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Autoclave Studies of Lignite Liquefaction

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AUTOCLAVE STUDIES OF LIGNITE LIQUEFACTION

by
Bruce G. Miller, M.S.

Bachelor of Science in Chemical Engineering
University of North Dakota, 1981

A Thesis

Submitted to the Graduate Faculty

of the

University of North Dakota

in partial fulfillment of the requirements

for the degree of

Master of Science

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Autoclave Studies of Lignite Liquefaction

Bruce G. Miller, M.S.

The University of North Dakota, 1982

Faculty Advisor: Dr. Thomas C. Owens

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at or near the reaction temperature (380-420°C) increased. Higher con-
versions and greater oil and gas yields were obtained when using
synthesis gas as compared to pure hydrogen. The increase in gas yield
for the synthesis gas runs can be attributed to increased carbon dioxide
production.

This Thesis submitted by Bruce G. Miller 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.

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This Thesis meets the standards for appearance and conforms to the style and format requirements of the Graduate School of the University of North Dakota, and is hereby approved.

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ii   497870

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Date _July 27, 1987_

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ABSTRACT

The effect of time at reaction temperature on the liquefaction of lignite using hydrogen or synthesis gas was studied. A slurry containing 200 grams of moisture-ash-free (MAF) lignite, 100 grams of water, and 400 grams of hydrogenated anthracene oil solvent was fed into the University of North Dakota Time-Sampling Hot-Charge Batch Autoclave System with the gas at an initial pressure of 400 psig.

Oil yields and conversions ranged from 0.9 percent to 35.7 percent and 66.7 percent to 90.6 percent, respectively, increasing as the time at or near the reaction temperature (380-420°C) increased. Higher conversions and greater oil and gas yields were obtained when using synthesis gas as compared to pure hydrogen. The increase in gas yield for the synthesis gas runs can be attributed to increased carbon dioxide production.

CHAPTER I

INTRODUCTION

Interest in converting coal to liquid products has been rather cyclic and affected by the cost and availability of petroleum. In the beginning of the industrial revolution, coal was the major source of energy in the United States and continued to dominate the United States' energy supply for the next hundred years, as shown in Figure 1 (1).[1] Petroleum quickly became the preferred energy source after its discovery in Pennsylvania in 1859 and its rapid commercial production in the early 1900's. By the early 1920's, worries that oil supplies were being depleted along with an expanding automobile industry caused coal liquefaction research to flourish. But this was short-lived; when oil was discovered in Texas in the mid-1920's, further work on coal liquefaction ceased. After World War II the United States experienced petroleum shortages, and coal liquefaction was again considered as an alternative. A sizeable research effort resulted. However, discovery of massive petroleum reserves in the Middle East in the mid-1940's once again made coal liquefaction uneconomical. In 1973 the United States' petroleum production began to decline and unrest developed in the Middle East. The limited availability of domestic supplies of natural gas and crude oil and the desire to reduce the country's dependence on foreign sources of energy have promoted considerable interest in this country in

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[1]Numbers in parenthesis refer to items on the List of References at the end of this paper.

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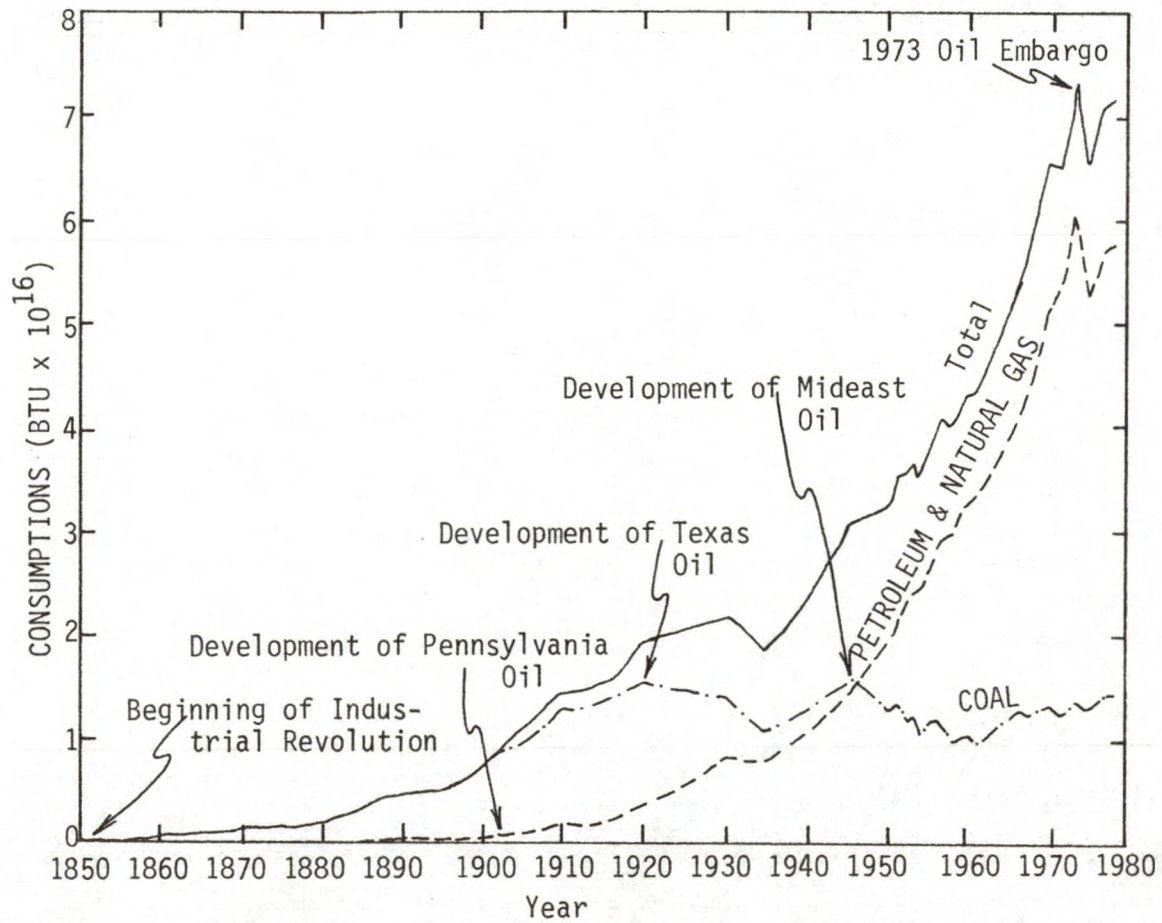
Figure 1. Consumption of Fossil Fuels in the United States.

developing alternative domestic sources of fuel. Because of the abundance of mineable coal reserves in the United States, coal liquefaction is once again being considered as a major source of liquid fuels.

The major differences between coal and petroleum are the ratio of hydrogen to carbon and the ash content (2). Coal has an atomic hydrogen to carbon ratio of approximately 0.8, while the ratio for oil is about 1.8. Coal has an ash content that can be as high as 15 percent, whereas oil seldom has over a few tenths of a percent. Thus, the problem in liquefaction is to increase the hydrogen content of the material and to eliminate the ash.

In this work, lignite liquefaction using hydrogen or synthesis gas was studied. The effects of temperature and feed gas composition on lignite liquefaction were examined.

CHAPTER II

PREVIOUS EXPERIMENTAL WORK

Coal was hydrogenated in the laboratory by Berthelot as early as 1869. The reaction was carried out with hydriodic acid at 270°C for 24 hours, and a 67 percent yield of oil containing aromatics and naphthenes was obtained (3).

In 1911 Bergius obtained oil by hydrogenating coal without a catalyst under hydrogen pressure at 300 to 350°C. In 1913 he applied for the first patent on coal hydrogenation, and in 1931 he was awarded the Nobel Prize in Chemistry (3,4). Bergius also observed that coal paste could be injected readily into a vessel under pressure. The role of catalysts in the hydrogenation of coal was not realized until later.

At the end of 1925, I. G. Farben hydrogenated coal using a molybdenum oxide catalyst. The presence of the catalyst allowed the hydrogenation of coal in the presence of excess hydrogen at low partial pressure and at temperatures of 400 to 450°C.

In the following year, Farben conducted the liquefaction process in two steps because high-molecular-weight materials in the intermediate hydrogenation product fouled the catalyst. Coal was mixed with catalyst and hydrogenated in the liquid phase to middle oil, which was further hydrogenated to gasoline in vapor-phase over a fixed bed of catalyst (3).

Pott and Broche showed that it was possible to liquefy coals to considerable extent, in some cases to 80 percent and higher, into

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suitable oils or mixtures of oils by the method of pressure extraction (5). Also, it was noted that in order to effect considerable liquefaction of the coal, the pressure extraction must be carried out at increasing temperatures up to 400°C. The temperature increase must be regulated so it follows the gradually increasing temperature of decomposition of the material undergoing extraction. The coal fractions going into solution were then easily converted into oils by pressure hydrogenation at temperatures of 430 to 450°C.

The Bureau of Mines started work on the hydrogenation of coal at Pittsburgh, Pennsylvania in 1934 and used batch autoclaves. This was followed by continuous liquid-phase hydrogenation in 1936.

The feasibility of using total extraction as a means for producing clean fuels from coals was investigated in the early 1960's by Spencer Chemical Company under a contract with the then U.S. Office of Coal Research and a Spencer affiliate, the Pittsburgh and Midway Coal Mining Company (4). This work led to the Solvent-Refined Coal (SRC) process and was based on the older Pott-Broche technology. The purpose of the SRC process is to produce an environmentally acceptable solid fuel from coal. Hydrogenation of the coal in the SRC process takes place at elevated pressure and temperature in the presence of hydrogen and without the addition of any catalyst.

In 1921, Fischer and Schrader showed that brown coal could be readily liquefied using carbon monoxide and water (6). This work was not pursued further until the 1960's when Appel, Wender, and other workers at the Pittsburgh Energy Research Center (PERC) demonstrated in autoclave experiments that high yields of a benzene soluble oil could be obtained by treating low rank coals by this method in the presence

of 1,1-a-naphthol-phenanthrene as a solvent (7,8). Most experiments were conducted at fairly high total pressures (270-340 atm) and moderate temperatures (380°C) and obtained as much as 89 percent conversion of lignite to benzene solubles in ten minute residence time.

From 1965 to 1970, batch autoclave runs were carried out at the University of North Dakota (UND) with support from the Great Northern Railway, to investigate the production of liquids from lignite. The process involved contacting lignite slurried with recycle solvent and synthesis gas (50-60% CO + 30-50% H_2) in a noncatalytic reactor. Conversions as high as 96 percent were obtained and optimum operating conditions of 750°F and 1500 psig initial hydrogen pressure were determined (9). Anthracene oil appeared to be the most promising commercial material for use as a starting solvent (9,10).

In 1972, UND signed a research contract with the U.S. Office of Coal Research to develop the necessary data to design a lignite refinery which would produce high-quality solid, liquid, and gaseous fuels from Northern Plains Province lignite (11,12). Primary effort was directed toward operating a 0.6 ton/day process development unit (PDU) designed for continuous solvent extraction of lignite at pressures up to 2500 psig and at temperatures up to 950°F in an atmosphere of reducing gases, usually synthesis gas, and with a hydrogen donor solvent. The Project Lignite PDU produced approximately 15 pounds per hour of solvent refined lignite (SRL) with a melting point of 300-400°F, as well as additional quantities of lighter liquids and gases (13,14). Continuous operation of the PDU for twenty-eight day periods was demonstrated, but a problem with solids buildup in the reactor was never completely solved (15).

A technique that was under active investigation at the PERC was the COSTEAM process which is intended to produce low-sulfur fuel oils from lignite and subbituminous coals and for this purpose reacts coal-oil slurries with synthesis gas (16). Conversion is assisted by the natural moisture content of the coal which increases the hydrogen partial pressure in the reactor because of the water-gas shift reaction, and by mild catalytic activity of iron-bearing compounds in the mineral matter of the coal.

The COSTEAM process has also been under investigation at the Grand Forks Energy Technology Center (GFETC) since 1975, with the design and construction of a 5 pound per hour continuous process unit (CPU) and a hot-charge time-sampled autoclave system (17,18). The present investigation was performed using the latter system.

CHAPTER III

COAL LIQUEFACTION

The term liquefaction as used here includes conversion of coal in which the major product is liquid. The liquid has been rather broadly defined on the basis of solubility in various solvents, and in many cases a major liquid product is solid at room temperature. Gases, water, and distillate oils are produced in addition to the heavy liquid product. Therefore, before an introduction to coal liquefaction is presented, terms used in this study will be defined.

Definitions of Terms

The percent conversion is defined as 100 minus the ash-free tetrahydrofuran (THF)-insoluble material as weight percent of MAF lignite charged:

$$\text{Percent Conversion} = \frac{\text{MAF lignite in} - \text{MAF THF-insoluble}}{\text{MAF lignite in}} (100)$$

Oil yield is the MAF ratio of cyclohexane solubles to lignite charged. Cyclohexane was chosen as a solvent based on trial extractions of previously analyzed samples from UND's hot-charged time-sampled batch autoclave studies. The amounts of cyclohexane soluble materials in these samples were closely related to the oil yields determined by microdistillation at 250°C and one torr as shown in Table 1.

SRL is the weight percent of the material soluble in THF but insoluble in cyclohexane expressed as percent of the MAF lignite charged.

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TABLE 1

COMPARISON OF OIL YIELDS DETERMINED BY EXTRACTION AND DISTILLATION

Sample	N-44	N-54	N-68
Distillable Oils	62.9%	66.2%	79.2%
Cyclohexane Solubles	69.5%	70.6%	79.9%

The insoluble organic matter (IOM) is the ash-free portion of the THF insoluble expressed as weight percent of the MAF lignite charged. Previous work at UND showed little difference in the change in mass of ash during liquefaction of Zap coal; therefore, the mass of ash in the THF insoluble material was assumed equal to the mass of ash in the lignite charged (19).

Gas yield is the increase in mass of gas expressed as percent of MAF lignite charged.

Direct Coal Liquefaction

Most direct coal liquefaction processes react coal, a solvent, and hydrogen gas in the presence of a catalyst at high temperatures and pressures. Catalysts have been omitted from the following discussion because they were not used in this study.

The primary liquefaction processes involve the consumption of hydrogen. The solvent is thought to play the essential role of transferring hydrogen from the gas phase to the coal. Most liquefaction processes are usually conducted between 375 and 465°C, that is, within the range in which pyrolysis or thermal decomposition of the coal becomes important (6). A number of competing chemical processes are taking place simultaneously; the more important ones are coal pyrolysis, coking, hydrogen transfer from solvent to coal, solvent rehydrogenation, and direct interaction of molecular hydrogen with the coal.

Effect of Solvent

The properties of the solvent can affect the primary liquefaction process in various ways. The donor properties of the solvent are of prime importance in donor solvent extraction. The yield structure will

depend on the nature and concentration of the donors in the solvent present in the system at any time. Once the donor concentration has been increased beyond a minimum value, the yield structure becomes relatively independent of further increases in donor concentration (6).

The operating procedure, conditions, and nature of the solvent can affect the yield structure. For example, previous work has shown that high heating rates such as those obtained when using microauto-claves and continuous units usually result in a lower conversion at the same hydrogen input than when using batch autoclaves (20). Yield structure may also be affected by operating temperature. Relatively high temperatures (350-425°C) cause the coal matrix to swell and also aid in overcoming the van der Waals forces holding the soluble molecules in place (6). It has been noted that lower yields are obtained for the same amount of hydrogen transfer at reduced temperatures (21). The upper limit for the yield of liquid products has been in the range of 40-50 percent of the moisture -and ash- free coal and has been achieved at temperatures in the range 450-460°C. Recent research has shown that it is possible to achieve almost complete conversion of coal to liquid products under relatively mild process conditions when basic nitrogen compounds are present in the solvent (22).

Effect of Feed Gas Composition

When carbon monoxide and water were used to liquefy low-rank coals in autoclave experiments, high yields of a benzene soluble oil were obtained (7,8). Low-rank coals were shown to react more readily with carbon monoxide and water than with hydrogen under comparable conditions (23). The relative advantages of carbon monoxide and water versus

hydrogen were also shown to decrease with increasing temperature. Despite this fact, higher conversion is obtained using carbon monoxide over the range of 375 to 425°C.

Experiments done by Appell using pure hydrogen gas have shown that some carbon dioxide is split from the lignite during processing (24).

The use of both pure carbon monoxide and synthesis gas has been investigated for liquefaction; improvements in operating conditions and yield structure were noted as compared with the use of pure hydrogen (25).

Synthesis gas has been used as a replacement for carbon monoxide because it is less expensive and hydrocracking occurs more readily in the presence of hydrogen than in the presence of carbon monoxide (24). Extensive hydrocracking is not desirable but some is needed to reduce the average molecular weight and viscosity of the product. The somewhat higher reactivity of carbon monoxide is offset by the lower cost of the synthesis gas and the need to increase the extent of hydrocracking sufficiently to obtain a liquid product.

The high activity of carbon monoxide in reducing carbonyl groups is believed to be the reason that low-rank coals are liquefied more readily in the presence of carbon monoxide than hydrogen (7). Low-rank coals not only contain more carbonyl groups than higher rank coals but also contain the alkaline materials that are converted to formates, the probable active reducing agents (16). In work done by Appell (25), the high reactivity of aldehydes, and to a lesser extent ketones, with carbon monoxide in the presence of alkali metal carbonates suggested that a crossed Cannizaro-type reaction was occurring between the carbonyl compound and the formate anion with its aldehydic hydrogen.

The effectiveness of carbon monoxide is, therefore, due to its ability to remove a cross-linking rather than any ability to cleave bonds in the lignite. The extent of the reducing action on carbonyl groups is not large because of the limited number of these groups, but the effect is believed to be a significant factor in the liquefaction process.

CHAPTER IV

EXPERIMENTAL PROCEDURE AND EQUIPMENT

Materials

The lignite used was strip-mined at the Indian Head Mine of the North American Coal Company located near Zap, North Dakota. It was obtained from the Grand Forks Energy Technology Center (GFETC) in powdered form. Size distribution, proximate, and ultimate analyses are shown in Table 2.

The lignite sample was dried at 75-85°F for 23 hours and stirred every half hour to reduce the moisture content from approximately 32 to 30 percent. After the coal was dried, it was stored in plastic garbage bags, double wrapped, with as much air forced out of the bags as possible.

A catalytically hydrogenated anthracene oil (HAO-61) was the solvent used for each run. It was obtained from the GFETC where it was made from an anthracene oil (AO-4). Table 3 shows the analyses of HAO-61 and AO-4.

The water used for each run was distilled water.

Tetrahydrofuran (THF), cyclohexane, and methanol were purchased from Fisher Scientific.

Hydrogen and synthesis gas (44.36 and 55.64 mole percent hydrogen and carbon monoxide, respectively) were purchased from the Linde Division of Union Carbide.

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TABLE 2

ANALYSES OF ZAP LIGNITE

Size Distribution

U.S. Screen Size	Percent Passing
60 mesh	100.0
100 mesh	97.5
150 mesh	87.3
170 mesh	75.7
200 mesh	62.8

Proximate Analysis[a]

Constituent	Percent
Volatile Matter	33.6
Moisture	30.6
Fixed Carbon	28.1
Ash	7.7
Total	100.0

[a] as received basis

Ultimate Analysis[b]

Constituent	Percent
Carbon	62.07
Hydrogen	3.81
Nitrogen	1.02
Sulfur	1.03
Oxygen (by diff.)	20.97
Ash	11.10

[b] moisture free basis

TABLE 3

ANALYSES OF SOLVENTS

Solvent	AO4(a)	HA061(b)
ASTM D-1160 Distillation @ 5 torr		
IBP, °C	94	42
Vol. % off at, °C	135	93
10	146	107
20	163	122
30	175	134
40	185	144
50	195	152
60	205	161
70	217	175
80	231	182
90	251	207
95	276	252
Max. Temp., °C	288	273
Vol. % off at Max. Temp.	96.5	97
Calculated from ASTM D-1160		
IBP - 120°C Fraction, Wt. %	3.1	19.2
120 - 260°C Fraction, Wt. %	85.0	77.5
260°C - Max. Temp. Fraction, Wt. %	7.6	1.3
Vacuum Bottoms, Wt. %	4.3	2.0
Density, Gms/ml @ RT	1.107	1.050
Elemental Analysis		
Carbon, Wt. %	90.17	90.29
Hydrogen, Wt. %	5.94	6.99
Nitrogen, Wt. %	0.83	0.37
Sulfur, Wt. %	0.68	0.15
Oxygen, Wt. % (by difference)	2.38	2.20
H/C Ratio	0.79	0.93

(a) As-received anthracene oil from Crowley Tar & Chemical

(b) Anthracene oil catalytically hydrogenated in Continuous Process Unit Run 61 at Grand Forks Energy Technology Center

Equipment

The UND hot-charge time-sample batch autoclave facility was used for this study. The autoclaves and primary support equipment such as the slurry charge and gas compression equipment are discussed briefly in this section. For a detailed description of the autoclaves, primary support equipment, instrumentation and control equipment, and building modifications, see Appendix A. Appendix A is a copy of a report on the facility prepared by Rindt, Severson, and Souby for presentation at the 88th National AICHE meeting on June 8-12, 1980 at Philadelphia, Pennsylvania.

Figure A-1 is an overall flow diagram of the components of the autoclaves and primary support equipment. Figure A-1 is broken down into seven areas as indicated by the dotted lines.

Figure A-2 is a detailed diagram of Area III, the hot-charge auto- clave. This autoclave was used for both hot- and cold-charge runs. The autoclave (AU-101) is a one-gallon stainless steel pressure vessel rated at 5,100 psi at 510°C. It is also equipped with an explosion proof, variable speed, packless, magnetically coupled stirrer. The autoclave (QV-146) used to quench the products instantaneously to room temperature is also in Area III.

Figure A-3 is a detailed diagram of Area II, the slurry charge system for the autoclave. The principal component of this system is the piston accumulator used as the slurry charge vessel (PA-102). The slurry charge vessel is a one-gallon stainless steel accumulator equipped with a movable 4-inch piston with a 10,000 psi rating at room temperature. The seals between the piston and the cylinder walls are made of Viton. The upper portion of the accumulator, above the piston,

contains hydraulic oil. The slurry is placed in the lower portion. When charging the slurry into the autoclave, the hydraulic oil may be pumped to pressures as high as 7,500 psi. This system is capable of charging one gallon of slurry into the autoclave at high temperature and pressure in two minutes.

Figure A-4 is a detailed diagram of Area IV, the gas compression system. The major components of this system are two 2-½ gallon piston accumulators (PA-201, PA-202) rated at 10,000 psi at room temperature. In this system gas is on the upper side of the piston and hydraulic oil on the lower side. Gas is supplied from cylinders shown in Area VII-B of Figure A-1. This system is capable of compressing as much as 100 SCF of gas at tank pressure (up to 2,200 psi) to 7,500 psi.

Cold-Charge Runs

The slurry and feed gas were charged into the autoclave and slowly heated to 410°C for the cold-charge runs. At this point the heaters were turned off and the product slurry temperature peaked at 420°C and began to cool down slowly. The product gas was removed at 204°C.

Hot-Charge Runs

The hot-charge runs consisted of two types: hot-charge at 320°C, and hot-charge at 360°C. The first type involved charging the feed gas into the autoclave and heating it to 340°C. The slurry was then charged into the autoclave and the temperature dropped below 320°C. The constituents were then heated to 420°C and upon reaching 420°C the products were quenched to room temperature. The residence time (time the constituents are in the reactor) was recorded; it was 29 minutes.

The second type of hot-charge run involved charging the feed gas into the autoclave and heating it to 380°C. The slurry was then charged into the autoclave and the temperature dropped below 360°C. The constituents were heated to 420°C and held at 420°C until the residence time of 29 minutes was attained. The products were then quenched to room temperature.

Slurry Preparation

Moisture and ash of the feed coal were determined by American Society for Testing and Materials (ASTM) procedures #D3173 and D3174, respectively. After the moisture content of the coal was determined, the slurry was prepared according to the ratio; Water:MAF lignite: Solvent = 100 grams:200 grams:400 grams. To compensate for losses of slurry during charging, 202 grams and 205 grams of MAF lignite were used for the cold-charge and hot-charge runs, respectively.

Addition of Slurry to the Reactor

The slurry was charged directly into the reactor for the cold-charge runs by drawing the slurry through the head with a vacuum. For the hot-charge runs the slurry was charged into the reactor from the charger. Weighed disposable wipes were used to recover any slurry that was not charged into the reactor.

Product Slurry Removal

Upon completion of a run, the reactor or quench vessel was opened and the products were transferred into a previously weighed quart can. Weighed disposable wipes were used to recover any remaining material. Small portions of the product slurry were analyzed to determine

solubility in cyclohexane, solubility in THF, moisture content, and ash content. Figure 2 is a flowsheet of a typical run and the subsequent analyses of the products.

Product Gas Analysis

The product gas was released from either the reactor or quench vessel through three cold traps located in series. The function of the cold traps was to remove water from the gas. Next, the gas passed through a meter calibrated for 60°F and atmospheric pressure before it was collected in a 15 cubic foot gas sampling bag. Hydrogen sulfide was determined by ASTM method #D2385, and ammonia was determined by the Nessler Method as found in APHA Standard Methods (26). The gas was then analyzed using a Hewlett Packard F and M Scientific 700 Laboratory Chromatograph using Porpak Q and 5A Mole Sieve columns. Carbon dioxide, ethane, and propane were analyzed from the Porpak Q column, and hydrogen, oxygen, nitrogen, methane, and carbon monoxide were analyzed from the Mole Sieve column. The specific gravity of the gas was determined by the Regnault method using a gas density bulb (27).

Solubility in Cyclohexane and THF

Approximately 1.0 gram of product slurry was extracted with cyclohexane and filtered through a preweighed 0.5 micron filter (Millipore, type FH). Dry nitrogen gas was used for pressure filtration. The filter cake was washed with cyclohexane until the filtrate ran clear. Approximately 200 ml of cyclohexane was used for the extraction and washing.

The residue from the cyclohexane extraction was extracted with THF by the same procedure. Conversion and oil yields were calculated
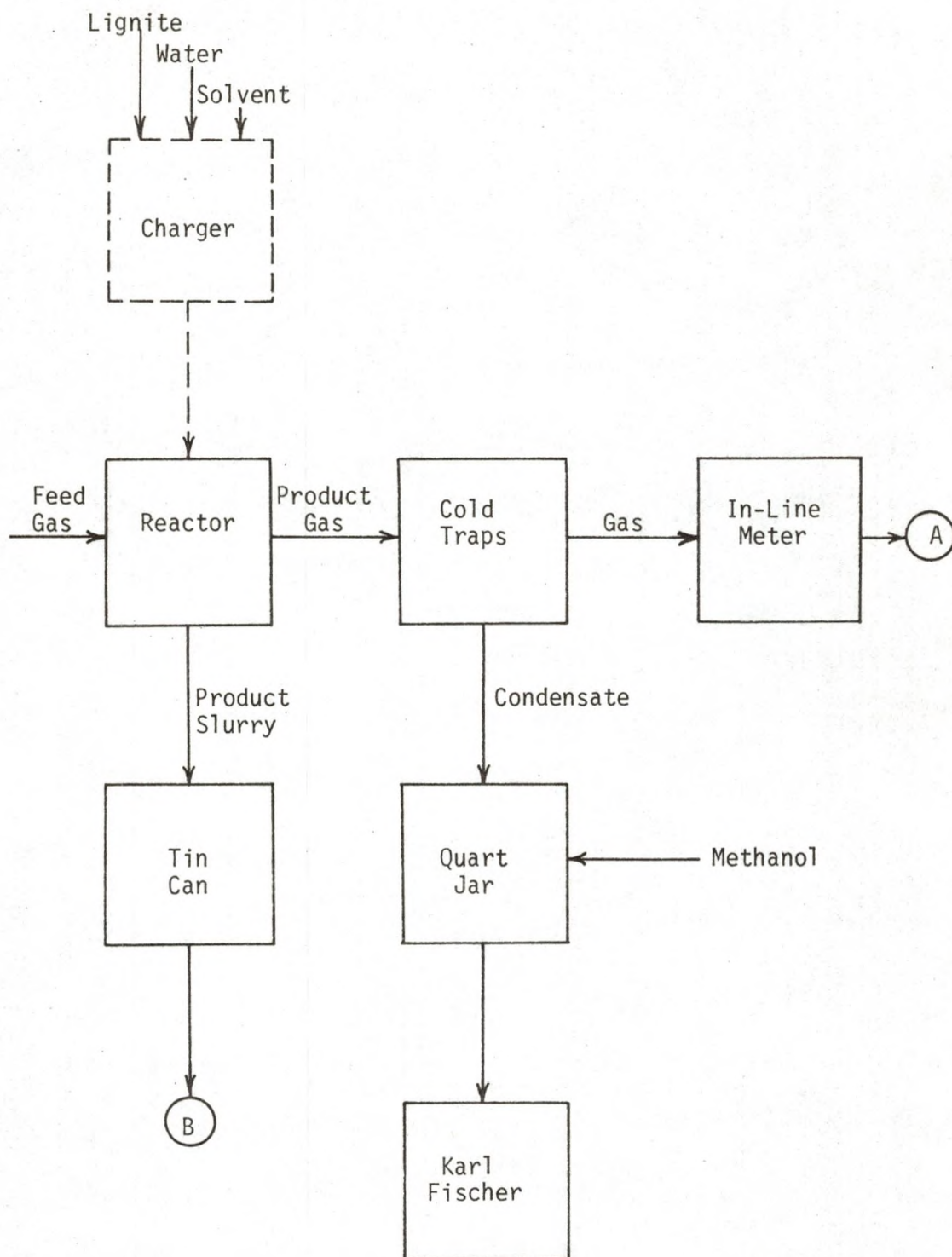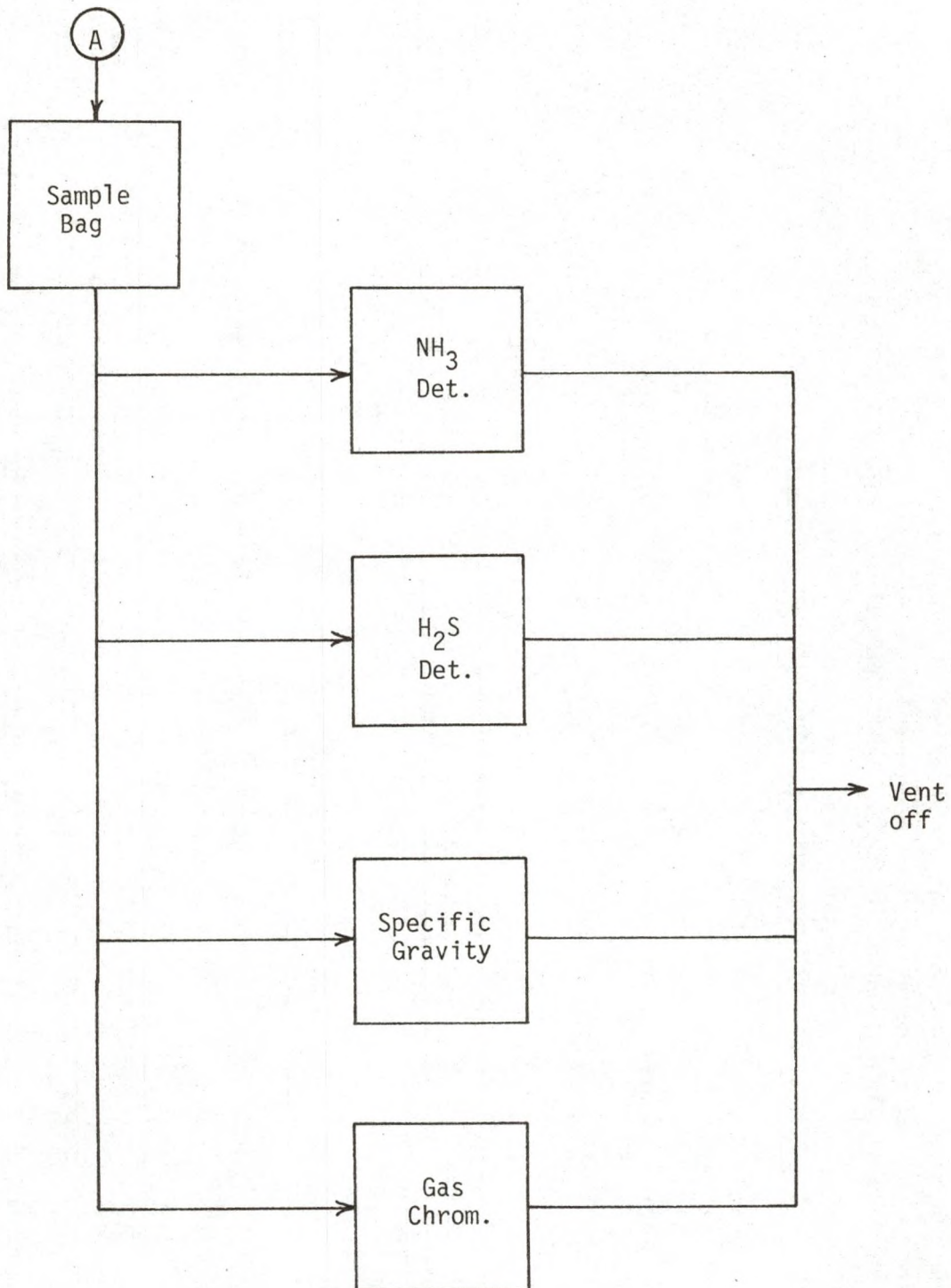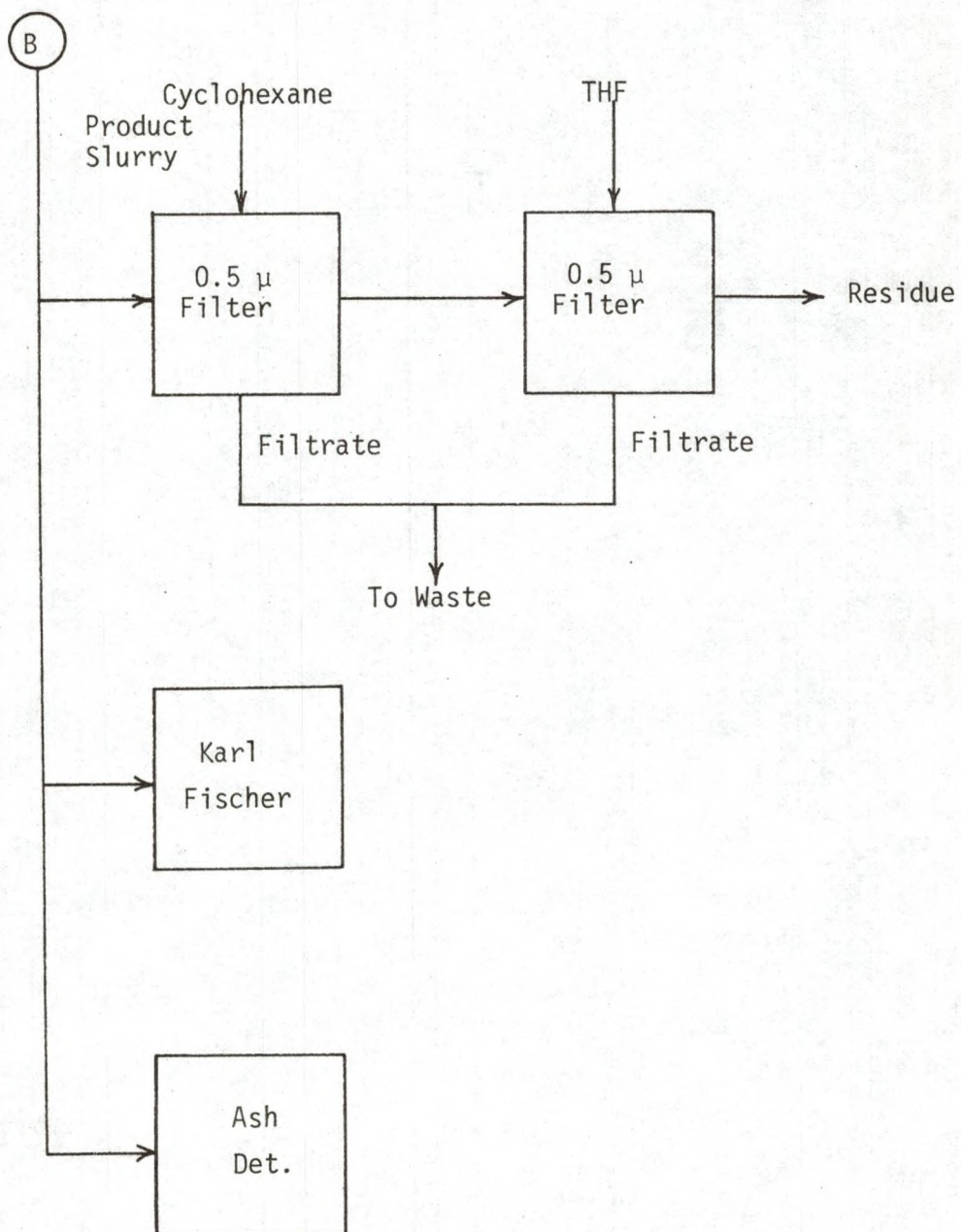
Figure 2. Flowsheet of A Typical Run and Analyses.

Figure 2. Continued.

Figure 2. Continued.

from the raw data as shown in Appendix B.

Moisture Determination

The moisture content of the product slurry from the cold-charge runs was expected to be low because the gas was removed from the reactor at 204°C with the moisture leaving the reactor as water vapor. Small portions of the product slurry were removed using a micropipette, weighed, and analyzed for moisture by the Karl Fischer method using a Photovolt Aquatest IV automatic titrator.

The moisture content of the product slurries from the remaining runs was expected to be higher because the products (slurry and gas) were quenched to room temperature before the gas was removed. Because of the expected high moisture content, small portions of the slurry were analyzed by the Karl Fischer method by hand titrating. The automatic titrator was not used because concentrations over 10 percent take a considerable amount of time to titrate.

Methanol was added to the cold trap condensate to dilute it to a 15:1 ratio. Upon complete mixing, small portions of the homogeneous methanol phase containing the moisture were removed and analyzed by the Karl Fischer method using the Photovolt Aquatest IV automatic titrator. The product moisture calculations are shown in Appendix B.

Ash Determination

Ash content of the product slurry was determined by ASTM procedure #D3174.

CHAPTER V

DISCUSSION OF RESULTS

A summary of the conditions of all runs appears in Appendix C.
Computer printouts of the run summaries are included in Appendix D. The
material balance closure for run B-4 was only 90.1 percent; therefore,
the results were not used in this study. Run B-6 is a repeat of run
B-4 and had material balance closure near 100 percent, so run B-6 was
used instead of B-4. The computer program used to do all calculations
is shown in Appendix E.

Oil yields and conversions ranged from 0.9 percent to 35.7 percent
and 66.7 percent to 90.6 percent, respectively, and are consistent with
earlier liquefaction work that used a non-basic nitrogen heterocyclic
solvent (22). Specifically, these results are consistent with similar
work done by Hanson at UND using HAO-61 and synthesis gas in a micro-
reactor (28).

Hydrogen as Feed Gas

Runs B-1, B-2, and B-3 were conducted using pure hydrogen as feed
gas and are summarized in Table 4. Run B-1, a cold-charge run, has high-
er conversion than either runs B-2 or B-3, hot charge runs at 320 and
360°C, respectively. This is consistent with results obtained by Gorin
and co-workers (20) in which it was found that the longer overall reac-
tion time, resulting from the slow heat-up and cool-down periods, has a
favorable effect on the extent of conversion. This is further

TABLE 4

SUMMARY OF RUNS USING HYDROGEN AS FEED GAS

Run Number	Temperature History	Normalized Net Yields as Weight % of MAF Lignite						
		Water	Oil	SRL	IOM	Gas	Conversion	% Closure
B-1	Cold Charge Heat to 420°C Slow Cooling	10.7	14.2	41.0	11.6	25.3	88.4	98.2
B-2	Hot Charge at 320°C Heat to 420°C Quench Residence time = 29 min.	10.9	0.9	38.8	33.3	16.7	66.7	101.1
B-3	Hot Charge at 360°C Heat to 420°C Hold at 420°C until total time = 29 min. Quench	7.5	19.6	45.4	15.9	11.4	84.1	96.6

demonstrated in run B-2 where the products were quenched to room temperature immediately upon reaching 420°C. In this run the conversion was approximately 75 percent of the conversion attained in run B-1.

Hydrogen becomes more effective in hydrogenating coal as the time at reaction temperature is increased; this is confirmed by the results shown in Table 5. Table 5 shows the product gas compositions for runs B-1, B-2, and B-3; the gas consisted primarily of hydrogen and carbon dioxide. More hydrogen was recovered in the product gas for runs that had shorter residence times at or near 420°C. Concurrently, carbon dioxide production decreased. Experiments using pure hydrogen have shown that some carbon dioxide is split from the lignite during processing (24). This could explain the increase in carbon dioxide production as the residence time at or near 420°C increased.

The SRL yields for all three runs are similar, while the oil yields for runs B-1 and B-3 are approximately equal and considerably larger than the oil yield for run B-2. Another similarity between runs B-1 and B-3 is seen in the IOM yields, which are again nearly equal but less than that observed for run B-2. This suggests that the IOM may be converted to SRL, which in turn is converted to oil during longer times at or near 420°C. Another possibility, and probably more likely because the SRL yields are similar, is that the IOM is converted directly to oils. Two statistically similar kinetic models were developed by Culpon (26) to describe the liquefaction of North Dakota lignite in a continuous stirred tank reactor. In his first model, Model B, coal is converted to asphaltenes (SRL) or directly to oils. Asphaltenes can be further converted to oils. In his second model, Model C, coal is either converted to asphaltenes or to oils. Culpon reports that more

TABLE 5

PRODUCT GAS COMPOSITION USING HYDROGEN AS FEED GAS

Run Number	CO_2	C_2H_6	C_3H_8	H_2	CH_4	CO	H_2S	NH_3
B-1	8.93	0.40	0.19	86.44	1.06	1.88	0.16	0.02
B-2	7.04	0.06	0.01	89.75	0.39	0.22	0.15	0.01
B-3	4.50	0.52	0.00	92.02	0.86	0.15	0.19	0.04

kinetic data is needed on the rate of conversion of the asphaltenes to oils. Therefore, there may be shortcomings to both models and no definite conclusion can be drawn for the above observation.

Synthesis Gas as Feed Gas

Runs B-5 and B-6 were conducted using synthesis gas as feed gas. A summary of these runs is shown in Table 6. It can be seen that SRL and IOM values for both runs are approximately the same. Run B-6, a cold-charge run, has slightly better conversion and higher gas and oil yields. Higher conversion and greater oil yield for the cold-charge run were expected because earlier batch studies using synthesis gas have shown similar trends (30).

The product gases consisted primarily of carbon monoxide, hydrogen, and a significant amount of carbon dioxide, as shown in Table 7. The greater yield of carbon dioxide agrees with prior results obtained when hydrotreating coal using synthesis gas, where it was determined that large amounts of the oxygen in the coal were removed as carbon dioxide (31).

Synthesis Gas Versus Hydrogen as Feed Gas

The cold-charge run using synthesis gas, run B-6, had higher conversion and oil production than run B-1 where hydrogen was used as the feed gas. This trend was also observed between runs B-5 and B-3, hot-charge runs at 360°C, using synthesis gas and hydrogen as feed gases, respectively. A comparison of hydrogen and carbon monoxide for liquefaction has shown that carbon monoxide is selective to reduction of the carbonyl group, whereas hydrogen causes more cracking. As mentioned earlier, the high activity of carbon monoxide for reducing carbonyl

TABLE 6

SUMMARY OF RUNS USING SYNTHESIS GAS AS FEED GAS

| Run Number | Temperature History | Normalized Net Yields as Weight % of MAF Lignite | | | | | | |
		Water	Oil	SRL	IOM	Gas	Conversion	% Closure
B-5	Hot Charge at 360°C Heat to 420°C Hold at 420°C until total time = 29 min. Quench	-18.9	27.2	45.6	10.8	34.7	89.2	101.5
B-6	Cold Charge Heat to 420°C Slow Cooling	-18.9	35.7	49.6	9.4	27.6	90.6	98.7

TABLE 7

PRODUCT GAS COMPOSITION USING SYNTHESIS GAS AS FEED GAS

Run Number	CO_2	C_2H_6	C_3H_8	H_2	CH_4	CO	H_2S	NH_3
B-5	29.71	0.53	0.00	41.81	0.70	26.45	0.18	0.02
B-6	22.98	0.27	0.10	46.13	0.73	28.87	0.20	0.02

groups is believed to be the reason that low-rank coals are liquefied more readily in the presence of carbon monoxide than hydrogen.

Gas yield was similar for both run B-6 and run B-1; however, run B-5 had three times as much gas produced as did run B-3. It was the large amount of carbon dioxide produced in run B-5 that caused this significant difference.

Water yields as shown in Tables 4 and 6 are positive for runs using hydrogen and negative for runs using synthesis gas. This implies that water is produced in the former runs and depleted in the latter. Water was expected to react with carbon monoxide from the synthesis gas and form carbon dioxide and hydrogen via the water-gas shift reaction.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

1. Higher conversions and greater oil yields were obtained when using
    synthesis gas as compared to pure hydrogen. This is consistent with
    previous work and occurred because of the presence of carbon monox-
    ide in the feed gas.

2. Longer times at or near the reaction temperature (380°-420°C)
    resulted in higher conversions and greater oil yields under the
    conditions used.

3. Synthesis gas produced more carbon dioxide than similar runs using
    hydrogen, resulting in a higher gas yield.

4. Oil yields and conversions ranged from 0.9 percent to 35.7 percent
    and 66.7 percent to 90.6 percent, respectively.

5. SRL yields were similar for all runs.

Recommendations

1. A hot-charge run should be performed to determine the identity of
    reactor contents at residence time equal to zero. As mentioned
    earlier, for a hot-charge run at 320°C the feed gas was heated to
    approximately 340°C before the slurry was charged. Upon slurry
    charging the temperature dropped below 320°C and it took several
    minutes before the temperature was back up to 320°C and timing of
    the residence period began. A run conducted where the contents of
    the autoclave are quenched as soon as they reach 320°C and

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subsequently analyzed would determine if there are products formed before timing begins. If products are formed, these could be subtracted from the final results to give a better overall picture of what is occurring during the residence time only.

2. A hot charge run could be conducted at 420°C using synthesis gas and the results compared with those obtained for the hot-charge run at 360°C.

APPENDICES

APPENDIX A

UNIVERSITY OF NORTH DAKOTA HOT-CHARGE TIME-SAMPLE
BATCH AUTOCLAVE FACILITY

UND HOT-CHARGE TIME-SAMPLE BATCH AUTOCLAVE FACILITY

By

Rindt, J. R., Severson, D. E., and Souby, A. M.

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UND HOT-CHARGE TIME-SAMPLE BATCH AUTOCLAVE FACILITY

The University of North Dakota (UND) Chemical Engineering Department is performing contract research with the Grand Forks Energy Technology Center (GFETC) on the liquefaction of low rank coals. One task under this contract is the design and construction of a versatile two autoclave system, with one autoclave run in a mode suitable for obtaining accurate material balances (charged cold) and the other for accurate kinetics data (charged hot). The autoclave facility is designed to meet current federal health and safety guidelines.

When operating to obtain accurate material balances (with the cold charge autoclave), the reactant materials, gas, solvent, and coal are charged to the autoclave at room temperature. The autoclave is then heated to the desired reaction temperature, held there for the desired reaction time, allowed to cool, and all products collected. This procedure allows 95 to 99 percent product recovery, and thus is quite useful in obtaining material balance data.[1]

The hot charge autoclave, operated to obtain kinetic data, is equipped so that the reactant materials may be charged rapidly into the preheated autoclave. This allows the reactants to reach operating temperatures in a few minutes. Both vapor and liquid phase reactants are sampled at intervals during the reaction to obtain data for kinetic studies. A hot charge, 1-liter autoclave facility operated at GFETC has resulted in product recoveries of 90 to 92 percent. This recovery is less than the 95 to 99 percent recovery reported for a cold charge

autoclave facility operated at UND. The lower recovery for the hot
charge system is due to unavoidable losses during sampling.

The new UND autoclave system was designed to minimize sampling
losses and enhance charging reliability with improvements based on past
autoclave experience. The UND autoclave facility will be discussed in
terms of three major elements, as follows:

1. The autoclaves and primary support equipment such as the slurry
   charge and gas compression equipment,

2. The instrumentation and control equipment which includes tem-
   perature, pressure, gas and liquid phase flow measurement
   systems, and,

3. The building modification primarily related to meeting require-
   ments suggested by current federal health and safety guidelines,
   as listed in the Fossil Energy Program, Environment and Safety
   Program.

The remainder of this paper will describe the features and innova-
tions of the UND Batch Autoclave Facility.

Figure 1 is an overall flow diagram of the components of the auto-
claves and primary support equipment. Figure 1 is broken down into seven
areas as indicated by the dotted lines.

Figure 2 is a detailed diagram of Area III, the hot charge auto-
clave. The autoclave (AU-101) is a one-gallon stainless steel pressure
vessel rated at 5,100 psi (35,000 kPa) at 510°C. It is also equipped
with an explosion proof, variable speed, packless, magnetically coupled
stirrer. The autoclaves are equipped with flush valves at the bottom
for liquid phase time sampling. When closed, the valves leave no pockets
or dead spots on the inside of the autoclave into which reactant materials

may accumulate or settle. This feature should provide reliable liquid sampling data with a minimum of sampling losses since fewer purge samples will be required.

In the one-liter time-sampled autoclave at GFETC, a minimum of 400-gram slurry charge is used to limit change in reactor contents during the run and allow reasonable material balances. This leaves so little remaining space in the reactor that the reaction is depleted of gas. Use of the one-gallon reactor will permit much higher gas-slurry ratio with adequate material balances, thus providing a substantially lengthened time during which the vapor phase reactant is not the limiting reactant. Also, the higher gas volume of the one gallon autoclave reduces the effect of vapor phase time sampling on pressure. The size of each of the time samples is approximately the same as that for the one-liter autoclave, while the reactive vapor volume increases significantly. The time sampling in the one-gallon autoclave produces a smaller pressure loss, resulting in less change in pressure during the reaction time.

Figure 3 is a detailed diagram of Area II, the slurry charge system for the hot charge autoclave. Principal components of this system are the low pressure slurry pump (PD-351) and the piston accumulator used as the slurry charge vessel (PA-102). The low pressure slurry pump is a double diaphragm, positive displacement, variable flow, metering pump, which charges the slurry into the slurry charge vessel. The slurry charge vessel is a one-gallon stainless steel accumulator equipped with a movable 4-inch piston with a 10,000 psi rating (69,000 kPa) at room temperature. The seals between the piston and the cylinder walls are made of Viton. The low-pressure slurry pump charges slurry to the accumulator below the piston. The upper portion of the accumulator

contains hydraulic oil. When charging the slurry into the autoclave, the hydraulic oil may be pumped up to pressures as high as 7,500 psi (52,000 kPa). Two valves between the charge vessel and the autoclave are used to control the charge amount and rate. This highly flexible positive displacement feed system is capable of charging one gallon of slurry into the autoclave at high temperature and pressure in two minutes. The system is also capable of injecting small increments of slurry or other liquid reactants during the reaction. The entire slurry system can be flushed and recharged to allow different materials to be added during a run, e.g., a catalyst may be added after a run is started. This system has several advantages over the use of a slurry pump for direct charging to an autoclave. These include low initial investment as compared to a slurry pump capable of metering slurry at pressure of 7,500 psi (52,000 kPa), improved reproducibility of quantity and composition of slurry charged, and positive displacement of the slurry which avoids the losses due to adherence to charger walls.

Figure 4 is a detailed diagram of Area IV, the gas compression system. The major components of this system are two 2-½ gallon piston accumulators (PA-201, PA-202) rated at 10,000 psi (69,000 kPa) at room temperature. In this system gas is on the upper side of the piston and hydraulic oil on the lower side. Gas is supplied from cylinders shown in Area VII-B of Figure 1. This system is capable of compressing as much as (100 SCF) of gas at tank pressure (up to 2,200 psi) (15,000 kPa) to 7,500 psi (52,000 kPa). This system enjoys the same versatility as the slurry charge system with the additional advantage of continuous feed capability when the two accumulators are used alternately.

Figure 5 is a detailed diagram of Area I, the high pressure hydraulic oil supply system. The major component of the system is the high-pressure, positive-displacement, packed-plunger, metering hydraulic pump (PD-301) which is capable of pumping hydraulic oil at 30 gallons/hour and 7,500 psi (52,000 kPa). It supplies oil to both the slurry charge system and the gas compressor system at a rate which allows both slurry and gas to be charged simultaneously. In addition, the hydraulic pump and slurry pump are driven by the same system to save space and expense. As both pumps have metering capabilities, they may be used simultaneously or independently in the operation of the gas compressor and slurry charge systems. The combination of these systems has greatly reduced initial investment, parts inventory, and maintenance expense, while affording a high degree of flexibility and system independence.

The cold charge autoclave, shown in Figure 1 as Area VII-A, is supplied by the same gas supply and compression system as the hot charge facility.

The second major element of the UND autoclave facility is the instrumentation and controls system. Figure 6 is a schematic diagram of the instrumentation for both the hot and cold charge autoclave. Because of the safety requirements, which will be discussed later, all pressure and temperature measurement are remote. Type J thermocouples are used for temperature signal generation and pressure transducers with 0-20 mA output for pressure signals. Four recorders and four digital displays show temperature and pressures. Autoclave temperature and pressure are recorded with continuous pen recorders, while other temperature and pressure data are recorded on multipoint dot recorders.

All recorders have one second full scale response times. The multipoint
recorders have a skip function enabling any point or points to be elimi-
nated during any given run. Digital display of points not requiring
recording is on four 5-place multi-display pressure and temperature
indicators.

The quality of slurry or gas charged is determined by measuring
the hydraulic fluid displaced during the charge procedure. The hydrau-
lic oil, under constant pressure, is measured by two independent methods,
one being by observation of a sight glass on the seven-gallon oil reser-
voir and the other by means of a turbine flow meter equipped with a
flow rate indicator and totalizer. The gas charged may also be mea-
sured with a gas phase turbine flow meter with a temperature and pres-
sure compensated flow rate indicator and totalizer.

The temperature programmed gas chromatograph (GC) used for analyz-
ing vapor samples is equipped with two columns with column packing
capable of separating H_2O, CO, CO_2, and light hydrocarbons. The analy-
sis of H_2O by the gas chromatograph, not usually incorporated into auto-
clave gas sampling systems, required that the sample collection system
be held at a temperature above the boiling point of H_2O at sample pres-
sure. A gas sample storage system is provided to improve data collection
versatility. Figure 7 is a drawing of the GC sample loops and hot box.
The sample loops are also shown diagramatically in Figure 1, Area IV.
The storage system provides for storage of up to 10 samples, which may
be collected at sampling intervals as short as 20 seconds, for a time
long enough for all 10 samples to be analyzed.

The GC sample loop storage system, as well as the vapor and liquid
phase sampling systems, have several simultaneous timed operations, all

of which can be handled by a programmable controller. The programmable controller provides reliable, reproducible timing for sequenced operations. It can be programmed to operate on a time table in increments as small as 0.01 seconds, and thus essentially eliminates variability for the timed sample events. The controller is also capable of controlling the GC operation, the slurry charge system, and the gas charge system, thus further standardizing operations.

A significant effort in the facility preparation program is the building modification for compliance with federal health and safety guidelines. Figure 8 is a floor plan of the portion of the UND building housing the project. The areas of major building modifications are cells 1 through 4, the lunchroom, and locker rooms 1 through 4.

One guideline employed at GFETC is that direct personnel exposure to high pressure equipment be limited to a vessel at 100°C or less and 3,000 psi (21,000 kPa) or less.[2] As the UND autoclave system is to be operated in excess of these limitations, special enclosures are required. The enclosures are cells 1 through 4 of Figure 8. Figure 9 is a detailed diagram of the barricade structure. The autoclave barricade system is set up to allow the cleaning and maintenance of one autoclave during the operation of the other. Cell 1 contains the hydraulic and slurry pumps; cell 2, the hot charge autoclave; cell 3, the gas compression equipment and GC sample loops; and cell 4, the cold charge autoclave. Each cell has a blast window which opens during an explosion, protecting operators behind the opposing barricade from the consequences of dangerous pressure buildups should an explosion occur. Beyond the blast windows are blast mats woven of ½-inch steel cables. The barracade itself is constructed of ½" Cor-ten steel plate. The

barricade and blast mats have been calculated to provide protection against shrapnel.

Federal health and safety guidelines[3] also specify conditions for extended work in an environment containing coal liquefaction products. Personnel in potential contact with coal liquefaction products are to be supplied with clean work clothing at the start of each work day and must properly dispose of them at the close of each work day. Further requirements include separate change facilities to isolate the area for changing work clothing from that for street clothing. These guidelines require the presence of two locker rooms if only one sex is employed and four if both male and female employees are present. Locker rooms 1 through 4 of Figure 8 are the change facilities planned for the UND autoclave installation.

There are also guidelines for break and lunch times during the work day. A break room isolate from the bulk of the work area, equipped with wash facilities, is required to provide a safe area in which food may be consumed. The lunchroom, shown in Figure 8, meets these requirements.

Ventilation requirements are also quite rigorous. Twenty changes of air per hour are suggested in the barricaded area with 10 changes per hour in the work and locker room areas.

The UND autoclave facility has enough flexibility to be useful for many different research programs and is expected to supply extensive data from studies on the liquefaction of low-rank western coals.

Legend (abbreviations)

AD - AUTOCLAVE
AC - CARRIER GAS CLEANUP APPARATUS
BA - BLADDER ACCUMULATOR
CP - COLLECTION PORT
CT - COLD TRAP
CV - CHECK VALVE
DV - DOUBLE VALVE
FI - FLOW INDICATOR
FIT - FLOW INDICATOR TOTALIZER
FL - FILTER
FM - FINE METERING VALVE
FV - FLUSH VALVE
GC - GAS CHROMATOGRAPH
GV - GAS SAMPLING VALVE
MT - MAGNETIC TACHOMETER PICKUP
PA - PISTON ACCUMULATOR
PD - POSITIVE DISPLACEMENT PUMP
PG - BACK PRESSURE REG. VALVE
PI - PRESSURE INDICATOR

PIR - PRESSURE INDICATOR RECORDER
PR - PRESSURE RELIEF VALVE
PV - SOLENOID VALVE
QV - QUENCH VESSEL
RS - RESERVOIR
RSI - REMOTE SAMPLE INLET
RV - PRESSURE REGULATOR VALVE
RVS - REMOTE VACUUM SOURCE
SB - SURGE CHECK BYPASS VALVE
SC - SURGE CHECK VALVE
SL - SAMPLE LOOP
SP - SURGE PISTON ACCUMULATOR
ST - SAMPLE TRAY
SV - SHUTOFF VALVE
TI - TEMPERATURE INDICATOR
TIC - TEMPERATURE INDICATOR CONTROLLER
TIR - TEMPERATURE INDICATOR RECORDER

PIPE SCHEDULE

A	9/16" O.D.	20,000 psi (S.S.)
B	3/8" O.D.	20,000 psi (S.S.)
C	1/4" O.D.	Plastic Instrument Tubing
D	9/16" O.D.	60,000 psi (S.S.)
E	1/4" O.D.	60,000 psi (S.S.)
F	3/8" O.D.	60,000 psi (S.S.)
G	1/8" O.D.	11,000 psi (S.S.)
H	1/4" O.D.	11,000 psi (S.S.)

FITTING SCHEDULE

1	20BF39964	Bulkhead	(9/16" - 20K) A.E.
2	20N94Z6	Adaptor	(9/16" 20K x 3/8" 20K) A.E.
3	6M49M6	Adaptor	(1/4" NPTM - 9/16" 20K) A.E.
4	6M49M6	Adaptor	(1/4" NPTM - 9/16" 20K) A.E.
5	6M129M6	Adaptor	(3/4" NPTM - 9/16" 20K) A.E.
6	6NX9121X8	Adaptor	(3/4" NPTF - 9/16" 20K) A.E.
7	6M46M6	Adaptor	(1/4" NPTM - 3/8" 20K) A.E.
8	20N96M6	Adaptor	(9/16" 20K x 3/8" 20K) A.E.
9	6M169M6	Adaptor	(1" NPTM - 9/16" 20K) A.E.
10	20BF2566	Bulkhead	(3/8" 20K) A.E.
11	6M126M6	Adaptor	(3/4" NPTM - 3/8" 20K) A.E.
12	20N96M6	Adaptor	(9/16" 60K - 3/8" 20K) A.E.
13	60N94B3	Adaptor	(9/16" 60K - 1/4" 60K) A.E.
14	6M166M6	Adaptor	(1" NPTF - 3/8" 20K) A.E.
15	6M126M6	Adaptor	(3/4" NPTM - 3/8" 20K) A.E.
16	60BF4433	Bulkhead	(1/4" 60K) A.E.
17	6M166M3	Adaptor	(1" NPTM - 3/8" 60K) A.E.
18	6N46M6B3	Adaptor	(1/4" 60K + 3/8" 60K) A.E.
19	6M46B3	Adaptors	(1/4" NPTM - 1/4" 60K) A.E.
20	6M86M3	Adaptors	(1/2" NPTM - 1/4" 60K) A.E.
21	6M46B2	Adaptor	(1/4" 60K + 1/4" 10K) A.E.
22	OCS-B-600/OCS-0-600	Quick Connect	(3/8") Swagloc
23	601PC-4	Adaptor	(3/8" 11K - 1/4" 11K) Swagloc
24	601-PC/4B6-316/NPTM4-116	Adaptor	(3/8"-1/4"-TLI-1/8") Swagloc
25	6M42D1	Adaptor	(1/4" 10K - 1/8" 10K) A.E.
26	15M42B1	Adaptor	(1/4" 60K + 1/8" 11K) B.E.
27	15BF2211	Bulkhead	(1/8" 11K) A.E.
28	6M26C8	Adaptor	(1/4" NPTF - 1/8" 10K) A.E.
29	ST2220	Tee	(1/8" 11K) A.E.
30	SA-2-TSW-3	Weld Tee	(1/8" 11K) Cajon
31	6M44M2	Adaptor	(1/4" NPTM - 1/4" 11K) A.E.
32	6M412D8	Adaptor	(3/4" NPTF + 1/4" 11K) A.E.

Figure A-1. Overall Flow Diagram.

AD - AUTOCLAVE
AC - CARRIER GAS CLEANUP APPARATUS
BA - BLASTTER ACCUMULATOR
CP - COLLECTION PORT
CT - COLD TRAP
CV - CHECK VALVE
DV - DOUBLE VALVE
FI - FLOW INDICATOR
FIT - FLOW INDICATOR TOTALIZER
FL - FILTER
FM - FINE METERING VALVE
FV - FLUSH VALVE
GC - GAS CHROMOTOGRAPH
GV - GAS SAMPLING VALVE
MT - MAGNETIC TACHOMETER PICKUP
PA - PISTON ACCUMULATOR
PD - POSITIVE DISPLACEMENT PUMP
PG - BACK PRESSURE REG. VALVE
PI - PRESSURE INDICATOR

PIR - PRESSURE INDICATOR RECORDER
PR - PRESSURE RELIEF VALVE
PV - SOLENOID VALVE
QV - QUENCH VESSEL
RS - RESERVOIR
RSI - REMOTE SAMPLE INLET
RV - PRESSURE REGULATOR VALVE
RVS - REMOTE VACUUM SOURCE
SB - SURGE CHECK BYPASS VALVE
SC - SURGE CHECK VALVE
SL - SAMPLE LOOP
SP - SURGE PISTON ACCUMULATOR
ST - SAMPLE TRAY
SV - SHUTOFF VALVE
TI - TEMPERATURE INDICATOR
TIC - TEMPERATURE INDICATOR CONTROLLER
TIR - TEMPERATURE INDICATOR RECORDER

PIPE SCHEDULE

Ⓐ	9/16" O.D.	20,000 psi (S.S.)
Ⓑ	3/8" O.D.	20,000 psi (S.S.)
Ⓒ	1/4" O.D.	Plastic Instrument Tubing
Ⓓ	9/16" O.D.	60,000 psi (S.S.)
Ⓔ	1/4" O.D.	60,000 psi (S.S.)
Ⓕ	3/8" O.D.	60,000 psi (S.S.)
Ⓖ	1/8" O.D.	11,000 psi (S.S.)
Ⓗ	1/4" O.D.	11,000 psi (S.S.)

FITTING SCHEDULE

1	20BF39966	Bulkhead	(9/16" - 20K) A.E.
2	20M9486	Adaptor	(9/16" 20K + 3/8" 20K) A.E.
3	6M49M6	Adaptor	(1/4" NPTM - 9/16" 20K) A.E.
4	8M49M6	Adaptor	(1/4" NPTM - 9/16" 20K) A.E.
5	8M12M6	Adaptor	(3/4" NPTM - 9/16" 20K) A.E.
6	8H09128B	Adaptor	(3/4" NPTF - 9/16" 20K) A.E.
7	6M46M6	Adaptor	(1/4" NPTM - 3/8" 20K) A.E.
8	20M96X6	Adaptor	(9/16" 20K - 3/8" 20K) A.E.
9	6M16M6	Adaptor	(1" NPTM - 9/16" 20K) A.E.
10	20BF1666A	Bulkhead	(3/8" 20K) A.E.
11	6M12M6	Adaptor	(3/4" NPTM - 3/8" 20K) A.E.
12	20M9686	Adaptor	(9/16" 60K - 3/8" 20K) A.E.
13	60M9483	Adaptor	(9/16" 60K - 1/4" 60K) A.E.
14	6M16606	Adaptor	(1" NPTM - 3/8" 20K) A.E.
15	6M12M6	Adaptor	(3/4" NPTM + 3/4" 20K) A.E.
19	60BF4433	Bulkhead	(1/4" 60K) A.E.
20	6M166M3	Adaptor	(1" NPTM - 3/8" 60K) A.E.
21	60M4683	Adaptor	(1/4" 60K + 3/8" 60K) A.E.
22	6M46M3	Adaptors	(1/4" NPTM - 1/4" 60K) A.E.
23	6M84M3	Adaptors	(1/2" NPTM - 1/4" 60K) A.E.
24	6M44M2	Adaptor	(1/4" 60K + 1/4" 10K) A.E.
25	QC6-B-600/QC6-D-620	Quick Connect	(1/8") Swaglok
26	601PC-4	Adaptor	(1/8" 11K + 1/4" 11K) Swaglok
27	601-PC/4M6-316/67MT4-316	Adaptor	(3/8"-1/4"-TEE-1/8") Swaglok
28	6M42P1	Adaptor	(1/4" 10K + 1/8" 10K) A.E.
29	CT-4440	Tee	(1/4" 60K) A.E.
30	15M42B1	Adaptor	(1/4" 60K + 1/8" 11K) A.E.
31	15BF2211	Bulkhead	(1/8" 11K) A.E.
32	6M26CB	Adaptor	(1/4" NPTF - 1/8" 10K) A.E.
33	CT2220	Tee	(1/8" 11K) A.E.
34	SS-2-TSW-1	Weld Tee	(1/8" 11K) Cajon
35	6M44M2	Adaptor	(1/4" NPTM - 1/4" 11K) A.E.
36	6M41206	Adaptor	(3/4" NPTF + 1/4" 11K) A.E.

Figure A-2. Detail diagram of the UND hot charge autoclave components.

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Figure A-3. Detail diagram of the UND autoclave facilities slurry charge components.

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AREA II

ENG.: J. RINDT   DRN. BY: J. BETCHER
DATE: 11-7-79   DRG. NO.: FY79-TO-4-12

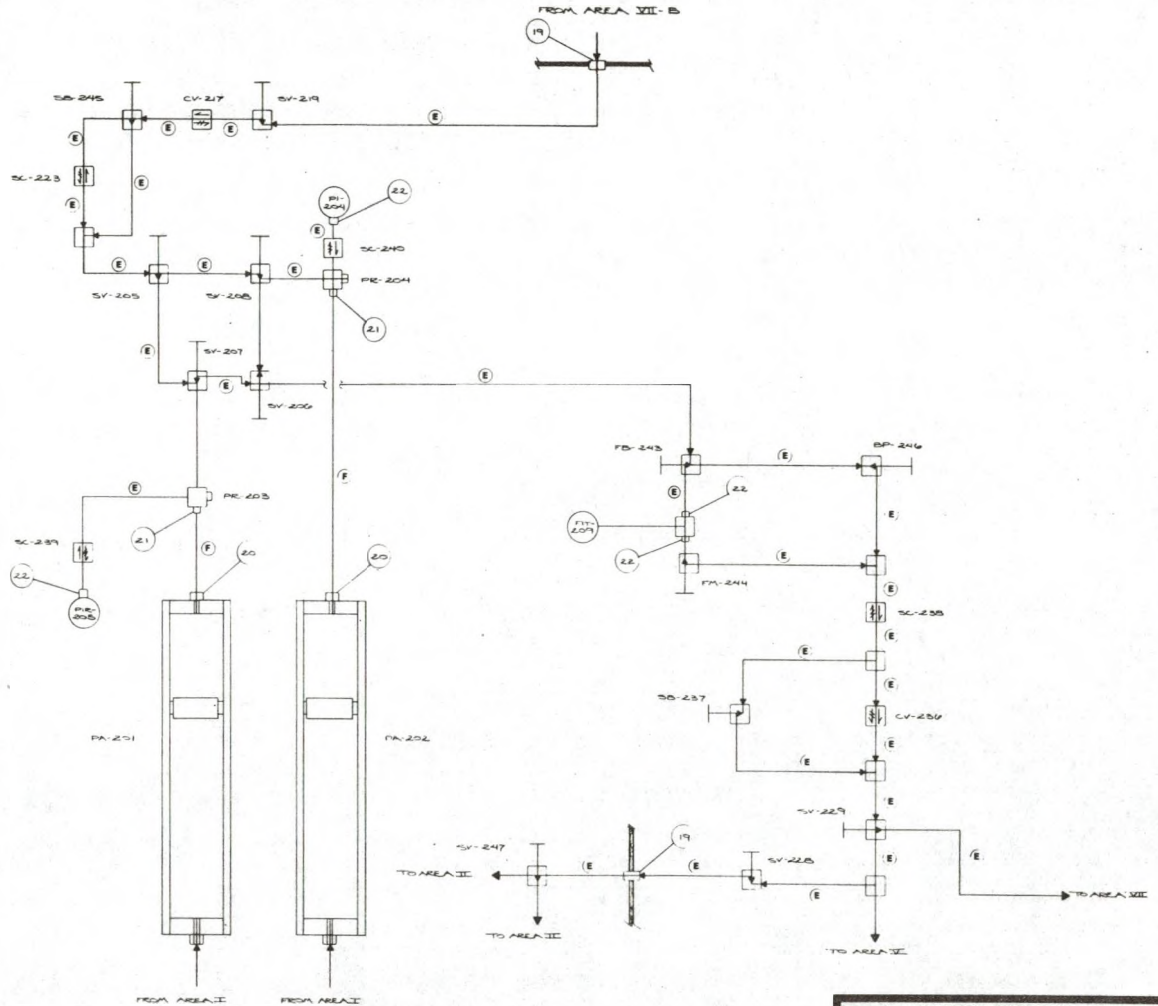Figure A-4. The Gas Compression System.

Figure A-5. Detail diagram of the UND autoclave facilities high pressure hydraulic oil supply system.

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AREA I

Figure A-6. Schematic flow diagram of the UND autoclave facilities instrumentation.
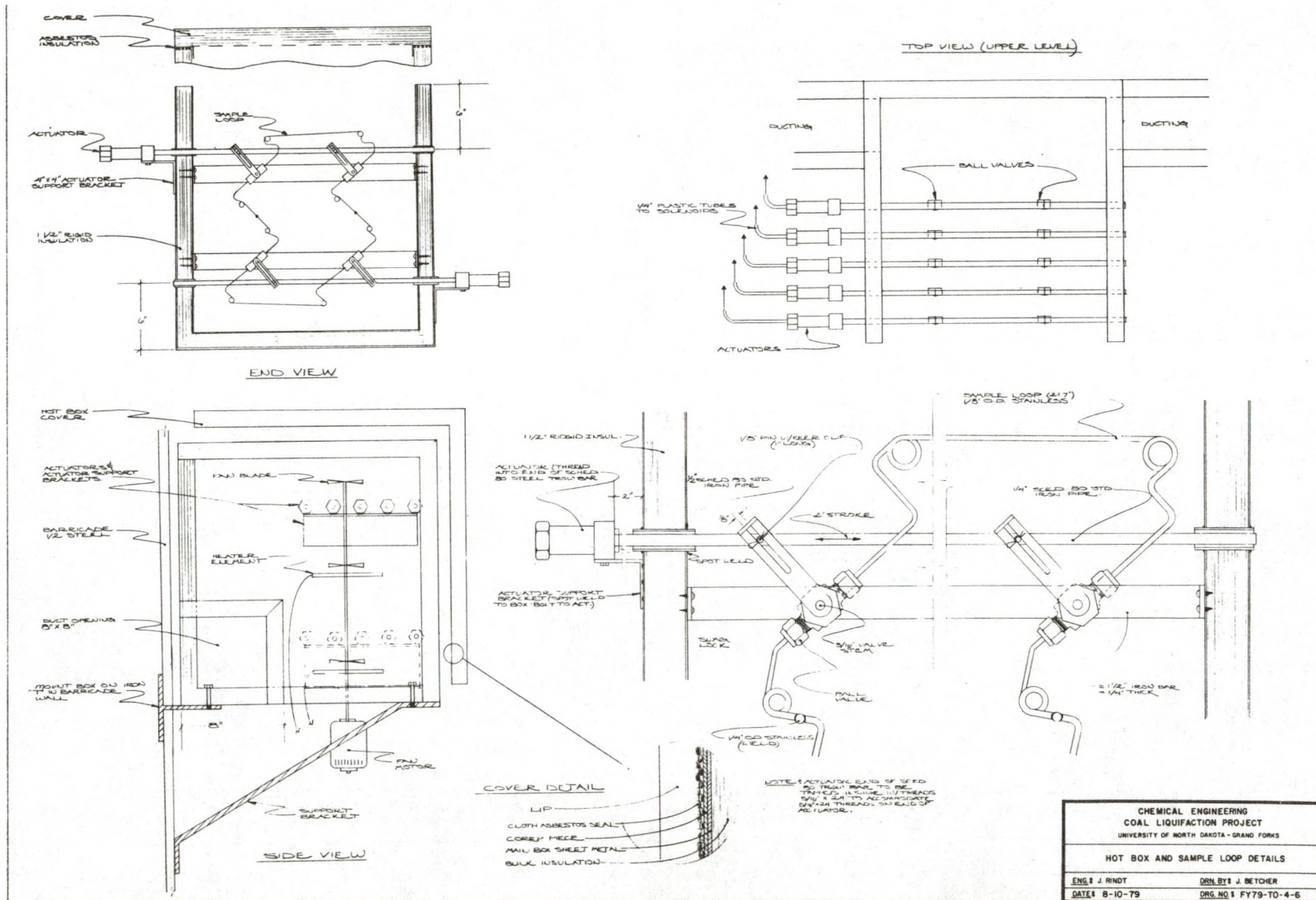
Figure A-7. Drawing of UND autoclave facilities GC sample loops and hot box.

Figure A-8. Floor plan of the UND building housing the autoclave facilities.

Figure A-9. Detail diagram of the UND autoclave facility barricade system.

REFERENCES

1. Wilson, W., Knudson, C., Baker, G., and Owens, T., Severson, D., Application of Liquefaction Process to Low-Rank Coals. DOE publication for Presentation at the 1979 Lignite Symposium, May 30-31, 1979, Grand Forks, ND, p. 34

2. Knudson, C., Private Communication, 1979, Available on request from C. Knudson, Grand Forks Energy Technology Center, Grand Forks, ND

3. U.S. Department of Health, Education, and Welfare, Recommended Health and Safety Guidelines for Coal Gasification Pilot Plants, DHEW (NIOSH) Publication #78-120, p. 239

APPENDIX B

SAMPLE YIELD CALCULATIONS FOR RUN B-1

Calculate initial pressure in reactor.[1]

```
P(1)=P(1)+(P(3)*0.49131)
    =400+(29.03*0.49131)
P(1)=414.2627 psig
```

```
C(1)=((273+T(1))/293)*(Y1/100*(M1*P(1)+R1)+((1-Y1/100)*(P(1)*M2+R2)))
C(1)=((273+20)/293)*(100/100*(0.023776*414.2627-0.137239)+((1-100/100)*
    (414.2627*0.024935+-0.030819)))
    =(1)*((9.7123)+(0)*(10.2988)
    =9.7123 g-moles
```

H2S Pressure
```
P(2)=P(2)+(P(3)*0.49131)
    =0+(29.03*0.49131)
    =14.2627 psig
```

```
C(2)=((273+7(2))/293)*(Y1/100*(M1*P(2)+R1)+((1-Y1/100)*(P(2)*M2+R2)))
    =((273+0)/293)*(100/100*(0.023776*14.2627-0.137239)+((1-100/100)*
    (14.2627*0.024935-0.030819)))
    =(0.9317)*((0.2019)+(0)*(0.3248))
    =0.1881 g-moles
```

Moles of H2 in Feed Gas Corrected for Temperature and Pressure
```
C(3)=((1)-C(2)
    =9.7123-0.1881
    =9.5242 g-moles
```

Moles of Reactant Gas

```
N1=C(3)+C(4)
  =9.5242+0
  =9.5242 g-moles
```

Mole Percent of H2S in Reactant Gas
```
H2=(C(4)/N1)*100
  =(0/9.5242)*100
  =0
```

Mole Percent of H2 in Reactant Gas
```
H3=((Y1/100*C(3))/N1)*100
  =((100/100*9.5242/9.5242)*100
  =100
```

Mole Percent CO in Reactant Gas
```
Cl=100-H2-H3
  =100-0-100
  =0
```

---

[1]See Appendix E for meaning of the symbols used.

Mass of Reactant Gas
M7=N1C1/100*28.01+N1*H3/100*2.016+N1*H2/100*34.08
  =9.5242*0/100*28.01+9.5242*100/100*2.016+9.5242*0/100*34.08
  =0+19.2008+0
  =19.2008 grams

Moles of Product Gas
N2=P(3)*V1/25.01512
  =29.03*8.891/25.01512
  =10.3180 g-moles

Mass of Product Gas
M8=N2*61/100*44.01+N2*62/100*30.07+N2*63/100*44.09+N2*64/100*1.016+N2*
  65/100*16.04+N2*66/100*28.01+N2*67/100*34.08+N2*68/100*17.08
  =10.318*8.925/100*44.01+10.318*0.395/100*30.07+10.318*0.193/100*
  44.09+10.318*86.436/100*2.016+10.318*1.064/100*16.04+10.318*1.88/100*
  28.01+10.318*0.164/100*34.08+10.318*0.02/100*17.08
  =68.4174 grams

Mass of Water in Slurry
X1=M4/(7+(2/((100-@5-@4)/100)*@4/100))
  =724.14/(7+(2/((100-29.31-7.91/100)))
  =99.8540 grams

Mass of HAO-61 Slurry
H6=4*X1
  =4*99.8540
  =399.4160 grams

Mass of MAF Lignite in Slurry
L1=2*X1
  =2*99.8540
  =199.7080 grams

Mass of Water out of Reactor
X2=@2/100*M6+@3/100*M5
  =0.128/100*536.87+95.17/100*124.34
  =119.0216 grams

Mass of Distillates out of Reactor
D1=S1/100*M6-@2/100*M6+(100-@3)/100*M5
  =77.2/100*536.87-0.128/100*536.87+(100-95.17)/100*124.34
  =419.7821 grams

Mass of SRL out of Reactor
S3=(S2-S1)/100*M6
  =(92.17-77.20)/100*536.87
  =80.3694 grams

Mass of IOM out of Reactor
I1=(100-S2)/100*M6-M6*(@1/100)
  =(100-92.17)/100*536.87-536.87*(3.58/100)
  =22.8170 grams

Mass of Ash in Endpot
A2=M6*(@1/100)
=536.87*(3.58/100)
=19.2199 grams

Mass of Ash in Slurry
A1=(2*X1/((100-@4-@5)/100)*@4/100)
=(2*99.8540/((100-7.91-2931)/100)*7.91/100)
=25.1623 grams

Total Mass into Reactor
I2=M7+L1+X1+A1+H6
=19.2008+199.7080+99.8540+25.1623+399.4160
=743.3411 grams

Total Mass out of Reactor
O=M8+X2_D1+S3+I1+A2
=68.4174+119.0216+419.7821+80.3694+22.8170+19.2199
=729.6274 grams

Percent Closure
C6=O/I2*100
=729.6274/743.3411*100=98.1551

Net Percent Distillates per MAF Lignite
D=((D1-4*X1)/(2*X1))*100
=((419.7821-4*99.8540)/(2*99.8540))*100
=10.1979

Net Percent SRL per MAF Lignite
S=S3/(2*X1)*100
=80.3694/(2*99.8540)*100
=40.2435

Net Percent Gas per MAF Lignite
G=((M8-M7)/(2*X1))*100
=((68.4174-19.2008)/(2*99.8540))*100
=24.6443

Net Percent IOM per MAF Lignite
I=(I1/(2*X1))*100
=(22.8170/(2*99.8540))*100
=11.4252

Net Percent Water per MAF Lignite
H=((X2-X1)/(2*X1))*100
=((119.0216-99.8540)/(2*99.8540))*100
=9.5978

Net Percent Ash per MAF Lignite
A=((A2-A1)/(2*X1))*100
=((19.2199-25.1623)/(2*99.8540))*100
=-2.9755

Percent Conversion
C7=100-I
  =100-11.4252
  =88.5748

Total Net Yield per MAF Lignite
T=D+S+G+I+H+A
 =10.1979+40.2435+24.6443+11.4252+9.5978-2.9755
 =93.1332

Normalize Data
Weight of Endpot
M6=M6*100/C6
  =536.87*100/98.1551
  =546.9609 grams

Mass Condensate in Cold Traps
M5=M5*100/C6
  =124.34*100/98.1551
  =126.6771 grams

Mass or Product Gas
M8=M8*100/C6
  =68.4174*100/98.1551
  =69.7034 grams

Mass Water out of Reactor
X2=@2/100*M6+@3/100*M5
  =0.128/100*546.9609+9517/100*126.6771
  =121.2587 grams

Mass Distillates out of Reactor
D1=S1/100*M6-@2/100*M6+(100-@3)/100*M5
  =77.2/100*546.9609-0.128/100*546.9609+(100-95.17)/100*126.6771
  =427.6722 grams

Mass SRL out of Reactor
S3=(S2-S1)/100*M6
  =(92.17-77.20)/100*546.9609
  =81.8800 grams

Mass of IOM out of Reactor
I1=(100-S2)/100*M6-M6*(@1/100)
  =(100-92.17)/100*546.9609*(358/100)
  =23.2458 grams

Mass of Ash in Endpot
A2=M6*(@1/100)
  =546.9609*(3.58/100)
  =19.5812 grams

Mass of Ash in Slurry
A1=(2*X1/((100-@4-@5)/100)*@4/100)
  =(2*99.8540/((100-7.91-29.31)/100)*7.91/100)
  =25.1623 grams

Total Mass into Reactor
I2=M7+L1+X1+A1+H6
  =19.2008+199.7080+99.8540+25.1623+399.4160
  =743.3411 grams

Total Mass out of Reactor
O=M8+X2+D1_S3_I1+A2
 =69.7034+121.2587+427.6722+81.8800+23.2458_19.5812
 =743.3413 grams

Percent Closure
C6=O/I2*100
  =743.3413/743.3411*100
  =100.0000

Net Percent Distillates per MAF Lignite
D=((D1-4*X1)/(2*X1))*100
 =((427.6722-4*99.8540)/2*99.8540))*100
 =14.1488

Net Percent SRL per MAF Lignite
S=S3/(2*X1)*100
 =81.8800/(2*99.8540)*100
 =40.9999

Net Percent Gas per MAG Lignite
G=((M8-MT)/(2*X1))*100
 =((69.7034-19.2008)/(2*99.8540))*100
 =25.2882

Net Percent IOM Per MAF Lignite
I=(I1/(2*X1))*100
 =(23.2458/(2*99.8540))*100
 =11.6399

Net Percent Water per MAF Lignite
H=((X2-X1)/(2*X1))*100
 =((121.2587-99.8540)/(2*99.8540))*100
 =10.7180

Net Percent Ash per MAF Lignite
A=((A2-A1)/(2*X1))*100
 =((19.5812-25.1623)/(2*99.8540))*100
 =-2.7946

Percent Conversion
$C7=100-I$
$=100-11.6399$
$=88.3601$

Total Net Yield per MAF Lignite
$T=D+S+G+I+H+A$
$=14.1488+40.9999+25.2882+11.6399+10.7180-2.7946$
$=100.0002$

APPENDIX C

RUN CONDITIONS

RUN CONDITIONS

Run Number	Temperature History	Lignite Moisture	Lignite Ash	Initial Pressure	Maximum Pressure	Feed Gas
B-1	Cold Charge Heat to 420°C Slow Cooling	29.31%	7.91%	400	3880	H_2
B-2	Hot Charge at 320°C Heat to 420°C Quench Residence time = 29 min	19.91%	7.85%	400	4025	H_2
B-3	Hot Charge at 360°C Heat to 420°C Hold at 420°C until total time = 29 min	29.14%	7.93%	400	3950	H_2
B-4	Cold Charge Heat to 420°C Slow Cooling	29.39%	7.90%	400	3325	$CO-H_2$
B-5	Hot Charge at 320°C Heat to 420°C Hold at 420°C until total time = 29 min	29.96%	7.84%	400	3900	$CO-H_2$
B-6	Repeat of B-4	29.95%	7.84%	400	3900	$CO-H_2$

RUN 1

Run #, Date of Run, Atm Press, H2 Press, H25 Press, % H2 in Feed Gas

B-1 ,   41682   ,   29.03 ,   400,   0   ,   100

H2-CO Temp,   H2S Temp,   Mass Slurry In,   Mass Condensate Out

  20.0   ,   0.00 ,   724.1   ,   124.34

Vol Gas Out,   Mass Endpot,   % Ash in Endpot,   % H2O in Lignite

    8.90 ,   536.9 ,   3.58 ,   29.31

% H2O in Endpot,   % Cychex Soluble,   % THF Soluble

   0.13   ,   77.20   ,   92.17

% H2O in Condensate,   % Ash in Lignite

     95.17   ,   7.91

Product Gas Composition CO2, C2H6, C3H8, H2, CH4, CO, H2S, NH3
                  8.93,   0.40, 0.19, 86.44, 1.06, 1.88, 0.16, 0.02

RUN 2

Run #, Date of Run, Atm Press, H2 Press, H25 Press, % H2 in Feed Gas

B-2,   42782,   29.50,   400,   0,   100

H2-CO Temp,   H2S Temp,   Mass Slurry In,   Mass Condensate Out

20,   0 ,   716.5 ,   12.60

Vol Gas Out,   Mass Endpot,   % Ash in Endpot,   % H2O in Lignite

8.77 ,   678.2,   3.51 ,   29.91

% H2O in Endpot,   % Cychex Soluble,   % THF Soluble

16.21   ,   75.25   ,   86.68

% H2O in Condensate,   % Ash in Lignite

92.67   ,   7.85

Product Gas Composition CO2, C2H6, C3H8, H2, CH4, CO, H2S, NH3

7.04, 0.06, 0.01, 89.75, 0.39, 0.22, 0.15, 0.01

RUN 3

Run #, Date of Run, Atm Press, H2 Press, H25 Press, % H2 in Feed Gas

B-3,   50482,   28.91 ,   400 ,   0 ,   100

H2-CO Temp,   H2S Temp,   Mass Slurry In,   Mass Condensate Out

  20 ,   0 ,   726.7 ,   2.03

Vol Gas Out,   Mass Endpot,   % Ash in Endpot,   % H20 in Lignite

  8.27 ,   677.9 ,   3.67 ,   29.14

% H20 in Endpot,   % Cychex Soluble,   % THF Soluble

  16.13 ,   78.33 ,   91.78

% H20 in Condensate,   % Ash in Lignite

  95.0 ,   7.93

Product Gas Composition CO2, C2H6, C3H8, H2, CH4, CO, H2S, NH3

                4.50, 0.52, 0.00, 97.02, 0.86, 0.15, 0.19, 0.04

RUN 4

Run #, Date of Run, Atm Press, H2 Press, H25 Press, % H2 in Feed Gas

   B-4,   51882,   28.96,   400 ,   0 ,   44.36

H2-CO Temp,   H2S Temp,   Mass Slurry In,   Mass Condensate Out

   20 ,   0 ,   719.9   ,   105.88

Vol Gas Out,   Mass Endpot,   % Ash in Endpot,   % H2O in Lignite

   7.92 ,   532.7 ,   4.12   ,   29.39

% H2O in Endpot,   % Cychex Soluble,   % THF Soluble

   0.14   ,   76.29   ,   93.09

% H2O in Condensate,   % Ash in Lignite

  100   ,   7.90

Product Gas Composition CO2, C2H6, C3H8, H2, CH4, CO, H2S, NH3

       17.42, 0.48, 0.00, 50.66, 1.43, 28.01, 0.09, 0.03

RUN 5

Run #, Date of Run, Atm Press, H2 Press, H25 Press, % H2 in Feed Gas

    B-5,   52182 ,   29.26 ,   400 ,   0   ,   44.36

H2-CO Temp,   H2S Temp,   Mass Slurry In,   Mass Condensate Out

    20 ,   0 ,   705.7 ,   3.89

Vol Gas Out,   Mass Endpot,   % Ash in Endpot,   % H2O in Lignite

    9.17 ,   643.9 ,   4.04   ,   29.96

% H2O in Endpot,   % Cychex Soluble,   % THF Soluble

    8.95   ,   78.66 ,   92.65

% H2O in Condensate,   % Ash in Lignite

    100   ,   7.84

Product Gas Composition CO2, C2H6, C3H8, H2, CH4, CO, H2S, NH3

                    29.71, 0.53, 0.00, 41.81, 0.70, 26.45, 0.18, 0.02

RUN 6

Run #, Date of Run, Atm Press, H2 Press, H25 Press, % H2 in Feed Gas

B-6,   60882,   29.19 ,   400 ,   0 ,   44.36

H2-CO Temp,   H2S Temp,   Mass Slurry In,   Mass Condensate Out

     20 ,   0 ,   722.9   ,   105.97

Vol Gas Out,   Mass Endpot,   % Ash in Endpot,   % H2O in Lignite

    9.80 ,   544.1 ,   3.27   ,   29.55

% H2O in Endpot,   % Cychex Soluble,   % THF Soluble

   0.16   ,   75.70   ,   93.39

% H2O in Condensate,   % Ash in Lignite

   56.25   ,   7.84

Product Gas Composition CO2, C2H6, C3H8, H2, CH4, CO, H2S, NH3

           22.98, 0.27, 0.01, 46.13, 0.73, 28.87, 0.20, 0.20

APPENDIX D

COMPUTER RUN SUMMARIES

```
RUN NUMBER        B1              DATE            41682

INPUT
.......

COMPONENT                         GRAMS IN
..........                        .........
MAF LIGNITE                       199.708
H20                                99.854
ASH                                25.162
HAO-61                            399.416
GAS                                19.201
   TOTAL                          743.340
..........................................................
OUTPUT
..........
                  GRAMS           NET YIELDS
COMPONENT         OUT             WTZ MAF LIG
..........        .......         ...........
H20               119.022           9.598
OIL               419.782          10.198
SRL                80.369          40.243
IOM                22.817          11.425
ASH                19.220          -2.976
GAS                68.417          24.644
   TOTAL          729.627          93.133

% CLOSURE                98.155
% CONVERSION             88.575
..........................................................
NORMALIZED
OUTPUT
..........
                  GRAMS           NET YIELDS
COMPONENT         OUT             WTZ MAF LIG
..........        .......         ...........
H20               121.259          10.718
OIL               427.672          14.149
SRL                81.880          41.000
IOM                23.246          11.640
ASH                19.581          -2.795
GAS                69.703          25.288
   TOTAL          743.340         100.000

% CLOSURE               100.000
% CONVERSION             88.360
..........................................................
TIME 0.2 SECS
```

```
RUN NUMBER        B2              DATE           42782

INPUT
........

COMPONENT                         GRAMS IN
..........                        .........
MAF LIGNITE                       197.594
H2O                                98.797
ASH                                24.921
HAO-61                            395.188
GAS                                19.201
   TOTAL                          735.701
.........................................................
OUTPUT
...........
                  GRAMS           NET YIELDS
COMPONENT         OUT             WTZ MAF LIG
...........       ........        ............
H2O               121.619          11.550
OIL               401.356           3.122
SRL                77.523          39.233
IOM                66.535          33.673
ASH                23.806          -0.564
GAS                52.843          17.026
   TOTAL          743.682         104.039

% CLOSURE            101.085
% CONVERSION          66.327
.........................................................
NORMALIZED
OUTPUT
...........
                  GRAMS           NET YIELDS
COMPONENT         OUT             WTZ MAF LIG
...........       ........        ............
H2O               120.314          10.890
OIL               397.049           0.942
SRL                76.691          38.812
IOM                65.821          33.311
ASH                23.551          -0.694
GAS                52.276          16.739
   TOTAL          735.701         100.000

% CLOSURE            100.000
% CONVERSION          66.689
.........................................................
TIME 0.2 SECS
```

```
RUN NUMBER        B3                  DATE              50482

INPUT
........

COMPONENT                             GRAMS IN
..........                            .........
MAF LIGNITE                            200.418
H20                                    100.209
ASH                                     25.255
HAO-61                                 400.832
GAS                                     19.201
   TOTAL                               745.920
.............................................................
OUTPUT
..........

                  GRAMS               NET YIELDS
COMPONENT         OUT                 WTX MAF LIG
..........        ........            ............
H20               111.265                  5.516
OIL               425.177                 12.145
SRL                87.792                 43.804
IOM                30.846                 15.391
ASH                24.880                 -0.187
GAS                40.527                 10.641
   TOTAL          720.486                 87.309

% CLOSURE                  96.590
% CONVERSION               84.609
.............................................................
NORMALIZED
OUTPUT
..........

                  GRAMS               NET YIELDS
COMPONENT         OUT                 WTX MAF LIG
..........        ........            ............
H20               115.193                  7.476
OIL               440.186                 19.633
SRL                90.891                 45.351
IOM                31.935                 15.934
ASH                25.758                  0.251
GAS                41.958                 11.355
   TOTAL          745.920                100.000

% CLOSURE                 100.000
% CONVERSION               84.066
.............................................................
TIME 0.2 SECS
```

```
RUN NUMBER        B4              DATE            51882

INPUT
.......

COMPONENT                         GRAMS IN
..........                        .........
MAF LIGNITE                        198.534
H2O                                 99.267
ASH                                 25.011
HAO-61                             397.068
GAS                                268.109
   TOTAL                           987.988
......................................................
OUTPUT
..........
                  GRAMS           NET YIELDS
COMPONENT         OUT             WT% MAF LIG
..........        ........        ...........
H2O               106.636             3.712
OIL               405.648             4.321
SRL                89.495            45.078
IOM                14.863             7.486
ASH                21.948            -1.543
GAS               155.312           -56.815
   TOTAL          793.901             2.240

% CLOSURE               80.355
% CONVERSION            92.514
......................................................
NORMALIZED
OUTPUT
..........
                  GRAMS           NET YIELDS
COMPONENT         OUT             WT% MAF LIG
..........        ........        ...........
H2O               132.706            16.843
OIL               504.817            54.272
SRL               111.374            56.098
IOM                18.496             9.316
ASH                27.313             1.160
GAS               193.282           -37.690
   TOTAL          987.989           100.000

% CLOSURE              100.000
% CONVERSION            90.684
......................................................
TIME 0.2 SECS
```

```
RUN NUMBER        B5              DATE              52182

INPUT
. . . . . . . .

COMPONENT                             GRAMS IN
. . . . . . . . .                     . . . . . . . .
MAF LIGNITE                            194.620
H20                                     97.310
ASH                                     24.531
HAO-61                                 389.240
GAS                                    161.280
    TOTAL                              866.980
. . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . .
OUTPUT
. . . . . . . . . .
                       GRAMS             NET YIELDS
COMPONENT              OUT               WTX MAF LIG
. . . . . . . . . .    . . . . . . .     . . . . . . . . . . .
H20                    61.515            -18.392
OIL                    448.835            30.621
SRL                    90.076            46.283
IOM                    21.312            10.950
ASH                    26.012             0.761
GAS                    232.292           36.487
    TOTAL              880.041           106.711

% CLOSURE                       101.507
% CONVERSION                     89.050
. . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . .
NORMALIZED
OUTPUT
. . . . . . . . . .
                       GRAMS             NET YIELDS
COMPONENT              OUT               WTX MAF LIG
. . . . . . . . . .    . . . . . . .     . . . . . . . . . . .
H20                    60.602            -18.861
OIL                    442.173           27.198
SRL                    88.739            45.596
IOM                    20.995            10.788
ASH                    25.626             0.563
GAS                    228.844           34.716
    TOTAL              866.980           100.000

% CLOSURE                       100.000
% CONVERSION                     89.212
. . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . .
TIME 0.2 SECS
```

```
RUN NUMBER        B6                 DATE            60882

INPUT
........

COMPONENT                           GRAMS IN
..........                          .........
MAF LIGNITE                         199.398
H2O                                  99.699
ASH                                  24.968
HAO-61                              398.795
GAS                                 161.279
   TOTAL                            884.139
.........................................................
OUTPUT
..........
                  GRAMS             NET YIELDS
COMPONENT         OUT               WT% MAF LIG
..........        .......           ............
H2O               60.457            -19.680
OIL              457.359             29.370
SRL               96.242             48.267
IOM               18.171              9.113
ASH               17.790             -3.600
GAS              222.194             30.549
   TOTAL         872.213             94.019

% CLOSURE              98.651
% CONVERSION           90.887
.........................................................
NORMALIZED
OUTPUT
..........
                  GRAMS             NET YIELDS
COMPONENT         OUT               WT% MAF LIG
..........        .......           ............
H2O               61.283            -19.266
OIL              463.612             32.506
SRL               97.558             48.927
IOM               18.420              9.238
ASH               18.034             -3.478
GAS              225.232             32.073
   TOTAL         884.139            100.000

% CLOSURE             100.000
% CONVERSION           90.762
.........................................................
TIME 0.2 SECS
```

APPENDIX E

COMPUTER PROGRAM FOR RUN CALCULATIONS

LIST OF SYMBOLS IN MATERIAL BALANCE PROGRAM

DO	Date of Run
P$	Run Number
P(1)	H2 or Synthesis Gas Pressure (psig)
P(2)	H2S Pressure (psig)
P(3)	Barometric Pressure (inches of Hg)
Y1	Percent H2 in Feed Gas
T(1)	H2 or Synthesis Gas Temperature (°C)
T(2)	H2S Temperature (°C)
C(1)	Calibration Factor
C(2)	Calibration Factor
C(3)	Moles of H2 in Feed Gas
C(4)	Moles of H2S in Feed Gas
N1	Moles of Feed Gas
H2	Mole Percent of H2S in Feed Gas
H3	Mole Percent of H2 in Feed Gas
C1	Mole Percent CO in Feed Gas
M7	Moles of Feed Gas
N2	Moles of Product Gas
M8	Mass of Product Gas
X1	Mass of Water in Slurry
H6	Mass of HAO-61 in Slurry
L1	Mass of MAF Lignite in Slurry
X2	Mass of Water Out of Reactor
D1	Mass of Distillates Out of Reactor
S3	Mass of SRL Out of Reactor
I1	Mass of IOM Out of Reactor
A2	Mass of Ash in Endpot
A1	Mass of Ash in Slurry
I2	Total Mass into Reactor
O	Total Mass Out of Reactor
C6	Percent Closure
D	Net Percent Distillates per MAF Lignite
S	Net Percent SRL for MAF Lignite

G	Net Percent Gas Per MAF Lignite
I	Net Percent IOM Per MAF Lignite
H	Net Percent Water Per MAF Lignite
A	Net Percent Ash Per MAF Lignite
CT	Percent Conversion
T	Total Net Yield Per MAF Lignite
M4	Mass of Slurry in Autoclave
M5	Mass Condensate in Cold Traps
V1	Volume of Product Gas
M6	Mass of Endpot
@1	Percent Ash in Endpot
@2	Percent Water in Endpot
S1	Percent of Endpot that is Cyclohexane Soluble
S2	Percent of Endpot that is THF Soluble
@3	Percent Water in Condensate
G1	Mole Percent CO_2 in Product Gas
G2	Mole Percent C_2H_6 in Product Gas
G3	Mole Percent C_3H_8 in Product Gas
G4	Mole Percent H_2 in Product Gas
G5	Mole Percent CH_4 in Product Gas
G6	Mole Percent CO in Product Gas
G7	Mole Percent H_2S in Product Gas
G8	Mole Percent NH_3 in Product Gas
@5	Percent H_2O in Lignite

```
   5  PRINT "RUN #, DATE OF RUN, ATM PRESS, H2-CO PRESS, H2S PRESS, %H2
IN FEED GAS"
  10  INPUT P$,D0,P(3),P(1),P(2),Y1
  15  PRINT "H2-CO TEMP, H2S TEMP, MASS SLURRY IN, MASS CONDENSATE OUT"
  20  INPUT T(1),T(2),M4,M5
  25  PRINT "VOLUME GAS OUT, MASS ENDPOT OUT, %ASH IN ENDPOT, %H2O IN LIG
NITE"
  30  INPUT V1,M6,@1,@5
  35  PRINT "%H2O IN ENDPOT, %CYCLOHEXANE SOLUBLE, %THF SOLUBLE"
  40  INPUT @2,S1,S2
  45  PRINT "%H2O IN CONDENSATE, %ASH IN LIGNITE"
  50  INPUT @3,@4
  70  PRINT "PRODUCT GAS COMPOSITION: CO2,C2H6,C3H8,H2,CH4,CO,H2S,NH3"
  80  INPUT G1,G2,G3,G4,G5,G6,G7,G8
  90  M1= 2.377600E-02
 100  M2= 2.493500E-02
 110  M3= 1.985780E-02
 120  R1= -1.372390E-01
 130  R2= -3.081900E-02
 140  R5= 2.653510E-02
 150  FOR A6=1 TO 2
 160  P(A6)= P(A6) + (P(3)*0.49131)
 170  C(A6)= ((273+T(A6))/293)*(Y1/100*(M1*P(A6)+R1)+((1-Y1/100)*(P(A6)*M
2+R2)))
 180  NEXT A6
 190  C(3)= C(1)-C(2)
 200  IF T(2)=0 THEN GOTO 220
 210  C(4)= ((273+T(1))/294)*(M3*P(2)+R5)
 220  N1= C(3)+C(4)
 230  H2= (C(4)/N1)*100
 240  H3= ((Y1/100*C(3))/N1)*100
 250  C1= 100 -H2-H3
 260  M7= N1*C1/100*28.01+N1*H3/100*2.016+N1*H2/100*34.08
 270  N2= P(3)*V1/25.01512
 280  M8= N2*G1/100*44.01+N2*G2/100*30.07+N2*G3/100*44.09+N2*G4/100*2.016
+N2*G5/100*16.04+N2*G6/100*28.01+N2*G7/100*34.08+N2*G8/100*17.08
 290  X1= M4/(7+(2/((100-@5-@4)/100)*@4/100))
 293  H6= 4*X1
 297  L1= 2*X1
 300  X2= @2/100*M6+@3/100*M5
 310  D1= S1/100*M6-@2/100*M6+(100-@3)/100*M5
 320  S3= (S2-S1)/100*M6
 330  I1= (100-S2)/100*M6-M6*(@1/100)
 335  A2= M6*(@1/100)
 337  A1= (2*X1/((100-@4-@5)/100)*@4/100)
 340  I2= M7+L1+X1+A1+H6
 350  O= M8+X2+D1+S3+I1+A2
 360  C6= O/I2*100
 370  D= ((D1-4*X1)/(2*X1))*100
```

```
380 S=S3/(2*X1)*100
390 G= ((M8-M7)/(2*X1))*100
400 I= (I1/(2*X1))*100
410 H= ((X2-X1)/(2*X1))*100
415 A= ((A2-A1)/(2*X1))*100
420 C7= 100-I
455 T= D+S+G+I+H+A
460 IF Z=1 THEN 675
470 PRINT
480 PRINT "RUN NUMBER", P$,                "DATE",  DO
490 PRINT
495 :                   ###.###
500 PRINT "INPUT"
510 PRINT "........."
520 PRINT
530 PRINT "COMPONENT                        GRAMS IN"
540 PRINT ".........                        ........."
550 PRINT "MAF LIGNITE",
560 PRINT USING 495,L1
570 PRINT "H2O",
580 PRINT USING 495,X1
590 PRINT "ASH",
600 PRINT USING 495,A1
610 PRINT "HAO-61",
620 PRINT USING 495,H6
630 PRINT "GAS",
640 PRINT USING 495,M7
650 PRINT "   TOTAL",
660 PRINT USING 495,I2
670 PRINT ".............................................................
"
673 IF Z=0 THEN 680
675 PRINT "NORMALIZED"
680 PRINT "OUTPUT"
690 PRINT "..........."
700 PRINT "              GRAMS            NET YIELDS"
710 PRINT "COMPONENT      OUT             WIZ MAF LIG"
720 PRINT "...........   ........         ............."
730 :####.###         ###.###
740 PRINT "H2O",
750 PRINT USING 730,X2,H
760 PRINT "OIL",
770 PRINT USING 730,D1,D
773 PRINT "SRL",
777 PRINT USING 730,S3,S
780 PRINT "IOM",
790 PRINT USING 730,I1,I
800 PRINT "ASH",
810 PRINT USING 730,A2,A
820 PRINT "GAS",
830 PRINT USING 730,M8,G
```

```
840 PRINT "   TOTAL",
850 PRINT USING 730,0,T
860 PRINT
870 :        ###.###
880 PRINT "% CLOSURE",
890 PRINT USING 870,C6
900 PRINT "% CONVERSION",
910 PRINT USING 870,C7
920 PRINT ".....................................
"
930 IF Z=1 THEN 1000
940 M6= M6*100/C6
950 M5= M5*100/C6
960 M8= M8*100/C6
970 Z=1
980 GOTO 300
1000 STOP
1010 END
```

APPENDIX F

LIST OF ABBREVIATIONS

MAF	Moisture Ash Free
°C	Degrees Celcius
°F	Degrees Fahrenheit
psig	Pounds per square inch, guage
psi	Pounds per square inch
SRC	Solvent Refined Coal
SRL	Solvent Refined Lignite
UND	University of North Dakota
PDU	Process Development Unit
CPU	Continuous Process Unit
PETC	Pittsburgh Energy Technology Center
GFETC	Grand Forks Energy Technology Center
COSTEAM	Carbon Monoxide and Steam
ASTM	American Society of Testing and Materials
APHA	American Public Health Association
IOM	Insoluble Organic Matter
HAO-61	Hydrogenated Anthracene Oil from Run Number 61
AO-4	Anthracene Oil - Batch Number 4
THF	Tetrahydrofuran
ml	Milliliters
min	Minute
Hg	Mercury

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