3. ENGINEERING RESEARCH AND DEVELOPMENT (Reporting Category 3)

Engineering research and development studies were carried out under the Catalytic Coal Gasification Process Predevelopment Program to provide economic evaluations of process alternatives and to prepare a conceptual study design and economics for a commercial-scale plant.

The work to evaluate process alternatives is described below under three main headings: (1) Catalyst Source/Recovery Studies, (2) Gasification Reactor System Studies, and (3) Acid Gas Removal Studies. The commercial study design and economics are described separately in Section 4 of this report.

The engineering studies described below led to the following major conclusions:

(1) Catalytically active potassium salts such as KOH and K_2CO_3 must be manufactured from naturally occurring source minerals (i.e., KCl or K_2SO_4). The potassium source minerals necessary to supply a mature catalytic coal gasification industry are readily available; very large reserves of KCl exist in the United States and Canada.

(2) Based on current market prices and studies of alternative catalyst manufacturing processes, KOH solution produced by electrolysis of KCl is expected to be the preferred form of makeup catalyst for catalytic gasification. The technology for KCl electrolysis in diaphragm or membrane cells (which will probably replace mercury cells in future electrolysis plants) is commercial or near-commercial today, and thus is expected to be available for license when needed.

(3) Screening studies of KCl electrolysis indicated that KOH produced specifically for catalytic gasification may be 25-45% cheaper than KOH purchased currently on the open market. Such savings may be achievable if dedicated electrolysis plants are used to manufacture KOH solution in the relatively large quantities and low purities (98-99%) required for commercial catalytic gasification plants.

(4) A screening evaluation showed that $Ca(OH)_2$ digestion to recover water insoluble catalyst from spent gasifier solids is justified in addition to water washing to recover water soluble catalyst, with make-up KOH priced at or somewhat below the current market level. Further development work will be required to better define the relative costs of recovered versus manufactured catalyst salts.

(5) Only a small economic incentive -- a saving of less than one percent in gas cost -- was shown for adding a secondary gasification step to raise carbon conversion over the base level of 90%. This saving was judged insufficient to justify further development in view of the more complex reactor system required.

(6) A two-stage gasification reactor concept with the upper stage used for drying catalyst solution was evaluated and found to be higher in cost than the base single-stage reactor. Thus, there is no incentive for further pursuit of this option.

(7) Additional screening studies to evaluate the commercial impacts of alternative catalytic gasifier operating conditions indicated that gas cost savings may be obtainable by reducing gasifier temperature from 1300°F to 1200°F. Little or no savings were found for reducing feed catalyst loading below 15 wt.% K_2CO_3 on dry coal or for increasing gasifier steam rate above the base level of about 1.5-1.6 lb/lb dry coal. The potential for cost savings associated with changes in these fundamental process variables will be analyzed as more data become available from the future process development program.

(8) A preliminary comparison of three conventional acid gas (CO_2 and H_2S) removal alternatives showed that selective heavy glycol scrubbing is the preferred process for a catalytic gasification plant. This is closely followed by nonselective hot potassium carbonate scrubbing. The third alternative, selective refrigerated methanol scrubbing, is significantly less attractive due to high methane absorption and subsequent loss with the vented CO_2.

(9) A study to assess the technical feasibility of a nonconventional cryogenic fractionation concept for acid gas removal indicated that the technique evaluated cannot be applied without freezing CO_2 in the cryogenic system.

3.1 CATALYST SOURCE/RECOVERY STUDIES

Catalyst recovery studies were carried out to define alternative approaches to catalyst recovery and makeup which minimize overall costs. These studies considered the probable source and cost of catalyst makeup in the quantities required for a commercial gasification industry.

3.1.1 Commercial Sources of Potassium and Sodium Catalyst

An assessment was made of the potential sources and costs of potassium (K) and mixed potassium/sodium (K/Na) catalysts when produced in the quantities required for a commercial catalytic gasification industry. Estimates of catalyst costs help to establish incentives for reducing catalyst makeup requirements. One approach to reduce catalyst makeup is to incorporate facilities for the recovery of water insoluble catalyst into a gasification plant in addition to multistage countercurrent water washing facilities.

An extensive literature investigation was carried out to determine the domestic consumption patterns of alkali metal carbonates, potential catalyst source minerals and compositions, and commercial and developing technology used to produce potassium hydroxide and carbonates. The results of this investigation are summarized in Tables 3.1-1 and 3.1-2.

TABLE 3.1-1

PRINCIPAL SOURCES OF POTASSIUM AND SODIUM SALTS

Chemical	Current Sources	Potential Alternate Sources	1975 Domestic Consumption (k ST/yr)	Identified Domestic Mineral Reserves (MST)
Sodium Compounds:				
• Na_2CO_3	Trona deposits in Wyoming and brines in California; also manufactured from NaCl via Solvay process	--	7,500(1)	50,000
• $NaHCO_3$	Carbonation of Na_2CO_3 solution; also as a Solvay process intermediate	Nahcolite deposits in Utah, Wyoming and Colorado	200	Very large
Potassium Compounds:				
• K_2CO_3	Carbonation of KOH	Various chemical processes using KCl or K_2SO_4 feed	65	Nil
• $KHCO_3$	Carbonation of K_2CO_3 solution	Engel-Precht process using KCl feed	Small	Nil
• KOH	Electrolysis of KCl (Hg cells)	Electrolysis of KCl (diaphragm and membrane cells)	200	Nil
• KCl	Deposits in New Mexico, Utah, California, and Saskatchewan	Deposits in Arizona, Montana, Nebraska, N. Dakota, New Brunswick, U.S.S.R., and Israel	7,900	300(2)
• K_2SO_4	Deposits in New Mexico, Utah, California, and Texas	Various chemical processes using KCl	400	Large

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Notes: (1) 4,500 kST/yr from trona and 3,000 kST/yr from Solvay process.

(2) An additional 100,000 MST reserve of KCl is in Canada.

(3) $k = 10^3$, $M = 10^6$

Table 3.1-2

ALTERNATIVE PROCESSES FOR PRODUCTION OF POTASSIUM CARBONATE

Process	Developmental Status	Reactions
Electrolysis of KCl	Presently commercial in U.S. (Hg cells). Final development work required to apply diaphragm or membrane cells.	$2KCl + 2\,H_2O \rightarrow 2KOH + Cl_2 + H_2$ $2KOH + CO_2 \rightarrow K_2CO_3 + H_2O$
Engel-Precht Process	Commercial in Germany prior to 1938 as a batch operation: during past several years, University of Saskatchewan has done bench-scale work to modify batch operation to continuous.	$MgO + H_2O \rightarrow Mg(OH)_2$ $Mg(OH)_2 + CO_2 + 2H_2O \rightarrow MgCO_3 \cdot 3H_2O\downarrow$ $3(MgCO_3 \cdot 3H_2O) + CO_2 + 2KCl \rightarrow$ $2(KHCO_3 \cdot MgCO_3 \cdot 4H_2O)\downarrow + MgCl_2$ $KHCO_3 \cdot MgCO_3 \cdot 4H_2O \rightarrow KHCO_3 + MgCO_3 \cdot 3H_2O\downarrow + H_2O$
Formate Process	Commercial in pre-WWII Germany, *ca* 1938.	$K_2SO_4 + Ca(OH)_2 + 2CO \rightarrow 2KHCO_2 + CaSO_4\downarrow$ $2KHCO_2 + O_2 \rightarrow K_2CO_3 + CO_2 + H_2O$
Reduction of K_2SO_4	Bench-scale studies.	$K_2SO_4 + 3H_2 + CO \rightarrow K_2S + 3H_2O + CO_2$ $K_2S + CO_2 + H_2O \rightarrow K_2CO_3 + H_2S$
Electrolysis of K_2SO_4	Bench-scale studies on analogous Na_2SO_4.	$2K_2SO_4 + 2H_2O + 4Hg \rightarrow 4K(Hg) + O_2 + 2H_2SO_4$ $2K(Hg) + 2H_2O \rightarrow 2KOH + H_2 + 2Hg$ $2KOH + CO_2 \rightarrow K_2CO_3 + H_2O$

As shown in Table 3.1-1, there are substantial deposits of sodium carbonates in the United States. Na_2CO_3 exists in conjunction with other Na salts in brine from Searles Lake and Owens Lake in California. Larger sources of naturally occurring Na_2CO_3 are found in Wyoming in the form of trona ($Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$). A currently untapped natural source of $NaHCO_3$ is nahcolite. Nahcolite deposits are found in Colorado, Utah, and Wyoming, usually in association with oil shale deposits. Large quantities of technical grade Na_2CO_3 manufactured from trona or via the Solvay process are marketed domestically. Thus, availability of Na_2CO_3 would not be a problem. However, as discussed previously in Section 2.2, a potassium-only catalyst appears to be the best choice for catalytic coal gasification.

Presently, only limited quantities of potassium are marketed as K_2CO_3 in the United States, and no significant deposits of K_2CO_3 are found in nature. However, the United States and Canada do have large deposits of other K salts from which substantial quantities of KCl and some K_2SO_4 are extracted for sale as fertilizer. Such K salts are commonly known as "potash". Potassium carbonate - and other catalytically active K salts such as KOH, $KHCO_3$, and perhaps $KHCO_2$ - must be manufactured from these available KCl or K_2SO_4 source minerals. The K_2CO_3 which is sold today is manufactured by carbonation of KOH produced by electrolysis of KCl.

In addition to electrolysis of KCl, four other processes have been identified for conversion of K salts to K_2CO_3. The development status and major reaction steps for these five K_2CO_3 processes are also shown in Table 3.1-2. The final step in some of the processes involves conversion of KOH, $KHCO_3$, or $KHCO_2$ to K_2CO_3. This step may be unnecessary, since these salts are likely to be active gasification catalysts based on earlier bench-scale screening tests. Literature sources indicate adequate reagent availability for the Engel-Precht reaction and the formate reaction. Large quantities of both MgO and $Ca(OH)_2$ are available from normal market sources.

Potassium salt manufacturers were contacted to obtain non-proprietary information on commercial and developing routes to make KOH and K_2CO_3. At present, almost all domestic KOH is made via mercury cell electrolysis of KCl. The small remainder is made via diaphragm cell electrolysis of KCl. K_2CO_3 is made subsequently by carbonating KOH. By the 1985-1990 time frame, the presently developing membrane cell technology will be commercially available for KCl electrolysis.

3.1.2 "Cash Flow" Analysis of Alternative Catalyst Manufacturing Processes

Scoping studies were carried out to define and compare the "cash flows" for the alternative processes for potassium catalyst manufacture listed in Table 3.1-2. The objective of these studies was to screen the manufacturing alternatives to select candidates for further, more detailed evaluation.

The initial step in defining the "cash flows" was to develop costs and values for the various raw materials and byproducts involved in these processes. Representative prices (f.o.b. source) were developed for all chemicals of interest based on Chemical Marketing Reporter cost trends and vendor contacts. Typical rail shipping costs to the Illinois area were added to the f.o.b. prices of the raw materials.

The results of the catalyst manufacture "cash flows" studies are summarized in Table 3.1-3. For each process, the "minimum catalyst cost" shown in the table consists of the estimated catalyst manufacture plant raw materials costs, the estimated investment charges and operating costs for utilities, and any additional costs due to changes required in the SNG plant. It excludes the investment charges (maintenance and return) for the catalyst manufacturing facilities and associated product tankage.

The "minimum catalyst costs" are shown as percentages of the cost of KOH solution purchased on the open market at the price listed in the Chemical Marketing Reporter. This price was confirmed by contacts with KOH manufacturers. As indicated previously, all domestic KOH is produced by electrolysis of KCl. As shown in Table 3.1-3, purchased K_2CO_3 is more expensive than KOH at market prices. This is a reflection of the fact that K_2CO_3 is presently manufactured from KOH using additional carbonation and drying steps. Since KOH has been shown to be at least as effective a gasification catalyst as K_2CO_3 in fixed bed gasification tests, it appears that KOH is the preferred form of makeup catalyst for catalytic gasification if electrolysis is the method of catalyst manufacture.

"Cash flows" for two major categories of manufacturing processes were developed for comparison with purchased KOH: electrolysis processes and chemical processes. On an economic basis consistent with the basis used for gasification screening studies, the "minimum cost" for KOH manufacture via KCl electrolysis ranges from 26-33 percent of the KOH market price. As indicated above, this "cash flow" is based on estimated feedstock and utilities requirements, and does not include capital charges on electrolysis investment. Since the investment for electrolysis is expected to be fairly large, the "gap" between the "minimum cost" and the market price could be eliminated when investment charges are included. On the other hand, projected costs for catalyst makeup, even for KOH from KCl electrolysis, could differ from current market prices because of differences in factors such as plant size and location, electrolysis technology, KCl feedstock grade and cost, costs of utilities, acceptable return on investment, and the contractual basis for supply. As an example of the latter, KOH might be supplied by a chemical company under long-term contract at a price below that prevailing in the open market. In order to better define the potential economics of KOH manufacture, more detailed studies of KCl electrolysis were carried out, as described in Section 3.1.4.

"Cash flows" were also estimated for presently non-commercial manufacturing alternatives: electrolysis of K_2SO_4 and three "chemical" processes (the Engel-Precht process, the formate process, and direct reduction of K_2SO_4). The chemistry and development status of each of these alternatives was discussed in Section 3.1.1. Although different makeup catalyst forms are involved, all have similar catalytic activity per potassium equivalent. The relative "minimum catalyst costs" have been expressed on a potassium-equivalent basis to eliminate the effect of the differences in form. To put these minimum cash flows in better perspective, the last column of Table 3.1-3

TABLE 3.1-3

CATALYST MANUFACTURE CASH FLOW STUDIES

ECONOMIC SUMMARY

Catalyst Source	Catalyst Form	Relative Minimum Catalyst Cost (1) (% of Purchased KOH Cost on K-Equivalent Basis)	Estimated Added Investment Level
• Purchased Chemicals at Market Price:			
+ Purchased KOH	45% KOH Solution	100 (Base)	Base
+ Purchased K_2CO_3	Calcined K_2CO_3	121	Nil
• Catalyst Manufacture via Electrolysis:			
+ KCl Electrolysis	30-45% KOH Solution	26-33	High
+ K_2SO_4 Electrolysis	45% KOH Solution	71	High
• Catalyst Manufacture via "Chemical" Processes:			
+ Engel-Precht Process (KCl Feed)	25% $KHCO_3$ Solution	74	Medium
+ Formate Process (K_2SO_4 Feed)	87% $KHCO_2$ Solution	96	Low/Medium
+ K_2SO_4 Reduction	Calcined K_2CO_3	105	Medium

Note:

(1) Minimum Catalyst Cost consists of the raw materials costs, investment charges and operating costs for utilities, and any additional costs (investment and operating) due to changes in the SNG plant. It excludes the cost of investment for the catalyst manufacturing facilities and associated product tankage.

indicates the relative magnitudes of added investment for the catalyst manufacturing alternatives based on current information and judgement.

Based on these scoping studies, the most attractive chemical process appears to be the KCl based Engel-Precht process. The K_2SO_4-based processes (K_2SO_4 electrolysis, formate process, and K_2SO_4 reduction) all suffer from the fact that potassium from K_2SO_4 is estimated to cost approximately twice as much as potassium from KCl. With investment charges included, it is likely that these processes would exceed the cost of purchased KOH.

Although the Engel-Precht process is more costly on this "cash flow" basis than KCl electrolysis, the latter is expected to require the larger investment. Thus, it is not apparent, from these studies alone, how the total cost of KOH from a grass-roots KCl electrolysis plant would compare with purchased KOH or the equivalent $KHCO_3$ from a grass-roots Engel-Precht plant. To help in this comparison, a more definitive screening evaluation of the Engel-Precht process was carried out, including an estimate of the investment required. The results of this study are presented in the following section.

3.1.3 Screening Evaluation of the Engel-Precht Process

A screening-quality evaluation of the Engel-Precht process for manufacturing potassium catalyst for the catalytic gasification process was completed. Based on the "cash flow" scoping studies reported above, the Engel-Precht process appeared to be the most economically attractive of the alternative chemical processes which were considered.

Historically, the Engel-Precht process was used in Germany to manufacture potassium carbonate and bicarbonate commercially as a batch operation from about 1900 to 1938. In about 1938, the formate process (K_2SO_4 to $KHCO_2$) superseded the Engel-Precht process. In the last 20 years, Israel and Saskatchewan have had renewed interest in the Engel-Precht process to convert their KCl deposits to K_2CO_3 or $KHCO_2$ in a continuous operations. All the process basis information used in developing this study was taken from the open literature. Significant uncertainties exist as to the quality and consistency of the available data. Based on the literature, no commercial Engel-Precht plants, continuous or batch, are presently in operation.

The Engel-Precht process involves four reaction steps, as shown below:

(1) $MgCl_2 + CaO\cdot MgO + 2H_2O \rightarrow 2Mg(OH)_2 \downarrow + CaCl_2$

(2) $Mg(OH)_2 + CO_2 + 2H_2O \rightarrow MgCO_3\cdot 3H_2O \downarrow$

(3) $3(MgCO_3\cdot 3H_2O) + CO_2 + 2KCl \rightarrow 2(KHCO_3\cdot MgCO_3\cdot 4H_2O) \downarrow + MgCl_2$

(4) $KHCO_3\cdot MgCO_3\cdot 4H_2O \rightarrow KHCO_3 + MgCO_3\cdot 3H_3O \downarrow + H_2O$

Reaction (4) requires careful control of reaction conditions to produce reusable $MgCO_3 \cdot 3H_2O$, and thus, only a dilute $KHCO_3$ solution can be made directly (about nine weight percent maximum). Steam-heated evaporators were included in the screening case to concentrate the product solutions to 25 weight percent for feed to the catalyst addition facilities.

Investment costs for this Engel-Precht screening evaluation fall into three main categories: costs of materials handling and processing equipment to carry out the Engel-Precht reactions, costs of facilities required to supply needed utilities (principally the steam for the evaporators), and net costs of modifying the catalytic gasification plant to receive catalyst makeup as 25 percent $KHCO_3$ solution. The Engel-Precht process facilities were cost-estimated based on individual equipment specifications. The remaining facilities were prorated from the catalytic gasification "Base Case" completed prior to the start of the Predevelopment Program.

The breakdown of the product $KHCO_3$ cost for the Engel-Precht process screening evaluation is shown in Table 3.1-4. Costs are shown as percentages of the cost of KOH solution purchased on the open market (on a potassium-equivalent basis). This is consistent with the basis used in presenting the results of the "cash flow" analyses in Table 3.1-3. As shown in Table 3.1-4, the total estimated cost of $KHCO_3$ catalyst from an Engel-Precht plant is about 94 percent of the cost of purchased KOH. This six percent advantage appears to be insufficient to justify further development work on the Engel-Precht process as a catalyst source for catalytic gasification. This conclusion was confirmed by subsequent studies of the cost of catalyst via KCl electrolysis as reported in the next section.

3.1.4 Screening Evaluation of Alternative Electrolysis Technologies

A rough screening study was completed of the alternative KCl electrolysis technologies for producing potassium catalyst for a commercial catalytic gasification plant. Vendor contacts were made to define investment and operating cost factors for use in this study. The results of this study, along with the previous catalyst manufacturing cost studies reported above, indicate that KCl electrolysis is the most economical method for producing makeup potassium catalyst for catalytic gasification plants. The three electrolysis technologies evaluated were diaphragm cells, membrane cells, and mercury cells at both 180 T/D and 470 T/D KOH product rate. The KOH makeup requirement for the Catalytic Coal Gasification Commercial Plant Study Design is 189 T/D KOH.

The estimated relative catalyst costs of these alternatives are as follows:

	180 T/D KOH	470 T/D KOH
Purchased KOH Cost	-------- 100 (Base) ---------	
Diaphragm Cells	76	56
Membrane Cells	75	62
Mercury Cells	67	54

TABLE 3.1-4

ENGEL-PRECHT PROCESS SCREENING EVALUATION BREAKDOWN OF RELATIVE PRODUCT CATALYST COST

Basis: Cost of Purchased KOH = 100(1)

• Raw Materials:	
- KCl (Agricultural Grade)	32
- $\mathrm{CaO \cdot MgO}$ (Calcined Dolomite)	6
• Utilities:	
- Coal Fuel	4
- Raw Water	Nil
- Cooling Water	Nil
- Electric Power	5
- Low Pressure Steam(2)	(3)
• By-product Sulfuric Acid	(1)
• Labor and Related Costs	5
• Investment-Related Costs	7
• Capital Charges(3)	39
Total Product Catalyst Cost	94

Notes:

(1) On a potassium-equivalent basis.

(2) Operating cost credit for low-pressure steam based on using non-condensing steam turbine drivers to back out purchased power.

(3) Capital charges based on 100% equity financing with 10% constant dollar DCF return.

These economics reflect an f.o.b. cost for 50 percent KOH solution produced in the diaphragm and mercury cells and for 31 percent solution from the membrane cells. Capital charges are based on 100 percent equity funding and 10 percent constant dollar DCF return.

As indicated from these figures, potassium catalyst produced specifically for catalytic gasification plants may be significantly cheaper than purchasing KOH from the open market. The cost differences between purchased and manufactured KOH may be attributable to the differences in project basis. KOH for use in catalytic gasification is assumed here to be manufactured by a dedicated plant producing large quantities of relatively impure KOH (98-99 percent dry basis) as makeup catalyst. The current market reflects supplies of small quantities of high purity KOH (99.6^+ percent dry basis) to multiple users. Specifically, the electrolysis screening cases presented here are based on "white" grade KCl feedstock (rather than high purity "chemical" grade), unit train shipment of feed KCl, and use of electrolysis by-product hydrogen for fuel in the SNG plant.

KOH production from mercury cells is the most attractive technology economically. However, increasingly stringent mercury emissions regulations will likely obviate large scale use of this technology in the future. At the smaller 180 T/D KOH scale, the alternative diaphragm or membrane cell technologies are about equal in cost. Both produce KOH for catalytic gasification plants at about 75 percent of the cost of purchased KOH. Since membrane cells are at an earlier stage of development than diaphragm cells (pioneer plant vs. commercial plant), further improvements during development may make membrane cells the preferred technology in the long run.

Due to differing economies of scale, diaphragm cells are currently more economical than membrane cells at the larger 470 T/D KOH scale. However, the potential applicability of larger-size dedicated electrolysis plants is more limited. Such plants may be applicable in the context of a mature catalytic gasification industry or if recovery of water insoluble catalyst is not carried out.

3.1.5 "Cash Flow" Analysis of Alternative Catalyst Recovery Processes

Scoping studies were conducted to evaluate the "cash flows" for several alternatives to recover water-insoluble catalyst from spent gasifier char and fines. The alternatives studied include two cases involving aqueous digestion of gasifier solids with $Ca(OH)_2$ and three processes which combine recovery of water insoluble catalyst using acid wash with catalyst manufacture via electrolysis of potassium salts or the formate process. These screening economics provided an initial estimate of the incentives for the recovery of insoluble catalyst to help guide ongoing laboratory studies.

To provide economic basis information for these "cash flow" studies, the current sources and costs of lime (CaO) and hydrated lime ($Ca(OH)_2$) were investigated. Inquiries were made to vendors of these materials in the Illinois area. Also, estimates of typical transportation costs for the shipment of calcium compounds to a commercial gasification plant were developed. Raw materials costs favor the use of lime rather than hydrated lime as the source calcium chemical. In turn, lime is normally produced by calcination of limestone ($CaCO_3$) at plants located near natural limestone deposits.

The results of the catalyst recovery "cash flows" are summarized in Table 3.1-5. As in Table 3.1-3, the minimum catalyst cost estimates for the alternatives are compared to the cost of purchased KOH. In each case, this cost consists of chemicals costs, utilities operating costs, and additional costs due to changes required in the existing SNG plant. However, the "minimum catalyst cost" excludes charges associated with the additional catalyst recovery system investments required for recovery of the water insoluble catalyst. The last column of Table 3.1-5 indicates the relative magnitudes of these investments based on current information and judgement. For the $Ca(OH)_2$ digestion cases, the "minimum catalyst cost" refers to the incremental catalyst which is recovered over and above the catalyst recovered in water washing only. For the acid wash cases which incorporate catalyst manufacture, this cost refers to the total catalyst supplied by the combined system.

Based on these scoping studies, catalyst recovery via aqueous digestion with $Ca(OH)_2$ offers the potential for substantial savings relative to purchased KOH at the market price. The "minimum cost" of the incremental potassium recovered via this route was estimated to be 36-54 percent of the cost of purchased KOH, depending on the $Ca(OH)_2$ requirement. This evaluation was based on bench-scale experiments described in Section 2.4 which showed at least 80 percent recovery of water-insoluble potassium with a calcium-to-potassium mole ratio ranging from 0.53-0.80 ($Ca(OH)_2$ added per total potassium originally present). Although investment charges for the digestion are not included in the "minimum cost", the added investment required for these facilities is expected to be relatively small.

Catalyst recovery via acid wash integrated with catalyst manufacture appears less attractive. Three process concepts of this type were screened. The first two combine recovery of water-insoluble catalyst using acid wash with electrolysis of potassium salts (i.e., KCl and K_2SO_4). These salts are produced by acidifying the water-washed gasifier solids (char and fines) with HCl or H_2SO_4, and then neutralizing with KOH to precipitate and separate catalytically inactive cations such as aluminum, silicon, and iron. Makeup potassium in the form of KCl or K_2SO_4 is also fed to electrolysis. The KOH produced is sent to the neutralization step and to the catalyst addition step upstream of the gasifier. The third process concept also begins by acidifying the gasifier solids with H_2SO_4. Then, the solids are neutralized with $Ca(OH)_2$, precipitates are removed, and carbon monoxide is added along with additional $Ca(OH)_2$ to carry out the "formate" process reaction producing catalytically active $KHCO_2$ and solid $CaSO_4$. Since all three of these cases are expected to require large investments, it is apparent from the "minimum catalyst costs" in Table 3.1-5 that the total costs for these alternatives will probably exceed the cost of purchased KOH.

Based on the results of these "cash flow" studies, a screening study was carried out to compare catalyst recovery via $Ca(OH)_2$ digestion with water washing only. This screening study is described in the next section.

TABLE 3.1-5

CATALYST RECOVERY CASH FLOW STUDIES

ECONOMIC SUMMARY

Catalyst Source	Catalyst Form	Relative Minimum Catalyst Cost (1) (% of Purchased KOH Cost on K-Equivalent Basis)	Estimated Added Investment Level
• Purchased KOH at Market Price	45% KOH Solution	100 (Base)	Base
• Catalyst Recovery via $Ca(OH)_2$ Digestion			
+ Gasifier Solids + $Ca(OH)_2$ (Ca/K = 0.53)	35% Mixed K-Salt Solution	36(2)	Low
+ Gasifier Solids + $Ca(OH)_2$ (Ca/K = 0.80)	35% Mixed K-Salt Solution	54(2)	Low
• Catalyst Recovery via Acid Wash Integrated with Catalyst Manufacture			
+ Gasifier Solids + HCl + KCl Electrolysis	30% KOH Solution	83	Very High
+ Gasifier Solids + H_2SO_4 + K_2SO_4 Electrolysis	30% KOH Solution	92	Very High
+ Gasifier Solids + H_2SO_4 + Formate Process	30% $KHCO_2$ Solution	100	High

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Notes:

(1) Minimum Catalyst Cost consists of chemicals costs, operating costs for utilities, and any additional costs (investment and operating) due to changes in the existing SNG plant facilities. It excludes the cost of investment for catalyst recovery and, where present, catalyst manufacturing and associated product tankage.

(2) Minimum Catalyst Cost for the $Ca(OH)_2$ digestion alternatives reflects the cash flow per unit of incremental catalyst recovered above that recoverable by water wash.

3.1.6 Screening Study of $Ca(OH)_2$ Digestion

A screening study was carried out to evaluate catalyst recovery using hot, aqueous $Ca(OH)_2$ digestion of the catalyst-containing char and fines withdrawn from the gasifiers. The objective was to compare the investment and operating costs for this case with costs for water washing alone to quantify the relative economics of the two alternatives.

Water washing alone has been shown to recover readily only about 70% of the potassium salts in the spent gasifier solids when starting with 15 wt % K_2CO_3 equivalent on Illinois coal (dry basis). The remaining salts are tied up as water insoluble complexes with the coal mineral matter. $Ca(OH)_2$ digestion has been shown in laboratory experiments to solubilize most of this water insoluble potassium. Then, countercurrent water washing can be used to recover 90% or more of the total potassium.

A simplified process flow plan for the base "Water Wash Only" Case is shown in Figure 3.1-1. Gasifier char solids from the char withdrawal system and gasifier fines from the tertiary cyclone catch are separately slurried with portions of the semi-rich catalyst solution from the second stage of catalyst recovery. The two slurries are then depressured into the first-stage water wash mixing drum which operates at 20 psia and 230°F. The mixing drum effluent slurry is pumped through the first-stage hydroclone separators. The first-stage hydroclone overflow, which is the most concentrated potassium solution in the system, is fed into the rich catalyst solution holding drum. Makeup 30 wt % KOH solution is also fed into this drum to replace the potassium not recovered in the washing sequence. The recovered catalyst solution is pumped to the catalyst addition facilities where it is reimpregnated on the feed coal to the gasifiers. The first-stage hydroclone underflow slurry is mixed with the third-stage hydroclone overflow solution in the second-stage mixing drum. The mixture is then pumped through the second-stage hydroclones. The semi-rich overflow from this stage is used to slurry the char and fines, and the underflow is fed into the third-stage mixing drum. This countercurrent water washing sequence continues in a similar manner until the fifteenth stage, where clean makeup wash water is preheated and added to the system. The leached solids in the last stage underflow slurry are sent to offsites waste solids handling facilities. Catalyst solution from filtration of venturi fines slurry stripper bottoms enters catalyst recovery in the tenth stage, where the concentrations are similar.

A simplified process flow plan for the "$Ca(OH)_2$ Digestion with Water Wash" Case is shown in Figure 3.1-2. In this case, the gasifier char and fines feed slurries are depressured into a $Ca(OH)_2$ digestor, operating at 70 psia and 300°F. A portion of the semi-rich solution is fed to a lime feed slurry drum and mixed with lime (CaO) solids and makeup catalyst (30 wt% KOH solution). This lime slurry is then mixed and reacted with the char and fines slurries in the $Ca(OH)_2$ digestor. The residence time is two hours, and the Ca/total K ratio is maintained at 0.7 mol/mol. These digestion conditions have been shown in laboratory tests to solubilize at least 90% of the total potassium in the gasifier solids (see Section 1.5). The $Ca(OH)_2$ digestor effluent is pumped through the first-stage hydroclone separators. The first-stage hydroclone overflow, again the most concentrated potassium

FIGURE 3.1-1
CATALYTIC COAL GASIFICATION CATALYST RECOVERY SYSTEM
"WATER-WASH ONLY" CASE

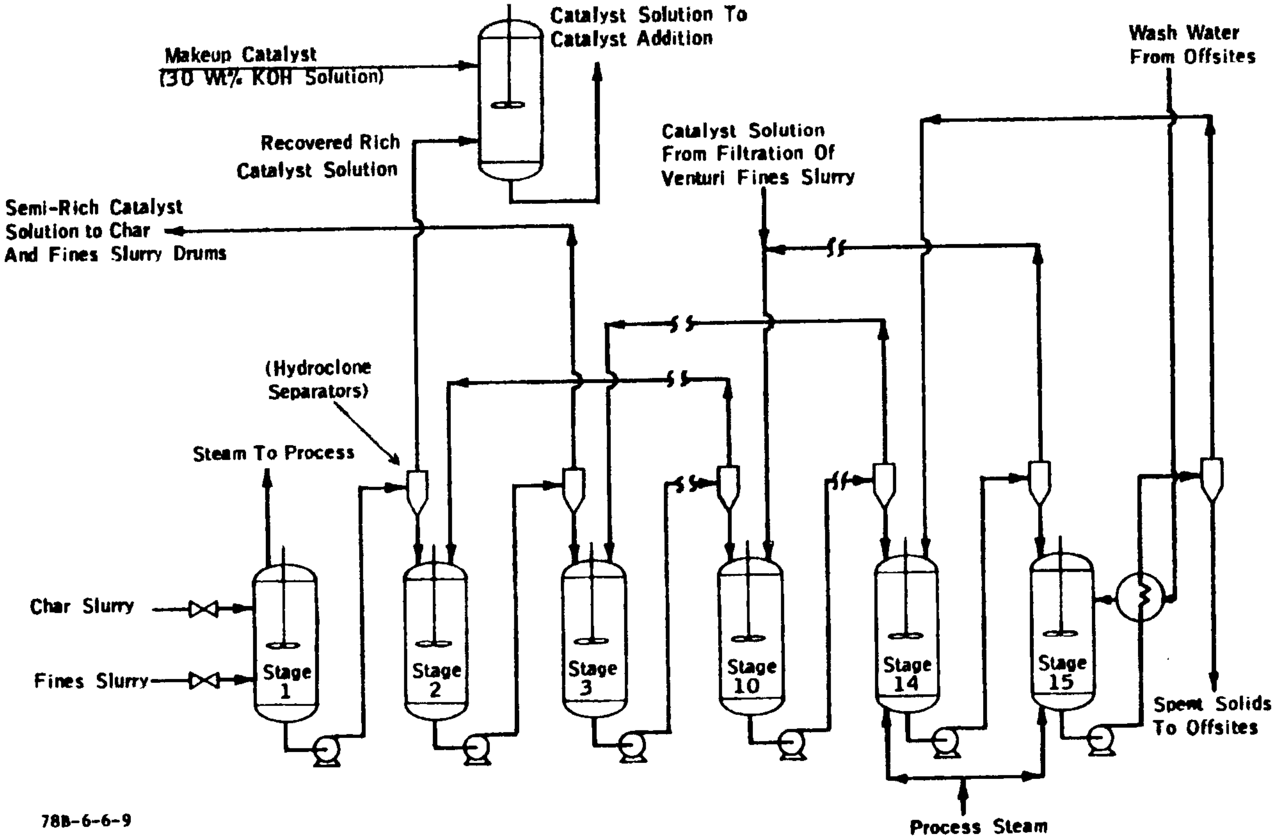
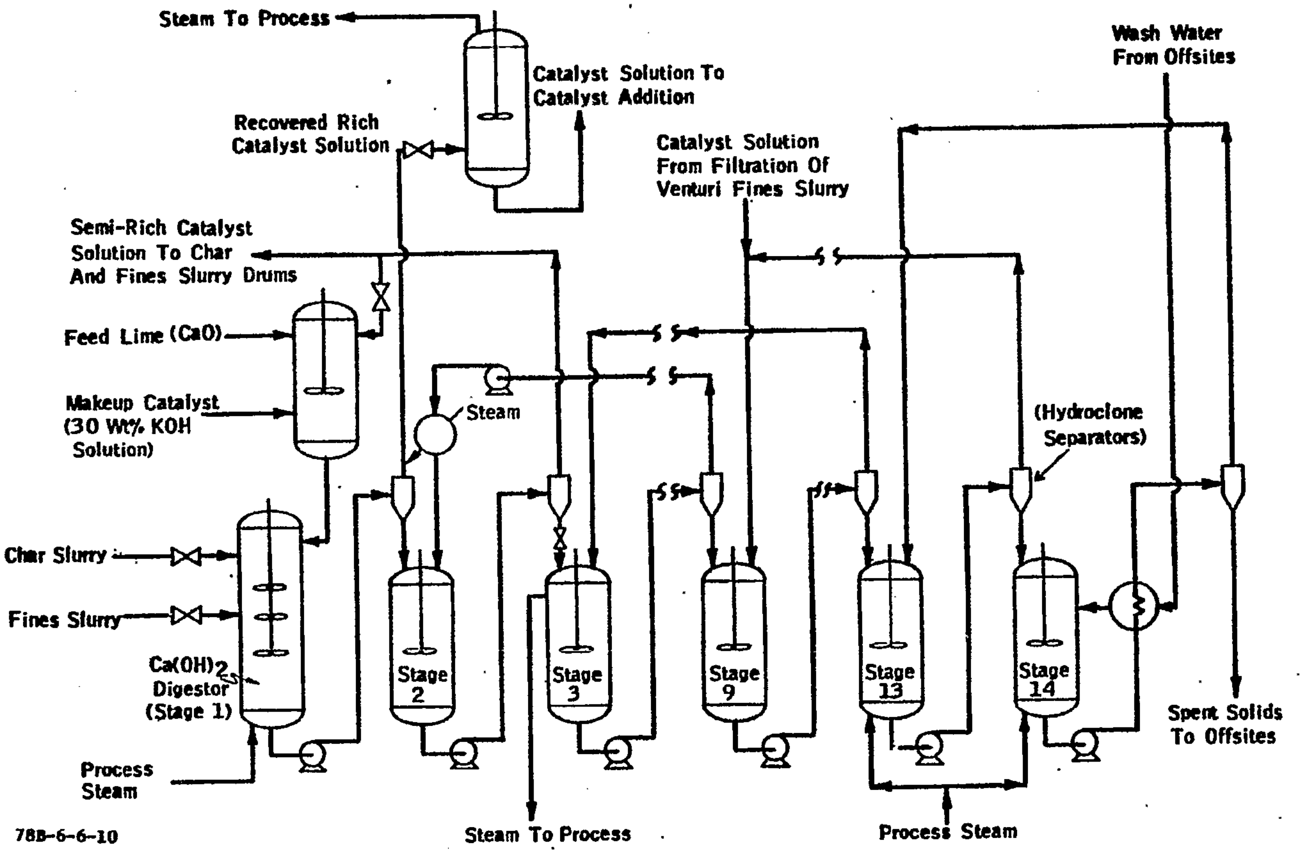


FIGURE 3.1-2

CATALYTIC COAL GASIFICATION CATALYST RECOVERY SYSTEM "$Ca(OH)_2$ DIGESTION WITH WATER WASH" CASE



solution in the system, is depressured into the rich catalyst solution holding drum and pumped into the catalyst addition facilities. The downstream water washing sequence is similar to the "Water Wash Only" Case, except that: (1) solids throughput is greater due to the presence of insoluble calcium salts, and (2) one less stage of washing is required to obtain the target 98.5% recovery of solubilized potassium salts.

The investment costs considered in this screening evaluation fall into two main categories: (1) costs for facilities directly related to recovery and handling of catalyst, i.e., costs for the catalyst recovery system, associated raw materials handling, and facilities to supply required utilities; and (2) costs for changes to other facilities in the gasification plant, i.e., coal drying/catalyst addition, preheat furnaces, waste solids handling, and flue gas desulfurization. The facilities for catalyst recovery and raw materials handling for "$Ca(OH)_2$ Digestion with Water Wash" were cost estimated based on individual equipment specifications. The facilities costs for catalyst recovery and raw materials handling for the Water Wash Only Case were pro-rated from these costs. Investment cost impacts for changes to other facilities in the gasification plant were pro-rated from earlier catalytic gasification studies.

Table 3.1-6 presents a breakdown of the incremental costs for catalyst recovery by "$Ca(OH)_2$ Digestion with Water Wash" versus the costs for "Water Wash Only". The incremental costs have been divided by the incremental tons of KOH equivalent recovered by using $Ca(OH)_2$ digestion, and these costs per ton have in turn been expressed as percentages of the cost of purchased makeup KOH at the current market price. As shown, the total cost of the incremental catalyst recovered by including $Ca(OH)_2$ digestion in the catalyst recovery system is 68% of the cost of an equivalent amount of purchased KOH. This potential advantage of over 30% justifies further development work on the $Ca(OH)_2$ digestion process.

Obviously, the incentive for recovering water-insoluble catalyst via $Ca(OH)_2$ digestion would be lower if makeup KOH could be manufactured at a cost substantially below the current market price. As reported earlier in this report, this may indeed be possible, since special factors associated with manufacturing KOH for use in catalytic gasification tend to lower the cost relative to the present market. In the next development phase, a more detailed study of catalyst manufacturing facilities will be needed to better define the costs of KOH for catalytic gasification. Results of future laboratory experiments on $Ca(OH)_2$ digestion and water wash will also help to firmly establish the relative economics of $Ca(OH)_2$ digestion.

3.2 GASIFICATION REACTOR SYSTEM STUDIES

Studies were undertaken to identify preferred reactor system configurations for catalytic gasification and estimate the impacts of reactor operating conditions on reactor volume and other process variables.

3.2.1 Evaluation of the Incentive for Secondary Gasification

An engineering screening study was carried out to determine whether there is an economic incentive for adding a secondary gasification step to the

TABLE 3.1-6

SCREENING STUDY OF CATALYST RECOVERY USING $Ca(OH)_2$ DIGESTION

BREAKDOWN OF INCREMENTAL COSTS WITH RESPECT TO WATER WASH ONLY

Basis: Cost of Purchased KOH = 100

Cost Items	Incremental Costs Per Increment of KOH Equivalent Recovered
• Raw Materials	
- Lime, 97% CaO	39
• Utilities	
- Power	1
- Intermediate Pressure Steam(1)	(1)
• Coal for Dryer Fuel	(1)
• Fuel Gas	(1)
• Labor and Related Costs	4
• Investment-Related Costs	4
• Capital Charges(2)	23
Total Cost of Incremental Catalyst Recovered	68

Notes:

(1) Operating cost credit for intermediate pressure steam is based on using noncondensing steam turbine drivers to back out purchased power.

(2) Capital charges are based on 100% equity financing with 10% constant dollar DCF return.

Exxon Catalytic Coal Gasification Process. The objective of secondary gasification is to raise overall process efficiency by increasing carbon conversion above that attainable in a single fluidized bed. The gas cost with secondary gasification was estimated to be only 0.8 percent less than the gas cost in the Catalytic Gasification "Base Case" developed prior to the Predevelopment Program. This small economic credit does not appear to offset the development risks due to greater system complexity and the potential for added technical problems. However, this conclusion could change if it were not practical to obtain high carbon conversions in a single reaction step or if coal or catalyst costs increase significantly. The basic assumptions, results, and economic sensitivities for the secondary gasification case are discussed below.

A schematic of the reactor system flow plan with secondary gasification is shown in Figure 3.2-1. The primary stage of the gasifier gasifies 90 percent of the feed carbon as in the "Base Case," and the secondary stage gasifies enough additional carbon so that the overall carbon conversion is 95 percent. The secondary gasifier operates at a slightly lower pressure than the primary gasifier and receives as feed all of the entrained solids which can be captured from the primary effluent gas by an overhead cyclone, as well as all of the char withdrawn from the primary gasifier. The secondary gasifier is fed a portion of the preheated steam/recycle mixture and operates at a relatively low gas velocity to minimize fines entrainment. The coal injection gas supplies a second source of recycle gas for the primary gasifier. Since the steam and recycle mixture is split on the basis of the steam required for each gasifier, the two gasifiers are not individually in recycle gas balance. (Recycle gas balance is achieved when CO + H_2 in equals CO + H_2 out.) Recycle gas balance could have been achieved by heating the steam and recycle streams separately and blending the appropriate mixture for each gasifier. Since this would have increased the complexity and cost of the preheat furnace, it was judged that the simpler scheme would be better.

The process basis and some results of the material and energy balances are presented in Table 3.2-1. The key process basis items are unchanged from the Base Case except where indicated in the table. The material balance was calculated assuming shift, methanation, and steam-graphite equilibrium in each gasifier. The assumption of steam-graphite equilibrium results in feed steam conversions of 43 percent in the primary gasifier and 54 percent in the secondary gasifier. These conversions appear reasonable based upon the available kinetic data. The temperature in the primary gasifier was fixed at 1300°F. The secondary gasifier temperature was determined by a trial-and-error material and energy balance. The secondary gasifier temperature was found to be essentially the same as that for the primary gasifier, 1300°F. Also, the steam/recycle preheat furnace coil outlet temperature was calculated to be almost identical to the Base Case value of 1540°F.

Stream rates are presented in Table 3.2-1 for the Secondary Gasification Incentive Case for a plant producing 257 GBtu/SD net SNG product. Steam and recycle rates are up slightly from the Base Case, but the gasifier coal rate is down about 5 percent because of the higher overall carbon conversion. In sizing the secondary gasifier, the outlet gas velocity was assumed to be 22.5 percent of the Base Case primary velocity, and the volumetric carbon gasification rate was assumed to be 50 percent of the rate in the primary gasifier.

FIGURE 3.2-1

EXXON CATALYTIC COAL GASIFICATION PROCESS WITH SECONDARY GASIFICATION

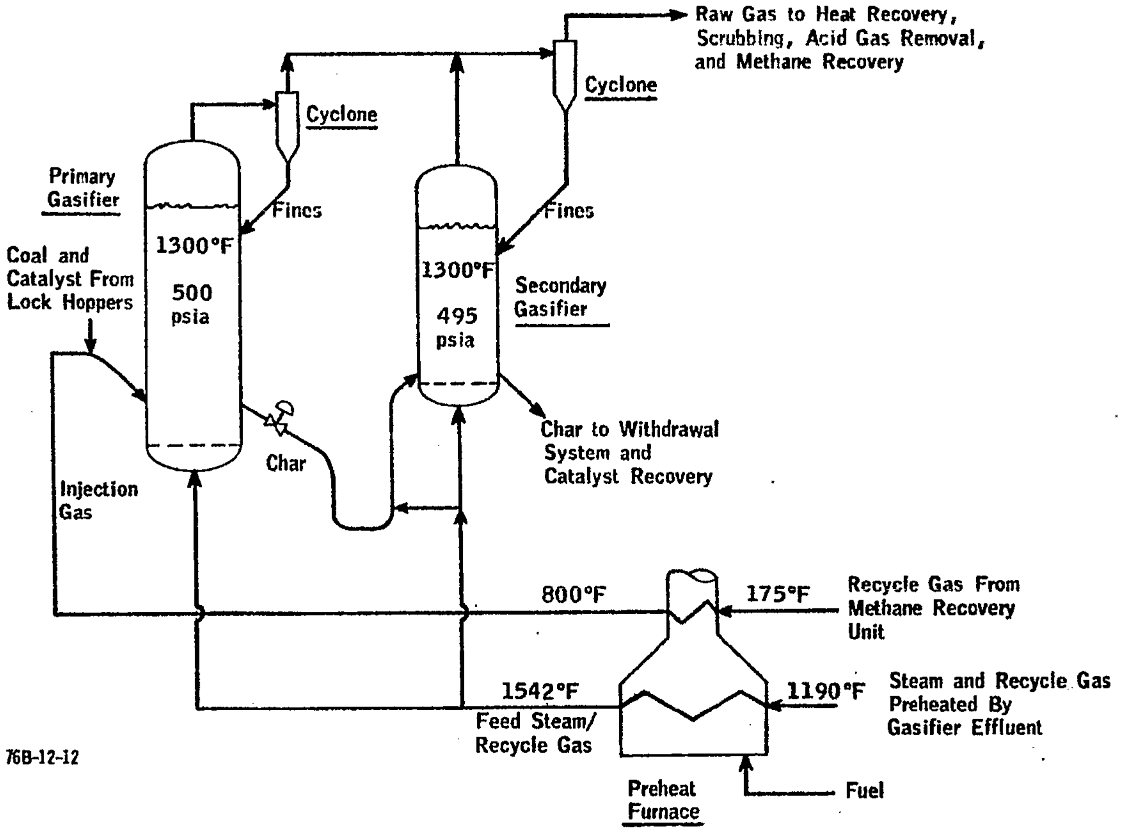


TABLE 3.2-1

INCENTIVE FOR SECONDARY GASIFICATION
SUMMARY OF PROCESS BASIS AND HEAT AND MATERIAL BALANCE(1)

	Base Case	Secondary Gasification Incentive Case
Reactor System	"Primary" Gasifier Only	Primary and Secondary Gasifiers
Feed Carbon Conversion:		
Primary Gasifier	90%	90%
Overall	90%	95%
Conditions:		
Primary Gasifier	1300°F/500 psia	1300°F/500 psia
Secondary Gasifier	--	1300°F/495 psia
Secondary Gasifier Sizing Bases:		
Superficial Outlet Velocity	--	22.5% of Primary
Volumetric Gasification Rate	--	50% of Primary
Preheat Furnace Coil Outlet Temperature	1540°F	1542°F
Key Stream Rates:(2)		
Coal Feed to Gasifiers	14,490 ST/SD	13,835 ST/SD
Coal to Boiler Fuel	1,860 ST/SD	1,925 ST/SD
Coal to Dryer Fuel	650 ST/SD	620 ST/SD
Total Coal	17,000 ST/SD	16,380 ST/SD
Total Gasifier Steam Rate	84,164 moles/hr	85,633 moles/hr
Total Recycle Rate	51,292 moles/hr	51,605 moles/hr
Split of Preheated Steam/Recycle	All to Primary	94.0/6.0% to Primary/Secondary
By-Product Rates:		
Ammonia	239 ST/SD	234 ST/SD
Sulfur	400 LT/SD	403 LT/SD
Sulfuric Acid	177 ST/SD	179 ST/SD
Utilities Requirements:		
Electric Power	159 MW	157 MW
Raw Water	5,500 GPM	5,500 GPM

Notes:

(1) For plant sized to produce 257 GBtu/SD SNG.

(2) All coal rates are for Illinois coal as received from coal cleaning. Higher heating value is 10,620 Btu/lb.

A breakdown of the relative investment for the Secondary Gasification Incentive Case as compared to the Base Case is presented in Table 3.2-2. The total plant investment with secondary gasification has increased by 1.0 percent over the Base Case investment. The addition of the secondary gasifier increased the investment for gasifier vessels by about 20 percent. Reductions in the investment for other areas of the plant offset about half the added investment in the gasifier area. The reduced coal rate decreased the investment for the coal feed and catalyst handling areas. The lower coal rate and higher overall carbon conversion reduced the spent solids rate to the catalyst recovery area to 84 percent of the Base Case rate. This resulted in investment savings in the char withdrawal, catalyst recovery, and waste treating areas.

A breakdown of the relative gas cost for the Secondary Gasification Incentive Case as compared to the Base Case is shown in Table 3.2-3. The total gas cost with secondary gasification is 0.8 percent less than the Base Case gas cost. Savings in coal and catalyst are partially offset by increased capital charges associated with the net added investment. Thus, there appears to be only a marginal incentive for adding a secondary gasification step at this stage in the development.

This conclusion is dependent on the validity of the basis assumptions. If conversion of 90 percent of the feed carbon in a single reactor is not practically obtainable (e.g., if a coal feed is relatively friable and produces excessive fines), or if coal cost or catalyst cost increases significantly, then there would be increased incentive to develop secondary gasification. The incentive would also be larger if the disposal of char containing nearly 50 percent carbon becomes an economic or environmental problem. For example, if a substantial charge per ton is added for solid waste disposal, the savings shown for secondary gasification could increase from the present 0.8 percent to about 1.5-2.5 percent, depending on the assumptions made. Another area of uncertainty is gasification rate. If the volumetric carbon gasification rate in the secondary gasifier is equal to the rate in the primary gasifier, rather than 50 percent of that rate, then the secondary gasification case would save an additional 0.5 percent relative to the Base Case.

There may be benefits in catalyst recovery performance due to the reduced carbon content of the residual solids from secondary gasification. The present study takes credit only for the reduced weight of char/ash solids to be washed. If catalyst recovery can be operated with more concentrated slurries of char/ash solids after those solids are processed in a secondary gasifier, the gas cost savings for secondary gasification might increase from 0.8 percent to about 2 percent. If two or more of these revised assumptions prove to be applicable, the potential gas cost savings for secondary gasification could increase to 3 percent or more. Thus, the secondary gasification alternative should be held in reserve pending further definition of the catalytic gasification process performance in the base configuration.

3.2.2 Evaluation of Two-Stage Gasifier with Upper Drying Stage

A screening study was prepared to evaluate the incentive for a two-stage gasification reactor with the upper stage used for coal plus

TABLE 3.2-2

INCENTIVE FOR SECONDARY GASIFICATION INVESTMENT BREAKDOWN

Basis: Base Case Total Investment = 100

	Base Case	Secondary Gasification Incentive Case
Coal Prep. and Materials Handling		
Coal Handling	5.3	5.2
Char/Ash Handling	1.1	1.1
Catalyst Handling	1.2	1.2
Coal Drying/Catalyst Addition	3.7	3.6
Subtotal	11.3	11.1
Onsites		
Reactor System	17.4	19.1
Preheat Furnace	5.6	5.6
Product Gas Cooling/Scrubbing	9.7	9.7
NH_3/H_2S Recovery	2.7	2.6
Acid Gas Removal/Sulfur Recovery	14.2	14.2
Methane Recovery/Refrigeration	8.6	8.6
Catalyst Recovery	1.9	1.5
Common Facilities	4.4	4.4
Subtotal	64.5	65.7
Offsites		
Waste Treating	2.9	2.8
By-product Handling	0.7	0.7
Miscellaneous Offsites	4.7	4.7
Subtotal	8.3	8.2
Utilities		
Raw Water/CW/BFW Treating	2.0	2.0
Steam Generation	7.2	7.3
Flue Gas Desulfurization	3.4	3.4
Electric Power Distribution	2.9	2.9
Miscellaneous Utilities	0.4	0.4
Subtotal	15.9	16.0
TOTAL	100.0	101.0

TABLE 3.2-3

INCENTIVE FOR SECONDARY GASIFICATION SUMMARY OF RELATIVE GAS COSTS

Basis: Base Case Total Gas Cost = 100

	Base Case	Secondary Gasification Incentive Case
• Coal	26.1	25.2
• Gasification Catalyst	6.3	5.9
• By-products		
- Ammonia	(3.2)	(3.2)
- Sulfur	(1.9)	(1.9)
- Sulfuric Acid	(0.6)	(0.6)
Subtotal	(5.7)	(5.7)
• Operating Costs		
- Electric Power	7.9	7.8
- Raw Water	0.1	0.1
- Labor and Related Costs	5.6	5.6
- Investment-Related Costs	9.3	9.4
- Other Catalysts and Chemicals	0.6	0.6
Subtotal	23.5	23.5
• Capital Charges(1)	49.8	50.3
TOTAL GAS COST	100.0	99.2

Note:

(1) Capital charges based on 100% equity financing with 10% constant dollar DCF return.

catalyst solution drying and the lower stage used for catalytic coal gasification. The heat to dry the coal plus catalyst solution is supplied by the hot gasifier effluent.

The major process bases for this study were as follows:

- Conversion of Illinois No. 6 coal to 257 Billion Btu/SD of SNG.
- Gasifier conditions of 1300°F and 500 psig.
- Feed coal is dried to 4 wt % moisture prior to catalyst solution addition to ensure adequate catalyst dispersion onto the coal.
- The "wet" catalyzed coal from catalyst solution addition is fed to the upper stage via lock hoppers.
- The catalyzed coal is dried to essentially zero moisture and preheated to 600°F in the upper drying stage.

There are several differences between this "Two-Stage Gasifier with Upper Drying Stage" Case and the earlier "Base Case" with regard to flow scheme, flow rates, and heat integration. The major differences are:

- The coal drying/catalyst addition facilities are simplified by deleting the second drying stage which was used in the Base Case to evaporate the moisture in the recycle catalyst solution.
- The catalyzed feed coal is injected into the upper stage dryer rather than the fluid bed gasifier. As a result, coal injection gases bypass the gasification stage. These gases go directly to the downstream gas cleanup and methane recovery facilities and, hence, appear as incremental flows in the recycle loop. Additionally, vaporized moisture from the upper stage dryer also goes to the downstream gas cleanup and cooling facilities. In total, the gas rate to the gas cooling and scrubbing equipment increases by 30 percent.
- Approximately half of the raw 1300°F gasifier product gas must bypass the upper stage dryer in order to keep the temperature of the drying bed at 600°F and thus avoid significant devolatilization of the coal. The combined temperature of the bypassed gasifier product gas and the gas present in the upper stage dryer is 924°F. Much of the high level heat associated with the new raw gasifier product gas is used to dry and preheat the feed coal. Hence, the use of gas-gas exchangers is probably not justified. Therefore, the gas-gas exchangers were deleted and the combined 924°F product gas is sent directly to a waste heat boiler for steam generation.
- The design of the preheat furnace is significantly different from that used in previous catalytic gasification studies. The heat duty is approximately double, but the normal coil outlet temperature has decreased by about 300°F to 1220°F. The duty is larger primarily because

of the deletion of the gas-gas heat exchangers. The coil outlet temperature is lower mainly because the coal feed to the gasifier is now preheated to 600°F rather than 200°F.

- Additional gross methane product is needed as fuel to supply the additional duty to the preheat furnace. Therefore, in order to maintain the same product methane rate, about 6% more coal must be fed to the gasifiers. The increased demand for process coal is somewhat offset by the decreased demand for coal used in the drying facilities and the offsite boilers. As a result, total coal feed rate to the plant has increased by only about 2%.

The relative economics for the Base Case and the Two-Stage Gasifier with Upper Drying Stage are as follows:

	Base Case	Two-Stage Gasifier with Upper Drying Stage
Reactor System	One-Stage Gasifier	Two Stages: Upper for Drying Lower for Gasification
Relative Investment	1.000	1.000
Relative Gas Cost		
Coal	0.261	0.267
Gasification Catalyst	0.063	0.066
By-Product Credits	(0.057)	(0.059)
Operating Costs	0.235	0.240
Capital Charges	0.498	0.498
Total Gas Cost	1.000	1.012

Both cases are sized to produce 257 GBtu/SD SNG from Illinois coal. Capital charges are based on 100% equity funding and 10% constant dollar DCF return.

The investment for the two cases is the same. Use of an upper stage dryer permits a significant reduction in the duty of the catalyst addition/drying facilities in the coal preparation section. The gas-gas exchangers are eliminated because the incentive for their use is greatly reduced when the gasifier effluent high level heat is used for coal drying. These savings are offset by the more complicated two-stage gasifier reactor and larger recycle gas handling facilities.

The gas cost calculated for the Two-Stage Gasifier Case is about 1% greater than for the Base Case. There are two main reasons for this increase. First, total process coal and makeup catalyst requirements are about 6% higher for the same net SNG product rate. This is due to increased consumption of methane as preheat furnace fuel. Second, utilities demands are greater because of larger overall processing requirements. Thus, there appears to be no incentive for further pursuit of this two-stage gasifier concept.

3.2.3 Impacts of Catalytic Gasifier Operating Conditions

Engineering screening studies were carried out in the middle of the Predevelopment Program to estimate the commercial impacts of alternative catalytic gasifier operating conditions such as catalyst composition and loading, temperature, and steam rate. Four commercial-scale cases with K_2CO_3 catalyst were evaluated for economic impacts as variations to the earlier "Base Case" with mixed K_2CO_3/Na_2CO_3 catalyst. They are as follows:

(1) base temperature (1300°F) and 15 wt % K_2CO_3 catalyst loading on feed coal (rather than the base 7.5% K_2CO_3/ 7.5% Na_2CO_3)

(2) lower catalyst loading (10% K_2CO_3)

(3) lower temperature (1200°F) and 15% K_2CO_3 catalyst

(4) higher steam rate and 15% K_2CO_3 catalyst

In addition, the Mixed Catalyst Base Case itself was revised to reflect laboratory data showing a low activity for sodium and a selective tie-up of potassium as inactive aluminosilicates in the mixed K_2CO_3/Na_2CO_3 system, discussed in Section 1.3.3.

A summary of the cases evaluated is presented in Table 3.2-4. In each of these cases, the steam and recycle gas rates were determined based on assumptions made about the extent of three reactions in the gasifier effluent gases:

Shift	$CO + H_2O = CO_2 + H_2$
Methanation	$CO + 3H_2 = CH_4 + H_2O$
Steam-Carbon	$C(s) + H_2O = CO + H_2$

The gases were assumed to be in shift equilibrium in all cases. The gasifier model described below was used to predict the effective methanation equilibrium temperature for each case. Methanation was estimated to be essentially at equilibrium for all of the 1300°F cases. However, the methanation equilibrium temperature for the 1200°F case was estimated to be 1210°F, i.e., a 10°F approach. In all cases except the "Higher Steam Rate" case, the approach to steam-carbon equilibrium was held constant so that the volumes calculated by the gasifier model would reflect differences due only to reaction kinetics and not to equilibrium. The technique used to do this was to set the steam rate so that the gasifier effluent gas was "at equilibrium" for the steam-carbon reaction over graphite. (Since the carbon in coal-derived chars has a thermodynamic activity greater than graphite, the steam-carbon gasification reaction still proceeds at a significant rate when the gases are at steam-graphite "equilibrium.")

The gasifier volumes for the sensitivity cases and the present evaluation of the Mixed Catalyst Base Case were predicted using a fluidized bed

TABLE 3.2-4

IMPACTS OF CATALYTIC GASIFIER OPERATING CONDITIONS
SUMMARY OF CASES AND ECONOMICS(1)

	15% Mixed Catalyst Base Case		Sensitivity Cases			
	Previous Evaluation	Present Evaluation	15% K_2CO_3 Catalyst	10% K_2CO_3 Catalyst	Lower Temperature	Higher Steam Rate
• Gasifier Operating Conditions						
+ Pressure, psia	500	500	500	500	500	500
+ Temperature, °F	1300	1300	1300	1300	1200	1300
+ Catalyst Loading, Wt% on Dry Coal						
- K_2CO_3	7.5	7.5	15	10	15	15
- Na_2CO_3	7.5	7.5	--	--	--	--
• Extent of Gasifier Reactions						
+ Steam Conversion, % Feed Steam	43.0	43.0	43.0	43.0	40.3	35.8
+ Carbon Conversion, % Feed Carbon	90.0	90.0	90.0	90.0	90.0	90.0
+ Approach to Methanation Equilibrium, °F	0	0	0	0	10	0
• Results of Heat and Material Balance						
+ Coal Rates, ST/SD(2)						
- Coal to Process, ST/SD	14,490	14,520	14,505	14,480	14,360	14,550
- Coal to Boilers, ST/SD	1,860	1,865	1,865	1,860	2,050	2,370
- Coal to Dryers, ST/SD	650	640	635	470	625	635
- Total Coal, ST/SD	17,000	17,025	17,005	16,810	17,035	17,555
+ Gasifier Feed Steam, moles/hr	84,164	84,291	84,225	84,062	88,907	101,458
+ Total Recycle Rate, moles/hr	51,292	51,353	51,353	51,253	34,804	61,328
+ Normal Steam/Recycle Preheat, °F	1,540	1,554	1,548	1,534	1,397	1,502
• Relative Gasifier Volume(3)	100	201	88	119	135	71
• Relative Plant Investment(4)	100.0	113.3	103.0	101.4	98.0	102.4
• Relative Gas Cost(4)	100.0	111.0	105.4	104.9	103.6	107.5

Notes:

(1) For plants sized to produce 257 GBtu/SD SNG.

(2) Coal rate is for Illinois coal as received from coal cleaning. Higher heating value is 10,620 Btu/lb.

(3) Relative fluid bed volumes are shown as percentages of the volume previously estimated for the "Base Case."

(4) Relative investments and gas costs are shown as percentages of the totals for the previous evaluation of the "Base Case."

kinetics/contacting model of the catalytic gasifier developed with Exxon funds prior to the start of the Predevelopment Program. (This model was partially revised later in the Program as described in Sections 1.3.6 and 2.2.) The model predictions were based on preliminary estimates of the gasifier char properties. These estimates were based largely on data obtained in Fluid Bed Gasifier operations conducted prior to the present program. Sensitivity studies using the gasifier model have identified the weight fraction catalyst in the gasifier char as the most important char property. Char bulk and particle densities also have a moderate impact on predicted gasifier volumes.

The predicted gasifier volumes are shown in Table 3.2-4 as percentages of the corresponding value for the previous evaluation of the Mixed Catalyst Base Case. As shown, the new fluid bed volume predicted for the Mixed Catalyst Base Case is roughly twice the previous estimate. However, with 15% K_2CO_3, the volume is 12 percent less than the previous case. With 10% K_2CO_3, the volume is only 19 percent greater than the previous estimate. All cases are sized to produce 257 GBtu/SD SNG. Four gasifier trains are provided in all cases except the present evaluation of the Base Case, which has six trains because of the large volume required.

Total plant investments and gas costs are also shown in Table 3.2-4 as percentages of the corresponding values for the previous evaluation of the Mixed Catalyst Base Case. The gas cost with mixed catalyst increased by 11.0%. This reflects increased gasifier volume and increased catalyst makeup cost due to the preferential tie-up of potassium as inactive aluminosilicates.

The sensitivity cases using K_2CO_3 catalyst all provide investment and gas cost savings relative to mixed catalyst in the <u>present</u> evaluations. However, the gas costs are increased by 3-5% relative to the previous evaluation of the Mixed Catalyst Base Case due to the higher cost of K_2CO_3 relative to Na_2CO_3. With K_3CO_3 catalyst, the incentive increases to reduce catalyst makeup cost by recovering water insoluble catalyst tied up with the ash. Laboratory and engineering studies described previously in this report address the catalyst recovery alternatives.

To identify the impacts of gasifier conditions, it is best to compare the 15% K_2CO_3 catalyst case with each of the other three sensitivity cases in turn. Based on these comparisons, lowering the gasifier temperature from 1300°F to 1200°F saves about 2%, reducing K_2CO_3 catalyst loading from 15% to 10% saves about 0.5%, and increasing the gasifier feed steam rate by 20% costs an extra 2%.

It is premature to draw firm conclusions regarding preferred gasifier operating conditions from these early screening studies, because the bases do not necessarily reflect the extensive data obtained in bench and FBG runs over the course of the Predevelopment Program. In particular, the updated gasifier model was not used. Also, the economic impacts are not necessarily linear or additive because of the complexity of the various gasification plant balances. However, it is clear that data on FBG and fixed bed operations at temperatures lower than 1300°F or at K_2CO_3 catalyst loadings lower than 15% should be closely reviewed to determine whether the gasifier volumes used in these sensitivity studies are representative and, hence, whether the savings shown are attainable.

TABLE 3.2-5

IMPACT OF CATALYTIC GASIFIER OPERATING CONDITIONS ON GASIFIER VOLUME REQUIREMENT

Cases are Defined in Terms of Changes Made from the Following Common Gasifier Basis:

500 psia, 1300°F, 15% K_2CO_3 Catalyst Loading, 90% Carbon Conversion(1)

	Percentage Change in Flow Rates			Normal Preheat Temperature	Relative Gasifier Volume	
Cases	Coal	Steam	Recycle		vs. Previous Base Case(2)	vs. Common Basis Case
Impact of Catalyst Composition						
• Previous Evaluation of Base Case: 7.5% K_2CO_3/7.5% Na_2CO_3 Catalyst	Base	Base	Base	1540°F	100	114
• Present Evaluation of Base Case: 7.5% K_2CO_3/7.5% Na_2CO_3 Catalyst	0%	0%	0%	1554°F	201	229
Impact of Catalyst Loading						
• Common Basis Case: See Above (15% K_2CO_3 Catalyst)	0%	0%	0%	1548°F	88	100
• 10% K_2CO_3 Catalyst	0%	0%	0%	1534°F	119	136
Impact of Gasifier Temperature						
• 1200°F	-1%	+6%	-32%	1397°F	135	154
• 1350°F	+1%	+1%	+29%	1603°F	77	88
Impact of Gasifier Steam Rate						
• Base Steam + 20%	0%	+20%	+20%	1502°F	71	81
• Base Steam - 20%	0%	-20%	-17%	1616°F	142	162
Impact of Two Simultaneous Changes						
• 1200°F and Base Steam + 32%	-1%	+32%	-12%	1353°F	115	131
• 10% K_2CO_3 Catalyst and Base Steam + 20%	0%	+20%	+19%	1491°F	97	111
Impact of Gasifier Pressure						
• 350 psia	0%	+1%	+27%	1491°F	129	147
• 700 psia	+1%	0%	-19%	1630°F	66	75
Impact of Carbon Conversion						
• 80% Carbon Conversion	+10%	-4%	-2%	1601°F	100	114

Notes:

(1) For plant sized to produce 257 GBtu/SD SNG.

(2) In this column, fluid bed volumes are shown as percentages of the volume previously estimated for the Base Case.

Heat and material balances and gasifier model volume predictions were developed for several cases in addition to the cases presented in Table 3.2-4. Table 3.2-5 presents the key results for all cases studied. The cases in the table are sensitivities to the 15% K_2CO_3 case. This catalyst and loading was maintained as a common basis in all but the catalyst composition and loading sensitivities. However, the process stream rates are shown relative to the previous evaluation of the 15% Mixed Catalyst Base Case. Gasifier volumes are shown relative both to that case and to the 15% K_2CO_3 common basis case. All cases were sized to produce 257 GBtu/SD SNG.

3.3 ACID GAS REMOVAL STUDIES

Screening studies were carried out to make a preliminary selection of the preferred acid gas removal system for use with the Exxon Catalytic Coal Gasification Process.

3.3.1 Evaluation of Conventional Acid Gas Removal Processes

A screening quality evaluation of conventional acid gas (CO_2 and H_2S) scrubbing alternatives for use with catalytic gasification was prepared. The alternatives were limited to processes that are commercially demonstrated and have reasonable compatability with the catalytic gasification process. Three systems were considered: (1) selective scrubbing with a heavy glycol solvent, (2) selective scrubbing with refrigerated methanol, and (3) non-selective scrubbing with hot potassium carbonate.

The selective processes recover essentially all the H_2S from the gasifier effluent in an H_2S-rich stream. This stream is concentrated enough to feed to a Claus sulfur recovery plant. Most of the CO_2 is recovered in a second stream and vented. The non-selective process recovers H_2S and CO_2 together in a single stream. The H_2S is then scrubbed from this more dilute stream and converted to sulfur in a process suited for this service. Since this type of sulfur recovery process is more expensive than the Claus process, costs for conversion of H_2S to by-product sulfur are significantly higher with the non-selective process.

The three systems were compared based on the processing conditions and acid gas removal requirements for the Catalytic Coal Gasification Commercial Plant Study Design. Non-confidential vendor design and cost information were used to evaluate the first two acid gas scrubbing alternatives. The vendor cost information was reviewed and put on a consistent basis. An equipment list and cost estimate was prepared on the same basis for hot potassium carbonate scrubbing.

A major problem in comparing these alternative acid gas removal processes is differences in the degree of engineering detail developed for each of the three cases. The basic inputs for these cases were prepared by different engineering organizations. This makes absolute comparison of the processes very difficult. The results of this evaluation must, therefore, be viewed as preliminary. A more thorough and consistent approach would be needed to arrive at definitive conclusions.

The relative investments and gas cost impacts of the three alternative processes are as follows:

	Selective Heavy Glycol Solvent	Selective Refrigerated Methanol	Non-Selective Hot Potassium Carbonate
Relative Investment			
Acid Gas Removal	0.706	0.875	0.337
Sulfur Recovery	0.097	0.074	0.280
Associated Facilities	0.197	0.220	0.690
Total	1.000	1.169	1.307
Relative Gas Cost Impact			
Operating Costs	0.356	0.285	0.223
Capital Charges	0.602	0.708	0.783
Methane Losses	0.042	0.145	0.011
Total	1.000	1.138	1.017

For each case, these economics include the acid gas removal process and its associated facilities (e.g., feed pretreatment, sulfur recovery, final gas cleanup for feed to cryogenic methane recovery, and prorated utilities costs). Capital charges are based on 100% equity funding and 10% constant dollar DCF return.

Based on this preliminary analysis, selective heavy glycol scrubbing was the preferred acid gas removal process for a catalytic gasification SNG plant, but only by a small margin. This system was included in the Commercial Plant Study Design. A non-selective hot potassium carbonate system would have only a 2% greater gas cost impact, and thus, can be considered about equal to the heavy glycol system. The high associated facilities charge for this case is due to hot carbonate's high steam usage. The selective refrigerated methanol system was the least attractive; it increased the gas cost contribution due to acid gas removal by about 14%. One of the major debits for this process is a relatively high methane loss due to high methane solubility in the methanol solvent.

3.3.2 Evaluation of Cryogenic Fractionation for Acid Gas Removal

The objective of this study was to evaluate the technical feasibility of cryogenic fractionation for separating acid gases (CO_2 and H_2S) from the rest of the catalytic gasifier effluent gas, which consists principally of CH_4, CO, and H_2. Conventional methods for removal of CO_2 and H_2S from gas streams generally utilize gas scrubbing with either a chemical or a physical solvent. Typically, acid gases are removed down to desired specification levels by scrubbing the feed gas with the solvent in an absorber. The solvent is then stripped and/or reboiled to separate the acid gases in a regenerator. The three acid gas removal processes reported above represent the conventional approach to acid gas removal.

Fractionation is thermodynamically more reversible than either chemical or physical absorption processes, and, therefore, may be attractive due to lower energy requirements. Additionally, since cryogenic methane recovery is required for CH_4 separation in the catalytic gasification SNG process, integration of the two cryogenic processing blocks could be particularly attractive.

In work done with Exxon funds prior to the current predevelopment phase, a proprietary fractionation scheme had been proposed for separating acid gases without CO_2 freeze-out. However, based on these additional simulation studies of system process variables, it was concluded that CO_2 freeze-out is likely to occur in some part of the acid gas fractionation system throughout the range of tower operating conditions necessary to meet other system limitations. In the course of this study, several fractionation tower heat and material balances were developed using Exxon proprietary correlations of literature data on vapor-liquid equilibria and CO_2 freeze-out in CH_4/CO_2 solutions.

The proposed acid gas fractionation system is severely constrained by phase behavior and process requirements. The operating pressure must be selected to avoid both CO_2 freeze-out and the CO_2 critical point. In addition, the overhead operating temperature must be kept low to maintain a low outlet CO_2 concentration to avoid excessive costs in the downstream molecular sieve final cleanup step preceeding the cryogenic methane recovery system. Furthermore, feed cooling is limited to temperatures above the CO_2 triple point to avoid CO_2 freeze-out in the feed cooler. The combination of these limitations does not appear to provide any feasible operating regime for the tower which could avoid CO_2 freeze-out.

The primary cause of CO_2 freeze-out in the acid gas fractionation scheme is the good separation between CH_4 and CO_2 at the top of the tower. In this part of the tower, the temperature is low enough to allow CO_2 freeze-out, and the volatility of methane relative to CO_2 is sufficiently high so that CO_2 is the primary component in the liquid phase. Since this liquid phase CO_2 concentration is above the limit of CO_2 solubility in CH_4 at these conditions, freeze-out of solid CO_2 would occur. No further engineering work was done under the Predevelopment Program on possible approaches to operation in the CO_2 freeze-out regime.