

EXXON CATALYTIC COAL GASIFICATION PROCESS  
AND LARGE PILOT PLANT DEVELOPMENT PROGRAM

H. A. Marshall  
Exxon Research and Engineering Co.

F. C. R. M. Smits  
Esso Steenkool Technologie, B.V.

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Harry A. Marshall  
Exxon Research and Engineering Co.  
Florham Park, New Jersey 07932  
United States of America

and

Frans C. R. M. Smits  
Esso Steenkool Technologie, B.V.  
3100 AE Schiedam  
The Netherlands

Introduction

Exxon Research and Engineering Company (ER&E) has been engaged since the early 1970's in the development of a unique process for the conversion of coal to substitute natural gas (SNG).<sup>1,2</sup> The development started with the discovery that coal catalyzed with potassium salts promotes methanation of coal gasification products. From this discovery stemmed a one-reactor process concept which offers an efficient route to produce methane from coal.

The objective of this paper is to describe this process concept, recent development activities, and plans to bring the process to commercial readiness by constructing and operating a large pilot plant. The process is called Catalytic Coal Gasification, or CCG.

CCG Process Concept

The fundamental reaction in coal gasification, as shown in Figure 1, is the reaction of carbon with steam to form a mixture of carbon monoxide and hydrogen. When producing methane for use as a substitute natural gas, this is followed by the water-gas shift reaction in which steam reacts with some of the carbon monoxide to form additional hydrogen. The last step in the sequence is methanation, the reaction of carbon monoxide and hydrogen to form methane and water. The overall reaction is thus carbon plus steam yielding the desired product methane and a by-product, carbon dioxide.

The heats of the individual reaction steps are shown in Figure 1. The gasification reaction is highly endothermic, requiring the addition of 64 kcal of heat for each 2 moles of carbon. The shift reaction is slightly exothermic, releasing 8 kcal of heat for each mole of carbon monoxide shifted. The methanation reaction, however, is highly exothermic, releasing 54 kcal for each mole of methane formed. The overall reaction, as shown, is slightly endothermic, and requires very little heat input. Therefore, from a heat balance standpoint, it is clearly beneficial to carry out gasification, shift, and methanation in a single reactor, rather than in three separate reactors as in most coal gasification processes.

The overall reaction can be made to take place in a single reactor by recycling the carbon monoxide and hydrogen. Unfortunately, a gasifier operating at 1700°F or higher would require an unacceptably high recycle rate because of unfavorable methanation equilibrium at high temperatures. The recycle gas rate could be reduced to a reasonable level by dropping the gasifier temperature to 1300°F, if the methanation reaction rate were high enough to approach equilibrium in the gasifier at that temperature. However, the gasification and methanation rates are much too slow at 1300°F, that is, too slow without the use of a catalyst.

It has been known for over half a century that alkali metal salts of weak acids, such as potassium carbonate ( $K_2CO_3$ ), catalyze the steam gasification of coal. Exxon's research has confirmed that commercially acceptable gasification rates can be obtained at a temperature of 1300°F using a catalyst, versus temperatures of 1700-1800°F without a catalyst. Catalyst loadings on the order of 10-20 wt%  $K_2CO_3$  on dry coal are required to achieve acceptable gasification rates.

The discovery that this same catalyst system also promotes the methanation reaction is relatively new and is essential to the Exxon CCG process. Figure 2 presents some bench-scale fixed bed reactor data for the methanation reaction, with  $K_2CO_3$  catalyst on an Illinois No. 6 bituminous coal char. At temperatures above about 1300°F, conversions near equilibrium are obtained even at high space velocities. This figure also shows the effect of temperature on equilibrium. Since the catalyst permits the steam gasification reaction to take place at lower temperatures, it permits more conversion of the resulting carbon monoxide and hydrogen to methane. The ability of the catalyzed char to promote methanation is the key to the CCG process, since it allows a one-reactor process to use directly the heat released in methanation to balance the heat requirement for coal gasification.

#### Commercial Flow Scheme

The proposed commercial plant flow scheme for the CCG process is shown in Figure 3.

Feed coal is crushed to minus 1/8 in., partially dried, and fed to a catalyst mixer. Catalyst is added in the mixer as an aqueous solution at a loading of about 15 wt% (as  $K_2CO_3$ ) on dry coal. The damp catalyzed coal is dried with a mixture of air and recycle flue gas. For some caking and swelling coals, this drying step will also incorporate pretreatment by mild oxidation to reduce swelling in the gasifier. The prepared coal is then fed via a lock hopper system to a fluidized bed gasifier operating at 1300°F and 500 psia. The gasifier contains no internals other than a gas distributor. Here the coal is gasified with a mixture of steam and recycle synthesis gas (carbon monoxide and hydrogen).

The gasifier effluent is primarily  $CH_4$ , CO,  $H_2$ ,  $CO_2$ , and unconverted steam. This effluent flows through cyclones in which the coarser entrained fines are recovered for return to the fluid bed. After high level heat recovery from the gas, the remaining fines are removed by cyclones and a venturi scrubber, and ammonia, hydrogen sulfide, and carbon dioxide are removed using conventional technology. Product methane is separated from CO and  $H_2$  by cryogenic distillation, and the methane is sent to sales. The CO

and H<sub>2</sub> are recycled to the gasifier. Since the amount of CO and H<sub>2</sub> fed balances the amount of CO and H<sub>2</sub> leaving the gasifier, the net products of gasification are only methane and carbon dioxide along with small amounts of hydrogen sulfide and ammonia.

As previously described, this overall reaction is essentially thermally neutral, and only a small amount of heat is required in the gasifier to heat up the feed coal and offset heat losses. This heat is supplied by preheating the feed gases to about 1500°F before they enter the fluid bed. A small steam/methane reformer may also be included to provide a supplemental source of synthesis gas which methanates in the gasifier and thus supplies additional heat. This approach is more economical than raising the preheat temperature much above 1500°F.

Also shown on the flow diagram is a catalyst recovery step. This step is required because catalyst leaves the gasifier with the ash/char residue, and the catalyst is too costly to discard. Fortunately, most of the catalyst is water soluble and can be recovered in a counter-current water washing operation. However, a portion of the catalyst reacts with the coal ash to form insoluble compounds, principally potassium aluminosilicates. The degree of catalyst tie-up is a function of the coal ash content and composition. With a typical Illinois coal about 70% of the catalyst is water soluble. Thus, some makeup catalyst in the form of potassium hydroxide or potassium carbonate is required.

Figure 4 summarizes both the benefits and debits of using potassium catalyst in the CCG process. First among the benefits, the rate of steam gasification is accelerated allowing gasification temperatures to be reduced. Second, and most significant, the rate of methanation is promoted so that this reaction is close to equilibrium. This results in an almost thermally neutral overall reaction which requires little heat input. In contrast to thermal gasification processes, no oxygen is required, and no separate shift and methanation reactors are needed. Third, the catalyst reduces the swelling and caking tendencies of bituminous coals during devolatilization, thus making CCG capable of processing a wide range of coals. And fourth, the potassium-char bed effectively destroys all hydrocarbons heavier than methane, eliminating any tars and oils which can raise costs and create operating problems in gasifier effluent heat recovery equipment and waste water treating facilities.

The use of potassium as a catalyst in the CCG process also brings some debits. One debit is the facilities required to recover catalyst. Also, fresh makeup catalyst is needed. Another is the higher quality construction materials required to offset the corrosive effects of the potassium salts. This problem is somewhat mitigated by the relatively low 1300°F operating temperature of this gasification process. Last is the volume of residual ash to be disposed, consisting of the coal ash, some unconverted carbon (since carbon conversion is limited by the fluid bed concept used), and unrecovered insoluble potassium salts. The unconverted carbon and insoluble potassium are not expected to cause any environmental disposal problems beyond those present with coal ash. Exxon is developing several disposal and utilization options for CCG residual solids.

### CCG Process Development

In developing a process to commercial readiness, ER&E follows a development path through four major phases as shown in Figure 5: exploratory research, predevelopment, development, and precommercialization. Each phase involves a mix of activities including fundamental research and process testing in the laboratory, and engineering studies of commercial systems to provide critical guidance to the development. Exxon's exploratory research on catalytic coal gasification began in 1971. The discovery that a mixture of potassium carbonate and coal char catalyzes the methanation reaction led to the definition of a new coal gasification process concept, which is now called CCG.

Major component technologies of CCG were examined in the predevelopment phase, which took place in 1975 through 1977.<sup>3</sup> This work included bench-scale research, operation of a 0.25 T/D Fluidized Bed Gasifier (or FBG) at 115 psia, and engineering support studies including a conceptual "study design" for a commercial-scale CCG plant.

The process development phase of work covered the period 1978 through early 1981 and was aimed at advancing CCG technology sufficiently to make it ready for further scale-up in a large pilot plant.<sup>4</sup> The major task in this phase was the operation of a 1 T/D Process Development Unit (or PDU) at a pressure of 500 psia. Bench-scale research and engineering studies were also carried out to support the integrated development effort.

A major portion of the funding for the predevelopment and development phases was provided by the U. S. Department of Energy and the Gas Research Institute. ER&E wishes to express its gratitude for this support. Currently the program is totally funded by Exxon.

The CCG process has now entered the final or precommercialization phase of its development. This phase will involve a 100 T/D large pilot plant (or LPP) which is now being designed. Supporting laboratory and engineering programs will continue during the precommercialization phase, which is expected to be completed in 1989. The large pilot plant project will be described in more detail later in this paper.

Figure 6 illustrates the key pilot unit sizes for the last three development stages and the projected commercial plant. The capacity of the fluid bed unit used during predevelopment was 0.25 T/D of coal. The process development unit now in operation feeds 1 T/D. The two pictures on the right look ahead to the future large pilot plant of 100 T/D and commercial gasifier reactors of 3,000-5,000 T/D which could be in operation in the late 1990's.

The current development effort centers on the 1 T/D PDU located at ER&E's Synthetic Fuels Research Laboratory in Baytown, Texas.<sup>5</sup> This unit is large enough to permit continuous feed and withdrawal, and it operates at the projected commercial conditions. The PDU includes complete facilities for coal preparation, gasification, product gas cleanup and separation, and catalyst recovery. The gasifier is a slender tube 10 inches in diameter and 80 feet long. The purpose of the PDU has been to confirm the operability of the process at commercial conditions and to provide the data base for design of the large pilot plant. To date, the unit has been run for over 9,500 hours,

with the longest uninterrupted run period being 33 days. ER&E is proud of these operating achievements, especially in view of the substantial challenge which operation of high pressure coal gasification pilot plants presents. During the large pilot plant phase, continued operation of this 1 T/D unit is envisioned.

The PDU achieved its most significant milestone to date in April, 1981, with a 23-day demonstration run.<sup>5,6</sup> This run showed the operability, sustainability, and control of the CCG process at the target commercial conditions. The results of this run are shown on Figure 7. Temperature and pressure were controlled at 1280°F and 500 psia, and coal and steam rates were maintained near the targets. The fluid bed density was held at 16 lbs/ft<sup>3</sup>, steam conversion was 35%, and carbon conversion was 85-90% -- all met the original targets. Entrained fines were not recycled during the demonstration run, and it is expected that carbon conversion would increase with fines recycle. Methane content in the product gas was 20-25%, somewhat lower than target, but this level was consistent with the higher steam/coal ratio used. Material balances within 5% were recorded, and no gasifier plugging was observed. This run was a major success. The PDU demonstrated process operability and provided data necessary for the next phase of the program: the design, construction, and operation of the large pilot plant. The PDU is now focusing on evaluation of alternative coals, process improvements, and improved carbon conversion.

#### Large Pilot Plant Project Basis

Figure 8 presents the project planning basis for the CCG large pilot plant. The pilot plant will be built and operated in Rotterdam Europoort in Holland by Esso Steenkool Technologie, B.V., an Exxon affiliate. A site next to an existing Exxon facility has been selected to take advantage of certain available utilities. The prime purposes for the large pilot plant are to develop process and equipment data and scale-up capability to design commercial plants and to demonstrate the applicability of the process on a range of coals of interest. An in-depth size study taking into account process and hardware issues, scale-up capability, and commercial representativeness resulted in a size selection for the large pilot plant based mainly upon the gasifier section. The conclusion was that a large pilot plant of about 100 T/D is needed to bring the process to commercial readiness.<sup>2</sup>

Bituminous coals which are reasonably representative of coals expected to be internationally traded in the future will be tested in the large pilot plant. The product gas will be SNG, which will be sent to the adjacent Exxon facilities as fuel. The 100 T/D large pilot plant, its operation, and the associated R&D activities are expected to cost over 500 million dollars.

The facilities which will be included in the large pilot plant are illustrated in Figure 9, which repeats the commercial flow scheme shown previously in Figure 3. The facilities indicated with shading were identified during the size study as areas which should be demonstrated on the large pilot plant scale in order to obtain adequate scale-up data for commercialization. Included in this category are:

- The fluid bed pretreatment step.
- The gasifier, including coal feeding, cyclones, and char withdrawal and depressuring equipment.
- The gasifier effluent high temperature heat recovery equipment, consisting of a gas-gas heat exchanger and a waste heat boiler.
- The catalyst recovery facilities.

The remaining facilities will probably be included in the large pilot plant, but they represent conventional technology or can be demonstrated separately without inclusion in the LPP. To enable the plant to operate, it will be necessary to provide for coal crushing/drying, coal/catalyst mixing, fines removal, and preheat. The steam reformer will be included to provide additional heat input for the gasifier which is essential at the large pilot plant scale to offset relatively high heat losses from small equipment. Acid gas removal and cryogenic separation will be included to close the recycle gas loop.

#### Large Pilot Plant Process Basis

A major effort, carried out in late 1981 and early 1982, established the process bases for all large pilot plant equipment. An important aspect of this work was the fact that the large pilot plant must have the flexibility to handle a variety of coal feeds and a range of operating conditions. A series of flexibility studies was carried out to estimate the impacts of alternative operating conditions on the material and energy balance and to establish design ranges for major process variables, such as coal feed rate, gasifier temperature and pressure, steam rate, and gasifier effluent rate. The ranges in some of the key process variables and a few operating modes presented in Figures 10 and 11 reflect such flexibility considerations. Some of the ranges are very wide, and therefore present significant challenges in designing the LPP.

The base coal feed rate to the large pilot plant is set at 100 T/D of Illinois No. 6 coal. Illinois No. 6 has been used as the primary design feed because the data base to date is mainly on this coal. As mentioned before, several bituminous coals will be run in the LPP. Since no specific coals have been selected yet, the LPP will be designed for a considerable range of coal properties. Ash contents ranging from 1.5-17 wt% have been specified. Ash is an important parameter since aluminosilicates in the coal tie up active potassium and form water-insoluble compounds which cannot be recovered by the counter-current water wash train in the catalyst recovery section. Coal feed heating values in the range of 8,000-13,500 Btu/lb, moisture levels between 3.5 and 16.5 wt%, and sulfur levels between 0.5 and 4 wt% have been assumed in the basis. The catalyst loading will be in the range of 10-20 wt% as potassium carbonate on dry coal, depending on the ash content of the coal and required carbon conversion.

The fluid bed pretreater which is used to dry the coal/catalyst mixture and to reduce coal swelling and caking tendencies will be designed to run at temperatures between 350 and 400°F at a pressure of about 17 psia. Designing for this range of temperatures, along with the capability to vary

residence time and inlet gas oxygen content, will provide flexibility to adjust pretreater operations to best satisfy the pretreatment requirements of individual coal feeds. For mildly caking coals, the pretreater will be used as a drier only and oxygen consumption will be minimal. When strongly caking coals are processed, conditions will be adjusted to obtain oxygen consumptions in the range of 2.5-10 wt% on dry coal.

Considerable flexibility has been provided in the gasifier process basis as indicated in Figure 11. A temperature range of 1275 to 1325°F at a pressure of 500 psia has been specified. Steam-to-coal weight ratios ranging from 1.3 to 2.0 and carbon conversions of up to 95% have been assumed in the heat and material balance calculations. Together with kinetic and fluidization correlations incorporated in a computerized CCG Reactor Model, heat and material balance calculations have led to the sizing of the gasifier and showed the need to be able to run at a range of bed heights from 60 to 100 ft to allow operations under all conditions likely to be of commercial interest.

Heat recovery from the gasifier effluent gas will be by a gas-gas exchanger which preheats gasifier feed steam and recycle gas, followed by a waste heat boiler producing 600 psig steam. Because it may be desirable to vary the exchanger configurations to determine the best operating conditions for the high temperature, dusty environment, the LPP will be designed to run with either the gas-gas exchanger or the waste heat boiler or both bypassed. These operating modes will allow modifications to the exchangers while continuing to operate the gasifier.

Catalyst recovery will be designed for a 95% recovery of water-soluble potassium, which represents for Illinois No. 6 coal about 70% of the total potassium added to the coal. Six stages of settlers and several filters will be required to handle all potential solids rates. Significant extra allowances will be specified as a result of uncertainties in solid properties and the large range of ash content of the feed coals for the large pilot plant.

#### Large Pilot Plant Project Schedule

The current schedule outlook for the large pilot plant project is shown in Figure 12. The planning effort is nearly completed, and the design activities started earlier this year are expected to be completed in 1983. Detailed engineering and construction are scheduled in the 1983-1986 time frame. Operation of the plant will take 2-3 years.

Supporting R&D activities will continue throughout the large pilot plant program. Much remains to be done to bring CCG to commercial readiness. As in any major process development, some technical challenges must be resolved, and unexpected findings may occur. On the other hand, ER&E's continuing work on process improvements could lead to enhancements to the current commercial process concept. Either the process development or process improvement activities may lead to changes in this development schedule.



### Conclusion

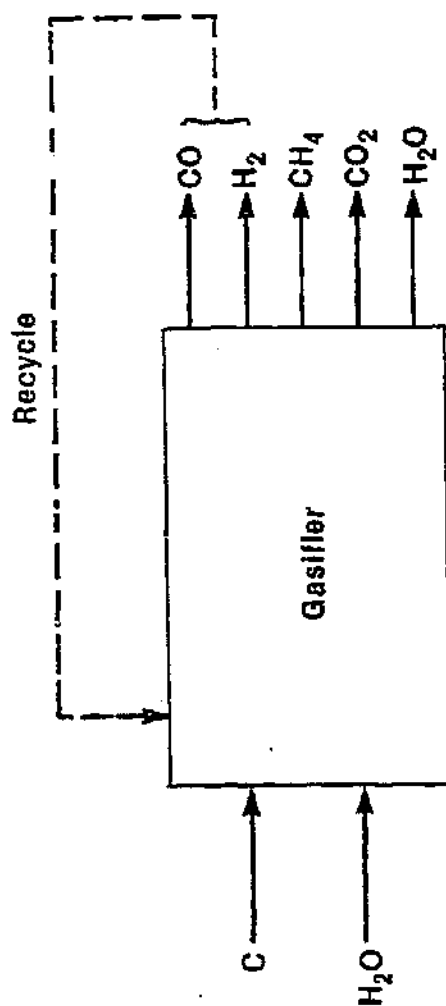
In conclusion, Exxon Research and Engineering and Esso Steenkool Technologie, B.V. believe that, in the longer term, CCG offers an efficient route to SNG from coal, particularly from bituminous coals. More than a decade of development work has brought the process from an early concept to a point where process feasibility has been demonstrated. The Department of Energy and the Gas Research Institute played an important part in CCG's evolution through their financial support and encouragement. Exxon is now proceeding with the final development step — the design and operation of a large pilot plant — to ready CCG for commercial application.

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# COAL GASIFICATION CHEMISTRY

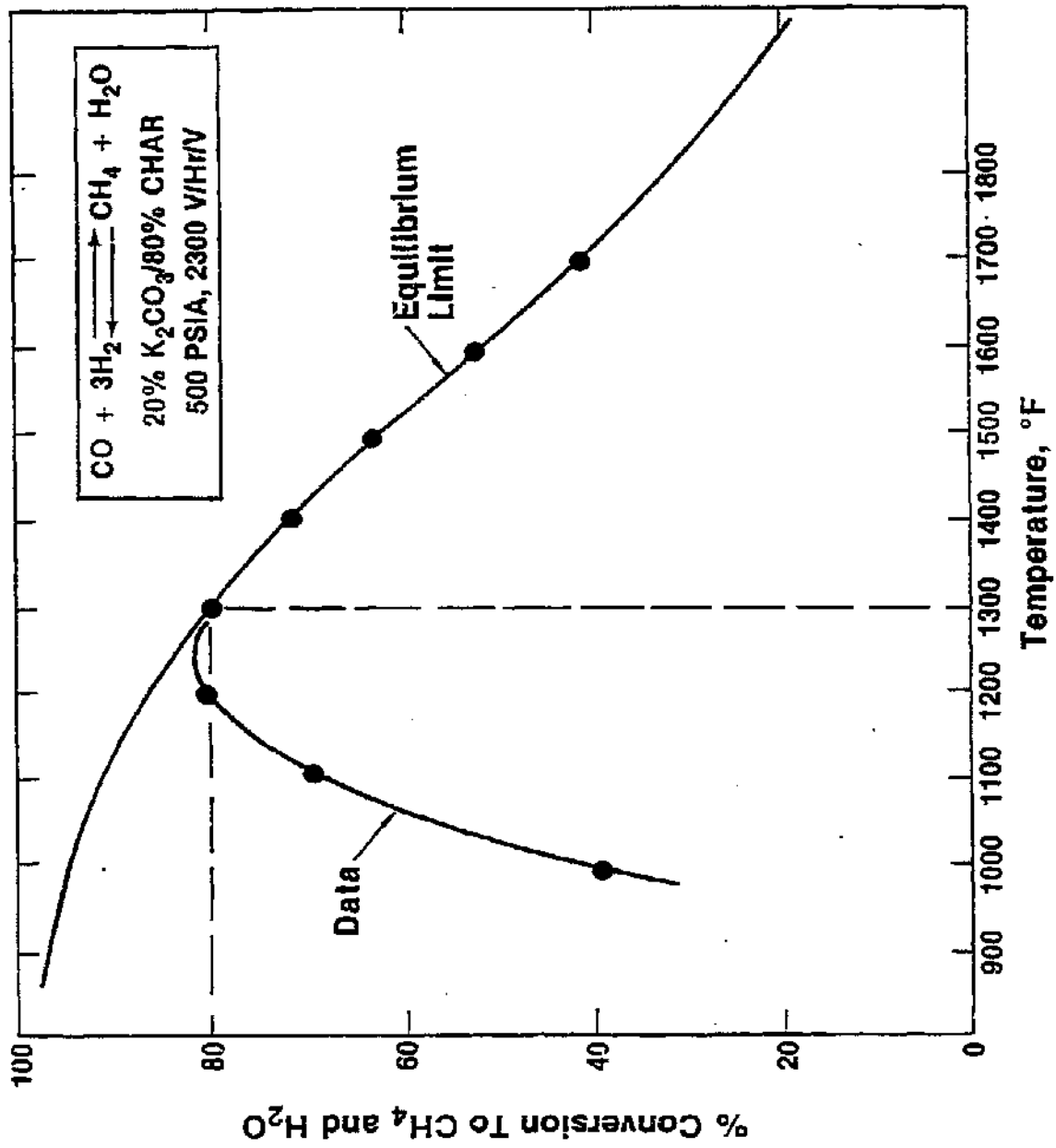
Figure 1



Gasification	$2C + 2H_2O \longrightarrow 2CO + 2H_2$	$\Delta H_R = 64 \text{ KCAL/MOLE}$
Shift	$CO + H_2O \longrightarrow CO_2 + H_2$	$\Delta H_R = -8 \text{ KCAL/MOLE}$
Methanation	$CO + 3H_2 \longrightarrow CH_4 + H_2O$	$\Delta H_R = -54 \text{ KCAL/MOLE}$
Overall	$2C + 2H_2O \longrightarrow CH_4 + CO_2$	$\Delta H_R = 2 \text{ KCAL/MOLE}$

Figure 2

# POTASSIUM-CHAR IS A METHANATION CATALYST



# EXXON CATALYTIC COAL GASIFICATION PROCESS

Figure 3

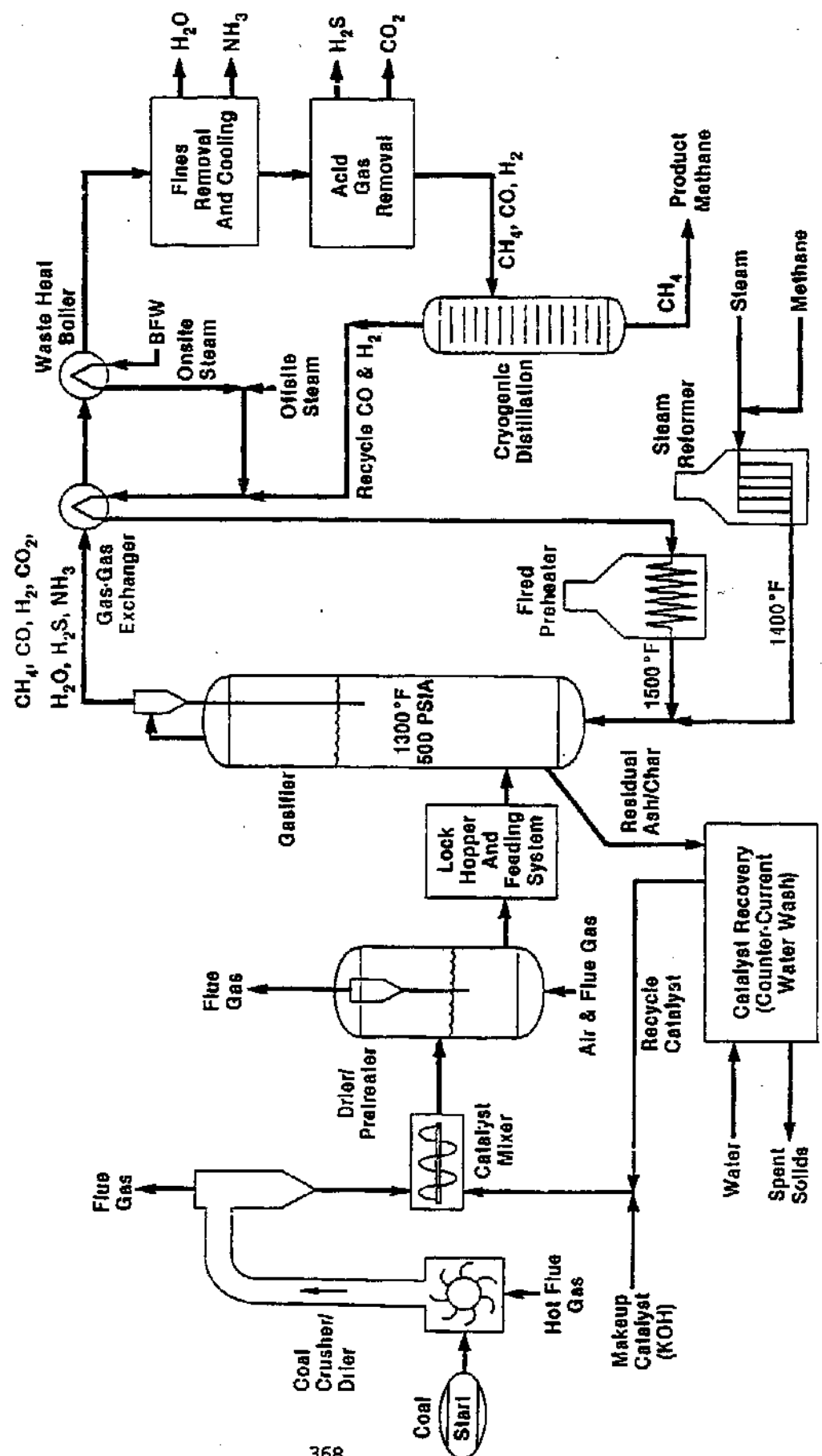


Figure 4

## **BENEFITS AND DEBITS FOR CCG PROCESS**

- **Process Benefits of Potassium Catalyst**
  - **Accelerates Steam Gasification Rate**
  - **Promotes Methanation Rate**
  - + **Gasifier Almost Thermally Neutral**
  - + **No Oxygen Required**
  - + **No Separate Shift and Methanation Reactors**
  - **Reduces Swelling and Caking of Bituminous Coals**
  - **Destroys Tars and Heavy Oils in Gasifier Bed**
- **Process Debits of Potassium Catalyst**
  - **Requires Catalyst Recovery and Makeup**
  - **Requires Higher Quality Materials for Corrosion Resistance**
  - **Produces Residual Solids Containing Coal Ash, Unconverted Carbon, and Insoluble Potassium Salts**

Figure 5

# CCG PROCESS DEVELOPMENT PHASES

Activity	Time Frame
• Exploratory Research	1971-1974
— Methanation Activity of Potassium-Char Found	
• Predevelopment	1975-1977
— 0.25 T/D FBG Operation at 115 PSIA	
— Commercial Plant Study Design	
• Development	1978-1981
— 1 T/D Process Development Unit (PDU) Operation at 500 PSIA	
— Supporting R&D Programs	
• Precommercialization	1981-1989
— 100 T/D Large Pilot Plant (LPP)	
— Supporting R&D Programs	

Figure 6

# GASIFIER SIZE VS. STAGE OF DEVELOPMENT

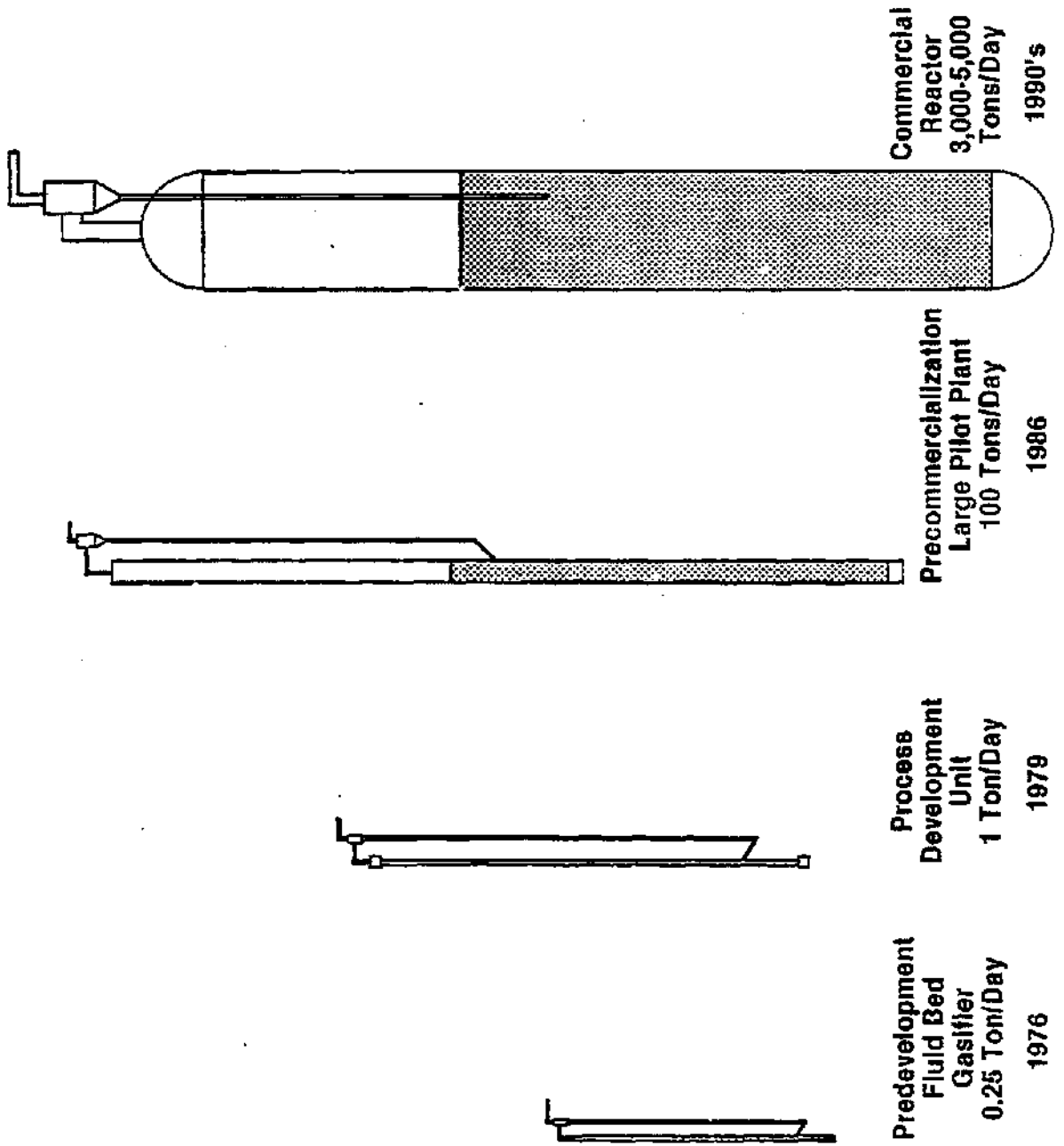


Figure 7

## SUCCESSFUL 23-DAY PDU GASIFIER DEMONSTRATION RUN WAS ACHIEVED IN 1981

	<u>Target</u>	<u>Achieved</u>
Temperature, °F	1300	1280
Pressure, PSIA	500	500
Coal + Catalyst, Lbs/Hr	132	132
Steam/Coal Ratio	1.7	1.9
Bed Density, Lbs/Ft <sup>3</sup>	>10	16
Steam Conversion, %	30-40	35
Carbon Conversion, %	>85	85-90
CH <sub>4</sub> In Product Gas, %	>25	21*
Run Lengths, Days	14-21	23

\* Consistent with Operating Conditions



**Figure 8**  
**LARGE PILOT PLANT PROJECT PLANNING**  
**BASIS**

- **Location** Rotterdam Europoort
- **Operator** Esso Steenkool Technologie, B.V.
- **Facilities** Grass Roots Except for Some Utilities
- **Size** 100 T/D Coal Feed (As Received)
- **Feed Coal** Bituminous Coals
- **Product** SNG
- **Program Cost** 500 Million \$ +

# FACILITIES IN CATALYTIC COAL GASIFICATION LPP

- Shading Shows Facilities Which Must Be Demonstrated in LPP to Obtain Scale-up Data

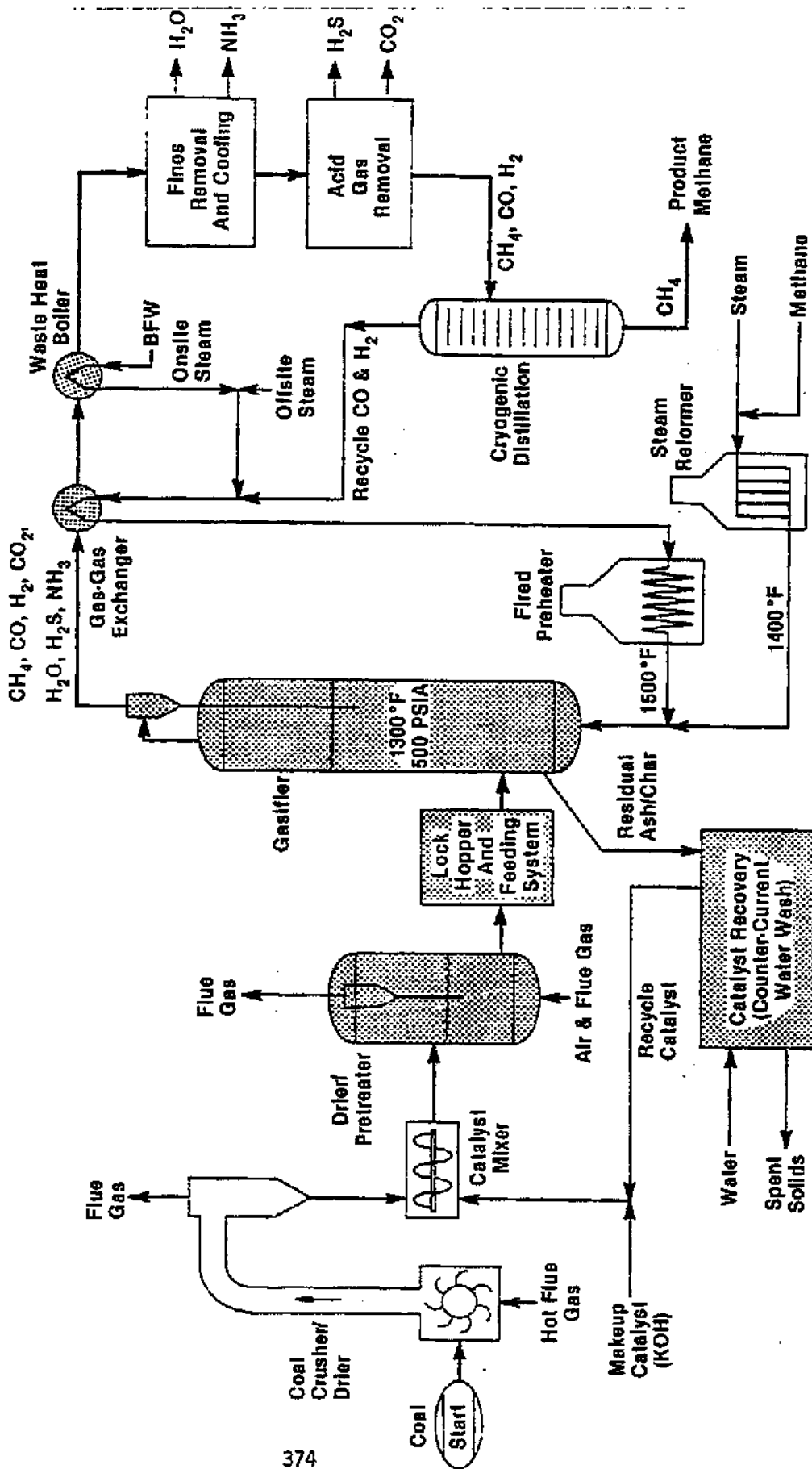


Figure 10  
**LARGE PILOT PLANT PROCESS BASIS**

- **Base Coal Feed** — 100 T/D Illinois No. 6
- **Other Coals** — 1.5-17% Ash
  - 8,000-13,500 Btu/Lb
  - 3.5-16.5% Moisture
  - 0.5-4% Sulfur
- **Catalyst Loading** — 10-20%  $K_2CO_3$  on Dry Coal
- **Pretreatment** — 350-400 °F/17 PSIA
  - Oxygen Consumption 0-10% on Dry Coal

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Figure 11

## LARGE PILOT PLANT PROCESS BASIS (Continued)

- Gasifier
  - 1275-1325 °F/500 PSIA
  - 1.3-2.0 Steam/Coal Ratio
  - Up to 95% Carbon Conversion
  - 60 to 100 Ft Bed Heights
- Heat Recovery
  - Gas-Gas Exchanger and/or Waste Heat Boiler or Both Bypassed
- Catalyst Recovery
  - 6 Stages of Settlers
  - 95% Recovery of Water-Soluble Potassium

**Figure 12**  
**LARGE PILOT PLANT SCHEDULE OUTLOOK**

- **Planning** 1981-1982
- **Design** 1982-1983
- **Detailed Engineering/Construction** 1983-1986
- **Operations** 1986-1989
- **Supporting R&D** Through 1989