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Osanloo, Morteza Gholi

# CHEMICAL COMMINUTION FOR DEEP AND THIN BITUMINOUS COAL BY USING CARBON DIOXIDE + WATER AS A SOLVENT

*The University of Oklahoma* PH.D. 1982

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THE UNIVERSITY OF OKLAHOMA

GRADUATE COLLEGE

# CHEMICAL COMMINUTION FOR DEEP AND THIN BITUMINOUS COAL BY USING $CO_2$ + $H_2O$ AS A SOLVENT

A DISSERTATION

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the

degree of

DOCTOR OF PHILOSOPHY

By

MORTEZA OSANLOO

Norman, Oklahoma

1982

CHEMICAL COMMINUTION FOR DEEP AND THIN BITUMINOUS

COAL BY USING $CO_2$ + $H_2O$ AS A SOLVENT

A DISSERTATION

APPROVED FOR THE DEPARTMENT OF PETROLEUM AND

GEOLOGICAL ENGINEERING

APPROVED BY

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ABSTRACT

In the past decade, mine engineers have had a difficult task in trying to increase the production of coal, particularly from deep and thin deposits. The two main mining techniques, open-pit and underground operations, are not feasible for deep and thin reservoirs. Although in open-pit the production is high, the cost of operation is also high, in addition to causing air and water pollution. In the underground mining methods, the operation is dangerous as a result of roof collapse, gas explosion (particularly methane), in addition to low production. These problems became more complicated for the engineer when the demand for higher production of coal combined with the demand for better quality of coal. These problems in the mining industries led to a new technique called "chemical comminution." Chemical comminution of coal involves reducing the size of the coal by injection and penetration of a suitable solvent through the natural discontinuities of coal such as fractures, pores and fissures. In this study, $CO_2 + H_2O$ was proposed as a solvent for the chemical comminution process. Three different bituminous coal samples from eastern Oklahoma, (1) McAlester (Latimer County), (2) Croweburg (Okmulgee County), and (3) Secor (Wagoner County), and one unknown coal sample (the origin of the coal is unknown) were examined with the proposed solvent. A 500 ml stainless steel bomb reactor was used for treatment of the coal with

the proposed solvent. The conditions of the treatment of the coal in each test were different. The temperature ranged from 200°C to 325°C. The pressure ranged from 2150 psi to 3600 psi. The results of the research indicated that, at higher temperature and pressure and higher ratio of solvent to coal with longer period of experiment, the percentage of the fragmented coal was higher and the size of the fragmented coal became finer. Results of ultimate analysis of the fragmented coal showed that at 275°C and 3300 psi with 3.5 solvent to coal ratio for 24 hours, the total sulfur of the coal declined from 3.51 percent to 2.23 percent; and the ash was reduced from 18.65 to 17.5 percent. As a result of this investigation, it is believed that $CO_2$ and its aqueous solution in water is a suitable solvent in the chemical comminution process; and it is capable of breaking the coal and reducing the sulfur and ash contents of the coal.

## ACKNOWLEDGEMENTS

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## UNITS USED IN THIS STUDY

MTOE - Million tons of oil equivalent which represents the amount of energy which exists in one short ton of oil*

One ton of oil is roughly equal to:

1. one ton of anthracitic coal
2. 1.5 tons** of bituminous coal
3. 3 tons of lignite coal
4. 5.3 tons of peat
5. 1167 thousand cubic meters of natural gas
6. 39 million Btu (British thermal units)
7. 11.5 million watts
8. 9.8 billion calories

One pound = 453.4 grams

One short ton = 2000 lb

One long ton = 2210 lb

One Btu = 0.293 watts = 252 calories = 1055 Joules

One atmosphere = 14.70 psi

One bar = $10^6$ dyn/$cm^2$ = 14.5 psi

---

*Don Hedley, World Energy: The Facts and Future, "Energy Units," published by Facts on File, Inc., 1981.

**This number can range from 1.2 to 1.8 tons depending on the type of bituminous coal.

1 inch = 2.54 cm

1 ft = 30.48 cm

1 mile = 1609 meter = 5280 ft

$°F = \frac{9}{5}$ °C + 32 where °C is a symbol for measuring temperature in Celsius and °F is a symbol for measuring temperature on Fahrenheit scales.

°K = 273.15° + °C where °K is a symbol for measuring temperature on Kelvin scale.

# CHEMICAL COMMINUTION FOR DEEP AND THIN BITUMINOUS COAL BY USING $CO_2 + H_2O$ AS A SOLVENT

## CHAPTER I

## INTRODUCTION

### A. GENERAL STATEMENT OF THE PROBLEM

In the past decade, the quality and higher production of coal from deep and thin reservoirs has become extremely important for the mining industries. Inefficient mining techniques, such as underground and open pit, for coal production and mechanical methods of removing the impurities of coal such as ash and sulfur have led to a new technology for both quality and improvement of coal production called "chemical comminution". Underground mining methods are too risky for deep reservoirs in addition to their lower production. On the other hand, surface mining or the open pit method is not a feasible technique from an economic point of view for deep and thin reservoirs. In addition, water and air pollution and damage to natural resources occurs as a result of this operation. Also, up-to-date mechanical methods, such as crushing and milling, are not able to remove organic sulfur from coal compounds, which account for 30 to 70 percent of the total sulfur in coal.

As a result of these problems in the mining industries, this study was proposed to study a chemical agent, carbon dioxide and its aqueous solution in water, for the chemical comminution process in order to improve the quality and production of coal. The suggested chemical agent has the following advantages for the mining industries and energy division: (1) The cost of operations is reduced in comparison with open-pit techniques for deep and thin reservoirs. (2) Many coal reservoirs would change from being resources to reserves because of the feasibility of this technique from an economic point of view. (3) Less processing is required for coal production compared to both mining methods. (4) The risky operations of the underground mining methods and the air and water pollution of the open-pit method are unnecessary. (5) Carbon dioxide is a cheap and plentiful substance. (6) The substance is nonflammable, nonhazardous and nonexplosive with regard to humans and rock formation. (7) The substance is low density and less complicated which is desirable in separating solid (coal) from solvent.

## B. REVIEW OF PREVIOUS INVESTIGATION

In 1920 in West Germany, Pott and H. Broch developed a technique which could produce relatively clean burning fuel from coal under hydrogen pressure in either the form of a solid called Solvent Refined Coal I (SRCI) or a liquid called SRCII. But this process was stopped for two reasons. First, at that time the washability method was unknown or less developed and second because of World War II.

From 1950 to 1960 in the United States, research and development work on a modification of the Pott-Broch method was carried out by

Spencer Chemical Company. Then in 1962, Gulf Oil Corporation obtained this project through the Office of Coal Research (OCR) and reassigned it to the Pittsburgh and Midway Coal Mining Company (P&M). As a result, P&M designed a pilot-plant capable of processing 50 tons of pure coal per day by SRCI.[1]

In early 1971, Syracuse University Research Corporation examined and introduced the first new chemical agent for the chemical comminution process. The chemical agent proposed was ammonia (gas and liquid) in order to remove the impurities of coal such as ash and sulfur and consequently reduce the size of the coal (fragment).[2,3,4,5] In this research, four different types of coal samples (two thousand pounds) were selected for experimental study: (1) Illinois No. 6 coal (Franklin County); (2) Pittsburgh seam coal (Greene County, PA); (3) Upper Freeport seam coal (Westmoreland County, PA); and (4) Lower Freeport seam coal. All of them were run-of-mine samples (ROM). The process was carried out in a bomb reactor with different pressures, times, temperatures and different phases and various percentages of ammonia. They discovered the rate and extent of fragmentation of coal and the release of sulfur depended on several factors: (a) coal characteristics, higher ranks of coal have less response to ammonia than lower ranks of coal; (b) reaction conditions, the results of the experiment showed that increasing the pressure increases the percentage of fragmentation. Also, they discovered that higher pressure will yield finer coal than lower pressure.

Although how the chemical comminution process actually breaks the coal was not fully understood by the Syracuse University Research

Corporation, it is thought that the accessible hydrogen atoms of the ammonia molecule disrupt the weak bonding energy along the coal's internal boundaries.[6] It has been reported by the Syracuse University Research Corporation that chemical comminution with ammonia is capable of liberating more pyritic sulfur ($FeS_2$) than mechanical methods for a given size. The cost of chemical comminution was estimated between $2.5 to $3.00/ton; this includes the cost of washability.

In 1974 Duane R. Skidmore, Professor of Mineral and Energy Resource, and Calvin J. Konya, Associate Professor of Mining Engineering at the College of Mineral and Energy Resource at West Virginia University, presented a paper at the AIME National meeting at Dallas, Texas (February 25-28), under Chemical Comminution of Coal.[7] This paper was a summary of two experimental studies on chemical comminution with two different solvents. First, the Pittsburgh seam coal from Morgantown, West Virginia, was examined with pyridine solvent. Pyridine was refluxed through coal samples held in Soxhlet extractor sleeves (19 x 90 mm) at atmospheric pressure and room temperature for 6 to 42 hours. The results of U.S. Standard sieve analysis showed longer reaction times caused finer particle size. The second experimental work was done with anthracane oil solvent on the same coal seam bed but at higher temperatures and pressures. The study was carried out in a 750 ml carbon steel batch autoclave. The temperature ranged from 240°C to 320°C and pressure up to 900 psi for 60 minutes of operation. The results of the second experiment were reported as follows: Higher temperature with longer period of experimentation with relatively high pressure would yield more fine coal. Addition of water to the system

would increase the pressure but not change the size of particles. The water was added to the system in order to reduce the cost of operations.

In March 1980, Bruce W. Davis from Chevron Research Company, San Francisco, California, introduced a new chemical agent that successfully affected several coal types from lignite to bituminous.[8] The coal samples were selected from Alberhill County (lignite), Karpowitz and Carbonado No. 3, 7 (bituminous). In this research, gaseous $NO_2$-$O_2$ mixture was used as a chemical agent, and ethanolamine was selected as an aqueous solution. First the gaseous $NO_2$-$O_2$ mixture contacted the coal for the desired length of time, allowing the $NO_2$-$O_2$ mixture to penetrate into the pores and along grain boundaries in order to create permeability. Then an ethanolamine solution, containing from 0.25 to 0.5% by weight ethanolamine, was added to the coal-$NO_2$-$O_2$ mixture. $NO_2$ was selected in order to create permeability, and $O_2$ was chosen to control the rate of rection. Finally, aqueous ethanolamine was added to the compounds to break up and slurry the treated coal. The temperature applied in this study ranged from 20°C to 90°C.

At the University of Oklahoma Department of Chemistry, Dr. Arnulf P. Hagen proposed fluorinated solvents [mainly, trifluoracetic acid (TFA) and difluorophosphoric acid (DFPA)] for bituminous coal fragmentation and liberation of ash and sulfur. At physical conditions up to 300 C and 5000 psi pressure, preliminary experiments have shown that TFA and DFPA have potential for the comminution of Oklahoma high volatile bituminous coal.[9]

Besides the above compounds, the following compounds have also been found effective in tests for the chemical comminution process of

coal by Syracuse Research Corporation:[10] (1) anhydrous methanol, (2) anhydrous methanol plus 1/4 mol NaOH/liter, (3) anhydrous ethanol, (4) anhydrous ethanol plus 1/4 mol NaOH/liter, (5) anhydrous isopropanol, (6) anhydrous isopropanol plus 1/4 mol NaOH/liter, (7) 40 percent methylamine/anhydrous methanol, (8) 70 percent ethylamine/anhydrous ethanol, (9) anhydrous methanol/acetone, (10) anhydrous ethanol/actone, (11) glacial acetic acid/acetone, (12) hydrous isosporpanol/acetone, (13) hydrogen peroxide and acetone.

In the past, several compounds have also been developed and introduced for the liberation of both organic and inorganic sulfur, but not necessarily for in situ mining industries, and results were reasonable. At Pittsburgh Energy Research Center, Sidney Friedman, Robert B. LaCount and Robert P. Warzinski injected air as a source of oxygen for the oxidation of organic sulfur, then used NaOH for the elimination of $SO_2$. The pressure applied in this experiment ranged from 800 to 1000 psi and temperatures up to 300°C.[11] The same group explored nitrogen dioxide ($NO_2$) as a good reagent for converting organic sulfide to sulfones and then used NaOH in aqueous solution as a solvent in order to eliminate $SO_2$.[12] The same group at Pittsburgh Energy Research Center also discovered that pyrite in coal can be minimized with compressed air at 1000-1200 psi and at 150 -160°C.[13]

At Ledgemont Laboratory of Kennecott Copper Corporation, S. S. Sareen was able to remove almost all of the pyritic sulfur and 25% of the organic sulfur at 130°C temperature and up to 300 psi pressure by using an ammonia/oxygen/water mixture for 2 hours.[14]

## C. SPECIFIC STATEMENT OF THE PROBLEM

In the past the recovery of deep coal in thin deposits has always been extremely expensive and difficult. Many unsolved problems exist in both open-pit and underground mining methods. In open-pit, despite advances in technology which increased the coal production, air and water pollution plus the destruction of natural resources still remain without sufficient solution. At the same time, the price of equipment and operations in open-pit mining has increased to unpredictable levels. On the other hand, it is well known that the production of coal by underground mining operations is very low and very risky. (In 1981 itself, more than 100 people died in the United States and Japan as a result of this operation. Events: April 15, 1981 in Colorado of U.S.; October 16, 1982 in Japan; December 7, 1981 in southeast Kentucky in U.S.; December 8, 1981 in East Tennessee of U.S.; and January 20, 1982 in Japan.)

These factors are complicating the production of coal not only from deep but also from shallow deposits; and, as a result of these, coal production is low, thus serving to worsen the energy crisis. In Oklahoma itself, the Oklahoma Geological Survey reported in 1974[15] that in 19 counties in eastern Oklahoma, there are 24 bituminous coal beds covering 1.5 million acres with more than 7 billion tons of resources. However, 90 percent of this coal is more than 100 feet deep and less than three feet thick. Only 0.5 billion tons of this coal has been mined in the past 100 years. From the remaining coal, 2.3 billion tons are not recoverable at the present time by present technology and

probably will not be mined in the near future unless there is some improvement in the mining industry. Among this 2.3 billion tons of coal, 240 million tons is suitable for liquefaction and gasification, 650 million tons is suitable for generating electricity, and more than one billion tons is suitable for the coke industry if sulfur and ash can be removed from the coal. It is also interesting to note that, according to Keyston,[16] in the United States, there have been more than 3 trillion tons of coal resources recognized. Among this figure, almost 50% of coal located between 0 and 3000 feet deep has been mapped and explored (identified) by geological methods and the other half unmapped and unexplored (indicated and probable). But among this large resource only 150 billion tons can be reasonably extracted with present technology.

At the same time, many energy planners in the United States estimate 1.2 billion tons of coal production would be required by 1985 and 2 billion tons by the year 2000 in order to meet the energy demand.[16] To meet this production, according to a federal energy administration source, the following actions need to be taken in order to provide 1.2 billion tons of coal by 1985: (1) Develop 140 new 2-million-ton-per-year mines in the eastern United States by underground mining operations. (2) Develop 30 new 2-million-ton-per-year mines in the eastern U.S. by open-pit technology. (3) Develop 100 new 5-million-ton-per-year mines in the western United States by open-pit (surface mining) technology. (4) Train and provide 80 thousand new coal miners in the eastern United States. (5) Train and create 45 thousand new coal miners in the western United States.

To bring this plan to productivity would not be so easy—especially in the short term. To open and develop one underground mine with two million tons production per year requires at least five solid years. This can be increased to ten years depending on many factors, such as where the mine is located, weather, etc. Also, to develop one open-pit or surface mine with 2 to 5 million tons production per year requires from two to five years. Again, this period can be extended to many years for many reasons.

In addition to difficulties in coal mining, the demand for pure coal recently increased for the following reasons: (1) to reduce the cost of transportion by reducing and removing the impurities from the coal; (2) to enhance salability; (3) to reduce the sulfur oxide ($SO_2$) emissions as a result of coal combustion. In the United States in 1972, of the 600 million tons of coal produced, almost 50% of the total coal required some type of purification in order to remove the sulfur (Figure 1).

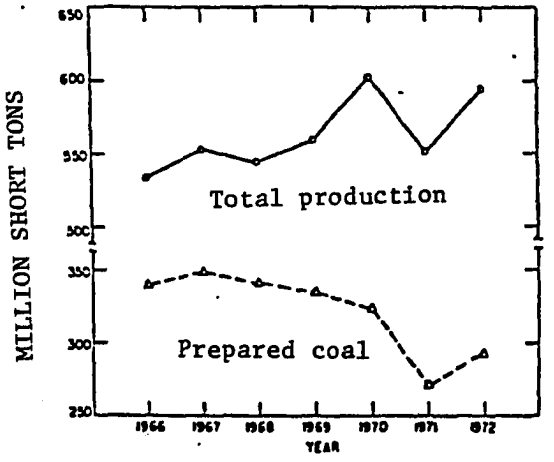



FIGURE 1. Total and prepared coal production.

From: Howard, Philip, Hanchett, Arnold, and Aldrich, Robert G., "Chemical Comminution for Cleaning Bituminous Coal," Clean Fuels from Coals Symposium II, sponsored by Institute of Gas Technology, June 23-27, 1975, p. 735.

Up to mid 1970, mainly mechanical methods (crushing, grinding, milling) were used to remove the sulfur from the coal; but first, the mechanical methods were producing too fine particles of coal during the process, consequently complicating the washability or separation process. Second, the mechanical methods are not able to remove organic sulfur from coal which is 30 to 70 percent of the total sulfur in coal. Therefore, the chemical communition process is necessary and can be a part of the solution for the difficulties involved in both production and impurities of coal. As a result, the specific problem of this study is to attempt to answer the following questions:

1. Can $CO_2$ and its aqueous solution in water be used as a chemical agent in the chemical comminution process for in situ mining with a deep and thin coal bed for which open-pit and underground mining operations are not suitable?

2. Can $CO_2$ and its aqueous solution in water be used as a chemical agent in the chemical comminution process to remove sulfur and ash instead of mechanical methods?

## D. SCOPE AND LIMITATION OF THE RESEARCH

1. Can a laboratory research be developed to obtain sufficient results with regard to McAlester bituminous coal-carbon dioxide-water mixture that can supply the basic data for use in the theoretical calculations necessary to predict the behavior of bituminous coal-$CO_2$-$H_2O$ mixture?

2. What are the minimum and maximum temperatures and pressures required for fragmentation of a McAlester coal-$CO_2$-$H_2O$ mixture?

3. What are the percentages of coal fragmentation with regard to time, temperature, and pressure?

4. What percent of sulfur and ash will be removed from McAlester coal with regard to at least one typical temperature, pressure, and time of experiment?

5. Are there any other coal beds of Oklahoma which can be reacted with a $CO_2$-$H_2O$ mixture? If so, determine breakpoint and distribution of particle size at that particular point.

## E. EXPERIMENTAL PROCESS FOR CHEMICAL COMMINUTION OF COAL

1. Weigh desirable amount of coal and place inside the bomb reactor and add desirable amount of water in the bomb (not more than 75% of bomb reactor capacity). At this stage, there is coal + $H_2O$ in the bomb reactor.

2. Inject $CO_2$ to the bomb rector which contains coal + $H_2O$.

3. Heat bomb reactor by any device such as electrical heater for desirable time.

4. Turn off heat after desirable period and leave bomb reactor and its contents for 3-5 hours depending on temperature in order to cool off bomb reactor for further operations.

5. Remove the cap of bomb rector and separate fragmented coal from solvent.

## F. DEFINITIONS OF TERMS AS APPLIED IN THIS STUDY

Chemical Comminution: The process that fragments the coal along naturally occurring systems of fractures, pores, faults and other

discontinuities by usually low molecular weight chemical compounds. Although the mechanism of chemical comminution in many cases is not fully understood, it is believed the chemical compounds penetrate the coal, weakening and disrupting the bonding forces at the natural interfaces of the coal structure where ash and pyrite are located. Therefore, in chemical comminution, not only can coal be fragmented, but also impurities of coal such as ash and pyrite can be removed.

Washability: Washability (or difference method) is the technique which separates solid from liquid by using gravity property.

MTOE: Million tons of oil equivalent. This represents the amount of energy contained in one ton of oil.

ROM (run of mine): The raw coal (or ore) as it is delivered by the mine cars, conveyor, etc.

Resource: This is the broadest term applied to ore (coal) deposits which are identified to exist within a mineral (coal) field, based on interpretation of geologic data and geological judgement but not necessarily recoverable at the present time by present technology from an economic point of view. This is the maximum estimation of mineral or ore (coal). There are three classes of resources. They are (1) measured, (2) indicated and probable, and (3) inferred.

1. Measured resources (proven): They lie within 1/2 mile of a point of observation and are based on mapped coal beds in which the thickness and continuity of coal are determined by observation in natural exposures along the outcrops, drill holes, mine workings and trenches. They usually account for 20 percent of true tonnage and are also considered to be as an identified coal or reserve coal.

2. Indicated (probable) resources: The points of observation and measurement which are used to calculate indicated resources are widely spaced. In general, the points between observation and measurement are about one mile or approximately up to 1 1/2 mile, but not more than 1-1/2 mile. The thickness and continuity of the coal bed is determined by geological evidence, and information obtained from proven resources (measured).

3. Inferred resources: Those resources which lie more than 2 miles from points of precise information. Although some knowledge of geological characteristics of the coal bed, the enclosing rocks and the region in which they occurred are available, mostly the thickness and continuity of the coal bed is estimated on the basis of the assumption that the coal bed continued beyond the measured and indicated area. Inferred resource area cannot be more than 4 miles.

Coal bed: A bed or stratum of coal, a layer with more than 14 inches in thickness. In United States, also called coal seam.

Coal bed thickness, bed thickness, coal thickness: Coal thickness is divided into three categories for different ranks of coal; they are (1) thin, (2) intermediate, and (3) thick.[24, 52]

| Categories | Bituminous and anthracite (in) | Subbituminous and lignite (ft) |
|---|---|---|
| Thin | 14-28 | 2.5-5 |
| Intermediate | 24-42 | 5-10 |
| Thick | > 42 | > 10 |

Vessel, pressure vessel or reactor or bomb reactor: Has a cylindrical shape with 2 1/2 inch inside diameter with 6 1/4 inch inside depth and constructed from stainless steel material by Parr Instrument Company and used in this study as a container of coal and solvent for high temperature and high pressure operation.

Reserve: This is the term that is applied for maximum recoverable ore (coal) with present technology with reasonable cost.

Chemical agent (solvent): Chemical compound used in the chemical comminution process for fragmentation and purification of coal ($CO_2$ + $H_2O$).

Agglomerating: Agglomerating usually refers to the behavior of coal when heated rapidly in a volatile matter test. Sometimes, coal is classified as agglomerating and nonagglomerating.

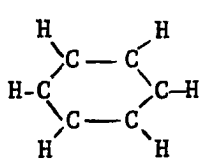
Transparency: This is the property of minerals in which a thin section of a mineral can transmit light and vision. Transparent minerals can transmit both light and vision.

Translucent mineral: Those minerals which can transmit light but not vision.

Opaque: Those minerals which cannot transmit either light or vision.

Hydrocarbon: Contains only two elements: carbon and hydrogen. The hydrocarbons can be divided into two groups.

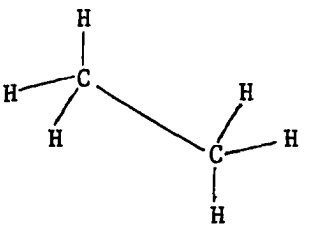
1. Aromatic. The best example is benzene and has the following geometrical structure.



Any hydrocarbons which do not have above geometrical structure are called aliphatic.

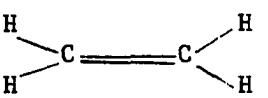
2. Aliphatic. Aliphatics are divided into three subclassifications.

a. Alkane. The best example is ethane which has the following structure

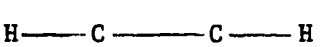


Its special characteristic is the existence of only single carbon-carbon bonds.

b. Alkene is hydrocarbon that has at least one or more carbon-carbon double bonds. The best example is ethylene, $CH_2=CH_2$, which has the following structure. Alkenes are sometimes referred to as olefins or unsaturated hydrocarbons.



c. Alkyne. The best example is acetylene, CH≡CH, which has the following structure



and has at least one or more than one carbon-carbon triple bond.

Homologous series: All the compound of the series can be described by the same general formula and contain common structural elements, but differ in number of atoms making up the molecule.

Open-pit mining, strip mining, surface mining, open cut mining or open cast mining: All of them have the same definition. A form of operation designed to extract minerals that lie near the surface. Recently, this definition was used more generally by eliminating "near the surface" and has been used to describe the technique or operation which removes waste and overburden first to reach the mineral.

Underground mining methods: A form of operation designed to extract mineral from the waste beneath the surface of the ground, such as room-pillar, long wall and short wall, etc., methods.

Fragmented: The coal was arbitrarily considered fragmented if the particles were 1/2 inch or less in diameter.

# CHAPTER II

## COAL AND GENERAL PROPERTIES OF COAL

### A. DEFINITIONS, CLASSIFICATION, STRUCTURE AND COMPOUNDS OF COAL

#### 1. Definition

It is generally agreed that coal is a heterogeneous substance that originates primarily from plants[19] in which the composition of the plants are changed under varying conditions of moisture, temperature, and pressure. Depending on the varying conditions, the type of plants, and the completeness of the decomposition, the resulting product is far from uniform. It ranges from the initial stage of humic acid to peat, lignite (brown coal), subbituminous coal, bituminous coal, anthracite and the final stage graphite.[20] It is possible under unique and similar conditions of moisture, temperature, pressure, plants and extent of decomposition for coal to become unique and uniform in composition and structural properties; but usually factors such as faults, fractures in the coal and surrounding rock, weathering of the coal near an outcrop and some other factors acting during the period of formation modify and change the final product (coal). As a result of these factors, coal from different portions of the same bed or even different portions of the same mine is different in some important properties such as the content of ash and sulfur.[21] There are two major stages required from

a geological point of view in order for plant or organic substances to become coal: (1) the biochemical phase and peat stage, and (2) metamorphic phase or dynamochemical.

(a) Biochemical phase and peat stage: At this stage, the organic substance and plants are accumulated in the sedimentary environment for a long period of time. During this period, because of the activity of microorganisms and particularly bacteria, there are some chemical changes in the organic substance.[22] The original plant or organic substance gains more carbon and loses oxygen; and it becomes a new form of organic substance which is called peat. The plants are heterogeneous in composition and are usually compounds of cellulose, hemicellulose, lignin, resins, waxes and fats.[23] Since it is recognized by many researchers that the major composition of plants are cellulose and lignin, it is safe to say cellulose and lignin are the principle constituents of coal. Figure 2 shows the structure of these compounds.

(b) Metamorphic stage or dynamochemical phase: Following the biochemical process, the remaining plants or peat are under different temperature and pressure for a long period of time (millions of year) and, depending on the starting plants, organic substance and nature of change during the biochemical process, can result in distinctly different coals.[24] These changes of the original organic substance into coal are known as <u>coalification</u> or <u>carbonification</u> which includes both the biochemical and metamorphic stages.[25]

2. <u>Classification of Coal Based on Degree of Metamorphosis</u>

As one may expect, coal has been classified on the basis of the degree of metamorphosis. This classification is recognized as the

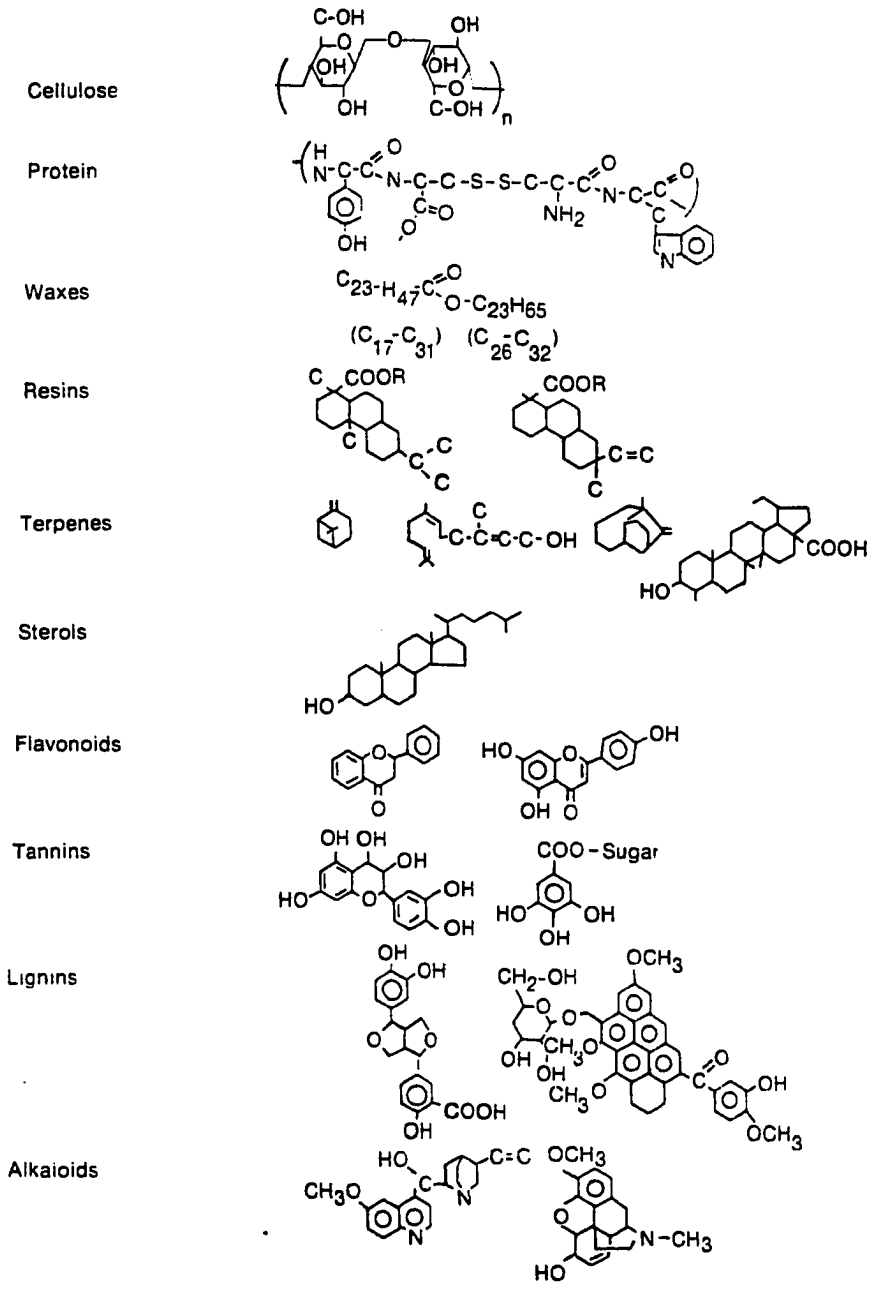



FIGURE 2. Structures of coal precursors.

From: Yatish T. Shah, Reaction Engineering in Direct Coal Liquefaction (Addison-Wesley Company, Inc., 1981), p. 36.

rank of coal. Peat is not regarded as a coal although it has similar characteristics to lignite. But generally, it is recognized that the lignite has undergone the least metamorphosis. As a result, coal which has above 86% carbon is classified as anthracite, and further subclassifications of anthracite depends on the range of percentage of carbon. Sometimes this group is also classified as a nonagglomerating coal. The anthracitic group has a high Btu value (15,000 Btu/lb) but is usually less abundant. Relatively less research has been done on this type of coal. On the other hand, those coals that have less than 86% carbon, distinguished from their burning characteristics (heating value), are mainly divided into three categories: (a) bituminous coal (at least 10,500 Btu/lb); (b) subbituminous (at least 8300 Btu/lb); (c) lignite (at least 6300 Btu/lb). These three coals have been divided into further subclassifications on the basis of both heating value and volatile value. Generally, bituminous coal is called agglomerating and subbituminous and lignite are called nonagglomerating. Among these coals, bituminous is more abundant around the world. As a result, relatively more research has been done on this particular coal. Table 1[26] shows the classification of coal on the basis of the degree of metamorphosis. Figure 3 shows the relation between the carbon content of coals and their geologic age.[27]

Classification of Coal Based on Coal Petrography

Coal petrography usually refers to the study of coal by microscopic observation, and classifications are based on different compounds of plants observed in coal. Generally speaking, optically organic substances in coal are referred to as macerals or petrographic

TABLE 1. Classification* of coals by rank

| Class, group | Fixed carbon limits (dry, mineral-matter-free basis), % | | Volatile matter limits (dry, mineral-matter-free basis), % | | Calorific value limits (moist, mineral-matter-free basis), †Btu/lb | | Agglomerating character |
|---|---|---|---|---|---|---|---|
| | Equal or greater than | Less than | Equal or greater than | Less than | Equal or greater than | Less than | |
| I. Anthracitic: | | | | | | | |
| 1. Meta-anthracite | 98 | | | 2 | | | |
| 2. Anthracite | 92 | 98 | 2 | 8 | | | |
| 3. Semianthracite | 86 | 92 | 8 | 14 | | | Nonagglomerating† |
| II. Bituminous: | | | | | | | |
| 1. Low-volatile bituminous coal | 78 | 86 | 14 | 22 | | | |
| 2. Medium-volatile bituminous coal | 69 | 78 | 22 | 31 | | | |
| 3. High-volatile *A* bituminous coal | | 69 | 31 | | 14,000§ | | Commonly, agglom- |
| 4. High-volatile *B* bituminous coal | | | | | 13,000§ | 14,000 | erating.¶ |
| | | | | | 11,500 | 13,000 | |
| 5. High-volatile *C* bituminous coal | | | | | 10,500 | 11,500 | Agglomerating |
| III. Subbituminous: | | | | | | | |
| 1. Subbituminous *A* coal | | | | | 10,500 | 11,500 | Nonagglomerating |
| 2. Subbituminous *B* coal | | | | | 9,500 | 10,500 | |
| 3. Subbituminous *C* coal | | | | | 8,300 | 9,500 | |
| IV. Lignitic: | | | | | | | |
| 1. Lignite *A* | | | | | 6,300 | 8,300 | |
| 2. Lignite *B* | | | | | | 6,300 | |

*This classification does not include a few coals, principally nonbanded varieties, which have unusual physical and chemical properties and which come within the limits of fixed carbon or calorific value of the high-volatile bituminous and subbituminous ranks. All these coals either contain less than 48 percent dry, mineral-matter-free fixed carbon or have more than 15,500 Btu per pound, calculated on the moist, mineral-matter-free basis.

†Moist refers to coal containing its natural inherent moisture but not including visible water on the surface of the coal.

‡If agglomerating, classify in low-volatile group of the bituminous class.

§Coals having 69 percent or more fixed carbon on the dry, mineral-matter-free basis shall be classified according to fixed carbon, regardless of calorific value.

¶It is recognized that there may be nonagglomerating varieties in these groups of the bituminous class, and there are notable exceptions in the high-volatile *C* bituminous group.

From:[26] Schmidt, R. A., "Origin and Properties of Coal," Coal in America, McGraw Hill, 1979, p. 36.

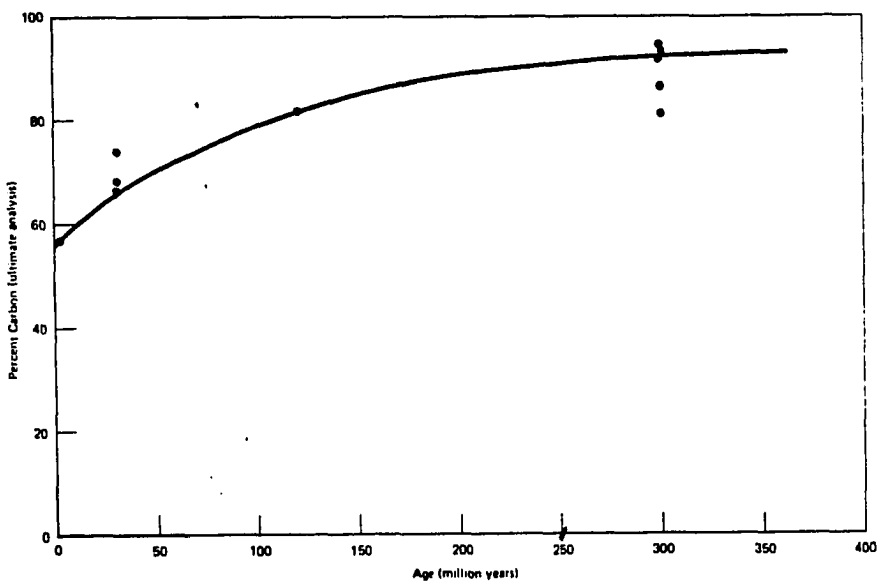



FIGURE 3. Relationship of carbon content of coals to geologic age. (From I. A. Williamson, Coal Mining Geology, Oxford University Press, London, 1967.)

components.[28] However, further classification of macerals or petrographic components are related to the methods applied for microscopic observation. As a result of different methods, there is a difference between U.S. and European coal researchers on this issue. In the United States (1920) R. Thiessen[29,30,31] used translucency properties to classify coal. In his research, Thiessen prepared coal samples of 5-15 $\mu$ in thickness and then examined the samples in transmitted light.[32] Furthermore, he classified the coal components as (1) anthraxylon, (2) attritus, (3) fusain. This classification depended on the translucent appearance in the coal.

(a) Anthraxylon: Anthraxylon's appearance in transmitted light varies from yellowish-orange to orange, red, reddish-brown, and finally to dark brown; and its composition is recognized to be from undisintegrated wood and bark of plants such as stems, branches and roots.

(b) Attritus: The appearance of atttritus in transmitted light varies from yellow to yellow-orange and reddish brown; and its composition is mostly from more resistant plant and organic substances which remained after the biochemical process and have been changed less in their compounds during the biochemical process.

(c) Fusain: This group of macerals is opaque to transmitted light and is similar to charcoal and is commonly derived from wood. Fusain is noncoking and has less heating value compared to anthraxylon and attritus.

In 1919 in England, Marie D. Stopes used reflection properties in order to classify the coal.[33] She polished the coal sample either

in lump or granule form, then immersed it in resin. The difference in reflectance of the various coal constituents makes possible their recognition from the polished surface. Furthermore, she classified coals as (1) vitrain, (2) clarin, (3) durain, and (4) fusain. This terminology is derived from the French language: "vitro" means glass; "clara" means bright; "dur" means hard; and finally, "fusain" means charcoal. Comparing these classifications, vitrain is analogous to anthraxylon which com prises between 70-90% of any coal bed. Clarin and durain are found to be attritus in Thiesson's classification. And, finally, fusain in both classifications covers the opaque matter of the coal components.

Table (2)[23] shows these two classifications which are based on petrographic study. Column 1 shows the appearance of transmitted light of the macerals. Column 2 shows Thiessen's classification; and column 3 shows the appearance of the macerals in reflected light. Finally, column 4 shows the lists of terminology used for macerals in both transmitted light and reflected light. As Table 2 indicates, the color appearance in transmitted light becomes darker when coal rank increases, and in reflected light the color of coal becomes lighter when rank of coal incrases.

3. Structure and Compounds of Coal

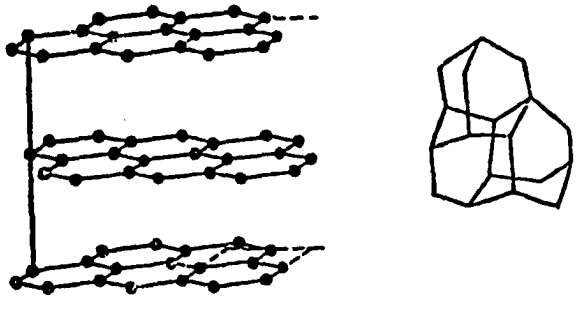
Studies of the structure of coal indicate that coal is primarily graphite, but others argue that coal has a diamond-like structure (Figure 4).[34] The results depended on the methods applied for recognition of the coal structure. Both of these theories were based on oxidation of coal by different compounds. The first groups used

Table 2.

Description of Macerals in Thiessen-Bureau of Mines System and Comparison with Stopes-Heerlen System

| Appearance in Transmitted Light[a] | Thiessen System | Appearance in Reflected Light[a] | Maceral | |
|---|---|---|---|---|
| Yellowish orange to dark red; material defined as collinite in RL may show structure in TL | Anthraxylon and humic matter | Groundmass for other macerals; often cell filling of telinite; no visible structure, gray to yellowish white | Vitrinite | Collinite |
| | | Occurs with collinite in discrete bands; shows cell structure; gray to yellowish white | | Telinite |
| Golden-yellow to reddish brown | Spores and pollen | Elongate, discrete bodies; dark gray to light gray | Exinite | Sporinite |
| Orange-yellow to rust | Cuticles | Narrow bands one edge of which is often serrate, dark gray to light gray | | Cutinite |
| May sometimes show cell structure, yellow to orange | Algal remains | Derived from algae; weaker reflectivity than associated vitrinite and sporinite | | Alginite |
| Yellow to reddish orange | Resinous and waxy substances | Discrete, small bodies; round, oval, or rod-shaped; black to gray | | Resinite |
| Generally opaque; in very thin sections dark brown | Opaque matter, brown matter (in part) | Variable form; finely to coarsely granular; light to white | Inertinite | Micrinite |
| Opaque | Fusain | Discrete lenses, bands, and fragments, good cellular structure; yellowish white | | Fusinite |
| Orange-red to opaque | Fusain (in part), brown matter (in part) | Intermediate between vitrinite and fusinite; cell structure not as well defined as fusinite; light gray to white | | Semifusinite |
| Dark red-brown to opaque | Fusain (in part), brown matter (in part) | Round or oval bodies or interlaced fibrous masses; light gray to yellowish white | | Sclerotinite |

From:[23] Wen, C. Y. and Stanley, Lee E., Coal Conversion, 1979, p. 8.



Graphite Diamond

FIGURE 4

From: Whitehurst, D. D., Coal Liquefaction (Academic Press, 1980), p. 9.

$HNO_3$, $K_2Cr_2O_7$, $HNO_3$, $KMNO_4$-OH, and they came to the conclusion from the reaction that coal must contain aromatic structures which are close to the graphite structures.[35] On the other hand, those researchers which used NaOH/OH have come to the conclusion that coal must contain a large amount of aliphatic carbon which is close to the diamond structure.[36] X-ray techniques were also applied in order to confirm whether the structure of coal is aromatic or less aromatic; but this technique, like the oxidation method, has given conflicting results. In 1958 P. B. Hirsh reported that more than 80 percent of the carbon was arranged in an aromatic structure order.[37] But in 1959, S. Ergun and W. Tiesun, by using the same method (x-ray), reported coal is less aromatic and more likely aliphatic.[38] In the same year, R. A. Fiedel published a paper in a fuel magazine and indicated, by using an ultraviolet technique, that coal cannot be aromatic and must be an aliphatic structure.[39] In 1973 A. Pines, by applying a nuclear magnetic resonance (NMR) technique, confirmed there is a correlation between the H/C ratio and the percentage of aromatic carbon (Figure 5).[40] He indicated that, as the rank of coal increased, the aromatic carbon content increased, too; but the H/C ratio decreased. The aromatic carbon content for anthracite becomes 90% and for lignite 50-60%. (Table 3 shows H/C ratios for paraffins, olefins, and aromatic structures.) Finally, the most aceptable structures of coal were presented by Given[41] and Wiser.[42] In Given's structure (Figure 6), the structures do not really represent the true structure of coal. Rather, it is representative of the kind of structure which one can expect to see in coal. However, Wiser's structure (Figure 7) is a more complicated one but has been more accepted

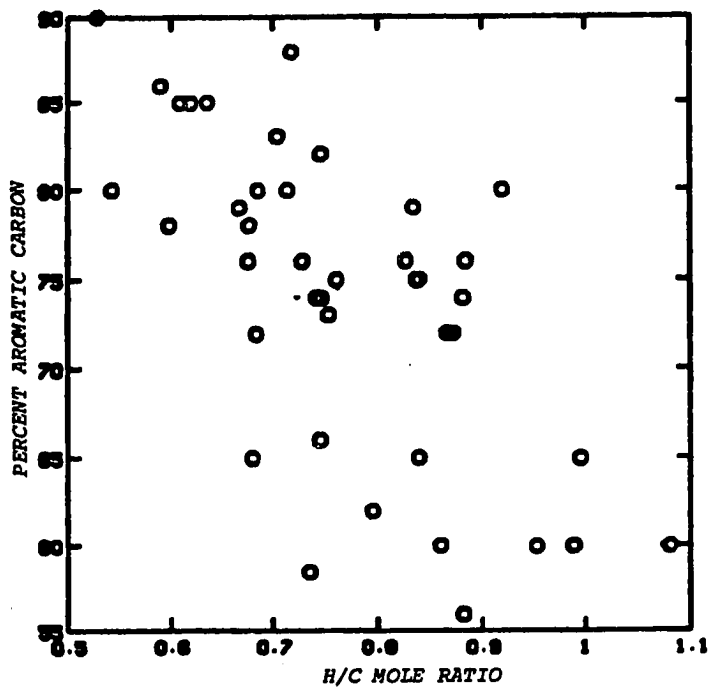



FIGURE 5. Aromatic Carbon vs. H/C

From: Pines, A., Journal of Chemical Physics, 1973, Vol. 59, p. 569.

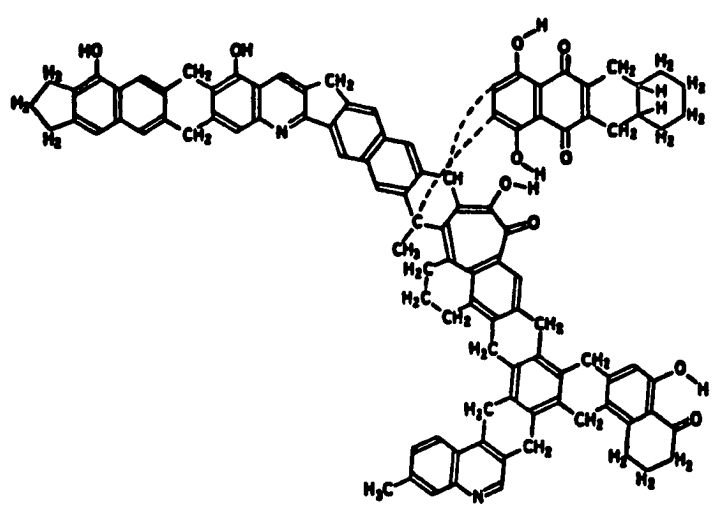


FIGURE 6. Proposed Structural Elements of Coal by Given.

From: Whitehurst, D. Duayne, Mitchell, O., Thomas and Farcasiu, Malvina, Coal Liquefaction, 1980, p. 21-22.

TABLE 3

Hydrogen/Carbon Atom Ratios in Hydrocarbons

| Hydrocarbons | H/C Ratio | Normal State |
|---|---|---|
| Paraffins | | |
| Methane | 4.0 | G |
| Ethane | 3.0 | G |
| Propane | 2.67 | G |
| Butane | 2.5 | G |
| Isooctane | 2.25 | L |
| Decane | 2.2 | L |
| Octadecane | 2.1 | S |
| Olefins | 2.0 | G, L |
| Acetylene | 1.0 | G |
| Aromatics | | |
| Benzene | 1.0 | L |
| Toluene | 1.143 | L |
| Naphthalene | 0.80 | S |
| Anthracene | 0.71 | S |
| Hexacene | 0.62 | S |
| Gasoline | 1.78 | L |
| Fuel oil | 1.56 | L |
| Coals (dry, ash-free) | | |
| Lignite | 0.87 | S |
| Subbituminous | 0.87 | S |
| Bituminous | 0.75 | S |
| Anthracite | 0.34 | S |

From: Wen, C. Y., Coal Conversion (Addison-Wesley Company, Inc., 1979), p. 319.

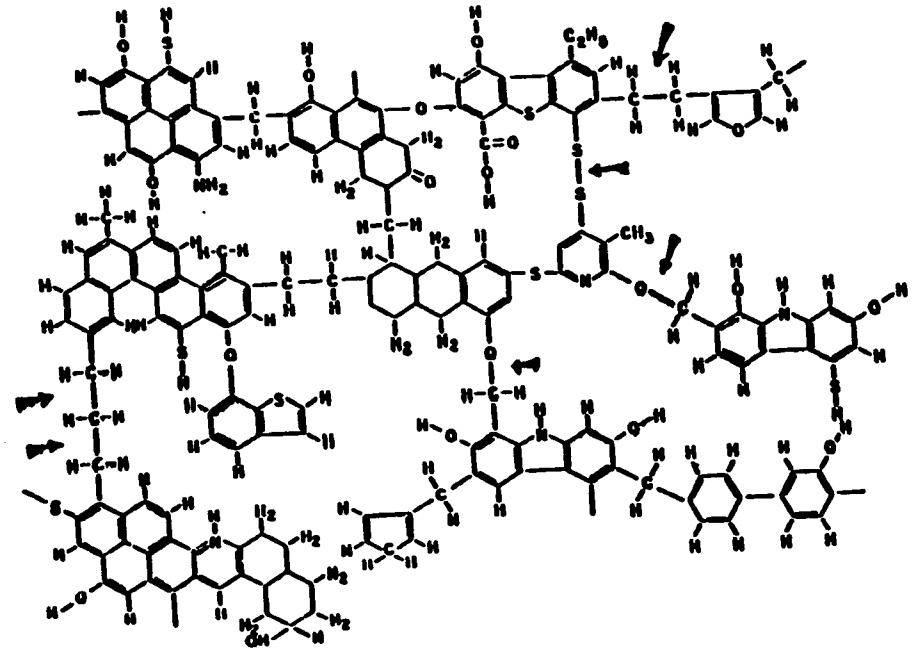


FIGURE 7. Representation of Functional Groups in Coal (2-26). Arrows indicate weak bonds.

From: Whitehurst, D. Duayne, Mitchell, O., Thomas and Farcasiu, Malvina, Coal Liquefaction, 1980, p. 21-22.

recently by many coal researchers around the world. In Wiser's structure, the weakest bonds have been shown by arrows. However, some coal researchers do not agree with him. Furthermore, in both cases, coal has a more aromatic arrangement of hydrocarbon than aliphatic.

Knowing the structure of coal is very important in the chemical comminution, liquefaction and gasification processes because it provides enough knowledge about the reactions that take place in order to break the coal and convert it to liquid or gas.

4. Compounds of Coal

The major elements commonly found in coal are carbon, hydrogen, nitrogen, oxygen and sulfur. Among these, elements carbon and hydrogen are the two most important elements of coal. The percentage of carbon and hydrogen in coal depends on their rank. As rank increases the percentage of carbon increases, but hydrogen decreases. As seen in Figure 8, lower ranks of coal (lignite and subbituminous) have a higher percentage of hydrogen than higher ranks of coal (anthracite).

Nitrogen is a minor element in coal ranging from approximately 0.5 to at most 2% by weight in coal. As Figure 9 indicates, higher ranks of coal (anthracite) have a lower percentage of nitrogen when compared to lower ranks of coal such as bituminous or subbituminous. The percentage of oxygen in coal can be up to 30% by weight. Like the hydrogen and nitrogen content in coal, the percentage of oxygen in anthracite is very low but in lignite is very high (approximately 30%---Figure 10).

Recently, sulfur in coal has become one of the important issues for coal miners. Coal combustion, either for generating

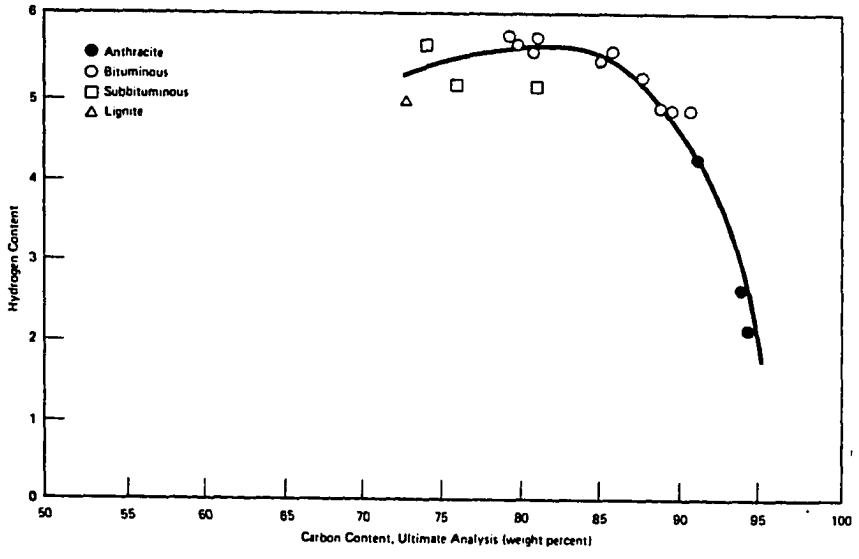



FIGURE 8. Relationship of hydrogen content to carbon content for coals of varying rank. (From: Schmidt, R. A., Coal in America, McGraw Hill Publication Company, 1979, p. 32.

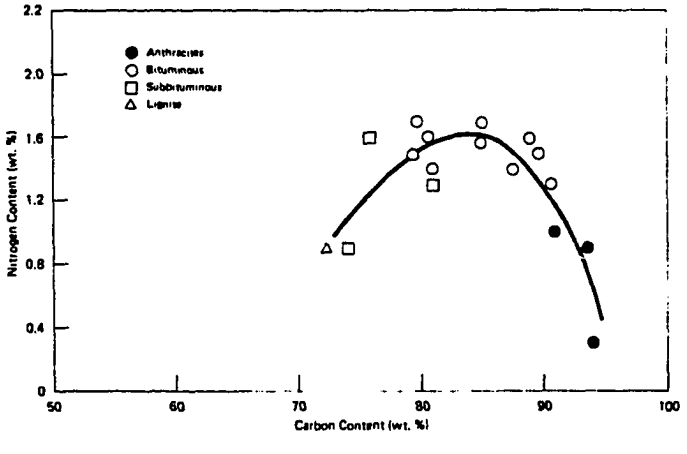



FIGURE 9. Relationship of nitrogen content to carbon content in coals of varying rank. (From: Schmidt, R. A., Coal in America, McGraw Hill Publication Company, 1979, p. 33.

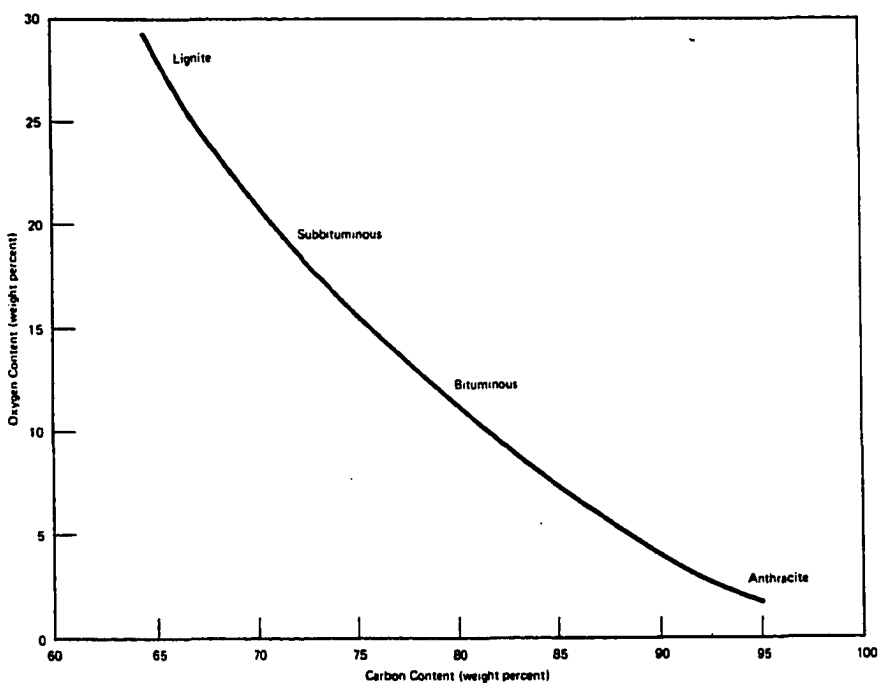



FIGURE 10. Continuous variation in coal composition. (From: Schmidt, R. A., Coal in America, McGraw Hill Publication Company, 1979, p. 31.

electricity or converting coal to oil and gas, causes $SO_2$ emission which is one of the most unpleasant and harmful of the common pollutant gases. Sulfur in coal as a waste and useless material increases the cost of transportation of coal and at the same time reduces the salability of coal. Up to now, several researches have been performed on the distribution and quantity of sulfur in coal. The results indicated that the primary forms of sulfur in coal are:

(1) Inorganic sulfur including:

  (a) pyrite ($FeS_2$ cubic) or marcasite ($FeS_2$, orthorhombic)

  (b) sulfate sulfur ($CaSO_4$, $2H_2O$)

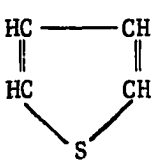
(2) Organic sulfur including:

  (a) thiol or mercaptan R-S-H

  (b) thio-ether or sulfide R-S-R'

  (c) disulfide R-S-S-R

  (d) aromatic systems containing the thiophene ring




The source of sulfur in coal is recognized to be the original plants which normally contained between 0.2 and 0.5% sulfur. The higher percentage of sulfur in coal is caused by microorganisms, particularly bacterial, activities in the organic materials. As Figure 11 shows, during the biochemical period and after the deposition of the organic substance in the ocean which contains some amount of sulfate, especially sulfate sulfur $CaSO_4$, the bacteria use part of the organic

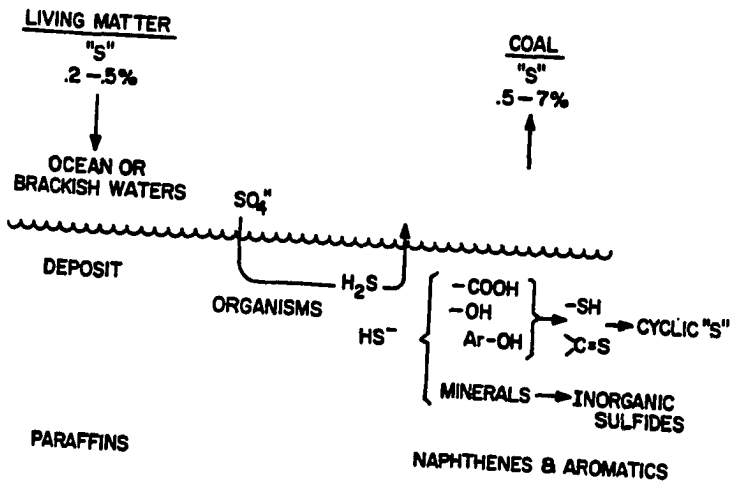



FIGURE 11. Origin of Organic Sulfur in Coal.

From: Whitehurst, Duayne, D. Mitchell, Thomas, O and Farcasiu, Melvina, Coal Liquefaction (Academic Press, 1980), p. 19.

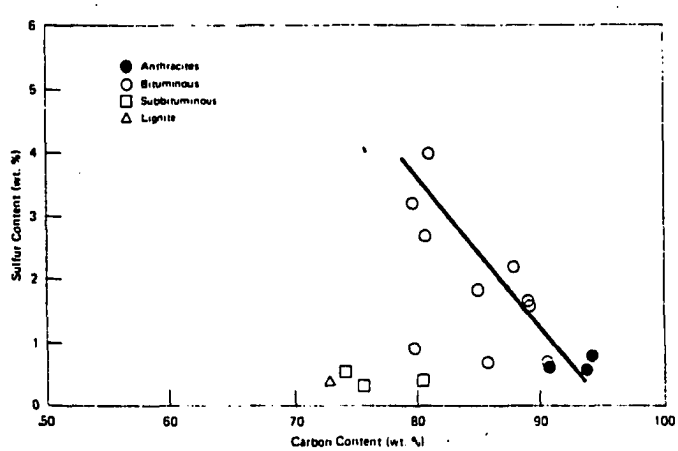



FIGURE 12. Relationship of sulfur content to carbon content in coals of varying rank. (From Steam, Babcock & Wilcox Company, New York, 1972. In Schmidt, R. A., "Coal in America," McGraw-Hill, 1979, p. 33.)

substance which has $SO_4$ as a source of oxygen. At the same time, iron ions present in water help to precipitate producing pyrite. As a result of these actions and reactions for a long period of time (geological period), the sulfur percentage in coal becomes higher than its original compounds. The sulfur content in coal is direct related to the percentage of carbon in coal. The relation of carbon content of various coals to the sulfur content is shown in Figure 12.

In recent efforts, Polish coal researchers[44] using eighteen solvents at room temperature (18-22°C) were able to identify more than 300 compounds. (Table 4 shows the results of their experiment.) This experiment used high-volatile bituminous coal. However, it is possible by using different techniques and different coals, the number of compounds becomes more or less; but, early work in 1945 by H. H. Lowry,[45] indicated at atmospheric pressure from low to high temperature carbonization of coal, there are more than 300 compounds in coal (386 compounds). Besides those compounds, there are some minerals which are associated with coal but not necessarily during the process of coalification. The majority of them were recognized by present technology and are presented in Table 5.[23]

## B. PHYSICAL AND MECHANICAL PROPERTIES OF COAL

There have been many studies by many investigators using different methods in order to determine the physical and mechanical properties of coal. Among these techniques are: x-ray diffraction, ultraviolet and visible absorption, reflectance and refractive index, infrared absorption, electron spin resonance, proton spin resonance,

TABLE 4. Substances identified in high-volative bituminous coal.

| $Z^a$ | First member of homologous series | Carbon numbers experimentally determined | Possible structures |
|---|---|---|---|
| 1 | 2 | 3 | 4 |
| | | | *Hydrocarbons* |
| −6 | $C_6H_6$ | 9–11, 15, 17–18 | benzene, dodecahydrophenanthrene, perhydrochrysene |
| −8 | $C_9H_{10}$ | 9–11, 18–19 | indane, tetrahydronaphthalene, hexahydrochrysene |
| −10 | $C_9H_8$ | 9–14, 17–18 | indene, dihydronaphthalene, octahydrophenanthrene |
| −12 | $C_{10}H_8$ | 10–18 | naphthalene, azulene, hexahydroanthracene |
| −14 | $C_{12}H_{10}$ | 12–16, 18–19 | diphenyl, acenaphthene, dihydrophenalene, tetrahydrophenanthrene |
| −16 | $C_{12}H_8$ | 13–18 | acenaphthylene, diphenylene, fluorene |
| −18 | $C_{14}H_{10}$ | 14–18 | anthracene/phenanthrene |
| −20 | $C_{14}H_{18}$ | 14–15, 17–19 | methanophenanthrene, phenylnaphthalene |
| −22 | $C_{16}H_{10}$ | 16–19 | pyrene/fluoranthene, aceanthrylene, dihydronaphthacene |
| −24 | $C_{18}H_{12}$ | 18, 20–21 | tetracene/chrysene, tetraphene |
| −26 | $C_{18}H_{10}$ | 18–20 | benzo[*ghi*] fluoranthene, phenylphenanthrene |
| −28 | $C_{20}H_{12}$ | 20–21, 23 | benzopyrene, perylene, naphthofluorene |
| −34 | $C_{24}H_{14}$ | 24 | dibenzopyrene |
| | | | *Nitrogen Compounds CHN* |
| −3 | $C_4H_5N$ | 7–8, 11 | pyrrole |
| −5 | $C_5H_5N$ | 7–15 | pyridine, aniline |
| −7 | $C_7H_7N$ | 7–9, 14 | azaindane, tetrahydroquinoline |
| −9 | $C_8H_7N$ | 8–15 | indole, dihydroquinoline, methylbenzonitrile |
| −11 | $C_9H_7N$ | 9–10, 12–15 | quinoline, naphthylamine |
| −13 | $C_{11}H_9N$ | 11–16 | phenylpyridine, phenylaniline, tetrahydroacridine |
| −15 | $C_{11}H_7N$ | 11–15 | carbazole, dihydroacridine |
| −17 | $C_{13}H_9N$ | 13–17, 19 | acridine, phenylindole, benzoquinoline |
| −19 | $C_{14}H_9N$ | 13–19 | benzo[*def*] carbazole, methylenephenanthridine, fluorenenitrile |
| −21 | $C_{15}H_9N$ | 15–21 | azapyrene, benzocarbazole, azafluoranthene |
| −23 | $C_{17}H_{11}N$ | 17–22 | benzacridine |
| −25 | $C_{17}H_9N$ | 18–23 | azabenzofluoranthene, benzofluorenenitrile |
| −27 | $C_{19}H_{11}N$ | 19–22 | azabenzopyrene |
| −29 | $C_{21}H_{13}N$ | 22–23 | azapicene |
| −31 | $C_{21}H_{11}N$ | 21–24 | azabenzoperylene |
| −33 | $C_{23}H_{13}N$ | 24 | azadibenzopyrene |
| | | | *Nitrogen Compounds $CHN_2$* |
| −6 | $C_8H_{10}N$ | 9–10, 13 | diazatetrahydronaphthalene, azatetrahydroquinoline |
| −8 | $C_7H_6N_2$ | 9–10 | diazaindene |
| −10 | $C_8H_6N_2$ | 10 | diazanaphthalene |
| −12 | $C_{10}H_8N_2$ | 10, 13 | bipyridine |
| −14 | $C_{11}H_8N_2$ | 11–14 | diazafluorene |
| −16 | $C_{12}H_8N_2$ | 11–14 | diazaanthracene/phenanthrene |
| −18 | $C_{13}H_8N_2$ | 19 | diazabenzofluorene, diazaphenylnaphthalene |
| −20 | $C_{14}H_8N_2$ | 15–18 | diazapyrene, diazaaceanthrylene |
| −22 | $C_{16}H_{10}N_2$ | 19–20 | diazachrysene, diazanaphthacene |
| −24 | $C_{16}H_8N_2$ | 20 | diazabenzofluoranthene |
| −26 | $C_{18}H_{10}N_2$ | 20, 22 | diazabenzopyrene |
| | | | *Oxygen Compounds CHO* |
| −6 | $C_6H_6O$ | 8–9, 11, 13 | phenol |
| −8 | $C_8H_8O$ | 7, 9, 11–13 | acetophenone, indanol |
| −10 | $C_8H_6O$ | 11–15, 17 | benzofuran, indenol, indanone, chromene |
| −12 | $C_{10}H_8O$ | 12–15 | naphthol, phenylfuran |
| −14 | $C_{11}H_8O$ | 11–14, 16–17 | indenofuran, phenylphenol, diphenyl ether |
| −16 | $C_{12}H_8O$ | 12–16, 18, 21 | dibenzofuran, naphthofuran, hydroxyfluorene, xanthene |
| −18 | $C_{14}H_{10}O$ | 14–18 | hydroxyphenanthrene/anthracene |
| −20 | $C_{16}H_{12}O$ | 13, 16–19 | hydroxyphenylnaphthalene, diphenylfuran |
| −22 | $C_{16}H_{10}O$ | 18–19, 21 | benzonaphthofuran, hydroxypyrene |
| −24 | $C_{18}H_{12}O$ | 24 | hydroxytetracene/chrysene, naphthenophenanthrenenofuran |

| $Z^a$ | First member of homologous series | Carbon numbers experimentally determined | Possible structures |
|---|---|---|---|
| 1 | 2 | 3 | 4 |
| | | | *Oxygen Compounds $CHO_2$* |
| −6 | $C_6H_6O_2$ | 7–10 | dihydroxybenzene, methoxyphenol |
| −8 | $C_8H_8O_2$ | 9, 13, 16 | hydroxyacetophenone, benzoic acid, hydroxyindanol |
| −12 | $C_{10}H_8O_2$ | 14–15 | dihydroxynaphthalene |
| −14 | $C_{12}H_{10}O_2$ | 14–17 | biphenol |
| −16 | $C_{12}H_8O_2$ | 13–15, 17–19 | hydroxydibenzofuran, dihydroxyacenaphthylene |
| −18 | $C_{14}H_{10}O_2$ | 14–16, 17–20 | dihydroxyanthracene, flavanone |
| −20 | $C_{16}H_{12}O_2$ | 17–18 | dihydroxyphenylnaphthalene, anthraquinone, flavone |
| −22 | $C_{17}H_{12}O_2$ | 20 | hydroxybenzoxanthene, dihydroxypyrene |
| −26 | $C_{18}H_{10}O_2$ | 21 | benzanthraquinone |
| −30 | $C_{21}H_{12}O_2$ | 21 | benzopyrene carboxylic acid, benzopyrenequinone |
| | | | *Oxygen-Nitrogen Compounds CHON* |
| −5 | $C_5H_5ON$ | 6, 8–12 | hydroxypyridine, aminocresole |
| −7 | $C_8H_9ON$ | 8–11 | hydroxyazaindane, acetylpyridine |
| −9 | $C_8H_7ON$ | 8–9, 11, 13–14 | hydroxyindole, aminobenzofuran |
| −11 | $C_9H_7ON$ | 9, 11, 13 | hydroxyquinoline |
| −13 | $C_{11}H_9ON$ | 11, 13 | hydroxyphenylpyridine, hydroxytetrahydroacridine |
| −15 | $C_{12}H_9ON$ | 12–16 | hydroxycarbazole, aminodibenzofuran, azaxanthene |
| −17 | $C_{13}H_9ON$ | 14–19 | hydroxyacridine, aminohydroxyphenanthrene, x*H*-azaphenanthrenone |
| −19 | $C_{15}H_{11}ON$ | 15–16, 20 | hydroxyphenylquinoline, 1*H*-2 oxa-xaza-pyrene |
| −21 | $C_{15}H_9ON$ | 17, 19, 20 | hydroxyazapyrene, aminobenzonaphthofuran |
| −23 | $C_{17}H_{11}ON$ | 22 | hydroxybenzacridine, aminohydroxytetracene |
| | | | *Oxygen-Nitrogen Compounds $CHON_2$* |
| −10 | $C_8H_6ON_2$ | 9 | hydroxydiazanaphthalene |
| −12 | $C_{10}H_8ON_2$ | 14 | hydroxybipyridine |
| −16 | $C_{12}H_8ON_2$ | 15–18 | hydroxydiazaanthracene |
| −18 | $C_{14}H_{10}ON_2$ | 18 | hydroxydiazaphenylnaphthalene, dipyridylfuran |
| −22 | $C_{16}H_{10}ON_2$ | 20 | hydroxydiazachrysene |
| | | | *Oxygen-Nitrogen Compounds $CHO_2N$* |
| −11 | $C_9H_7O_2N$ | 14 | dihydroxyquinoline |
| −13 | $C_{11}H_9O_2N$ | 14, 17 | dihydroxyphenylpyridine |
| −15 | $C_{12}H_9O_2N$ | 15, 17, 20 | dihydroxycarbazole, hydroxyazadibenzofuran |
| | | | *Other Oxygen-Nitrogen Compounds* |
| −14 | $C_{11}H_8O_2N_2$ | 17 | dihydroxydiazafluorene |
| −11 | $C_{10}H_9N_3O$ | 10, 14 | hydroxyaminobipyridine |
| | | | *Sulphur Compounds* |
| −8 | $C_{10}H_{12}S$ | 10 | indanethiol |
| −10 | $C_8H_6S$ | 10 | benzothiophene |
| −12 | $C_{10}H_8S$ | 10 | naphthalenethiol |
| −14 | $C_{11}H_8S$ | 16 | indenethiophene |
| | | | *Oxygen-Sulphur Compound CHOS* |
| −12 | $C_{11}H_{10}OS$ | 18 | hydroxynaphthenebenzothiophene |
| | | | *Nitrogen-Sulphur Compound CHNS* |
| −10 | $C_{10}H_7NS$ | 15 | thiopheneindole |

a In $C_nH_{2n-z}$ or in $C_nH_{2n-z}X$

From: Dantua, Bodzek and Marzec, Anna, "Molecular Components of Coal and Coal Structure," Department of Petroleum and Coal Chemistry, Fuel, Vol. 60, January 1981, p. 47-51.

TABLE 5. Minerals Associated with Bituminous Coals

| Group | Species | Formula |
|---|---|---|
| Shale | Muscovite<br>Hydromuscovite<br>Illite<br>Bravaisite<br>Montmorillonite | $(K, Na, H_3O, Ca)_2(Al, Mg, Fe, Ti)_4(Al, Si)_8O_{20}(OH, F)_4$ |
| Kaolin | Kaolinite<br>Livesite<br>Metahalloysite | $Al_2(Si_2O_5)(OH)_4$ |
| Sulfide | Pyrite<br>Marcasite | $FeS_2$ |
| Carbonate | Ankerite<br>Ankeritic calcite<br>Ankeritic dolomite<br>Ankeritic chalybite | $(Ca, Mg, Fe, Mn)CO_3$ |
| Chloride | Sylvine<br>Halite | KCl<br>NaCl |
| Accessory minerals | Quartz | $SiO_2$ |
| | Feldspar | $(K, Na)_2O \cdot Al_2O_3 \cdot 6SiO_2$ |
| | Garnet | $3CaO \cdot Al_2O_3 \cdot 3SiO_2$ |
| | Hornblende | $CaO \cdot 3FeO \cdot 4SiO_2$ |
| | Gypsum | $CaSO_4 \cdot 2H_2O$ |
| | Apatite | $9CaO \cdot 3P_2O_5 \cdot CaF_2$ |
| | Zircon | $ZrSiO_4$ |
| | Epidote | $4CaO \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot H_2O$ |
| | Biotite | $K_2O \cdot MgO \cdot Al_2O_3 \cdot 3SiO_2 \cdot H_2O$ |
| | Augite | $CaO \cdot MgO \cdot 2SiO_2$ |
| | Prochlorite | $2FeO \cdot 2MgO \cdot Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ |
| | Diaspore | $Al_2O_3 \cdot H_2O$ |
| | Lepidocrocite | $Fe_2O_3 \cdot H_2O$ |
| | Magnetite | $Fe_3O_4$ |
| | Kyanite | $Al_2O_3 \cdot SiO_2$ |
| | Staurolite | $2FeO \cdot 5Al_2O_3 \cdot 4SiO_2 \cdot H_2O$ |
| | Topaz | $(AlF)_2SiO_4$ |
| | Tourmaline | $H_9Al_3(BOH)_2Si_4O_{19}$ |
| | Hematite | $Fe_2O_3$ |
| | Penninite | $5MgO \cdot Al_2O_3 \cdot 3SiO_2 \cdot 2H_2O$ |

From: Wen, C. Y. and Stanley, Lee E., Coal Conversion, 1979, p. 36.

electrical conductivity, diamagnetic susceptibility, dielectric constant, sound velocity, porosity, strength and heating value.[46] These researches are due to the higher demand of coal and the fact that the utilization and workability of coal is partly dependent on the physical and mechanical properties of coal.

Among the physical and mechanical properties determined to date, the following are more valuable in mining, preparation and utilization of coal.

(a) Porosity: Coal is a porous rock with porosities which can range from 2 to 20% depending on the rank of the coal, structure and deposition of the coal. Among these factors, there is a little evidence that shows a correlation between the rank and porosity of coal. As Figure 13[24] indicates, the porosity of coal is high up to 85% carbon content which covers lignite and subbituminous. Between 85 and 91% carbon content, which covers bituminous, the porosity is its lowest value. Above 91%, the porosity is again as high as subbituminous (20%). This property mainly depends on the type of structure as suggested by Hirsh in 1954 who used an x-ray diffraction technique.[47] This is illustrated in Figure 14. Hirsh defined the structure of coal as follows:

1. Open structure. This structure is described for a low rank of coal (up to 85% carbon in coal) and has porosity as high as 20%. Very seldom are the layers connected to each other. Lignite and subbituminous have been described to have this type of structure.

2. Liquid structure. In this type of structure, some of the layers are connected to each other through the cross link; and, as a

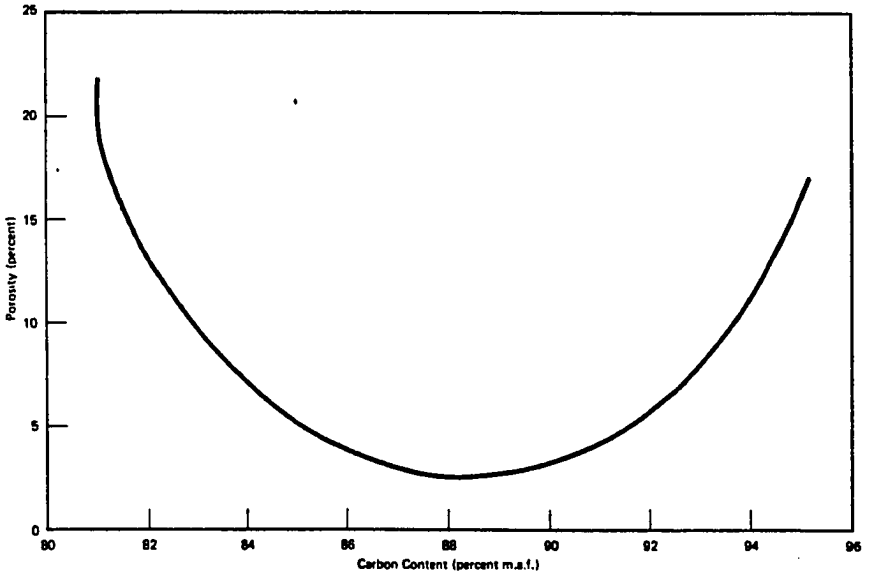



FIGURE 13. Variation in coal porosity with rank. (From J. G. King, and E. T. Wilkins,"The Internal Structure of Coal," Proc. Conf. Ultra-Fine Structure of Coals and Cokes, BCURA, p. 46-56, 1944. In Schmidt, R. A., Coal In America, McGraw-Hill, 1979, p. 28.)

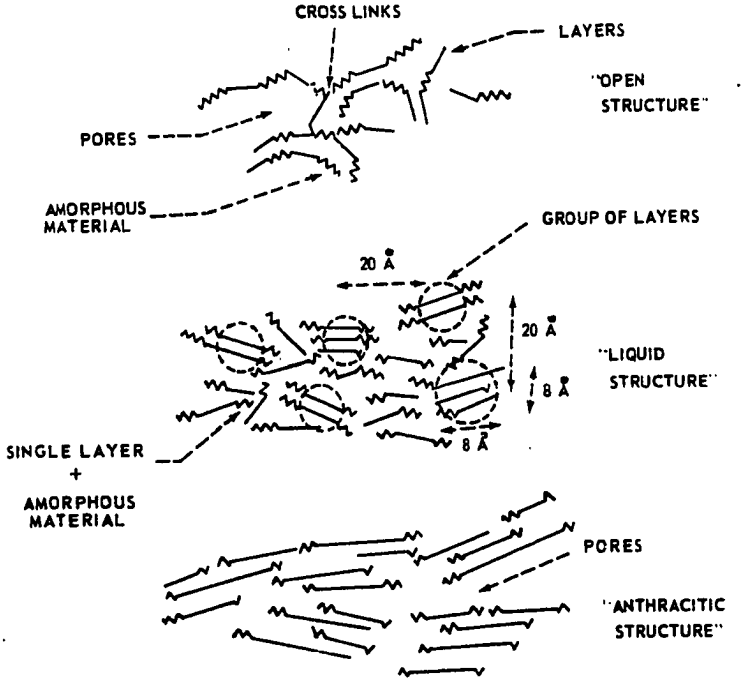



FIGURE 14. Schematic model of coal structure. (From Clarence, K., Analytical Methods for Coal and Coal Products, Academic Press, 1978, p. 126.)

result, the pore value is low so it has a low porosity. This structure has 85 to 91% carbon and this structure is similar to the bituminous coal structure.

3. Anthracitic structure. This structure again has no cross links between layers. As a result of the large pore volume, it has a higher porosity. Mostly this structure has been observed in high ranks of coal with high percent of carbon content (anthracite).

The porosity of coal has a significant role in chemical comminution, liquefaction and gasification processes. It is believed in those three processes that the chemical penetrates the coal and dissolves some of the mineral material through the pores of coal, or it reaches these minerals through the other discontinuities at the pore surface area which shapes the mineral materials.

In underground mining operations, porosity also plays a major role in the safety of mine operations. Recent events in Japan and the United States indicated the explosion of methane in underground coal mines caused the death of many mine workers. Usually, those coal reservoirs which are not near the surface or under light cover contain significant quantities of adsorbed methane in their natural state in the seam. As a result of this, during mining operations, as soon as methane contacts the air or oxygen, there would be an explosion and consequently cause a disaster in the mine. A knowledge of pore volume or the porosity of coals determines the extent and ease of diffusion of methane out of the pore structure during mining operations.

(b) Density: The density of coal is an important factor in the preparation of various coals or in the chemical comminution process

where the washability process becomes important in order to separate pure and solid coal from some impurity material such as pyrite or any other mineral material in the general case. However, it is very difficult to determine the true value of the density of coal because coal is a porous solid, and it is hard to determine the exact value of the volume. Therefore, measurements of coal density are apparent instead of true densities. As Figure 15[48] shows, the densities of coals range from 1.29 to approximately 1.6. The lowest density occurs in the range of about 85% carbon, which is believed to be bituminous.

(c) Strength: The strength of coal is one of the important mechanical properties of coal which has a major role in mining, particularly in the crushing and milling process in order to remove the impurities and fragment the coal. Up to now a number of laboratory tests have been applied to many different coal beds, and results of those tests have been used as the basis for theoretical analysis of coal strength. However, it would be unwise and unreasonable to obtain the data from strength analysis of coal in the laboratory and to believe that is the behavior of coal at 2000 or 3000 feet deep under tremendous overburden pressure compared with free coal in the laboratory. The strength analysis of coal can be made more accurate if one simulates the field conditions in the coal laboratory.

Up to now, both compression tests and tension tests have been applied to coal. The results of compression tests of coal in the laboratory have shown that strength can vary by as much as 30% from the strength of seam coal (field conditions).[49] Both of these methods are largely influenced by heterogeneity characteristics of coal and the

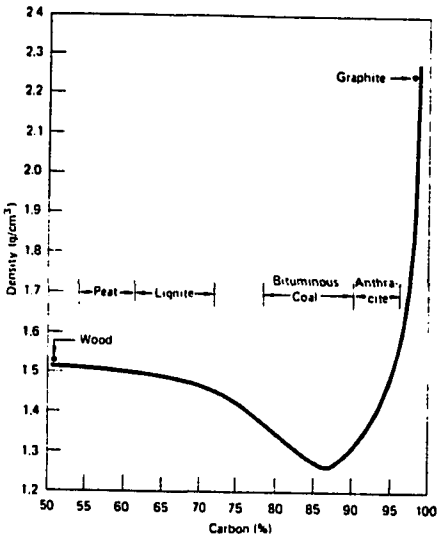



FIGURE 15. Relationship between apparent density and the rank of coal (as indicated by carbon content). (From I. A. Williamson, Coal Mining Geology, Oxford University Press, London, 1967.)

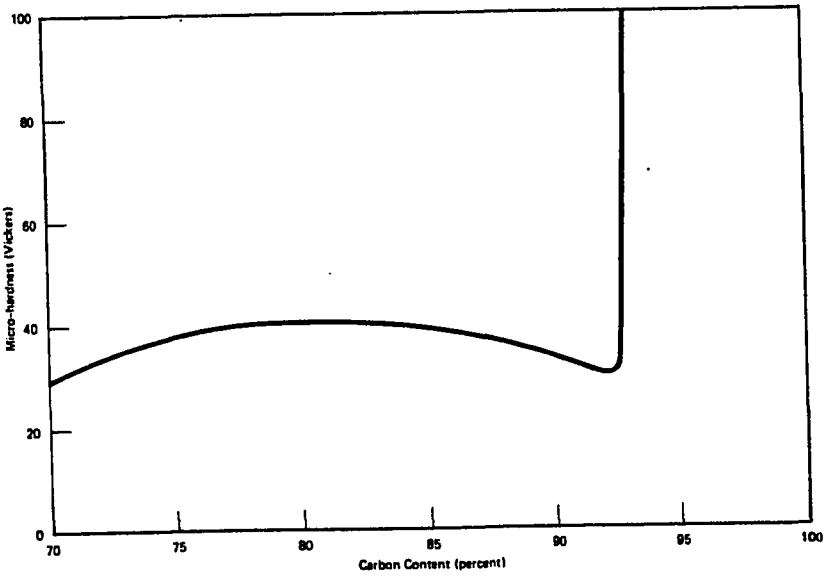



FIGURE 16. Variation in Vickers microhardness with coal rank. (From D. W. Van Krevelen, Coal, American Elsevier, New York, 1961.)

different conditions which exist between the field and the laboratory. As a result, none of the laboratory tests were able to represent and predict the behavior of seam coal. Furthermore, it was suggested by D. W. Vankrevelen[51] in 1961 that the strength of coal is mainly related to the hardness and friability of coal. Therefore, by measuring hardness and friability of coal, the strength of coal can be estimated. The hardness of coal in his proposal was determined by the Vickers microhardness test in which a pyramidal or spherical indention is made with some exact and precise amount of force for a specific period of time in the coal sample. Then the depth and area of penetration are taken as a measure of hardness. This test indicated (Figure 16) the maximum hardness is in coal which has 83% carbon and minimum in the coal that contains 90% carbon. Tests have shown coal which has above 90% carbon has elastic properties.

Friability is the tendency of coal to fragment under light force during transportation or storage of coal,[51] and friability can be determined by the impact strength index. The impact strength index is measured by dropping a steel plunger for a constant number of times into a coal sample at the base of a steel cylinder. As a result, the percentage of coal remaining in the initial size range after the test is called the impact strength index.

## C. RESOURCES AND RESERVES OF COAL IN THE UNITED STATES AND THE WORLD AND ITS FUTURE AS A SOURCE OF ENERGY

In January 1974 the United States Geological Survey published a bulletin[52] which indicated the total remaining coal resources in the

United States. It was estimated as 3968 billion tons and is distributed as shown in Table 6. Of the total identified coal, 91 percent is located at less than 1000 feet, 7.7 percent is between 1000 and 2000, and 1.3 percent is between 2000 and 3000 feet. Among 1731 billion tons (short tons), 1.1 percent is anthracite, 43.1 percent is low-volatile

TABLE 6: Coal Resources in the United States

| | Billions of Short Tons |
|---|---|
| Mapped and explored (Identified) | |
| 0 to 3000 feet deep | 1731 |
| Unmapped and unexplored (indicated and probable) | |
| 0-3000 feet deep | 1849 |
| 3000-6000 feet deep | 388 |
| Total remaining resources | 3968 |

bituminous coal, 28.1 percent is subbituminous and 27.7 percent is lignite (Table 7).

The Geological Survey bulletin defined reserve base for coal beds of specific depth and thickness in the mapped and explored (identified) resource category. It was defined as those coal beds with a minimum of 28 inches of thickness for bituminous and anthracite coal with 0 to 1000 feet overburden which could be suitable for both surface and underground mining methods and 60 inches or more in thickness for subbituminous and lignite with 0 to 120 foot overburden which is suitable for surface or open pit mining methods. The total amount of reserve base was estimated to be about 430 billion tons. Among mapped

TABLE 7

(a) Identified Coal in U.S.

| Depth | Percent | Billion short tons of coal |
|---|---|---|
| 0-1000 | 91 | 1575 |
| 1000-2000 | 7.7 | 134 |
| > 2000 | 1.3 | 22 |
| Total | 100.0 | 1731 |

(b) Different Rank of Identified Coal in U.S.

| Type of Coal | Percent | Billion short tons of coal |
|---|---|---|
| Anthracite | 1.1 | 19 |
| Bituminous | 43.1 | 746 |
| Subbituminous | 28.1 | 487 |
| Lignite | 27.7 | 479 |
| Total | 100.0 | 1731 |

and explored (identified) resources, only about 150 billion tons is practically minable with present mining methods. It is believed approximately 100 billion tons of the total 150 billion tons is suitable for the underground mining method and about 50 billion tons (short tons) is suitable for surface mining methods. This 150 billions tons of minable coal is called reserve or recoverable coal which can be distinguished from reserve base. It is interesting to note that this recoverable coal (reserve) is only 4 percent of the total coal estimated in the United States. Table 8 shows minable coal in the U. S. with regard to its rank.

Paul Averitt in U.S. Geological Survey Bulletin 1412, 1974, indicated that coal comprised 69 percent of the total estimated recoverable resource of fossil fuel in the U.S. while petroleum and natural gas together comprised 7 percent and oil in oil shale, which is not currently used as a fuel, counted for 23 percent of the total recoverable fossil fuel. The United States also has the largest recoverable reserves (25-28% of total world reserves). This is followed by the Soviet Union which accounts for 22 percent of the world reserves. However, the situation in world resources is different. In this category, 45 percent of the total world coal resource is located in the Soviet Union.[53,54] The total resource of coal in the Soviet Union is estimated to be 8.6 trillion tons. As Figure 17 indicates, about 90 percent of the total coal reserves are located in the Soviet Union, United States and China. As Figure 18 shows, the total possible coal resource in billion ton oil equivalent is estimated to be 26 times greater than the total possible oil resource around the world.

TABLE 8. Recoverable Coal in U.S.
(million tons)

| Rank | Surface Mining | Underground Mining | Total |
|---|---|---|---|
| Anthracite | 68 | 2,166 | 2,344 |
| Bituminous | 13,597 | 54,596 | 68,340 |
| Subbituminous | 24,318 | 32,320 | 56,227 |
| Lignite | 8,895 | -- | 8,895 |
| Total | 46,878 | 89,082 | 135,696 |

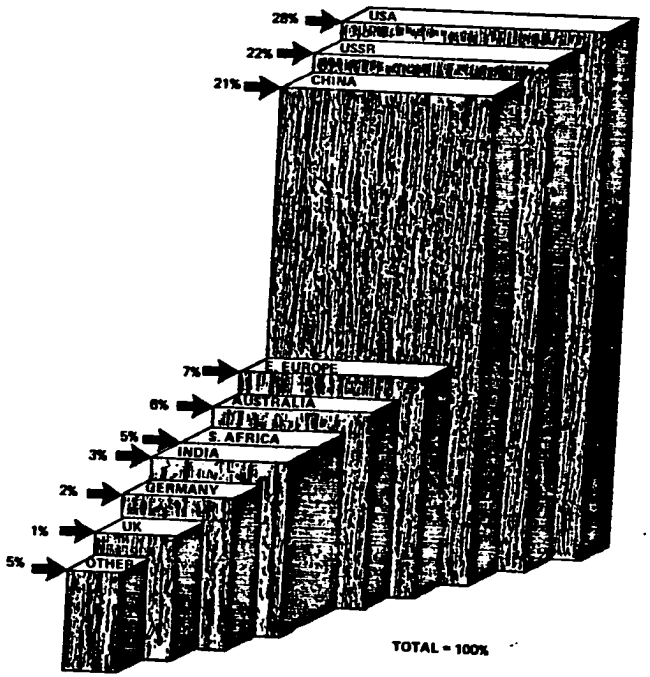



FIGURE 17

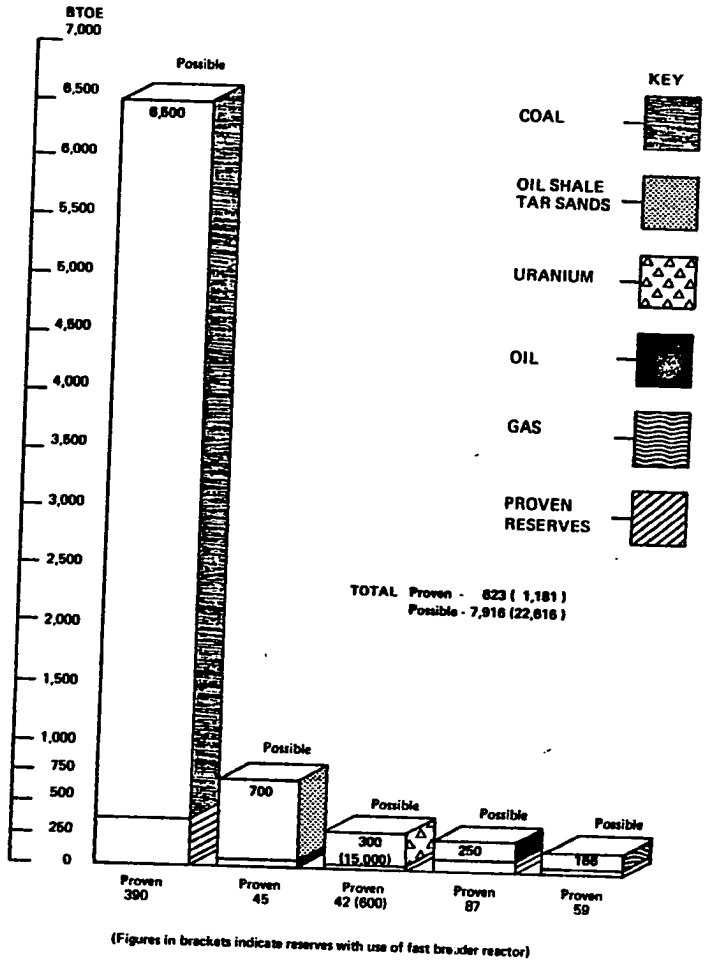



FIGURE 18

From Hedley, Don, World Energy, published by Facts on File, Inc., 1981, p. 40, 34.

Because of higher demand in energy, the role of coal as a major source of energy in the future is almost unavoidable. In 1979, the world used 6.9 billion tons oil equivalent (BTOE) which was 3.2 percent more than 1978 and four times larger than 1950. Among this figure in 1979, coal represented 28 percent, oil 45 percent, gas 19 percent, water 6 percent, and nuclear 2 percent. But this will change by the year 2000 when the demand for energy will be 75 percent higher than 1979. By the year 2000, coal will account for 37 percent of the total fossil fuel consumption while oil will account for 33 percent, gas for 17 percent, water 5 percent, and nuclear for 8 percent (Figure 19).[53] As Figure 18 shows, in 1979 the proven world equivalent of 623 billion tons of oil existed to meet the energy demand. It is interesting to note that the same year, the world used 6.9 billion tons of oil equivalent. It is projected by increasing the demand for energy by 2.7 percent each year up to the year 2000, that 32 percent of the present energy reserve would be gone and by the year 2010 80 percent and finally the world energy reserve at its present level would be lost by the year 2023.[55] Despite attempts made by many countries to reduce their dependency on energy, particularly on oil, there was only a little success in the United States, Switzerland, and Turkey between 1978-1979. In the same period, several countries in Europe and around the world were more dependent on oil than at any other time. Among them Denmark's dependency on oil accounted for 79% of total energy consumed by that country. Second was Japan with 70 percent, Italy 69 percent, Sweden 64 percent, Spain 61 percent and finally France with 60 percent.[56] The question arises whether or not the present fuel in common terms

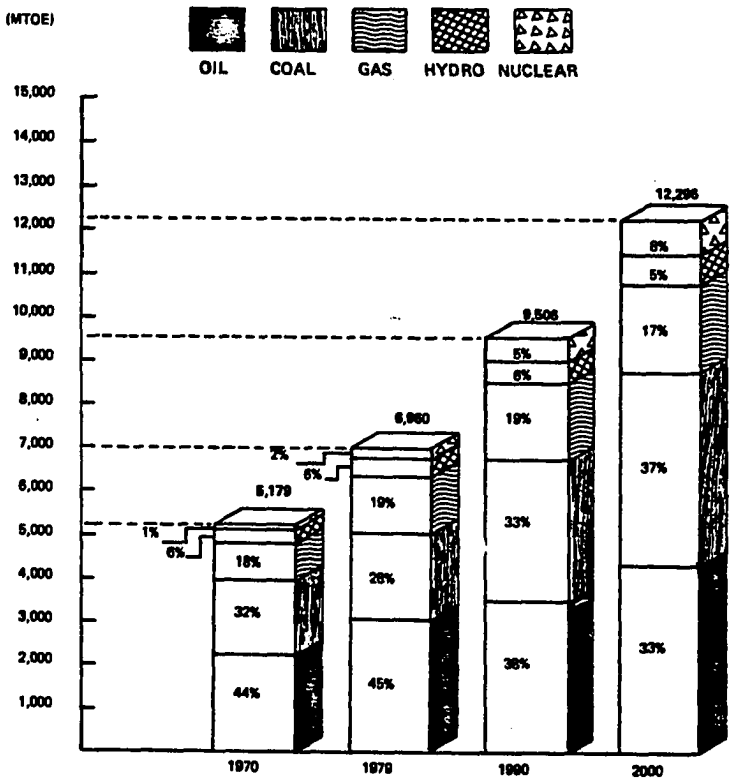



FIGURE 19

From: Hedley, Don, World Energy, published by Facts on File, 1981, p. 26.

which exists in the ground is enough to meet the future energy demand of humans. The answer is yes, but it has been shown in this research and indicated by many energy analysts that coal is going to play a major role in the near future. Coal has been called the "bridge to the future." Also, it has been shown (Figure 18) that the proven coal reserve is a few times larger than proven combined oil and several other possible sources of energy. Unmapped and unexplored coal (so-called coal resource) is more than twenty times larger than the oil resource. But it is doubtful the present forms of technology, especially mining methods, are adequate to produce the large amount of coal which many energy planners are predicting will be needed by the year 2000 in order to meet the energy needs in developed, less developed and nondeveloped countries. But there are not any other realistic alternatives except coal.

Unfortunately, in the last 30 years because of political and economic reasons, large discoveries of oil reservoirs in a short period, easy production and transportion of oil have brought the mining industries in general and coal mining in particular to the stage where they are at present. There are many problems in both open-pit and underground mining methods which are not suitable for large amounts of coal production in the near future. For example, it was proposed in 1976 by the United States government to increase U.S. coal production from 600 million tons to 1.2 billion tons by 1985. But in 1981, there had been only a 7 percent increase in coal production from 1976 production. It is doubtful that the goal will be achieved by 1985 mostly because of lack of high technology development in mining and environmental issues. Coal is a very complicated rock or substance difficult

to deal with. It is a dirty substance and in some cases has relatively high percentage of impurities.

Recently there were some attempts among coal researchers and miners, particularly in the United States (including the University of Oklahoma), to develop the technique called chemical comminution which can help achieve higher production with better quality. However, there are some practical and theoretical problems in this technique. Without further improvement, the result of chemical comminution cannot be better than open-pit and underground mining methods. Furthermore, since this technique is very new in its present form (started 1971), it is hoped more research and study will eliminate most of the problems in this type of mining in the near future and lead to higher production and better quality. As a result, the energy crisis may be reduced.

# CHAPTER III

## GENERAL PROPERTIES OF SUGGESTED SOLVENT

## ($CO_2$ + $H_2O$)

### A. $CO_2$, ITS PHYSICAL AND CHEMICAL PROPERTIES

$CO_2$ or carbon dioxide was first recognized as a distinct gas by Van Helmont (1577-1644) when he discovered its presence as a byproduct of charcoal combustion and fermentation.[57] Carbon dioxide exists in the atmosphere in relatively large quantities through the combustion of coal and other carbonaceous fuels (about 3 vols of $CO_2$ in 10,000). $CO_2$ is a colorless gas which also can exist as a liquid, solid or all three phases together simultaneously. In the form of gas, its density under standard conditions is 1.5 times the density of air.[58] Carbon dioxide does not exist in the liquid phase at room temperature and atmospheric pressure, but it can be liquified at any temperature between its triple point (-56.6°C) and its critical point (31°C) by compressing it to the corresponding liquefaction pressure and removing the heat of condensation. Figure 20[59] shows the phase diagram of $CO_2$ in the P-T plane where pressure is plotted as log P rather than P. The characteristic points of the phase equilibrium curve are the normal sublimation point, the triple point and the critical point. The normal sublimation point is -108°F (-78.35°C) at one atmosphere pressure. The

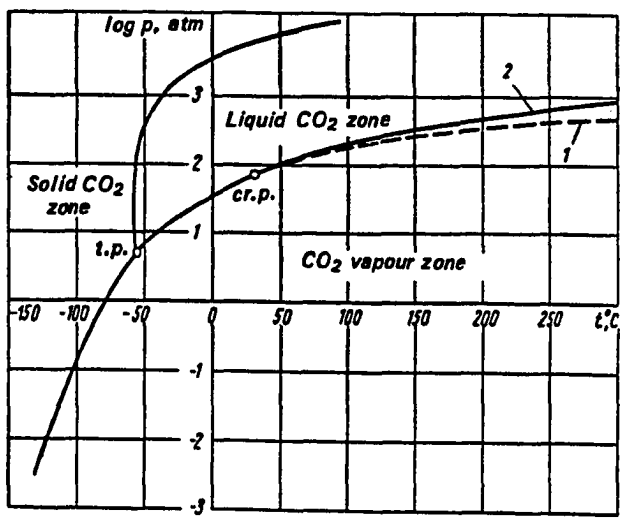



FIGURE 20. $CO_2$ phase equilibrium diagram

1 - Critical isochore; 2 - line of maxima

From: Vukalovich, M. P. and Altunin, V. V., "Phase Equilibrium," Thermophysical Properties of Carbon Dioxide, London & Welling Borough, 1968, p. 72-100.

triple point is -70.6°F (-57°C) and 5.113 atmospheres pressure. And, finally, the critical point is 87.8°F (31.04°C) and 72.85 atmospheres pressure. In Table 9 $\rho_{CR}$ (g/cm$^3$), $V_{CR}$ (cm$^3$/g) are the critical density and critical volume. Table 10[60] shows the general physical properties of $CO_2$.

Carbon dioxide is not a very reactive substance at ordinary temperature and pressure. However, in water solution it forms carbonic acid which is classified as a weak acid and is unstable. Figure 21[57] shows the solubility of carbon dioxide in water at temperatures between 0 and 120°C. As the figure indicates, the solubility of $CO_2$ at relatively low pressure (up to 200 atmospheres) decreases despite increasing temperature. But, above 200 atmospheres, the case is different. Generally, the minimum value of solubility occurs between 60-90°C; then, the solubility value increses with increasing temperature above 200 atmosphere pressure.

Carbon dioxide also can be reduced to carbon monoxide by reacting with hydrogen. The reaction with hydrogen is reversible at proper temperature and pressure.

$$CO_2 + H_2O \rightleftharpoons CO_3H_2$$

$$CO_2 + H_2 \rightarrow CO + H_2O$$

Although carbon dioxide is very stable, at higher temperature, it can be dissociated into carbon monoxide and oxygen.

$$2CO_2 \rightleftharpoons 2CO + O_2$$

Table 11 shows the number of molecules dissociated per 100 molecules of $CO_2$ at different temperatures.[61] Carbon dioxide also can be reduced

TABLE 9

| $T_{cr}$ °C | $P_{cr}$ atm | $T_{tp}$ °C | $P_{tp}$ atm | $T_{nsp}$ °C | $P_{nsp}$ atm | $\rho_{cr}$ g/cm$^3$ | $V_{cr}$ cm$^3$/g |
|---|---|---|---|---|---|---|---|
| 31.04 | 72.85 | -57 | 5.113 | -78.5 | 1 | 0.467 | 2.1413 |

TABLE 10. Physical Constants of Carbon Dioxide

**TABLE** Physical Constants of Carbon Dioxide

| | |
|---|---|
| Molecular weight | 44.01 |
| Density of the gas at 60°F and 14.696 lb/in$^2$abs | 0.1166 lb/ft$^3$ |
| Critical temperature | 88°F (31.0°C) |
| Critical pressure | 1073 lb/in$^2$abs (73.01 atm) |
| Specific heat: | |
| Gas at 60°F and 14.696 lb/in$^2$abs; constant pressure | 0.201 Btu/lb · °F |
| Gas at 60°F; constant volume | 0.1546 Btu/lb · °F |
| Ratio of specific heat at constant pressure to specific heat at constant volume, 60°F | 1.30 |
| Specific gravity (air = 1.0) | 1.528 |
| Triple point (solid, liquid, and gas co-exist) | 75.1 lb/in$^2$abs and −70°F (5.11 atm and −56.6°C) |
| Atmospheric sublimation point | −109°F (78.5°C) |
| Thermal conductivity: | |
| at −58°F (−50°C) | 0.0064 Btu/hr · ft$^2$ · °F/ft |
| at 32°F (0°C) | 0.0084 Btu/hr · ft$^2$ · °F/ft |
| at 212°F (100°C) | 0.0128 Btu/hr · ft$^2$ · °F/ft |
| Viscosity, gas: | |
| at 0°F (−17.8°C) | 0.013 cP |
| at 100°F (37.8°C) | 0.0155 cP |
| at 200°F (93.3°C) | 0.018 cP |
| Latent heat of vaporization: | |
| at triple point (−70°F; −56.6°C) | 149.7 Btu/lb |
| at 0°F (−17.8°C) | 120.1 Btu/lb |
| at 32°F (0°C) | 100.9 Btu/lb |

From: McKetta, J. J., Encyclopedia of Chemical Processing and Design, Vol. 6, 1978, p. 281.

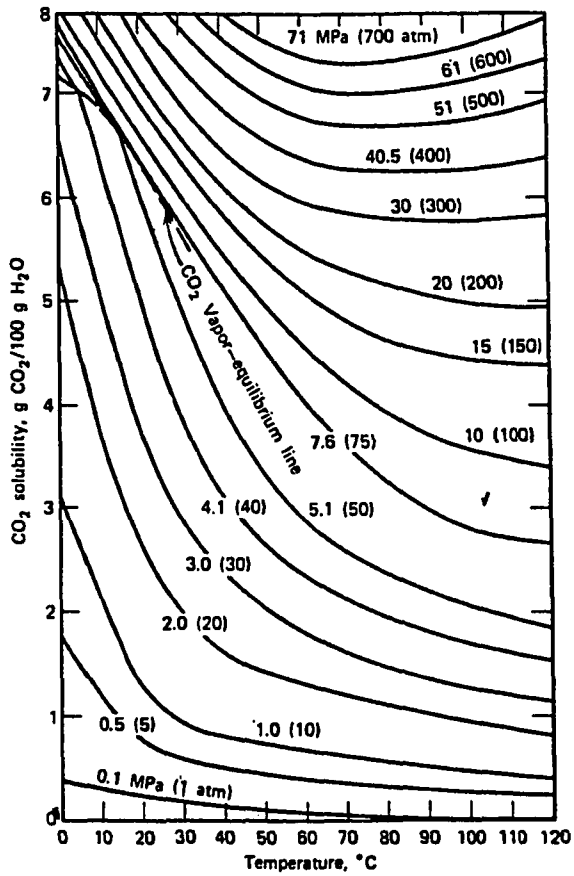



FIGURE 21. Solubility of carbon dioxide in water.

From: Kirth-Othmer, Encyclopedia of Chemical Technology, 1977, Vol. 4, p. 727.

with various hydrocarbons and even with carbon itself at high temperature. This reaction happens in almost all coal combustion processes which are usually used to produce carbon monoxide.

$$CO_2 + C \rightarrow 2CO$$

Carbon dioxide is not considered a hazardous substance in its present concentration of 300 ppm (0.03 vol%) in the atmosphere except in an industrial evnironment, in which case approximately 16 times the normal concentration of $CO_2$ in air or at most 5000 ppm becomes acceptable. Beyond that, $CO_2$ is recognized as a hazardous substance in air and consequently dangerous.

Besides the natural occurrence of $CO_2$ in air, carbon dioxide has been produced commercially from natural gas wells in the United States. But this type of $CO_2$ frequently contains hydrogen, sulfur, methane, propane, and ethane and requires further chemical processing is order to obtain pure $CO_2$. However, there are several other commercial methods which have been used to produce $CO_2$;[62] they are (1) synthetic ammonia and hydrogen plants in which methane or other hydrocarbons are converted to hydrogen and carbon dioxide.

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$$

(2) lime-kiln operations in which carbonates are thermally decomposed to carbon dioxide and calcium oxide.

$$CaCO_3 \rightarrow CO_2 + CaO$$

(3) sodium phosphate manufacture

$$3Na_2CO_3 + 2H_3PO_4 \rightarrow 2Na_3PO_4 + 3CO_2$$

(4) flue gases resulting from the combustion of carbonaceous fuel, and

TABLE 11

Dissociation of $CO_2$ at Different Temperatures

| T °K | 1000 | 1500 | 2000 | 3000 | 3500 |
|---|---|---|---|---|---|
| % dissociation | 0.000024 | 0.0483 | 2.05 | 54.8 | 83.2 |

TABLE 12

Sublimation, Triple, Critical Points of $H_2O$

at Different Temperatures and Pressures

| Point | Sublimation | Triple Point | Critical Point |
|---|---|---|---|
| Temperature °C | -10 | 0.01 | 374.14 |
| Pressure atm | $2.56 \times 10^{-3}$ | $6 \times 10^{-3}$ | 218 |

(5) fermentation in which a sugar is converted to ethyl alcohol and carbon dioxide

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$$

Carbon dioxide is generally considered an inexpensive substance and in liquid form can be purchased for $0.30/lb.

## B. WATER, ITS PHYSICAL AND CHEMICAL PROPERTIES

Water is one of the most widely dispersed of natural substances but is never found in a pure state. Its molecular weight is 18. The characteristic points of the phase equilibrium diagram are the normal sublimation point, the triple point and the critical point. Its sublimation point is -10°C (14°F) at 0.26 kPa ($2.56 \times 10^{-3}$ atmospheres) pressure; the triple point is 0.01°C (32.018°F) and 0.611 kPa ($6 \times 10^{-3}$ atmospheres) pressures; and the critical point is 374.14°C (705.4°F) at 22.09 MPa (218 atmospheres) pressure. Table 12 shows the sublimation point, triple point and critical point.[63,64]

Figure 22 shows how water changes to steam at different temperatures and pressures.[65] The points marked D represent the saturated liquid phase, and those marked E represent the saturated vapor state. The latent heat of vaporization (heat needed to form steam from liquid water), or the heat required to go from point D to point E, depends on pressure. At atmospheric pressure (14.7 psi), it requires approximately 970 Btu in order to convert one pound of water to vapor. At 100 psi, it requires 889 Btu to convert one pound of water to steam. As pressure increases, the latent heat value decreases. Just below the critical point (3204 psi), the latent heat value is 62 Btu; but when

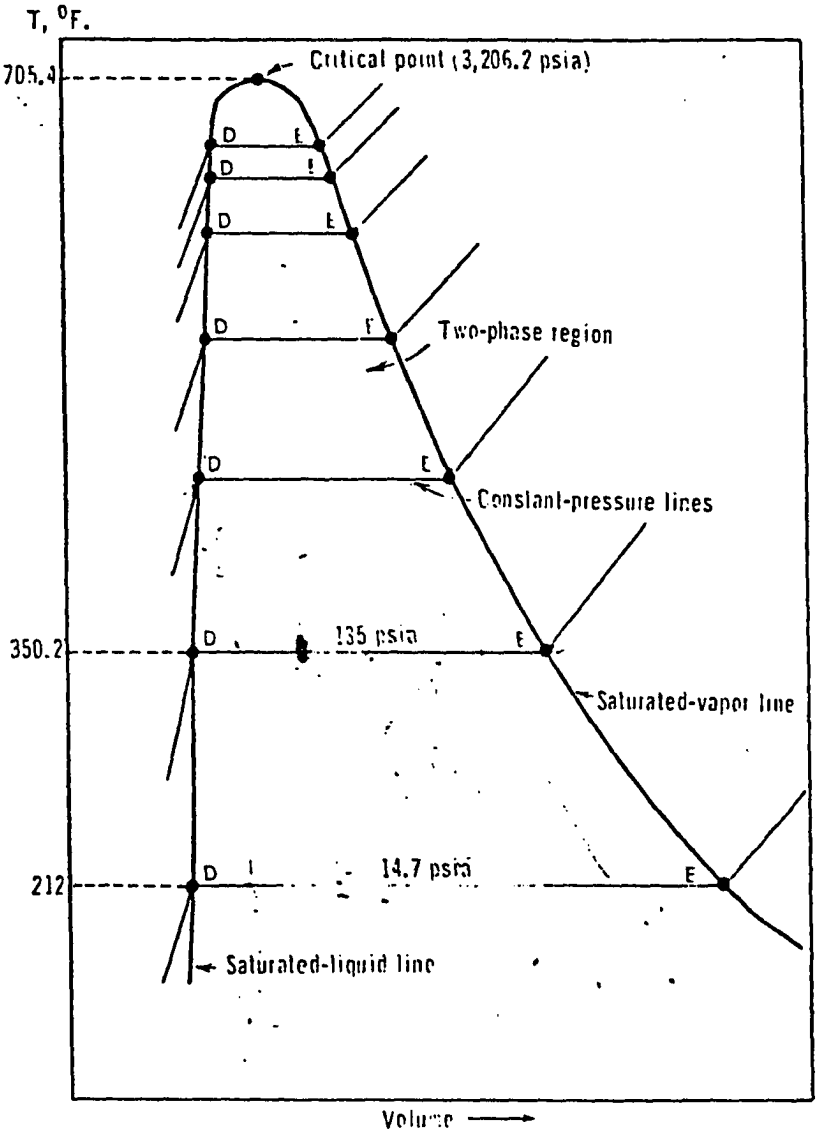



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FIGURE 22

Phase Diagram of $H_2O$

the pressure reaches 3204 psi, the latent heat value is eliminated. Table 13 shows the general physical properties of water.[66]

Usually, water in its natural form contains some solid matter or minerals in a very fine size. Even when water looks clear, it still has solutions of acids and salts. Water has been classified into three categories[67] according to the compounds it contains and their effect on the water's use. They are

(1) Corrosive--Corrosive substances are usually in the form of an acid solution or as a dissolved gas such as oxygen, hydrogen sulfide and ammonia.

(2) Foam producing substance--Organic and inorganic substances present in water cause foaming during any heating process of the water. Normally, oil and decomposed humic matter are the chief causes of foaming.

(3) Scale-forming substances--The presence of these frequently reduces the solubility of water. The most common scale-forming substances are calcium carbonate and calcium sulfate.

All of these substances can be removed from water by chemical treatment. Some of them may be removed by boiling the water, but some of them require special chemical treatment.

## C. THE BINARY SYSTEM OF $CO_2$-$H_2O$ MIXTURE AT HIGH TEMPERATURE AND PRESSURE

There have been many studies by different groups of researchers of the binary system of carbon dioxide and water. These studies cover the range from lower temperatures and pressures up to relatively

TABLE 13

General Physical Properties of Water*

| | Water |
|---|---|
| Chemical formula | $H_2O$ |
| Molecular weight | 18 |
| Specific gravity at 212°F | 0.958 |
| Melting point, °F | 32 |
| Boiling, °F (atm. pressure) | 212 |
| Flash point, COC, °F | --- |
| Specific heat of liquid, B.t.u./(lb)(°F) | 1.005 (212°F) |
| Heat of vaporization, B.t.u./lb | 970.2 |
| Heat of fusion, B.t.u./lb | 143.3 |
| Critical expansion coefficient | 0.0024 |
| Absolute viscosity of liquid, centipoise | 0.284 (212°F) |
| Surface tension (contact with air), dynes/cm | 72.8 |
| Thermal conductivity liquid, B.t.u./(ft)(hr)(sq.ft)(°F) | 0.393 |

*From Perry, J. H., Chemical Engineering Handbook, "Water Constituents," 4th Edition, McGraw Hill Series, 1960, p. 9-51.

high temperatures and pressures.[68,69,70] This includes 0 to 350°C temperature and up to approximately 5000 psi pressure. Depending on the methods and equipment used, different results were obtained, particularly at high temperature and pressure. However, these differences are not large enough to dismiss or discredit the attempts or data obtained from the studies.

Most of these results are classified on the basis of experimental search. In 1924, Pollitzer and Strebel[68] studied various gases mixed in the water. The temperature ranged up to 70°C and pressure up to 87 atmospheres (1280 psi). They discovered $CO_2$ mixed in the water increased the partial pressure of water in the vapor phase. In 1937, Zelvenskii determined the solubility of $CO_2$ in water up to 100°C temperature and 100 atmospheres (1470 psi) pressures.[68] He reported that Henry's law* yields better results below 100°C and below 100 atmospheres pressure. In 1939-1941, Welbe and Gaddy investigated the $CO_2$-$H_2O$ binary systems at 100°C temperature but pressures up to 700 atmospheres (10,290 psi).[68] Their research mostly investigated vapor phase compositions. In 1958 Khitarov and Malinin studied the $CO_2$-$H_2O$ mixture for the first time at higher temperatures (range 200-300°C) and higher pressure [approximately 580 atm (8500 psi)].[68] As a result, they discovered the critical temperature of the solution is lower than the critical temperature of water in the gas-liquid system. By 1959 and 1963 two series of attempts were made by Ellis[69] and Ellis and Golding[70] on the solubility of carbon dioxide in water at higher

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*$k = P_g/x$ where k is called the Henry's law coefficient, $P_g$ is the partial pressure of the gas and x is the ratio of the moles of the gas to the sum of moles of gas and water in solution.

temperatures up to 350°C and up to 160 atmospheres pressure (2350 psi). They indicated the Henry's law coefficient which was obtained by equation was not the same as the one which they obtained by experiment. In 1959 Frank and Todheide investigated supercritical conditions of the $CO_2$-$H_2O$ binary sytstem.[68] They reported in their study that the behavior of the carbon dioxide-water system is typical of a binary system which consists of a nonpolar and a strongly polar component. In this study the temperature applied was 750°C and pressures to 2000 atmospheres (29,400 psi). Recently in 1963 Sukune Takenouch and George C. Kennedy at the Institute of Geophysics and Planetary Physics at the University of California, Los Angeles, studied the $CO_2$-$H_2O$ binary system. Their primary equipment consisted of an autoclave or bomb reactor with 105 ml capacity which was made of stainless steel material and contains a pressure gauge, valve, tubing and several pumps for injecting $CO_2$ and $H_2O$ inside the bomb reactor. The temperature ranged from 110°C to 350°C and the pressure up to 1500 bar (22000 psi). The period of the experiment ranged from 6 to 7 hours depending on the temperature. Table 14 shows the concentration of $CO_2$ in liquid and gas phase in the $CO_2$-$H_2O$ mixture at various temperatures and pressures. In Table 14, $X_C$ shows the critical concentration of carbon dioxide and $P_C$ is the critical pressure. The results of the experiment by Sukune Takenouchi and George C. Kennedy which were shown in Table 14 are also expressed in diagrams for the mole percent of liquid and gas phase of $CO_2$ with regard to temperature and pressure (Figures 23-26).

Figure 23 indicates the concentration of $CO_2$ in both the liquid and gas phase in the $H_2O$-$CO_2$ mixture at temperatures ranging from

TABLE 14

| bars | 350°C liq phase | 350°C gas phase | 325°C liq phase | 325°C gas phase | 300°C liq phase | 300°C gas phase |
|---|---|---|---|---|---|---|
| 100 | — | — | — | — | 0.4 | 8.0 |
| 150 | — | — | 1.0 | 10.6 | 1.6 | 29.0 |
| 200 | 1.5 | 9.0 | 2.6 | 24.6 | 2.9 | 39.0 |
| 250 | 4.0 | 16.2 | 4.3 | 32.1 | 4.1 | 43.4 |
| 300 | 6.4 | 16.6 | 6.1 | 34.2 | 5.4 | 45.4 |
| 350 | | | 8.2 | 33.4 | 6.8 | 45.6 |
| 400 | $P_c = 325^{bars}$ | | 11.2 | 28.6 | 8.4 | 44.8 |
| 450 | $X_c = 10.5\%$ | | | | 10.4 | 42.2 |
| 500 | | | $P_c = 435^{bars}$ | | 12.7 | 38.0 |
| 550 | | | $X_c = 18.0\%$ | | 17.0 | 32.0 |
| | | | | | $P_c = 575^{bars}$ | |
| | | | | | $X_c = 23.6\%$ | |

| bars | 275° liq phase | 275° gas phase | 270°C liq phase | 270°C gas phase | 260°C liq phase | 260°C gas phase |
|---|---|---|---|---|---|---|
| 100 | 1.0 | 25.6 | | | | |
| 150 | 1.9 | 42.6 | | | | |
| 200 | 2.8 | 50.0 | 2.7 | 53.0 | 2.7 | 57.2 |
| 250 | 3.8 | 54.0 | 3.6 | 57.0 | 3.5 | 62.0 |
| 300 | 4.9 | 55.8 | 4.6 | 59.0 | 4.4 | 64.0 |
| 400 | 7.2 | 55.8 | 6.7 | 59.0 | 5.9 | 64.2 |
| 500 | 9.6 | 53.0 | 8.7 | 57.0 | 7.3 | 62.4 |
| 600 | 12.0 | 49.6 | 10.6 | 54.6 | 8.7 | 60.4 |
| 700 | 14.4 | 46.0 | 12.5 | 52.0 | 10.0 | 58.0 |
| 800 | 17.5 | 42.0 | 14.5 | 49.6 | 11.3 | 56.0 |
| 900 | $P_c = 885^{bars}$ | | 16.6 | 46.2 | 12.5 | 54.8 |
| 1000 | $X_c = 27.0\%$ | | 19.0 | 42.4 | 13.5 | 53.6 |
| 1100 | | | 21.5 | 38.2 | 14.5 | 52.4 |
| 1200 | | | 25.0 | 34.0 | 15.5 | 51.0 |
| 1300 | | | | | 16.0 | 50.4 |
| 1400 | | | $P_c = 1230^{bars}$ | | 16.5 | 50.2 |
| 1500 | | | $X_c = 28.8\%$ | | 17.5 | 50.0 |

| bars | 250°C liq phase | 250°C gas phase | 200°C liq phase | 200°C gas phase | 150°C liq phase | 150°C gas phase |
|---|---|---|---|---|---|---|
| 100 | 1.2 | 41.0 | 1.3 | 71.5 | 1.35 | 88.0 |
| 200 | 2.7 | 63.6 | 2.6 | 82.0 | 2.15 | 91.0 |
| 300 | 4.2 | 68.0 | 3.4 | 82.5 | 2.60 | 90.0 |
| 400 | 5.5 | 67.6 | 4.1 | 81.6 | 2.90 | 88.2 |
| 500 | 6.4 | 66.0 | 4.7 | 80.0 | 3.20 | 86.2 |
| 600 | 7.4 | 63.6 | 5.2 | 78.0 | 3.45 | 84.0 |
| 700 | 8.4 | 61.3 | 5.6 | 76.0 | 3.70 | 82.4 |
| 800 | 9.4 | 59.3 | 5.8 | 74.5 | 3.90 | 80.8 |
| 900 | 10.4 | 58.0 | 6.1 | 73.2 | 4.05 | 79.4 |
| 1000 | 11.5 | 56.7 | 6.3 | 72.0 | 4.20 | 78.0 |
| 1100 | 12.5 | 55.5 | 6.5 | 71.6 | 4.40 | 77.0 |
| 1200 | 13.2 | 54.8 | 6.7 | 70.6 | 4.50 | 76.4 |
| 1300 | 13.6 | 54.2 | 6.9 | 70.0 | 4.60 | 75.8 |
| 1400 | 14.0 | 54.0 | 7.0 | 69.4 | 4.70 | 75.4 |
| 1500 | 14.4 | 54.0 | 7.2 | 69.0 | 4.80 | 75.2 |

| bars | 110°C liq phase | 110°C gas phase | bars | 110°C liq phase | 110°C gas phase |
|---|---|---|---|---|---|
| 100 | 1.40 | 95.6 | 900 | 3.45 | 84.0 |
| 200 | 2.10 | 95.8 | 1000 | 3.60 | 83.0 |
| 300 | 2.40 | 94.8 | 1100 | 3.70 | 82.2 |
| 400 | 2.60 | 93.2 | 1200 | 3.75 | 81.6 |
| 500 | 2.80 | 91.4 | 1300 | 3.85 | 81.0 |
| 600 | 3.00 | 89.3 | 1400 | 3.90 | 80.4 |
| 700 | 3.15 | 87.2 | 1500 | 4.00 | 80.0 |
| 800 | 3.30 | 85.4 | | | |

From: Sukune Takenouchi and George C. Kennedy, "The Binary System of $H_2O$-$CO_2$," American Journal of Science, 1964, Vol. 262, p. 1059-1060.

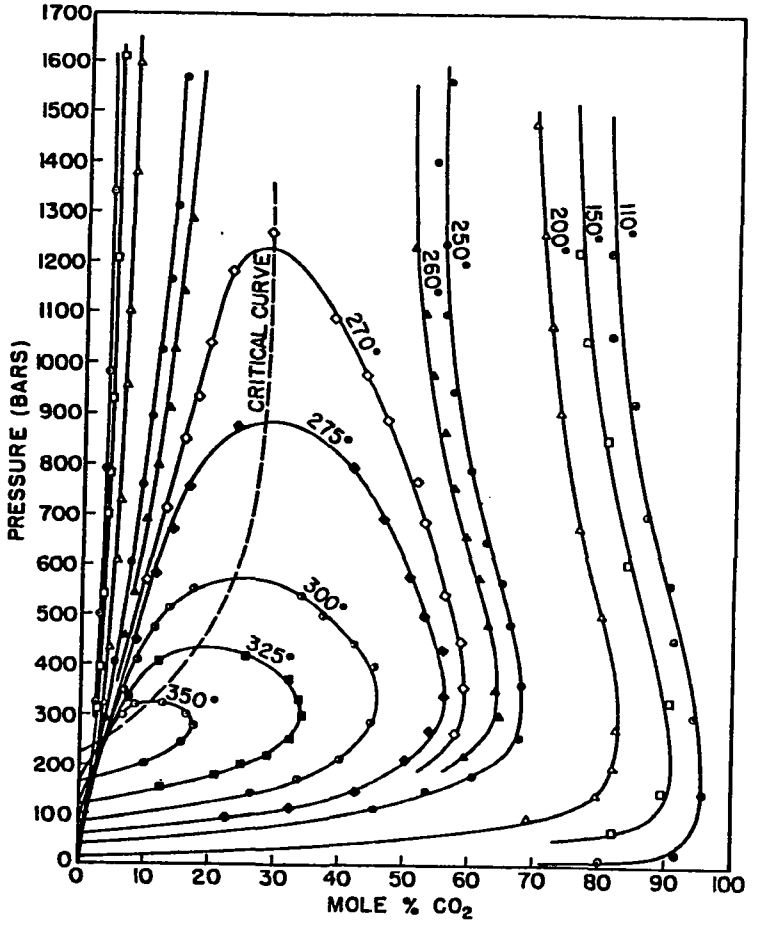



FIGURE 23. Isotherms showing the compositions of gas and liquid phases in the system $H_2O$-$CO_2$. (From: Sukune Takenouchi and George C. Kennedy, American Journal of Science, 1963, Vol. 261, p. 1061.)

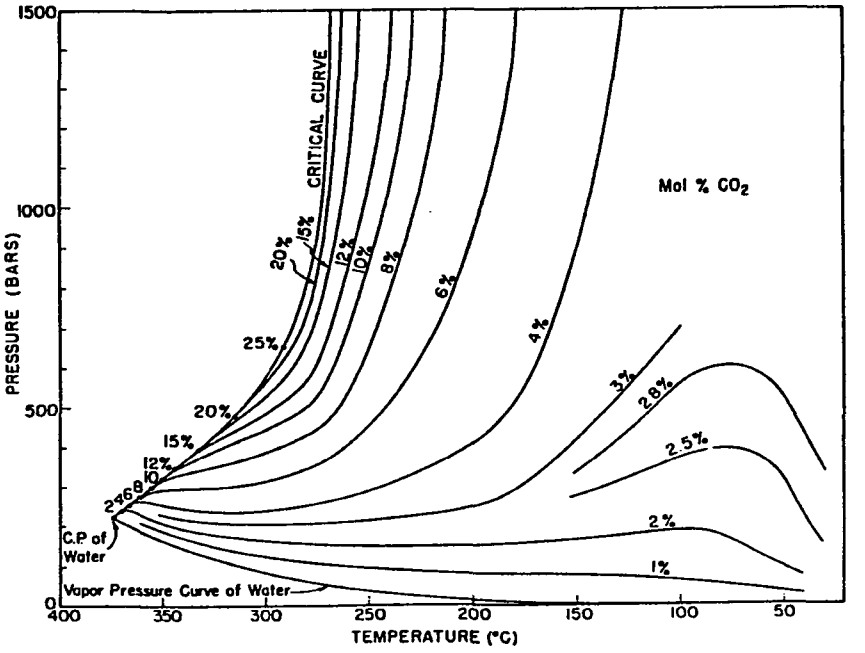



FIGURE 24. Isocompositional curves of the liquid phase in equilibrium with the gas phase in the system $H_2O$-$CO_2$. (From: Sukune Takenouchi and George C. Kenedy, American Journal of Science, Vol. 262, 1963, p. 1063.)

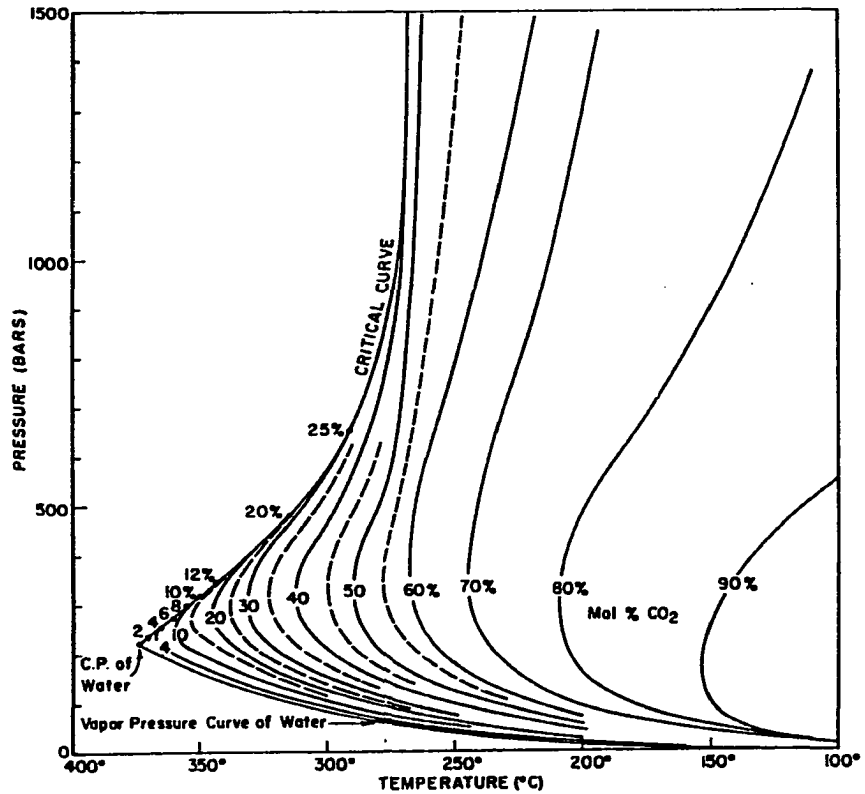



FIGURE 25. Isocompositional curves of the gas phase in equilibrium with the liquid phase in the system $H_2O$-$CO_2$. (From Takenouchi and Kennedy, American Journal of Science, Vol. 262, 1963, p. 1064.)

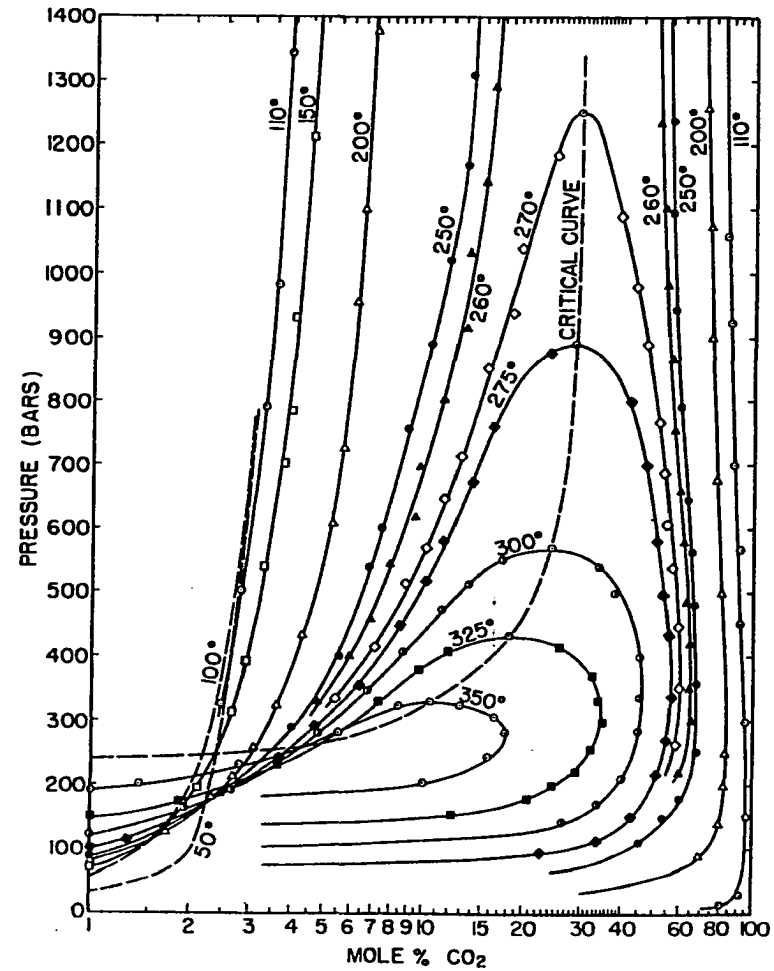



FIGURE 26. Semi-logarithmic diagram of isotherms showing the composition of coexisting gases and liquids in the system $H_2O$-$CO_2$. (From: Takenouchi and Kennedy, American Journal of Science, Vol. 262, 1963, p. 1066.)

110° to 350°C and pressures up to 1600 bars (23200 psi). Figure 24 and Figure 25 show the liquid phase and gas phase of $CO_2$ in the binary system. Figure 26 shows the coexistence of the liquid and gas phases of $CO_2$ in the binary system of $CO_2$-$H_2O$ in a semilogarithmic diagram. And, finally, the density of carbon dioxide and water is shown in Figure 27 at different temperature and pressures. As Table 14 and Diagrams 23-26 indicate, the mole percent of $CO_2$ in the gas and liquid phases from 110°C up to 350°C at different pressures can be determined. Also, the amount of $CO_2$ which has been dissolved in the water can be calculated by subtracting the sum of moles of $CO_2$ in the gas and liquid phases from 100. For instance, at 110°C temperature and 100 bars (99 atm) pressure, Table 14 and Figures 23-26 indicate 95.6 percent of $CO_2$ in the binary system is gas and 1.4 percent is liquid. Therefore, 3 percent of the $CO_2$ has been dissolved in the water. These results can also be obtained by using Figure 21 which shows the solubility of $CO_2$ in water below 120°C temperature. By using this figure, at pressure of 99 atm and temperature of 110°C, the solubility of $CO_2$ per 100 gram water is going to be 3-3.5 gram or 3-3.5 percent. The small difference can be related to various procedures and human error by researchers.

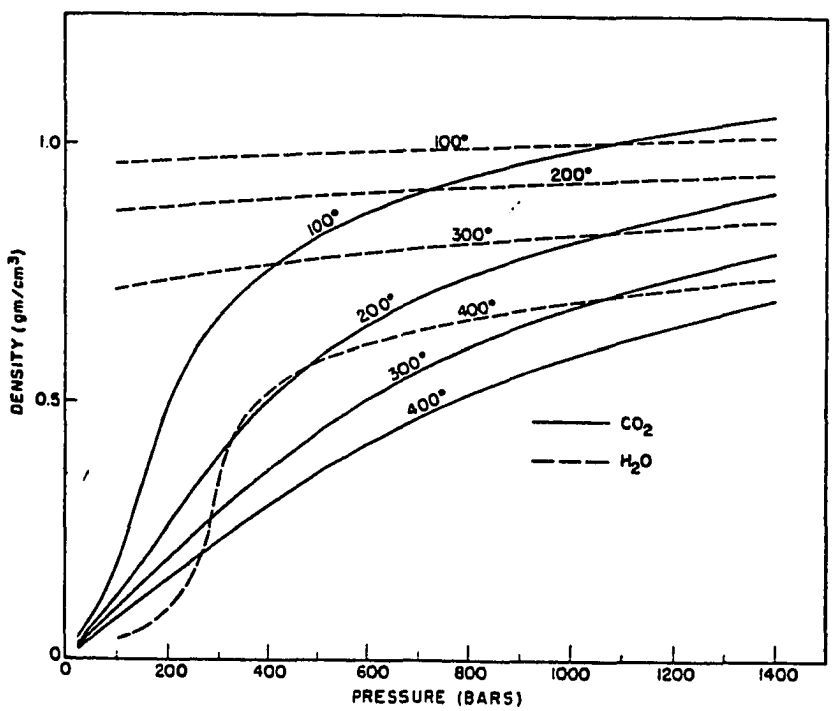



FIGURE 27. The density of water and carbon dioxide at various temperatures and pressures. (From: Takenouchi and Kennedy, American Journal of Science, Vol. 262, 1963, p. 1071.)

# CHAPTER IV

## PROCEDURE OF THE INVESTIGATION

### A. EXPERIMENTAL APPARATUS

The experimental apparatus for this study included the following equipment.

(1) Pressure vessel or pressure reactor which consisted of the following pieces:

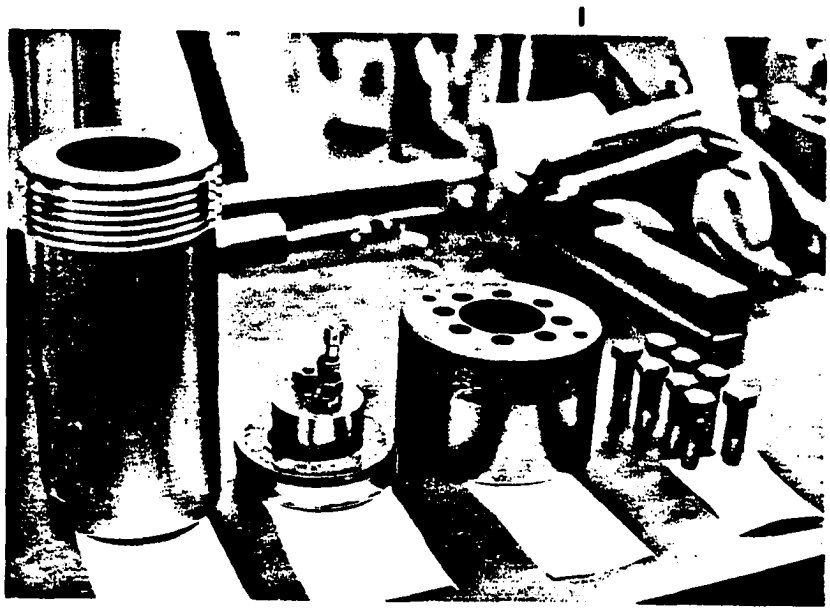
(a) Body--the body had been constructed from stainless steel 316 with a right circular cylindrical shape with 500 ml capacity. Its inside diameter is 2.5 inches and outside diameter is 3.85 inches. Its inside depth is 6.25 inches. The body was used as a container of coal and solvent. The stainless steel construction of the body was designed to withstand relatively high pressure and high temperature and corrosion which might be caused by the reaction. Two holes had been machined on the bottom of the vessel for the convenience of holding the vessel with a disk while removing cap, cover and bolts. The body weight is 19.2 pounds (8.6 kg).

(b) Cover or head which was made from stainless steel 316 and covered the top and open portion of the vessel. The cover had a 1/2 millimeter diameter hole that was used for the purpose of gas or liquid injection from the gas cylinder through the stainless steel fitting and

union type connectors into the vessel (body). The weight of the cover is 3.6 pound (1.6 kg).

(c) Cap--the cap was machined from stainless steel and had an inside diameter of 2 inches and outside diameter of 4 3/4 inches and height of 3 1/8 inches. The cap consisted of the following portions: (1) outside cap that screws onto the body of the reaction vessel, (2) eight thrust bolts with furrow made from steel. The bolts were used to compress the cap and thrust ring and cover in order to become tight enough for high temperature and high pressure operations. The diameter of each bolt is 1/2 inch; the length is 1 1/2 inches from below the head of the bolt. The average weight of each bolt is 45 grams. The bolts must be loosened in a staggered pattern before unscrewing the cap. The bolts must be tightened in the same fashion, and each bolt is torqued equally to approximately 80 ft-lb. (3) hardened steel thrust ring that separates the cover from the bolts. The cap also has two tapped holes for eye bolts for use in lifting the vessel from the heating device (furnace). Finally, there is an O-ring unit which is used as a gasket and constructed of stainless steel 316. This unit helps to seal the head onto the top of the vessel and prevent leakage. Figure 28 shows the body, cover and cap of the pressure vessel, and Figure 29 and Table 15 show the dimensions of the vessel which was used in this research.

(2) Three pressure gauges: (a) Matheson type pressure gauge (0-3000 psi) run by oil with 2.5 inch diameter dial. The Matheson pressure gauge was used to measure the pressure of $CO_2$ injected into the cylinder; (b) Maxisafe pressure gauge (0-5000 psi) with 5 inch



1 2 3 4

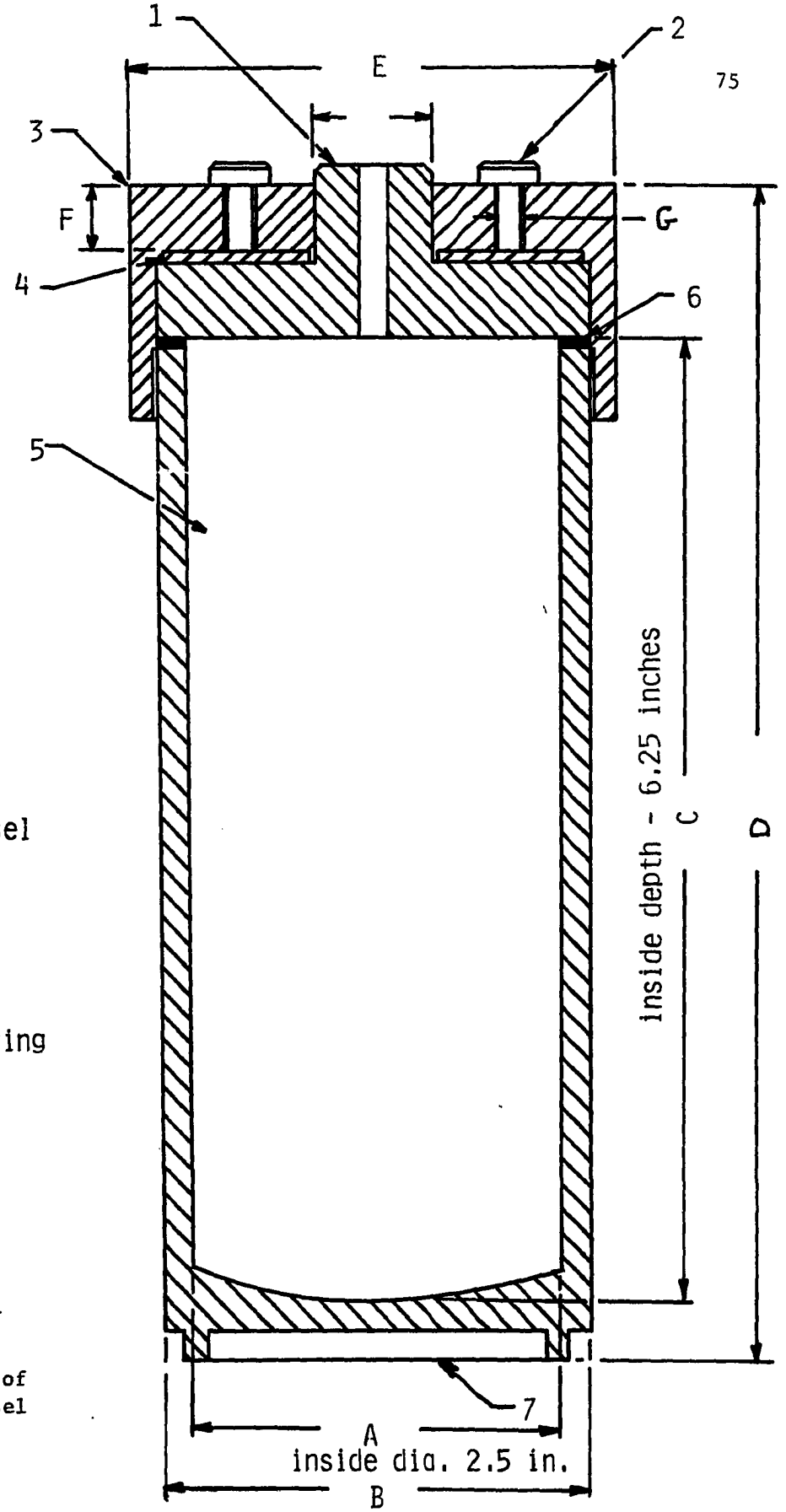
FIGURE 28: Different Portions of Pressure Vessel

1 - Body 2 - Cover or head with stainless steel thrust ring
3 - cap 4 - bolts

TABLE 15

| Name | Pressure Vessel | Dimensions (inches) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | A | B | C | D | E | f | G | h |
| | | 2.5 | 3.85 | 6.25 | 10 | 4.70 | $1\frac{1}{2}$ | $\frac{1}{2}$ | 2 |

(See Figure 29, next page)




Pressure Vessel

Including

1. Cover
2. Bolt
3. Cap
4. Thurst ring (washer)
5. Body
6. Gasket
7. Disk

FIGURE 29

Illustration of Pressure Vessel

diameter dial with AISI 316 tube filled with mercury; (c) Wika pressure gauge (0-10000 psi) with 3.51 inch diameter dial and tube filled with mercury. Maxisafe and Wika pressure gauges were used for high pressure and high temperature operations in different periods of the experiment.

(3) Standard $CO_2$ gas cylinder with approximately 1050 psi pressure. Figure 30 shows how the various pieces of equipment used for coal-$CO_2$ + $H_2O$ reaction at high temperature and high pressure were connected together with high pressure stainless steel laboratory valves, fittings and tubing. The $CO_2$ cylinder was connected to the pressure vessel with 1/16 inch OD stainless steel tubing.

(4) CENCO-Meinzer sieve shaker with U.S. Standard sieve series was used to determine the distribution of coal particles after treatment of the chunk coal with $CO_2$-$H_2O$ mixture. The sieve number and opening sizes are: 4 (0.185 inches), 16 (0.0469 inches), 50 (0.0116 inches), 60 (0.0098 inches) and 70 (0.0083 inches), 100 (0.0059 inches) and -100 (0.00291 inches).

(5) Galbraith Laboratory, Inc. in Knoxville, Tennessee performed ultimate analyses and sulfur form analyses before and after the coal was treated. Also, the same laboratory determined the Btu value of the McAlester coal before and after treatment.

In the ultimate analysis, the following elements were measured: carbon, oxygen, hydrogen, nitrogen, sulfur, chlorine, ash. In the sulfur form analysis, pyrite, sulfate sulfur and organic sulfur was measured.

(6) A Beckman Irlo Infrared Spectrophotometer was used to measure the absorption of seven inorganic and organic compounds after

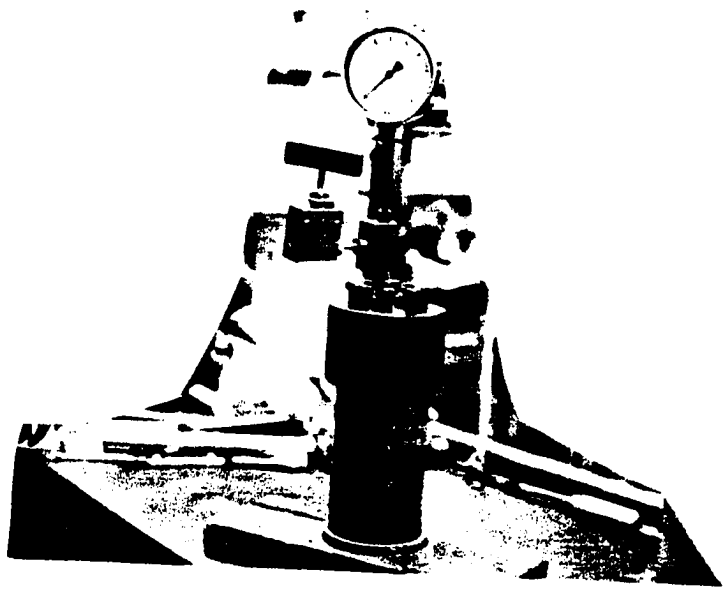


FIGURE 30

Illustration Indicating Pressure Vessel with Contents of Coal + $H_2O$ Ready for Injection of $CO_2$

treatment with the $CO_2$-$H_2O$ mixture. These compounds are believed to have linkage bonds similar to the coal compounds. The physical conditions for the treatment of these compounds with the $CO_2$-$H_2O$ mixture were similar to the coal and $CO_2$-$H_2O$ mixture. In this system the wave number (the number of waves per centimeter, $cm^{-1}$) is used to measure the position of a given infrared absorption. There are two types of vibration for molecules: (a) stretching, in which the distance between the two atoms decreases or increases but the atoms stay in the same bond axis; (b) bending or deformation, in which the positions of the atoms change relative to their original position.[71,75] Bending vibrations usually occur at a longer wavelength (lower wave number) and require very low energy. In the Beckman Irlo Infrared spectrophotometer used in this study, the infrared region extended from 4000 to 300 $cm^{-1}$. The stretching vibrations were found to happen in the order of bond strength. For instance, the triple bond absorption C≡C with 2300-2000 $cm^{-1}$ is stronger than the double bond absorption C=C (1900-1500 $cm^{-1}$) which is stronger than the single bond absorption such as C-C, C-N, C-O (1300-800 $cm^{-1}$). However, the O-H bonds, such as in water, have the highest infrared absorption. The O-H absorbed around 3500 $cm^{-1}$. This was particularly obvious in those compounds used in this study because of the very small amounts of water remaining in the compounds after the vaporization process.

(7) An Elconap type oven was used to dry the fragmented samples. The heat supplied by this oven is up to 200°C (392°F). The temperature used to dry the samples was around 110°C. This oven is manufactured by Electric Heat Control Apparatus Company in the United States.

(8) An electrical heater was used to provide heat for the reaction. This device had a furnace with an inside diameter of 4 inches and outside diameter of 10 inches and inside depth of 10 inches. The temperature was measured by a thermocouple. The maximum temperature which could be provided by this heater was 400°C (752°F). The temperature was controlled by a temperature controller device. Figure 31 shows the pressure vessel with gauge inside the furnace and electrical heater device.

(9) Some evaporation apparatus, beaker, funnel, filter, hot plate and chemical agents such as ether and $MgSO_4$ were used in this study. Ether and $MgSO_4$ were used to extract water from the chemical compounds which had been treated with the $CO_2$-$H_2O$ binary system. These chemical compounds have bond linkages similar to coal; and after treatment with $CO_2$-$H_2O$, the water was removed from the remaining compounds before infrared absorption analysis in order to find out whether or not the solvent ($CO_2$ + $H_2O$) had any effect on selected chemical compounds. (This was an attempt to prove the fragmentation of coal by the $CO_2$-$H_2O$ binary system occurs through these linkages which are believed to exist in the coal structure.) This series of tests were done with a small reactor with 25 ml capacity.

Except for the U.S. Standard sieve shaker and screen and Elconap oven which were provided by the Geological and Petroleum Engineering Department, the other equipment was provided in Professor A. Hagen's Chemistry Laboratory at the University of Oklahoma.

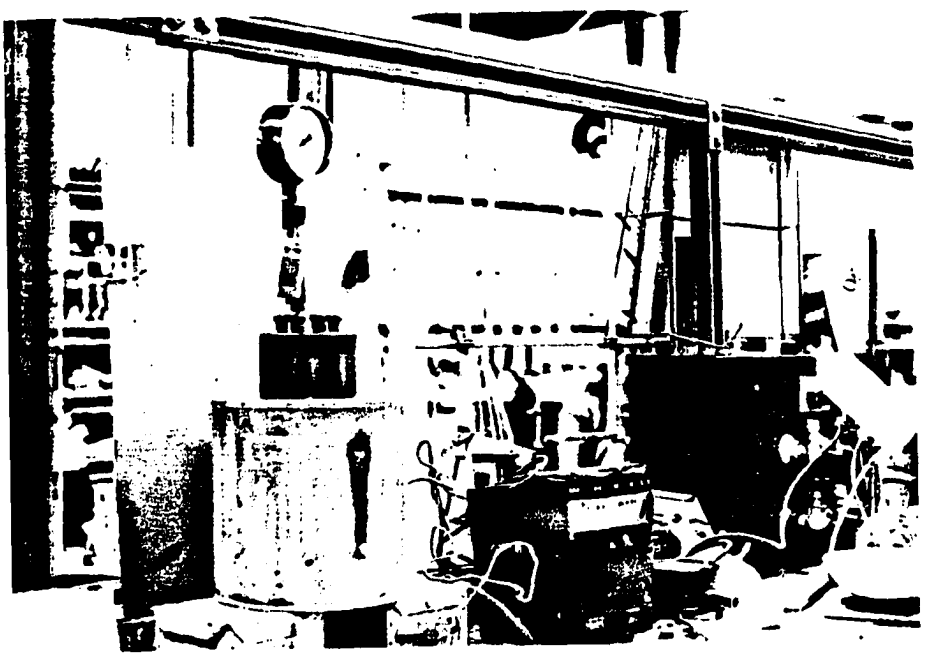


FIGURE 31

Pressure Vessel with Contents of Coal + $H_2O$ + $CO_2$

Inside Furnace Ready for Heating

## B. MATERIALS

### 1. Coal:

Three different run-of-mine (ROM) bituminous coal beds from eastern Oklahoma and one unknown coal were used in this study. The three bituminous coals of Oklahoma are: (a) McAlester coal--The McAlester coal was selected from Latimer County and supplied by Farrel-Cooper Mining Co. The McAlester coal of Latimer County is 1.5-3.5 feet thick with more than 200 million short tons of resources. Among this, 40% has thickness between 29 and 42 inches; 55% is 15-28 inches thick; and less than 5% of the total coal resources is between 12 and 14 inches thick. The sulfur content of this coal ranged from 2 to 4.5 percent. Up to 1974 less than one percent of this coal had been mined by underground coal mining methods. This coal bed has been recognized as a suitable coal for use in electric power generation, liquefaction, gasification and coking manufacture. (b) Secor coal--The Secor coal samples were selected from Wagoner County in the northeastern part of Oklahoma. The average thickness has been identified as 1.5 feet with an average of 2.8 percent sulfur in the coal. There has been mining activity in this county by Bill's Coal Co. using the open-pit technique. The average overburden thickness is 35 feet. The total Secor coal resource of this county is not included in the Geological Survey report of January 1974. However, the Secor coal production of Wagoner County is reported by the Geological Survey of Oklahoma to be less than 100,000 short tons.[73] In general, the Secor coal bed in Oklahoma has been recognized as suitable for liquefaction, gasification and even for electric power generation within the limits of sulfur and ash. This

coal sample was provided by Bill's Coal Company through the Petroleum and Geological Department of the University of Oklahoma. (c) Croweburg coal—The Croweburg coal sample was selected from Okmulgee County of northeast Oklahoma. The total Croweburg coal resources of this county are estimated to be more than 300 million short tons.[74] Among this, 5 percent is 42 inches or more in thickness; more than 80 percent is between 29 and 42 inches in thickness; and less than 15% of the total Croweburg coal bed of Okmulgee county is less than 28 inches in thickness. The sulfur content ranges from 0.9 to 4.2 percent. Less than 20 percent of the total coal has been mined by both surface and underground mining methods up to 1974. In January 1977,[75] the Geological Survey reported two mine companies had activities in this county, and the coal production by these two mines was reported to be between 100,000 and approximately 500,000 short tons in that year. The Croweburg coal bed is recognized to be one of the most useful coal beds in the state of Oklahoma for both domestic heating and industrial purposes.[75] Table 16 shows the mining characteristics of the McAlester and Croweburg coal beds of Latimer and Okmulgee Counties of eastern Oklahoma. Also, Figure 32 shows the distribution of bituminous coal in these counties, and arrows indicate the approximate location where the samples were collected. The total samples provided for study were approximately 50 pounds.

The unknown coal (its origin is unknown) had been provided by the Transportation Department of Oklahoma to the Chemistry Department and was used in this study.

TABLE 16

## --Original and Mined Coal Resources, Latimer County, Oklahoma (in thousands of short tons)

| COAL AND RANK[1] | COAL DEPTH (FEET) | SULFUR CONTENT[2] (PERCENT) | ORIGINAL RESOURCES | | | | | | | | | | MINED AND LOST IN MINING | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | 12-14 INCHES | | 15-28 INCHES | | 29-42 INCHES | | 42+ INCHES | | TOTAL | | SURFACE | | UNDERGROUND | | TOTAL | |
| | | | ACRES | TONS | ACRES | TONS | ACRES | TONS | ACRES | TONS | ACRES | TONS | ACRES | TONS | ACRES | TONS | ACRES | TONS |
| UPPER MC ALESTER (hvb) | 0-100 | 4.1 (4.1) | 5 | 11 | 1,461 | 4,950 | 86 | 464 | -- | -- | 1,552 | 5,425 | 52 | 166 | -- | -- | 52 | 166 |
| | 101-1,000 | 4.1 (4.1) | 27 | 58 | 22,574 | 74,893 | 1,856 | 9,025 | -- | -- | 24,457 | 83,976 | -- | -- | -- | -- | -- | -- |
| | 1,001-2,000 | 4.1 (4.1) | -- | -- | 5,125 | 15,184 | 555 | 2,497 | -- | -- | 5,680 | 17,681 | -- | -- | -- | -- | -- | -- |
| | Total | 4.1 (4.1) | 32 | 69 | 29,160 | 95,027 | 2,497 | 11,986 | -- | -- | 31,689 | 107,082 | 52 | 166 | -- | -- | 52 | 166 |
| LOWER MC ALESTER (hvb) | 0-100 | 2.3 (1.9-3.2) | 8 | 17 | 3,379 | 10,195 | 556 | 2,676 | -- | -- | 3,943 | 12,888 | 342 | 1,129 | -- | -- | 342 | 1,129 |
| | 101-1,000 | 2.3 (1.9-3.2) | 29 | 63 | 25,365 | 77,475 | 14,473 | 65,898 | -- | -- | 39,867 | 143,436 | -- | -- | -- | -- | -- | -- |
| | 1,001-2,000 | 2.3 (1.9-3.2) | -- | -- | 7,928 | 25,536 | 3,030 | 13,169 | -- | -- | 10,958 | 38,705 | -- | -- | -- | -- | -- | -- |
| | 2,001-3,000 | 2.3 (1.9-3.2) | -- | -- | -- | -- | 1,758 | 7,595 | -- | -- | 1,758 | 7,595 | -- | -- | -- | -- | -- | -- |
| | 3,000+ | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- |
| | Total | 2.3 (1.9-3.2) | 37 | 80 | 36,672 | 113,206 | 19,817 | 89,338 | -- | -- | 56,526 | 202,624 | 342 | 1,129 | -- | -- | 342 | 1,129 |

## --Original and Mined Coal Resources, Okmulgee County, Oklahoma (in thousands of short tons)

| COAL AND RANK[1] | COAL DEPTH (FEET) | SULFUR CONTENT[2] (PERCENT) | ORIGINAL RESOURCES | | | | | | | | | | MINED AND LOST IN MINING | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | 12-14 INCHES | | 15-28 INCHES | | 29-42 INCHES | | 42+ INCHES | | TOTAL | | SURFACE | | UNDERGROUND | | TOTAL | |
| | | | ACRES | TONS | ACRES | TONS | ACRES | TONS | ACRES | TONS | ACRES | TONS | ACRES | TONS | ACRES | TONS | ACRES | TONS |
| CROWEBURG (hvb) | 0-100 | 2.2 (0.9-4.2) | 1,011 | 2,037 | 3,443 | 13,286 | 2,605 | 12,101 | -- | -- | 7,059 | 27,424 | 1,069 | 4,387 | -- | -- | 1,069 | 4,387 |
| | 101-1,000 | 2.2 (0.9-4.2) | 975 | 1,972 | 6,515 | 25,153 | 60,199 | 322,135 | 3,149 | 20,972 | 70,838 | 370,232 | -- | -- | 13,209 | 68,966 | 13,209 | 68,966 |
| | Total | 2.2 (0.9-4.2) | 1,986 | 4,009 | 9,958 | 38,439 | 62,804 | 334,236 | 3,149 | 20,972 | 77,897 | 397,656 | 1,069 | 4,387 | 13,209 | 68,966 | 14,278 | 73,353 |

From: S. A. Friedman, Investigation of the Coal Reserves in the Ozark Section of Oklahoma, Oklahoma Geological Survey, January 1974, p. 88, 90.

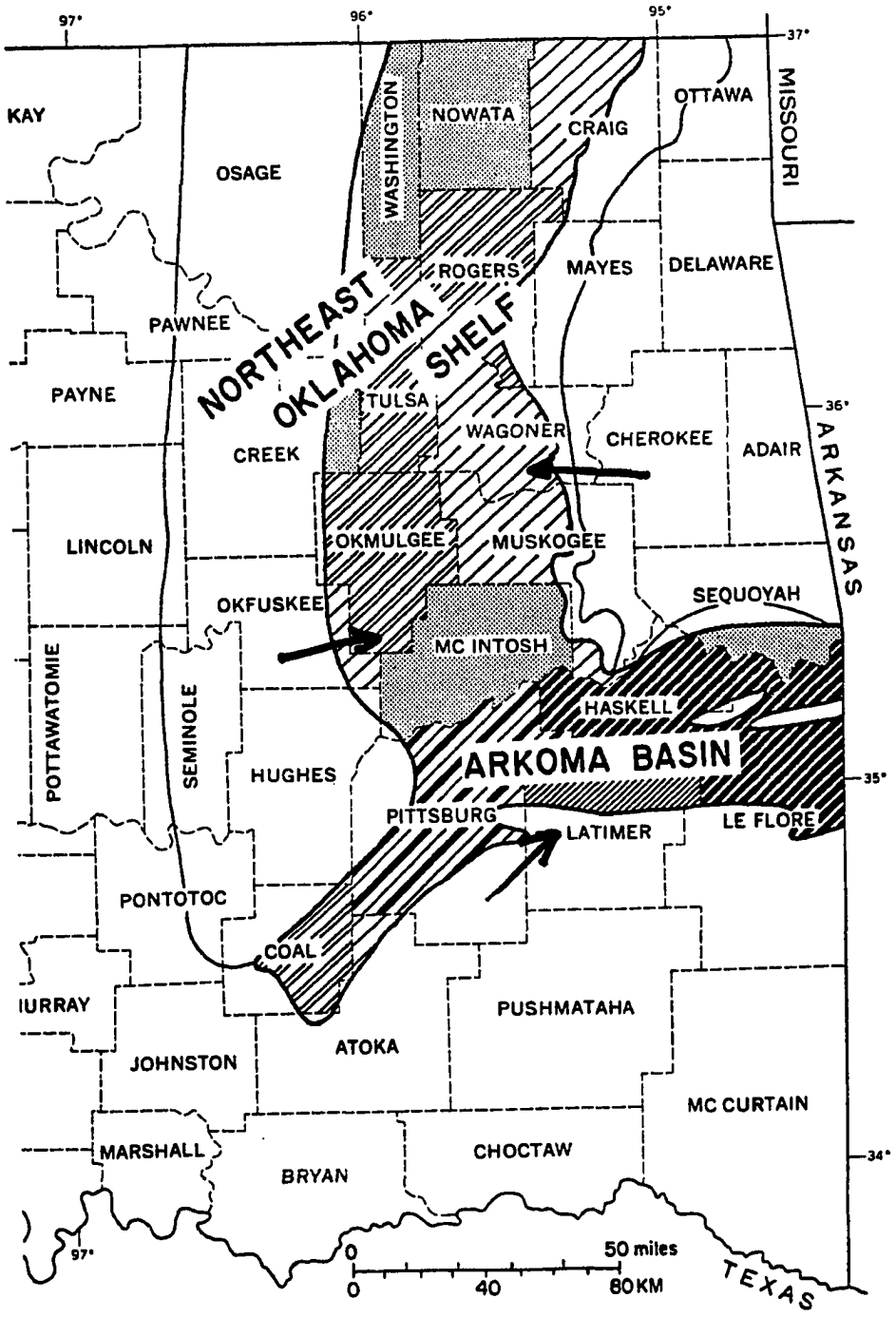



FIGURE 32. Map outlinging boundary of the Oklahoma part of the Western Region of the Interior Coal Province and showing distribution by county of remaining resources of bituminous coal in Oklahoma (as of January 1, 1974). (From S. A. Friedman, Investigation of the Coal Reserves in the Ozark Section of Oklahoma, Geological Survey, Jan. 1974, p. 10.)

2. Chemical Compounds:

Besides the three different coal beds from the eastern part of Oklahoma and one unknown coal which had been used in this study with $CO_2$-$H_2O$ solvent, seven other inorganic and organic compounds, some of which exist in coal compounds and some of which have similar linkages to the coal structure in their structure, were used in this research in order to discover whether or not the fragmentation of coal by the suggested solvent was caused by these compounds. These compounds were provided by Professor A. Hagen. They are:

(a) Benzyl-ether $(C_6H_5CH_2)_2O$—a liquid with molecular weight 198.27, boiling point 298°C, melting point 3.6°C and specific gravity 1.043.

(b) Diphenyl-disulfide $(C_6H_5\text{-}S\text{-}S\text{-}C_6H_5)$—a solid with molecular weight 218, boiling point 310°C, melting point 61-62°C and specific gravity 1.353.

(c) Benzyl phenyl ether $(C_6H_5CH_2\text{-}O\text{-}C_6H_5)$—a solid with molecular weight 184, boiling point 297°C and melting point 40-44°C.

(d) Pyritic sulfur (pyrite) $(FeS_2)$—molecular weight 120, melting point 1171°C and specific gravity 5.00.

(e) Benzyl-alcohol $(C_6H_5CH_2OH)$—a liquid with boiling point 204-205°C, melting point -15°C, and specific gravity 1.04.

(f) Phenethyl-alcohol $(C_6H_5CH_2\text{-}CH_2OH)$—a liquid with molecular weight 122, boiling point 219-221°C at 745 mm, melting point 20°C and specific gravity 1.023.

(g) 2-Naphthyl-benzoale $(C_6H_5COOC_{10}H_7)$—a solid with molecular weight 248.

The test of these compounds with the $CO_2$-$H_2O$ mixture was conducted under similar temperature conditions to the coal-$CO_2$-$H_2O$ mixture; but, generally, the pressures were higher. However, they are not the only compounds which exist in coal or have similar structural linkages. As indicated in Chapter II (Coal Structure), there are more than 300 compounds found in coal; and many other compounds have similar structures to coal. These compounds were selected because some of them are believed to have weak bonds and because they are not hazardous.

## C. GENERAL PROCEDURE OF THE EXPERIMENT

The general procedure of the experiment included several steps. They are:

1. One to three pieces of coal (size--gms) were placed inside the pressure vessel.

*2. A known amount of water was added to the pressure vessel.

3. The head or cover was put on top of the pressure vessel and covered by the cap and the closure system (cover and cap) was tightened with the bolts.

4. The pressure gauge and valves were installed on the top of the cover (head) and connected to the vessel by fittings and coupling connectors.

*5. $CO_2$ was injected from the $CO_2$ cylinder into the vessel through the stainless steel tube which was connected to the vessel by fittings and connectors.

---

*Step 2 is not required if only $CO_2$ was used as a solvent in the experiment while Step 5 is not required if only $H_2O$ is used as a solvent in the experiment.

6. The $CO_2$ was disconnected from the cylinder when the pressure shown by the pressure gauge installed on the vessel (reactor) was approximately equal to the pressure of the $CO_2$ cylinder, and the reactor was prepared for heating.

7. The vessel (reactor), which included the pressure gauge, with approximately 900 psi pressure was placed inside the furnace and heated for the desired time to the desired temperature.

8. After the desired period, the heat was turned off and the reactor (vessel) was left inside the furnace for at least four to five hours, depending on the temperature, in order for the reactor to become cool. Then the bomb reactor (pressure vessel) was removed from the furnace and the closure system was opened by loosening the bolts and removing bolts, cap and head (cover).

9. The solution was separated from the fragmented coal by passing through the filter and evaporating the solution. The fragmented coal was prepared for further purposes (size distribution analysis).

10. The U.S. standard sieve series was used to determine the size distribution of the fragmented coal.

11. Some of the broken samples were placed in the oven at 110°C for 24 hours in order to remove the moisture and dry the sample for further chemical analysis (ultimate, sulfur form, Btu analysis).

12. Samples of 3 to 10 grams—60 mesh no. (those fragmented samples which can pass through mesh no. 60 and have less than 0.0098 inch diameter) were provided for ultimate analysis, sulfur form analysis and Btu measurement.

## D. SPECIFIC PROCEDURE OF THE EXPERIMENT

### Step 1. Preparation of Selected Coal

A total of approximately 50 pounds of McAlester, Secor and Croweburg run-of-mine coal from eastern Oklahoma had been delivered to the laboratory. The Secor and Croweburg coal had been divided into reasonable sizes. The McAlester coal was in a large chunk and was broken into smaller pieces for the experiment. A total of more than 50 tests were performed on these three different coals in a period of approximately eleven months (May 1981-March 1982). The majority of the tests were done on the McAlester coal because of the difficulties involved in the mining operations for the production of this particular coal bed and also its high sulfur content. These coal samples were kept in a plastic bag during the period of the experiment. For each test, from one to three pieces of the coal samples with 30 to 176 grams weight were used. Each sample was 2 to 2 1/4 inches wide and approximately 2 1/2 to 3 1/2 inches long. Before the sample or samples were placed in the reactor, both the coal sample and the vessel (reactor) were cleaned). Then the coal sample was carefully placed into the vessel (bottom of vessel).

### *Step 2. Addition of Water to the Vessel (Reactor)

Between 125 and 300 cc of water was poured into the vessel. This range depended on the amount of coal being used for the test--less coal required less water and consequently, a large amount of coal required a larger volume of water. The water always covered the coal in

*Step 2 was not required for those tests in which only $CO_2$ was used as a solvent.

the reactor. The minimum amount of water used in the experiment was 125 cc. This amount is reasonable for a coal sample with 30 to 50 grams weight; but specifically, for more than one piece of coal (about 100 grams), approximately 300 cc water was reasonable. In any case, there was always at least 2 inches between the surface of the water inside the reactor and the top portion of the reactor to avoid very high pressures as a result of heating a liquid-filled reactor. Also it helped prevent leakage and damage to the pressure gauge and cover. The water used in this experiment was not distilled or purified.

*Step 3. Injection of $CO_2$ into the Reactor

After water was added to the coal inside the reactor, the reactor (vessel) was covered with the head (cover). The cap was screwed clockwise by a belt or hand until the cap was tight. The bolts were screwed down symmetrically. Either a torque wrench or an air impact wrench was used to tighten the bolts. In both cases, approximately 78-85 ft-pounds torque was used to tighten the bolts. This value is standard and depended on the pressure used in the test and the type of gasket. Figure 33[76] shows how to select the torque with regard to pressure and type of gasket. After the bolts were tightened, the pressure gauge was installed on the vessel, and it was connected to the vessel through the fittings and coupling connectors with a 1/16 inch outside diameter tube. Then carbon dioxide gas at approximately 1000 psi was injected into the vessel (reactor) by a capillary stainless steel tube which was connected to the reactor through the fitting and

*Step 3 was not applied for those tests in which $H_2O$ was used as the only solvent.

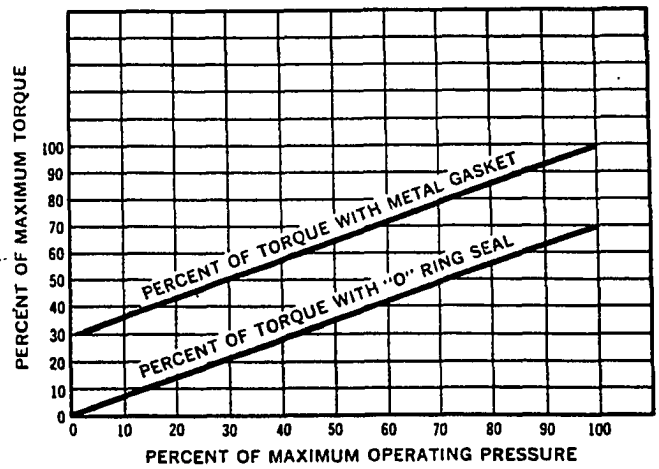



FIGURE 33. Selection of torque. From: Autoclave Engineering, High Pressure Information, Autoclave Eng., Inc., Bulletin 857.[76]

connectors with an inside diameter of 1/2 millimeter. This procedure was continued for about 15 minutes until the pressures of the $CO_2$ cylinder and vessel (reactor) were balanced. Then the $CO_2$ line was disconnected, and the reactor was prepared with contents for further operations.

Summary of the First 3 and Important Steps of Experiment:

Figure 34 illustrates the first three important steps of the experiment. First, the reactor (A) was placed on a flat disk that was fitted on a piece of wood (W) which was 5 1/4 inches wide, 14 inches long and 2 1/2 inches thick. The disk was located exactly in the middle of the piece of wood with an outside diameter of 4 1/2 inches. This disk contained two bars 1 1/2 inches long which fit into the two holes machined at the bottom of the reactor (vessel). This device (W) helped to hold the vessel during closing and removing closure system such as cap, cover and bolts. Then a piece or pieces of coal (I) ranging from 30 to 176 grams were placed inside the reactor (A). After

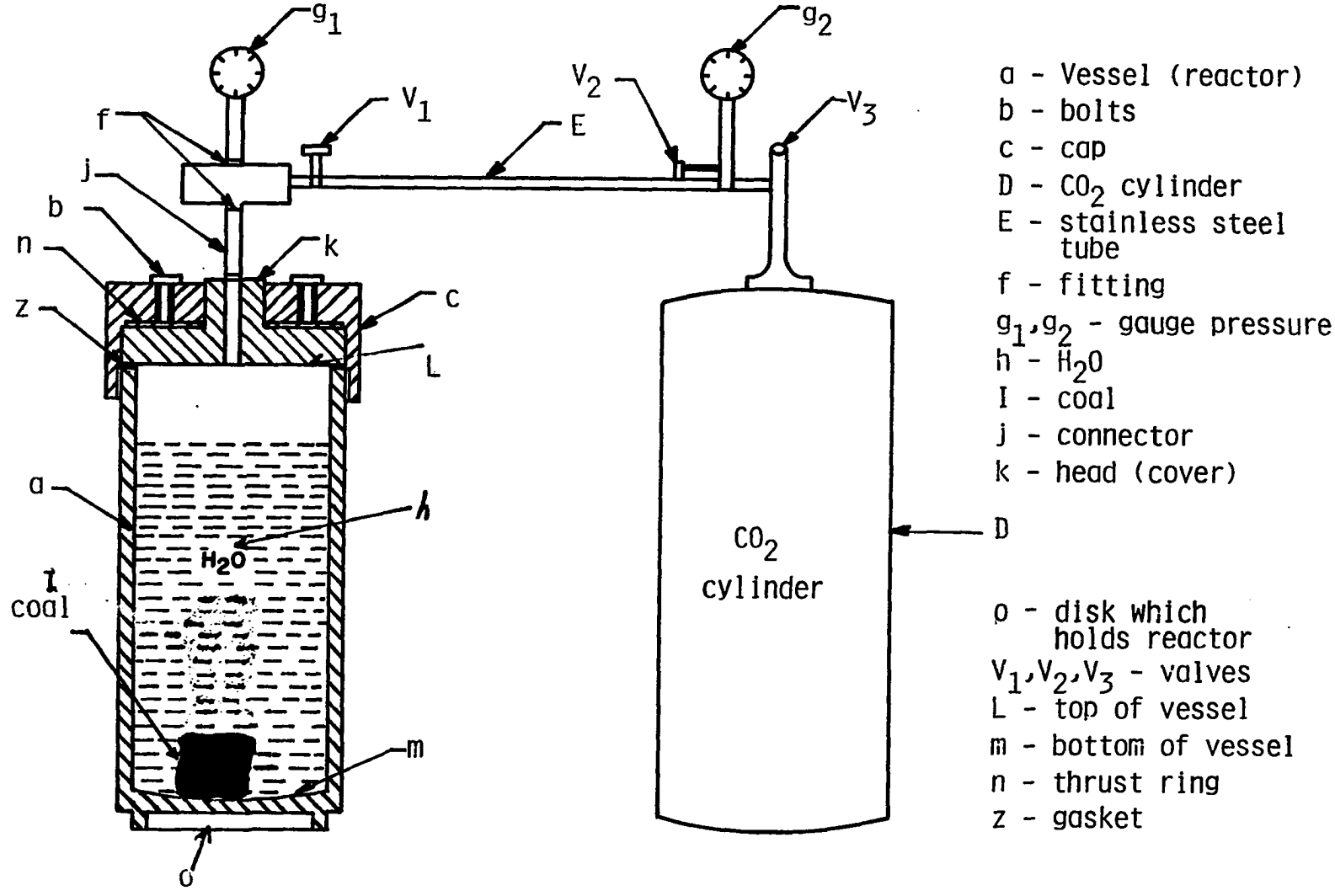



FIGURE 34. Illustration of injection of $CO_2$ into reactor.

that, from 150 to 300 cc water (h) was poured into the reactor (depending on the amount of coal). The water always completely covered the coal as Figure 34 indicates. However, there was at least two inches distance between the surface of the water inside the reactor (h) and the top of vessel (L). Then the head or cover (K) with thrust ring (N) was put on top of the vessel (L). After that the cap (C) was located and turned clockwise around the top portion of the vessel until it became tight enough for operations. In most tests, a belt was used to tighten the cap. Otherwise, there could have been leakage or probable explosion at high temperature and pressure. After the cap was screwed on, eight bolts (b) were tightened in a manner that began by tightening any two diametrically opposed bolts by hand, then two more in the same fashion until all eight bolts were tightened by hand. Then a torque wrench or air impact wrench was used to tighten the bolts completely. The amount of torque used ranged from 75 to 85 ft-pounds. Two diametrically opposed bolts are preferred in order to prevent leakage or explosion. Then the pressure gauge, Maxisafe or Wike model type of gauge ($g_1$) and the three-way stainless steel valve ($V_1$) were installed on the vessel through the head by a union coupling connector tube with 1/16 inch outside diameter (j). Then the $CO_2$ cylinder (D) was used to inject $CO_2$ through the 24 inches of capillary stainless steel tube with 1/2 mm inside diameter (E) and fitting into the reactor. After the pressure vessel with pressure gauge was set up, the $CO_2$ cylinder was connected to the reactor by stainless steel tube (E). At this stage of the test, valve (3) was opened; and pressure gauge (2) was used to indicate the $CO_2$ pressure of the cylinder which normally

was about 1050 psi. In cool weather, this pressure reduced to 900 psi. Finally, valve (2) was used to control the flow of gas to the reactor. Sometimes it required a few minutes to reach the same amount of pressure in the reactor and in the $CO_2$ cylinder (10-15 minutes). At this point, pressure gauge ($g_1$) and pressure gauge (2) indicated approximately the same pressure. Then $V_3$ and $V_1$ were closed; and the $CO_2$ injection was disconnected by disconnecting stainless steel tube (E). First, $V_1$ was closed, then $V_3$ was closed. After closing $V_1$ and $V_3$ the stainless steel tubing was disconnected from the $CO_2$ cylinder by loosening the fitting until pressure gauge ($g_2$) indicated approximately zero. Finally stainless steel (E) was also disconnected from the reactor. At this stage, the reactor with its contents (coal + $CO_2$ + $H_2O$) were ready for the heating process. Before the heating process began, a solution of soap and water was used to test for any leakage. In the case of leakage, the procedure was repeated from the first step.

Step 4. Heating the Reactor

After the leakage test, the reactor was placed inside the furnace with inside diameter of 4 inches for heating purposes, and the temperature was controlled by a controller device. The period of heating ranged from 2 hours up to 42 hours. However, this period did not include the time for warming the reactor up to the desired temperature. Normally, it required from 60 minutes up to 150 minutes to increase the temperature of the reactor from room temperature (25°C) to the temperature range of 200 to 350°C. After the desired period of heating, the electrical heater was turned off. The reactor remained in the furnace for a few hours (minimum of four) until the reactor was

cool and could be removed from the furnace. The reactor can be cooled in a shorter period if the reactor can be removed from the furnace.

Step 5. Release of Gas Pressure in Reactor and the Closure System

This step began with releasing the remaining gas pressure ($CO_2$ pressure) either by loosening the gauge connector or loosening the three-way stainless steel valves. In most tests, the gauge connector (j in Figure 34) was used to relieve the pressure (approximately 900 psi). Furthermore, in both cases, the procedure for removing the gas pressure was very slow, in order to prevent any damage to the gauge connectors or fitting or valves. Then in the same manner in which the bolts were closed, they were loosened by using a torque wrench or air impact wrench. The torque used to loosen the bolts was slightly higher than the torque used to tighten the bolts. After all bolts were loosened, they were removed from the head. Then the cap was turned counterclockwise. In most cases, the belt was used to open the cap and remove it from the vessel. However, in some tests, because of the high temperature, the cap or vessel expanded to such a degree that the cap was difficult to remove from the vessel. In those cases, either cool water was used to cool the bottom portion of the vessel in order to create a temperature difference between the top portion of the vessel which the cap covered and the bottom portion of the vessel, or heat was applied slightly to the top portion of the vessel. After removing the cap in any case, the head (cover) was removed from the top of the vessel. In this step in some tests, the gas smelled like $H_2S$ which indicated there had been some reaction between solvent and coal and some mineral matter of the coal.

Step 6. Sieve Analysis of the Fragmented Coal

In this step, the contents of the vessel, fragmented coal and solution, were separated from each other through a filter. The solution was then vaporized to remove the water. In many cases, the results of evaporization indicated a small portion of the coal had been dissolved (< 1 gm). Then the U.S. standard sieve series with the following screen sizes was used to determine the percentage of size distribution of fragmented coal. The period of time used to shake the U.S. standard sieve series was 30-35 minutes.

Step 7. Preparation of Samples for Ultimate Analysis, Sulfur Analysis and Btu Measurement

Two samples were prepared for ultimate, sulfur and Btu analysis. Among these two samples, one sample was before treatment and the other sample was after treatment (treatment of coal by $CO_2$-$H_2O$ mixture). The physical conditions of the treatment were 275°C temperature and 3300 psi pressure. The period of the test was 24 hours. This analysis was conducted by Galbraith Laboratories, Inc. Both samples (before and after treatment) were selected from McAlester bituminous coal. After sieve analysis of each sample, between 3 and 10 grams of Mesh No. 60 (< 0.0098 inches) were collected separately. Then except for the original sample (before treatment), the other sample was placed in a watch glass with 24 gram weight and then kept in the oven for at least 24 hours. Finally, the two samples were placed in a plastic jar with 20 gram weight and sent to Galbraith Laboratories, Inc. for ultimate, sulfur and Btu analysis.

In the ultimate analysis, the percents of the following elements were determined using ASTM (American Society for Testing and materials) standards: carbon, hydrogen, oxygen, nitrogen, sulfur, moisture, and chlorine. In the sulfur form analysis, three different forms of sulfur were measured. They are: pyrite (pyritic sulfur), sulfate sulfur, organic sulfur. Also in both samples, the Btu value was measured by ASTM test. (The results are shown in Tables 1 and 2 of Appendix A.)

Step 8. Test Procedure for Treatment with $CO_2$-$H_2O$ mixture of Seven Organic and Inorganic Compounds Which Exist in Coal or Have Similar Linkage Compared to Coal Structure

On the basis of Wiser's theory about coal structure which is the latest theory and most accepted by coal researchers in the United States (Chapter II, Figure 7), seven inorganic (pyrite) and organic compounds were selected in this study for the chemical reaction with carbon dioxide-water mixture. These compounds either exist in coal, such as pyrite ($FeS_2$), or they have linkages similar to coal structure. Two reasons affected the selection of these compounds. First, some of them are believed to have weak bonds such as benzyl ether $(C_6H_5CH_2)_2O$ and pyrite ($FeS_2$). This is the view of Wiser[42] and indicated by arrows in Figure 7 of Chapter II. However, this view is not shared by some coal researchers. Second, they were not hazardous compounds. The compounds used and the physical conditions of the reactions are:

1. Benzyl ether $(C_6H_5CH_2)_2O$--a liquid, boiling point 298°C and melting point 3.6°C with specific gravity 1.043. Benzyl ether was mixed with $CO_2$ (gas) and water in the small bomb reactor. The physical

conditions were temperature of 305°C and pressure up to 8000 psi. No chemical reaction obtained after 24 hours.

2. Diphenyl-disulfide ($C_6H_5$-S-S-$C_6H_5$)—a solid with boiling point 310°C, melting point 61-62°C with specific gravity 1.353. Diphenyl-disulfide was mixed with $CO_2$ (gas) and water at temperature of 305°C and pressure up to 6000 psi for 24 hours. No reaction chemical occurred.

3. Benzyl phenyl ether ($C_6H_5CH_2$-O-$C_6H_5$)—a solid with boiling point 297°C, melting point 40-44°C was mixed with $CO_2$ (gas) and water at temperature 305°C and pressure up to 7000 psi. No chemical reaction obtained after 24 hours.

4. Pyrite ($FeS_2$)—a solid with melting point 1171°C with specific gravity 5.00 was mixed with $CO_2$ and water at 305°C and pressure up to 3400 psi for 24 hours. No chemical reaction occurred.

5. Benzyl-alcohol ($C_6H_5CH_2OH$)—a liquid with boiling point 203-205°C, melting point -15°C and specific gravity 1.045 was mixed with $CO_2$ (gas) and water for 24 hours at 305°C and pressure up to 7000 psi. No chemical reaction obtained.

6. Phenethyl-alcohol ($C_6H_5CH_2$-$CH_2OH$) with melting point 20°C, boiling point 219-221°C at 750 mm and specific gravity 1.023 was mixed with $CO_2$ (gas) and water for 24 hours at 305°C and pressure up to 7000 psi. No chemical reaction occurred.

7. 2-Naphtyl-benzoal ($C_6H_5COOC_{10}H_7$)—a solid was mixed with $CO_2$ gas and water for 24 hours at 305°C and up to 7000 pressure. No chemical reaction obtained.

The procedure of the tests of these compounds with the $CO_2$-$H_2O$ mixture was similar to the coal-carbon dioxide-water mixture. The bomb reactor (vessel) used in these tests was constructed of stainless steel but with smaller capacity compared to the one which was used in the coal-$CO_2$-$H_2O$ tests. The reactor had 12 mm (1.2 centimeter) inside diameter and 2.5 cm outside diameter with 21.5 cm inside depth. The volume of the cylindrical reactor was 25 ml. In this reactor, a glass liner was used in order to prevent any corrosion by the reaction. The capacity of the glass liner was 20 ml. In all seven tests, the procedure was similar. First, a small amount of the compound was placed inside the glass liner (between 1-2 gram), then between 8 and 10 ml water was added to the compound in the glass liner. After that, the glass liner was carefully placed inside the reactor. The pressure gauge and three-way valve were connected to the reactor through the fitting and connectors, and $CO_2$ was added to the reactor through the 24 inch capillary stainless steel tube to the reactor. The temperature applied was 305°C (desired temperature on the basis of coal fragmentation by the $CO_2$-$H_2O$ mixture), and the pressure, depending on the compound, ranged from 3400 psi to 8000 psi. The period for tests was 24 hours. The heating system was similar to the one used in the coal carbon dioxide-water mixture. After 24 hours, the reactor was allowed to cool off. The closure system was removed, and the glass liner with its contents was carefully removed from the reactor. The contents were mixed with ether (except for pyrite which has a high specific gravity so that the lack of reaction with the $CO_2$-$H_2O$ mixture was obvious) in a funnel for extraction of water from the compound. Because ether is a

good solvent except for water, the layer of water could be recognized easily and was extracted from the compounds. A very small amount of water could remain within the compounds so $MgSO_4$ was added to the remaining compounds (for 24 hours) in order to eliminate this amount of water in the compounds. After this period, the $MgSO_4$ was separated from the chemical compounds by filter, and the chemical compounds were evaporated by hot plate for approximately one hour in order to remove the ether. For pyrite, the result was obvious and did not require infrared spectroscopy. In the other cases, whatever compounds remained were tested using the Beckman Irlo infrared spectrophotometer. The results showed that there was not much difference between the chemical after treatment with the $CO_2$-$H_2O$ mixture and before treatment (original compound)*. In other words, there was no reaction between these chemicals and the carbon dioxide-water mixture.

*The original infrared spectrum of some of the these compounds was provided by Professor Hagen at the University of Oklahoma Chemistry Department. But some of the above seven chemicals were test by infrared spectroscopy in this study in order to compare the original infrared spectrum of the chemical (before treatment with the $CO_2$-$H_2O$ mixture) with the infrared spectrum of the chemical compound after treatment with the $CO_2$-$H_2O$ mixture.

# CHAPTER V

## CALCULATIONS AND THEORETICAL CONSIDERATIONS

### A. CALCULATIONS

1. Volume of reactor (cylindrical shape).

Diameter of reactor = 2.5 inches

Inside depth of reactor = 6.25 inches

Volume of reactor = $\pi r^2 h$

$h = 6.25$ inches $\Rightarrow$ $r = \frac{2.5}{2} = 1.25$ inches

1 ft = 12 inches = 30.48 cm

$$V = \pi\left(\frac{1.25}{12}\right)^2 \left(\frac{6.25}{12}\right) = 0.0177 \text{ ft}^3$$

$$V = 0.0177 \text{ ft}^3 \left(\frac{30.48 \text{ cm}}{\text{ft}}\right)^3 = 500 \text{ cm}^3 = 500 \text{ ml}$$

$V = 500$ ml

2. Amount of $CO_2$ injected for each test:

Total $CO_2$ injected into reactor = $CO_2$ dissolved in water + $CO_2$ gas

The $CO_2$ dissolved in water for temperatures from 0 to 120°C and pressures up to 700 atmospheres is given in gram per 100 gram water in Figure 21 of Chapter III. Since the initial conditions of each test are similar (room temperature, 25°C, and 900 psi or 61 atmospheres), the amount of carbon dioxide dissolved per 100 gram water would be the same. However, because different amounts of water were used in each

test, the total amount of $CO_2$ dissolved in the water for each test varies. By using Figure 21 of Chapter III for T = 25°C and pressure = 61 atm, the $CO_2$ dissolved in 100 grams water is determined in the following manner. Since for T = 25°C and P = 61 atm, the $CO_2$ dissolved is not given directly, the interpolation technique was used. Therefore, for T = 25° and P = 61 atms, 5.86 g $CO_2$ is dissolved in 100 gram water.

The number of moles of $CO_2$ gas which was injected into the reactor at room temperature (25°C) and 61 atm pressure that did not dissolve in the water is calculated as follows:

$$n_g = \frac{PV}{ZRT} \qquad (1)$$

where P is injection pressure, 900 psi (61 atm); V is the volume of $CO_2$ gas; Z is the compressibility factor for $CO_2$; R is the gas constant; and T is the temperature (25°C). In Equation (1), V is equal to

$$V_{CO_2\ gas} = \text{Total volume of reactor} - (V_{coal} + V_{H_2O} + V_{air})$$

where total volume of reactor = 500 ml

$$V_{coal} = \frac{M}{\rho}$$

where M is the amount of coal used in each test and $\rho$ is the density of the coal which was determined from Figure 15 of Chapter II. By knowing the percent of carbon in McAlester coal (86%), the density was estimated as 1.3 gram/$cm^3$. (This value had also been measured in the Petrophysics Laboratory of the Petroleum and Geological Engineering Department.)

$$V_{air} = \frac{nRT}{P} \quad \text{(air was assumed an ideal gas)}$$

is the volume which is occupied by air inside the reactor at 25°C (room temperature) and 61 atm pressure (initial pressure of $CO_2$).

By knowing $V_{coal}$, $V_{H_2O}$, and $V_{air}$, the volume of gas ($CO_2$) can be calculated. Then, knowing $V_{gas}$, Equation (1) was applied to determine the number of moles of $CO_2$ (gas). Finally, by knowing the amount of $CO_2$ dissolved in the water and the amount of gas ($CO_2$) in the reactor, the total amount of $CO_2$ used for each test was calculated.

Since the procedure for calculating the $CO_2$ injected into the reactor for each test is similar, the only difference being in the amount of coal and water used for each test, instead of repeating the procedure of the calculation for all tests, only the procedure for Test One is illustrated. For the remaining tests, the results of the calculation are shown in Table 17 (p. 107) and Table 18 (p. 108).

TEST #1:

Total $CO_2$ injected into the reactor = $CO_2$ dissolved + $CO_2$ gas

The $CO_2$ dissolved in 100 grams of water was calculated in the last section to be 5.86 g $CO_2$/100 g $H_2O$. Since 250 grams water was used in Test #1, the total $CO_2$ dissolved is:

$$5.86 \times 2.5 = 14.65 \text{ grams}$$

$CO_2$ dissolved for Test #1 = 14.65 g

$CO_2$ gas (Test #1):

$$V_{CO_2 g} = \text{total volume of reactor} - (V_{coal} + V_{H_2O} + V_{air})$$

$$= 500 \text{ ml} - (V_{coal} + V_{H_2O} + V_{air})$$

$V_{coal} = \frac{M}{\rho}$, where M is the amount of coal used in Test #1, which was 160 grams and $\rho = 1.3 \text{ g/cm}^3$. Therefore,

$$V_{coal} = \frac{160}{1.3} = 123 \text{ cc or } 123 \text{ ml}$$

$V_{H_2O}$ = 250 ml or 250 cc, the volume of water used in Test #1.

$V_{air}$ - Assuming air is an ideal gas, then the following relation can be justified to calculate $V_{air}$.

$V_{air} = \frac{nRT}{P}$, where n is number of moles of air and R is gas constant = 0.08205 liter-atm-$K^{-1}$-$mole^{-1}$, T is room temperature (298.2 K) and P is initial pressure of $CO_2$ gas, 61 atm (900 psi).

$n_{air}$ for one atmosphere pressure and T = 25°C can be calculated as:

$$n = \frac{PV}{RT}$$

where V is equal to:

$$V = 500 \text{ (total volume of reactor)} - (V_{coal} + V_{H_2O})$$

$$V = 500 - (123 + 250) = 127 \text{ ml or } 127 \text{ cm}^3$$

$$n = \frac{(1)(0.127)}{(0.08205)(298.2)} = 0.0052 \text{ mole}$$

and $V_{air}$ at 61 atm (900 psi), 298.2 K is calculated as:

$$V_{air} = \frac{nRT}{P} = \frac{(0.0052)(0.08205)(298.2)}{61}$$

$$V_{air} = 0.0021 \text{ liter or } 2.1 \text{ ml or } 2.1 \text{ cm}^3$$

and

$$V_{CO_2 g} = \text{total volume of reactor} - (V_{coal} + V_{H_2O} + V_{air})$$

$$V_{CO_2 g} = 500 - (123 + 250 + 2.1) = 124.9 \text{ cm}^3$$

Since $CO_2$ is a non-ideal gas,

$$n_{CO_2 \text{ gas}} = \frac{PV}{ZRT}$$

where P is initial pressure of $CO_2$ (61 atm); V = 0.1249 liter, R is gas constant = 0.08205 lit-atm-$K^{-1}$-$mole^{-1}$, T is 298.2 K (room temperature) and Z is compressibility factor which is calculated as follows:

Using Chart #1,[77]

$$P_r = \frac{P}{P_C}$$

where P is $CO_2$ injection pressure, $P_C$ is critical pressure of $CO_2$ (73 atm) and $P_r$ is reduced pressure which is equal to:

$$P_r = \frac{61}{73} = 0.84$$

$$T_r = \frac{T}{T_C}$$

where $T_r$ is the reduced temperature, $T_C$ is the critical temperature (31° C) and T is room temperature (25°C). Thus,

$$T_r = \frac{25}{31} = 0.81$$

In Chart #1, the compressibility factor Z for $P_r = 0.84$, $T_r = 0.81$ is not given, but Z at $P_r = 0.84$ and $T_r = 1.00$ and $P_r = 0.84$ and $T_r = 0.7$ are given. Therefore, by using interpolation, we can calculate Z = 0.51 for $P_r = 0.84$, $T_r = 0.81$.

By using Chart #2,[78] the Z compressibility factor for $P_r = 0.84$, $T_r = 0.81$ is approximately equal to the value which had been calculated by using Chart #1. Therefore, by finding Z, $n_{CO_2\ gas}$ can be calculated.

$$n_{CO_2\ gas} = \frac{PV}{ZRT}$$

$$n_{CO_2\ gas} = \frac{(61)(0.1245)}{(0.51)(0.080205)(298.2)} = 0.61 \text{ mole}$$

Since 1 mole of $CO_2$ = 44 g

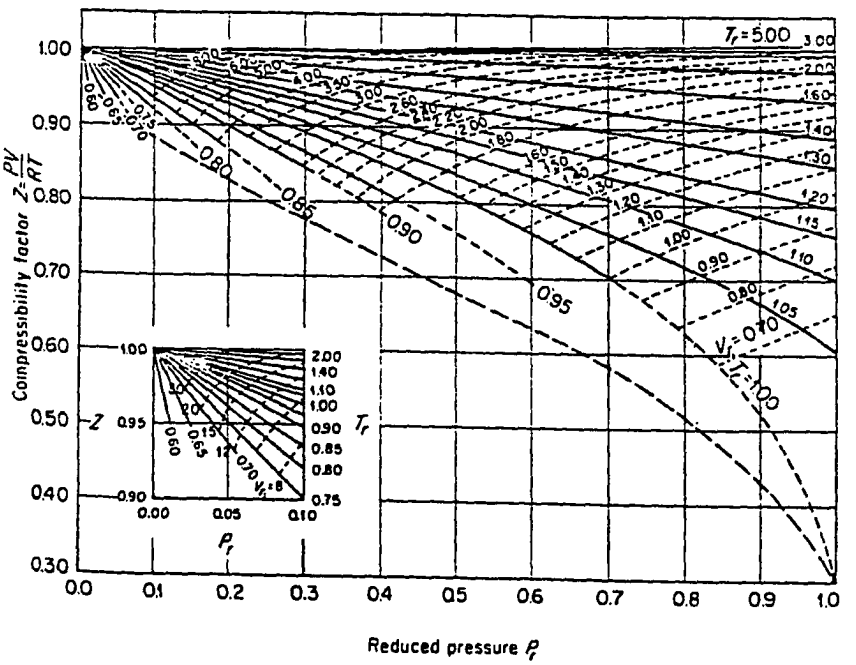
$$CO_2 \text{ gas} = 0.61 \times 44 = 26.7 \text{ gram}$$

Therefore, the total $CO_2$ in the reactor is equal to

$$CO_2 = CO_2 \text{ gas} + CO_2 \text{ dissolved}$$

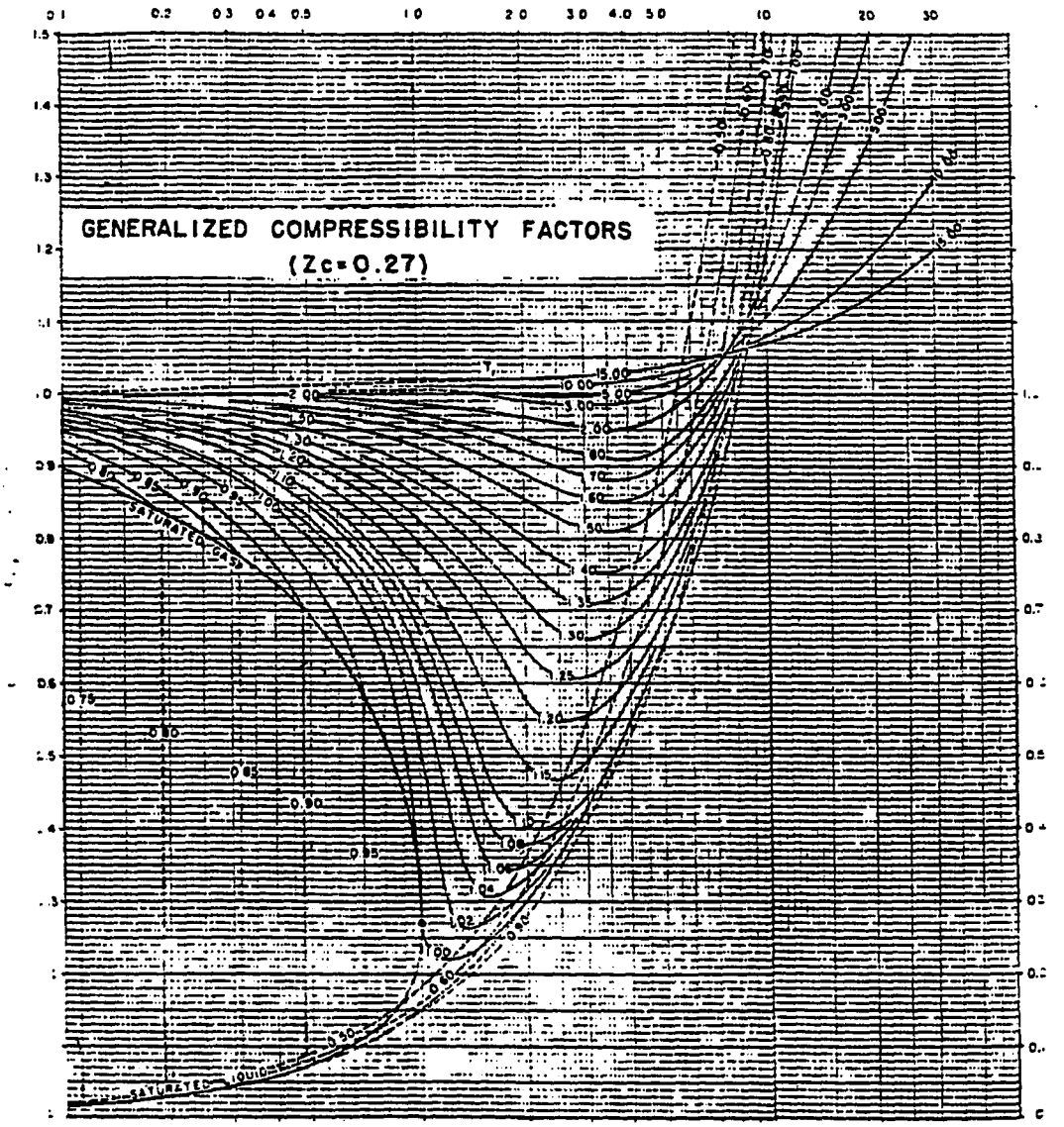
$$CO_2 = 26.7 + 14.65 = 41.35 \text{ grams}$$

Total water = 250 grams




Generalized compressibility chart. (*From Ref.* )

From: Reid, R. C., Prausnitz, J. M. and Sherwood, T. K., "Pressure-Volume-Temperature Relation of Pure Gases and Liquids," The Properties of Gases and Liquids, McGraw Hill Book Company, 1977, Third Edition, p. 27.




Generalized compressibility chart.

From: Van Wylen, G. J. and Sonntag, R. E., Fundamentals of Classical Thermodynamics, John Wiley and Sons, Inc., Second Edition, 1976.

TABLE 17: The Results of Calculations of $CO_2$ Used in This Study for McAlester Coal

| Test No. | 1 Coal g | 2 $H_2O$ g | 3 $CO_2$ Dissolved g | 4 $CO_2$ gas (g) | 5 Total $CO_2$ g | 6 Total Solvent g | 7 $\%CO_2$ | 8 $\%\ H_2O$ | 9 Total Solvent + Coal g | 10 % Coal | 11 % Solvent |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 160 | 250 | 14.65 | 26.7 | 41.35 | 291.35 | 14.2 | 85.8 | 451.35 | 35.4 | 64.5 |
| 2 | 128 | 225 | 13.185 | 37.4 | 50.585 | 275.585 | 18.4 | 81.6 | 403.585 | 31.7 | 67.3 |
| 3 | 132 | 215 | 12.6 | 38.7 | 51.3 | 266.3 | 19.2 | 80.7 | 398.3 | 33 | 67 |
| 4 | 69 | 135 | 7.9 | 66 | 73.9 | 208.9 | 35 | 65 | 277.9 | 24.5 | 74.5 |
| 5 | 79.5 | 175 | 10.255 | 56 | 66.255 | 241.255 | 27.5 | 72.5 | 320.8 | 24.8 | 75.2 |
| 6 | 59.7 | 135 | 7.9 | 67.32 | 75.2 | 210.23 | 35.7 | 64.3 | 269.93 | 22.1 | 77.8 |
| 7 | 52 | 125 | 7.325 | 71 | 78.325 | 203.325 | 38.5 | 61.5 | 255.3 | 20.4 | 79.6 |
| 8 | 50.8 | 125 | 7.32 | 70.8 | 78.1 | 203.1 | 38.8 | 61.2 | 253.9 | 20 | 80 |
| 9 | 47.5 | 125 | 7.325 | 71.625 | 78.958 | 203.95 | 38.7 | 61.2 | 251.3 | 18.9 | 81.1 |

Column 1 - Amount of coal used in each test.

Column 2 - Amount of water used in each test.

TABLE 18: The Relationship Between Dependent Variable (d) and Independent Variables

| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | % Remaining on Mesh No. | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Test No. | T °C | P psi | Period of Test (h) | S/C | h/C | M gm | d inch | 4 0.185 | 16 0.0469 | 50 0.0116 | 70 0.0082 | 100 0.0059 | -100 0.0029 |
| 1 | 200 | 2150 | 21.5 | 1.8 | 6 | 451.3 | 0.135 | 55 | 27.2 | 6.3 | 2.2 | 4.5 | 5 |
| 2 | 225 | 2700 | 23 | 2 | 4.5 | 403.58 | 0.126 | 33.9 | 50.4 | 9.3 | 3.4 | 1 | 2 |
| 3 | 235 | 2850 | 24 | 2 | 4 | 398.3 | 0.124 | 42 | 38.4 | 12.6 | 4.2 | 0.5 | 2.3 |
| 4 | 250 | 2950 | 24 | 2.9 | 1.85 | 277.9 | 0.119 | 44 | 30 | 11.2 | 7.7 | 4.6 | 2.2 |
| 5 | 275 | 3300 | 18 | 3 | 2.6 | 320.8 | 0.145 | 60 | 28 | 7 | 1.5 | 0.63 | 3 |
| 6 | 275 | 3300 | 24 | 3.5 | 1.8 | 269.93 | 0.094 | 30 | 27.5 | 17.2 | 9.2 | 8.1 | 8 |
| 7 | 275 | 3300 | 30 | 3.9 | 1.6 | 255.3 | 0.082 | 25 | 23.4 | 18.5 | 11.7 | 8.8 | 12.6 |
| 8 | 275 | 3300 | 36 | 4 | 1.59 | 253.9 | 0.072 | 21 | 22 | 16.4 | 12.6 | 10.5 | 17.5 |
| 9 | 325 | 3600 | 18 | 4.3 | 1.59 | 251.49 | 0.074 | 23.3 | 20.3 | 16 | 10.2 | 12.8 | 17.4 |

Column 1 - Temperature in degrees Centigrade
Column 2 - Pressure in psi
Column 3 - Period of experiment in hours
Column 4 - Solvent to coal ratio
Column 5 - Water to $CO_2$ ratio
Column 6 - Total mass in reactor in grams (coal + $CO_2$ + $H_2O$)
Column 7 - Average particle size in inches

Total solvent ($CO_2$ + $H_2O$) = 250 + 41.35 = 291.35 grams

Total coal = 160 grams

$$\% \ CO_2 \text{ in solvent} = \frac{41.35}{291.35} \times 100 = 14.2\%$$

$$\% \ H_2O \text{ in solvent} = \frac{250}{291.35} = 85.8\%$$

Total solvent + total coal = 291.35 + 160 = 451.35 grams

$$\% \text{ coal in reactor} = \frac{160}{451.35} \times 100 = 35.4\%$$

$$\% \text{ solvent in reactor} = \frac{291.35}{451.35} \times 100 = 64.6\%$$

B. THEORETICAL CONSIDERATIONS OF THE EXPERIMENT

Coal has such a complicated structure and composition that it is difficult for many coal researchers to work with in a normal fashion. Its composition is sometimes variable from one coal bed to another and even from one location to another in the same coal bed. To date, more than 300 organic and inorganic compounds have been recognized in coal.[44,45] The way they are bound together is not clear. On one hand, Wiser in his theory indicated that the organic compounds of coal are bound together by sulfur and ash.[19,42] On the other hand, there are researchers who believe the organic and inorganic compounds of coal are connected to each other by hydrogen.[4] Therefore, those who support Wiser's hypothesis believe that in the chemical comminution process, the suggested solvent disrupts the sulfur bonds and permits the whole macromolecular compounds of coal to fall apart. Those who are followers of the second group believe the suggested solvent disrupts and disconnects the hydrogen bonds, thereby causing the fragmentation of the coal. This division depends mainly on the results of the

fragmented coal and solvent suggested for the chemical comminution process, and interpretation of the results in order to justify the cause of the fragmentation as a result of the treatment of the coal by the suggested solvent. In relation to this research, since the total sulfur of the coal was reduced from 3.51% by weight to 2.23% by weight (37% of the total sulfur was eliminated) and the total ash was reduced from 18.65 to 17.5% by weight, the Wiser hypothesis is most suitable. As indicated in the Ph.D. dissertation proposal,[79] the primary forms of sulfur in coal are inorganic and organic sulfur.

1. Inorganic Sulfur:

a. Pyritic sulfur ($FeS_2$)—Pyritic sulfur occurs in coal in two forms: (1) cubic shape in which a = b = c and is called pyrite; or (2) orthorhombic in which $a \neq b \neq c$ (unequal axes) which is called marcasite.

b. Sulfate sulfur ($CaSO_4 \cdot 2H_2O$)

One of the most significant forms in which it occurs is pyrite ($FeS_2$). In some cases, the pyrite is scattered in large masses and is readily recognized as such. In other cases it occurs in a very finely divided form with separate particles being too small to be recognized.

2. Organic Sulfur in Coal:

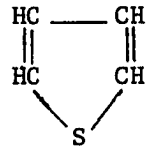
Another important form in which sulfur occurs is organic sulfur which can be

a. Thiol or mercaptan RSH

b. Sulfide or thio-ether RSR'

c. Disulfide RSSR'

d. Aromatic system containing the thiophen ring



R and R' are alkyl or aryl groups.

The reaction of coal with the suggested solvent in this research ($CO_2$ + $H_2O$) is expected to follow the following two stages in order to fragment the coal as a result of removing and disconnecting the sulfur bonds from organic compounds. The first stage is oxidation of organic sulfur to sulfone.

$$R\text{-}S\text{-}R \xrightarrow[T^\circ+P]{[O]} R\text{-}SO_2\text{-}R$$

The second stage is to eliminate the $SO_2$ from the sulfone by aqueous $H_2O$

$$R\text{-}SO_2\text{-}R \xrightarrow[H_2O]{T^\circ + P} R\text{-}OH\text{-}R + SO_3$$

In the case of inorganic sulfur, where pyrite is considered to be the main portion of inorganic sulfur, the stages are:

1. $$FeS_2 + 2CO_2 \xrightarrow{T^\circ + P} Fe + 2SO_2 + 2C$$

$$FeS_2 + 4CO_2 \xrightarrow{T^\circ + P} Fe + 2SO_2 + 4CO$$

$$2FeS_2 + 11CO_2 \xrightarrow{T^\circ + P} Fe_2O_3 + 4SO_2 + 11CO$$

2. $$Fe_2O_3 + SO_2 \xrightarrow[H_2O]{T^\circ + P} Fe(OH)_3 + SO_3$$

These stages and reactions are the most reasonable ones for the chemical interactions of $CO_2$ with coal, but the reaction of

$$CO_2 \rightarrow CO + O_2$$

has such a thermodynamic property (high positive free energy, $\Delta H$), it is hard to believe the $CO_2$ can act as a source of oxygen at temperatures up to 325°C and pressure up to 3300 psi. However, since the coal was fragmented in the presence of $CO_2 + H_2O$ and sulfur was also reduced by 37%, $CO_2$ probably acted as a medium to dissolve mineral matter which existed between the boundaries of the coal and provided better sources of oxygen for further reaction with pyrite and organic sulfur. Also, since water is in the system, the role of carbonic acid could become important. It is interesting to note that recently there have been many studies[80,81,82,83,84,85] on the presence of sulfur in coal and how it can be removed from the coal at relatively low temperature and pressure (the temperature ranged from 25-400°C at atmospheric pressure) despite the thermodynamic properties of pyrite which indicate that pyrite is very stable and strong at these temperatures. These studies claimed[80,82] $FeS_2$ appears in the form of loose crystals which form vein-like structures in the organic coal bed because the density of pyrite is high (5.0 $g/cm^3$) and the density of the organic compounds are relatively low (1.2-1.5 $g/cm^3$). Since the float-sink technique, centrifugation method and froth flotation technique can easily remove the pyrite from the coal compounds, it is not surprising that pyrite in coal compounds has loose connections compared to the structure of pyrite itself. In other words, the pyrite alone is much stronger and established compared to the one which exists in coal compounds.

To justify this analogy, two series of tests were done on coal in the presence of oxygen and hydrogen. In the first series, coal was heated at different temperatures ranging from 25°C to 400°C in the

presence of an oxygen atmosphere on Illinois No. 6 coal.[81] The results of this study showed the oxidation of pyrite ($FeS_2$) in Illinois No. 6 coal occurs in three steps: (1) at temperatures between 25-310°C, pyrite is converted to iron sulfate; (2) at temperatures between 310-325°C pyrite is changed to $\gamma$-$Fe_2O_3$; and (3) at 325-400°C temperature, pyrite is converted to $\alpha$-$Fe_2O_3$. It has been concluded as a result of this study that the oxidation of pyrite in coal is highly affected by the compounds and structure of the coal. A similar test was done on the same coal bed in the presence of a hydrogen atmosphere at temperatures ranging from 25°C to 400°C. The results of this study showed the pyrite could be removed from the coal below 400°C with the presence of hydrogen.

In addition, seven compounds which are believed to exist in coal or which have similar structure were treated with $CO_2 + H_2O$. The temperature of all tests was set up at 305°C which was predicted to have a reaction with $CO_2$-$H_2O$ compared to the range of temperatures, 200-325°C, at which coal fragmented as a result of the treatment with the $CO_2$-$H_2O$ mixture. The pressures are different because there was no control on pressure, and pressure depended on temperature and type of compound. These compounds were believed to have weak bonds, but as Appendix D shows, no reaction occurred between these compounds and $CO_2 + H_2O$.

It is believed the fragmentation of McAlester, Croweburg and Secor coal by the suggested solvent ($CO_2 + H_2O$) is mainly due to dissolving of the mineral matter which holds the coal particles together by $CO_2$. However, the mechanical effect of the procedure should be considered. As Figure 10 of Appendix A shows, in the treatment of coal by

only water, the vapor pressure developed and extended fractures in the coal which could help the penetration of the solvent; but the mechanical factor is not the main cause of fragmentation. Therefore, the role of $CO_2$ and carbonic acid becomes much more important in this study. It is possible the $CO_2$ dissolved the mineral matter between the boundaries of coal and caused or provided a better source of oxygen for further reaction with pyrite which led to removing the pyrite and breaking the whole macrocompounds of coal. Also, sulfur removal could have occurred due to the solubility of sulfur-containing materials, especially organic sulfur (not necessarily the compounds which had been examined with $CO_2 + H_2O$), in the liquid $CO_2$ which was present at the conditions of the experiment.

# CHAPTER VI

## INTERPRETATION OF EXPERIMENTAL RESULTS

From the results of about 60 experiments, the results of 30 tests were selected and are presented in this research. The rest of the tests either had similar or close physical conditions, or the tests had been repeated. Among these 30 tests, 17 of them were performed on Oklahoma bituminous coal (McAlester, Croweburg and Secor), but most emphasis and tests were done on the McAlester coal which was the target of this study. The results of these tests are illustrated in Appendices A, B, and C. Also, there were seven tests on chemical compounds which exist in coal or have similar structure to coal on the macromolecular level. The results of these tests are presented in Appendix D. Finally, six tests were done on the unknown coal (the origin of the coal is not known), and the results of these tests are presented in Appendix E.

### A. RESULTS OF FRAGMENTED COAL AT TYPICAL TEMPERATURE AND PRESSURE

In Appendix A, Figures 1, 3 and Figures 2, 4 show the McAlester coal before and after treatment with the $CO_2$-$H_2O$ mixture. Figure 1 shows one piece of McAlester coal of approximately 60 gram weight before treatment. Figure 2 shows the same piece of coal after treatment

with the $CO_2$-$H_2O$ mixture (35.7% $CO_2$ and 64.3% $H_2O$). The coal was placed in the reactor with the $CO_2$- $H_2O$ mixture for 24 hours under physical conditions of 275°C temperature and pressure up to 3300 psi. The average size of the fragmented coal (after treatment) is 0.094 which is approximately 1/22 of the original coal size (before treatment). 84% of the fragmented coal remained above mesh no. 70 (> 0.0995 inches), and less than 20% passed through mesh no. 70 (< 0.00995 inches).

Figure 3 shows a piece of McAlester coal of approximately 50 grams weight before treatment. The coal was treated with $CO_2$-$H_2O$ (38.8% $CO_2$ and 61.2% $H_2O$) at the same physical conditions--275°C temperature and pressure up to 3300 psi, but the test lasted for 36 hours instead of 24 hours. As Figure 4 indicates, the size of the fragmented coal is smaller; and the results of the U.S. Standard sieve analysis showed the average size of the fragmented coal is 0.072 inches which is approximately 1/30 of the original coal size (before treatment). Also, the U.S. Standard sieve analysis showed 70% of the fragmented coal remained above mesh no. 70 (> 0.00995), and 30% of the broken coal passed through mesh no. 70 (< 0.00995).

Figure 5 of Appendix A shows a piece of Croweburg coal of approximately 60 grams weight before treatment, and Figure 6 shows the results of the Croweburg coal after treatment with the $CO_2$-$H_2O$. The coal was placed in the reactor; then water and $CO_2$ were added to the coal under physical conditions of 305°C temperature and pressure up to 2550 psi for 24 hours. These are the minimum physical conditions required to break the Croweburg coal. The result of the U.S. Standard

sieve analysis showed the average fragmented coal had a size of 0.150 inch, which was approximately 1/15 of the original coal size (before treatment). Also, the U.S. Standard sieve analysis showed 95% of the fragmented coal was retained above mesh no. 60 (> 0.0098 inch), and only 5% passed through mesh no. 60 (< 0.0098 inch).

Figure 7 shows 136.5 grams by weight of Secor coal before treatment, and Figure 8 shows the fragmented Secor coal as a result of treatment with the $CO_2$-$H_2O$ solvent. The coal was placed inside the reactor; then the coal was treated with the $CO_2$-$H_2O$ mixture under physical conditions of temperature up to 315°C and pressure up to 2750 psi for 24 hours. These are the minimum physical conditions required to break the Secor coal. The result of the U.S. Standard sieve analysis showed the average fragmented coal had a size of 0.135 inch, which is approximately 1/16 of the original coal size (before treatment). Also the U.S. Standard sieve analysis showed 86% of the fragmented coal remained above mesh no. 60 (> 0.0098 inches), and 24% passed through mesh no. 60 (< 0.0098 inches).

Figure 9 of Appendix A shows the result of treatment of 34.5 grams by weight of McAlester coal by only $CO_2$ (solid + gas). The coal was placed in the reactor, then 20 grams by weight solid $CO_2$ (dry ice) was added to the coal in addition to injection of $CO_2$ gas. The test was set up at 325°C for 24 hours, and the pressure went up to 3250 psi. As a result, the coal became slightly friable but not fragmented.

Figure 10 shows the results of treatment of 36 grams of McAlester coal by only $H_2O$. The coal was placed in the reactor, then 150 grams of water was added to the coal. The experiment was set up for 24

hours at 325°C. The pressure increased to 2850 psi. As a result, the coal became friable, as Figure 10 of Appendix A indicates, but not broken.

## B. ANALYTICAL RESULTS OF MCALESTER COAL BEFORE AND AFTER TREATMENT WITH $CO_2$-$H_2O$ AT TYPICAL TEMPERATURE AND PRESSURE

Table 1 of Appendix A shows the analytical results of the McAlester coal before treatment and after treatment with the $CO_2$-$H_2O$ mixture on the basis of free moisture (fmb). Table 1 shows the H/C ratio is slightly increased; that means hydrogen increased and carbon decreased slightly as a result of coal treatment by the $CO_2$-$H_2O$ mixture. There was also an increase in the amount of oxygen and a decline in the amount of nitrogen.

But the most important element in this experiment is sulfur. The analytical results of the fragmented coal (after treatment) shows in Table 1 that sulfur decreased from 3.51% to 2.23% by weight. That means 37% of the total sulfur in the McAlester coal had been reduced as a result of treating the McAlester coal with the $CO_2$-$H_2O$ solvent. It is interesting to note that the pyritic sulfur ($FeS_2$) decreased from 2.06% by weight to 1.24% by weight, about 40% reduction of pyrite. Sulfate sulfur decreased by approximately 50%, and finally, the most important compound of sulfur, inorganic sulfur, had been decreased from 1.07% by weight to 0.82% by weight, about 23% reduction of inorganic sulfur.

Table 2 of Appendix A shows basically the same data, but the values are calculated on the basis of moisture, ash free (fmab). The

ratio of H/C is increased slightly after treatment which indicates the carbon decreased and the hydrogen increased slightly. There also was some increase in nitrogen and oxygen. Again, on the basis of fmab calculations, the total sulfur was reduced by 37% by weight, pyrite was reduced by 37%, sulfate sulfur by approximately 50%, and finally, inorganic sulfur decreased by 23% by weight. The physical conditions for the coal treatment in both tables are the same, 275 C temperature and pressure up to 3300 psi, and the experiment was set up for 24 hours with 38.5% $CO_2$ and 61.5% water in the solvent.

## C. RESULT OF TREATMENT OF THREE DIFFERENT COALS WITH $CO_2$-$H_2O$ AT DIFFERENT TEMPERATURES AND PRESSURES

Appendix B shows the results of the treatment of seventeen tests on Oklahoma bituminous coals with the $CO_2$-$H_2O$ solvent, with only $CO_2$, and finally with only $H_2O$. The first nine tests are related to McAlester coal, test number ten belongs to Croweburg coal, and test number eleven is with Secor coal; the solvent used in these was the $CO_2$-$H_2O$ mixture. The physical conditions of these eleven tests are different. The temperature ranged from 200°C to 325°C, the pressured ranged from 2150 psi to 3600 psi, and the period of experiment ranged from a minimum of 18 hours up to 36 hours. The results of the U. S. Standard sieve analysis of these eleven tests showed the average size of the fragmented coal (after treatment) varied from 0.072 inches to 0.150 inches. For each test, there are five figures and two tables. The figures are: (1) temperature in degrees centigrade (Celsius) versus time in minutes which indicates the time required to warm up the

reactor to the desired degree; (2) pressure in psi versus time in minutes which indicates the time required to increase the pressure of the reactor from initial pressure (900 psi) to the desired point with regard to temperature; (3) pressure in psi versus temperature in degrees centigrade. These were to study the relationships between temperature and time, temperature and pressure, and pressure and time since the hypothesis and results indicated (Table 1 of each test) that pressure and temperature increase with time. Also, vapor pressure increases as temperature increases. Therefore, the following models and SAS* were used in order to describe the relationship between (1) pressure and temperature, (2) pressure and time, and (3) temperature and time. The models are: (1) $y = M*x + B$, (2) $y = M*z + B$, (3) $x = M*z + B$ where y represents pressure in psi, x represents temperature in Celsius and z represents time in minutes. M is the coefficient (slope of the line) and B is the intercept value. These models are called regression equations. By using SAS and plotting these regression equations, the regression lines (the lines that best fit the points on the graph) were obtained. The technique used to obtain the regression lines is called the "least-squares curve fitting." Table 1 of Appendix B shows the general program which was used for each test in order to obtain the regression lines that indicate the relationship between temperature and time, pressure and time, and pressure and temperature with regard to data obtained from laboratory experiment for each test. Furthermore, Figure 4 of each test shows the percentage of fragmented coal versus

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*SAS is a computer system for data analysis and stands for Statistical Analysis System.

mesh no.; and, finally, Figure 5 shows the cumulative distribution of fragmented coal versus the size of fragmented coal in inches. Table 1 of each test shows the data obtained in each test and indicates the relationship between pressure-temperature, pressure-time, and temperature-time which was used to find the regression lines. Table 2 of each test shows the results of the U.S. Standard sieve analysis of fragmented coal with regard to percentage of broken coal as a result of the treatment of the coal by the solvent ($CO_2$ + $H_2O$).

Table 2 of Appendix B shows each mesh number with its opening size which was used in this research. Table 3 shows the period, temperature and pressure of the nine tests on McAlester coal. As Table 3 indicates, the break point occurs at 200°C and 2150 psi which is the minimum temperature and pressure required for fragmentation of McAlester coal. In tests 5, 6, 7, and 8 the temperature and pressure remain constant, but time is variable. The period of tests, as Table 3 shows, changed from 18 to 36 hours.

Table 4 of Appendix B illustrates the fragmented size distribution from the McAlester bituminous coal-$CO_2$ + $H_2O$ mixture. As Table 4 indicates, at lower temperature and pressure a higher percentage of the fragmented coal remained above mesh no. 70; and a lower percentage passed through mesh no. 70. But at higher temperature (275 C) and higher pressure (up to 3300 psi), a lower percentage of the fragmented coal remained above mesh no. 70. Also, Table 4 of Appendix B shows the period of the tests becomes the major factor from the point of view of size. As the period of the tests increased, the size of the fragmented coal decreased.

Test 1, McAlester Coal: A total of 160 grams of coal (three pieces) was treated with the $CO_2$-$H_2O$ solvent at a temperature of 200°C and pressure of 2150 psi for 21.5 hours. Only 11 grams of the coal (6% by weight) fell apart, and the average size of the fragmented coal was 0.135 inches. It required 80 minutes in order to increase the temperature of the reactor from room temperature (25°C) up to 200°C. The period of the experiment (21.5 hours) does not include the 80 minutes which was used to warm up the reactor to 200°C. In Test 1, Table 1.1 shows the relationship between the time required to increase the temperature of the reactor up to 200°C and pressure up to 2150 psi. As a result of this table, Figures 1.1, 1.2, and 1.3 show time versus temperature, time versus pressure and temperature versus pressure. The initial temperature was 25°C (room temperature), and the initial pressure was approximately 900 psi ($CO_2$ pressure). Table 1.2 shows the results of the U.S. Standard sieve analysis on the 11 grams of fragmented coal. As Table 1.2 indicates, 90% by weight of this 11 grams remained above mesh no. 70 (> 0.00995 inches) and 10% by weight passed through mesh no. 70 (< 0.00995 inches). As a result of Table 1.2, Figure 1.4 and Figure 1.5 show the normal and cumulative distribution of the fragmented coal. Figure 1.4 shows 55% by weight of the fragmented coal remained on mesh no. 4 (> 0.185 inches), 27% on mesh no. 16 (> 0.116 inches), 6.3% on mesh no. 50 (> 0.0273 inches), 2.2% on mesh no. 70 (> 0.00995 inches), 4.5% on mesh no. 100 (> 0.0071 inches), and finally 5% by weight passed through mesh no. 100 (< 0.0071 inches).

Test 2, McAlester Coal: A total of 128 grams by weight of coal (three pieces) was treated with the $CO_2$-$H_2O$ solvent at a temperature of 225°C and pressure of 2700 psi for 23 hours. This period (23

hours) does not include the time used (102 minutes) to increase the temperature of the reactor up to 225°C. Only 48.6 grams of the total coal fell apart (38% by weight), and the average size of the fragmented coal was 0.126 inches. Table 2.1 shows the relation between the time required to increase the temperature of the reactor up to 225°C and pressure up to 2700 psi. As a result of this table, Figures 2.1, 2.2, and 2.3 show time versus temperature, time versus pressure, and temperature versus pressure. The initial temperature of Test 2 was 25°C (room temperature), and the initial pressure was approximately 900 psi ($CO_2$ pressure). Table 2.2 shows the results of the U.S. Standard sieve analysis on the 48.6 grams of fragmented coal. As Table 2.2 indicates, 97% of the fragmented coal remained above mesh no. 70 (> 0.00995 inches), and only 3% by weight passed through mesh no. 70 (< 0.00995 inches). As a result of Table 2.2, Figure 2.4 indicates the normal distribution and Figure 2.5 the cumulative distribution of the fragmented coal. Figure 2.4 shows 34% by weight of the fragmented coal remained on mesh no. 4 (> 0.185 inches), 50.4% on mesh no. 16 (> 0.116 inches), 9.3% on mesh no. 50 (> 0.0293 inches), 3.4% on mesh no. 70 (> 0.0095 inches), 1% on mesh no. 100 (> 0.0071 inches), and finally, 2% by weight of the fragmented coal passed through mesh no. 100 (< 0.0071 inches).

Test 3, McAlester Coal: A total of 132 grams by weight of coal sample (three pieces) was treated with the $CO_2$-$H_2O$ solvent at a temperature of 235°C and pressure up to 2850 psi for 24 hours. This period does not include the time used (105 minutes) to increase the temperature of the reactor up to 235°C. After 24 hours, only 107.5

grams of the coal fell apart (81% by weight), and the average size of the fragmented coal was 0.124 inches. Table 3.1 shows the relation between the time required to increase the temperature of the reactor up to 235°C and pressure up to 2850 psi. As a result of this table, Figures 3.1, 3.2, and 3.3 show time versus temperature, time versus pressure, and temperature versus pressure. The initial temperature of Test 3 was 25°C (room temperature), and the initial pressure was approximately 900 psi ($CO_2$ pressure). Table 3.2 shows the result of the U.S. Standard sieve analysis on the 107.5 grams of fragmented coal. As Table 3.2 indicates, 97% of the fragmented coal remained above mesh no. 70 (> 0.00995 inches), and less than 3% passed through mesh no. 70 (< 0.00995 inches). As a result of Table 3.2, Figures 3.4 and 3.5 show the normal and cumulative distribution of the fragmented coal. Figure 3.4 shows 42% by weight of the fragmented coal remained on mesh no. 4 (> 0.185 inches), 38.5% on mesh no. 16 (> 0.116 inches), 12.6% on mesh no. 50 (> 0.0293 inches), 4.2% on mesh no. 70 (> 0.00995 inches), 0.5% on mesh no. 100 (> 0.0071 inches) and finally, 2.3% of the fragmented coal passed through mesh no. 100 (< 0.0071 inches).

Test 4, McAlester Coal: A total of 69 grams by weight of coal (one piece) was treated with the $CO_2$-$H_2O$ solvent at a temperature of 250°C and pressure up to 2950 psi for 24 hours. This 24 hours does not include the time used (118 minutes) to increase the temperature of the reactor to 250°C. After 24 hours, 100% of the coal sample fragmented, and the average size of the fragmented coal was 0.119 inches. Table 4.1 shows the relation between the time required to increase the temperature of the reactor up to 250°C and the pressure up to 2950 psi.

As a result of this table, Figures 4.1, 4.2, and 4.3 show time versus temperature, time versus pressure, and temperature versus pressure. The initial temperature for Test 4 was 25°C (room temperature), and the initial pressure was 900 psi ($CO_2$ pressure). Table 4.2 shows the result of the U.S. Standard sieve analysis of the fragmented coal. As Table 4.2 indicates, 92.9% by weight of the fragmented coal remained above mesh no. 70 (> 0.00995 inches), and only 7% passed through mesh no. 70 (< 0.00995 inches). As a result of Table 4.2, Figures 4.4 and 4.5 show the normal distribution and cumulative distribution of the fragmented coal. Figure 4.4 shows 44% by weight of the fragmented coal remained on mesh no. 4 (> 0.185 inches), 30% on mesh no. 16 (> 0.116 inches), 11.2% on mesh no. 50 (> 0.0293 inches), 7.7% on mesh no. 70 (> 0.00995 inches) and 4.6% on mesh no. 100 (> 0.0071 inches). Finally, only 2.2% by weight passed through mesh no. 100 (< 0.0071 inches).

Test 5, McAlester Coal: A total of 79.5 grams by weight of coal sample (one piece) was treated with the $CO_2$-$H_2O$ solvent at a temperature up to 275°C and pressure up to 3300 psi for 18 hours. This period does not include the time used (132 minutes) to warm up the reactor to 275°C. After 18 hours, the total coal sample was broken, and the average size of the broken coal was 0.145 inches. Table 5.1 shows the relation between the time used to increase the temperature of the reactor from room temperature up to 275°C and pressure up to 3300 psi. The initial temperature of Test 5 was room temperature (25°C), and the initial pressure was 900 psi ($CO_2$ pressure). As a result of Table 5.1, Figures 5.1, 5.2, and 5.3 show time versus temperature, time versus pressure, and temperature versus pressure. Table 5.2 shows the

result of the U.S. Standard sieve analysis of the fragmented coal. As Table 5.2 indicates, more than 96% by weight of the fragmented coal remained above mesh no. 70 (> 0.00995 inches), and approximately 3% passed through mesh no. 70 (< 0.00995 inches). As a result of Table 5.2, Figures 5.4 and 5.5 show the normal and cumulative distribution of the fragmented coal. In Figure 5.4, 60% of the fragmented coal in Test 5 remained on mesh no. 4 (> 0.185 inches), 28% on mesh no. 16 (> 0.116 inches), 7% on mesh no. 50 (> 0.0193 inches), 1.5% on mesh no. 70 (> 0.00995 inches), 0.63% on mesh no. 100 (> 0.0071 inches). Only 3% by weight passed through mesh no. 100 (< 0.0071 inches). Figure 5.5 shows the cumulative distribution of the fragmented coal which was inicated in the last column of Table 5.2.

Test 6, McAlester Coal: A total of 59.7 grams of coal by weight was treated with the $CO_2$-$H_2O$ solvent at a temperature of 275°C and pressure up to 3300 psi for 24 hours. This period (24 hours) does not include the time required (130 minutes) to increase the temperature of the reactor from room temperature to 275°C. After 24 hours, 100% of the coal sample was broken to smaller size, and the average size of the fragmented coal was 0.094 inches. Table 6.1 shows the relation between the time used to increase the temperature from room temperature to 275°C and pressure up to 3300 psi. The initial pressure of the experiment was 900 psi ($CO_2$ pressure), and the initial temperature of the experiment was 25°C (room temperature). As a result of Table 6.1, Figures 6.1, 6.2, and 6.3 show time versus temperature, time versus pressure, and temperature versus pressure. Table 6.2 shows the results

of the U.S. Standard sieve analysis of the fragmented coal of Experiment No. 6. As Table 6.2 shows, approximately 84% of the fragmented coal remained above mesh no. 70 (> 0.00995 inches), and approximately 16% of the broken coal passed through mesh no. 70 (> 0.00995 inches). As a result of Table 6.2, Figures 6.4 and 6.5 show the normal and cumulative distribution of the fragmented coal. In Figure 6.4, 30% by weight of the fragmented coal stayed on mesh no. 4 (> 0.185 inches), 27.5% on mesh no. 16 (> 0.116 inches), 17.2% on mesh no. 50 (> 0.0293 inches), 9.2% on mesh no. 70 (> 0.00995 inches), 8.1% on mesh no. 100 (> 0.0071 inches), and finally, 8% by weight passed through mesh no. 100 (< 0.0071 inches). Figure 6.5 shows the cumulative distribution of the fragmented coal which appeared in the last column of Table 6.2.

Test 7, McAlester Coal: In Test No. 7, a total of 52 grams of coal (one piece) by weight was treated with the $CO_2$-$H_2O$ solvent at a temperature of 275°C and pressure up to 3300 psi for 30 hours. This period (30 hours) does not include the time used (135 minutes) to warm up the reactor to 275°C. The average size of the fragmented coal was 0.082 inches, and 100% of the coal broke. Table 7.1 shows the relation between the time used to increase the temperature of the reactor to 275°C and pressure up to 3300 psi. The initial temperature of Experiment No. 7 was approximately 25°C (room temperature), and the initial pressure was approximately 900 psi ($CO_2$ pressure). As a result of Table 7.1, Figures 7.1, 7.2 and 7.3 show time versus temperature, time versus pressure and temperature versus pressure. Table 7.2 shows the result of the U.S. Standard sieve analysis of the fragmented coal of Test No. 7. As the table indicates, 78% by weight of the fragmented

coal remained above mesh no. 70 (> 0.00995 inches), and 22% passed through mesh no. 70 (< 0.00995 inches). As a result of Table 7.2, Figures 7.4 and 7.5 show the normal and cumulative distribution of the fragmented coal. Figure 7.4 shows 25% by weight of the fragmented coal stayed on mesh no. 4 (> 0.185 inches), 23.4% on mesh no. 16 (> 0.116 inches), 18.5% on mesh no. 50 (> 0.0293 inches), 11.7% on mesh no. 70 (> 0.00995 inches), 8.8% on mesh no 100, and finally, 12.6% by weight of the fragmented coal passed through mesh no. 100 (< 0.0071 inches). Figure 7.5 shows the cumulative distribution of the fragmented coal which was presented in the last column of Table 7.2.

Test 8, McAlester Coal: In Test No. 8, a total of 50.8 grams by weight of coal (one piece) was treated with the carbon dioxide-water solvent at a temperature of 275°C and pressure up to 3300 psi for 36 hours. This period (36 hours) does not include the time which was spent (130 minutes) to increase the temperature of the reactor to 275°C. After 36 hours, as a result of the coal treatment by the $CO_2$-$H_2O$ mixture, the total coal sample had been broken to smaller size, and the average broken size of the coal was 0.072 inches. Table 8.1 shows the relation between the time used to increase the temperature of the reactor up to 275°C and pressure up to 3300 psi. As a result of Table 8.1, Figures 8.1, 8.2, and 8.3 show time versus temperature, time versus pressure and temperature versus pressure. Table 8.2 shows the results of the U.S. Standard sieve analysis of the broken coal of Test No. 8. As the table indicates, approximately 72% by weight of the broken coal remained above mesh no. 70 (> 0.00995 inches), and 28% passed through mesh no. 70 (< 0.00995 inches). As a result of Table

8.2, Figures 8.4 and 8.5 show the normal and cumulative distribution of the broken coal. Figure 8.4 indicates 21% by weight of the broken coal remained on mesh no. 4 (> 0.185 inches), 22% on mesh no. 16 (> 0.116 inches), 16.4% on mesh no. 50 (> 0.0293 inches), 12.6% on mesh no. 70 (> 0.00995 inches), 10.5% on mesh no. 100 (> 0.0071 inches), and finally, 17.5% by weight of the broken coal passed through mesh no. 100 (< 0.0071 inches). Figure 8.5 shows the cumulative distribution of the fragmented coal as shown in the last column of Table 8.2.

Test 9, McAlester Coal: In Test No. 9, despite Tests 5, 6, 7, and 8, the temperature and pressure were not constant and a total of 47.5 grams by weight of coal (one piece) was treated with the carbon dioxide-water solvent at a temperature of 325°C and pressure up to 3600 psi for 18 hours. It required 148 minutes to warm up the reactor to 325°C. The period of the experiment (18 hours) does not include the time to warm up the reactor (148 minutes). The initial temperature of Test 9 was 25°C (room temperature), and the initial pressure was 900 psi. After 18 hours, 100% of the coal broke, and the average size of the fragmented coal was 0.074 inches. Table 9.1 shows the relation of time required to increase the temperature of the reactor to 325 C and pressure up to 3600 psi. As a result of Table 9.1, Figures 9.1, 9.2, and 9.3 show time versus temperature, time versus pressure, and temperature versus pressure. Table 9.2 shows the results of the U.S. Standard sieve analysis of Test 9, and Table 9.2 shows approximately 70% of the broken coal remained above mesh no. 70 (> 0.00995 inches) while approximately 30% of the broken coal by weight passed through mesh no. 70 (< 0.00995 inches). As a result of Table 9.2, Figures 9.4

and 9.5 show the normal and cumulative distribution of the fragmented coal of Test 9. As Figure 9.4 shows, 23% by weight of the fragmented coal remained on mesh no. 4 (> 0.185 inches), 20.6% on mesh no. 16 (> 0.116 inches), 16% on mesh no. 50 (> 0.0293 inches), 10.2% on mesh no. 70 (> 0.00995 inches), 12.8% on mesh no. 100 (> 0.0071 inches), and finally, 17.4% by weight passed through mesh no. 100 which has size less than 0.0071 inches. Figure 9.5 shows the cumulative distribution of the fragmented coal of Test 9 which was presented in the last column of Table 9.2.

Generally speaking, the results of these nine tests on McAlester bituminous coal shows that higher temperature and pressure with relatively long period of tests increased the percentage of fragmented coal that has smaller size.

Test 10, Croweburg Coal: In Test 10, instead of McAlester coal, a total of 60 grams by weight of Croweburg coal (one piece) was treated with the $CO_2$-$H_2O$ solvent at a temperature up to 305°C and pressure up to 2550 psi for 24 hours. This period (24 hours) does not include the time spent to increase the temperature of the reactor from room temperature to 305°C and pressure up to 2550 psi. The initial temperature of the reactor was approximately 25°C (room temperature), and the initial pressure of the reactor was 900 psi which was the $CO_2$ pressure. After 24 hours, 100% of the coal broke to a smaller size, and the average broken size was 0.150 inches. Table 10.1 shows the relation between the time used to warm up the reactor from room temperature to 305 C and pressure up to 2550 psi. As a result of Table 10.1, Figures 10.1, 10.2, and 10.3 show the time versus temperature,

time versus pressure and temperature versus pressure. Table 10.2 shows the results of the U.S. Standard sieve analysis of the broken Croweburg coal. As Table 10.2 shows, approximately 95% by weight of the broken coal remained above mesh no. 60 (> 0.011 inch), and approximately 5% by weight passed through mesh no. 60 (< 0.011 inches). As a result of Table 10.2, Figures 10.4 and 10.5 show the normal and cumulative distribution of the fragmented Croweburg coal. Figure 10.4 shows 66% by weight of the broken coal stayed on mesh no. 4 (> 0.185 inches), 21.7% on mesh no. 16 (> 0.116 inches), 6.7% on mesh no. 50 (> 0.0293 inches), 0.8% on mesh no. 60 (> 0.0011 inches), 1.6% on mesh no. 100 (> 0.0079 inches), and finally, only 3.2% by weight of the Croweburg fragmented coal of Test 10 passed through mesh no. 100 (< 0.0079 inches). Figure 10.5 shows the cumulative distribution of the broken coal which appeared in the last column of Table 10.2.

Test 11, Secor Coal: A total of 136.5 grams of coal (three pieces) by weight was treated with the $CO_2$-$H_2O$ solvent at a temperature up to 315°C and pressure up to 2750 psi for 24 hours. After this period, 100% of the coal had broken to a smaller size, and the average size of the broken coal was 0.135 inches. Table 11.1 shows the relations between the time used to warm up the reactor to 315°C temperature and pressure up to 2750 psi. As a result of Table 11.1, Figures 11.1, 11.2, and 11.3 show the time versus temperature, time versus pressure and temperature versus pressure. Table 11.2 shows the result of the U.S. Standard sieve analysis of the Secor broken coal (after treatment). As Table 11.2 shows, 86% by weight of the broken coal remained above mesh no. 60 (> 0.011 inches), and approximately 14% by weight

passed through mesh no. 60 (< 0.0011 inches). As a results of Table 11.2, Figures 11.4 and 11.5 show the normal and cumulative distribution of the fragmented Secor coal. Figure 11.4 shows that 64% by weight of the fragmented coal of Test 11 stayed on mesh no. 4 (> 0.185 inches), 10.7% by weight on mesh no. 16 (> 0.116 inches), 7.3% on mesh no. 50 (> 0.0293 inches), 4.4% on mesh no. 60 (> 0.011 inches), 4.8% on mesh no. 100 (> 0.0079 inches), and only 8.6% by weight of the Secor fragmented coal passed through mesh no. 100 which has size less than 0.0079 inches. Figure 11.5 shows the cumulative distribution of the Secor fragmented coal which appeared in the last column of Table 11.2.

The results of the tests on Croweburg and Secor coal show that the minimum temperature required to break the coal is higher than the McAlester coal and the size of the fragmented coal is coarser. These differences are due to the different properties of the coal which probably exists in these three coal beds.

There were several treatments of McAlester coal with only carbon dioxide or only water. In this series of experiments, like previous tests, coal was placed inside the reactor; then $CO_2$ or water alone, instead of the mixture of $CO_2$-$H_2O$ was added to the coal. But in both cases ($CO_2$ or water alone), no fragmentation was obtained. Most of these tests were performed at the three different temperature which resulted in the coal being broken as a result of the treatment by the carbon dioxide-water mixture. In both cases, $CO_2$ or water, the temperatures were 250°C, 275°C and 325°C, and the period of the experiment ranged from 24 hours to 48 hours.

In Appendix B, Tables 12.1, 13.1, and 14.1 represent the relationship between the time required to warm up the reactor and temperature and pressure of the three tests. In these three tests, McAlester coal was treated with only $H_2O$ at different physical conditions, but no fragmentation occurred. However, some fracture in the coal which was due to vapor pressure became obvious. In Test 12.1 a total of 45 grams of coal with 150 grams of water was examined under 250°C and 2250 psi pressure for 24 hours. In Test 13.1 a total of 55 grams of coal was treated with 150 grams of water, and the temperature was 275°C and the pressure went up to 2600 psi. The period of the test was 24 hours. In Test 14.1 a total of 35.5 grams of sample was treated with $H_2O$ at 325°C for 24 hours. The pressure went up to 2900 psi. In all three cases, no fragmentation occurred. But it is interesting to note that the coal became friable after treatment.

Tables 15.1, 16.1 and 17.1 represent the relationship of time required to warm up the reactor with temperature and pressure as a result of the McAlester coal treatment with only $CO_2$ at three different conditions. In these three tests, both solid and gas $CO_2$ were used, but no fragmentation occurred. Again, the coal became friable compared to its original state. In Test 15, 80 grams of coal (McAlester) was examined with 15 grams solid $CO_2$ (dry ice) and $CO_2$ gas. The temperature was set up for 250°C for 24 hours, and the pressure went up to 2600 psi. In Test 16, a total of 50 grams of coal with 22 grams solid $CO_2$ (dry ice) in addition to $CO_2$ gas were used. The temperature was arranged at 275°C for 24 hours, and the pressure went up to 2900 psi. In Test 17, a total of 34.5 grams of coal sample was treated with $CO_2$

gas in addition to 20 grams of solid $CO_2$. The temperature for Test 17 was 325°C, and the pressure went up to 3250 psi after 24 hours. In these three tests, the initial $CO_2$ gas pressure was 900 psi, and no fragmentation was obtained.

In Appendix C, Figure 1 shows the relation between the percentage of McAlester coal broken and pressure and temperature. As Figure 1 shows, an increase in the pressure and temperature caused an increase in the percentage of fragmented coal. At point (1) with temperature of 200°C and pressure of 2150 psi, only 6% of the coal fell apart; but at point (4) with temperature of 250°C and pressure of 2950 psi, 100% of the coal fell apart. Figure 2 shows expansion of the period of the experiment resulted in smaller size of the fragmented coal. In these figures, temperature and pressure are constant, and the period of the experiment is variable. All these points had a pressure of 3300 psi and a temperature of 275°C. As the figure shows, for a period of 18 hours, the average particle size of the fragmented coal was larger than the size of the fragmented coal for a period of 36 hours. Figure 3 of Appendix C shows how the period of the experiment affected the distribution of the fragmented coal. At a shorter period of experiment, most of the broken coal remained on a lower mesh no. In other words, the shorter the period of experiment, the coarser the particle size.

In Appendix C, Figure 4 shows the relationship between the average fragmented size of McAlester coal and pressure (P), temperature (T), period of experiment (A), solvent to coal ratio (S), and water to $CO_2$ ratio (H). As Figure 4 indicates, the size of fragmentation is directly related to pressure, temperature, solvent to coal ratio, and

period of experiment which means that increasing temperature and pressure, the fragmented coal becomes smaller. However, there is a limitation on both temperature and pressure. Above 325°C, the McAlester coal became sticky (so-called plastic state) instead of fragmenting. Further increase of the temperature begins to change the phase (solid to liquid). Therefore, the highest temperature and pressure for fragmentation of McAlester coal are 325°C and 3600 psi. The minimum temperature and pressure required to fragment McAlester coal are 200°C and 2150 psi. Between the range of 200 to 325°C temperature and 2150 to 3300 psi pressure, the percentage of fragmented coal became higher and the size of the fragmented coal became smaller. However, these are not the only factors which cause higher percentage of fragmentation. The period of experiment and larger ratio of solvent to coal generally cause smaller fragments of coal. With regard to fragmentation of McAlester coal by $CO_2$ + $H_2O$, 24 hours for the period of experiment and between 3.5 to 4.5 ratio of solvent to coal are favorable. This recommendation is based on approximate uniform distribution of fragmented coal on different mesh numbers. Finally, as Figure 4 of Appendix C shows, the larger the ratio of $H_2O$ to $CO_2$ the coarser the fragmented coal became; and the range of 1.58 to 2.6 of water to carbon dioxide gave better results with regard to fragmented size of coal.

From the McAlester coal experimental results a relationship was found between the size of the fragmented coal (d, dependent variable) and independent variables which included temperature (T), pressure (P), period of experiment (t), total mass placed in the reactor (coal + $H_2O$ + $CO_2$) and specific heat of coal ($c_p$). (It would be more

representative to use an apparent $c_p$ for the total mass in the reactor. However, under the experimental conditions, it was not possible to measure directly the fraction of liquid water and vapor and the $CO_2$ content in each phase.) The method of dimensionless analysis was used in order to reduce the number of independent variables and to form the number of variables into two dimensionless groups. Consequently, an empirical correction was develped to predict the size of the fragmented bituminous coal in the chemical comminution process as a result of treatment of McAlester bituminous coal with the proposed solvent. Therefore, the $\Pi$ theorem was used in dimensionless analysis to identify the groups from the independent variables as follows:

$$d = f(t,T,c_p,P,M)$$

where d is size of fragmented coal, t is period of experiment, T is temperature, $c_p$ is specific heat of coal, P is pressure, M is total mass in reactor expressed by M = coal + $CO_2$ + $H_2O$. Therefore, in MLT system

$$F(d,t,T,c_p,M,P) = 0$$

and

$$\Pi_1 = d,\ t,\ T,c_p$$

$$d = L$$

$$c_p = L^2t^{-2}T^{-1}$$

Then

$$\Pi_1 = d^x t^y T^z L^2 t^{-2} T^{-1}$$

$$L^x t^y T^z L^2 t^{-2} T^{-1} = 0$$

$$x + 2 = 0 \Rightarrow x = -2$$

$$y - 2 = 0 \Rightarrow y = 2$$

$$z - 1 = 0 \Rightarrow z = 1$$

Therefore,

$$\Pi_1 = \frac{t^2 T c_p}{d^2} \qquad (1)$$

And

$$\Pi_2 = P, M, d, t$$

$$t^x L^y M^z M L^{-1} t^{-2} = 0$$

$$x - 2 = 0 \Rightarrow x = 2$$

$$y - 1 = 0 \Rightarrow y = 1$$

$$z + 1 = 0 \Rightarrow z = -1$$

Therefore,

$$\Pi_2 = \frac{t^2 dP}{M} \qquad (2)$$

Furthermore, by multiplying $\Pi_1$ and $\Pi_2^2$, a new group was constituted called $\Pi_3$:

$$\Pi_3 = \frac{c_p T P^2 t^6}{M^2} \qquad (3)$$

T, P, M, t, $c_p$, and d are known from experiment. Thus, $\Pi_2$ and $\Pi_3$ could be calculated and are shown in Table 19 (p. 138). Then log $\Pi_3$ was plotted versus $\Pi_2$ in Figure 5 of Appendix C. From this plot, the mathematical model was developed which will predict the size of fragmented bituminous coal (with reference to McAlester coal of Oklahoma) in chemical comminution by using $CO_2 + H_2O$ as a solvent. The equation for the line in Figure 5 of Appendix C is found to be

$$\log_{10} \Pi_3 = A + b\Pi_2 \qquad (4)$$

This equation can be written in the following form:

TABLE 19

VALUES OF DIMENSIONLESS VARIABLES

| $\Pi_1$ | $\Pi_2$ | $\Pi_3$ |
|---|---|---|
| 1521811 | 297.26 | $13.45 \times 10^{10}$ |
| 2249150 | 445.90 | $44.72 \times 10^{10}$ |
| 2640999 | 510.43 | $68.81 \times 10^{10}$ |
| 3050632 | 727.62 | $161.51 \times 10^{10}$ |
| 1271344 | 483.27 | $29.69 \times 10^{10}$ |
| 5377999 | 661.93 | $235.64 \times 10^{10}$ |
| 11042534 | 953.94 | $1004.87 \times 10^{10}$ |
| 20625000 | 1212.80 | $3033.69 \times 10^{10}$ |
| 5768809 | 343.26 | $67.97 \times 10^{10}$ |

$$\log_{10}\left(\frac{\Pi_3}{A}\right) = b\Pi_2 \qquad (5)$$

$$\Pi_2 = \frac{1}{b}\log_{10}\left(\frac{\Pi_3}{A}\right) \qquad (6)$$

Therefore, substituting the expressions for $\Pi_2$ and $\Pi_3$ and rearranging Equation (3), the size of fragmented coal can be obtained as

$$d = \frac{1}{b}\frac{M}{Pt^2}\log_{10}\frac{c_p TP^2 t^6}{AM^2}$$

where A is the intercept and b is the slope. For Figure 5 of Appendix C, these were found to be A = 24.4 and b = 0.0055. Therefore, as Equation (5) shows, as the period of experiment in chemical comminution becomes longer and the pressure gets higher, the size of fragmented coal can be expected to become smaller.

In Appendix D Table 1 shows the seven chemical compounds which were examined with the proposed solvent. These compounds exist in coal or are believed to have similar structures compared to the coal structure. These compounds were treated with $CO_2 + H_2O$ under similar conditions as the coal had been treated with $CO_2 + H_2O$ in this study. As the last column of this table indicates, no reaction occurred between these compounds and the proposed solvent even though, in most tests, the pressure was much higher than the pressure which was obtained as a result of the McAlester coal treatment with $CO_2 + H_2O$ at different temperatures.

Table 1 of Appendix E shows the results of treatment of the unknown coal with only $CO_2$ at different temperatures and pressures. As Table 1 indicates, at temperatures ranging from 200°C to 350°C and

pressures ranging from 1650 to 2175 psi, the coal did not break. Table 2 of Appendix E shows the result of one test of the coal with only $H_2O$ at a temperature of 350°C and pressure up to 7500 psi. This table indicates no fragmentation occurred as a result of treatment of the coal by only $H_2O$. Table 3 of Appendix E shows the results of treatment of the unknown coal with $CO_2 + H_2O$; 100% of the coal fragmented. Since this particular coal was not part of the original research, only one set up of temperature was arranged. The temperature was set up for 350°C, and the pressure went up to 3600 psi. All these tests were run for 24 hours. Table 4 of Appendix E shows the distribution of the fragmented coal of Test 6 of Table 3 (unknown coal + $CO_2 + H_2O$) on the U.S. Standard sieve series. As Table 3 shows, 60% of the broken coal has less than 0.185 inches diameter and 40% of the fragmented coal remained above mesh no. 40 ($> 0.185$ inches). The results of this series of tests indicated that the combination of $CO_2$ and water is required for the fragmentation of the coal, but the conditions of the reaction are different which is due to the different characteristics of the coal.

## D. SUMMARY OF RESULTS

The laboratory experiments proved that carbon dioxide in aqueous solution with water can be used as a chemical agent for the chemical comminution process (technically, but without economic considerations) in mining industries in order to fragment McAlester coal to a smaller size.

Ultimate analysis of laboratory experimentally fragmented coal indicated the total sulfur in the coal decreased from 3.51% to 2.23% (mfb), ash decreased from 18.65% to 17.5%, and heating value increased from 11808 Btu per pound to 11923 Btu per pound.

This investigation indicated the minimum temperature and pressure required for fragmentation of McAlester bituminous coal by the suggested solvent ($CO_2$ + $H_2$)) were 250°C and 2950 psi. However, the results of the study showed that at 200°C and 2150 psi, the coal (McAlester) began to fall apart. The maximum temperature and pressure applied in this investigation were 325°C and 3600 psi. Further increase of temperature was not attempted in order to avoid the plasticity characteristic of coal which usually occurs in the range of temperature between 325°C-350°C.

The minimum time required for the chemical reaction between the suggested solvent ($CO_2$ + $H_2O$) and the coal in order to dissolve the impurities of coal such as pyrite and ash and fragment the coal was established to be 18 hours.

The physical and chemical characteristics of the coal were found to significantly alter the size of the fragmented coal. The McAlester coal reacted more favorably than the Croweburg and Secor with regard to size of the fragmented coal.

With regard to the result of fragmentation of McAlester coal by $CO_2$ + $H_2O$, a series of calculations were done in order to determine the amount of $CO_2$ and $H_2O$ used for each test. These calculations would be helpful for further investigation of this series of tests either in the laboratory or in actual field operations.

The Statistical Analysis System (SAS computer system) and least squares curve fitting technique were used for each test in order to achieve the best fit line for (1) pressure versus temperature, (2) pressure versus time (time required to warm up the reactor with its contents to the desired temperature), and (3) temperature versus time.

U.S. Standard sieve analysis of the fragmented McAlester coal indicated that at higher temperature and pressure and longer time, the fragmented coal is finer than at lower temperature and pressure and shorter period of tests.

This investigation also proposed a theory along with formulae of possible chemical reactions to explain the fragmentation of McAlester coal by $CO_2 + H_2O$. It is also possible vapor pressure helped to develop fractures on the surface of the coal that made the penetration of $CO_2$ easier and faster. But in the final analysis, the chemical reaction between $CO_2$ and the mineral matter of coal played the major role in the fragmentation of McAlester coal. Probably, $CO_2$, after reaching the mineral matter which exists between the boundaries of the coal, dissolved this mineral matter and caused the fragmentation; or else it provided a better and unstable source of oxygen which had further reaction with pyrite or any other organic sulfur and let to the fragmentation of coal. Also, this investigation showed that this type of experiment is very sensitive and requires care and patience with regard to setting up the experiments. Any lack of care or patience could result in different results and conclusions.

Finally, this study found that the treatment of McAlester coal with $CO_2$ itself or with only water does not cause fragmentation. Therefore, the combination of carbon dioxide and water is required in the chemical comminution process for McAlester bituminous coal, and the percentage and size of fragmented coal depended on temperature, pressure, solvent to coal ratio and period of experiment.

# CHAPTER VII

# SUMMARY AND CONCLUSIONS

## A. STATEMENT OF THE PROBLEM

In the past decade, the recovery of deep coal in thin deposits has become extremely expensive and difficult. Many unsolved problems exist in both open-pit and underground mining methods. In open-pit, despite advances in technology which increase the coal production, air and water pollution plus the destruction of natural resources still remain without solution. At the same time, the price of equipment and operations in open-pit mining has risen to high levels. It is also recognized that the production of coal by underground mining operations is very low, and the mining operations are risky. On the other hand, the demand for pure coal without impurities such as sulfur by industry has increased recently. In the past, the mine engineer did not pay attention to the purification of coal because it was assumed the mine engineer's task was to produce the coal from the reservoir. But now the view of the mine engineer has changed. On the one hand, the mechanical methods (crushing, grinding, milling) which have been used for a long period of time in order to extract sulfur from the coal are not sufficient because the mechanical methods are not able to separate organic sulfur. Such sulfur accounts for 30 to 70 percent of the

total sulfur. On the other hand, the impurities of coal such as ash and sulfur reduce the salability of coal and increase the cost of transportation. These factors complicate the production of coal; and, as a result of this, coal production is low and thus serves to worsen the energy crisis. Therefore, new effective mining methods for higher production and better quality are necessary. An example is the fragmentation of of coal by the chemical comminution process.

The objective of this research was to answer the following questions:

1. Can $CO_2$ and its aqueous solution in water be used in the chemical comminution process for in situ mining operations of deep and thin coal beds for which both underground and open-pit methods are not suitable (with reference to McAlester coal of Oklahoma)?

2. Can $CO_2$ and its aqueous solution in water be used in the chemical comminution process in order to reduce the total amount of sulfur and ash instead of using a mechanical method (with reference to McAlester bituminous coal of Oklahoma)?

## B. PROCEDURE OF THE INVESTIGATION

A 500 ml stainless steel pressure vessel (bomb reactor) with 2.5 inch inside diameter and 6.25 inch inside depth was used in this investigation. Three coals from eastern Oklahoma and one unknown coal (origin of coal is unknown) were treated with $CO_2 + H_2O$. In each test, one to three pieces of coal were placed inside the reactor; then water was added to the coal; and finally, $CO_2$ (gas) was injected into the reactor. The initial temperature of the reactor was 25°C (room temperature) and the initial pressure of the reactor with its contents was

900 psi ($CO_2$ cylinder pressure). The reactor with its contents was heated (an electric type heater was used to heat the reactor and a thermocouple was used to measure the temperature) for the desired period of time. Then the heat was turned off, and the reactor was allowed to cool. Finally, the contents of the reactor (solid + liquid) were separated from each other through a filter. The fragmented coal was analysed with a U.S. Standard sieve series to obtain the size distribution of the fragmented coal. Then 3 to 5 grams of the fragmented McAlester coal were sent to Galbraith Laboratories, Inc. for ultimate, sulfur form, and heating value analyses. These samples included coal both before and after treatment of the coal with $CO_2$ + $H_2O$.

The result of thirty tests were analysed in this study. Fifteen of these were of McAlester coal, and two of these were of Croweburg and Secor coal from eastern Oklahoma. Six of them belonged to the unknown coal, and seven tests were of compounds which had similar structure with regard to coal structure or which exist in coal. The physical conditions for the chemical reaction between the suggested solvent ($CO_2$ + $H_2O$) and the coal ranged in temperature from 200°C to 325°C and pressure from 2150 psi to 3600 psi. The period of the experiments ranged from 18 hours to 36 hours.

## C. RESULTS AND CONCLUSIONS

This study established the following:

1. The proposed solvent ($CO_2$ + $H_2O$) can be used in the chemical comminution process for fragmentation of McAlester bituminous coal.

2. The suggested solvent ($CO_2$ + $H_2O$) also may be used in the chemical comminution for purification of the coal. In the sample tested the total percentage of sulfur, including both organic and inorganic forms, was reduced; and the amount of ash in McAlester coal was also decreased.

3. Experimental data can be used to predict the future performance of a McAlester coal-$CO_2$ + $H_2O$ mixture.

4. The minimum temperature and pressure required for fragmentation of McAlester coal by $CO_2$ + $H_2O$ are 250°C temperature and 2950 psi pressure. However, at 200°C and 2150 psi, the bituminous coal of Oklahoma began to fall apart.

5. The minimum time required for chemical reaction between the suggested solvent and McAlester coal is 18 hours.

6. At higher temperature and higher pressure and longer period of experiment and relatively higher ratio of solvent to coal (3.5-4.5) and lower ratio of water to $CO_2$ (1.6-2.6), the fragmented coal is smaller, and the percentage of fragmented coal is higher.

7. The physical and chemical characteristics of the coal affect the results of the chemical comminution by the proposed solvent. Three different coal beds of Oklahoma, McAlester, Croweburg, and Secor, reacted differently with regard to the size of the fragmented coal and physical conditions of treatment.

8. Mechanical effects should be considered. In particular, gas pressure probably helped to develop fractures which made the penetration of $CO_2$ easier and faster. However, the major factor for the fragmentation of the three eastern Oklahoma coals is the chemical reaction between the suggested solvent and coal.

9. Water itself without $CO_2$ and $CO_2$ without water at 250°C, 275°C and 325°C for 24 hours did not break the coal. But in all cases, fracture of the coal was obvious and wider. On the other hand, for the same period of test (24 hours) and same temperature with the presence of both $CO_2$ and $H_2O$ (the proposed solvent), the same coal bed (McAlester) had been broken (fragmented) to a finer size.

10. Despite the fact that the proposed solvent ($CO_2$ + $H_2O$) was able to break and reduce the size of three coals from eastern Oklahoma and decrease the amount of ash and sulfur, because coal is a heterogeneous type of rock and has such a complicated structure, it is not obvious that the treatment of other bituminous coals with the proposed solvent ($CO_2$ + $H_2O$) will have the same results. However, the possibility of the chemical comminution of other bituminous coals as a result of this investigation exists.

## D. SUGGESTIONS FOR FURTHER RESEARCH

Further research should be developed into the following categories:

1. Treatment of other bituminous coals from different regions with the suggested solvent ($CO_2$ + $H_2O$). In the case of the U.S., these bituminous coals can be obtained from the Appalachian region (Pennsylvania and West Virginia), Alabama region, eastern midwest region (Illinois, Indiana), western region (Montana, Colorado) and possibly from other regions such as Arkansas and Iowa. These various types of coals will provide more extensive conclusions regarding the chemical comminution process on bituminous coal by using the proposed solvent ($CO_2$ + $H_2O$).

2. Treatment of all four types of coal, anthracite, bituminous, subbituminous and lignite, with the proposed solvent in order to discover the effect of the rank of coal in the chemical comminution process

with the proposed solvent. These series of tests will help to determine the effect of the physical characteristics of coal, such as porosity, permeability, density and moisture content, on the chemical comminution process with the suggested solvent.

3. After conducting these two series of tests, it is useful to develop the kinetic equation in order to predict the factor or factors which affect the chemical comminution process of coal with the proposed solvent for field applications.

4. The final steps of research should involve the application of the results obtained from this investigation to the in situ mining operation. Figure 35 and Figure 36 show the hypothesis of in situ mining operations for thin coal deposits. The equipment which are required in field operations are indicated in Figures 35 and 36. However, the amout of heat loss from the surface of ground to the bottom of the hole must be calculated in order to add this amount of heat to the binary system in Tank 5. The operation in the field can be as follows:

a. Open valve 3 and allow water to flow into tank 5. Then close valve 3 and allow $CO_2$ to flow from tank 2 into tank 5. The preferred ratio of $H_2O/CO_2$ is 1.5 to 1. Close valve 4.

b. Heat binary system to the desired temperature by a favorable heating device. At this stage, the amount of heat loss from the ground surface to the bottom hole must be calculated. Also it is necessary to calculate the amount of temperature and pressure which exists at the bottom hole of the in situ mine.

c. Open valve 7 and allow the solvent to flow through the injection well for the desired time. Then close valve 7.

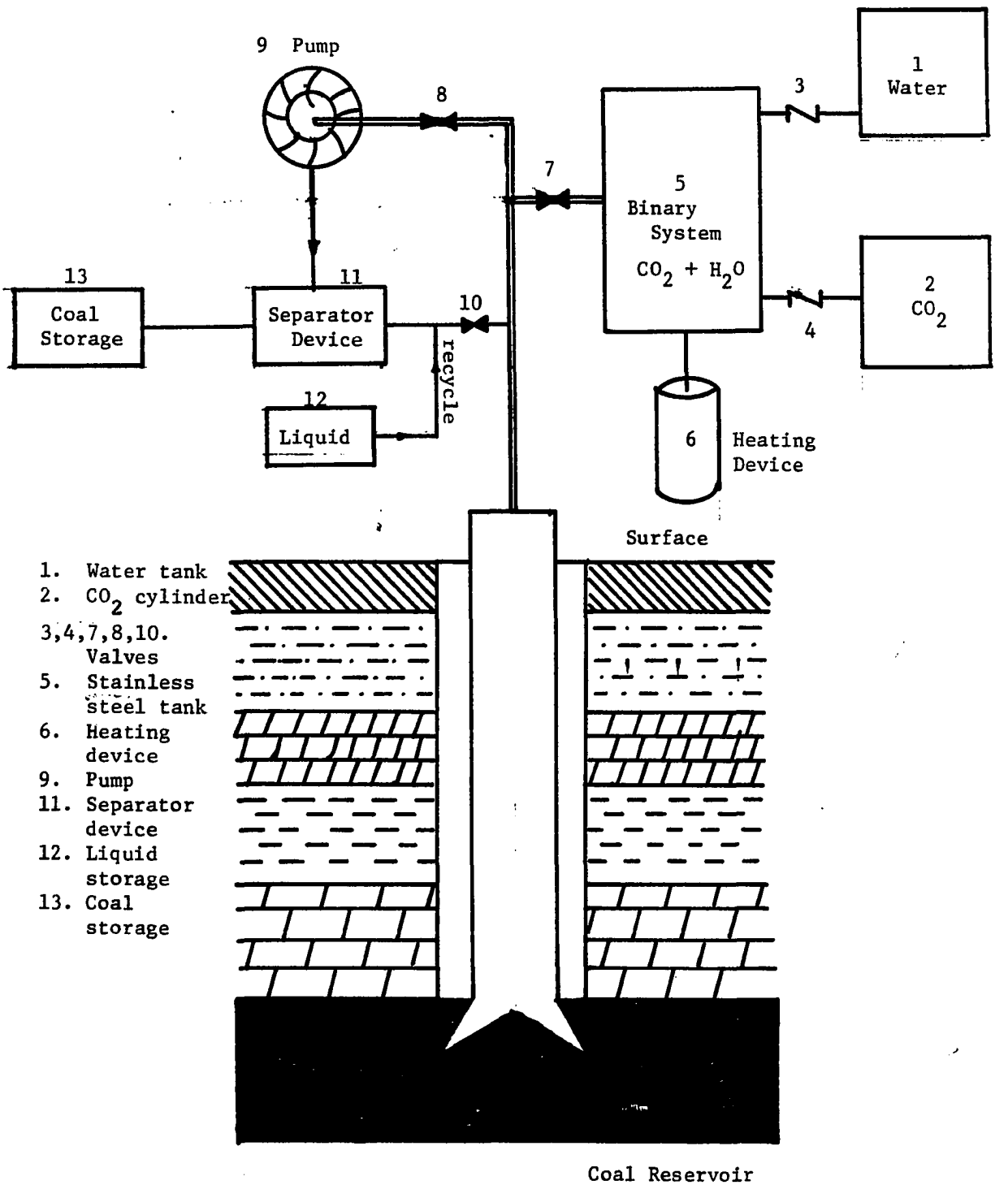


FIGURE 35

Illustration of Field Operations Before Chemical Comminution.

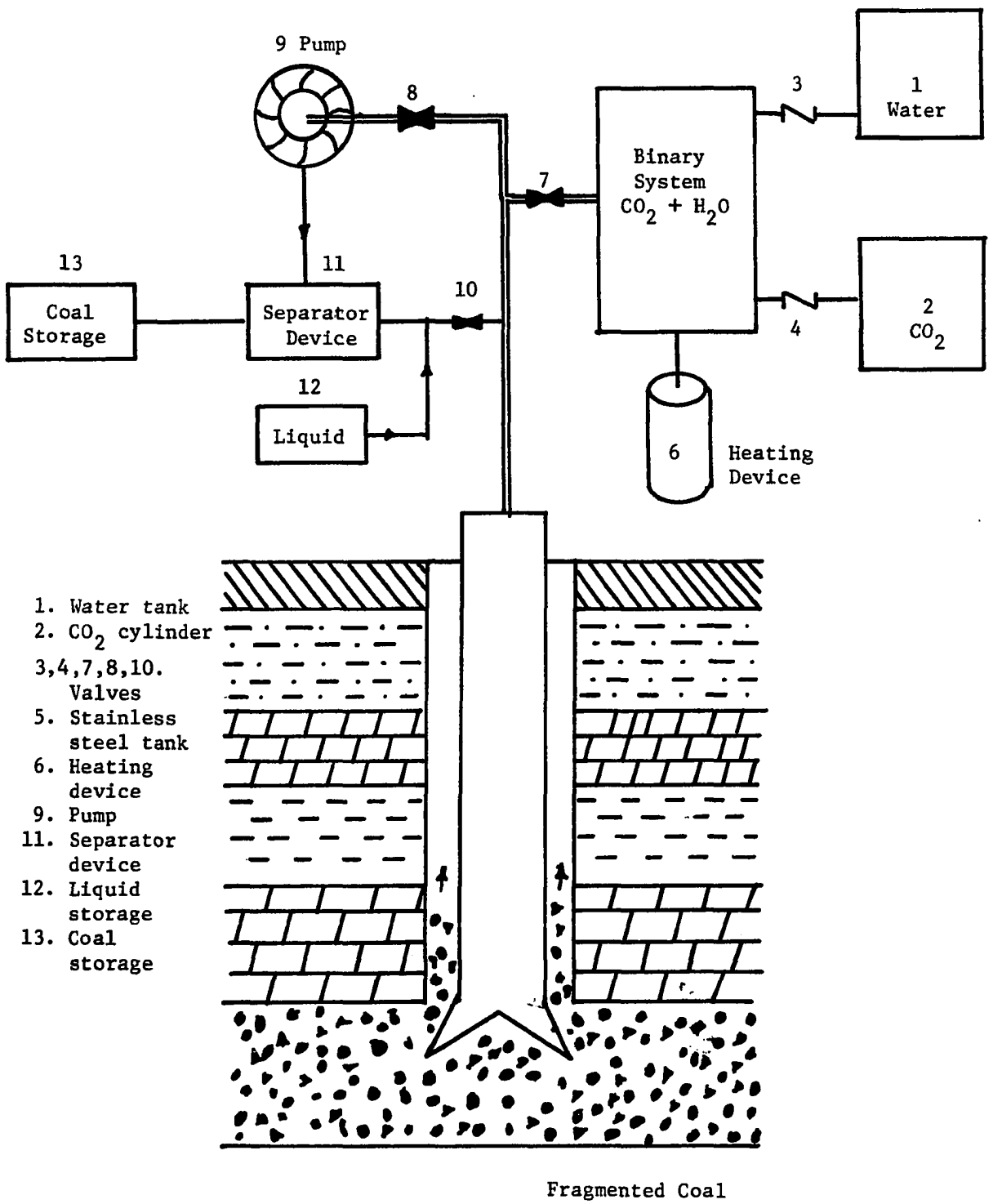


FIGURE 36

Illustration of Field Operations After Chemical Comminution.

d. After the coal is broken (Figure 36), the fragmented coal can be moved to the surface by using a single hydraulic pump (9) with enough pressure. Open valve 8 and open valve 10 at the production well (in this operation, the production well and injection well are not separate). After removing fragmented coal, close valve 8 and valve 10.

e. Use favorable separation device (11) and separate liquid (12) ($H_2O$ and $CO_2$) from solid (fragmented coal), then keep the coal in storage (13). Probably, for economic considerations, the liquid can be recycled, and the operation can be repeated with the same procedure.

5. The accuracy of the correlation equation which was developed (page 140, Eqn. 6) could be improved if the following steps are carried out in further research.

a. Instead of using the figure and empirical calculation, the $CO_2$ can be determined from the difference in the weight of the reactor before and after injection of the $CO_2$.

b. Since dimensional analysis is applied to develop the correlation between the dependent variable (size of fragmented coal) and independent variables (T, P, solvent to coal ratio, etc.), better correlation might be obtained if the coal is a specific shape instead of its natural form (unshaped).

c. Also, better results and correlation would occur if the coal can be stored in such a way to prevent its oxidation.

d. A better understanding of fragmentation can be gained if the process of chemical comminution can be observed inside the reactor in order to determine the conditions (vapor, liquid or mixture) while the coal is fragmenting. For this purpose, a piece of glass (5 x 3 inches) which can resist high temperature and pressure can be installed on the reactor. The rest of the equipment would be similar to that used in this research.

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# APPENDIX A

## PHOTOGRAPHS INDICATING THREE COAL BEDS, McALESTER, CROWEBURG AND SECOR, BEFORE AND AFTER TREATMENT WITH $CO_2 + H_2O$




FIGURE 1

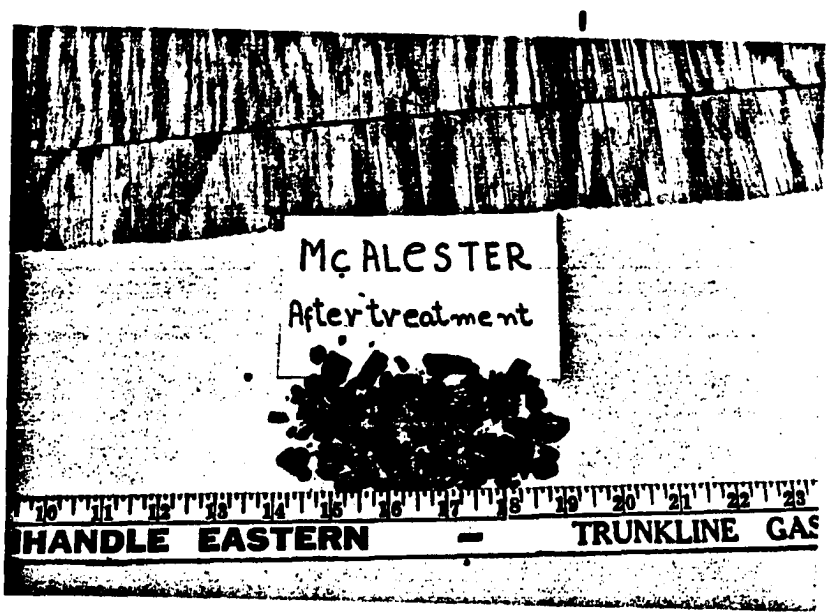



FIGURE 2

T = 275°C, P = 3300 psi, Period of Test = 24 hours

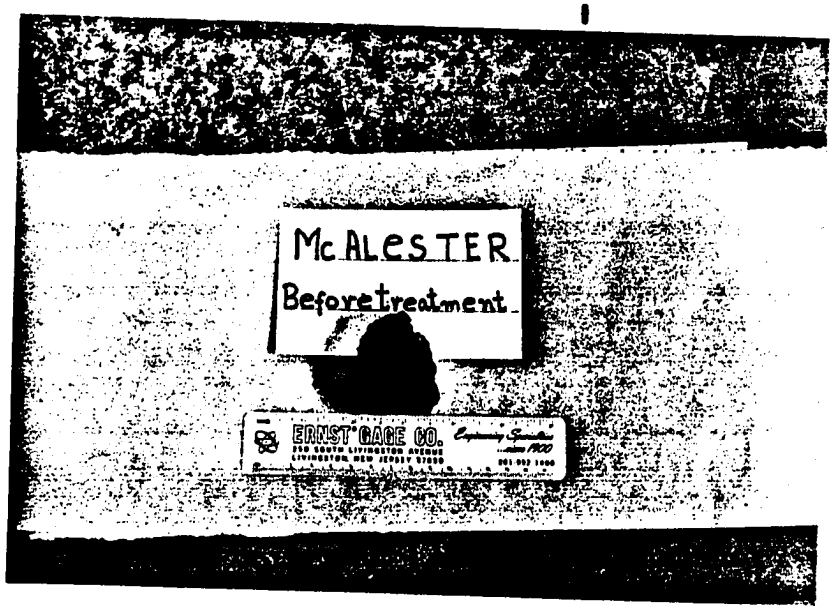



FIGURE 3

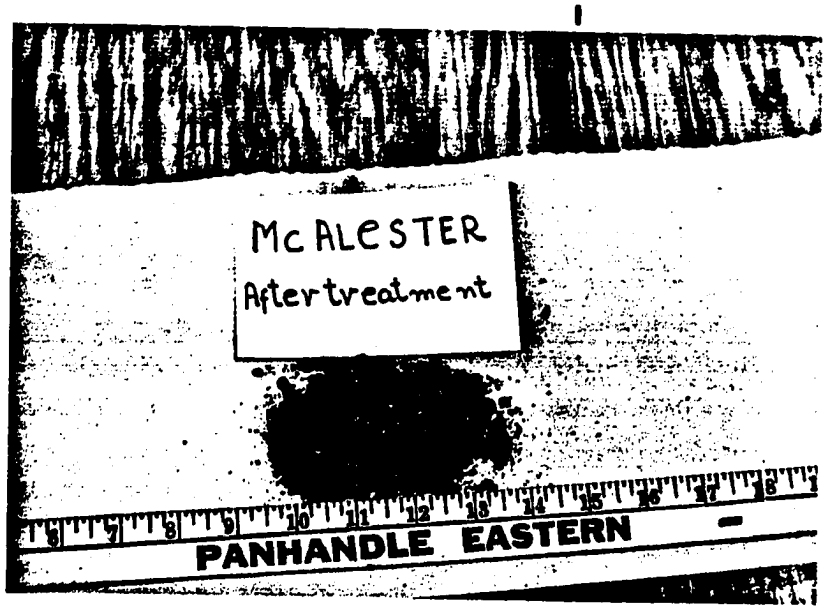



FIGURE 4

T = 275°C, P = 3300 psi, Period of Test = 36 hours

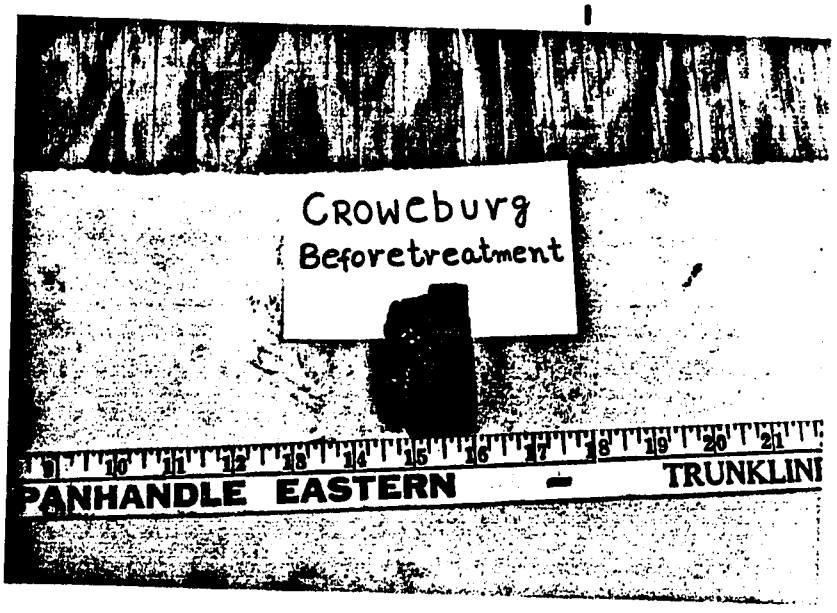



FIGURE 5

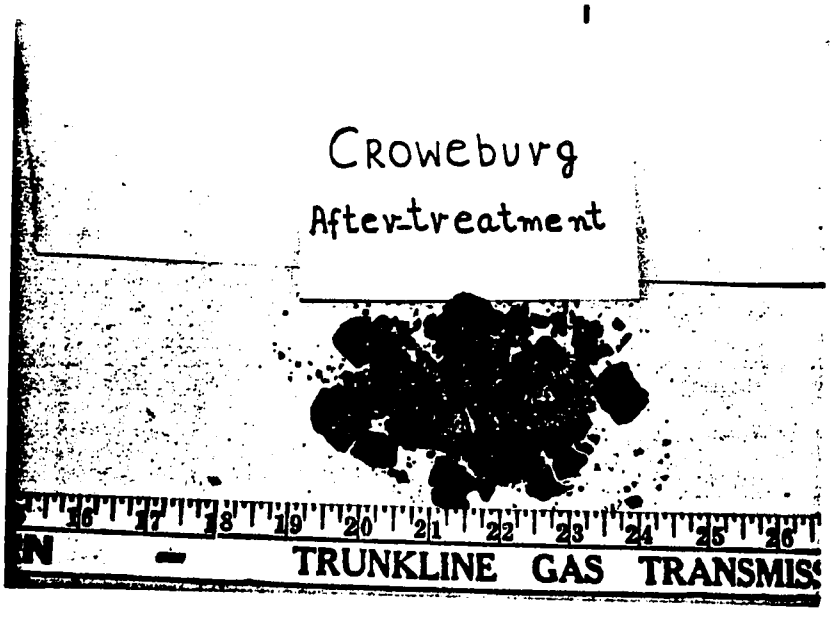



FIGURE 6

T = 305°C, P = 2550 psi, Period of Test = 24 hours

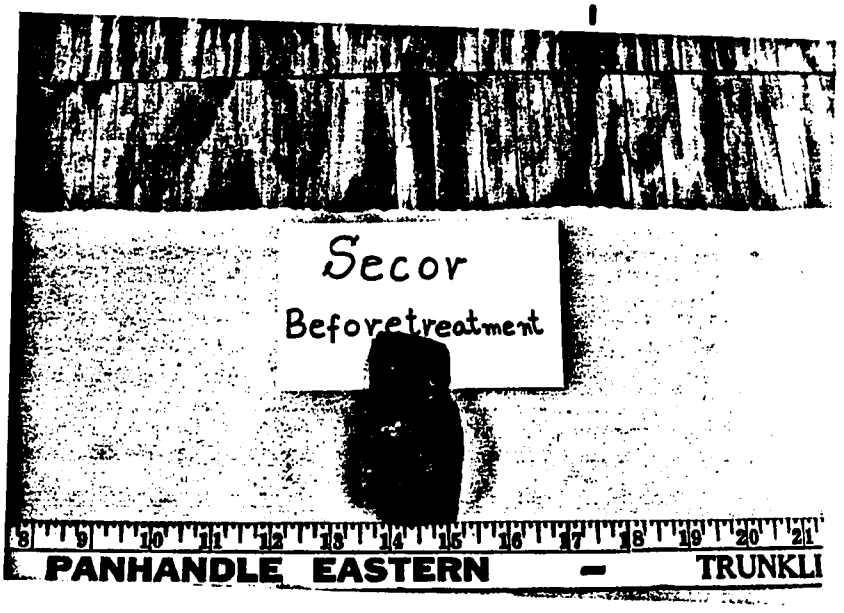



FIGURE 7

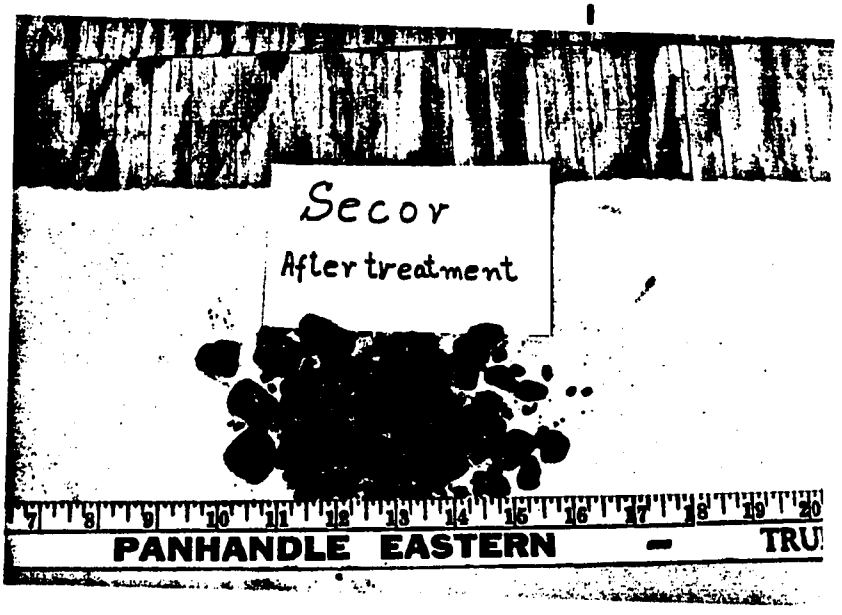



FIGURE 8

T = 315°C, P = 2750 psi, Period of Test = 24 hours

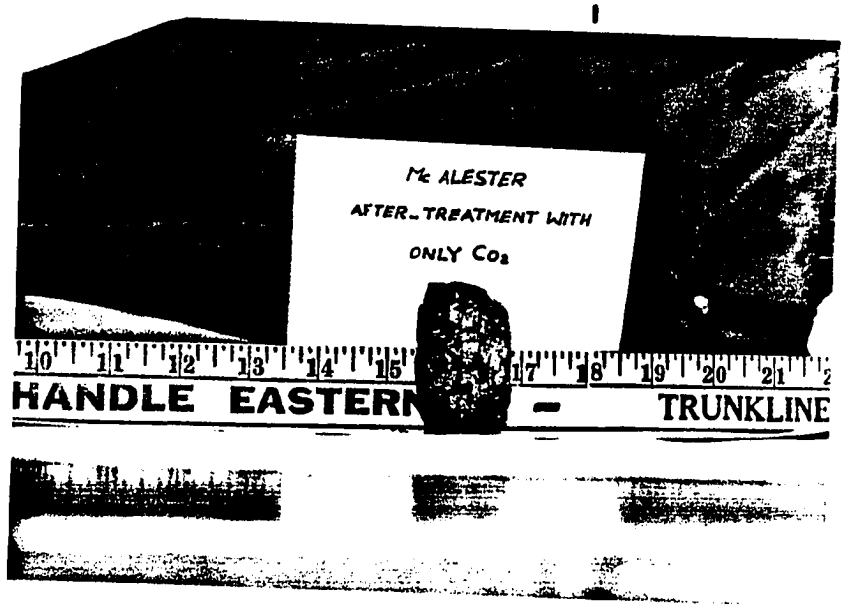



FIGURE 9

T = 325°C, P = 3250 psi, Period of Test = 24 hours



FIGURE 10

T = 325°C, P = 2900 psi, Period of Test = 24 hours

TABLE 1

Analytical Data: McAlester Bituminous Coal of Oklahoma

(Moisture free basis)

T = 275°C, P = 3300 psi

| Weight % of Ultimate Analysis | Untreated | Treated |
|---|---|---|
| | $CH_{0.67}$ | $CH_{0.69}$ |
| Carbon (C) | 70.4 | 69.54 |
| Hydrogen (H) | 3.95 | 4.01 |
| Nitrogen (N) | 1.25 | 1.12 |
| Sulfur (S) | 3.51 | 2.23 |
| Chlorine (Cl) | 0.02 | 0.04 |
| Oxygen (O) by difference | 2.22 | 5.56 |
| Moisture | [0.04] | [0.10] |
| Ash | 18.65 | 17.5 |
| Sulfur Form | | |
| Pyritic Sulfur ($FeS_2$) | 2.06 | 1.24 |
| Sulfate Sulfur | 0.38 | 0.17 |
| Organic Sulfur | 1.07 | 0.82 |
| Total | 3.51 | 2.23 |
| Heating Value (Btu/lb) | 11808 | 11924 |

TABLE 2

Analytical Data: McAlester Bituminous Coal of Oklahoma

(Moisture, ash free basis)

T = 275°C, P = 3300 psi)

| Weight % of Ultimate Analysis | Untreated | Treated |
|---|---|---|
| | $CH_{0.67}$ | $CH_{0.69}$ |
| Carbon (C) | 86.55 | 84.3 |
| Hydrogen (H) | 4.86 | 4.87 |
| Nitrogen (N) | 1.53 | 1.36 |
| Sulfur (S) | 4.32 | 2.71 |
| Chlorine (Cl) | 0.024 | 0.049 |
| Oxygen (O) by difference | 2.73 | 6.71 |
| Moisture | [0.04] | [0.10] |
| Ash | [18.65] | [17.5] |
| Sulfur Form | | |
| Pyritic Sulfur ($FeS_2$) | 2.53 | 1.5 |
| Sulfate Sulfur | 0.47 | 0.22 |
| Organic Sulfur | 1.32 | 0.99 |
| Total | 4.32 | 2.71 |
| Heating Value (Btu/lb) | 14522 | 14471 |

# APPENDIX B

THE RESULTS OF 17 TESTS ON McALESTER, CROWEBURG, AND SECOR COAL INCLUDING FIGURES: TEMPERATURE VERSUS TIME, PRESSURE VERSUS TIME, PRESSURE VERSUS TEMPERATURE, THE DISTRIBUTION OF FRAGMENTED COAL VERSUS MESH NO. AND SIZE OF FRAGMENTED COAL VERSUS PERCENT OF CUMULATIVE

TABLE 1

"SAS" General Computer Program of Regression Analysis for:

1. Pressure-Temperature Relationship
2. Pressure-Time Relationship
3. Temperature-Time Relationship

```
//JOB
//EXEC  SAS
//SYSIN  DD  *
DATA NAME;
INPUT X Y Z;
CARDS;
Data here
Proc print;
Proc NLIN Data=Name Best=10;
Model Y = M*X + B;
Parameter M=0 to 10 by .1
          B=0 to 10 by .1;
Output out = One predicted = PY;
Proc print;
Proc GPLOT Data = One;
Plot Y*X PY*X/overlay;
Symbol 1 V = Star;
Symbol 2 V = None I = Join;
Label Y = Pressure in psi;
Label X = Temperature in Degree Centigrade;
```

TABLE 1 (Continued)

```
Title .H=2 Pressure vers Temperature;
Footnote 1 .H=1 Test No. Temperature in degree Centigrade .H=
1 Pressure in psi;
Footnote 2 .H=1 Period of Test in hours;
Run;
Proc NLIN Data = Name Best = 10;
Model Y = M*Z+B;
Parameter M=0 to 10 by .1
          B=0 to 10 by .1;
Output out = One Predicted = PY;
Proc Print;
Proc GPLOT Data = One;
Plot Y*Z PY*Z/overlay;
Symbol 1 V = Star;
Symbol 2 V = None I = Join;
Label Y = Pressure in psi;
Label Z = Time in minutes;
Title .H=2 Pressure vers Time;
Footnote .H=1 Test No.
Run;
Proc NLIN Data = Name Best = 10;
Model X = M*Z + B;
Parameter M=0 to 10 by .1
          B=0 to 10 by .1;
Output out = One Predicted = PX;
```

TABLE 1 (Continued)

```
Proc Print;
Proc GPLOT Data = One;
Plot X*Z PX*Z/overlay;
Symbol 1 V = Star;
Symbol 2 V = None I = Join;
Label X = Temperature in degrees Centigrade;
Label Z = Time in minutes;
Title .H=2 Temperature vers Time
Footnote .H=1 Nest No.
//
JCL Final Control Card
```

TABLE 2

U.S. STANDARD SIEVE

| Mesh No. | Opening Size Inch | Average Opening Size Inch | Average Opening Size cm |
|---|---|---|---|
| 4 | 0.185 | 0.185 | |
| 16 | 0.0469 | 0.116 | 0.295 |
| 50 | 0.0116 | 0.0293 | 0.074 |
| 70 | 0.0083 | 0.00995 | 0.0252 |
| 100 | 0.0059 | 0.0071 | 0.018 |
| -100 | 0.0029 | 0.0044 | 0.011 |

1 inch = 2.54 cm or 25.4 mm

1 cm = $10^4$ micron

1 inch = 25400 micron

TABLE 3

| Test No. | Period Hours | T °C | P psi |
|---|---|---|---|
| 1 | 21.5 | 200 | 2150 |
| 2 | 23 | 225 | 2700 |
| 3 | 24 | 235 | 2850 |
| 4 | 24 | 250 | 2950 |
| 5 | 18 | 275 | 3300 |
| 6 | 24 | 275 | 3300 |
| 7 | 30 | 275 | 3300 |
| 8 | 36 | 275 | 3300 |
| 9 | 18 | 325 | 3600 |

All tests were run on McAlester Coal of Oklahoma.

TABLE 4

Fragmented Size Distribution from McAlester

Coal-$CO_2$ + $H_2O$ Mixture

| Test No. | Time Hours | % Retained on U.S. Standard Screen Mesh 4 | 16 | 50 | 70 | 100 | -100 |
|---|---|---|---|---|---|---|---|
| 1 | 21.5 | 55 | 27.2 | 6.3 | 2.2 | 4.5 | 5 |
| 2 | 23 | 33.9 | 50.4 | 9.3 | 3.4 | 1.00 | 2 |
| 3 | 24. | 42 | 38.4 | 12.6 | 4.2 | 0.5 | 2.3 |
| 4 | 24 | 44 | 30 | 11.2 | 7.7 | 4.6 | 2.2 |
| 5 | 18 | 60 | 28 | 7 | 1.5 | 0.63 | 3 |
| 6 | 24 | 30 | 27.5 | 17.2 | 9.2 | 8.1 | 8 |
| 7 | 30 | 25 | 23.4 | 18.5 | 11.7 | 8.8 | 12.6 |
| 8 | 36 | 21 | 22 | 16.4 | 12.6 | 10.5 | 17.5 |
| 9 | 18 | 23.3 | 20.3 | 16 | 10.2 | 12.8 | 17.4 |

TEST #1

T = 200°C

Pressure = 2150 psi

Period = 21.5 hours

6% of total coal fell apart

Total coal sample = 160 grams (3 pieces)

Water added = 250 gm

$CO_2$ added = 41.4 gm

Total fragmented coal = 11 grams

Average particle size = 0.135 inches

TABLE 1.1*

Time, Temperature, Pressure Relation of Test #1

| Time Minute | Temperature °C | Pressure psi |
|---|---|---|
| 10 | 50 | 1100 |
| 22 | 75 | 1300 |
| 31 | 100 | 1475 |
| 55 | 150 | 1825 |
| 68 | 175 | 1950 |
| 80 | 200 | 2150 |

80 minutes were required to warm reactor up to 200°C.

*These data are used to plot Figures 1.1, 1.2, 1.3.

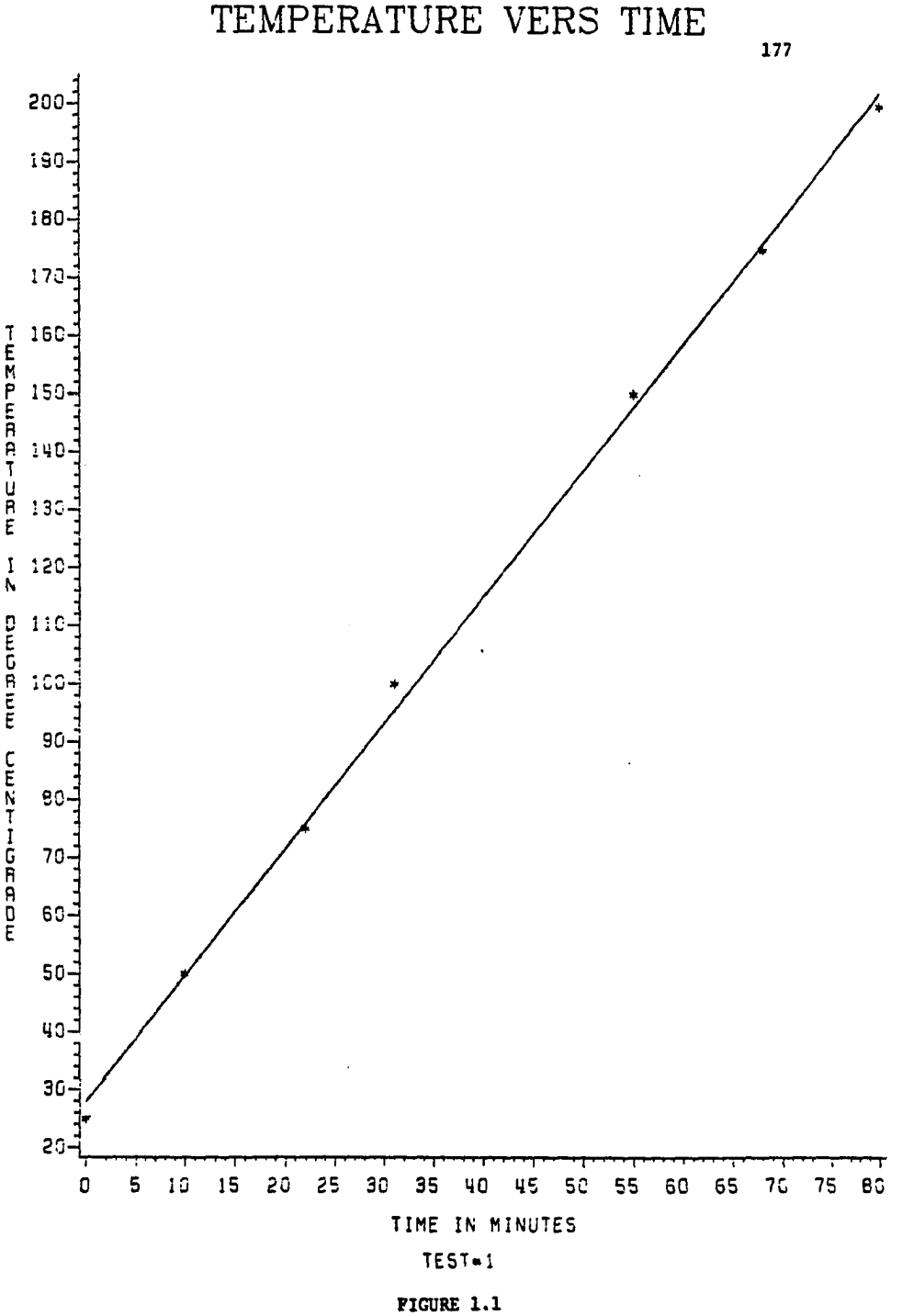

TEMPERATURE VERS TIME
TEMPERATURE IN DEGREE CENTIGRADE
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
0 5 10 15 20 25 30 35 40 45 50 55 60 65 70 75 80
TIME IN MINUTES
TEST=1

FIGURE 1.1

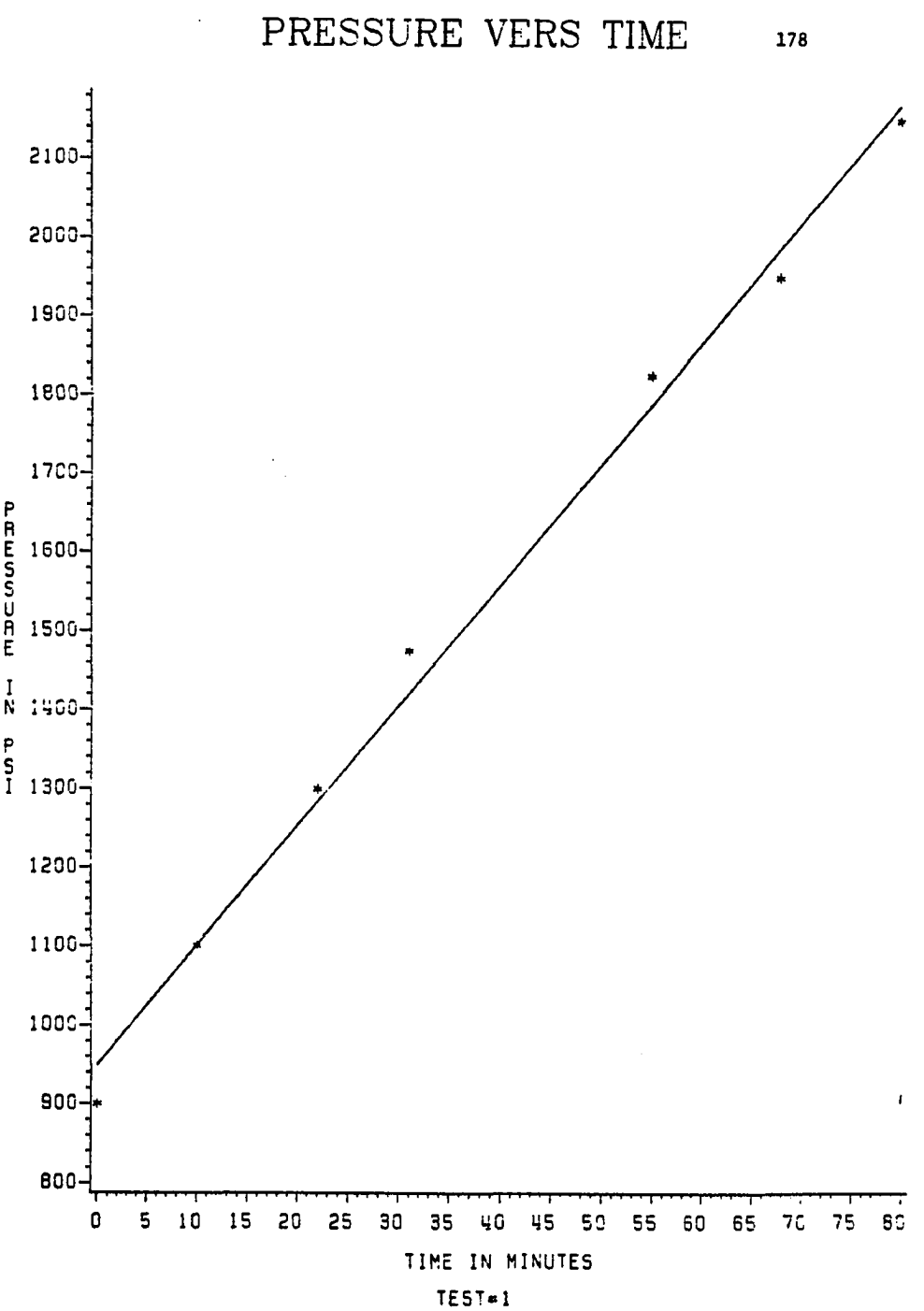
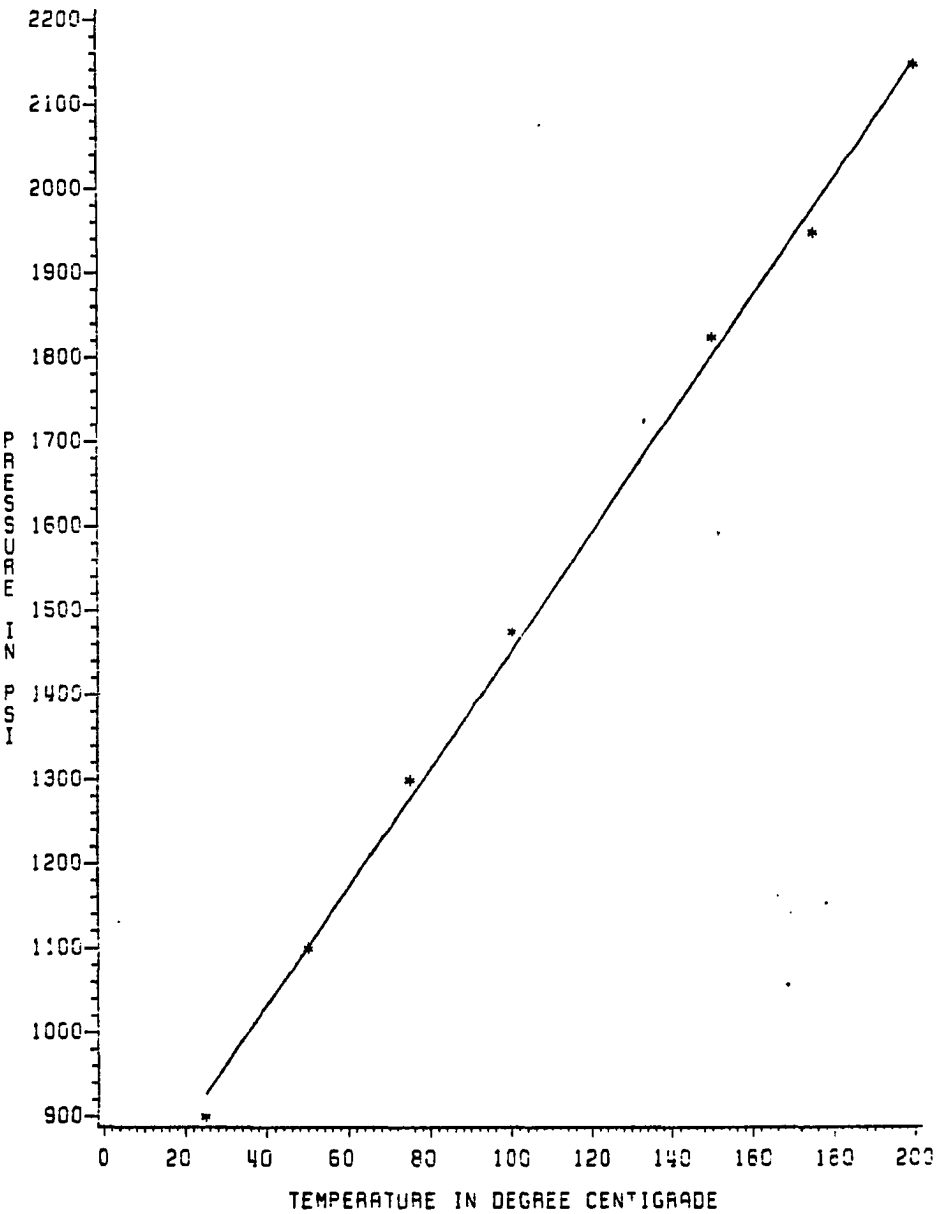

PRESSURE VERS TIME
PRESSUAE IN PSI
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
0 5 10 15 20 25 30 35 40 45 50 55 60 65 70 75 80
TIME IN MINUTES
TEST=1

**FIGURE 1.2**

# PRESSURE VERS TEMPERATURE






TEST=1 TEMPERATURE=200 DEGREE CENTIGRADE PRESSURE=2150 PSI
AND PERIOD OF TEST 21.5 HOURES

**FIGURE 1.3**

TABLE 1.2

The Result of U.S. Standard Sieve Analysis of Particular Distribution

| Mesh No. | Opening Size Inch | $X_i$ Average Opening Size Inch | $f_i$ Weight Retained on Mesh No. (g) | % by Weight | % Cumulative by Weight |
|---|---|---|---|---|---|
| 4 | 0.185 | 0.185 | 6 | 55 | 55 |
| 16 | 0.0469 | 0.116 | 3 | 27.2 | 82.2 |
| 50 | 0.0116 | 0.0293 | 0.7 | 6.3 | 88.6 |
| 70 | 0.0083 | 0.00995 | 0.25 | 2.2 | 90.8 |
| 100 | 0.0059 | 0.0071 | 0.5 | 4.5 | 95 |
| -100 | 0.0029 | 0.0044 | 0.55 | 5 | |
| | | | 11 g | | 100% |

$$\text{Average particle size} = \frac{\sum f_i x_i}{\sum f_i} = 0.135 \text{ inches}$$

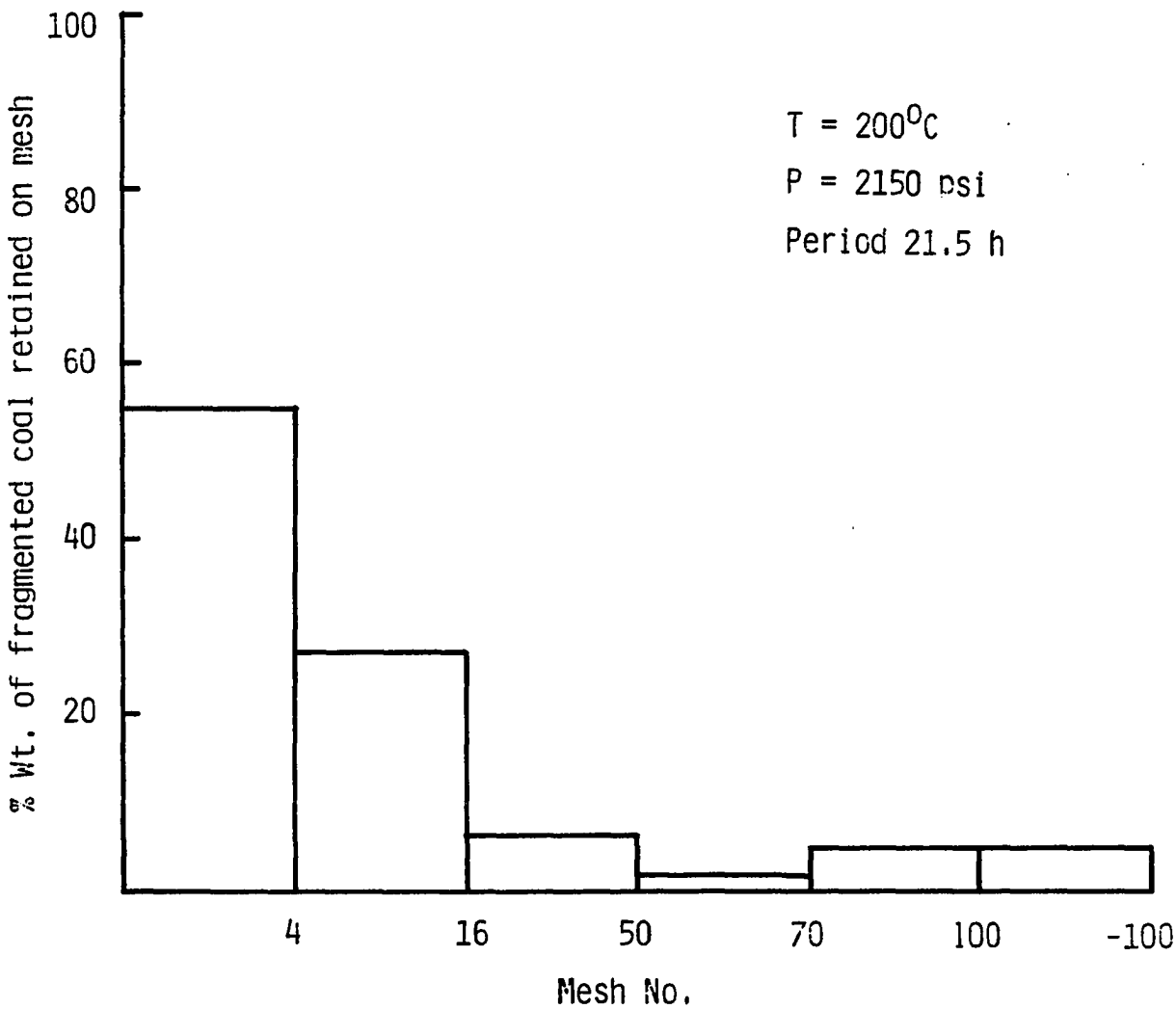



FIGURE 1.4 Distribution of fragmented coal on mesh no.

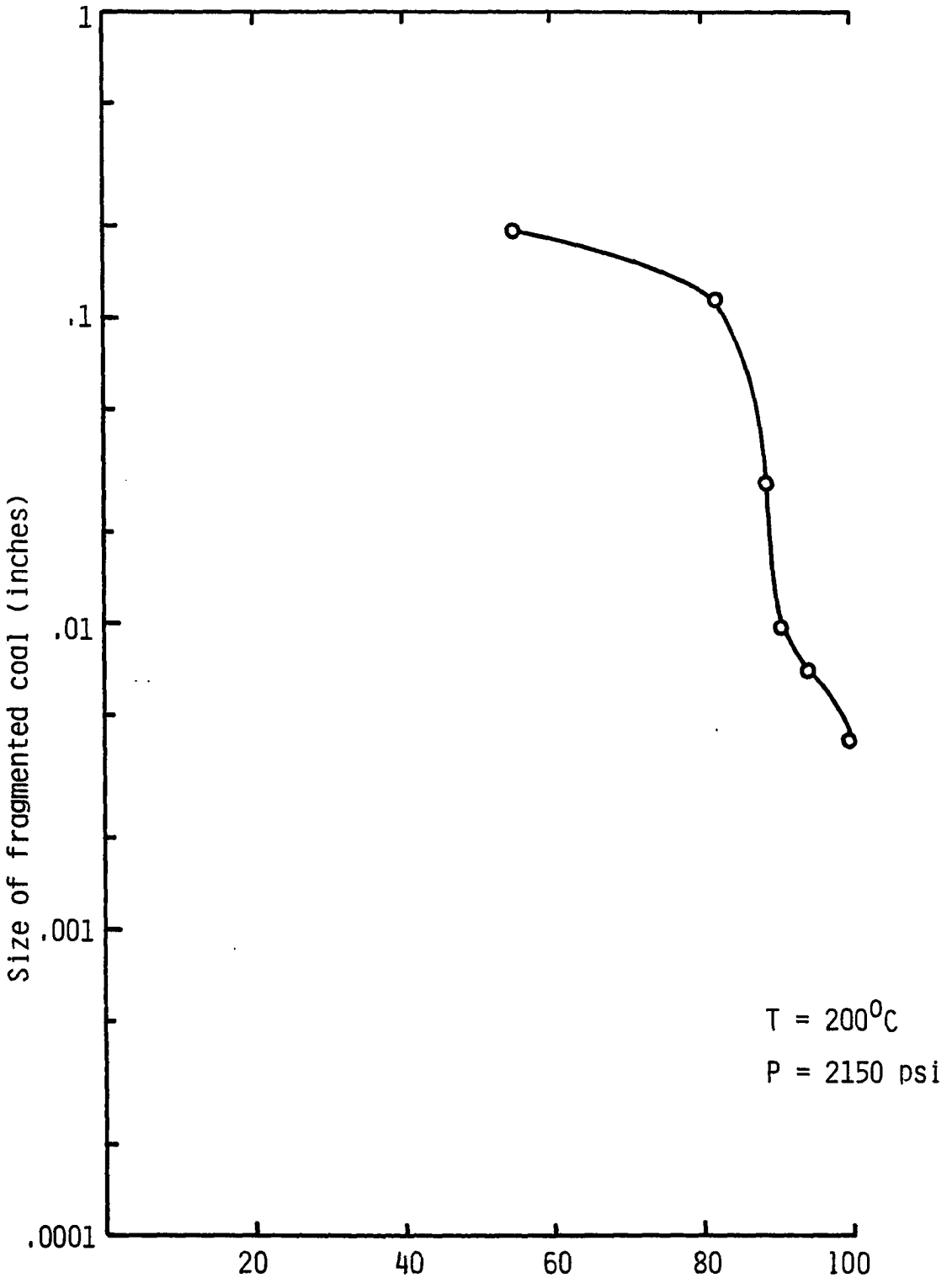



FIGURE 1.5 % Cumulative of fragmented coal.

TEST #2

T = 225°C

Pressure = 2700 psi

Period = 23 hours

38% of total coal fell apart

Total coal sample = 128 grams (3 pieces)

Water added = 225 gm

$CO_2$ added = 50.58 gm

Total fragmented coal = 48.6 grams

Average particle size = 0.126 inches

TABLE 2.1*

Time, Temperature, Pressure Relation of Test #2

| Time Minute | Temperature °C | Pressure psi |
|---|---|---|
| 22 | 75 | 1250 |
| 37 | 100 | 1600 |
| 55 | 125 | 1850 |
| 72 | 150 | 2100 |
| 88 | 200 | 2500 |
| 102 | 225 | 2700 |

102 minutes were required to warm reactor up to 225°C

*These data are used to plot Figures 2.1, 2.2, 2.3.

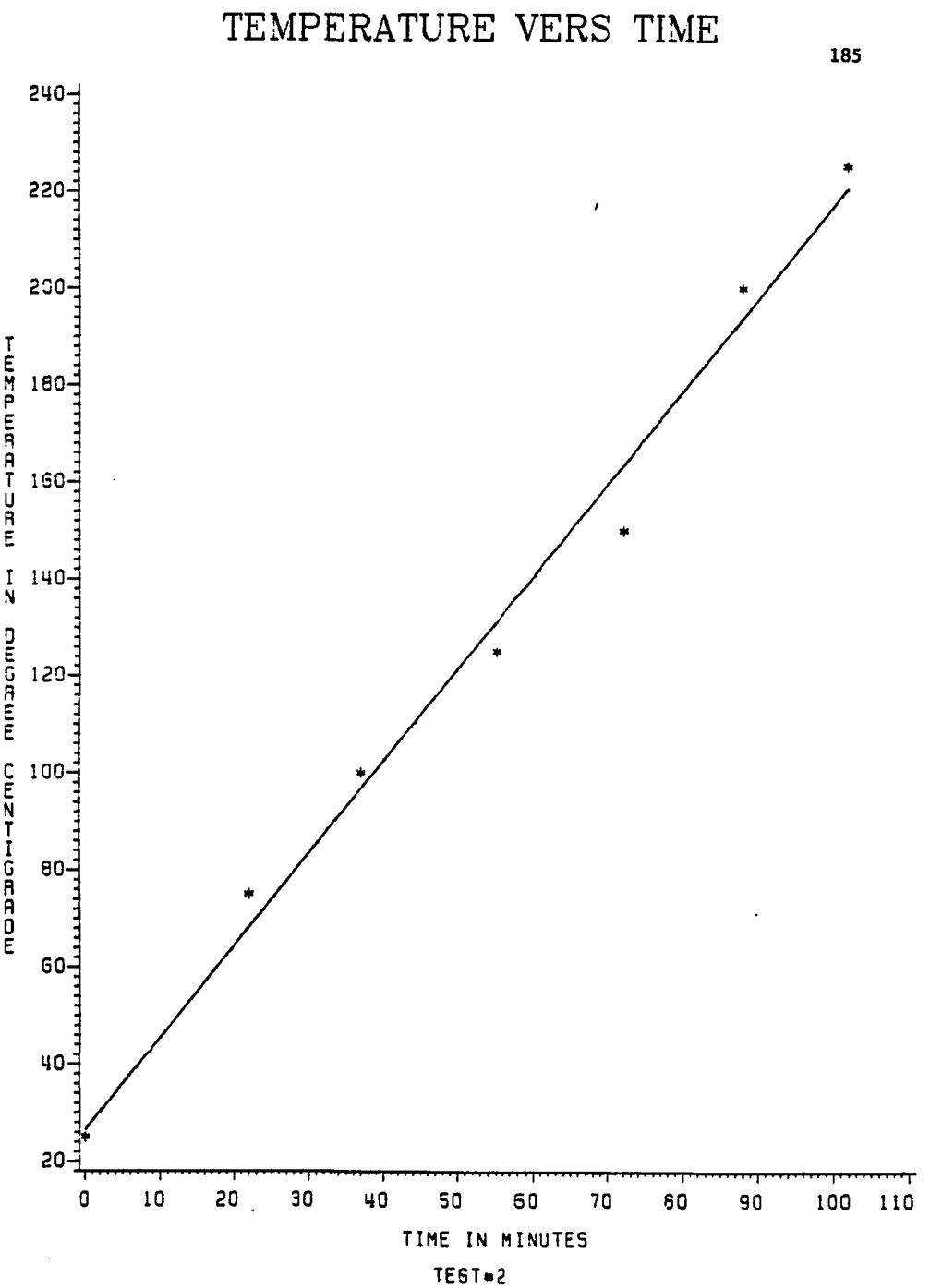

TEMPERATURE VERS TIME
TEMPERATURE IN DEGREE CENTIGRADE
240
220
200
180
160
140
120
100
80
60
40
20
0
10
20
30
40
50
60
70
80
90
100
110
TIME IN MINUTES
TEST=2

FIGURE 2.1

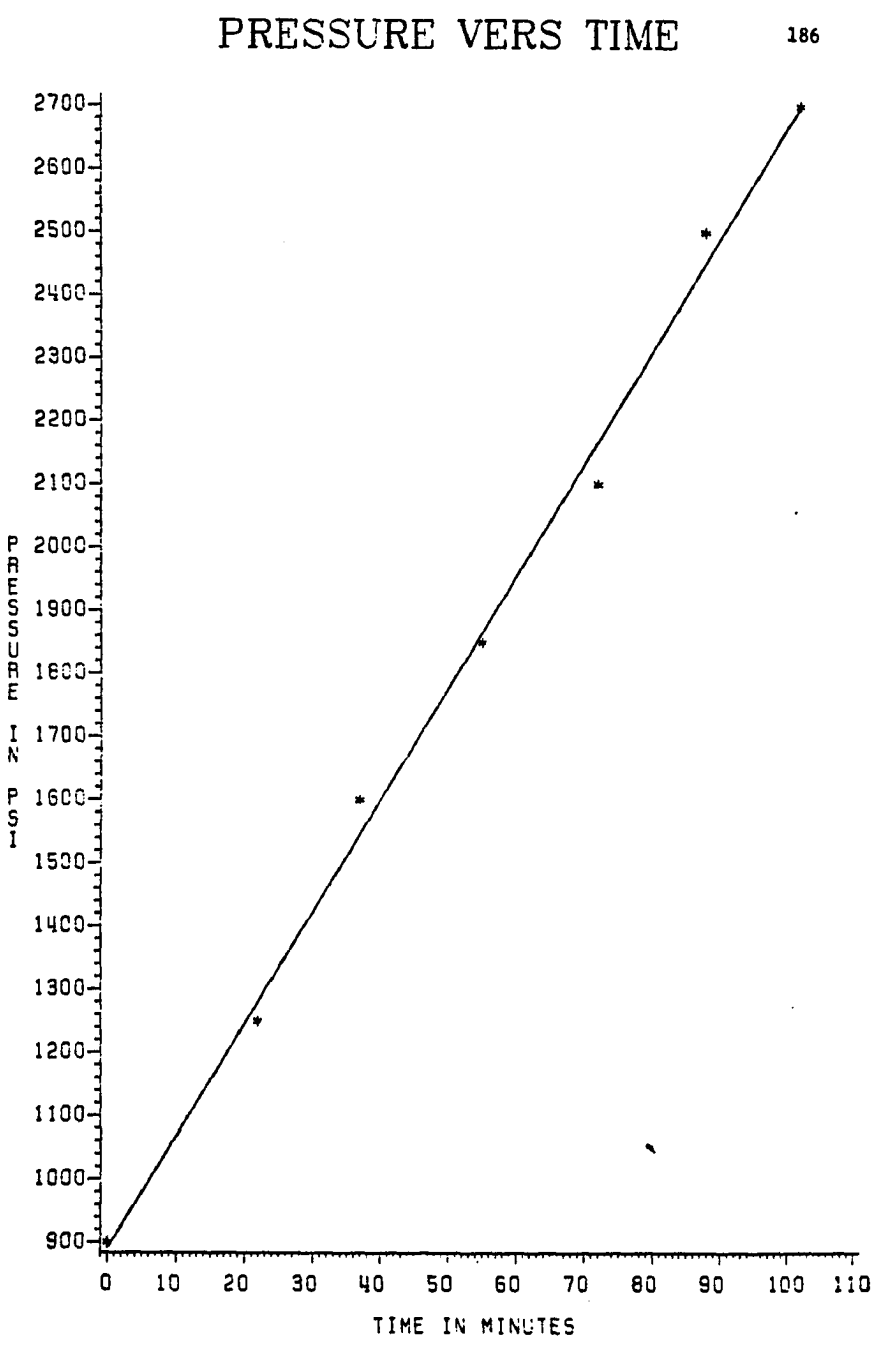

PRESSURE VERS TIME
2700
2600
2500
2400
2300
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
PRESSURE IN PSI
0
10
20
30
40
50
60
70
80
90
100
110
TIME IN MINUTES
TEST=2

**FIGURE 2.2**

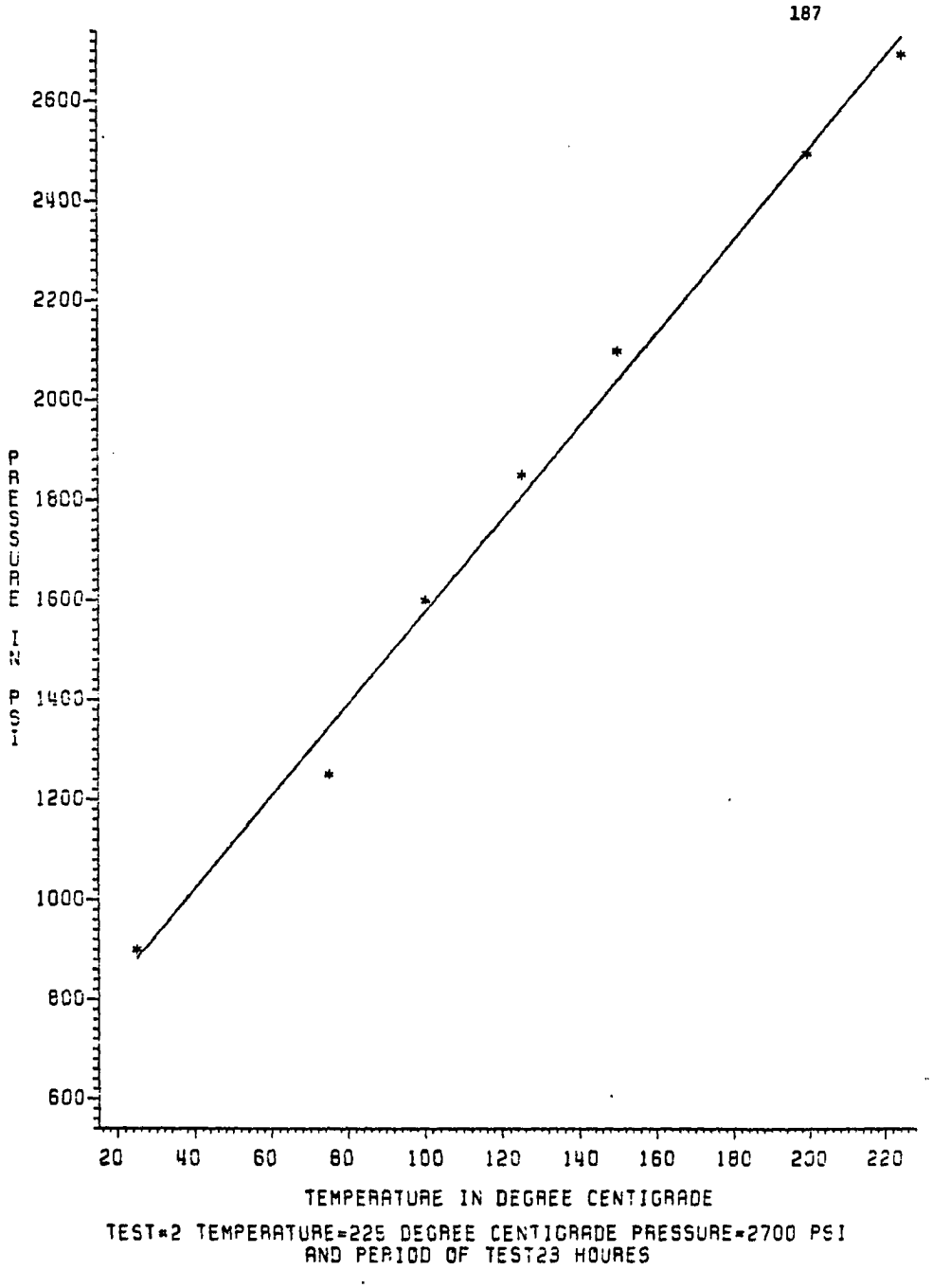

PRESSURE VERS TEMPERATURE
PRESSURE IN PSI
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
20
40
60
80
100
120
140
160
180
200
220
TEMPERATURE IN DEGREE CENTIGRADE
TEST*2 TEMPERATURE=225 DEGREE CENTIGRADE PRESSURE=2700 PSI
AND PERIOD OF TEST23 HOURES

**FIGURE 2.3**

TABLE 2.2

The Result of U.S. Standard Sieve Analysis of Fragmented Coal Distribution

| Mesh No. | Opening Size Inch | $x_i$ Average Opening Size Inch | $f_i$ Weight Retained on Mesh No. (g) | % by Weight | % Cumulative by Weight |
|---|---|---|---|---|---|
| 4 | 0.185 | 0.185 | 16.5 | 33.9 | 33.9 |
| 16 | 0.0469 | 0.116 | 24.5 | 50.4 | 84.3 |
| 50 | 0.0116 | 0.0293 | 4.5 | 9.3 | 93.6 |
| 70 | 0.0083 | 0.00995 | 1.6 | 3.4 | 97 |
| 100 | 0.0059 | 0.0071 | 0.5 | 1.00 | 98 |
| -100 | 0.0029 | 0.0044 | 1.00 | 2 | 100% |
| | | | 48.6 | 100% | |

$$\text{Average particle size} = \frac{\sum f_i x_i}{\sum f_i} = 0.126 \text{ inches}$$

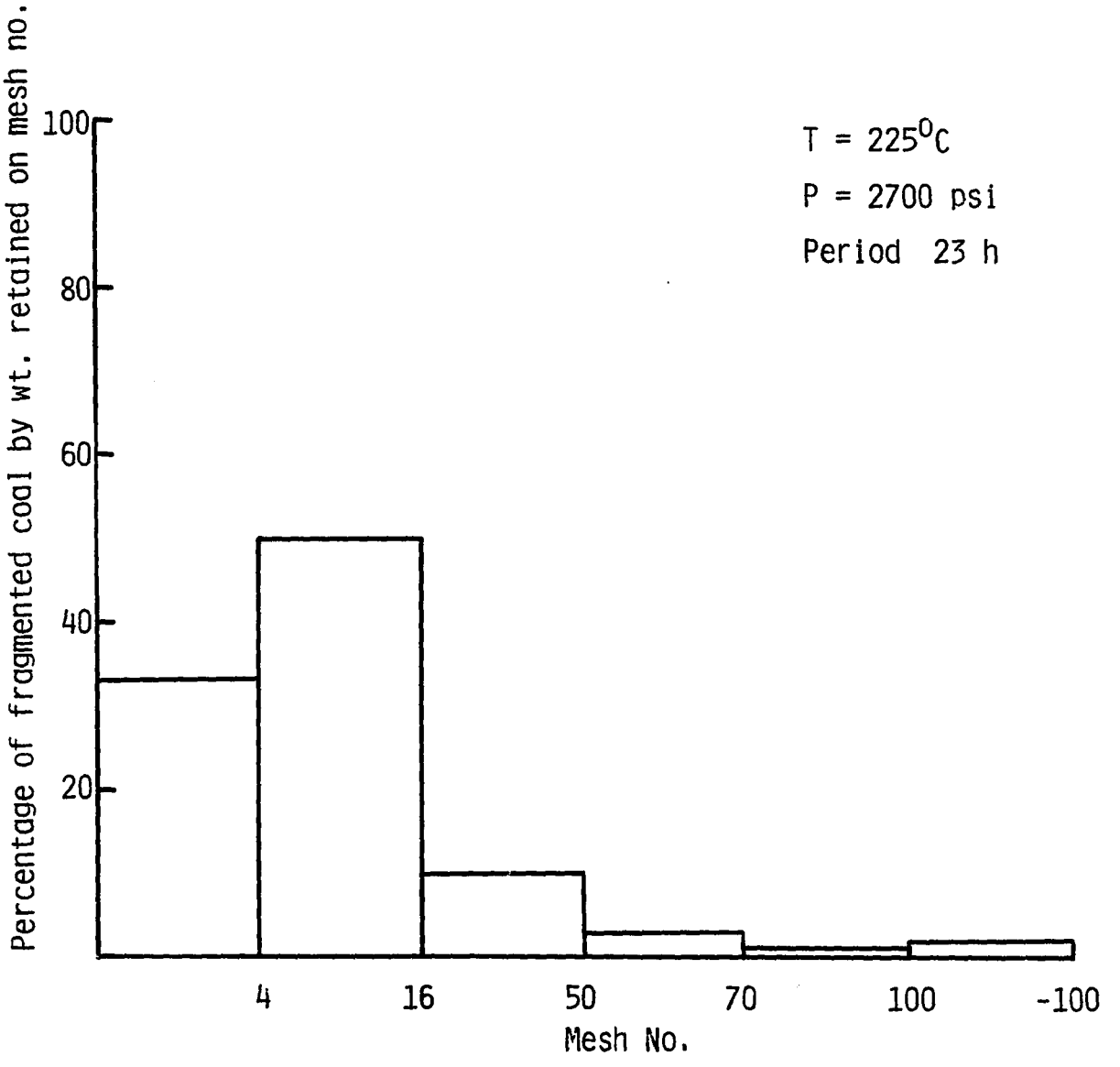



FIGURE 2.4 Distribution of fragmented coal on mesh no.

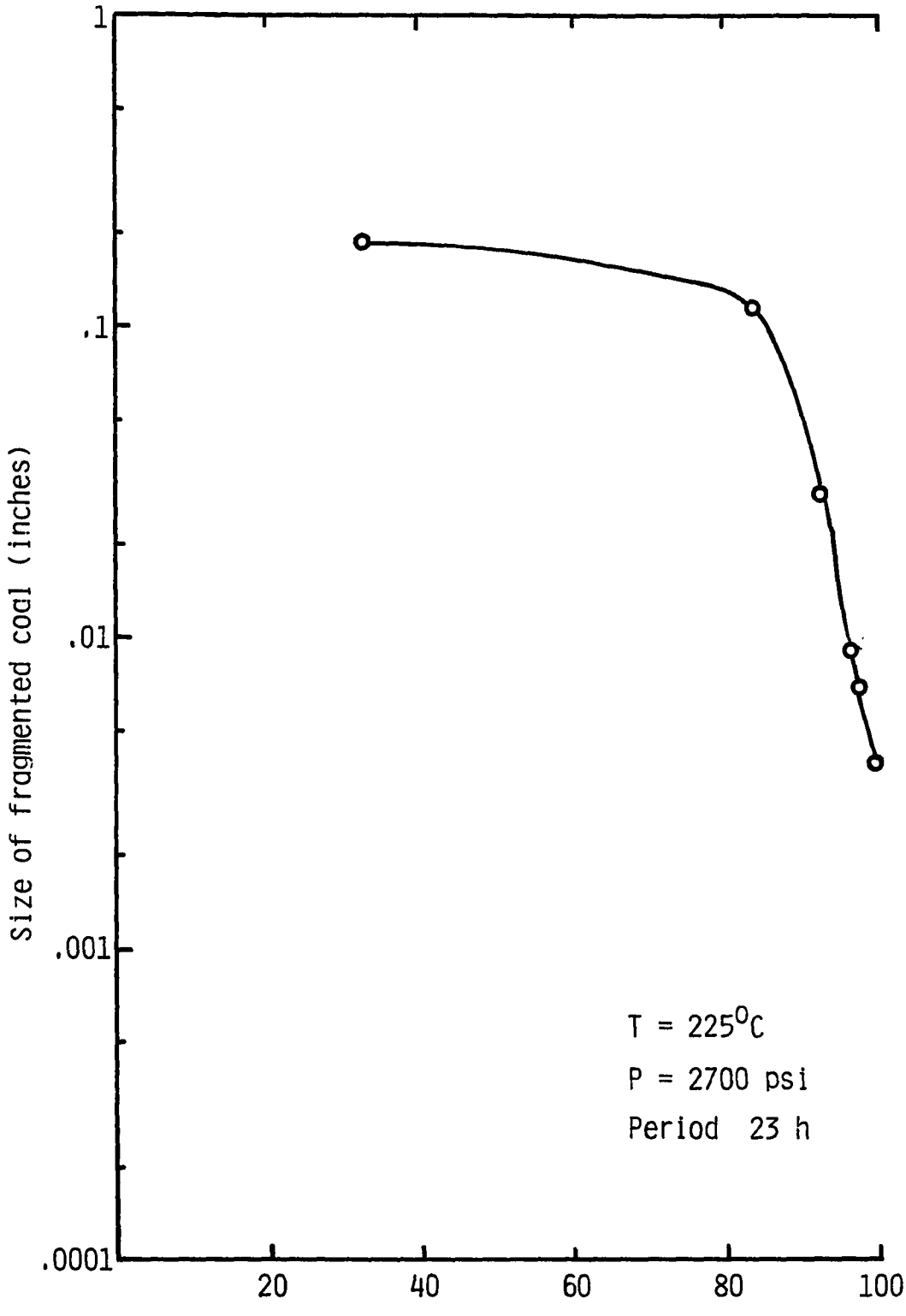



FIGURE 2.5 % Cumulative by weight

TEST #3

T = 235°C

Pressure = 2850 psi

Period = 24 hours

81% of total coal fell apart

Total coal sample = 132 grams (3 pieces)

Water added = 215 gm

$CO_2$ added = 51.3 gm

Total fragmented coal = 107.5 grams

Average particle size = 0.124 inches

TABLE 3.1*

Time, Temperature, Pressure Relation of Test #3

| Time Minute | Temperature °C | Pressure psi |
|---|---|---|
| 11 | 50 | 1100 |
| 34 | 100 | 1550 |
| 58 | 150 | 1875 |
| 88 | 200 | 2450 |
| 100 | 225 | 2750 |
| 105 | 235 | 2850 |

105 minutes were required to warm reactor up to 235°C.

*These data are used to plot Figures 3.1, 3.2, 3.3.

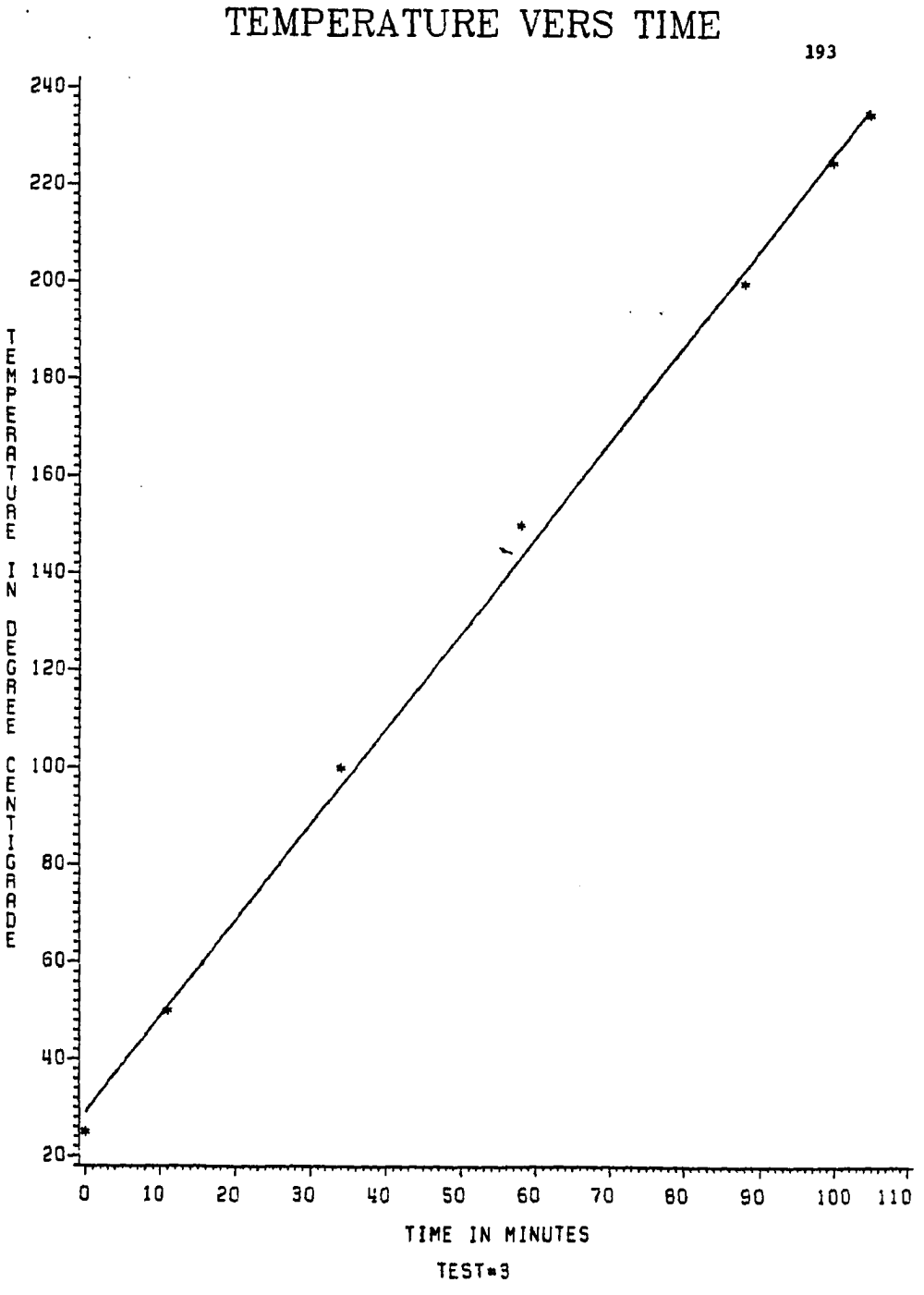

TEMPERATURE VERS TIME
TEMPERATURE IN DEGREE CENTIGRADE
240
220
200
180
160
140
120
100
80
60
40
20
0
10
20
30
40
50
60
70
80
90
100
110
TIME IN MINUTES
TEST=3

**FIGURE 3.1**

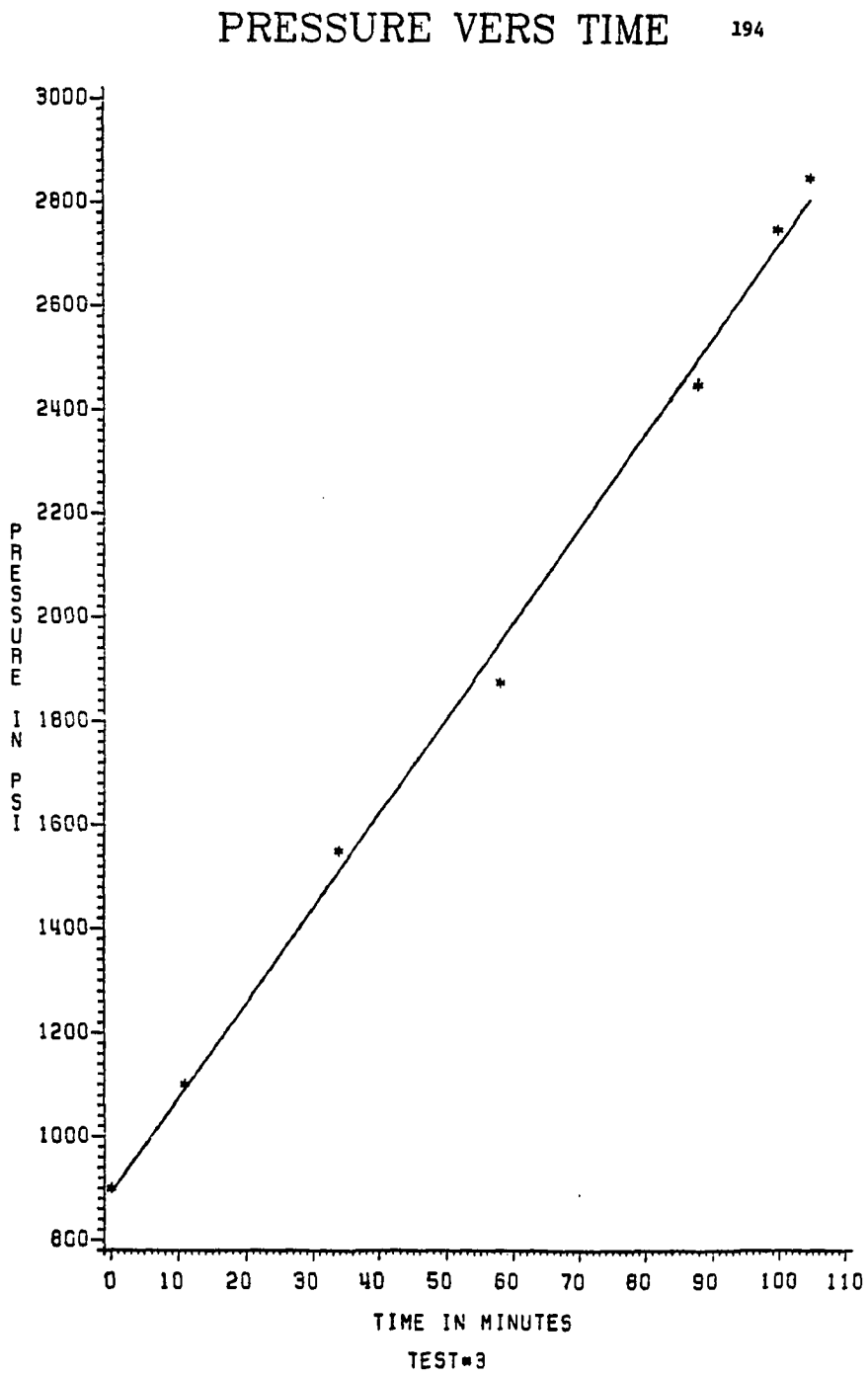

PRESSURE VERS TIME
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
PRESSURE IN PSI
0
10
20
30
40
50
60
70
80
90
100
110
TIME IN MINUTES
TEST#3

**FIGURE 3.2**

# PRESSURE VERS TEMPERATURE



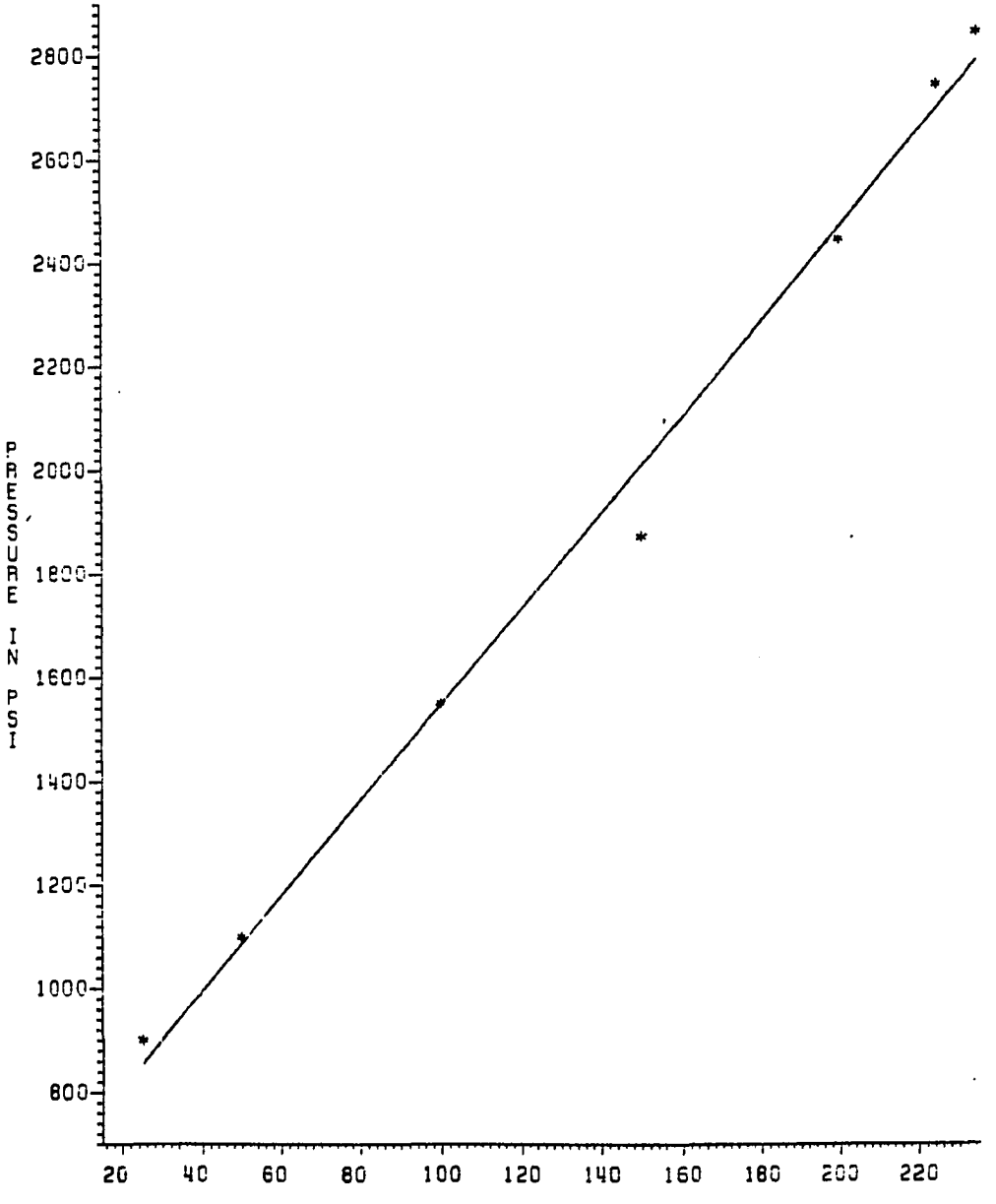



**FIGURE 3.3**

TABLE 3.2

The Result of U.S. Standard Sieve Analysis of Fragmented Coal Distribution

| Mesh No. | Opening Size Inch | $x_i$ Average Opening Size Inch | $f_i$ Weight Retained on Mesh No. (g) | % by Weight | % Cumulative by Weight |
|---|---|---|---|---|---|
| 4 | 0.185 | 0.185 | 45 | 42 | 42 |
| 16 | 0.0469 | 0.116 | 41.5 | 38.4 | 80.8 |
| 50 | 0.0116 | 0.0293 | 13.5 | 12.6 | 93 |
| 70 | 0.0083 | 0.00995 | 4.5 | 4.2 | 97.2 |
| 100 | 0.0059 | 0.0071 | 0.5 | 0.5 | 97.7 |
| -100 | 0.0029 | 0.0044 | 2.5 | 2.3 | 100 |
| | | | 107.5 | 100% | |

$$\text{Average particle size} = \frac{\sum f_i x_i}{\sum f_i} = 0.124 \text{ inches}$$

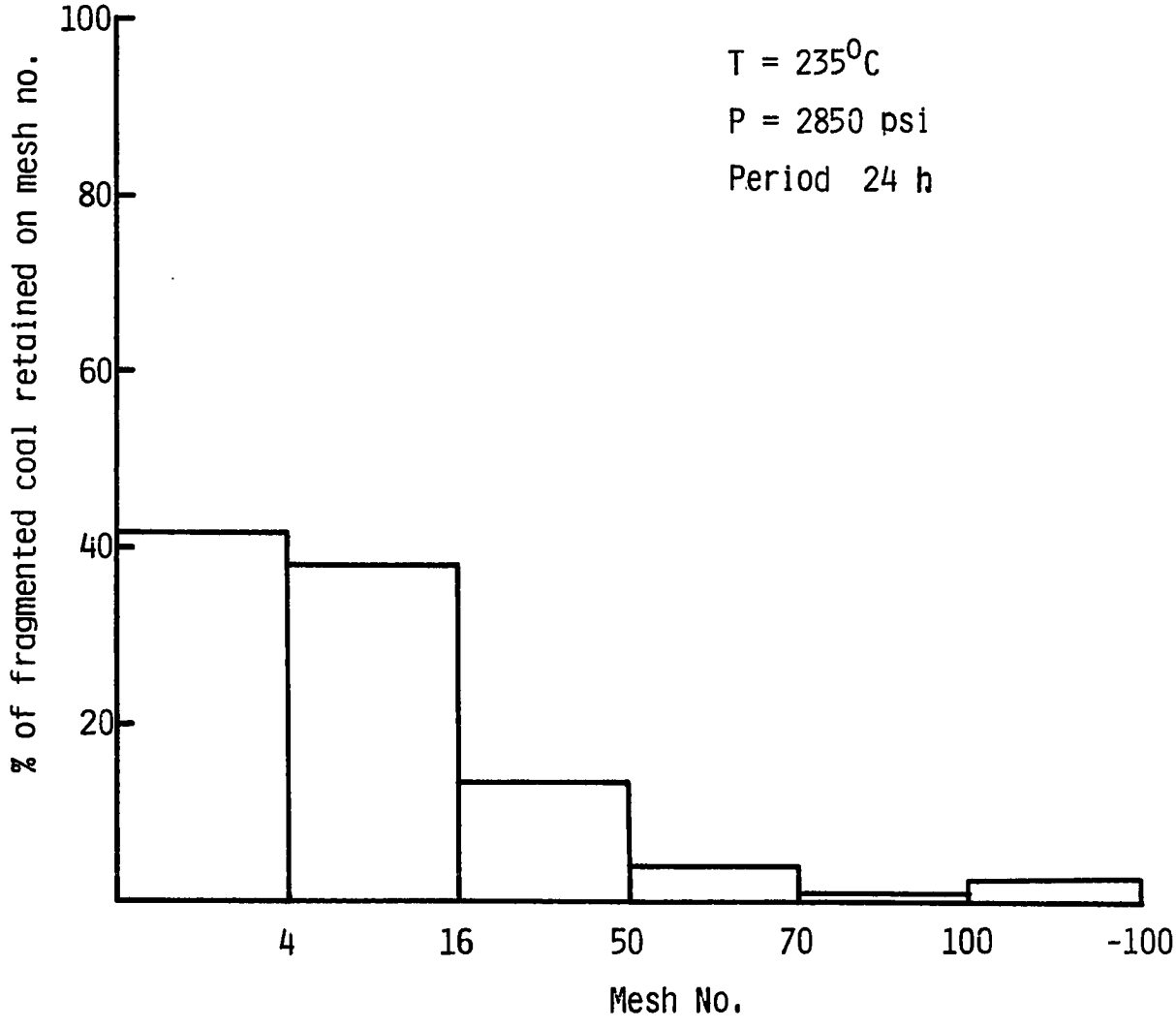



FIGURE 3.4 Distribution of fragmented coal on mesh no.

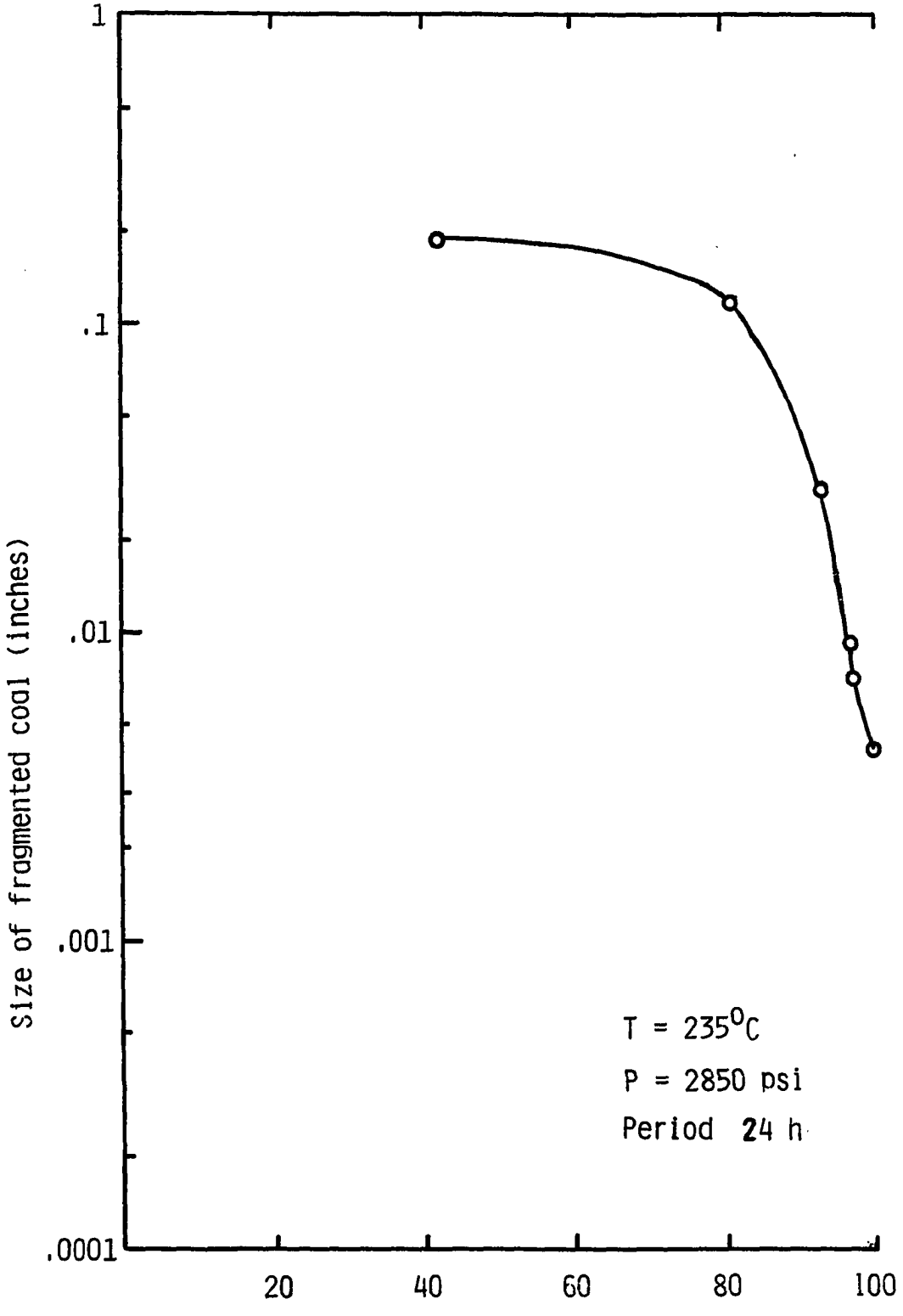



FIGURE 3.5 % Cumulative of fragmented coal.

TEST #4

T = 250°C

Pressure = 2950 psi

Period = 24 hours

100% of total coal fell apart

Total coal sample = 69 grams (1 piece)

Water added = 135 gm

$CO_2$ added = 73.9 gm

Total dissolved coal = 0.8 grams

Average particle size = 0.119 inches

TABLE 4.1*

Time, Temperature, Pressure Relation of Test #4

| Time Minute | Temperature °C | Pressure psi |
|---|---|---|
| 11 | 50 | 1150 |
| 35 | 100 | 1425 |
| 60 | 150 | 1900 |
| 72 | 175 | 2200 |
| 87 | 200 | 2450 |
| 101 | 225 | 2650 |
| 118 | 250 | 2950 |

118 minutes were required to warm up reactor to 250°C.

*These data are used to plot Figures 4.1, 4.2, 4.3.

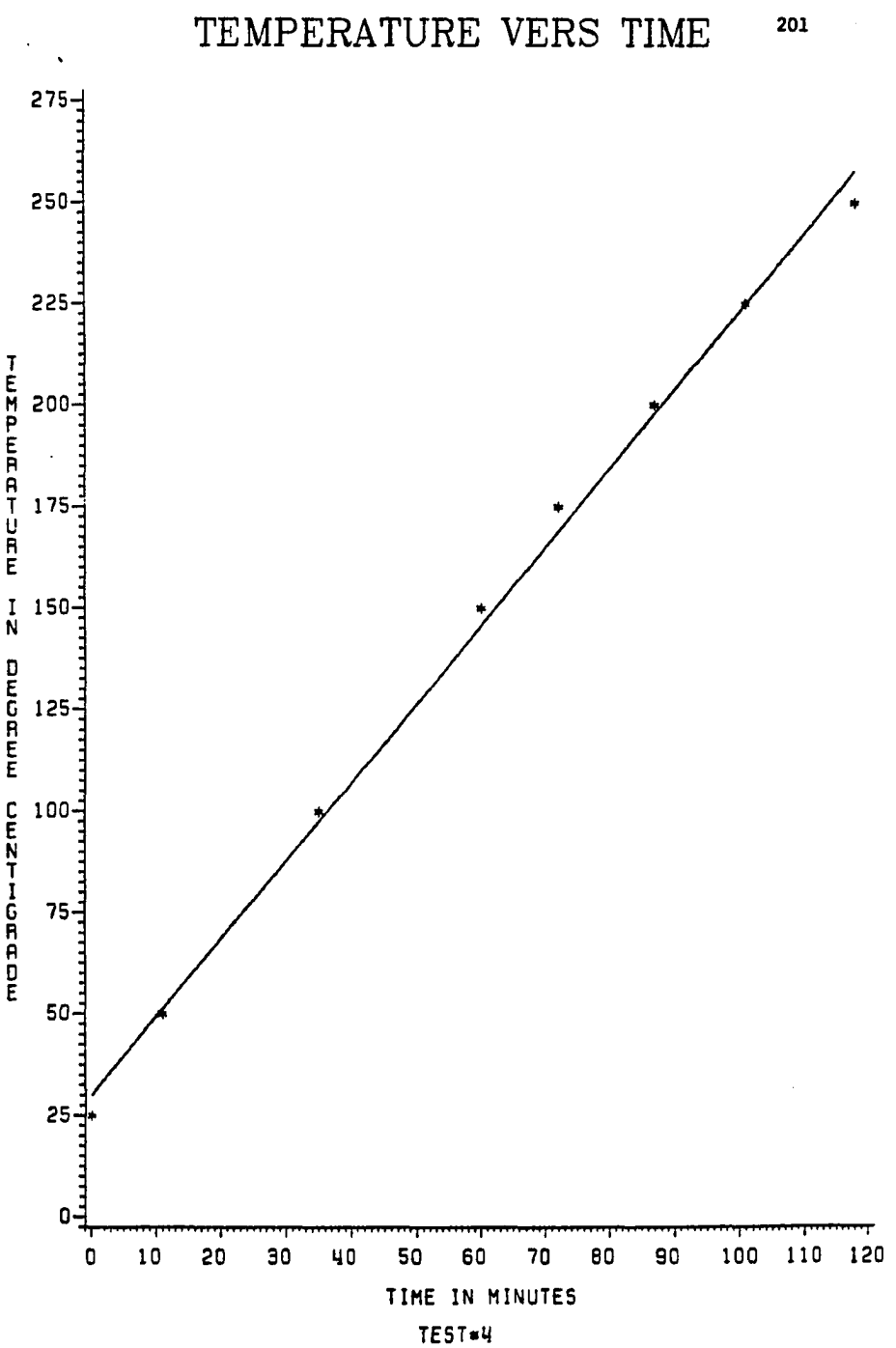

TEMPERATURE VERS TIME
TEMPERATURE IN DEGREE CENTIGRADE
275
250
225
200
175
150
125
100
75
50
25
0
0 10 20 30 40 50 60 70 80 90 100 110 120
TIME IN MINUTES
TEST=4

FIGURE 4.1

# PRESSURE VERS TIME

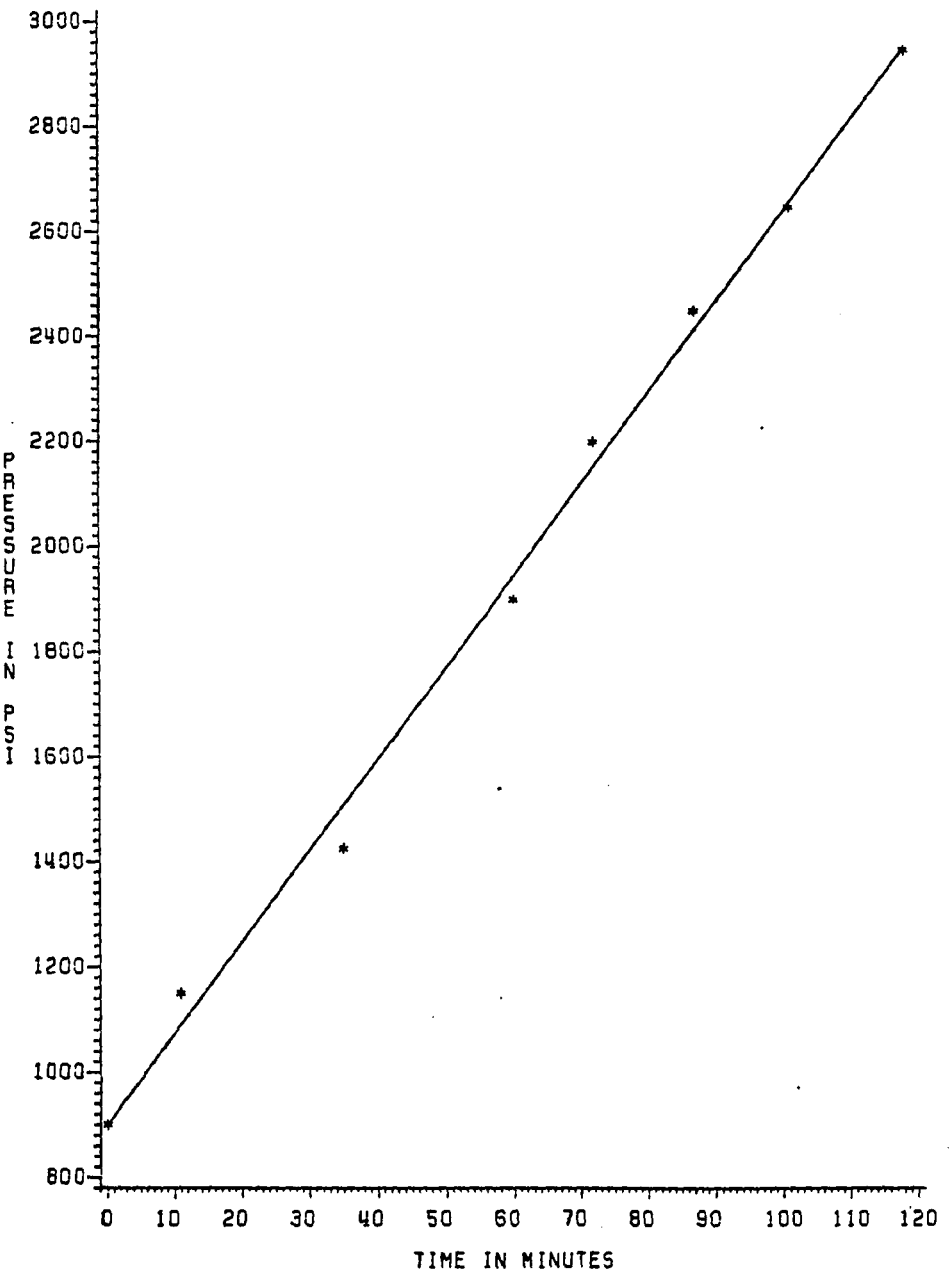



FIGURE 4.2

# PRESSURE VERS TEMPERATURE

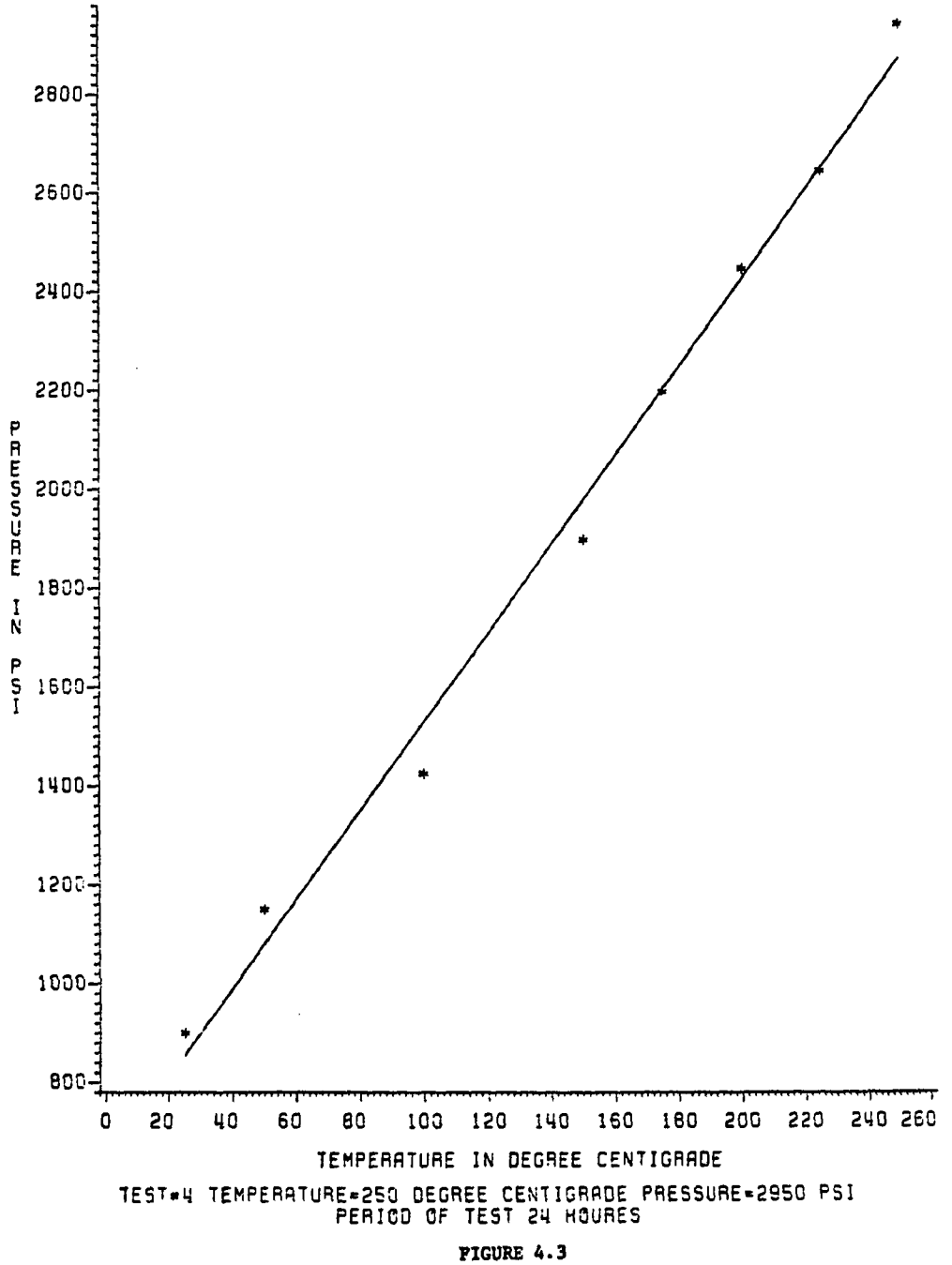



**FIGURE 4.3**

TABLE 4.2

The Result of U.S. Sieve Analysis Distribution of Fragmented Coal by % Wt.

| Mesh No. | Opening Size Inch | $x_i$ Average Opening Size Inch | $f_i$ Weight Retained on Mesh No. (g) | % by Weight | % Cumulative by Weight |
|---|---|---|---|---|---|
| 4 | 0.185 | 0.185 | 30 | 44 | 44 |
| 16 | 0.0469 | 0.116 | 20.5 | 30.0 | 74 |
| 50 | 0.0116 | 0.0293 | 7.6 | 11.2 | 85.2 |
| 70 | 0.0083 | 0.00995 | 5.3 | 7.7 | 92.9 |
| 100 | 0.0059 | 0.0071 | 3.2 | 4.6 | 97.5 |
| -100 | 0.0029 | 0.0044 | 1.5 | 2.2 | 100% |
| | | | 68.1 | 100% | |

$$\text{Average particle size} = \frac{\sum x_i f_i}{\sum f_i} = 0.119 \text{ inches}$$

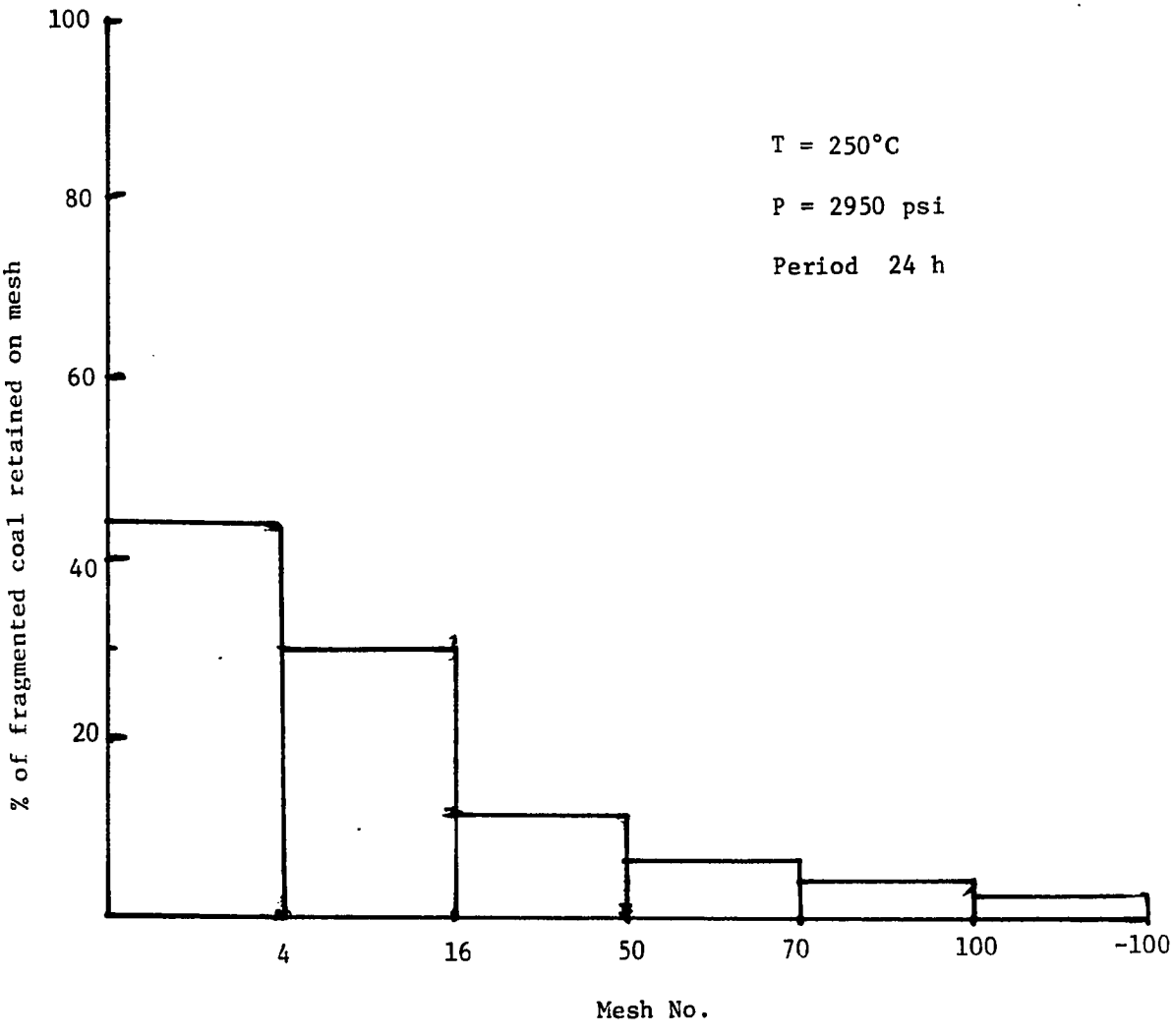



FIGURE 4.4: Distribution of fragmented coal on mesh no.

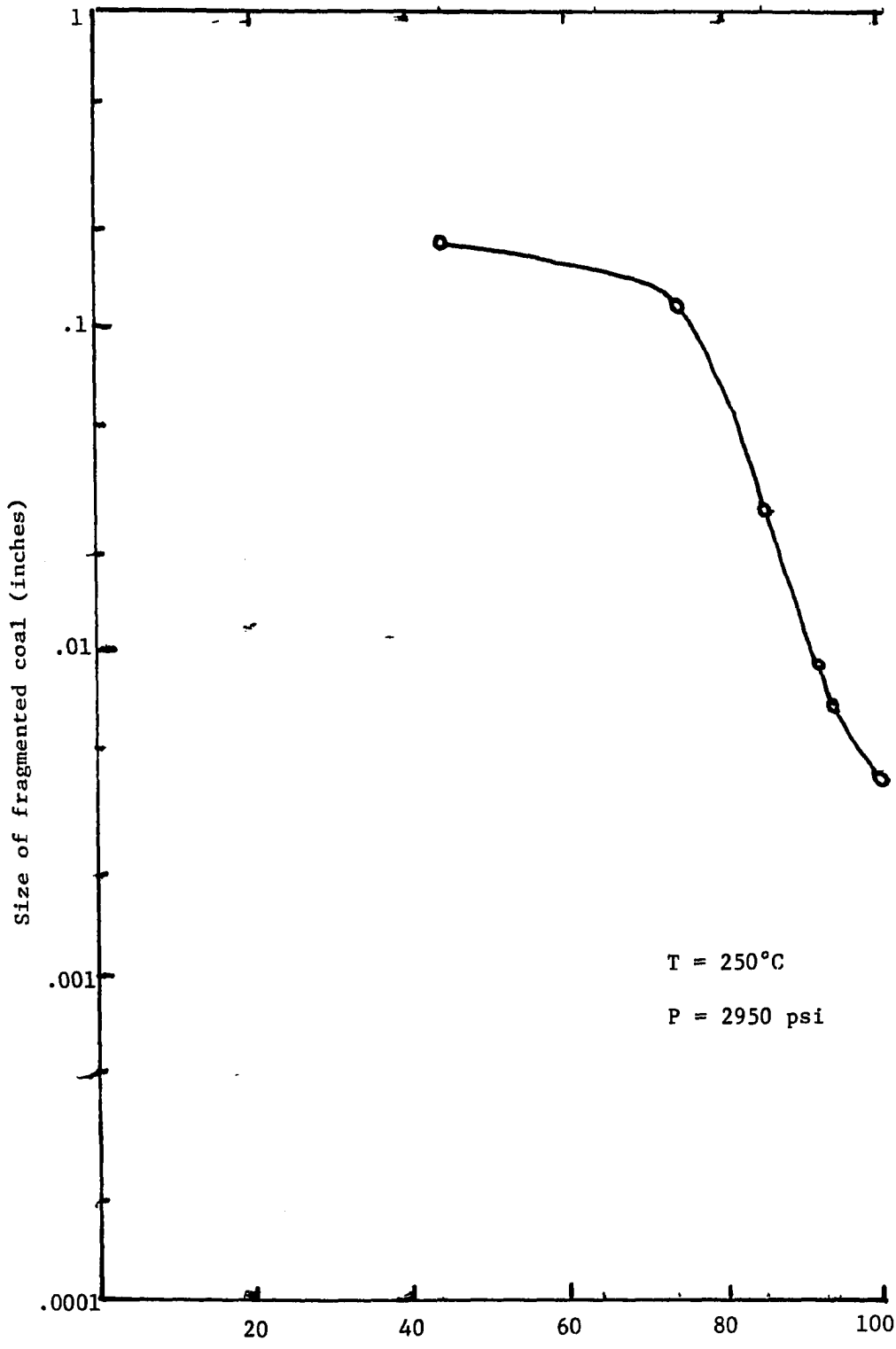



FIGURE 4.5: % Cumulative of fragmented coal.

TEST #5

T = 275° C

Pressure = 3300 psi

Period = 18 hours

100% of total coal fell apart

Total coal sample = 79.5 grams (1 piece)

Water added = 175 gm

$CO_2$ added = 66.255 gm

Total dissolved coal = 0.7 grams

Average particle size = 0.145 inches

TABLE 5.1*

Time, Temperature, Pressure Relation of Test #5

| Time Minute | Temperature °C | Pressure psi |
|---|---|---|
| 10 | 50 | 1150 |
| 38 | 100 | 1500 |
| 62 | 150 | 1850 |
| 74 | 175 | 2050 |
| 100 | 225 | 2750 |
| 118 | 250 | 2950 |
| 132 | 275 | 3300 |

132 minutes were required to warm up reactor to 275°C

*These data are used to plot Figures 5.1, 5.2, 5.3.

# TEMPERATURE VERS TIME

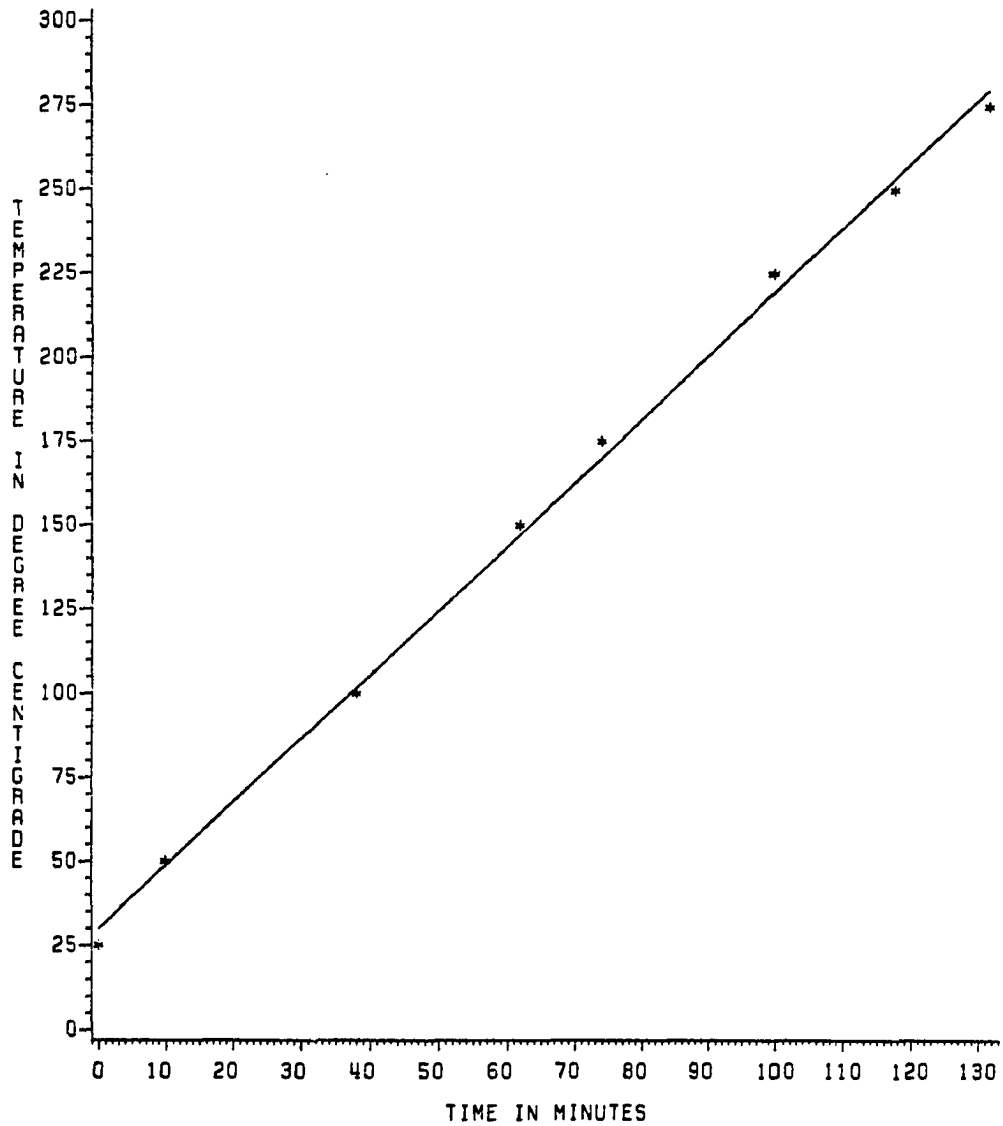



**FIGURE 5.1**

TEST=5

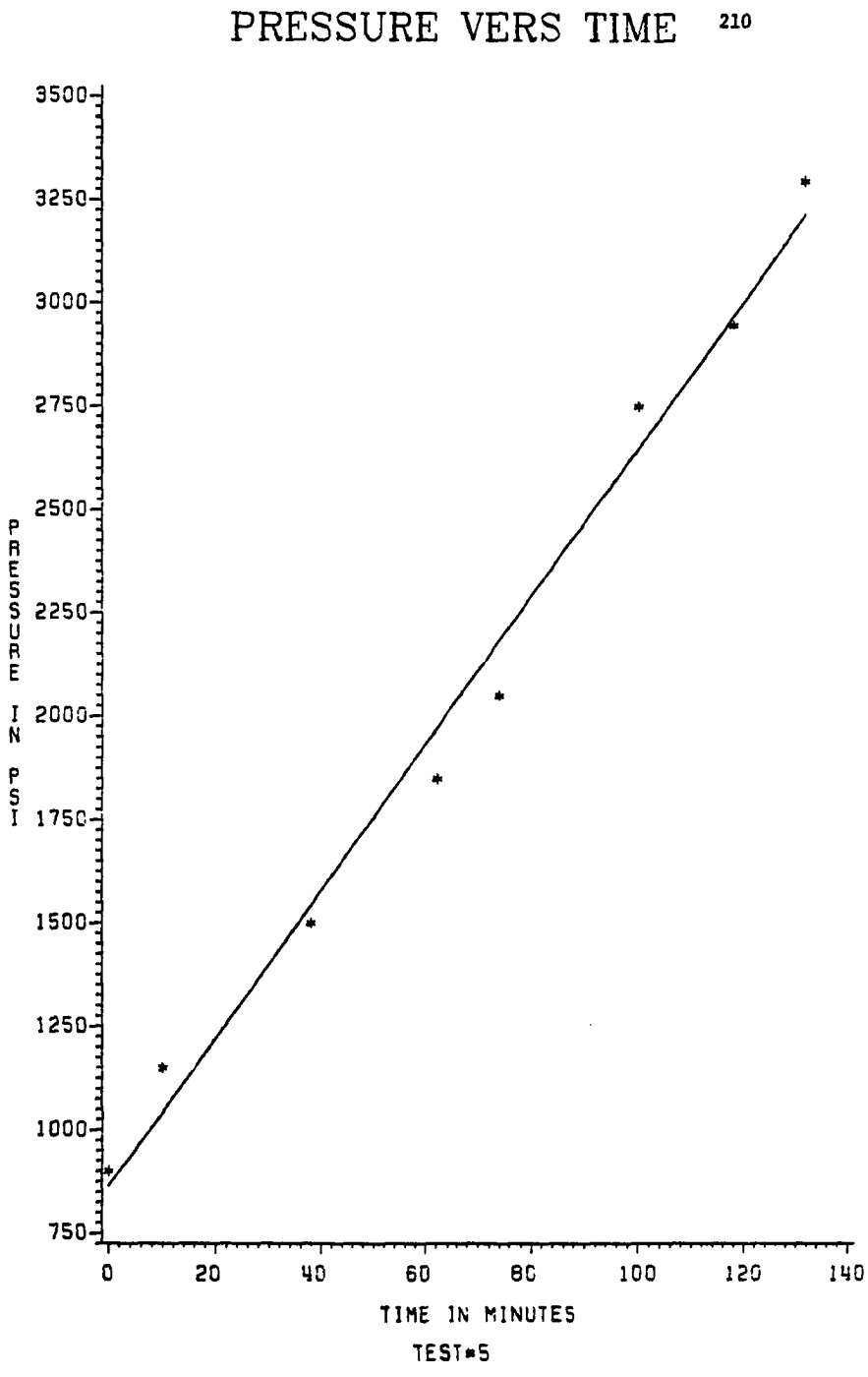
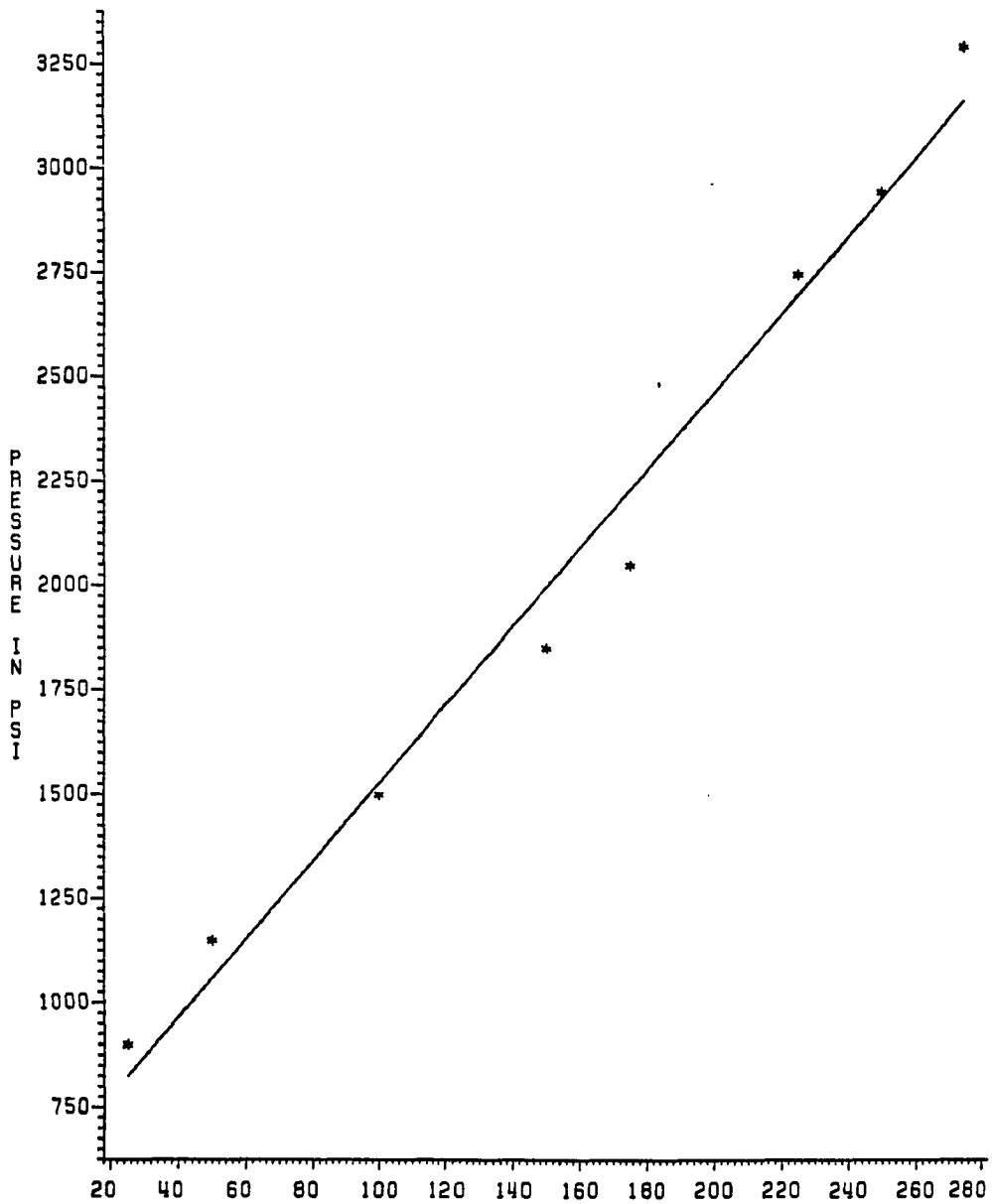

PRESSURE VERS TIME
3500
3250
3000
2750
2500
2250
2000
1750
1500
1250
1000
750
PRESSURE IN PSI
0
20
40
60
80
100
120
140
TIME IN MINUTES
TEST#5

FIGURE 5.2

# PRESSURE VERS TEMPERATURE




TEST=5 TEMPERATURE=275 DEGREE CENTIGRADE PRESSURE=3300 PSI
PERIOD OF TEST 18 HOURES

FIGURE 5.3

TABLE 5.2

The Result of U.S. Sieve Analysis, Distribution of Fragmented Coal

| Mesh No. | Opening Size Inch | $x_i$ Average Opening Size Inch | $f_i$ Weight Retained on Mesh No. (g) | % by Weight | % Cumulative by Weight |
|---|---|---|---|---|---|
| 4 | 0.185 | 0.185 | 47 | 60 | 60 |
| 16 | 0.0469 | 0.116 | 22 | 28 | 88 |
| 50 | 0.0116 | 0.0293 | 5.6 | 7.00 | 95 |
| 70 | 0.0083 | 0.00995 | 1.2 | 1.5 | 96.5 |
| 100 | 0.0059 | 0.0071 | 0.5 | 0.63 | 97 |
| -100 | 0.0029 | 0.0044 | 2.5 | 3 | 100 |
| | | | 78.8 | 100% | |

$$\text{Average particle size} = \frac{\sum x_i f_i}{\sum f_i} = 0.145 \text{ inches}$$

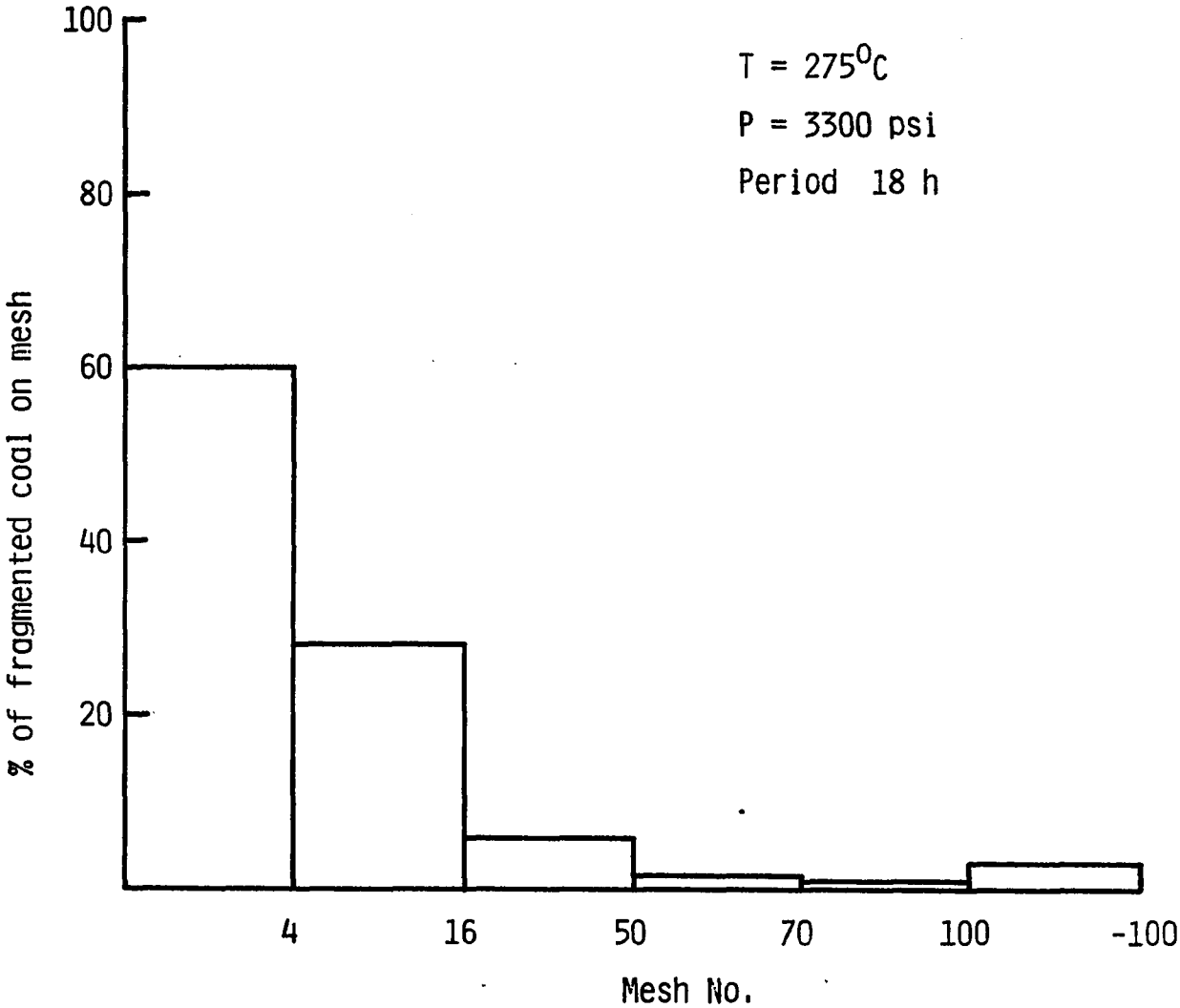



FIGURE 5.4 The distribution of fragmented coal on mesh no.

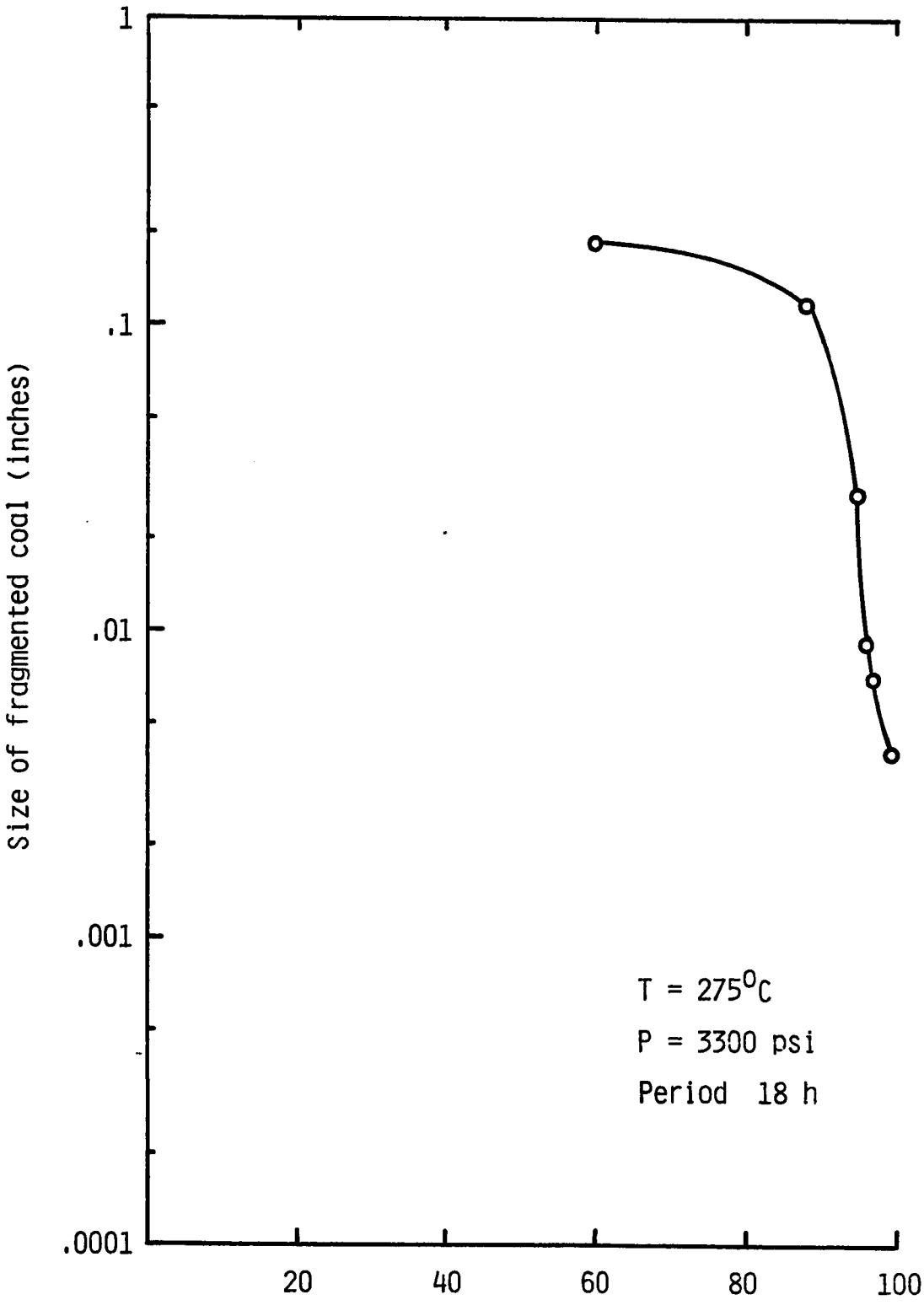



FIGURE 5.5 % Cumulative of fragmented coal.

TEST #6

T = 275°C

Pressure = 3300 psi

Period = 24 hours

100% of coal fragmented

Total coal sample = 59.7 grams

Water added = 135 grams

$CO_2$ added = 75.2 grams

Total dissolved coal = 0.3 grams

Average particle size = 0.094 inches

TABLE 6.1*

Time, Temperature, Pressure Relation of Test #6

| Time Minute | Temperature °C | Pressure psi |
|---|---|---|
| 10 | 50 | 1150 |
| 38 | 100 | 1500 |
| 56 | 150 | 1900 |
| 86 | 200 | 2325 |
| 101 | 225 | 2725 |
| 130 | 275 | 3300 |

130 minutes were required to warm reactor up to 275°C.

*These data are used to plot Figures 6.1, 6.2, 6.3.

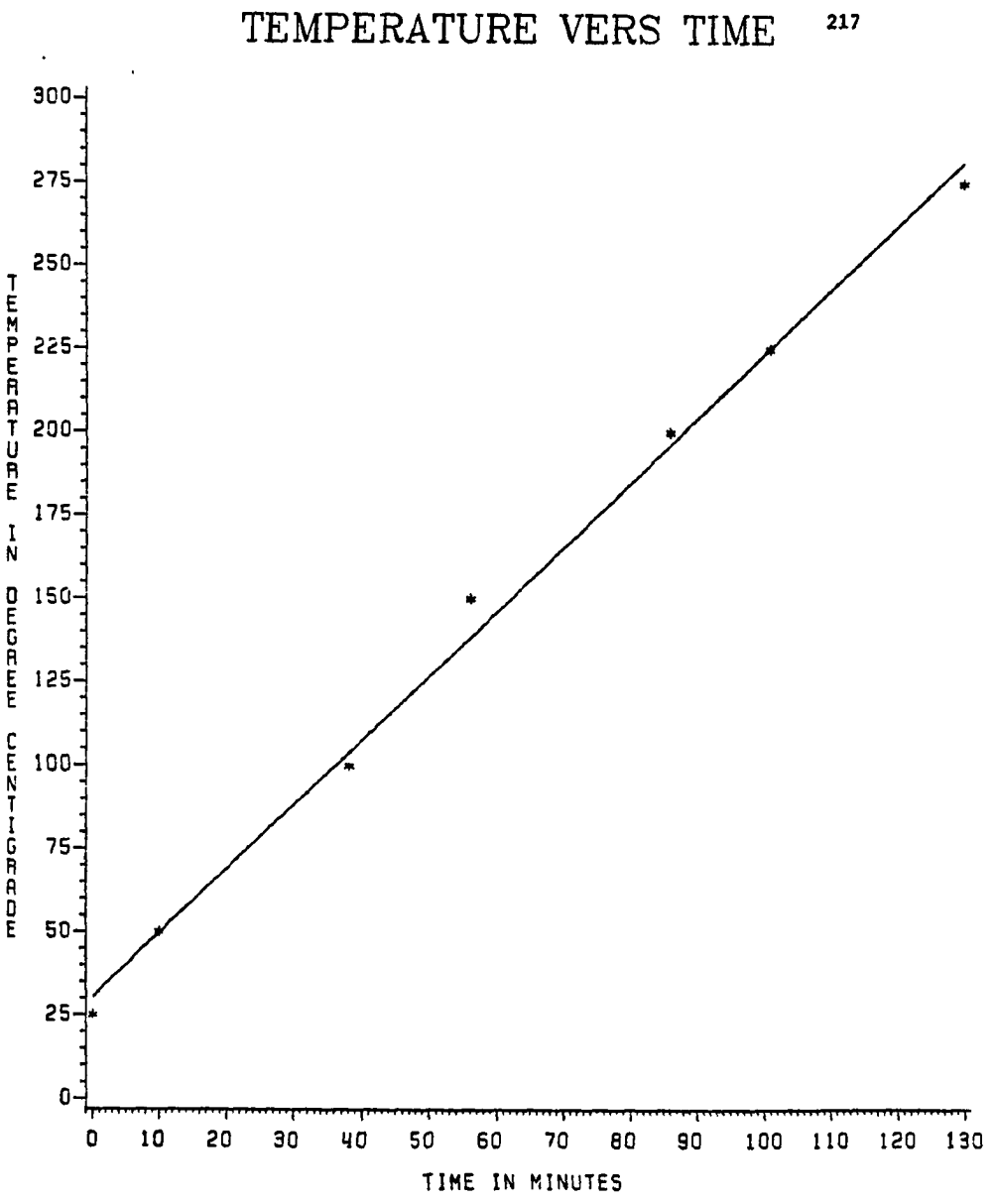



**FIGURE 6.1**

TEST*6

# PRESSURE VERS TIME

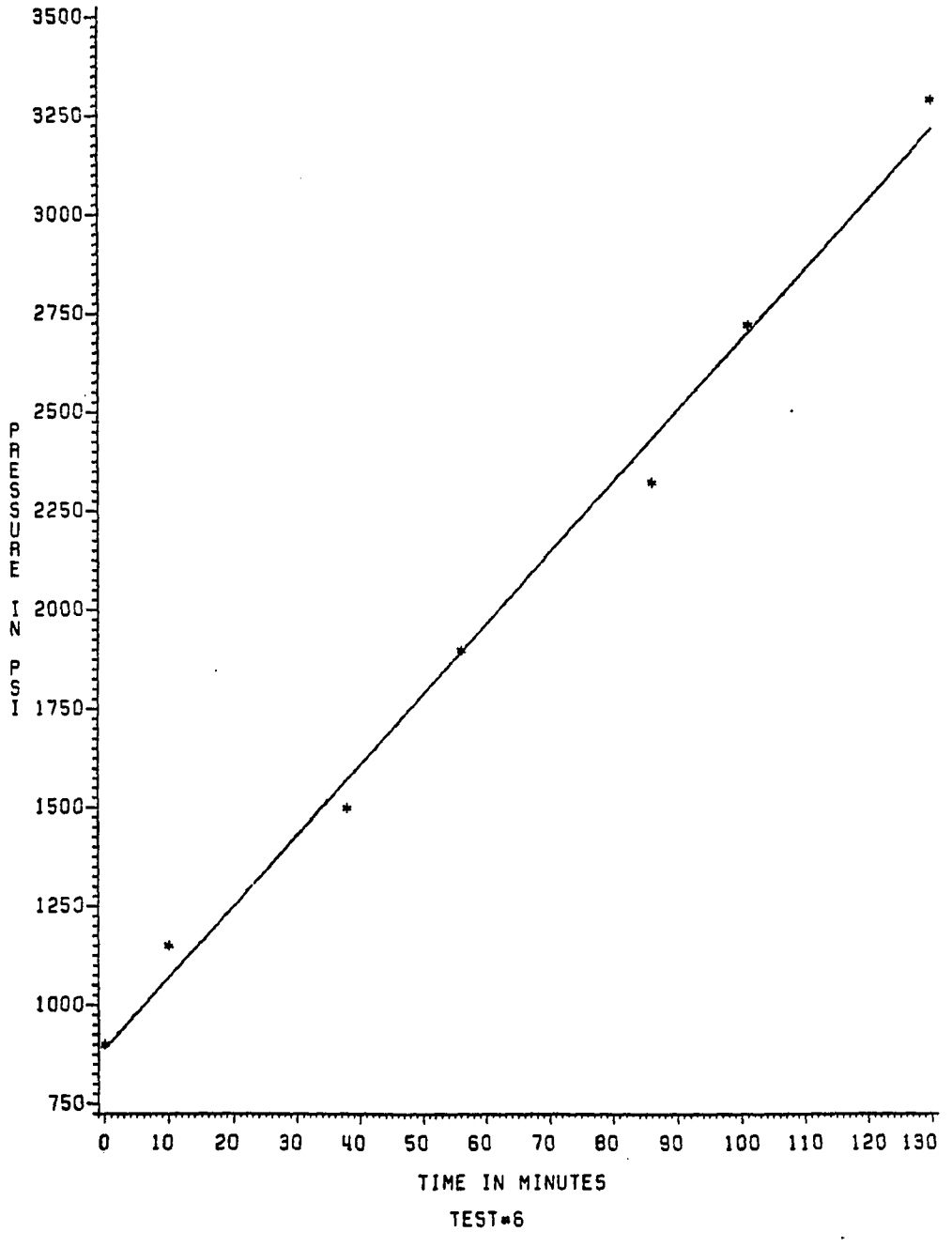



FIGURE 6.2

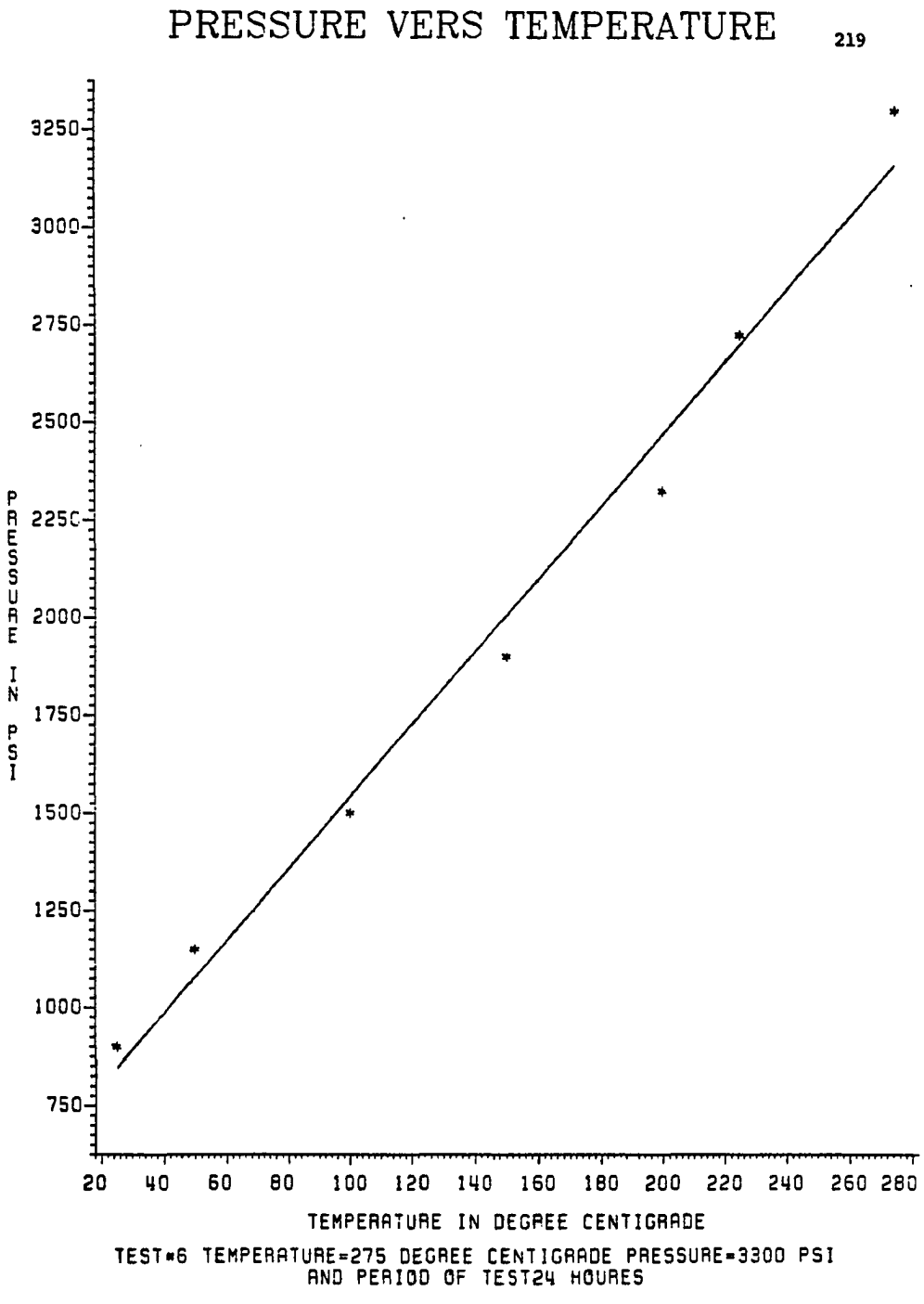

PRESSURE VERS TEMPERATURE
PRESSURE IN PSI
3250
3000
2750
2500
2250
2000
1750
1500
1250
1000
750
20
40
60
80
100
120
140
160
180
200
220
240
260
280
TEMPERATURE IN DEGREE CENTIGRADE
TEST#6 TEMPERATURE=275 DEGREE CENTIGRADE PRESSURE=3300 PSI
AND PERIOD OF TEST24 HOURES

**FIGURE 6.3**

TABLE 6.2

The Result of U.S. Sieve Analysis, Distribution of Fragmented Coal on Mesh

| Mesh No. | Opening Size Inch | $x_i$ Average Opening Size Inch | $f_i$ Weight Retained on Mesh No. (g) | % by Weight | % Cumulative by Weight |
|---|---|---|---|---|---|
| 4 | 0.185 | 0.185 | 17.5 | 30 | 30 |
| 16 | 0.0469 | 0.116 | 16.3 | 27.5 | 57.5 |
| 50 | 0.0116 | 0.0293 | 10.2 | 17.2 | 74.7 |
| 70 | 0.0083 | 0.00995 | 5.7 | 9.2 | 83.9 |
| 100 | 0.0059 | 0.0071 | 4.8 | 8.1 | 92.0 |
| -100 | 0.0029 | 0.0044 | 4.7 | 8 | 100 |
| | | | 59.3 | 100% | |

$$\text{Average coal particle} = \frac{\sum f_i x_i}{\sum f_i} = 0.094 \text{ inches}$$

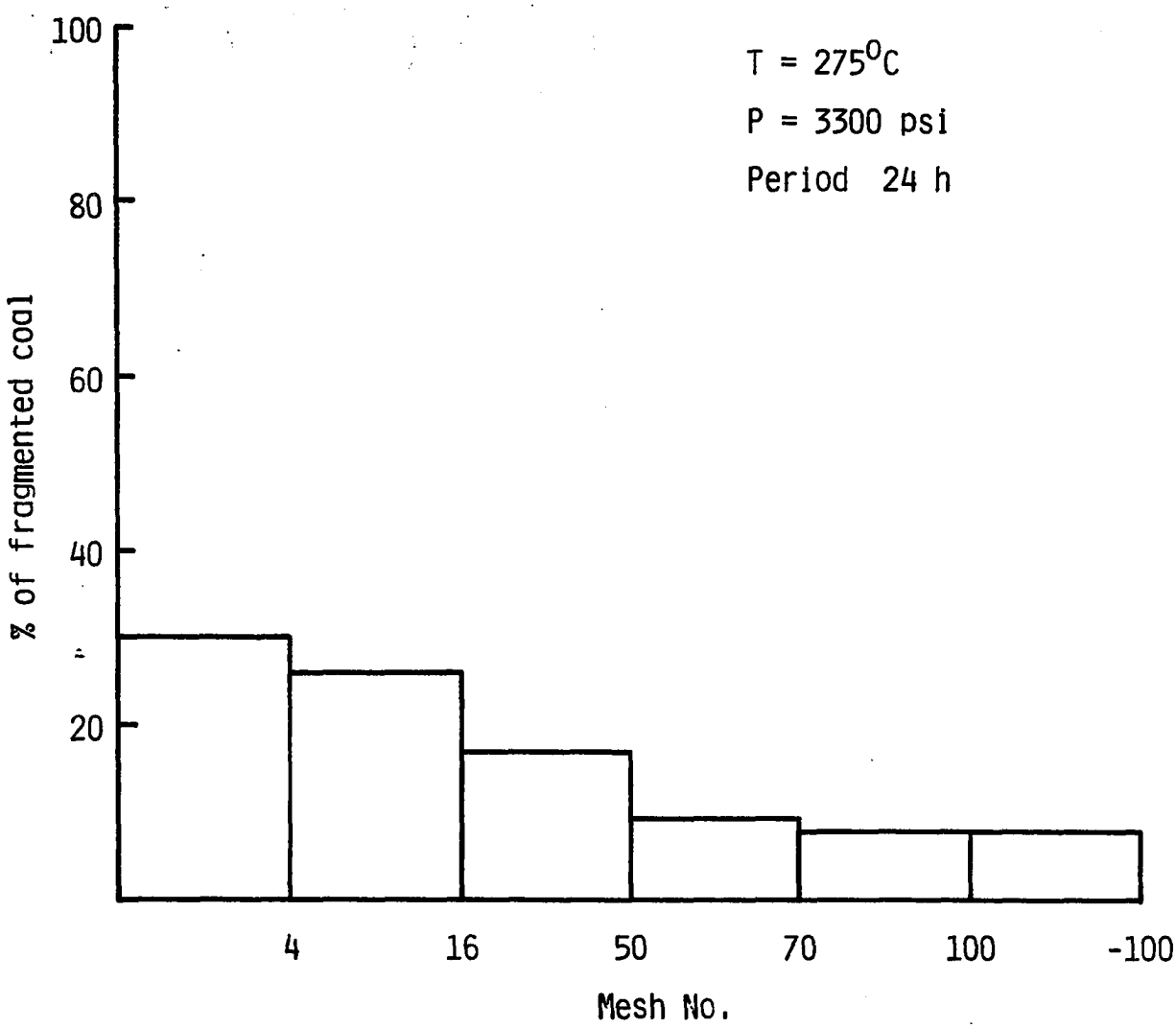



FIGURE 6.4 The distribution of fragmented coal on mesh no.

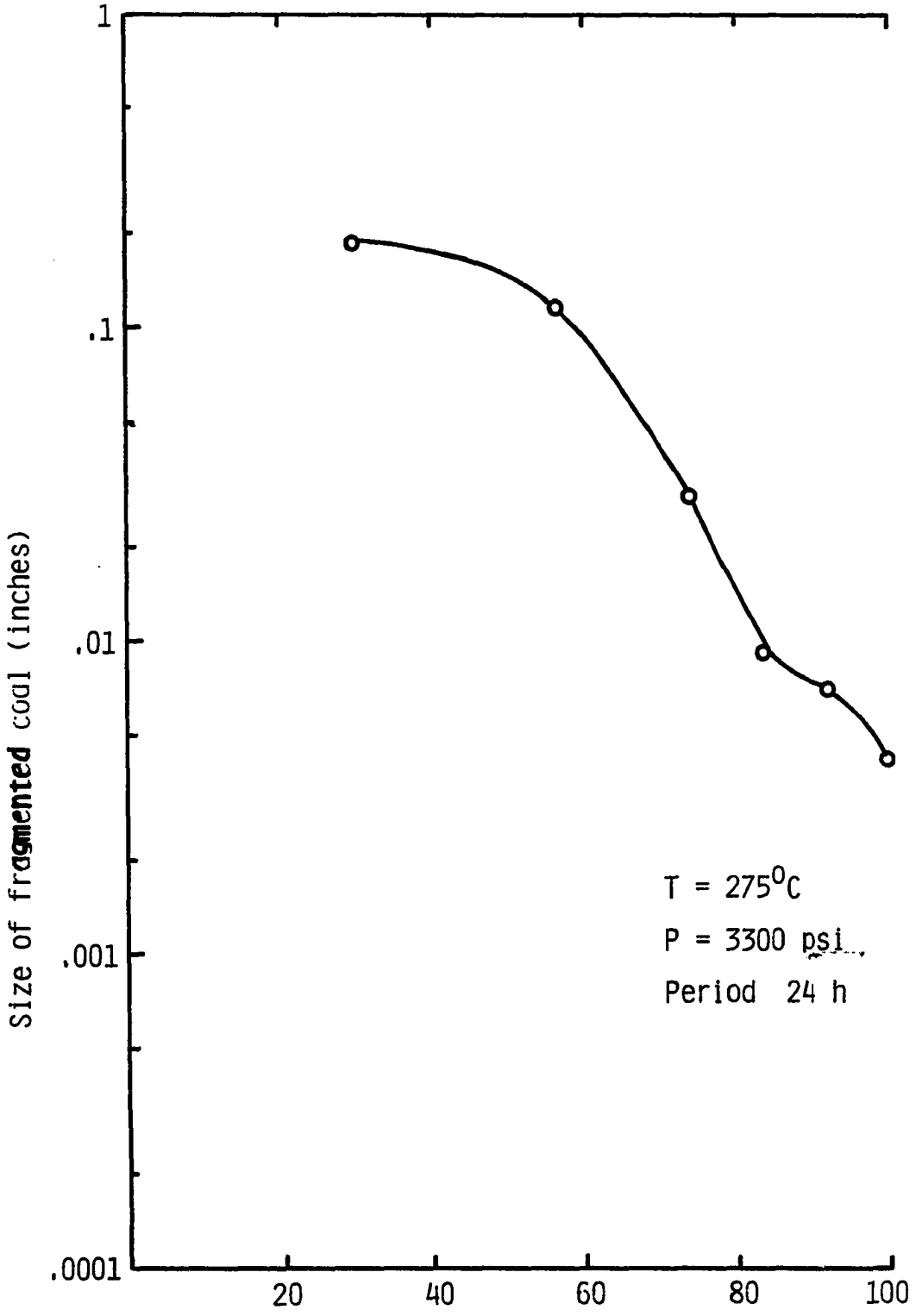



FIGURE 6.5 % Cumulative of fragmented coal

TEST #7

T = 275° C

Pressure = 3300 psi

Period = 30 hours

100% of coal fragmented

Total coal sample = 52 grams (1 piece)

Water added = 125 grams

$CO_2$ added = 78.325 grams

Total dissolved coal = 0.7 grams

Average particle size = 0.082 inches

TABLE 7.1*

Time, Temperature, Pressure Relation of Test #7

| Time Minute | Temperature °C | Pressure psi |
|---|---|---|
| 10 | 50 | 1070 |
| 35 | 100 | 1475 |
| 62 | 150 | 1800 |
| 92 | 200 | 2400 |
| 103 | 225 | 2850 |
| 135 | 275 | 3300 |

135 minutes were required to warm reactor up to 275°C.

*These data are used to plot Figures 7.1, 7.2, 7.3.

# TEMPERATURE VERS TIME 

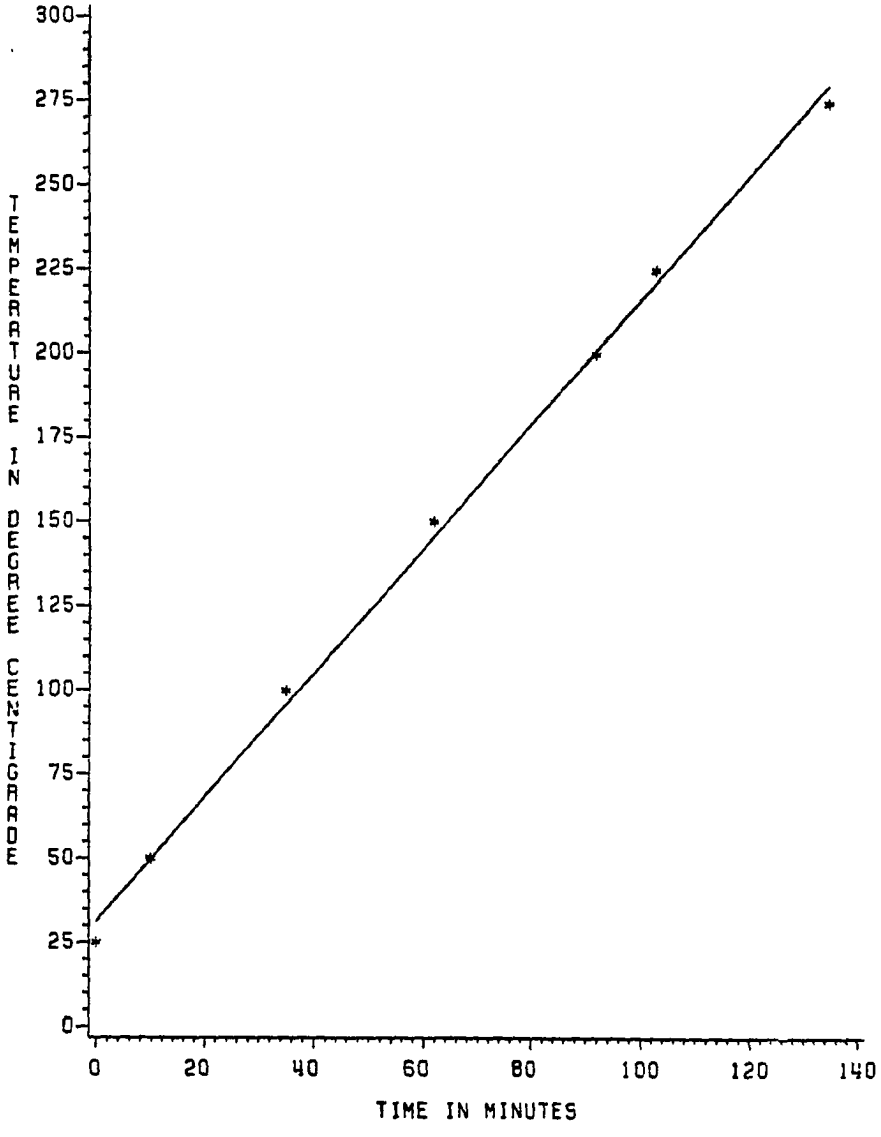



**FIGURE 7.1**

TEST=7

# PRESSURE VERS TIME

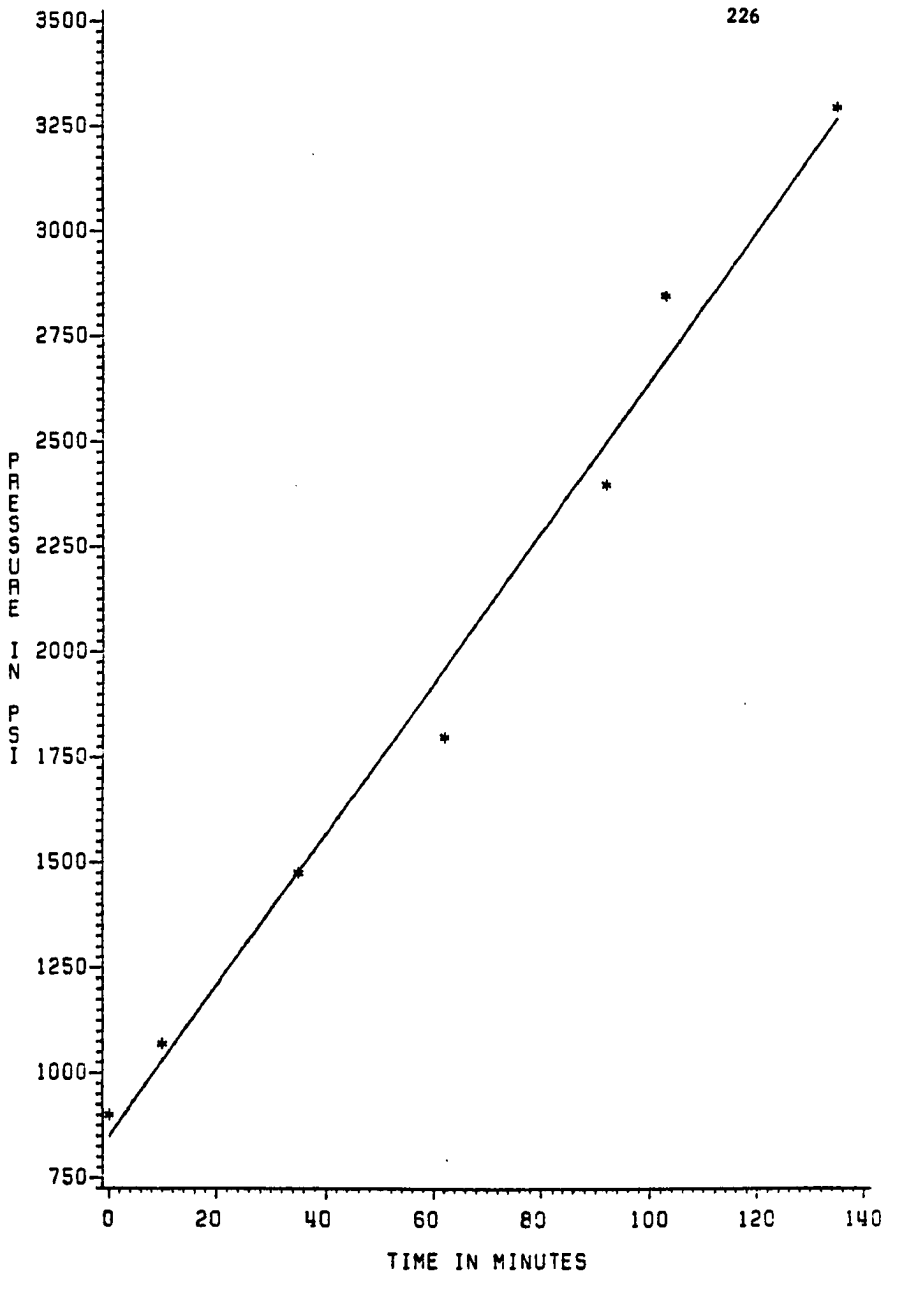



FIGURE 7.2

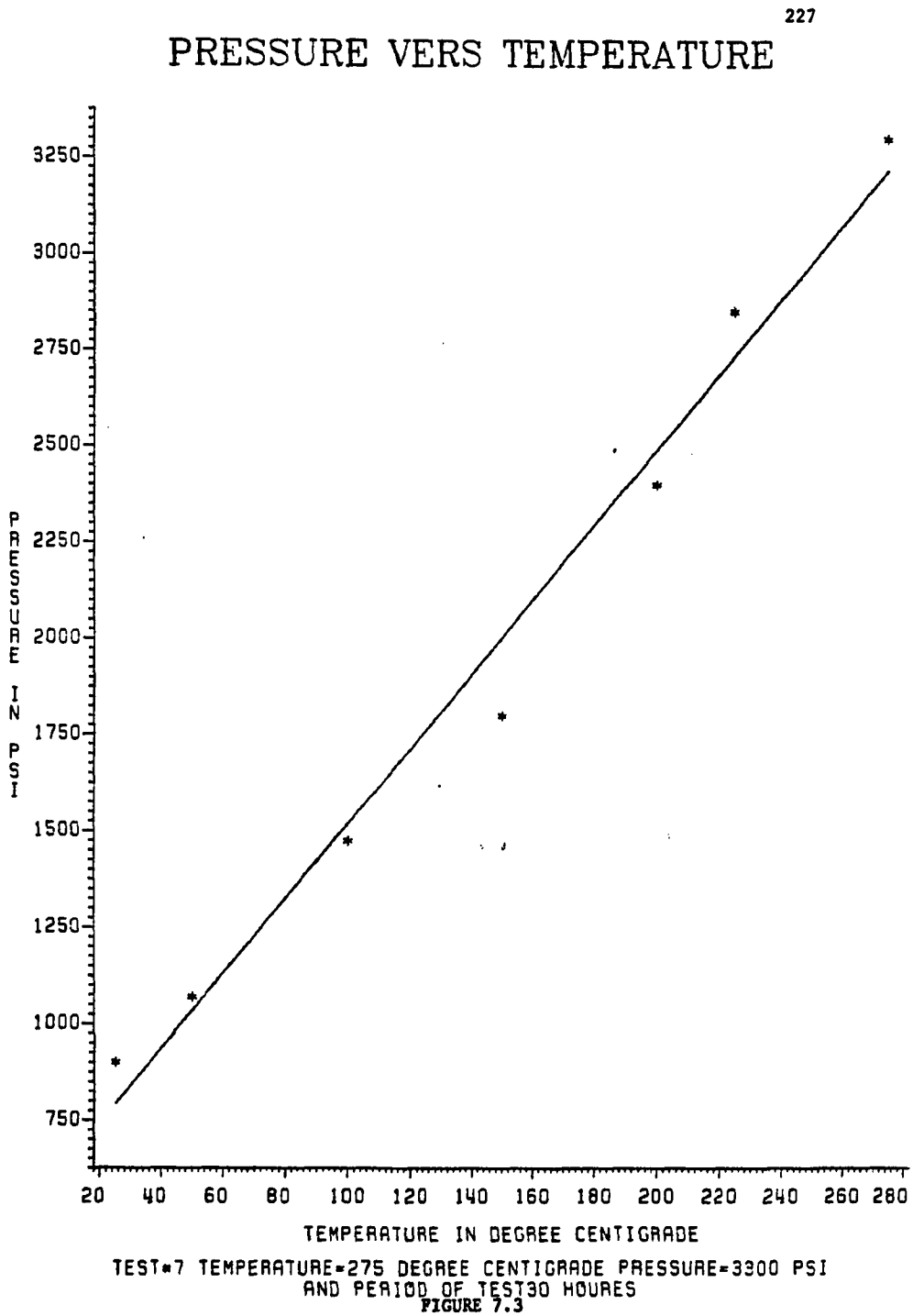

PRESSURE VERS TEMPERATURE
PRESSURE IN PSI
3250
3000
2750
2500
2250
2000
1750
1500
1250
1000
750
20 40 60 80 100 120 140 160 180 200 220 240 260 280
TEMPERATURE IN DEGREE CENTIGRADE
TEST#7 TEMPERATURE=275 DEGREE CENTIGRADE PRESSURE=3300 PSI
AND PERIOD OF TEST30 HOURES

FIGURE 7.3

TABLE 7.2

The Result of U.S. Sieve Analysis, Distribution of Fragmented Coal at T = 275-280°C and P = 3300 psi

| Mesh No. | Opening Size Inch | $x_i$ Average Opening Size Inch | $f_i$ Weight Retained on Mesh No. (g) | % by Weight | % Cumulative by Weight |
|---|---|---|---|---|---|
| 4 | 0.185 | 0.185 | 12.8 | 25 | 25 |
| 16 | 0.0469 | 0.116 | 12 | 23.4 | 48.4 |
| 50 | 0.0116 | 0.0293 | 9.5 | 18.5 | 66.9 |
| 70 | 0.0083 | 0.00995 | 6.00 | 11.7 | 78.6 |
| 100 | 0.0059 | 0.0071 | 4.5 | 8.8 | 87.4 |
| -100 | 0.0029 | 0.0044 | 6.5 | 12.6 | 100% |
| | | | 51.3 | 100% | |

$$\text{Average coal particles} = \frac{\sum f_i x_i}{\sum f_i} = 0.082 \text{ inches}$$

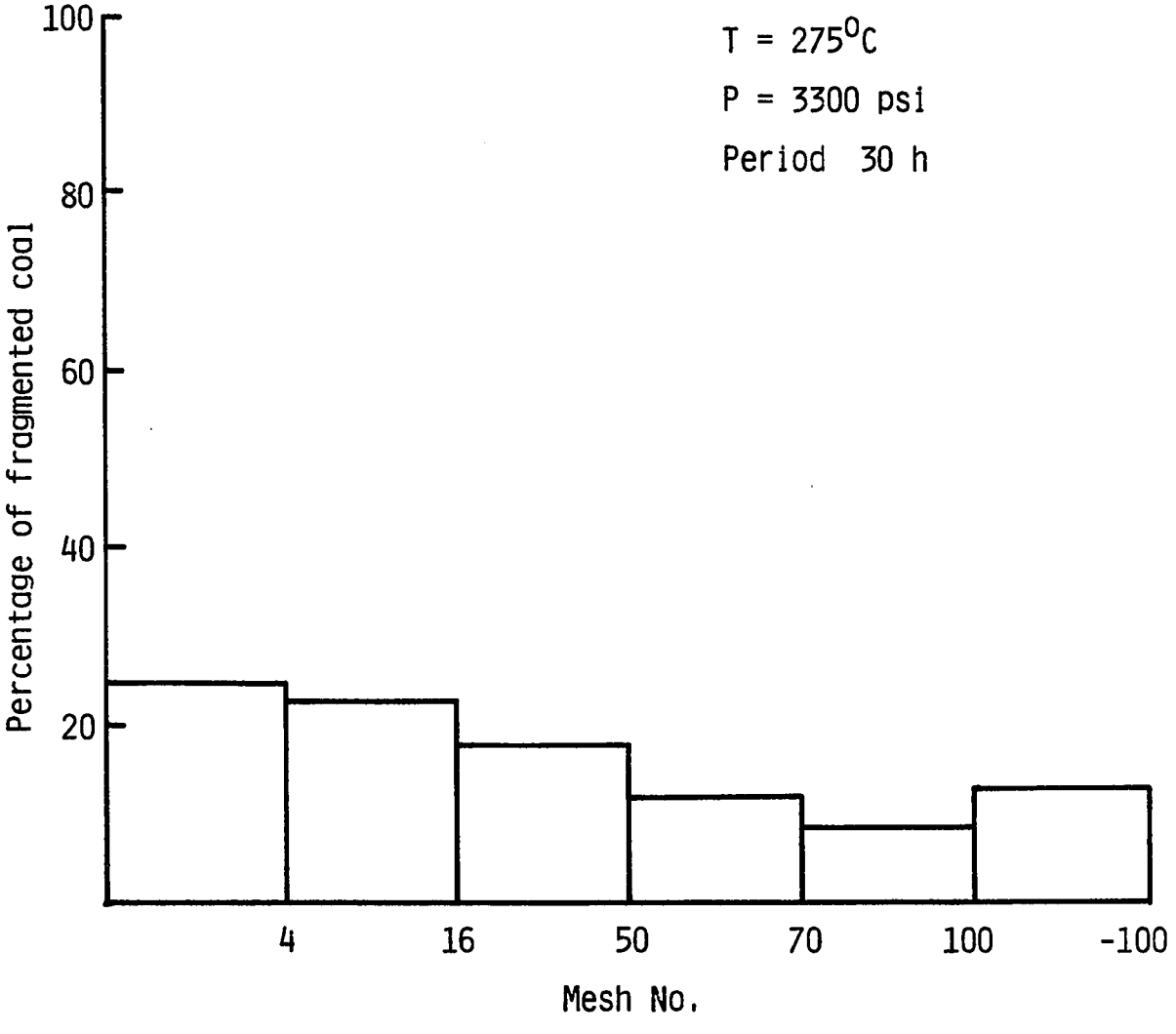



FIGURE 7.4 The distribution of fragmented coal on mesh no.

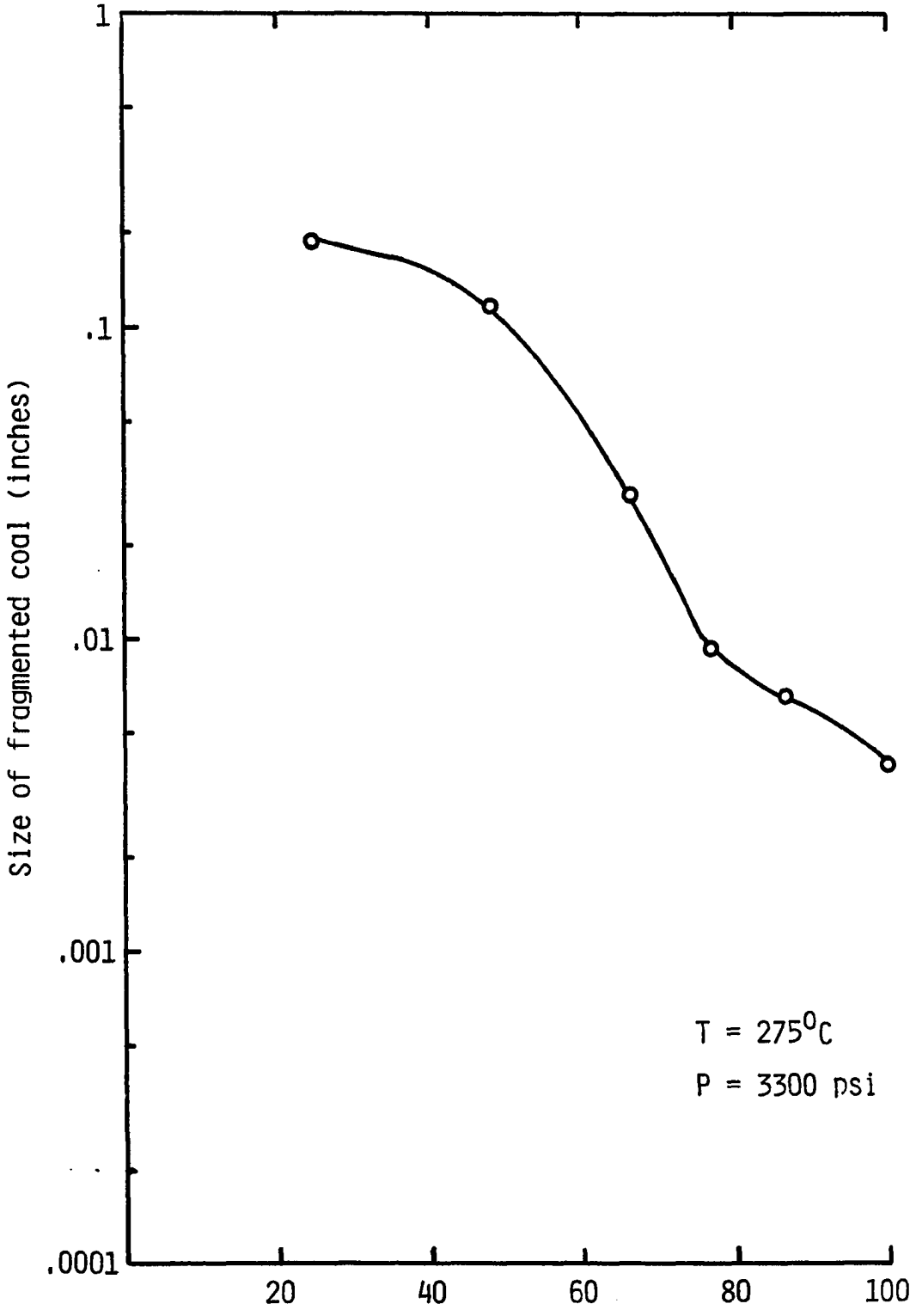



FIGURE 7.5 % Cumulative of fragmented coal

TEST #8

T = 275°C

Pressure = 3300 psi

Period = 36 hours

100% of coal fragmented

Total coal sample = 50.8 grams (1 piece)

Water added = 125 grams

$CO_2$ added = 78.1 grams

Total dissolved coal = 0.3 grams

Average particle size = 0.072 inches

TABLE 8.1*

Time, Temperature, Pressure Relation of Test #8

| Time Minute | Temperature °C | Pressure psi |
|---|---|---|
| 10 | 50 | 1075 |
| 29 | 100 | 1450 |
| 58 | 150 | 1775 |
| 80 | 200 | 2250 |
| 95 | 225 | 2500 |
| 110 | 250 | 2950 |
| 130 | 275 | 3300 |

130 minutes were required to warm reactor up to 275°C.

*These data are used to plot Figures 8.1, 8.2, 8.3.

# TEMPERATURE VERS TIME

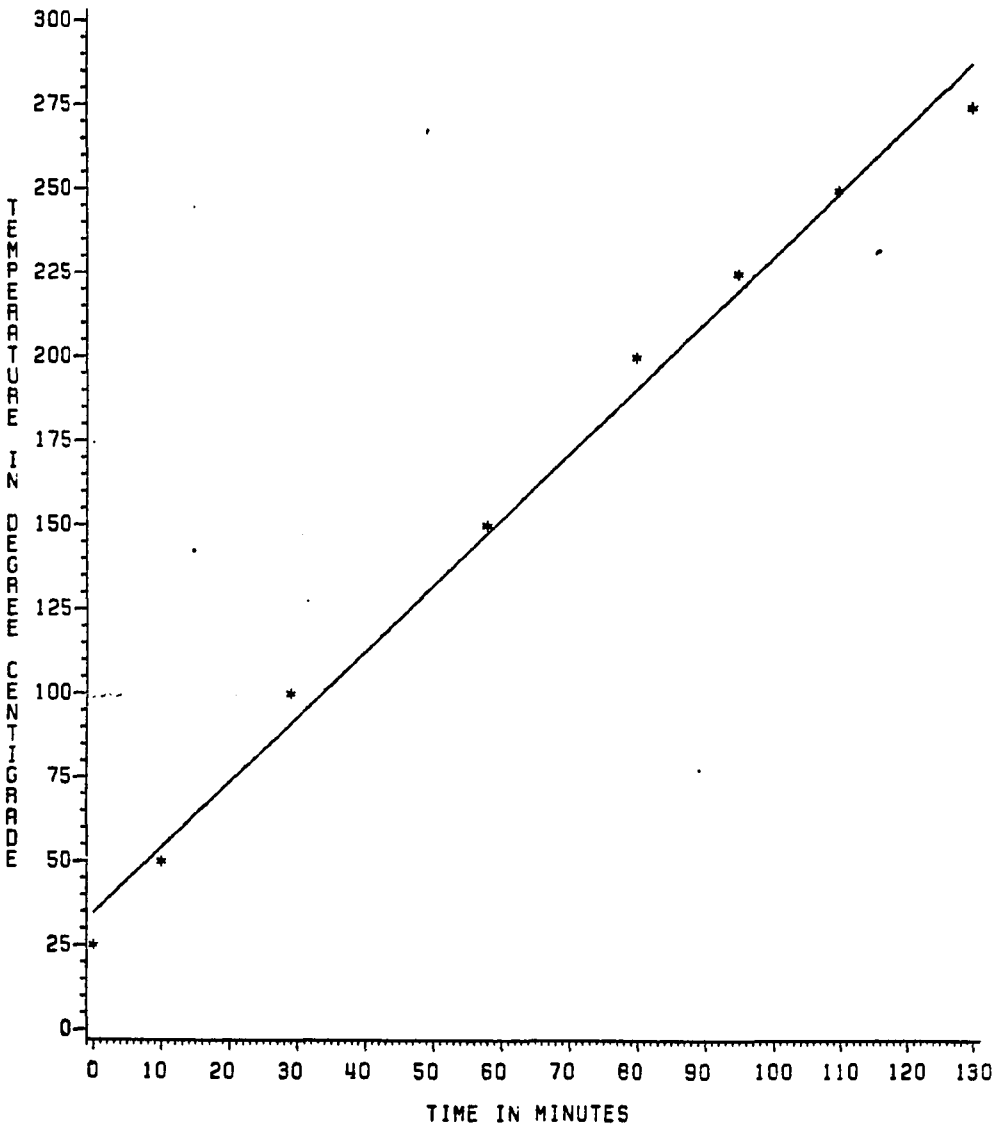



**FIGURE 8.1**

# PRESSURE VERS TIME

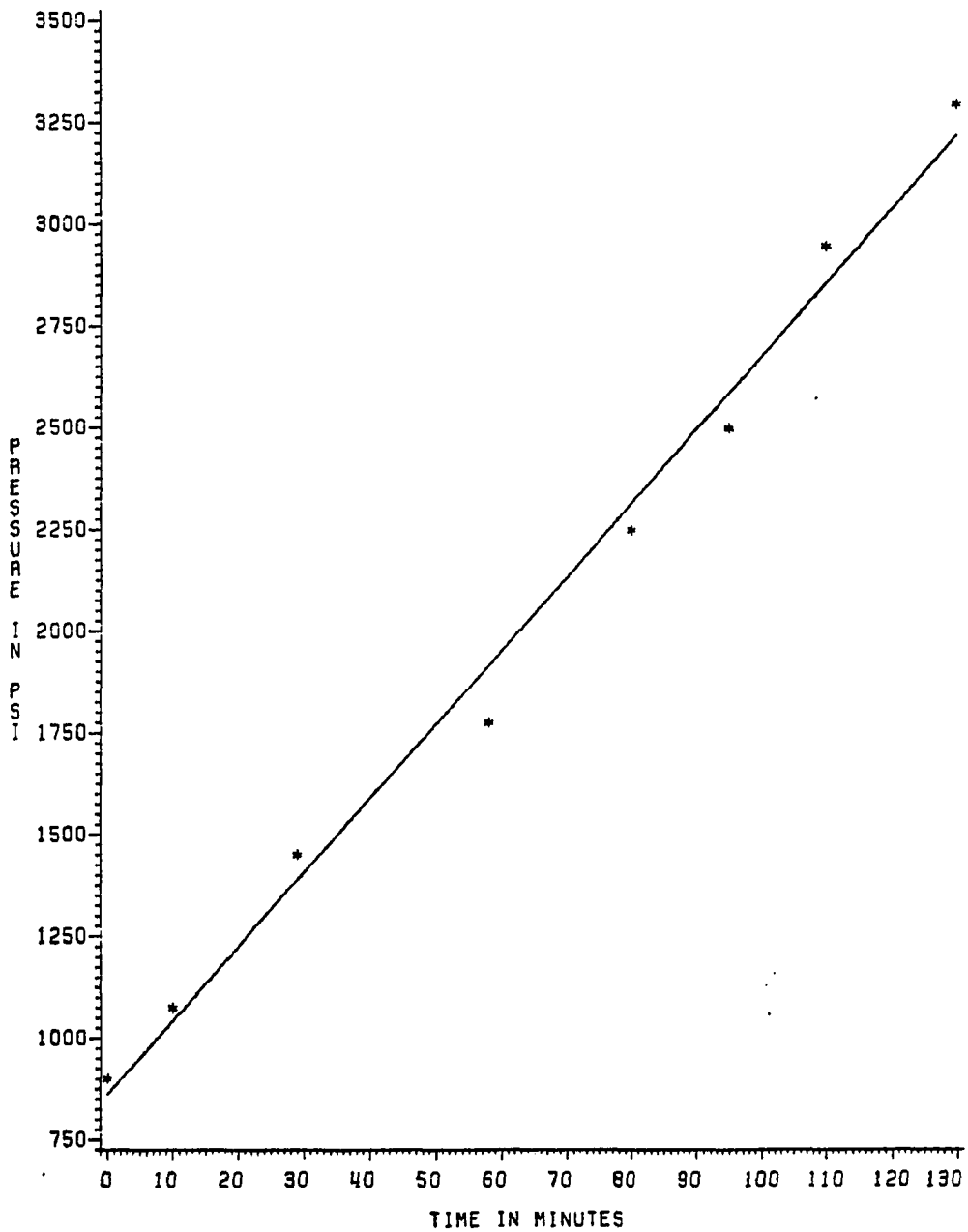



FIGURE 8.2

# PRESSURE VERS TEMPERATURE 235

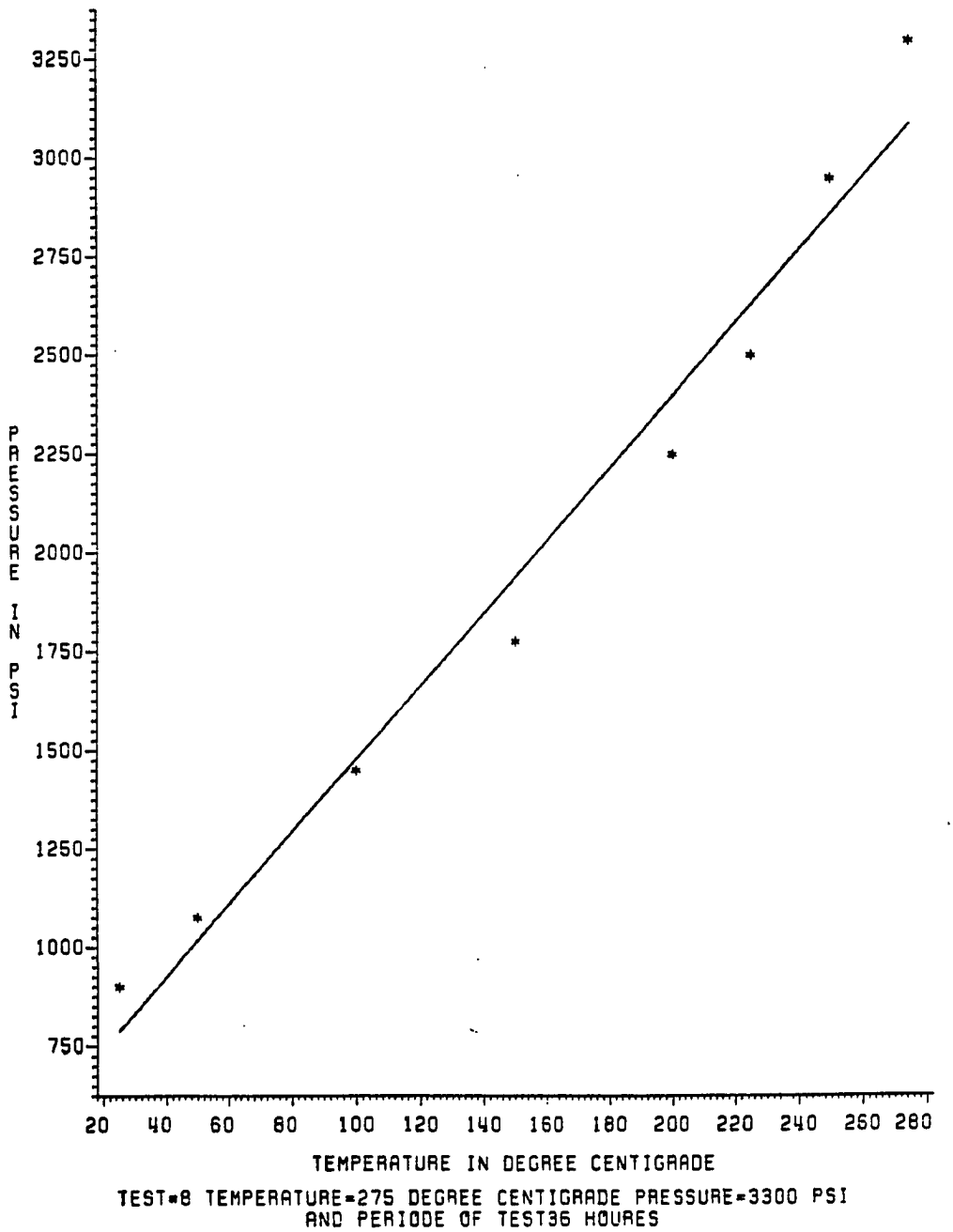



**FIGURE 8.3**

TABLE 8.2

The Result of U.S. Standard Sieve Analysis, Distribution of Fragmented Coal at 275°C and 3300 psi

| Mesh No. | Opening Size Inch | $x_i$ Average Opening Size Inch | $f_i$ Weight Retained on Mesh No. (g) | % by Weight | % Cumulative by Weight |
|---|---|---|---|---|---|
| 4 | 0.185 | 0.185 | 10.5 | 21 | 21 |
| 16 | 0.0469 | 0.116 | 11.3 | 22 | 43 |
| 50 | 0.0116 | 0.0293 | 8.3 | 16.4 | 59.4 |
| 70 | 0.0083 | 0.00995 | 6.4 | 12.6 | 72.0 |
| 100 | 0.0059 | 0.0071 | 5.3 | 10.5 | 82.5 |
| -100 | 0.0029 | 0.0044 | 8.7 | 17.5 | 100 |
| | | | 50.5 | 100.0 | |

$$\text{Average particle size} = \frac{\sum f_i x_i}{\sum f_i} = 0.072 \text{ inches}$$

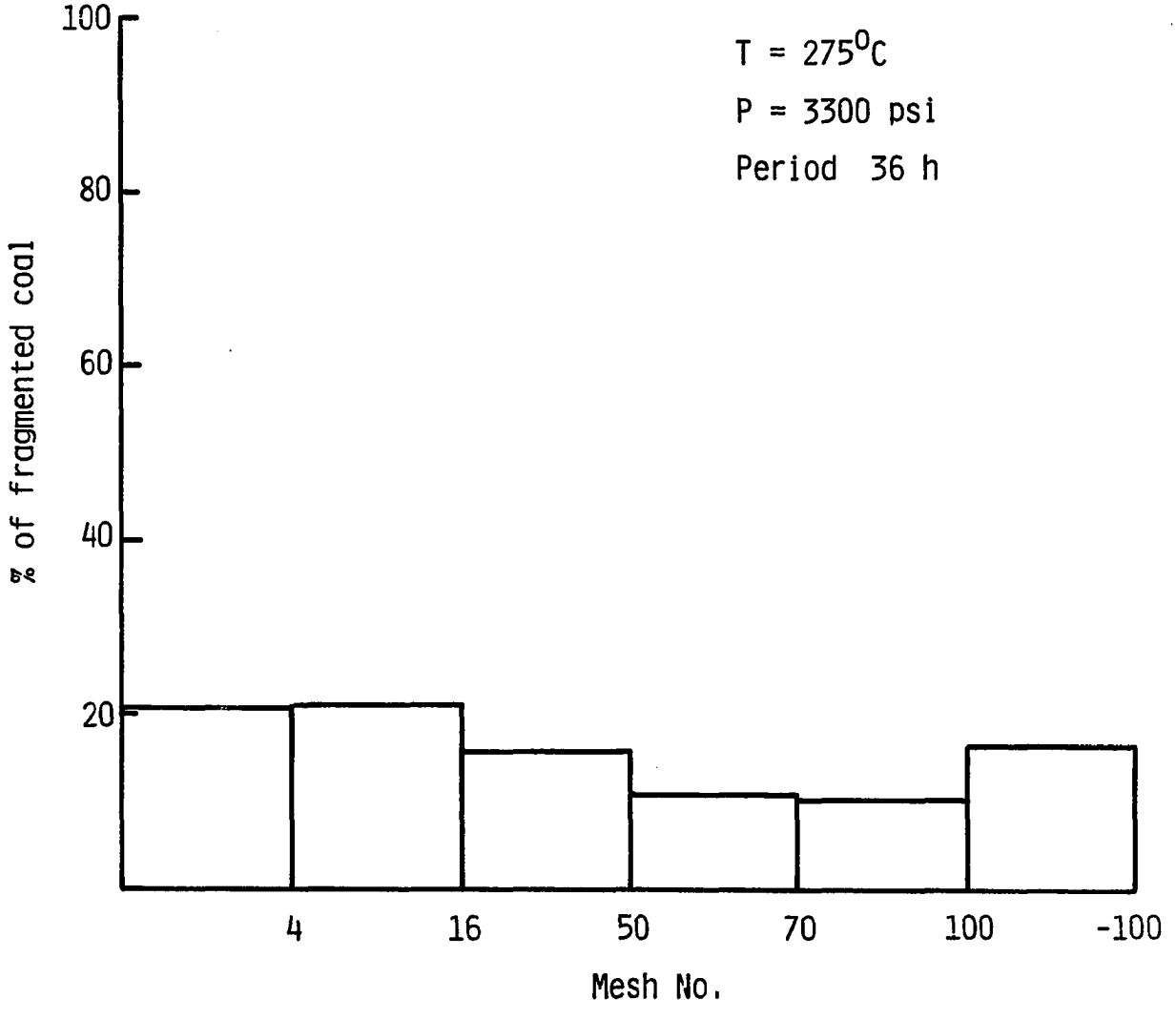



FIGURE 8.4 The distribution of fragmented coal on mesh no.

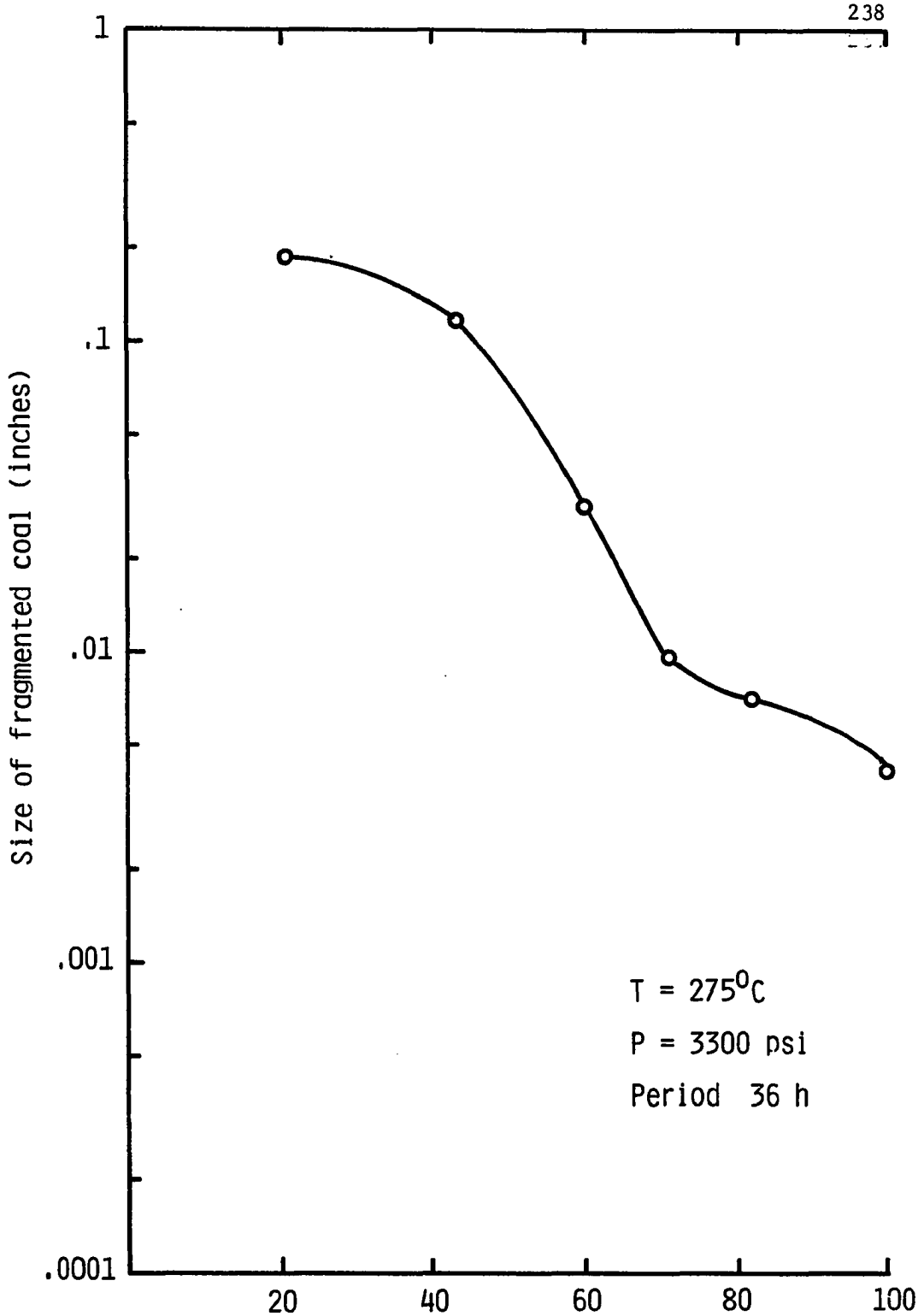



FIGURE 8.5 % Cumulative of fragmented coal

TEST #9

T = 325°C

Pressure = 3600 psi

Period = 18 hours

100% of coal fragmented

Total coal sample = 47.5 grams (1 piece)

Water added = 125 grams

$CO_2$ added = 71.625 grams

Total dissolved coal = 0.1 grams

Average particle size = 0.074 inches

TABLE 9.1*

Time, Temperature, Pressure Relation of Test #9

| Time Minute | Temperature °C | Pressure psi |
|---|---|---|
| 10 | 50 | 1100 |
| 40 | 125 | 1600 |
| 60 | 175 | 2200 |
| 90 | 225 | 2825 |
| 118 | 275 | 3250 |
| 148 | 325 | 3600 |

148 minutes were required to warm reactor up to 325°C.

*These data are used to plot Figures 9.1, 9.2, 9.3.

# TEMPERATURE VERS TIME

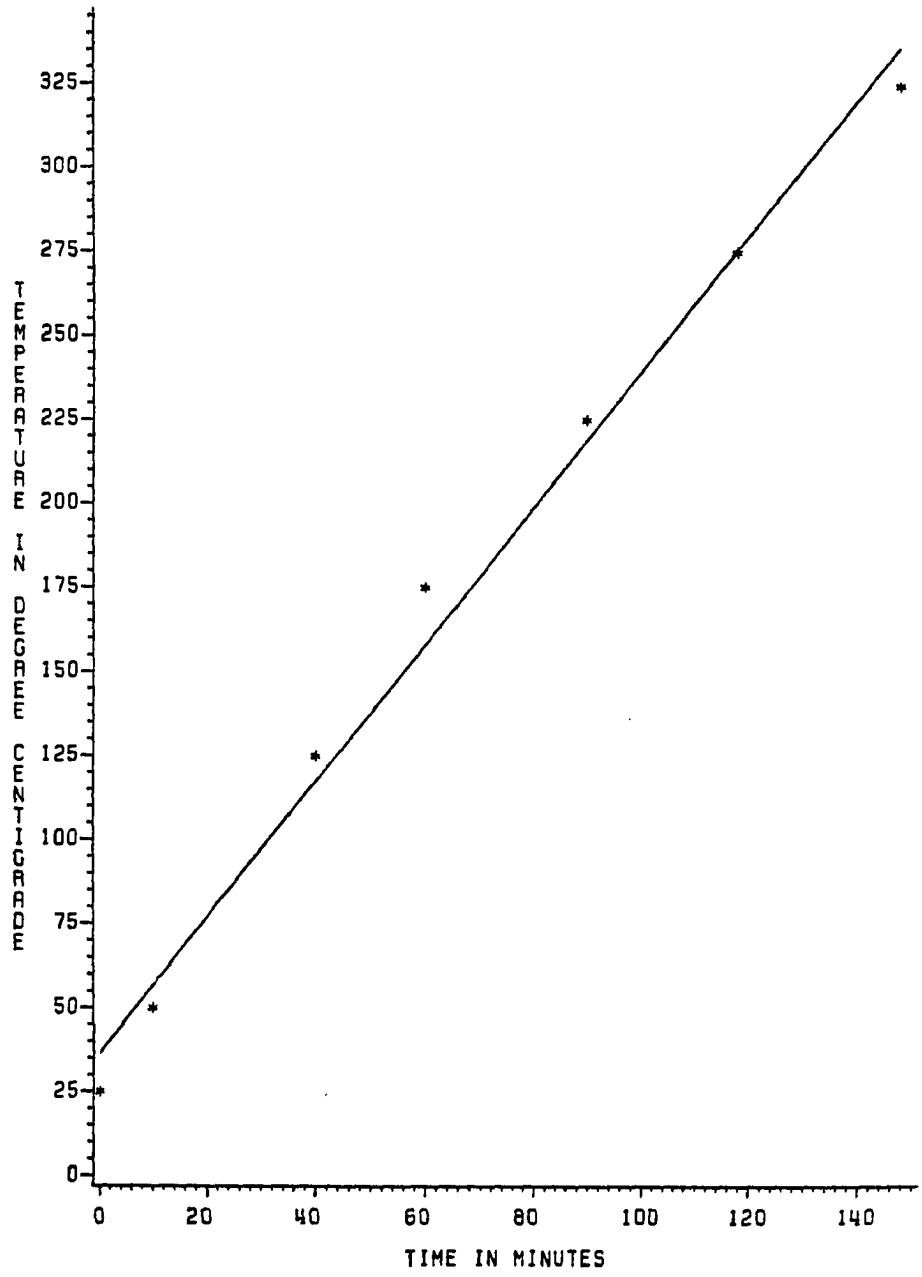



FIGURE 9.1

# PRESSURE VERS TIME

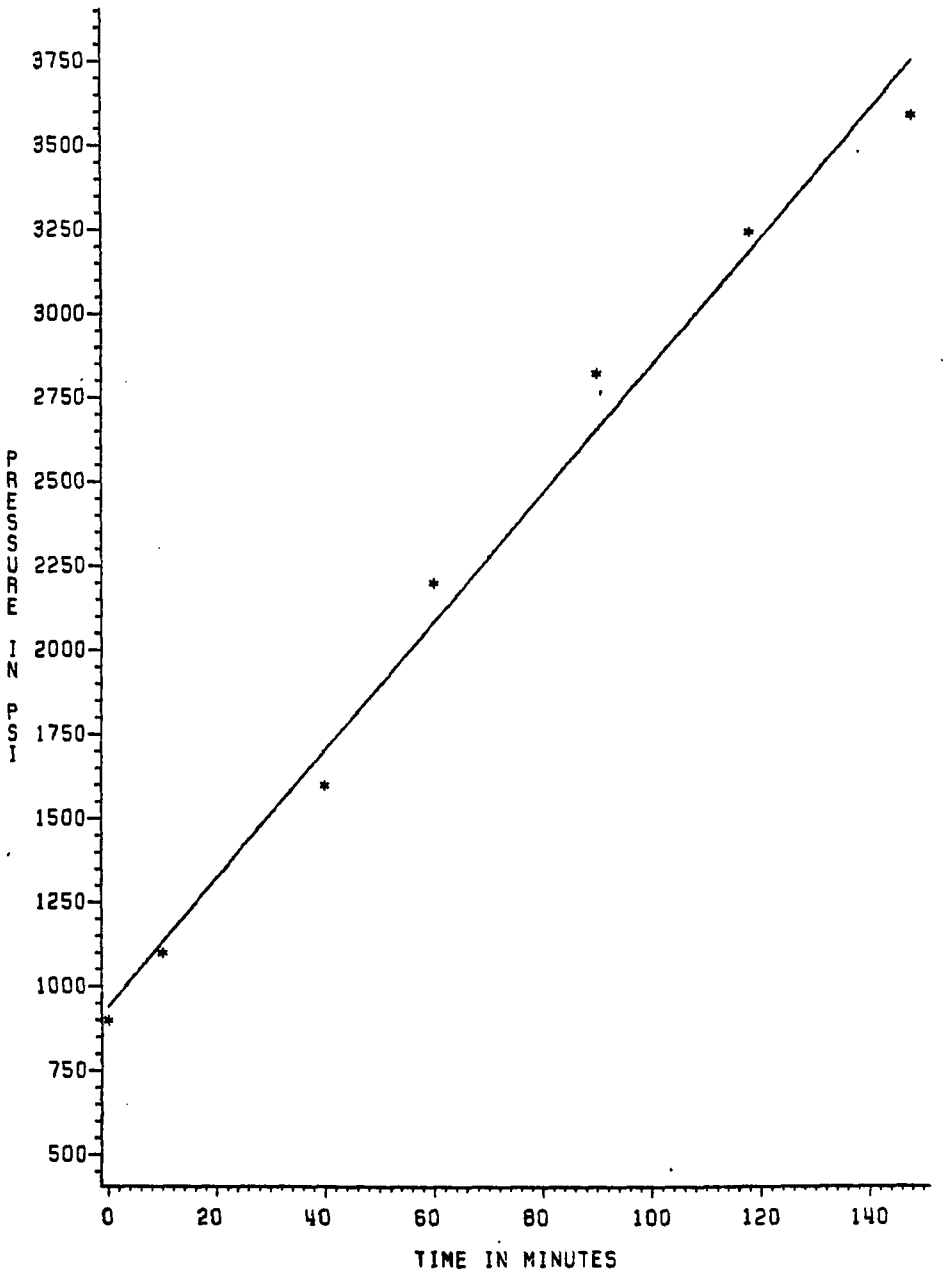
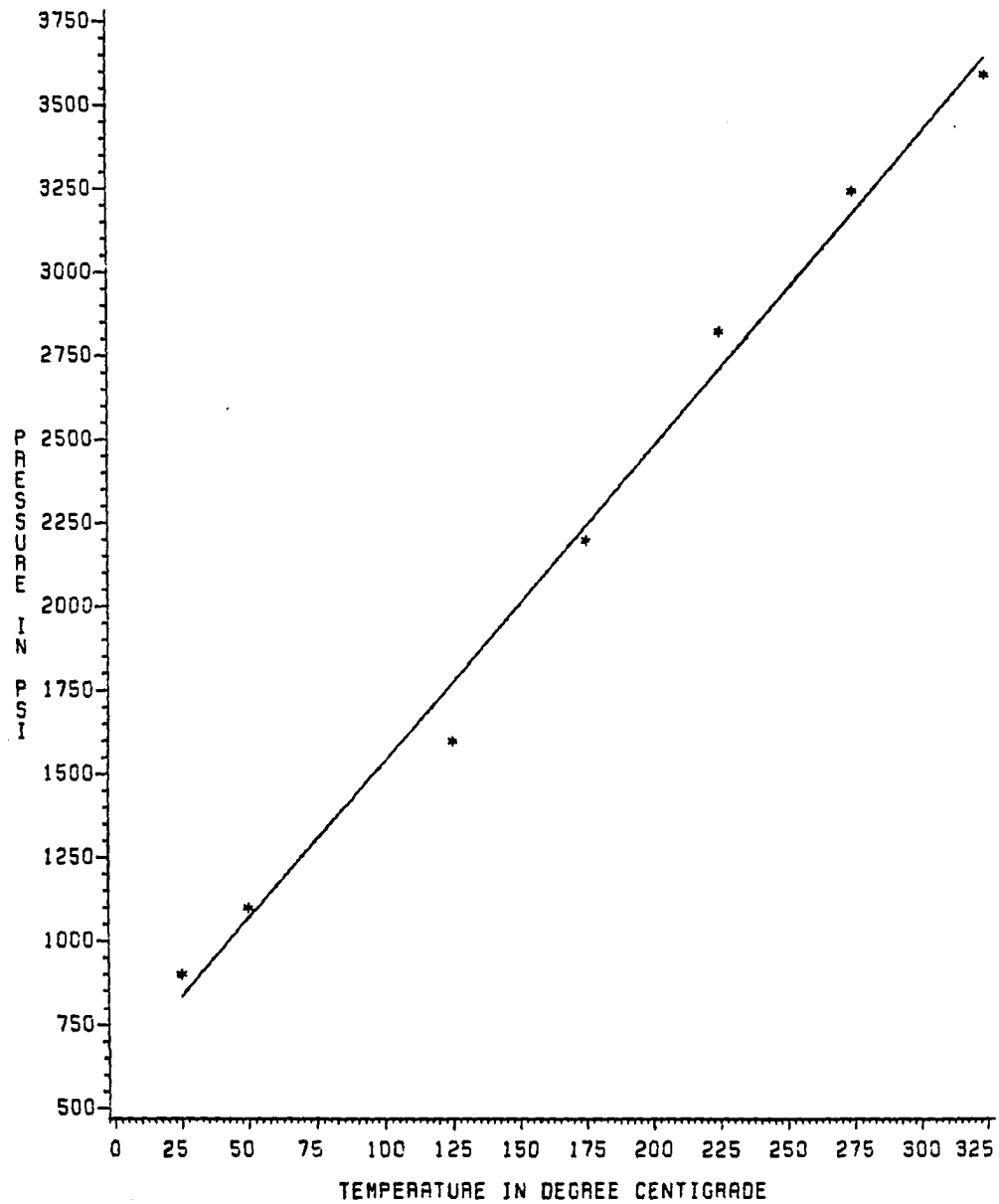



FIGURE 9.2

# PRESSURE VERS TEMPERATURE




TEST=9 TEMPERATURE=325 DEGREE CENTIGRADE PRESSURE=3600 PSI
AND PERIOD OF TEST29 HOURES

FIGURE 9.3

TABLE 9.2

The Result of U.S. Sieve Analysis, The Distribution of Fragmented Coal at 325°C and 3600 psi Pressure

| Mesh No. | Opening Size Inch | $x_i$ Average Opening Size Inch | $f_i$ Weight Retained on Mesh No. (g) | % by Weight | % Cumulative by Weight |
|---|---|---|---|---|---|
| 4 | 0.185 | 0.185 | 11 | 23.3 | 23 |
| 16 | 0.0496 | 0.116 | 9.5 | 20.3 | 43.6 |
| 50 | 0.0116 | 0.0293 | 7.6 | 16 | 59.6 |
| 70 | 0.0083 | 0.00995 | 4.9 | 10.2 | 69.8 |
| 100 | 0.0059 | 0.0071 | 6.2 | 12.8 | 82.6 |
| -100 | 0.0029 | 0.0044 | 8.2 | 17.4 | 100 |
| | | | 47.4 | 100.0 | |

$$\text{Average particle size} = \frac{\sum f_i x_i}{\sum f_i} = 0.074 \text{ inches}$$

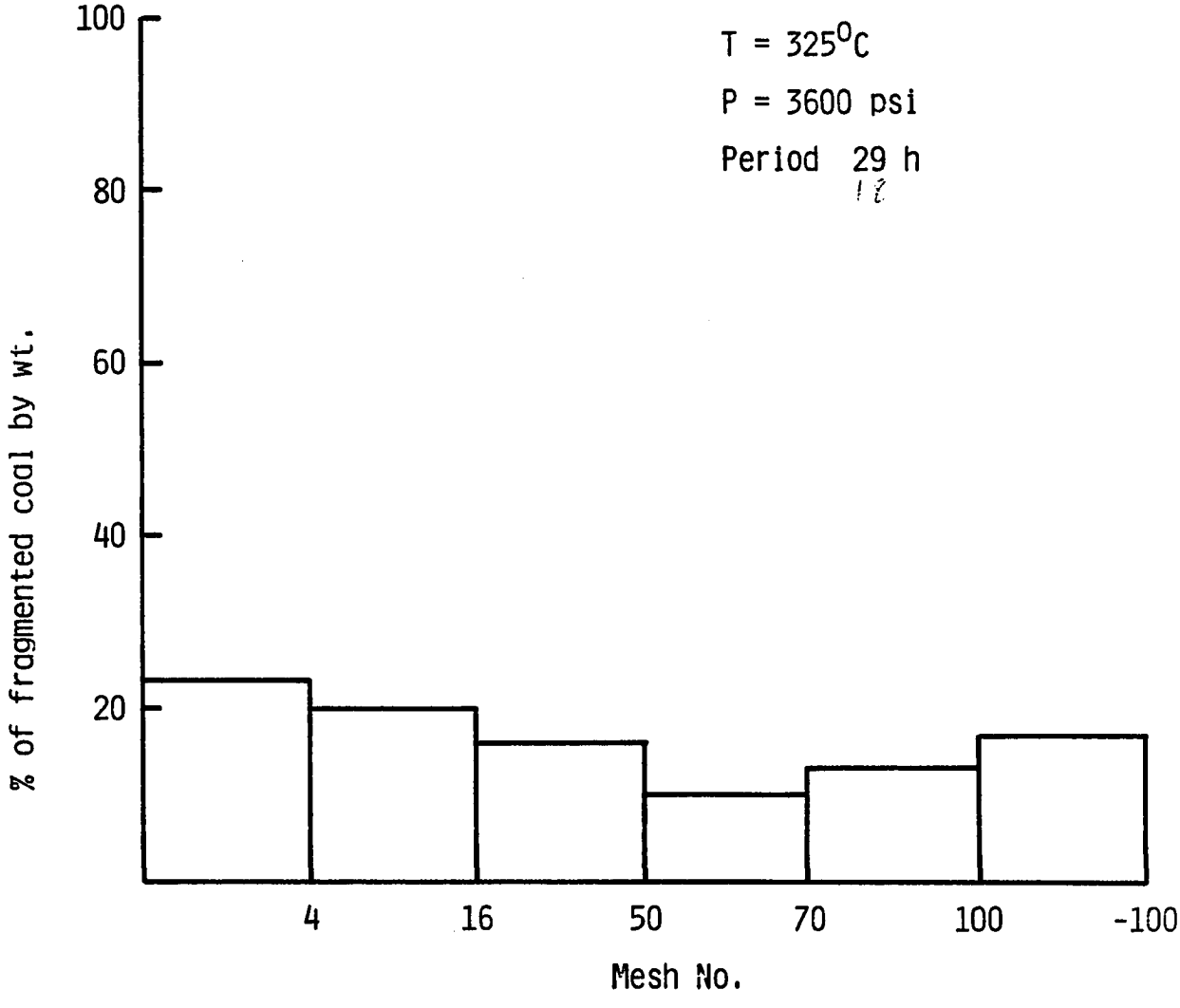



FIGURE 9.4 The distribution of fragmented coal on mesh no.

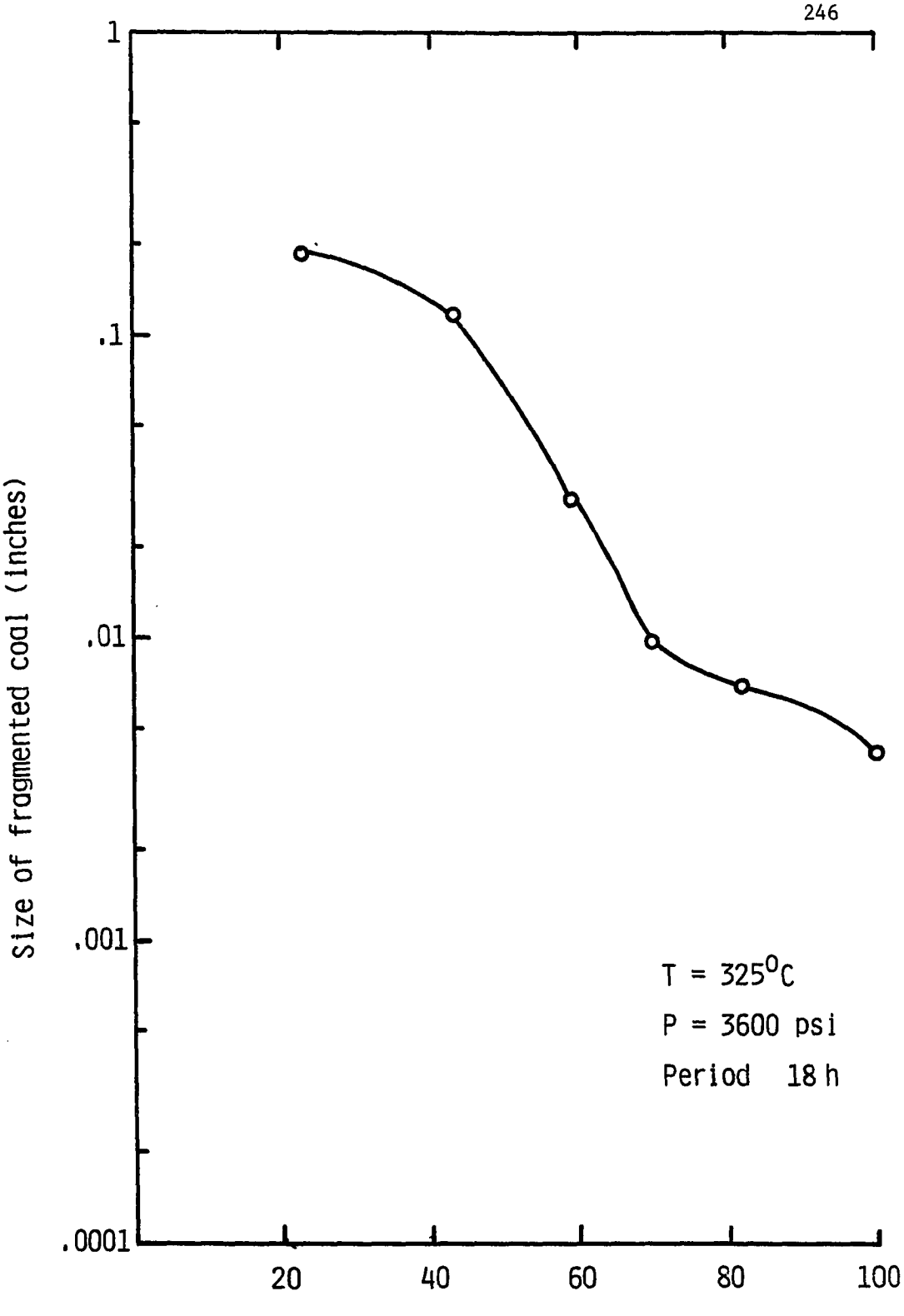



FIGURE 9.5 % Cumulative of fragmented coal

TEST #10

T = 305°C

Pressure = 2550 psi

Period = 24 hours

100% of coal fragmented

Total coal sample = 60 grams (1 piece)

Water added = 200 grams

$CO_2$ added = 65.3 grams

Total dissolved coal = 0.3 grams

Average particle size = 0.150 inches

TABLE 10.1*

Time, Temperature, Pressure Relation of Test #10

| Time Minute | Temperature °C | Pressure psi |
|---|---|---|
| 10 | 50 | 1050 |
| 22 | 100 | 1300 |
| 35 | 150 | 1550 |
| 55 | 200 | 1800 |
| 78 | 250 | 2200 |
| 90 | 275 | 2350 |
| 106 | 305 | 2550 |

106 minutes were required to warm reactor up to 305°C.

*These data are used to plot Figures 10.1, 10.2, 10.3.

# TEMPERATURE VERS TIME 

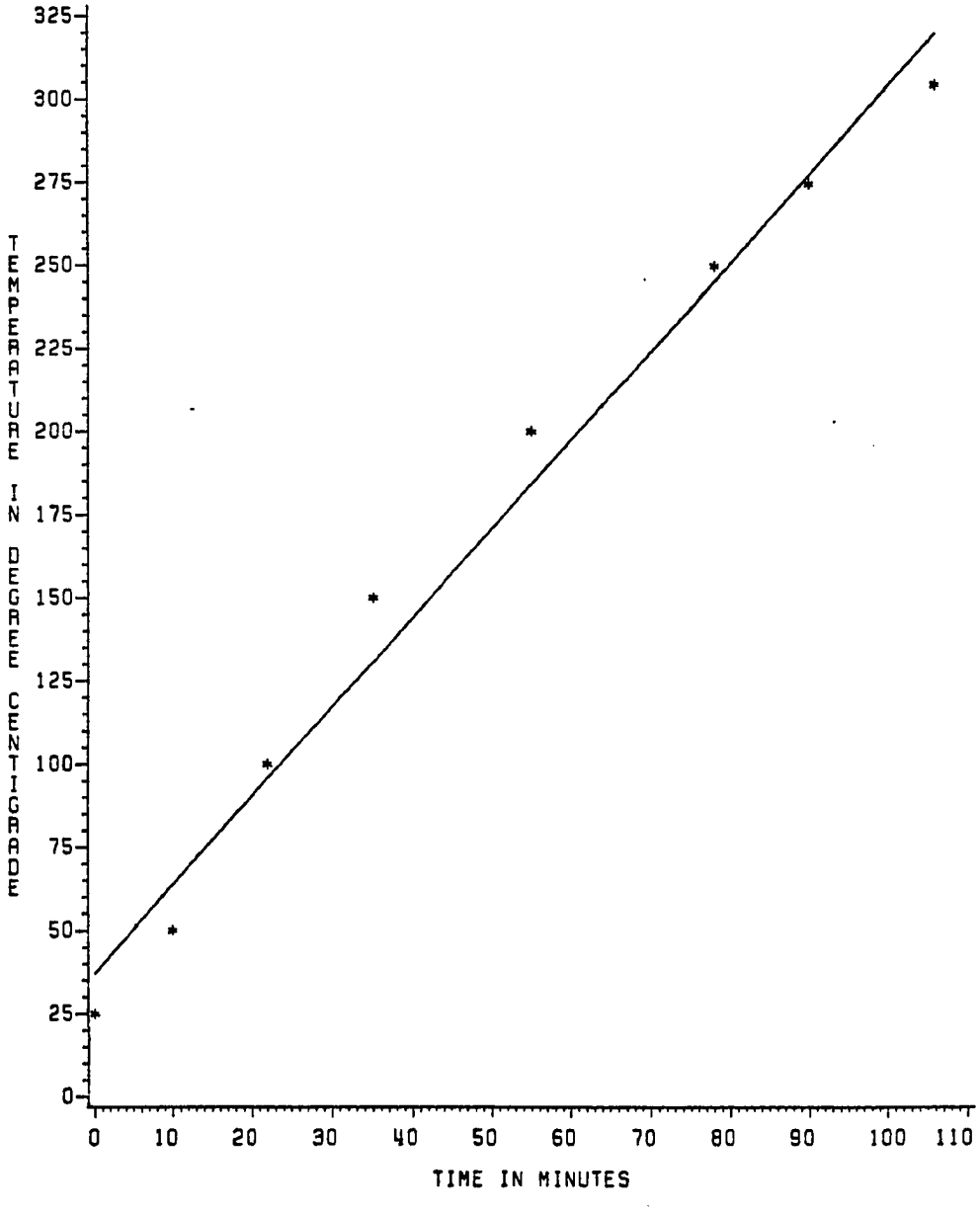



**FIGURE 10.1**

TEST=10

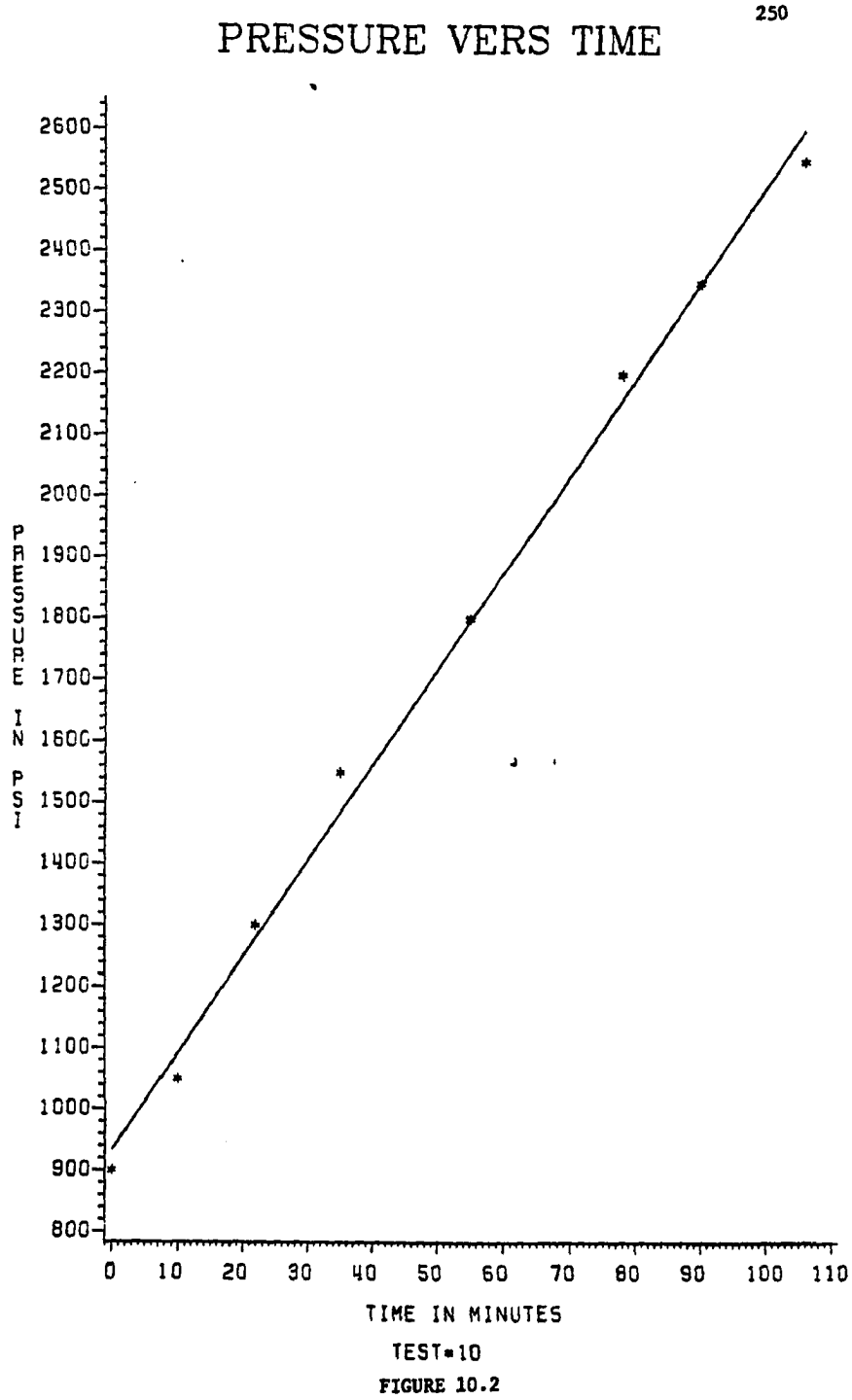

PRESSURE VERS TIME
PRESSURE IN PSI
2600
2500
2400
2300
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
0
10
20
30
40
50
60
70
80
90
100
110
TIME IN MINUTES
TEST=10

FIGURE 10.2

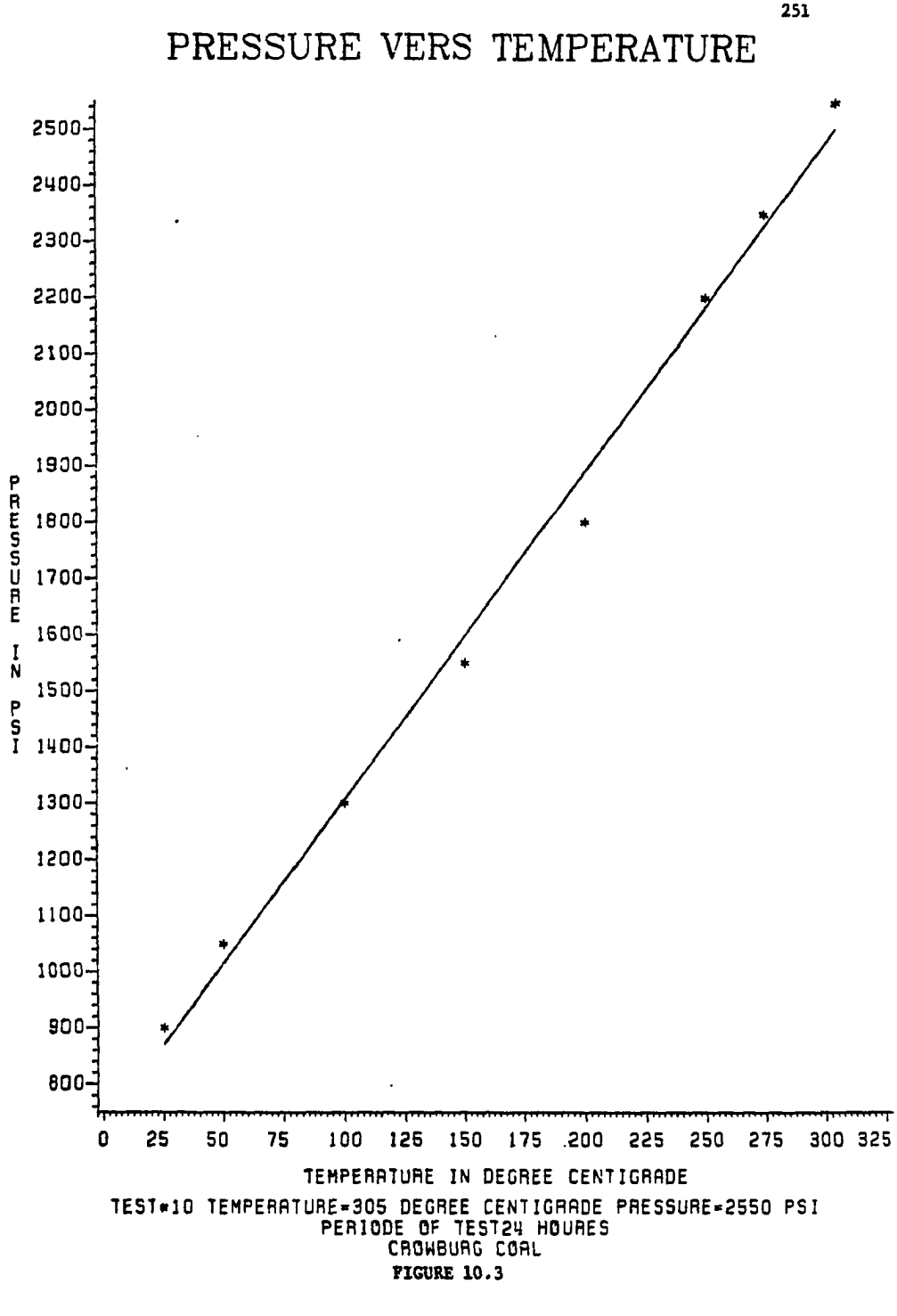

PRESSURE VERS TEMPERATURE
PRESSURE IN PSI
2500
2400
2300
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
0 25 50 75 100 125 150 175 200 225 250 275 300 325
TEMPERATURE IN DEGREE CENTIGRADE
TEST#10 TEMPERATURE=305 DEGREE CENTIGRADE PRESSURE=2550 PSI
PERIODE OF TEST24 HOURES
CROWBURG COAL

FIGURE 10.3

TABLE 10.2

The Result of U.S. Standard Sieve Analysis of Croweburg Coal, Distribution of Fragmented Coal at T = 305°C and P = 2550 psi

| Mesh No. | Opening Size Inch | $x_i$ Average Opening Size Inch | $f_i$ Weight Retained on Mesh No. (g) | % by Weight | % Cumulative by Weight |
|---|---|---|---|---|---|
| 4 | 0.185 | 0.185 | 39.2 | 66 | 66 |
| 16 | 0.0469 | 0.116 | 13 | 21.7 | 87.7 |
| 50 | 0.0116 | 0.0293 | 4 | 6.7 | 94.4 |
| 60 | 0.0098 | 0.011 | 0.5 | 0.8 | 95.2 |
| 100 | 0.0059 | 0.0079 | 1 | 1.6 | 96,8 |
| -100 | 0.0029 | 0.0044 | 2 | 3.2 | 100 |
| | | | 59.7 | 100 | |

$$\text{Average coal particle size} = \frac{\sum f_i x_i}{\sum f_i} = 0.150 \text{ inches}$$

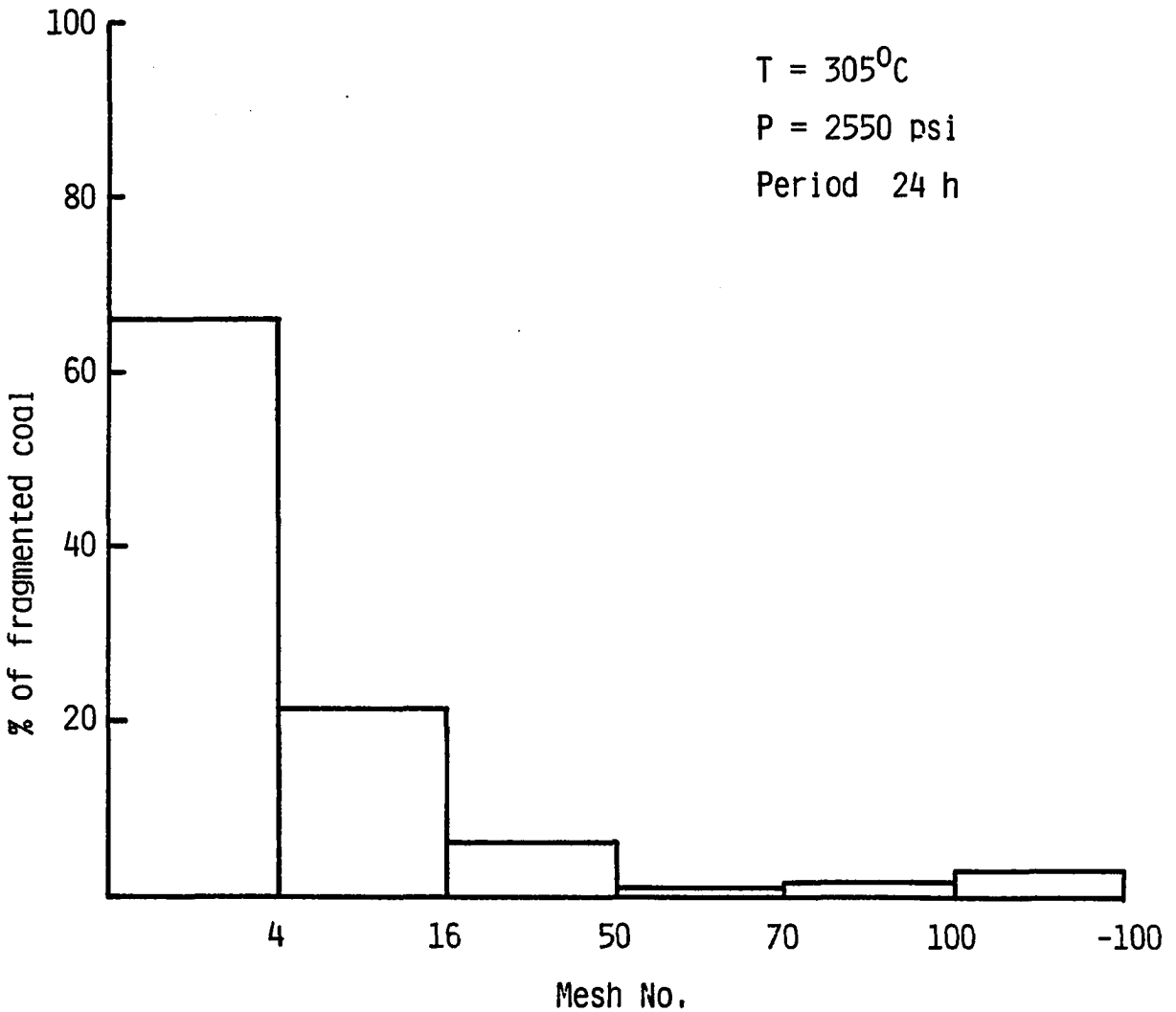



FIGURE 10.4 The distribution of fragmented coal (Croweburg) on mesh no.

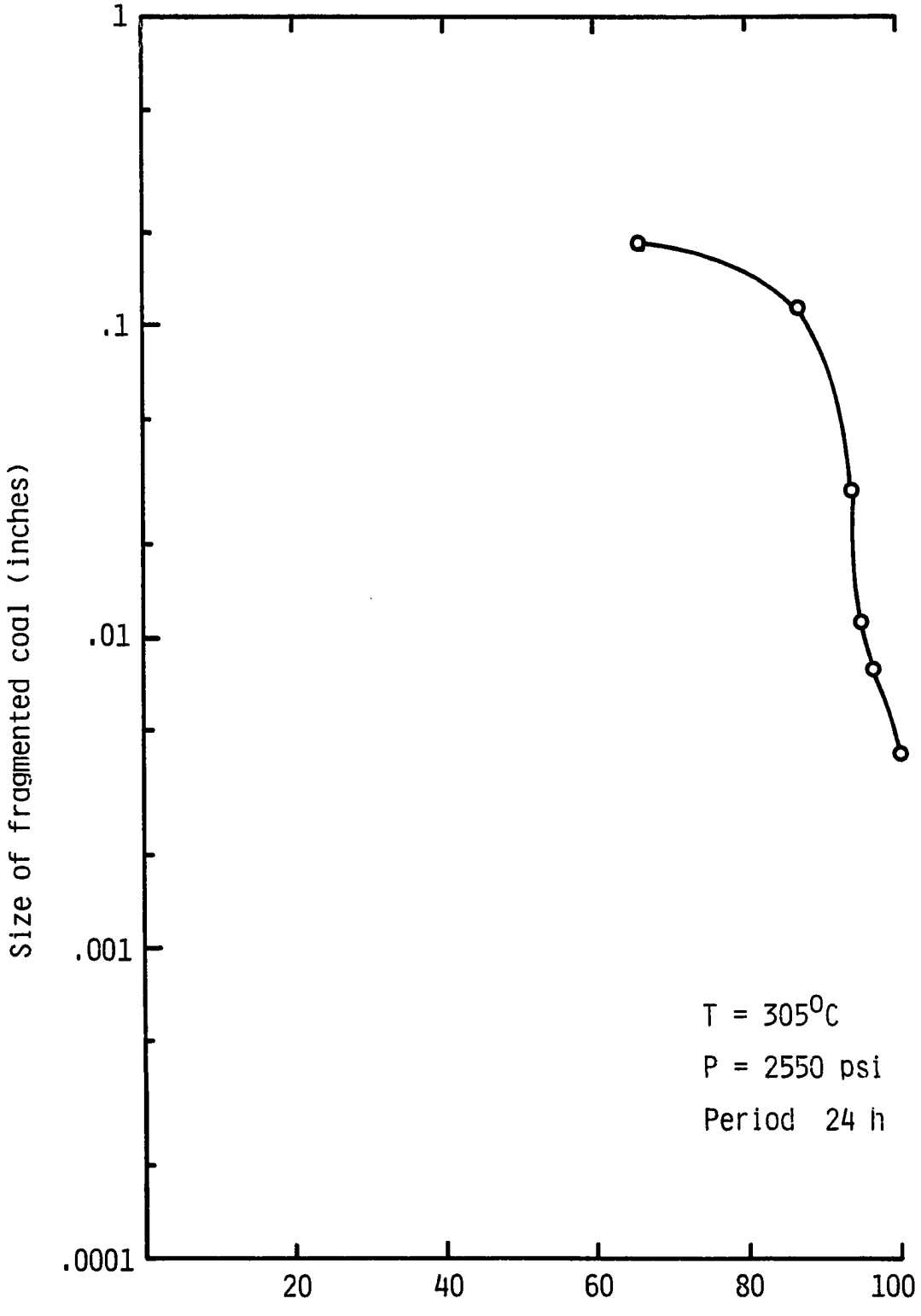



FIGURE 10.5 % Cumulative of Croweburg fragmented coal.

TEST #11

T = 315°C

Pressure = 2750 psi

Period = 24 hours

100% of coal broke

Total coal sample (Secor) = 136 grams

Average particle size = 0.135 inches

TABLE 11.1*

Time, Temperature, Pressure Relation of Test #11

| Time Minute | Temperature °C | Pressure psi |
|---|---|---|
| 10 | 50 | 1050 |
| 29 | 100 | 1350 |
| 46 | 150 | 1600 |
| 65 | 200 | 2000 |
| 90 | 260 | 2450 |
| 120 | 315 | 2750 |

120 minutes were required to warm reactor up to 315°C.

*These data are used to plot Figures 11.1, 11.2, 11.3.

# TEMPERATURE VERS TIME

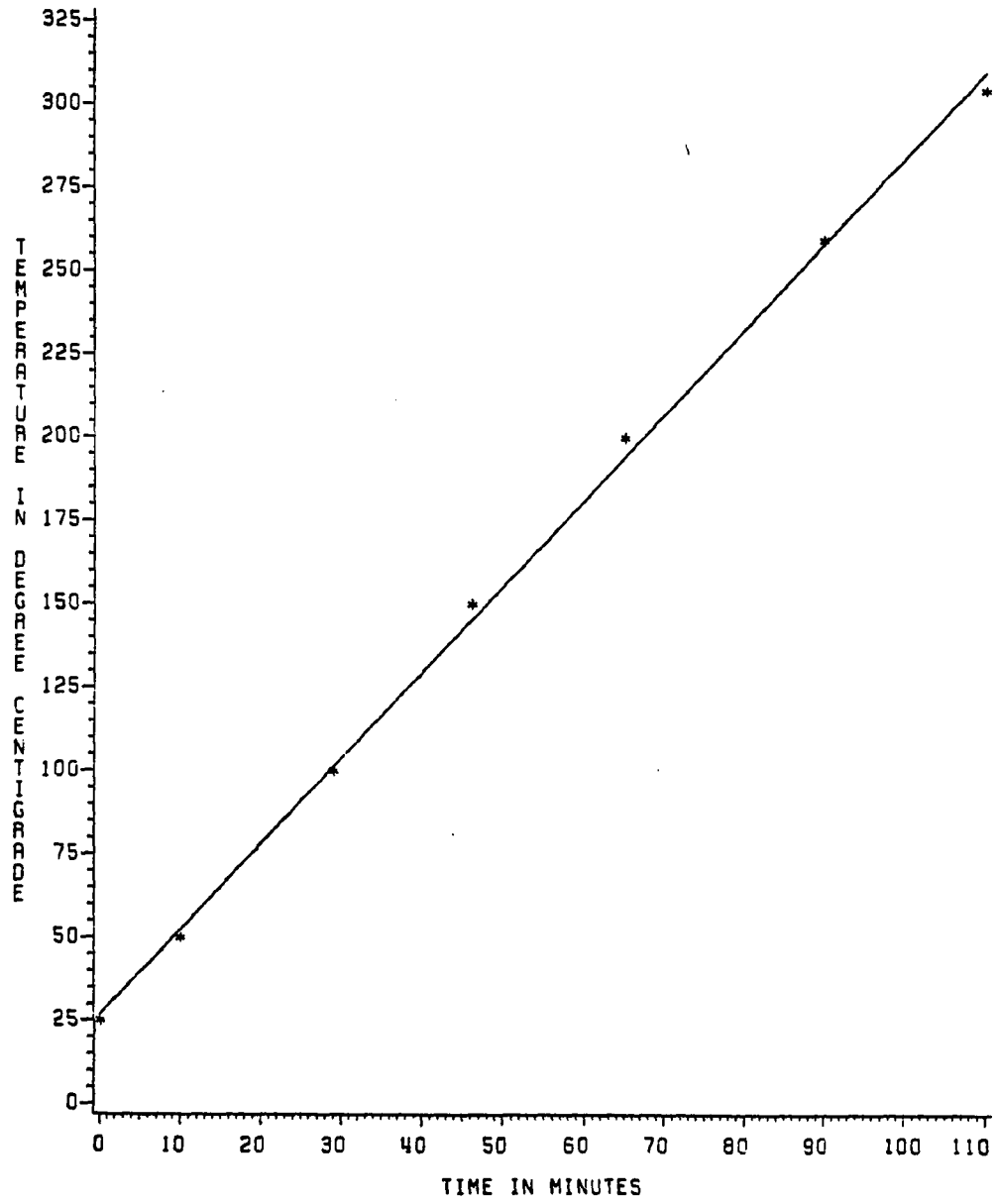
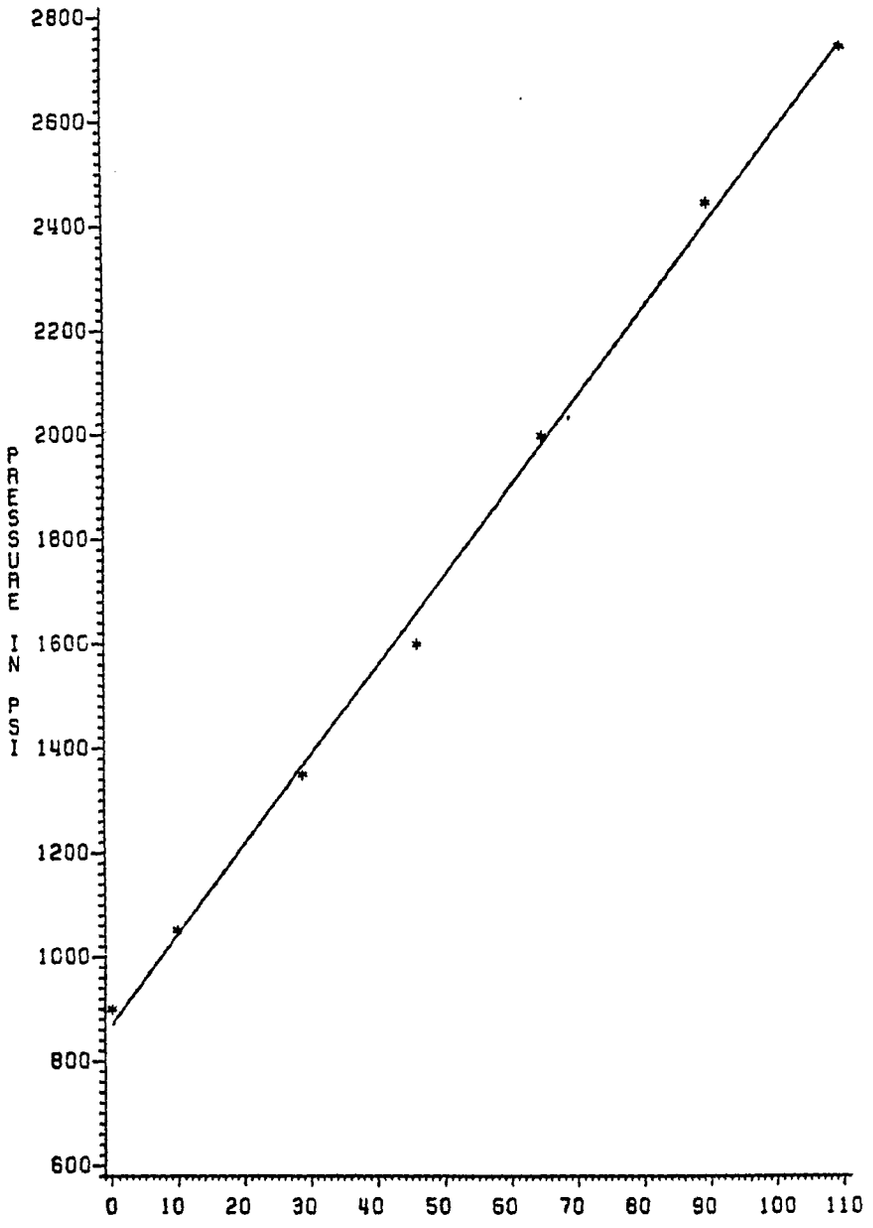



**FIGURE 11.1**

TEST=11

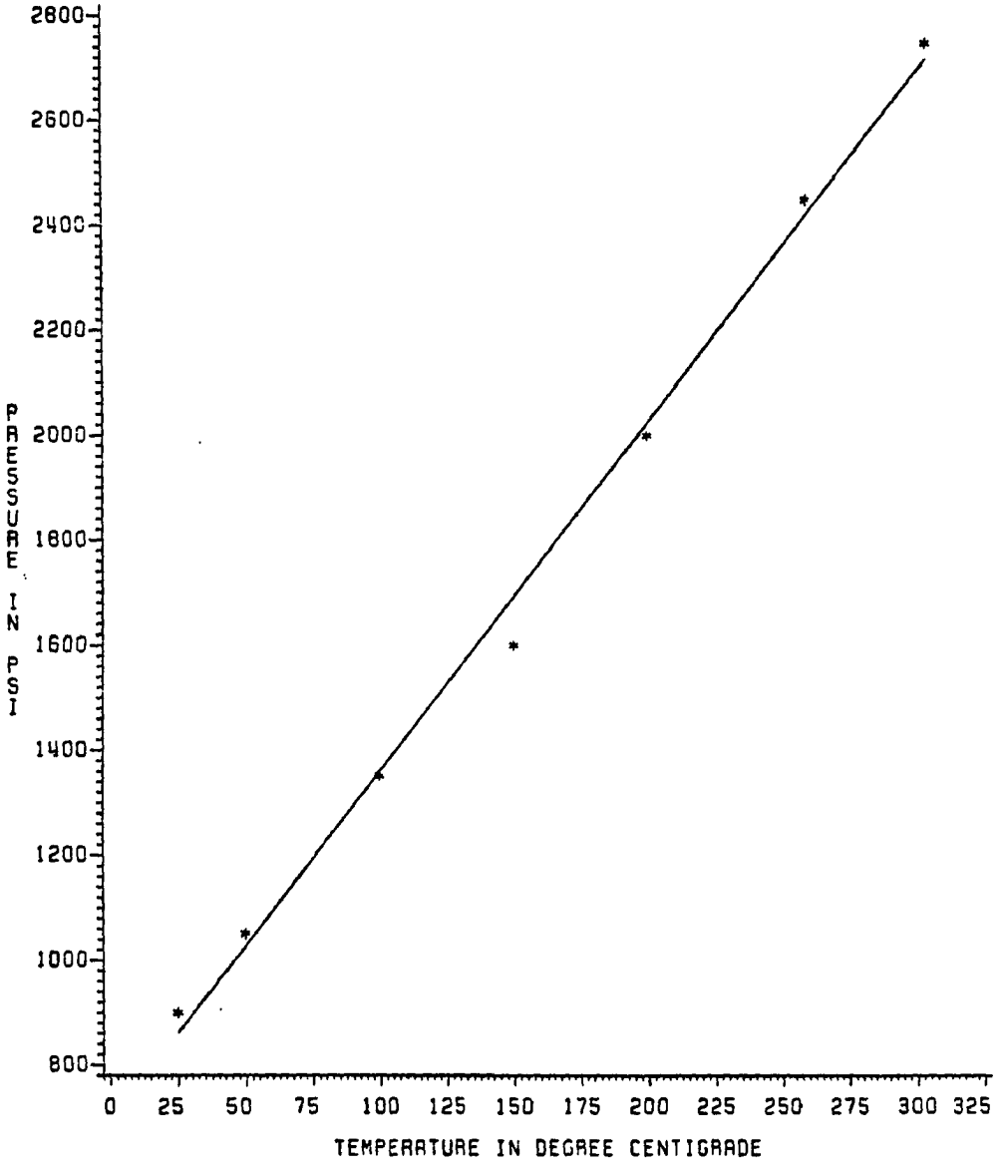
# PRESSURE VERS TIME




TEST*11

FIGURE 11.2

# PRESSURE VERS TEMPERATURE 259




TEST=11 TEMPERATURE=315 DEGREE CENTIGRADE PRESSURE=2750 PSI
AND PERIOD OF TEST 24 HOURES
SECOR COAL

**FIGURE 11.3**

TABLE 11.2

The Result of U.S. Standard Sieve Analysis of Secor Coal

| Mesh No. | Opening Size Inch | $x_i$ Average Opening Size Inch | $f_i$ Weight Retained on Mesh No. (g) | % by Weight | % Cumulative by Weight |
|---|---|---|---|---|---|
| 4 | 0.185 | 0.185 | 87.5 | 64 | 64 |
| 16 | 0.0469 | 0.116 | 14.5 | 10.7 | 74.7 |
| 50 | 0.0116 | 0.0293 | 10 | 7.3 | 82.0 |
| 60 | 0.0098 | 0.011 | 6 | 4.4 | 86.6 |
| 100 | 0.0059 | 0.0079 | 6.5 | 4.8 | 91.4 |
| -100 | 0.0029 | 0.0044 | 11.5 | 8.6 | 100 |
| | | | 136.0 | 100 | |

$$\text{Average coal particle} = \frac{\sum f_i x_i}{\sum f_i} = 0.135 \text{ inches}$$

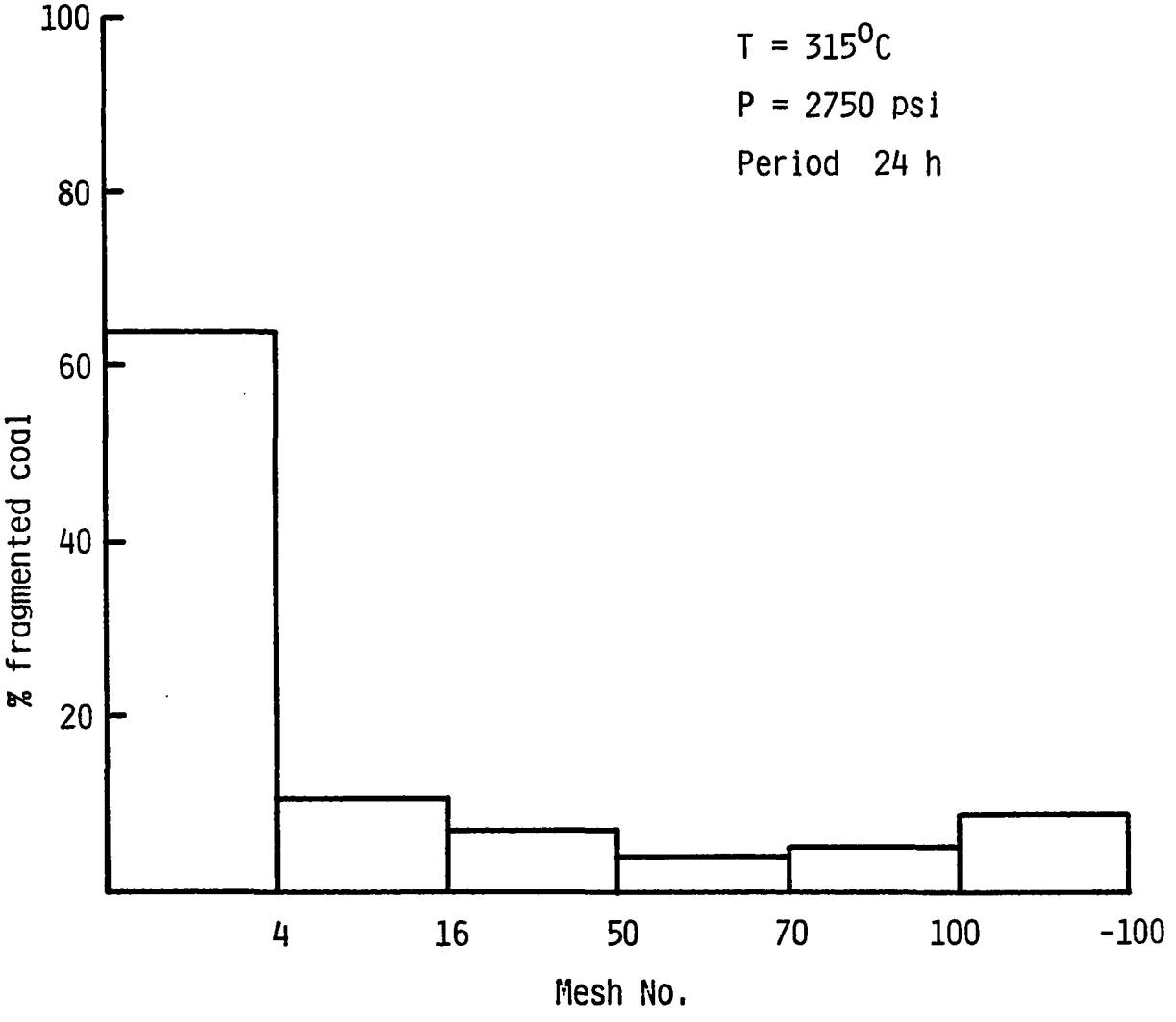



FIGURE 11.4 The distribution of fragmented coal (Secor) on mesh no.

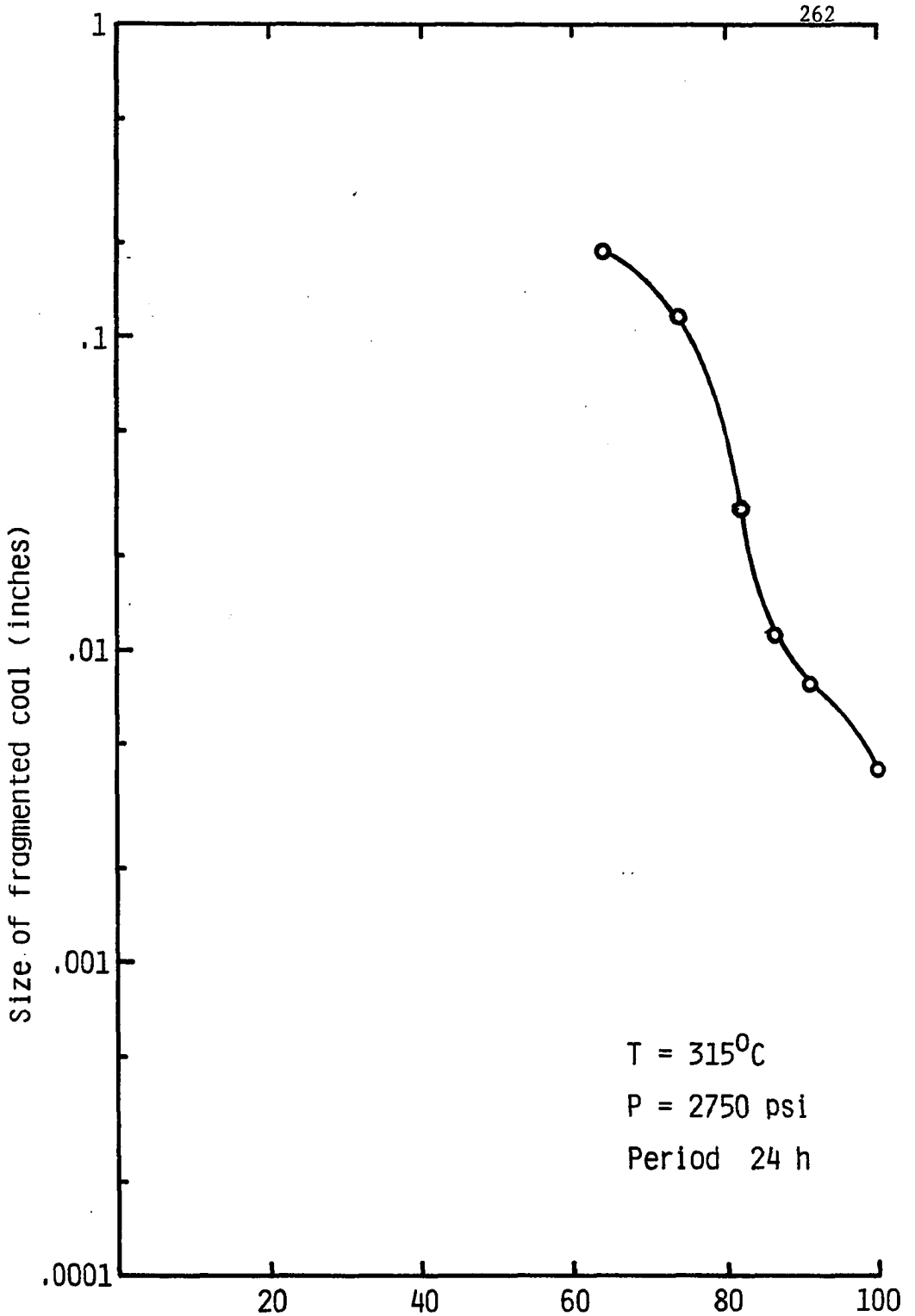



FIGURE 11.5 % Cumulative of Secor fragmented coal

TABLE 12.1

Time, Temperature, Pressure Relation

for Coal + $H_2O$

Period of Test: 24 hours

| Time Minutes | Temperature °C | Pressure psi |
|---|---|---|
| 20 | 75 | 50 |
| 29 | 100 | 275 |
| 47 | 150 | 1075 |
| 66 | 200 | 1800 |
| 77 | 225 | 2100 |
| 89 | 250 | 2250 |

TABLE 13.1

Time, Temperature, Pressure Relation

for Coal + $H_2O$

Period of Test: 24 hours

| Time Minutes | Temperature °C | Pressure psi |
|---|---|---|
| 18 | 75 | 50 |
| 28 | 100 | 300 |
| 46 | 150 | 1150 |
| 67 | 200 | 1850 |
| 90 | 250 | 2375 |
| 102 | 275 | 2600 |

TABLE 14.1

Time, Temperature, Pressure Relation

for Coal + $H_2O$

Period of Test: 24 hours

| Time Minutes | Temperature °C | Pressure psi |
|---|---|---|
| 18 | 75 | 50 |
| 30 | 100 | 300 |
| 49 | 150 | 1100 |
| 70 | 200 | 1750 |
| 92 | 250 | 2425 |
| 104 | 275 | 2575 |
| 130 | 325 | 2900 |

TABLE 15.1

Time, Temperature, Pressure Relation

for Coal + $CO_2$ g+s

Period of Test: 24 hours

| Time Minutes | Temperature °C | Pressure psi |
|---|---|---|
| 0 | 25 | 900 |
| 17 | 75 | 1150 |
| 25 | 100 | 1300 |
| 32 | 125 | 1650 |
| 40 | 150 | 1800 |
| 51 | 175 | 2150 |
| 59 | 200 | 2325 |
| 82 | 250 | 2600 |

TABLE 16.1

Time, Temperature, Pressure Relation

for Coal + $CO_2$ g+s

Period of Test: 24 hours

| Time Minute | Temperature °C | Pressure psi |
|---|---|---|
| | 25 | 900 |
| 18 | 75 | 1200 |
| 31 | 125 | 1625 |
| 50 | 175 | 2050 |
| 68 | 225 | 2500 |
| 80 | 250 | 2650 |
| 93 | 275 | 2900 |

TABLE 17.1

Time, Temperature, Pressure Relation

for Coal + $CO_2$ g+s

Period of Test: 24 hours

| Time Minutes | Temperature °C | Pressure psi |
|---|---|---|
| | 25 | 900 |
| 17 | 75 | 1200 |
| 33 | 125 | 1700 |
| 48 | 175 | 2175 |
| 66 | 225 | 2575 |
| 88 | 275 | 2875 |
| 102 | 325 | 3250 |

# APPENDIX C

## FIGURES INDICATING THE RELATION BETWEEN THE PERCENTAGE OF FRAGMENTED McALESTER COAL VERSUS TEMPERATURE, PRESSURE, AND PERIOD OF EXPERIMENT

TABLE 1

"SAS" GENERAL COMPUTER PROGRAM OF REGRESSION ANALYSIS

```
//JOB
//EXEC SAS
//SYSIN DD*
//DATA NAME:
INPUT P T t SC  HC AV;
CARDS;
Data here
PROC PRINT;
PROC GLM DATA=MAIN;
Model AV= P T t SC HC AV;
OUTPUT OUT=One Predicted = PAV;
PROC PRINT;
DATA NON;
MERGE MAIN ONE;
PROC GPLOT;
PLOT PAV*P PAV*T PAV*t PAV*SC PAV*HC/OVERLAY;
SYMBOL1 V='P' I=RL C=1;
SYMBOL2 V='T' I=RL C=2;
SYMBOL3 V='A' I=RL C=3;
SYMBOL4 V='S' I=RL C=4;
SYMBOL5 V='H' I=RL C=5;
LABEL PAV= Fragmented size in inches;
TITLE .H=2 Multiple Regression Analysis;
FOOTNOTE .H = Explain P, T, A, S, H
// Final JCL Card
```

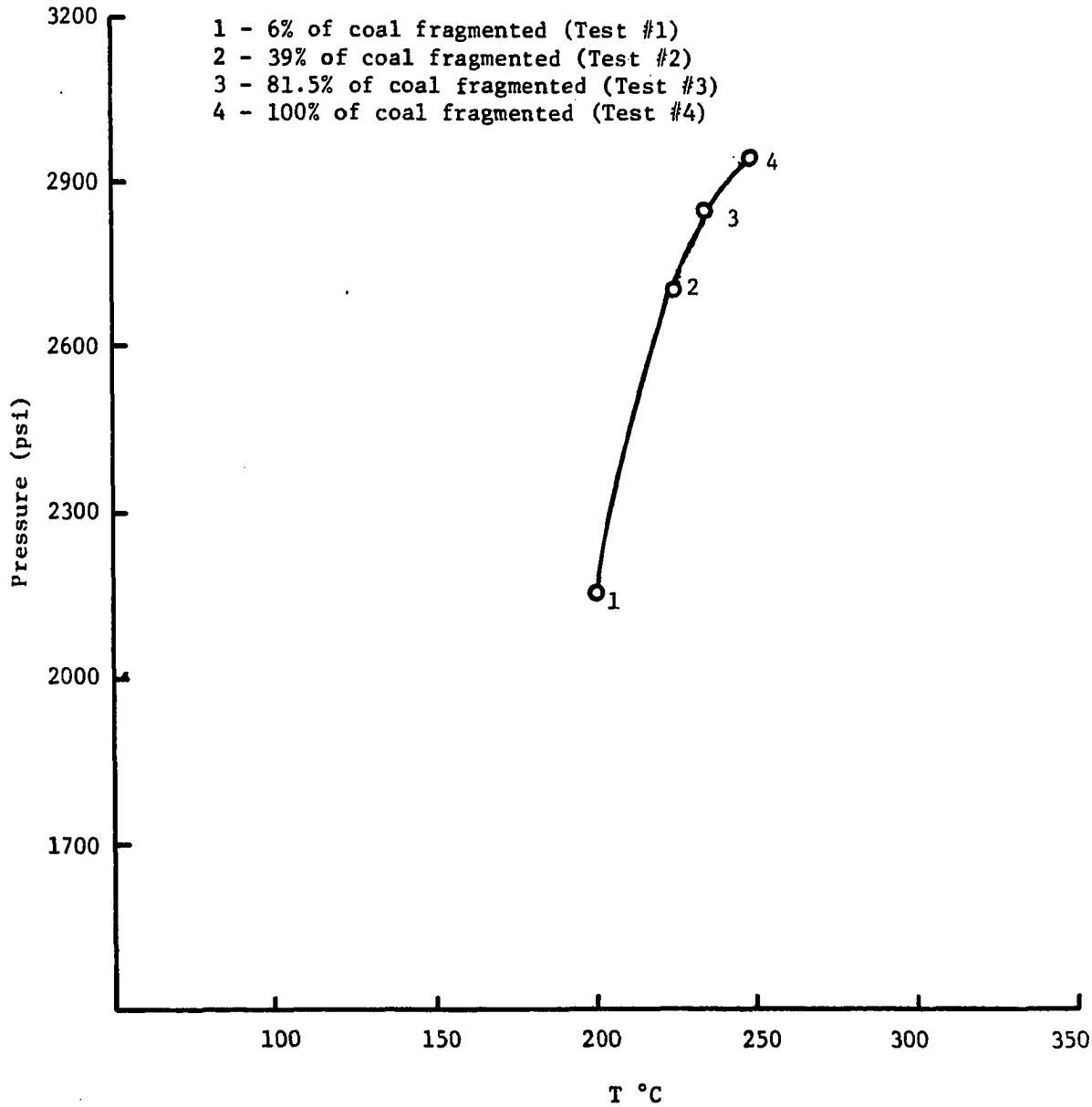



FIGURE 1

Increase of the percentage of fragmented coal as P, T increased.

T, P are relatively constant, time variable.

$T = 275^{0}C$

P = 3300 psi

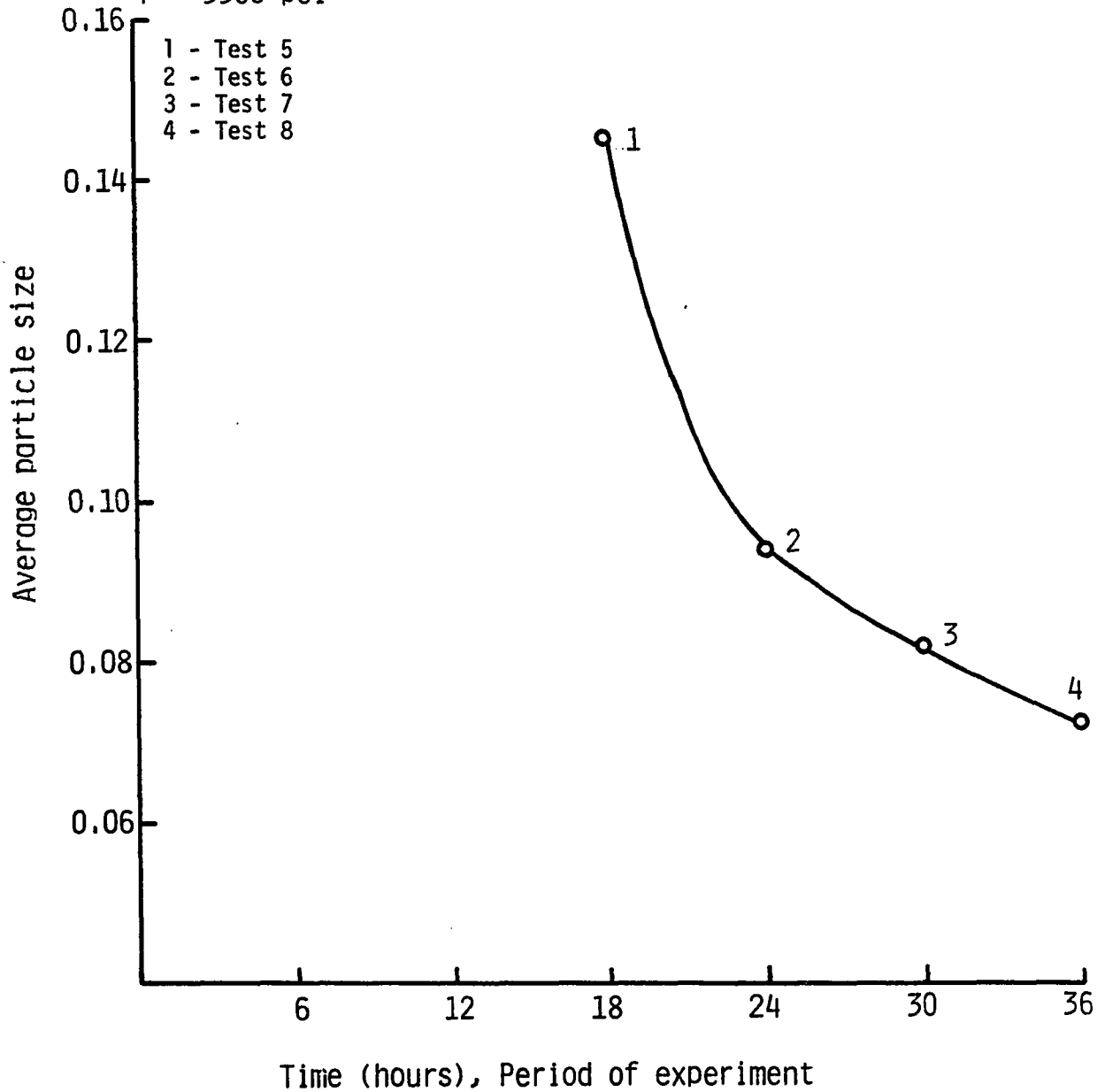



FIGURE 2

At constant temperature and pressure, the fragmented coal becomes smaller with longer period of experiment.

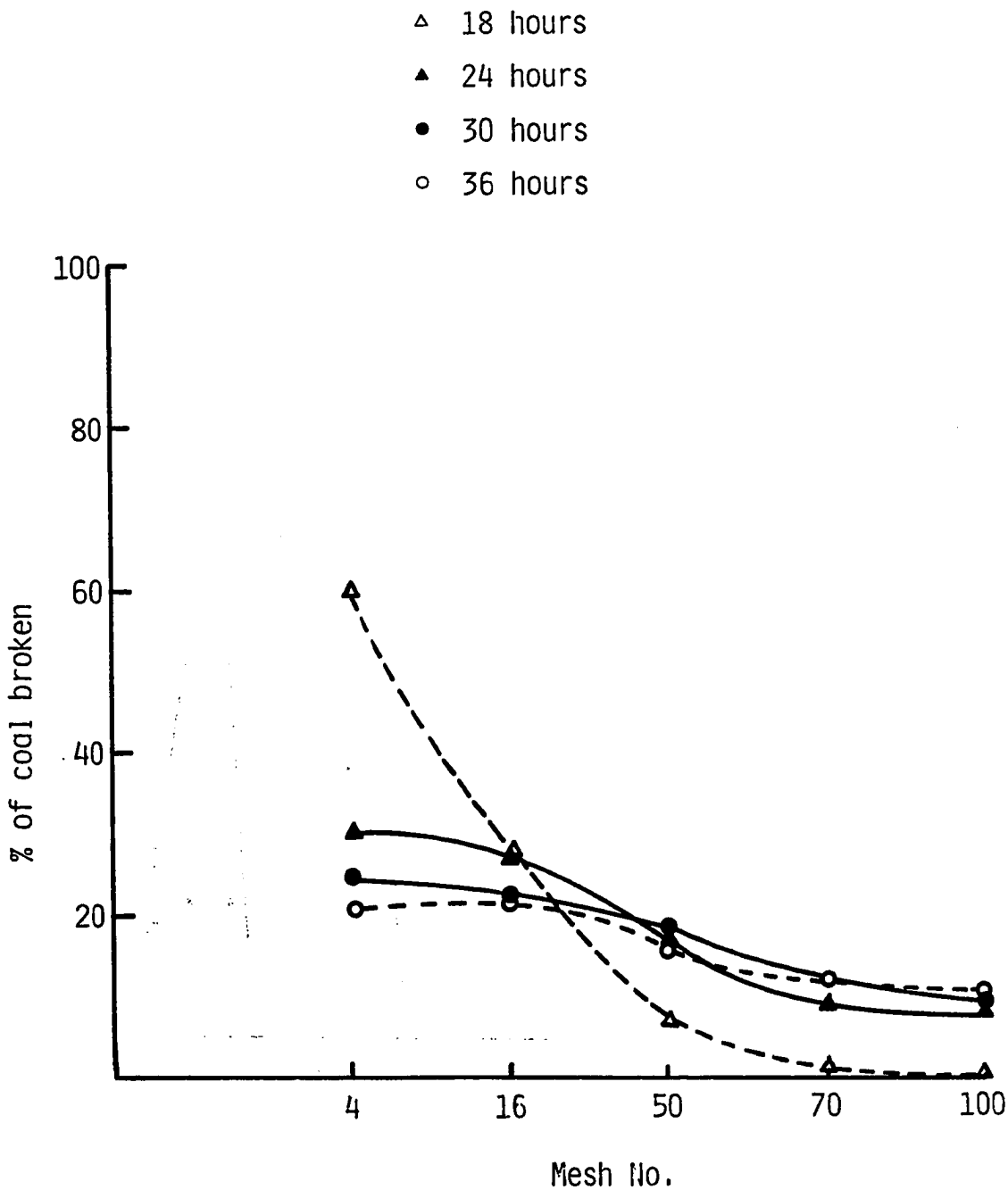



FIGURE 3

For shorter time periods, a higher percentage of fragmented coal remains coarser.

# MULTIPLE REGRESSION ANALYSIS [274]

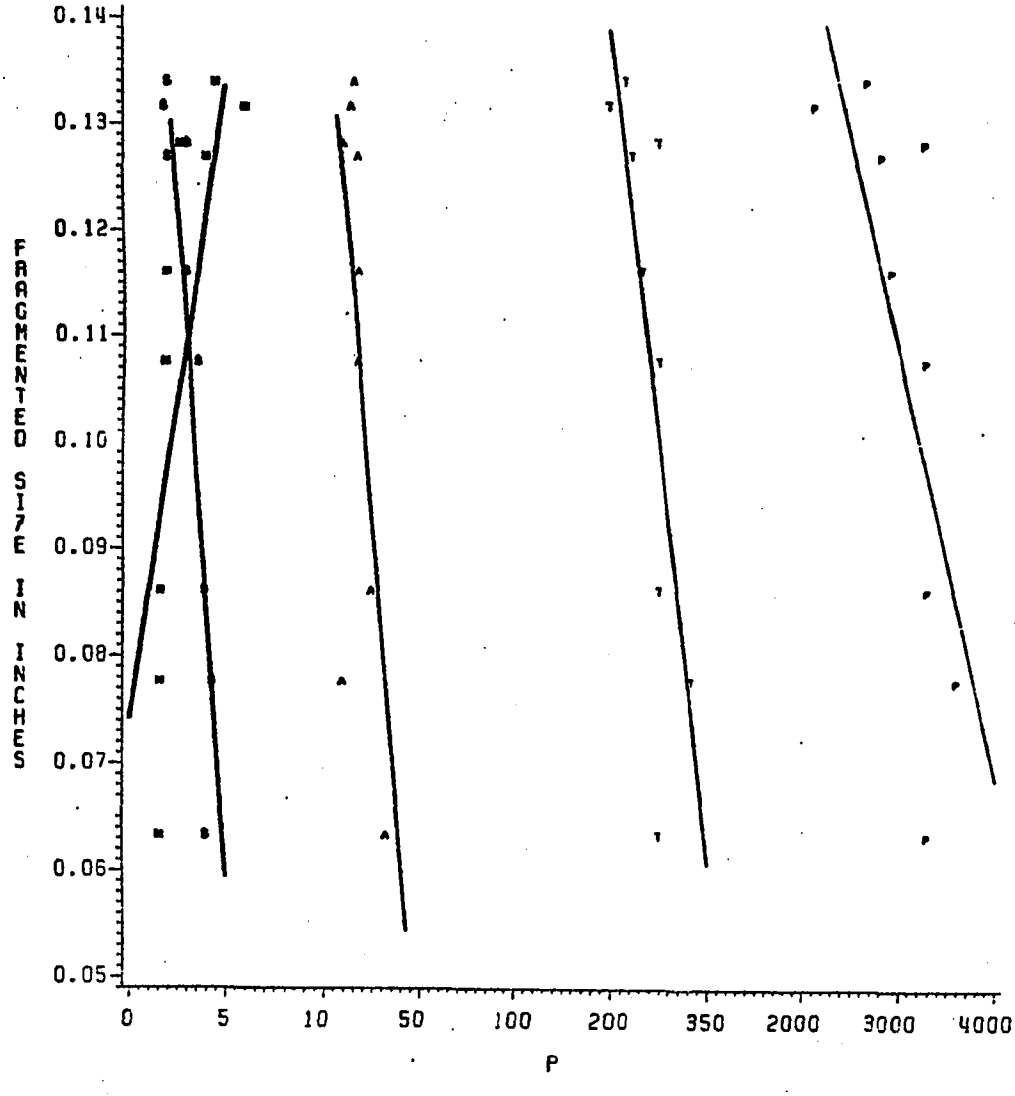



FIGURE 4

P PRESSURE RANGE FROM 2150 TO 3000 PSI
T TEMPERATURE RANGE FROM 200 TO 325 DEGREE CENTIGRADE
A PERIODE OF EXPERIMENT RANGE FROM 18 TO 36 HOURES
S THE RATIO OF SOLVENT TO COAL RANGE FROM 1.8 TO 4.3
H THE RATIO OF WATER TO CO2 RANGE FROM1.58 TO 6

THESE DATA OBTAINED FROM TREATMENT OF MCALESTE COAL BY MIXTURE OF CO2+H2O

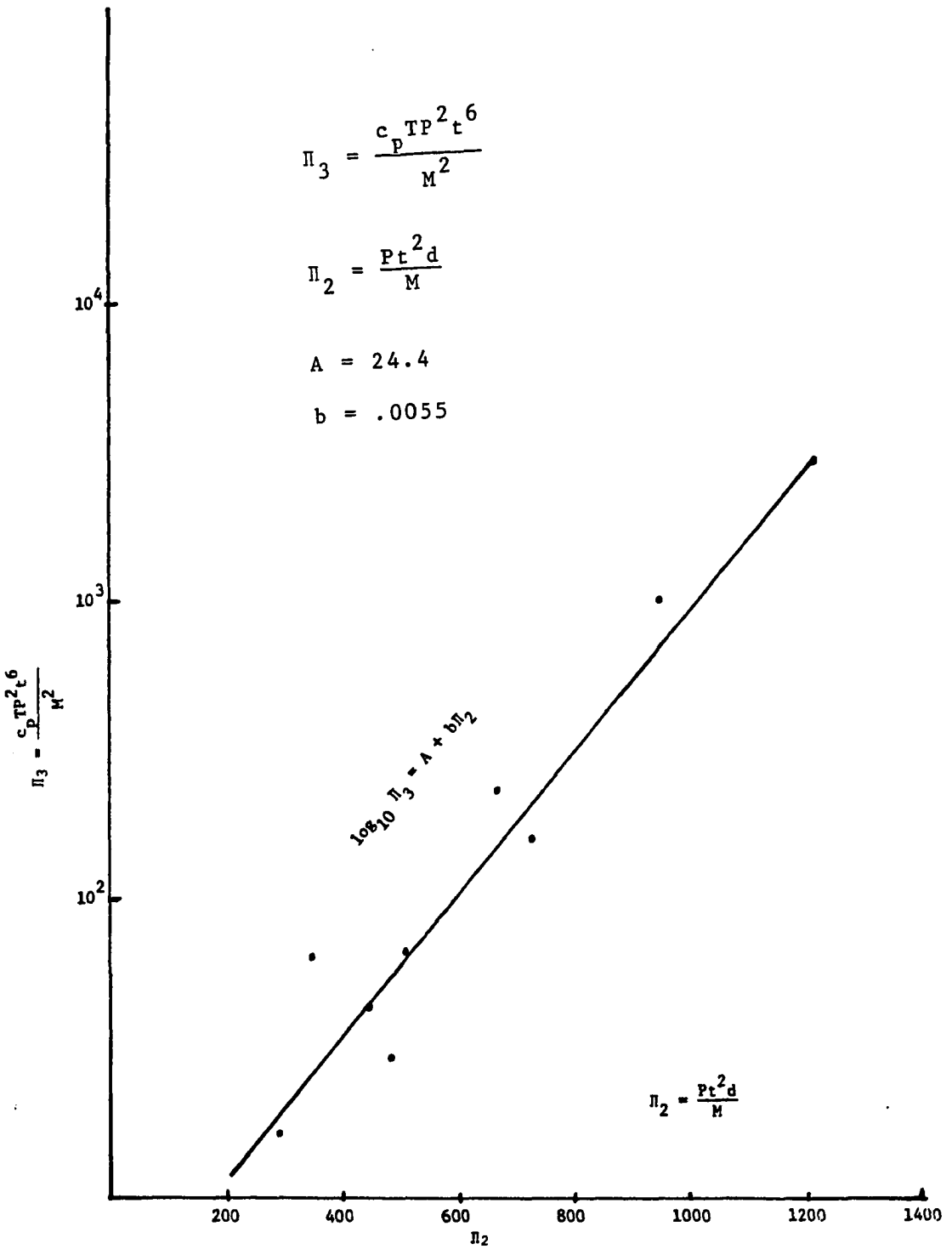



FIGURE 5: Relation between $\Pi_3$ and $\Pi_2$ (predictions of fragmented size of coal).

# APPENDIX D

## THE RESULTS OF TREATMENT OF SEVEN COMPOUNDS WITH $CO_2 + H_2O$

TABLE 1

COMPOUNDS TREATED WITH $CO_2 + H_2O$

| Compound Name | Compound Formula | T °C | Pressure psi | Period of Test Hours | Reaction |
|---|---|---|---|---|---|
| Benzyl-ether | $(C_6H_5CH_2)_2O$ Liquid | 305 | 8000 | 24 | No reaction |
| Diphenyl-disulfide | $C_6H_5-S-S-C_6H_5$ Solid | 305 | 6000 | 24 | No reaction |
| Benzyl-phenyl ether | $C_6H_5CH_2-O-C_6H_5$ Solid | 305 | 7000 | 24 | No reaction |
| Pyrite | $FeS_2$ Solid | 305 | 3400 | 24 | No reaction |
| Benzyl-alcohol | $C_6H_5CH_2OH$ Liquid | 305 | 7000 | 24 | No reaction |
| Phenethyl-alcohol | $C_6H_5CH_2-CH_2OH$ Liquid | 305 | 7000 | 24 | No reaction |
| 2-Naphthyl-benzoal | $C_6H_5COOC_{10}H_7$ | 305 | 7000 | 24 | No reaction |

# APPENDIX E

## THE RESULTS OF TREATMENT OF UNKNOWN COAL WITH $CO_2 + H_2O$, $CO_2$ AND $H_2O$

*TABLE 1: Coal + $CO_2$ (gas)

| Test No. | T °C | P psi | Reaction |
|---|---|---|---|
| 1 | 200 | 1650 | None |
| 2 | 200 | 1700 | None |
| 3 | 300 | 2100 | None |
| 4 | 350 | 2175 | None |

TABLE 2: Coal + $H_2O$

| Test No. | T °C | P psi | Reaction |
|---|---|---|---|
| 5 | 350 | > 3000 | None |

TABLE 3: Coal + $CO_2$ + $H_2O$

| Test No. | T °C | P psi | Reaction |
|---|---|---|---|
| 6 | 350 | 3600 | 100% of coal broke |

*The origin of coal is unknown. Coal had been provided by Chemistry Department by Professor A. Hagen.

This series of tests were done in advance in order to prove dissertation proposal and obtain grant from OMMRRI.

TABLE 4

Distribution of Fragmented Coal on Mesh No. of

Test 6 of Table 3 of Appendix E

| Mesh No. | Opening Size Inch | $x_i$ Inch | $f_i$ Weight gram | Percent by Weight | Percent Cumulative by Weight |
|---|---|---|---|---|---|
| 4 | 0.185 | 0.185 | 70 | 39.7 | 39.7 |
| 16 | 0.0469 | 0.116 | 64.5 | 36.6 | 76.3 |
| 50 | 0.0116 | 0.0293 | 20 | 11.4 | 87.7 |
| 70 | 0.0083 | 0.00995 | 4 | 2.3 | 89.9 |
| 100 | 0.0059 | 0.0071 | 3 | 1.8 | 91.7 |
| -100 | 0.0029 | 0.0044 | 14.5 | 8.3 | 100.0 |
| | | | 176.0 | 100.0 | |

$$\text{Average particle size} = \frac{\sum f_i x_i}{\sum f_i} = \frac{21.1425}{176} = 0.12 \text{ inches}$$