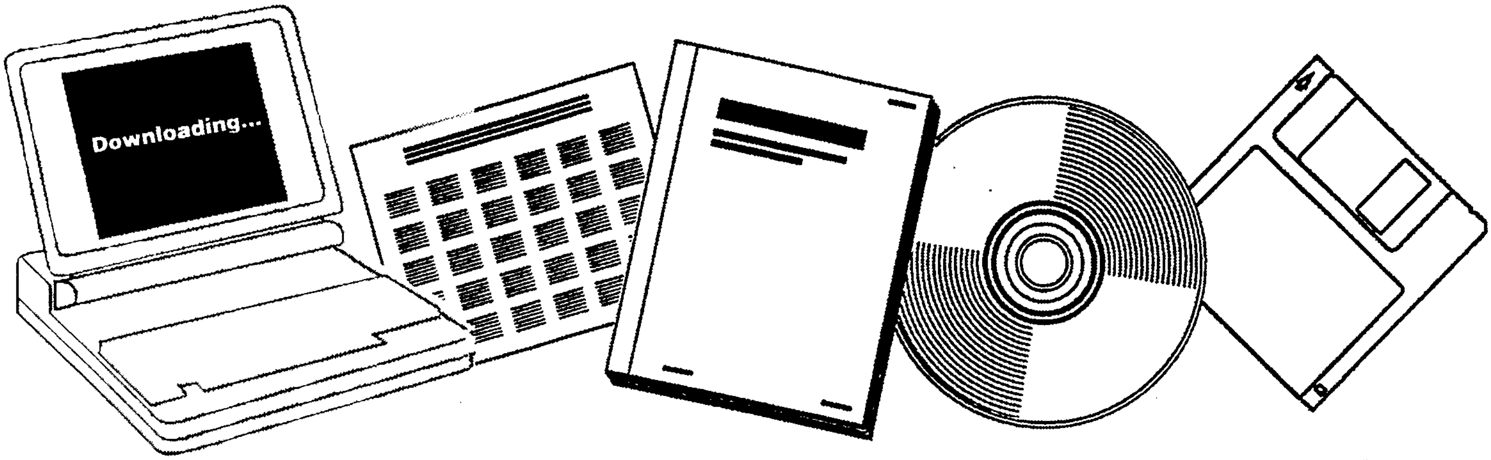
EXXON CATALYTIC COAL GASIFICATION PROCESS DEVELOPMENT PROGRAM. QUARTERLY TECHNICAL PROGRESS REPORT, JULY 1-SEPTEMBER 30, 1978

EXXON RESEARCH AND ENGINEERING CO.
BAYTOWN, TX

NOV 1978

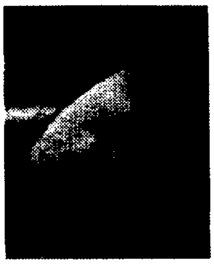


One Source. One Search. One Solution.

NTIS

Providing Permanent, Easy Access to U.S. Government Information

National Technical Information Service is the nation's largest repository and disseminator of government-initiated scientific, technical, engineering, and related business information. The NTIS collection includes almost 3,000,000 information products in a variety of formats: electronic download, online access, CD-ROM, magnetic tape, diskette, multimedia, microfiche and paper.



Search the NTIS Database from 1990 forward

NTIS has upgraded its bibliographic database system and has made all entries since 1990 searchable on **www.ntis.gov.** You now have access to information on more than 600,000 government research information products from this web site.

Link to Full Text Documents at Government Web Sites

Because many Government agencies have their most recent reports available on their own web site, we have added links directly to these reports. When available, you will see a link on the right side of the bibliographic screen.

Download Publications (1997 - Present)

NTIS can now provides the full text of reports as downloadable PDF files. This means that when an agency stops maintaining a report on the web, NTIS will offer a downloadable version. There is a nominal fee for each download for most publications.

For more information visit our website:

www.ntis.gov

U.S. DEPARTMENT OF COMMERCE
Technology Administration
National Technical Information Service
Springfield, VA 22161

FE-2777-1
Distribution Category UC-90c

EXXON CATALYTIC COAL GASIFICATION PROCESS DEVELOPMENT PROGRAM

Quarterly Technical Progress Report
for the period
July 1 - September 30, 1978

C. A. Euker, Jr. - Program Manager

Exxon Research and Engineering Company
Baytown, Texas 77520

November, 1978

PREPARED FOR THE UNITED STATES
DEPARTMENT OF ENERGY UNDER
Contract No. ET-78-C-01-2777

ABSTRACT

This report covers the activities for the Exxon Catalytic Coal Gasification Development Program during the quarter from July 1 - September 30, 1978. This work is being performed by the Exxon Research and Engineering Company Company (ER&E) and is supported by the United States Department of Energy under Contract No. ET-78-C-01-2777.

The highlights of this report are summarized below:

- Bench Scale Research and Development

The separation of the char-lime residue from the recovered potassium solution in the catalyst recovery system has been identified as a troublesome step in pilot plant operations. Many of the char-lime particles are smaller than 10 microns, and the effective density of the char particles is close to that of the recovered potassium solution. Promising approaches for improving this separation have been identified and include:

- Combusting the char residues to increase the particle size and density;
- Diluting the recovered potassium solution to reduce the liquid density and viscosity.

- Advanced Study of the Exxon Catalytic Coal Gasification Process

The present kinetic model for catalytic gasification is based almost entirely on data from devolatilized coal at 1300°F and some limited data at 1200°F. Plans have been made to expand the data base to include the gasification kinetics of steady state char from the fluid bed gasifier (FBG) to determine the effect of carbon conversion on reaction rate and to better define the effect of temperature.

- Engineering Research and Development

A study has been initiated to update the offsite design and cost estimate which were completed in the predevelopment contract (E49-18)-2369. This update will include a more detailed study of water quality and reuse options as well as a revised flue gas desulfurization study design based on a lime scrubbing system.

Engineering cost reduction studies have identified a potential economic incentive to reduce the methane content of the recycle gas stream below the 10% CH_4 level in the current study. This step would require more cryogenic refrigeration but would significantly reduce the amount of recycle gas, reduce the offsite stream required, and reduce the gas feed to acid gas recovery. A more detailed study is planned.

An additional incentive study has begun to determine the potential for a cryogenic separation system to remove the acid gases from the product gas. Since the acid gas separation system makes up about 15% of the gas cost, savings here could be very beneficial.

TABLE OF CONTENTS

LABORATORY PROCESS RESEARCH AND DEVELOPMENT

1. Bench Scale Research and Development (Reporting Category C01)

1.1 Catalyst Recovery Studies

Background

Under the predevelopment contract E(49-18)-2369, potassium carbonate and potassium hydroxide were used as coal gasification catalysts. Since these potassium compounds are relatively expensive, they must be recovered from the gasified coal char.

Fluid Bed Gasifier (FBG) pilot plant operations with catalyst recycle during July, 1977, demonstrated that water washing of the char would remove up to 65% of total potassium. This was accomplished using a series of leaching tanks with hydroclones as solid-liquid separation devices between each tank. Operation of the hydroclones in these pilot plant tests was troublesome. Relatively high levels of fines carryover in the overflow was observed which necessitated intermittent filtering of the liquid during the pilot plant operation. This work identified two needs in catalyst recovery:

- Increased level of potassium recovery
- Improved solid-liquid separation in catalyst leaching operation

Hydrothermal Catalyst Recovery

Bench work under the predevelopment contract identified a way of increasing the level of potassium recovery. This research showed that part of the potassium impregnated on the coal reacts with the coal mineral matter. The following are the major mineral potassium reactions.

$$K_2CO_3 + 2SiO_2 \cdot Al_2O_3 \cdot 2H_2O \rightarrow 2KAlSiO_4 + 2H_2O + CO_2$$

$$K_2CO_3 + 2FeS_2 + H_2 \rightarrow 2KFeS_2 + H_2O + CO_2$$

Both $KAlSiO_4$ and $KFeS_2$ are water insoluble and catalytically inactive forms of potassium. However, a hydrothermal reaction of char with $Ca(OH)_2$ at high pH and temperatures at or above 300°F causes the following chemical reactions to proceed:

$$2KAlSiO_4 + 4Ca(OH)_2 + 2H_2O \rightarrow Ca_3Al_2SiO_4(OH)_8 + 2KOH + CaSiO_3 \cdot H_2O$$

$$2KFeS_2 + 6KOH \rightarrow Fe_2O_3 + 4K_2S + 3H_2O$$

Consequently, the water insoluble and inactive forms of potassium can be converted to soluble and catalytically active forms of potassium (KOH and K_2S, respectively).

This hydrothermal chemistry was studied in a 100 gallon batch digester as shown in Figure 1.1-1. Approximately 50 lbs of char, 25 lbs of lime, and 300 lbs of KOH solution were charged to the digester. Steam and resistance heaters were used to rapidly heat the slurry to process conditions between 300-400°F. After digestion, water was fed to the coil which rapidly cooled the slurry down to approximately 120°F. The solids were then filtered from the liquid and washed. Results shown in Figure 1.1-2 demonstrate that potassium recoveries of 90% and greater can be achieved with this hydrothermal chemistry.

Properties of Solids and Liquids in Catalyst Leaching Operation

To improve solid-liquid separation in the catalyst leaching oprations, bench scale work was carried out to better characterize the properties of the solids and liquids. A particle size distribution of a typical solids residue from the digestion experiments described previously was determined by wet sieving. The results are as follows:

PARTICLE SIZE DISTRIBUTION OF
DIGESTION SOLIDS RESIDUE

Sieve Size Microns	Particles Less than Sieve Size % Weight
300	84
75	61
10	34

This shows that approximately 1/3 by weight of the char-lime particles are smaller than 10 microns, and this small size makes solid-liquid separation difficult. Work is underway to identify where these smaller particles are produced.

The density difference between the particles and the catalyst solution is small which also contributes to difficulties in solid-liquid separation. Porosimetry studies have shown that the skeletal density of a char particle is approximately 2 g/cc, and the pore volume is about 2/3 of the particle volume. Thus, the effective density of this char in the water leaching process would be 1.33 g/cc. The effective density is the density of the particle where its pore volume is filled with leaching solution. Since the density of water is 1.0 g/cc, the density difference between the char particle and water is only 0.3 g/cc in this leaching environment.

Further, if the leaching solution is 35 wt.% K_2CO_3 in water (1.35 g/cc), then the density difference between the particle and solution is smaller yet. Using the same pore volume as before, the effective particle density is <u>1.56</u> g/cc which is only <u>0.2</u> denser than the K_2CO_3 solution.

FIGURE 1.1-1

100 GALLON RAPID HEATUP-COOLOFF DIGESTER

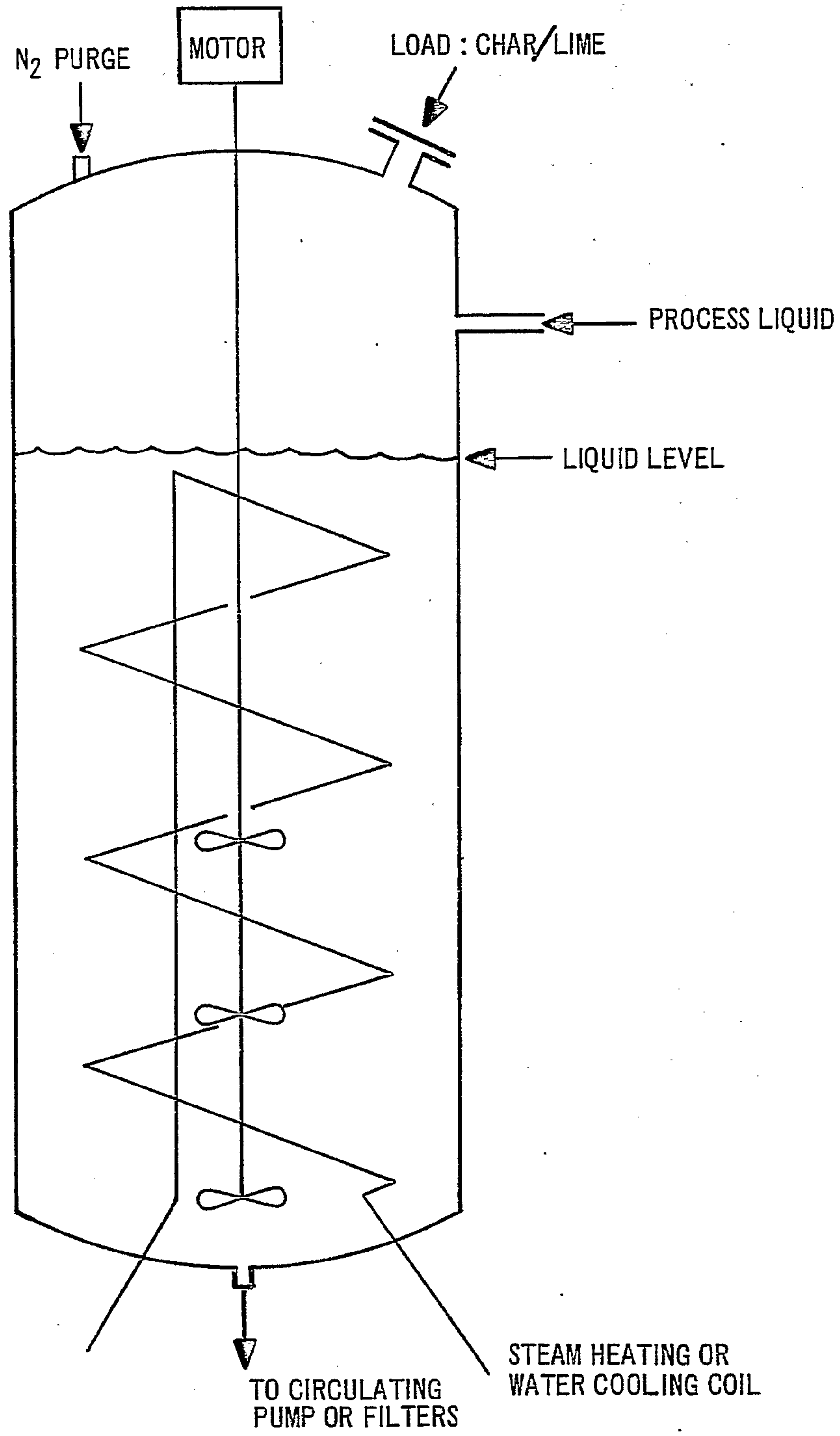
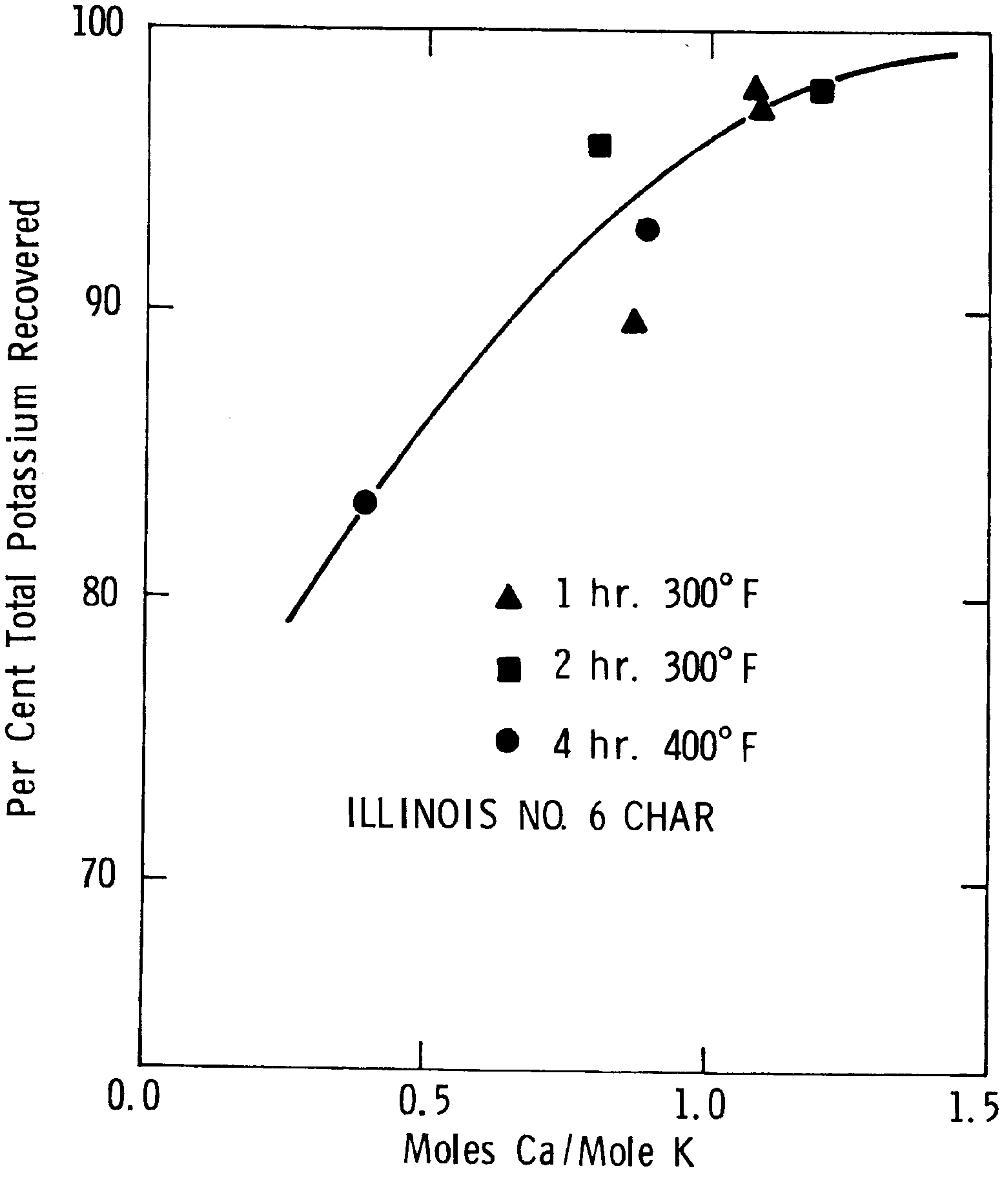


FIGURE 1.1-2

CALCIUM HYDROXIDE DIGESTION RECOVERS POTASSIUM

100 gallon batch digester



To enchance this solid-liquid separation, the solids properties, the liquid properties, or both could be changed. An increase in the solid density or size would be advantageous as would be a decrease in the liquid density. Several encouraging approaches have been identified and are discussed below.

Potential Improvements in Solid-Liquid Separation

One of the sources of fine particles in the leaching operation is the fine lime added in the hydrothermal digestion. These fines could be eliminated by using coarse lime. Preliminary tubing bomb experiments using coarse lime particles have been conducted. Instead of using the normal lime which is mostly -325 mesh, a -20 + 100 mesh cut was used. At digestion conditions of 400°F, two hours residence time and Ca/K=1.0, a three run average potassium recovery of 85% was attained in the tubing bomb. This is the same recovery as that obtained with normal lime which indicates that coarse lime is as effective as normal lime. Since mixing is a problem in tubing bombs, a better mixing digester should improve the results.

Another approach to decrease both the density and size of the solids is to combust the char residue. Combustion will remove the carbon from the particle, and this should increase the particle density. In addition, the particles may also sinter, and this will increase the particle size. Illinois No. 6 char was combusted in a ceramic boat to test this idea. Some sintering was observed and the bulk density of dry char increased from 0.24 g/cc to 0.47 g/cc during combustion. These results are encouraging.

For combustion to be a part of the potassium recovery process, the feasibility of recovering potassium from this combusted material needs to be determined. Below is a table of hydrothermal tubing bomb results using large lime and combusted Illinois No. 6 char.

POTASSIUM RECOVERY FROM ILLINOIS NO. 6 CHAR
(400°F FOR 4 HOURS)

Ca/K (Mole ratio)	% Potassium Recovered from Ash
0.52	95
0.52	98 (better mixing)
1.02	97
1.02	97
2.04	96

These runs show that potassium recovery from combusted char can be accomplished and that the combustion step did not create unrecoverable potassium.

Overall then, the screening runs show that coarse lime is effective in catalyst recovery, larger and denser char particles can be made by combustion, and potassium can be recovered from combusted char. We plan to construct bench units to study these options further.

An alternate approach for improving this solid-liquid separation is to reduce the concentration of the recovered potassium solution below the planned 35 wt.% K_2CO_3 solution. This change would lower the liquid density, decrease the liquid viscosity, and decrease the solids loading. All of the changes directionally favor solid-liquid separation. Bench work is planned to define the effect of decreased potassium concentration on the solid-liquid separation.

2. Process Development Unit Operations (Reporting Category C02)

No work was scheduled in this category for this reporting period.

3. Data Acquisition and Correlations (Reporting Category C03)

No work was scheduled in this category for this reporting period.

4. Advanced Study of the Exxon Catalytic Coal Gasification Process (Reporting Category C04)

4.1 Kinetics of Gasification and Devolatilization

The conversion of coal to gaseous products via Exxon's catalytic gasification process can be envisioned as a two-step process. First, the coal undergoes rapid devolatilization to yield coal char and numerous volatile products. The resulting char is then gasified with steam and recycle gas to produce a mixture of methane, hydrogen, and carbon oxides. Additional amounts of these products are also produced from the devolatilization products as they pass through the bed of char. The purpose of this work is to better characterize the reaction rates and yield structures for the devolatilization and char gasification steps. The results of this investigation can then be combined with appropriate mass transfer correlations to predict reaction rates and conversions in fluid bed gasifiers and help define optimum process conditions.

Char Gasification

The kinetics of char gasification have previously been investigated during the predevelopment phase of catalytic gasification research [Contract No. E(49-18)-2369)]. The majority of the kinetic data was obtained using a fixed bed reactor at 1300°F and catalyst loadings of 10 and 20 wt.% potassium carbonate on dry Illinois coal. The coal was devolatilized under an inert atmosphere before loading in the fixed bed reactor. Some data was also obtained at 1200°F.

On the basis of these data, engineering studies have established 15 wt.% potassium carbonate as the preferred catalyst loading. The optimum gasifier temperature, however, has not yet been clearly defined. Engineering sensitivity studies using the limited temperature data have indicated an economic incentive for lowering the gasifier temperature below 1300°F. Additional kinetic data at various temperatures on steady state char is necessary before a confident optimization of the gasifier conditions can be made.

In view of this need, a laboratory program has been initiated to expand the kinetic data base for steam gasification of Illinois char. Feed for these studies will be Illinois char produced at various levels of carbon conversion by the Fluid Bed Gasification Unit (FBG) under steady state conditions rather than the devolatilized coal used previously. The initial process variable studies will include:

- Effects of variations in potassium/carbon ratio in the steady state char.
- Variations in temperature and pressure around the base conditions of 1300°F and 500 psig, respectively.

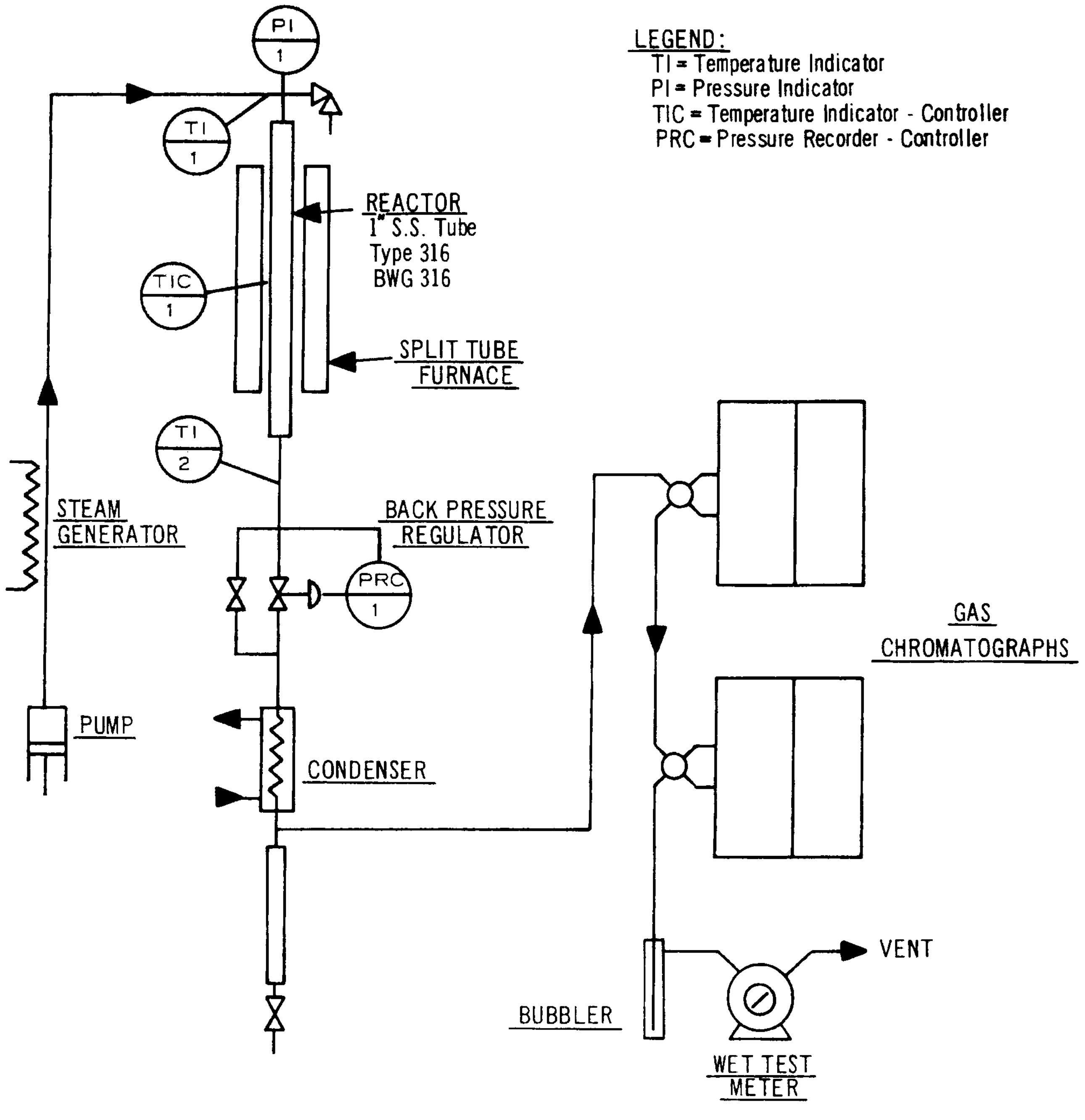
The experimental data required for this study will be obtained in a bench scale fixed bed and a mini-fluid bed gasification unit. A simplified flow diagram of the fixed bed unit is shown in Figure 4.1-1. The unit consists of a high pressure water pump, steam generator, fixed bed reactor, unreacted steam condenser, gas chromatographs, and dry gas flow measurement system. The entire fixed bed unit is presently being recommissioned. Shakedown runs are planned in order to check out the various systems before embarking on the process variable study. The components of the mini-fluid bed have been ordered and a description of this unit will be presented in a later report.

Devolatilization

Current hypotheses about the devolatilization step are based on limited data in inert gas at atmospheric pressure. No information exists regarding quantity of yield structure of gas, tar, and coke resulting from devolatilization at commercial conditions or the eventual fate of these products. An experimental unit will be designed and constructed to address these concerns. Consideration is presently being given to the specific characteristics of such a unit.

FIGURE 4.1-1

SIMPLIFIED FLOW DIAGRAM OF BENCH SCALE GASIFICATION UNIT



LEGEND:
TI = Temperature Indicator
PI = Pressure Indicator
TIC = Temperature Indicator - Controller
PRC = Pressure Recorder - Controller

ENGINEERING RESEARCH AND DEVELOPMENT
(Reporting Category (C20)

Engineering research and development studies are being carried out under the Catalytic Coal Gasification (CCG) Process Development Contract in conjunction with the laboratory bench-scale research and PDU operations. This work will include engineering and cost studies to evaluate process improvements and guide the continuing laboratory programs, and engineering technology programs to develop fundamental process and equipment technology to support the laboratory and engineering efforts. The overall objective of the engineering work is to define the conceptual commercial CCG process at the end of the contract period.

The engineering research and development work under the CCG Process Development Contract is divided into four major sub-tasks:

Cost Reduction and Laboratory Guidance Studies
Systems Modeling
Process Definition
Engineering Technology Studies

During the period covered by this report engineering work proceeded only on the first sub-task. Systems Modeling and Engineering Technology Studies were deferred pending contract signing. Work on the Process Definition is not scheduled until January, 1980.

5.1 Cost Reduction and Laboratory Guidance Studies

CCG Commercial Plant Study Design -- Offsites Revision

A Catalytic Coal Gasification Commercial Plant Study Design was prepared during the latter part of the CCG Predevelopment Program which was completed in January, 1978 under Contract No. E(49-18)-2369. The results of the "CCG Study Design" are documented in the final report for that contract. This detailed engineering study design will serve as the "base case" for evaluating new data, process improvements, and optimum process conditions under the present Process Development Contract.

Offsites facilities (including materials handling, utilities, and general offsites) constituted 40% of the total plant direct and indirect investment cost for the CCG Study Design. Although considerable effort was involved in specifying the offsites facilities for the Study Design, for the most part these areas were studied in less engineering depth and specified in less detail than the onsites process sections. Because the onsites and offsites design work proceeded at the same time, some inconsistencies developed between the final onsites utilities demands and the estimated demands used in specifying the utilities sections. Also, the process waste water rate used in sizing the wastewater treating facilities was underestimated. A preliminary plant layout was used in specifying piping for utilities distribution and for industrial sewers. A final look at onsites layout indicated that these piping requirements were probably overestimated.

In view of these factors, a revised offsites facilities definition and cost estimate is being prepared to firm up the CCG Study Design in this important area. As a result of this offsites revision, the accuracy of screening studies which use the Study Design as a "base case" will be improved. Most of the changes in this offsites revision are a matter of adjusting equipment sizes to correct for inconsistencies between the initial and final utilities demands and plant layout requirements. However, more extensive changes are being made in two sections. First, in the wastewater treating section, more detailed consideration is being given to water quality and reuse options to better define treating needs and further reduce plant makeup and effluent water rates. Second, the flue gas desulfurization (FGDS) process is being changed from a regenerative system using sodium carbonate to a once-through system using lime scrubbing. The objective of this change is to capture potential economic benefits from integration of lime scrubbing offsites with other CCG plant offsites. In particular, lime receipt for FGDS can be integrated with lime receipt for onsite catalyst recovery, which uses lime as feed to $Ca(OH)_2$ digestion. Common absorbers can be utilized to handle flue gas from the coal-fired boilers, the coal-fired feed coal dryers, and catalyst addition dryers. Other integration possibilities have also been considered. In addition to these integration advantages, the technology and costs for lime (and limestone) scrubbing are better defined today than costs for regenerative FGDS.

Equipment lists for the revised CCG Study Design offsites neared completion in September. The investment cost estimate is scheduled for the fourth quarter of 1978. Updated utilities balances for the Study Design will also be prepared in the fourth quarter.

Incentive Study for Removing Methane from Recycle Gas

A brief screening study was carried out to determine whether there is an incentive for reducing the methane content of the recycle gas stream. In the CCG Study Design base case, the recycle gas contained 10% CH_4. This was thought to be the lowest methane content in the recycle gas that could be practically achieved without adding a lower temperature level refrigerant (such as a nitrogen cascade) to cool the methane recovery tower overhead to a lower temperature (below the -239°F base case temperature). Since recycle of methane product to the gasifier inhibits the gasification reactions, this study was carried out to evaluate the effect of eliminating the methane from the recycle gas.

The effect of removing methane from the recycle gas was simulated with an in-house heat and material balance program for catalytic coal gasification. The process basis and conditions were identical to the CCG Study Design base case except for the removal of methane. The design changes required in the cryogenic methane recovery system were not evaluated at this time. The key differences between the "no methane in recycle gas" case and the CCG Study Design base case are listed in Table 5.1-A and summarized below:

TABLE 5.1-A

SUMMARY OF SCREENING STUDY FOR REMOVAL OF CH_4 IN CCG RECYCLE GAS

Study Design Base Case - 10% CH_4 in Recycle Gas

Incentive Study - 0% CH_4 in Recycle Gas

	Base Case	No CH_4 in Recycle Gas	% Change
Gasifier Temperature, °F	1,275	1,275	-
Coal Feed to Gasifier, ST/SD	14,490	14,490	-
Plant Rates and Operating Conditions			
Net CH_4 Product, Moles/hr	27,973	28,015	+ 0.2
Total Recycle Gas, Moles/hr	57,225	47,461	-17.5
Gasifier Steam/Recycle Gas, Moles/hr	131,004	117,179	-10.5
Raw Gasifier Product, Moles/hr	164,783	151,048	- 8.3
Acid Gas Removal Feed, Moles/hr	110,357	100,399	- 9.0
Methane Recovery Feed, Moles/hr	87,111	77,244	-11.3
Normal Preheat Furnace COT, °F	1,543	1,575	+32°F
Preheat Furnace Fuel Fires, MBtu/Hr	528	502	- 6.3
Steam Consumption, Moles/hr(1)	38,878	37,455	- 3.7
Steam Conversion, %	43.1	43.5	+ 0.9
Overall Net CH_4 Product, GBtu/SD	257.04	257.4	+ 0.2
Steam Generated Offsite, Moles/hr	59,268	55,263	- 6.8
Relative Gasifier Volume	100	96	- 4.0

Note:

(1) Steam consumption = steam in preheat furnace inlet + water with coal + cooling steam - steam in reactor effluent

- The total recycle gas rate was reduced by 17%.
- The raw gasifier effluent gas rate was reduced by 8%.
- The feed to methane recovery tower was reduced by 11%.
- The preheat furnace fuel fired was down by 6%.
- Overall net methane product was increased by 0.2%.
- The offsite steam requirement was reduced by 6.8%.
- The feed to acid gas removal was reduced by 9%.
- The gasifier volume was reduced by 4%.

Although the preheat furnace duty requirement to heat balance the gasifier was lower in the "no methane in recycle gas" case, the furnace coil outlet temperature was calculated to be 32°F higher. This is due to the steam/recycle gas rate being about 10.5% lower than in the base case.

In the methane recovery section of the plant, more refrigeration would be required to reduce the methane content of the recycle gas stream. This would require somewhat greater investment and operating cost in that section.

Overall, it was concluded that there are incentives for reducing the methane content of the recycle gas stream. More detailed studies, including the impact of higher methane recovery section refrigeration requirements, will be made at a later time.

Cryogenic Acid Gas Removal Incentive Study

In the conceptual commercial Catalytic Coal Gasification flow scheme, as defined by the CCG Study Design, a conventional physical solvent process (heavy glycol) is specified to remove acid gases (CO_2 and H_2S) from the product gas. Since fractionation is thermodynamically more reversible than conventional acid gas removal processes using chemical or physical absorption, fractionation may be attractive from the standpoint of lower energy requirements. Also, since cryogenic methane separation is already required in the process, integration of the two cryogenic processing blocks could be very attractive.

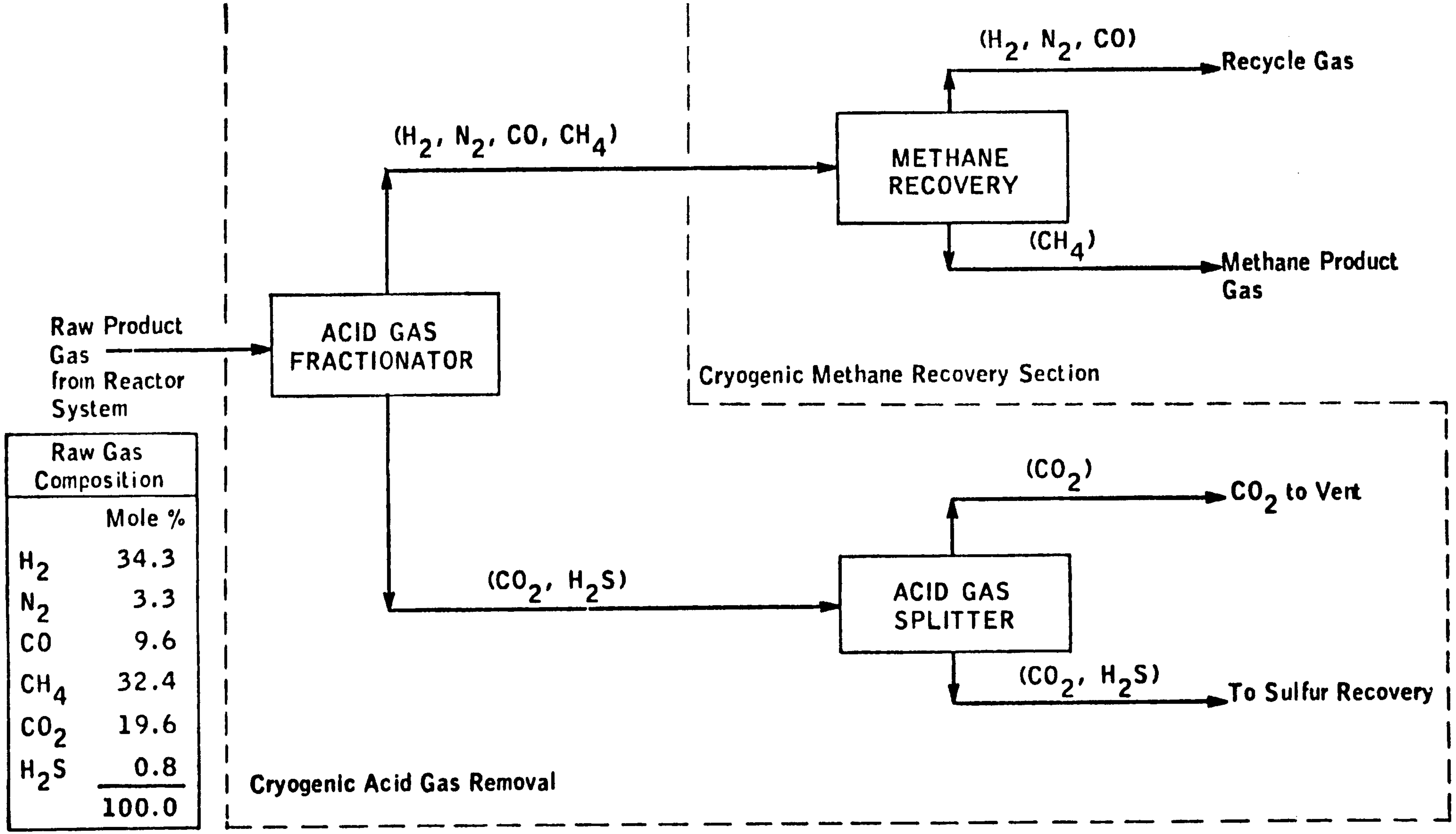
Work was begun in July, 1978 to evaluate the economic incentive associated with using a cryogenic fractionation scheme for acid gas removal. This study involves the definition of the process flow scheme for the separation, detailed heat and material balances, design of the required equipment, and development of investment and operating costs for this plant section. Overall process economics will then be developed and compared with the costs for the CCG Study Design to identify the economic incentive for cryogenic acid gas removal. Technical uncertainties and data needs will also be identified.

Previous work done under the CCG Predevelopment Contract led to the conclusion that carbon dioxide (CO_2) freeze-out will occur in some part of the acid gas fractionation system throughout the range of possible tower operating conditions. For the purpose of this study, it has been assumed that the freeze-out problem can be handled in a simple manner within the system. Further work to determine the actual effect of CO_2 freeze-out would then be undertaken if the economics for this alternative acid gas removal scheme were favorable.

A simplified block flow plan of the Cryogenic Acid Gas Removal scheme is presented in Figure 5.1-1. This figure shows the inlet gas composition and the flow of the raw product gas (from product gas cooling and scrubbing) through the Cryogenic Acid Gas Removal and Cryogenic Methane Recovery Sections. Heat and material balances and heat integration studies for this scheme are currently underway and should be completed during the fourth quarter of 1978.

FIGURE 5.1-1

CRYOGENIC ACID GAS REMOVAL FLOW SCHEME



Raw Gas Composition	
	Mole %
H_2	34.3
N_2	3.3
CO	9.6
CH_4	32.4
CO_2	19.6
H_2S	0.8
	100.0

U.S. GOVERNMENT PRINTING OFFICE:1980 740-145/594

Reproduced by NTIS

National Technical Information Service
Springfield, VA 22161

This report was printed specifically for your order from nearly 3 million titles available in our collection.

For economy and efficiency, NTIS does not maintain stock of its vast collection of technical reports. Rather, most documents are custom reproduced for each order. Documents that are not in electronic format are reproduced from master archival copies and are the best possible reproductions available.

Occasionally, older master materials may reproduce portions of documents that are not fully legible. If you have questions concerning this document or any order you have placed with NTIS, please call our Customer Service Department at (703) 605-6050.

About NTIS

NTIS collects scientific, technical, engineering, and related business information – then organizes, maintains, and disseminates that information in a variety of formats – including electronic download, online access, CD-ROM, magnetic tape, diskette, multimedia, microfiche and paper.

The NTIS collection of nearly 3 million titles includes reports describing research conducted or sponsored by federal agencies and their contractors; statistical and business information; U.S. military publications; multimedia training products; computer software and electronic databases developed by federal agencies; and technical reports prepared by research organizations worldwide.

For more information about NTIS, visit our Web site at http://www.ntis.gov.

NTIS

Ensuring Permanent, Easy Access to U.S. Government Information Assets

SATISFACTION GUARANTEED

NTIS strives to provide quality products, reliable service, and fast delivery. Please contact us for a replacement within 30 days if the item you receive is defective or if we have made an error in filling your order.

▶E-mail: info@ntis.gov
▶Phone: 1-888-584-8332 or (703)605-6050

U.S. DEPARTMENT OF COMMERCE
Technology Administration
National Technical Information Service
Springfield, VA 22161 (703) 605-6000