Reduction of subbituminous coal with carbon monoxide and water
by Dat Nguyen

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY in Chemical Engineering
Montana State University

Abstract:
This research studied the effects of temperature, pressure and the type and concentration of a selected number of solvents and catalysts on the reduction of Colstrip (Montana) subbituminous coal through the use of carbon monoxide and water. The reactor was a 500-cc rocking autoclave. Conversion was calculated based on the amount of moisture-and ash-free coal that was converted into benzene-soluble products in a run.

The operating time--during which the autoclave was maintained at the final temperature--was fixed at 5 minutes. Temperatures under investigation ranged from 300 to 475 °C and the initial pressure, from 1000 to 1500 psi.

The conversion, varying with the individual coal batch as well as with the time of storage, was close to zero at 300 °C but increased steeply as long as the temperature was raised. Increasing the initial carbon monoxide pressure also resulted in drastic increases in conversion, but the pressure effect became less significant as the 1500 psi region was approached.

Of the six solvents studied (decalin, tetralin, naphthalene, anthracene, phenanthrene and FMC coal tar), phenanthrene was found to perform best. When present at a 2:1 weight ratio with respect to coal, phenanthrene resulted in conversions twice as high as those of runs without any solvent. Among the five catalysts investigated.(sodium formate, sodium bicarbonate, sodium carbonate, ferric oxide and stannous chloride), the bicarbonate appeared most promising, raising the conversion by about 10 percentage points when present at a ratio of 1:100 with respect to coal.

Less than 5 per cent of the converted coal went into the gas phase as methane and ethane. The remainder was a tar having a H/C ratio of about 1.1, a sulfur content close to 0.3 per cent and' an ash content of about 0.1 per cent. Preliminary estimates for a plant to produce the tar yielded production costs ranging from 50 to 90 cents per million Btu's worth of tar, depending upon the plant capacity and the total direct cost employed.

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I. INTRODUCTION

That we are today facing an increasingly grave shortage of energy has been reiterated often enough by authoritative voices (4,12). To meet this upcoming crisis, a great deal of effort has been devoted to the development of latent and yet more abundant energy from the sun, the atom and the traditional family of fossil fuels, of which coal is the most voluminous member (4,13).

The great abundance of coal, together with the ever-increasing cost of fuel, have of late caused much attention to be turned again to coal conversion technology, and more specifically to the gasification and liquefaction of coal (12,15). The present research on the batchwise reduction of Colstrip (Montana) subbituminous coal using carbon monoxide and water is a small part of this general effort to develop cleaner and affordable fuels from low-rank coals.

It is hoped that the information gained on the behavior of this particular--and yet to be popular--process will encourage additional studies on a larger scale, leading to more detailed knowledge which can some day be successfully applied to the conversion of our vast low-rank coal reserves.

II. TECHNICAL BACKGROUND

A great deal of research and development work on coal hydrogenation has been carried out in various countries in the past fifty years, resulting in a large volume of literature on the subject. These many research projects and their results have been ably summarized by various authors (5,27).

The question one may ask at this point is then: Why further studies on coal hydrogenation? In order to answer this, it is necessary to look at some of the more technical aspects of coal hydrogenation in the past and see how these aspects affect the present state-of-the-art.

From the patented process by Bergius, conceived in 1913, to its eventual modification and adaptation to large scale production during World Was II by Germany, the principle behind coal hydrogenation had been merely to break up the coal "molecules" into reactive fragments and subject the latter to the presence of hydrogen, supplied from outside sources, for hydrogenation through a number of steps.

Only four of the eighteen coal hydrogenation plants in Germany still operated after World War II because the process was extremely expensive, largely from the high cost of generating hydrogen (27).

Besides these large scale operations in Germany, a must at the time because of the country's war-time fuel shortage, much additional

research had been carried out at research institutions in France, Japan, Germany, Great Britain, the Soviet Union and the United States. These works involved studies on the effects of pressure, temperature, various catalysts and solvents, and have been well summarized by Donath (5).

Despite all these efforts, no major breakthrough has been made, and the use of hydrogen from an outside source remains to this day a main feature. Hence the continued high cost of coal hydrogenation.

From these observations, it is only too clear that drastic changes in major concepts regarding coal hydrogenation must be made if the latter is to be more economically attractive. This is explained clearly by the Chief of the Division of Coal, Energy Research, U.S. Bureau of Mines, Dr. G. A. Mills (11), who in the same article enumerates a number of new ideas on coal hydrogenation, presently considered to be of great significance by Bureau of Mines scientists. Among these ideas is the use of water and carbon monoxide in coal reduction.

The main difference between the carbon monoxide-water approach and the ordinary approach to coal hydrogenation is that in the former case, the hydrogen does not come from an outside source. Instead, it is supplied by the water-gas "shift" reaction

$$CO + H_2O = H_2 + CO_2,$$

to take place directly in the hydrogenation reactor. With the elimination of the expensive hydrogen generation step, this simpler scheme should result in large cost reductions. It is worth noting that for

this particular approach, the carbon monoxide would come, say, from a synthesis gas generator using the unconverted char, or from the reaction between the latter and the CO_2 from the shift reaction

$$C + CO_2 = 2CO,$$

thereby making the process CO self-sufficient.

Although the idea of using carbon monoxide and water in coal reduction was conceived as early as in the 1920's (7), published works on the approach have been scarce. Interest in it was renewed only after some sketchy but encouraging results were reported by Bureau of Mines scientists in 1968, showing a remarkable increase in conversion with the CO-water approach over that with the hydrogen approach on the hydrogenation of North Dakota and Texas lignites (1). In particular, these authors reported a striking 89 per cent conversion in the hydrogenation of North Dakota lignite for only 10 minutes at 380 °C.

Additional research has since been carried out by the Bureau, which reported further findings on the CO-water approach in the 1971 North Dakota Lignite Symposium (2). Their results showed a significantly faster conversion rate when CO was used. Regardless of the solvent and the operating time, highest conversions always resulted from runs made at 380-400 °C final temperature. Conversion up to 95 per cent was obtained during a 2-hour operating time at 380 °C. In the same paper, the authors hypothesized the formation and decomposition of alkaline metal formates as possible intermediate steps in coal reduction reactions.

At Montana State University, research to adapt the CO-water approach to Montana coals began in 1969. The effects of temperature, pressure, mode of coal grinding and various solvents on the conversion of a number of North Dakota lignites and Montana subbituminous coals were briefly investigated to yield support data for a number of designs of coal hydrogenation plants (28).

Although the economics of these proposed designs appear promising, it was felt that by additional, systematic studies of the various process variables involved, significant improvements in conversion could still be made, giving a more accurate and more realistic process picture, helpful not only to future economic analyses but also to the operation of future larger, pilot-plant types of equipments should commercialization be eventually visualized.

III. RESEARCH OBJECTIVE

The objective of this research was to study the effects of

1. Temperature,
2. Pressure,
3. The type and concentration of a selected number of solvents,
4. The type and concentration of a selected number of catalysts

on the batchwise, short operating time reduction of Colstrip (Montana) subbituminous coal via the water-gas "shift" reaction between carbon monoxide and water.

The ultimate aim of these studies was to arrive at the most suitable operating conditions based on which

1. More realistic and detailed economic analyses of the process could be made in the future,
2. Provisions for the construction and operation of pilot-plant scale equipment for the process could be obtained.

IV. MATERIALS, EQUIPMENT, AND PROCEDURE

A. Materials The materials to be used in each run were subbituminous coal, the solvent, the catalyst, water and carbon monoxide.

1. Coal and Analyses of Coal The subbituminous coal was obtained specifically from the Colstrip mine in Eastern Montana, a part of the Fort Union coal formation. The proximate, ultimate and ash analyses of the coal are given in table 1. It is worth noting that the values shown in this table are average values and often tend to be misleading. For example, it was found that 30-gram samples from any one, say, 20-pound chunk of coal could differ considerably in ash contents, as typified in the following table:

Sample number	Per cent ash
163	9.4
165	7.3
167	6.0
169	7.9
171	8.1

These variations presented great difficulties in the interpretation of moiture- and ash-free (m.a.f.) conversion data, especially when, in order to avoid the considerable loss of water and severe oxidation in the coal due to prolonged periods of exposure to air, it was not possible to obtain completely uniform samples by grinding up at any one time an amount of coal large enough for a series of runs. To remedy this in the later experiments, an ash analysis had to be made with each run.

TABLE 1. Analyses for Colstrip Subbituminous Coal (28).

Proximate Analysis

Moisture	23.9%
Volatile matters	30.9
Fixed carbon	37.6
Ash	7.6

Ultimate Analysis

Moisture	23.9
Carbon	50.3
Hydrogen	3.4
Nitrogen	0.7
Sulfur	0.4
Oxygen	13.7
Ash	7.6

Ash Analysis

SiO_2	36.4
Al_2O_3	17.6
Fe_2O_3	4.6
TiO_2	0.4
P_2O_5	0.8
CaO	22.7
MgO	9.4
Na_2O	0.3
K_2O	0.5
SO_3	14.9

The merit of this additional step will be discussed in Part V. The ash content determination was done by heating up a ground coal sample in a covered porcelain crucible. The heating was slow at first to prevent other materials from being carried away along with the volatile matter, then was accelerated until the crucible became red hot. Combustion of the sample was complete when the weight of the crucible became constant. The per cent of ash was defined as 100 times the ratio of the weight of the non-combustible materials to that of the original coal sample.

As the coal lost approximately 1.5 per cent of its water per month of storage, this water was determined monthly to ensure accuracy in the calculation of the m.a.f. conversion. In a water test, the ground coal sample was distilled with toluene, the water volume in the condensed two-phased distillate being read off on a graduated distillate trap.

2. Solvent The purpose of the solvent is to dissolve the organic matter in coal, making it more susceptible to attack by the available hydrogen. In order to be effective, therefore, a solvent should have a molecular structure similar to those of the organic compounds constituting coal. From the basic conjecture that coal contains organic clusters of compounds having two, three or four aromatic rings (5), the following chemicals were selected for testing: decalin, tetralin, naphthalene, anthracene, phenanthrene and FMC coal tar. The structural formulae for the first five chemicals are shown in figure 1. The structure of FMC coal tar, a product of FMC Corporation's COED (Char-Oil-

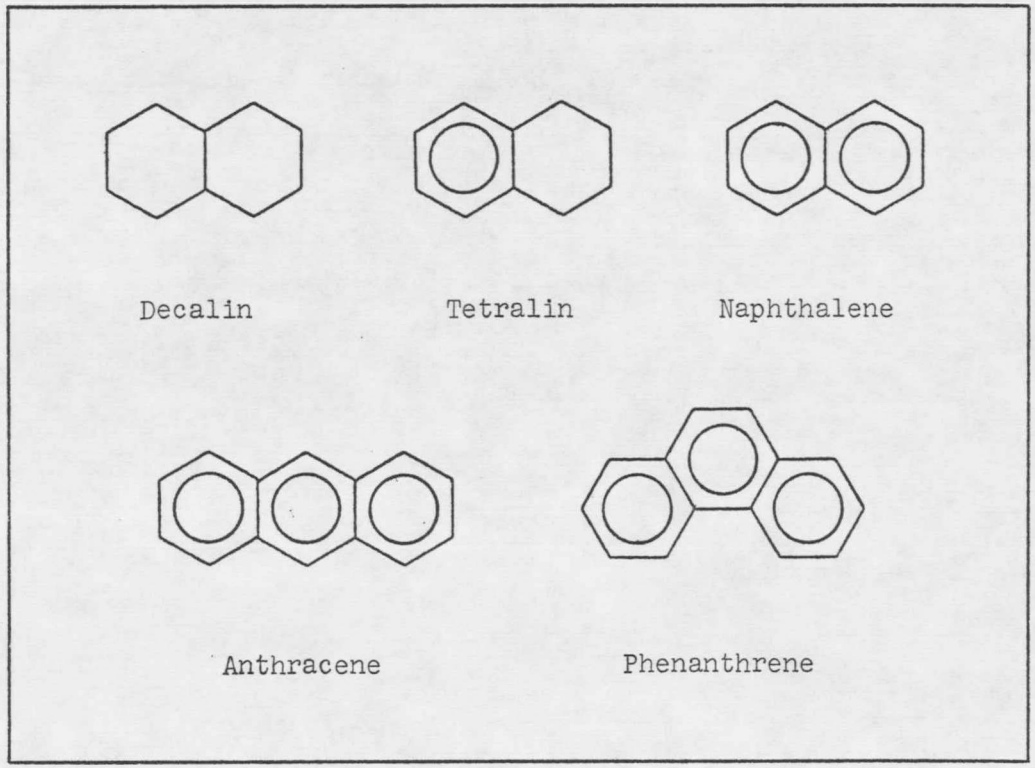

FIGURE 1. Structural Formulae of Tested Solvents.

Energy-Development) process (8), is not known.

Figure 1 does not show any four- or five-ring compounds, which were not tested because of their high melting points. Nitrogen-based compounds such as isoquinoline, which have been shown to be quite effective (2), were not included due to environmental problems that are conceivable in the large scale application of the process.

Except for the naphthalene, available in reagent grade, and for the FMC coal tar, all the other chemicals were technical grade.

3. Catalyst For this particular process, two types of catalysts had to be tested. The first type would catalyze the hydrogen-forming reaction

$$CO + H_2O = H_2 + CO_2,$$

and the second type would catalyze the reduction and stabilization reactions between the newly-formed hydrogen and the thermally cracked coal, the reactive fragments of which now dispersed in the solvent. The following compounds were tested for catalytic effects: sodium formate, sodium bicarbonate, sodium carbonate, ferric oxide and stannous chloride.

The sodium compounds were selected because of (a) their catalytic effects on the water-gas shift reaction (28), (b) their relatively low price, which would be a must if they were to be used commercially on an once-through basis, and (c) their solubility in water, which ensured their even distribution among the reaction mass.

Ferric oxide was included also because of the well known catalytic

action of iron compounds on the shift reaction (20).

The selection of stannous chloride was based on observations elsewhere (24) that tin compounds were moderately effective as catalysts for the stabilization of the reactive coal fragments through hydrogenation reactions. Stannous chloride was also water-soluble, a desirable property not found in most tin compounds. Used at very low concentrations, the tin salt was comparable in cost to the sodium salts. And finally, the corrosiveness of $SnCl_2$ to the reactor could be expected to be negligible at these levels of concentrations.

Tin metal and other tin compounds were not used either because they were not soluble in water, which at low concentrations would have made them even more difficult to be dispersed among the reactants, or because they would conceivably cause environmental problems in large scale operations. This was also the reason for the exclusion of ammonium chloride in spite of the fact that the latter has been reported to be particularly effective when used in conjunction with tin compounds (24).

4. Carbon Monoxide Technical grade carbon monoxide was used. In order for the gas to be continually available at 1500 psi, a pressurization system was used in which CO was let flow to a high pressure cylinder where it was subjected to a decrease in volume by hydraulic oil being pumped in from an oil reservoir. From the high pressure cylinder, the CO flowed directly into the reaction autoclave (figure 2).

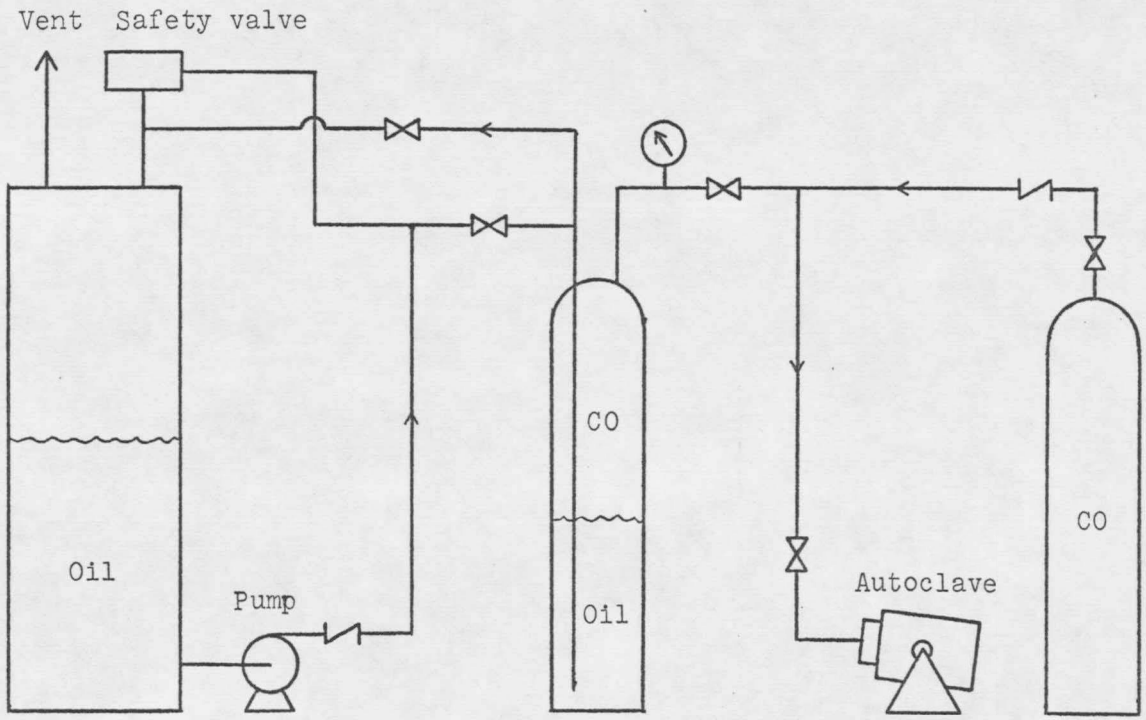

FIGURE 2. Pressurization System.

B. Experimental Procedure and Equipment Figure 3 shows the major steps taken in each run. More specifically:

1. Coal Preparation The Colstrip subbituminous coal, under storage in three-layer plastic bags or bottles as lumps approximately two inches in diameter, was hand-ground with a mortar and pestle to -40 mesh. Ball-milling enough coal for more than one run was avoided because of the adverse effects such prolonged exposure to air would cause, through oxidation and loss of water, on conversion.

It was felt that at -40 mesh, the coal would still be fine enough to be easily disintegrated further in the presence of the solvent at the high final temperature. This was in fact the case because the unconverted coal from each run was always found to be in an extremely fine powder form.

2. Charging Thirty grams of the ground coal, 30 grams of water and the appropriate amounts of solvent and catalyst were charged to the reaction autoclave. To ensure even catalyst distribution, the catalyst was first completely dissolved in the water, and the fine coal then added and allowed to soak up the solution. Where a catalyst was not water-soluble, as in the case of ferric oxide, it was manually mixed with the coal and the solvent before the addition of water. Ball-milling the catalyst with coal would have created better mixing, but was not done because of the negative effects of this type of operation on conversion, as has been previously discussed.

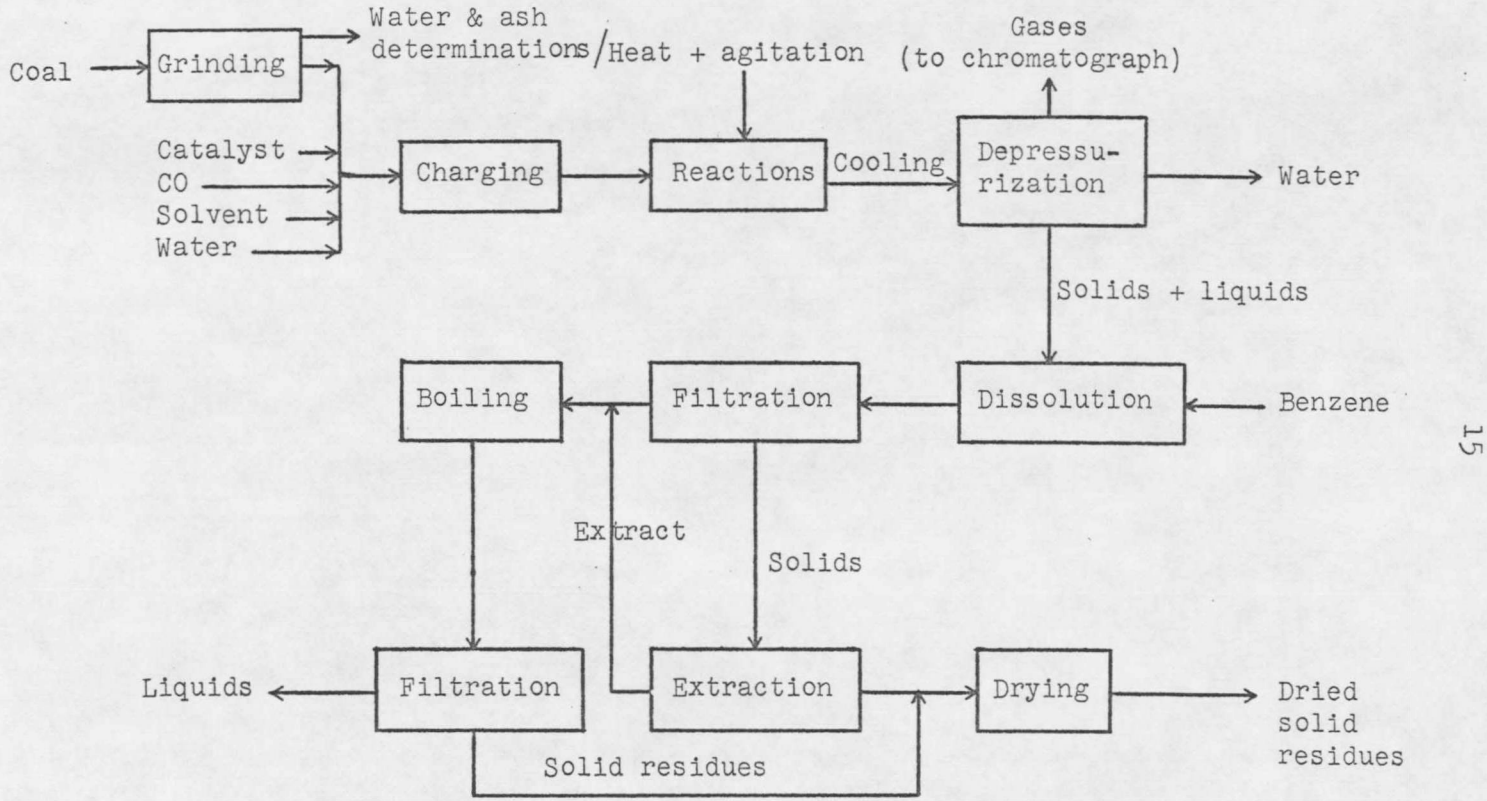

FIGURE 3. Steps for an Experimental Run.

After the addition of coal, water, catalyst and solvent, the autoclave was sealed and pressurized with carbon monoxide until the desired initial pressure--ranging from 1000 to 1500 psi--was reached.

The reaction autoclave, manufactured by Parr Instrument Company, was made of Inconel 600 (figure 4). At 500 °C, it could withstand a pressure of 7000 psi. The autoclave had a capacity of 500 cc. Its head was equipped with a breather tube connected to a pressure gage which read from zero to 10,000 psi. Between the body and the head was a copper gasket which expanded upon heating and effectively sealed the autoclave. An 8000-psi rupture disc was also installed in the head for safety purposes.

3. Reacting The reaction autoclave was brought to final temperature by heating in an electric jacket-type heater which rocked at about 36 cycles per minute at an angle of approximately 30 degrees of the horizontal. The temperature was measured by means of a thermocouple inserted through the heating jacket, touching the base of the autoclave. It took about 30 minutes for the autoclave to reach 300 °C, 45 minutes to reach 400 °C, and 55 minutes to reach 475 °C. As the temperature rose, the pressure rose accordingly to a final value three to four times the initial pressure. Figure 5 shows the temperature-pressure relationships for a number of similar runs. During the last part of the heat-up period and especially during the time the autoclave was maintained at the final temperature--the "operating time," always 5 minutes

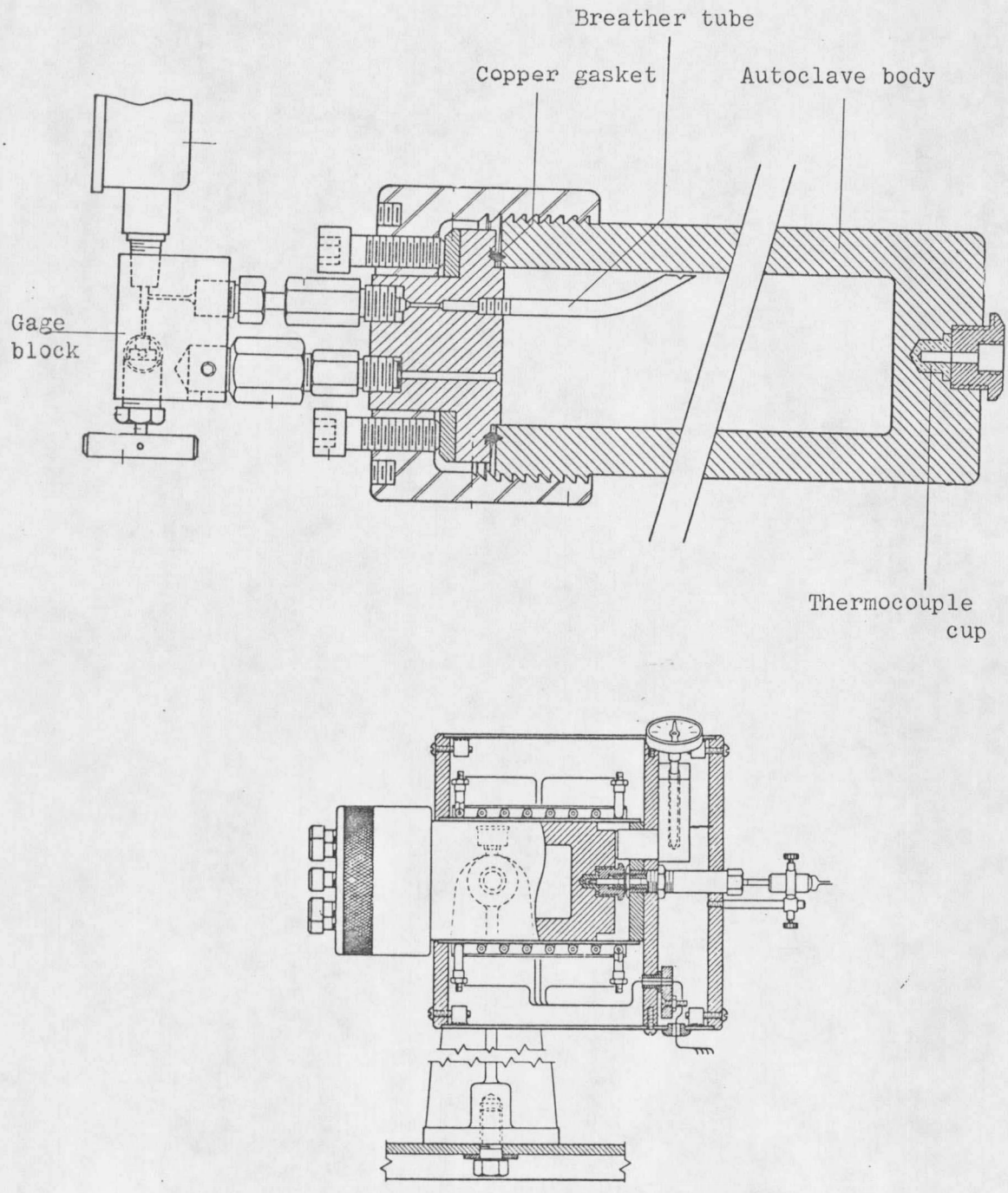

FIGURE 4. Autoclave and Heater Details.(17)

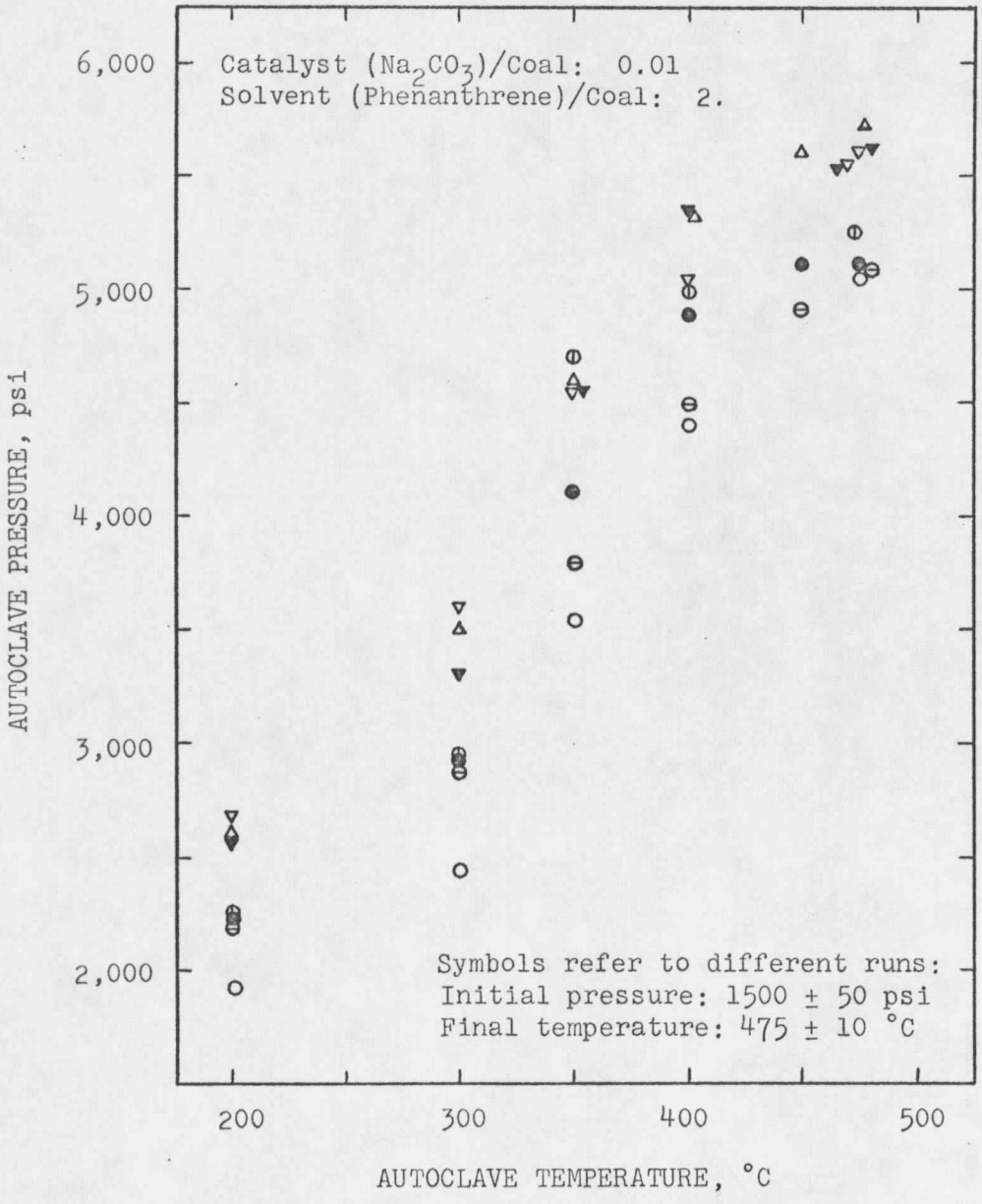

FIGURE 5. Reaction Autoclave Temperature-Pressure Relations.

unless otherwise specified--before being removed from the heater to cool in open air, the coal was dissolved and thermally cracked. The coal fragments then combined with the hydrogen formed by the water-gas shift reaction to give the final hydrogenated products.

4. Depressurization and Gaseous Products Analyses After the reactor had cooled to room temperature, it was slowly depressurized, the bled-off gas being collected in sample bottles for chromatographic analyses. The techniques for these analyses were developed by York (28). The gas's carbon dioxide and hydrocarbon contents were determined through a Porapak Q column (1/4" by 6'), and the carbon monoxide, oxygen and nitrogen through a Linde 5A molecular sieve column (1/4" by 9'). The hydrogen content was determined by difference. The chromatograph's oven temperature was 75 °C and the hydrogen carrier flow rate was 40 cc per minute, with the gas samples being 0.5 ml. One of the three standard gases was air. The second standard gas contained CO, CO_2 and H_2, and the third one contained H_2, N_2, CH_4 and C_2H_6.

5. Separation of Benzene-soluble Products After the gaseous products had been removed, the autoclave assembly was taken apart. The unreacted water, ranging from 10 to 25 grams, was poured off. The remaining mixture of the reaction products, the unconverted coal and the solvent was then dispersed in benzene.

The operation was continued with a series of filtration and extraction steps aiming at separating the benzene-soluble products

from the unconverted coal. Whatman No. 5 filter papers were used for the filtration. Each extraction with benzene as the solvent was carried out for at least 24 hours with a Soxhlet extractor and a 43 X 123 mm Whatman double-thickness cellulose extraction thimble.

C. Conversion Analysis The materials that remained behind in the extraction thimble due to their insolubility in benzene were defined as the residues. After extraction, the residues were dried at 100 °C for 12 hours. Their total weight was then determined and used to calculate the moisture- and ash-free (m.a.f.) per cent conversion, defined as

$$\frac{\text{(m.a.f. weight of original sample)} - \text{(m.a.f. weight of residues)}}{\text{(m.a.f. weight of original sample)}} \times 100.$$

D. Non-gaseous Products Analyses The extract from the extraction step was a solution of both the solvent and the converted coal in benzene. Flashing off the benzene gave a solid product which was sent to Huffman Laboratories, Inc. (Wheatridge, Colorado) to be analyzed for the hydrogen, carbon, sulfur and ash contents.

V. RESULTS AND DISCUSSION

A. Effects of Various Factors on Conversion Most of the results on conversion will be reported in the form of graphs, and some in tables. Each point on a graph is the average of two, and occasionally three or four runs. Upper and lower experimental extremities have been included to show the magnitude of the variation involved at the particular point. Where no such extremities are drawn, only one run had been made.

Since conversion depended very much on the particular batch from which the coal came and on the time the coal had been in storage (figure 6), these properties--batch name and storage time--are included with every set of data.

As mentioned in Part IV, the differences in ash content between run samples could also cause considerable errors in the calculation of the m.a.f. per cent conversion. These errors could amount up to 4 percentage points in extreme cases. In the later experiments, the ash content of every run sample was determined and used (instead of an average value) in the particular conversion calculation, but it is difficult to tell how much this procedure improved the results' accuracy because very often the errors due to the ash content were overshadowed by other errors due to variations in the ash (and again the coal) chemical compostions.

The large degree of variation at each experimental point has

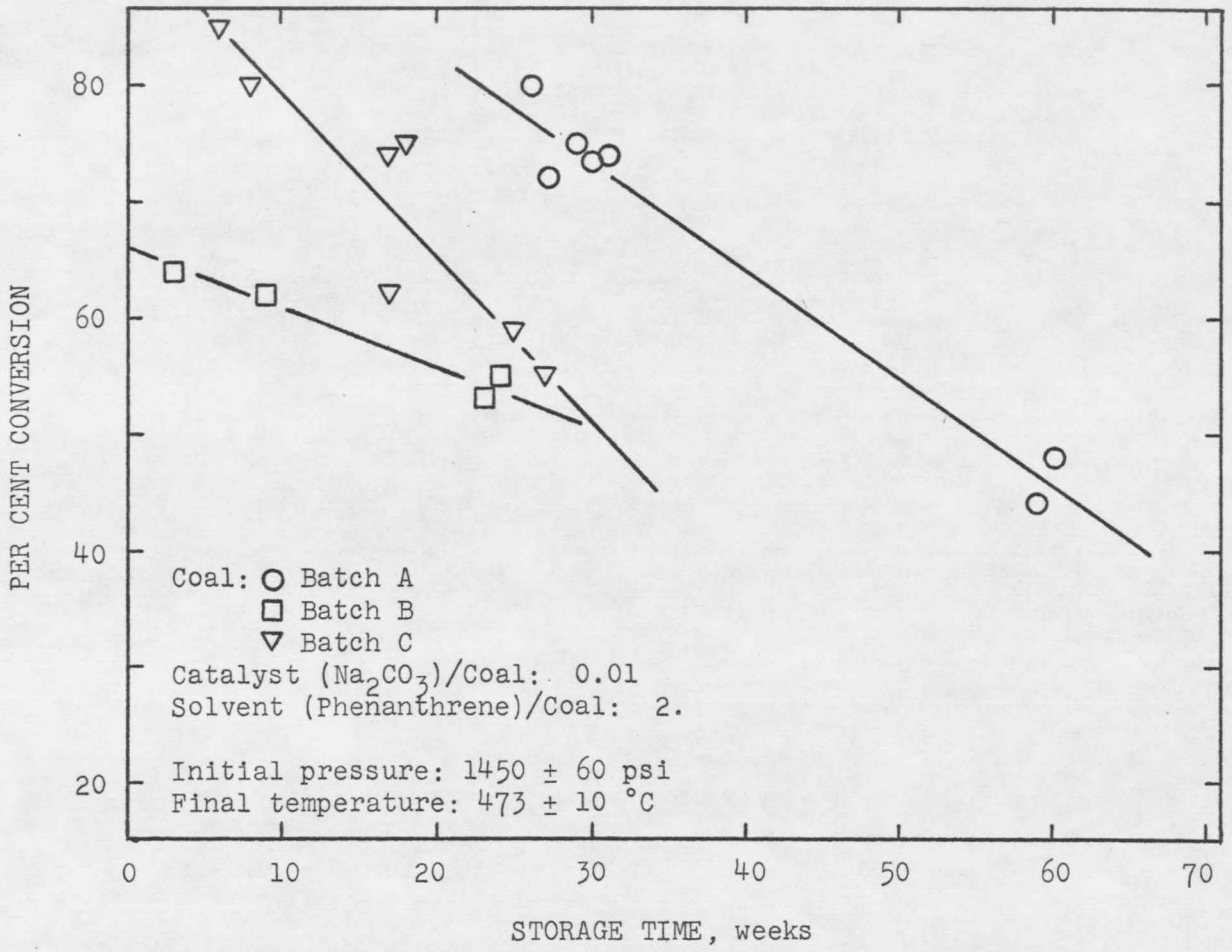

FIGURE 6. Effect of Storage Time.

necessitated statistical analyses, carried out to provide more meaningful interpretation of the results by separating experimental errors from the real effects of the particular treatment under consideration, be it temperature, catalyst concentration, or whatever else. The techniques for these simple analyses may be found in standard textbooks on applied statistical methods (16,21). The outcome of the analyses are reported together with a "significance level," denoted by the letter "α." An α of 0.05 means that there is a $100\alpha = 5$ per cent chance of concluding erroneously that there is a departure from the hypothesis that the particular treatment is non-significant--the Null Hypothesis.

Whenever there is doubt as to whether a real difference exists between any two levels of treatment in a multi-level experiment, LSD (Least Significant Difference) tests (16,21) are performed to determine if the experimentally observed difference is statistically significant.

1. Effects of Temperature and Heating Time The final reactor temperature has a significant effect on conversion. As shown in figure 7, very little of the coal was converted into benzene-soluble products when the final temperature was 300 °C, whereas at 475 °C, the conversion was over 70 per cent. Although the effects of temperature as shown are quite obvious, the difference in conversion between 400 °C and 475 °C for the sake of completeness has been computed to be very significant at $\alpha = 0.025$ (Appendix A).

At 400 °C, time does not have much effect on conversion, as

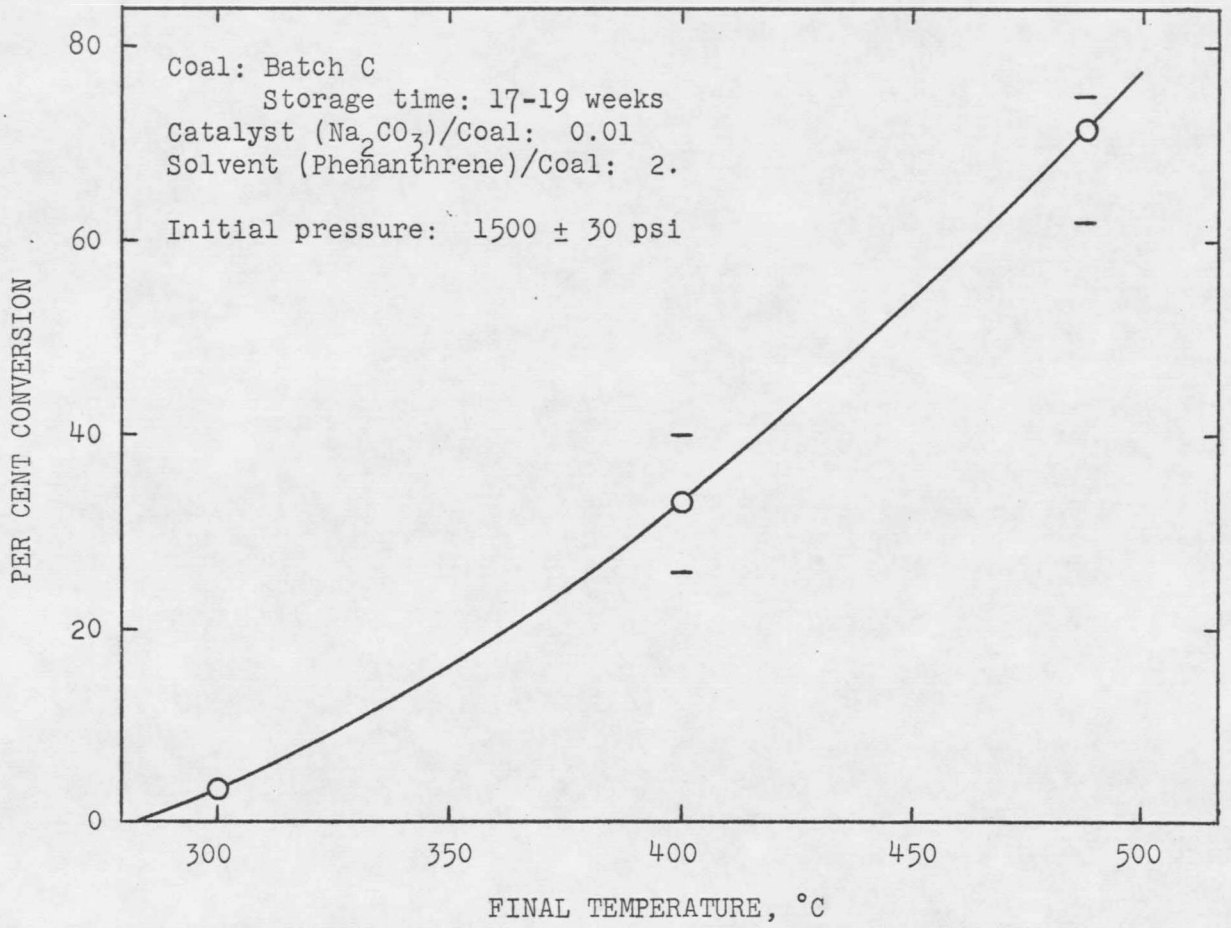

FIGURE 7. Effect of Final Temperature.

evidenced from the runs shown in table 2:

TABLE 2. Effect of Operating Time at 400 °C Final Temperature.

Operating time	% conversion
5 min.	40.
5 min.	26.
15 min.	32.

*Characteristics of runs:
Coal: Batch C
Storage time: 18-20 weeks
Catalyst (Na_2CO_3)/Coal: 0.01
Solvent (Phenanthrene)/Coal: 2.

Initial pressure: 1510 ± 40 psi.

Thus the increase in conversion in the first portion of the curve in figure 7 was due to the difference in temperature only. For final temperatures above 400 °C, however, this increase would have to be attributed partly to the heat-up time, which normally was about 10 minutes between 400 and 475 °C. This observation is important in the future design of large scale equipments because when technically feasible, arrangements could be made to bring the reactants to 400 °C in the shortest time possible without negatively affecting the conversion.

Finally, it is necessary to examine the indirect effects of temperature on conversion via pressure, which by itself has a great influence on conversion, too, as will be shown immediately. Fortunately, the

final pressures in the 400 °C runs ranged from 5300 to 5500 psi, well in the range attained in runs at the higher level of final temperature, 475 °C. From this observation, it may be safely concluded that in these ranges of operation, there is no interaction between the final temperature and pressure, and consequently the effect of the latter may be studied independently. The fact that no noticeable difference existed between the final pressures in the 400 °C runs and those in the 475 °C runs was itself not very surprising because one would reasonably expect better hydrogen consumption at the higher temperature, where the coal was better fragmented due to the thermal breaking of a larger number of chemical bonds linking its colloidal size units.

2. Effect of Pressure The effect of reactor pressure on conversion is shown in figure 8. When no carbon monoxide was used, i.e., when the initial CO pressure was zero, the solvent alone dissolved close to 40 per cent of the coal, no hydrogenation having taken place. The conversion increased roughly to 80 per cent at 1500 psi CO initial pressure. A routine statistical test (Appendix B) indicates, as expected, the significance of pressure at $\alpha = 0.01$.

Beyond the 1500 psi mark, which would correspond to a final pressure between 5000 and 5800 psi, the effect of pressure was no longer as pronounced. It can be concluded from this behavior that pore diffusion, important due to the presence of capillaries in the coal particles (6), is no longer a controlling factor above the 1500 psi

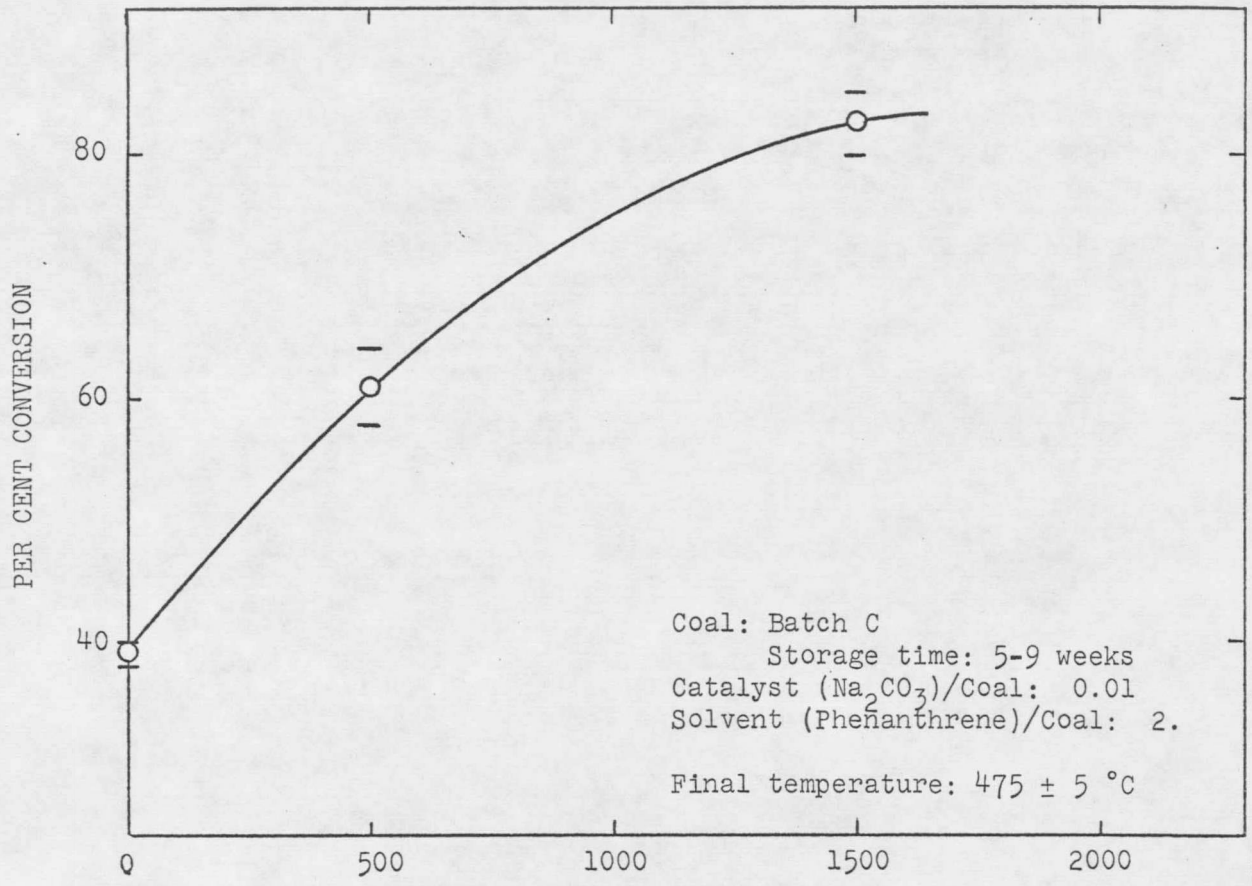

FIGURE 8. Effect of Initial Pressure.

inital pressure region.

Attempts to improve conversion by raising the final pressure through an increase of either the initial water (from 30 to 40 grams) or the initial CO pressure (from 1500 to 2000 psi) were not successful (table 3). A statistical analysis on the data in this table (Appendix C) revealed no significant effect by either of the particular treatments just mentioned, even at an α as high as 0.25.

TABLE 3. Effect of Increased Initial Pressure and Water.

Water, grams	30	40	15
Initial pressure, psi	1500	1500	2000
Per cent conversion*	53.	58.	41.
	62.	49.	55.
	55.	--	60.
Average % conversion	57.	54.	52.

*Characteristics of runs:
Coal: Batch B
Storage time: 21-27 weeks
Catalyst (Na_2CO_3)/Coal: 0.01
Solvent (Phenanthrene)/Coal: 2.
Final temperature: 468 ± 8 °C.

3. Effects of Solvent Type and Concentration Figure 9 shows the decrease in conversion as one goes from a double ring aromatic solvent (naphthalene) to a non-aromatic one (decalin). To be sure, the effect of the solvent's aromaticity is statistically significant only at $\alpha = 0.15$ (Appendix D), but it is reasonable to expect α to have been

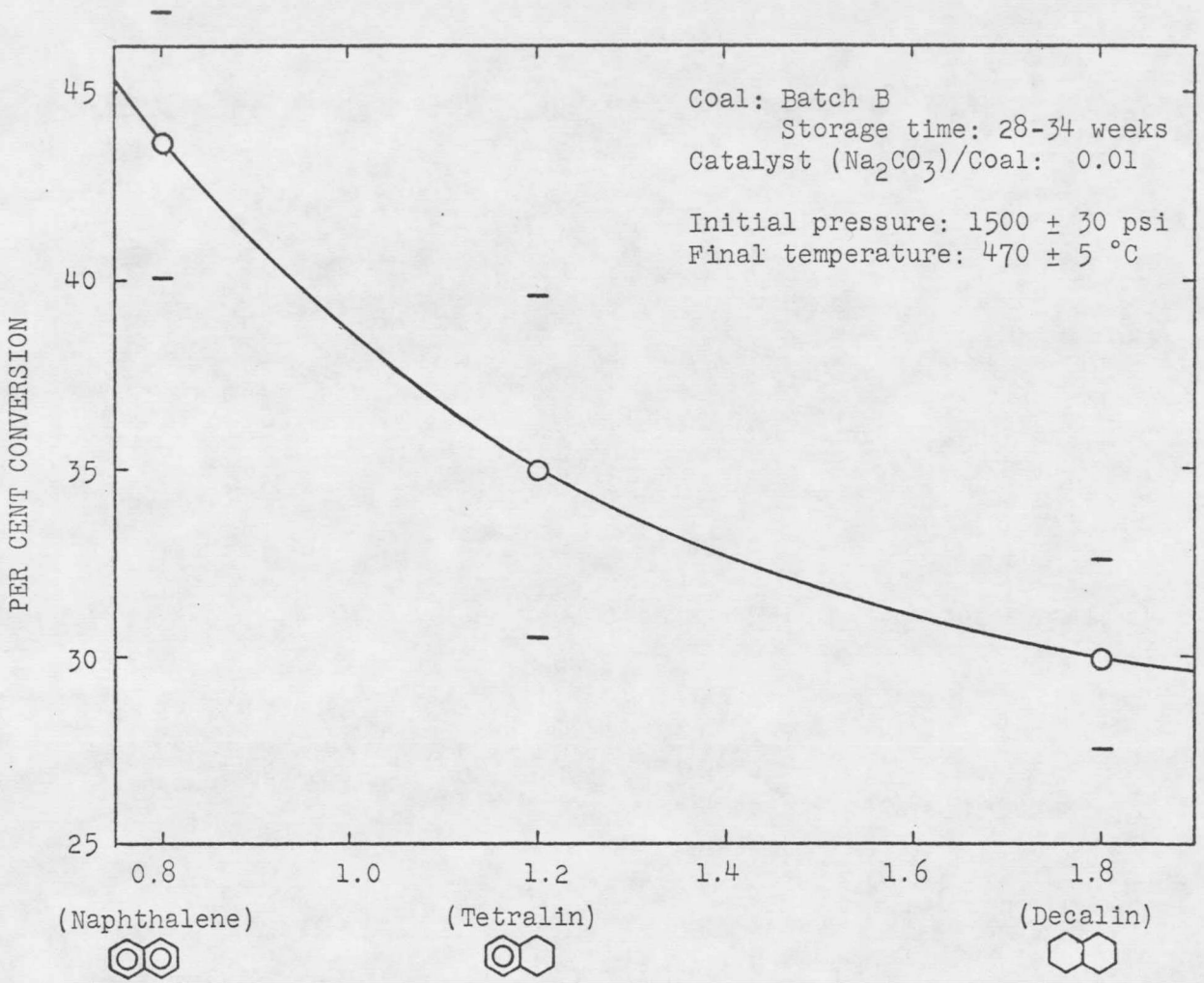

FIGURE 9. Effect of Solvent Aromaticity.

lower had more experiments been performed. (This was not done because the conversions involved were too low to be worth additional investigations.)

Three-ring solvents performed better than double-ring ones, with phenanthrene exceeding anthracene by about 20 conversion per cent (figure 10).

Regarding solvent concentration, no appreciable change in conversion was observed as the anthracene:coal weight ratio was increased beyond 1:1 (figure 10).

Phenanthrene, however, gave the highest conversion when present at a 2:1 ratio with respect to coal (figure 11). This behavior was significant at $\alpha = 0.05$ (Appendix E), and could be attributed to a compromise between the adequacy and over-adequacy of the unsaturated solvent, which in the latter case would tend to compete with the coal for the available hydrogen, thereby decreasing the conversion.

Relevant LSD tests (Appendix E) show that the difference between the 1:1 and 2:1 phenanthrene:coal ratios was significant at $\alpha = 0.05$, whereas α would have to be at least 0.10 in order for the difference between the 2:1 and 3:1 ratios to be significant.

Neither anthracene nor phenanthrene appeared to be chemically affected to any great extent by run conditions. (The solid product of a run with phenanthrene alone had a melting point of 100 ± 1 °C, and a C/H ratio of 1.4, which are the properties of phenanthrene itself.)

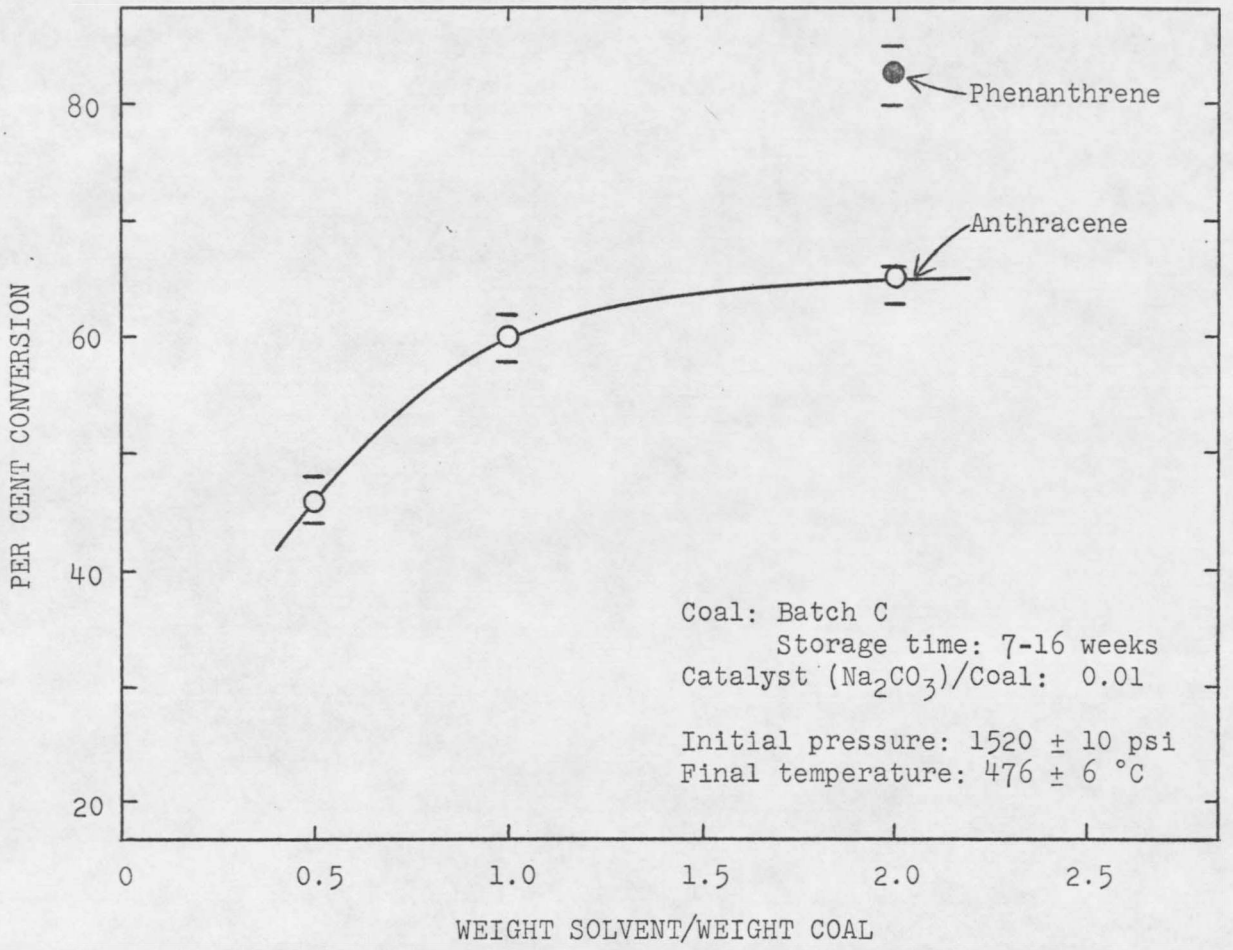

FIGURE 10. Effect of Anthracene Solvent Concentration.

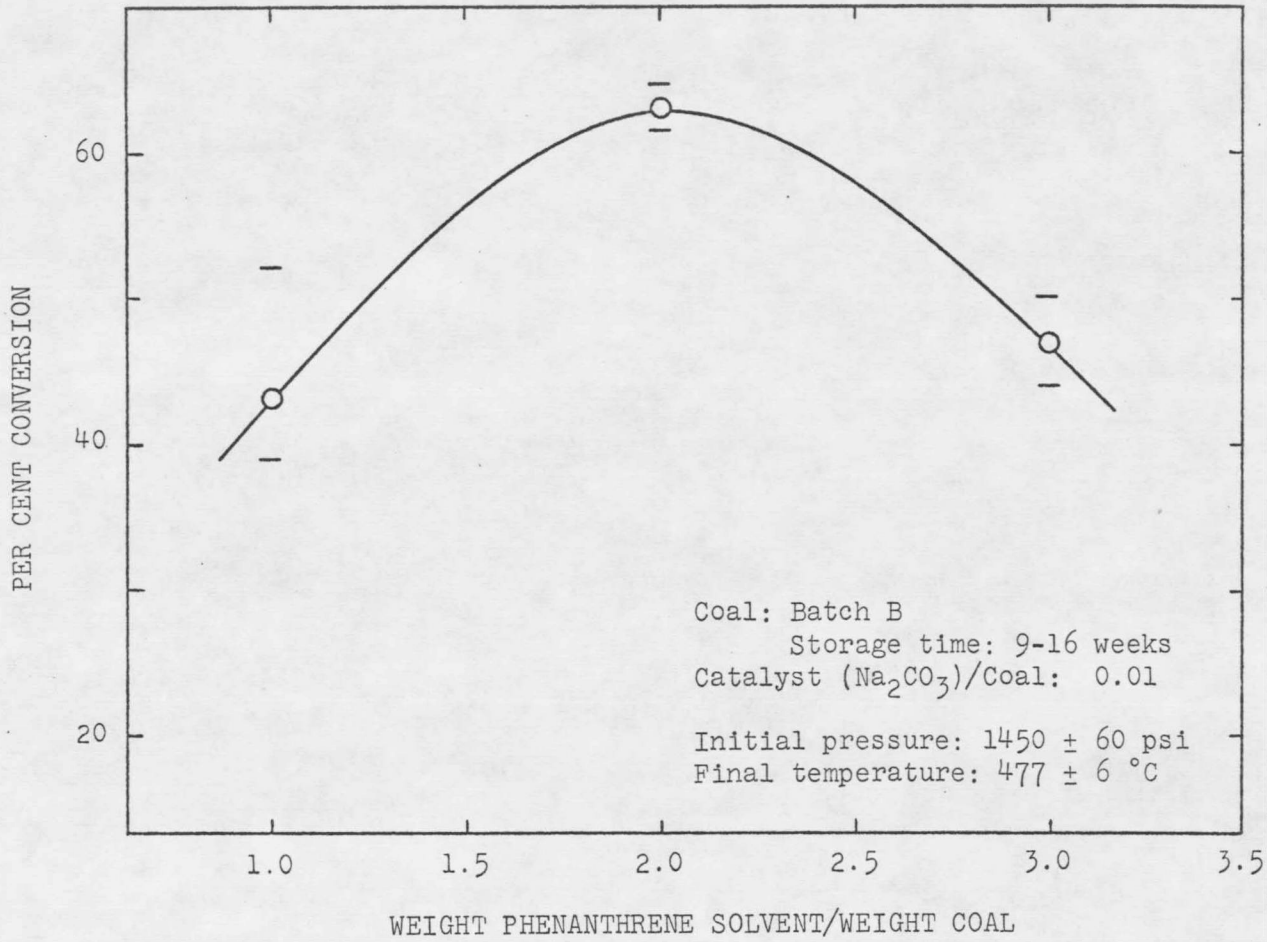

FIGURE 11. Effect of Phenanthrene Solvent Concentration.

In other comparisons between anthracene and phenanthrene as solvents, it is worth noting that in addition to the higher conversion (figure 10), the extraction of the products from a phenanthrene run took only 24 hours instead of the 36 hours normally required to extract the product from an anthracene run. The cause of this longer time was the lower solubility in benzene of anthracene and associated hydrogenation products. In commercial operations, this would cause a great deal of mechanical difficulty to the filtration steps.

The conversions with FMC coal tar, the last solvent to be tested, are shown in table 4. These conversions are totally too low to be of any practical interest. Large experimental errors are apparent, and a statistical analysis (Appendix F) shows neither solvent nor the catalyst tested with it to be significant even at an α as high as 0.25.

From a commerical standpoint, FMC coal tar then does not appear suitable for this process. Examination of the products of a run made with 60 grams of the tar alone, i.e., without any coal, revealed about 2.7 grams of carbon lay-down. The carbon obviously came from the overcracked tar. Although the lay-down itself may not have affected the real conversion, it still would, in large scale operations, represent a great loss of solvent and would cause much additional work in product separation.

4. Effects of Catalyst Type and Concentration The general trend with the sodium salt catalysts tested was that conversion increased

TABLE 4. Conversion with FMC Coal Tar as Solvent.*

Weight Na_2CO_3 / Weight coal	Weight FMC coal tar/Weight coal 1.	2.
0.01	30.%	29.%
	44.	29.
0.02	34.	41.
	21.	27.

*Characteristics of runs:
Coal: Batch A
Storage time: 9-10 months

Initial pressure: 1150 ± 50 psi
Final temperature: 480 ± 3 °C.

with increasing salt concentration (figures 12, 13, 14).

In the particular case of sodium formate (figure 12), there was an appreciable decrease in conversion at lower formate concentrations, followed by a gradual increase. As shown in Appendix G, the effect of sodium formate was significant at $\alpha = 0.05$. In addition, associated LSD tests (Appendix G) show that the difference between the conversion at the "no catalyst" level and that at the "1%"= 0.01 level is significant at the same α. This is also true between the "1%" and "5%" levels, as can be seen directly by referring again to figure 12. It would seem that at higher formate concentrations, the catalytic effects of the salt begin to overcome the negative effects resulted from its own alkalinity on conversion.

The effects of the concentration of sodium bicarbonate are shown in figure 13. These effects are very significant at $\alpha = 0.05$ (Appendix H), where the difference between any pair of concentration levels are shown by LSD tests (Appendix H) to be also significant.

Although we would expect sodium carbonate to behave similarly to sodium bicarbonate, the large experimental errors involved made the conversion increase in figure 14 statistically significant only at $\alpha = 0.10$ (Appendix I). It is seen from the LSD tests in Appendix I that the difference between the "no catalyst" and "3% catalyst" levels is significant.

The last of the water-gas shift reaction catalysts to be tested

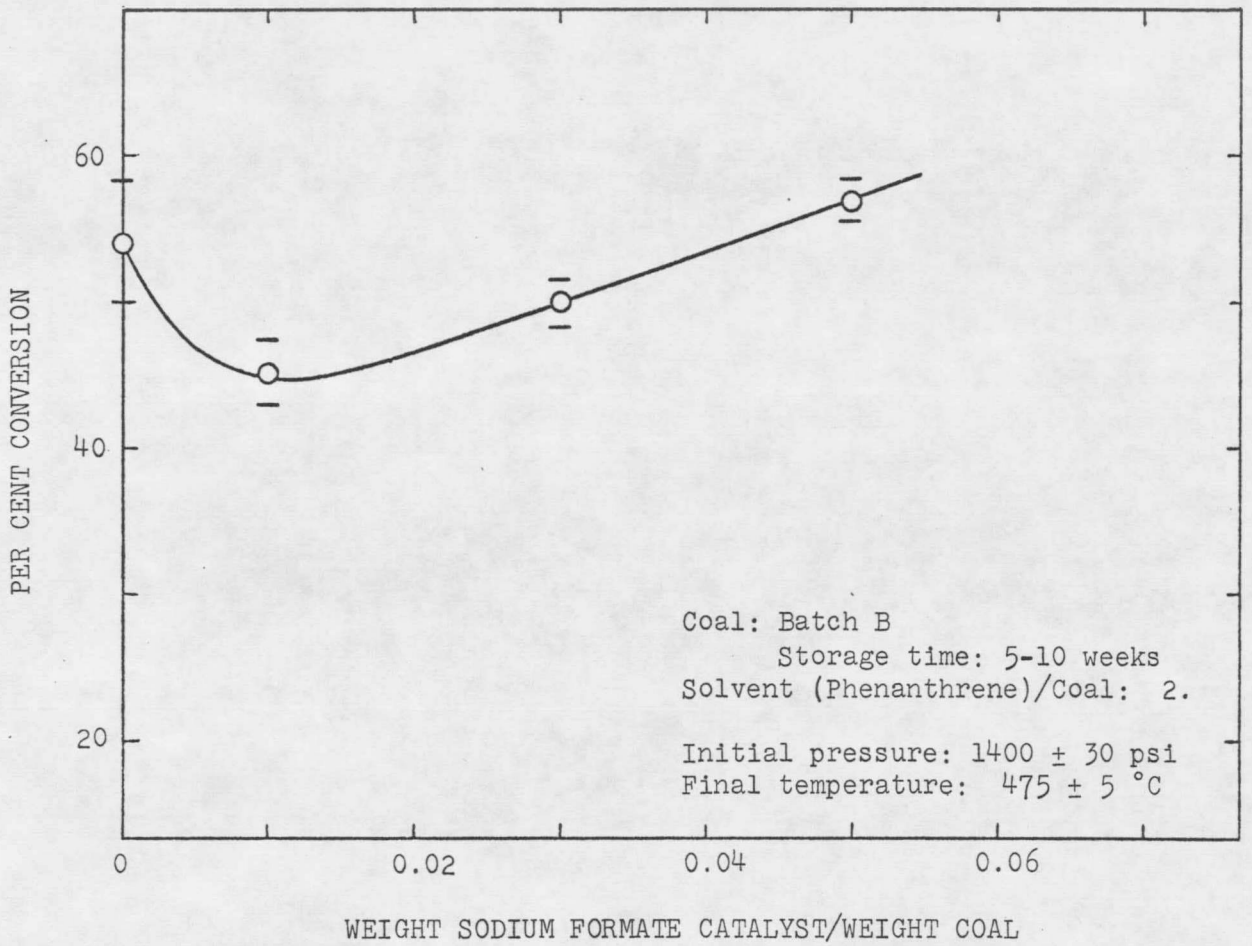

FIGURE 12. Effect of Sodium Formate Catalyst Concentration.

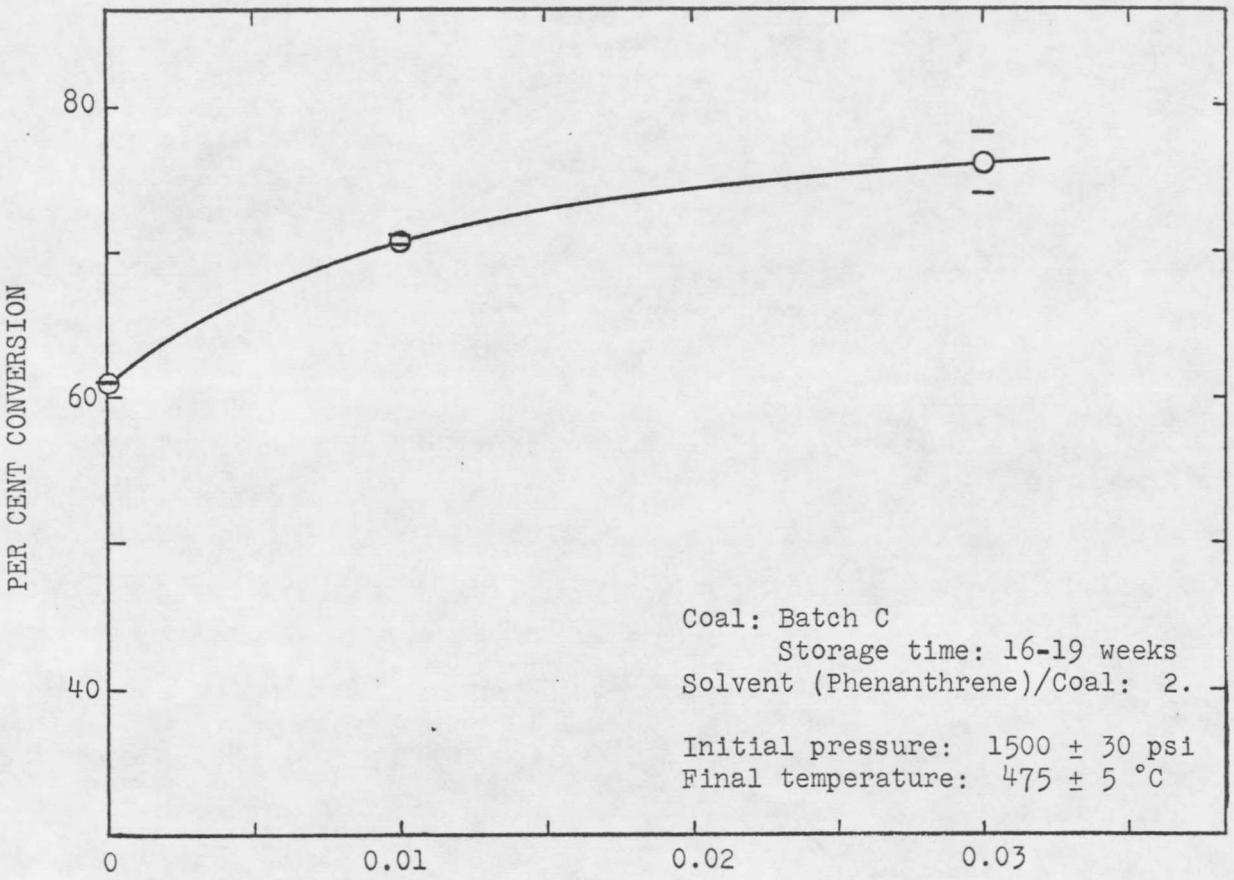

FIGURE 13. Effect of Sodium Bicarbonate Catalyst Concentration.

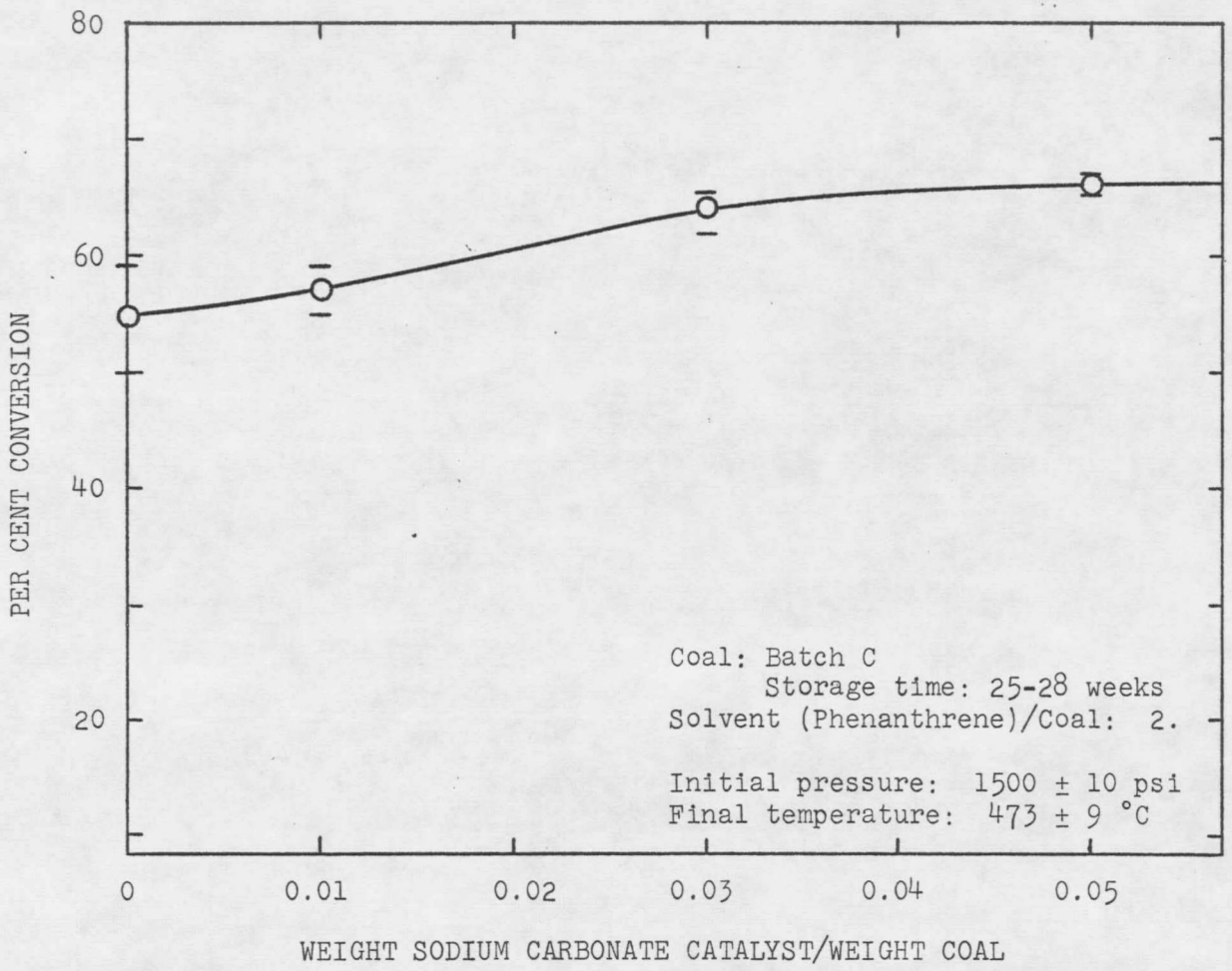

FIGURE 14. Effect of Sodium Carbonate Catalyst Concentration.

was ferric oxide. The least square line in figure 15 shows the slight effect of this chemical on conversion. Statistically speaking, the slope of this line is significant only at $\alpha = 0.35$ (Appendix J). It should be noted that figure 15 shows the effect of Fe_2O_3 on the conversion of coal samples from batch A, which at the time of the runs had already been stored for 47-52 weeks. The initial pressure used in these runs was close to 1200 psi. From the behavior of batch A coal with respect to storage time (figure 6) and from the general trend in conversion with respect to initial pressure (figure 8), it is reasonable to expect conversions with Fe_2O_3 to be in the 70 per cent region if the runs are made with fresh coal and at 1500 psi initial pressure.

The last of the catalysts to be tested was stannous chloride. As mentioned earlier, $SnCl_2$ was the only catalyst belonging to the second type--catalyzing the coal reduction and stabilization reactions--that was selected. In the low range of concentration shown in figure 16, $SnCl_2$ did not show any catalytic effect even at an α as high as 0.25 (Appendix K). This conclusion of non-significance comes from the scattered nature of conversion data, especially at the "no catalyst" level. Due to the fact that the autoclave interior was not equipped with a glass liner, the higher conversion obtained at this level could have been caused by "memory" effects left on the reactor wall by chlorine compounds during the preceding runs with $SnCl_2$. The use of a glass liner in a reactor large enough to process hundreds of tons of

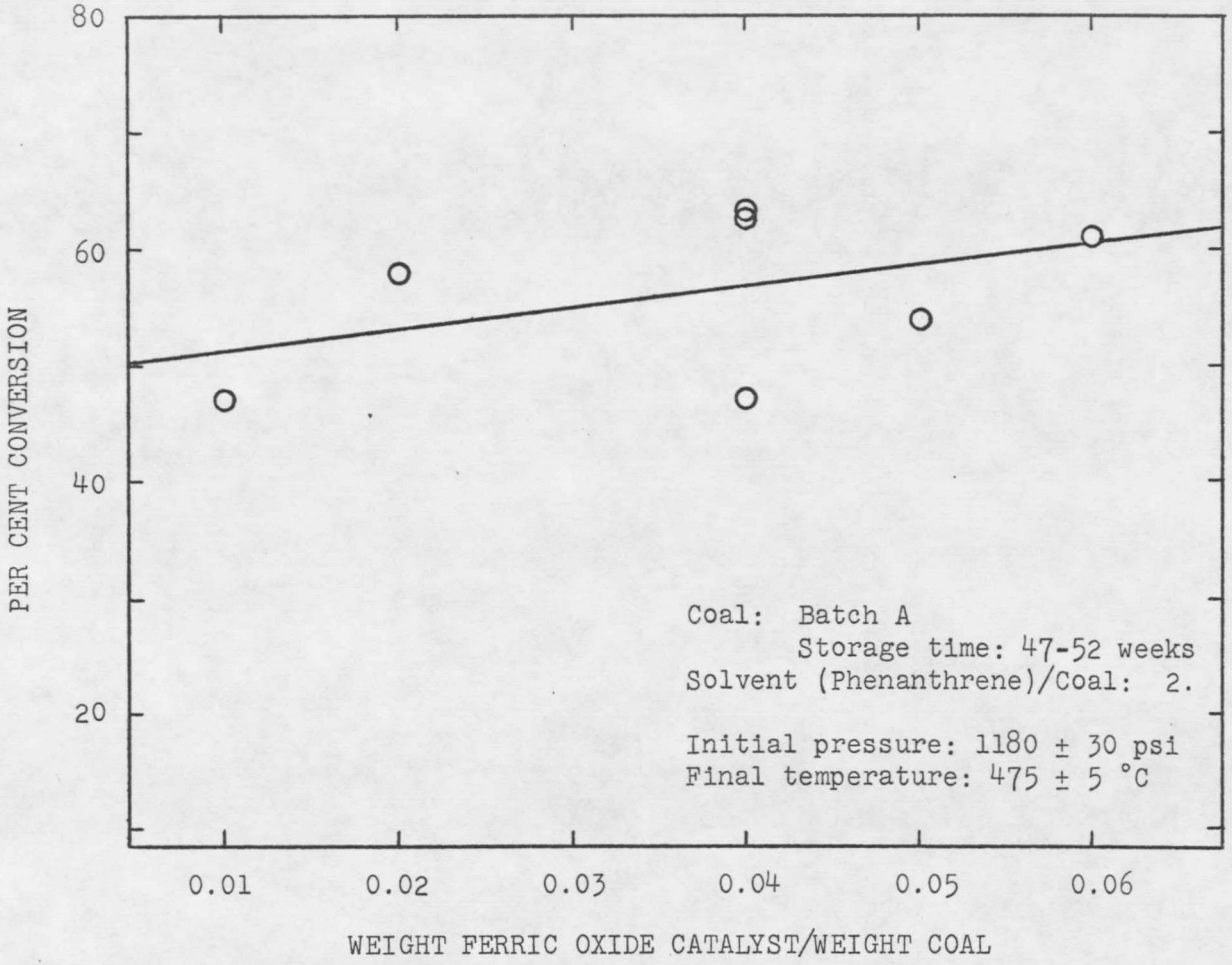

FIGURE 15. Effect of Ferric Oxide Catalyst Concentration.

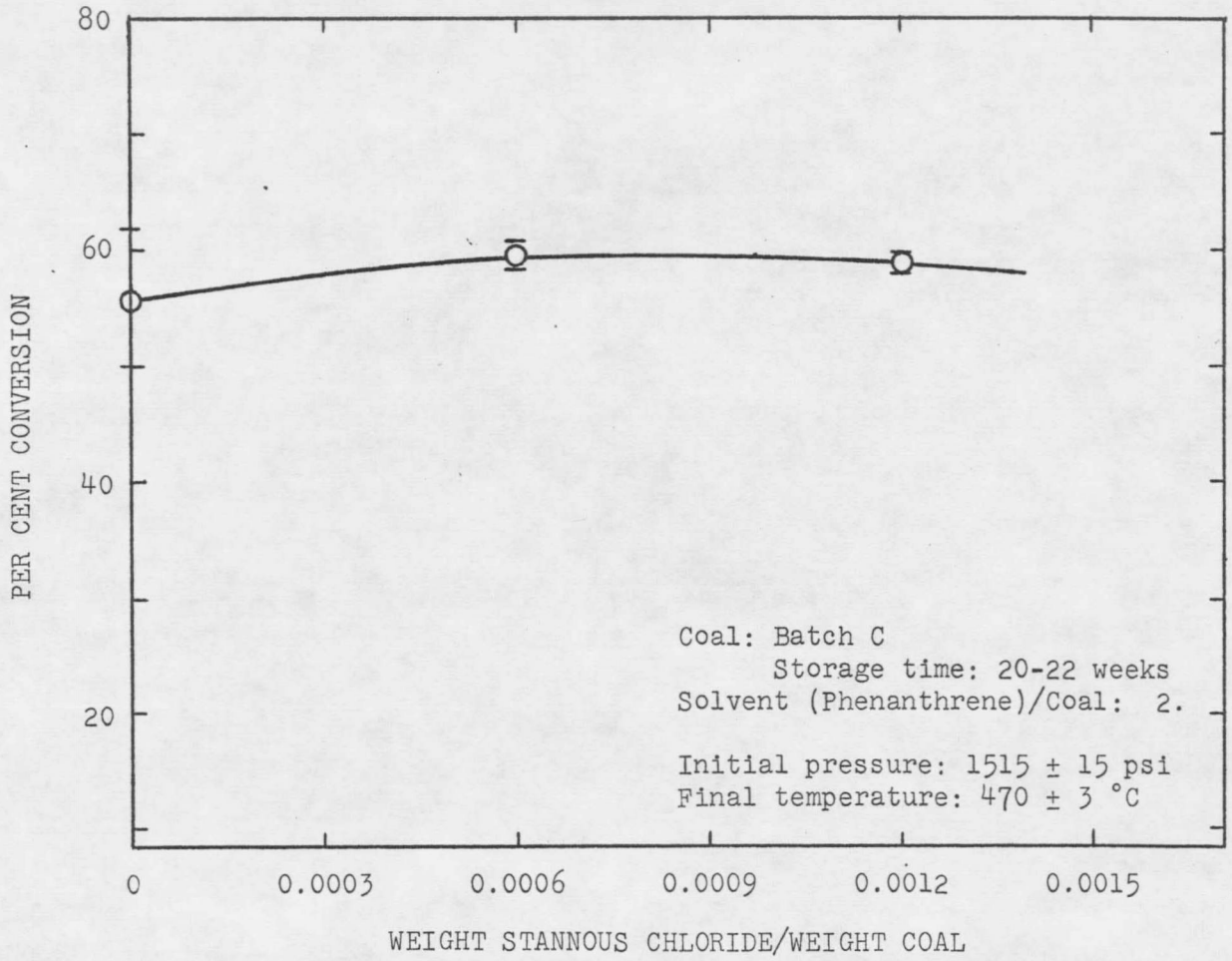

FIGURE 16. Effect of Stannous Chloride Catalyst Concentration.

coal per hour, however, would not be realistic, and this question concerning $SnCl_2$ was not pursued any further.

B. Products Analyses: Results and Discussion

1. Gaseous Products In the earlier phase of this research, gaseous products from a run were ordinarily collected in gas sample bottles and analyzed by the chromatographic techniques described earlier. The purpose of these analyses was to gain some idea on the composition of these products. Table 5 shows the analysis of the gas mixture from a typical run:

TABLE 5. Analysis for Gaseous Products from a Typical Run.

Gas*	Volume per cent
CO	52.4
CO_2	28.8
CH_4	0.9
C_2H_6	0.4
H_2	17.5 (by difference)

*Run characteristics:
Coal: Batch A
Storage time: 27 weeks
Catalyst (Na_2CO_3)/Coal: 0.01
Solvent (Phenanthrene)/Coal: 2.

Initial pressure: 1260 psi
Final temperature: 474 °C.

It could be seen from the above analysis that a large portion of carbon monoxide went through the process unreacted. The presence of both hydrogen and carbon dioxide attests to the occurrence of the shift

reaction

$$H_2O + CO = H_2 + CO_2,$$

with some hydrogen having been consumed by simultaneous hydrogenation reactions with coal. From the per cent conversion of a particular run and from the amounts of methane and ethane found in the resulting gas mixture, the percentage of the converted coal going into the gas phase could be calculated. From the data obtained, it is safe to say that this percentage is less than 5 per cent--an exact value would not be possible due to the inaccuracy involved in the measurement of the minute methane and ethane.

2. Solid Product: Tar Table 6 shows the analysis of the resulting mixture of phenanthrene--the solvent--and the tar product from a typical run:

TABLE 6. Analysis for Solid Products from a Typical Run.

Analysis*	Weight per cent Sample 1	Sample 2
Carbon	91.54	91.44
Hydrogen	5.86	5.89
Sulfur	0.27	0.29
Ash	0.01	0.13

*Run characteristics:
Coal: Batch C
Storage time: 27 weeks
Catalyst (Na_2CO_3)/Coal: 0.01
Solvent (Phenanthrene)/Coal: 2.

Initial pressure: 1500 psi
Final temperature: 471 °C.

Back calculations using the above analysis, the per cent conversion for this particular run assuming no interaction with or by the phenanthrene solvent yielded a H/C ratio of 1.1 for the tar. This value agrees with that obtained by York through analyses of products from runs without solvent. This confirms York's assumption and the observation earlier in this work that the solvent essentially goes through the process chemically unaffected. The loss of solvent due to unwanted hydrogenation therefore could be expected to be minimal.

With a H/C ratio of 1.1, the resulting tar from this process still contains too little hydrogen to be at all suitable as a refinery feedstock. It must be observed however that this ratio represents a considerable improvement upon the original coal, the H/C ratio of which is only 0.81.

Besides the possibility of being further hydro-treated to yield a synthetic crude, the other conceivable use of the tar would be as a combustion fuel in the MHD (magnetohydrodynamic) generator, where it is suitable not only because of its still low H/C ratio but also because it contains only a small percentage of ash and would cause less erosion to the MHD tunnel components (28).

VI. CONCLUSIONS

The major conclusions that can be drawn from this research on the reduction of Colstrip subbituminous coal with carbon monoxide and water are:

1. Less than 5 per cent of the converted coal will go into the gas phase as methane and ethane. The remaining tarry product has a H/C ratio of about 1.1, a sulfur content close to 0.3 per cent, and an ash content of about 0.1 per cent,

2. At the 300 °C final temperature level, practically no coal is reduced (i.e., converted). The conversion is highest--over 70 per cent--at 475 °C, which was the highest final temperature experimented with,

3. The initial, and therefore final reactor pressure has a very significant effect on conversion. The effect is most pronounced below the 1000 psi initial pressure mark, and becomes less so around 1500 psi, where the conversion begins to level out close to 80 per cent,

4. To some extent, the conversion increases with the solvent's aromaticity. Three-ring solvents are better than double-ring ones, with phenanthrene being better than anthracene by about 20 percentage points. The optimal phenanthrene:coal ratio is around 2:1. FMC coal tar is not suitable for this process,

5. The conversion increases with increasing sodium salts' concentrations. In the case of sodium bicarbonate, the conversion increase is

about 10 percentage points as one goes from a bicarbonate:coal ratio of zero to 0.01:1. The effects of sodium formate and sodium carbonate are similar in nature, though not as pronounced. On a coal that has been in storage for about a year, ferric oxide causes a conversion increase of only a few percentage points, but the effect of this oxide can be expected to be stronger on a fresh coal. At low concentrations ($SnCl_2$: coal = 0.0006 to 0.0012), stannous chloride shows no significant effect.

In short, it may be concluded that it is possible at a short operating time of 5 minutes to convert 70-80 per cent of a low-rank coal such as Colstrip subbituminous into benzene-soluble products by reduction with carbon monoxide and water. The conversion may be expected to vary somewhat with the particular batch (of coal) under treatment and with the time the coal has been stored, but the highest possible conversion at this short operating time can be warranted if the reduction is carried out at a final temperature around 475 °C and under an initial carbon monoxide pressure of 1500 psi. Phenanthrene, present at a 2:1 ratio with respect to coal, appears to be the best solvent for the process, and from 1 to 3 parts of sodium bicarbonate per 100 parts of coal will be required.

It is felt that the conditions just enumerated, in particular the short operating time, present a process picture that is much more realistic than previously depicted by York (28). Using York's design figures derived from an economic evaluation by the Pittsburg and

Midway Coal Mining Company (19) and the simplifying assumption of a fixed average operating cost, and based on the technical feasibilities ascertained by the present research (75% conversion, 5 minute operating time), the cost of producing 1 million Btu's worth of tar by this process has been calculated to be between 50 and 90 cents depending upon the plant capacity desired and the the fixed capital investment projected (Appendix L, figure 18).

VII. RECOMMENDATIONS FOR FURTHER STUDIES

The present study has shown that it is possible to convert 70 to 80 per cent of subbituminous coal to benzene-soluble products by reduction with carbon monoxide and water at 475 °C and under 5000-5800 psi final pressure for 5 minutes, heat-up time excluded. To develop the process further toward commercialization, additional studies will have to be made not only on the process itself but on the product as well.

Regarding the process, it is felt first of all that conversion can still be improved by more vigorous mixing. Studies in this direction will involve the use of baffles or steel balls inside the present autoclave, various rocking rates, or a new magnetic-stirred reactor.

Secondly, it has been assumed all along that the solvent can be recycled without losing its effectiveness. Although it has been shown that the solvent does not appear to be chemically affected after a run, the solvent's effectiveness should still be checked by subjecting it to more than one coal-less run and finally using it in a normal run to see how well it still works. In addition, the combined product of a number of "first generation" normal runs should be used as solvent in new "second generation" runs to see how well it performs, the procedure being continued through at least three such "generations" of runs.

Thirdly, as it appears that the large variations experienced at each treatment level in a series of runs have been due to a great

extent to the non-uniformity in coal samples even from the same batch, chemical analyses should be made with each run to determine the nature of this non-uniformity (e.g., the sodium content in the ash) and to correlate it with the particular conversion variations. This endeavor will involve a great deal more sophisticated analytical work which is not possible with the present facilities.

Finally, as far as the process is concerned, it can be expected that the conditions specified in the present batchwise studies will be far from identical to those in a continuous operation. Therefore, some sort of continuous system should be set up and its operating conditions examined and modified if a more realistic picture of the process is to be gained.

Regarding the product, various avenues should be explored for its use. Most immediate perhaps is its suitability as a direct combustion fuel for the MHD power generation process, in which the tar's low H/C ratio and low ash content are the assets. To this aim, large quantities of the tar will have to be produced if the total amount is to be sufficient for test runs in the MHD tunnel. This will require larger equipments than presently available.

Toward further developments of the product into a synthetic crude --the second logical use of it--, analytical methods will have to be used to determine its exact chemical composition. This will hopefully shed some light on how the product can be further hydro-treated to

increase its H/C ratio, making it a more suitable feed to oil refineries.

VIII. APPENDICES

APPENDIX A. F-test (16,21) for the Effects of Final Temperature.

1. Data

	Temperature level, °C	
	400	475
Per cent conversion	40.	74.
	26.	75.
	--	62.

2. AOV Table

Source of Variation	Degress of Freedom	Sum of Squares	Mean Square	F_c
Total	5	17221		
Mean	1	15345.8000		
Among temperatures	1	1672.5333	1672.5333	24.8
Experimental error	3	202.6667	67.5556	

3. F-test

H_o: Temperature has no effect

H_a: H_o not true

Critical region: F_c greater than $F_t = F_{.975(1,3)} = 17.4$

Test statistic: $F_c = 24.8$, greater than F_t

Conclusion: Reject H_o at the 2.5% significance level.

APPENDIX B. F-test for the Effects of Pressure.

1. Data

	Pressure level, psi		
	0	500	1500
Per cent conversion	38.	64.	80.
	40.	58.	85.

2. AOV Table

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Square	F_c
Total	6	24129		
Mean	1	22204.1667		
Among pressures	2	1892.3333	946.1667	87.3
Experimental error	3	32.5000	10.8333	

3. F-test

H_o: Pressure has no effect

H_a: H_o not true

Critical region: F_c greater than $F_t = F_{.99(2,3)} = 30.8$

Test statistic: $F_c = 87.3$, greater than F_t

Conclusion: Reject H_o at the 1% significance level.

APPENDIX C. F-test for the Effects of Higher Initial (CO) Pressure (2000 psi) and Higher Initial Water (40 grams).

1. Data

Same as in table 3.

2. AOV Table

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Square	F_c
Total	8	23652		
Mean	1	23328		
Among treatments	2	35.3333	17.6667	0.306
Experimental error	5	288.6667	57.7333	

3. F-test

H_o: The special treatments have no effects

H_a: H_o not true

Critical region: F_c greater than $F_t=F_{.95(2,5)}=5.79$

Test statistic: $F_c=0.306$, much smaller than F_t

Conclusion: Not reject H_o.

Note: Even if an $F_t=F_{.75(2,5)}=1.85$ were allowed, we still could not reject H_o.

APPENDIX D. F-test for the Effects of Various Solvents.

1. Data

	Solvents		
	Decalin	Tetralin	Naphthalene
Per cent conversion	32.	39.	40.
	27.	30.	47.

2. AOV Table

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Square	F_c
Total	6	7983		
Mean	1	7704.1667		
Among solvents	2	201.3333	100.6667	
Experimental error	3	77.5000	25.8333	

3. F-test

H_o: No difference exists between solvents

H_a: H_o not true

Critical region: F_c greater than $F_t = F_{.95(2.3)} = 9.55$

Test statistic: $F_c = 3.90$, smaller than F_t

Conclusion: Not reject H_o.

Note: H_o could still be rejected, but only at the 15% significance level.

APPENDIX E. F-test and LSD Tests (16,21) for the Effects of Phenanthrene Concentration.

1. Data

	Weight phenanthrene/Weight coal		
	1. (Level 1)	2. (Level 2)	3. (Level 3)
Per cent conversion	39.	64.	50.
	52.	62.	44.
	38.	--	--

2. AOV Table

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Square	F_c
Total	7	18045		
Mean	1	17400.1429		
Among concentrations	2	502.8571	251.4286	7.08
Experimental error	4	142.0000	35.5000	

3. F-test

H_o: Phenanthrene concentration has no effect

H_a: H_o not true

Critical region: F_c greater than $F_t = F_{.95(2,4)} = 6.94$

Test statistic: $F_c = 7.08$, greater than F_t

Conclusion: Reject H_o at the 5% significance level.

4. LSD Tests

Let y_i be the mean conversion for the "ith" concentration level.

Then $y_1 = 43.$, $y_2 = 63.$, $y_3 = 47.$.

Now $s^2_{y_1-y_2} = s^2_{y_1-y_3} = s^2_{13}=35.5/3 + 35.5/2=29.5833$, thus $s_{13}=5.439$. Likewise, $s^2_{23}=35.5/2 + 35.5/2= 35.5$, and $s_{23}=5.5982$.

At the 5% significance level, $t_{.975,3}=3.182$, and $LSD_{1 \text{ vs. } 2} = LSD_{1 \text{ vs. } 3}=s_{13} \cdot t_{.975,3}=(3.182)(5.439)=17.3072$. Also, $LSD_{2 \text{ vs. } 3} = (5.5982)(3.182)=18.9590$. For the 10% significance level, $t_{.95,3}=2.353$ and therefore $LSD_{2 \text{ vs. } 3}=13.1726$.

The results of the three LSD tests involved are summarized in the following table:

Between these concentration levels	% conversion difference (PCD)	5% sign. level LSD	5% sign. level Is PCD significant?	10% sign. level LSD	10% sign. level Is PCD significant?
1 and 2	20.	17.	Yes	---	---
1 and 3	4.	17.	No	---	---
2 and 3	16.	19.	No	13.	Yes

APPENDIX F. F-tests for the Effects of FMC Coal Tar Concentration and the Presence of 1% Na_2CO_3.

1. Data

Same as in table 4.

2. AOV Table

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Square	F_c
Total	8	8525		
Mean	1	8128.1250		
Treatments				
Tar concentration	1	1.1300	1.1300	0.0107
Na_2CO_3	1	10.1250	10.1250	0.0963
Tar X Na_2CO_3	1	105.1200	105.1200	1.4990
Experimental error	4	280.5000	70.1250	

3. F-tests

a. Effect of Interaction between Tar Concentration and Na_2CO_3

H_o: No significant interaction exists

H_a: H_o not true

Critical region: F_c greater than $F_t = F_{.95(1,4)} = 7.71$

Test statistic: $F_c = 1.5$, much smaller than F_t

Conclusion: Not reject H_o.

Note: Even if the significance level were chosen at 25%, one still would not be able to reject H_o.

b. Effect of Tar Concentration

Same conclusion as above.

c. Effect of Na_2CO_3 Presence

Same conclusion as above.

APPENDIX G. F-test and LSD Tests for the Effects of Sodium Formate Concentration.

1. Data

	Weight sodium formate/Weight coal			
	0 (Level 1)	0.01 (Level 2)	0.03 (Level 3)	0.05 (Level 4)
Per cent conversion	58.	43.	51.	56.
	50.	47.	48.	58.
	53.	--	--	--

2. AOV Table

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Square	F_c
Total	9	24136		
Mean	1	23921.7778		
Among concentrations	3	167.0555	55.6852	5.90
Experimental error	5	47.1667	9.4333	

3. F-test

H_o: Formate concentration has no effect

H_a: H_o not true

Critical region: F_c greater than $F_t = F_{.95(3,5)} = 5.41$

Test statistic: $F_c = 5.90$, greater than F_t

Conclusion: Reject H_o at the 5% significance level.

4. LSD Tests

Let y_i be the mean conversion at the "ith" concentration level. Then $y_1 = 54.$, $y_2 = 45.$, $y_3 = 50.$, and $y_4 = 57.$

Using the method similar to that in Appendix E, we have $s_{12}=s_{13}=s_{14}=2.8038$, and $s_{23}=s_{24}=s_{34}=3.0714$.

At the 5% significance level then, $LSD_{1 \text{ vs. } 2}=LSD_{1 \text{ vs. } 3}=LSD_{1 \text{ vs. } 4}=7.2086$, and $LSD_{2 \text{ vs. } 3}=LSD_{2 \text{ vs. } 4}=LSD_{3 \text{ vs. } 4}=7.8965$. For the 10% significance level, $LSD_{2 \text{ vs. } 3}=LSD_{2 \text{ vs. } 4}=LSD_{3 \text{ vs. } 4}=6.1889$. The results of the six LSD tests involved are summarized in the following table:

Between these concentration levels	% conversion difference (PCD)	5% sign. level		10% sign. level	
		LSD	Is PCD significant?	LSD	Is PCD significant?
1 and 2	9.	7.2	Yes	---	---
1 and 3	4.	7.2	No	5.6	No
1 and 4	3.	7.2	No	5.6	No
2 and 3	5.	7.9	No	6.2	No
2 and 4	12.	7.9	Yes	---	---
3 and 4	7.	7.9	No	6.2	Yes

APPENDIX H. F-test and LSD Tests for the Effects of Sodium Bicarbonate Concentration.

1. Data

	Weight sodium bicarbonate/Weight coal		
	0 (Level 1)	0.01 (Level 2)	0.03 (Level 3)
Per cent conversion	61.	70.	78.
	61.	71.	74.

2. AOV Table

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Square	F_c
Total	6	28943		
Mean	1	28704.1667		
Among concentrations	2	230.3333	115.1667	40.6
Experimental error	3	8.5000	2.8333	

3. F-test

H_o: Bicarbonate concentration has no effect

H_a: H_o not true

Critical region: F_c greater than $F_t = F_{.95(2,3)} = 9.55$

Test statistic: $F_c = 40.6$, much greater than F_t

Conclusion: Reject H_o at the 5% significance level.

Note: H_o could still be rejected at the 1% significance level.

4. LSD Tests

Let y_i be the mean conversion at the "ith" concentration level.

Then y_1=61., y_2=70.5 and y_3=76. .

Using the method shown in Appendix E, we have $s_{12}=s_{13}=s_{23}=$ 1.6832. At the 5% significance level, $LSD_{1 \text{ vs. } 2}=LSD_{1 \text{ vs. } 3}=LSD_{2 \text{ vs. } 3}=$ 5.3561.

The results of the three LSD tests involved are summarized in the following table:

Between these concentration levels	% conversion difference (PCD)	5% sign. level LSD	5% sign. level Is PCD significant?	10% sign. level LSD	10% sign. level Is PCD significant?
1 and 2	10.	5.4	Yes	---	---
1 and 3	15.	5.4	Yes	---	---
2 and 3	5.5	5.4	Yes	---	---

APPENDIX I. F-test and LSD Tests for the Effects of Sodium Carbonate Concentration.

1. Data

	Weight sodium carbonate/Weight coal			
	0 (Level 1)	0.01 (Level 2)	0.03 (Level 3)	0.05 (Level 4)
Per cent conversion	50.	59.	62.	67.
	59.	55.	65.	65.

2. AOV Table

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Square	F_c
Total	8	29270		
Mean	1	29040.5000		
Among carbonate conc'ns	3	174.5000	58.1667	4.23
Experimental error	4	55	13.7500	

3. F-test

H_o: Carbonate concentration has no effect

H_a: H_o not true

Critical region: F_c greater than $F_t = F_{.95(3,4)} = 6.59$

Test statistic: $F_c = 4.23$, smaller than F_t

Conclusion: Not reject H_o.

Note: It would be possible to reject H_o at the 10% significance level.

4. LSD Tests at the 10% Significance Level

Using the method of Appendix E, we have $s_{ij}=3.7081$. At the 10% significance level then, $LSD_{i \text{ vs. } j}=7.9057$. The results of the six LSD tests involved are summarized in the following table:

Between these concentration levels	% conversion difference (PCD)	10% sign. level LSD	10% sign. level Is PCD significant?
1 and 2	2.5	7.9	No
1 and 3	9.0	7.9	Yes
1 and 4	11.5	7.9	Yes
2 and 3	6.5	7.9	No
2 and 4	9.0	7.9	Yes
3 and 4	2.5	7.9	No

APPENDIX J. Regression Analysis (16) for the Effects of Ferric Oxide Concentration.

1. Data

Weight Fe_2O_3/Weight coal	0.01	0.02	0.04	0.04	0.04	0.05	0.06
Per cent conversion	47.	58.	63.	63.	47.	54.	61.

2. Regression Equation

$$\hat{Y} = b_o + b_1 X$$

$$= 49.475934 + 179.493402\ X$$

3. t-test for Significance of Slope

H_o: Slope not significant

H_a: H_o not true

Critical region: t_c greater than $t_t = t_{.975(5)} = 2.571$

Test statistic: $t_c = (b_1 - 0)/s_{b_1} = 1.089$, smaller than t_t

Conclusion: Not reject H_o.

Note: Interpolation shows that H_o could be rejected only at the 35% significance level.

APPENDIX K. F-test for the Effects of Stannous Chloride Concentration.

1. Data

	Weight stannous chloride/Weight coal		
	0	0.0006	0.0012
Per cent conversion	52.	58.	59.
	62.	61.	58.
	50.	--	--
	59.	--	--

2. AOV Table

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Square	F_c
Total	8	26459		
Mean	1	26335.1250		
Among concentrations	2	22.1250	11.0625	0.54
Experimental error	5	101.7500	20.3500	

3. F-test

H_o: Chloride concentration has no effect

H_a: H_o not true

Critical region: F_c greater than $F_t = F_{.95(2,5)} = 5.79$

Test statistic: $F_c = 0.54$, much smaller than F_t

Conclusion: Not reject H_o.

Note: Even if the significance were chosen to be 25%, one still would not be able to reject H_o.

APPENDIX L. Preliminary Estimates for a Coal Conversion Plant.

In the design of York's (28) "Alpha" process (figure 17), the total direct cost of a plant to convert 417 tons of coal per hour (75% conversion, 60 minute operating time) is estimated to be $64 million. This figure has been based on an economic report submitted to the U.S. Office of Coal Research by the Pittsburg and Midway Coal Mining Company in 1970 (19).

It is felt that based on the results ascertained by the present research (75% conversion, 5 minute operating time), the figure given by York can now be used more realistically in another preliminary but still conservative estimate of the production cost for a plant using the "Alpha" scheme.

Due to the lack of experimental data, uncertainties still exist regarding the exact total direct cost of such a plant. Based on York's figure, it is reasonable to assume that this cost lies between 60 and $100 million. In this preliminary estimate then, let x be the total direct cost and y be the tonnage of coal to be processed per hour.

A. Total Annual Cost (TAC) Taking the total direct cost to be 70% of the fixed capital investment (3), the latter is $(x)/0.7 = 1.429\ x$. We have the three general cost areas:

1. Depreciation Using the simple straight-line rule, the annual depreciation at 15 years is $(1.429\ x)/15 = 0.0952\ x$/year.

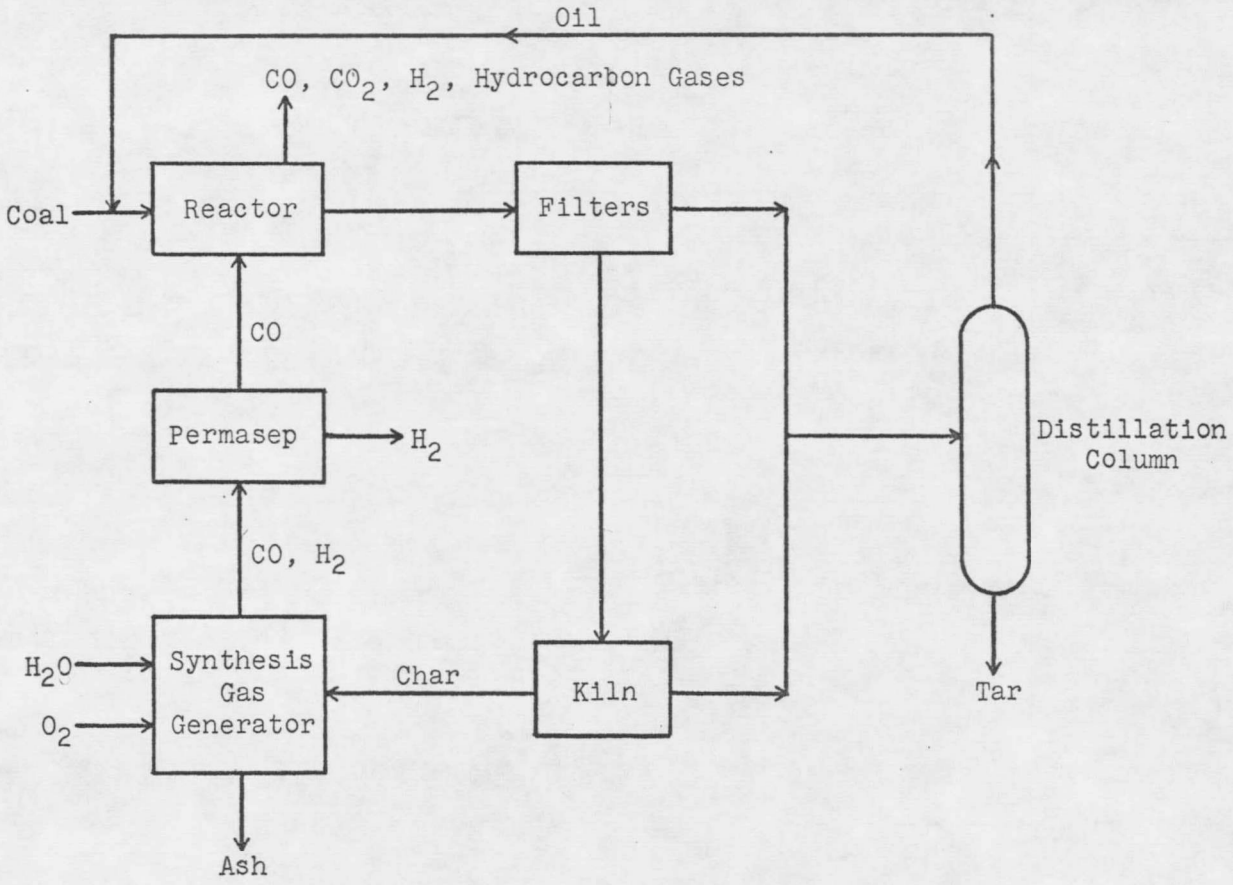

FIGURE 17. York's "Alpha" Scheme for a Coal Conversion Plant (28).

2. Coal Cost At y tons/hour, 24 hours/day, 350 days/year, and \$2/ton, the coal cost is \$16,800 y/year.

3. Operating Cost Since the overriding cost in this analysis can clearly be seen to be the fixed capital investment once the profit is included, an average value of the operating cost can be used without altering to any great extent the economic picture of the process. York's figure for the operating cost is \$12 million. Allowing an additional \$2.43 million for the average sodium bicarbonate catalyst tonnage used annually (1% of the coal tonnage), the average operating cost for the plant becomes \$14.43 million/year.

The total annual cost (TAC) is then

TAC = Depreciation + Coal Cost + Operating Cost

= \$0.0952 x + \$16,800 y + \$14,430,000

B. Annual Btu Production At 24% water and 7% ash, the annual tonnage of moisture- and ash-free coal processed is (8400 y)(0.69) tons of coal. At 75% conversion, the tonnage of tar produced annually is (8400 y)(0.69)(0.75) = 4340 y tons of tar/year. At an approximate heating value of 15,000 Btu/lb of tar, the total number of Btu produced yearly is (4340 y)(2000)(15,000) = $(1.303)10^{11}$y Btu/year.

C. Production Cost (Profit excluded)

$$\text{Production Cost} = \frac{\text{Annual Total Cost}}{\text{Annual Btu Production}}$$

$$= 100 \cdot \frac{0.0952\,x + 16{,}800\,y + 14{,}430{,}000}{(1.303)10^{11}y} \frac{\text{cents}}{\text{Btu}}$$

Figure 18 shows the production cost as a function of both $\underline{x}$ and $\underline{y}$. It can be seen that in the reasonable range of $\underline{x}$ (i.e., the total direct cost) considered, the cost to produce the tar varies from 50 to 90 cents/million Btu.

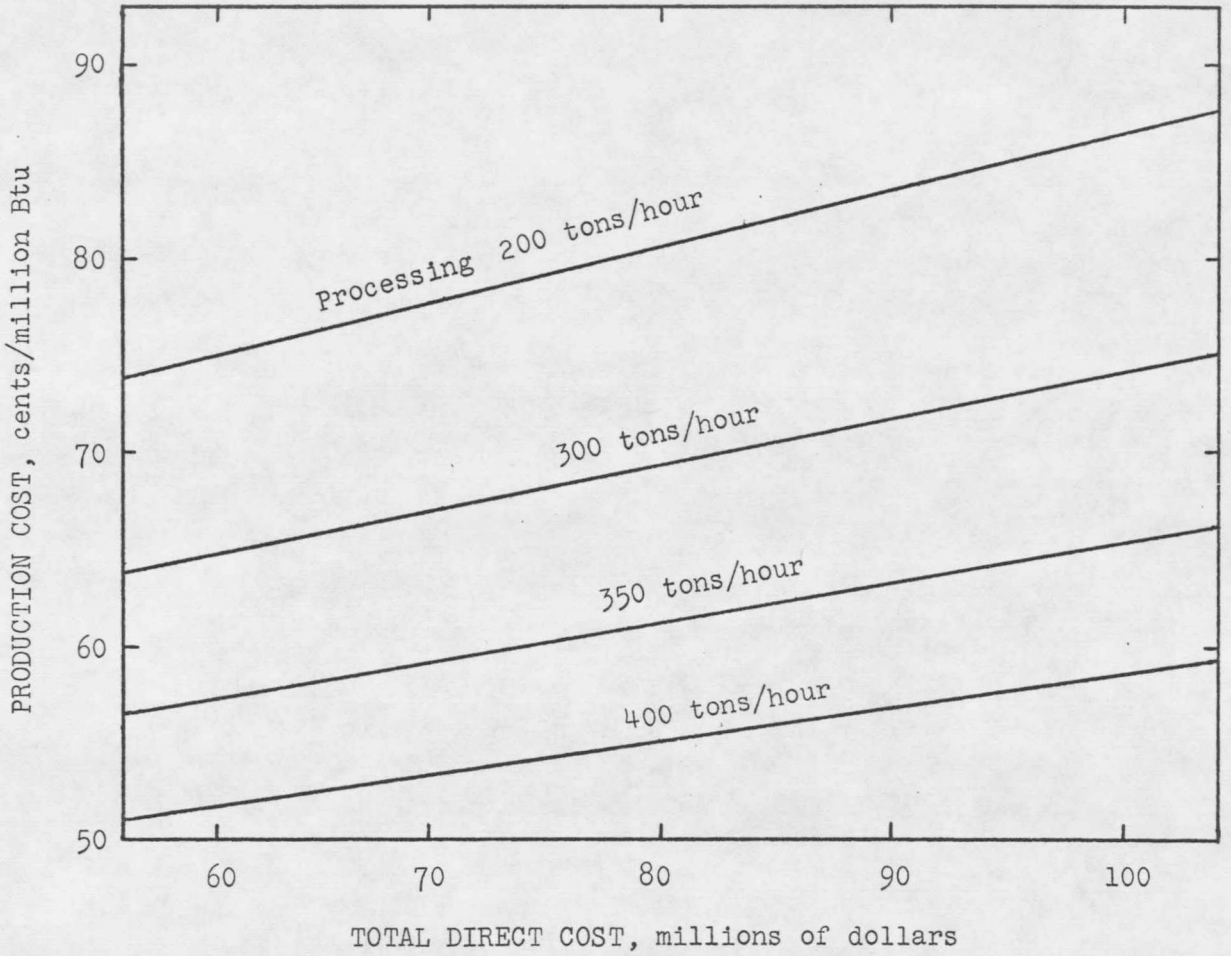

FIGURE 18. Estimated Production Cost for a Coal Conversion Plant using York's (28) "Alpha" Scheme.

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