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CATALYTIC GASIFICATION PREDEVELOPMENT RESEARCH

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CATALYTIC GASIFICATION PREDEVELOPMENT RESEARCH

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ABSTRACT

Significant progress has been made in the predevelopment research phase of catalytic coal gasification for the production of substitute natural gas (SNG). The potassium catalyst and the processing sequence permit the direct reaction of steam and coal to form methane and carbon dioxide, a reaction which is thermally neutral and does not require oxygen for heat balance or downstream methanation of synthesis gas. A model of the reaction kinetics has been developed and a preferred approach has been identified to recover about 90 percent of the potassium catalyst for reuse.

EXXON RESEARCH AND ENGINEERING COMPANY has been actively engaged in coal gasification research since the late 1960's. The predevelopment phase of catalytic gasification was recently completed under DOE sponsorship. The status of research prior to this phase was described in 1976 by Epperly and Siegel (1) at the Eleventh Intersociety Energy Conversion Engineering Conference. The process concept had been identified, and a limited data base had been generated. An early engineering design of a commercial SNG plant indicated that there was a significant incentive over thermal approaches, but key feasibility questions remained.

This paper presents a review of the process concept and summarizes the resolution of the key technical issues.

The concept was identified when it was found that the combination of coal char and alkali metal is an active methanation catalyst It had been known that weak acid salts of alkali metals, such as potassium carbonate, are active in the steam gasification of coal. Fixed bed kinetic experiments showed that satisfactory steam conversion and carbon gasification rates could be obtained at temperatures as low as about 1300°F (700°C) with potassium catalyst versus about $1700^{\circ}F$ (925°C) for comparable performance without catalyst. During the course of these experiments, it was observed that the gas composition was essentially in chemical equilibrium with respect to its five major components, H₂O, H₂, CO, CO₂, and CH₄. In similar experiments without catalyst, it was found that all but methane were generally in equilibrium. This was interpreted to mean that the water-gas shift reaction,

$$H_20 + C0 \leftrightarrow H_2 + C0_2$$

is catalyzed by the char alone, but the addition of alkali metal gasification catalyst also promotes another gas phase reaction involving methane and some of the other constituents, for example, the methanation-reforming reaction:

$$3H_2 + CO \leftrightarrow CH_4 + H_2O$$

This was independently confirmed by carrying out the above reaction from both directions at space velocities up to ten times gasification space velocities. Neither char alone nor potassium carbonate alone were catalytic for the methanation-reforming reaction. However, a mixture of the two, heated to an elevated temperature, produces a combination which catalyzes the gas phase reactions even more readily than it catalyzes the decomposition of steam reacting with carbon (2). This effect is shown in Figure 1 where the methane content content of the product gas is plotted as a



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percentage of the equilibrium methane content. This data at 500 psig (3.5 MPa) was generated with both Wyoming and Illinois coal chars. The relative residence time for the gas phase in a commercial gasifier would lie between 1 and 2 on this plot, and indicates that essentially equilibrium levels of methane are to be expected in the raw product gas.

The application of this finding to the manufacture of methane from steam and coal is illustrated conceptually in the chemistry diagrams shown in Figure 2 which contrasts





Fig. 2 - Chemistry of coal gasification

thermal gasification with catalytic gasifica-Reaction heat effects are shown for tion. generating 1000 units of heating value in the product methane. The steam-carbon reaction needs 300 units to generate H2 and CO. This endothermic heat of reaction is the thermodynamic equivalent of shaft work and supplying it is limited by Carnot's theorem to a maximum efficiency of about 50 percent. Most of the heat load is returned at a lower temperature as the mixture is converted to methane by a combination of the water-gas shift and methanation reactions. When steam and carbon are reacted in the presence of potassium catalyst, the product gas also contains some H2 and CO. These components, however, can be separated and recycled to the gasifier which will maintain their equilibrium relationship with methane. Because all of the H₂ and CO mixture withdrawn is replaced, there is no net production of these endothermic reaction products, and the net reaction products are methane and carbon dioxide. Forming these products from steam and graphite is very slightly endothermic. With coal as the feed, rather than graphite, the reaction is slightly exothermic, uses less steam, and generates less C07:

Graphite: $2C + 2H_2O \rightarrow CH_4 + CO_2$

Coal: $1.7CH_{0.9}O_{0.1} + 1.2H_{2}O \rightarrow CH_{4} + 0.7CO_{2}$

Because the reaction is not endothermic, the only heat input to the gasifier is the preheat of the reactants to the gasification temperature. A simplified diagram of the Exxon catalytic gasification process is shown in Figure 3.



Fig. 3 - Exxon catalytic coal gasification process

Coal is prepared for gasification by being crushed to minus 8 mesh, a size consist suitable for fluidization. Catalyst is added as an aqueous solution of potassium hydroxide, and the mixture is dried before being fed to a fluidized bed reactor operating at 500 psig (3.5 MPa), and 1300°F (700°C). The reactor is fluidized with a preheated mixture of steam with recycled hydrogen and carbon monoxide. The product gas contains all five of the major constituents already mentioned plus most of the coal sulfur as H2S and essentially all of the organic nitrogen as NH3. The unreacted steam condenses in waste heat recovery equipment and dissolves ammonis. Entrained particulates are wet scrubbed out in this step also. The gas mixture is then further treated for removal of CO2 and H2S. The remaining constituents are separated by cryogenic distillation into methane product and recycle gas. Ash must be purged from the reactor, and catalyst is unavoidably withdrawn. About two-thirds of the catalyst is recoverable by water leaching as a mixture of potassium carbonate and potassium hydroxide. The unique features of this process are the gasification reaction itself, the catalyst recovery step and the cryogenic distillation step.

No experimental work was done on the cryogenic distillation, shown in Figure 4.





The available data base on the vapor-liquid equilibria is sufficient to design the distillation equipment for this three-component The feed gas is cooled and partially avstem. liquefied by exchange with the separated prodects. With a system pressure of 400 psig and 10% methane in the recycle gas, the coldest part in the system, the overhead condenser, can be - interated to -241°F (-152°C) by boiling suchane. The liquid methane is the third migarane of a coscade which supplies the net up refrigeration. The reboiler itself acts se part of the refrigeration system by liquefyand methane and returning it to the cascade. The catalyst recovery step was originally

conceived as a counter-current water leaching operation as shown in Figure 5.



Sig. 5 - Catalyse recovery

Dist tackmining occurs as a result of particle contrainment in the hydroclone overflow and water intrainment in the underflow. Even allowing for technizing, nearly all the water soluble catalyst can be recovered by having enough toget. The main technical issue is whether that new soluble constituents in the coal will be up on the pathbyst recycle loop.

satifier design is another significant interactions During the predevelopment into a literia codel was developed to aid in a static provider size requirements. The into a static to addl is illustrated in base in The major independent variables



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which can be selected by the process designer are the volume, temperature, pressure, catalyst loading and desired carbon conversion. The last two determine the composition of the steadystate solids, and the first three can be used as inputs to the kinetic model, which predicts steam conversion when only the reaction kinetics are limiting. In a real reactor, steam conversion will be slightly lower because of less than perfect contacting between gas and solids. When estimates are made of these effects, the computed steam conversion, equilibrium calleur lations, and reaction stoichiometry can be used with the independent variables to completely describe the gasifier material balance and energy balance. Clearly the key element in this effort is the kinetic model. A detailed description of the model will be presented by Vadovic and Eakman (3) at the September ACS Symposium in Miami. The reaction rate was found to be controlled by strong product in-hibition, and a kinetic expression of the classical Langmuir-Hinshelwood form was used to correlate the data shown in Figure 7.



Fig. 7 - Covelation of data with fized bed kinetic model

Catalyst loading, temperature, and steam flow rate were incorporated into the definition of equivalent steam residence time. This residence time is the single independent variable needed to predict steam conversion in the gasification reaction, expressed as moles of carbon gasified per mole of steam fed.

The correlation is seen to be adequate ise the data base represented in Figure 7, but the test of more significance is the capability of the model to translate these results from $\{0\}$ baten to continuous operation, $\{b\}$ fixed bed on fluidized bed, (c) that to cost, and (d) steet feed to a mixture of steam and recycle gas

This test was carried out in a six-inch 115 cm) diameter fluidized bed gasifier shown in the flowplan in Figure 8. This unit 14 limited in



Fig. 8 - Fluid bed gasifier (FBG) flowplan

pressure to 100 psig (0.8 MPa), but is otherwise capable of simulating anticipated commercial conditions with respect to continuous feeding and solids withdrawal, temperature, coal size consist, catalyst loading, fluidizing gas velocity, steady-state solids composition (carbon conversion), and steam conversion. Recycle gas is simulated by a blend of H₂ and CO to match the output of these components in the product gas. Feed coal at about 5 kg/hr is entrained in the recycle gas from a continuous lockhopper into the bottom of the gasifier where it is mixed with steam. Entrained particles are recovered dry by a combination of cyclones and filters before the gas is cooled to its dewpoint. This operation is performed to obtain good material balance, while in a commercial plant the solids would be removed by wet scrubbing. After solids removal the gas is cooled, scrubbed in its own condensate, analyzed by gas chromatograph, metered, and flared. The unit was operated for eight months during the predevelopment period. During the last six months, the average service factor was 70 percent with one month at 96 percent. Fifty material balance periods were identified, usually of 24 hours duration each. Eighteen of these periods were selected for detailed material balance work-up, the selection being made to represent a variety of process variables. Water-soluble catalyst was recovered and reused during the last 45 days, with final operation at 94 percent recovery of water-soluble catalyst. The end of the operation corresponded to about ten cycles of catalyst through the system. Sodium cation and sulfate anion, both present in the raw coal, were the only species observed to build up in the catalyst recovery loop, to a level of about two percent of the catalyst loading. There was no observable loss of activity during this operation. During the latter months, raw material balances closed typically within two percent for total input and output, and within five percent for individual carbon, hydrogen, and oxygen balances, as shown in Figure 9. The Fluid Bed Gasifier performance compared adequately with predictions based on the fixed



Fig. 9 - Fluid bed gasifier material balance

bed kinetic model as shown in Figure 10, where the range of interest is 0.4 to 0.6 mole carbon gasified per mole of steam fed. Based on a



Fig. 10 - Comparison of FBG data with reactor model predictions

similar prediction for the commercial plant study design, a 250 G Btu/day (63 x 10⁹ kcal/day) SNG plant would require four gasifiers, each 22 feet (6.7 m) in diameter with about 100 feet (30m) of bed depth. Fluidized beds of comparable size are used in commercial operations in the petroleum industry. More information about the commercial plant study design will be presented by Gallagher and Marshall (4) at the November AIChE Symposium in Miami. Other engineering studies carried out during the predevelopment phase showed that makeup catalyst can be made available in large quantities and identified KOH manufactured by electrolysis of KCl as the preferred form.

As a further result of this research project, a preferred route was identified for the recovery of water insoluble potassium. For most coals, the mixture of coal and catalyst will contain about 8 percent potassium. As much as one-third of the potassium can react with clay minerals found in coal to make insoluble potassium aluminum silicate, a form which is not active as a catalyst. The formation of this material completes a cycle which began in nature while the coal was being formed some 50-300 million years ago. The chemistry is that of the most abundant elements. More than half of the earth's crust is composed of feldspars. These minerals are aluminosilicates of potassium, sodium, and calcium. They are the chief constituents of igneous rocks such as granite. The six elements which constitute the feldspars rank among the first seven in abundance. The clay minerals found in coal are the products of the weathering process illustrated in Figure 11. By a variety of natural processes, normetal oxides





Fig. 11 - Chemistry of catalyst reactions with mineral matter

enter the atmosphere and are absorbed in rain water, making it slightly acidic. As an acid, rain water can extract alkali and alkaline earth metals from feldspars. The remaining aluminosilicates lose their structural integrity, wash down as silt in the runoff, and settle out to form clay deposits in regions where drainage is poor, such as coal-forming swamps. The solubilized potassium ultimately appears as the residue of extinct salt lakes, commonly referred to as potash, the source mineral for potassium catalyst. When these materials are recombined in catalytic gasification, minerals such as kaliophilite are formed. The chemistry of this cycle suggests several approaches to recovery of the potassium, such as acid extraction or displacement by cheaper sodium or calcium. Extraction by strong acids does in fact solubilize all of the potassium, but other materials such as iron and silica are also brought into solution and the potassium is recovered as the salt of a strong acid, a catalytically inactive form. The use of cheaper sodium carbonate as an ash scavenger was explored, but it was found that although sodium aluminosilicates were formed, the sodium was subsequently displaced by potassium. The preferred approach identified during this research was the aqueous digestion of the char with calcium hydroxide. It was found that with a suitable calcium loading, a reaction time of two hours at 300°F (150°C) was sufficient to solubilize more than



Fig. 12 - Potassium recovery by calcium hydroxide digestion

90 percent of the potassium, mainly as KOH as shown in Figure 12. This high level of recovery raises the need to reexamine the potential buildup of other soluble species which did not cause problems at the 60-70% level of catalyst recovery.

Further investigation of catalyst recovery and integration of all the process steps will be carried out in the process development phase which is expected to last through 1980. A Process Development Unit now under construction will be capable of gasifying 100 lb/hr (45 kg/hr) of coal at 500 psig (3.5 MPa). Its operation will be carried out in parallel with bench-scale research and engineering studies aimed at readying the process for further scale-up.

ACKNOWLEDGEMENT

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KINETICS OF POTASSIUM CATALYZED GASIFICATION

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INTRODUCTION

The Exxon Catalytic Coal Gasification Process(2) is based upon a new combination of processing steps which avoid thermodynamic constraints inherent in the previous art. The use of the catalyst in the reaction step and the manner in which the reactor is integrated into the overall process are the keys to this concept. The goal of the work reported here is the formulation of a kinetic relationship for catalytic gasification which can be used in developing a model for the fluid bed reactor used in this process. This model is needed to correlate pilot unit conversion data and as a design tool for commercial scale units. This paper reports on the work which culminated in the successful formulation of the required kinetic expression.

Alkali metal gasification catalysts increase the rate of steam gasification(3,4,5) promote gas phase methanation equilibrium, (2,5) and minimize agglomeration of caking coals.(1) The catalytic gasification process uses an alkali metal gasification catalyst (K₂CO₃) with a novel processing sequence which maximizes the benefits of the catalyst. The process combines a relatively low gasifier temperature (1300°F) and high pressure (500 psig) with the separation of syngas (CO + H₂) from the methane product. The syngas is recycled to the gasifier so that the only net products from gasification are CH₄, CO₂, and small quantities of H₂S and NH₃. The resulting overall gasification reaction can be represented as follows:

 $Coal + H_2O + CH_4 = CO_2$

Since this reaction is essentially thermoneutral, major heat input to the gasifier at high temperature is not required. Thus, as discussed by Nahas and Gallagher(5), second law constraints on thermal efficiency inherent in other processes are avoided.

A simplified flow plan for the process is shown in Figure 1. Coal is impregnated with catalyst, dried and fed via a lockhopper system to a fluidized bed gasifier which operates at about 1300°F and 500 psig. The coal is gasified with a mixture of steam and recycled syngas. The major gasifier effluents are CH4, CO2, CO, H2, and unconverted steam. No tars or oils are produced. The gaseous products are cooled and the unconverted steam is condensed. The dry product gas is treated in a series of separation steps including acid gas scrubbing to remove CO2 and H2S, and cryogenic fractionation to separate methane from syngas. The syngas is combined with feed steam and recycled to the gasifier at approximately 150°F above the gasification temperature. Although there is no net heat required for the gasification reactions, some small amount of heat input is required to heat up the feed coal, to vaporize residual water, and to provide for gasifier heat losses. Ash/char residue from the gasification step is sent to a catalyst recovery unit in which a large fraction of the catalyst is leached from the residue using countercurrent water washing. The recovered catalyst, along with some makeup catalyst, is reimpregnated on the coal to complete the catalyst recovery loop.

EXPERIMENTAL

Design of the gasifier for this process requires a quantitative description of the kinetics of the catalytic gasification reaction. Bench scale studies were conducted in a fixed bed reactor to provide the necessary data for the development of the rate equation.

Apparatus

The high pressure apparatus used in this study is shown in Figure 2. The main components of the system are the fixed bed reactor, water pump and steam generation equipment, pressure and temperature control systems, unreacted steam condenser, a gas chromatograph and a dry gas flow measurement system. Provisions were included for the optional use of an inert or reactant gas (such as $H_2 + CO$) as a feed supplementing steam.

A high pressure pump was used to supply H₂O at a constant rate to the steam generator which consisted of 1/4" stainless steel tubing coiled around the fixed bed reactor. Both the steam generator and the reactor were mounted vertically in a split tube furnace. The reactor temperature was measured and controlled at the center of the bed of char. The product gas stream, consisting primarily of E_2 , CO, CH₄, CO₂ and unreacted H₂O, was filtered and then depressurized through the pressure control valve. The unreacted H₂O was condensed and the gas stream was further dried by calcium sulfate. The dry gas stream passed through a gas constant gas flow was measured by a wet test meter connected to a cubie generator. The signals from the pulse generator were accumulated as a customer of total gas volume produced.

The fixed bad reactor was constructed from 1-inch Schedule 80 stainless that gips and was approximately 30 inches in length. The reactor was filled to a depth of 15 inches by 1/8-inch mullite beads which supported the bed of there.

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Samples were prepared by soaking 30 to 100 mesh Illinois coal No. 6 in a pinction containing the desired weight of catalyst, typically between 10 and 15 gas kgC03/100 gas of coal (referred to as 10 and 20% KgC03). Normally, the verght ratio of water to coal was slightly greater than one. The samples were here dried overnight in a vacuum oven. A scanning electron microscope study showed a fairly even dispersion of potassium throughout the coal particle. The impregnated coal samples were then devolatilized at atmospheric pressure for 30 minutes in a muffle furnace under a nitrogen atmosphere at 1200°F. The impregnate to cool to room temperature and then stored in bottles under nitrogen.



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A run was made by loading the reactor with a 20 gram char sample. The reactor was purged with helium and the temperature was raised to the desired level. At that point the pressure in the reactor was raised to operating conditions by manually injecting water through the pump. When the run pressure was achieved, the pump was set in the automatic mode. If syngas was used, the supplementary gas valve was also opened at the start of the run. Steam and syngas (if used) were then fed to the reactor. At the end of a run, the feed was shut off and the unit depressured.

During the run, gas analyses and cumulative dry gas volumes were obtained. From this data the carbon gasified is calculated. Assuming that the oxygen content of the char is small in relation to the oxygen content of the steam fed, the steam conversion is obtained from the oxygen content of the dry product gases.

Runs were made in the fixed bed reactor with Illinois coal catalyzed with 10% and 20% K₂CO₃ with steam as the gasifying medium. Temperatures of 1200°F and 1300°F were used and pressures varied from 0 to 500 psig. Steam flows ranged from 3 to 100 gm/hr. With these conditions, steam conversions from 10% to 80% and total carbon conversions from 50% to 100% were obtained. Material balances on hydrogen were used to check the consistency of the data. The balance closures ranged from 100% to 105% for typical runs.

Results

During the runs it was observed that the steam gasification rate was independent of pressure. The gasification rate was found to increase with an increasing rate of steam fed to the reactor. Additionally, at high steam flow rates, or low steam conversions, the gasification rate was directly proportional to the catalyst loading. One explanation for these observations is that the kinetics are controlled by a strong product inhibition. This suggests that a kinetic expression in the classical Langmuir-Hinshelwood form may be used to fit the data. It was further seen that methane and carbon dioxide were in chemical equilibrium with the other gas phase components for the conditions studied, i.e., the methanation and shift reactions are at equilibrium.

DATA INTERPRETATION

Fixed Bed Reactor Model

A mathematical model for the fixed bed reactor was developed based upon the observed behavior. Plug flow of gas through the bed is assumed. It is also assumed that strong product inhibition results in a high rate of gasification over a very short distance of the bed followed by a slower rate over the remaining length of the bed where higher partial pressures of products exist. This assumption leads to a simplified picture for the fixed bed reactor shown in Figure 3. In this model the reaction proceeds so as to form a sharp "carbon burnoff front." If little or no carbon is present, gasification will not take place. Therefore, the potassium catalyst which is left behind this "burnoff front" does not contribute to the reaction rate. The equation describing conversion in the plug flow reactor is

$$\int_{0}^{V} \frac{dV}{N_{H_{2}0}^{o}} = \int_{0}^{X} \frac{dx}{-r_{G}}$$
(1)

where \underline{V} is the reactor volume, $N_{H_2O}^{\mu}$ is the molar rate of steam fed to the reactor, $r_{\underline{G}}$ is the molar rate of the carbon-steam gasification reaction per unit volume and \underline{x} is the extent of reaction defined as moles carbon gasified per mole steam fed. The sharp burnoff front model provides a relationship between the carbon remaining in the bed and the effective fixed bed reactor volume,

$$n_{c} = C_{c} V$$
 (2)

where n_c is the instantaneous moles of carbon in the bed, V is the effective reactor volume, and C_c is the proportionality constant with the dramation moles carbon per unit volume. Based upon initial bed conditions C_c will have a value of approximately 0.045 gmole/cc. Substitution of Equation (2) into Equation (1) provides

$$\frac{n_c}{N_{H_20}^{\circ} C_c} = \int_0^x \frac{dx}{-r_G}$$
(3)

This model may now be used for the identification of acceptable forms for the rate, rg, and to obtain best fit values for the parameters in these approachings.

A Langmuir-Hinshelwood type expression for heterogeneous catalytic kinetics as applied to the carbon-steam reaction may be written in the generalized form.

$$r_{G} = \frac{k[p_{H_{2}0} - p_{C0} p_{H_{2}}/K_{G}]}{1 + \sum_{i} (b_{i}p_{i} + \sum_{j} b_{i}jp_{i} p_{j})}$$
(4)

where pH_20 , pC0, pH_2 , etc. represent the partial pressures of these components, \underline{k} is the kinetic rate constant for the carbon-steam reaction, K_G

is the equilibrium constant for this reaction, and the b's represent the adsorption constants, no more than four of which will be allowed to be nonzero in any one model being tested.

Equation (4) when substituted into Equation (3) gives

$$e = \frac{n_c}{N_{H_2}^{\circ}0} = \frac{C_c}{\kappa} \int_0^{\infty} \frac{dx}{R_G} + \sum_j \frac{b_j C_c}{\kappa} \int_0^{\infty} \frac{p_j}{R_G} dx + \sum_j \sum_j \frac{b_j C_c}{\kappa} \int_0^{\infty} \frac{p_j p_j}{R_G} dx$$
(5)

where the reaction driving force term in the denominator of each of the integrals is given by

$$R_{G} = -[PH_{2}O - PCOPH_{2}/K_{G}]$$
(6)

For a given conversion, the shift and methanation equilibrium relationships are sufficient to calculate the partial pressures of all components (H₂, CO, 1H₄, CO₂, H₂O) in the gas phase. Using a closely spaced series of increcontrol closes for x, the partial pressures were accurately mapped over a range of conversions. This needed to be done only once. These partial pressures were the conversion of the expressions under the integrals shown in control (The The values of these integrals for any specified conversion are the observed by a Simpson's rule numerical integration of the expression under the factored.

a collected in the fixed bed steam gasification experiments department - control uses to calculate and cabulate conversion, x, moles carbon gasified. the stars fed as a function of holding time, 0, moles instantaneous bed the stand steam flow rate. The "carbon oursoff front's model for fixed In generalized paralysing as if ication requires that the data for \underline{x} as a function in the cost for different steam flow makes must all mesh together to give a game for any fixed temperature, pressure, and catalyst loading. this collected for steam gasification over a range of steam flowrates . Still party and 20% kpt0g on the india could are at the model of figure 4. The series of the model of the india could be at the model and the data of the could be data of the where the configure 4 represence the equiprimental limit for the various scheme that the This include corresponds to a carbon activity of about twice that The region at the lower left of the diagram shows the carbon of the second divide by the rate of reaction. The data points at the different of solution in the required manner over three orders of magnitude of a consistent with the experimental observations are consistent with the conductores. This reactor model was then used as the basis for the analysis

Parameter Estimation

The coefficients in front of the integrals in a series of particular forms of Equation (5) were estimated by regression analysis. The regression data base used consisted of the results of the steam gasification runs at 500 psig described above as well as runs at 0, 100 and 250 psig at steam rates of 6, 12 and 24 gm H₂O/hr. Two additional series of runs were conducted at 500 psig and the same three steam rates. The first was at 1200°F and 20% K₂CO₃ and the second was at 1300°F and 10% K₂CO₃. The data from these runs were used to assess the effect of temperature and catalyst loading on gasification rate.

Numerous kinetic models were formulated and tested by regression for the constants in Equation (5). These models consisted of all combinations of from one to four terms involving the partial pressures of H₂, CO, and H₂O and the cross products of the partial pressures of H₂ and CO, and H₂O and the Those which gave negative coefficients on regression were discarded as being physically unreal. Four additional models were discarded because they gave an infinite rate in the limit of zero steam conversion. The three models which remained are

(A)
$$r_{G} = \frac{k(p_{H_{2}0} - p_{C0} p_{H_{2}}/K_{G})}{p_{H_{2}} + b_{1} p_{H_{2}0}}$$
 (7)

(B)
$$r_{G} = \frac{k(p_{H_2O} - p_{CO} p_{H_2}/K_G)}{p_{H_2} + b_1 p_{H_2} p_{CO} + b_2 p_{H_2O}}$$
 (8)

(C)
$$r_{G} = \frac{k(p_{H_20} - p_{C0} p_{H_2}/K_G)}{p_{H_2} + b_1 p_{C0} + b_2 p_{H_20}}$$
 (9)

All are independent of pressure. The variance of the residuals around the regression line for these are A: 0.0556, B: 0.0519, and C: 0.0562. Since Model B has a smaller variance than A or C, it was chosen as the basis for further analysis. However, further studies should be done to better discriminate between these and possibly other kinetic expressions. The coefficients obtained by regression of Model B are

$$\frac{C_c}{k} = 1.603 \text{ hr}$$

$$\frac{b_1 C_c}{k} = 0.3371 \text{ hr/atm}$$

$$\frac{b_2 C_c}{k} = 0.0954 \text{ hr}$$

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These coefficients were used in Equation (5) to compute the values of θ required to achieve the various measured conversion levels. These calculated values are compared to the actual holding times in Figure 5. While there is scatter to the data, it is seen that the model provides a reasonable fit over the broad range of pressures (0-500 psig) and flowrates (3-100 gm/hr) considered.

Using the approximate value of $C_c = 0.045$ gmole/cc, the values for the parameters at 1300°F and 20% K₂CO₃ loading may be expressed as

 $k = 0.0281 \frac{\text{gmole C}}{\text{hr} \cdot \text{cc}}$ $b_1 = 0.210 \text{ atm}^{-1}$ $b_2 = 0.0595$

It was found by comparing the 1200°F and 1300°F data that the rate constant, k, has an activation energy of 30 kcal/gmole in the Arrhenius expression. Furthermore, its value at the 10% K₂CO₃ loading was approximately half that at the 20% K₂CO₃ level. Hence, within this range <u>k</u> may be expressed as

$$k = k_0 C_K \exp(-E/RT).$$
(10)

where k_0 is the frequency factor, C_K is the moles of catalytically active potassium per unit volume, \underline{E} is the activation energy, \underline{R} is the universal gas constant and \underline{T} is the absolute temperature. For 20% K_2CO_3 on Illinois coal the value of \overline{C}_K for the fixed bed of char is typically

$$C_K = 0.0021 \text{ gmole/cc}$$

On this basis the value of the frequency factor may be computed as

$$k_0 = 6.80 \times 10^7$$
 gmole C/hr-gmole K

for

$$E = 30 \text{ kcal/gmole.}$$

The ratio of holding times necessary to attain a given conversion level, \underline{x} , at two different temperatures and catalyst levels is given by

$$\frac{\partial 1}{\partial 2} = \frac{k_2}{k_1} = \frac{C_{K_2}}{C_K} \exp\left[-\frac{E}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right]$$
(11)

This assumes that the temperature difference does not significantly affect the equilibrium calculation for the partial pressures. Equation (11) allows the definition of an "equivalent residence time," $\underline{\Theta}^*$, which can be used to combine data collected at different temperatures and catalyst levels. The quantity $\underline{\Theta}^*$ is defined as the holding time at \underline{T}^* and C_K^* which will give the same conversion as that obtained with a holding time $\underline{\Theta}$ at temperature T and catalyst concentration C_K . Specifically,

$$\Theta^{\star} = \Theta \frac{C_{K}}{C_{K}^{\star}} \exp\left[-\frac{E}{R}\left(\frac{1}{T}-\frac{1}{T^{\star}}\right)\right]$$
(12)

This relationship was tested for its ability to correlate 500 psig fixed bed reaction data collected at $10\% K_2C0_3-1300^{\circ}F$ and $20\% K_2C0_3-1200^{\circ}F$ with the data base collected at $20\% K_2C0_3-1300^{\circ}F$. The result is given by the data points shown in Figure 6 where conversion, <u>x</u>, is plotted as a function equivalent residence time, <u>e</u>^{*}, with all data adjusted if needed to $1300^{\circ}F$ and $20\% K_2C0_3$. It is seen that the data appear uniformly correlated by this expression.

Generalized Fixed Bed Model

The above kinetic relationships apply to a pure steam feed. In order to apply them to the synthesis gas recycle case, they must be generalized for mixed gas input to the fixed bed. This may be done by writing the differential equations describing the molar flow of each molecular species through the bed and numerically integrating these over the effective volume. These equations are

$$\frac{d n_{H_2}}{dz} = A (-3 r_M + r_S + r_G)$$
(13)

$$\frac{d N_{CO}}{dz} = A \left(-r_{M} - r_{S} + r_{G}\right)$$
(14)

$$\frac{d NCH_4}{dz} = A r_M$$
(15)

$$\frac{d N_{CO_2}}{dz} = A r_S$$
(16)

$$\frac{d N_{H_20}}{dz} = A (r_M - r_S - r_G)$$
(17)

where N_i is the molar flow rate of component <u>i</u>, <u>z</u> is the distance down the bed, <u>A</u> is the cross-sectional area of the bed, and <u>rm</u>, <u>rs</u> and <u>rg</u> are the

rates of the methanation, shift, and carbon-steam gasification reactions respectively expressed as moles per unit reactor volume per unit time.

The reaction rate expressions used for the shift and methanation reactions are

$$r_{\rm S} = k_{\rm S} \left(p_{\rm CO} \, p_{\rm H_2O} - p_{\rm CO_2} \, p_{\rm H_2} / K_{\rm S} \right)$$
 (18)

$$r_{M} = k_{M} (p_{C0} p_{H_{2}}^{3} - p_{CH_{4}} p_{H_{2}0}/K)$$
(19)

where $k_{\rm S}$ and $k_{\rm M}$ are the respective rate constants and $K_{\rm S}$ and $K_{\rm M}$ are the respective equilibrium constants. These reactions may be forced to equilibrium by assigning arbitrarily large rate constants. The reaction rate expression used for the potassium catalyzed carbon-steam reaction is obtained by combining Equations (8) and (10)

$$r_{G} = \frac{k_{0} C_{K} exp(-E/RT) [p_{H_{2}0} - p_{C0} p_{H_{2}}/K_{G}]}{p_{H_{2}} + b_{1} p_{C0} p_{H_{2}} + b_{2} p_{H_{2}0}}$$
(20)

The ordinary differential Equations (13)-(17) were numerically integrated by a Runga-Kutta-Fehlberg procedure for a series of cases considering pure steam fed to a fixed bed reactor at 500 psig, 1300°F and $C_{\rm K}$ = .0021 gmoles potassium per cc (corresponding to 20% K₂CO₃ on Illinois coal). The conversion, <u>x</u>, was determined at various distances, z, down the bed from

$$x = \frac{N_{C0} + N_{CH_4} + N_{C0_2}}{N_{H_20}}$$
(21)

The residence time corresponding to each conversion was computed as

$$\Theta = \frac{C_c A z}{N_{H_20}}$$
(22)

The integrations performed in this manner for various steam flowrates overlapped to give the single correlation line shown in Figure 6. This line is seen to provide a reasonable fit to the data.

Model Verification Experiments

To test the predictive capability of the kinetic model with a mixed gas feed, two fixed bed gasification runs were made with steam plus syngas (H₂ + CO)

at 1300°F. One run was made with 5 liter per hour syngas at 500 psig. The second was made with 15 liter per hour syngas at 100 psig. Both runs were made with 12 grams per hour steam feed. In both cases the syngas composition was 75 mole % H2 and 25 mole % CO. In these experiments the conversion, \underline{x} , was computed as

$$x = \frac{N_{CO} + N_{CH_4} + N_{CO_2} - N_{CO}^2}{N_{H_2O}^2}$$
(23)

where N_{CO} is the molar rate of carbon monoxide fed to the reactor. The residence time is computed by Equation (22). A comparison between the predicted and experimental conversions for these two experiments is shown in Figure 7. Good agreement is observed in the 500 psig case. The conversions obtained here are essentially the same as observed above for pure steam feed. At 100 psig with higher syngas flow, the data show a lower conversion than at 500 psig for the same residence time. It is also seen that the model underpredicts the actual conversion. This may be due, in part, to the use of parameters which are derived from pure steam data.

CONCLUSIONS

An empirical Langmuir-Hinshelwood kinetic model for the potassium catalyzed gasification of Illinois #6 bituminous coal has been developed. This model provides a good fit to fixed bed reactor data over pressures ranging from thospheric to 500 psig and a 30-fold range of steam flow rates. It also predicts conversions for the temperature range 1200°F to 1300°F and catalyst loadings from 0.1 to 0.2 grams K2C03 per gram of coal. For the catalyst levels examined, the gasification rate was proportional to the amount of catalyst present. Additional studies need to be performed over a broader range of catalyst loadings to determine the limits of this relationship. It was also shown that these kinetics can be applied to predict trends in conversion for H_2O , H_2 and CO mixed gas feeds.

The kinetic expression obtained has been shown to have adequate predictive capabilities in the range of interest. It is in a form which can be used directly in the development of models for fluid bed gasification reactors. Thus, the goal for this study has been achieved. Future work will be directed toward formulating a fluid bed reactor model.

ACKNOWLEDGEMENT

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Nomenclature

A	cross-sectional area of reactor
Ь	adsorption constant in Langmuir-Hinshelwood rate expression
Сc	carbon concentration, moles C per unit reactor volume
с _к	potassium concentration, moles K per unit reactor volume
Ε	activation energy in Arrhenius expression for carbon-steam reaction rate constant
k	rate constant for carbon-steam reaction
k _o	frequency factor in Arrhenius expression for carbon-steam reaction rate constant
к <mark>м</mark>	rate constant for methanation reaction
ks	rate constant for shift reaction
KG	equilibrium constant for carbon-steam reaction, atm
KM	equilibrium constant for methanation reaction, atm ⁻²
Κs	equilibrium constant for shift reaction
Ną	molar flow rate of component \underline{i}
110 1	molar flow rate of component \underline{i} fed to reactor
nc	moles carbon (total in reactor)
p;	partial pressure of component <u>i</u> , atm
R	universal gas constant
R_{G}	driving force for carbon-steam reaction, see Equation (6)
rG	molar rate of carbon-steam reaction per unit reactor volume
rM	molar rate of methanation reaction per unit reactor volume
rs	molar rate of shift reaction per unit reactor volume
¥	volume of fixed bed reactor
x	extent of reaction, moles carbon reacted per mole H2O fed
z	distance from start of fixed bed reactor
θ	residence time in fixed bed, moles bed carbon-hr/mole H ₂ O fed

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FIGURE 1. OVERALL FLOW PLAN OF THE EXXON CATALYTIC COAL GASEFECTION PROCESS





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FIGURE 3. SIMPLIFIED MODEL FOR FIXED BED REACTOR IN POTASSIUM CATALYZED STEAM GASIFICATION

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78B-6-4-11

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78B-6-4-12



78B-6-4-13

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CATALYTIC COAL GASIFICATION PROCESS RESEARCH AND DEVELOPMENT

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October 1978 Chicago, Illinois CATALYTIC COAL GASIFICATION - PROCESS RESEARCH AND DEVELOPMENT L. E. Furlong and N. C. Nahas Exxon Research and Engineering Company

Abstract

The technical progress during the recently completed predevelopment phase of catalytic coal gasification supports the transition to a development phase program. This process research focuses on production of substitute natural gas (SNG) from bituminous coals using a potassium catalyst and a thermally neutral reaction of steam and coal. After a review of the basic process concept, this paper concentrates on defining the current technical base and delineating the major questions to be addressed during the development Remaining needs for commercialiphase. zation are also outlined.

Process Description and Background

Exxon Research and Engineering Company has been pursuing coal gasification since the late 1960's and catalytic coal gasification (CCG) since 1971. Our early work was described in 1976 by Epperly and Siegel (1). They presented the process concept and discussed the role of the catalyst in depth. The major points are summarized here.

First, it had been known for some time that alkali metal salts of weak acids (e.g. K_2CO_3 , Na_2CO_3 , K_2S , Na_2S) catalyzed the steam gasification of coal. Our research confirmed that at catalyst concentrations on the order of 10-20 wt.% K_2CO_3 on Illinois bituminous coal, commercially acceptable gasification rates could be obtained at 1300°F (700°C) versus about 1700°F (925°C) without catalyst. Figure 1 presents some of this data showing a relative carbon gasification rate as a function of catalyst concentration at 1300°F. Catalyst concentration is expressed here as the atomic ratio of the alkali metal (K) to carbon (C) in the average bed char particle. An initial loading of 20 wt.% K_2CO_3 on coal, when gasified to 80% carbon conversion, translates to 0.3 K/C on this scale. The catalyst increases the gasification rate by an order of magnitude and the effect of catalyst concentration on rate is essentially linear over this range. Note that relatively high catalyst loadings are required to achieve acceptable rates. The high cost of catalyst necessitates catalyst recovery systems for economic balance.



Figure 1.

This first part of the concept was well known by researchers in the field. The second part of the concept was the discovery that this same catalyst system also promoted the methanation reaction

Figure 2 presents some data for the methanation reaction, again with K_2CO_3 catalyst on Illinois bituminous coal. At temperatures above 1250-1300°F equilibrium conversions are obtained even at





very high space velocities.

The third element of the process concept relates to the thermal balances for the individual reaction steps and for the overall steam gasification to methane and carbon dioxide reaction. Figure 3 illustrates these heats of reaction for an ideal system of graphite and steam.



Figure 3

The gasification reaction is highly endothermic, requiring the addition of 64 kcal of heat for each 2 moles of carbon.

The shift reaction (which is at equilibrium in our system) is slightly exothermic, releasing 8 kcal of heat for each mole of CO shifted.. By contrast, the methanation reaction is highly exothermic releasing 54 kcal for each mole of methane formed. The overall reaction shown is slightly endothermic for graphite, and slightly exothermic for real coals. In Exxon's catalytic coal gasification concept all three reactions are carried out in one vessel avoiding the need for heat input via air or oxygen. Using the catalyst, commercially acceptable rates are obtained at 1300°F. The catalyst equilibrates both the shift and methanation reactions at this temperature. The net products are forced to CH₄ and CO₂ by recycling the CO and H2.

The embodiment of this concept in a process is illustrated in Figure 4.



Figure 4.

The feed coal is crushed to minus 8 mesh, a size distribution suitable for fluidization. Catalyst is added as an aqueous solution, the feed is dried and fed through lock hoppers to a fluid bed gasifier. The gasifier operates at $1300^{\circ}F$ (700°C) and 500 psi (3.5 MPa). The fluidizing gas is a mixture of steam and recycle CO and H₂ which has been preheated as shown. Unreacted scales is conventional and CC2 and NyS screwed of conventional acid gas treating into call sciwens). The priod wethane to separated procenically from the convola CO and N2. Char containing the covarysay correlated purples and cool minerals is removed continuously. Most of the catalyst is recovered and recycled.

The parts of this system unique to conalytic gasification are the catalyst addition/recovery block, the fluid bed posifier, and the cryogenic distillation contains. The technical states and major and is these three areas are considered confolioming sections.

in fevelocing a compact into c lefe undreit we annretie conquere to says phases of anotessing scale and President As names potatible, key . 1011 RESIDENCE DE SUPRESSED dÉ VIE Linest stand Major Consider, Ked оргос низте вкажского со з ровбеко∛о contain leannacel busc derives from tratition of the preducelusment phase superneed of the resk. Predevely creat results star incleated in August er numes and Gallagner (2). Negotiations ers recently completes for a 15.8 MS revencement phase of the also under indicability the Department of Emergy: Section conclusion tegen in all 1000 sectors. News too much tegan in a . sug: EBC. Exxon is fonding the instruction of a 3 MS, fully integrated allow eleast for this program.

TRATUS OF KEY AREAS

Catalyst Addition and Recovery

At the beginning of the predevelopment phase, the major catalysts being studied were K_2CO_3 and mixtures of K_2CO_3 and Na_2CO_3 . K_2CO_3 was found to be significantly more active than



Magding at the sanification can all constructions. The subscreams construction looking at alternatic construction an atomic K basis) to KpCGa. Since the preferred catalyst. Addition of either KOH or KpCO3 to coal as a spraword water solution is uncomplicated. Recovery of the catalyst from the catalystchar-mineral matter solid withdrawn from the fluidized bed is more challenging. Figure 5 illustrates the chemistry involved.



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KON reacts with the coal in the ways nen form an active site los des ficos fieldestad path, or it name class t anatos Jinates in the ender 1 au пно дер Алдебіна сдярасного bed with messonable solid real orable c all of the aluminum in the coal was with K. High alumina deals cont higher catalyst loading to produce to same active catalyst levels and which require recovery more effective that water wash since only the excess K is present as an active catalyst. Further, this KAISiO4 cannot be recovered by water wash. However, Ca(OH)2 will displace the K from this compound to yield KOH, the desired catalyst form, and insoluble calcium aluminosilicates.

recycle) and is projected to be operating in a borderline bubbling contacting mode. (That is 2-3 inch bubbles in a TO-inch I.D. fluid bed.) Representative carbon and steam conversions should be obtainable in all units.

In order to integrate our knowledge of bench and pilot plant results, we have developed a mathematical reactor model. Figure 8 describes the elements of the model.



Figure 8.

Effects of independent variables are determined from tests in fixed bed reactors. A kinetic equation of the Langmuir-Hinshelwood form was developed to correlate this data. The kinetic equation was described in September, 1978 by Vadovic and Eakman (3). Incorporation of char physical property data and contacting equations allow generation of a fluid bed gasifier reactor model which predicts steam conversion. Gas phase equilibria and material and energy balance constraints define the product gas composition.

We have compared model predictions from fixed bed data with results from our 10 lb/hr pilot plant. The data quality from the pilot plant was exceptional as illustrated in Figure 9. Mass balances were done for individual elements C, H, O as well as on an overall basis. During the latter months of unit operation material balances were within 2% for total input/output and 5% for individual elements. Additionally, the unit service factor for the last 6 months averaged 70% of real time with all systems at design conditions.



Figure 9

Figure 10 compares prediction from our mathematical model with observed pilot plant conversions.



Figure 10.



The current recovery process is shown in Figure 6.



Figure 6.

The catalyst-char-mineral matter solid from the gasifier is digested under mild conditions (300°F, 150°C) with Ca(OH)2 and the residue is washed countercurrently with water. The chemistry of this process has been well defined in bench tests. The Ca(OH)₂ digestion and the countercurrent water wash were demonstrated during predevelopment in a semi-batch mode. K recoveries above 90% were shown to be feasible. However. there has been no integrated, continuous test of this system. The water wash alone, obtaining 60-70% K recovery, was used to study build-up of trace components in the catalyst recycle stream. At this recovery level trace ion accumulation was acceptable. However, build-up of trace elements at 90% recovery must also be defined. Thus one key need of the development program will be the definition of a continuous, integrated process for recovery of potassium catalyst at target commercial conditions.

Fluid Bed Gasifier Operation

The envisioned commercial scale fluid bed gasifier would be over 20 ft. in diameter with 100 ft of bed operating in a freely bubbling mode at 1300°F (700°C) and 500 psi (3.5 MPa). Approximation of flow characteristics of this unit in small pilot plants is difficult. Figure 7 gives one a feel for the degree of approximation.

	ASILICA	UPERATING CUT		
	NENCH UNITS	PREDEVELOPMENT PROT DATA	CONNERCIAL DESIGN	PROCESS DEVELOPMENT UN
RED RATE LUSAR	R. 🖷		230, 689	100
PRESSURE, PSIG	I - 100	100	500 1	10
TEMPERATURE T	1300	1309	1300	1380
INTEGRATION	SIMULATED	SIMULATED	COMPLETE	COMPLETE
STEAM CONVERSION, 1	40 - 10	40 - 10	•	
CARBON CONVERSION, 1		D - 41	•	-
RUIDIZING MORE	FIXED-DED	SLUGGING	N/88, HIS	NOR BEAL INE

Figure 7.

The first data column is for fixed bed bench units of about 1-inch diameter. Most of our kinetic data have been generated in these reactors. They are flexible allowing coverage of desired temperature and pressure ranges but the bed is not fluidized (mixed solid phase) and gas feeds are simulated.

Our largest predevelopment unit fed about 10 lb/hr (5kg/hr) of coal to a fluid bed gasifier about 30 feet deep This unit had a maximum operating pressure of 100 psi (0.8 MPa) versus the design of 500 psi (3.5 MPa) and due to this low pressure and small diameter operated in a slugging mode (large gas bubbles relative to reactor diameter). Additionally, the output of CO and H₂ was measured and an equivalent amount fed to the reactor to simulate the CO/H₂ Thus build-up of trace comporecycle. nents in the recycle gas stream has not been addressed. Design criteria for the Process Development Unit are shown in the last column. This unit is fully integrated (catalyst recovery and gas

Considering the broad range of steam conversions the fit is quite good. Obviously, fluid bed data are needed at 500 psi, the design operating condition to confirm predicted conversion at commercial conditions.

Cryogenic Distillation

The third unique area of the CCG process is the cryogenic separation of methane (CH₄) from carbon monoxide (CO) and hydrogen (H₂). A schematic is shown in Figure 11.



Figure 11.

 H_2S and CO₂ are removed with conventional technology using physical absorption. The feed gas is cooled to -195°F by heat exchange with the recycle gas. The recycle overhead from the cryogenic tower contains all of the H₂, almost all of the CO and is 10% by volume methane (CH_A) . At the system pressure of 400 usig, the overhead condenser operates at -240°F (-150°C). This is the coldest The bottom of part of the system. the tower, the reboiler, operates at -143°F (-96°C). The product methane contains 0.1% CO. The vapor-liquid equilibria for this system are well characterized and the design of this distillation tower is within the state of the art. In fact, the separation of CO from CH_A is easier than the separation

of 02 from N2 and 02 from Argon because CO and CH₄ are further apart in relative volatility. The investment and operating energy requirements of the cryogenic CO/CH₄ separation system are less than those of a conventional oxygen plant sized for the same Btu output of CHA from a thermal process. The ability to operate this system has been demonstrated in small scale, continuous distillation apparatus using mixtures of pure components as feed. Design concentrations were easily achieved. Integrated operation with actual reactor effluent has not been demonstrated and will be one of the key components of the development program. Build-up of trace components in the gas recycle loop will be examined as well as the ability of the cryogenic system to handle trace components which could freeze out. No major needs are anticipated beyond the development phase.

Economics of CCG

Use of absolute investment and product gas costs require a careful definition of bases. In addition to the design of the process itself (flow rates, yields, equipment size, specifications, materials, service factor, environmental standards, utilities and off-sites) the projected gas costs also depend on major external factors (project timing, financing, location, size and feed coal). Because of these many factors, it is hard to compare costs projections made by different studies. A second major item is the use of continaencies.

Exxon's experience in process development has shown that as a process moves through development the estimated cost invariably rises. To compensate for this historical trend we add contingencies to estimate the investment required for a first commercial plant. Prior to the predevelopment phase, Exxon developed comparative investments and costs for CCG versus Lurgi technology. On consistent bases and using appropriate contingencies for catalytic Exxon concluded that for Eastern coals the first commercial CCG plant could have a cost advantage which would increase as the catalytic technology matured. Based on this study, research and development of Exxon's second generation thermal process was discontinued. As part of the predevelopment phase, a commercial study design was prepared and economics estimated on an explicit basis. This aspect of the predevelopment contract will be described in depth at the November AIChE meeting in Miami by Gallagher and Marshall (4). A comparison with thermal technology is being updated.

The long term potential of catalytic gasification technology deserves special comment. Figure 12 illustrates the effects on relative investment in constant dollars of both the contingencies before the first commercial plant and improved technology following commercialization.



Figure 12.

The estimated cost in the early development of a new process contains large uncertainties represented by the shaded area. Process and project contingencies are added to bring these early investment estimates to the probable level for the first commercial plant.

For subsequent plants investment

costs normally decrease following a The decline in costs curve as shown. results from knowledge gained from the first plant and to a greater extent from the impact of continuing process research and development. One of the major anticipated areas of improvement lies in the area of more efficient catalysts. The catalyst provides a major degree of freedom which should allow more substantive improvements in this technology than for thermal processes. Engineering improvements in feed systems, reactor design and gas treating would also be anticipated.

Summary

In Figure 13, the current status, the anticipated status after completion of the development program and needs anticipated at this time beyond the development phase are summarized.

		EVW MARY	
	AFTER PREVENCIPALIN		NEMA INING NEEDS
LATAL VST A BOITION / RECOVERY	CHEMISTRY REFINED BOICH DATA SUS RECOVERY	CONTINUOUS OPERATION IMPROVED SEPARATION	SCALABLE EQUIPMENT
R. UH D- OCH GA SIFNER	300 psi - FLU10 300 psi - F1320 m0081, u2V8,0413	102 pil - RU18 SORDERLISE BUSHLING WOOD, CONFIRMATION	FREELY-BUBBLING CONTACT FINE'S CONTROL AT RESIGN GAS VELOCITY
CHYOGENIC SLPARATION	SMALL - SCALE SEAT - CONTHERDYS NON- UNICAN ILD	HITEGRAVED, CONTHLUCUS AND LONG TERM	ND OLSYGN NOLDS

Figure 13.

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In the catalyst addition and recovery area, the chemistry is understood and we expect to demonstrate continuous, integrated catalyst recovery and recycle in development. Remaining needs are for demonstration of separation in scalable equipment. In the gasifier area, the reactions and kinetics are again well defined. After development, the process

- 334 -

which be demonstrated at design temperaand pressure and at borderline le bling condition. Our reactor model to belong condition. We swer, the development pilot plant will the be completely representative of commercial fluid-beds and larger scale within would be prudent. Contacting could be better on the larger scale at design velocities but control of fines could be more difficult. On cryogenic station design needs should be filled within the development program. Addiinterval needs will likely be identified where the advelopment program, some of at it may require larger scale testing to 1 - 5¹48.

On balance we feel this technology in anothis by. Technical needs identified tasks that the technology and prospects for a technology and transmiss appear favorable.

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PRODUCTION OF SNG FROM ILLINOIS COAL VIA CATALYTIC GASIFICATION

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> November, 1978 Miami Beach, Florida

PRODUCTION OF SNG FROM ILLINOIS COAL VIA CATALYTIC GASIFICATION

J. E. Gallagher, Jr. and H. A. Marshall

Exxon Research and Engineering Co.

INTRODUCTION

Exxon Research and Engineering Company is engaged in research and development on Catalytic Coal Gasification (CCG) for the production of substitute natural gas (SNG). The Predevelopment phase of catalytic gasification research was completed recently under DOE sponsorship. During this phase of work, several key technical questions were resolved and the technology has now moved into the process development phase.⁽¹⁾ The objective of this paper is to describe a conceptual design of a commercial-scale CCG plant which was completed as part of the Predevelopment research program.

BENEFITS FOR THE USE OF CATALYTIC GASIFICATION

The catalysts studied in the Predevelopment program were the basic and weak acid salts of potassium. The preferred form of makeup catalyst was identified as potassium hydroxide. The principal benefits from using potassium catalyst in a gasification reactor system are as follows: First, it increases the rate of gasification. Secondly, it prevents swelling and agglomeration when handling caking coals. Thirdly, and most importantly, it promotes gas phase methanation equilibrium.

These key features of the catalyst are combined in a novel processing sequence which maximizes their benefit. A schematic flow plan for this processing sequence is shown in Figure 1. Catalyst is added to the feed coal and the mixture is gasified at about $1300^{\circ}F$ and 500 psia. At these conditions, the gasification rates are high enough to allow reasonable size commercial reactor vessels while at the relatively low temperature, equilibrium favors the formation of methane. Thus the production of CO and H₂ is decreased and high direct methane yields can be achieved. The components in the gasifier overhead are separated into CO₂ which is vented, product methane which is sent to the pipeline, and carbon monoxide and hydrogen which are recycled to the gasification stage. Since the amount of CO and H₂ fed balances the amount of CO and H₂ leaving the gasifier, the net products of gasification are only methane and CO₂ along with smaller amounts of H₂S and NH₃. The chemistry of this reaction can be represented as follows:

$$Coal + H_2O = CH_4 + CO_2 \qquad \Delta H \stackrel{>}{_{\sim}} O$$

As indicated, this reaction is thermally neutral and in fact only a small amount of heat is required in the gasifier to preheat the feed coal and provide for heat losses. Also shown on the flow diagram is a catalyst recovery step. This is required because the catalyst leaving the gasifier with the ash/char residue is too costly to discard. The unique features of the Catalytic Coal Gasification (CCG) process can be summarized as follows: (1) All the methane is formed in one reactor, the gasifier; no separate shift and methanation reactors are required. (2) No significant heat input is required to the reactor; the oxygen plant and potential slagging problems from oxygen use are exfaning (3) No pretreatment is required for taking coals due to the action of the catalyst. (4) Significant future improvements are possible through the development of improved catalysts.

OBJECTIVES AND SCOPE OF THE STUDY DESIGN

The main engineering task of the CCG Predevelopment phase program was the completion of a conceptual design or "Study Design" for a commercial scale CCG plant. Study designs have a number of objectives as shown in Table 1. First, they can be used to project the investment and product cost for a pioneer plant employing new technology. Secondly, they can identify uncertainties in the data/technology base and thus provide guidance for direction of the research program. Thirdly, study designs provide a framework - a base case - which can be used to evaluate new data and process improvements, and to conduct optimization studies to direct the research effort toward the most favorable operating conditions. To generate this fairly detailed engineering involvement early in a process development effort helps maximize the probability of successful development of the technology.

Table 1 also lists the steps that are involved in developing a study design and economics. The first step involves setting the project basis. This includes factors such as plant focation and size, feed note the product slate and the basis for the source of plant utilities. The second trap involves setting the process basis. For the current OCG Study Decision the date and correlations developed during the Predevelopment research erignam were used for this purpose. Fotential future improvements out for identified or for which a reasonable data base is not yet available, were controlated. Also, contingencies were added to the investment estimate to tablect historical Excon experience that costs increase during the course of process development.

The next step is to develop detailed material and energy uploans to serve as the basis for equipment specifications. In the case of ansite facilities and specialized offsites, individual equipment specifications and usually prepared. These list equipment type, major dimensions, menorics, we construction, design temperatures and pressures and special methan def facility forwardinan offsites systems are specified based on the oversel conversion of system

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Investment estimates are developed by a variety of techniques. To the entrop possible proprietary Exten computer programs are used. There programs estimate equipment costs and, based on historical scorel flow. Testing from situal Extens projects, also have be restricted four and the and had equipment qualities for structure over situation projects. Appropriate contingencies are added to the investment based on Exxon practices for actual commercial projects, and, as indicated above, based on historical data for other developments.

PROJECT AND PROCESS BASIS FOR THE STUDY DESIGN

For the CCG Study Design done after the Predevelopment research phase, the project basis is presented in Table 2. The plant is assumed to be at the minemouth in Illinois and feeds Illinois No. 6 coal. The plant produces 257 billion Btu per stream day of SNG. Steam is generated in coal fired offsite boilers with flue gas desulfurization, and electric power is purchased.

As discussed above, the second major step in developing a study design is to set the process basis. Table 3 lists the major independent variables which must be specified for the catalytic gasifier. These are the coal feed rate, temperature, pressure, catalyst loading, steam rate and bed volume. Specification of these variables fixes the steam conversion, carbon conversion, recycle gas rate and gas preheat temperature. Even in the early stages of a development it is important to optimize these variables so that the research effort can be focused on the range of conditions in which the gas cost is minimized.

The effect of pressure on the CCG process has been described previously.(2) The pressure was set at 500 psia as a balance between increased recycle gas rates at lower pressure and the potential for increased costs and mechanical problems at higher pressures. Engineering studies during the Predevelopment phase established 90% carbon conversion as the preferred target based on a balance between poor resource utilization at substantially lower levels and the more complex reactor system probably required for higher levels.

Having set the pressure and target carbon conversion, studies were undertaken to establish the preferred operating temperature, catalyst loading, steam rate and volume. This was done using a gasifier model which combines an empirical Langmuir-Hinshelwood kinetic equation for the potassium catalyzed gasification of Illinois No. 6 coal with contacting equations which predict mass transfer effects in the fluid bed. The kinetic aspects of this model were described in a recent paper.(3)

The base case conditions for this series of studies is shown in Table 4. The operating temperature was 1300° F, the catalyst loading 15 wt% K₂CO₃ equivalent on feed coal and the steam/coal feed ratio 1.25 lbs/lb. Changes in temperature, catalyst loading and steam rate were analyzed via heat and material balances for their impact on recycle gas rate, gasifier volume and preheat temperature.

Lowering the gasifier temperature to 1200° F significantly decreases the recycle gas rate but at the expense of increasing the gasifier volume by over 50%. Raising the temperature to 1350° F increases the

recycle gas rate substantially while the gasifier volume is reduced by only 12%. Reducing the catalyst loading from 15 wt% on coal to 10 wt% reduces the amount of catalyst to be recovered but increases the gasifier volume by 36%. A 20% increase in steam rate decreases the gasifier volume only 19% while a 20% lower steam rate increases the gasifier volume by 62%.

Based on these estimates, three cases were chosen for more detailed analysis: lower catalyst loading, lower temperature and higher steam rate. The higher temperature and lower steam rate options were discarded because of the judgement that the net economic effect would be increased cost, and because both options would increase the recycle furnace preheat temperature to the point where technical feasibility could be a concern.

Investments and economics for the three cases were developed reflecting the impact of the change in gasifier conditions on the entire plant, both onsites and offsites. The results of this analysis are shown in Table 5. The case with lower catalyst loading was essentially a standoff with the base case. The case with higher steam rate showed increases in both investment and gas cost of about two percent. On the other hand, reducing the temperature to 1200°F decreased both investment and gas cost by about two percent. In this instance, the effects of decreased recycle gas rate and preheat furnace temperature more than offset the effect of increased gasifier volume.

It was concluded from these studies that the economics are not extremely sensitive to changes in operating conditions over the range studied and that the base case conditions are close to being optimum. Higher steam rates appear unjustified. Thus, directionally, the most favorable option appears to be operating at reduced gasifier temperature.

Based on these conclusions, gasifier conditions for the study design were set at $1275^{\circ}F$ and 15 wt% catalyst loading with 1.25 pounds of steam per pound of coal. The temperature was not reduced all the way to $1200^{\circ}F$ because the bulk of the current data base was obtained at temperatures in the range of $1300^{\circ}F$. Future research will expand the data base in the $1200-1250^{\circ}F$ temperature range to allow further optimization of the operating temperature.

The key process basis items for the study design are summarized in Table 6. The operating conditions for the gasifier have already been discussed. The major steps employed for processing the gasifier overhead stream are high level heat recovery using a gas-gas exchanger, venturi scrubbing to remove fines, acid gas removal using a physical solvent and cryogenic distillation for methane recovery.

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The catalyst recovery design is based on the use of calcium hydroxide digestion to free part of the water-insoluble catalyst followed by a staged counter-current washing operation to recover soluble catalyst from the spent solids. The digestion operating conditions are 300°F and two hours residence time with a calcium to potassium weight ratio of 0.7. Additional information on the catalyst recovery step can be found in a recent paper.(1)

FACILITIES DESCRIPTION FOR A COMMERCIAL - SCALE CCG PLANT

After setting the process basis, the next steps in the CCG Study Design were the preparation of heat and material balances and equipment specifications. Figure 2 presents a simplified flow diagram for the commercial system envisioned for catalyst addition, recovery and recycle. Coal is crushed to minus 8 mesh and is dried by a circulating flue gas stream in an entrained system. Catalyst is then added to the dried coal in a gentle mixing step. The catalyst is a solution of potassium hydroxide in water. A small makeup of purchased KOH is required to supplement that which has been recovered and recycled. The mixture is then dried before being fed via a lock hopper system to the fluidized bed gasifier operating at 1275°F and 500 psia.

In the catalyst recovery system, char withdrawn from the bottom of the gasifier and part of the fines entrained overhead are slurried, mixed with Ca(OH)₂ and soaked at 300°F for two hours. This "digestion" step frees additional water-soluble catalyst such that about 90% of the catalyst is recovered in a downstream staged counter-current washing operation. The balance of the catalyst leaves the plant in the form of water-insoluble compounds. For this study the solid-liquid separation design was based on the use of hydroclones. A major objective of the next stage of research will be to obtain more data on the catalyst recovery system and on the preferred recovery hardware.

Figure 3 presents a simplified flow diagram for the synthesis gas recycle system envisioned for a commercial CCG plant. The reactor is fluidized with a preheated mixture of steam and recycled hydrogen and carbon monoxide. The coal is fed to the bottom of the fluidized bed and the residence time is sufficient at 1275°F with catalyst to gasify 90% of the feed carbon. Pyrolysis products are cracked and essentially no hydrocarbons heavier than methane leave the gasifier. Since the gasifier exit temperature is only 1275°F and heavy hydrocarbons are present in only ppm quantities, the high level sensible heat in the overhead gas can be recovered and used for steam/recycle gas preheat and for high pressure steam generation. A venturi scrubber is used for fines removal prior to low pressure steam generation. H₂S and CO₂ are removed using a physical solvent acid gas removal system. At this point the stream contains only H2, CO, and CH4. The methane is separared in a simple cryogenic distillation system and sent to the pipeline. The CO and H₂ are mixed with gasification steam, preheated to about 1550°F and recycled to the bottom of the gasifier. The sensible heat above 1275°F in the steam/recycle gas mixture provides all the heat required in the gasifier to compensate for heat losses and for coal preheat. As mentioned above the overall gasification reaction is essentially thermoneutral.

A sketch of the catalytic gasifier itself is shown in Figure 4. The coal is fed to the gasifier via a lock hopper system which pressures the coal to the gasification pressure of 500 psia. Injection gas picks up the feed coal and conveys it dense phase to the gasifier and injects it into the bottom of the bed. A number of coal injection points are used to assure good mixing and distribution of coal into the bed. The feed coal pyrolyzes rapidly and the pyrolysis products flow up through the bed where they are cracked to light gaseous products. The bed dimensions for each of four gasifiers are 22 feet inside diameter by 97 feet in height.

The feed steam and recycle synthesis gas are injected into the bottom of the bed through a distributor. Thus, the gasification medium also fluidizes the bed. The principal reactions taking place are the highly endothermic steam gasification reaction, the mildly exothermic water gas shift reaction and the highly exothermic methanation reaction. The fluidized bed is characterized by the existence of a continuous emulsion phase with intimate gas solids contact and with gas bubbles rising up through the emulsion phase. Since steam passes through the bed in bubbles it must be transferred into the emulsion to react with the carbon. CO and H₂ from the recycle gas are also transferred across the bubble-emulsion interface to react via the catalytic action of the catalyst-char combination to form methane. The reaction rate in the gasifier is primarily kinetically limited, although bubble-emulsion mass transfer effects are not insignificant.

As stated previously, the overall reaction is essentially thermoneutral. Although a detailed analysis has not yet been made, it appears that the different zones of the gasifier will not differ greatly in temperature. The feed coal is the major external heat sink added to the gasifier and the preheated steam plus recycle gas is the major external heat source. These are both added at the same zone in 'he bottom of the gasifier in a fashion conducive to good mixing and heat mansfer. In the bulk of the bed, the primary heat effects are the heat-balanced steam-carbon and methanation reactions. In addition, of course, the solids mixing resulting from bed fluidization further promotes a uniform bed temperature.

The top section of the vessel contains a de-entrainment zone and external cyclones. The use of internal cyclones is an option that could be investigated. At the bottom of the bed, a solids stream is withdrawn to control bed level and prevent the buildup of ash. This solids stream flows into a small fluidized bed where it is cooled with recycle synthesis gas and then into a vessel where it is slurried with water for feed to catalyst recovery.

The catalytic gasifier is a simple, single vessel reactor with only one bed and without complicated internals. It is believed that this gasification system has the potential for a reliable, high service factor operation because it is simple, because the catalyst prevents caking and because the use of synthesis gas for heat input prevents slagging. A summary of the offsite facilities included in the study design is presented in Table 7. These include materials handling facilities to receive and handle coal, catalyst and chemicals and facilities to handle and dispose of waste solids and byproducts. General offsites include wastehave creating, safety and fire protection systems, buildings and miscellanous items such as maintenance and mobile equipment, communications systems, etc. A full range of utility systems are included such as water treating, steam generation, flue gas desulfurization, cooling water and electric power distribution. It is important to note that the utilities system capacities lociude an allowance of up to 25% to cover increases in utilities rates as project definition improves and to provide spare capacity for startup and emergency needs. The utilities capacity allowance is based on Exxon experituce for a broad range of commercial process plants.

MUVESTMENT FOR A PIONEER COMMERCIAL PLANT

The investment developed for the CCG Study Design is presented in Table 8. The investment is 1640 M\$ for the pioneer commercial plant feeding Illinois No. 6 coal and producing 257 billion Btu per stream day of CMG. This is for a January, 1978 cost level. Caution must be used when comparing this investment with published projections of the plant investment Car other developing coal gasification processes. Most of the investments toperted to date in the literature have been significantly lower.

Analysis of many published estimates indicates that the differences are caused by three major factors. First, the CCG Study Design basis-setting and equipment specification approach is aimed at providing the error likely final cost for a pioneer conmercial plant. Thus, the investment is based on a process basis supported by the current data base - potential future process improvements are not considered. Also, the design philosophy incorporates features to achieve a high service factor. In addition, as inationed above, utilities capacities include allowances which historical imperiated by a process. Some or all of these elements are not included in Huny published estimates of coal gasification plant investments.

The second major factor contributing to a higher investment for the CCS Study Pesign relative to many published numbers for either developing or aristing technology, is the inclusion of investment contingencies in the detailed CCF cost estimate to allow prediction of the most likely pioneer plant investment at this early stage of process and project development. As shown in Table 8, the total investment includes a 25% "project" contingency. The detailed to all estimates at each stage of project development to cover historical increases in cost resulting from more detailed design definition, firming of the project execution plan, site factors, and estimate corrections. The investment estimate also includes a process developtent showned of 25% applied to the onsite facilities. This allowance is applied to estimates for new technology to cover historical increases in investment as processes proceed from initial research and development to the pioneer plant.

The third major area of difference between the CCG estimate and many published estimates is the inclusion of added costs to cover the effect of "diseconomies of scale" on field labor construction costs for large projects. This unanticipated ineffiency associated with very large projects is often omitted when using estimating techniques which have been developed primarily for conventional-sized projects. In summary, the Study Design investment is believed to be a realistic prediction of the expected final cost for a pioneer plant.

With regard to the breakdown of investment cost by plant area, it is worth noting that facilities for catalyst addition and recovery and methane recovery amount to only 10% of the total investment. For a thermal process, the cost of shift conversion, methanation, and heat input via an oxygen plant or other system are likely to be substantially higher. In addition, offsite steam requirements are reduced relative to thermal processes as a result of the high level heat recovery from the gasifier overhead and the inherent high efficiency of combining all reactions in one vessel. Also, the absence of heavy hydrocarbons in the gasifier overhead minimizes wastewater treating requirements and eliminates the need to incinerate the vent gas from acid gas removal to meet hydrocarbon emissions standards.

GAS COST FOR A PIONEER COMMERCIAL PLANT

Consistent with an investment of 1640 M\$, the cost of SNG produced from deep mined Illinois coal is estimated to be 6.40 \$/MBtu for a January 1978 investment cost level, as shown in Table 9. This is based on 100% equity financing with a 15% DCF return assuming product revenues escalate at 6% per year and operating costs escalate at 5% per year. This economic basis has been described in a detailed report covering a study design for the Exxon Donor Solvent Coal Liquefaction Process.(4) On a financing basis of 30% equity/70% loan, with 9% interest on the loan, the gas cost is 4.80 \$/MBtu. For the 100% equity gas cost, about 20% results from the coal cost and about 50% from capital charges. Purchased makeup KOH catalyst contributes only about 4% to the gas cost.

It is important to recognize that several factors could reduce the gas cost for a pioneer CCC plant below the study design range of \$4.80-6.40/MBtu. For example, as shown in Table 9, the construction of plants larger than 250 billion Btu/SD could reduce gas cost between 0.25 and 0.50 \$/MBtu, depending on the actual size constructed. The use of surfacemined instead of deep-mined coal could reduce gas cost 0.50 to 0.75 \$/MBtu depending on heating value and mining costs. The combined effect of these items could result in a total reduction in gas cost from the pioneer plant of 0.75 to 1.25 \$/MBtu. In addition, tax credits, loan guarantees, or other government incentives could further reduce gas cost from the pioneer plant.

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For plants built after the ploneer plant, gas cost savings can be expected by incorporating the learning experience of the ploneer plant and the results of further research. Historical data from other Exxon process developments suggest that the gas cost from mature technology plants could be 0.75 to 1.00 $\$ /MBtu less than that for the pioneer plant, on a 1978 cost basis.

As shown above, estimates of coal gasification costs can vary widely depending on the approach to the investment estimate, maturity of the technology, plant size, coal type, method of financing, etc. The time frame for which costs are presented is also an important factor. This emphasized the difficulty of comparing the CCG Study Design costs with coal gasification costs published by others. A consistent comparison of CCG with state of-the-art gasification technology has been made by Exxon Research and Engineering Company and it has been concluded that significant incentive exists for development of the Catalytic Coal Gasification process.

ACKNOWLEDGEMENT

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FIGURE 1

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EXXON CATALYTIC GASIFICATION PROCESS



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FLOWPLAN FOR CATALYST ADDITION, RECOVERY, AND RECYCLE



- 348 -

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FIGURE 3

FLOWPLAN FOR RECYCLE GAS LOOP



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SCOPE AND OBJECTIVES OF STUDY DESIGN

OBJECTIVES

- STIMATE THE INVESTMENT AND PRODUCT COST FROM A PIONEER PLANT
- IDENTIFY NEEDS FOR FURTHER TECHNOLOGY DEVELOPMENT
- PROVIDE A FRAMEWORK FOR EVALUATING NEW DATA, PROCESS IMPROVEMENTS AND OPTIMUM PROCESS CONDITIONS

SCOPE

- PROJECT BASIS SETTING
- PROCESS BASIS SETTING
- DETAILED MATERIAL AND ENERGY BALANCES
- GOUIPMENT SPECIFICATION FOR ONSITES AND OFFSITES
- Investment estimate and economics

PROJECT BASIS FOR STUDY DESIGN

- FEED COAL -- ILLINOIS NO. 6
- PRODUCT -- SNG
- LOCATION MINEMOUTH ILLINOIS
- SIZE 257 BILLION BTU/STREAM DAY
- UTILITIES -- STEAM: COAL FIRED BOILERS WITH FLUE GAS DESULFURIZATION ELECTRIC POWER: PURCHASED

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KEY PROCESS VARIABLES FOR CATALYTIC GASIFIER

INDEPENDENT VARIABLES

COAL FEED RATE TEMPERATURE PRESSURE CATALYST LOADING STEAM RATE BED VOLUME

DEPENDENT VARIABLES

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STEAM CONVERSION CARBON CONVERSION RECYCLE GAS RATE PREHEAT TEMPERATURE

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IMPACT OF OPERATING GONDITIONS ON RECYCLE RATE AND GASIFIER VOLUME

BASE CASE:	COAL FEED RATE, T/D	14,490
	STEAM TO GASIFIER, T/D	18,200
	TEMPERATURE, °F	1,300
	PRESSURE, PSIA	500
	CATALYST LOADING, W1% K2CO3	15

RELATIVE	RELATIVE
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VARIATION FROM BASE CASE	RECYCLE RATE	GASIFIER VOLUM
BASE CASE	100	1 00
1200°F	68	15 2
1350°F	129	8 30
10% K2CO3	100	13
BASE STEAN + 20%	120	6 P P
BASE STEAM - 209	83	182

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ECONOMIC IMPACT OF ALTERNATIVE GASIFIER OPERATING CONDITIONS

	BASE CASE	····· SENSITIVITY CASES ······		
	15% K ₂ CO ₃ CATALYST	10% K ₂ CO ₃ CATALYST	HIGHER STEAM RATE	LOWER TEMPERATURE
GASIFIER OPERATING CONDITIONS				
+ PRESSURE, PSIA	500	500	500	500
+ TEMPERATURE, °F	1300	1300	1300	1200
+ CATALYST LOADING WT% ON DRY COAL	15	10	15	15
RELATIVE GASIFIER VOLUME	100	136	81	154
RELATIVE PLANT INVESTMENT	100.0	101.4	102.4	98.0
• RELATIVE GAS COST	100.0	99.5	102.0	98.3

TABLE 6 KEY PROCESS BASES FOR STUDY DESIGN

GASIFIER

OPERATING TEMPERATURE, °F	1275
OPERATING PRESSURE, PSIA	500
CATALYST LOADING, WT% K2CO3	15

GAS PROCESSING

HIGH LEVEL HEAT RECOVERY	GAS-GAS EXCHANGER
SOLIDS REMOVAL	VENTURI SCRUBBER
ACID GAS REMOVAL	PHYSICAL SOLVENT
METHANE RECOVERY	CRYOGENIC DISTILLATION
METHANE RECOVERY	CRYOGENIC DISTILLATION

CATALYST RECOVERY

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PROCESSING BASIS SOLID-LIQUID SEPARATIONS	Ca(OH) ₂ DIGESTION PLUS WATER WASH HYDROCLONES
DIGESTION CONDITIONS TEMPERATURE °F	300
Ca/K. LB/LB	0.7
RESIDENCE TIME, HRS.	2

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OFFSITE FACILITIES FOR STUDY DESIGN

MATERIALS HANDLING

- COAL RECEIPT AND STORAGE
- COKE/CHAR HANDLING
- CHEMICALS HANDLING AND STORAGE
- BY PRODUCTS STORAGE AND SHIPPING
- WASTE SOLIDS HANDLING AND DISPOSAL

GENERAL OFFSITES

- WASTEWATER TREATING
- SAFETY AND FIRE PROTECTION
- **BUILDINGS**
- LAYOUT AND SITE PREPARATION
- MISCELLANEOUS

UTILITIES

- RAW WATER/BFW TREATING
- STEAM GENERATION AND DISTRIBUTION
- FLUE GAS DESULFURIZATION
- COOLING WATER
- ELECTRICAL POWER DISTRIBUTION
- COMPRESSED AIR, INERT GAS, FUEL GAS

INVESTMENT FOR CATALYTIC COAL GASIFICATION **PIONEER PLANT**

BASIS: JANUARY 1978 COST LEVEL EASTERN ILLINOIS LOCATION

ONSITES	<u>M\$</u>
COAL CRUSHING AND DRYING	35
CATALVET ADDITION AND DRYING	25
DEACTOR SYSTEM	200
CAS COOLING AND SCRUBBING	85
COUD WATER STRIPPING	20
ACID CAS DEMOVAL / SILL FUR RECOVERY	155
METHANE RECOVERY AND REFRIGERATION	75
	40
COMMON FACILITIES	<u> 65</u>
ONSITES SUB-TOTAL	700
MATERIALS HANDLING	115
CENERAL OFESITES	95
UTILITIES	260
TOTAL DIRECT AND INDIRECT COSTS	1170
PROCESS DEVELOPMENT ALLOWANCE	175
PROJECT CONTINGENCY	295
TOTAL INVESTMENT	1,640

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COST OF SHE FROM CATALVING CASIFICATION

STUDY DESIGN FOR MOMEER PLANT

BASIS

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- Illinois No. 6 Deep mined Coal
- 257 BILLION BTU/STREAM DAY
- JANUARY 1978 COST LEVEL
- 15% DCF RETURN ON EQUITY (CURRENT DOLLAR)
- 9% INTEREST ON BOBROWED CAPITAL

GAS COST BREAKDOWN	\$/MBTU		
	<u>100% Equity</u>	70% DEBT/30% EQUITY	
Coal Feed	1.40	1.40	
GASIFICATION CATALYST	0.25	0.25	
OTHER OPERATING COSTS	1.60	1.60	
BY-PRODUCT CREDITS	(0.20)	(0.20)	
CAPITAL CHARGES	3.38 	1.75	
total gas cost	6.40	4.80	

POTENTIAL ROUTES TO LOWER COST GAS FROM PIONEER PLANT

		GAS COST CAMINGS CAMPTIN
		CALLAND, OF MICH
٩	LARGER PLANT	0.25 - 0.50
Ø	Surface Mined Coal	<u>0.50</u> - <u>0.75</u>
	TOTAL	0.75 - 1.25

POTENTIAL ADDITIONAL GAS COST REDUCTION FOR MATURE PLANTS

0.70 - 1.00 s/mstu



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