Several process configurations for CO_2 stripping were devised. All of the configurations were based on Catalyst Recovery Screening Study Case 2, Water Wash with Rotary Drum Filters. Preliminary material balances were completed and were used to select the most promising alternatives. A combination of semi-rich and rich solution CO_2 treatment was selected as the most feasible configuration for Case 2. This configuration is presented in Figure 5.1-17. Semi-rich solution treatment lowers the concentration of potassium silicate in the water wash by pH control. As a result, potential fouling problems are avoided in the rich solution treatment step, where final removal of potassium silicates is accomplished. In addition, potassium sulfides are converted to potassium carbonate by releasing H_2S. It is desireable to remove potassium sulfides, since they have the tendency to oxidize and form inactive potassium sulfate.

Work was completed on a quick study aimed at evaluating the potential for buildup of various inert potassium compounds in the catalyst recycle loop. The purpose of this study was to give guidance to ongoing laboratory programs. Recent data, combined with preliminary material balances, indicated the potential for buildup of potassium chloride, potassium borate, potassium sulfate, potassium phosphate, and other trace impurities, such as sodium, in the CCG catalyst loop. The method used to determine buildup at steady state conditions was also applied to unsteady state conditions, such as might be encountered in the PDU, to determine buildup as a function of PDU run length.

5.2 Systems Modeling

Systems modeling work was carried out as part of the CCG Process Development Program to develop material and energy balance tools which reduce the engineering effort required to do screening studies and process definition studies. A material balance model was completed for the catalyst recovery system. A material and energy balance model for the CCG reactor system was also developed.

5.2.1 Catalyst Recovery Material Balance Model

Catalyst recovery as incorporated in the CCG Commercial Plant Study Design prepared during the Predevelopment Program involves "digestion" of gasifier char and fines with lime to solubilize most of the catalytic potassium salts, followed by multi-stage countercurrent leaching with water to remove the soluble catalyst from the gasifier and calcium solids. Material balances for this system required extensive stage-by-stage hand calculations, as well as some simplifying assumptions. A new catalyst recovery material balance model was developed to perform rigorous stage-by-stage calculations taking into account the solid-liquid separation efficiencies for individual stages. This computer model was used in catalyst recovery system screening studies to evaluate alternative processing approaches and solid-liquid separation techniques.

FIGURE 5.1-17

CATALYST RECOVERY SYSTEM WITH CO_2 TREATMENT

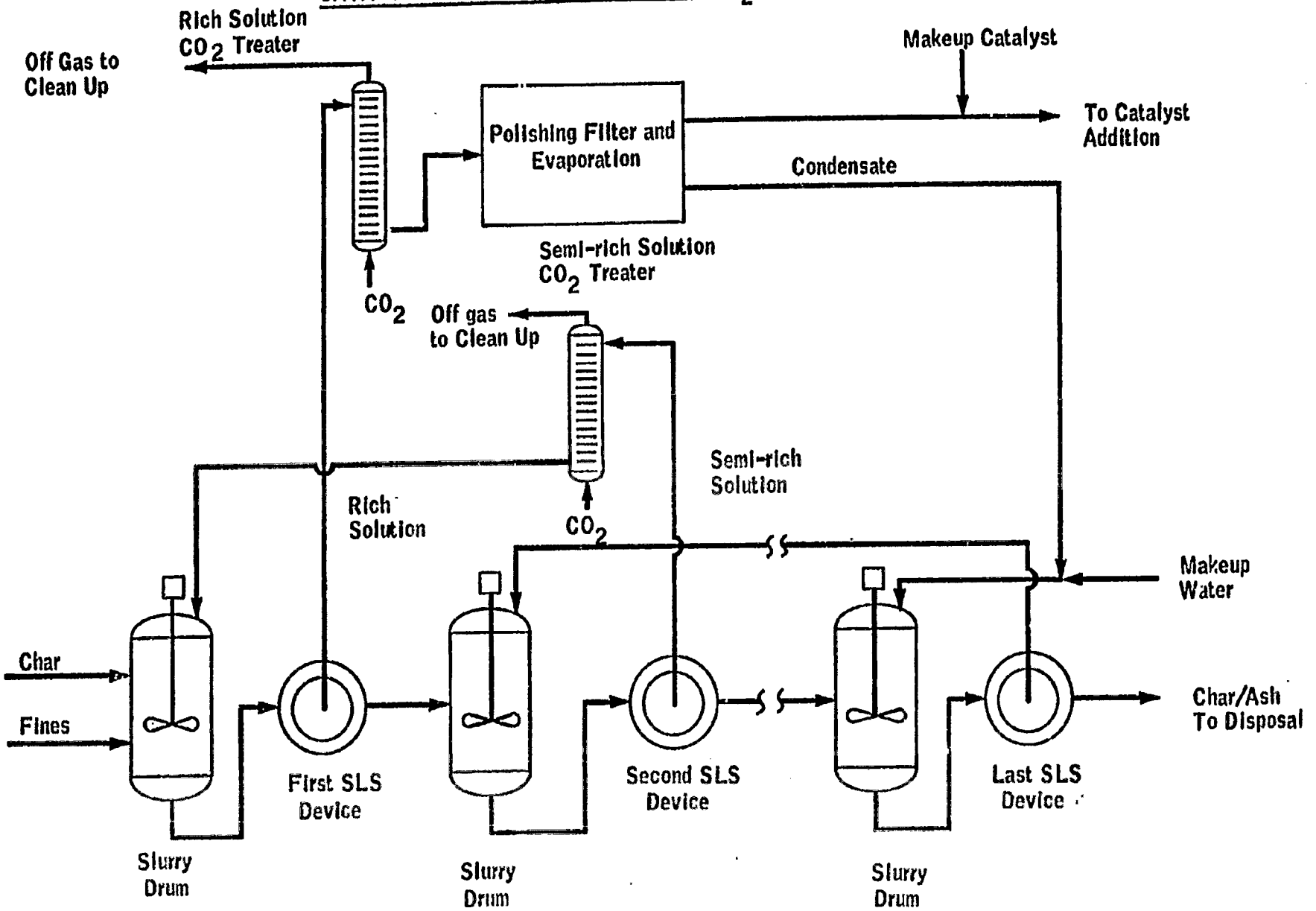


Figure 5.2-1 represents one stage in the countercurrent leaching sequence. Each stage involves mixing of solids from a richer (more concentrated) stage with solution from a leaner (less concentrated) stage, followed by solid-liquid separation to produce a richer solution stream and a leaner solids stream. The catalyst recovery model is capable of handling these four streams, as well as an internal stream representing the feed to the solid/ liquid separation device, and a net side feed stream. The latter stream can be used to represent any special feeds or products that may be involved. One example is lime digestion, where calcium solids are added and water is consumed in chemical reactions. Provision is also made within the model to reflect adsorption of soluble potassium salts on the solids.

The model is capable of calculating any one of the following three parameters, with the remaining two specified by the user:

- Overall catalyst recovery
- Recovered "rich" solution concentration
- Number of washing (leaching) stages

Varying rich solution concentration is equivalent to varying wash water rate. Other required inputs are the rich solids feed to the first (richest) stage as well as the solid-liquid separation performances and side feed streams for all stages.

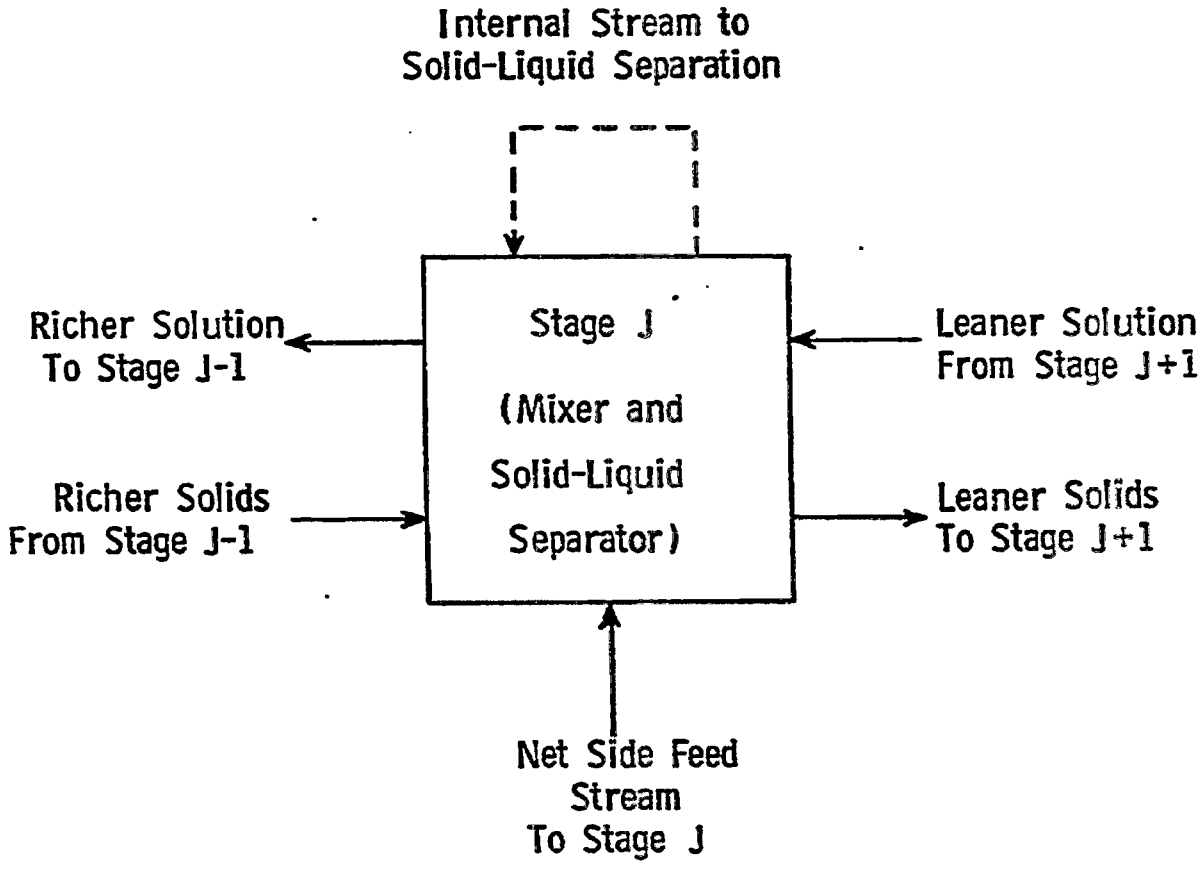
The material balance routines in the model were validated by duplicating the catalyst recovery material balance for the CCG Study Design. The material balances for soluble catalyst salts, water, and insoluble solids all closed to within $\pm$ 0.01%. Numerous test cases were run to validate various material balance convergence and output options. After minor modifications to improve the convergence methods, all cases converged satisfactorily. Computer costs per run were very low. The model was used extensively in the engineering and laboratory studies of the catalyst recovery system reported in Section 5.1.21.

5.2.2 CCG Reactor System Material and Energy Balance Model

A systems modeling effort to develop improved material and energy balance tools for the CCG reactor system was completed in December, 1979. The catalytic gasification reactors and the associated recycle synthesis gas loop and preheat fired heaters are key parts of the commercial process flowsheet. Five of the eight process blocks in the CCG Commercial Plant Study Design were involved in the reactor system modeling effort. These include the Reactor, the Product Gas Cooling and Scrubbing, the Acid Gas Removal, the Methane Recovery, and the Refrigeration sections. These sections carry out the gasification step and the cleanup and separation of the raw gasifier product gases.

Figure 5.2-1

CATALYST RECOVERY MATERIAL BALANCE MODEL:
STAGE CONFIGURATION AND STREAMS



A "first pass" reactor system material and energy balance model was used in preparing the CCG Commercial Plant Study Design. Although this computer model was accurate and proved satisfactory for use in the Study Design effort, the gasifier material balance routine was not specifically intended for coal gasification and the energy balance calculations were complex and cumbersome. In applying this first-pass model, extensive hand calculations were necessary to set up the material balance and to develop solids enthalpy terms for the overall energy balance. Improved reactor system material and energy balance techniques and computational tools were needed to allow the laboratory guidance and process definition studies planned under the current program to be carried out efficiently and consistently.

The new CCG reactor system computer model calculates the overall material and energy balance for the gasifiers, recycle gas loop, and preheat facilities in a commercial CCG plant. The major independent variables which must be specified by the user are as follows:

- Coal feed rate and composition
- Catalyst feed rate (or loading) and composition
- Gasifier pressure and temperature
- Carbon conversion in the gasifiers
- Approaches to shift and methanation equilibria in the raw gasifier product gas
- Steam-carbon gasification reaction equilibrium constant (or steam conversion or steam rate)
- Gasifier heat losses and heat input control allowance
- Extent of shift reaction (if any) in the preheat fired heater

Additional information defining the composition and properties of the solids in the gasifier fluid bed must be provided if the user wants the model to calculate gasifier bed volume using the current gasifier kinetics/contacting model.

The new CCG model is incorporated within the framework provided by Exxon's proprietary process network simulation program, known as "COPE". Four main blocks have been programmed to model the gasifier itself:

- The first block models the CCG gasifier solids material and energy balance. This block feeds coal and catalyst and produces "reacting coal" (the portion of the solids feed which is gasified) and spent solids (residual char, ash, and catalyst). Solids stream enthalpies, including the effects of catalyst-coal reactions, are also calculated.

- The second block feeds the "reacting coal" and the various gaseous feed streams and produces a product gas at specified shift and methanation equilibria.

- The third block carries out the overall gasifier energy balance. The model has the flexibility to energy-balance other related reactor systems, such as steam reformers.

- The fourth block incorporates the current gasifier kinetics/contacting model. This optional feature allows calculation of the gasifier bed volume along with the material and energy balance.

The gasifier model was broken down into these four independent functional blocks to facilitate modeling of flowsheets or gasifier configurations different from the base case in future lab guidance and process improvement studies.

In order to simulate the material and energy balance for a CCG reactor system, the model blocks are incorporated in a COPE process network. The network used to model the reactor system for the CCG Commercial Plant Study Design is illustrated in simplified form in Figure 5.2-2. The network joins together the three required blocks, models the material balances for the product gas cleanup and separations steps downstream of the gasifier, and converges the overall material balance and gasifier/preheat fired heater energy balance.

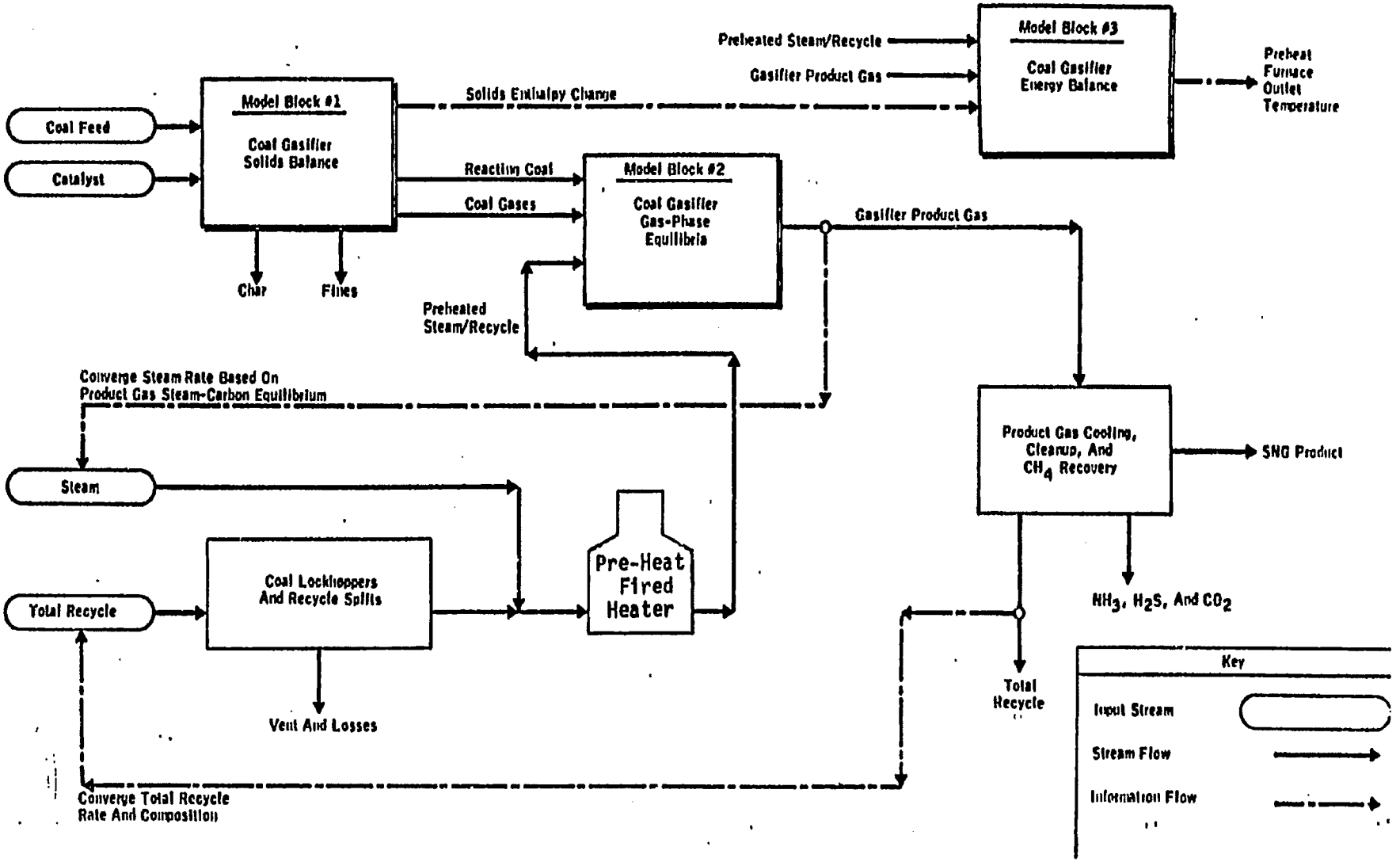
The calculations are relatively complex. Two nested loops are used to converge the overall material balance. The inner loop determines the steam rate to the gasifier based on product gas steam-carbon equilibrium (or gasifier steam conversion). Within this inner loop, the gasifier material balance is calculated by model blocks one and two. The principal feeds are coal, catalyst and preheated steam/recycle, and the principal products are char, fines, and gasifier product gas. The outer loop converges the recycle (synthesis gas) stream rate and composition, using a series of COPE operations. After the material balance is converged, the gasifier energy balance is closed by model block three. The gas-phase feed and product streams are fed to model block three directly. The impact of solids on the gasifier energy balance is accounted for by using a solids enthalpy change transferred from model block one. Model block three calculates the steam/recycle preheat fired heater outlet temperature required to maintain the desired gasifier operating temperature, with or without allowance for potential shift reaction in the fired heater.

In developing the converged overall balance, the COPE network is used to simulate the material balance impacts of several process systems. For example, the network models, in simplified fashion, the acid gas removal, molecular sieve, and cryogenic methane recovery steps. The effects on the recycle gas loop of the coal lock hopper pressurization system, the coal injection system, the gasifier char withdrawal system, and gas losses in the various processing steps are also simulated.

The majority of the CCG model development effort centered on programming the four main blocks described above. Additional details on each of these blocks are provided in the following paragraphs.

FIGURE 5.2-2

FLOW DIAGRAM FOR COMPUTER SIMULATION
OF CCG COMMERCIAL PLANT STUDY DESIGN



First, the coal gasifier solids balance block feeds coal and catalyst, produces char and fines streams which include the catalyst leaving the gasifier, and calculates the total enthalpy change of the solids across the gasifier. The routine requires knowledge of the coal pyritic sulfur, sulfatic sulfur, alumina, silica, and "inert" ash (excluding alumina and silica) to calculate the extent of reactions between catalyst and coal mineral matter. This information is inputted by specifying the coal feed stream analysis in the manner shown in the left column of the table below. The components listed in the right column of the table are accepted in the catalyst streams to and from the model block.

COMPONENTS FOR CCG GASIFIER SOLIDS BALANCE BLOCK

Coal Stream	Catalyst Streams	
Carbon	KOH	Principal forms
Hydrogen	K_2CO_3	in catalyst fed
Oxygen	K_2S	to gasifier
Nitrogen	$KHCO_3$	
Organic Sulfur	KHS	
Pyritic Sulfur	K_2SO_3	
Sulfatic Sulfur	K_2SO_4	
Ash*	$K_2S_2O_3$	
Alumina (Al_2O_3)	K_2S_2	
Silica (SiO_2)	Inert Forms	
Coal Moisture	K (in K-Char)**	Principal forms
	$KFeS_2$	in catalyst leav-
	$KAlSiO_4$	ing gasifier,
	$K_2O \cdot xSiO_2$	along with K_2CO_3

*Excluding alumina and silica.

**K-Char represents the complex formed between catalytically active potassium salts and coal-derived char under gasification conditions. E.g., the reaction for its formation from K_2CO_3 can be written $K_2CO_3 + 2H\text{-Char} \rightarrow 2K\text{-Char} + H_2O + CO_2$.

A key objective of the CCG Process Development Program was to better define the catalyst forms and amounts which will be present when the CCG catalyst recycle loop is closed. It is expected that the first three catalyst components listed will be the predominant forms in the catalyst fed to the gasifier. The last four catalyst forms, along with K_2CO_3, are expected to be predominant in the catalyst leaving the gasifier. Smaller amounts of the other components may also be present in the closed loop.

The enthalpy change of the solids across the gasifier is calculated in this first model block beginning with the complete material balance for feed and product solids broken down into the components listed above. Heats of

formation for the organic portions of the coal, char, and fines streams are calculated using an equation derived from the Mott-Spooner heat of combustion correlation (Mott, R. A, and C. E. Spooner, Fuel, 19 (10), 226-231, 242-251 (1940)). Heats of formation for most of the catalyst components and for alumina and silica compounds in the coal mineral matter were available in the general literature. It was necessary to estimate heats of formation for $KFeS_2$ and $K_2O \cdot xSiO_2$. An approximate heat of formation for K·Char was developed from calorimetry data on the heat of mixing catalyzed char with water. The heat of dehydration for any $K_2CO_3 \cdot 1.5\ H_2O$ in the catalyzed feed coal can be reflected in the energy balance at the user's option. Heat capacity relationships for coal, char, and ash were developed from a paper by Lee (Lee, A. L., "Heat Capacity of Coal," Am. Chem. Soc., Div. of Fuel Chemistry, Preprints, 12 (3), 19-31 (1968)). Heat capacities were not available in the literature for a few of the catalyst compounds. These were set equal to the heat capacity (on a weight basis) of either K_2O or K_2SO_4, as judged appropriate. Because of the approximations and assumptions involved, there is some uncertainty in the CCG gasifier enthalpy balance as currently calculated by the model. Work to reduce this uncertainty is planned later in the current program.

The second block calculates the gasifier product gas rate and composition based on simultaneous shift and methanation equilibria. For specified coal and gas feed streams, shift equilibrium temperature, methanation equilibrium temperature, and gasifier pressure, an equilibrium product gas is calculated. The two reactions considered along with their associated equilibrium expressions are:

- Shift reaction:

$$CO + H_2O = CO_2 + H_2 \qquad K_S(T_S) = \frac{(CO_2)(H_2)}{(CO)(H_2O)}$$

- Methanation reaction:

$$CO + 3H_2 = CH_4 + H_2O \qquad K_m(T_m) = \frac{(CH_4)(H_2O)}{(CO)(H_2)^3} \cdot \frac{G^2}{P^2}$$

where:

$K_S(T_S)$ = shift equilibrium constant at equilibrium temperature T_S
$K_m(T_m)$ = methanation equilibrium constant at equilibrium temperature T_m, atm^{-2}
P = gasifier pressure, atm
G = total product flow rate, lb-moles/hr
(x) = flow rate of component x, lb-moles/hr

Equilibrium constants are calculated by the program but may be overriden by the user. First order non-ideality corrections are made using calculated fugacity coefficients. The model block calculates the apparent steam-carbon equilibrium constant based on the composition of the product gas so that the COPE network can converge on equilibrium for this gas-solid reaction. The steam-carbon reaction and the associated equilibrium expression are:

- Steam-carbon reaction:

$$C + H_2O = CO + H_2 \qquad K_c(T_c) = \frac{(CO)(H_2)}{A_c(H_2O)} \cdot \frac{P}{G}$$

where:

$K_c(T_c)$ = steam-carbon equilibrium constant at equilibrium temperature T_c, atm
A_c = carbon activity (graphite = 1.0)
P, G, (x) are defined as above

In addition to CCG reactors, the equilibrium block can be used to model the material balance for other related reactor systems, including steam reformers, shift reactors, and methanation reactors.

The third block performs an overall energy balance around the CCG gasifier with a total of up to nine feed and product gas streams. Heats of formation at 100°F for the CCG gas components were taken from the literature. Stream sensible enthalphies at conditions and at the reference state (ideal gases at 100°F) are obtained from the proprietary data base built into the COPE program. In calculating the overall enthalpy change around the gasifier, the model takes into account the solids enthalpy change, gasifier heat losses, and heat input control allowance as well as the gas stream enthalpies. The program operates in one of two modes:

- One routine energy-balances the gasifier by varying the temperature of the steam/recycle gas feed, with or without allowance for water-gas shift reaction in preheat. Under this option, the computer routine will converge upon the required preheat temperature assuming a specified percentage (0-100%) of the shift reaction which would occur if the stream were in full shift equilibrium.

- The alternative routine does not attempt to energy-balance the gasifier, but instead uses the specified stream temperatures to calculate the energy balance "miss", or delta enthalpy. This option allows the COPE network to balance the gasifier outside of this block by, for example, varying the flow rate of a feed stream to the unit. (Most cases using steam reforming for heat input to the gasifier are balanced in this manner.)

This block also performs a consistency check to see if the streams to be energy-balanced are in material balance. The model can also close the energy balance by varying the temperature of a product rather than a feed, which may be appropriate in some modeling situations.

To enable its use in conjunction with the material and energy balance routines, the existing stand-alone reactor kinetics/contacting model was incorporated into its own block. This reactor model block receives as feeds the catalyzed coal, the bottom-fed steam/recycle gas mixture, and the coal