



12-1-1970

Thermal Dissolution of Lignite Under Pressure of Carbon Monoxide and Water

Michael Kuo-Tay Peng

Follow this and additional works at: <https://commons.und.edu/theses>

Recommended Citation

Peng, Michael Kuo-Tay, "Thermal Dissolution of Lignite Under Pressure of Carbon Monoxide and Water" (1970). *Theses and Dissertations*. 3531.
<https://commons.und.edu/theses/3531>

This Thesis is brought to you for free and open access by the Theses, Dissertations, and Senior Projects at UND Scholarly Commons. It has been accepted for inclusion in Theses and Dissertations by an authorized administrator of UND Scholarly Commons. For more information, please contact und.common@library.und.edu.

THERMAL DISSOLUTION OF LIGNITE UNDER PRESSURE
OF CARBON MONOXIDE AND WATER

by
Michael Kuo-Tay Peng

Diploma, Taipei Institute of Technology, Taiwan 1966

A Thesis

Submitted to the Faculty

of the

University of North Dakota

in partial fulfillment of the requirements

for the Degree of

Master of Science

Grand Forks, North Dakota

December
1970

T1970
P37
eng.

This Thesis submitted by Michael K. T. Peng in partial fulfillment of the requirements for the Degree of Master of Science from the University of North Dakota is hereby approved by the Faculty Advisory Committee under whom the work has been done.

Donald E. Swenson
(Chairman)

Deane R. Bidmore

David J. Verka

William Johnson
Dean of the Graduate School

Permission

Title Thermal Dissolution of Lignite Under Pressure of
Carbon Monoxide and Water

Department Chemical Engineering

Degree Master of Science

In presenting this thesis in partial fulfillment of the requirements for a graduate degree from the University of North Dakota, I agree that the Library of this University shall make it freely available for inspection. I further agree that permission for extensive copying for scholarly purposes may be granted by the professor who supervised my thesis work or, in his absence, by the Chairman of the Department or the Dean of the Graduate School. It is understood that any copying or publication or other use of this thesis or part thereof for financial gain shall not be allowed without my written permission. It is also understood that due recognition shall be given to me and to the University of North Dakota in any scholarly use which may be made of any material in my thesis.

Signature Michael Peng

Date December 10, 1970

ACKNOWLEDGEMENTS

The author wishes to express gratitude to Dr. D. E. Severson and Dr. D. R. Skidmore for guiding the research to its meaningful conclusion and for their invaluable suggestions and stimulating discussions during the course of this research. He would like to express his sincere thanks to Professor W. R. Kube and Dr. D. J. Uherka for many helpful suggestions during the course of work.

Last, the author expresses his deepest gratitude to his fiancée Margaret Ming-Chia Chen for her encouragement, patience, and understanding.

TABLE OF CONTENTS

ACKNOWLEDGEMENTS	iv
LIST OF TABLES	vi
LIST OF ILLUSTRATIONS	vii
ABSTRACT	viii
INTRODUCTION	1
DESCRIPTION OF EQUIPMENT	3
MATERIAL TESTED	6
EXPERIMENTAL PROCEDURES	7
DESIGN OF EXPERIMENTS	9
EXPERIMENT RESULTS	12
DISCUSSION OF RESULTS	16
CONCLUSIONS	20
APPENDICES	
A. Data on Reaction of Lignite with Carbon Monoxide And Water	21
B. Proximate Analysis of Lignite	22
C. Sample Calculations and a Typical Temperature Pressure History of A Run	23
D. Calculations of Analysis of Variance	25
REFERENCES	27

LIST OF TABLES

Table		Page
1.	Design of Greco-Latin Square for Solubilization of Lignite with Carbon Monoxide and Water	10
2.	Levels and Coding of Variables	10
3.	Per cent Solubilization of Lignite with Carbon Monoxide and Water	13
4.	Per cent Solubilization of Lignite with Carbon Monoxide and Water	14
5.	Analysis of Variance Table for Greco-Latin Square Design	17
6.	Data on Reaction of Lignite with Carbon Monoxide and Water	21
7.	Proximate Analysis of Lignite	22
8.	Sample Calculations and A Typical Temperature Pressure History of a Run	23

LIST OF ILLUSTRATIONS

Figure		Page
1.	Schematic Diagram of Reactor Assembly	4
2.	Effect of Independent Variables on Lignite Conversion	15

ABSTRACT

The relative effects of different operating conditions in the reaction of lignite with carbon monoxide and water were studied in a microautoclave.

A Greco-Latin square experimental design was employed to test four independent variables at four levels. Independent variables were reaction temperature, initial pressure of carbon monoxide, reaction time, and the ratio of water to lignite. The dependent variable was the per cent solubilization of lignite calculated from the amount of residue recovered and initial moisture- and ash- free weight of lignite charged.

An analysis of variance indicated that at the 99 per cent confidence level only the temperature was significant. At the 95 per cent confidence level, all the four independent variables were significant.

The maximum solubilization was achieved at 460°C reaction temperature, 600 psig initial pressure of carbon monoxide, ratio of water to moisture- and ash- free lignite of 4:1, and at 60 minutes of reaction time.

INTRODUCTION

The disadvantages of coal relative to liquid fuel are that coal is solid and contains a large amount of ash. Recently, the consumption of energy has been increasing rapidly, and the sources of liquid fuel, petroleum, and nuclear energy may not fill this demand. Large reserves of coal and the ability to convert coal to liquid fuel will help fill future demands.

Compared to petroleum, coal is relatively low in hydrogen content. Therefore, the fundamental method in converting coal to liquid hydrocarbons is to add hydrogen to coal. One attractive method of conversion of coal to fluid fuels in recent years has been the hydrogenation of coal with carbon monoxide and water. The rate and degree of conversion depend on the temperature and time of reaction, the particle size and chemical composition of the coal, the initial pressure of carbon monoxide, the amount of water used, and the effect of a catalyst if used.

Conversions of coal to benzene-soluble and volatile materials, as high as 90 per cent, were obtained using carbon monoxide, water, and organic solvents by Appell and Wender (1).

For experiments with lignite, Appell and Wender (1) conclude that: 1) the conversion increases with temperature and the amount of conversion reaches a maximum between 375° and 400°C. The decrease in conversion above 400°C could be the result of changing some of the soluble products

to insoluble, high molecular weight material, 2) conversion of lignite to benzene-soluble materials at the optimum conditions seems to be complete within 10 minutes, and 3) the conversion of lignite increases sharply with increases in the initial pressure, but above 1000 psig the increases in conversion are smaller.

Other data obtained by Severson and Skidmore (2) in their work on lignite are shown in Appendix A. These experiments were performed within a one-gallon autoclave.

The behavior of carbon monoxide plus water and of hydrogen in coal hydrogenation have been reported in another article by Appell, Wender, and Miller (3). They suggest that the reaction of carbon monoxide and water to solubilize low rank coal results from: 1) hydrogenation with activated hydrogen generated by the water gas shift reaction between CO and H₂O, 2) the introduction of alkyl groups, and 3) the ability of carbon monoxide to produce some kinds of bond or to prevent condensation reactions which lead to benzene-insoluble materials.

The major purpose of the present research was to investigate the relative effects of different operating conditions and to determine the optimum operating conditions.

DESCRIPTION OF EQUIPMENT

The reaction was carried out in a microautoclave reactor with approximately one gram samples of lignite.

The equipment used in the present research work was essentially the same as that of Desai (4) and Yuan (5). The equipment is shown in Figure 1. The only modification was that the 1/16 in. stainless steel rod which was placed inside the reactor was removed.

The apparatus consisted of a main reactor, heater, shaker-vibrator, pressure gauge, and temperature recorder.

The main reactor was a stainless steel tube, 9/16 in. o.d., 5/16 in. i.d., 6 in. in length, and 8 ml. in internal volume.

The pressure gauge was connected to the reactor by a stainless steel tubing, couplings, and nipples which were designed for 15,000 psig at 100°F and were supplied by Autoclave Engineers, Inc.

The heater was a 1.5 in. i.d. and 8 in. long pipe; wound around the outside of the pipe was a heater coil controlled by a variable transformer. The assembly was insulated with a 1.5 in. magnesia layer.

The whole assembly was attached to a shaker-vibrator¹ which produced vertical and lateral gyratory agitation. The shaker-vibrator was driven by an electric motor and controlled by a rheostat.

¹Manufactured by Central Scientific Co.

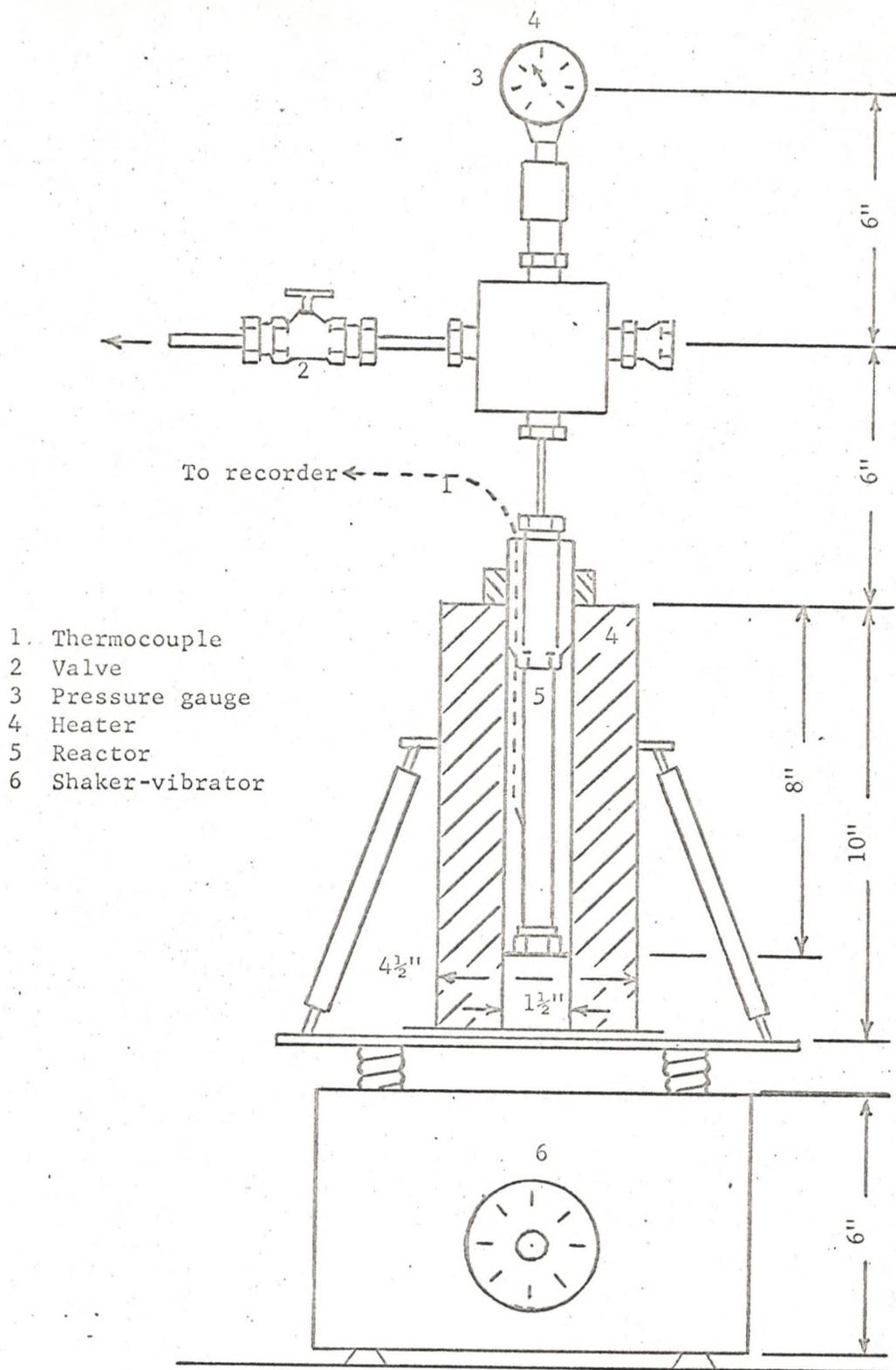


Figure 1--Schematic diagram of reactor assembly.

By Desai (4), "Thermal Dissolution of Lignite Under Hydrogen Pressure," M.S. Thesis, University of North Dakota (1969), p. 13.

A chromel-alumel thermocouple was soldered to the outside wall of the reactor, 2 in. from the bottom of the tube, and connected to a Honeywell temperature recorder.

Desai (4) showed that the difference between the external temperature and the internal temperature was not more than 10°F at reaction temperature.

MATERIALS TESTED

Lignite from Velva mine, Ward County, North Dakota, was used in the present work. The lignite was pulverized to minus 200 mesh, sealed in the jar, and kept in a refrigerator to prevent loss of moisture. The proximate analysis of the lignite is shown in Appendix B.

Demineralized water was used and the carbon monoxide was obtained from a commercial supplier¹ in a tank at 1500 psig, and was used directly from the tank.

¹The Matheson Co., Inc., East Rutherford, New Jersey.

EXPERIMENTAL PROCEDURES

The reactor was charged with pulverized lignite (about 0.6 gram on MAF¹ basis) and with demineralized water in the desired ratio by weight. After sealing, the reactor was pressurized to the desired initial pressure with carbon monoxide and held at room temperature for one hour to test for leakage by observation of the constancy of pressure. The reactor was then inserted into the heater assembly, heated to the desired temperature and maintained at that temperature for the specified reaction time.

The vibrator-shaker speed was set at No. 2 rheostat position, and operated intermittently for 5 minutes of every 10 minutes. The vibrator was operated periodically in order to minimize the possibility of leakage. Yuan (5) had investigated two otherwise identical runs with hydrogen, and found that there was no noticeable difference in results between shaking continuously and shaking for 5 minutes out of every 10 minutes. The pressure was recorded at 10 minute intervals during the reaction period.

After the desired reaction time, the reactor was removed from the heater assembly, cooled to room temperature, and the pressure was released slowly. The reacted material was washed from the reactor into 500 ml. beaker with about 300 ml. of benzene.

¹Moisture- and ash- free

The material collected and the benzene were boiled together for 30 minutes, and then the mixture was vacuum filtered through an asbestos mat on a gooch crucible. The crucible containing the residue was dried at 110°C for 30 minutes and weighed.

Sample calculations and a typical temperature-pressure history of a run are shown in Appendix C.

DESIGN OF EXPERIMENTS

The Greco-Latin square with four independent variables was used for the basic experimental design.

Using the Greco-Latin square design, the four independent variables can be tested with the same number of experiments as two variables ordinarily require. The design also provides sufficient degrees of freedom to give a low critical value of "F" for error factor estimate.

The details of Greco-Latin square design can be found in previous publications. (6, 7, 8, 9, 10)

The present experimental design is a 4-by-4 Greco-Latin square. This is developed from the Latin square in which Greek and Latin alphabets are used, each individually becoming a Latin square such that each letter of one alphabet occurs with each letter of the other alphabet just once. Thus, each of the 16 blocks contained a different combination of the four experimental variables. Each level of each variable occurred only once in each row and in each column.

The initial pressures were assigned as the row factors, reaction temperatures as column factors, the ratio of water to lignite as Greek letters, and the time of reaction as Latin letters, as shown in Table 1.

The order of performance of the total 16 tests was randomized to minimize the possibility of bias due to unavoidable changes in conditions with time.

TABLE 1

DESIGN OF GRECO-LATIN SQUARE FOR SOLUBILIZATION
OF LIGNITE WITH CARBON MONOXIDE AND WATER

ROW-VARIABLE LEVEL	COLUMN-VARIABLE LEVEL			
	I	II	III	IV
1	A α (6)	B β (14)	C γ (2)	D δ (10)
2	B δ (3)	A γ (7)	D β (1)	C α (4)
3	C β (12)	D α (5)	A δ (15)	B γ (16)
4	D γ (11)	C δ (13)	B α (9)	A β (8)

TABLE 2

LEVELS AND CODING OF VARIABLES

TEMPERATURE		INITIAL PRESSURE OF CO		WEIGHT RATIO OF WATER TO MAF LIGNITE		TIME OF REACTION	
°C	Code	psig	Code	Ratio	Code	Minutes	Code
380	I	900	1	3	α	140	A
460	II	1200	2	1	β	20	B
420	III	1500	3	2	γ	60	C
340	IV	600	4	4	δ	100	D

The actual order of performance is indicated in each block of Table 1 with a number in a circle.

EXPERIMENT RESULTS

The per cent solubilization was calculated from the weight of MAF residue retained on the crucible filter-mat and weight of MAF lignite charged as follows:

$$\text{Per cent solubilization} = \left(1 - \frac{\text{Weight of MAF Residue}}{\text{Weight of MAF Lignite}}\right) \times 100\%$$

The per cent solubilization from the reaction of lignite with carbon monoxide and water for each of the 16 tests in the designed experiment is given in Table 1.3

After the designed experiment had been completed, further tests were made to explore the effect of specific operating variables in the vicinity of the maximum solubilization obtained in Run 13. In these experiments, results of which are shown in Table 3⁴ and plotted in Figure 2, the conditions of Run 13 were used except that values of one variable immediately above or immediately below that giving the maximum solubilization were used. In separate series of experiments, changing one variable at a time, the maximum solubilization was found to occur at 600 psig, 460°C, 60 minutes reaction time, and a water-lignite ratio of 4:1.

TABLE 3

PER CENT SOLUBILIZATION OF LIGNITE WITH CARBON MONOXIDE AND WATER

RUN	TEMP. °C	INITIAL PRESSURE psig	MAXIMUM PRESSURE psig	WEIGHT RATIO OF WATER TO MAF LIGNITE	TIME minutes	SOLUBILIZATION per cent
1	420	1200	2900	1	100	33.7
2	420	900	2860	2	60	35.0
3	380	1200	2600	4	20	36.5
4	340	1200	2350	3	60	30.6
5	460	1500	3950	3	100	43.5
6	380	900	2620	3	140	42.7
7	460	1200	3680	2	140	43.4
8	340	600	1600	1	140	31.4
9	420	600	2500	3	20	42.2
10	340	900	2000	4	100	32.5
11	380	600	1800	2	100	41.5
12(1)	380	1500	3010	1	60	36.3
12(2)	380	1500	3210	1	60	36.7
13(1)	460	600	2850	4	60	48.5
13(2)	460	600	2400	4	60	45.6
14	460	900	2750	1	20	39.1
15	420	1500	3800	4	140	43.1
16	340	1500	2580	2	20	23.3

TABLE 4

PER CENT SOLUBILIZATION OF LIGNITE WITH CARBON MONOXIDE AND WATER

RUN	TEMPERATURE °C	INITIAL PRESSURE psig	WEIGHT RATIO OF WATER TO MAF LIGNITE	TIME minutes	SOLUBILIZATION per cent
17	460	300	4	60	30.2
18	460	900	4	60	44.6
21	460	600	3	60	42.1
22	460	600	6	60	34.9
23	420	600	4	60	44.1
24	500	600	4	60	41.9
26	460	600	4	100	46.0
27	460	600	4	20	42.4

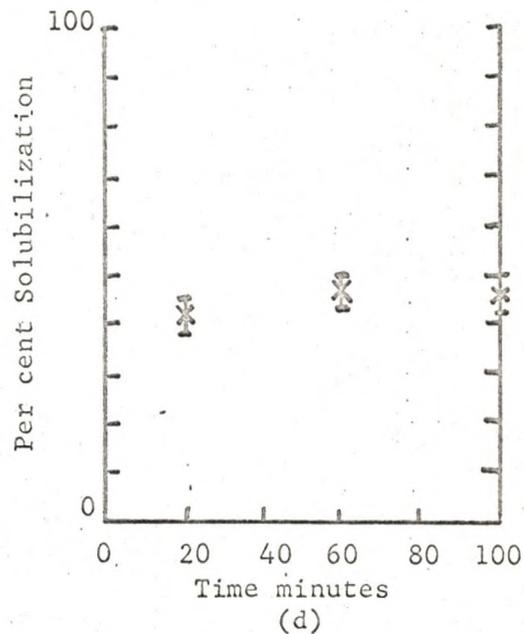
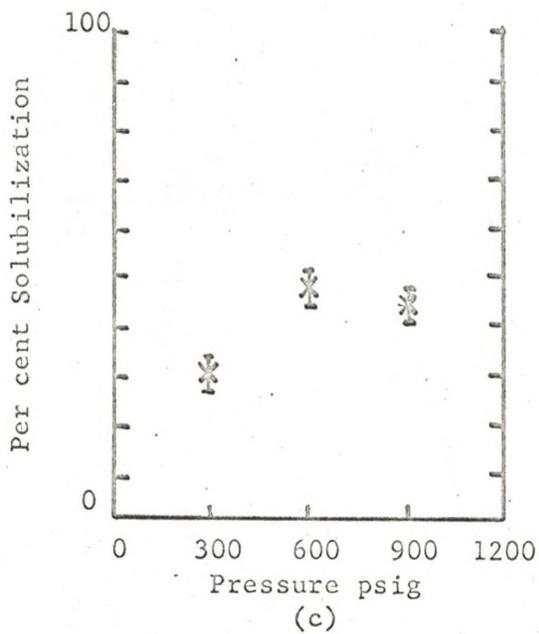
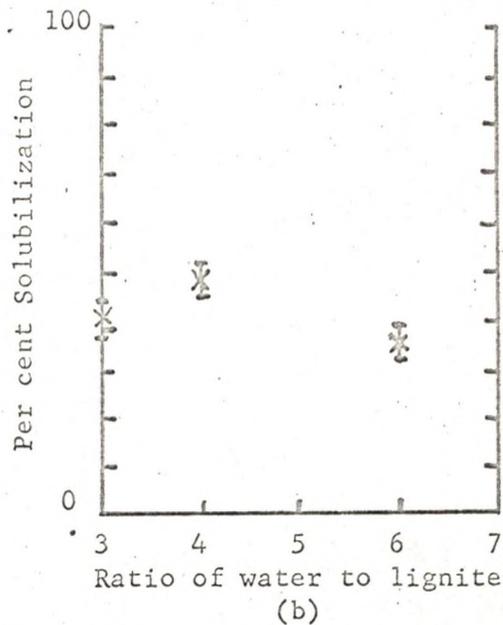
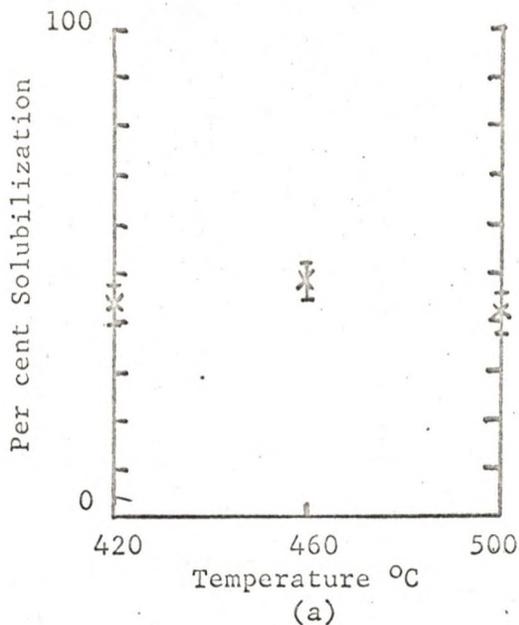


Figure 2--Effect of independent variables on lignite conversion

DISCUSSION OF RESULTS

Statistical Analysis:

In this designed experiment, the mean square of the variables is not only an estimate of the variable effect σ_i^2 (where i indicates the variable i) but also an estimate of the random population variance (σ_e^2). Consequently, the calculated F- value is the ratio of mean square of the variable to the mean square of the error factor.

If the calculated F- ratio is larger than a critical F at the significant level selected, then the variable effect (σ_i^2) is significant.

The calculated value of each of the four dependent variables is compared to the critical F- value at the selected significance level having 3 and 3 degrees of freedom.

Analysis of Variance:

The Analysis of Variance Table is shown in Table ⁵ A, and the calculations are in Appendix D.

Tests of significance at 99- and 95- per cent confidence levels were selected for the four independent variables.

This analysis of variance indicates that the temperature of the reaction has a highly significant (99-per cent confidence level) effect on the solubilization of lignite with carbon monoxide and water. It also indicates that the other three independent variables, i.e.,

TABLE 5
ANALYSIS OF VARIANCE TABLE FOR
GRECO-LATIN SQUARE DESIGN

SOURCE	SS ^a	DF ^b	MS ^c	CALCULATED F	CRITICAL F		ESTIMATED MS
					0.05	0.01	
Temper- ature	423.314	3	141.105	101.51	9.28	29.5	$\sigma_e^2 + 4 \sigma_{temp}^2$
Initial Pressure	58.012	3	19.337	13.91	9.28	29.5	$\sigma_e^2 + 4 \sigma_{press}^2$
Reaction Time	47.429	3	15.810	11.37	9.28	29.5	$\sigma_e^2 + 4 \sigma_{time}^2$
Ratio of Water to Lignite	81.724	3	27.241	19.60	9.28	29.5	$\sigma_e^2 + 4 \sigma_{ratio}^2$
Residual	4.169	3	1.3897				σ_e^2
Total	614.648	15					

^aSum of Squares

^bDegree of Freedom

^cMean Squares

initial pressure of carbon monoxide, ratio of water to lignite, time of reaction, as well as the temperature are significant at the 95- per cent confidence level.

The most significant effect is temperature; the second is the weight ratio of water to lignite, then the initial pressure of carbon monoxide, and the least significant effect is the time of reaction.

The mean square of residual term includes experimental error and possible interactions.

The low residual sum of squares (4.169) compared with sum of squares of main effects plus residual sum of squares, indicates that most of the variance can be attributed to the main effects. It would be expected that the mean square due to replication would be lower, as the estimate includes possible interactions.

Assuming little or no interaction between main effects, the 95-per cent confidence interval for error is $\pm 3.8^1$ per cent solubilization for one measurement, which is considered reasonably low for this type of experimental work.

Optimum Operating Conditions:

The optimum operating conditions of temperature, weight ratio of water to MAF lignite, initial pressure, and time of reaction are 460°C, .4, 600 psig, and 60 minutes, respectively.

¹The 95-per cent confidence interval for error is $\pm t_{0.025(3)} \times \sqrt{\frac{SSE}{4}}$, where $t_{0.025(3)} = 3.182$, SSE = sum of square of error = 4.169.

As shown in Figure 2(a), a maximum conversion of lignite to benzene-soluble and volatile materials was obtained at 460°C. The decrease in conversion above the optimum temperature is probably due to the production of insoluble materials, coking, and polymerization.

The initial pressure of carbon monoxide and the ratio of water to lignite also have yield maxima.

All these independent variables reach optima at conditions similar to those reported by Appell and Wender (1), who used solvents in most of their experiments. The optimum values of per cent solubilization are considerably lower for this work than those reported by Appell and Wender. The data obtained by Severson and Skidmore (2) indicate significantly higher solubilization than the present work, but maxima under similar conditions. These differences can be attributed to the different apparatus and experimental procedures which were applied to the present research work.

The ratio of the volume occupied by lignite in the reactor to the total inner volume of the reactor, the time required to heat-up and shut-down, and the maximum pressure that could be reached during the reaction which were obtainable in the reactor used in the present work are smaller than those obtained from the reactor that was used by Severson and Skidmore (2).

CONCLUSIONS

Solubilization tests on North Dakota lignite with carbon monoxide and water, using Greco-Latin square design, were performed in a microautoclave reactor.

Four selected independent variables--reaction temperature, initial pressure of carbon monoxide, ratio of water to lignite, and time of reaction--were tested at four different levels.

The following conclusions are provided by the present study:

- 1) The reaction temperature had a highly significant effect (at the 99-per cent confidence level) upon the conversion of lignite to benzene-soluble product and volatile material.
- 2) The weight ratio of water to MAF lignite was the second most highly significant effect.
- 3) All the four independent variables were significant at the 95-per cent confidence level.
- 4) The optimum reaction temperature, initial pressure of carbon monoxide, the ratio of water to lignite, and the reaction time are 460°C, 600 psig, 4, and 60 minutes. A solubilization of 48.5 per cent was obtained under these conditions.

APPENDIX A

TABLE 6

DATA ON REACTION OF LIGNITE WITH CARBON MONOXIDE AND WATER^a

RUN	WEIGHT OF COAL gram	WEIGHT OF WATER gram	MOISTURE OF COAL per cent.	INITIAL PRESSURE psig	MAXIMUM TEMPER- ATURE °F	TIME hour	PER CENT OF BENZENE EXTRACTABLE
308	350	0	36.1	1200	724	2	47.0
315	550	100	35.7	1180	725	2	46.7
320	175	100	35.0	1200	716	2	70.7
322	175	206	35.0	1200	725	2	76.2
327	125	147	34.9	1200	845	2	49.1
330	175	206	34.9	1200	672	2	55.8
331	341	13.5	34.9	1200	680	2	45.7
333	118	262	4.6	1200	725	2	76.6
334	391	33	30.5	1200	735	2	14.1
338	162.5	218.5	29.9	1200	725	4	71.7
339	115.5	156.5	29.9	1200	835	0.1	57.8
340	162	219.0	29.9	1200	680	4	73.1
341	100	135	29.9	1200	950	0.1	30.7
342	161.5	269	29.7	900	725	2.1	69.5
343	161.5	369	29.7	600	723	2	53.1

^aData from Severson and Skidmore¹⁰

APPENDIX B

TABLE 7

PROXIMATE ANALYSIS OF LIGNITE^a

PROXIMATE ANALYSIS	Moisture	Volatile Matter	Fixed Carbon	Ash
Per cent Content	30.4	31.7	32.4	5.5

^aLignite from Velva mine, Ward County, North Dakota

APPENDIX C

TABLE 8

SAMPLE CALCULATIONS AND A TYPICAL TEMPERATURE
PRESSURE HISTORY OF A RUN

Run No.: 15
Initial pressure of CO: 1500 psig
Reaction temperature: 420°C
Ratio of water to lignite: 4
Time: 140 Minutes

Time in Minutes	Temperature Degree F	Pressure psig
0	90	1500
10	320	1600
20	680	2200
30	790	3580
40	790	3510
50	788	3600
60	786	3680
70	785	3680
80	784	3650
90	786	3700
100	780	3700
110	788	3750
120	785	3750
130	793	3760
140	788	3800
150	788	3780
160	786	3880
170	780	3800

Complete Sample Calculation: Run No. 15.

Weighing bottle + lignite	18.4271 g
Weight of weighing bottle	<u>17.4855 g</u>
Weight of lignite	0.9416 g
Weight of dropper + water	7.3328 g
Weight of dropper	<u>5.1951 g</u>
Weight of water	2.1277 g
Weight of crucible + residue	21.5747 g
Weight of crucible	<u>21.1798 g</u>
Weight of residue	0.3949 g

Moisture (30.485%): $0.9416 \times 0.30458 = 0.2864$ (g)

Ash (5.465%): $0.9416 \times 0.05465 = 0.0515$ (g)

Lignite (MAF):

0.9416 g
-0.2864 g
<u>-0.0515 g</u>
0.6033 g

Residue (MAF):

0.3949 g
<u>-0.0515 g</u>
0.3434 g

Percent solubilization = $(1 - \frac{0.3434}{0.6033}) \times 100\%$
 $= \frac{0.2599}{0.6033} \times 100\%$
 $= 43.08\%$

APPENDIX D

CALCULATIONS OF ANALYSIS OF VARIANCE

Row total:

900 psig: 149.22
 1200 psig: 144.16
 1500 psig: 146.15
600 psig: 163.60
 Grand Total: 603.13

Column total:

380° C: 157.01
 460° C: 174.34
 420° C: 154.00
340° C: 117.78
 Grand Total: 603.13

Latin total:

140 Min.: 160.56
 20 Min.: 141.10
 60 Min.: 150.31
100 Min.: 151.16
 Grand Total: 603.13

Greek total:

1: 140.54
 2: 143.07
 3: 158.95
4: 160.57
 Grand Total: 603.13

$$(\text{Grand Total})^2 = (603.13)^2 = 363765.7969$$

$$\begin{aligned} \sum (\text{Row total})^2 &= (149.22)^2 + (144.16)^2 + (146.15)^2 + (163.60)^2 \\ &= 91173.4965 \end{aligned}$$

$$\sum (\text{Column total})^2 = 92634.7041$$

$$\sum (\text{Latin total})^2 = 91131.1653$$

$$\sum (\text{Greek total})^2 = 91268.3439$$

$$\frac{(\text{Grand Total})^2}{16} = 22735.362$$

$$\sum_{i=1}^{16} (X_i)^2 = (42.7)^2 + \dots + (31.42)^2 = 23350.0101$$

Calculations of sum of square:

$$\begin{aligned} \text{Column sum of square} &= \frac{\sum (\text{Column total})^2}{4} - \frac{(\text{Grand Total})^2}{16} \\ &= \frac{92634.7041}{4} - 22735.362 \end{aligned}$$

$$= 423.314$$

$$\text{Row sum of square} = \frac{\sum (\text{Row total})^2}{4} - \frac{(\text{Grand Total})^2}{16}$$

$$= \frac{91173.4965}{4} - 22735.362$$

$$= 58.012$$

$$\text{Latin sum of square} = \frac{\sum (\text{Latin total})^2}{4} - \frac{(\text{Grand Total})^2}{16}$$

$$= \frac{91131.1653}{4} - 22735.362$$

$$= 47.429$$

$$\text{Greek sum of square} = \frac{\sum (\text{Greek total})^2}{4} - \frac{(\text{Grand Total})^2}{16}$$

$$= \frac{91268.3439}{4} - 22735.362$$

$$= 81.724$$

$$\text{Total sum of square} = \frac{\sum_{i=1}^{16} (x_i)^2}{16} - \frac{(\text{Grand Total})^2}{16}$$

$$= 23350.0101 - 22735.362$$

$$= 614.648$$

$$\text{Error sum of square} = \text{Total sum of square} - (\text{Row SS} + \text{Column SS} + \text{Latin SS} + \text{Greek SS})$$

$$= 4.169$$

REFERENCES

1. Appell, H. R. and Wender, I., 156th National Meeting, American Chemical Society, Fuel Division Preprints, Vol. 12, No. 3, 220 (1968).
2. Severson, D. E., Skidmore, D. R., Unpublished data on reaction of lignite with CO and H₂O., Chemical Engineering Department, University of North Dakota, n.d.
3. Appell, H. R., Wender, I., and Miller, R. D., 158th National Meeting, American Chemical Society, Fuel Division Preprints, Vol. 13, No. 4, pp. 39 (1969).
4. Desai, S. N., "Thermal Dissolution of Lignite under Hydrogen Pressure," M.S. Thesis, University of North Dakota, June, 1969.
5. Yuan, K. C., "Solubilization of Lignite under Hydrogen Pressure in Various Organic Solvents," M.S. Thesis, University of North Dakota, June, 1969.
6. Wine, R. L., Statistics for Scientists and Engineers, pp. 434-444, N.J.: Prentice-Hall, Inc., 1964.
7. Li, C. C., Introduction to Experimental Statistics, pp. 189-206, New York: McGraw-Hill Book Company, 1964.
8. Fisher, R. A., The Design of Experiments, pp. 70-92, New York: Hafner Publishing Company, Inc., 1960.
9. Cox, D. R., Planning of Experiments, pp. 205-218, New York: John Wiley & Sons, Inc., 1958.
10. Kempthorne, O., The Design and Analysis of Experiments, pp. 184-205, New York: John Wiley & Sons, Inc., 1952.