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SYSTEMS STUDIES OF COAL-CONVERSION PROCESSES
USING A REFERENCE SIMULATOR

Final Report for the Period
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1. Overview

1.1 Project Objectives

This project had two principal objectives. The first was to construct a modular computer simulation/design package suitable for coal conversion systems modelling and analysis. The second objective was to use this package to study in a programmatic fashion an array of coal conversion flowsheet alternatives. The computerized package was to have sufficient flexibility to permit the user to incorporate reasonable process alternatives and engineering design modifications without extensive restructuring of the coding. The package was also to have the capability for physical properties estimation, detailed plant capital cost estimation and project economic evaluation. The detailed process unit models specific to selected coal conversion processes were to have been based on bench and large scale pilot data developed by other organizations under ERDA/DOE contracts. The "Clean Boiler Fuels from Coal" (CBFC) Conceptual Demonstration Plant defined in a 1975 ERDA Study by the Ralph M. Parsons Company was the first conversion process to have been investigated. Other variations to this flowsheet which retained the BIGAS and SRC primary conversion sections were next to have been investigated, followed by other possible alternations involving conversion technologies to be proposed by DOE/ERDA. The CBFC process was subsequently abandoned as base case flowsheet for study. This process was replaced at DOE/ERDA request by the ICGG process and later by a modified COED flowsheet which incorporated the general ICGG design concept but employed non-proprietary process units.

1.2 Project History

The project concept was formulated after discussion with OCR Staff early in 1974. A formal proposal was submitted to OCR in November 1974. A revised

proposal was resubmitted in November 1975 and the project was initiated on March 12, 1976 under the aegis of the newly formed ERDA Fossil Demonstration Plants Division. As part of the initial contract task schedule the BIGAS/SRC based "Clean Boiler Fuels from Coal" conceptual process was selected as project base case flowsheet. Purdue University proceeded with data gathering activities for this process including meetings with representatives of the Pittsburgh & Midway Coal Company, the ERDA SRC contractor; the Bituminous Coal Research Laboratory, the BIGAS gasifier developer; PERC; IGT; Oak Ridge; the Bureau of Mines, Morgantown, and other relevant data sources.

On July 20, 1976 by letter from the contract technical representative, ERDA requested that the CBFC process be abandoned in favor of the conceptual process proposed by the Illinois Coal Gasification Group. This process had been presented to ERDA in response to an RFP for Pipeline Gas Demonstration Plants, and incorporated concepts tested during project COED, involved a proprietary COGAS gasification/combustion section, the proprietary H-oil hydrotreating unit, as well as the RMP bulk methanation system. By letter dated August 2, 1976, Purdue University informed ERDA that the change was acceptable but that it would result in a four month delay in project time tables, assuming process data were released to Purdue by the end of August, 1976. By May of the following year such data were still not forthcoming because of complications in the negotiations between (now) DOE and ICGG. At that time, (Contract Amendment Dated 7/7/77 DOE requested, and Purdue agreed, to undertake an additional task under the existing contract. This task involved the formulation of and literature

review for a conceptual base case process which paralleled the ICGG proposal but which substituted project COED or other publically disclosed process units for the proprietary process sections of the ICGG process.

In the interim, work proceeded on the other project tasks; development of the process simulation, the physical properties, the costing, pyrolysis, and flowsheet balancing calculation packages. Throughout this period, efforts by Purdue as well as the DOE technical representative were continued to obtain quantitative information about the conditions and design specifications of the ICGG process but no process information beyond that available as qualitative presentations made by ICGG at AIChE and AGA meetings were forthcoming. This status remained unchanged until the termination of the contract.

In spite of the repeated modifications of the project objectives and the disruptive organizational and personnel changes during the history of the project, the primary project objectives were met. The simulation package was completed and models of the main process sections of the modified COED flowsheet were implemented. However, as a result of the major time delays which were incurred and the three months required for the conceptual flowsheet study, the sequence of flowsheet case studies as well as the intended studies involving alternative primary conversion units could not be carried out within the time and budgetary constraints of this contract.

1.3 Summary of Project Technical Accomplishments

The primary project achievements consist of the following:

- i) a conceptual flowsheet study defining a modified COED coal conversion process
- ii) the development of a steady state chemical process simulation system
- iii) the formulation and execution of models of the key sections of the modified COED process using the simulation system
- iv) the development of reactor models for the pyrolysis, gasification, and combustion sections of the process

The conceptual process which was developed employs Illinois No.6 coal and incorporates the basic processing sequence proposed by the Illinois Coal Gasification Group. The flowsheet differs from the ICGG proposal in that proprietary or otherwise ill-defined processing steps are replaced with units whose operating data are adequately reported in the open literature and for which satisfactory design models can be formulated. The key steps of the process are: fluidized bed pyrolysis using a sequence of three reactors, steam-char gasification using a fluidized bed reactor with heat transfer via a recycle char stream, a fluidized bed char combustor using a limestone bed additive, a water quench pyrolysis vapor recovery system, oil hydrotreating using conventional trickle bed reactors, acid gas removal using a DEA system, shift-methanation via a sequence of packed bed reactors, hot carbonate CO_2 removal, and a reformer based

hydrogen plant. A review of the key details of the flowsheet is given in Section 2. A detailed report including the process flowsheets, preliminary material balances, discussion of the pertinent literature, and justification of the unit selection was given in FE-2275-5. This flowsheet study has served to define the base case flowsheet used by both Purdue University and Lehigh University (EX-76-C-01-2338) in subsequent steady state and dynamic modeling work, respectively.

The steady state process simulation system LSP (Large Scale Steady State Program) developed under this project is a general purpose package for modeling chemical process flowsheets. In this system flowsheets are represented in terms of equipment nodes and process streams and the equipment nodes are modeled using a library of process equipment modules. In LSP a process simulation is formulated by identifying the chemical components present, defining the process input streams and the stream-node connections, selecting the modules for each node and specifying the node equipment parameters as well as the appropriate design constraints. LSP can accomodate streams containing pure component, boiling fractions, solid components, as well as user selected auxiliary stream characteristics such as heteroatom flows or size fraction flows. The system incorporates an efficient stream and equipment parameter storage scheme which allows execution of realistically sized simulations on middle size range machines without complex overlays. Finally, LSP offers the choice of either an advanced form of the sequential modular strategy or a two level strategy in which calculations alternate between an approximate (linearized) upper level process model

and one or more, lower-level, process section simulations.

The LSP package consists of the executive, an information management system, an equipment module library, a numerical calculation library, as well as a program (LINBAL) for executing the upper level model, and is directly linked to a physical properties estimation package (PPROPS). The equipment library contains some 40 unit modules ranging from general purpose routines, such as equilibrium stage column, plug flow reactor, and two or three phase flash modules; to non-conventional modules such as Venturii scrubbers, electrostatic precipitator, and ejector; to specialized modules such as a steam reformer and coal oil hydrotreating reactor.

The physical properties package is a general purpose program designed for stand-alone use or use in conjunction with LSP. The package has been designed for computational efficiency and simplicity; hence, does not include roadmapping features, data regression facilities; or extensive equation of state options. Properties which are provided include: enthalpy, entropy, and density for vapor-liquid streams; heats of reaction and combustion, chemical equilibrium constants and K values for two phase mixtures and stream viscosities. Flash calculations are performed as part of this package. Ideal solution Redlich-Kwong, regular solution, Grayson-Streed, Chao-Seader, and Wilson options are provided. Boiling fraction component properties are estimated using Kesler-Lee and API Data Book methods. A properties constant data base consisting of 53 constants per species is included for common species of interest in refinery and coal conversion process applications. The data base may be easily expanded on a permanent basis or overridden for a given application.

The LINBAL program is a general purpose mass and energy balancing package which can either be used on a stand-alone basis or linked with LSP when the two level execution strategy is used. In LINBAL the mass and energy

balances are decoupled into two separate calculation segments. LINBAL uses linear multiple input-multiple output unit modules but can handle linear and nonlinear equality as well as linear inequality constraints. The solution procedure employs a novel mixer equation approach under which at most as many equations must be solved simultaneously as there are tear streams which would have to be converged in the conventional sequential modular approach. Constraints are accommodated by generating a parametric solution. Input requires description of the flowsheet in terms of unit modules, each with its module parameters. Three general types of constraints are allowed: linear equations in the species flows, linear inequalities, and nonlinear equations. The user may specify system of units and mass or molar flow basis. Output consists of echo of input data; notes on how the solution was obtained; calculated values of module parameter which had not been specified by the user; and, a complete tabulation of the flowsheet stream table.

Associated with LSP is a capital cost estimation and profitability analysis program PCOST. The package contains an extensive data base of equipment cost correlating functions, an efficient data base management system, a library of routines for equipment cost estimation, and programs for total plant cost estimation. Total plant cost is based on a detailed estimate of utilities and other off-sites and a factored estimate of major process equipment installation and other costs. An optional economic evaluation calculation based on a DCF analysis can also be made. The user has the option of selecting specific cost correlations or of obtaining a range of cost estimates based on all available correlations for a given equipment item. Required user input consists primarily of equipment specifications with the level of detail depending upon the level of estimate required. The user may enter actual quoted costs for any item, may supply special multipliers for FOB cost, installation labor and materials,

and may select any particular cost escalation index. Flexible report generating options are provided including detailed plant section-wise or equipment class-wise summaries. Further details of the LSP system and its components will be reviewed in Section 3 of this report.

The LSP package has been used to formulate models of the following key process sections of the modified COED process: the vapor recovery system, the hydrotreating system, the hydrogen plant, two types of acid gas removal systems, the bulk methanation system, and a process utilities system. Each of these process section models is a moderately sized simulation requiring some 100 K octal words of storage and perhaps 100 to 500 secs of CPU time for converged solution. Details of these systems are given in Section 4.

Finally, detailed reactors models were developed of the primary coal conversion reactors: the fluidized bed reactors for pyrolysis, gasification, and combustion and the entrained flow lift-tube partial combustor. The pyrolysis reactor system model accomodates up to five fluidized bed reactors with char and gas recycle between stages. Pyrolysis is modelled using the kinetics developed by Suuberg et al.(1977) for lignite. Analogous kinetics were fitted to COED data for Illinois No.6 coal. The pyrolysis reactor system program includes an optional Monte Carlo simulation calculation which allows a convenient check of the key model assumptions when other kinetics are substituted into the model.

The fluidized bed gasifier and combustor models are treated within a single general purpose fluidized bed reactor model. The model uses a two phase mixing model and includes provisions for plug flow grid region and freeboard region calculations. Detailed particle population balances are performed which allow particles to vary in both size and density. Since the model allows both heterogeneous reactions and homogeneous gas phase reactions, it can be used for

either gasifier or combustor modelling by adjustment of program calculation option parameters and insertion of the appropriate reaction stoichiometry and kinetics. Both gasifier and combustor cases have been implemented.

The lift-tube model involves a plug flow representation with combustion on the solid surface and homogeneous CO-oxidation in the interstitial gas. Particle population balances are incorporated by using a discretized representation of the distribution. Discretization was required because of severe stiffness encountered in the numerical integration. In addition to accounting for reaction and dilute phase transport, the model also incorporates an exponential gas mixing mechanism which allows representation of the effects of incomplete mixing of the gas and solid phases.

Finally, an integrated but simplified model of the pyrolysis, gasifier, lift-tube and combustor units has been implemented. Because of computational difficulties and time limitations the detailed combustor-gasifier models had to be replaced by simplified models for purposes of integrated simulation of this coal conversion section.

1.4 Project Publications

The technical details of the work of this project have been reported in DOE/ERDA reports available through NTIS, regular journal publications, conference papers, comprehensive program manuals, as well as graduate student theses.

A list of these documents follows:

1. Reports

a. Regular Quarterly Reports

2275-1 through 2275-4

2275-6 through 2275-11

b. Special Reports

2275-5 Conceptual Modified COED Flowsheet Study

"Coal Conversion Plant Computer Simulation", in Proc. of Conference on Mathematical Modelling of Coal Conversion Processes, Michael J. Biallas (ed.) CONF-761104 Nov. 1976, pp. 78-94.

c. Summary Reports

Annual Summaries Submitted for DOE/EODA Annual Report 1977, 1978

"Systems Studies of Coal Conversion Processes Using a Reference Simulator" Proceedings 5th Annual DOE/Fossil Energy Conference on University Coal Research, August, 1978.

2. Publications

a. Journal Publications

- a.1 "Solution of Material Balances for Flowsheets Modelled with Elementary Modules: The Unconstrained Case", AICHE J. 25, p. 220, 1979
(presented AIChE Annual Meeting, New York, Nov. 1977).
- a.2 "Solution of Material Balances for Flowsheets Modelled with Elementary Modules: The Constrained Case", AICHE, J. 25, p. 109, 1979.
(presented AIChE Nat'l Meeting, Philadelphia, PA. June, 1978).
- a.3 "Solutions of Balances for Flowsheets Modelled with Elementary Modules: Extension and Computational Aspects", to appear in Computers and Chemical Engineering, 1979.

- a.4 "A Hierarchical Strategy for Large Scale Process Calculations", to appear in Computers and Chemical Engineering, Spring 1980.
(presented 12th Symposium on Computer Applications in Chemical Engineering, Montreux, Switzerland, April, 1979).
- a.5 "Modeling of Staged Fluidized Bed Pyrolysis Reactors",
I & EC Process Design and Development, 19, p. 15, (1980).
(presented AIChE Nat'l Meeting, Philadelphia, PA. June, 1978).
- b. Conference papers (distributed at meetings but not yet published).
 - b.1 "Modeling and Analysis of an Integrated Coal Pyrolysis, Gasification, and Combustion Reactor System", AIChE Annual Meeting, Miami Beach, Nov. 1978.
 - b.2 "Simulation of a Coal Oil Hydrotreating Section", AIChE Nat'l Meeting, Houston, Texas, April, 1979.
 - b.3 "A Two Level Approach Exploiting Sparsity in Material Balancing", AIChE Nat'l Meeting, Houston, Texas, April, 1979.

3. Project Manuals

A Physical Properties Package for Computer-Aided Process Design, May, 1979.

PCOST: Costing Program, May, 1979 revised Dec. 1979.

Material Balance Program-II, December, 1977 revised July, 1978.

Energy Balance Program-II, September, 1978.

SS/PP: Steady State Pyrolysis Program, May, 1978 revised May, 1979.

DSP: Detailed (Steady State) Simulation Program May, 1979 (obsolete)

LSP: Large Scale Steady State Program Version II November, 1979.

LSP Equipment Library Manual, December 1979.

LSP Process Application Documentation, December, 1979.

BED: Generalized Fluidized Bed Reactors Model, December, 1979.

4. Graduate Student Thesis (all at Purdue University)

M. Tanzio, "Computer Models for Entrained Coal Gasification and Fluidized Bed Methanation", M.S. ChE., Dec. 1977.

G. Fazzoni, "Computer Aided Costing and Applications to Acid Gas Removal Systems", M.S. ChE. August, 1978.

J.R. Ford, "Computer Model for Coal Oil Hydrotreating Simulation" M.S. ChE. December, 1978.

C.R. Wilkinson, "Computer Models for Heat Recovery and Utilities Systems in Chemical Process Plants", M.S. ChE. August, 1979.

J.S. Boo, "Computer Model of a Coal Conversion Hydrogen Plant", M.S. ChE. December, 1979.

W. Wiede, Jr., "Steady State Simulation of Water and Oil Quench Vapor Recovery Systems in a Coal Conversion Process", M.S. ChE. December, 1979.

B. Overturf, "Gas-Solid Reactor Models with Application to Coal Conversion", Ph.D. ChE. May, 1980.

P. Buchanan, "Comparative Study of Methanation Reactors in Coal Conversion", M.S. ChE. May, 1980.

2. Conceptual Flowsheet Study

2.1 Objectives of Study

Because of difficulties in securing design details for the ICGG process, DOE initiated a study to define a flowsheet similar in concept to that proposed by ICGG but differing in that proprietary or ill-defined process units were to be replaced by suitable alternatives chosen from the open literature. The criteria for choosing alternatives were thus suitability for the intended service and availability of modelling data. The resulting conceptual flowsheet was intended to serve as base case for the Purdue University modeling efforts as well as those of a parallel project conducted by Lehigh University involving dynamic modeling.

2.2 Definition of Flowsheet

A block diagram of the flowsheet which resulted from this study is shown in Fig. 1. The process employs the following key steps:

1. Coal Injection and Drying

Sized coal from the crushing and preparation facility is raised to 85 psia pressure using a dense phase injection system and transported to a fluidized bed dryer. In that unit the coal is preheated to 350°F and dried using combustor flue gases.

2. Fluidized-Bed Pyrolysis

Three pyrolysis reactors are operated at 600, 850 and 1000°F and 65 psia with char recycle between stages. Heat for this unit is supplied entirely by the synthesis gas generated in the char gasifier.

3. Char Gasifier

Char from the last pyrolysis stage is reacted with steam in a fluidized bed gasifier operated at 90 psia and 1550°F. Heat for gasification

FIG. 1. BLOCK DIAGRAM OF COED CONCEPTUAL PROCESS

is supplied indirectly by heating a recycle char stream with combustor flue gases.

4. Char Combustor

Residual char from the gasifier and fines from the process are burned with air in a pressurized fluidized bed combustor. The combustor employs limestone as SO_2 scavenger and is operated at 1820°F and 125 psia. Limestone is not regenerated.

5. Water Quench Pyrolysis Vapor Recovery

Hot pyrolysis vapors are quenched and separated using two stages of venturi scrubbers, decanters, electrostatic precipitator, and dehydrators.

6. Rotary Pressure Precoat Filtration

Condensed pyrolysis oil containing the entrained fines is filtered prior to hydrotreating using rotary filters with precoat at 350°F and 60 psia.

7. Oil Hydrotreating

Filtered oil is treated with hydrogen in conventional downflow trickle-bed catalytic reactors to remove heteroatoms and decrease viscosity. Two fixed bed reactor stages are used operating at 2400 psia and 650°F inlet conditions.

8. DEA Acid Gas Removal

Pyrolysis gases are compressed to 500 psia and scrubbed of H_2S and a portion of the CO_2 using a standard DEA absorber stripper system.

9. Light Hydrocarbon Recovery

Desulfurized pyrolysis gases are stripped of light hydrocarbons using a pressurized oil scrubbing system.

10. Fixed Bed Bulk Methanation

The carbon oxides in the process gas product are converted to CH_4 using six stages of steam moderated combined methanation shift reactors analogous to the RMP process.

11. Hot Carbonate Bulk CO_2 Removal

Methanated product gases are purified of CO_2 using hot carbonate absorption system.

12. Final Compression and dehydration

The resulting high Btu gas is compressed to pipeline gas pressures and dried using a standard glycol dehydration unit.

13. Hydrogen Production Unit

A portion of the desulfurized product gas is fed to a conventional hydrogen generation plant. The plant involves steam reforming, two stage shift reaction, CO_2 removal using the hot carbonate process, and clean-up methanation.

14 & 15. Clean-up of process waste streams

The H_2S bearing gases from the acid gas removal unit are processed in a Claus plant the design of which is not detailed. The sour waters generated in the process are reclaimed using existing phenol absorption and ammonia as well as H_2S stripping operations.

2.3 Discussion of Choices

The reasons for the selection of the process units enumerated above will be briefly recounted in this section. For a detailed discussion the reader is directed to FE-2275-5.

1. Coal Injection and Drying

The system selected is analogous to that employed by Holmes, et. al. [1977]. That design is essentially based on a design developed by PETROCARB to feed coal at 120 psia using CO_2 as injection gas. The coal drying via a fluid bed was recommended by FMC in their conceptual COED process studies [1975].

2. Pyrolysis Section

A three stage pyrolysis system involving fluid beds at 65 psia and 600, 850, and 1000°F was chosen based on ICGG disclosures. Both forward and recycle char flows between stages are used. All of the heat required by the system and the fluidizing gas for the last pyrolysis stage is supplied by the gasifier product gas as proposed by ICGG. Char transport is carried out in dense phase using scrubbed and compressed pyrolysis gas as transport gas, analogous to FMC designs [1975]. Kinetics for reactors modelling were obtained by fitting COED data to expressions suggested by the work of Sunberg, et. al. [1977].

3. Char Gasifier

A conventional steam-char fluid bed was selected. The kinetics reported by IGT are appropriate [1976]. The heat transfer via recirculating hot solids is as proposed by IGT. Modelling of the lift tube requires char combustion kinetics which are available in the literature. Correlations for choking velocities and dilute phase transport pressure drops are also available. Detailed data for the operating lift-tubes are not available.

4. Char Combustor

No data could be found in the open literature for designing or scaling of cyclone combustors. Consequently a moderate pressure (120 psia) fluid bed with limestone sorbent was selected. Data on such units are increasingly available

from DOE funded projects. The combustor uses air as oxidant and does not incorporate regeneration because of the continuing uncertainties over the chemical and physical properties of regenerated limestone. While a cyclone combustor would operate under slagging conditions, the fluid bed combustor must operate at temperatures substantially below slagging. Preliminary calculations indicate that the lower temperature fluid bed combustor will thus lead to lower lift-tube char temperatures and consequently increased char recycle rates between the gasifier and the lift tube, perhaps as high as 25 times the gasifier feed.

5. Water Quench Vapor Recovery

The system used is essentially that employed in the COED pilot plant. Adequate three phase equilibrium data cannot be derived from COED pilot plant reports. However, the Peng-Robinson correlations can be used with caution.

6. Filtration

Extensive but unsystematic data for pressure filtration of Illinois No. 6 Coal Oil is reported in COED pilot plant reports. Rotary units were employed in COED work and recommended by FMC in their conceptual design report.

7. Oil Hydrotreating

Since no publicly available data on ebullating bed hydrotreating could be found, a conventional multiple fixed bed system was selected. Data for Illinois No. 6 Coal Oil hydrotreating in such reactors was collected in project COED. The standard design reported by Parsons in another conceptual study was followed [1975].

8 & 11 Acid Gas Removal

A standard DEA system was selected for scrubbing H_2S and CO_2 from the pyrolysis gases. DEA data is readily available in the literature. A non-catalyzed hot potassium carbonate system was selected for CO_2 removal in the bulk methanation

plant and in the H_2 plant. Data on catalyzed systems are not publicly available.

9. Light Hydrocarbon Recovery

A system analogous to that reported by Foster-Wheeler in a conceptual Consol design [1972] was adopted. Vapor-liquid equilibrium data for absorber and flash units must be estimated from API correlations.

10. Bulk Methanation

The flowsheet selected is patterned after that reported by Parsons in describing their RMP shift-methanation process. The kinetics used were those developed by Lehigh by adjusting the parameters for the accepted form of the kinetic expressions so that scattered Parsons results could be matched as closely as possible.

12. Fluid Compression and Dehydration

The standard design reported in Campbell [1970] is used.

13. Hydrogen Production

The standard design given by Holmes, et. al. [1977] is used. The reformer is designed based on heat transfer limitations. The shift reactors and clean-up methanator is designed using Girdler kinetics.

2.4 Design Basis

The feed rate to the process was assumed to be 1200 T/Hr of coal on a moisture free basis as fed to the pyrolysis unit. The coal was assumed to have the properties of the Illinois No. 6 Coal most extensively studied in COED operations. The averaged analysis of the coal as given in COED reports [1975] is:

Proximate Analysis, dry wt %

Volatile Matter	38.0
Fixed Carbon	49.8
Ash	12.2

Ultimate Analysis, dry wt %

Carbon	67.1
Hydrogen	4.8
Nitrogen	1.3
Sulfur	4.1
Oxygen	10.5
Ash	12.2

Moisture as received, wt % 14

The principal products of the process are high Btu gas meeting pipeline gas standards and a synthetic oil meeting No. 4 fuel oil specifications.

Properties of the high Btu gas [Skamser, 1976].

CO concentration $\leq$ 0.1% (mole)

H₂ concentration $\leq$ 3% (mole)

H₂O content $\leq$ 7 lbs/MMSCF

H₂S content $\leq$ 0.25 grains/100 SCF

total Sulfur content $\leq$ 10 grains/100 SCF

Properties of the oil product [FMC Corp., 1974].

API gravity 25°

Sulfur, weight % 0.3 max

Ash, weight % 0.3 max

Ash, weight % 0.1 max

Flash point, °F 130 min

Based upon these assumptions, the preliminary balances indicate a production of:

235 MMSCFD of high Btu coal
32,460 BBL/D of synthetic oil

3. Generalized Simulation/Design Programs

The LSP simulator packages consists of an executive, the module equipment library, the properties estimation package, the linear balancing program and the process cost estimation package. In this section a brief review of the stages in the development of these programs and a summary of their key features is presented.

3.1 The LSP Executive and Module Library

3.1.1 Development Overview

In order to expedite the assembly of process simulation models, and standardize the results such models will yield in comparative process studies it is highly desirable to employ a steady state process simulator. Recognizing this fact, one of the key tasks of this project has been the development of such a simulator. In the initial stages of this project, it had been the intention of ERDA to secure for this purpose portions of the Flowtran flowsheeting system under lease agreement with Monsanto. However, when it appeared that the negotiations with Monsanto would be protracted, this plan was abandoned. Purdue therefore proceeded with the development of a new process simulation package based on the prototype system developed by Prof. J.M. Woods at Purdue.

The important requirements for the simulation system was that it should be able to accommodate large flowsheets with multiple, interconnected recycle loops. Recognizing that even moderately sized flowsheets with perhaps 12-15 equipment

nodes, 30-40 streams including two or three recycle streams, and a dozen species can require 100-200 K octal storage and 100-500 seconds execution time on a large main-frame computer, it is clear that simulation of a flowsheet of the complexity of that shown in Fig. 1 will present a severe computational challenge to conventionally structured simulators. Accordingly, Purdue set about designing a system which would minimize storage requirements and yet maintain acceptable computation times. This was accomplished in three ways: compact one-dimensional storage of stream and equipment parameter data, use of a stream-lined physical properties package and formulation of a hierarchical decomposition scheme in which individual detailed process section simulations would be linked by overall process section material and energy balance models. These concepts were discussed in reports FE-2275-1 and FE-2275-2.

A prototype simulation system incorporating the first design feature, called S4 (Steady State Simulation System), demonstrated that significant savings in core simulation data storage could be achieved. However, the basic coding and COMMON block structure of the information management system proved to be too cumbersome. A new version of the system called DSP (Detailed Simulation Program) was implemented, tested, and shown to be quite satisfactory. Concurrent with these developments, work proceeded both in the physical properties package and on efficient programs for executing large scale material and energy balances. The latter was particularly essential for the implementation of the proposed hierarchical calculation strategy. While the properties estimation package underwent only a single version with minor modifications, the latter programs were developed through stages. This occurred because the structure of physical properties packages has been repeatedly discussed in the literature and, consequently, the design of such a program could be clearly defined without extensive experimentation. However, a computational strategy

and computer program for the large scale balance computations required for our purposes was not available in the literature. Considerable new computational research was required which we reported in a series of publications listed in Section 1.4. The balancing programs underwent three versions in which the computational strategies and program capabilities were successively refined. The final version called LINBAL incorporated several computational features that could not be adequately exploited using the DSP structure. Consequently, the DSP executive was revised to allow convenient linkage of the upper level process model with the lower level process section simulation models, to incorporate design constraint handling capability, and to standardize the data structure used by both programs. The resulting system, called LSP (Large Scale Steady State Program), is the final version delivered to DOE.

3.1.2 Features of LSP

The primary features of LSP are:

- i) use of an advanced sequential modular design
- ii) use of optional multi-job step calculation strategies
- iii) efficient stream and equipment node parameter storage
- iv) ability to incorporate solids; hydrocarbon boiling fraction, as well as other non-standard stream entities.

LSP simulations can be executed using either a single job step employing an advanced sequential modular strategy or a number of multi-job calculation strategies. In the normal sequential modular mode the flowsheet will be calculated in iterative solution passes. However, in contrast to conventional implementations, in LSP the recycle tear streams are all updated at a single level after execution of each pass of node calculations. Design constraints are accommodated either locally by iterating around individual nodes or globally by simultaneously updating all

adjustable node parameters. Node calculation sequences can either be generated completely automatically by the LSP executive, or generated by LSP incorporating user selected tear streams, or totally fixed by the user via a calculation sequencing routine provided by him. The first option is of significant help to the novice user because he neither needs to concern himself with the recycle loop structure nor does he have to provide initial recycle stream estimates. However, since zero initial recycle stream estimates will be used, the automatically generated calculation sequence may require longer calculation times for convergence. If the user can identify some or all of the key recycle tear streams from physical insight into the flowsheet and if he can provide good initial estimates of the tear streams, then the second option is highly desirable and will generally lead to more efficient solutions. Finally, if for specialized applications conditional logic and branching are required in the calculation sequence or if because of particular problem structures nested iterative calculations prove efficient, then the third option, the user coded calculation sequencing routine or process routine is appropriate. In this case, the user process routine would act as calculation executive replacing the LSP sequencer.

An additional novel design feature of the LSP computational architecture is the fact that equipment modules are separated into default parameter definition segment, output stream calculations, specification calculations, and node report generation. Segregation of the output stream calculations and the specification or design calculations allows the latter module computations to be deferred until all flowsheet balances have converged.

Although the single job step sequential modular strategy is convenient to use it is generally useful only for moderately sized flowsheets. For more complex applications, it becomes appropriate to separate the calculations into multiple

execution steps. At the simplest level, if the recycle iteration calculations require too much computation time, it becomes expedient to terminate a run after a fixed number of iterations, to save the current simulation results, to print the current values for user analysis, and then to restart the calculations from the current stream and parameter values, possibly somewhat modified as a result of user analysis of the printed intermediate results. This strategy is known as the restart feature. In LSP, by setting the appropriate flags, the user can have all of the data associated with a simulation stored in an appropriate file upon termination of a specified number of flowsheet passes. Again by setting appropriate flags, the user can, as a subsequent separate job step, restart the simulation run using this file and may if he desires read additional stream and equipment parameter modifiers for this run. The restart feature thus allows the user to conveniently interrupt the simulation to check the progress of the calculations and modify their course.

For larger scale flowsheet studies it is often convenient to decompose a flowsheet into several process sections each of which is assembled and executed as a single job step. The LSP system provides the interface which stores the required inter-section output stream values generated during the execution of each individual process section simulation and which retrieves the required inter-section input stream values. LSP allows arbitrary sequencing of species in the process section simulations and arbitrary multiple numbering of common process streams. The user thus can simulate the entire flowsheet by executing a series of process section simulations without having to be concerned with updating common streams and defining all streams to be of identical species structure.

As a further alternative for complex recycle cases, whether formulated as single process section or multiple process section simulations, it is possible to significantly accelerate convergence by employing a two level solution strategy

available in LSP. Under this strategy an upper level linearized model is used to predict values of all recycle streams as well as unspecified process input streams. This model is efficiently solved using a specialized structure and sparsity exploiting equation solving strategy. The detailed lower level simulation models are used to update the coefficients of the linearized model. The LSP system provides the interface which stores the required stream values generated during a single pass through the detailed simulations; assists in the formulation of the upper level model; automatically updates the coefficients of the linearized model; directs the solution of the linearized model; stores the required recycle and input stream values; and reinitiates the next pass of detailed model evaluations. Thus, the two level strategy can be executed with minimum user intervention and without requiring any restructuring of the lower level models that the user has developed.

In conventional systems, the streams and equipment parameters are stored in two dimensional arrays which have predefined maximum sizes. When the actual sizes are different from the predefined values considerable unused space will be allocated in the computer. Moreover, when the number of equipment and stream items in a simulation exceed the predefined limits, the whole package must be updated and recompiled. In LSP, the streams, equipment parameters, and all additional simulation data are stored in a head to tail fashion in a single one dimensional array. The length of this array can be selected to suit a specific simulation and can be modified by dimensioning and recompiling the main program only. In addition, in large scale process simulations the species present in one portion of the flowsheet may be absent in other portions. In conventional systems using fixed two dimensional stream arrays, the stream vector length must be assigned based on the total of all species in the flowsheet, resulting in considerable wasted storage. In LSP the leading and trailing zero species flow in a stream vector are not stored. Thus a judicious sequencing of species may result

in a large savings in storage space.

The storage, retrieval, and expansion of simulation information required under this compressed storage design are conveniently grouped into several utility routines. Moreover, the LSP information management system is structured so that key module input parameters will be automatically transferred whenever a module is entered. This design allows convenient isolation of the storage and retrieval details from user written equipment modules. Thus, it is very easy to add new equipment modules, derived from other packages or newly written, to the LSP module library inspite of the more complex LSP storage structure.

Finally, LSP allows the stream vector to contain several categories of stream components: pure species, boiling fraction components, solids, and up to three categories of auxiliary stream characteristics. This allows non-standard stream information such as heteroatom flows or size fraction flows or density fraction flows to be accommodated. Of course, only those categories must be defined that are actually needed in the simulation run.

Because of these features, LSP is ideally suited for a user who:

- 1) requires a system that can run in a minimum of storage space, especially on a machine which does not have a virtual memory system.
- 2) is likely to encounter applications with extensive recycles and design specifications which would severely tax conventional sequential modular systems.
- 3) is likely to encounter applications for which new modules will continuously have to be created and introduced.
- 4) is involved with streams containing more complex constituents than pure component vapor-liquid mixtures.
- 5) has an existing library of stand-alone equipment routines which he wants to merge into a simulation executive.

LSP uses the American Engineering System of units exclusively. That is, the units used are feet, pound, pound-mole, psia, °R, Btu, and hour. Stream input and output can be provided either in mass or in mole units.

3.2 The LINBAL Program

The LINBAL program is a specialized flowsheet simulation program suitable for solving the decoupled material and energy balances for flowsheets modelled in linear equipment modules. The program can be used in a stand-alone basis or to execute the upper level LSP model for a simulation when the two level LSP strategy is selected. LINBAL incorporates computational strategies which are unavailable in other existing software.

3.2.1 Development Overview

The design and implementation of a linear balancing program was deemed an appropriate task for this project because such a program could serve a very useful function in the preliminary stages of process design calculation and because it was essential for the implementation of the LSP two level calculation strategy. At the inception of this contract there was available a proto-type program developed as a Purdue Ph.D Thesis. This program proved to require excessive storage for large problems. Consequently efforts were initiated at exploring ways of reducing the storage requirements. A new mixer equation generation and ordering scheme was devised which reduced storage by $1/3$ (FE-2275-3). The revised program, called MBP-I, proved more efficient in CPU time as well but consumed excessive computational time when linear and nonlinear design constraints were included in the problem formulations (FE-2275-4). A new formulation of the parametric solution strategy was subsequently devised which reduced computational times by about $1/2$. The code was thoroughly revised and the result called MBP-II. Two papers describing the methodology embodied in MBP-II were published in the AIChE Journal (See Section 1.3). A similar strategy was devised to solve flowsheet energy balance program and a program called EBP-II was developed (FE-2275-6,-7). Manuals for MBP-II and EBP-II were written and the code was distributed for further testing by ORNL and Edgewood Arsenal.

Further use of the program as well as attempts at using MBP-II within the two level LSP strategy indicated that it would be desirable to extend the program to allow generalized (multiple-input/multiple output plus reaction) modules and to further exploit the species level problem sparsity. The ideas underlying these extensions were discussed in a paper published in Computers and Chemical Engineering (See Section 1.3). A new version of MBP-II was implemented and the same concepts were transferred to the energy balance calculation program. The revised program is called LINBAL and includes the material and the energy balance computations as separate calling programs. The features of LINBAL are discussed in the following sections.

3.2.2. Features of MBP3

The features of the material balance portion of LINBAL can be divided into two categories: user oriented features and implementation concepts. From a user point of view the following features of the program are of note:

- i) LINBAL allows modeling of process units in terms of linear modules which have multiple input streams, multiple output streams, stoichiometric reactions, as well as stream or stream component splitting.
- ii) the program permits the user to impose various types of design constraints involving the component flows: linear equations, nonlinear equations, and nonlinear inequalities.
- iii) the user may assign relative weights to the inequality constraints thus assigning preference to satisfying some constraints over others.
- iv) the program permits the user to leave unspecified some of the normal problem specifications such as: process input streams, reaction conversions, stream or component split fractions.

- v) the user does not need to identify tear streams or provide initial estimates of tear streams
- vi) the program can identify dependent specifications and inconsistent specifications and will issue diagnostic messages.

LINBAL incorporates a number of novel calculation and implementation features which makes it unique and computationally quite efficient. Some of these are:

- i) All recycle loops in a flowsheet are accounted for explicitly in the form of generalized mixer equations. A generalized mixer equation is simply a vector equation formed by tracing upstream in the flowsheet each input of any multiple input unit until another multiple input unit is encountered and aggregating the linear module transformation matrices which are encountered.
- ii) the generalized mixer equations are generated in symbolic rather than numerical form and are precedence ordered to locate the smallest independently solvable blocks.
- iii) the structure of the coefficient matrices of the blocks of generalized mixer equations can be generated in binary form purely from a knowledge of the identity of the key reactants and of the presence or absence of a species in output streams.
- iv) the binary form of the equations can be efficiently processed for solution using sparse matrix techniques and the calculation map can be saved for repeated solutions.
- v) Linear and nonlinear problem constraints are accommodated using a parametric solution strategy. Under this strategy a generalized parametric solution is generated for the underlying, underspecified unconstrained problem. The constraints are thus only used to determine the parameters in the generalized parametric solution.

- vi) Nonlinear constraints are solved using a Newton-Raphson method. The Jacobian is only as large as the total number of nonlinear constraints.
- vii) Linear inequality constraints are accommodated by solving a linear program involving as many rows as there are inequalities.

These implementation strategies have resulted in a very robust and efficient code suitable for stand-alone use or use within the LSP framework. Some sample results obtained using the material balance portion of LINBAL are shown in Table 1. As a rough guide to problem difficulty, the number of equivalent equations being solved is equal to the number of streams times the number of species plus the number of constraints. For example, the Chess example is roughly equivalent to 221 linear equations and 9 nonlinear equations. For detailed definition of the problems refer to the MBP-II or LINBAL manuals. For details of the methodology the reader is referred to papers a.1, a.2, and a.3.

3.2.3 Features of EBP3

From an operational point of view, flowsheet energy balance calculations can be separated into two parts: the thermodynamic part which is concerned with the intraconversion between composition, temperature, pressure, enthalpy and phases of a stream and the conservation law part which is concerned with the accounting of heat, work, and enthalpy flows. If the material and energy balances are assumed to be decoupled and if, as is usually the case, stream pressures are assumed known, then the key complicating factor in the thermodynamic part is the relationship between temperature, phase distribution and enthalpy. The calculation of one of these quantities given the other two is known to often constitute the main computational burden in carrying out detailed

TABLE 1. Sample Linear Results

Problem	Modules	Streams (External)	Species	Constraints		Core K Octal (to load)	Cpu Secs (CDC 6500)
				Linear	N. Linear		
Thatchers Chlorobenzene Flowsheet	6	13	5	0	0	63	.4
Reklaitis's Ammonia Flowsheet	7	16	9	16	0	67	6.4
Nagiev's Cracking Gas Flowsheet	9	16	6	0	2	64	1.0
Chess-Natural Gasoline Flowsheet	10	22	10	1	9	72	5.1
Parson's COED Coal Conversion Flowsheet	52	86	22	0	0	130	11.7
Parson's SRC Coal Conversion Flowsheet	64	106	17	12	0	110	54.1
	64	106	17	10	0	110	47.0

flowsheet simulations. Accordingly, in the simplified energy balancing approach used in EBP3, it is assumed that the phase distribution is always specified. With this assumption it proves convenient to represent the different phase flows of a species as separate pseudo species flows. Each pseudo species will have associated with it a heat capacity and a heat of transition at a selected reference temperature, that heat of transition being the difference between the enthalpy of the pseudo species in its phase and the enthalpy of the species in its phase at the selected reference conditions. Under this pseudo-species formulation, species phase changes can be conveniently represented as "reactions" in which a unit of one pseudo-species is converted to a unit of another pseudo species with an associated "heat of reaction", the heat of transition.

To further simplify the conversion between stream enthalpy and temperature, the species heat capacities are assumed to be constant over the range in question. The inaccuracies introduced by this assumption can be somewhat mitigated by judicious selection of the reference temperature. Finally, the enthalpy of each species in its reference phase at the reference conditions is assumed to be zero. One could, alternatively select the elements at standard conditions to have zero enthalpies and then could include the heats of formation of the species as part of the species enthalpy. However, this requires the introduction of additional data for each species regardless of whether or not that species will be involved in chemical reaction. In addition, the possibility of numerical errors is increased. Consequently, the total enthalpy method was not employed in EBP3.

By means of these assumptions and conventions, the thermodynamic calculations required to carry-out the flowsheet energy balances, namely the calculation of stream enthalpies from composition, phase, and temperature information and the recovery of temperatures from calculated stream enthalpies, are kept free

of iterations. The enthalpy-temperature relation for a stream is simply

$$E = \sum_{s=1}^S E_s = \sum_{s=1}^S N_s (H_{sr} + cp_s (T - T_r) + \Delta H_{sr})$$

where E is the stream enthalpy flow

E_s is the enthalpy flow of species s

H_{sr} is the unit enthalpy of the species in its reference phase r at reference temperature T_r

ΔH_{sr} is the enthalpy of transition from phase r to phase s at T_r

cp_s is the mean heat capacity of species s

Since the above is linear in T , intraconversion between E and T is straight-forward. The main focus can thus be directed towards the actual first law calculations.

Given these assumptions, the structure of the energy balance equations becomes quite similar to those of the material balance equations. For instance, stream mixing is represented by the equation,

$$E^{out} = \sum E^{in}$$

where E^i is the enthalpy flow of stream i

stream separation by the equation

$$E^{(j)} = t_j E^{(in)}$$

with

$$\sum_j t_j = 1, \text{ where the } t_j \text{ are the enthalpy split fractions;}$$

a stoichiometric reactor by the balance:

$$E^{\text{out}} = E^{\text{in}} + X_k \Delta H_k (T_r)$$

where X_k is the conversion of key reactant k and $\Delta H_k (T_r)$ is the heat of reaction per unit of key reactant k converted;

and a heat exchanger, a device through which heat is added or recovered at specified rate Q , by the balance equation,

$$E^{\text{out}} = E^{\text{in}} + Q.$$

These equations are linear in the enthalpy flows and thus can be aggregated into generalized modules analogous to those defined in the material balance case.

The natural specification parameters for the energy balance modules are, paralleling the material balance case:

- i) the temperatures (or enthalpy flows) of all process input streams
- ii) the enthalpy split fractions of all separators
- iii) the heats of reactions of all reactors
- iv) the heat transfer rate of all heat exchangers

As in the material balance case, design constraints can be imposed which can take the form of linear or nonlinear equations involving the enthalpy flows, the heat transfer rates, or the stream temperatures. In EBP-3 three constraint types are allowed: linear equations in stream temperatures, in stream enthalpies and in heat addition or removal rates. All specifications involving temperature are converted to enthalpies, the problem is solved in terms of stream enthalpies, and, upon solution, all enthalpies are converted to stream temperatures for outputting.

Given the formulation of the problem in terms of enthalpy flows, flowsheet energy balances can be solved using exactly the same strategy as was employed in the material balance case. The main difference lies in the fact that the energy balance equations for a module is a scalar equation and, hence, the stream level strategy employed in MBP3 collapses to a manipulation of scalar equations. Because of the similarity in the problem structure, it was also possible to structure the input data of EBP3 so that the results of an MBP3 run can be directly used in EBP3 and to structure the EBP3 output report so that the two output reports are complementary.

For further details on EBP3, the reader is referred to paper a.3, the EBP-II manual or the LINBAL manual.

3.3 The Physical Properties Package

The PPROPS program is a package designed to estimate physical properties of process streams. It is designed to be used either on a stand-alone basis or in conjunction with LSP. The basic design criteria employed in implementing PPROPS consist of the following:

- i) Emphasis on computational efficiency. PPROPS does not include road-mapping features and employs a compressed stream vector.
- ii) Use of the best general purpose estimation techniques. The number of estimation options is thus intentionally limited.
- iii) Design for easy program expansion. The computations are modularized and the properties array is of a readily expandable two dimensional form.
- iv) Use of a simple interface between applications programs and PPROPS.

All mixture specifications are transferred via a stream vector; estimation constants for the application are stored in two local arrays; the calls to the package involve only eight user routines.

The package can accommodate vapor-liquid pure components and mixtures, boiling fraction components, and, to a limited extent, solids. PPROPS estimates the following thermodynamic properties: volumetric properties, enthalpy, entropy, K-values; equilibrium constants, heats of reaction and combustion. The only transport property provided is the viscosity. All quantities in PPROPS are dimensioned in the AE system of units at DOE insistence.

3.3.1 Development Overview

The initial plan for this project provided that one of the proprietary physical packages available through software vendors or private developers be adapted for use in the steady state simulator. However, inquiries undertaken in the early summer of 1976 indicated that while several developers were willing to make their packages available on a lease basis, none would allow the disclosure and wide dissemination of their programs desired by ERDA unless the purchase price allowed them to recover their development costs. At the July 22, 1976, project review meeting it was therefore decided that Purdue would proceed to develop a package suitable for use within the steady state simulation system. In cooperation with Lehigh University, Purdue presented preliminary specifications for this program (FE-2275-2). The AIChE package, and programs developed at the University of Houston were selected to serve as references for the Purdue PPROPS package. The basic design of the program library was reported in FE-2275-3. Preliminary versions of the proto type program were sent to Lehigh and PERC in late 1977. Capability for estimating properties of boiling fractions pseudo-components was added by spring, 1978 (FE-2275-7) and revised program

decks were sent to ORNL and Edgewood Arsenal for preliminary testing. Specialized correlations for predicting the properties of steam were added in the following quarter (FE-2275-8). These correlations were modifications of the equations used to generate the 1936 and 1967 steam tables. Finally, PPROPS was expanded to include the calculation of entropy of mixtures (FE-2275-9). The need for entropy arose in compressor and turbine design calculations. Further minor modifications were reported in FE -2275-10 and a final program manual was issued in May, 1979.

3.3.2 Program Capabilities

PPROPS consists of an estimation constant data base, a library of main user routines, a support library of secondary routines, an interface routine LOADP and various diagnostic message print routines. The main user routines are summarized in Table 2 and some of the more important secondary routines in Table 3. The properties estimation constant data base consists of two arrays: the PPROPA array, whose entries are defined in Table 4, and the PPROPB array which contains binary interaction coefficients for selected species. The latter are used for Wilson activity coefficient estimation. At present the data base is complete for the pure components listed in Table 5. The data base is easily expanded to include more species, however, the list of species shown was satisfactory for coal conversion process modelling.

The pure component methods employed in PPROPS are summarized in Table 6. Note that options exist for calculating liquid activity coefficients and liquid reference fugacities. Boiling fraction component properties are estimated using the correlations given in Table 7. Given three user specified characterizing parameters for a boiling cut, PPROPS estimates the key remaining constants and uses these directly in the appropriate pure component formulas.

TABLE 2
MAIN USER ROUTINES

<u>ROUTINE</u>	<u>PURPOSE</u>
GFLASH	General flash calculation routine -isothermal flash -adiabatic flash -general flash
DENSITY	Density of stream
ENTHAL	Enthalpy of stream
EQK	Equilibrium constant for specified reaction stoichiometry
DTCAP	Ideal heat capacity of stream
HTCOMB	Heat of combustion of stream
HTREAC	Heat of reaction for specified reaction stoichiometry
KVALTX	Bubble pressure calculation
KVALPX	Bubble temperature calculation
KVALPY	Dew temperature calculation
KVALTY	Dew pressure calculation
KVALTA	Overspecified bubble point calculation
SGM	Entropy of Stream
VISGM	Viscosity of vapor stream
VISLM	Viscosity of liquid stream

TABLE 3

SECONDARY USER ROUTINES

<u>ROUTINE</u>	<u>PURPOSE</u>
AVMOL	Mole fraction average of any property
EGM	Enthalpy of gas mixture
ELM	Enthalpy of liquid mixture
ENTH	Low pressure enthalpy
ENTR	Entropy of single vapor component
HCPI	Integrated ideal heat capacity
MIX	Pseudo-critical properties of mixture
VAPRE	Vapor pressure of single component
VG	Viscosity of single component vapor
VGLOP	Viscosity of single component vapor at low pressure
VL	Viscosity of single component liquid
VLM	Volume of liquid mixture
ZRWM	Volumetric properties of gaseous mixture

TABLE 4

PROPA (I,J)

For each component J

LOCATION IENTRIES

1	ID Number
2,3,4	Chemical Formula
5,6,7,8	Critical Properties (T,P,V,Z)
9	Normal Boiling Point
10	Molecular Weight
11	Acentric Factor
12,13	Redlich-Kwong Constants
14,15,16	Antoine Equation Constants
17,18	Lower & Upper T bounds for Antoine Equation
19	Std. Free Energy
20	Std. Heat of Formation
21	Std. Heat of Combustion
22,23,24,25	Ideal Gas Ht Capacity Coeff's
26,27	Upper & Lower T bounds for Cp equation
28,29,30	Liquid Molar Volume Coeff's
31,32,33,34	Ideal Liquid Ht cap. coeff's
35,36	Lower & Upper T limits for liquid Cp
37	Heat of vap at normal B.P.
38	Solubility Parameter
39	Phase of Std. State
40,41,42	No. of C,H,S atoms per molecule
43	Melting Point
44	Heat of Fusion
45,46,47,48	Solid Ht cap. coeff's
49	Molecular Diameter
50,51	Potential Energy Parameters
52,53	Liquid Viscosity Parameters

TABLE 5. Pure Components In Physical Property Data Bank

<u>ID</u>	<u>COMPONENT</u>	<u>FORMULA</u>
1	Nitrogen	N ₂
2	Oxygen	O ₂
3	Hydrogen	H ₂
4	Carbon Monoxide	CO
5	Carbon Dioxide	CO ₂
6	Carbonyl Sulfide	COS
7	Carbon Disulfide	CS ₂
8	Sulfur Dioxide	SO ₂
9	Hydrogen Sulfide	H ₂ S
10	Ammonia	NH ₃
11	Hydrochloric Acid	HCl
12	Water	H ₂ O
13	Methane	CH ₄
14	Ethylene	C ₂ H ₄
15	Ethane	C ₂ H ₆
16	Propene	C ₃ H ₆
17	Propane	C ₃ H ₈
18	1-Butene	C ₄ H ₈
19	n-Butane	C ₄ H ₁₀
20	n-Pentane	C ₅ H ₁₂
21	Cyclopentane	C ₅ H ₁₀
22	Benzene	C ₆ H ₆
23	Toluene	C ₇ H ₈
24	para Xylene	C ₈ H ₁₀
25	n-Propyl Benzene	C ₉ H ₁₂
26	Mesitylene	C ₉ H ₁₂
27	Decane	C ₁₀ H ₂₂
28	Naphthalene	C ₁₀ H ₈
29	1-Methyl Naphthalene	C ₁₁ H ₁₀
30	Phenanthrene	C ₁₄ H ₁₀
31	1-2 Benzoflorene	C ₁₇ H ₁₂
32	Chrysene	C ₁₈ H ₁₂
33	Phenol	C ₆ H ₆ O
34	ortho Cresol	C ₇ H ₈ O
35	3,5-Xylenol	C ₈ H ₁₀ O
36	2-Naphthol	C ₁₀ H ₈ O
37	Thiophene	C ₄ H ₄ S
38	Pyridine	C ₅ H ₅ N
39	ortho Xylene	C ₈ H ₁₀
40	meta Xylene	C ₈ H ₁₀
41	Ethyl Benzene	C ₈ H ₁₀
42	n-Propanol	C ₃ H ₇ OH
43	Acetic Acid	C ₂ H ₄ O ₂

TABLE 6
PURE COMPONENT METHODS

<u>PROPERTY</u>	<u>SINGLE COMPONENT</u>	<u>MIXTURE</u>
Critical T	constants	Kay's Rule
Critical Z	constants	
Critical P	constants	Prausnitz-Gunn
Ideal Cp (gas, liq., solid)	constants	molar average
Real Gas Properties (volumetric properties gas enthalpy gas entropy)	Redlich-Kwong	R-K mixing rule
Liquid Density	constants	Yen-Woods, Lydersen, et.al.
Liquid Enthalpy	constants	Yen-Alexander

TABLE 6

<u>PROPERTY</u>	<u>SINGLE COMPONENT</u>	<u>MIXTURE</u>
GAS VISCOSITY	LOW P	
	CHAPMAN-ENSKOG	CHAPMAN-ENSKOG
	NEUFELD (non-polar)	WILKE
	STOCKMEYER (polar)	
	HIGH P	
	JOSSI, et.al.(non-polar)	
	STIEL & THODOS (polar)	
LIQUID VISCOSITY	CONSTANTS (low T_R)	LOG MOLAR AVERAGE
	LETSON & STIEL (high T_R)	
VAPOR PRESSURE	CONSTANTS (ANTOINE)	
	(in range)	
	RIEDEL-PLANK-MILLER	
	(outside range)	

PROPERTIES OF PURE
WATER & STREAM

ASME STEAM
TABLE CORRELATIONS

TABLE 6

VAPOR FUGACITY

REDLICH-KWONG

LIQUID ACTIVITY COEFF.

IDEAL

REGULAR SOLUTION

WILSON

LIQUID REF. FUGACITY

CLASSICAL, LYCKMAN, et.al.

CHAO-SEADER

GRAYSON-STREED

PARTIAL MOLAR VOLUME

LYCKMAN, et.al.

PRAUSNITZ, et.al.

TABLE 7

BOILING FRACTION COMPONENTS

CHARACTERIZING PARAMETERS

API Gravity

Mean Average Boiling Point

Molecular Weight (optional)

ESTIMATED PROPERTIESCORRELATION

Watson Factor

Definition

Molecular Weight

Kesler-Lee

Critical T

"

Critical P

"

Critical V

Hall & Yarborough

Acentric Factor

Edminster

Heat of Vap.

Kistiakowsky-Vetere

Solubility Parameter

Definition & Watson

Gas Viscosity

API Data Book

Liquid Viscosity

Not Available

Cp (vapor)

Kesler & Lee

Cp (liquid)

"

Heat of formation

Not Available

3.3.3 Program Usage and Limitations

To use PPROPS the user only needs to know the structure of the stream vector by means of which stream properties are transferred to the appropriate PPROPS routine; the calling form of the primary user routines, the definitions of the PROPA & PROPB arrays if he desires to store or retrieve specific properties constants, the structure of the input data deck, and the list of the species whose constants are available. If PPROPS is used within LSP then the input will be as defined in the LSP manual. If the program is being used on a stand-alone basis then the user will need to consult the PPROPS manual. In either case, the required user data is quite limited. Table 8 shows the structure of the data deck used in stand-alone applications.

The accuracy of PPROPS is of course limited by the nature of the methods used to estimate properties, the quality of the data in the data base, and the robustness of the numerical calculations that are incorporated in the code. For instance, it is well known that the R-K equation of state has very definite limitations. For specific mixtures and conditions more elaborate equations would give increased accuracy. Similarly the flash calculations which are an integral part of any properties package employ a Newton-Raphson algorithm. Convergence of this algorithm can not be generated under all conditions. It is possible to increase the reliability of flash calculations by including several levels of alternate numerical algorithms which would provide a back-up if the N-R iterations should diverge. Such alternate estimation methods and numerical algorithms were not included in PPROPS because of time and budgetary limitations. However, the program design is such that if deemed necessary by future users these features can be readily added without modification to the basic program structure.

TABLE 8

TYPICAL DATA DECK

RECORD 1:

COMPONENT CLASSIFICATION

Number of Components with user supplied constants

Number of boiling fraction components

Number of pure components from data bank

RECORD 2:

COMPONENT IDENTIFICATION

Sequence of Component ID's

RECORD 3:

BOILING FRACTION SPECIFICATIONS

for each cut,

Component ID

API Gravity

Molecular Weight (optional)

MEAN Ave. Boiling Point

Alphanumeric Name

RECORD 4:

USER SUPPLIED PROPA CONSTANTS

RECORD 5:

USER SUPPLIED STREAM VECTORS

(0000 card used as delimiter)

3.4 The Process Economics Package

Once a process flowsheet simulation has been satisfactorily executed, the results naturally should be used to calculate the capital cost of the project and to conduct an analysis of the process profitability. These types of calculations lend themselves readily to computer implementation and, hence, it was deemed appropriate that a process economics program be developed as adjunct to the LSP system. In this section, we will briefly describe the PCOST package developed to fill this need.

3.4.1 Development Overview

The three subtasks which comprised the bulk of this development effort were: equipment cost data gathering, evaluation, and correlation; design and implementation of the plant cost program; and design and implementation of the profitability analysis program. The cost data gathering activity was initiated early in the project life. As described in FE-2275-2 an extensive body of cost data was accumulated from various literature, institutional, and industrial sources. Cost correlations were constructed when required and a preliminary computerized data base was developed (FE-2275-3,4). Equipment cost estimation calculations were organized into a library of subroutines specific for each equipment class. Test cases presented indicated good numerical agreement with cost estimates available using alternate methods (FE-2275-7). However, testing and discussions with ORNL indicated that it would be highly desirable if the costing-evaluation package could operate on a stand-alone basis, separate from the simulation system. The decision was consequently made in consultation with DOE to redesign the capital cost estimation and economic evaluation package. The basic program design was detailed in FE-2275-8. Additional plant cost factor estimation correlations developed by Culbertson were incorporated and a detailed output report options implemented (FE-2275-9). The profitability

analysis portion of the program was assembled by adapting major portions of the PRP program developed at ORNL [Salmon, 1977]. Test runs with the complete program were completed in late 1978 and sample results reported in FE-2275-10. The resulting PCOST program is a data base oriented package which estimates the capital equipment cost for a chemical plant using a modified form of the factored approach proposed by Guthrie (1968) and which performs an economic analysis using a revised form of the Discounted Tax Flow technique reported by Salmon (1977). Although several proprietary programs employing these types of techniques have been reported in the literature, the design of PCOST incorporates novel features which make it unique. The noteworthy program capabilities are:

- i) easily modified data structure
- ii) multi-optional f.o.b. equipment cost estimation
- iii) calculation of means and ranges of estimates
- iv) flexible cost factor handling
- v) wide range of detailed costing options
- vi) flexibility in depreciation and tax schedule computation
- vii) product price and return on equity calculation options

The program implementation features of note are:

- i) flexible data base design
- ii) variable dimensioning
- iii) free or fixed format input, flexibility in input units
- iv) extensive program default options
- v) complete data echo and input validation
- vi) user oriented diagnostic messages
- vii) extensive output reports

3.4.2 Program Capabilities

3.4.2.1 Costing Data Base

One of the inherent limitations of any cost estimation program is the short useful life of the economic data which it employs. Especially within the last five years the process industries have experienced rapid changes in equipment f.o.b. costs, installation materials and labor costs, as well as costs of plant auxiliary equipment. For a cost program to be an accurate estimation tool, these data must continually be updated, revised, and expanded. This is an expensive and time consuming activity whose repeated execution can be considerably facilitated by careful design of the form in which this data is stored in the costing program. The typical form used in costing programs is aggregation of this data by equipment type and its storage within separate subroutines each of which performs the cost estimation for a given equipment type. Although this structure simplifies the program design, it is quite inconvenient for data updating, because the addition of new correlating equations and coefficients for a new equipment type requires modification of the coding of the corresponding costing subroutine. In PCOST this problem has been eliminated by using a data base to store all numerical cost data. Thus all of the equipment f.o.b. cost correlating parameters, correlation ranges and accuracy parameters as well as the field material, labor and indirect cost estimating coefficients are stored in two program data files, one of which is sequential, the other of which is a random access file.

As a consequence of this design, the revision of existing correlations or addition of new correlations for equipment in the data base requires only the modification or addition of a few records in the data bank. Multiple correlating equations for the f.o.b. cost of a given equipment type from different sources can be easily maintained in the data base and used either

selectively or simultaneously. Addition of new equipment categories or types within a category can be accomplished without coding a new equipment costing subroutine by merely defining new equipment type identifiers. Creation of new correlating equations can be accomplished by merely coding an expression for this new functional form. Periodic updating of the entire cost data bank can be carried out directly by accessing the data files themselves rather than by modifying algebraic equations scattered throughout a library of equipment costing subroutines.

The data base which is supplied with PCOST is based on data reported by Guthrie (1969, 1974) and Woods (1974) with additions by Salmon and Culbertson (1978). It incorporates f.o.b. cost correlating equations for 79 equipment classes such as pumps and shell/tube heat exchangers with multiple types within each class. Some 250 correlating equations are included. The program structure allows up to 999 equipment classes and up to 99 types within a class.

3.4.2.2 Cost Estimation Method

The program provides for a cost build-up from the equipment f.o.b. to the installed cost using the scheme proposed by Guthrie (1969) and modified by Salmon and Culbertson (1978). This includes estimates of field material and labor costs for items such as foundations, structures, insulation, instruments, electrical or piping as well as other direct and indirect costs. In addition to the installed costs for all the equipment, the program also provides an estimate for the cost of buildings, site preparation, storage facilities, auxiliary facilities, utilities and other costs within and outside the battery limits. In all these cases various levels of accuracy are provided. The factored estimates which are provided in all cases can be replaced by more accurate estimates if additional details are available from the user.

The f.o.b. costs themselves can be determined using two procedures: single item costing and aggregate costing. Most equipment items such as heat exchangers or pumps can be adequately costed directly as single items using appropriate size parameters and cost correlation. However, more complex units such as distillation towers can be costed by estimating separately the cost of various components which are standard pieces of equipment such as shell sections, trays or packing, and reboilers. These costs can then be added to give an aggregate cost. The program accomodates both these procedures. However, separate subroutines are needed for each type of equipment requiring aggregate cost.

In addition to employing available f.o.b. cost estimating correlations, the program also has the capability of accomodation user quotations for selected equipment items. These may either be exclusive in which case only the user supplied quote is used for the given item or non-exclusive in which case the quote is used for the given item or non-exclusive in which case the quote is used together with the correlation from the data base. Those provisions allow for the convenient incorporation of past quotes for similar pieces of equipment retained in company cost files as well as current quotation for costs of specialized items.

PCOST also incorporates material of construction indices for the various equipment types. By means of these multipliers the base f.o.b. cost of an item can be corrected for a different material of construction. A recommended classwise list of cost indices for various materials is provided with PCOST but user supplied values are also accommodated. It is thus possible to estimate the cost of an equipment with a material of construction not contained in the data base.

Finally, provisions are made in PCOST to take into account both the ranges of validity of the applicable correlations as well as the probable error in the cost predictions provided by the correlating equations. In general, cost correlations can only be used within their specified range of validity. The program will always first search for those applicable cost correlations which do not require extrapolation. In case none is found, then the correlations requiring minimum extrapolation are used and the user is appropriately informed.

The f.o.b. cost correlations, as all correlations, always involve considerable estimation error. In PCOST confidence limits are stored for all cost correlating equations. The standard deviation of the cost estimate for a given piece of equipment is computed by aggregating the confidence limits associated with each applicable cost correlating equation. These are then combined to compute a mean and range (± 2 standard deviation) for the plant cost estimate.

3.4.2.3 Costing Options

The program provides for the following options which can result in a custom-made cost estimate for any given application:

- Data Source: The user can opt for cost data from a particular source or from all the sources contained in the data base. Whenever the preferred data source does not produce an applicable cost correlation, the program would automatically relax this constraint and use the entire data base.

- Inflation Index: The program provides for a variety of cost inflation indices: the Marshall & Stevens indices. The Marshall & Stevens Cost Index for the chemical process industry is used as a default value.

- Labor Rate: Any preferred average labor rate can be used. The program provides a suitable default value.

- Cost Multipliers: In order to reflect the particular circumstances of a user, the program provides an easy and consistent means to modify the cost estimates. Cost modification factors are provided for the following:

- equipment f.o.b. cost (for every kind of equipment)
- cost of field materials for foundations, piping, insulation, etc.
- cost of field labor for foundations, piping, etc.
- equipment erection labor cost
- indirect costs
- Time Base: The cost estimates can be provided with any year as the time basis. If none is specified the program defaults to the run date.

3.4.2.4 Economic Analysis

As an option, PCOST will carry out an economic analysis of the project. Discounted cash flow calculations are performed to either compute the rate of return on equity or the price of the main product. These calculations were implemented by adapting elements of the program developed by Salmon (1977). The economic analysis calculations allow considerable flexibility in choosing depreciation methods, different depreciable lives for various plant cost components, various tax accounting options, variable plant operating rates over the project life, multiple plant products and feedstocks, as well as construction loan and interest calculations. Moreover, the program is structured to allow automatic generation of parametric studies.

The economic analysis portion of PCOST is directly linked to the plant investment estimation program so that the calculated yearwise capital cost estimates will be automatically used in the analysis.

3.4.3 Program Implementation Features

In addition to using a flexible data base design, PCOST incorporates a number of implementation features which facilitate its efficient use.

First of all, PCOST uses variable dimensioned arrays. Thus, the program can be easily expanded in dimension to accommodate very large jobs or precisely dimensioned to minimize storage requirements in computing environments in which this is important by dimensioning arrays in the main program only. Diagnostics are given which allow the user to compare the program dimensions with the array sizes actually used in his program run.

The program allows either free or fixed format input. The fixed format input uses only two format types: one for floating point (E10.2) and one for integer data (I5), thus simplifying input file preparation. PCOST allows the user wide flexibility in input units. The user only needs to supply the dimension code for an entry and the program will perform the necessary conversions to correspond to the dimensions required by the correlations in the data base. If illogical units are specified, the corresponding entries are disregarded and user warning messages are provided.

PCOST provides direct as well as formatted input data echoes and performs exclusive data validation. The input data is immediately echoed and printed at the beginning of the output report. This provides a convenient means to detect any errors in the input data. The program checks for fatal errors in the data and whenever possible disregards the input data if errors are detected. Thus cost calculations are performed for all the equipment with correctly specified data while at the same time the ones with incorrect data are disregarded. Furthermore, the program does not impose any restrictions on the order in which data for various equipment may be read and will sort out the equipment in

appropriate categories for printing output summaries.

Finally, PCOST provides extensive output in the form of appropriate tables and summaries. The first part of the report contains an echo of user's data as described earlier. The output includes a description of costing options, general notes, sectionwise directory and a summary of cost calculations. It then gives yearwise total capital payout, overall cost summaries, costs of off-site facilities and a summary of equipment with specific cost quotations. The next part of the report is optional and contains detailed equipmentwise cost estimates arranged first by plant sections and then by equipment classes. The last part of the report contains discounted cash flow tables and other economic analysis summaries.

Both the capital cost and the economic analysis report are presented with title pages and adequate explanatory statements so that they can be directly used as stand-alone study reports.

4. Process Section Applications

In this section, a brief review is given of the six process section simulation applications carried out using the LSP system. In each case, the basic flow-sheet will be presented and some of the key unit models will be discussed. Since the output reports for these simulations are typically quite voluminous, results will not be detailed here. Sample results are given in various quarterly reports and full output reports are available in the LSP applications manual.

4.1 Acid Gas Removal Systems

4.1.1 Introduction

In the modified COED flow sheet which formed the framework for the modelling studies, there are three locations in the processing sequence at which removal of CO_2 and H_2S from process streams is desirable. These are:

- i) removal of H_2S and CO_2 from the quenched and scrubbed gas produced by the vapor recovery section
- ii) removal of CO_2 from the product gas resulting from bulk methanation
- iii) removal of CO_2 from the high H_2 content stream produced in the hydrogen plant

Removal of H_2S and CO_2 is desirable in the first instance because the H_2S will poison both the bulk methanation and the stream reforming and/or shift reactor catalysts. Removal of CO_2 is desirable because it adversely affects methanation equilibrium, acts as uneconomical diluent in reforming, and adversely affects shift reaction equilibrium.

CO_2 removal is desirable after bulk methanation because the CO_2 reduces the heating value of the product gas and because it adversely affects the equilibrium in the clean-up methanation reactor.

Removal of CO_2 from the hydrogen plant product stream is necessary since it reduces the H_2 partial pressure in the feed gas to the hydrotreating section and thus would force higher reactor pressures in that plant section.

There are a number of candidate processes available to perform the removal of these constituents from gaseous process streams. These processes are collectively referred to as acid gas removal systems.

The large number of systems currently available can be divided into five general categories:

- i) chemical solvent processes
- ii) physical solvent processes
- iii) direct-conversion processes
- iv) dry bed processes
- v) speciality-solvent processes

The solvent based processes are most commonly used for the duties envisioned in the modified COED process. For purposes of our study, we have selected the DEA and uncatalyzed potassium carbonate processes for modelling. We will employ the single DEA process for clean-up of the quenched pyrolysis vapor and the uncatalyzed potassium carbonate system for CO_2 removal after bulk methanation and in the hydrogen plant. Although proprietary variants of these processes (Benfield, Giammarco-Vetricoke, etc) may well be more economical, adequate data on the solutions used is not reported in the open literature. In principle, the models developed are sufficiently flexible so that they can be adapted to other processes by inserting appropriate changes in the equilibrium and physical properties data. For illustrative purposes we will restrict our attention to the hot carbonate process. The development of the DEA simulation is very similar to that of the hot carbonate process.

Figure 2. Basic hot potassium carbonate flow sheet

4.1.2 Description of the Process

The hot potassium carbonate system employs a chemical reaction to remove the carbon dioxide and hydrogen sulfide from the sour gas. The reactions occurring are the following:

From the stoichiometry, two moles of potassium bicarbonate are produced for each mole of acid gas reacted in the solution. As shown by the second reaction the hot carbonate system can also be used to remove hydrogen sulfide from a gas. However, the potassium bisulfide salt is very difficult to regenerate causing the hot carbonate system to become uneconomical if high partial pressures of hydrogen sulfide are experienced.

A flow sheet for a typical hot-carbonate process is shown in Figure 2. The major pieces of equipment needed are the

- 1) absorber - which utilizes sieve trays as the contacting plates
- 2) flash separator - which is used as a form of pressure reduction and primary solution stripping
- 3) stripper - which utilizes sieve trays as the contacting plates and a reboiler to produce stripping steam
- 4) water mixer - which supplies the make-up requirements for water consumed and evaporated by the system
- 5) surge drum - which insures continuous flow between the absorber and stripper
- 6) pumps - which return the lean solution to the pressure of the absorber

The sour gas enters the absorber at its base and passes upward in counter-current flow to the lean solution. The sweetened gas leaves the top of the absorber and is sent to the dehydration and compression phase of the COED process, while the rich solution flows out the bottom of the tower. The stream temperatures are approximately:

sour gas entering	200°F
sweet gas exiting	228°F
lean solution entering	228°F
rich solution exiting	240°F

The system pressure in our application is 500 psia.

The rich solution is then sent to the flash separator where the solution pressure is lowered to approximately 18 psia. A knock-out drum is used to split the resulting streams. Nearly half of the absorbed carbon dioxide is released in this operation. The liquid fraction is then sent to the stripper for further regeneration.

The regenerator is a reboiled stripper. Steam is generated in the reboiler and passes up counter-currently to the descending rich solution. The lean solution passes out the bottom of the stripper, and the remaining carbon dioxide and hydrogen sulfide along with some water pass as a vapor from the top stage of the stripper. This vapor stream along with that of the flash operation is sent to a condenser where the majority of the water is condensed and sent back to the process. The stripper reboiler operates at about 230°F.

4.1.3 Modelling Approach

The key design variables in both of the described systems are: the column operating temperatures and pressures, the number of trays used in each column, and the solution recirculation rates. Normally the pressure of the

absorber will be dictated by processing requirements external to the acid gas system. The stripper pressure will be dictated by regeneration requirements. The column temperatures will be substantially constrained by the rather limited ranges allowed by the solution equilibrium properties. The main design parameters thus remain the number of trays and the solution recirculation rates. Evaluation of the effects of these parameters upon the system performance requires the development of suitable column models.

Three basic modelling/design approaches can be used for acid gas systems:

- i) short cut design using solution flux values
- ii) tray by tray column calculation assuming pseudo physical gas/liquid equilibrium
- iii) rigorous tray by tray calculation which includes ionic solution equilibrium and mass transfer effects

The short cut design approach is described by Maddox (1977) and is suitable for rough preliminary design. It involves neither consideration of column temperature distribution nor effects of interval composition variations. The rigorous calculations as described by Zemaitis (1979) and Gautam and Seider (1979) which would include ionic equilibrium in solution and chemical reaction offer the best likelihood of a detailed description of column concentration and temperature profiles. However, in view of the very low tray efficiencies typically occurring in such columns (5-15%), Maddox and Burns (1967) and the large effect the variation in these uncertainties can have on predicted column performance it is highly questionable whether the additional computational effort is justifiable. Accordingly, we have selected the second modelling approach for our purposes. It appears to offer a reasonable balance between calculation complexity and model parameter uncertainty.

The absorption/desorption and chemical reaction phenomena in the columns will thus be modelled by assuming that the concentration of CO_2 (lbs) in solution (actually existing as an amine or potassium bicarbonate (sulfide)) can be related to the CO_2 partial pressure in the gas via a physical equilibrium distribution constant K_i . The reactions will be accounted for by including a heat of reaction term in the tray enthalpy balance and by adjusting the tray species balances to reflect the changes in the number of moles of H_2O . Solute balances will be disregarded in the tray calculations.

Equilibrium data for the potassium carbonate/ CO_2 system are presented by Bocard and Mayland [1962] in the form of a series of curves expressing CO_2 vapor pressure as a function of temperature and CO_2 concentration in potassium carbonate solutions ranging from 20 to 40%. Since typical carbonate solutions employed in acid gas removal are 25-30%, the data for 25% solutions was fitted to the following correlating equations:

$$P_{\text{CO}_2} = 1.689 \exp(.0162 \cdot T - 129.25 \cdot X_{\text{CO}_2} - .0411/X_{\text{CO}_2} + 3921.3 \cdot X_{\text{CO}_2}^2)$$

$$P_{\text{H}_2\text{O}} = \exp(14.224 - 6869.59/(T + 377) - 3.96 \cdot X_{\text{CO}_2})$$

where P_{CO_2} and $P_{\text{H}_2\text{O}}$ are in psi and T is in $^{\circ}\text{F}$

From this, the distribution coefficient is calculated by the following equation:

$$K_{\text{CO}_2} = P_{\text{CO}_2} / (P_T \cdot X_{\text{CO}_2})$$

where P_T is the total pressure K_{CO_2} is the distribution coefficient

The reaction of CO_2 with carbonate

indicates that one mole of water is consumed with each mole of CO_2 reacted.. Thus, in the species balances the water balance must be adjusted for each mole of CO_2 absorbed or stripped. However, the total liquid molar now remains unchanged since two moles of KHCO_3 are formed from one mole each of H_2O and K_2CO_3 .

In addition to the corrections to the mass balance equations, the conventional equilibrium stage enthalpy balance must be modified to include the heat of reaction of the above reaction. Bocard and Mayland [1962] report a value of -13,400 Btu/lb-mole of CO_2 reacted.

ABSORBER AND STRIPPING COLUMN SIMULATION

The simulation of the absorber column as well as the stripping column is achieved by a simultaneous solution of mass and energy balances coupled with an equilibrium relationship on each stage in the column. These equations take on a modified form of the Napthali-Sandholm equations (1971) for simple two phase multicomponent distillation in that chemical reaction terms must be incorporated into the set of equations on each stage. In the approach outlined by Napthali and Sandholm, the solution of the set of column equations is carried out using the Newton-Raphson method. This can be done quite effectively even though the equation set is large because the intermediate linearized equations form a block tri-diagonal matrix which can be effectively handled using a generalized Thomas algorithm.

There is very little difference between the model used for the absorber and the reboiled stripper. The balance equations and calculations are the same except for one major difference. This difference lies in the additional degree of freedom that arises in the stripping column because no second feed is introduced as in the absorber. This degree of freedom is removed by fixing the temperature for the reboiler. When the calculations have converged the reboiler heat duty is determined by an enthalpy balance around the first stage.

FLASH DRUM EQUATIONS

As indicated in the acid gas flowsheet, an adiabatic flash on the stream leaving the bottom portion of the absorber column is performed before it enters the stripping column. This will lower the concentration of CO_2 entering the stripping column as well as reduce the stream pressure from 500 psia to approximately 20 psia.

The simulation of the adiabatic flash drum is carried out by solving a set of mass and equilibrium equations to determine the degree of phase splitting of the inlet feed stream into effluent liquid and vapor compositions of all the species present in these streams. In addition, an enthalpy balance is used to compute a temperature of the outlet vapor and liquid streams.

Since a chemical reaction is occurring within the flash tank, the simple two phase flash equation must be modified to take into account the formation and depletion of certain species. The flash algorithm used in the acid gas removal model is a simplified version of the sum of rates method presented by King (1971). The sum of rates is most efficient when the total flows of a system are dependent upon composition rather than temperature which is true for wide boiling mixtures as well as for absorption and extraction problems.

PROCESS SIMULATION

Once the individual process unit models are assembled and tested, a complete flowsheet simulation can be formulated using the LSP system. The information flow diagram for the hot carbonate process is shown in Fig.3. Node 8, the recycle convergence module, is not actually used in the LSP system but is inserted only to show the point at which the flowsheet iterations are initiated.

4.1.4 Results

The simulation output for a typical case will consist of the detailed stream table for the flowsheet plus the equipment parameter summaries. As reported in FE-2125 and summarized in Table 9 the results obtained are generally in good agreement with literature design cases. For instance, when compared to the design calculations reported by Maddox and Burns (1967) the simulation predicts somewhat less efficient acid-gas removal. These differences can be in part explained by differences in the actual

calculations. Maddox and Burns:

- 1) assumed constant molal overflow in their calculations
- 2) applied an overall stage efficiency to the fractional number of theoretical plates for determining the actual number of trays
- 3) introduced a lean solution containing a different acid-gas loading than was found in simulation
- 4) made no corrections in flows for water depletion by the chemical reaction with carbon dioxide and potassium carbonate
- 5) employed a simple calculation for the adiabatic flash

The constant molal overflow assumption used by Maddox and Burns does not introduce a large error in the number of stages as long as a vapor efficiency of one is being used. However, with the stage efficiency being much less than one and being included in the stage stepping, noticeable variations can take place. Also, in their design the equilibrium data was plotted over a temperature range and the values were averaged to produce a uniform curve. Finally, determination of fractional stages from a McCabe-Thiele diagram is hardly likely to lead to accurate results. The simulation model contains the vapor stage efficiencies within the equilibrium equations. It also corrects the water concentrations as carbon dioxide is absorbed.

Since the model utilized an accurate calculation for the flash, some differences are experienced. The result is a less efficient removal of carbon dioxide from the stripper's feed stream. This factor resulted in a higher reboil duty for the model, causing a less efficient regeneration of the rich solution in the stripper for the allotted number of stages. The results also show that a different product stream results from the stripper. This change is a result of the 100% efficiency assumed in the reboiler.

Table 9. Stream descriptions for the hot carbonate model

ABSORBER	gas in	gas out		
		Maddox and Burns	Simulation dry	Simulation wet
CO ₂	11.90	1.75	3.02	3.12
H ₂ O	-	-	-	2.31
CH ₄	79.66	79.66	79.66	79.66
TOTAL	91.56	81.41	82.68	85.09
T °F	200	230	230.4	230.6
P psia	500	<500	<500	<500
stage efficiency		0.05	0.05	0.05
actual number of plates		26	26	26

FLASH	Maddox and Burns			Simulation		
	liquid in	liquid out	vapor out	liquid in	liquid out	vapor out
CO ₂	20.03	15.03	5.00	14.55	12.73	1.82
H ₂ O	606.90	590.90	16.00	609.94	602.98	8.78
CH ₄	-	-	-	-	-	-
liquid inerts	27.07	27.07	-	27.07	27.07	-
TOTAL	654.00	633.00	21.00	651.56	642.78	10.60
T °F	238	210	210.0	242.0	224.2	224.2
P psia	~500	18	18	~500	18	18

STRIPPER	Maddox and Burns			Simulation		
	liquid in	liquid out	vapor out	liquid in	liquid out	vapor out
CO ₂	15.03	10.03	5.00	12.73	5.77	6.96
H ₂ O	630.90*	606.90	24.00	642.98*	602.04	47.90
liquid inerts	27.07	27.07	-	27.07	27.07	-
TOTAL	673.00	644.00	29.00	682.78	634.88	54.86
T °F	210	230	210.0	224.2	230.0	225.0
P psia	18	18	18	18	18	18
stage efficiency		0.10			0.10	
actual number of trays		22			22	
reboiler heat duty						
RTU/min		730100			1068300	

All flows in lb moles/min

*40 lb mole/min reflux is added to the feed

Average cp secs 250

Average storage 145 K

4.2 Methanation Process

4.2.1 Introduction

One of the main products of the pyrolysis and gasification sections of the modified COED process is a synthesis gas with a H_2 to CO ratio of about 2 to 1. To convert this gas to CH_4 it is necessary to adjust this ratio to 3:1 and then to react the resulting mixture to produce CH_4 and the by-product H_2O . In the modified COED process this is to be accomplished using a combined shift-methanation process of the type offered by the Ralph M. Parsons Company. The simulation model of this process will be summarized in this section.

4.2.2 Description of the Process

The principal reactions occurring in the methanation process are

Various other reactions such as the formation and the gasification of carbon are also possible. However, these are generally undesirable and are avoided by using excess H_2 or steam in the reactor. The above reactions are highly exothermic with ΔH of -52,730 cal/mole for the first, -43,680 cal/mole for the second, and -9700 cal/mole for the third. The key to methanation process design is therefore to control the temperature of the reactor so as to avoid sintering the catalyst.

All methanation processes require a $H_2:CO$ ratio of 3:1 which must be provided by a CO-shift reactor upstream of the methanator. The basic idea behind steam-moderated methanation process is to mix the Syngas with steam and carry out simultaneous methanation and shift reactions. An excess of steam provides the necessary mass to absorb the heat of reaction. This concept is utilized by the Ralph M. Parsons Co. in their RMPProcess. This process has the following major advantages:

- elimination of shift reactors
- no recycle of the product gas
- avoidance of carbon laydown by using excess steam
- heat recovery at high temperature

Some pilot plant data is reported in literature (White et al., 1975) but no details regarding the catalyst are available.

The complete process flow diagram for the methanation unit is shown in Figure 4. Six stages of fixed-bed reactors with interstage cooling are shown. As stated by White et al.(1975), the reactors are considered to be fixed-bed, catalytic, adiabatic with steam generation at 1500 psig in conventional heat-exchange equipment between the reactors. The inlet temperature to various reactors is taken between 500 - 1000⁰F as shown in Figure 4. Based on the design evaluated by Professor Faust (1977), it is assumed that the last two stages of heat exchange will be boiler feed water preheaters, while the first four will be steam generators. Each steam generation stage consists of a boiler in which 10% of the boiler feed water is vaporized. A common vapor liquid separation drum (steam drum) is used to which the vapor-liquid mixture from each boiler is fed. The saturated steam is separated in the steam drum and the saturated liquid is recycled to each boiler. After the first six stages, the process gas will be

FIGURE 4. Process Flow Diagram for Methanation Process

scrubbed of CO_2 in a potassium carbonate system after which the final CO level would be further reduced by a conventional clean-up methanation stage consisting of a fixed bed reactor with feed-effluent heat exchanger and a final cooler.

4.2.3 Process Modelling

Reaction Kinetics: One of the main difficulties in modelling a reactor system is in obtaining specific rate equations appropriate to the catalyst used. Although both ICI (Woodward, 1977), Girdler (Beuhler, 1977), and apparently Parsons have suitable high temperature methanation catalysts, the specific kinetic information has not been released. In the present model the approximate kinetic expressions developed by Schiesser et al. (1977) at Lehigh University are used. The kinetics for the combined shift and methanation reaction are based on the high temperature methanation kinetics reported by Vatcha (1976) which are based on reversible Langmuir-Hinshelwood rate function together with kinetics of Girdler's high temperature shift catalyst as reported in their sales literature. The pre-exponent constant and the Arrhenius activation energy for the methanation reaction were then determined by matching the steady state exit conditions to those reported by Parsons. The parameters thus determined provided a very good fit though these are not unique. Kinetics for the clean-up methanation reaction are based on Girdler G-33 and G-35 catalysts as reported by Stein (1979).

The key unit models required in the simulation of this flowsheet are: plug flow, packed bed, reactor models, heat exchangers, pumps, and flash units.

Reactor: Adiabatic, plug flow catalytic reactors are simulated by a conventional plug flow reactor model. The rate of reaction is computed by the following subroutines:

REAMTS - Combined methanation and shift reaction

REAMTH - Clean up methanation using Girdler G-33 and G-65

REAHTS - High temperature shift reaction using Girdler G-3 catalyst

REACT2 - can model adiabatic as well as externally cooled plug flow

reactors. For heat transfer, the temperature of the heat transfer medium and the overall heat transfer coefficient are user supplied. The reactor module employs a Runge-Kutta integration technique to integrate the differential balance equation. The reactor sizing can be carried out by multiple criteria such as a predefined temperature or mole fraction of any species. The reactor volume is computed along with other design parameters for determining the vessel cost.

Heat Exchanger: The interstage heat exchangers are sized by a module which can simulate a heat exchanger with 2 input and 2 output streams. The subroutine is written in most general form and multi-component stream with phase changes can be handled for both the hot and cold streams as shown in the temperature-enthalpy profiles in Figure 5. The user specifies both the inlet streams, amount of heat transferred or the hot or cold stream conditions. The individual heat transfer film coefficients are either user-specified or else suitable default values are used. The program divides the heat exchanger in five segments as shown in Figure 5. For each of these segments, the amount of heat transferred, log mean temperature difference and the overall heat transfer coefficient computed from the appropriate film coefficients of the hot and cold streams (gas, liquid, condensing vapors or boiling liquid) is determined and the clean and dirty heat transfer surface is determined as:

$$A_c = \sum_{i=1}^5 \frac{q_i}{U_{c_i} (LMTD)_i}$$

and

$$A_d = \sum_{i=1}^5 \frac{q_i}{U_{c_i} (LMTD)_i} [1 + U_{c_i} * RD]$$

where q_i is the segmental heat transferred, Btu/hr

FIGURE 5. . . . Temperature Profiles within a Heat Exchanger

TABLE 10. Input and Recycle Stream Information

Stream No.	Description	Temp. °R	Pres. psia	Vapor Frac.	Component Flow Rates lb moles/hr					
					CO	H ₂	CH ₄	CO ₂	N ₂	H ₂ O
1	Feed gas	1359	500	1.0	10361.9	18759.9	1313.9	1518.2	370.9	-
4	Feed steam	1380	500	1.0	-	-	-	-	-	10361.9
28	Gas exit clean-up methanator (guess)	1110	400	1.0	412.0	4250.0	7500	30.0	370.9	100.0
33	C. W.	537	30	0.0	-	-	-	-	-	500000
35	C. W.	537	30	0.0	-	-	-	-	-	1000000
37	Inlet BFW	660	1530	0.0	-	-	-	-	-	67500
38	BFW exit first pre- heater (guess)	889.6	1515	0.0	-	-	-	-	-	67500
40	BFW exit steam drum (guess)	1056.2	1515	0.0	-	-	-	-	-	675000

TABLE 11. Simulation Synopsis

Reactor	Diameter ft	Bed Length ft	Inlet Volumetric/flow ft ³ /hr $\times 10^{-5}$	CO Conversion %	Temperatures (°R)	
					In	Out
1	10	4.93	6.79	60.0	1362	1877
2	11	4.33	10.28	37.6	1461	1816
3	12	3.84	13.57	28.5	1469	1790
4	12.75	3.24	13.36	29.7	1460	1720
5	12.25	4.44	9.51	67.0	1060	1541
6	12.0	4.88	8.14	95.0	960	1234
7	6.5	6.17	3.01	39.0	900	925

Compositions (mole fractions)

	<u>EXIT</u>	<u>FEED</u>
CO	0.0327	0.3206
H ₂	0.3379	0.5804
CH ₄	0.5960	0.0406
CO ₂	0.0024	0.0470
N ₂	0.0295	0.0115
H ₂ O	0.0014	0.0

Export Steam: $\frac{4.5578 \times 10^4 \text{ moles/hr Steam}}{3.2325 \times 10^4 \text{ moles/hr feed gas}}$

Product Gas: $\frac{7.4933 \times 10^3 \text{ moles/w CH}_4}{1.3194 \times 10^4 \text{ moles/hr feed C}}$

U_{c_i} is the segmental heat transfer coefficient, $\text{Btu/hr ft}^2 \text{ } ^\circ\text{F}$

LMTD_i is the segmental log mean temperature difference, and R_d is a user-specified dirt coefficient, $\text{hr ft}^2 \text{ } ^\circ\text{F/Btu}$.

The computed heat transfer area is used to determine the equipment cost.

In addition to the equipment types described above the process simulation uses equipment nodes such as SUM, SPLIT or SEPP which are described in detail in the LSP Manual (1979). These equipment nodes are called in the sequence determined by the information flowsheet shown in Figures 6. The results of example runs based on the process flowsheet is discussed in the next section.

4.2.4 Sample Results

A simulation run utilizing the information flow diagram shown in Fig.6 was carried out. Execution of the simulation of course requires that process input streams and initial values of process recycle streams be specified. A set of such values was given in Table 10. In addition it is necessary to prepare a problem data deck following the data specifications given in the LSP manual. The results of a simulation will include complete stream tables and equipment parameter summaries. For illustrative purposes a summary of the output results is shown in Table 11.

4.3 Water Quench Vapor Recovery

4.3.1 Introduction

The design of an efficient and reliable vapor recovery system which will quench and remove the entrained condensible and solid components generated during the high temperature processing of coal is a key element in many coal conversion processes. The vapor recovery system is a particularly central unit in the operation of the modified COED process shown in Fig.1. It is the unit which defines the flows and purities of the gas, oil, and liquor streams which will be fed to the gas processing, oil hydrotreating, and liquor treating segments of the plant.

In the modified COED process, the feed stream to the vapor recovery system is produced via fluid bed pyrolysis of coal. It thus contains substantial quantities of oil and tars, fine particulates, water and a range of noncondens-ible components. The functions of the vapor recovery system are thus threefold:

- 1) quenching of the hot vapors.
- 2) separation of the condensible water and hydrocarbon phases
- 3) scrubbing of the non-condensable gases to remove entrained solids

The system to be reviewed in this section uses an aqueous liquor stream as quench medium and was tested on a pilot plant scale as part of project COED.

4.3.2 Process Descriptions

The water quench vapor recovery process, shown in Fig.7. consists of venturi scrubbers, multiple liquid phase, vapor-liquid flash separators as well as electrostatic precipitators. The flowsheet contains two stages of venturi scrubbers followed by an electrostatic precipitator to remove any entrained oil mist as well as residual particulates. The condensed oil and liquor mixture is separated into oil, water and vent gas phases in a decanter. The aqueous liquor phase is largely recycled back to the Venturii scrubbers as the quench

Figure 7 WATER QUENCH VAPOR RECOVERY FLOWHEET

medium for the incoming pyrolysis vapor stream and the rest of the liquor is sent to a waste water treatment facility. The quenched vapor product is sent to an acid gas removal system from which hydrogen sulfide along with other impurities are removed. The heavy oil is dehydrated in two stages and is sent to a filtration unit.

4.3.3 Unit Modeling

The simulation of this system requires the development of models for a venturi scrubber, a three phase flash drum, and an electrostatic precipitator. The design of the venturi scrubbers is based on the design equations developed by Goel and Holland (1975,1977). The model takes into account the physical shape of the venturi duct (circular or rectangular cross-section) and accommodates convergent, parallel or divergent fluid flow through the scrubbers. Further details of this model were reported in FE-2275-9.

A second type of key process unit in the flowsheet are the phase separation units. The simulation of the phase separation devices requires that the degree of phase miscibility be known at various process conditions. For the wide boiling mixtures characteristic of pyrolysis vapor, one or two liquid phases along with a vapor phase will occur at the process conditions being considered. To predict this phase behavior, a general multi-phase flash algorithm must be developed. The multi-phase flash strategy employed proceeds as follows. First a two phase flash is carried out using the methods described in the PPROPS manual (1979). This two phase (i.e., vapor-liquid) routine will check the feed conditions using the standard bubble and dew point tests before the actual flash calculation is made. From these calculations, the resulting effluent liquid phase is tested for phase stability. The details of the phase stability test computations are reported in FE-2275-10. If the test indicates

that a three phase system will be stable, a three phase flash calculation is executed. If not, the computations terminate with the two phase results. The three phase flash calculations involve an iterative calculation which is outlined in FE-2275-10. The algorithm employs concepts first reported by Boston [1978] and has proven to be quite efficient. Sample test runs are given in FE-2275-10.

The remaining key unit is the electrostatic precipitator the function of which is to remove entrained fine particles and, possibly, oil droplets. The basic design equations to be used in deriving an efficiency equation are described by H.J. White (1963). This efficiency equation is a function of the total collection area available, charging and precipitating voltages as well as gas volumetric flowrate and gas viscosity. Of course, the efficiency of the precipitator depends on the given particle size distribution and thus the median particle size enters into the calculations. In addition, the efficiency will be dependent on the electrical properties of the particles being sent through the precipitator, particularly, the particle dielectric constant. Once these input parameters are specified a precipitator efficiency can be computed and hence the final effluent particulate concentration in the gas stream is also determined. Further details of the precipitator model were outlined in FE-2275-9.

4.3.4 Flowsheet Modeling

Using the above models for the venturi scrubber, electrostatic precipitator, and multi-phase flash drums, a complete water quench vapor recovery flowsheet can now be assembled for computer simulation. The information flow diagram for the simulation of the water-quench vapor recovery system is given in Figure 8. As indicated by Figure 8, the computer simulation of this water quenching effect will involve three steps. First, the hot pyrolysis vapor stream

Figure 8. Water Quench Vapor Recovery Information Flow Diagram

(stream 1) is mixed with a colder aqueous stream (stream 2) in a sum node (node 1). Once an initial temperature estimate is provided for the effluent stream (stream 3), this stream is then flashed adiabatically in a flash drum (node 2) from which heavy oil, aqueous, and vapor phases are removed. In addition, a final temperature is also determined for these phase streams. Some of the remaining solids in the vapor stream (stream 4) are then removed in a venturi scrubber (node 4). The effluent streams are summed together and sent to a surge tank (node 6) for the next quenching stage.

After the two stages of water quenching is completed, the resulting vapor stream (stream 29) is split into two streams. One stream is sent off to be processed in the acid removal system (stream 34). The other stream is used as a recycle stream for the gasifier reactor (stream 35).

The combined heavy oil and aqueous stream (stream 33) is introduced into a large decanter tank where the heavy oil and aqueous phases settle out. The heavy oil stream (stream 45) is further processed in a series of surge tanks from which any remaining liquor water is removed. The final quenched pyrolysis oil is then pumped into a filtration unit for removal of any solids (stream 52). The aqueous phases which are removed in these operations are combined and recycled back as quench water (stream 38).

The convergence of the overall water quench vapor recovery process requires two loops. The inner loop which contains the two stages of water quenching along with the particulate scrubbing units must be converged (node 27) before the process streams can enter the second loop representing the decanter and surge tanks (node 31). In both convergence loops, the chemical species which will change the most are the water and pseudo-oil components. Hence, in the recycle computation, these components must be treated as the convergence variables.

TABLE 12

Capital Cost Estimate Using PCOST Routine*

Basis: Water Quench Vapor Recovery Simulation Results

Fixed Capital Costs(\$M)	
<u>Description</u>	
Total Bare Module Cost	22429
Buildings and Storage	4704
Site Preparation	979
Off-Site Piping	620
Utility Generation	1017
Spare Parts	480
Contractor Fee	1487
Contingencies	4685
<hr/>	
Total Plant Investment	36401
<hr/>	
Total Number of Equipment Costed:	39
<hr/>	

* Soni Y., Sood M.K., Reklaitis G.V., PCOST Costing Program, May 1979.

The Wegstein successive substitution method is used to achieve convergence on each of the components. An example simulation of the complete water quench vapor recovery process was presented in FE-2275-11 along with complete stream tables and equipment node summaries.

4.3.5 Plant Investment Cost

As an illustration of the use of PCOST to perform an estimate of the plant investment cost, the simulation results were used as input to PCOST. Typical results based on a plant processing 25 M ton/day of Illinois No.6 coal are shown in Table 12. The cost compares favorably with the fixed capital investment of 25 million projected by Jones, et al. in COED report FE-1212-T-9 for this process section.

4.4 Oil Hydrotreating

4.4.1 Introduction

The raw oil produced by pyrolysis of Illinois No.6 coal in the COED pilot plant contained about 2.1% sulfur, 1.1% nitrogen, 8.1% oxygen, and had an API gravity of -4. In order to make this oil environmentally acceptable as a fuel, chemically suitable as a refinery feed stock, and generally more convenient to ship, process, and use, it is necessary to substantially lower the heteroatom (S, N, and O) contents as well as to decrease the density of the oil to 25 API. These objectives are conventionally achieved in the petroleum industry by a limited catalytic reaction of the oil with hydrogen in a process known as hydrotreating.

Based on commercial practice, hydrotreating of heavy oils can be achieved in catalytic reactors using any of three flow configurations:

- 1) Fixed bed reactor
 - a) cocurrent down flow
 - b) cocurrent up flow

- 2) Ebullating bed reactor

Ebullating bed reactors have found application in the petroleum industry and an ebullating bed reactor has been proposed for use with coal oils by HRI. However, there is no publicly available data on the operation of an ebullating bed reactor with coal oils. Fixed bed reactors of the downflow type, often referred to as trickle bed reactors, are quite common and have been extensively studied. The experiments carried out under project COED were all of the fixed bed cocurrent downflow type. Some experiments carried out by ARCO with upflow reactors showed no particular improvements. The model developed in this work is that of a fixed bed reactor. The model could in principle be used for an upflow configuration but has only been verified for the more conventional downflow configuration.

4.4.2 Process Description

Flowsheets for hydrotreating of heavy oils whether of petroleum or coal origin follows a rather standard design. They generally involve one or more stages of adiabatic reactor beds followed by a series of let-down flash separations. The flash separations result in three phases: a gas phase, a hydrocarbon phase, and a water phase. Part of the gas phase material is purged, while the remainder is recompressed and recycled to the reactors along with a make-up H_2 stream. The hydrocarbon phase is usually stripped to remove light constituents while the water phase is sent to sour water treatment.

Since hydrotreating is overall an exothermic process, hydrotreating is generally carried out in multiple reactor beds. Gulf Oil Company's hydrodesulfurization process (Fowler 1973) uses a three stage system where product can be taken after any stage depending upon the sulfur level desired. Several other processes (Mosby et al. 1973; Radford and Rigg 1970) use multiple stages for interstage cooling to avoid high temperature coking, cracking, and excess

hydrogen consumption. Coal oils are a little different as some cracking is desired to obtain a higher gravity product.

Most problems in obtaining a high quality hydrotreated product occur with the heavy oil fractions (boiling over 900°F). Watkins et al.(1973) have shown in the Universal Oil Product's RCD ISOMAX process, that the sulfur level in the product heavy oil fraction is ten times greater than that of the gas oil fraction for a feed in which it was only four times greater. In ARCO bench scale studies (Jones et al.) of Illinois No.6 coal oil, the gas oil fraction had over ten times the sulfur and eight times the nitrogen and oxygen as the heating oil fraction. Also the residual oil from the pyrolysis section showed little desulfurization and only moderate denitrogenation as compared with the total coal oil.

It appears that if a higher quality synthetic crude is desired, a second or third stage could be applied to only the heavy oil fractions from the first stage. Jones in his design report to FMC Corporation suggests a partial condensation and recycle of heavy fractions in the char section of the COED pyrolyzer. A similar idea could be applied in the product recovery part of the hydrotreating plant. Heavy oil fractions could be partially condensed and sent for second stage hydrotreating.

The flowsheet shown in Figure 9 contains most of the design features discussed above. In addition to cooling of the reactor effluent by injection of cold recycle hydrogen, a recycle of heavy oil is incorporated as is rotary precoat filtration of the raw feed oil to remove solid fines.

4.4.3 Unit Modeling

The key model required in simulating this flowsheet is that of the trickle bed reactor. The model which was developed is basically a plug flow adiabatic fixed bed reactor model. As discussed in detail in FE-2275-7 this model is

generally satisfactory. Since the kinetic expressions used were fitted to COED pilot plant data the effects of mass transfer limitations and incomplete catalyst wetting are implicitly accounted for in the kinetic correlations.

The complex chemistry of the reactions occurring in hydrotreating can for modelling purposes be broken down into four phenomena:

- i) cracking and hydrogenation
- ii) heteroatom removal
- iii) catalyst deactivation
- iv) hydrogen consumption

Each of these phenomena is taken into account in the semi-empirical model that has been developed. The form of the model is based largely on suggestions drawn from the literature. The model thus is quite general in formulation but involves a number of kinetic parameters which must be evaluated by fitting experimental data for any new feedstock.

The four reaction phenomena are modelled as follows

- i) cracking and hydrogenation

The hydrocarbon mixture is discretized into m pseudo components. Each pseudo-component is assumed to crack and/or hydrogenate to produce lighter components in a first order fashion. The distribution of products resulting from the cracking and hydrogenation is assumed to fit a Chi-squared distribution. The distribution parameters are determined by data fitting.

- ii) hetero-atom removal

Removal of S, N, and O is considered. The removal of each heteroatom type is assumed to occur via an infinite number of parallel reactions each of which is first order in the amount of that heteroatom present and whose activat-

energies follow a Gaussian distribution. The kinetics is assumed to be independent of H_2 partial pressure. This restricts the validity of the model to H_2 partial pressures of 1500 psi or greater.

iii) catalyst deactivation

Deactivation is modelled by including empirically fit activity correction factors derived from COED deactivation tests.

iv) hydrogen consumption

Since cracking and hydrogenation are lumped, hydrogen consumption is assumed to be proportional to the rates of cracking and hydrogenation as well as proportional to the rates of heteroatom removal.

In addition, heats of formation of the pseudo-components are predicted using a modification of the Mlott-Spooner heat of combustion formula. API gravities are estimated using correlations recommended in the API Technical Data Book. Complete details of the model are given in FE-2275-7 including the parameters determined for Illinois No.6 coal from data reported by FMC as part of project COED. Sample results are also reported there, hence, will not be duplicated in this report.

The second key model required in this process is that of the raw oil filters. Parameters to the standard incompressible filter equation were fit to data reported by project COED. Finally, the let-down phase decanter vessels used in the process had to be modelled. These are complicated by the presence of H_2S , NH_3 , and H_2O . Satisfactory prediction of the phase separations at the high pressures (2500 psia) and temperatures used in the process require consideration of both physical and ionic equilibrium. In the absence of detailed equilibrium data, the water was assumed to separate as a separate liquid phase.

Figure 10. Information Flow Diagram for Hydrotreating Section

All of the NH_3 was assumed to dissolve in the water phase together with an equimolar amount of H_2S (forming ammonium sulfide). The remaining H_2S was assumed to remain in the vapor phase. The other stream components were assumed to distribute following normal two phase flash calculation predictions.

4.4.4 Flowsheet Modeling

The information flow diagram of the flowsheet corresponding to Figure 9, is shown in Fig.10. The model involves some 61 equipment nodes, 84 streams, and 23 stream components. Note that the flowsheet contains two main recycle loops: that of the recycle Oil, stream 32, and that of the recycle hydrogen gas, stream 52. Sample comparisons to a Parsons design are given in FE-2275-8 and detailed simulation outputs in the LSP Applications Manual.

4.5 Hydrogen Generation Section

4.5.1 Introduction

As discussed in FE-2275-5, the modified COED facility requires a hydrogen generation plant to produce the hydrogen required in the coal oil hydro-treating section. This hydrogen could be produced a number of different ways using various alternative plant internal streams as feed stocks. In the section simulation model developed in part of this contract, the feed stream is taken to be a portion of the sweetened synthesis gas that also serves as feed to the bulk methanation section.

4.5.2 Process Description

The available feed gas to the hydrogen generation plant has a hydrogen composition of 47% (mole basis) while the feed gas to the hydrotreating section must contain 95% H_2 . Upgrading of the stream can be accomplished using a modification of the syn gas generation section of conventional NH_3 plants. As shown in Fig.11, the feed gas is steam reformed to convert all hydrocarbons to

CO and CO₂. The resulting mixture is subjected to two stages of shift reactors in which CO is oxidized to CO₂ and additional H₂. The CO₂ formed is removed using a conventional hot carbonate system (See Section 4.1). The resulting gas is compressed and could optionally be processed through a clean-up methanation reactor. If the feed hydrocarbon content is low enough, then reforming may not be worthwhile, and the steam reformer may be deleted from the design.

4.5.3 Unit Models

The models required in this case are those of the reforming unit, the shift reactors, and the acid gas removal process. The latter process section model was already described in Section 4.1 and the shift reactor models are analogous to those discussed for the methanation section (4.2). Hence, the remaining key unit is the steam reformer.

The catalytic reaction of light hydrocarbons with steam at elevated temperatures and pressures is known as steam reforming. It is an important industrial reaction for producing hydrogen. The overall reaction is endothermic thus favored by high temperature. The reaction is generally carried out at 900-1500°F and at pressures up to 450 psi in catalyst packed tubes which are heated externally. Though high pressure does not favor equilibrium conversion, the reaction is still carried out at elevated pressures mainly because compression before reforming is economical.

The reactions are rather complex. Generally it is assumed that light hydrocarbons will immediately crack and hydrogenate to produce CH₄ and CO₂ and then that the resulting CH₄ and CO₂ will react via the reactions

It is generally accepted that the effluent from a reformer is normally near its equilibrium composition with respect to these reactions. Consequently, it is

Figure 11. Hydrogen Generation Plant

FIG. 12 INFORMATION FLOW DIAGRAM

accepted practice to design reformers on the assumption that the heat flux supplied to the gas is the limiting factor and not the kinetics (Morse (1973), Yen (1977)). As a precaution, however, some value of the minimum required space time for contacting a given gas with a given catalyst should be known. Moreover, a check for the possibility of carbon formation should be incorporated.

The reformer model developed uses the exit gas equilibrium and radiative heat flux limitation assumptions. The calculation procedures for the model is detailed in FE-2275-7,-8,-9, and basically follow the method outlined by Morse (1973). The radiative and convective section calculations are performed as follows. The enthalpy difference between the inlet and outlet streams determine the needed heat input to the process fluid in the radiant section. The input values of average heat flux and mass velocity along with catalyst data will determine a design of the radiant section. The tube length is determined by the Ergun equation for pressure drop. The number and diameter of tubes are determined from the best match between the surface area required for heat transfer and the cross sectional flow area for the mass flow rate. The large amount of heat produced in the radiant section is utilized in the convection section. Four heat recovery sections in addition to a feed preheater are provided in the reformer module. These sections in a fixed order are the feed gas preheater, steam superheater, steam generator, boiler feed water heater, and combustion air preheater. The procedure for designing the convection sections is adopted from Schweppe and Torrijos (1964). Some iteration is required to ensure that temperature profiles between the flue gas and heat recovery fluid have an approach temperature of at least thirty degree R. Also because an integral tube row number needs to be used for each section an iterative adjustment may be made on the flow rate. The convective heat transfer coefficient equations used for each fluid were the ones recommended by Lord et al.(1970). The final calculation in each convective section is the pressure drop the flue gas

Figure 13. Combined Hydrotreater - H_2 Plant Subsystem

Figure 14: Plant Steam Balance Flowsheet

undergoes in flowing past the bank of tubes. The total heat requirement for the reformer is used to calculate the fuel usage for the reformer.

The fuel heat of combustion as well as the flue gas heat capacity and flame temperature will determine the fuel rate if an exit stack temperature is set. The exit temperature may rise above the set value though because of the minimum temperature required in the radiant section. If too little heat recovery is specified the flue gas may not drop to a low enough level and hence an iteration in the design is required.

The model used for the shift reactors is simply the adiabatic plug flow reactors discussed in Section 4.2. The rate expressions used were supplied by Girdler for their high temperature shift catalysts G-3 and low temperature shift catalyst G-66B.

4.5.4 Flowsheet Simulation

The simulation of this section follows the information flow diagram shown in Fig.12. The only recycle is that in the hot carbonate system. For purposes of studying the H_2 plant, this recycle can be deleted. A representative simulation run for this plant section is given in FE-2275-10. The H_2 plant simulation has been run in conjunction with the hydrotreater and acid gas removal section models as a series of separate job steps. Fig.13 shows the typical flows and compositions for one such run. For simplicity only the dominant chemical species are listed.

4.6 Plant Steam Distribution Network

4.6.1 Introduction

A coal conversion process can in many ways be viewed as a large steam distribution network. Large flows of process steam at pressures varying from 500 to 100 psia are required in the methanation, H_2 plant, and gasification sections. Large high pressure steam flows are required to drive the pyrolysis

vapor compressors, the H_2 plant compressors, and the final SNG product compressors. Significant amounts of steam will be raised in the methanation section, the steam reformer, the combustor, the flue gas economizer, as well as between the shift reactor stages. Clearly, the efficient design of this steam network is an important part of the overall process design. Accordingly an LSP-II model has been developed for a general steam distribution system. The model allows for four steam pressure levels, can accommodate input and/or export of different pressure level steam as well as horsepower, and incorporates an optional combined cycle steam generator.

4.6.2 Steam Network Description

A typical steam distribution network is shown in Fig.14. The network consists of four pressure headers: for high, level I, level II, and low pressure steam. The steam at each header can be divided into steam generated from waste heat boilers, steam injected into the process without condensate return, steam used for heating, as well as steam used for generating horsepower or electricity. Accordingly there is associated with each pressure level:

- 1) A waste heat boiler representing all such boilers for that pressure level. These boilers are not simulated explicitly, but are accounted for as black boxes with fixed condensate input requirements and fixed quantities of steam and blowdown.
- 2) A fixed quantity of process injection steam
- 3) A fixed quantity of steam that is used for process heating.
Once again the process side is only accounted for by the fixed streams going into and coming out of the heating block.
- 4) A pump that compresses the condensate to the desired pressure before it is returned to the appropriate boiler.

Associated with the high and the two intermediate pressure levels are the following:

- 1) A let-down station to throttle steam to the next lower pressure level
- 2) A back pressure turbine that generates power and at the same time reduces pressure to the next lower level
- 3) A network of flash units that flash the condensate returned from the process as well as the back pressure turbines to separate a desired pressure steam from the condensate.
- 4) A second network of flash units that flash the blowdown from the boilers.

Associated with the low pressure header is a condensing turbine. Also a small quantity of the low pressure steam is needed for deaerating the condensate before returning to the boilers. A condensing turbine is also provided for the high pressure header. However, this turbine is inefficient to operate and will be operated only if additional steam must be used for producing horsepower. An auxiliary boiler is included. This boiler will be operated only if the waste heat boilers cannot meet all of the steam requirements. The fuel for this boiler is the hot gases that are obtained by burning compressed air and methane in a combustor. The hot gases, at user option, are passed through a turbine before coming into the boiler. This combined cycle option is thermodynamically more efficient.

4.6.3 Unit Modeling

The individual model required in the simulation of the steam flowsheet are those of an expansion turbine, an auxiliary boiler, an air compressor, a flash unit and various mixing, splitting, and heat exchanger units. The details of these unit models are relatively straight forward. Turbine and

compressor simulations are carried out assuming isentropic expansion/compression with specified efficiencies. The calculations are performed using the PPROPS entropy routines and the special PPROPS steam properties routines.

4.6.4 Flowsheet Simulation

The network is simulated using the LSP-II system. The calculation procedure for this application differs from a conventional flowsheet simulation in that two objectives need to be met: convergence of the condensate flow loop and minimization of the auxiliary steam requirements. The basic principle involved in developing a thermodynamically efficient design is to generate power by expanding higher pressure steam through back-pressure turbines and then to use the expanded steam for process heating or injection needs. This process is called cogeneration since both mechanical and heat energy are generated. By careful matching of power and heat needs efficiencies higher than those of a normal Rankine cycle can be attained. In the LSP-II implementation, the minimization objective is achieved by shifting as much as possible of the power generation to the higher pressure steam headers. The minimization of auxiliary steam requirements could be achieved by using an optimization algorithm such as a direct search method in which the simulation would be executed for each trial point. However, given the dimensionality of the problem, this is computationally quite inefficient. The procedure described here is quite efficient requiring typically only three to four flowsheet passes.

Given the waste heat boiler steam flows and conditions, the boiler blow-down flows, the process steam requirements and condensate return flows, the required driver horsepower, the let-down steam flows, as well as upper bounds on the export steam and export horsepower allowed, the calculation proceeds as follows:

- 1) Perform blow-down flash and balance calculations to estimate blow-down steam and condensate flows
- 2) Reset node parameters for those nodes that require the header pressure to the pressures set for the waste heat boilers
- 3) Given the specified condensing turbine exhaust pressure, calculate the corresponding saturation temperature and set the condenser operating temperatures
- 4) Using the correct stream values perform the flash and material balance calculations associated with the flash trains
- 5) For each steam header beginning with the lowest level header
 - a) determine the net steam requirements
 - b) select how to satisfy these requirements: either from the extraction turbine in the next higher pressure level or from the let-down stream.

This selection is made by calculating the outlet flow of the turbine and the horsepower generated for a unit inlet flow. The residual unsatisfied horsepower requirements are then checked to determine how much horsepower could be generated using the extraction turbine. The flow chosen corresponds to the smaller of either the net steam requirement or the unsatisfied horsepower requirements. If the latter requirement determines the extraction turbine flow then the remaining steam flow is obtained by simple let-down.

- 6) The calculations at the highest pressure level header are identical to those for the lower levels with the following exceptions. If there is an excess steam supply at the highest level, then a check is made to determine if additional horsepower

needs to be generated. If so, the appropriate amount of steam is sent to the condensing turbine. The remaining steam is sent down the let-down stations.

- 7) If a shortage of steam exists at the highest pressure level then the auxiliary boiler or combined cycle system must be used. First these units are simulated using a unit input to determine the resulting output. Then the input is scaled to produce the required output and the auxiliary boiler or combined cycle system is simulated to produce the precise output flows
- 8) The complete high pressure level is next simulated to fix the condensate flows to the low pressure level
- 9) Next, the deaerator is simulated. Given the total condensate flow and the user selected operating pressure, the lower level steam requirements for the deaerator are computed. If the steam requirements are negative, the pressure level is adjusted until a zero flow is obtained.
- 10) The make-up water flow is next computed by material balance. The condensate flows to the boilers are emptied and the condensate pumps horsepower requirements are evaluated
- 11) Finally, the deaerator steam flow and total BFW pump horsepower requirements are computed to the values at the previous iteration to determine whether convergence was attained. If not, the computations continue with step 4.

The above computational procedure represents a departure from the conventional sequential modular calculation strategy in three respects:

- 1) node loops involving module computations using unit input flows followed by a repeat simulation using scaled input flows
- 2) execution of flowsheet segments as separate entities and against the direction of flow
- 3) execution of flowsheet entities controlled by conditional logic.

These features require a simulation executive that admits a user supplied flowsheet calculation sequencer. This feature is available in LSP but not in most flowsheeting packages. Sample simulation results and further simulation details are given in FE-2275-11.

5. Coal Conversion Units

5.1 Development Overview

One of the key tasks of this contract has been the formulation and implementation of reactor models of several primary coal conversion reactors. The initial contract objectives included the two-stage BIGAS gasifier, the BIGAS fluid bed methanator, and the SRC dissolver. After four months of development work, the objectives were altered and these three reactor models were dropped at ERDA request. Because of thesis requirements the work on the two BIGAS reactors was nonetheless completed and reported in the thesis by M. Tanzio (See Section 1.4). After August, 1976 work commenced on the pyrolysis reactor system model and the model of the lift-tube partial combustor. Detailed model development for the gasifier and combustor reactors was delayed pending release of COGAS data. When this was not forthcoming and, as a consequence of the conceptual study, FE-2275-5, effort was directed at modelling a steam-char gasifier using IGT kinetics and a fluidized bed combustor using the simple CSTR solids assumption. The pyrolysis system model was completed in the third quarter of 1977 and an integrated pyrolysis, gasifier, combustor, lift-tube

model (using the simplified gasifier/combustor models) in the third quarter of 1978. At that time, work was initiated to develop a more detailed generalized fluidized bed model which could accommodate with suitable changes both char gasification and char combustion. That model was completed at contract termination.

In this section, a brief review is given of the key elements of the pyrolysis section, the lift-tube, and the generalized fluid bed model. The section concludes with a summary of the integrated coal conversion system model.

5.2 The Pyrolysis System

5.2.1 System Description

As proposed by ICGG and piloted by FMC under project COED, low temperature, low pressure, pyrolysis of coal is carried out in a series of fluidized bed reactors as shown in Fig.15. Dry coal is fed to the first stage, partially devolatilized, and sent on to the next stage. In the second reactor the char is further devolatilized at a higher temperature. Part of the char is recycled to the first stage as heat carrier and the remainder is transferred to the third stage. In the third stage the coal is devolatilized at a still higher temperature with part of the residual again recycled while the remainder is transferred to the char gasifier. All of the heat for the system is supplied by the synthesis gas from the gasifier available at about 1600°F. Note that this synthesis gas combined with the devolatilized species serves as fluidizing gas for the three fluid beds. Note further that the char recycle streams are transferred pneumatically in dense phase using as transport gas a portion of the gas stream leaving the vapor recovery section. Depending upon the type of coal processed and the temperatures selected, the system can be expanded to five beds and the gas streams can be rerouted. However, the counter-current solids flow pattern is retained.

Fig.15

FLOW DIAGRAM OF A THREE STAGE PYROLYSIS PLANT

5.2.2 Reactor Modeling

Modeling of any one of the pyrolysis beds requires consideration of the devolatilization kinetics, the reactor flow patterns, the gas-solid heat transfer, and the fluidization phenomena: bed expansion, elutriation, attrition, and pressure drop. On the basis of single particle models employing total devolatilization kinetics it could be shown that the gas-solids heat transfer and devolatilization occur very fast compared to the solids residence time in even a shallow bed. Moreover, it could be shown using the detailed devolatilization kinetics reported by Suuberg, et al. (1977) that devolatilization at low pressures was primarily temperature dependent. That is, the kinetics were such that at a given temperature a conversion plateau was reached very quickly and that subsequent extended residence times at the same temperature produced very little additional devolatilization. These studies are reported in paper(a.5) referenced in Section 1.4.

In addition, at low temperatures and pressures, particularly, low hydrogen partial pressures, the solid particles do not react with the surrounding gas nor are there any appreciable homogeneous gas phase reactions. Thus, there is no need to represent gas-solid interactions or reactor flow patterns. It is sufficient to treat the solids as well mixed and as being unaffected by the surrounding gas. These observations substantially simplify the resulting reactor model and allow a satisfactory approximate model to be formulated.

In the approximate model, the particle temperature history is quantified in terms of mass fractions x_{nj} which represent the fraction of the char in reactor n which has been treated at temperature T_j of reactor j . The discretizing assumption made is that all particles in mass fraction x_{nj} will have the same properties (density, enthalpy, and volatiles content). It is also assumed on the basis of available experimental data that once a particle has been

treated at a given temperature, it will be inert during the course of any subsequent lower or same temperature treatment.

In spite of these convenient but reasonable assumptions the solution of the linked kinetic models is complicated because of the counter-current gas and solids flows between the units. A sequential modular strategy is quite impractical. Instead, it is expedient to use a simultaneous solution strategy. The solution strategy proceeds through the following steps:

- 1) simultaneous solution of the flowsheet total mass, char, and energy balance equations to determine the flows of all system streams
- 2) sequential solution of the char fraction balance equations to calculate all char stream compositions x_{nj}
- 3) recursive solution of the gaseous species balance equations to update the gaseous species compositions
- 4) estimation of minimum and actual fluidizing velocities and void fractions as well as bed diameter
- 5) prediction of bed heights
- 6) determination of transport disengaging heights
- 7) calculation of particle size distributions in the reactors and estimation of fines elutriation
- 8) determination of average particle residence times and average ages of particles
- 9) updating of stream enthalpies and other physical properties.

These calculations are repeated until a satisfactory specified tolerance between successive iterations is achieved.

TABLE 13. HIGHLIGHTS OF THE PROGRAM

. PARTICLE SIZE DISTRIBUTION IN ALL STREAMS

. ATTRITION

. ELUTRIATION AND CYCLONE LOADING

. CYCLONE EFFICIENCY WITH PARTICLE SIZE

. PARTICLES PERFECTLY MIXED IN FLUIDIZED BED

. CHOICE OF DEVOLATILIZATION KINETICS

. GASEOUS SPECIES CONCENTRATIONS

. CHANGING PARTICLE DENSITY

. VARIABLE PHYSICAL PROPERTIES

. NON-ADIABATIC REACTORS

. CHAR FLOWRATES AND REACTOR SIZES CALCULATED

. CHOICE OF FLUIDIZING GAS SOURCE

. UNFEASIBLE OPERATIONS DETECTED

. CHOICE OF NUMBER OF REACTORS

. HISTOGRAMS FOR PARTICLE SIZE AND DENSITY

. MONTE-CARLO SIMULATION AS AN OPTION

. CHOICE OF ENGINEERING OR METRIC UNITS

5.2.3 The SS/PP Program

The above calculations have been implemented into a stand-alone program SS/PP (Steady State Pyrolysis Program) the key features of which are summarized in Table 13. This program consisting of some 3000 lines of code, is self contained: it includes all fluidization and properties correlations and includes the kinetics for Montana lignite and approximate devolatilization kinetics for Illinois No.6 coal. The program is structured so that processing of different coal types only requires the insertion of a user supplied devolatilization kinetics subroutine. As shown in Fig.16 flexibility is included to allow various routings of the gas streams and to accomodate an arbitrary number of reactor stages. Finally, the program includes as an option a Monte-Carlo simulation of the particle history in the multi-bed system. This model allows the validity of the discretization assumption to be verified for new coals or radically different reactor conditions. The details of these calculations are discussed in paper a.5, in FE-2275-4, as well as in the program manual.

5.2.4 Simulation Results

Sample results achieved using SS/PP are reported in FE-2275-3 and two different cases are described in detail in the program manual. Direct comparison of the model results with project COED data could not be made because oxygen was injected into some of the pyrolysis stages in the pilot runs, thus substantially altering the devolatilization behaviour and recycle flows. Oxygen injection is not desirable if maximum devolatilization yields are intended and was consequently not proposed either by ICGG or in FE-2275-5.

5.3 The Lift-Tube

5.3.1 Introduction

In the process proposed by ICGG the initial pyrolysis portion of the COED process remained largely intact. However, the final oxygen/steam fed

fluidized bed was replaced by the gasifier/combustor configuration shown in Fig.17. Rather than add both steam and oxygen to a single fluidized bed reactor, steam alone is added to a fluidized bed gasifier. Heat for the endothermic gasification reactions is provided by the heating of an external recycle char stream by the combustor flue gas. The flue gas is generated by burning the collected process fines in a cyclone combustor. This process has the following advantages over the original COED process:

- 1) Since gasification and combustion are done in different reactors, air, rather than O_2 , can be used as an oxidant with SNG still one of the possible products
- 2) The char to be gasified may have had less of an exposure to an oxidizing atmosphere
- 3) The slow char gasification reactions will be carried out at lower levels of char conversion.

The process also has the following potential disadvantages:

- 1) Indirect heat transfer via the char lift-tube will not be as efficient as direct contact heating
- 2) The gasifier char will have been exposed to a higher temperature
- 3) For high char recycle rates and normal levels of excess oxidant in the combustor, the gasifier char may still undergo significant oxidation
- 4) Increased solids handling for the lift-tube recycle will result in more particle attrition.

In the modified COED process studied in FE-2275-5, the cyclone combustor was replaced with a fluidized bed combustor. The resulting flowsheet is shown in Fig.18. Since a fluidized bed combustor operates below slagging conditions

Figure 17 COGAS Gasification/Combustion Section

Figure 18. Gasification/Combustion Section of Modified COED Process

(2200-2450°F), the flue gas temperature of the modified process will be lower and the temperature driving force in the lift-tube reduced. However, the possibility exists of adjusting the flue gas oxygen concentration so that a small but significant amount of char oxidation does occur in the lift-tube thus compensating for this loss of temperature driving force. On the other hand, if the flue gas oxygen concentration is set too low, then CO formation in the lift-tube via the char-CO₂ reaction may lower the char temperature and thus further reduce the temperature driving force. In order to investigate such effects as well as to carry-out systematic studies of the combined reactor system, it is desirable to develop a reasonably detailed model of the lift-tube/partial combustor.

5.3.2 Reactor Modeling

The lift-tube reactor involves the following three key phenomena:

- 1) Entrained flow reaction with changing particle size
- 2) Dilute phase solid transport
- 3) Reaction of a char particle in a N₂-O₂-CO₂ environment.

For the simplest situation an entrained flow reactor can be modelled as a plug flow reactor with complete mixing in the radial direction, no mixing in the axial direction, and no entrance effects. If we do not further classify the solids flow, say according to size, density, or temperature, then the lift-tube design equation can be written as:

$$-\frac{dW}{dz} = \frac{1}{u_s \rho_s v_s f_r} R W$$

where

W = solid mass flow rate

z = axial position

U_s = particle velocity

ρ_s = particle density (apparent)

V_s = particle volume

R = solid reaction rate

f_r = fraction of solid particle which is reactive material

The char fed to the lift-tube will, however, consist of a distribution of sizes and consequently the above solid balance equation must be modified to include a balance on each size cut. Each such balance must further account for the fact that particles shrink in size with reaction and, hence, will grow out of one size cut and into another. The resulting solids balances will thus expand into a set of differential equation, one for each size cut. Furthermore, since the particle reactions will affect their temperature and since the flue gas char heat transfer is a key issue, these equations must be augmented by a differential energy balance equation for each size cut. A parallel set of differential mass balances must be written for the gaseous species and a differential energy balance must be written to follow the mixed gas temperature. The gas balances include an exponential mixing term which allow the effects of incomplete gas mixing to be modelled. Finally, a mass balance equation must be written on the ash since the solids size cut balances only consider the active material and not the attrited ash created as the particles react and shrink. The formulation of these equations is discussed in FE-2275-9,11 and, hence, will not be repeated here. For ten size cuts as well as the four gaseous species O_2, N_2, CO , and CO_2 , the entrained flow balance equations amount to 26 differential equations.

The balance equations include several terms which must be evaluated using subsidiary design equations. These terms involve the size cut velocities, void fractions and reaction rates. The particle velocities and void fractions involve considerations of dilute phase solids transport. As discussed in FE-2275-11, dilute phase transport is a fluidization regime which occurs at gas velocities behind the slugging regime which forms the practical upper bound for fluidized reactor operation. Beyond a characteristic velocity known as the choking velocity, dilute phase transport sets in, that is, solids move in entrained flow with the gas. Since it is generally desirable to operate at conditions safely above choking, the model must include a prediction of this critical velocity. Punwani's extension of Yeng's correlation, as reported by IGT (1978) is suitable for this purpose. Yeng (1975,1976) also gives further correlations which predict voidage, particle velocity, and pressure drop. These are incorporated into the lift-tube model.

To predict the char-particle reaction rates in an $N_2-O_2-CO_2$ atmosphere, it is necessary to consider the mechanisms of reaction and diffusion for single particles subject to the heterogenous reactions

and the homogeneous gas phase reaction

Such a boundary layer model was developed following the work of Mon and Amundsen (1978). On the basis of parametric studies, a sample result of which is given in Fig.19, it could be concluded that for the range of temperature and composition which are likely to be encountered in lift-tube operations,

Figure 19. Boundary Layer Profiles for the Oxidation of a 50 μ m Char Particle

essentially no CO oxidation occurs in the boundary layer. Consequently, a single film model with diffusion controlled reaction is satisfactory for representing the char reaction rates.

The complete lift-tube design model thus forms a set of ordinary initial value differential equations plus a set of algebraic equations which must be integrated along the length of the tube. The ease with which this integration can be carried out depends upon the nature of the kinetic expressions and the range of solid particle sizes under consideration. Initially a fourth-order Runge-Kutta integration technique was used for this purpose. However, the variation of particle temperature and particle reaction rate with particle size results in a "stiff" set of differential equations. Gear's method for integration, an implicit method allowing variation of both integration order and step size, was able to satisfactorily integrate the set of design equations.

5.3.3 Results

The lift-tube model was used to conduct a series of parameter studies which are reported in FE-2275-11. The results of these studies were the following:

- i) constant physical properties of the gas may be used over the tube length
- ii) the particle size distribution is not substantially altered in the lift-tube
- iii) the char temperature is significantly higher than would result if no char reaction would occur
- iv) particle size cut calculations are necessary in order to predict temperature peaks or "hot spots"
- v) incomplete gas-solids mixing at the inlet can be important if the tube is not long enough to allow a final steady-state temperature profile to be reached.

On the basis of these studies it was possible to conclude that for purposes of an integrated model it is satisfactory to use an average char size in the lift-tube model. Once the integrated reactor calculations have converged, the multi-size cut model can be executed to determine the detailed lift-tube profiles and design.

5.4 The Generalized Fluid Bed

5.4.1 Introduction

The remaining two reactors, the gasifier and the combustor, are both fluidized beds in which char particles are consumed by reaction with a gas. In spite of the substantial differences in the chemistry of the reactions, the calculations required to evaluate the design of these reactions are quite similar in structure. In fact the following general design procedure must be followed for any fluidized bed reactor in which solid reacts:

FLUIDIZED BED REACTOR DESIGN PROCEDURE

- 1) Specify the known operating conditions
 - operating temperature and pressure
 - gaseous reactant inlet composition and temperature
- 2) Specify inlet solid and gas flow rates and solid conversion
(or outlet solid flow rates)
- 3) Estimate the unknown reactor conditions
 - reactor bed particle distributions
 - fines flow rate and particle distribution
 - minimum fluidization velocity
 - bed void fraction
 - bed height
- 4) Guess solid conversion for each of the heterogeneous reactions

- 5) Use the reactor flow model and the component balance equations to update the gas compositions and char conversions
- 6) Solve the particle distribution calculations to find the
 - bed weight
 - bed particle distribution
 - fines rate
 - fines distribution
- 7) Re-evaluate the gas phase physical properties
- 8) Use the updated gas phase compositions and particle distributions to compute
 - minimum fluidization velocity
 - fluidizing velocity
 - bed void fraction
 - bed diameter
- 9) Compute the reactor height
- 10) Check for convergence and either stop or return to step 5.

Given these common features, a generalized fluid bed reactor model has been developed which, with the appropriate single particle kinetic expressions and specification of the gas and solid flow characteristics, can be applied to either gasification or combustion or any other application involving solid reactions. In the next section we will summarize the salient features of this model.

5.4.2 The Fluid Bed Model

5.4.2.1 Conceptual Formulation

Following the Davidson-Harrison two phase fluid bed reactor representation, a fluid bed reactor can be viewed as consisting of basically two regimes: a dilute (bubble) phase and a dense or emulsion phase. The dilute phase consists

FIG. 20 GENERALIZED D-H MODEL

of gas bubbles rising through the fluidized bed; while the emulsion phase consists of the solids plus the interstitial gas. The bubbles are assumed to be of constant size and to be uniformly distributed over the reactor cross-section. The emulsion void fraction is assumed to be that of the bed at minimum fluidization conditions; consequently, all of the gas in excess of that required to maintain that void fraction is assumed to form the bubble phase. As shown in Fig.20, the emulsion phase can further be subdivided into the solid particles and the interstitial gas. Finally, because of the special flow patterns which arise in the vicinity of the gas distributor, it is appropriate to incorporate a grid (or jet) region. The extent of this region will be defined by a jet penetration depth for which empirical correlations are available. The complete reactor can thus be viewed as consisting of four compartments.

The feed gas to the reactor is assumed to enter through the grid region. After the grid reactions it is divided into bubble gas and interstitial gas on the basis of void fractions. Solid feed(s), by definition must enter the solid compartment and elutriated solids as well as the solids overflow must leave from that compartment. The overhead gas from the reactor will of course be a mixture of the exit bubble gas and an outlet flow from the interstitial gas.

The central compartment in this representation is the interstitial gas. It transfers heat and mass with the particles, with the dilute phase, with the grid region and with the reactor walls or immersed surfaces. In order to model each of these compartments it is next necessary to associate with each compartment an appropriate flow pattern. It is generally accepted that the bubble phase is moving in plug flow, that the solids particles are well mixed (CSTR); and that the grid region gas is in plug flow. The choice of flow pattern for the interstitial gas is less obvious, both plug and CSTR flow have been proposed. Following Gordon and Amundsen (1976) we chose the CSTR flow pattern for the

interstitial gas. Finally, it is appropriate to assign reaction classes to each compartment. It is usually assumed in fluid bed modelling that the bubbles and jets contain no solids; hence, that only homogeneous gas phase reactions will occur in the bubbles and in the jets. By definition only homogeneous reactions will occur in the interstitial gas and only heterogenous reactions will occur in the solid phase. These conceptual features can be used to define any gas-solid bed reactor and form the framework for our model.

5.4.2.2 The Basic Design Equations

The design equations required to model each of these compartment are the following:

- i) Grid region: ordinary differential equations, a mass-balance for each species and an energy balance for the entire jet zone
- ii) Bubble phase: ordinary differential equations, a mass balance for each species and an energy balance defining the bubble temperature
- iii) Interstitial gas: the algebraic CSTR mass balance for each species and an energy balance defining the gas temperature
- iv) Particle phase: a partial differential equation the solution of which defines the particle distribution function
This reduces to an ordinary differential equation if the distribution function depends on only a single variable.
A mass balance for each particle size relating the particle surface concentrations to the interstitial gas concentrations. An energy balance equation for each particle size which serves to define the particle temperature.

Complicating features arise in two of these equation sets. The interstitial gas equations are complicated by the fact that the bubble to interstitial gas mass (heat) transfer term included in these equations has a driving force which varies over the reactor length. This term must consequently be integrated over the reactor length. Similarly, the interstitial gas balance equations contain a term corresponding to the mass (heat) transfer from the particles. This term is the sum of the contributions from all particles and must be calculated by evaluating an integral over the particle distribution function. The interstitial gas balances thus become integral equations.

The particle population balance equation is in general a nonlinear partial differential equation. If the particle distribution function depends on diameter (d_p) and density (ρ_a), then that equation takes the form,

$$R(d_p, \rho_a) \frac{\partial P_1(d_p, \rho_a)}{\partial d_p} + R_1(d_p, \rho_a) \frac{\partial P_1(d_p, \rho_a)}{\partial \rho_a} = \alpha_1(d_p, \rho_a) P_1(d_p, \rho_a) + \alpha_2(d_p, \rho_a)$$

Where

$R(d_p, \rho_a)$ is the total heterogeneous rate for all shrinking core reactions

$R_1(d_p, \rho_a)$ is the total heterogeneous rate for all constant size reactions

and $\alpha_1(d_p, \rho_a)$ and $\alpha_2(d_p, \rho_a)$ are nonlinear functions involving the bed weight, feed rate, R and R_1 , and the elutriation constants. (For derivation see the BED manual or Overturf (1980)).

FIG. 21 OVERTURF CALCULATION SCHEME

Since this equation is highly coupled to the other bed variables (the rates depend on particle temperatures and interstitial gas compositions), it must be solved repeatedly within the overall reactor calculation scheme. Efficient solution is thus quite critical. Fortunately this can be accomplished by using a double collocation scheme. The double collocation scheme is advantageous because it allows convenient evaluation of the integrals involving the particle distribution function using quadrature formulas.

A further complicating feature arises with the ordinary differential equations defining the temperature of each particle. As observed in the lift-tube model, over a wide particle size (density) range, these equations can in general be quite stiff and hence very time consuming to evaluate. As a model simplification, it is assumed that particles react to temperature changes instantaneously, that is particle temperatures are at quasi-steady state. As in the pyrolysis reactor case, it can be shown that even for shallow beds, particles as large as 10 mm, and diffusion limited char combustion this is a very good assumption. For endothermic or kinetically limited reactions this approximation is even better.

5.4.2.3 The Solution Procedure

The above complex model consisting of integral, ordinary differential, partial differential, and algebraic equations can be solved using an adaptation of the strategy reported by Gordon et al.(1978) for a simplified fluid bed model. A schematic of the strategy is shown in Figure 21.

The calculations are initialized by performing the complete design calculations assuming a mono-sized feed with average feed properties. Using the resulting interstitial gas compositions and temperature, the grid and bubble phase ODE'S are integrated. Next the particle surface composition and particle temperature equations are solved at selected quadrature points. The particle

FIG. 22 STEAM - CHAR GASIFIER

balance PDE is then solved and the integrals involving the distribution function evaluated. Finally, the interstitial gas equations are solved for new estimates of the interstitial gas compositions and temperature using a Newton-Raphson algorithm. During the N-R iterations, the values of the integrals are not updated although strictly speaking they are implicit functions of the interstitial gas variables. The new estimates of the emulsion gas compositions and temperature are used to reinitiate the computational loop. A convergence promotion step is inserted to update the successive interstitial gas variable estimates.

The entire computational scheme is independent of the particular stoichiometry and kinetics used, although the solution time may well be affected. Consequently, it has proved possible to use this model for both gasifier and combustor applications.

5.4.3 Gasifier Application

The first application of this model was to a steam-char gasifier, the conceptual diagram for which is shown in Fig.22. The char is assumed to be devolatilized and rapid rate methane formation is assumed not to occur. Since no oxygen is introduced into the bed, it is not necessary to include the grid region. Heat transfer to the bed is handled in two ways: transfer through the reactor wall or immersed surfaces (the fluidization is assumed not to be affected) or transfer via a recirculating heat carrier solid. In the latter mode two solids are assumed to exist in the bed. Multiple solids are readily handled in BED providing that the solids are assumed to be super posable, that is, they do not interfere with each other. The heterogeneous reaction kinetics are represented using the IGT semi-empirical kinetics. The difference in the solids is handled via the reactivity term in the kinetic expressions.

Table 14a. Sample Combustor Run

```

*****
* FLUIDIZED BED COAL COMBUSTION - DATA OF BABCOCK AND WILCOX *
*
*****

```

REACTOR DESIGN

***GAS FLOW CHARACTERISTICS

VELOCITIES:

MINIMUM FLUIDIZATION
FLUIDIZING
INTERSTITIAL
BUBBLE
BUBBLE RISE
JET ZONE

9.6244E-01 FT/SEC
8.4443E+00 FT/SEC
9.6244E-01 FT/SEC
1.1013E+01 FT/SEC
3.5310E+00 FT/SEC
4.0987E+02 FT/SEC

FLOW RATES:

INTERSTITIAL
JET ZONE
BUBBLE
TOTAL

9.5879E+00 CU FT/SEC
8.5000E+01 CU FT/SEC
7.5312E+01 CU FT/SEC
8.5000E+01 CU FT/SEC

BUBBLE SIZE:

INITIAL
MAXIMUM
AVERAGE
FRACTION

2.0754E-01 FT
6.9659E+00 FT
7.8555E-01 FT
6.7937E-01

REACTOR LENGTHS:

JET ZONE
FLUIDIZED BED
FREELBOARD
TOTAL

2.5048E-01 FT
2.3392E+00 FT
0 FT
2.3392E+00 FT

REACTOR VOLUMES:

SOLID
INTERSTITIAL
JET ZONE
BUBBLE
FLUIDIZED BED
FREELBOARD
TOTAL REACTOR

1.7747E+00 CU FT
2.1747E+01 CU FT
1.1013E+01 CU FT
1.1013E+01 CU FT
2.3392E+00 CU FT
0 CU FT
2.3392E+00 CU FT

Table 14 b. Sample Combustor Run

***STEADY-STATE DESIGN SOLID FLOW RATES

SOLIDS: CHAR

FEED RATE (DESIGN)	7.4000E-02	LBS/SEC
WITHDRAWAL RATE	8.5484E-03	LBS/SEC
ELutriATION RATE (LESS FINES)	1.5111E-02	LBS/SEC
FINES RATE	0.1429E-03	LBS/SEC
RED WEIGHT OF SOLID 1	1.1749E+02	LBS
SPACE TIME	1.5877E+03	SEC
SOLID CONVERSION	6.8032E-01	

SOLIDS: LIMESTONE

FEED RATE (DESIGN)	1.4000E-02	LBS/SEC
WITHDRAWAL RATE	1.4000E-02	LBS/SEC
ELutriATION RATE (LESS FINES)	1.6463E-07	LBS/SEC
FINES RATE	0	LBS/SEC
RED WEIGHT OF SOLID 2	1.9241E+02	LBS
SPACE TIME	1.3744E+04	SEC

Table 14 c. Sample Combustor Run

***STEADY-STATE DESIGN (POINT) GAS COMPOSITIONS AND TEMPERATURES

COMPONENT	CONCENTRATION - LB MOLES PER CUBIC FEET					
	INLET BED	EXIT JET	EXIT BUBBLE	EMULSION	ENTER FREEBOARD	EXIT REACTOR
O ₂	1.2420E-04	4.6907E-05	3.8803E-05	8.4651E-06	3.5416E-05	3.5416E-05
CO	-0	3.7676E-06	8.1959E-08	1.6497E-05	2.1008E-06	2.1008E-06
CO ₂	6.8030E-06	6.8007E-05	7.9098E-05	9.0962E-05	8.1362E-05	8.1352E-05
H ₂ O	2.5950E-05	6.2151E-05	6.5780E-05	8.1371E-05	6.7557E-05	6.7557E-05
N ₂	5.1930E-04	5.1966E-04	5.1969E-04	5.1988E-04	5.1972E-04	5.1972E-04
SO ₂	-0	5.7052E-07	6.3739E-07	1.0244E-06	6.8150E-07	6.8150E-07
TEMPERATURE	8.5800E+02	2.0456E+03	2.0790E+03	2.0000E+03	2.0699E+03	2.0699E+03

***STEADY-STATE DESIGN (AVERAGE) GAS COMPOSITIONS AND TEMPERATURES

COMPONENT	CONCENTRATION - LB MOLES PER CUBIC FEET		
	AVERAGE JET	AVERAGE BUBBLE	AVERAGE FREEBOARD
O ₂	8.1361E-05	4.2868E-05	3.5416E-05
CO	3.8589E-06	1.2923E-07	2.1008E-06
CO ₂	4.0130E-05	7.5453E-05	8.1362E-05
H ₂ O	4.7057E-05	6.4030E-05	6.7557E-05
N ₂	5.1951E-04	5.1968E-04	5.1972E-04
SO ₂	3.2397E-07	6.0485E-07	6.8150E-07
TEMPERATURE	1.8533E+03	2.0968E+03	2.0699E+03

Table 14d. Sample Combustor Run

***STEADY-STATE GAS PROFILES FOR DISTRIBUTED PARAMETER REGIONS

JETS:

COMPONENT	AXIAL POSITION - FEET							
	0	1.0077E-02	3.2716E-02	6.5384E-02	1.0454E-01	1.4594E-01	1.8509E-01	2.1776E-01
O ₂	1.8377E-01	1.7678E-01	1.6216E-01	1.4335E-01	1.2348E-01	1.0498E-01	8.9865E-02	7.9007E-02
CO	0	1.0279E-03	3.1773E-03	5.7590E-03	7.2425E-03	6.9327E-03	6.1041E-03	5.6032E-03
CO ₂	1.0155E-02	1.4777E-02	2.4512E-02	3.7294E-02	5.1845E-02	6.6760E-02	7.9516E-02	8.8739E-02
H ₂ O	3.7715E-02	4.1076E-02	4.8062E-02	5.6506E-02	6.5898E-02	7.3846E-02	8.0123E-02	8.4568E-02
H ₂	7.6836E-01	7.6629E-01	7.6193E-01	7.5640E-01	7.5111E-01	7.4693E-01	7.4373E-01	7.4134E-01
SO ₂	0	4.8703E-05	1.5159E-04	2.8557E-04	4.2664E-04	5.5621E-04	6.6281E-04	7.4131E-04
TEMPERATURE (DEG R)	8.5800E+02	1.1209E+03	1.5116E+03	1.7929E+03	1.9392E+03	2.0087E+03	2.0363E+03	2.0442E+03

BUBBLES:

COMPONENT	AXIAL POSITION - FEET							
	2.5048E-01	3.3451E-01	5.2329E-01	7.9571E-01	1.1222E+00	1.4674E+00	1.7939E+00	2.0664E+00
O ₂	6.9564E-02	6.6945E-02	6.5417E-02	6.3772E-02	6.1858E-02	5.9897E-02	5.8100E-02	5.6642E-02
CO	5.3580E-03	6.7341E-04	9.1803E-05	9.2323E-05	9.8338E-05	1.0413E-04	1.0909E-04	1.1288E-04
CO ₂	9.6729E-02	1.0188E-01	1.0369E-01	1.0507E-01	1.0669E-01	1.0835E-01	1.0987E-01	1.1111E-01
H ₂ O	8.8401E-02	8.8814E-02	8.9321E-02	8.9586E-02	9.0759E-02	9.1547E-02	9.2267E-02	9.2848E-02
H ₂	7.3914E-01	7.4065E-01	7.4066E-01	7.4024E-01	7.3974E-01	7.3924E-01	7.3877E-01	7.3839E-01
SO ₂	8.1148E-04	8.1729E-04	8.2647E-04	8.3902E-04	8.5370E-04	8.6881E-04	8.8273E-04	8.9406E-04
TEMPERATURE (DEG R)	2.0456E+03	2.1117E+03	2.1169E+03	2.1084E+03	2.0997E+03	2.0922E+03	2.0864E+03	2.0824E+03

The results, reported in detail in the BED manual, are in good agreement with available test cases.

5.4.4 Combustor Application

The second application is to a fluidized bed combustor. The basic kinetics and fluidization correlations are those used by Gordon and Amundsen (1976) in an earlier combustor study. Two solid feeds are assumed: char and limestone. The char is assumed to react via a shrinking core model in which the ash is attrited instantaneously. The size distribution of the limestone is assumed to be unchanged. The grid region model is included and an enhanced jet-to-emulsion transfer is assumed. Good agreement is achieved with data reported by Babcock and Wilcox for a shallow experimental bed. Sample results are shown in Tables 14 a,b,c, and d. Further details are given in the BED manual.

5.5 The Integrated Coal Conversion Section Model

5.5.1 Introduction

The complete modified COED coal conversion section consists of multiple pyrolysis reactor beds, the gasifier, the lift tube, and the combustor bed. This reactor system involves extensive recycle of solid and gaseous streams as well as indirect heat transfer between the beds. An integrated simulation of the complete multi-bed system would require highly nested recycle convergence calculations if the sequential modular calculation strategy were employed. To avoid such iterations a form of the simultaneous solution strategy employed in the stand-alone pyrolysis program was used. However, even with this strategy, solution time become prohibitive if the detailed forms of the gasifier, lift-tube, and combustor models are used. For purposes of integrated systems studies, simplified models of these reactors were developed and incorporated into an overall system model. In this section, a brief discussion is given of model and some sample results obtained using it.

5.5.2 The Simplified Reactor Models

The simplified gasifier model consists of a CSTR gas/solid reactor with low rate gasification kinetics as reported by IGT in the Technical Data Book (IGT, 1978). IGT recommendations, given in the same reference on the basis of operating experience with pilot plant fluid-beds, suggest that, in beds with L/D ratios of less than 4, the assumption of perfectly mixed gas and solid phases is satisfactory for predicting carbon conversion and exit gas composition.

The simplified combustor model is an adaptation of the model reported by Campbell and Davidson (1975). This model is an extension of the two-phase Avedesian and Davidson (1973) model which assumed that the overall rate of

reaction was controlled by the diffusion of oxygen through the gas bubbles and/or subsequent diffusion through the ash bed. The extension primarily consists of including particle size distribution. In our adaptation, the kinetics of the SO_2 -limestone reaction as well as the prediction of NO_x emissions were not taken into account. Instead a conservative CA/S ratio and bed char composition were selected based on literature values.

Also for purposes of the overall model, the lift tube calculations were performed using a single average particle size and assuming that the solid and flue gas will reach an approach ΔT .

The complete reactor system calculations were broken down into five phases:

1. Simultaneous solution of the flowsheet total mass, solids flow, and energy balance equations to determine estimates of the flows of all process streams.
2. Individual reactor particle size balance calculations to update stream particle size distribution and reactor bed weights. When applicable these calculations include the solution of char fraction balances.
3. Solution of the individual reactor gaseous species balance equations to obtain updated species compositions.
4. Updating of stream enthalpies and other physical properties.
5. Reactor sizing and fluidization calculations.

These calculations are performed repeatedly until all stream variables converge to within specified tolerances. This decomposition of the total flow and component balances is possible because the primary coupling occurs through the physical properties and the reactor residence times or conversions. The properties are relatively insensitive to composition, the pyrolysis residence times have a relatively weak effect on extent of volatilization; while the

Figure 23. Gasifier and Char Lift Tube Operating Lines

coupling effect of the gasifier and combustor conversions is eliminated by making these variables design specifications.

For the gasifier the following variables are set at user specified values: temperature, pressure, steam/fixed carbon ration, and fixed carbon conversion. For the combustor, the specified design variables are: temperature, pressure, percent excess air, and fixed carbon conversion.

5.5.3 Results

Representative results obtained for the reactor system using the overall model were reported in FE-2275-9 and in paper b.1.

A further series of runs was made to define a feasible operating range for the system. Figure 23 shows a typical set of superimposed operating lines for the three units.

As can be seen, acceptable operating char recycles of 10 (char recycle/gasifier fresh feed) can be obtained with solids return temperatures of 1750°F and reasonable gasifier conversions of 30 to 50%. Given such operating ranges, the detailed reactor models can next be used to further refine the design conditions.

6. Conclusions and Recommendations

Methodology and general purpose software were developed which do allow computer-aided design and analysis of large scale coal conversion processes. The LINBAL package for larger scale balance calculations was demonstrated to be quick and efficient in solving problems involving over 100 streams, 20 species, and 80 or more flowsheet units. The LSP simulation package embodies constraint handling, recycle calculation, and information management features which are an advance of the state of the art. The two level strategy available in LSP

was demonstrated on a reasonable sized simulation and shown to result in a 1/3 reduction of CPU time over conventional calculation strategies.

The Physical Properties Package was used in all of the simulation models developed under this project and proved to be satisfactory within the limits of the thermodynamic correlations and estimation methods which are encoded. Although the package is largely conventional in overall design, it does employ features which make it convenient to use both within LSP and on a stand-alone basis. The PCOST package represents a new approach to the design of this type of program. The program has proved to be simple to use, robust, and accurate within the limitations of the literature cost correlations that it contains.

The conceptual flow sheet study defining the modified COED process indicated that a COED type process which employed a fluidized bed combustor, gasifier, and a char lift-tube was technically feasible and had many desirable features. Studies carried out using the integrated reactor system model showed that acceptable design operating regions could be found. However, further studies are needed using the detailed fluid bed models developed under this project to better define the best conditions. The analysis of the pyrolysis section indicated quite clearly that reaction kinetics are secondary in this system and that reactor design must be based primarily on agglomeration and fluidization considerations. Studies with the model showed that considerable flexibility exists in the selection of gas routing and that conditions do exist under which char recycle can be avoided. The developed model and solution strategy have proven to be quick and robust under all conditions tested.

The process section simulations, in addition to serving to test the LSP system, have demonstrated the feasibility of reasonably detailed process simulation involving a range of unit operations. Some but not all of the models could be verified against literature data. The hydrotreater model kinetics was fitted to COED pilot plant data with reasonable success. Prediction of the heats of

of formation of the coal oil cuts proved to be the key uncertainty in calculating fixed bed reactor exit temperature. Better correlations are clearly required. The steam system model is a unique development not only in that it models a key but typically neglected process section, but also in that the system executive developed for this purpose can directly optimize the stream routings as part of the simulation logic.

The lift-tube model was a novel development in that it incorporated detailed two variable particle size distribution calculations not considered in literature models. The model predictions indicated that control of the O_2 concentration in the lift tube is the key and very sensitive parameter in the performance of this unit. The generalized fluidized bed model is an advance in the state of the art due to its solids population balance calculations and its capabilities for alternative solids reaction models. Good agreement could be obtained with the model to literature FBC operating data.

In summary, the project has accomplished its primary objectives. However, time and fiscal limitations did not permit the completion of an adequate slate of case studies. The case studies which would be of particular interest include:

- Integrated simulation of the entire modified COED flowsheet.

- Process section case studies involving alternate vapor recovery, bulk methanation, and hydrogen plant design.

- More extensive studies of the coal conversion reactor system model using the detailed fluid-bed and lift-tube models

- Investigation of alternate gasifier-combustor section designs. For instance, a comparative study involving a cyclone combustor as well as a study involving an oxygen fed steam-carbon gasifier would be extremely interesting. This would, however, require the development of additional reactor models.

On the basis of the work accomplished under this contract the stage has been set for interesting and significant computer-aided process design studies. Such studies ought to be pursued as a high priority item.

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