set of noise-free data (30 data points) using the exact solution (equation 6.10). All of the methods approximated the exact solution fairly well. In Case 2, uniformly distributed random noise was added to the data from Case 1. The maximum noise added to any data point was seven percent of the maximum concentration on the response curve. The Marquardt algorithm handled the noisy data the best of the three methods.

Cases 3-6 use concentration data taken during our experiments. Case 3 is illustrated in Figure 6.3 where the points are the experimental data, and the lines are those calculated using equation 6.10 and the axial dispersion coefficients predicted from the data by the various methods. The data is quite noisy, but appears to be symmetrical as in Case 2. It is not obvious which of the methods gives the "best" answer although from a statistical point of view, the answers are essentially equal.

Case 4 graphically illustrates the differences in the techniques and is shown in Figure 6.4. This example shows some tailing of the tracer concentration. It is obvious that both the method of moments and weighted moments put more weight on the tail end of the data than the Marquardt algorithm. Since the Marquardt technique minimizes the sum of the squares, the most improvement in the objective function (equation 6.11) is achieved by minimizing the error at the peak of the curve. The method of moments, on the other hand, emphasizes the tail of the concentration curve where the experimental data has a tendency to be in the most error. Most of the criticism of the method of moments centers around this emphasis, and methods such as weighted moments¹⁰ or optimal data truncation¹⁵ have been proposed to remedy the drawback. This improvement can be seen in the Figure

Figure 6.3: Impulse tracer response curves—Indian Head, Temp = 21°C; Flow = 0.4 ml/min.

6.4, where the effective dispersion coefficient calculated by weighted moments is between the values calculated by moments and the current algorithm.

Cases 5 and 6 are situations where the Marquardt estimator calculated values between those of moments or weighted moments. The purpose of these cases is to illustrate that none of the methods predict values that are always higher or lower than the others.

Based on these results, we conclude that our Marquardt method is a valid and accurate technique for the determination of the effective axial dispersion coefficient from pulse tracer data in unconsolidated porous media. It should be emphasized that we have assumed a noncapacitive model and that use of this technique on data that has significant capacitance effects will result in errors. This technique is also very useful in cases where there is a slow change in porosity due to leaching of water soluble material.

6.4 Results and Discussion of Results

The results from our experiments are presented in Table 6.3. Figures 6.5–6.7 are the effective axial dispersion coefficient data plotted in the form of equation 6.9. The solid line in each of the figures is a plot of the least squares fit of the experimental data. It is apparent that while there is scatter in the data (particularly for the Indian Head experiments) there is a linear relationship. This is also demonstrated by the correlation coefficients (R^2 in Table 6.3) obtained from the least squares regression for each coal. While this does not prove that our model is the correct one, it does demonstrate that there is a strong correlation between the model and the experimental data. Based on these results, we conclude that the model should be a good representation of the physical system.

The coefficients A, B, and τ_m are obtained from a least squares regression of the experimental data. In order to obtain A we need the molecular diffusion coefficient of tritiated water in distilled water. Equation 6.4 was used to estimate this value ($D_{AB} = 2.6 \times 10^{-5}$ at 21°C). Once the value of A is calculated, it is a constant for the water-tritiated water system used. This is shown in Table 6.3. The intercept of the least squares line is then used to calculate τ_m and the slope of the line is the value B. The least squares fit is shown as a line in Figures 6.5–6.7.

Figures 6.8–6.10 are plots of the effective axial dispersion coefficient versus superficial velocity for the three isotherms studied. The points represent experimental data and the lines represent the values predicted by our model (equation 6.6) using

Figure 6.4: Impulse tracer response curves—South Hallsville, Temp = 65°C; Flow = 0.6 ml/min.

Figure 6.5: Correlation plot-South Hallsville.

Figure 6.6: Correlation plot—Usibelli.

Figure 6.7: Correlation plot-Indian Head.

A, B, and τ_m for the particular coal. For the South Hallsville coal (Figure 6.8), the model fits extremely well, while there is appreciable scatter in the data for the Indian Head coal (Figure 6.10). The variability in the data for the Usibelli and Indian Head coals may be attributed to experimental error, the use of a new core at each temperature, and the fact that powdered coal presents some problems with experimental consistency due to water soluble material and variability in particle sizes. It is interesting to look at the extremes of superficial velocity and temperature in order to check the validity of the model. First, note in Figures 6.8–6.10 that as the velocity approaches zero, the isotherms cross. At zero flow, molecular diffusion becomes dominant, and we only need to look at the temperature effects on the diffusion process. The crossing is consistent with what we know about the molecular diffusion coefficient as a function of temperature (equation 6.5) in that as the temperature increases, the diffusion coefficient increases. This effect is particularly noticeable with the Usibelli coal (Figure 6.9). This is because the mass tortuosity is small, thus equation 6.6 approaches the molecular diffusion equation (equation 6.4). The Indian Head coal, on the other hand, has such a large mass tortuosity that the effective dispersion coefficient is very nearly zero at no flow conditions. The implication of this is that the Indian Head coal particles are so tightly packed, that at no flow, there is little or no self diffusion occurring. By comparing the mass tortuosity for each coal in Table 6.3 with the permeabilities in Table 6.1, it can be seen that as the absolute value of the mass tortuosity increases, the permeability decreases. This is consistent with the idea that under no external flow, the tighter the flow path is, the more the interstices in the core act as individual pockets and molecular diffusion is limited.

As the superficial velocity increases, the velocity term dominates equation 6.6. In this region, viscous effects are the major cause for the difference in the isotherms. This can be seen in Figures 6.8–6.10. At lower temperatures, the carrier fluid is more viscous, therefore it undergoes more shear as it moves through the pores in the core. This shearing causes more mixing and thus a higher effective axial dispersion coefficient. This is the cause of mechanical mixing effects as discussed by Ramirez et. al.⁵ At higher temperatures, the viscous effect is much less causing the curve to flatten out.

Thus, our model is consistent with what should occur at the extremes of temperature and flow. This leads to the conclusion that the model should be useful as a predictive tool to extend limited experimental data to other temperatures and flow rates.

Figure 6.8: Axial dispersion vs. velocity-South Hallsville.

Figure 6.9: Axial dispersion vs velocity-Usibelli.

Figure 6.10: Axial dispersion vs. velocity-Indian Head.

6.5 Conclusions

The nonlinear least squares parameter estimation technique provides an accurate and useful method for calculating the effective axial dispersion coefficient from pulse tracer data in nonreacting unconsolidated porous media that does not exhibit capacitance effects. The major advantages over the standard techniques of moments and weighted moments are the calculation of porosity in conjunction with the calculation of the dispersion coefficient, the elimination of the assumption of constant porosity, and the ability to handle noisy data.

The effective axial dispersion coefficient model presented here includes the effects of temperature on molecular diffusion and viscosity, the effects of flow rate on mixing, and the effects of the differences in the coals themselves. Based on the results shown, we believe that this model accounts for most of the major contributions to the effective dispersion coefficient in porous media and should provide a consistent means of extending data to a wide range of flows and temperatures.

Nomenclature

A	Experimentally determined parameter (equation 6.9)
A_c	Cross sectional area of core (cm^2)
a	Experimentally determined parameter (equation 6.1)
B	Experimentally determined parameter (equation 6.9)
C	Tracer concentration (mCi/ml)
D_z	Axial dispersion coefficient (cm^2/sec)
D_{AB}	Self diffusion coefficient (cm^2/sec)
E	Lumped parameter (equation 6.3)
k	Permeability to water (md)
Q	Quantity of tracer injected (mCi)
R^2	Correlation coefficient from least squares regression
S	Dimensionless constant characteristic of cross section (equation 6.2)
T	Absolute temperature (K)
t	Time (sec)
V	Molar volume of solute as liquid at normal boiling point (ml/gmole)
v	Superficial velocity (cm/sec)
X	Core length (cm)
Y	Vector containing experimentally measured dependent variable
$\hat{Y}$	Vector containing model predictions of dependent variable

Greek Symbols:

α	Velocity power term (equation 6.1)
ψ_B	Association parameter
κ	Velocity characteristic parameter (equation 6.2)
Φ	Performance index
ϕ	Porosity
τ_m	Mass tortuosity
μ	Absolute viscosity (cp)

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Table 6.1: Coal Analysis
Proximate Analysis (Air Dried)

Coal	(%)			
	Moisture	Ash (ASTM)	Volatile Matter	Fixed Carbon
South				
Hallsville	5.5	0.9	40.0	43.6
Usibelli	10.8	6.7	42.7	39.8
Indian				
Head	7.6	6.7	38.4	47.3

Table 6.2: Coal Analysis
Ultimate Analysis (Air Dried)

Coal	(%)					
	C	H	N	S	O	Heating (Cal/g)
South						
Hallsville	60.4	4.7	1.2	1.2	21.6	5630
Usibelli	57.9	6.6	0.7	0.3	28.7	4560
Indian						
Head	61.7	4.5	0.9	0.5	25.7	5700

Table 6.3: Coal Analysis				
Coal	Sieve Anal.	D_p	Perm* (k)	Poros* (ϕ)
	Range (μm)	(μm)	(md)	
South				
Hallsville	<100	70	10	0.60
Usibelli	<110	70	25	0.57
Indian				
Head	<100	60	7	0.64

*Measured as part of the experimental procedure

Table 6.4: Comparison of Data Analysis Techniques for Pulse Tracer Data D_z ($\times 10^{-5}$) cm^2/sec

Case Number	Data Type	Exact	Marquardt	Weighted Moments	Moments
1	Exact	15.0	14.8	15.1	15.1
2	7% Noise	15.0	15.4	17.5	16.8
3	Noisy	—	3.9	3.2	3.4
4	Long Tail	—	10.1	12.3	20.2
5	Short Tail	—	20.7	17.3	26.7
6	Good Data	—	5.0	4.1	5.8

Table 6.5: Model Parameters

Coal	A	B	τ_m	R^2
South Hallsville	8.84×10^{-8}	62.66	-0.76	0.99
Usibelli	8.84×10^{-8}	36.86	-0.20	0.96
Indian Head	8.84×10^{-8}	172.8	-0.92	0.93

7 VAPOR-PHASE DIFFUSIVITY MEASUREMENTS OF ORGANIC SOLVENTS IN CONSOLIDATED LIGNITE COAL

7.1 Introduction

The diffusion of organic vapors in low-rank coal is of critical importance in the process specification of advanced coal gasification plants and in solvent extraction of coal. Measurement of the diffusion rate is hampered by the natural anisotropy of coal, adsorption of the vapor on the coal surface, and the sample to sample variability of low-rank coal structure. Although usual methods for measuring effective dispersion coefficients are steady-state approaches, unsteady-state methods have several advantages which are attractive for a study on a material such as coal. First, steady-state methods measure the net flux of diffusing species through samples in one direction, whereas our unsteady-state approach measures the diffusion flux from all directions at once. This is particularly valuable for an anisotropic material such as coal. Second, irregular-shaped consolidated samples can be handled conveniently using the unsteady-state approach, whereas cylindrical consolidated samples usually must be used in a steady-state apparatus. The difficulty in producing regular, machined shapes from consolidated low-rank coal samples is well known. Third, the unsteady-state approach can be used to obtain average diffusion coefficients on several consolidated samples at once, whereas only one consolidated sample can be run at one time using the steady state approach. This is particularly valuable for coal, where between sample variability in physical properties may be higher than variability between types. Finally, adsorption of a vapor phase on the surface of a sample cannot be directly determined using the steady-state approach, while the unsteady state approach provides direct measurement of adsorption coefficients along with the diffusion coefficients.

The unsteady-state approach had not been previously used extensively due to the limitations of the electronic data acquisition systems to record a rapid pressure transient. However, the recent upgrade of microcomputer-based data acquisition and control hardware provided an opportunity to use the unsteady-state approach in this project. We used an unsteady-state pressure transient technique to estimate the diffusion coefficient of pentane vapor in Indian Head and Usibelli lignite at temperatures from 50 to 170°C. We also attempted to measure diffusion coefficients

of toluene and steam in these coals at temperatures from 120 to 170°C, and qualitatively determined the effectiveness of these solvents for extraction of low-boiling point components of lignite coal. Diffusivity data for nitrogen were also collected to compare with the reactive solvent results.

7.2 Experimental Approach

The unsteady-state diffusion coefficient measurement apparatus is shown in Figure 7.1. The sample and flash chambers are evacuated after the coal samples are placed in the sample chamber. Liquid solvent (water, toluene, or pentane) is introduced through the septum port while the butterfly valve is closed. The liquid flashes to the vapor phase. The butterfly valve is opened, and the resulting pressure transient is measured with the pressure transducer. The initial and final pressures in the sample chamber are directly related to the amount of vapor adsorbed by the coal sample. The pressure transient is analyzed to obtain the effective diffusion coefficient. Operation of the butterfly valve, data acquisition, and data analysis of the pressure transient is performed by an IBM-XT personal computer outfitted with a Data Translation DT-2801 Data Acquisition and Control Board. Data acquisition and valve control programs were written in BASIC and compiled using the IBM CBASIC compiler. Consolidated lignite was stored under water until prepared for the experiments. Lignite samples were cut from these large "chunks" into cubic shaped pieces approximately 1 cm to a side. These samples were dried to constant weight in a partial vacuum under N_2 purge at 160-180°C to remove water and other volatile components. Some samples were sent to an independent laboratory for porosity determination using a helium injection apparatus.

7.3 Mathematical Approach

The mathematical analysis of the pressure data provides the diffusion coefficient and adsorption coefficient. The approach assumes that an effective spherical radius is known for the samples, the diffusion coefficient is constant, the adsorption isotherm is linear, and the adsorption rate is much faster than the diffusion rate. Operation of the apparatus at around one atmosphere pressure helps ensure the validity of the linear adsorption isotherm. We also assume the vapor is an ideal gas due to the low pressures and temperatures of the experimental conditions.

Figure 7.1: Mass diffusivity measurement apparatus (unsteady state).

The equation for diffusion of a gas into a porous solid is

$$(1 + A) \frac{\partial C}{\partial t} = \frac{D_e}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C}{\partial r} \right) \quad (7.1)$$

where D_e is the diffusion coefficient, and A is the adsorption coefficient defined as

$$A \equiv \frac{C_s}{C} \quad (7.2)$$

C_s is the adsorbed concentration (moles adsorbed/free container volume) and C is the pore concentration (moles/free container volume). The initial condition is

$$C = 0 \quad -R < r < R \quad \text{at } t = 0 \quad (7.3)$$

and the boundary conditions are

$$\frac{\partial C}{\partial r} \Big|_{r=0} = 0 \quad \text{for all } t \quad (7.4)$$

$$V_F \frac{\partial C}{\partial t} \Big|_{r=R} = -A_p D_e \frac{\partial C}{\partial r} \quad (7.5)$$

where V_F is the free volume in the chamber, and A_p is the total open area of all samples at $r = R$. A_p can be defined as

$$A_p \equiv 4\pi R^2 \epsilon n \quad (7.6)$$

where *epsilon* is the internal porosity and n is the number of samples in the chamber.

The flux boundary condition (equation 7.5) can be written

$$\frac{\partial C}{\partial t} \Big|_{r=R} = - \frac{4\pi R^2 \epsilon n D_e}{V_F} \frac{\partial C}{\partial r} \Big|_{r=R} \quad (7.7)$$

If we define α as

$$\alpha \equiv \frac{V_F}{4/3\pi R^3 n \epsilon} \quad (7.8)$$

Then equation 7.7 becomes

$$\frac{\partial C}{\partial t} \Big|_{r=R} = - \frac{3D_e}{\alpha R} \frac{\partial C}{\partial r} \Big|_{r=R} \quad (7.9)$$

Equations 7.1-7.4 and 7.9 constitute the mathematical formulation for the conditions of the unsteady-state measurement apparatus. Here α is the ratio of the free gas volume surrounding the samples to the total pore volume of the samples.

Crank (1956) solved this system of equations to obtain the following solution:

$$\frac{C(r, t)}{C(R, \infty)} = 1 + \sum_{n=1}^{\infty} \frac{6(1 + \alpha) \exp[-D_e q_n^2 t / R^2(1 + A)]}{9 + 9\alpha + q_n^2 \alpha^2} \frac{R \sin(q_n r / R)}{r \sin q_n} \quad (7.10)$$

where the q_n 's are the non-zero roots of

$$\tan q_n = \frac{3q_n}{3 + \alpha q_n^2} \quad (7.11)$$

Equation 7.10 allows calculation of the internal concentration profile in the sample, and comparison to experimental data would provide a two-parameter fit (A and D_e) to measured concentrations. However, pressure is measured in the experiment rather than concentration, and two-parameter curve fits should be avoided if possible. Equation 7.10 can be modified if we note that

$$\frac{C(R, t)}{C(R, \infty)} = \frac{P(R, t)}{P(R, \infty)} \quad (7.12)$$

for moderate pressures and constant temperatures. We also want to evaluate equation 7.10 at $r = R$ where the pressure measurements are obtained. Thus, equation 7.10 becomes

$$\frac{P(R, t)}{P(R, \infty)} = 1 + \sum_{n=1}^{\infty} \frac{6(1 + \alpha) \exp[-D_e q_n^2 t / T^2(a + A)]}{9 + 9\alpha + q_n^2 \alpha^2} \quad (7.13)$$

Equation 7.13 still contains the two unknown parameters, D_e and A . We also know that

$$\frac{P(R, \infty)}{P(R, 0)} = \frac{C(R, \infty)}{C(R, 0)} = \frac{n(\infty)V(v)}{n(0)V(\infty)} \quad (7.14)$$

where n is the number of moles of vapor in the system.

The volume occupied by the gas at $t = \infty$ consists of the free volume $V_F (= \alpha \epsilon V_p)$ and the pore volume $V_v (= \epsilon V_p)$ where V_p is the bulk sample volume. The volume at $t = 0$ before any diffusion occurs is V_F . The number of moles contributing to the pressure at $t = \infty$ is the original number of moles ($n(0)$) minus the number of

moles that have adsorbed (n_{ADS}). The number of moles adsorbed can be computed as

$$n_{ADS} = C_s V_F = \frac{An(\infty)\alpha\epsilon V_p}{\alpha\epsilon V_p + \epsilon V_p} = \frac{An(\infty)}{\alpha + 1} \quad (7.15)$$

thus, after substitution of equation 7.15 into equation 7.14 and some algebraic manipulation,

$$\frac{P(R, \infty)}{P(R, o)} = \frac{\alpha}{\alpha + 1 + A} \quad (7.16)$$

or,

$$A = \alpha \left(\frac{P(R, o)}{P(R, \infty)} - 1 \right) - 1 \quad (7.17)$$

Equation 7.17 allows independent determination of A from knowledge of $P(R, o)$, $P(R, \infty)$, and α for each sample run.

Equation 7.13 can be expressed as

$$\frac{P(R, t)}{P(R, o)} = \frac{\alpha}{\alpha + 1 + A} \left[1 + \sum_{n=1}^{\infty} \frac{6(1 + \alpha) \exp[-D_e q_n^2 t / R^2 (1 + A)]}{9 + 9\alpha + q_n^2 \alpha^2} \right] \quad (7.18)$$

The IBM personal computer collects values of $P(R, t)/P(R, o)$ and solves equation 7.18 "on line" for each sample run to obtain the effective diffusion coefficient D_e .

7.4 Results and Discussion

Comparison of nitrogen diffusivity data with the results for the organic solvents in new lignite samples indicates the reactivity and the extraction capability of these solvents at relatively moderate temperatures and pressures. Figure 7.2 shows a typical pressure transient for nitrogen diffusion in lignite, along with the modeled transient based on equation 7.18 using the best fit diffusion coefficient. Very little nitrogen is adsorbed on the solid surface as indicated by initial pressure readings. The shallow transient indicates that the porosity of the coal is low, and the diffusion rate is slow compared to most porous catalysts. This particular experiment yielded a diffusivity of $3.3 \times 10^{-5} \text{ cm}^2/\text{sec}$.

The nitrogen pressure transient in Figure 7.2 is compared in Figure 7.3 with the pentane pressure transient obtained at the same temperature on the same sample. There is a dramatic pentane pressure increase which occurs within 40 to 60 sec after the pentane comes into contact with the sample. The pressure then generally decreases to an equilibrium value after nearly 1000 seconds of contact.

Figure 7.2: Measured and modeled nitrogen pressure transient in Usibelli lignite at 125°C.

Figure 7.3: Comparison of pentane and nitrogen pressure transients in Usibelli lignite at 125°C.

Figure 7.4 presents a similar comparison of the pressure transients for nitrogen and toluene. The toluene data were obtained at 140°C to ensure that toluene was not present in a liquid phase. The sharp pressure increase followed by the slow decrease is particularly dominant in the toluene pressure transient. Figure 7.5 shows data for steam, and these results are similar to the results for toluene and pentane. It is apparent from the pressure transient data that a reaction or extraction process is occurring during the experiment. The action of common organic solvents on coal is well known (Speight, 1983). Usually, little of the true coal substance is dissolved at low temperatures, and the solvent will extract only that material which is occluded within the coal matrix. Lower-rank coals are particularly susceptible to common solvents. The materials that are extracted are montan waxes consisting of aliphatic acids ($C_{24} - C_{32}$) and the corresponding esters and alcohols. Resins are also extracted which are derivatives of mono- and dibasic $C_{12} - C_{20}$ acids with aromatic nuclei. Phillip and Anthony (1978) found a long list of low-boiling point compounds which they extracted at super-critical conditions. It is probable that some of these compounds also could be present at low concentrations in our experiments.

The presence of gaseous extraction products precluded measurements of diffusivity using pressure transients. Thus, we decided to repeatedly subject a single sample to pentane vapor in order to gradually remove the extractable fraction of the lignite samples. We repeated the pressure transient experiment until consistent pressure transients were obtained, indicating that the extractable fraction was removed. Figure 7.6 shows the results of these multiple runs on Indian Head lignite. Approximately 20 runs were needed at 70°C to remove the extractable fraction. Six additional runs were performed to ensure that reproducible data could be obtained. This process was repeated at higher temperatures in order to obtain data at these conditions.

Figure 7.7 presents the final pressure transient for pentane in Indian Head lignite at 70°C. The mathematical model predictions are also shown. The model does not predict the initial pressure decrease in the experimental data. The model assumes that adsorption is much faster than diffusion, but the experimental data indicate that a slow adsorption step is also present. Figure 7.8 shows final pressure transient data for pentane at various temperatures. The slow adsorption process becomes more rapid and is less pronounced at higher temperatures, which is commonly seen during adsorption on other porous materials such as catalysts (Satterfield, 1980). Figure 7.9 presents the measured and modeled data for pentane at 1700C, and

Figure 7.4: Comparison of toluene and nitrogen pressure transients in Usibelli lignite at 125-140°C.

Figure 7.5: Comparison of steam and nitrogen pressure transients in Usibelli lignite at 125°C.

Figure 7.6: Pentane pressure transients after repeated operation on a single Indian Head lignite sample at 70°C.

the model does a credible simulation since the assumption of rapid adsorption is supported by the data at 170°C. Figure 7.10 shows the toluene pressure transient after repeated extraction of the same Indian Head lignite sample as used in the pentane study. Toluene removes a different set of coal components than pentane, and the amounts of these materials decrease after many extraction experiments.

Diffusion coefficient data were obtained from the pressure transients by fitting equation 7.18 to data obtained after 400 sec contact time. Table 7.1 provides a summary of these results. All diffusion coefficient results were obtained after repeated extraction experiments had removed low-boiling point coal components. Pentane diffuses at a slower rate than nitrogen, which is to be expected because of the relative size of the molecules. The diffusion coefficient data do not show definite trends with temperature, although it is to be expected that the diffusion coefficients should increase with temperature. It is probable that the slow adsorption processes interfere with the diffusion data, especially at the lower temperatures. However, the data are comparable to diffusion coefficients measured in other coals (Yang et al., 1977; Nandi and Walker, 1964, 1975). Adsorption coefficients (based on the model assumptions of rapid rate and linear isotherm) decrease with increasing temperature for a given gas-phase fluid.

Figure 7.7: Measured and modeled pentane pressure transient for Indian Head Coal at 70°C.

Figure 7.8: Measured pentane pressure transients for Indian Head coals at various temperatures.

Figure 7.9: Measured and modeled pentane pressure transient data for Indian Head lignite at 170°C.

Figure 7.10: Toluene pressure transients after repeated operation for a single Indian Head lignite sample at 170°C.

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Table 7.1: Summary of Experimental Results

Lignite	Gas Phase	Temperature (°C)	No. of Runs	Ave. Diffusion Coefficient (cm^2/sec)	Average Adsorption Coefficient
Usibelli	Nitrogen	23	2	6.7×10^{-5}	0.1
Usibelli	Pentane	50	1	3.9×10^{-6}	16
Usibelli	Pentane	70	1	3.6×10^{-6}	10
Usibelli	Pentane	90	1	1.5×10^{-6}	6
Usibelli	Pentane	140	1	4.8×10^{-5}	5
Indian Head	Nitrogen	70	4	1.8×10^{-6}	0
Indian Head	Pentane	70	7	7.2×10^{-6}	6
Indian Head	Pentane	115	2	1.5×10^{-6}	3
Indian Head	Pentane	170	3	2.0×10^{-6}	0.3