Mineral Processing Research Institute

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Chemical Complex Analysis System

User's Manual
And
Tutorial

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Abstract

This manual describes the Chemical Complex Analysis System that has been developed and used to demonstrate optimization of a chemical production complex. The System incorporates economic, environmental and sustainable costs, and solves a MINLP for the best configuration of plants. It incorporates a Pollution Index methodology to identify sources of pollution generation which targeted for reduction.

The manual includes a tutorial example to demonstrate the procedure to use the program. Then it gives application of the System to an chemical production complex with thirteen multiple plant production units as found in the lower Mississippi river corridor. The optimum configuration of plants was determined based on the triple bottom line that includes sales, economic, environmental and sustainable costs using the Chemical Complex Analysis System. With the additional plants in the optimal structure the triple bottom line increased from $343 to $506 million per year. Multicriteria optimization has been used with Monte Carlo simulation to determine the sensitivity of prices, costs, and sustainability credits/cost to the optimal structure of a chemical production complex. In essence, for each Pareto optimal solution, there is a cumulative probability distribution function that is the probability as a function of the triple bottom line. This information provides a quantitative assessment of the optimum profit versus sustainable credits/cost, and the risk (probability) that the triple bottom line will meet expectations. The capabilities of the Chemical Complex Analysis System have been demonstrated, and this methodology could be applied to other chemical complexes in the world for reduced emissions and energy savings. The System was developed by industry-university collaboration, and the program with users manual and tutorial can be downloaded at no cost from the LSU Mineral Processing Research Institute's website www.mpri.lsu.edu.

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I. Introduction and Methodology

Introduction

The business focus of chemical companies has moved from a regional to a global basis, and this has redefined how these companies organize and view their activities. As described by H. J. Kohlbrand of Dow Chemical Company (Kohlbrand, 1998), the chemical industry has gone from end-of-pipe treatment to source reduction, recycling and reuse. Pollution prevention was an environmental issue and is now a critical business opportunity. Companies are undergoing difficult institutional transformations, and emphasis on pollution prevention has broadened to include tools such as Total (full) Cost Assessment (accounting) (TCA), Life Cycle Assessment (LCA), sustainable development and eco-efficiency (*eco*nomic and *eco*logical). At this point in time there is no integrated set of tools, methodologies or programs to perform a consistent and accurate evaluation of new plants and existing processes. Some of these tools are available individually, e.g. TCA and LCA, and some are being developed, e.g. metrics for sustainability. An integrated analysis incorporating TCA, LCA and sustainability is required for proper identification of real, long-term benefits and costs that will result in the best list of prospects to compete for capital investment.

Chemical companies and petroleum refiners have applied total cost accounting and found that the cost of environmental compliance was three to five times higher than the original estimates (Constable, et. al., 1999). Total or full cost accounting identifies the real costs associated with a product or process. It organizes different levels of costs and includes direct, indirect, associated and societal. Direct and indirect costs include those associated with manufacturing. Associated costs include those associated with compliance, fines, penalties and future liabilities. Societal costs are difficult to evaluate since there is no standard, agreed-upon methods to estimate them, and they can include consumer response and employee relations, among others (Kohlbrand, 1998).

The Center for Waste Reduction Technology (CWRT) of the American Institute of Chemical Engineers (AIChE) published a detailed report with an Excel spreadsheet on Total Cost Assessment Methodology (Constable, et. al., 1999). This TCA report was the outgrowth of industry representatives working to develop the best methodology for use by the chemical industry. The AIChE/CWRT TCA program uses five types of costs. Type 1 costs are direct costs for the manufacturing site. Type 2 costs are potentially hidden corporate and manufacturing site overhead costs. Type 3 costs are future and contingent liability costs. Type 4 costs are internal intangible costs, and Type 5 costs are external costs that the company does not pay directly including those born by society and from deterioration of the environment by pollution within compliance regulations. This report states that environmental costs made up at least 22% of the nonfeedstock operating costs of the Amoco's Yorktown oil refinery. Also, for one DuPont pesticide, environmental costs were 19% of the total manufacturing costs; and for one Novartis additive these costs were a minimum of 19% of manufacturing costs, excluding raw materials. In addition, this TCA methodology was said to have the capability to evaluate the full

life cycle and consider environmental and health implications from raw material extraction to end-of-life of the process or product.

Sustainable development is the concept that development should meet the needs of the present without sacrificing the ability of the future to meet its needs. An effort is underway to develop these metrics by an industry group through the Center for Waste Reduction Technology of the American Institute of Chemical Engineers, and they have issued two interim reports (Adler, 1999) and held a workshop (Beaver and Beloff, 2000). Also, external or sustainable costs are the very difficult to quantify. Sustainable costs were estimated from results given for power generation in the AIChE/TCA report where CO_2 emissions had a sustainable cost of \$3.25 per metric ton of CO_2. A cost of \$3.25 was charged as a cost to plants that emitted CO_2, and a credit of twice this cost (\$6.50) was given to plants that utilized CO_2. In this report SO_2 and NO_X emissions had sustainable costs of \$192 per metric ton of SO_2 and \$1,030 per metric ton of NO_X. In addition, for gypsum production and use, an arbitrary but conservative sustainable cost of \$2.5 per metric ton for gypsum production was used, and a credit of \$5.0 per metric ton for gypsum consumption was used.

Methodology

Combining economic, environmental and sustainability costs with new methodology for the best configuration of plants is now feasible. The analyses and components exist. This paper describes the System shown in Figure 1 that combines these components into an integrated system for use by plant and design engineers. They have to convert their company's goals and capital into viable projects that are profitable and meet environmental and sustainability requirements and have to perform evaluations for impacts associated with green house gases, finite resources, etc.

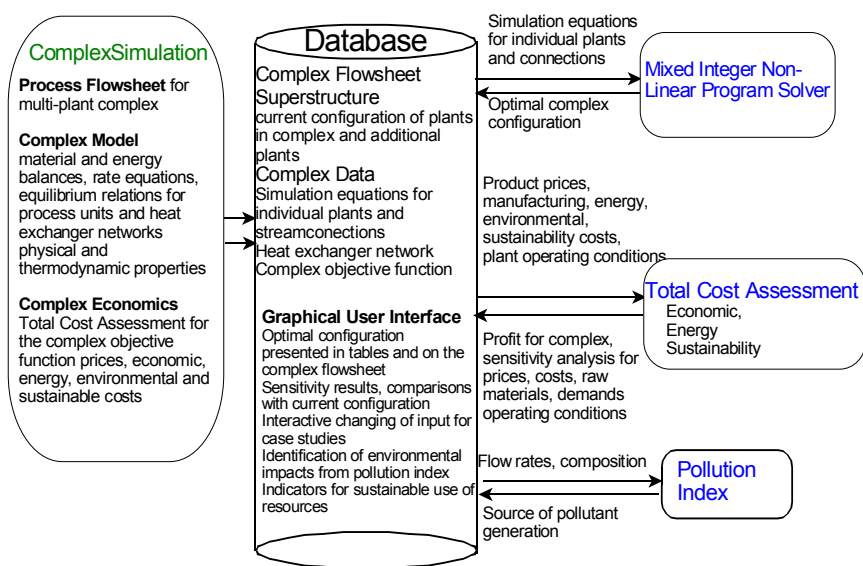Figure 1. Program structure for Chemical Complex System

This program can be used with these projects and evaluations and also can help demonstrate that plants are delivering environmental, social and business benefits that will help ameliorate command and control regulations.

The system has been developed in collaboration with engineering groups at Monsanto Enviro Chem, Motiva Enterprises, IMC Agrico and Kaiser Aluminum and Chemicals to ensure it meets the needs of the chemical and petroleum refining industries. The System incorporates TCA methodology from the AIChE/CWRT Total Cost Assessment Methodology (Constable, 1999) which provides the criteria for the best economic-environmental design.

Flowsheeting Optimization

The structure of the Chemical Complex Analysis System is shown in Figure 1. The system incorporates a flowsheeting component where the simulations of the plants in the complex are entered. Individual processes can be drawn on the flowsheet using a graphics program. The plants are connected in the flowsheet as shown in Figure 2. For each process material and energy balances, rate equations, equilibrium relations and thermodynamic and transport properties are entered through windows and stored in the database to be shared with the other components of the system. Also, the total cost assessment is entered as an equation associated with each process with related information for prices, economic, environmental and sustainable costs. The TCA component includes the triple bottom line for the complex that is a function of the economic, environmental and sustainable costs and income from sales of products. Then the information is used to solve the Mixed Integer Nonlinear Programming (MINLP) problem for the optimum configuration of plants in the complex. Also, the sources of pollutant generation are located by the pollution assessment component of the system using the EPA pollution index methodology (Cabezas, et. al., 1997).
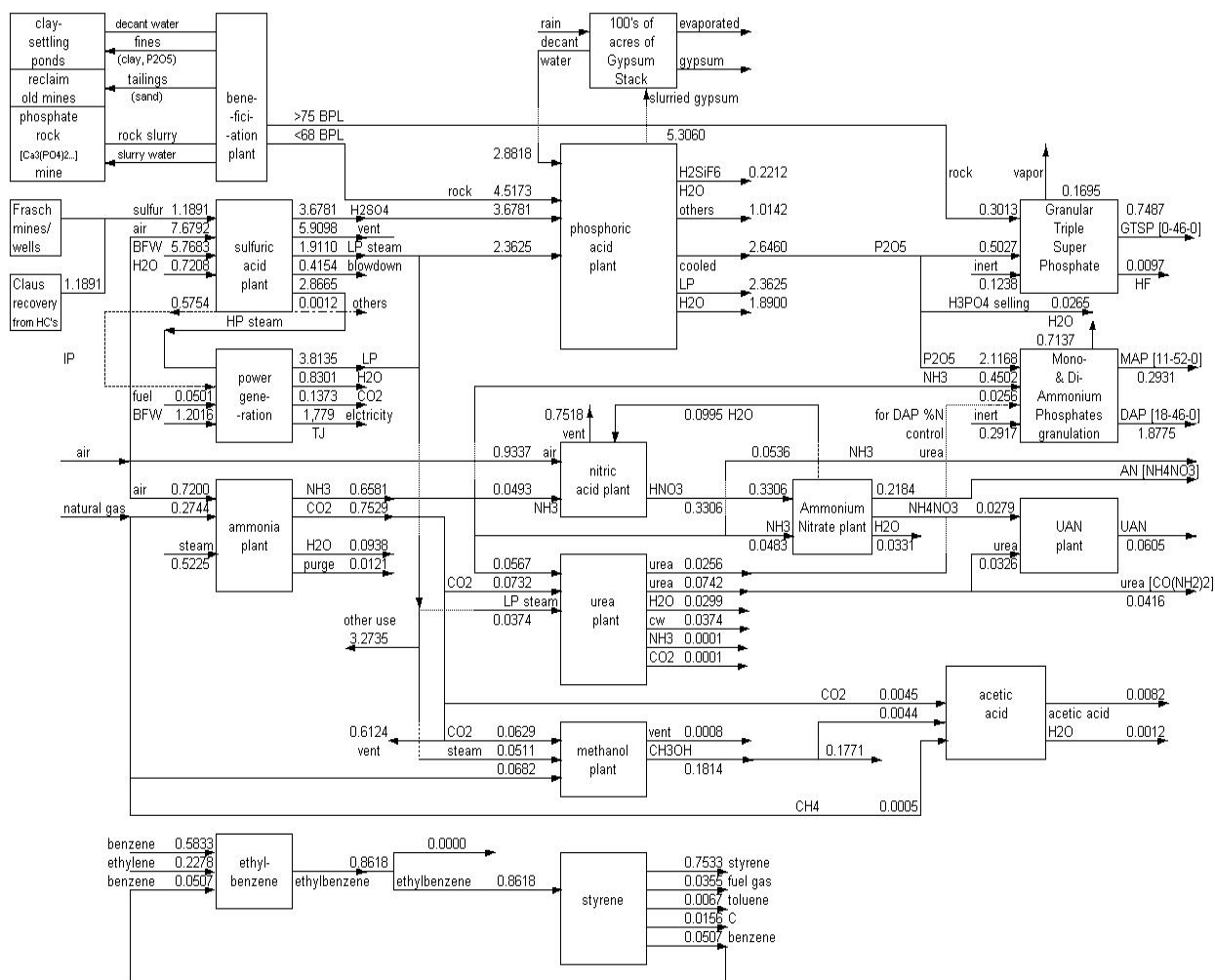
Figure 2 Base Case of Existing Plants in the Chemical Production Complex in the Lower Mississippi River Corridor, Flow Rates Million Metric Tons Per Year

All interactions with the system are through the graphical user interface of the system that is written in Visual Basic. As the process flow diagram for the complex is prepared, equations for the process units and variables for the streams connecting the process units are entered and stored in the database using interactive data forms as shown on the left side in Figure 1 and in section 4. Material and energy balances, rate equations and equilibrium relations for the plants are entered as equality constraints using the format of the GAMS programming language that is similar to Fortran. Process unit capacities, availability of raw materials and demand for product are entered as inequality constraints. Features for developing flowsheets include adding, changing and deleting the equations that describe units and streams and their properties. Usual Windows features include cut, copy, paste, delete, print, zoom, reload, update and grid, among others.

The system has the TCA component prepare the assessment model for use with determination of the optimum complex configuration. The AIChE/CWRT TCA program (Constable, D. et. al., 1999) is an Excel spreadsheet that has the cost in five types, as describe above. This Excel spreadsheet is an extensive listing of all possible costs. The TCA component combines these five categories of costs into three costs: economic, environmental and sustainable. Types 1 and 2 are included in economic cost, Types 3 and 4 are included in environmental cost, and Type 5 is sustainable cost. Economic costs are estimated by standard methods (Garrett, 1989). Environmental costs are estimated from the data provided by Amoco, DuPont and Novartis in the AIChE/CWRT report. Sustainable costs are estimated by the study of power generation in this report. It is an on-going effort to refine and update better estimates for these costs.

As shown in Figure 1, determining the optimal configuration of plants in a chemical complex is a mixed integer nonlinear programming problem where the equality and inequality constraints include material and energy balances, process unit capacities and others as described above. This type of optimization problem is solved using GAMS. GAMS (General Algebraic Modeling System) was developed at the World Bank for very large economic models, and it can be used to determine the optimal configuration of a chemical complex by solving a MINLP programming problem using the DICOPT solver or the SBB solver.

Pollution Assessment

The final step in the Chemical Complex Analysis System is the assessment of the pollution impact of the process on the environment. The pollution assessment module of the Chemical Complex Analysis System is based on the Waste Reduction Algorithm, WAR, (Hilaly, 1994) and the Environmental Impact Theory (Cabezas et. al., 1997). The WAR algorithm is based on the generic pollution balance of a process flow diagram.

Pollution Accumulation =
$$\text{Pollution Inputs + Pollution Generation - Pollution Output} \qquad (1\text{-}1)$$
It defines a quantity called as the 'Pollution Index' to measure the waste generation in the process. This pollution index is defined as:

$$I = \text{wastes/products} = -\left(\Sigma \text{Out} + \Sigma \text{Fugitive}\right) / \Sigma P_n \qquad (1\text{-}2)$$

This index is used to identify streams and parts of processes to be modified. Also, it allows comparison of pollution production of different processes. The WAR algorithm can be used to minimize waste in the design of new processes as well as modification of existing processes.

The Environmental Impact Theory (Cabezas et. al., 1997) is a generalization of the WAR algorithm. It describes the methodology for evaluating potential environmental impacts, and it can be used in the design and modification of chemical processes. The environmental impacts of a chemical process are generally caused by

the energy and material that the process takes from and emits to the environment. The potential environmental impact is a conceptual quantity that can not be measured. But it can be calculated from related measurable quantities.

The generic pollution balance equation of the WAR algorithm is now applied to the conservation of the Potential Environmental Impact in a process. The flow of impact $\dot{I}$, in and out of the process is related to mass and energy flows but is not equivalent to them. The conservation equation can be written as

$$\frac{dI_{sys}}{dt} = \dot{I}_{in} - \dot{I}_{out} + \dot{I}_{gen} \qquad (1-3)$$

where I_{sys} is the potential environmental impact content inside the process, $\dot{I}_{in}$ is the input rate of impact, $\dot{I}_{out}$ is the output rate of impact and $\dot{I}_{gen}$ is the rate of impact generation inside the process by chemical reactions or other means. At steady state, equation 1-3 reduces to

$$0 = \dot{I}_{in} - \dot{I}_{out} + \dot{I}_{gen} \qquad (1-4)$$

Application of this equation to chemical processes requires an expression that relates the conceptual impact quantity $\dot{I}$ to measurable quantities. The input rate of impact can be written as

$$\dot{I}_{in} = \sum_j \dot{I}_j = \sum_j \dot{M}_j^{in} \sum_k x_{kj} \Psi_k \qquad (1-5)$$

where the subscript 'in' stands for input streams. The sum over j is taken over all the input streams. For each input stream j, a sum is taken over all the chemical species present in that stream. M_j is the mass flow rate of the stream j and the x_{kj} is the mass fraction of chemical k in that stream. Ψ_k is the characteristic potential impact of chemical k.

The output streams are further divided into two different types: Product and Non-product. All non-product streams are considered as pollutants with positive potential impact and all product streams are considered to have zero potential impact. The output rate of impact can be written as

$$\dot{I}_{out} = \sum_j \dot{I}_j = \sum_j \dot{M}_j^{out} \sum_k x_{kj} \Psi_k \qquad (1-6)$$

where the subscript 'out' stands for non-product streams. The sum over j is taken over all the non-product streams. For each stream j, a sum is taken over all the chemical species.

Knowing the input and output rate of impact from the equations 1-5 and 1-6, the generation rate can be calculated using equation 1-4. Equations 1-5 and 1-6 need values of potential environmental impacts of chemical species. The potential environmental impact of a chemical species (Ψ_k) is calculated using the following expression

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$$\Psi_k = \sum_l \alpha_l \Psi^s_{k,l} \qquad\qquad (1\text{-}7)$$

where the sum is taken over the categories of environmental impact. α_l is the relative weighting factor for impact of type l independent of chemical k. $\Psi^s_{k,l}$ is the potential environmental impact of chemical k for impact of type l. Values of $\Psi^s_{k,l}$ for a number of chemical species can be obtained from the report on environmental life cycle assessment of products (Heijungs, 1992).

There are nine different categories of impact. These can be subdivided into four physical potential impacts (acidification, greenhouse enhancement, ozone depletion and photochemical oxidant formation), three human toxicity effects (air, water and soil) and two ecotoxicity effects (aquatic and terrestrial). The relative weighting factor α_l allows the above expression for the impact to be customized to specific or local conditions. The suggested procedure is to initially set values of all relative weighting factors to one and then allow the user to vary them according to local needs. More information on impact types and choice of weighting factors can be obtained from the report on environmental life cycle assessment of products (Heijungs, 1992).

To quantitatively describe the pollution impact of a process, the conservation equation is used to define two categories of Impact Indexes. The first category is based on generation of potential impact within the process. These are useful in addressing the questions related to the internal environmental efficiency of the process plant, i.e., the ability of the process to produce desired products while creating a minimum of environmental impact. The second category measures the emission of potential impact by the process. This is a measure of the external environmental efficiency of the process i.e. the ability to produce the desired products while inflicting on the environment a minimum of impact.

Within each of these categories, three types of indexes are defined which can be used for comparison of different processes. In the first category (generation), the three indexes are as follows.

1) $\dot{I}^{NP}_{gen}$ This measures the the total rate at which the process generates potential environmental impact due to nonproducts. This can be calculated by subtracting the input rate of impact ($\dot{I}_{in}$) from the output rate of impact ($\dot{I}_{out}$). Total rate of Impact generated based on Potential Environmemtal Impact is:

$$\dot{I}^{NP}_{gen} = \dot{I}_{in} - \dot{I}_{out} \qquad\qquad (1\text{-}8)$$

where $\dot{I}_{in}$ is calculated using equation 1-5 and $\dot{I}_{out}$ is calculated using Equation 1-6.

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2) $\hat{I}_{gen}^{NP}$ This measures the potential impact created by all nonproducts in manufacturing a unit mass of all the products. This can be obtained from dividing $\dot{I}_{gen}^{NP}$ by the rate at which the process outputs products. Specific Impact generated based on Potential Environmental Impact is:

$$\hat{I}_{gen}^{NP} = \frac{\dot{I}_{gen}^{NP}}{\sum_p \dot{P}_p} = \frac{\dot{I}_{out}^{NP} - \dot{I}_{in}^{NP}}{\sum_p \dot{P}_p} \qquad (1\text{-}9)$$

where $\sum_p \dot{P}_p$ is the total rate of output of products.

3) $\hat{M}_{gen}^{NP}$ This is a measure of the mass efficiency of the process, i.e., the ratio of mass converted to an undesirable form to mass converted to a desirable form. This can be calculated from $\hat{I}_{gen}^{NP}$ by assigning a value of 1 to the potential impacts of all non-products.

Rate of Generation of Pollutants per Unit Product is

$$\hat{M}_{gen}^{NP} = \frac{\sum_j \dot{M}_j^{(out)} \sum_k x_{kj}^{NP} - \sum_j \dot{M}_j^{(in)} \sum_k x_{kj}^{NP}}{\sum_p \dot{P}_p} \qquad (1\text{-}10)$$

The indexes in the second category (emission) are as follows.

4) $\dot{I}_{out}^{NP}$ This measures the the total rate at which the process outputs potential environmental impact due to nonproducts. This is calculated using equation 1-6.

5) $\hat{I}_{out}^{NP}$ This measures the potential impact emitted in manufacturing a unit mass of all the products. This is obtained from dividing $\dot{I}_{out}^{NP}$ by the rate at which the process outputs products.   Specific Impact Emission based on Potential Environmental Impact is:

$$\hat{I}_{out}^{NP} = \frac{\dot{I}_{out}^{NP}}{\sum_p \dot{P}_p} \qquad (1\text{-}11)$$

6) $\hat{M}_{out}^{NP}$ This is the amount of pollutant mass emitted in manufacturing a unit mass of product. This can be calculated from $\hat{I}_{out}^{NP}$ by assigning a value of 1 to the potential impacts of all non-products.   Rate of Emission of Pollutants per Unit Product is:

$$\hat{M}_{out}^{NP} = \frac{\sum_j \dot{M}_j^{(out)} \sum_k x_{kj}^{NP}}{\sum_p \dot{P}_p} \tag{1-12}$$

Indices 1 and 4 can be used for comparison of different designs on an absolute basis whereas indices 2, 3, 5 and 6 can be used to compare them independent of the plant size. Higher values of indices mean higher pollution impact and suggest that the plant design is can be improved.

II. Tutorial Example for Design of a Simple Chemical Complex

This section provides a tutorial example for demonstration of the use of the system. It is taken from the CACHE Design case Studies Series edited by Grossmann(1991).

As shown in the diagram below, a company is evaluating producing chemical C from B in either process 2 or 3. Also, B can be made in process 1, or B can be purchased from another company. This evaluation requires solving a mixed integer linear programming problem. The economic model includes fixed and operating costs as given in the table below. The constraints are material balances mass yields, demand for product and availability of raw materials as shown in the table. Integer variables are used to have C produced from B in either process 2 or process 3 and to have B either produced in process 1 or purchased from another company. The optimal solution will select either process 2 or 3 to produce C and determine if B is to be purchased or produced in process 1 by maximizing the profit. Also, the optimal amounts of B and C will be determined given the demand for C and the availability of A.
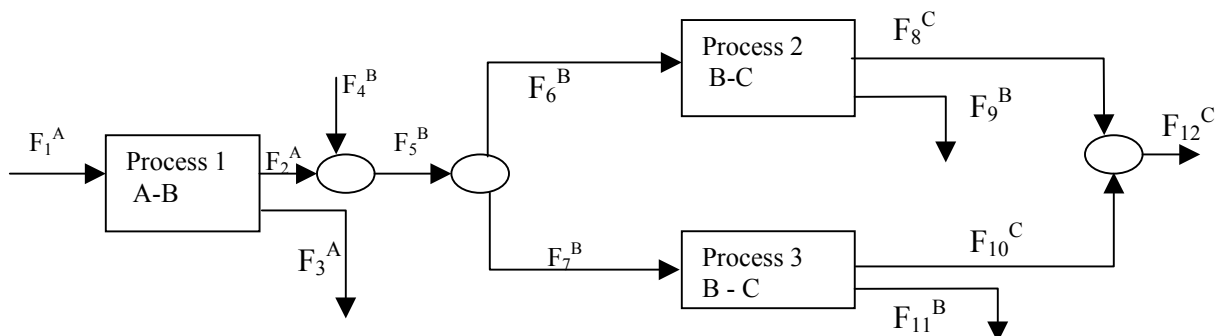
Economic Data :

Process	Fixed Cost ($/hr)	Operating Cost ($/hr)	Feed	Cost ($/hr)
1	1,000	250	A	500
2	1,500	400	B	950
3	2,000	550	**Product**	**Sales Price($/hr)**
			C	1800

Process Data:

Process	Mass Yield	Demand for Product
1 (A to B)	0.90	C <= 10 tons/hr
2 (B to C)	0.82	**Availability of Raw Material**
3 (B to C)	0.95	A <= 16 tons/hr

Diagram :

The process variables are defined as follows where F designates the mass flow rate in tons per hour. A subscript specifies the stream number and a superscript gives the component (chemical species) in the stream.

F_1^A flow rate of A to Process 1
F_2^B flow rate of B to either Process 2 or 3 if Process 1 is selected
F_3^A flow rate of unreacted A from Process 1
F_4^B flow rate of B purchased from a supplier if a supplier is selected
F_5^B flow rate of B to either Process 2 or 3
F_6^B flow rate of B to Process 2 if Process 2 is selected
F_{7B} flow rate of B to Process 3 if Process 3 is selected
F_8^C flow rate of C if Process 2 is selected
F_9^B flow rate of unreacted B if Process 2 is selected
F_{10}^C flow rate of C if Process 3 is selected
F_{11}^B flow rate of unreacted B if Process 3 is selected
F_{12}^C flow rate of C to sales

Integer variables are used to ensure either process A or B is purchased. Also, they are used to ensure that either Process 2 or 3 is selected. They are defined as follows:

y_1 = 1 if Process 1 is selected and 0 if not
y_2 = 1 if Process 2 is selected and 0 if not
y_3 = 1 if Process 3 is selected and 0 if not

The equations for the material balances, demand for product and availability of raw materials, and also the integer equations forcing the selection of Process 2 or 3 and the selection of Process 1 or purchasing B are as follows.

The material balances associated with the processes and the nodes in the diagram are as follows.

Conversion of A to B in Process 1:
$$F_2^B = 0.90\ F_1^A$$
$$F_3^A = 0.10\ F_1^A$$

Conversion of B to C in Process 2:
$$F_8^C = 0.82\ F_6^B$$
$$F_9^B = 0.18\ F_6^B$$

Conversion of B to C in Process 2:
$$F_{10}{}^C = 0.95 \, F_7{}^B$$
$$F_{11}{}^B = 0.05 \, F_7{}^B$$

Material balance on B at node between processes:
$$F_2{}^B + F_4{}^B = F_5{}^B$$
$$F_5{}^B = F_6{}^B + F_7{}^B$$

Material balance on C from Processes 2 and 3:
$$F_8{}^C + F_{10}{}^C = F_{12}{}^C$$

Availability of raw material A:
$$F_1{}^A \leq 16$$ must be modified to include the possibility of not having Process 1
$$F_1{}^A \leq 16 \, y_1$$ operating by incorporating binary integer variable y_1

Demand for product C:
$$F_{12}{}^C \leq 10$$ must be modified to include the possibility of only having Process 2 or 3
$$F_8{}^C \leq 10 \, y_2$$ operating by incorporating binary integer variables y_2 and y_3
$$F_{10}{}^C \leq 10 \, y_3$$

Integer equations include the integer equation forcing the selection of Process 1 or purchase of B:
$$y_1 \leq 1$$

and the integer equation forcing the selection of either Process 2 or 3.
$$y_2 + y_3 = 1$$

Combining the constraint equations with the economic model in the MILP format gives:

operating cost   fixed cost   feed cost

max: $-250 \, y_1 \, F_1{}^A - 400 \, y_2 \, F_6{}^B - 550 \, y_3 \, F_7{}^B - 1{,}000 y_1 - 1{,}500 y_2 - 2{,}000 y_3 - 500 \, y_1 \, F_1{}^A -$
$950 \, F_4{}^B$

sales
$+ \, 1{,}800 \, F_{12}{}^C$

subject to:
 mass yields
$$-0.90 \, F_1{}^A + F_2{}^B = 0$$
$$-0.10 \, F_1{}^A + F_3{}^A = 0$$
$$-0.82 \, F_6{}^B + F_8{}^C = 0$$
$$-0.18 \, F_6{}^B + F_9{}^B = 0$$

$$-0.95 \, F_7{}^B + F_{10}{}^C = 0$$
$$-0.05 \, F_7{}^B + F_{11}{}^B = 0$$

node MB
$$F_2{}^B + F_4{}^B - F_5{}^B = 0$$
$$F_5{}^B = F_6{}^B - F_7{}^B = 0$$
$$F_8{}^C + F_{10}{}^C - F_{12}{}^C = 0$$

availability of A $F_1{}^A \leq 16 \, y_1$
demand for C $F_8{}^C \leq 10 \, y_2$
       $F_{10}{}^C \leq 10 \, y_3$

integer constraint $y_2 + y_3 = 1$
        y_1 will be 0 or 1 since it is specified as a binary variable.

Sensitivity Analysis Optimization

   Sensitivity Analysis is used to analyze solution over the change in parameter values over different iterations. Complex Analysis System uses Monte-Carlo simulation method to perform sensitivity analysis. Refer to Monto-Carlo Simulation in Chapter 3 of (Xu, 2004) for further information.

Sensitivity Analysis data for tutorial example is as follows.
   Price Parameter (P) Members

Element Name	Mean	Standard Deviation
A	500	10
B	950	10
C	1800	10

   Price data is normally distributed and number of iterations are five.

New economic model in the MILP format in terms of price paramter P:
     operating cost   fixed cost   feed cost
max: $-250 \, y_1 \, F_1{}^A - 400 \, y_2 \, F_6{}^B - 550 \, y_3 \, F_7{}^B - 1{,}000 y_1 - 1{,}500 y_2 - 2{,}000 y_3 - P(\text{`A'}) \, y_1 \, F_1{}^A$
   $- P(\text{`B'}) F_4{}^B$
    sales
  $+ P(\text{'C'}) F_{12}{}^C$
   All the other constraints are same as above.

Multi-Criteria Analysis Optimization

   Multi-objective optimization (MOP), also called multi-criteria optimization, is the simultaneous optimization of more than one objective function. The general Multi-Objective Optimization Problem (MOP) can be formally defined as (Equation 2-1):

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Minimize: $F(\mathbf{x}) = [f_1(\mathbf{x}), f_2(\mathbf{x}), ..., f_k(\mathbf{x})]^T$

Subject to: $g_i(\mathbf{x}) \geq 0$ i = 1, 2, ..., m (2-1)

$h_j(\mathbf{x}) = 0$ j = 1, 2, ..., p

$\mathbf{a} \leq \mathbf{x} \leq \mathbf{b}$

Multi-criteria optimization is used to determine the optimal configuration of plants based on objective functions for economic, environmental and sustainable costs.

According to the influence of the decision maker (DM) in the optimization process, multi-objective optimization problem can be classified into different methods, refer to (Xu, 2004). The System implements parametric approach. Parametric approach is also called aggregating approach or weighted sum (Bhaskar, et al., 2000). It combines all the objectives into a single one using addition, multiplication or any other combination of arithmetical operations. Most important is weighted sum scalarization, $\min \sum_{i=1}^{k} w_i f_i(x)$, where $\sum_{i=1}^{k} w_i = 1$, $w_i \geq 0$, are the weighting coefficients representing the relative importance of the k objective functions of the problem. In other words, the DM has to assign the relative weights to each of the objective functions according to their relative importance. In order to produce desirable solutions in proportion to the ranges of the objective functions, the objective functions should be normalized or scaled to get approximately same magnitude of their objective values.

MOP data for tutorial example as follows.

Objective Variable : MultiProfit
Weight Parameters
W1   Independent variable Increment fraction value   0.1
W2   Dependent variable Increment fraction value   0.1

Additional Data
Econ Equation   MultiProfit =e= w2*IOcost+w1*GrossProfit
IOcost =E= -((1000*Y1) +((250*Y1)*F1A) + (1500*Y2) + ((400*Y2)*F6B) + (2000*Y3) + ((550*Y3)*F7B))
GrossProfit =E= - (P('A')*F1A) - (P('B')*F4B) + (P('C')*F12C)

Variables : GrossProfit, Iocost, MultiProfit.

The next section illustrates the use of the Complex Analysis System, and the solution to this problem will be obtained.

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III. Getting Started with the Chemical Complex Analysis System

Upon running the Chemical Complex Analysis System, the first window presented to the user is the 'Chemical Complex Analysis Desk'. This is shown in Figure 3.

By default, the Chemical Complex Analysis System opens a new model named 'untitled.ioo' in the program directory. The complete filename for this new model is shown in the bottom left corner of the window. The bottom right corner shows the date and the time the program was started. The file menu provides various options such as opening a new or an existing model. This is shown in Figure 4. The 'Recent Models' item in the file menu maintains a list of last four recently used models for easy access.
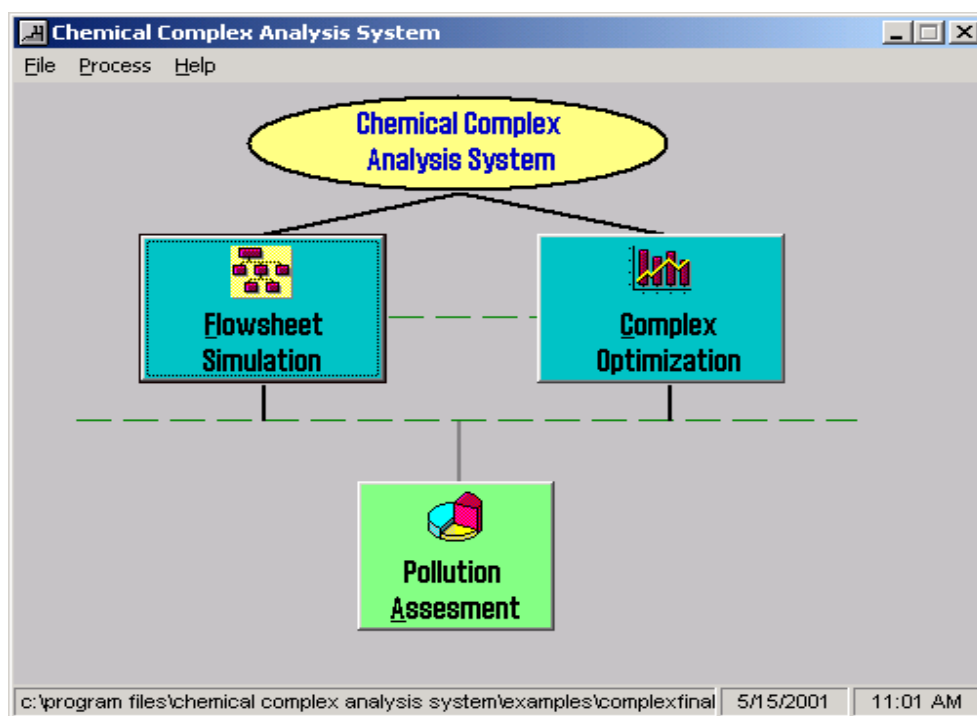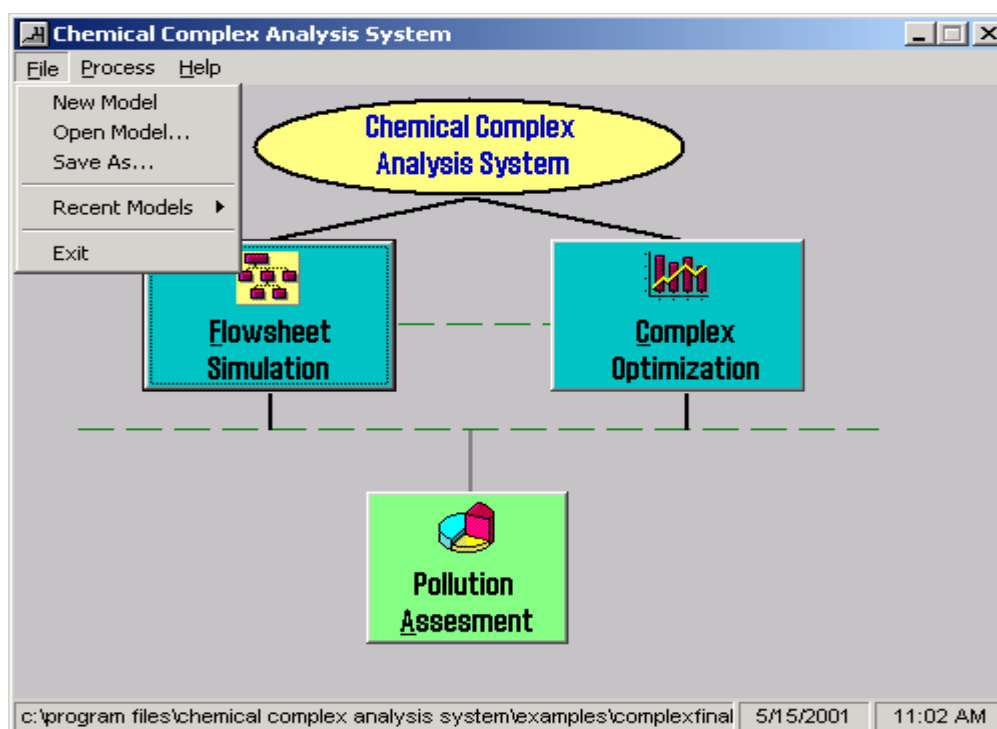

Figure 3: Chemical Complex Analysis Desk

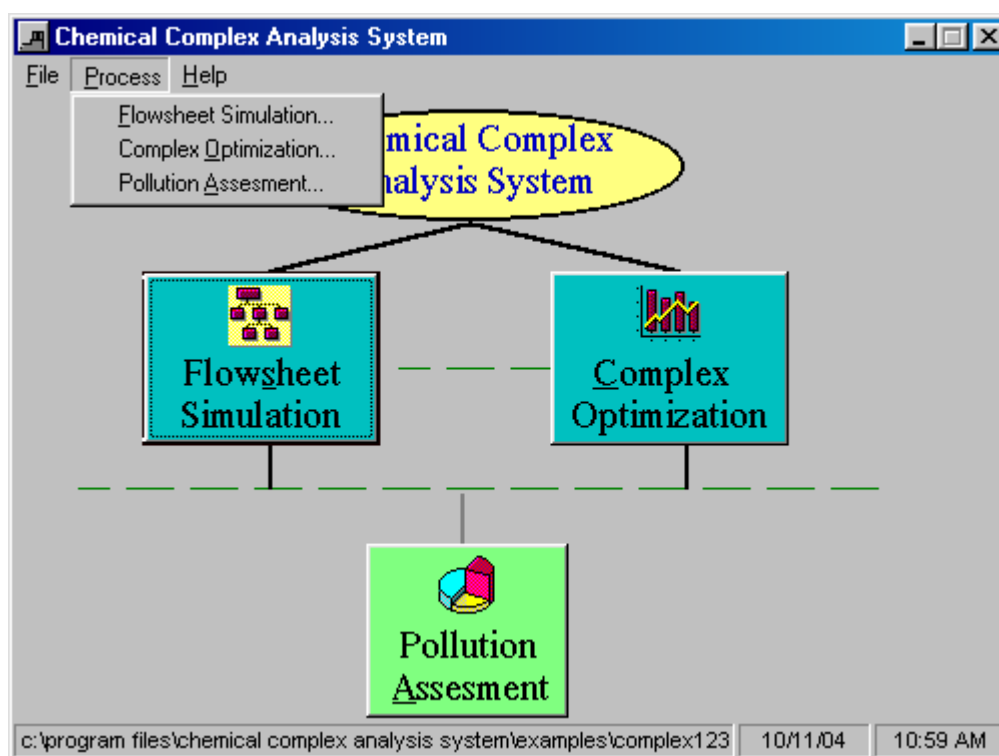Figure 4:The File Menu of the Chemical Complex Analysis Desk

Figure 5: The Process Menu of the Chemical Complex Analysis Desk

The Chemical Complex Analysis Desk has three buttons leading to the three component programs, which were described in earlier sections. All of these can also be called using the process menu at the top. This is shown in Figure 5.

When a new model is opened, only the 'Flowsheet Simulation' button is active. The development of the process model using Flowsim is the first step in using the Chemical Complex Analysis System. Until the flowsheet simulation part is completed, buttons for the other two programs remain dimmed and unavailable.

The application of Chemical Complex Analysis System is demonstrated using the chemical complex process described in the previous section. The first step is to develop the process model using the Flowsim program. The 'Flowsheet Simulation' button should be now clicked to open the Flowsim program.

IV. Using Flowsim

Upon clicking the 'Flowsheet Simulation' button in Figure 5, the FlowSim window is displayed with the 'General Information' box. In the space for model name, let us enter 'complex123'. In the process description box, let us enter "Example of MILP". The 'General Information' box with this information is shown in Figure 6.

By clicking the 'OK' button, the main screen of 'FlowSim' is displayed. This is the screen where the user draws the flowsheet diagram. The 'Model' menu shown in Figure 7 provides the various commands used to draw the flowsheet diagram. The menu commands are divided into two groups. The first group has commands for drawing the flowsheet diagram whereas the second group has commands for entering various kinds of process information.

The 'Add Unit' command should be used to draw a process unit. The 'Add Stream' command should be used to draw a process stream between two process units. The program requires that every stream be drawn between two units. However, the input and output streams of a process only have one unit associated with them. To solve this problem, the FlowSim program provides an additional type of unit called 'Environment I/O'. This can be drawn, shown in Figure 7, using the command 'Add Environment I/O'. The 'Lock' option makes the diagram read-only and does not allow any changes. The diagram can be unlocked by clicking on the 'Lock' command again.
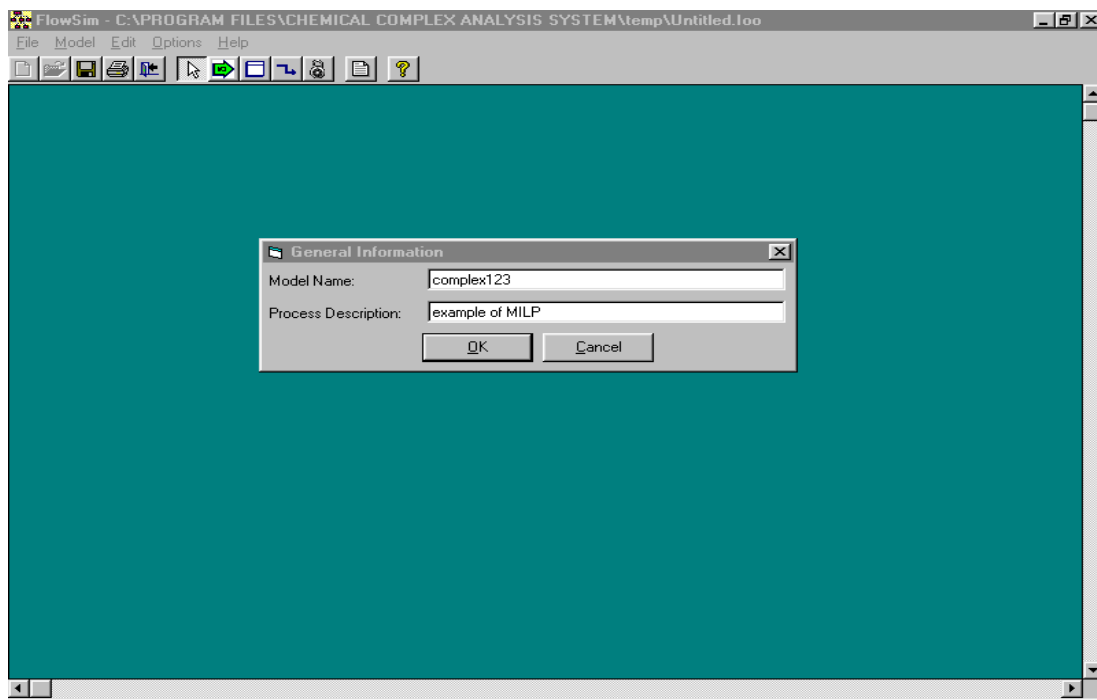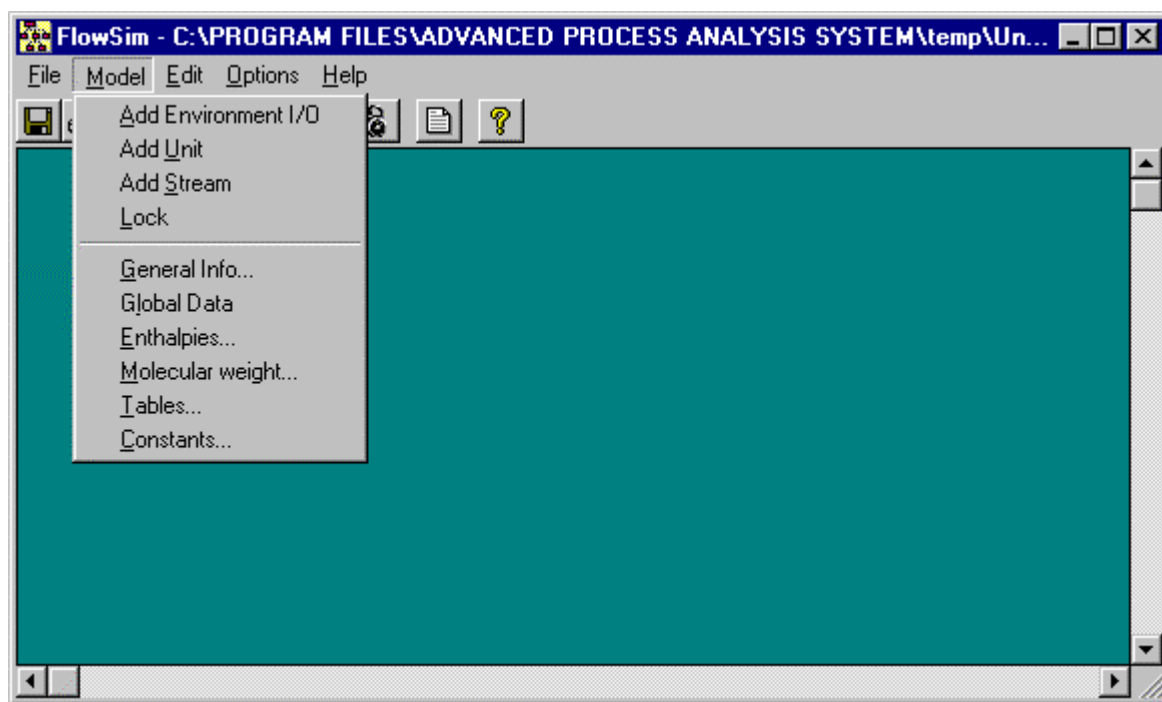

Figure 6: General Information Box

Figure 7: The Model Menu

Now, let us use these commands to draw the flowsheet diagram for the complex123 process. Although FlowSim allows the units and streams to be drawn in any order, it is recommended that while drawing a process model, one should start with the feed and then add units and streams in order. Let us draw the Unit 1, which is the unit with the feed stream from the Environmental I/O that is the input. Select the 'Add Unit' command from the 'Model' menu. The mouse cursor changes to a hand. The cursor can now be dragged to draw a rectangle. Once, the mouse button is released, a small input window appears on the screen as shown in Figure 8. For every process unit that is drawn in FlowSim, the user is required to enter a unique Unit ID and description. Let us enter 'U1' as the unit ID and 'Process I' as the description.

Now, let us draw the unit 'J1' in the flowsheet diagram. Let us enter the Unit ID 'J1' and description 'Mixer 1'. Mixers are units where any two streams converge into a single stream. With these two units, the screen looks like in Figure 9.
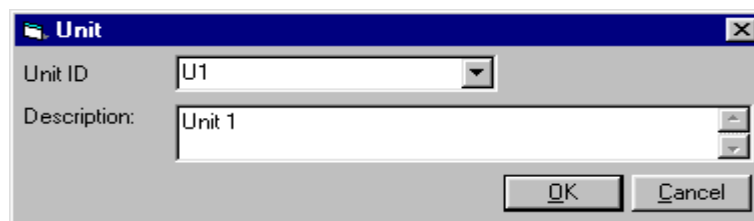

Figure 8: The Unit Window
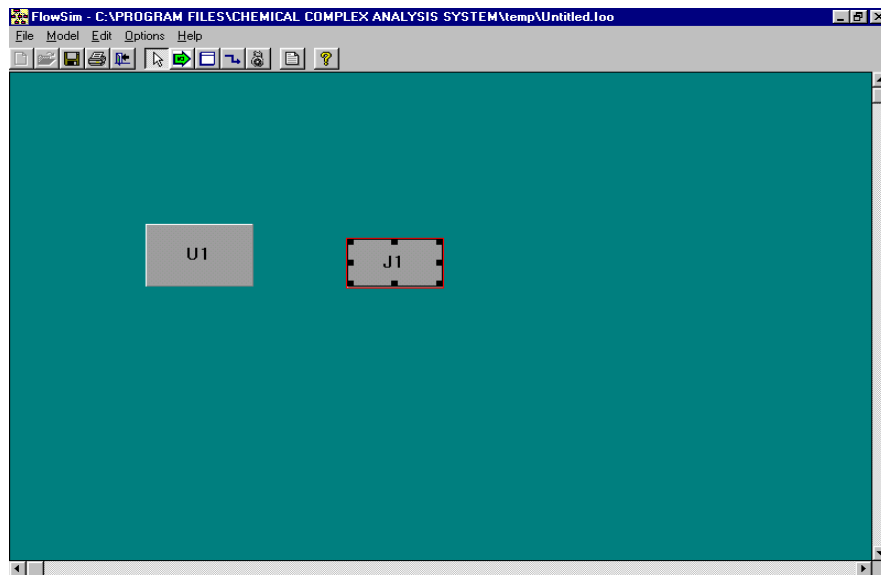
Figure 9: Flowsheet Screen with two Units.

Now, let us add the stream that leaves U1 (Process I) and enters J1 (Mixer 1). To do this, select the 'Add stream' command from the 'Model' menu. The cursor changes to a small circle. Position the cursor on the U1 unit and drag the cursor to the J1 unit. The program now displays a small box shown in Figure 10. Let us enter the stream ID 'FBI' and the description 'Production Rate of B in Process I'. With units U1 and J1 and stream S2, the FlowSim screen looks as shown in Figure 11. In this way, the entire process flow diagram for the MILP process can be drawn using the Model menu commands. After drawing the complete diagram, the FlowSim Screen Looks like as shown in Figure 12.

Figure 10: The Stream Window

Figure 11: FlowSim Screen with two Units and a Stream

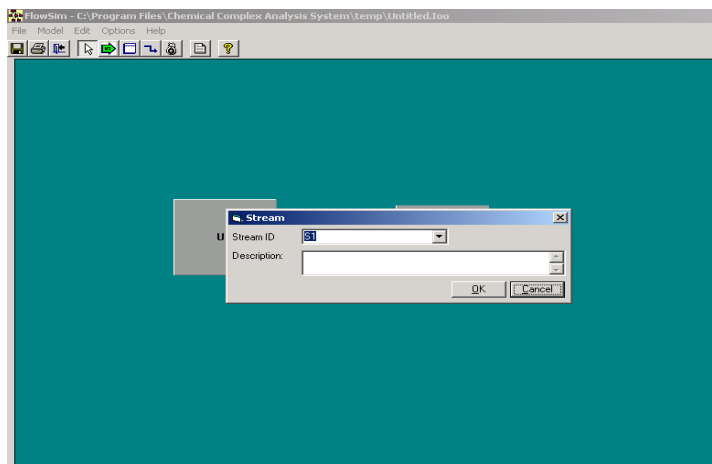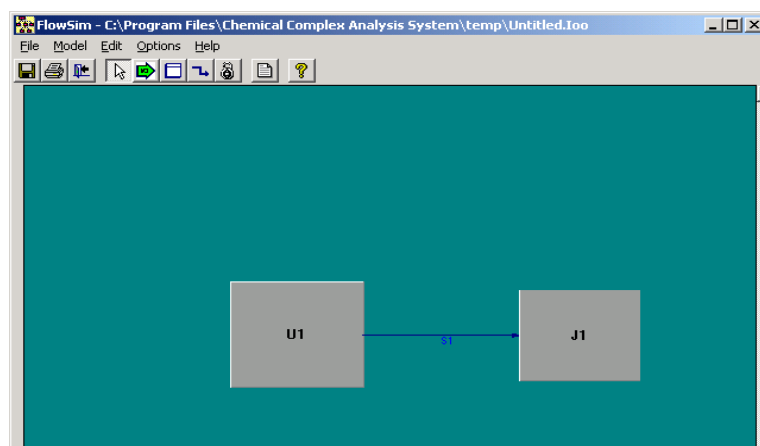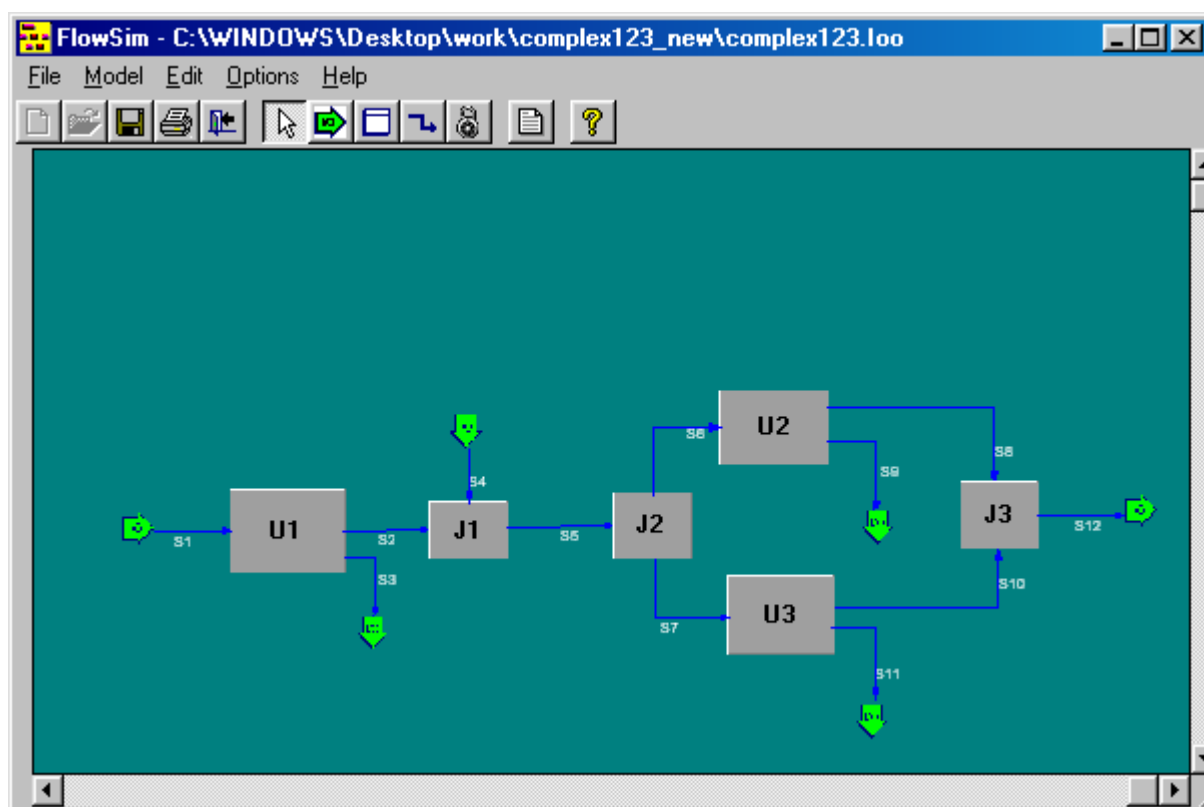Figure 12: The Flowsim Screen with the Process Diagram for Complex123 Process Model

The 'Edit' menu at the top of the FlowSim screen provides various options for editing the diagram. It is shown in Figure 13. To use the Edit commands, a unit in the flowsheet diagram has to be selected first by clicking on it. The cut, copy and paste commands can be used for both units as well as streams. The 'Delete' command can be used to permanently remove a unit or a stream from the diagram. The 'Rename' command can be used to change the unit ID for a unit or to change the stream ID for a stream. The 'Properties' command can be used to change the appearance of a unit or a stream. The 'Data' option used to Add/ Modify/Delete Process data, explained in detailed later part of the section (page 22).

The 'Options' menu in the FlowSim screen is shown in Figure 14. The zoom option can be used to change the magnification by zooming in and out. The 'zoom to fit' option automatically selects the appropriate magnification so that the diagram occupies the entire screen. The 'Grid Lines' command can be used to display grid lines on the FlowSim screen, to change the spacing between the grid lines and to change the grid line and background colors. The 'Object settings' command is useful to change the appearance of all the units and streams in the FlowSim screen. The object setting window is shown in Figure 15. To change settings for all the streams, click on the streams tab. To change settings for all the environment I/O units, click on the 'Environment I/O' tab. If you want the changes to remain effective even after you close the application, you must select 'Save the palette for future uses' box.
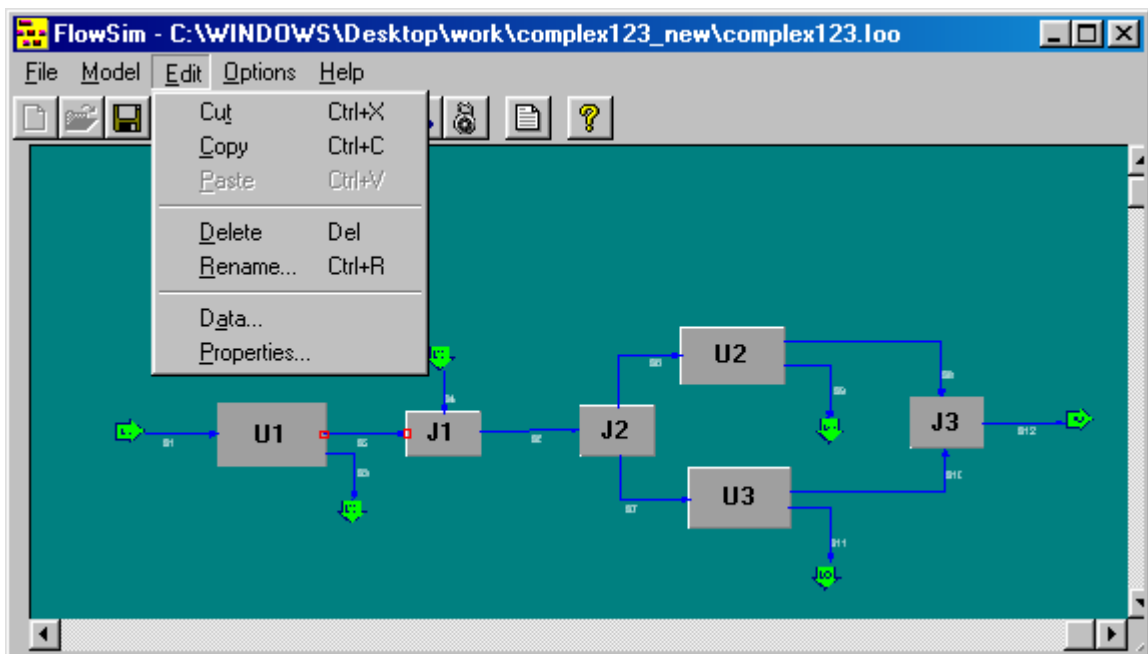
Figure 13: The Edit Menu
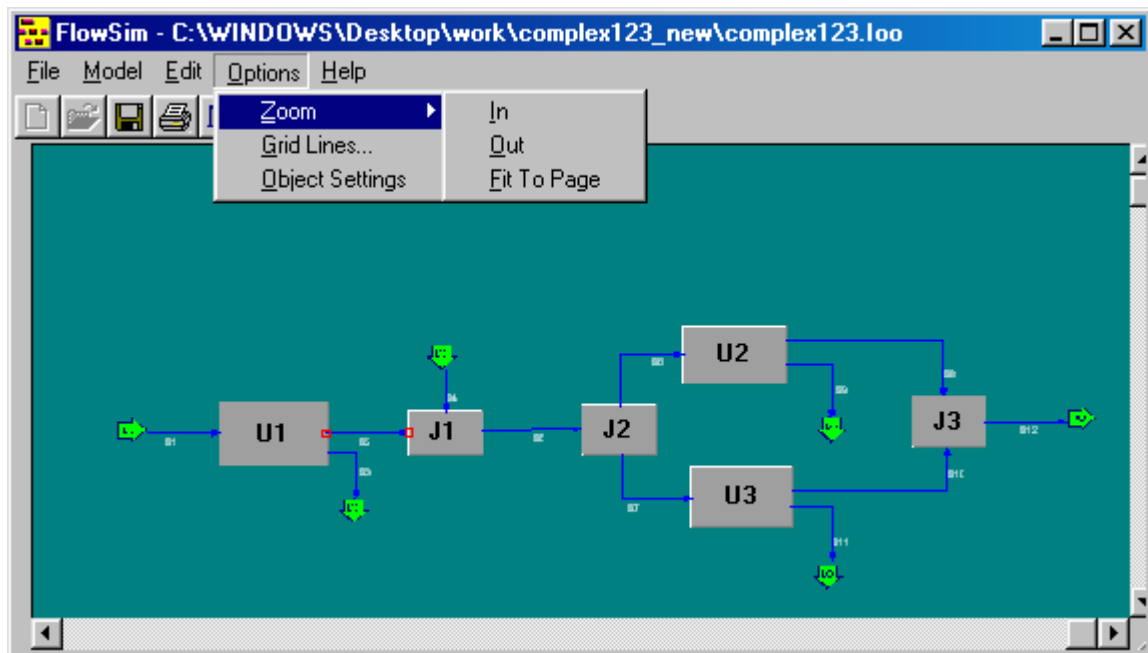
Figure 14: The Options Menu
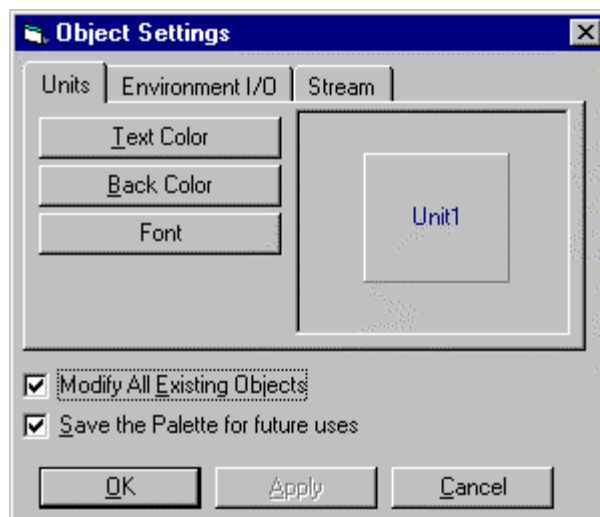
Figure 15: Object Settings Window

Once you have drawn a stream, the data associated with the stream can be entered by clicking on the data option in the edit menu or by double clicking on the stream. Let us enter the data associated with the stream S2. When you double click on this stream, a data form is opened. This is shown in Figure 16.

To enter the continuous variables associated with the stream/unit, the 'add' button should be clicked. When the 'add' button is clicked, the caption of the 'Refresh' button changes to 'Cancel'. Then the information about the variable such as

the name of the variable, the plant data, the standard deviation of the plant data should be entered. The description, initial point, scaling factor, lower and upper bounds and the unit of the variable are optional.

The changes can be recorded to the model by clicking on the 'Update' button or can be cancelled by clicking on the 'Cancel' button. When the update button is clicked, the caption of the cancel button reverts back to 'Refresh'. The Stream Data Window with the information appears as shown in Figure 16. In this way, all the other continuous variables associated with the stream 'S2' can be entered.

To enter the integer variables associated with the stream/unit, click on the 'Integer Vars' tab. As explained above for the continuous variables, click on the add button in the stream data window. Enter the name, initial point of the Integer variable. The scaling factor, description and unit of the variable are optional. The bounds should be entered for Integer Variables because the variable can hold a maximum of 1 and a minimum of 0. The Unit Data window with the Integer variable data is shown in Figure 17.

Figure 16: Stream Data Window

Figure 17: Integer Variables Tab in the Unit Data Window

To move to a particular variable, enter the record number in the box adjacent to 'Go to Record' button. Then press 'enter' or click on the 'Go to Record' button to move to that variable. To delete a variable, first move to that variable and then click 'Delete'. To return to the main screen, click on the 'close' button.

To enter the data associated with a unit, double click on the unit. When you double click on the unit, a data form similar to the one shown in Figure 16 is opened as shown in Figure 17. The continuous variables, Integer variables are entered in the same way as for the streams. Let us proceed to enter the equality constraints for the U1 unit. Click on the Equalities tab in the Unit Data window to enter the equality constraints. Energy balance equation for the unit U1 given in Section II can be added by clicking on the add button on the Unit Data window. Enter the equation in the box provided and click 'Update'. Note the use of '=e=' in place of '=' as required by the GAMS programming language. The screen now looks as shown in Figure18. Similarly, Inequality Constraints can be added in the next tab of Unit Data Form.
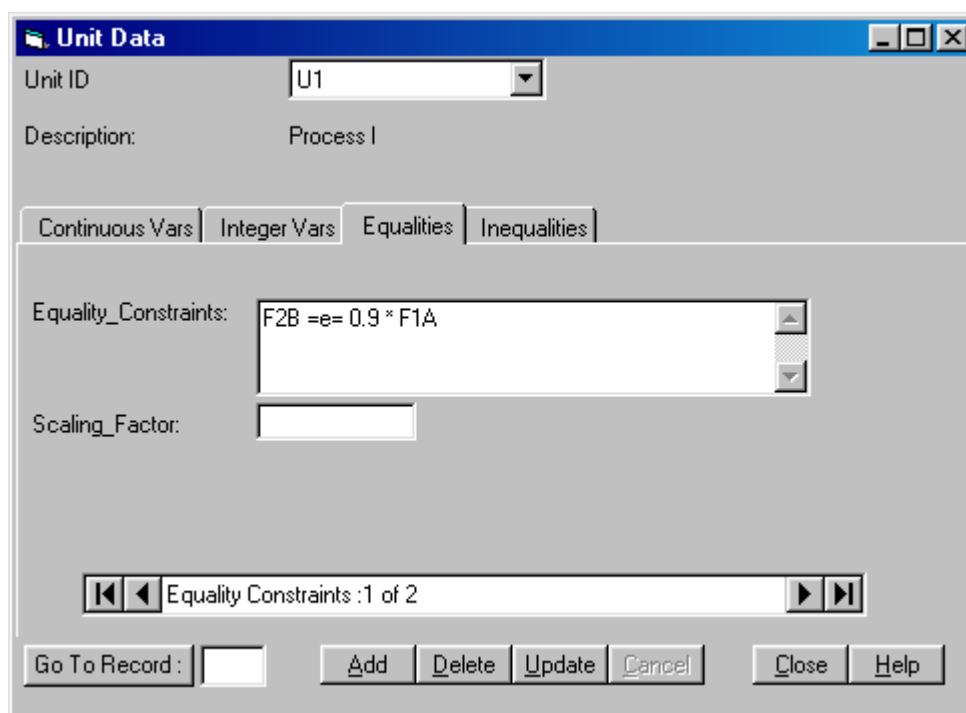
Figure 18: Equality Constraints Tab in the Unit Data Window

A. Global Data

If there are variables, parameters and equations that do not belong to either a unit or a stream, then they can be entered in the Global Data window. This includes the economic model and the equations to evaluate emissions and energy use. To enter this global data, right click on the background of the flowsheet diagram or click on the 'Global Data' option in the Model menu.

The Global Data window in Figure 19 shows the equality constraints in the Global Data section for the chemical complex process model. There are no equality constraints in the Global Data section for this chemical complex process so the window in Figure 19 shows empty in the equality constraint section.
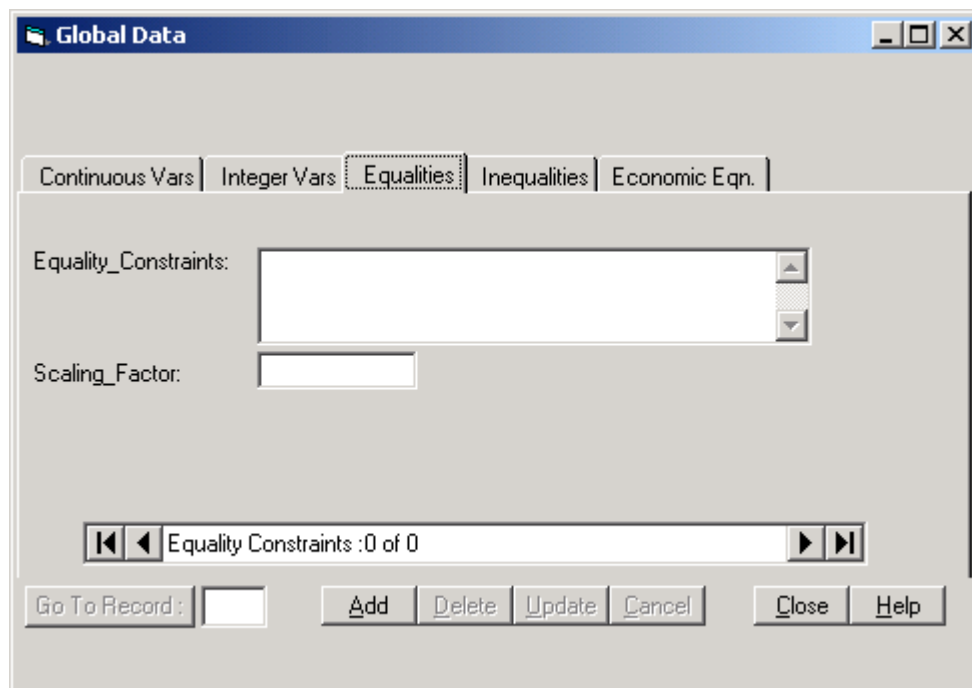
Figure 19: Equalities Tab in the Global Data Window
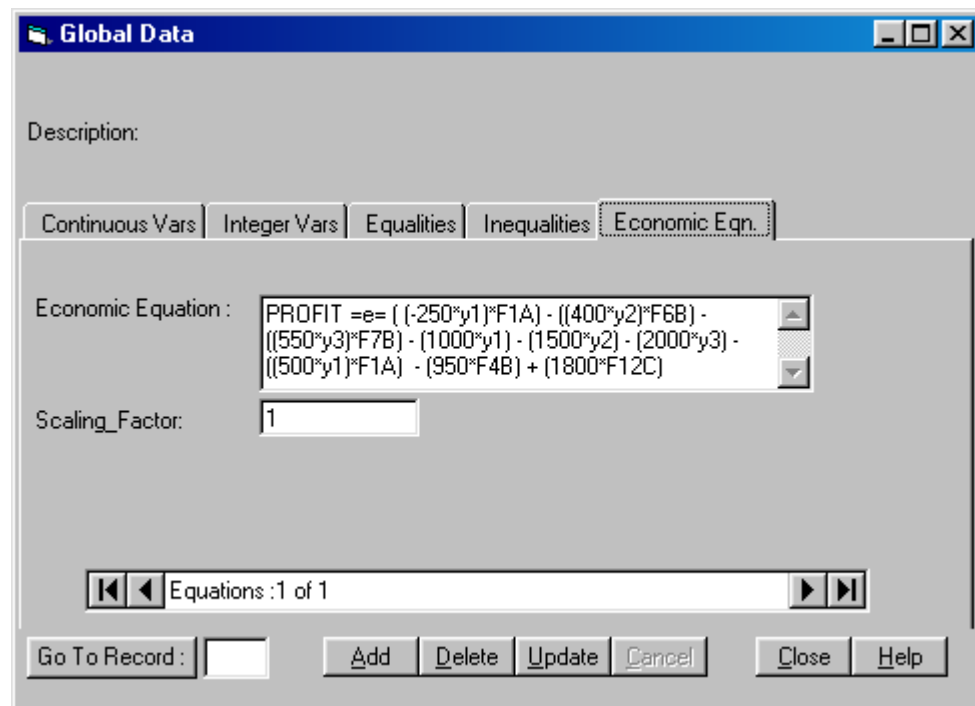
Figure 20 The Economic Equations Tab of Global Data

The last tab in the Global Data window is for the Economic Equations. These are equations, which can be used as the economic model and the left-hand side of one

of these equations is specified in optimization. For the complex123 process, let us enter the equation that defines the profit function for the whole process. Click on the 'Add' button and enter the equation shown in Figure 20. The variable 'profit' is used later to specify the objective function for economic optimization.

B. Constant Properties

The Constant Property window is where a list of constants is stored. Clicking on the 'Constants' option in the model menu opens the Constant Property window as shown in Figure 21. To create a set of constant properties, click on the 'Add New' button in Constant Property window to activate the window. As soon as the 'Add New' button is clicked, the caption of the 'Add New' button changes to 'Save' and that of 'Delete' changes to 'Cancel'. Then the general information of a constant property - the name and an optional description - must be entered in the Constant Property window. After entering the constant property information, the 'Save' button should be clicked to save the changes.
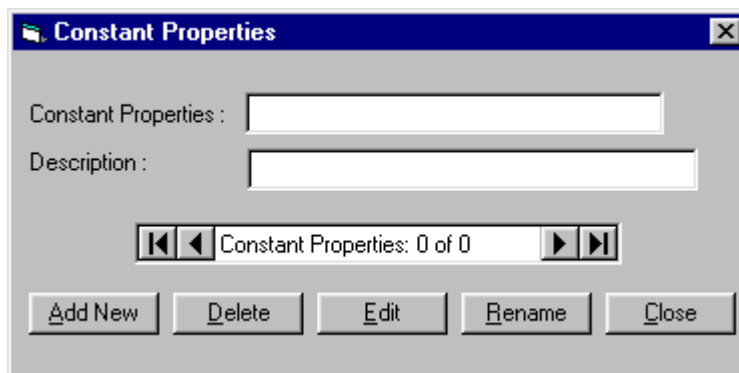
Figure 21: Constant Properties Window

To enter the data in the constant property window, click on the 'Edit' button. The Edit Constant Property window is opened for entering the name of the constant, the corresponding numerical value and an optional description.

After entering all of the above information, the model is complete. Save the changes by clicking on the 'Save' option in the File menu. If you click 'Exit' without saving the model, a message is displayed asking whether you want to save the changes or not. The 'Print' option in the File menu when clicked, prints the flowsheet diagram. When the 'Exit' button is clicked, the FlowSim window is closed and the user is taken back to the Chemical Complex Analysis Desk.

The development of the process model with basic features using FlowSim has been completed. The equations, parameters and constants have been stored in the database as shown in Figure 1. Save the model using the 'Save As' option in the File menu. A 'Save Model As' dialog box is opened. Save the model as 'complex123.ioo' in the 'Examples' subdirectory of the program folder.

Additional features such as Sets, Parameter Lists, One Dimensional Variables, and Multi-Dimension Variables which are useful for construction of large models and/or running Sensitivity Analysis or Multi-Criteria Analysis for the model. Steps to follow for using these features is described as below.

C. Sets
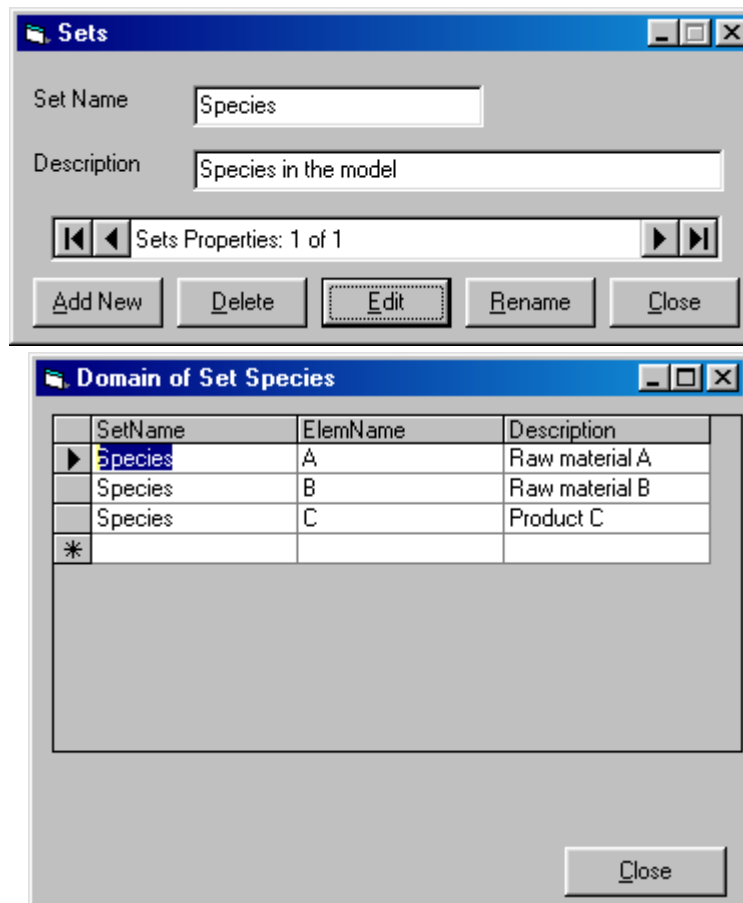
Figure 22. Set and Members of a set window

Each set consists of a collection of parameters. All these parameters can be added as a set to the system by clicking on 'Sets' menu item in the context sensitive menu shown by clicking on back ground of FlowSim window. Each set consists of set name and set description as attributes. These attributes can be added by clicking on 'Add New' button on sets window. 'Edit' button should be clicked to add parameters as members of the particular set. 'Delete' or 'Rename' buttons should be clicked to delete or modify the set attributes respectively. 'Close' button closes Sets window. Sets and Set members window snap shots of complex123.Ioo model are shown in Figure 22.

D. One Dimensional Variables and Lists

One Dimensional Variables and Lists are used to aceess a set of variables as a single unit. A set whose elements being used as members of the one dimensional variable or Lists must be defined before using the set in declaration of one dimensional variables or lists. One dimensional variables are especially useful in setting the same property values (lower bound and upper bound) for a set of variables. Lists are useful in setting different values for each of the parameters of the set and in accessing these parameter values with a single Name (List Name) and index or parameter name as subscript.

One dimensional variable or a list is added to the model by right clicking on the back ground window and clicking on the 'One D Variables' in the context sensitive menu shown. The input window for complex123.ioo model appears as shown in Figure 23. Click on 'Add New' button on the 'Lists' window and enter the List Name , select the Set Name associated with it, and enter the description. If Lower Bound and Upper Bound are zero, then List Name entered above will be treated as a list and the user can edit the values for members of the list by clicking on 'Edit' button and window appears as shown in Figure 24. Otherwise List Name is treated as one dimensional variable. Lower bound and upper bound values specified are lower and upper bounds for all members of the set. The bound values can be changed for specific members by clicking on 'Specify Bounds' button and window appears as shown in Figure 25. If lower and upper bound window is empty then all members of the variable use same lower and upper bound specified. Since complex123.Ioo model does not have any one dimensional variables, Figure25 is not of complex123.ioo model snapshot.
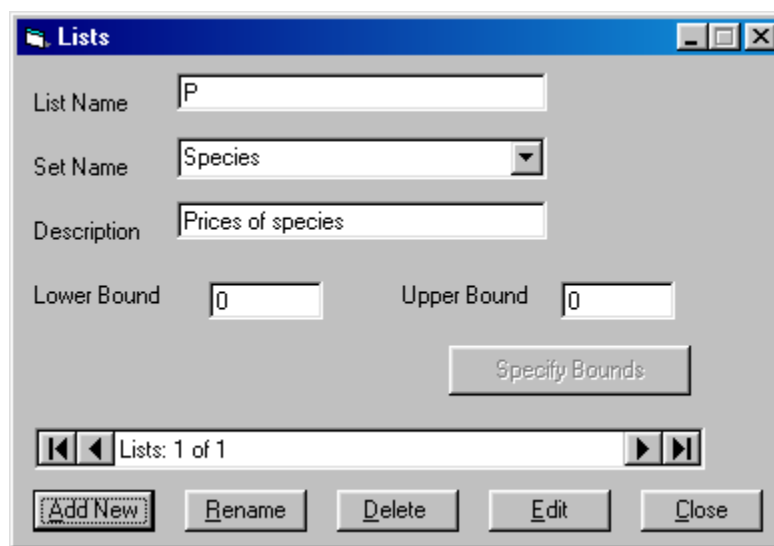
Figure 23. One Dimension Variables and Lists Window
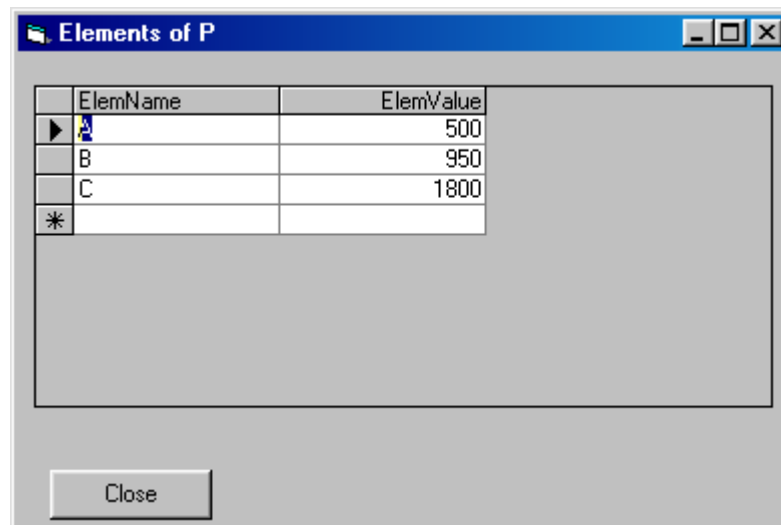
Figure 24. Elements of the List
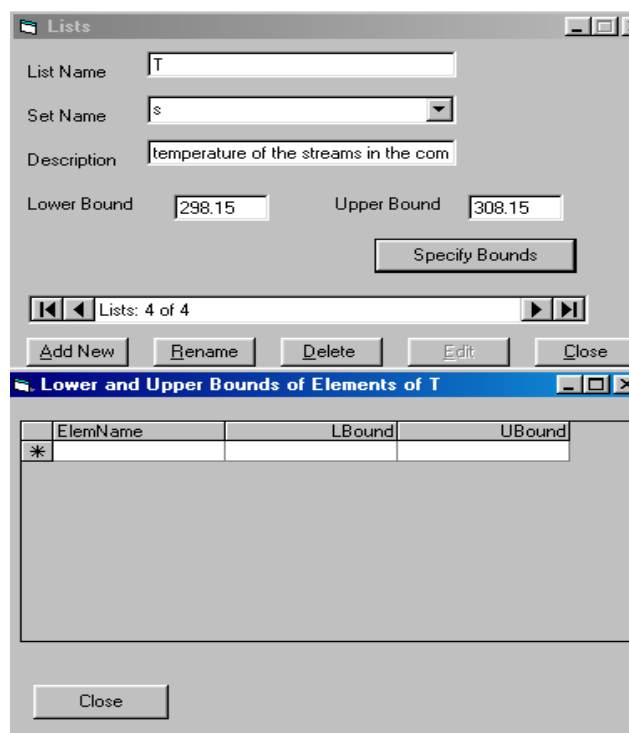
Figure 25. One Dimension Variable with different lower and upper bounds

E. Multi Dimensional Variables

Multi Dimensional (MD) variables are similar to one dimensional variables but MD variables use more than one set. These variables are added to system by clicking on 'Multi D Variables' on context sensitive menu shown by right clicking on back ground of 'FlowSim'. MD Variables window appears as shown in Figure 26.

MD Variables are added to the system by entering variable name, Names of the sets which are used by the variables separated with commas, and description of the variable (optional). Clicking on 'Close' button save the variables entered and close the window. This completes adding MD variables. Since complex123.ioo model does not have MD variables, table in Figure26 is empty. Further more, instead of sending to output all the variables (which is done by default),user can select only a set of variables for which you want see the result. This can be done by selecting 'Output Vbls..' option in the context sensitive menu (shown by right click on the back ground window). See Output Variables for sensitivity analysis for details.
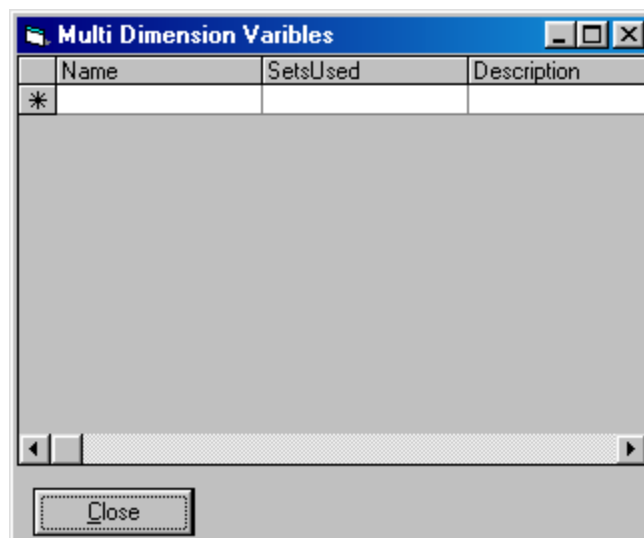
Figure26. Multi-Dimension Variables Window.

F. Sensitivity Analysis

Sensitivity Analysis is used to analyze solution over the change in parameter values over different iterations. System uses Monte-Carlo simulation method to perform sensitivity analysis.
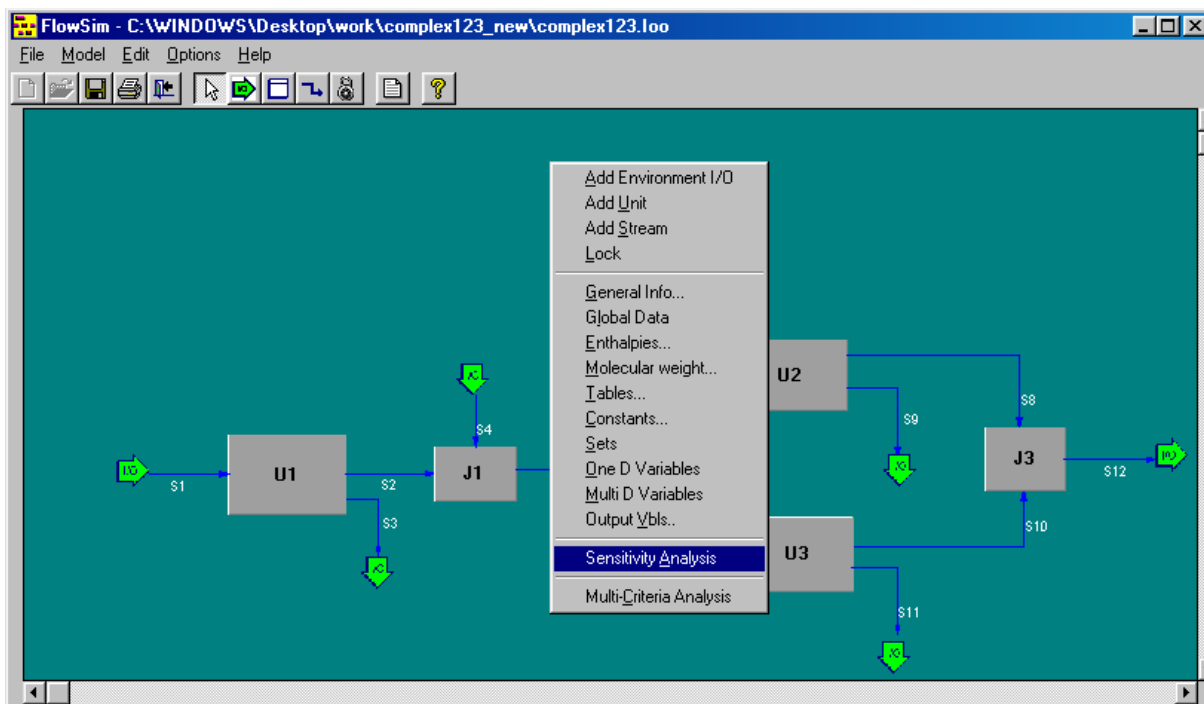
Figure 27. Select Sensitivity Analysis Option Menu

To run sensitivity analysis (henceforth SA) for the model the input data for must be entered Flow Sheet window. SA input data for complex123.Ioo model is entered by selecting 'Sensitivity Analysis' option on context sensitive menu for background window of FlowSim as shown in Figure 27. Input data such as number of iterations, input parameter, selection of distribution for the parameter, distribution data for each member of the parameter set is entered as shown in Figures 28 and Figure 29. Advanced options to run sensitivity analysis model can be added by clicking on Advanced Options button on the Sensitivity analysis window.
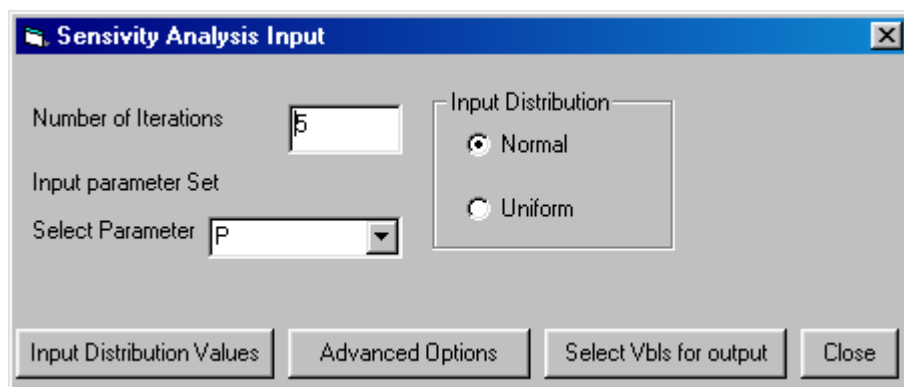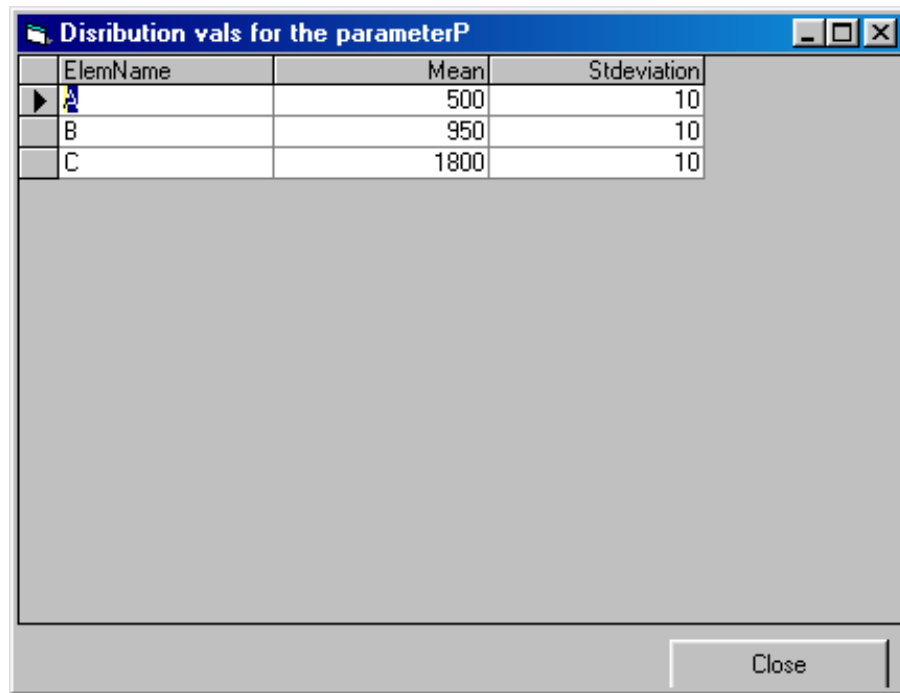
Figure 28. Sensitivity Analysis Input Window

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Figure 29. Distribution Data for Input Parameters

Output variables for sensitivity analysis can be selected by clicking on 'Select Vbls for output' Button. By clicking on the 'Select Vbls for output' button shows a 'Select Output Variables for Output' window shown in Figure 30 listing all variables of the model. In this window 'Select All' and 'Clear All' buttons select all the variables and none of the variables for output respectively. The user can select a particular variable for output by clicking on the check box on the left of the variable. By clicking on 'Output Selected Variables' saves selected variables for output and close the window. Selection of a particular set of variables can be done for all three types of analysis i.e. Complex Optimization, Sensitivity Analysis, and Multi-Criteria Analysis. This completes adding input for sensitivity analysis of the model.
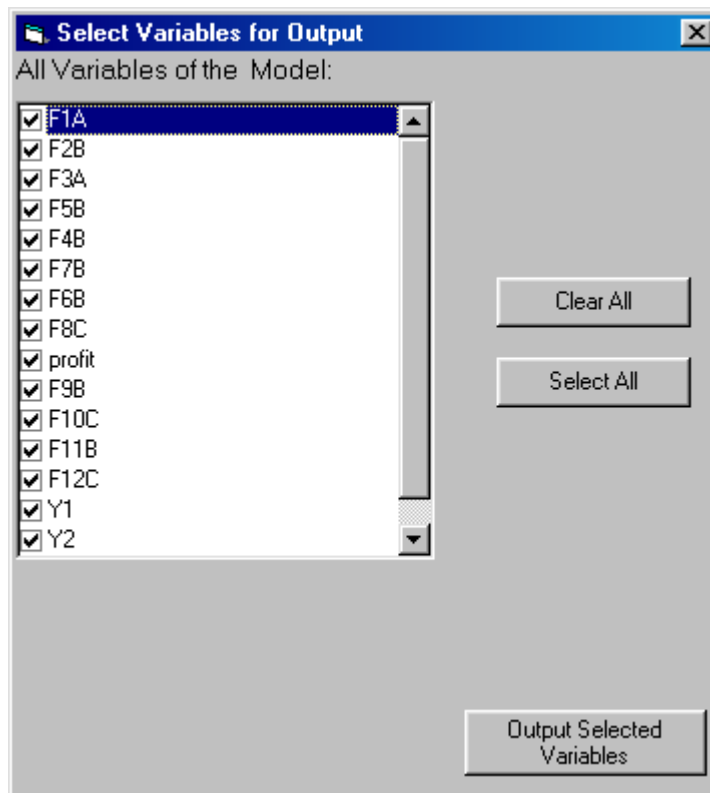
Figure 30. Select variables for Output Window

G. Multi-Objective Analysis

Multi-Objective Analysis (or Multi-Criteria Analysis, henceforth MCA) can be used to analyze the solution over the different objective functions (Ex: Maximizing Profit and Minimizing the cost). MCA allows the user to change weights for the objective parameters.
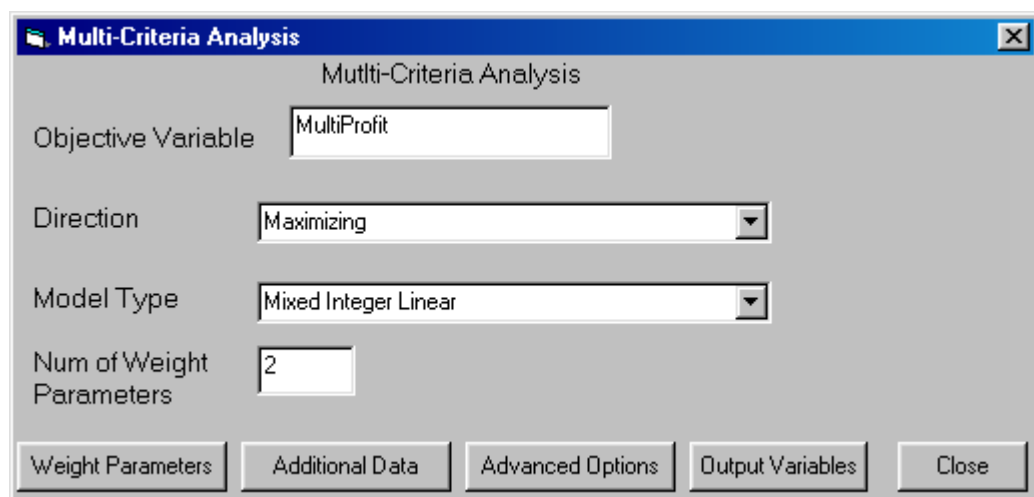
To execute MCA, input data for MCA, is entered in the FlowSim window as described below. MCA window is shown by clicking on the 'Multi Criteria Analysis' option on context sensitive menu for back ground window of FlowSim. Input window of MCA for complex123.Ioo model is as shown in Figure 31. Objective variable and number of weight parameters are added to the model by typing in the text boxes adjacent to the corresponding labels. Optimization direction, and type of the model are added to the model by selecting from the combo boxes adjacent to the corresponding labels. Weight parameters for the model are added to the model by clicking on 'Weight Parameters' button.
Note: Number of weight parameters value must be greater than zero to add the weight parameters.

Weight parameters window is shown as in Figure 32. Actual weight parameters for MCA are entered in the 'Weight Parameters' window shown by

clicking on 'Weight Parameters' button on the 'Multi-Criteria Analysis' window. 'Weight Parameters' window consists four columns: i.e. first column ("WtParamName") stores weight parameter name. Second column ("Option Type") whose value must be either "I" or "F", where "I" indicates Option value is specified as number of iterations, "F" indicates Option value is specified as fraction of increment. Third column ("Option Value") specifies increment value for the weight parameter which can either integer (number of iterations) or fraction value (Increment for each iteration), fraction value must be less than one. Fourth Column ("Param Type") which takes value either "I" or "D", I is for Independent variable, and "D" is for dependent variable. There must be only one dependent variable for the model. If more than one dependent variable exists, system considers only the first one. Value of the dependent parameter in each iteration is $1 - ($ sum of the values of independent parameters in the iteration). This completes adding weight parameters to the system. 'Help' button this window describes the syntax for adding weight parameters and 'Close' button validates the input data for weight parameter, saves the data in the database, and closes window.

Additional data (includes additional variables and constraint equations) that are specific to MCA are entered by clicking on the 'Additional Data' button on the 'Multi-Criteria Analysis' window. 'Additional Data' window is shown as in Figure 19 (Global data section). To enter the additional data in this window follow the steps in the Global Data section. All data entered in the additional data window is not used for executing complex optimization or sensitivity analysis tasks of the model. Advanced options specific to MCA can be specified by clicking on the 'Advanced Options' button on the MCA window.   Finally, specific variables for which the user want to see the output are selected by clicking on the 'Output Variables' button. Selection of variables for MCA is same as for Sensitivity Analysis. See Page 31 in Sensitivity Analysis Section. This completes adding input data for Multi-Criteria Analysis. Clicking on 'Close' button saves MCA data , and closes the window.
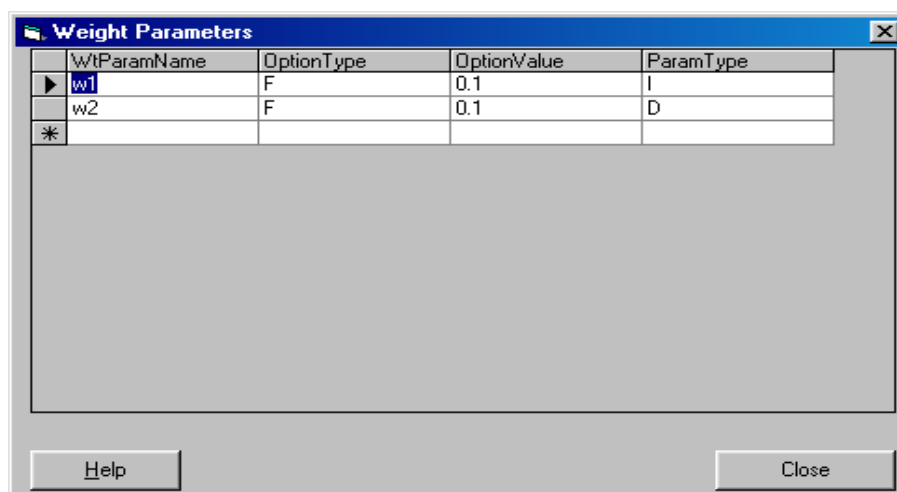
Figure 31. Multi-Criteria Analysis Input Window

Figure 32. Weight Parameters Window

The input data for the three (Optimization, Sensitivity analysis, Multi-Objective Analysis) process models entered above needs to be validated to make sure that it is representing the actual process accurately and it does not have any mistakes. This can be done by using the model to carry out a simulation and then comparing the results with the design data for the process.

The next step of the Chemical Complex Analysis System is optimization. The 'Optimization' button in Figure 5 should be now clicked to open the optimization program.

V. Using Complex Optimization Program

Upon clicking the ' Complex Optimization' button as shown in Figure 3, the Optimization main window is displayed with the Optimization Algorithm window as shown in Figure 33. This window includes the Objective function for Economic Optimization, the Optimization direction and the Economic Model type. In the Economic Optimization for the complexfinal process, the objective function is 'profit' as defined in Section V for the global economic equation (Figure 20). Let us choose the optimization direction to be 'Maximizing' and the Economic Model type to be 'Mixed Integer Linear'.
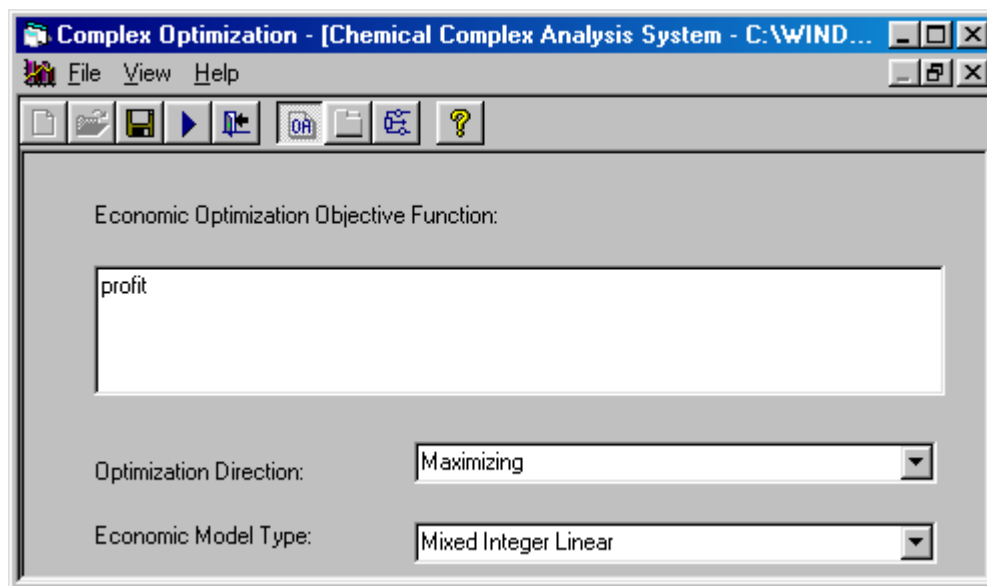
Figure 33. Optimization Algorithm Window
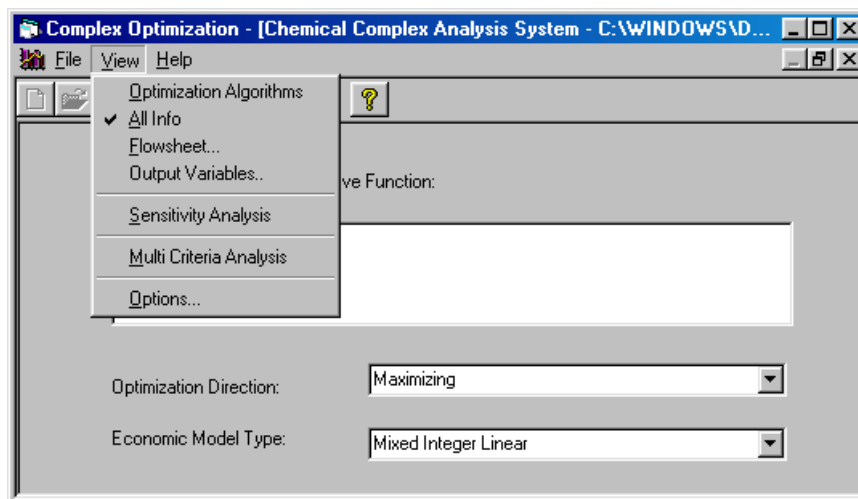
Figure 34. View Menu
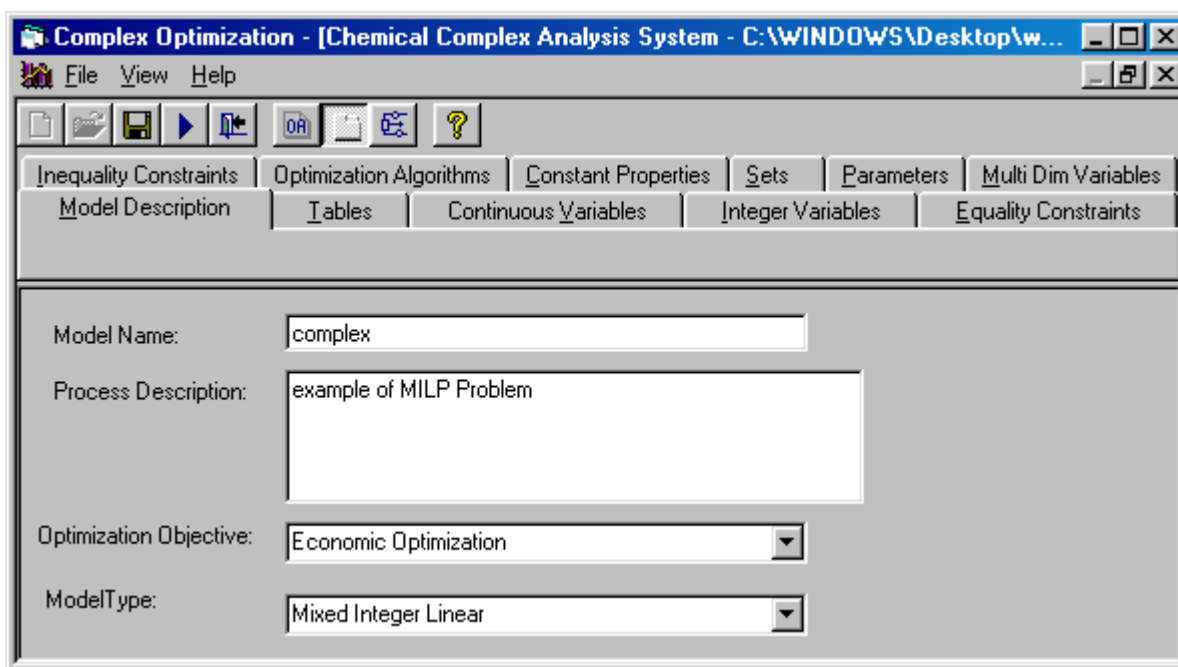
Figure 35: Model Description Window

When you click on the View menu in the Optimization Algorithm window, a pull-down menu is displayed as shown in Figure 34. The View menu includes commands for the Optimization Algorithm mode, the All Information mode and Flowsheet diagram. The 'Optimization Algorithm' mode displays the model description window. The 'All Information' mode contains the different windows combined together into one switchable window. The Flowsheet diagram option is

used to view the Flowsheet diagram, which is drawn using the Flowsheet simulation program.

To view the other windows used by the Optimization program click on the 'All Information' option in the view menu, which is shown in Figure 34. The Model Description window is shown in Figure 35.

For the Model Description window, the model name and the description were entered in the Flowsim program. This window includes the Optimization Objective and Model Type. The optimization objective has only one selection that can be selected from the drop-down list of 'Optimization Objective'. The selection is 'Economic Optimization'. Let us choose the ' Economic Optimization' option for the optimization objective. The model type of the plant model must be specified as either 'Linear' or 'Nonlinear' from the drop-down list. Let us choose 'Nonlinear' as the model type for the complex123 model.

When the information for the Model Description window is completed, you can proceed to the next window by clicking on the tab to move to any other window. Let us proceed to the Tables window by clicking on the 'Tables' tab. The Tables window is shown in Figure 36. it contains information about the tables that were entered in the FlowSim program.

Let us proceed to the Continuous Variables window by clicking the 'Continuous Variables' tab. The Continuous Variables window has a table with twelve columns which display the name, initial point, scaling factor, lower and upper bounds, stream number, process unit-ID, the unit and a short description of the continuous variables. The Continuous Variables window lists all the continuous variables that are associated with all the units and streams in the process model and the global continuous variables if any that were entered in the FlowSim program. The column 'Process Unit-ID' has the name of the process unit and the column 'Stream Number' has the name of the stream with which the variable is associated. The Continuous Variables window is shown in Figure 37. In this window, information can only be viewed. All of the data entered in FlowSim can only be viewed using the screens of optimization. To change the data, the user has to go back to the FlowSim program.

Then proceed to the Integer Variables window by clicking on the 'Integer Variables' tab. The Integer Variables window has nine columns for displaying the name, initial point, scaling factor, lower and upper bounds, stream number, process unitID, unit and description of the Integer variables. The Integer Variables window lists all the Integer variables, which were entered in the FlowSim program. The Integer Variables window is shown in Figure 38.
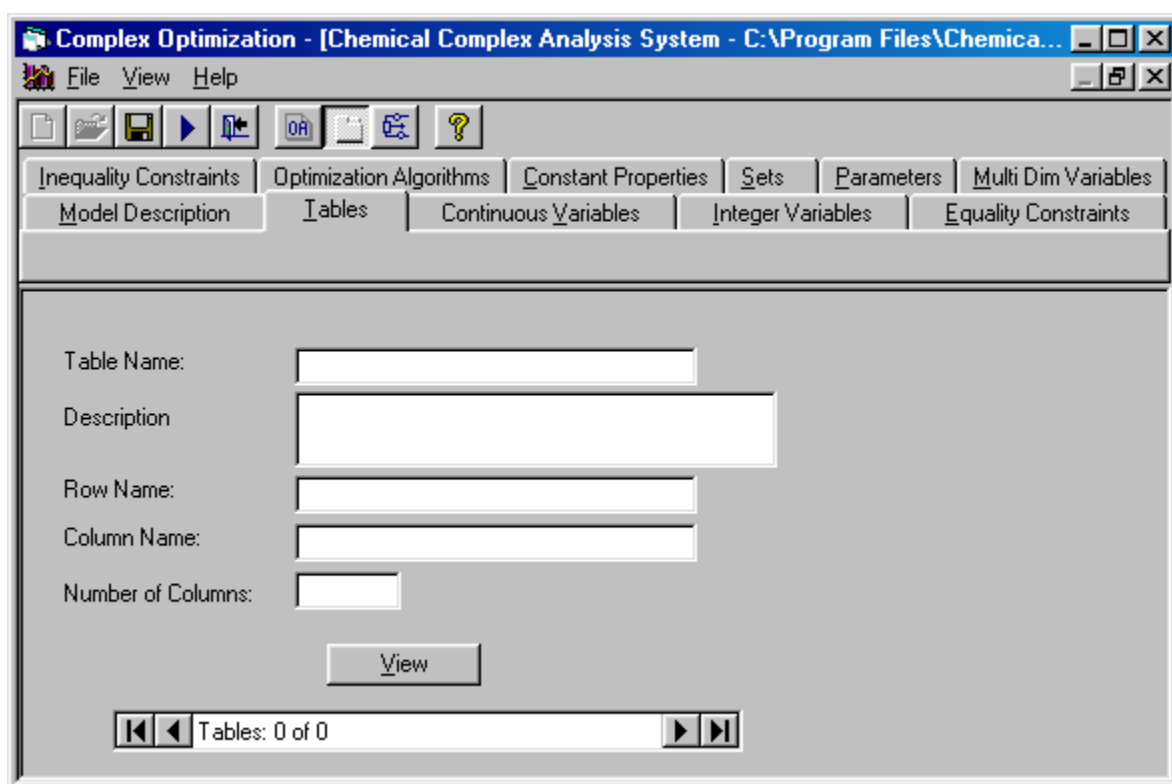
Figure 36. Tables Window of Complex Optimization
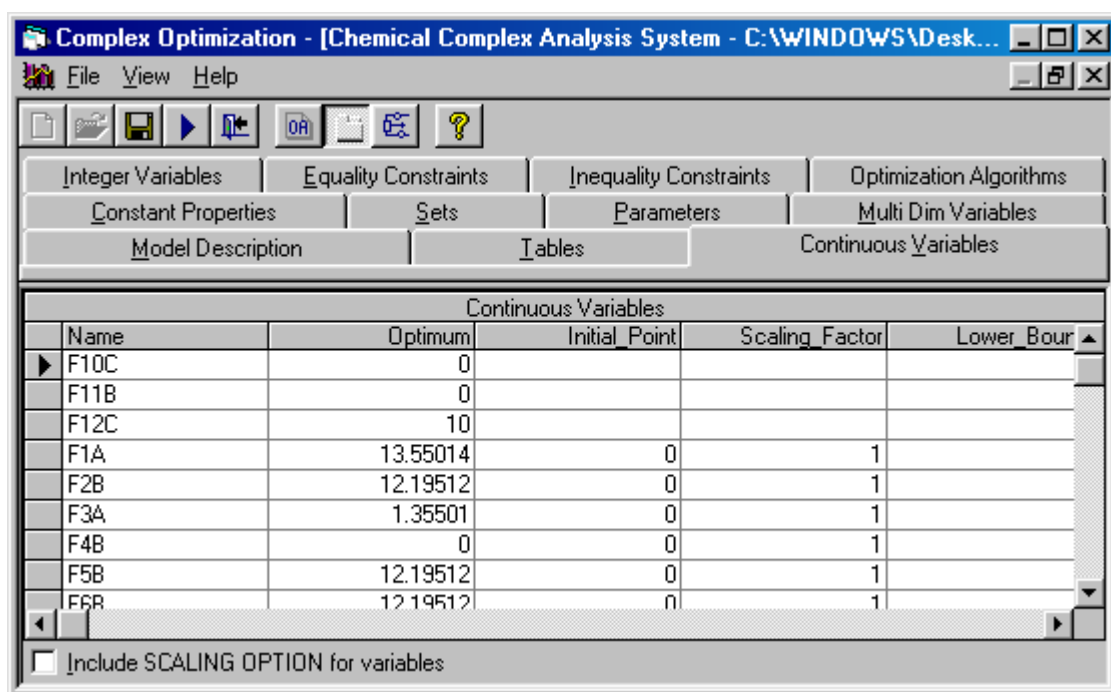
Figure 37. Continuous Variables Window
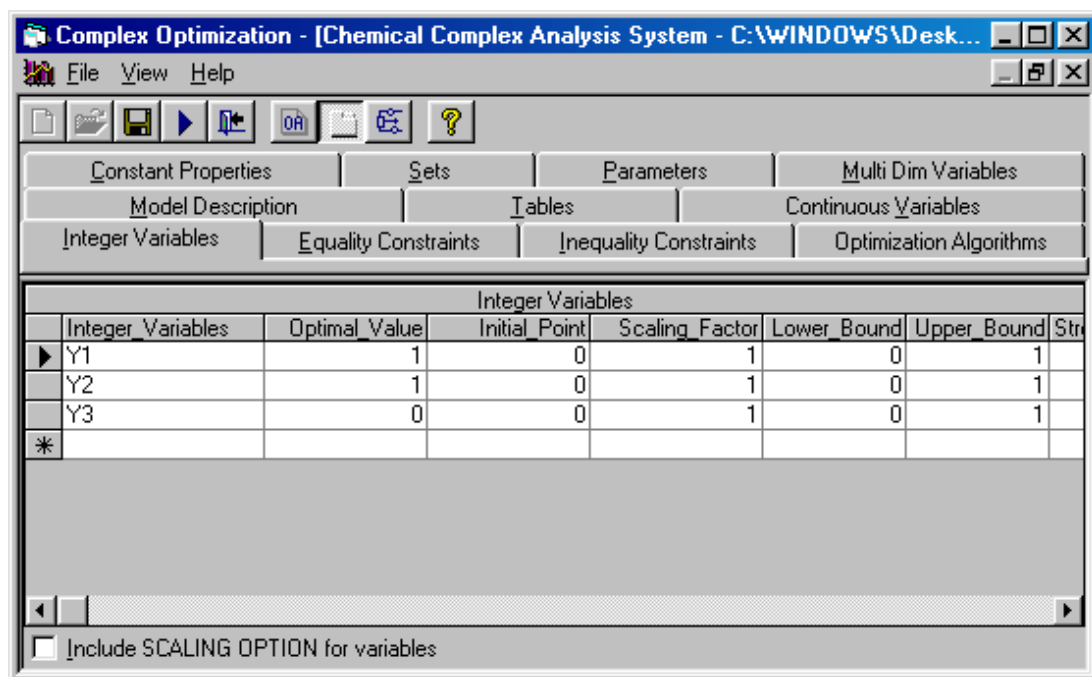
Figure 38. Integer Variables Window
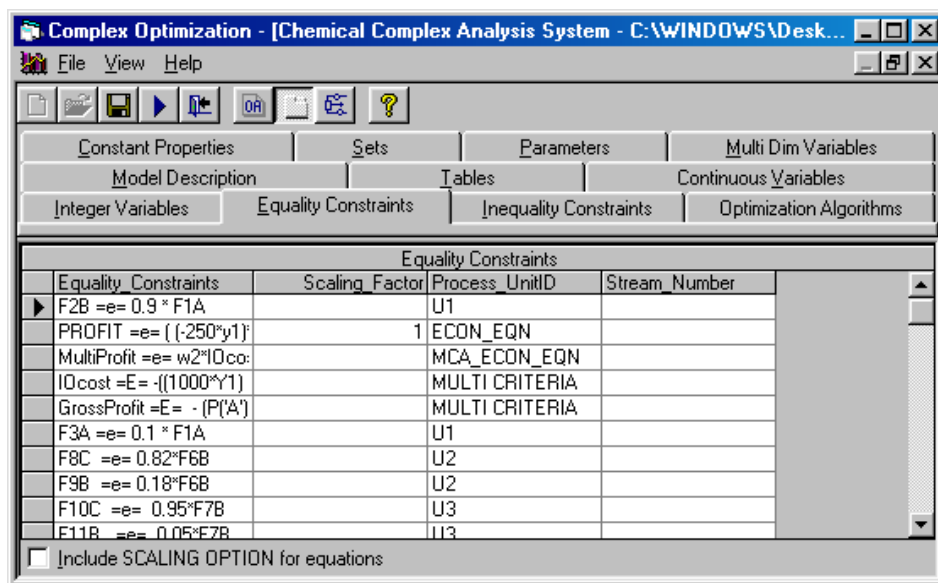
Figure 39. Equality Constraints Window

The Equality Constraints window has four columns for displaying the constraints, scaling factor, process unitID and stream number. All of the equality

constraints entered in the FlowSim program are listed in this window. The Equality Constraints window is shown in Figure 39. The next step is the Inequality Constraints window, which is similar to the Equality Constraints window.   The Inequality Constraints window has three columns for displaying the constraints, process unitID and stream number. Scaling factors are not available for inequality constraints.
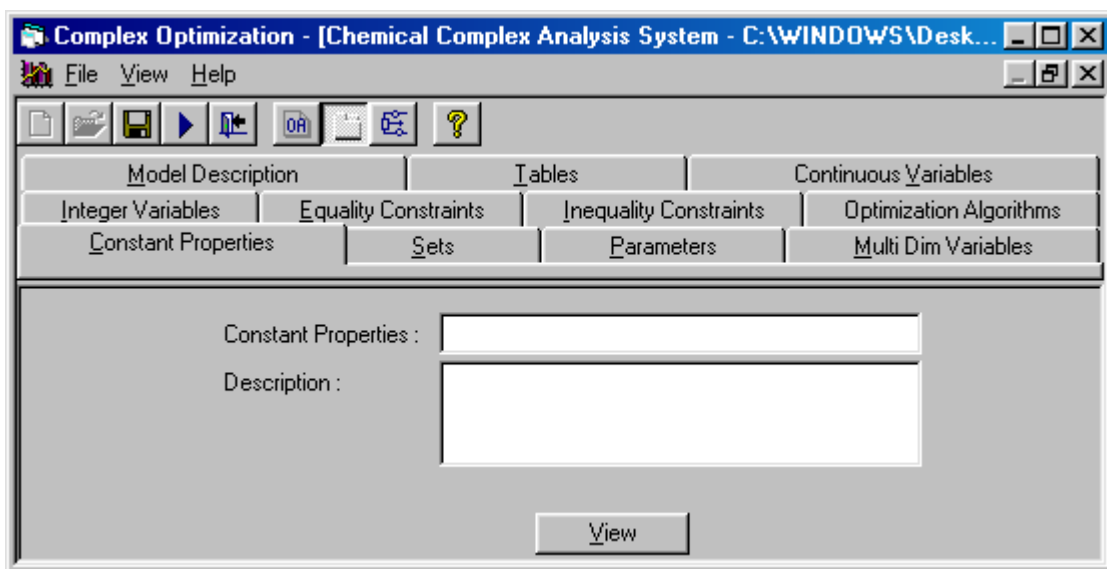
Figure 40. Constant Properties Window

The next step is the Constant Properties window. The constant properties window is shown in Figure 40. Since no constants has been defined in for complex123.ioo model, Constant Properties window empty.

Sets window shows the names of the sets and the associated elements of the set added in the FlowSheet simulation section window as shown in Figure 41. Navigation from one set to the other can be done by clicking on triangle icons at the bottom of the sets window. Each set consists of Set Name, Description of the set, and a set of elements. Each element of the set consists of element name and description.

The next tab is parameters window, which shows parameters associated to the model. Parameters are nothing but sets of constants grouped under a name. Parameters window show parameter name, associated set name, elements of the set and values of elements. As shown in Figure 42. Navigation of the parameters is same as sets.

Finally, The last tab is multi-dimension variables window, which shows all one and multi-dimension variables associated with the model. One dimension variables use single set, where as multi-dimension variables use more than one set. Multi-dimension variable window shows variable name, description, and sets used by the variables. Since there no Multi-Dimension variables defined for complex123 model, This window is empty as shown in Figure 43.
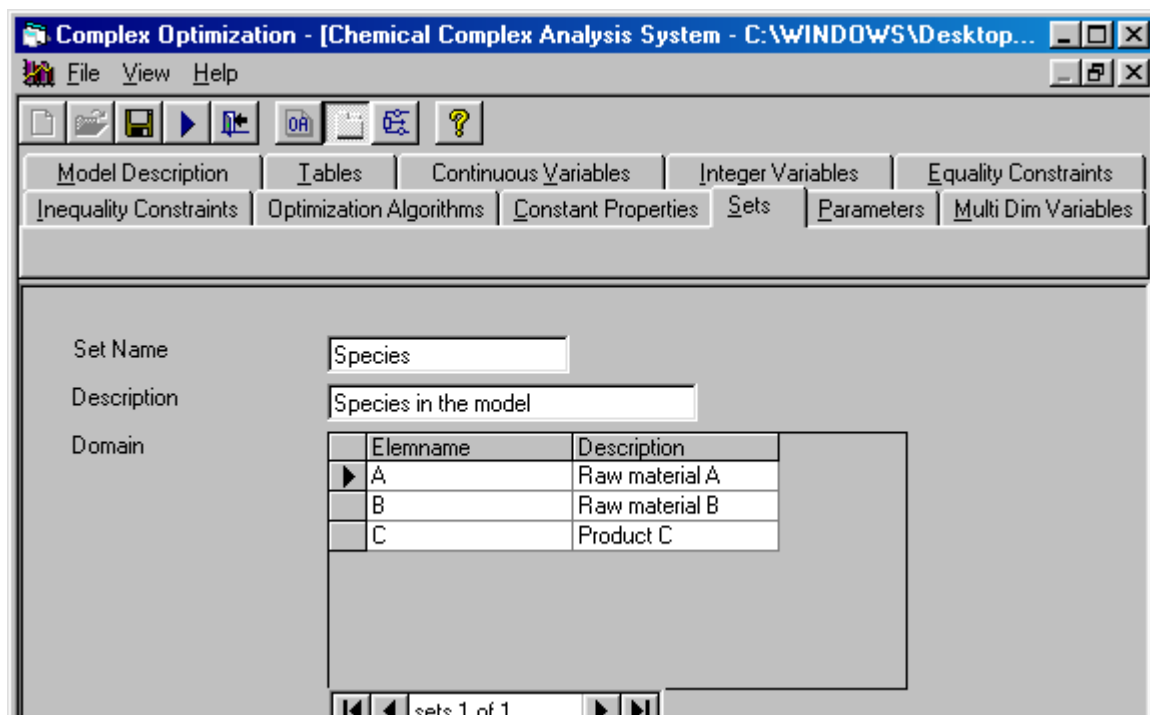
Figure 41. Sets window
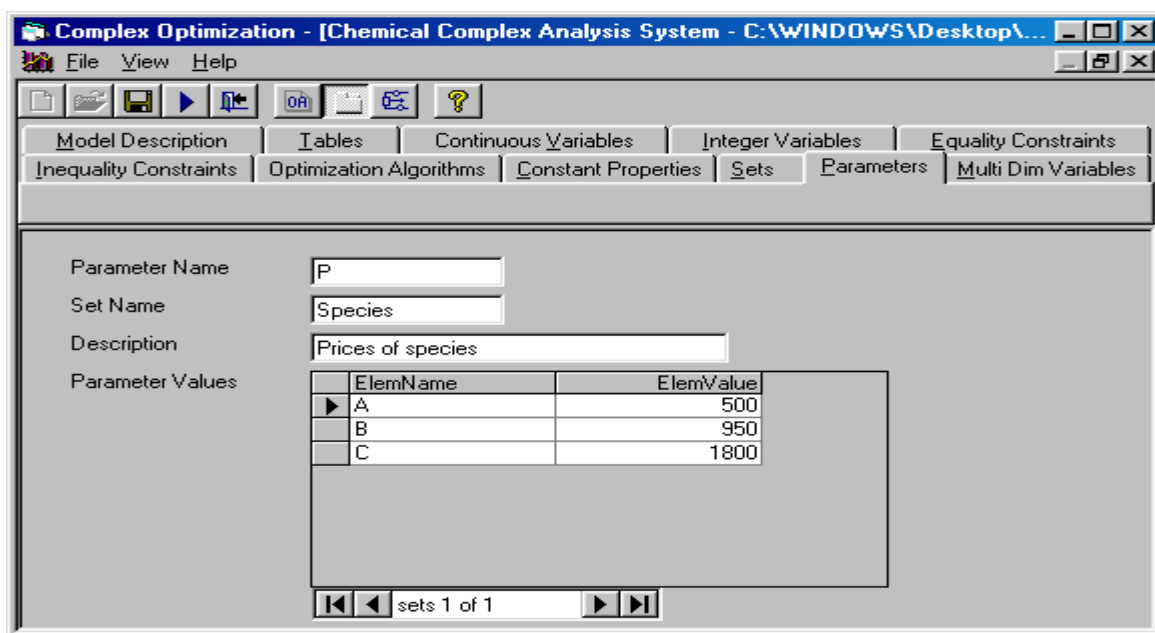
Figure 42. Parameters Window
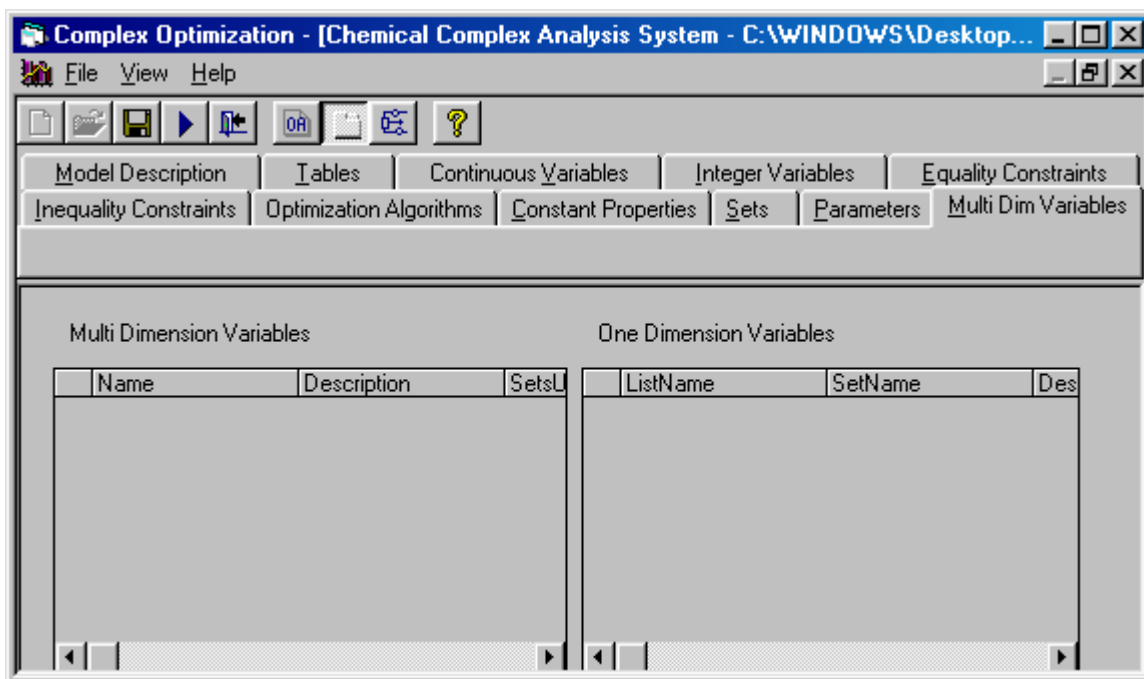
Figure 43. Multi-Dimension Variables Window.

The flowsheet diagram can be viewed by clicking on the 'FlowSheet Diagram' option in the view menu as shown in Figure 34. The flowsheet cannot be edited in the Optimization program. The flowsheet diagram is shown in Figure 41. Double clicking on a unit opens a data form, which displays all the continuous variables, Integer variables and plant parameters that are associated with that unit. Similarly, double clicking on a stream opens a data form, which displays the continuous, and Integer variables, associated with the stream. The global data can be viewed by double clicking on the background of the flowsheet.

Clicking on the 'Options' item in 'View' menu opens the Options window as shown in Figure 44. General GAMS Process options are set in the 'GAMS Process' tab as shown in the first window of Figure 44. The format for the GAMS output can be specified by clicking on the 'Output Format' tab. Model type can be selected in the Solver Tab or in Model Description window (shown in Figure 35). 'Select Solver' option shows the available solvers for the selected Model type. Since complex123 model is of type "MINLP", solver "SBB" is selected. The default values can be restored by clicking on the 'Use Defaults…' button. Solver Parameters like Number of Iterations; Number of Domain Errors and Amount of Time Used can be specified in the 'Solver Parameters' tab as shown in the fourth window of Figure 44.

The default values for Number of iterations 1000, Number of Domain Errors 0, and Amount of time used 1000 sec can be restored by clicking on the 'Use Defaults…' button. Default values are used for the complex123 model. Clicking on the 'Advanced Options' button, which brings up the window shown in Figure 45, can set other advanced (additional) options the user wants.

46
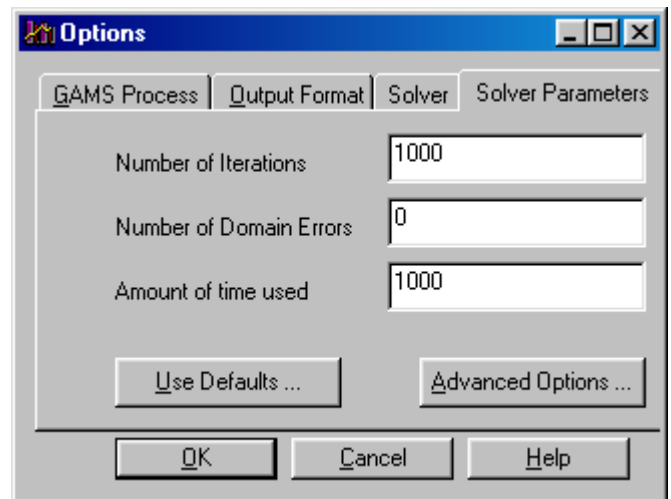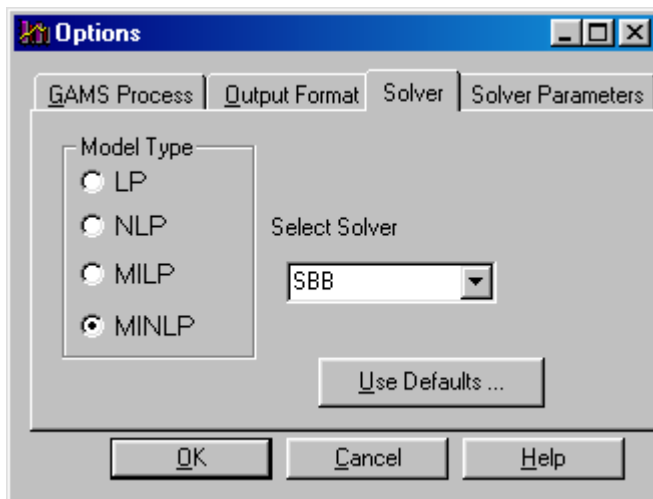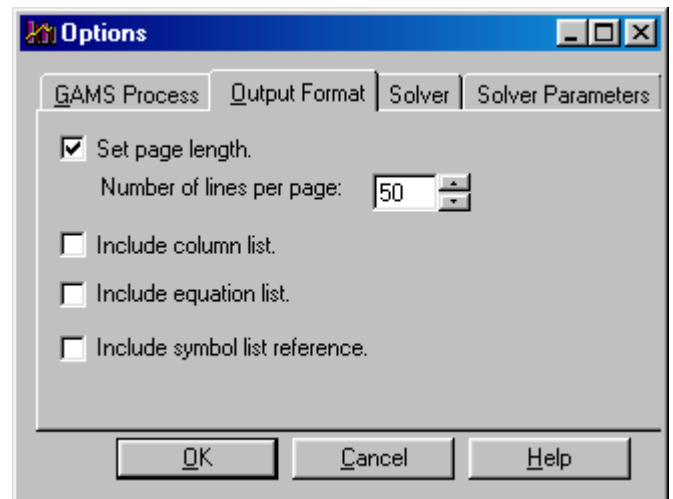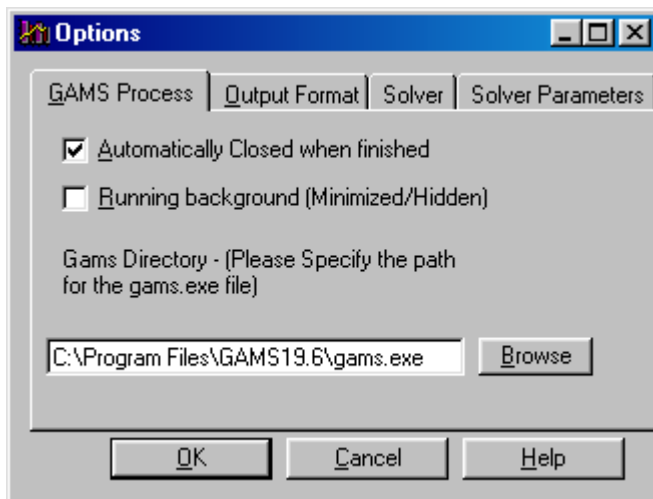
Figure 44. Options with **GAMS** process tab
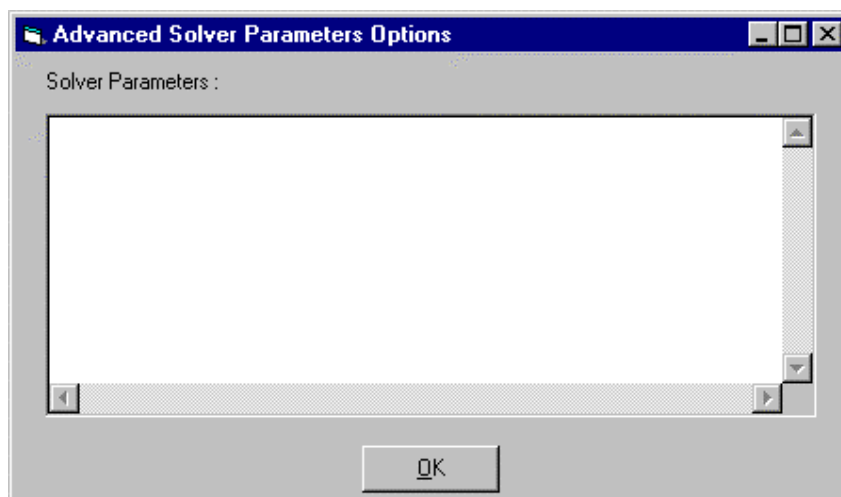
Figure 45. Advanced Parameters Options

When user clicks on the view (Figure 34) on the menu bar, it shows two additional options namely Sensitivity Analysis, Multi-Criteria Analysis. These options will be enabled if the model has the data to run the specified analysis. Otherwise, these options are disabled. Since the complex123 model has the data (entered in "FlowSim" part) to execute both Sensitivity Analysis and Multi-Criteria Analysis, both of these options are enabled in the 'View' menu as shown in Figure 34. Sensitivity Analysis window is shown as in Figure 46 when the user clicks on Sensitivity Analysis option on the 'View' menu. The data shown in this window is for viewing and verification only. To modify the data for sensitivity analysis, the user has to select Sensitivity Analysis option in the Flow Sheet Simulation window.

Similarly when the user clicks on the Multi-Criteria Analysis option on the view menu, MCA data window is shown as in Figure 47.

Once the user verifies that the input data is correct, The user proceeds to execute the model. To execute the model, click on the 'Execute' option in the File menu or click on the 'Execute' button (the button with the triangle) in the toolbar. Once the 'Execute' option is clicked the Model Summary and Execute window is shown as in Figure 48 . This window gives the summary of the chemical complex process, and shows three options i.e. Complex Optimization, Sensitivity Analysis, Multi-Criteria Analysis, to allow the user select the model to be executed. Sensitivity analysis and Multi-Criteria analysis options are disabled if the model do not have the associated information. By default Complex Optimization is selected.
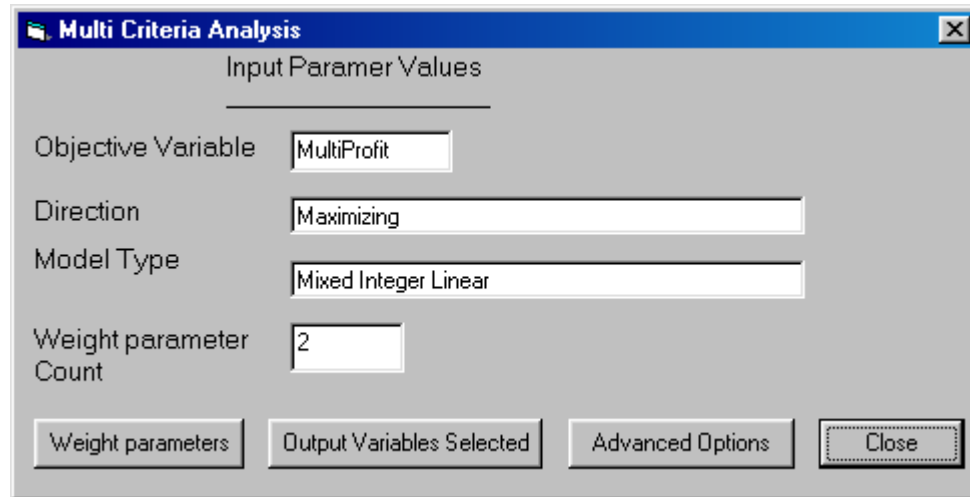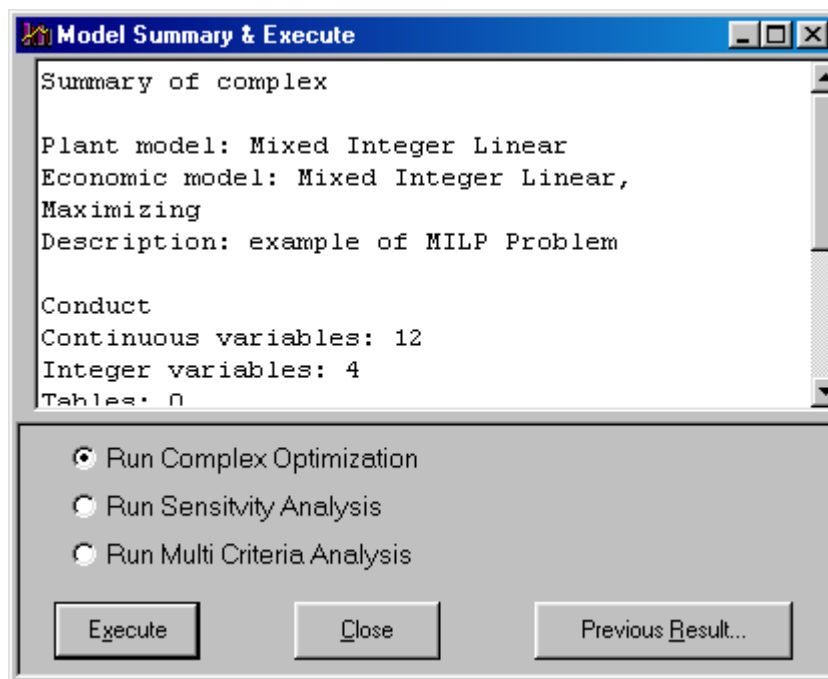
Figure 46. Sensitivity Analysis Data Window

When the 'Execute' button in the 'Model Execute and Summary' window is clicked, the program first extracts the model information from the database. Based on this information, it generates the GAMS input files and calls the GAMS solver. The progress of the GAMS program execution is shown in Figure 49. This window is automatically closed as soon as the execution is over. When the execution of the program is completed, it displays the results of the optimization in the Output window.

Figure 47. Multi-Criteria Analysis Data

Figure 48. Model Execution Summary Window

Figure 49. **GAMS** Program Execution Window

Figure 50. Final Report in the Output Window

After the program has been executed, GAMS output file is generated by GAMS for the selected analysis. The output file give a detailed solution for the Optimization of complex123 model. The output window with the Final Report which includes all the parameter of the complex 123 and their optimum values, of Complex Optimization, is shown in Figure 50. The View menu in the output window has three options named Final Report, Full Output and Flowsheet. The Final Report option has

50
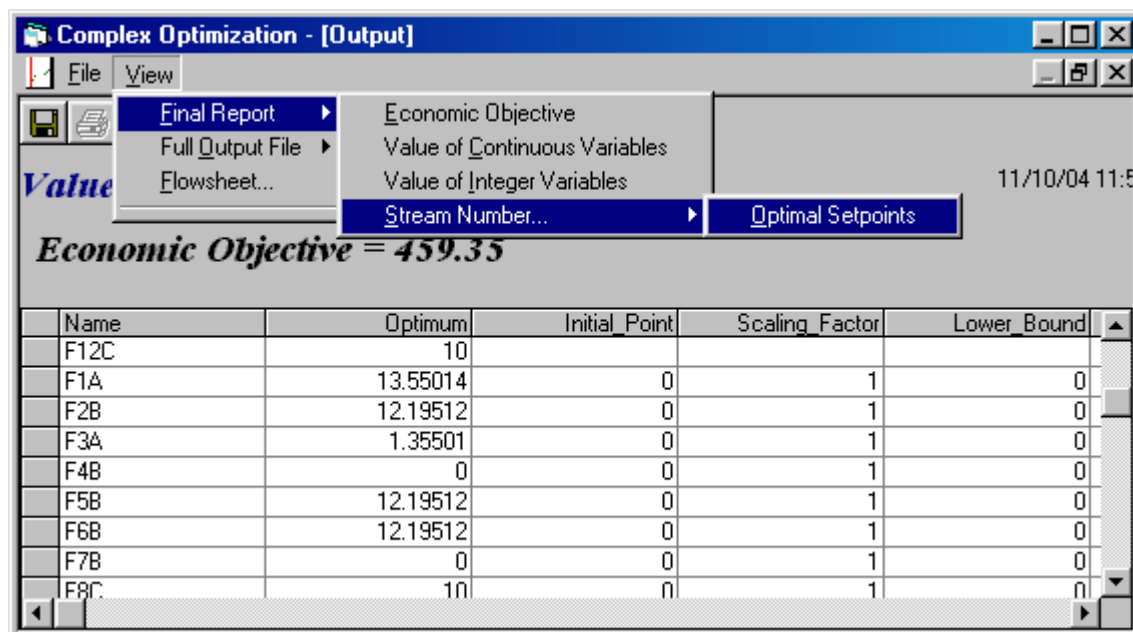
Figure 51. View Menu in the output Window
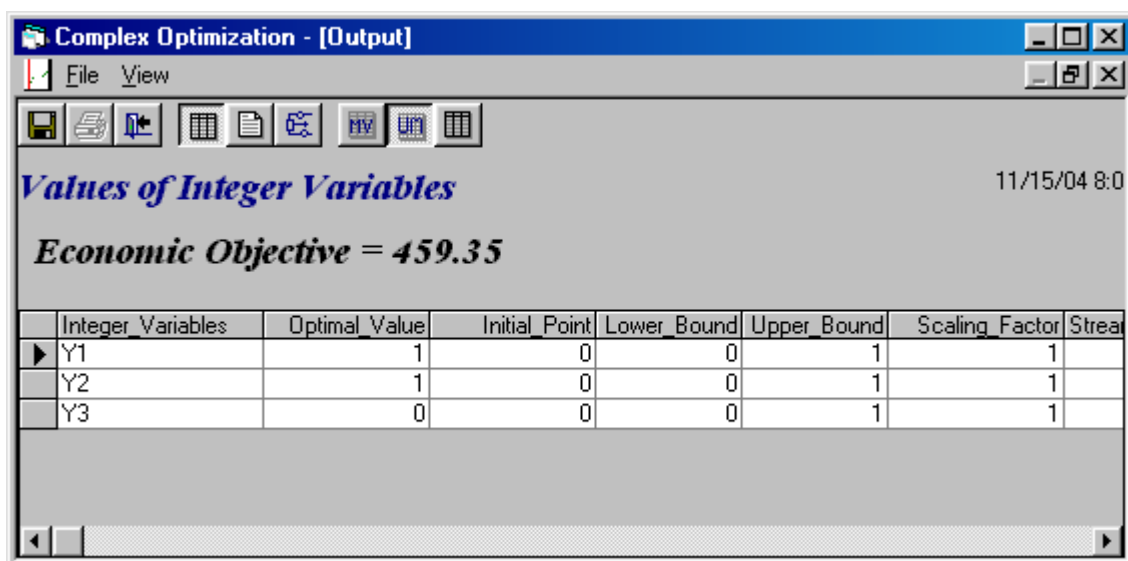
Figure 52. Optimal Values for Integer Variables

four options namely the Economic Objective, the Continuous Variables, the Integer Variables and the Stream Number as shown in Figure 51. Economic Objective value option shows the output as shown in Figure 50.

When the option 'Values of Continuous Variables' in the Final Report menu is clicked, the system opens a spreadsheet data form which includes the optimum values from economic optimization and the plant data as shown in Figure 50. The Final Report can be exported as an Excel file using the 'Export' option in the file menu.

Clicking on the 'Values of Integer Variables', the system opens a spreadsheet data form which includes the Integer Variables and their optimum values as shown in Figure 52. In the 'Stream Number' menu as shown in Figure 51, we see the 'Optimal Setpoints' option. 'Optimal Setpoints' option shows Optimum values for variables
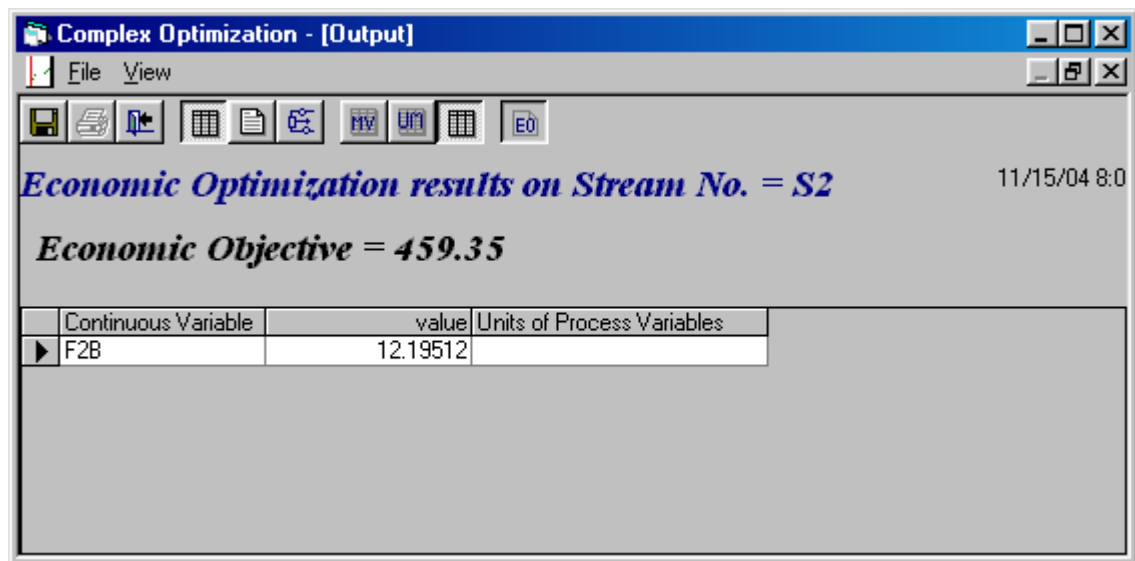
Figure 53. Information based on Stream Number

associated with the specified stream. When we click on the 'Optimal Setpoints' option, an input box appears. Let us enter 'S2' and click 'Ok'. The Continuous Variables and Integer Variables which are associated with the stream 'S2' with their optimum values from optimization are displayed as shown in Figure 53.
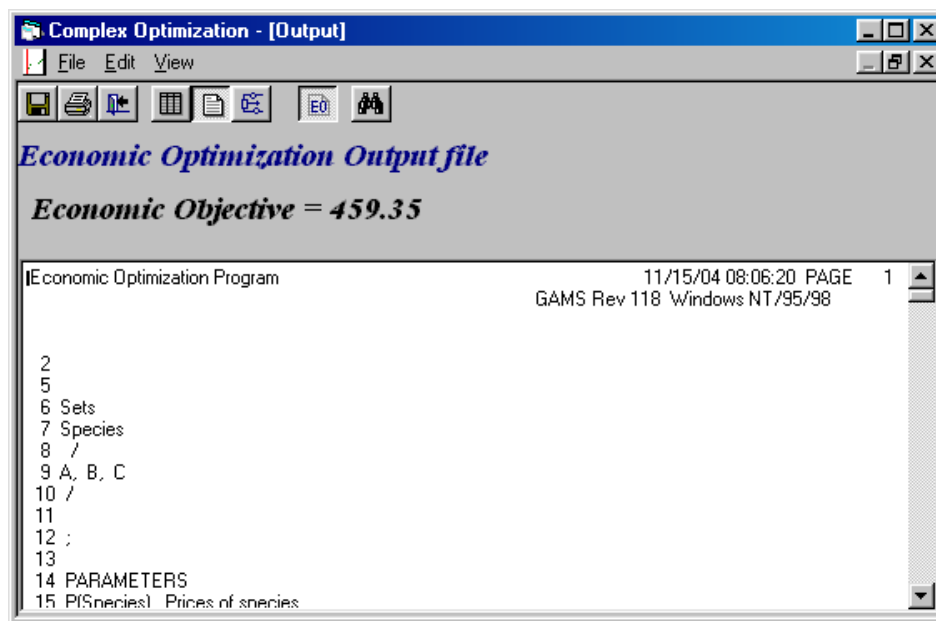
Figure 54. Full Output File of GAMS Programs

When the 'Full Output File' option in the view menu is selected, the Economic Optimization option is shown. When we click on the option, the output file of the Economic Optimization is shown as in Figure 54.

The user can use the 'Find' and 'Goto' options in the Edit menu to search for a

particular phrase or go to a particular section in the Full Output file. The Full Output file can also be exported as a text file using the 'Export' option.

The results can also be viewed from a flowsheet by double clicking on a stream or unit opens the corresponding data window. The Data window for stream 'S2' is shown in Figure 55. As seen in this figure, the values of the continuous variables are obtained as a result of optimization are displayed in the data window. When the user clicks on the flowsheet button in the output window, The streams whose data is less than 0.0002 (threshold) are shwon in black color. The units whose associated data is less than threshold are shwon in color red.

Clicking the 'Close' option in the file menu of the Output window returns the user to the main screen, which was shown in Figure 35. The model information can be exported to an Excel file using the 'Export' option in the file menu of the output window. Save the optimization results using the 'Save' option in the file menu. The
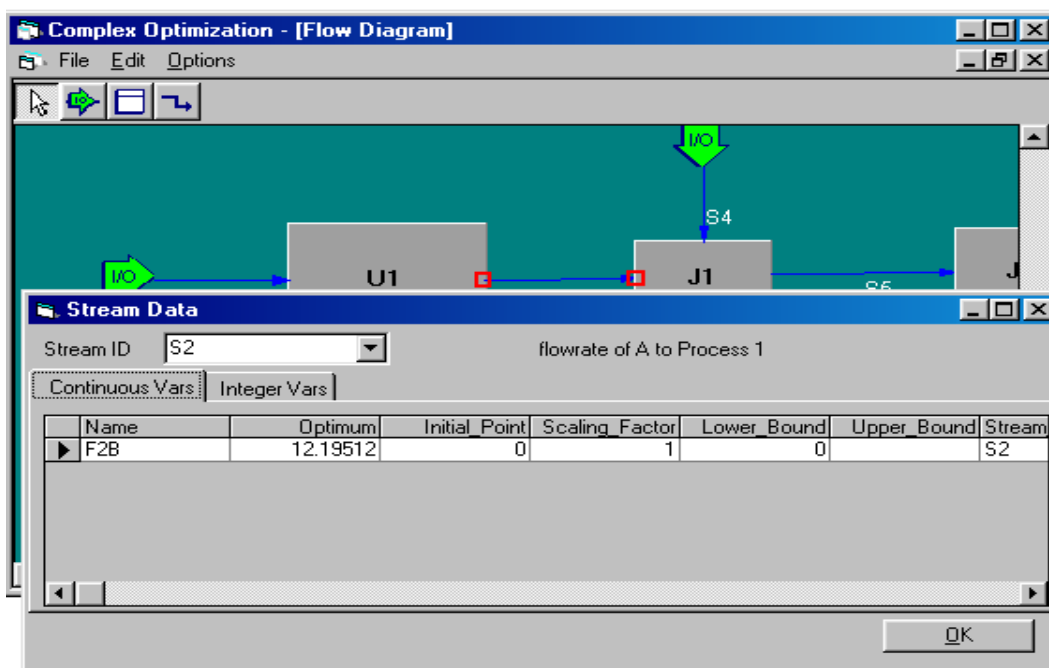
Figure 55. Stream Data Window
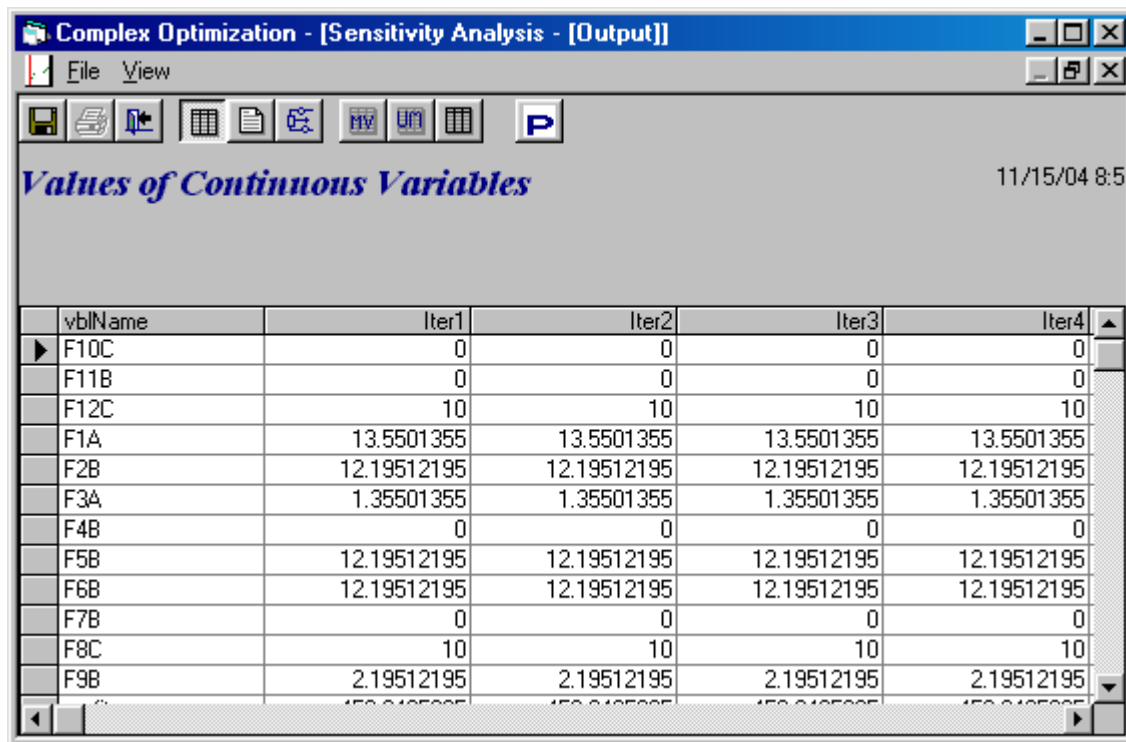
results including the full output files are stored along with the model. When the 'Exit' button is clicked, the Complex Optimization main window is closed and the user is taken back to the Chemical Complex Analysis Desk.

Sensitivity Analysis and Multi-Criteria Analysis Output

If the user selects 'Run Sensitivity Analysis' option from the execute window, shown in Figure 48. The system uses the sensitivity analysis data for complex123 model, and executes the sensitivity analysis. After finishing the execution, the System shows the sensitivity analysis output in Figure 56. The output window lists all the

continuous variables of the model and values of those variables in each of the iterations. If the specific variables are selected for output in the Flowsim window, only those variables is shown for output. Price parameter output values will be shown by clicking the button 'P' on the tool bar or selecting 'Sensitivity Model Parameter' from 'View' menu. For both Sensitivity Analysis and Multi-Criteria Analysis, If number of iterations is greater than 150, then only first 150 iterations results will be shown initially. All other iterations results can be viewed by selecting corresponding iteration range from the View menu. Each of the iterations results can be exported to an excel file by clicking on the 'Export' option from the 'File' menu. All other options in the sensitivity analysis model are same as the options in the Complex Optimization window.

Since each of iterations values may be different for the variables associated with the streams and units, when the Flowsheet button is clicked on the output window, the system asks for specific iteration number for which the user want to see the flow sheet diagram. Once the user enters the iteration number, flowsheet diagram for the specified iteration is shown. Flowsheet diagram may differ from one iteration to the other, in color of the some of the units and/or streams, depending on the data associated with those units and streams.

Figure 56. Sensitivity Analysis output window

Figure 57. Multi-Criteria Analysis Output window

When the user selects 'Run Multi-Criteria Analysis' option from the execute window shown in Figure 48. System executes Multi-Criteria analysis for specified model which is complex123 and shows the output as in Figure 57. All the options in the output window are same as of Sensitivity Analysis.

VI. Using the Pollution Assessment Program

Steps in Using the Pollution Assessment Program

The first step in performing pollution analysis is the selection of relevant streams. Environmental impact of a chemical process is caused by the streams that the process takes from and emits to the environment. Therefore, only these input and output streams are considered in performing the pollution index analysis. Other streams, which are completely internal to the process, are excluded. In the Pollution Index Program, this selection of input-output streams is automatically done based on the plant information entered in Flowsim.

The next step in the pollution index analysis is the classification of the output streams into product and non-product streams. All streams which are either sold as product or which are used up in a subsequent process in the production facility are considered as product streams. All other output streams, which are released into the environment, are considered as non-product streams. All non-product streams are considered as pollutant streams whereas all product streams are considered to have zero environmental impact.

Pollution index of a stream is a function of its composition. The composition data for the streams is retrieved from the results of optimization performed earlier. This can be either in terms of the molar flowrates or fractions. Additional data such as the specific environmental impact potential values for the chemical species is available in the report on environmental life cycle assessment of products.

The last piece of information required is the relative weighting factors for the process plant. These values depend on the location of the plant and its surrounding conditions. For example, the weighting factor for photochemical oxidation is higher in areas that suffer from smog.

Having finished all of the above prerequisite steps, the pollution index program is now called to perform the analysis. Mass balance constraints are solved for the process streams involved, and the equations of the Environmental Impact Theory are used to calculate the pollution index values. The pollution indices of the six types discussed earlier are reported for the process. Three of these are based on internal environmental efficiency whereas the other three are based on external environmental efficiency. Higher the values of these indices, higher the environmental impact of the process.

The pollution index program also calculates pollution indices for each of the individual process streams. These values help in identification of the streams that contribute more to the overall pollution impact of the process. Suitable process modifications can be done to reduce the pollutant content of these streams.

Every run of optimization for the process is followed by the pollution index calculations. The new pollution index values are compared with the older values. The comparison shows how the change in process conditions affects the environmental impact. Thus, the pollution index program can be used in continuous on-line monitoring of the process.

VII. Description of an Chemical Production Complex

The methodology and procedure to use the Chemical Complex Analysis System has been outlined in previous chapter. This chapter deals with the development of process simulation and optimization model for the chemical production complex in the lower Mississippi River corridor. This complex is ideally suited for demonstration of the system performance. A detailed description of the complex is given below.

A. Chemical Production Complex
A-1. Introduction to the Chemical Production Complex

As the world economy develops, it is good for chemical industry to incorporate all possible production units to make the maximum profit. A chemical production complex was assembled with production units in the lower Mississippi River corridor (Figure 7.1). This was done with information provided by the cooperating companies and other published sources. This complex is representative of the current operations and practices in the chemical industry and was used as the base case and starting point to develop a superstructure by adding plants. These additional plants gave alternate ways to produce intermediates that reduce and consume wastes and greenhouse gases and conserved energy. These additional plants could provide combinations leading to a complex with lower environmental impacts and greater sustainability. This superstructure was evaluated using the economic, environmental and sustainable criteria in the Chemical Complex Analysis System to obtain the optimum configuration.
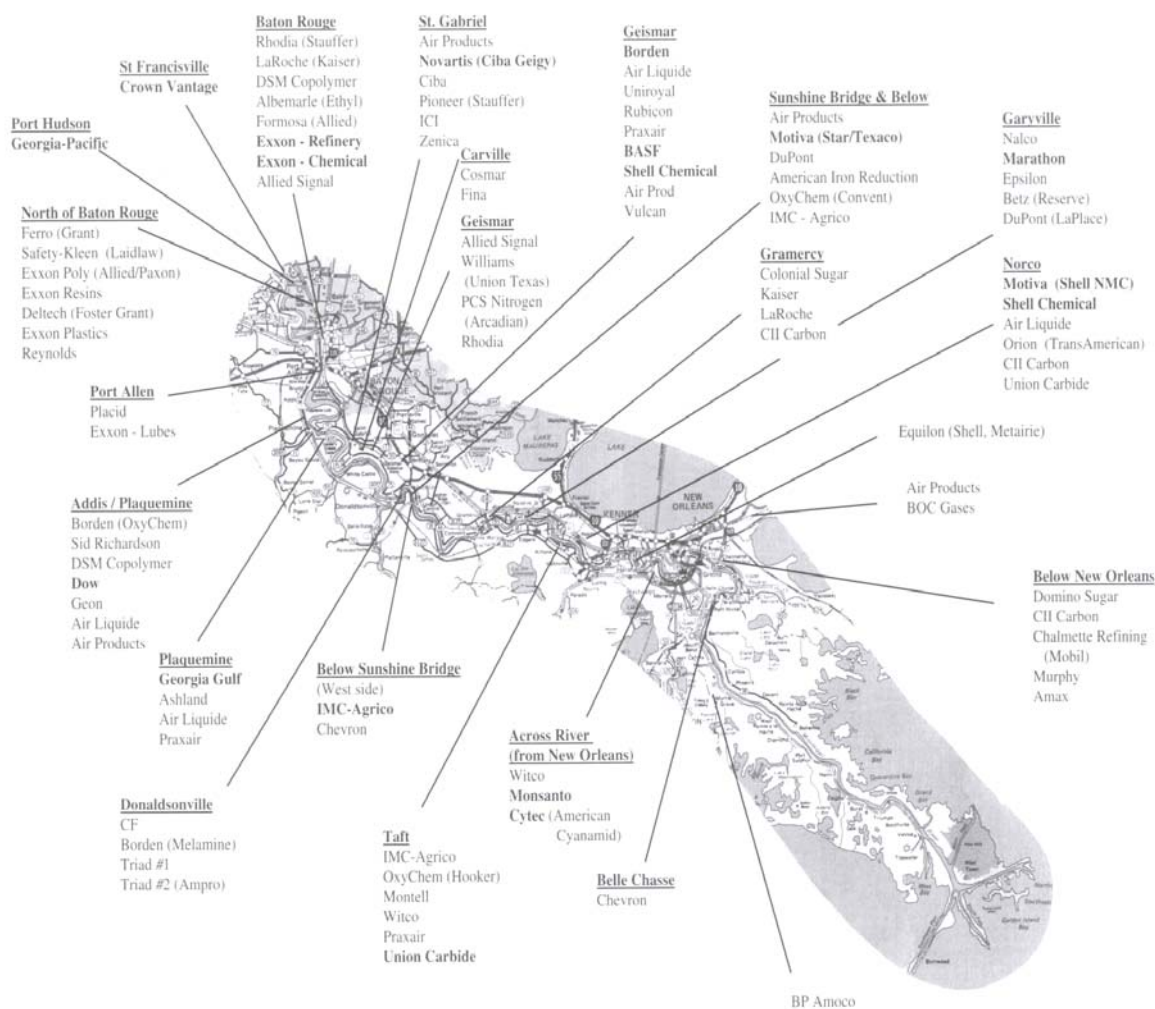
Figure 7.1 Chemical Plants along the Lower Mississippi River Corridor, from
Peterson (2000)

The process simulation of each unit in the chemical production complex is given in the
following section, along with how these plants are connected. First the process models
for the plants in the base case will be given. The base case of existing plants was
developed under the direction of the industrial advisory group. Then the process
models for the additional plants added to form the superstructure will be given.

A-2. Process Models in the Chemical Production Complex

The model (simulation) of a process includes material and energy balances,
rate equations and equilibrium relations. The material balance and energy balance

equations for a process are given in a table. For each process this includes the overall mass balance and the component or species mass balances. The mass balance for each component is established based on the conservation law. The steady state mass balance for a component is written as:

$$F_{in}^{(i)} - F_{out}^{(i)} + F_{gen}^{(i)} = 0 \qquad (7\text{-}1)$$

where i represents the name of component. F stands for the mass flow rate in the metric tons per year. The overall mass balance is the summation of all components mass balances.

The steady state overall energy balance is established based on the first law of thermodynamics. Neglecting changes in kinetic and potential energy, this equation is (Felder and Rousseau, 1986):

$$\Delta H = Q - W \qquad (7\text{-}2)$$

where Q is the net heat added to the system; W is the work done by the system on the surroundings; and ΔH is the change in enthalpy between input and output streams, i.e.,

$$\Delta H = \sum_{output} n^{(i)} H^{(i)} - \sum_{input} n^{(i)} H^{(i)} \qquad (7\text{-}3)$$

The reference condition for enthalpy is the elements that constitute the reactants and products at 25°C and the nonreactive molecular species at any convenient temperature. $H^{(i)}$ for a reactant or product is the sum of the heat of formation of the species at 25 °C and any sensible and latent heats required to bring the species from 25 °C to its inlet or outlet state. The reaction term is not required if elements are chosen as references, since this term is implicitly calculated when the heats of formation of the reactants are subtracted from those of the products.

Q is the net heat transferred to the process. It includes heat input in the form of steam in the heat exchanger and distillation column reboilers, and heat output which is removed by cooling water in heat exchanger and distillation column condensers. The heat output by cooling water can be estimated from HYSYS simulation and other sources as Q_{out} (energy per mass of reactant) times F_r (mass flow rate of reactant). Then the heat input by steam is Q_{in}, and the equation for Q can be written as Equation 7-4.

$$Q = Q_{in} - Q_{out} \times F_r \qquad \text{(r is for reactant)} \qquad (7\text{-}4)$$

where Q_{out} is a positive number. The negative sign indicates heat is removed from the process. The energy balance becomes Equation 7-5.

$$\sum_{output} n^{(i)} H^{(i)} - \sum_{input} n^{(i)} H^{(i)} = Q_{in} - Q_{out} \times F_r \qquad (7\text{-}5)$$

This form of the energy balance is used in the process models. Q_{in} is calculated from the solution obtained by the System, and it represents the heat required for separations and steam required for chemical reaction for an endothermic reaction in the chemical reactor. For an exothermic reaction, Q_{in} is the net of the heat released by the reaction and steam required for separations. Steam and heat required for chemical reactions are at a temperature level significantly above the temperature of heat removed by cooling water (~ 40°C). Also, shaft work for electricity energy for pumps and compressors is typically small compared to the other energy flows and is not included.

The expression for enthalpy is always expressed as a function of temperature (Equation 7-6).

$$H_k^i(T) = (a_1^i + \frac{1}{2}a_2^i T + \frac{1}{3}a_3^i T^2 + \frac{1}{4}a_4^i T^3 + \frac{1}{5}a_5^i T^4 + \frac{b_1^i}{T})RT \quad \text{J/mol} \qquad (7-6)$$

where a_1, a_2, a_3, a_4, a_5, and b_1 are coefficients; R is gas constant; T is temperature; i stands for species; and k stands for streams. The detailed enthalpy function for the species in the chemical production complex are given in Appendix A.

The next section describes the existing plants in the chemical production complex in the lower Mississippi River corridor as shown in Figure 3.3 called base case. A list of all of the stream designation and definition is given in Table B-1 of Appendix B, and stream splits and mixing parts are given in Table 7-46.

B. Processes in the Chemical Production Complex

B-1. Sulfuric Acid (Hertwig, 2004; Louisiana Chemical & Petroleum Products List, 1998).

In the chemical production complex, there is one option for sulfuric acid production, which is the contact process for sulfuric acid. The contact process is described below in detail. In the chemical production complex in the lower Mississippi River corridor the sulfuric acid production plants are as follow (Louisiana Chemical & Petroleum Products List, 1998).

- IMC-Agrico, Uncle Sam (2.2 million metric tons per year)
- IMC-Agrico, Faustina (1.1 million metric tons per year);
- PCS Nitrogen Fertilizer LP, Geismar (454 thousand metric tons per year);
- Dupont, Burnside (420 thousand metric tons per year);
- Rhodia, Baton Rouge (725 thousand metric tons per year);
- Cytec Industries, Westwego (572 thousand metric tons per year);

For the chemical production, the capacity of 10,932 tons per day was used in the base case (Hertwig, 2004).

B-1-1. Process Description of Contact Process for Sulfuric Acid

B-1-1-1. Sulfur Feedstock

There are two ways to obtain sulfur feedstock, Frasch and Claus processes.

Frasch process: In this process 160°C water is injected via double-pipe annulus into a porous sulfur-bearing rock formation and melted sulfur returns (along with some hot water) in the center pipe. Sulfur-melting water is heated in natural-gas-fired package boilers. This water is fresh onshore and sea/salt offshore. This sulfur well is typically called a "mine". However, Frasch sulfur is no longer practiced with excess Claus sulfur available. It is still in the model for the completeness.

Claus sulfur: There are two reactions in this process.

H_2S (g) + $1.5O_2$ = SO_2 (g) + H_2O (g) $\qquad\qquad\qquad$ (7-7)
SO_2 (g) + $2H_2S$ (g) = 3S(l) + $2H_2O$ (g) $\qquad\qquad\qquad$ (7-8)
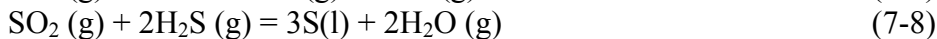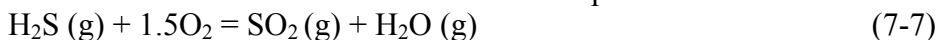
H_2S is recovered from sour natural gas and oil refining by absorbing it, then releasing it in fairly pure form. Environmental permits require 98% conversion of H_2S in 1984

(99.5% in Alberta province). Also environmental permits presume the balance is SO_2 air emissions.

B-1-1-2. Sulfur Storage

Trace hydrocarbon content in sulfur will react with S to produce H_2S, which must be air-stripped to prevent accumulation of lethal or explosive levels of H_2S.

B-1-1-3. Sulfuric Acid Reaction Theory

The contact process is a three-step process that produces sulfuric acid and steam from air, molten sulfur and water, i.e. the feed preparation, the reaction and the absorption. The block diagram is shown in Figure 7.2 with the steam definitions in Table 7-2.

The feed preparation equipment includes an air filter, air-drying tower, a main compressor and a sulfur burner. Molten sulfur feed is combusted with dry air in the sulfur burner which goes to completion. The reaction is:

$$S + O_2 = SO_2 + Heat \qquad (7-9)$$

The burner-exit gas is composed of sulfur dioxide, nitrogen, carbon dioxide, Ar, and unreacted oxygen at 1,800-2,100 °F. Much of the heat of reaction is recovered in a waste heat boiler. The compressor is power by a steam-driven turbine that has an efficiency of about 65% for the turbine itself.

For the reaction part there is a four (or five) - bed reactor packed with two different types of vanadium pentoxide catalyst where the gas mixture from the feed preparation section is further oxidized to produce sulfur trioxide according to the reaction:

$$2SO_2 + O_2 = 2SO_3 + Heat \qquad (7-10)$$

This is where the "contact" comes from. The alternate process is "chamber" and that has not been run for decades, and all further references to "contact" are dropped.
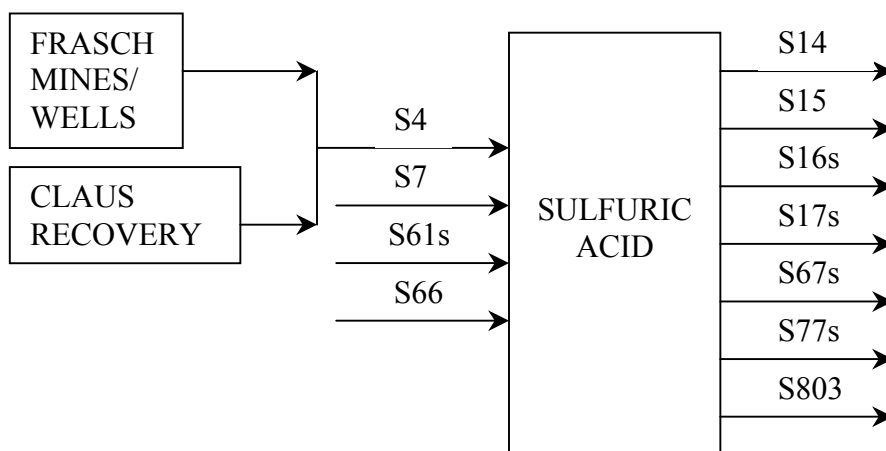
Figure 7.2 Block Diagram of Contact Process to Produce Sulfuric Acid

Table 7-2 Description of Process Streams in Contact Sulfuric Acid Production

Name of Streams	Description
Input Streams	
S2	S from Frasch mines/wells to sulfuric acid process (SAP)
S3	S from Claus recovery to SAP
S4	Total S to SAP
S7	Dry air to SAP
S61$_S$	Boiler feed water (BFW) to SAP
S66	Process water to SAP
Output Streams	
S14	H_2SO_4 solution produced from SAP
S15	Vent gases exiting from SAP
S16$_S$	Low pressure steam (LP) (40 psig) exiting from SAP
S17$_S$	High pressure steam (HP) (600 psig) exiting from SAP
S67$_S$	Boiler blowdown H_2O from SAP
S77$_S$	Intermediate pressure steam (IP) (150 psig) exiting from SAP
S803	Impurity of sulfur from SAP

Reaction 7-10 is exothermic, and the equilibrium conversion decreases with the increase in reaction temperature. The process uses multiple packed beds with heat exchangers between each bed to remove the liberated heat to reduce the temperature to allow further conversion. With the equilibrium constant $K_p = \dfrac{P_{SO_3}}{P_{SO_2} P_{O_2}^{0.5}}$, conversion is raised by adding interstage SO_3 absorption. With interstage absorption, P_{SO_3} is lower downstream and P_{SO_2} can be raised upstream by increasing burner-feed sulfur-to-air ratio.

In the absorbers, intermediate and final, essentially all of the SO_3 present is absorbed from the reaction gas mixture into 98.5wt% sulfuric acid to produce more concentrated acid and heat of absorption according to the equation:

$$SO_3 + H_2O = H_2SO_4 + Heat \qquad\qquad (7\text{-}11)$$

The equipment in this part includes the final acid absorption tower, inter-pass absorption tower, acid pump tank(s), dilution acid tank (optional) and heat exchangers which are one acid cooler per tower, gas-to-gas heat exchanger(s), and/or economizers or superheaters on gas streams to each absorber.

B-1-1-4. Air-Drying and SO_3-Adsorption Towers

Commercial processes add SO_3 to 98.5% H_2SO_4 and water to obtain 99% H_2SO_4. SO_3 absorption is maximized and essentially complete using 98.5% H_2SO_4.
Poorer-than-normal absorption can make the stack gas visible as a white plume of H_2SO_4 mist. Stack gas opacity is a concern because there are limits in the operating permit, and opacity may indicate a steam-system leak. High-performance demisters

will capture some of the mist and hide the steam-system problems for a while. Other potential causes for opacity include low absorber acid temperature and high absorber gas-inlet temperature.

Product H_2SO_4 can be produced as dilute as 93% with little extra risk of corrosion. Corrosion accelerates rapidly below 92%. Lower strengths (93% vs 98.5%) are valuable only to reduce heat of dilution in subsequent use.

Air drying is needed to reduce risk of acid condensing in the gas-side of the process. Air is dried with H_2SO_4. To improve drying, cooler acid is much better and 98.5% is slightly better than 93%. Dew point is typically about -40°C and can be estimated from H_2SO_4 partial-pressures tables.

B-1-1-5. Waste Heat Recovery

Waste heat is recovered from gas streams above 300°F as 600 or 900 psig superheated steam. Heat recovery from gas upstream of acid is limited by the gas dew point of 280-300°F. Dew point depends on the hydrocarbon content of the sulfur feed and drops about 20°F after being dried in the first SO_3-absorption tower. The 300 psig gap in steam-system designs (600 or 900 psig) is because turbine metallurgy must be more exotic above 750°F which is a reasonable superheat for 600 psig steam. Increasingly, lower-grade heat is recovered at an intermediate pressure. Heat of SO_3 absorption can be recovered with Monsanto Enviro-Chem's heat recovery system (HRS). This heat is recovered as steam at up to 150 psig. Process heat recovery is about 70% without HRS and about 80% with HRS. Most losses go to acid-cooling water.

B-1-1-6. Production Rates

H_2SO_4-STPD (short tons per day) -to-steam-KPPH (thousand pounds per hour) production ratio runs 9.2±0.5 without HRS. The ratio changes with ambient temperature, wind, rain, and fuel-to-air ratio, which is adjusted to keep stack SO_2 within environmental permit limits. H_2SO_4 production capacity is normally limited by blower capacity and increases at night and in winter when inlet air is denser because it is cooler.

B-1-2. Material Balance and Energy Balance

The material balance and energy balance equations for this process are given in Table 7-4. There are some parameters (Table 7-3) referred to Figure 7.2 for its material balance. In the constraints of Table 7-4, F denotes the component mass flow rate, metric tons per year (MTPY), and its superscript i and subscript k denote the component names and stream numbers, respectively.

Table 7-3 Parameters in Sulfuric Acid Production, from Hertwig (2004)

Name	Meaning	Value
SIPSA	S impurity (decimal fraction)	0.001
SO2EMSA	Stack SO_2 emissions, lb SO_2 / short ton H_2SO_4 produced (max 4.0 per short ton)	4.0
BBLSA	Boiler blowdown as fraction of boiler feed water (BFW) (typical = 0.05-0.10)	0.08
SHPSA	Short TPD H_2SO_4/ (Klb/hr of HP drum steam)	9.1
HPBTSA	Fraction of high pressure (HP) drum steam used by blower turbine (typically = 0.35-0.60)	0.40
IPCAPSA	Fraction of SAP capacity with heat recovery system producing intermediate pressure (IP) steam	0.3
CONCSASA	Sulfuric product concentration (0.93 (produced in drying tower or in dilution tank) - 0.99; 0.985 (for final abstraction tower) minimizes stack opacity)	0.985
IPHRSSA	Klb/hr IP steam (from a 3085 TPD SAP with heat recovery system (HRS))	150

Table 7-4 Constraint Equations for Contact Sulfuric Acid Production

Material Balances	
Overall	$(F_4 + F_7 + F_{S61} + F_{66}) - (F_{14} + F_{15} + F_{S16} + F_{S17} + F_{S67} + F_{S77} + F_{803}) = 0$
	where $F_7 = F_7^{(O_2)} + F_7^{(N_2)} + F_7^{(CO_2)} + F_7^{(Ar)}$
	$F_{14} = F_{14}^{(H_2SO_4)} + F_{14}^{(H_2O)}$
	$F_{15} = F_{15}^{(N_2)} + F_{15}^{(Ar)} + F_{15}^{(CO_2)} + F_{15}^{(SO_2)}$

Heat Exchange (boiler feed water and steam balance)

$$(F_{S16} + F_{S17} + F_{S67} + F_{S77}) - F_{S61} = 0$$

$$F_{S61} = F_{S61}^{(a)} + F_{S61}^{(b)}$$

Species

$$S : F_4(1 - SIPSA) - \frac{32.06}{98.08}F_{14}^{(H_2SO_4)} - \frac{32.06}{64.06}F_{15}^{(SO_2)} = 0$$

$$H_2O(\text{process water}) : F_{66} - \frac{18.02}{98.08}F_{14}^{(H_2SO_4)} - F_{14}^{(H_2O)} = 0$$

$$O_2 : F_7^{(O_2)} - (1.5)\frac{32}{98.08}F_{14}^{(H_2SO_4)} - \frac{32}{64.06}F_{15}^{(SO_2)} = 0$$

$$N_2 : F_{15}^{(N_2)} - F_7^{(N_2)} = 0$$

$$Ar : F_{15}^{(Ar)} - F_7^{(Ar)} = 0$$

$$CO_2 : F_{15}^{(CO_2)} - F_7^{(CO_2)} = 0$$

$$SO_2 : \frac{SO2EMSA}{2000} F_{14}^{(H_2SO_4)} - F_{15}^{(SO_2)} = 0$$

Impurity: $F_{803} = F_4 \times SIPSA$

Heat Exchange	BFW: $F_{S61}^{(a)} - \frac{(F_{S16} + F_{S17})}{(1 - BBLSA)} = 0$

HP: $F_{S17} - \frac{(12)(1 - HPBTSA)}{SHPSA} F_{14}^{(H_2SO_4)} = 0$

IP: $F_{S77} - \frac{IPCAPSA \times IPHRSSA(12)}{(3400)} F_{14}^{(H_2SO_4)} = 0$

LP: $F_{S16} - \frac{(12)HPBTSA}{SHPSA} F_{14}^{(H_2SO_4)} = 0$

Blowdown H_2O: $F_{S67} = BBLSA \times F_{S61}^{(a)}$

Energy Balance

Overall

$$(\frac{1}{M^{(H_2O)}} F_{S61}^{(H_2O)} H_{S61}^{(H_2O)} - (F_{S16}H^{(LP)} + F_{S17}H^{(HP)} + F_{S77}H^{(IP)}$$

$$+ \frac{1}{M^{(H_2O)}} F_{S67}^{(H_2O)} H_{S67}^{(H_2O)})) - Q_{SACID} = 0$$

where M^i is molecule weight, i= H_2O

Enthalpy Function

$$H_k^i(T) = (a_1^i + \frac{1}{2}a_2^i T + \frac{1}{3}a_3^i T^2 + \frac{1}{4}a_4^i T^3 + \frac{1}{5}a_5^i T^4 + \frac{b_1^i}{T})RT \quad J/mol$$

where R is gas constant

T is temperature

i = H_2O

k = 61, 67

$$H^{(LP)}(T) = ((72.558 + (0.5)(-0.66244)T + (\frac{1}{3})(0.002562)T^2 +$$

$$(0.25)(-4.3659E - 06)T^3 + (0.2)(2.7818E - 09)T^4 + \frac{(-41886)}{T})(8.3145)T$$

$$- 1893)\frac{1}{18.02} + ((-0.007)T^2 + (2.7838)T + 2292.0563)$$

J/g

$$H^{(IP)}(T) = ((72.558 + (0.5)(-0.66244)T + (\frac{1}{3})(0.002562)T^2 +$$

$$(0.25)(-4.3659E - 06)T^3 + (0.2)(2.7818E - 09)T^4 + \frac{(-41886)}{T})(8.3145)T$$

$$- 1893)\frac{1}{18.02} + ((-0.007)T^2 + (2.7838)T + 2292.0563)$$

J/g

$$H^{(HP)}(P,T) = 2.326((5.32661)((T-273.15)(1.8)+32) - 0.2839015P$$

$$- (7.352389E-03)((T-273.15)(1.8)+32)^2 + (3.581547E-06)$$

$$((T-273.15)(1.8)+32)^3 - (7.289244E-05)P^2 + (4.595405E-04)$$

$$((T-273.15)(1.8)+32)P) - 15861.82$$

J/g, P:psia

Note: LP and IP have no superheat, from Meyer, et al. (1977) and McBride, et al. (1993); HP has superheat, from Chen (1998).

In Table 7-4, the overall material balance for the whole process is given with the boiler feed water and steam balance in heat exchange part of the process. For the species material balance obtained using the reaction equations (7-9, 7-10 and 7-11), the first equation is for the sulfur balance; the second one is for the process water balance; the third one is for the oxygen balance; the fourth one is for the nitrogen balance; the fifth one is for the argon balance; the sixth one is for carbon dioxide balance; the last one is for the impurity balance, i.e., the impurity in the sulfur input is treated as an inert.

In the heat exchange part, all the streams starting with subscript S in Table 7-4 plus some number are steam and boiler feed water flow rates. They are only for heat exchange and are not reactants. Those equations in the heat exchanger are for the mass balance of steam and water. All of these steam outputs will be used as heat output by steam in the energy balance part. The first equation is for the boiler feed water (BFW) balance; the second one is for the high pressure steam (HP) balance; the third one is for the intermediate pressure steam (IP) balance; the fourth one is for the low pressure steam (LP) balance which equals the fraction of HP going to blower turbine; and the last one is for blowdown water balance to control scaling.

In the overall energy balance in Table 7-4, Q_{SACID} is the net of the heat released by the reactions (Equation 7-9 and 7-10). This energy is recovered in the waste boiler and is used by other processes in the chemical production complex. Q_{SACID} is calculated from the net steam output from the plant and does not include cooling water in the acid cooler. It is different from the energy balance method using the enthalpy changes from input reactants to output reactants and heat loss (Equation 7-2, 7-3, 7-4, and 7-5) because sulfuric acid plant can produce the steam output in the form of HP, IP and LP as given by the Heat Exchange equations in Table 7-4. HP and IP are used in the power plant to generate electricity and LP. LP is used to evaporate the phosphoric acid from 28% to 48% in the phosphoric acid plant. In enthalpy functions, the coefficients a_1, a_2, a_3, a_4, a_5, and b_1 for different species are given in Table A-1 in Appendix A in (Xu, 2004).

In the material balance part, there are 23 variables and 23 equations, including one dependent one (overall material balance). So the number of degrees of freedom is 1 for the material balance part. For the material and energy balances, there are 35 variables and 29 equations, including one dependent one (overall material balance). The number of degrees of freedom is 7.

B-2. Phosphoric Acid (H_3PO_4) Production (Wet Process) (Austin, 1984; Hertwig, 2004; Louisiana Chemical & Petroleum Products List, 1998).

The raw material for phosphoric acid production is phosphate rock ($CaF_2 \cdot 3Ca_3(PO_4)_2$, a fluorapatite). Although not included in the chemical production complex, phosphate rock is strip mining using giant draglines to remove overburden whose phosphatic value is too low for economic processing, placing it to the side, usually in a mined-out area. Then the dragline digs the phosphate rock matrix and dumps it in a pit where the rock is slurried by giant water jets for pumping to a beneficiation plant miles away. The matrix is composed of clay slimes, silica sand and phosphate pebble. Phosphate rock purity is measured as BPL or bone phosphate of lime as percent of pure $Ca_3(PO_4)_2$(Austin, 1984). Phosphate concentration in rock, acid, or fertilizers is usually referred to on its anhydrous basis, percent of P_2O_5. For example, 100% H_3PO_4 would be $(\frac{142}{2 \times 98} \times 100\% =)$ 72.4% P_2O_5. Sand removed goes to reclaim old strip mines. Clay slimes removed go to large settling ponds. Clay fractions carry significant amount of phosphate for which there is not an economical recovery process today.

In the existing chemical production complex, phosphoric acid is produced by the wet process. In the chemical production complex of the lower Mississippi River corridor, the companies producing phosphoric acid by wet process are as follow (Louisiana Chemical & Petroleum Products List, 1998).

- IMC-Agrico, Uncle Sam (805 thousand metric tons per year)
- IMC-Agrico, Faustina (525 thousand metric tons per year)
- PCS Nitrogen Fertilizer LP, Geismar (200 thousand metric tons per year)
- Rhodia, Geismar (90 thousand metric tons per year)

For the chemical production, the capacity of 3,833 tons per day was used in the base case (Hertwig, 2004).

Two other options are included in the superstructure, electric furnace process and Haifa process, which will be described in the complex extension part. The description of the wet process is given below.

B-2-1. Process Description

B-2-1-1. Reaction Theory - Digestion, Filtration, Evaporation and Clarification

In the wet process, phosphate rock is digested in H_2SO_4 to swap H^+ and Ca^{2+}. Digestion is conducted in a stirred chemical reactor with multi-compartments (called "attack" tank). Soluble H^+ is moved from the SO_4^{2-} to the PO_4^{3-}. Insoluble Ca is moved from the PO_4^{3-} to the SO_4^{2-}. Digestion is controlled to promote large and filterable gypsum crystals since filtration is the rate-limiting step. Product acid contains residual $CaSO_4 \cdot 2H_2O$ as solids (gypsum) as well as in solution. Careful control of digestion and clarification can maximize removal of $CaSO_4 \cdot 2H_2O$. Rock contains many impurities, especially F, Fe, Al, Mg and Si. Most of the Fe, Al, and Mg remain in solution, moving with the phosphoric acid into the downstream phosphates. Digestion product strength is typically 25-29% P_2O_5. Digestion product is usually evaporated to 45-55% P_2O_5 to help the water balance during ammoniation to produce solid/granular products and to allow for additional purge of impurities $CaSO_4 \cdot 2H_2O$

and F. SiF_4 is scrubbed from digestion fumes and evaporator vapors. Evaporator scrubbings are often recovered for salable H_2SiF_6.

Management of byproduct gypsum is a major environmental concern, mostly for gypsum's P, F and Radon contents. Gypsum is typically stacked 50-300 feet high on hundreds of acres next to the phosphoric acid plant. To minimize groundwater contamination, any sandy ground must be covered with clay or plastic before starting a new stack. Also, after the stack is as high as practical, it is covered with soil and grass to minimize contamination of runoff water.

The wet process block diagram is shown in Figure 7.3 with the definitions of streams shown in Table 7-5. The key reactions are:

$$Ca_3(PO_4)_2 + 3H_2SO_4 + 6H_2O = 3CaSO_4 \cdot 2H_2O + 2H_3PO_4 \qquad (7\text{-}12)$$
$$CaF_2 + H_2SO_4 + 2H_2O = CaSO_4 \cdot 2H_2O + 2HF \qquad (7\text{-}13)$$
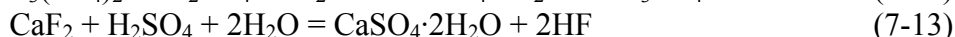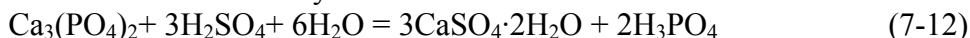
The general reaction from the summation of 3 times reaction equation (7-12) plus one times (7-13) is

$$CaF_2 \cdot 3Ca_3(PO_4)_2 + 10H_2SO_4 + 20H_2O = 10CaSO_4 \cdot 2H_2O + 6H_3PO_4 + 2HF \quad (7\text{-}14)$$

where $CaF_2 \cdot 3Ca_3(PO_4)_2$, is the fluorapatite.
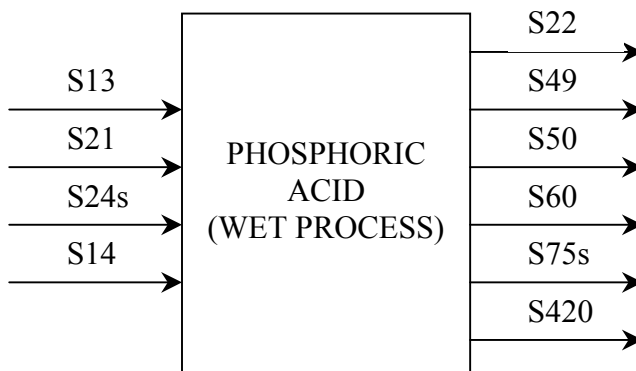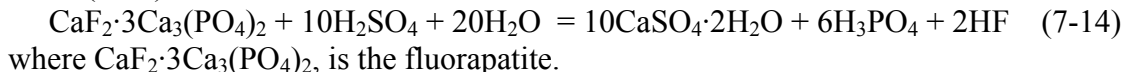
Figure 7.3 Block Diagram of Wet Process to Produce Phosphoric Acid

Table 7-5 Description of Process Streams in Wet Process

Name of Streams	Description
Input Streams	
S13	Phosphate rock slurry to phosphoric acid plant (PAP)
S21	Gypsum stack decant water to PAP
S24$_S$	LP steam to PAP
S14	Sulfuric acid to PAP
Output Streams	
S22	Slurried gypsum produced from PAP
S49	H_2SiF_6 solution produced from fluorides scrubbers in PAP
S50	Other inert materials in the phosphate rock from PAP
S60	Total phosphoric acid produced in PAP

S75$_S$	Condensate water from LP input in PAP
S420	Water evaporated from digestion and filtration in PAP

B-2-1-2. Fluoride Scrubbers

F is scrubbed because discharge to offsite water streams is regulated and because there is a market for the product. Fluorine fumes are drawn from the attack tank and filter, and scrubbed and recovered with H_2SiF_6 solution to which water is added. What is not scrubbed will go with the evaporator's barometric condenser water. This water is typically once-through river water or closed-circuit gypsum-pond water. The following reactions take place:

$$6HF + SiO_2 = H_2SiF_6 + 2H_2O \tag{7-15}$$

Reaction (7-15) is with small amount of fine sand present in feed rock. Most domestic phosphate rock has an excess of SiO_2 vs F. Heating under vacuum in an evaporator (or addition of strong acid like H_2SO_4) will shift reaction (7-16) to the right.

$$H_2SiF_6 = SiF_4 + 2HF \tag{7-16}$$

Scrubbing reaction (7-17) produces 1 mole of SiO_2 that will precipitate unless there are 6 more moles of HF present to react with it to form 1 more mole of H_2SiF_6 via reaction (7-15).

$$3SiF_4 + 2H_2O = 2H_2SiF_6 + SiO_2 \tag{7-17}$$
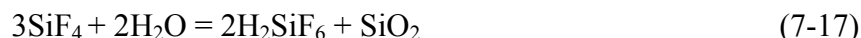
B-2-2. Material Balance and Energy Balance

Table 7-6 shows the parameters used in the material balance and energy balance (Table 7-7). Rock slurry is typically 66-68wt % solids. The percent is high enough to minimize water entering the process here in order to maximize water fed at filter wash where P_2O_5 gets recovered. The percent is low enough to let the cyclones or screens in the mill circuit give a good separation. The oversize is recycled back to the mill. Today's typical sulfuric acid concentration is 98%. Higher-than-98.5% will give poorer SO_3 absorption in the sulfuric plant (risks SO_3 emissions and visible stack plume) and lower than 93% accelerates corrosion of carbon steel. Typical P_2O_5 loss is 3-6%. Losses include undigested rock, P_2O_5 trapped in gypsum crystals, and aqueous P_2O_5 incompletely washed from the gypsum filter cake. Per ton of 64 BPL rock, 0.62 ton of [100%] H_2SO_4 is consumed to digest phosphate. The $CaCO_3$ present (a variable amount not tied to BPL) raises the actual ratio to about 0.802 T H_2SO_4 per T rock, which is roughly the 0.80 T H_2SO_4 / T rock used below.

Table 7-6 Parameters in Wet Process for Phosphoric Acid Production, from Hertwig (2004)

Name	Meaning	Value
DFPAP	P_2O_5 digested fraction	0.98
NRPPAP	Net P_2O_5 recovery in digestion and filtration	0.96
RBPLPAP	Fraction of pure $Ca_3(PO_4)_2$ (BPL/100)	0.64
FPBPPAP	Fraction of 28% H_3PO_4 bypassing the evaporators	0.00
EFCPAP	Evaporator feed strength %P_2O_5 (26-29%)	28%
EPCAP	Evaporator product strength %P_2O_5 (45-54%)	48%
ESEPAP	Evaporator steam efficiency lb water evaporated per lb steam condensed	0.80
FASPAP	Fluosilicic acid concentration(weight fraction)	0.24
FFEPAP	Fraction of F evaporated in evaporators (0.3-0.8)	0.60
FEFPAP	Fraction of evaporators with F scrubbers	0.80
C_1	T rock per T P_2O_5 produced	3.56
C_2	H_2SO_4 to rock ratio (T 100% H_2SO_4 / T 64-BPL rock)	0.80
C_3	T gypsum produced per T P_2O_5 produced	4.18
C_4	Net fraction of all fluorine recovered	0.36

In Table 7-7, the overall material balance for the whole process is given with the expressions of the process streams. For the species material balance obtained using the reaction equations (7-12, 7-13, 7-14, 7-15, 7-16 and 7-17), the first equation is for the P_2O_5 balance; the second one is for the sulfuric acid balance; the third one is for the gypsum balance; the fourth one is for the overall process water balance (H_2O-1); the fifth one is for the process water evaporation balance (H_2O-2); the last one is for the fluoride balance for the whole process. In the heat exchange part, the first equation

Table 7-7 Constraint Equations for the Phosphoric Acid Wet Process

Material Balance	
Overall	$(F_{13} + F_{14} + F_{21} + F_{S24}) - (F_{22} + F_{60} + F_{S75} + F_{49} + F_{50} + F_{420}) = 0$
	where $F_{14} = F_{14}^{(H_2SO_4)} + F_{14}^{(H_2O)}$
	$\quad\quad F_{60} = F_{60}^{(H_2O)} + F_{60}^{(P_2O_5)}$
	$\quad\quad F_{49} = F_{49}^{(H_2SiF_6)} + F_{49}^{(H_2O)}$
Species	$P_2O_5 : \dfrac{1}{C_1}F_{13} - F_{60}^{(P_2O_5)} = 0$
	$H_2SO_4 : F_{14}^{(H_2SO_4)} - F_{13}C_2 = 0$
	Gypsum: $F_{60}^{(P_2O_5)}C_3 - F_{22} = 0$

$$\text{H}_2\text{O-1:} \quad \begin{aligned} & F_{14}^{(H_2O)} + F_{21} - ((F_{60}^{(H_2O)} - \frac{(3)(18.02)}{141.94} F_{60}^{(P_2O_5)}) + F_{420} + F_{49}^{(H_2O)}) \\ & + \frac{(2)(18.02)}{144.11} F_{49}^{(H_2SiO_6)} = 0 \end{aligned}$$

$$\text{H}_2\text{O-2:} \quad F_{60}^{(P_2O_5)} (\frac{1}{\text{EFCPAP}} - \frac{1}{\text{EPCPAP}}) - F_{420} = 0$$

$$\text{F:} \quad \frac{(\text{RBPLPAP})(2)(144.11)\text{C4}}{(310.18)(3)(6)} F_{13} - F_{49}^{(H_2SiF_6)} = 0$$

Heat Exchange

$$\text{LP-1:} \quad F_{S24} - \frac{F_{420}}{\text{ESEPAP}} = 0$$

$$\text{LP-2:} \quad F_{S75} - F_{S24} = 0$$

Energy Balance

Overall

$$(F_{S24} H^{(LP)} - \frac{1}{M^{(H_2O)}} F_{S75}^{(H_2O)} H_{S75}^{(H_2O)}) - Q_{PPA} = 0$$

where $M^{(i)}$ is molecule weight.

$i = \text{H}_2\text{O}$

Enthalpy Function

$$H_k^i (T) = (a_1^i + \frac{1}{2} a_2^i T + \frac{1}{3} a_3^i T^2 + \frac{1}{4} a_4^i T^3 + \frac{1}{5} a_5^i T^4 + \frac{b_1^i}{T})RT \quad \text{J/mol}$$

$i = \text{H}_2\text{O}; \quad k = 75$

$$\begin{aligned} H^{(LP)}(T) = & ((72.558 + (0.5)(-0.66244)T + (\frac{1}{3})(0.002562)T^2 + \\ & (0.25)(-4.3659E-06)T^3 + (0.2)(2.7818E-09)T^4 + \frac{(-41886)}{T})(8.3145)T \\ & -1893)\frac{1}{18.02} + ((-0.007)T^2 + (2.7838)T + 2292.0563) \end{aligned}$$

J/g, LP has no superheat, from Meyer, et al. (1977) and McBride, et al. (1993)

is the steam requirement for the process (LP-1) and the other is steam input and output balance (LP-2). The steam input (S24$_S$) was from S16$_S$ (sulfuric acid plant) and S18$_S$ (power plant). The steams in the heat exchanger were used in the energy balance part.

In the overall energy balance, Q_{PPA} is equal to the heat from LP steam to evaporate the phosphoric acid from 28% to 48% in the phosphoric acid plant. Also, this steam is the only heat input for the process. Hence, Q_{PPA} is calculated directly from this LP steam input required to concentrate the phosphoric acid. The $Q_{out} \times F_r$ term in Equation 7-5 is not required since no cooling water is used in this process.

In enthalpy functions, the coefficients a_1, a_2, a_3, a_4, a_5, and b_1 for different species are given in Table A-1 in Appendix A in (Xu, 2004).

In the material balance part, there are 16 variables and 15 equations, so the number of degrees of freedom is 1 for the material balance part. For the material and energy balance, there are 21 variables and 18 equations, so the number of degrees of freedom is 3.

B-3. Granular Triple Super Phosphate (GTSP) (Hertwig, 2004; Austin, 1984; Brown, et al., 1985)

B-3-1. Process Description

In the chemical production complex in the lower Mississippi River corridor, granular triple super phosphate is produced by IMC-Agrico with the capacity of 2,259 tons per day (Hertwig, 2004). GTSP is made by the action of phosphoric acid on phosphate rock. This can be expressed as:

$$Ca_3(PO_4)_2 + 4H_3PO_4 = 3Ca(H_2PO_4)_2 \quad \text{digestion (not including F in rock)} \qquad (7\text{-}18)$$
$$CaF_2 + 2H_3PO_4 = Ca(H_2PO_4)_2 + 2HF \quad \text{(the F content)} \qquad (7\text{-}19)$$
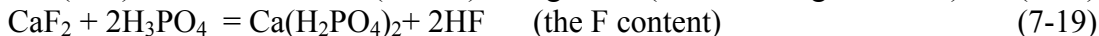
The general reaction from the summation of 3 times reaction equation (7-18) and 1 times reaction equation (7-19) is Equation (7-20), where $CaF_2 \cdot 3Ca_3(PO_4)_2$ is the mineral fluorapatite.

$$CaF_2 \cdot 3Ca_3(PO_4)_2 + 14H_3PO_4 = 10Ca(H_2PO_4)_2 + 2HF \quad \text{digestion} \qquad (7\text{-}20)$$

The block diagram is given in Figure 7.4 with the stream descriptions from Table 7-8. Pulverized phosphate rock is mixed with phosphoric acid in a two-stage reactor. The resultant slurry is sprayed into the granulator. The granulator contains recycled fines from the process. The product from the granulator is dried in the dryer with heat input, screened, crushed if oversize, and cooled again in the cooler by cooling water. The final product is conveyed to bulk storage where the material is cured for 4 to 6 weeks during which time a further reaction of acid and rock occurs which increases the availability of P_2O_5 as plant food. The exhaust gases from the
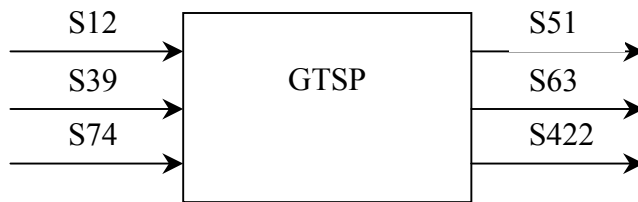
Figure 7.4 Block Diagram of GTSP Plant

granulator and cooler are scrubbed with water to remove silicofluorides which are represented in this material balance as HF (Austin, 1984).

B-3-2. Material Balance and Energy Balance

Using the parameters in Table 7-9, the material balance and energy balance of GTSP plant are given in Table 7-10.

In Table 7-10, first the overall material balance for this process is given. For the species material balance obtained using the reaction equations (7-18, 7-19 and 7-

20), the first equation is for the P_2O_5 balance; the second one is for the rock balance; the third one is for the HF balance; the last one is for the water balance.

Table 7-8 Description of Process Streams in GTSP Plant

Name of Stream	Description
Input Streams	
S12	Phosphate rock to GTSP
S39	Wet process phosphorous acid to GTSP
S74	Inert impurity to GTSP
Output Streams	
S51	GTSP produced from GTSP
S63	HF produced from GTSP
S422	Water evaporated from GTSP

Table 7-9 Parameters in GTSP Production, from Hertwig (2004)

Name	Meaning	Value
UPAGTSP	Utilization of H_3PO_4 in GTSP plant	0.999
PGTSP	GTSP fraction of P_2O_5 (0.45-0.46) (weight fraction)	0.46
BPLGTSP	Rock BPL(%)	75
URGTSP	Rock utilization	0.999

In the overall energy balance, Q_{GTSP} is the heat input for the process, such as the heat required to dry the product in the dryer, which is calculated from the energy balance. Q_{out} is the heat loss of unit operations in the GTSP plant, such as the heat removed by cooling water in the cooler, based on unit product output, 538 KJ per lb of GTSP (Brown, et al., 1985). In enthalpy functions, the coefficients a_1, a_2, a_3, a_4, a_5, and b_1 for different species are given in Table A-1 in Appendix A in (Xu, 2004).

In the material balance part, there are 9 variables and 8 equations, so the number of degrees of freedom is 1. For the material and energy balance, there are 21 variables and 15 equations, so the number of degrees of freedom is 6.

Table 7-10 Constraint Equations for GTSP Production

Material Balance	
Overall	$(F_{12} + F_{39} + F_{74}) - (F_{51} + F_{63} + F_{422}) = 0$
	where
	$F_{12} = F_{12}^{(ROCK)}$
	$F_{39} = F_{39}^{(P_2O_5)} + F_{39}^{(H_2O)}$

Species	
P_2O_5:	$\dfrac{UPAGTSP}{\dfrac{141.94}{(2)(98)}}F_{39}^{(P_2O_5)} - \dfrac{(PGTSP)(14)(98)}{\dfrac{141.94}{234.06}(10)(234.06)}F_{51} = 0$

ROCK:

$$F_{12}^{(ROCK)} - \frac{(UPAGTSP)(2)(98)(1008.62)(100)(3)(310.18)}{(141.94)(14)(98)(BPLGTSP)(1008.62)(URGTSP)}F_{39}^{(P_2O_5)} = 0$$

HF: $\dfrac{(UPAGTSP)(2)(98)(2)(20.01)}{(141.94)(14)(98)}F_{39}^{(P_2O_5)} - F_{63} = 0$

H_2O: $F_{422} - (F_{39}^{(H_2O)} - \dfrac{(3)(18.02)}{141.94}F_{39}^{(P_2O_5)}) = 0$

Energy Balance

Overall

$$((PGTSP)F_{51}^{(GTSP)}/M^{(P_2O_5)}H^{(GTSP)} + F_{63}^{(HF)}/M^{(HF)}H_{63}^{(HF)} + F_{422}^{(H_2O)}/M^{(H_2O)}H_{422}^{(H_2O)})$$

$$- ((BPLGTSP)/(100)F_{12}^{(ROCK)}/((3)M^{(Ca_3(PO_4))})H^{(ROCK)} +$$

$$\Sigma F_{39}^{(i)}/M^{(i)}H^{(i)}) + F_{51}Q_{out} - Q_{GTSP} = 0$$

$$i = P_2O_5, H_2O$$

Enthalpy
Function

$$H_k^i(T) = (a_1^i + \frac{1}{2}a_2^iT + \frac{1}{3}a_3^iT^2 + \frac{1}{4}a_4^iT^3 + \frac{1}{5}a_5^iT^4 + \frac{b_1^i}{T})RT \quad J/mol$$

$$i = H_2O, HF; \quad k = 39, 63, 422$$

$$H^{(ROCK)}(T) = (((-291.5)(1000) + (3)(-984.9)(1000)) + (16.02 + (3)(54.45))$$

$$(T - 298.15))(4.182)J/mol$$

Source: Lide (1982)

$$H^{(P_2O_5)} = (-1278.437)(1000) + (106.014)(T - 298.15)J/mol$$

Source: Lide (1982)

$$H^{(GTSP)}(T) = (-742.04)(1000)(4.182) + (246.4)(T - 298.15)J/mol$$

Source: Felder and Roussleu (1986)

B-4. Ammonia (Hertwig, 2004; Brykowski, 1981; Perry, 1997; Louisiana Chemical & Petroleum Products List, 1998)

In the chemical production complex in the lower Mississippi River corridor, the ammonia production plants are as follow (Louisiana Chemical & Petroleum Products List, 1998).

- IMC-Agrico, Faustina Plant (480 thousand metric tons per year)
- CF Industries, Donaldsonville (1.84 million metric tons per year)
- Triad Nitrogen, Donaldsonville (1.02 million metric tons per year)
- BCP, Geismar (400 thousand metric tons per year)
- PCS Nitrogen Fertilizer LP, Geismar (550 thousand metric tons per year)
- Monsanto, Luling (440 thousand metric tons per year)

- Cytec, Westwego (385 thousand metric tons per year)
- Air Product & Chemicals Inc., St. Gabriel (270 thousand metric tons per year)

For the ammonia production, the capacity of 1,986 tons per day was used in the base case (Hertwig, 2004).

B-4-1. Process Description

The block diagram for ammonia process is given in Figure 7.5 with the stream definitions in Table 7-11. After desulfurization the natural gas is fed to the primary reformer (steam reformer), where part of the methane is converted to carbon oxides and hydrogen over a nickel catalyst. Then the gas mixture enters the secondary reformer (autothermic reformer) where air is injected to provide nitrogen needed in ammonia synthesis. Because carbon oxides are highly poisonous to the ammonia synthesis catalyst, the reformed gas mixture is shifted for more H_2 and scrubbed for CO_2 removal, where carbon monoxide is oxidized to carbon dioxide. Then, in the methanator the remaining traces of CO_2 are removed by reaction with H_2 to produce methane and water. Finally, the synthesis gas is compressed and converted to ammonia in the synthesis reactor. More detail information about the plant is given below.
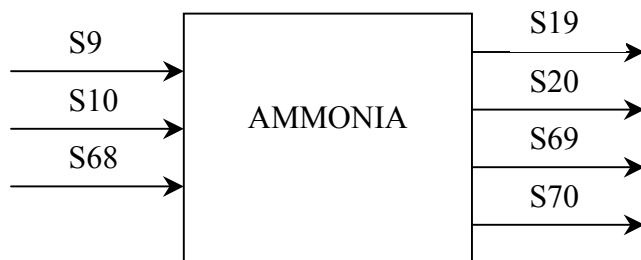
Figure 7.5 Block Diagram of Ammonia Plant

Table 7-11 Description of Process Streams in Ammonia Plant

Name of Streams	Description
Input Streams	
S9	Air to ammonia plant
S10	Natural gas to ammonia plant
S68	Steam (reactant) to ammonia plant
Output Streams	
S19	Total production of ammonia from ammonia plant
S20	Total production of CO_2 from ammonia plant
S69	Water from ammonia plant
S70	Purge from ammonia plant

B-4-1-1. Synthesis Gas Preparation

The steam reforming reaction is:

$$CH_4 + H_2O = CO + 3H_2 \tag{7-21}$$

The reaction is very endothermic, favored by high temperature and low pressure.

The water-gas shift reaction is employed to convert CO to CO_2 with additional H_2 production.

$$CO + H_2O = CO_2 + H_2 \qquad \Delta H(1000°C) = -32.18 \text{ MJ/Kgmol} \tag{7-22}$$
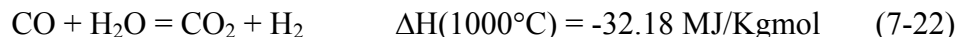
The reaction is mildly exothermic, favored by low temperature and unaffected by pressure. When the final product is CO_2, excess steam is used to prevent carbon formation. In the NH_3 plant, this reaction occurs with the reforming in the primary reformer that operates at 760-980°C. Product composition depends on process conditions, such as temperature, pressure, excess steam which determines equilibrium, and velocity through the catalyst bed which determines approach to equilibrium. Typical product is 75% H_2, 8% CO, 15% CO_2, 2% balance gases of N_2 and CH_4. Additional cooling and steam is provided to finish converting CO to CO_2 in the shift converters (Equation 7-22). After the secondary reformer air is introduced to provide N_2 to form NH_3. Oxygen from the introduced air will complete the oxidation of any remaining CH_4 and CO (Equation 7-23 and 7-24). Oxidation product H_2O is condensed out, and oxidation product CO_2 is scrubbed out using amines.

$$CH_4(g) + 2O_2(g) = CO_2(g) + 2H_2O(g) \quad \Delta H(25°C) = -191.759 \text{ Kcal/gmole} \tag{7-23}$$
$$CO + 0.5O_2 = CO_2 \qquad\qquad \Delta H(25°C) = -67.6361 \text{ Kcal/gmole} \tag{7-24}$$

The trace of CO_2 left is converted back to CH_4 in a methanator (Equation 7-25).

$$CO_2 + 4H_2 = CH_4 + 2H_2O \tag{7-25}$$

B-4-1-2. NH_3 Synthesis

The ammonia synthesis reaction is:

$$0.5N_2 + 1.5H_2 = NH_3 \tag{7-26}$$

The converter consists of a high-pressure shell containing a catalyst section and a heat exchanger. Both horizontal and vertical types of converter are used with cooling by quenching. Inlet gases conventionally pass along the shell, being preheated and reducing the maximum shell temperature. The conditions in the converter are 500 ^{o}C and 15 to 30 MPa. Outlet concentrations of ammonia are 16 to 25%. Product can be liquid or gas. Liquification makes storage practical but requires energy and equipment to produce, and ammonia is usually re-vaporized in the customer's process. A trace of water is added to the NH_3 liquid product to control corrosion of carbon steel.

Steam demand within the NH_3 plant usually is a close match to the NH_3 plant's steam production. Extra steam can be produced within the NH_3 plant for users inside or outside the NH_3 plant by firing the auxiliary burners in the heat-recovery section of the exhaust gas from the primary reformer.

The biggest yield losses are due to the inerts purge: inerts include Ar from the air feed and CH_4 from the CO_2 Methanator. The purge is usually passed through a H_2-recovery unit (HRU). When the remaining purge contains enough CH_4 and H_2, it is sent to the primary reformer as a fuel.

B-4-2. Material Balance and Energy Balance

     With the parameters shown in Table 7-12, the material and energy balances of the ammonia plant are given in Table 7-13.

     In Table 7-13, the overall material balance for the whole process is given with the mixture stream expressions. For the species material balance obtained using the reaction equations (7-21,7-22, 7-23, 7-24, 7-25 and 7-26), the first equation is for the methane balance; the second one is for the steam used as a reactant balance; the third one is for the CO_2 balance; the fourth one is for the NH_3 balance; the fifth one is for the purge N_2 balance; the sixth one is for the purge H_2 balance; the seventh one is for the purge Ar balance; the last one is for the water balance.

Table 7-12 Parameters in Ammonia Production, from Hertwig (2004)

Name	Meaning	Value
UHAMM	Utilization of H_2 in ammonia plant(higher than N_2 utilization due to H_2 recovery unit)	0.999
UNAMM	Utilization of N_2 in ammonia plant	0.995
	Trace of water added to NH_3 product for corrosion control (not used in any calculation yet)	0.0
	Air composition:	
	N_2 in air	78.084%
	O_2 in air	20.946%
	Ar in air	0.934%
	CO_2 in air	0.036%

     In the overall energy balance, Q_{AMM} is the heat from steam in the primary reformer for synthesis gas preparation (Equation 7-21), heat exchanger, and distillation column reboilers, which is calculated from the energy balance. $Q_{utilities}$ is the heat output removed by cooling water in heat exchanger and distillation column condensers during unit operations, such as methanation and ammonia separation, in the ammonia plant based on the unit of ammonia product, 3 MJ per lb of ammonia (Brykowski, 1981). Q_{purge} is the heat from the combustion of purge H_2 used as fuel gas, -54 MJ per lb of H_2 (Perry, 1997). In enthalpy functions, the coefficients a_1, a_2, a_3, a_4, a_5, and b_1 for different species are given in Table A-1 in Appendix A in (Xu, 2004).

Table 7-13 Constraint Equations for Ammonia Production

Material Balance

Overall $(F_9 + F_{10} + F_{68}) - (F_{19} + F_{20} + F_{69} + F_{70}) = 0$

where $F_9 = F_9^{(O_2)} + F_9^{(N_2)} + F_9^{(CO_2)} + F_9^{(Ar)}$

$F_{70} = F_{70}^{(N_2)} + F_{70}^{(H_2)} + F_{70}^{(Ar)}$

Species CH_4:

$$F_{10} - \frac{(0.5)(0.20946)(16.05)}{(17.04)(0.78084)(2)(UNAMM)}F_{19} - \frac{(1.5)(16.05)}{(17.04)(4)(UHAMM)}F_{19} = 0$$

Steam: $F_{68} - \frac{(1.5)(18.02)(2)}{(17.04)(4)(UHAMM)}F_{19} = 0$

CO_2:

$$F_9^{(CO_2)} + (\frac{(1.5)(44.01)}{(17.04)(4)(UHAMM)} + \frac{(0.5)(0.20946)(44.01)}{(17.04)(0.78084)(2)(UNAMM)})F_{19}$$

$$- F_{20} = 0$$

NH_3: $\frac{(17.04)(UNAMM)}{(0.5)(28.02)}F_9^{(N_2)} - F_{19} = 0$

N_2 purge: $-F_{70}^{(N_2)} + \frac{(0.5)(28.02)(1 - UNAMM)}{(17.04)(UNAMM)}F_{19} = 0$

H_2 purge: $-F_{70}^{(H_2)} + \frac{(1.5)(2.02)(1 - UHAMM)}{(17.04)(UHAMM)}F_{19} = 0$

Ar purge: $F_9^{(Ar)} - F_{70}^{(Ar)} = 0$

H_2O: $-F_{69} + \frac{(0.5)(0.20946)(2)(18.02)}{(17.04)(0.78084)(2)(UNAMM)}F_{19} = 0$

Energy Balance

Overall $(F_{19}^{(NH_3)}/M^{(NH_3)}H_{19}^{(NH_3)} + F_{20}^{(CO_2)}/M^{(CO_2)}H_{20}^{(CO_2)} + \Sigma F_{70}^{(j)}/M^{(j)}H_{70}^{ji}$

$+ F_{69}^{(H_2O)}/M^{(H_2O)}H_{69}^{(H_2O)}) - (F_{10}^{(CH_4)}/M^{(CH_4)}H_{10}^{(CH_4)} + \Sigma F_9^{(i)}/M^{(i)}H_9^{(i)}$

$+ F_{68}^{(H_2O)}/M^{(H_2O)}H_{68}^{(H_2O)}) + F_{19}^{(NH_3)}Q_{utilities} + F_{70}^{(H_2)}Q_{purge} - Q_{AMM} = 0$

$i = CO_2, O_2, N_2, Ar; j = H_2, N_2, Ar$

Enthalpy Function $H_k^i(T) = (a_1^i + \frac{1}{2}a_2^i T + \frac{1}{3}a_3^i T^2 + \frac{1}{4}a_4^i T^3 + \frac{1}{5}a_5^i T^4 + \frac{b_1^i}{T})RT$ J/mol

$i = H_2O, CO_2, CH_4, O_2, N_2, Ar, NH_3$
$k = 9, 10, 19, 20, 68, 69, 70$

In the material balance part, there are 14 variables and 14 equations including one dependent equation (overall material balance), so the number of degrees of freedom is 1. For the material and energy balance, there are 34 variables and 27

equations including the dependent overall material balance, so the number of degrees of freedom is 8.

B-5. Nitric Acid (Hertwig, 2004; Keleti, 1985; Louisiana Chemical & Petroleum Products List, 1998)

In the chemical production complex in the lower Mississippi River corridor, the nitric acid plants are as follow (Louisiana Chemical & Petroleum Products List, 1986).
- CF industries, Donaldsonville (380 thousand tons per year)
- PCS Nitrogen Fertilizer LP, Geismar (923 thousand tons per year)
- Rubicon, Geismar (120 thousand tons per year)

For nitric acid production, the capacity of 539 tons per day was used in the base case (Hertwig, 2004).

B-5-1. Process Description
The reaction can be expressed as:
$$NH_3 \text{ (g)} + 2O_2 \text{ (g)} = HNO_3 \text{ (aq)} + H_2O \text{ (l)} \qquad (7\text{-}27)$$
Commercial grades of the product range 0.534-0.687 w/w (36-42°Be). The product concentrating to 0.95 is possible with additional processing cost for extractive distillation with a dehydrating agent as H_2SO_4 with $MgSO_4$. Manufactured acid contains some HNO_2 when 0.20-0.45 HNO_3 and contains dissolved N_2O_4 when greater than 0.55 HNO_3.

Atmospheric-pressure plants have been replaced by pressurized plants to reduce plant size and capital cost, and to be able to produce more than 0.50-0.55 HNO_3. Single-pressure/American/DuPont plants have lower capital cost and produce more by-product steam than dual-pressure/European plants that have lower catalyst cost and slightly higher yield. But overall costs are roughly similar for single- vs dual-pressure processes.

A block process diagram is given in Figure 7.6 with the stream definitions from Table 7-14. In order to get to the production grade and reduce operating cost, the water from ammonium nitrate plant is used.

Figure 7.6 Block Diagram of Nitric Acid Plant
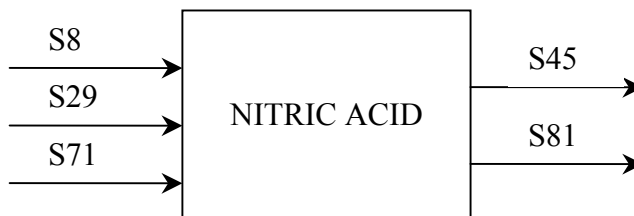
Table 7-14 Description of Process Streams in Nitric Acid Plant

Name of Streams	Description
Input Streams	
S8	Air to nitric acid plant
S29	Ammonia to nitric acid plant
S71	Water from ammonium nitrate plant to nitric acid plant
Output Streams	
S45	Nitric acid solution produced from nitric acid plant
S81	Vent gases from nitric acid plant

B-5-2. Material Balance and Energy Balance

Using the parameters in Table 7-15, the material balance and energy balance of nitric acid plant are given in Table 7-16.

In Table 7-16, the overall material balance for the whole process is given with the mixture stream expressions. For the species material balance obtained using the reaction equations (7-27), the first equation is for the O_2 (reactant) balance; the second one is for the NH_3 balance; the third one is for the H_2O balance; the fourth one is for the O_2 (inert) balance; the fifth one is for the N_2 balance; the sixth one is for the CO_2 balance; the seventh one is for the Ar balance; the last one is for the NO balance.

Table 7-15 Parameters in Nitric Acid Production, from Hertwig (2004)

Name	Meaning	Value
CONCNA	Product nitric acid concentration (0.54-0.68) (weight fraction)	0.54
ABNOL	NO absorption	0.980
	Weight fraction of the air required to "bleach" red NO_2 out of product HNO_3 in the total air input	0.15

In the overall energy balance, Q_{NIT} is the net heat released from the nitric acid plant in the form of steam in the heat exchanger because of the exothermic reaction (7-27), which is calculated from the energy balance. Q_{out} is the heat output removed by cooling water in the heat exchanger and absorption column in the nitric acid plant based on the unit of nitric acid product, 1 MJ per lb of nitric acid (100%) (Keleti, 1985). In enthalpy functions, the coefficients a_1, a_2, a_3, a_4, a_5, and b_1 for different species are given in Table A-1 in Appendix A in (Xu, 2004).

In the material balance part, there are 16 variables and 16 equations including one dependent equation (overall material balance), so the number of degrees of freedom is 1. For the material and energy balance, there are 35 variables and 30 equations including the dependent overall material balance, so the number of degrees of freedom is 6.

Table 7-16 Constraint Equations for Nitric Acid Production

Material Balance	

overall

$$(F_8 + F_{29} + F_{71}) - (F_{45} + F_{81}) = 0$$

where

$$F_8 = F_8^{(O_2)} + F_8^{(N_2)} + F_8^{(CO_2)} + F_8^{(Ar)}$$

$$F_{45} = F_{45}^{(HNO_3)} + F_{45}^{(H_2O)}$$

$$F_{81} = F_{81}^{(O_2)} + F_{81}^{(N_2)} + F_{81}^{(Ar)} + F_{81}^{(CO_2)} + F_{81}^{(NO)}$$

species

O_2: $\quad F_8^{(O_2)} - F_{81}^{(O_2)} - \dfrac{(2)(32)}{63.02} F_{45}^{(HNO_3)} - \dfrac{(5)(32)}{(30.01)(4)} F_{81}^{(NO)} = 0$

NH_3: $\quad F_{29} - \dfrac{17.04}{63.02} F_{45}^{(HNO_3)} - \dfrac{17.04}{30.01} F_{81}^{(NO)} = 0$

H_2O: $\quad F_{71} + \dfrac{18.02}{63.02} F_{45}^{(HNO_3)} + \dfrac{(6)(18.02)}{(30.01)(4)} F_{81}^{(NO)} - F_{45}^{(H_2O)} = 0$

O_2: $\quad F_{81}^{(O_2)} - 0.15 F_8^{(O_2)} = 0$

N_2: $\quad F_{81}^{(N_2)} - F_8^{(N_2)} = 0$

CO_2: $\quad F_{81}^{(CO_2)} - F_8^{(CO_2)} = 0$

Ar: $\quad F_{81}^{(Ar)} - F_8^{(Ar)} = 0$

NO: $\quad \dfrac{1}{30.01} F_{81}^{(NO)} - \dfrac{1 - ABNOL}{17.04} F_{29} = 0$

Energy Balance

Overall

$$(\Sigma F_{45}^{(i)} / M^{(i)} H_{45}^{(i)} + \Sigma F_{81}^{(j)} / M^{(j)} H_{81}^{(j)}) - (F_{29}^{(NH_3)} / M^{(NH_3)} H_{29}^{(NH_3)} +$$

$$F_{71} / M^{(H_2O)} H_{71} + \Sigma F_8^{(k)} / M^{(k)} H_8^{(k)}) + F_{45}^{(HNO_3)} Q_{out} - Q_{NIT} = 0$$

i = HNO$_3$, H$_2$O; j = CO$_2$, O$_2$, N$_2$, Ar, NO; k = CO$_2$, O$_2$, N$_2$, Ar

Enthalpy Function

$$H_k^i(T) = (a_1^i + \frac{1}{2}a_2^i T + \frac{1}{3}a_3^i T^2 + \frac{1}{4}a_4^i T^3 + \frac{1}{5}a_5^i T^4 + \frac{b_1^i}{T})RT \quad J/mol$$

i = H$_2$O, CO$_2$, O$_2$, N$_2$, Ar, NH$_3$, NO

k = 8, 29, 45, 71, 81

$$H_k^{(HNO_3)}(T) = (-174.1)(1000) + (109.9)(T - 298.15) J / mol \quad k=45$$

Source: Knovel (2003)

B-6. Urea (NH$_2$CONH$_2$) (Hertwig, 2004; Austin, 1984; Meyers, 1986; Louisiana Chemical & Petroleum Products List, 1998)

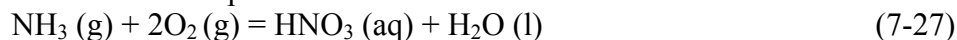In the chemical production complex in the lower Mississippi River corridor, the urea plants are as follow (Louisiana Chemical & Petroleum Products List, 1998).
- IMC-Agrico, Faustina Plant (260 thousand tons per year)

- CF Industries, Donaldsonville (1.6 million tons per year)
- BCP, Geismar (220 thousand tons per year)
- PCS Nitrogen Fertilizer LP, Geismar (412 thousand tons per year)
- Cytec Industries, Westwego (120 thousand tons per year)
- Triad Nitrogen, Donaldsonville (420 thousand tons per year)

For urea production, the capacity of 301 tons per day was used for the base case (Hertwig, 2004).

B-6-1. Process Description

There are two reaction steps (7-28 and 7-29) in the urea production. Usually, these two reactions can be expressed as overall reaction (7-30).

$$CO_2 + 2NH_3 = NH_2COONH_4 \qquad \Delta H = -155 \text{ MJ/Kgmol} \qquad (7\text{-}28)$$
$$NH_2COONH_4 = NH_2CONH_2 + H_2O \qquad \Delta H = +42 \text{ MJ/Kgmol} \qquad (7\text{-}29)$$
$$CO_2 + 2NH_3 = NH_2CONH_2 + H_2O \qquad (7\text{-}30)$$

Both (7-28) and (7-29) are equilibrium reactions. Carbamate (NH_2COONH_4) formation in Equation 7-28 goes to completion at 14 MPa and 170-190°C. Most of heat of reaction (7-28) goes into steam production.

Decomposition to urea (NH_2CONH_2) in Equation 7-29 is slow. It is less complete and driven by heat and pressure reduction. This is done in one or more decomposers at progressively lower pressures. Decomposer product is a urea solution that must be evaporated to be prilled or granulated. Heating the solution with the low pressure steam (LP) releases unreacted gases and undecomposes carbamate and evaporates water. Part of this heat comes from the heat of forming the carbamate.

Conversion of either reactant is helped by using an excess of the other reactants (NH_3 and CO_2). However, the theoretical amount of CO_2 is employed to make the material balance simple. Unconverted CO_2, NH_3 and undecomposed carbamate are recovered and recycled. This requires that all of the evolved gases must be repressurized to reactor pressure. Synthesis is further complicated by formation of a dimmer called biuret, $NH_2CONHCONH_2 \cdot 2H_2O$, which is toxic to many plant species at high concentrations. Biuret in urea can cause agronomic problems if placed near the seed. The major damage of biuret is to germinating seeds. Although some crops have been affected, there is little damage through plant absorption. So biuret content is typically around 0.3%. Overall, over 99% of both CO_2 and NH_3 are converted to urea, making environmental problems minimal. Air is introduced into the process with the CO_2 to provide O_2 to let 300 series stainless steels resist carbamate that is otherwise very corrosive to ordinary and stainless steels.

The block diagram is given in Figure 7.7 with the stream definitions from Table 7-17. CO_2 and NH_3 both come from an ammonia plant. NH_3 feed is as a gas for urea production in the chemical production complex. NH_3 can be liquid (Austin, 1984). Urea product is relatively pure. Product of 46% N used to be prilled but today it is usually granulated. Additives can slow storage decomposition losses to CO_2 and NH_3 that occurs over several months. Urea solutions are sometimes sold.
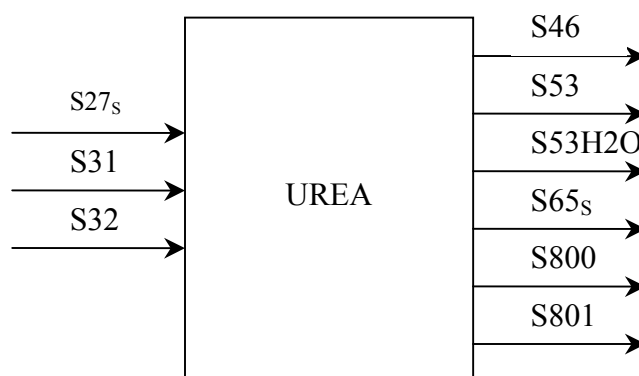
Figure 7.7 Block Diagram of Urea Plant

Table 7-17 Description of Process Streams in Urea Plant

Name of Streams	Description
Input Streams	
S27$_S$	LP steam to urea plant for heat exchange
S31	Ammonia to urea plant
S32	CO_2 to urea plant
Output Streams	
S46	Granular urea produced from urea plant
S53	Urea solid produced from urea plant for DAP N% control
S53H2O	Water produced from urea plant
S65$_S$	Condensed water from LP input in urea plant
S800	NH_3 emission from urea plant
S801	CO_2 emission from urea plant

B-6-2. Material Balance and Energy Balance

Using the parameters in Table 7-18, the material balance and energy balance of the urea plant are given in Table 7-19.

Table 7-18 Parameters in Urea Production, from Hertwig (2004)

Name	Meaning	Value
UAMMUR	NH_3 utilization in urea plant	0.999
UCO2UR	CO_2 utilization in urea plant	0.999

In Table 7-19, the overall material balance for the whole process is given with the heat exchange balance and mixture stream expressions. For the species material balance obtained using the reaction equations (7-28, 7-29 and 7-30), the first equation is for the water balance; the second one is for the total NH_3 balance; the third one is

for the NH_3 emission balance; the fourth one is for the CO_2 emission balance; the fifth one is for the total CO_2 balance; the last one is for the urea balance.

Table 7-19 Constraint Equations for Urea Production

Material Balance	
Overall	$(F_{S27} + F_{31} + F_{32}) - (F_{46} + F_{53} + F_{53}^{(H_2O)} + F_{S65} + F_{800} + F_{801}) = 0$
	where $F_{53} = F_{53}^{(UREA)}$
	Heat exchange: $F_{S27} - F_{S65} = 0$
Species	H_2O: $\dfrac{1}{EEVAUR} F_{53}^{(H_2O)} - F_{S27} = 0$
	NH_3: $F_{31} - \dfrac{(17.04)(2)}{(60.07)(UAMMUR)}(F_{53}^{(UREA)} + F_{46}) = 0$
	NH_3 emission: $-F_{800} + \dfrac{(17.04)(2)(1-UAMMUR)}{(60.07)(UAMMUR)}(F_{53}^{(UREA)} + F_{46}) = 0$
	CO_2 emission: $-F_{801} + \dfrac{(44.01)(1-UCO2UR)}{(60.07)(UCO2UR)}(F_{53}^{(UREA)} + F_{46}) = 0$
	CO_2: $F_{32} - \dfrac{44.01}{(60.07)(UCO2UR)}(F_{53}^{(UREA)} + F_{46}) = 0$
	Urea: $\dfrac{18.02}{60.07}(F_{53}^{(UREA)} + F_{46}) - F_{53}^{(H_2O)} = 0$
Energy Balance	
Overall	$(F_{53}^{(UREA)}/M^{(UREA)}H_{53}^{(UREA)} + F_{53}^{(H_2O)}/M^{(H_2O)}H_{53}^{(H_2O)} + F_{46}^{(UREA)}$
	$/M^{(UREA)}H_{46}^{(UREA)} + F_{800}^{(NH_3)}/M^{(NH_3)}H_{800}^{(NH_3)} + F_{801}^{(CO_2)}/M^{(CO_2)}H_{801}^{(CO_2)})$
	$-(F_{31}^{(NH_3)}/M^{(NH_3)}H_{31}^{(NH_3)} + F_{32}^{(CO_2)}/M^{(CO_2)}H_{32}^{(CO_2)}) + Q_{out}(F_{53}^{(UREA)} + F_{46})$
	$-Q_U = 0$
Enthalpy Function	$H_k^i(T) = (a_1^i + \dfrac{1}{2}a_2^i T + \dfrac{1}{3}a_3^i T^2 + \dfrac{1}{4}a_4^i T^3 + \dfrac{1}{5}a_5^i T^4 + \dfrac{b_1^i}{T})RT$ J/mol
	$i = H_2O, CO_2, NH_3$
	$k = 31, 32, 53H_2O, 800, 801$
	$H_k^{(UREA)}(T) = (-333.6)(1000) + (93.14)(T - 298.15) J/mol$ k=46, 53
	Source: Domalski, et al. (1984)

In the overall energy balance, Q_U is the heat input of the plant in the form of steam for heat for the reaction (Equation 7-29) and in the heat exchanger, and one-stage evaporator and vacuum evaporator, which is calculated from the energy balance. The reaction heat from Equation 7-28 is not enough for the total heat requirements of the plant. Q_{out} is the heat output removed by cooling water in the heat exchanger,

scrubber, condenser and stripper in the urea plant based on the unit of urea product, 1.6 MJ per lb of urea (Meyers, 1986). In enthalpy functions, the coefficients a_1, a_2, a_3, a_4, a_5, and b_1 for different species are given in Table A-1 in Appendix A in (Xu, 2004).

In the material balance part, there are 10 variables and 9 equations including one dependent equation (overall mass balance), so the number of degrees of freedom is 2. For the material and energy balance, there are 24 variables and 17 equations including the dependent overall mass balance, so the number of degrees of freedom is 8.

B-7. Methanol (CH_3OH or MeOH) (Hertwig, 2004; Brown, et al., 1985; Louisiana Chemical & Petroleum Products List, 1998)

In the chemical production complex in the lower Mississippi River corridor, the methanol plants are given as follow (Louisiana Chemical & Petroleum Products List, 1998).

- BCP, Geismar (330 million gallons per year)
- Ashland, Plaquemine (160 million gallons per year)
- Cytec, Westwego (Not available)
- Georgia Gulf, Plaquemine (160 million gallons per year)
- Praxair, Geisamr (10 million gallons per year)

For methanol production, the capacity of 548 tons per day was used in the base case (Hertwig, 2004).

B-7-1. Process Description

The block flow diagram is given in Figure 7.8 with stream definitions from Table 7-20 and the detailed process description is given below.
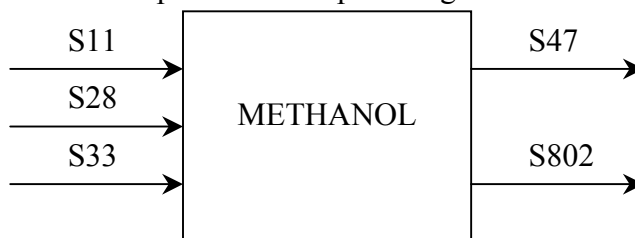
Figure 7.8 Block Diagram of Methanol Plant

Table 7-20 Description of Process Streams in Methanol Plant

Name of Streams	Description
Input Steams	
S11	Natural gas to methanol plant
S28	Steam to methanol plant
S33	CO_2 to methanol plant
Output Streams	
S47	Methanol produced from methanol plant
S802	Purge from methanol plant

B-7-1-1. Synthesis Gas Preparation

The steam reforming reaction is:

$$CH_4 + H_2O = CO + 3H_2 \tag{7-21}$$

The reaction is very endothermic, favored by high temperature and low pressure. This reaction produces 1:3 CO/H_2 instead of the 1:2 needed for MeOH synthesis, so another source of CO or CO_2 must be added. So CO_2 is imported in the MeOH plant instead of partial oxidation of CH_4 (7-31), which would supply CO, but with N_2 as an inert to this process.

$$CH_4 + 1.5O_2 = CO + 2H_2O \tag{7-31}$$

CO_2 is imported and in water-gas shift reaction (7-32), CO_2 is shifted back to CO by consuming some of the H_2 produced from CH_4 (7-21). The general reaction equation based on 7-21 and 7-32 of the synthesis gas preparation for methanol production using CH_4 and CO_2 as feedstock is Equation 7-33. The CO_2-to-CH_4 molar feeds ratio needs to be 1:3 to get 1:2 CO-to-H_2 for MeOH synthesis, though any incomplete conversion of CO_2 would call for a slightly higher feeds ratio. CO_2 conversion is hurt by the steam that is essential to H_2 generation. So careful control of steam-to-carbon ratio is needed to minimize CO_2 requirements. The stoichiometric molar ratio is 2:3 as calculated above. Unconverted CO_2 will waste CO_2 feed and carry MeOH, for example, with it when it has to be purged from the synthesis loop. Purge stream goes to the reformer to be burned as additional fuel.

$$CO_2 + H_2 = CO + H_2O \tag{7-32}$$

$$3CH_4 + 2H_2O + CO_2 = 4CO + 8H_2 \tag{7-33}$$

B-7-1-2. MeOH Synthesis in Catalytic Converter

$$CO + 2H_2 = CH_3OH \qquad \Delta H = -103 \text{ MJ/ Kgmol} \tag{7-34}$$
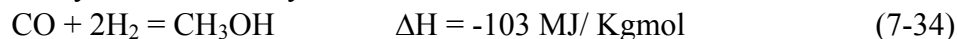
The converter in the Lurgi LP plant is a cooled multi-tubular reactor running at 5-8MPa and 250-260 ^{o}C. Liquid-entrained micron-sized copper-based catalysts can convert as much as 25% per pass (Equation 7-34). The heat of reaction is directly used to generate high pressure steam. MeOH is condensed by both heat exchange and pressure reduction. Condensed MeOH is collected and purified. Steam demand within the MeOH plant usually is a close match to the MeOH plant's steam production. Extra steam can be produced within the MeOH plant for users inside or outside the MeOH plant by firing the auxiliary burners in the heat-recovery section of the exhaust gas from the primary reformer.

B-7-2. Material Balance and Energy Balance

Using the parameters in Table 7-21, the material balance and energy balance of methanol plant are given in Table 7-22.

Table 7-21 Parameters in Methanol Production, from Hertwig (2004)

Name	Meaning	Value
UH2ME	Overall H_2 utilization in methanol plant	0.999
UCO2ME	Overall CO_2 utilization in methanol plant	0.99

In Table 7-22, the overall material balance for the whole process is given with the mixture stream expressions. For the species material balance obtained using the reaction equations (7-33 and 7-34), the first equation is for the CO_2 (reactant) balance; the second one is for the CH_4 balance; the third one is for the H_2O balance; the fourth one is for the purged H_2 balance; the fifth one is for the purged CO_2 (inert) balance; the last one is for the purged CO balance.

In the overall energy balance, Q_{MET} is heat input of the methanol plant in the form of steam in the heat exchanger and methanol separation units, which is calculated from the energy balance. Q_{out} is the heat output removed by cooling water in heat exchanger, cooler, condenser and methanol separation unit, based on the unit of methanol product, 4.6 MJ per lb of methanol (Brown, et al., 1985). In enthalpy functions, the coefficients a_1, a_2, a_3, a_4, a_5, and b_1 for different species are given in Table A-1 in Appendix A in (Xu, 2004).

Table 7-22 Constraint Equations for Methanol Production

Material Balance	
Overall	$(F_{11} + F_{28} + F_{33}) - (F_{47} + F_{802}) = 0$
	where $F_{802} = F_{802}^{(H_2)} + F_{802}^{(CO_2)} + F_{802}^{(CO)}$
Species	CO_2: $F_{33} - \dfrac{44.01}{(4)(32.05)(UCO2ME)} F_{47} = 0$
	CH_4: $F_{11} - \dfrac{(3)(16.05)}{(4)(32.05)(UH2ME)} F_{47} = 0$
	H_2O: $F_{28} - \dfrac{18.02}{16.05} F_{11} + \dfrac{(18.02)(UCO2ME)}{44.01} F_{33} = 0$
	H_2 purge: $-F_{802}^{(H_2)} + \dfrac{(1-UH2ME)(3)(2.02)}{16.05} F_{11} = 0$
	CO_2 purge: $-F_{802}^{(CO_2)} + (1-UCO2ME)F_{33} = 0$
	CO purge: $-F_{802}^{(CO)} + \dfrac{(1-UH2ME)(28.01)}{16.05} F_{11} = 0$

Energy Balance	
Overall	$F_{47}^{(MeOH)} / M^{(MeOH)} H_{47}^{(MeOH)} + \Sigma F_{802}^{(i)} / M^{(i)} H_{802}^{(i)} - (F_{11}^{(CH_4)} / M^{(CH_4)} H_{11}^{(CH_4)} +$
	$F_{28}^{(H_2O)} / M^{(H_2O)} H_{28}^{(H_2O)} + F_{33}^{(CO_2)} / M^{(CO_2)} H_{33}^{(CO_2)})$
	$+ Q_{out} F_{47} - Q_{MET} = 0$
	$i = CO_2, CO, H_2$
Enthalpy Function	$H_k^i(T) = (a_1^i + \frac{1}{2} a_2^i T + \frac{1}{3} a_3^i T^2 + \frac{1}{4} a_4^i T^3 + \frac{1}{5} a_5^i T^4 + \frac{b_1^i}{T}) RT \quad J/mol$
	$i = CO_2, CH_4, H_2O, CO, H_2$
	$k = 11, 28, 33, 802$
	$H_k^{(MeOH)}(T) = (-238.54)(1000) + (79.225)(T - 298.15) \; J/mol \; k=47$
	Source: Felder and Roussleu (1986)

In the material balance part, there are 8 variables and 8 equations including one dependent equation (overall material balance), so the number of degrees of freedom is 1. For the material and energy balance, there are 21 variables and 16 equations including one dependent equation (overall material balance), so the number of degrees of freedom is 6.

B-8. Ammonium Nitrate ($AmNO_3$ or NH_4NO_3) (Hertwig, 2004; Search and Reznik, 1977; Louisiana Chemical & Petroleum Products List, 1998)

In the chemical production complex in the lower Mississippi River corridor, ammonium nitrate is produced by the following plants (Louisiana Chemical & Petroleum Products List, 1998).

- PCS Nitrogen, Geimar (485 thousand metric tons per year)
- CF Industries, Donaldsonville (340 thousand metric tons)

For ammnium nitrate production, the capacity of 684 tons per day was used for the base case (Hertwig, 2004).

B-8-1. Process Description

$$NH_3 (g) + HNO_3 (aq.) = NH_4NO_3 (aq.) \qquad \Delta H = -86.2 \; kJ / gmol \; (7-35)$$
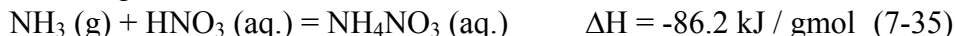
Ammonium nitrate is made by reacting nitric acid with ammonia (7-35). Both feeds are preheated and product is air-cooled. If feeds are properly heated and proportioned, the heat of reaction finishes drying the product. Continuous processes are employed instead of batch processes because of the labor and equipment costs. Figure 7.9 shows a block diagram with the stream definitions in Table 7-23.
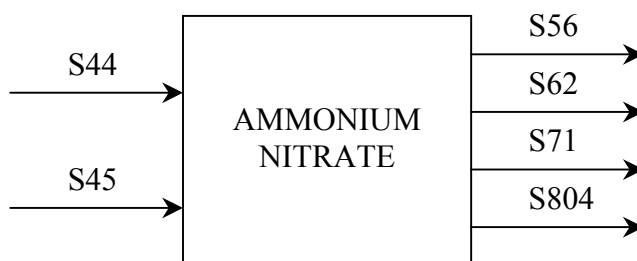
Figure 7.9 Block Diagram of Ammonium Nitrate Plant

Table 7-23 Description of Process Streams in Ammonium Nitrate Plant

Name of Streams	Description
Input Streams	
S44	Ammonia to ammonium nitrate plant
S45	Nitric acid solution to ammonium nitrate plant
Output Streams	
S56	Granular ammonium nitrate from ammonium nitrate plant
S62	Ammonium nitrate solution from ammonium nitrate plant
S71	Water from ammonium nitrate plant to nitric acid plant
S804	Water from ammonium nitrate plant but not to nitric acid plant

B-8-2. Material Balance and Energy Balance

Using the parameters in Table 7-24, the material balance and energy balance of the ammonium nitrate plant are given in Table 7-25. In Table 7-25, the overall material balance for the whole process is given with the mixture stream expressions. For the species material balance obtained using the reaction equations (7-35), the first equation is for the HNO_3 balance; the second one is for the NH_3 balance; the last one is for the H_2O balance.

In the overall energy balance, Q_{AN} is heat input of the ammonium nitrate plant in the form of steam in the heat exchanger and preheater, which is calculated from the energy balance. Q_{out} is the heat output removed by cooling water and the air for cooling in the prilling tower and cooler in ammonium nitrate plant, based on the unit of ammonium nitrate product, 62 KJ per lb of ammonium nitrate (Search and Reznik, 1977). In enthalpy functions, the coefficients a_1, a_2, a_3, a_4, a_5, and b_1 for different species are given in Table A-1 in Appendix A in (Xu, 2004).

In the material balance part, there are 10 variables and 8 equations including one dependent equation (overall material balance), so the number of degrees of freedom is 3. For the material and energy balance, there are 25 variables and 17 equations including one dependent equation (overall material balance), so the number of degrees of freedom is 9.

Table 7-24 Parameters in Ammonium Nitrate Production, from Hertwig (2004)

Name	Meaning	Value
UAMMAMN	NH_3 utilization in ammonium nitrate plant	1.0
UNITAMN	HNO_3 utilization in ammonium nitrate plant	1.0
CONCAMN	Concentration of ammonium nitrate solution product	0.30

Table 7-25 Constraint Equations for Ammonium Nitrate Production

Material Balance

Overall
$$(F_{44} + F_{45}) - (F_{56} + F_{62} + F_{71} + F_{804}) = 0$$
where
$$F_{45} = F_{45}^{(HNO_3)} + F_{45}^{(H_2O)}$$
$$F_{62} = F_{62}^{(AN)} + F_{62}^{(H_2O)}$$

Species
$$HNO_3: \ F_{45}^{(HNO_3)} - \frac{63.02}{80.06}(F_{62}^{(AN)} + F_{56}) = 0$$

$$NH_3: \ F_{44} - \frac{17.04}{80.06}(F_{62}^{(AN)} + F_{56}) = 0$$

$$H_2O: \ F_{45}^{(H_2O)} - F_{71} - F_{62}^{(H_2O)} - F_{804} = 0$$

Energy Balance

Overall
$$(F_{56}^{(AN)} / M^{(AN)} H_{56}^{(AN)} + \Sigma F_{62}^{(i)} / M^{(i)} H_{62}^{(i)} + F_{71}^{(H_2O)} / M^{(H_2O)} H_{71}^{(H_2O)} +$$

$$F_{804}^{(H_2O)} / M^{(H_2O)} H_{804}^{(H_2O)}) - (F_{44}^{(NH_3)} / M^{(NH_3)} H_{44}^{(NH_3)} + \Sigma F_{45}^{(j)} / M^{(j)} H_{45}^{(j)})$$

$$+ Q_{out} F_{56}^{(AN)} - Q_{AN} = 0$$
$$i = H_2O, AN; j = HNO_3, H_2O$$

Enthalpy Function
$$H_k^i(T) = (a_1^i + \frac{1}{2}a_2^i T + \frac{1}{3}a_3^i T^2 + \frac{1}{4}a_4^i T^3 + \frac{1}{5}a_5^i T^4 + \frac{b_1^i}{T})RT \quad J/mol$$

$$i = NH_3, HNO_3, H_2O$$
$$k = 44, 45, 62, 71, 804$$
$$H_k^{(AN)}(T) = (-365.381)(1000) + (139.261)(T - 298.15) \ J/mol \ k=56, 62$$
Source: Lide (1982)

B-9. Mono-/Di-Ammonium Phosphates (MAP/DAP) (Hertwig, 2004; Brown, et al., 1985; Louisiana Chemical & Petroleum Products List, 1998)

In the chemical production complex in the lower Mississippi River corridor, MAP and DAP are produced by the following plants (Louisiana Chemical & Petroleum Products List, 1998).

- IMC-Agrico, Faustina (Not available)

- IMC-Agrico, Taft (600 thousand tons per year for DAP)
- Avondale Ammonia, Westwego (125 thousand metric tons per year for DAP)

For the chemical production, the capacities of 885 tons per day for MAP and 5,666 tons per day for DAP were used for the base case (Hertwig, 2004).

B-9-1. Process Description

The standard grades for ammonium phosphate fertilizers are listed in Table 7-26. The product grades for MAP and DAP are set as 11-52-0 and 18-46-0 in Table 7-26, respectively.

Table 7-26 Ammonium Phosphate Standard Grades

%N - %P_2O_5 - %K_2O	N/P Mole Ratio
18-46-0	1.73 (if a true "di-" is 2.00)
10-50-0	0.90
10-52-0	0.85
11-52-0	0.94

The process feeds include anhydrous NH_3 as vapor, phosphoric acid at 40-54% P_2O_5, water for scrubber, and N boosters, such as NH_2CONH_2 (granular or solution), NH_4NO_3 (granular or solution), and $(NH_4)_2SO_4$ which comes from the reaction of NH_3 and feed H_2SO_4 in the granulator.

The overall reactions are:

$$H_3PO_4 + NH_3 = NH_4H_2PO_4 \qquad\qquad MAP \qquad (7\text{-}36)$$
$$NH_4H_2PO_4 + NH_3 = (NH_4)_2HPO_4 \qquad DAP \qquad (7\text{-}37)$$
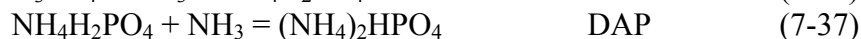
The block diagram is illustrated in Figure 7.10 with the stream definitions in Table 7-27. Ammonia and phosphoric acid are metered continuously to an agitated atmospheric tank (pre-neutralizer) in specific mole ratios to produce a liquid product. The liquid product, more NH_3, N-boosters, and recycled product fines are fed in specific mole ratios to a granulator to grow the fines into product granules. By adjusting feeds mole ratios and the N-boosters, different products of MAP and DAP can be manufactured. Granulator product is dried, cooled and screened. Screen fines and coarse material that get ground are each recycled to the granulator. Storage is indoors with big piles in a warehouse. Most products are shipped by barge and ship. Only small amounts get bagged for residential use.
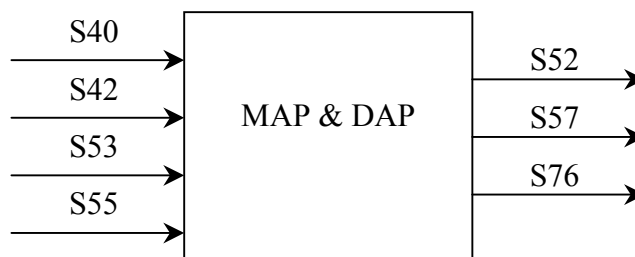
Figure 7.10 Block Diagram of MAP and DAP Plant

To control emissions of unreacted NH_3 and fluorides and of product dust, air is drawn through process vessels and scrubbed. By controlling H_3PO_4 additions, scrubber liquor pH is carefully controlled to be able to scrub both NH_3 and fluorides by Equation 7-38, 7-39, and 7-40. Permit limits apply though it is not yet feasible to measure these emissions on a continuous basis. Besides being a yield loss, emissions can cause NH_3-smell complaints from plant neighbors and formation of $(NH_4)_2SO_3$, a white haze, if NH_3 meets the trace amount of SO_2 from sulfuric plant stacks.

$$H_3PO_4 + NH_3 = NH_4H_2PO_4 \qquad \text{capture } NH_3 \quad (7\text{-}38)$$
$$NH_3 + HF = NH_4F \qquad \text{capture } HF \quad (7\text{-}39)$$
$$4NH_3 + 3SiF_4 + 2H_2O = 2(NH_4)_2SiF_6 + SiO_2 \qquad \text{capture } SiF_4 \quad (7\text{-}40)$$
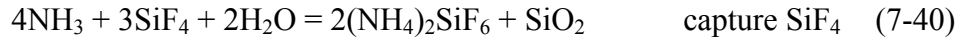
Table 7-27 Description of Process Streams in MAP and DAP Plant

Name of Streams	Description
Input Streams	
S40	Wet process phosphoric acid to MAP and DAP plant
S42	Ammonia to MAP and DAP plant
S53	Urea produced from urea plant as N-boosters to MAP and DAP plant
S55	Inert materials to MAP and DAP plant
Output Streams	
S52	MAP produced from MAP and DAP plant
S57	DAP produced from MAP and DAP plant
S76	Water vapor from MAP and DAP plant

B-9-2. Material Balance and Energy Balance

Using the parameters in Table 7-28 the material balance and energy balance of MAP and DAP plant are given in Table 7-29. In Table 7-29, the overall material balance for the whole process is given with the mixture stream expressions. For the species material balance obtained using the reaction equations (7-36 and 7-37), the first equation is for the P_2O_5 balance; the second one is for the NH_3 balance; the third one is for the urea (N-boosters) balance; the fourth one is for the water balance; the last one is for the MAP balance.

In the overall energy balance, Q_{APG} is heat input to MAP and DAP plant from steam in the heat exchangers and dryer, and it is calculated from the energy balance. Q_{out} is the heat output from reaction heat removed by cooling water in the heat exchanger with the reactor in MAP and DAP plant based on the unit of MAP and DAP product, 402 KJ per lb of MAP and DAP (Brown, et al., 1985). Since the overall energy balance is based on Equation 7-36 and 7-37, and urea as the N-booster is not in these reactions, urea and the inert impurities are not considered in energy balance, just the balance from the reaction equation directly is evaluated. In enthalpy functions, the coefficients a_1, a_2, a_3, a_4, a_5, and b_1 for different species are given in Table A-1 in Appendix A in (Xu, 2004).

In the material balance part, there are 9 variables and 8 equations, so the number of degrees of freedom is 1. For the material and energy balance, there are 21 variables and 15 equations, so the number of degrees of freedom is 6.

Table 7-28 Parameters in MAP and DAP Production, from Hertwig (2004)

Name	Meaning	Value
NMAP	% content of N in MAP	11
P2O5MAP	% content of P_2O_5 in MAP	52
NDAP	% content of N in DAP	18
P2O5DAP	% content of P_2O_5 in DAP	46
RPDAP	Ratio of P_2O_5 to DAP	0.68
RPMAP	Ratio of P_2O_5 to MAP	0.12
UPAGTSP	P_2O_5 utilization in ammoniation	0.999
NBRDAP	N-booster addition rate(urea solution) (T 100%-basis urea per T of DAP)	0.01362
PURMAP	Purity of $NH_4H_2PO_4$ in MAP	0.6357
PURDAP	Purity of $(NH_4)_2HPO_4$ in DAP (contains some MAP)	0.7705

B-10. Urea Ammonium Nitrate Solution (UAN) (Hertwig, 2004; Louisiana Chemical & Petroleum Products List, 1998)

In the chemical production complex in the lower Mississippi River corridor, UAN is produced by the following plants (Louisiana Chemical & Petroleum Products List,1998).

Table 7-29 Constraint Equations for MAP and DAP Production

Material Balance

Overall

$(F_{40} + F_{42} + F_{53} + F_{55}) - (F_{52} + F_{57} + F_{76}) = 0$

where

$F_{40} = F_{40}^{(P_2O_5)} + F_{40}^{(H_2O)}$

$F_{53} = F_{53}^{(UREA)}$

Species

P_2O_5: $F_{40}^{(P_2O_5)} - (\dfrac{P2O5MAP}{100} F_{52} + \dfrac{P2O5DAP}{100} F_{57}) = 0$

NH_3:

$\dfrac{1}{17.04} F_{42} - \dfrac{(RPDAP)(NDAP)}{(RPDAP + RPMAP)(P2O5DAP)(14.01)} F_{40}^{(P_2O_5)}$

$- \dfrac{(RPMAP)(NMAP)}{(RPDAP + RPMAP)(P2O5MAP)(14.01)} F_{40}^{(P_2O_5)} = 0$

UREA: $F_{53}^{(UREA)} - (NBRDAP)F_{57} = 0$

H_2O: $F_{76} - (F_{40}^{(H_2O)} - \dfrac{(3)(18.02)}{141.94} F_{40}^{(P_2O_5)}) = 0$

MAP: $F_{52} - \dfrac{(RPMAP)(100)}{(RPDAP + RPMAP)(P2O5MAP)} F_{40}^{(P_2O_5)} = 0$

Energy Balance

Overall

$((PURMAP)F_{52}^{(MAP)} / M^{(MAP)}H_{52}^{(MAP)} + (PURDAP)F_{57}^{(DAP)} / M^{(DAP)}H_{57}^{(DAP)} +$

$F_{76}^{(H_2O)} / M^{(H_2O)}H_{76}^{(H_2O)}) - (\Sigma F_{40}^{(i)} / M^{(i)}H_{40}^{(i)} + F_{42}^{(NH_3)} / M^{(NH_3)}H_{42}^{(NH_3)})$

$+ Q_{out}(F_{52} + F_{57}) - Q_{APG} = 0$

$i = P_2O_5, H_2O$

Enthalpy Function

$H_k^i(T) = (a_1^i + \dfrac{1}{2}a_2^i T + \dfrac{1}{3}a_3^i T^2 + \dfrac{1}{4}a_4^i T^3 + \dfrac{1}{5}a_5^i T^4 + \dfrac{b_1^i}{T})RT$ J/mol

$i = H_2O, NH_3$
$k = 40, 42, 76$

$H^{(P_2O_5)} = (-1278.437)(1000) + 106.014(T - 298.15)J/mol$

Source: Lide (1982)

$H_k^{(MAP)} = ((-345.38)(1000) + 34.00(T - 298.15))4.182$ J/mol k=52

Source: Lide (1982)

$H_k^{(DAP)} = ((-374.50)(1000) + 45.00(T - 298.15))4.182$ J/mol k=57

Source: Lide (1982)

- CF Industries, Donaldsonville (770 thousand metric tons per year)
- PCS Nitrogen Fertilizer LP, Geismar (1.1 million metric tons per year)

For UAN production, the capacity of 183 tons per day was used in the base case (Hertwig, 2004).

B-10-1. Process Description

UAN is simply manufactured by mixing granular urea and ammonium nitrate solution. The block diagram is shown in Figure 7.11 with the stream definitions in Table 7-30.

Figure 7.11 Block Diagram of UAN Plant
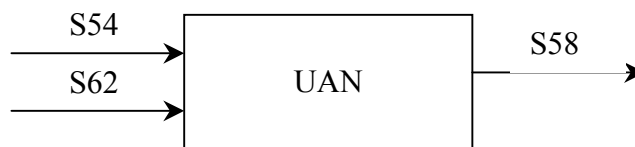
Table 7-30 Description of Process Streams in UAN Plant

Name of Streams	Description
Input Streams	
S54	Granular urea to UAN plant
S62	Ammonium nitrate solution to UAN plant
Output Streams	
S58	UAN solution produced from UAN plant

B-10-2. Material Balance and Energy Balance

Using the parameters in Table 7-31 the material balance and energy balance of UAN plant are given in Table 7-32. In Table 7-32, the overall material balance for the whole process is given with the mixture stream expressions. For the species material balance, the first equation is for the N balance; the second one is for the water balance.

An energy balance is not required because there is no significant energy change in this simple blending process. Hence, for the material and energy balance, there are 7 variables and 6 equations, so the number of degrees of freedom is 1.

Table 7-31 Parameters in UAN Production, from Hertwig (2004)

Name	Meaning	Value
CONCAMN	$AmNO_3$ solution strength, $AmNO_3$ weight fraction	0.30
CONCNUAN	UAN solution N weight fraction (commercial spec 0.28-0.32)	0.30

Table 7-32 Constraint Equations for UAN Production

Material Balance	
Overall	$(F_{54} + F_{62}) - F_{58} = 0$
	where
	$F_{58} = F_{58}^{(UAN)} + F_{58}^{(H_2O)}$
	$F_{62} = F_{62}^{(AN)} + F_{62}^{(H_2O)}$
Species	N: $(\dfrac{28.02}{60.07} F_{54} + \dfrac{28.02}{80.06} F_{62}^{(AN)}) - (CONCNUAN)F_{58} = 0$
	H_2O: $F_{62}^{(H_2O)} - F_{58}^{(H_2O)} = 0$

B-11. Power Generation (Hertwig, 2004)

In the chemical production complex in the lower Mississippi River corridor, the power generation plants are in the IMC-Argico Uncle Sam and Faustina plants (Hertwig, 2004).

B-11-1. Process Description

A steam turbine-driven generator is used in the complex. This is driven by steam produced from waste process heat. The steam turbine-driven power generation plant uses waste-heat steam from the sulfuric acid plant, and there are two generators; one is for high pressure steam (HP) and the other is for intermediate pressure steam (IP). Also there is a package boiler in the plant to provide needed steam not otherwise available. The block diagram is shown in Figure 7.12 with the stream definitions in
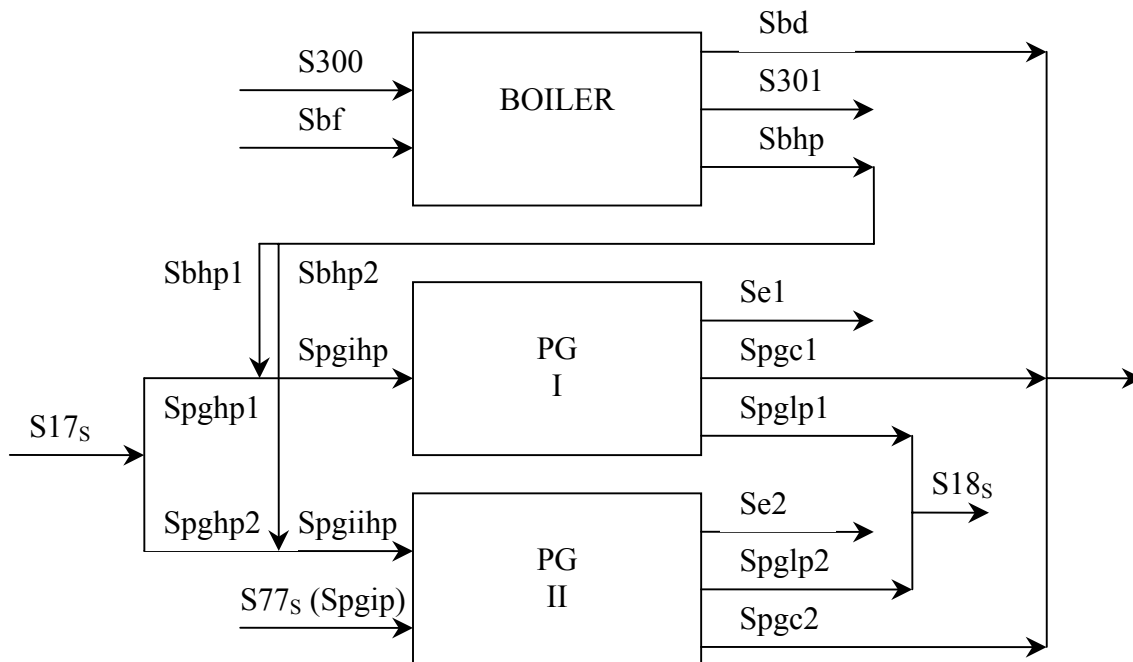
Figure 7.12 Block Diagram of Power Generation Plant

B-11-2. Material Balance and Energy Balance

Using the parameters in Table 7-34 the material balance and energy balance of power generation plant are given in Table 7-35. In Table 7-35, the overall water balance for the whole process is given with the expressions of mixing and splitting streams. For the species (water) material balance, the first equation is for the low pressure steam (LP) balance in power generator I (PGI); the second one is for the condensed water balance in PGI; the third one is for the LP balance in power generator II (PGII); the fourth one is for the condensed water balance in PGII; the fifth one is for the intermediate pressure steam (IP) balance in PGII; the sixth one is for the boiler feed water (BFW) balance in the package boiler; the seventh one is for the high pressure steam (HP) balance in the package boiler; the last one is for the distribution of HP from the package boiler to PGII. Meanwhile, the material balances of methane and CO_2 are also shown in Table 7-35 which gives the energy source and CO_2 emissions.

Table 7-33 Description of Process Streams in Power Generation Process

Name of Streams	Description
Input Streams	
$S17_S$	HP steam from sulfuric acid plant
$S77_S$	IP steam from sulfuric acid plant
Sbf	Water to the package boiler
S300	Natural gas to the package boiler
Intermediate Streams	
Spghp1	One branch of $S17_S$ to power generator I (PGI)
Spghp2	The other branch of $S17_S$ to power generator II (PGII)
Spglp1	LP from PGI
Spglp2	LP from PGII
Spgip	Branch of $S77_S$
Sbd	Blow-down water from the package boiler
Spgc1	Condensate water from PGI
Spgc2	Condensate water from PGII
Spgihp	HP to PGI
Spgiihp	HP to PGII
Sbhp	HP produced from the package boiler
Sbhp1	One branch of HP produced from the package boiler
Sbhp2	The other branch of HP produced from the package boiler
Output Streams	
S78	Water from power generation plant
$S18_S$	LP steam from power generation plant
S301	CO_2 emission from the boiler
Se1	Electricity generated from turbo generator
Se2	Electricity generated from IP turbo generator

In the overall energy balance, Q_{PG} is heat output of the power plant in the form of steam, and electricity. Part of the steam produced from power plant is used in the Table 7-34 Parameters in Power Generation, from Hertwig (2004)

Table 7-34 Parameters in Power Generation

Name	Meaning	Value
HPPLP	Conversion coefficient from HP to LP (KPPH HP per KPPH LP produced)	1.05
IPPLP	Conversion coefficient from IP to LP (KPPH IP per KPPH LP produced)	24.15
BDPG	Blowdown based on HP product	0.08
ENNATB	CH_4 combustion heat (MJ per cubic meter)	37.56
ROUNATB	CH_4 gas density (g per cubic meter)	653.921
HPNATB	Klb HP produced per MBTU CH_4 fired	0.9

Table 7-35 Constraint Equations for Power Generation Process

Material Balance	
Overall	$(F_{S17} + F_{S77} + F_{bf}) - (F_{S18} + F_{S78}) = 0$ (water balance)
	where
	$F_{S17} = F_{pghp1} + F_{pghp2}$
	$F_{S77} = F_{pgip}$
	$F_{S18} = F_{pglp1} + F_{pglp2}$
	$F_{S78} = F_{bd} + F_{pgc1} + F_{pgc2}$
	$F_{bhp} = F_{bhp1} + F_{bhp2}$
	$F_{pgihp} = F_{pghp1} + F_{bhp1}$
	$F_{pgiihp} = F_{bhp2} + F_{pghp2}$
Species (Water)	LP in PGI: $F_{pgihp} - (HPPLP)F_{pglp1} = 0$
	Condensed water in PGI: $F_{pgc1} - (F_{pgihp} - F_{pglp1}) = 0$
	LP in PGII: $(\dfrac{1}{HPPLP} F_{pgiihp} + \dfrac{1}{IPPLP} F_{pgip}) - F_{pglp2} = 0$
	Condensed water in PGII: $F_{pgc2} - (F_{pgiihp} + F_{pgip} - F_{pglp2}) = 0$
	IP in PGII: $F_{pgip} - 1.15 F_{pgiihp} = 0$
	BFW in boiler: $F_{bf} - (F_{bd} + F_{bhp}) = 0$
	HP in boiler: $F_{bd} - (BDPG)F_{bhp} = 0$

HP from boiler to PGII: $F_{bhp2} = 0$

Species (CH_4, CO_2)	CH_4: $F_{300} - \dfrac{(2204.62)(1.055)(ROUNATB)}{(HPNATB)(ENNATB)} F_{bhp} = 0$

Table 7-35 Continued

Material Balance (Continued)

Species (CH_4, CO_2)

CO_2: $\dfrac{F_{300}}{16.05} - \dfrac{F_{301}}{44.01} = 0$

Energy Balance

Overall

$$Q_{PG} - (-(S_{e_1} + S_{e_2}) + (\frac{-285830}{18.02} - H_{lpp})F_{18}) = 0$$

where

$S_{el} =$

$\dfrac{(365.25)(24)(3600)}{(9.6)}(\dfrac{2204.62}{(365.25)(24)(1000)}F_{pgihp} - 15E - 05$

$- \dfrac{2204.62}{(365.25)(24)(1000)(1.8)}F_{pglpl})$

1E+11 J/year, from Hertwig (2004)

$S_{e2} = \dfrac{(365.25)(24)(3600)}{(9.6)}(\dfrac{2204.62}{(365.25)(24)(1000)}F_{pgiihp}$

$+ \dfrac{2204.62}{(365.25)(24)(1000)(1.4)}F_{pgip} - 15E - 05 - \dfrac{2204.62}{(365.25)(24)(1000)(1.8)}F_{pglp2})$

1E+11 J/year, from Hertwig (2004)

Enthalpy Function

$H^{(LP)}(T) = ((72.558 + (0.5)(-0.66244)T + (\frac{1}{3})(0.002562)T^2 +$

$(0.25)(-4.3659E - 06)T^3 + (0.2)(2.7818E - 09)T^4 + \dfrac{(-41886)}{T})(8.3145)T$

$-1893)\dfrac{1}{18.02} + ((-0.007)T^2 + (2.7838)T + 2292.0563)$

J/g, LP has no super heat, from Meyer, et al. (1977) and McBride, et al. (1993).

phosphoric acid plant. The other part of the steam is used in other plants which require heat input in the base case. Electricity from the power plant is considered to be interchangable with steam since both steam and electricity can be used to drive pumps, compressors and other prime movers. The electrity Se1 and Se2 are calculated by the formulas in Table 7-35 provided by Hertwig (2004). In enthalpy functions, the

coefficients a_1, a_2, a_3, a_4, a_5, and b_1 for different species are given in Table A-1 in Appendix A in (Xu, 2004).

In the material balance part, only complete water balance is given in Table 7-35, where there are 22 variables and 19 equations, so the number of degrees of freedom is 3. For the material and energy balance of water, there are 40 variables and 30 equations, so the number of degrees of freedom is 10.

B-12. Conventional Acetic Acid Production (Rudd, et al., 1981; Louisiana Chemical and Petroleum Products List, 1998)

In the chemical production complex in the lower Mississippi River corridor, acetic acid is produced by the following plants (Louisiana Chemical & Petroleum Products List, 1998).

- Borden Chemicals and Plastics, Geismar (Not available)
- Dow Chemical, Hahnville (18 million pounds per year)

For acetic acid production, the production rate of the Dow Chemial's Hahnville plant, 18 million pounds per year (8,160 metric tons per year), was used in the base case (Louisiana Chemical & Petroleum Products List, 1998).

B-12-1. Process Description

A Monsanto developed low-pressure process to produce acetic acid from methanol and CO is used in Dow Chemical's Hahnville plant. The selectivity based on methanol was over 99%. CO was produced from methane and CO_2 (Equation 7-21 and 7-32). The specific reaction for producing acetic acid was Equation (7-41). The overall reaction was Equation (7-42) obtained from Equation (7-21), (7-32) and (7-41). The block diagram is illustrated in Figure 7.13 with the stream definitions from Table 7-36.

$$CH_4 + H_2O \rightarrow CO + 3H_2 \tag{7-21}$$
$$CO_2 + H_2 \rightarrow CO + H_2O \tag{7-32}$$
$$CH_3OH + CO \rightarrow CH_3COOH \tag{7-41}$$
$$CH_4 + 3CO_2 + 4CH_3OH \rightarrow 4CH_3COOH + 2H_2O \tag{7-42}$$
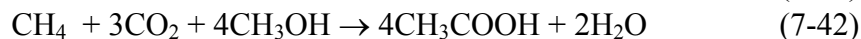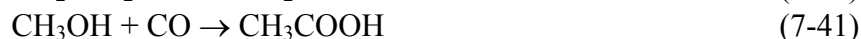
Figure 7.13 Block Diagram of Conventional Acetic Acid Plant

Table 7-36 Description of Process Streams in Conventional Acetic Acid Plant

Name of Streams	Description
Input Streams	
S82	CO_2 to conventional acetic acid plant
S83	Natural gas to conventional acetic acid plant
S424	Methanol from methanol plant to conventional acetic acid plant
Output Streams	
S84	Production of acetic acid from conventional acetic acid plant
S425	Water produced from conventional acetic acid plant

B-12-2. Material Balance and Energy Balance

Using the parameters in Table 7-37, the material balance and energy balance of conventional acetic acid plant are given in Table 7-38.

In Table 7-38, the overall material balance for the whole process is given first. For the species material balance obtained using the reaction equations (7-21, 7-32, 7-41 and 7-42), the first equation is for the CO_2 balance; the second one is for the CH_4 balance; the third one is for the methanol balance; the last one is for the H_2O balance.

Table 7-37 Parameters in Conventional Acetic Acid Plant

Name	Meaning	Value
	CO_2 utilization	1.0
	CH_4 utilization	1.0
	Methanol utilization	1.0

Table 7-38 Constraint Equations for Conventional Acetic Acid Plant

Material Balance	
Overall	$F_{82} + F_{83} + F_{424} - F_{84} - F_{425} = 0$
Species	CO_2: $\dfrac{1}{(44.01)(3)} F_{82} - \dfrac{1}{(60.06)(4)} F_{84} = 0$
	CH_4: $\dfrac{1}{16.05} F_{83} - \dfrac{1}{(60.06)(4)} F_{84} = 0$
	Methanol: $\dfrac{1}{(32.05)(4)} F_{424} - \dfrac{1}{(60.06)(4)} F_{84} = 0$
	H_2O: $-F_{425} + \dfrac{(2)(18.02)}{(60.06)(4)} F_{84} = 0$
Energy Balance	

Overall	$(F_{84}^{(aceticacid)} / M^{(aceticacid)} H_{84}^{(aceticacid)} + F_{425}^{(H_2O)} / M^{(H_2O)} H^{(H_2O)}) - (F_{82}^{(CO_2)}$
	$/ M^{(CO_2)} H_{82}^{(CO_2)} + F_{83}^{(CH_4)} / M^{(CH_4)} H_{83}^{(CH_4)} + F_{424}^{(CH_3OH)} / M^{(CH_3OH)} H_{424}^{(CH_3OH)})$
	$+ Q_{out} F_{84}^{(aceticacid)} - Q_{AA} = 0$
Enthalpy Function	$H_k^i(T) = (a_1^i + \frac{1}{2} a_2^i T + \frac{1}{3} a_3^i T^2 + \frac{1}{4} a_4^i T^3 + \frac{1}{5} a_5^i T^4 + \frac{b_1^i}{T}) RT$ J/mol
	$\quad i = CO_2, CH_4, H_2O; \; k = 82, 83, 425$
	$H_k^{(MeOH)}(T) = (-238.54)(1000) + (79.225)(T - 298.15)$ J/mol k=424
	Source: Felder and Roussleu (1986).
	$H_k^{(aceticacid)}(T) = ((-115.8)(1000) + (29.7)(T - 298.15))(4.185)$ J/mol k=425
	Source: Lide (1982).

In the overall energy balance, Q_{AA} is heat input of the acetic acid plant in the form of steam in the heat exchanger and acetic acid separation units, which is calculated from the energy balance. Q_{out} is the heat output removed by cooling water in the heat exchanger and condensers in acetic acid plant based on the unit of acetic acid product, 15 MJ per lb of acetic acid (Rudd, et al., 1981). In enthalpy functions, the coefficients a_1, a_2, a_3, a_4, a_5, and b_1 for different species are given in Table A-1 in Appendix A in (Xu, 2004).

In the material balance part, there are 5 variables and 5 equations including the dependent overall mass balance, so the number of degrees of freedom is 1. For the material and energy balance, there are 16 variables and 11 equations including the dependent overall mass balance, so the number of degrees of freedom is 6.

B-13. Ethylbenzene (EB) Produced from Benzene and Ethylene (Louisiana Chemical & Petrochemical Products List, 1998; Pellegrino, 2000; Speight, 2002; Brown, et al., 1985)

In the lower Mississippi River corridor, ethylbenzene is produced by the plants as follow (Louisiana Chemical & Petroleum Products List, 1998).

- Chevron Chemical Company, St. James (1.9 billion pounds per year)
- Cos-mar Company, Carville (2.2 billion pounds per year)
- Deltech Corporation, Baton Rouge (700 million pounds per year)

For ethylbenzne production, the production rate of ethylbenzene in St. James plant of Chevron Chemical Company, 1.9 billion pounds per year (862,000 metric tons per year), was used in the base case (Louisiana Chemical & Petrochemical Products List, 1998).

B-13-1. Process Description

Since 1980, EB has been produced using zeolite catalysts in a liquid phase operation (Equation 7-43) (Pellegrino, 2000). Ethylene and benzene are fed into a liquid-filled alkylation reactor that contains fixed beds of zeolite catalyst. The reaction needs excess benzene, in ratios of about 1:0.6 benzene to ethylene. The recyclable

alkylbenzenes and other by-products can be recycled to produce additional EB. A product with purity as high as 99.95 to 99.99% can be achieved. Since nearly all the EB produced (99%) is used to produce styrene, this process is usually integrated with styrene production, which is very energy-intensive. The block diagram of direct oxidation of ethylene process is in Figure 7.14 with the stream description in Table 7-39.

$$C_6H_6 + CH_2 = CH_2 \rightarrow C_6H_5CH_2CH_3 \tag{7-43}$$
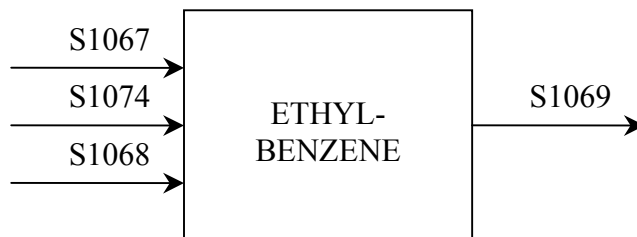
Figure 7.14 Block Diagram of Ethylbenzene Process

Speight (2002) reported that the overall yield of EB is 98% with the elaborate separations required, including washing with caustic and water and three distillation column, i.e. benzene column (benzene recycle), EB column and polyethylbenzene column (to transalkylator).

Table 7-39 Description of the Streams in the Ethylbenzene Process

Stream Name	Stream Description
Input Streams	
S1067	Benzene to Ethylbenzene process
S1068	Ethylene to Ethylbenzene process
S1074	Benzene recycled from Styrene process
Output Streams	
S1069	EB produced from Ethylbenzene process

B-13-2. Material Balance and Energy Balance

Using the parameters in Table 7-40, the material balance and energy balance of ethylbenzene process are given in Table 7-41.

In Table 7-41, the overall material balance for the whole process is given first. For the species material balance obtained using the reaction equation (7-43), the first equation is for the C_2H_4 balance; and the second one is for the benzene balance.

Table 7-40 Parameters in EB Production

Name	Meaning	Value
	Ethylene benzene yield in EG plant	100%
	Ethylene and benzene conversions	100%

Table 7-41 Constraint Equations for EB Production

Material Balance	
Overall	$(F_{1067} + F_{1074} + F_{1068}) - F_{1069} = 0$
Species	C_2H_4: $\dfrac{-F_{1068}}{mw(C_2H_4)} + \dfrac{F_{1069}}{mw(EB)} = 0$
	Benzene: $-\dfrac{(F_{1067} + F_{1074})}{mw(benzene)} + \dfrac{F_{1069}}{mw(EB)} = 0$
Energy Balance	
Overall	$F_{1069}^{(EB)} / M^{(EB)} H_{1069}^{(EB)} - (F_{1067}^{(BENZENE)} / M^{(BENZENE)} H_{1067}^{(BENZENE)}$
	$+ F_{1074}^{(BENZENE)} / M^{(BENZENE)} H_{1074}^{(BENZENE)} + F_{1068}^{(C_2H_4)} / M^{(C_2H_4)} H_{1068}^{(C_2H_4)})$
	$+ Q_{out} F_{1069}^{(EB)} - Q_{EB} = 0$
Enthalpy Function	$H_k^i(T) = (a_1^i + \dfrac{1}{2} a_2^i T + \dfrac{1}{3} a_3^i T^2 + \dfrac{1}{4} a_4^i T^3 + \dfrac{1}{5} a_5^i T^4 + \dfrac{b_1^i}{T})RT$ J/mol
	i = BENZENE, C_2H_4
	k = 1067, 1068, 1074
	$H_{1069}^{(EB)} = -12300 + 185.572(T - 298.15)$ J/mol
	Source: Lide (1990) and NIST (National Institute of Standards and Technology) (2002)

In the overall energy balance, Q_{EB} is heat input of the ethylbenzene process in the form of steam in the heat exchanger and separation distillation column reboilers, which is calculated from the energy balance. Q_{out} is the heat output removed by cooling water in the heat exchanger and separation distillation column condensers in the ethlbenzene process based on the unit of ethylbenzene product, 96 KJ per lb of ethylbenzene (Brown, et al., 1985). In enthalpy functions, the coefficients a_1, a_2, a_3, a_4, a_5, and b_1 for different species are given in Table A-1 in Appendix A in (Xu, 2004).

In the material balance part, there are 4 variables and 3 equations including one dependent one (overall material balance), so the number of degrees of freedom is 2. For the material and energy balance, there are 13 variables and 8 equations including one dependent one (overall material balance), so the number of degrees of freedom is 6.

B-14. Styrene from Catalytic Dehydrogenation of Ethylbenzene (Conventional Styrene Process) (Louisiana Chemical & Petrochemical Products List, 1998; Pellegrino, 2000; Wells, 1999; Brown, et al., 1985)

In the lower Mississippi River corridor, styrene is produced by the plants as follow (Louisiana Chemical & Petroleum Products List, 1998).

- Chevron Chemical Company, St. James (1.7 billion pounds per year)
- Cos-mar Company, Carville (2 billion pounds per year)
- Deltech Corporation, Baton Rouge (800 million pounds per year)

For styrene production, the production rate of Chevron Chemical Company in St. James plant, 1.7 billion pounds per year (771,000 metric tons per year), was used in the base case (Louisiana Chemical & Petroleum Products List, 1998).

B-14-1. Process Description

Styrene is widely used in copolymers as well as in homopolymers and rubber-modified styrene polymers. The major process for styrene manufacture involves a Friedel-Crafts reaction between benzene and ethylene to form EB. Styrene and hydrogen can be produced from dehydrogenation to styrene in the presence of steam and a catalyst (Equation 7-44).

Most of the styrene produced in the US is made by dehydrogenation of EB (Equation 7-44) (Pellegrino, 2000). The by-products are minor amounts of tar, toluene, and benzene (Equation 7-45, 7-46 and 7-47). Benzene, toluene and unreacted EB are recycled; tar residues are used as fuel. Conversion of EB can be as high as 80-90%. The catalysts are various metal oxides, such as zinc, iron, or magnesium oxides coated on activated carbon, alumina, or bauxite. The reaction temperature is 649°C and under vacuum. The yield of styrene is 90% (Wells, 1999).

The block diagram of conventional styrene process is in Figure 7.15 with the stream description in Table 7-42.
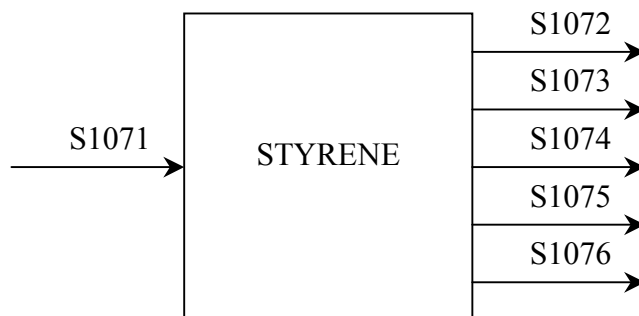
Figure 7.15 Block Diagram of Conventional Styrene Process

(4-44)

(4-45)

(4-46)

(4-47)
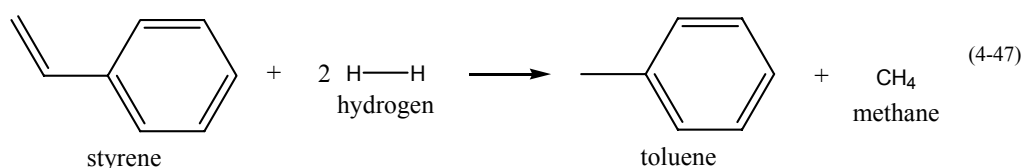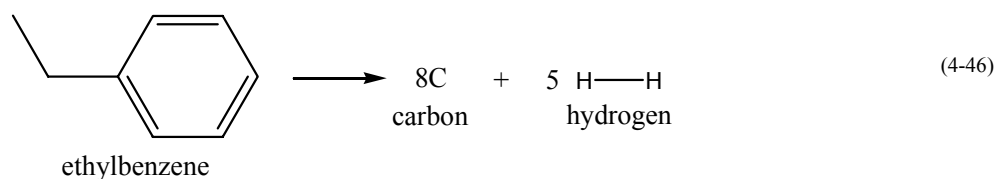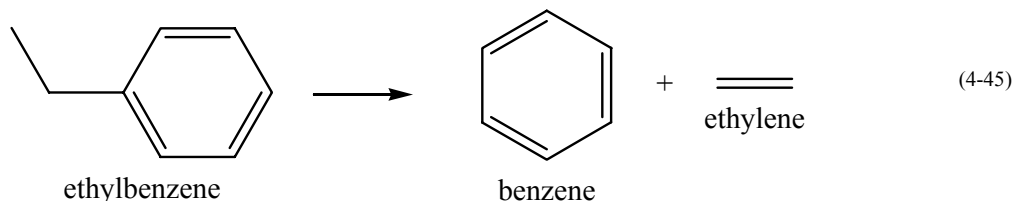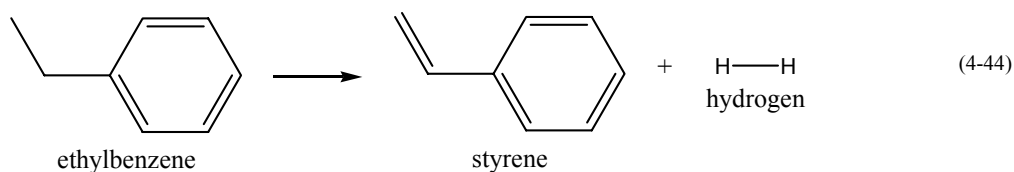
Table 7-42 Description of the Streams in Conventional Styrene Process

Stream Name	Stream Description
Input Streams	
S1071	Ethylbenzene to conventional styrene plant
Output Streams	
S1072	Styrene produced from conventional styrene plant
S1073	Fuel gas produced from conventional styrene plant
S1074	Benzene produced from conventional styrene plant
S1075	Toluene produced from conventional styrene plant
S1076	Carbon produced from conventional styrene plant

B-14-2. Material Balance and Energy Balance

Using the parameters in Table 7-43, the material and energy balances of conventional styrene process are given in Table 7-44.

In Table 7-44, the overall material balance for the whole process is given with the mixture stream expression. For the species material balance obtained using the reaction equations (7-44, 7-45, 7-46 and 7-47), the first equation is for the styrene balance; and the second one is for the benzene balance; the third one is for the toluene

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balance; the fourth one is for the carbon balance; the fifth one is for the H_2 balance; the sixth one is for the C_2H_4 balance; the last one is for the CH_4 balance.

In the overall energy balance, Q_{STY} is heat input of the conventional styrene process in the form of steam to supply enough heat for the endothermic reaction and for the product separation, which is calculated from the energy balance. Q_{out} is the heat output removed by cooling water in heat exchanger and condensers in the conventional styrene process based on the unit of styrene product, 1.4 MJ per lb of styrene (Brown, et al., 1985). In enthalpy functions, the coefficients a_1, a_2, a_3, a_4, a_5, and b_1 for different species are given in Table A-1 in Appendix A in (Xu, 2004).

In the material balance part, there are 9 variables and 9 equations including one dependent one (overall material balance), so the number of degrees of freedom is 1. For the material and energy balances, there are 24 variables and 18 equations including one dependent one (overall material balance), so the number of degrees of freedom is 7.

Table 7-43 Parameters in Conventional Styrene Process

Name	Meaning	Value
SSTS	Selectivity of EB to styrene in conventional styrene process	0.90
SSTB	Selectivity of EB to benzene in conventional styrene process	0.08
SSTC	Selectivity of EB to carbon in conventional styrene process	0.02
SSCTT	Conversion of styrene to toluene in conventional styrene process	0.01
	Conversion of EB in conventional styrene process	100%

Table 7-44 Constraint Equations for Conventional Styrene Process

Material Balance	
Overall	$F_{1071} - (F_{1072} + F_{1073} + F_{1074} + F_{1075} + F_{1076}) = 0$ where $F_{1073} = F_{1073}^{(H_2)} + F_{1073}^{(C_2H_4)} + F_{1073}^{(CH_4)}$
Species	Styrene: $\dfrac{F_{1072}}{mw(styrene)} - \dfrac{F_{1071} \times SSTS \times (1 - SSCTT)}{mw(EB)} = 0$ Benzene: $\dfrac{F_{1074}}{mw(benzene)} - F_{1071} \dfrac{SSTB}{mw(EB)} = 0$ Toluene: $\dfrac{F_{1075}}{mw(toluene)} - F_{1071} \dfrac{SSTS \times SSCTT}{mw(EB)} = 0$ C: $\dfrac{F_{1076}}{mw(C)} - \dfrac{F_{1071} \times SSTC}{mw(EB)} \times 8 = 0$ H_2: $\dfrac{F_{1073}^{(H_2)}}{mw(H_2)} - (F_{1071} \dfrac{SSTS}{mw(EB)} + F_{1071} \dfrac{SSTC \times 5}{mw(EB)} - \dfrac{2F_{1075}}{mw(toluene)}) = 0$

$$C_2H_4: \quad \frac{F_{1073}^{(C_2H_4)}}{mw(C_2H_4)} - \frac{F_{1074}}{mw(benzene)} = 0$$

$$CH_4: \quad \frac{F_{1073}^{(CH_4)}}{mw(CH_4)} - \frac{F_{1075}}{mw(toluene)} = 0$$

Energy Balance

Overall
$$(F_{1072}^{(STYRENE)} / M^{(STYRENE)} H_{1072}^{(STYRENE)} + \sum F_{1073}^{(i)} / M^{(i)} H_{1073}^{(i)}$$
$$+ F_{1074}^{(BENZENE)} / M^{(BENZENE)} H_{1074}^{(BENZENE)} + F_{1075}^{(TOLUENE)} / M^{(TOLUENE)} H_{1075}^{(TOLUENE)}$$
$$+ F_{1076}^{(C)} / M^{(C)} H_{1076}^{(C)}) - F_{1071}^{(EB)} / M^{(EB)} H_{1071}^{(EB)} + Q_{out} F_{1072}^{(STYRENE)} - Q_{STY} = 0$$
$$i = H_2, CH_4, C_2H_4$$

Enthalpy Function
$$H_k^i(T) = (a_1^i + \frac{1}{2}a_2^i T + \frac{1}{3}a_3^i T^2 + \frac{1}{4}a_4^i T^3 + \frac{1}{5}a_5^i T^4 + \frac{b_1^i}{T})RT \quad J/mol$$

$$i = H_2, CH_4, C_2H_4, BENZENE, C$$
$$k = 1073, 1074, 1076$$

$$H_{1071}^{(EB)} = -12300 + 185.572(T - 298.15) \quad J/mol$$

Source: Lide (1990) and NIST (2002)

$$H_{1072}^{(STYRENE)} = 103400 + 183.2(T - 298.15) \quad J/mol$$

Source: NIST (2002)

$$H_{1075}^{(TOLUENE)} = 12000 + 157.09(T - 298.15) \quad J/mol$$

Source: NIST (2002)

B-15. Electric Furnace Phosphoric Acid (Austin, 1984)

The capacity of this process is set as the same as the wet process for phosphoric acid production, 3833 TPD. This process can produce food grade phosphoric acid, and the wastes are $CaSiO_3$ and CO_2.

B-15-1. Process Description

This method uses phosphate rock, sand and coke to produce phosphoric acid as shown in the block diagram in Figure 7.16 with the description of streams shown in Table 7-48. This process produces high purity phosphoric acid which is used in food grade applications. The reaction can be expressed as:

$$CaF_2 \cdot 3Ca_3(PO_4)_2 + 9SiO_2 + 15C = CaF_2 + 6P + 15CO + 9CaSiO_3 \quad (7\text{-}48)$$

$$4P + 5O_2 = 2P_2O_5 \quad (7\text{-}49)$$

$$P_2O_5 + 3H_2O = 2H_3PO_4 \quad (7\text{-}50)$$

or, more simply expressed,

$$Ca_3(PO_4)_2 + 3SiO_2 + 5C + 5O_2 + 3H_2O = 3CaSiO_3 + 2H_3PO_4 + 5CO_2 \quad (7\text{-}51)$$

The phosphate rock was first ground and sized and mixed with sand and coke. Then the mixture is sintered and introduced into the electric furnace. After the mixture is heated and reduced at an elevated temperature, phosphorous vapor is condensed, and

CO is drawn off. Then in a separate step the phosphorus is burned in air and hydrated to become phosphoric acid solution.
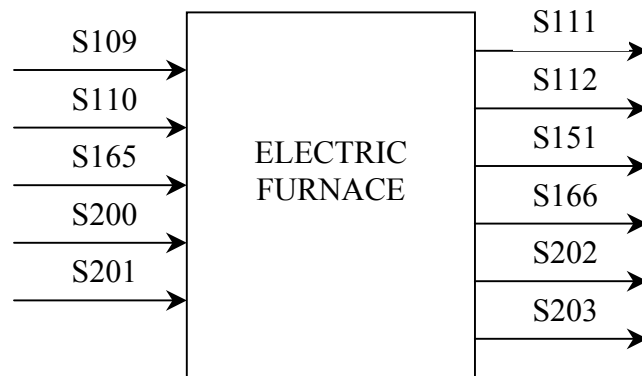
Figure 7.16 Block Diagram of Electric Furnace Process

Table 7-48 Description of Electric Furnace Process (EFP) Streams

Name of Streams	Description
Input Streams	
S109	Ore to EFP
S110	Sand to EFP
S165	C needed in EFP
S200	Air needed for EFP
S201	H_2O needed for EFP
Output Streams	
S111	Production of $CaSiO_3$ from EFP
S112	Production of H_3PO_4 from EFP
S151	Vent gas from EFP
S166	CO_2 produced from C in EFP
S202	CaF_2 produced from EFP
S203	Inert impurity in the ore separated in EFP

B-15-2. Material Balance and Energy Balance

The parameters in the electronic furnace process are shown in Table 7-49 and the constraint equations for the material and energy balances are given in Table 7-50.

Table 7-49 Parameters in Electric Furnace Process, from Austin (1984)

Name	Meaning	Value
CONCPEF	P_2O_5 concentration produced from EFP	0.6156
CONCPOR	P_2O_5 concentration in the rock (weight fraction)	0.365

Table 7-50 Constraint Equations for Electric Furnace Process

Material Balance

Overall

$$(F_{109} + F_{110} + F_{165} + F_{200} + F_{201}) - (F_{112} + F_{111} + F_{166} + F_{151} + F_{202} + F_{203}) = 0$$

where $F_{112} = F_{112}^{(P_2O_5)} + F_{112}^{(H_2O)}$

$$F_{151} = F_{151}^{(N_2)} + F_{151}^{(CO_2)} + F_{151}^{(Ar)}$$

$$F_{200} = F_{200}^{(O_2)} + F_{200}^{(N_2)} + F_{200}^{(CO_2)} + F_{200}^{(Ar)}$$

Species

P_2O_5 : $(CONCPOR)F_{109} - F_{112}^{(P_2O_5)} = 0$

CO_2 : $\dfrac{44.01}{12.01} F_{165} - F_{166} = 0$

SiO_2 : $\dfrac{CONCPOR}{141.94} F_{109} - \dfrac{1}{(60.09)(3)} F_{110} = 0$

C : $\dfrac{CONCPOR}{141.94} F_{109} - \dfrac{1}{(5)(12.01)} F_{165} = 0$

$CaSiO_3$: $\dfrac{1}{(60.09)(3)} F_{110} - \dfrac{1}{(3)(116.17)} F_{111} = 0$

O_2 : $\dfrac{CONCPOR}{141.94} F_{109} - \dfrac{1}{(5)(32)} F_{200}^{(O_2)} = 0$

N_2 : $F_{200}^{(N_2)} - F_{151}^{N_2} = 0$

Ar : $F_{200}^{(Ar)} - F_{151}^{Ar} = 0$

Vent CO_2 : $F_{200}^{(CO_2)} - F_{151}^{CO_2} = 0$

H_2O : $F_{201} - F_{112}^{(H_2O)} = 0$

CaF_2 : $\dfrac{(CONCPOR)(78.08)}{(3)(141.94)} F_{109} - F_{202} = 0$

Impurity : $(1 - \dfrac{(CONCPOR)(310.18)}{141.94}(1 + \dfrac{78.08}{(3)(310.18)}))F_{109} - F_{203} = 0$

Table 7-50 Continued

Energy Balance

Overall	$(\Sigma F_{112}^{(i)} / M^{(i)} H_{112}^{(i)} + \Sigma F_{151}^{(j)} / M^{(j)} H_{151}^{(j)} + F_{166} / M^{(CO_2)} H^{(CO_2)}$

$$+ F_{202} / M^{(CaF_2)} H^{(CaF_2)} + F_{111} / M^{(CaSiO_3)} H^{(CaSiO_3)})$$

$$- (CONCPOR / 141.94 / 3 F_{109}^{(ROCK)} H^{(ROCK)} + F_{110} / M^{(SiO_2)} H_{110}^{(SiO_2)}$$

$$+ F_{165} / M^{(C)} H^{(C)} + \Sigma F_{200}^{(k)} / M^{(k)} H_{200}^{(k)} + F_{201} / M^{(H_2O)} H^{(H_2O)}) + F_{112}^{(P_2O_5)} Q_{out}$$

$$- Q_{EF} = 0$$

where $i = P_2O_5, H_2O$; $j = N_2, Ar, CO_2$; $k = N_2, Ar, CO_2, O_2$

Enthalpy Function

$$H_k^i(T) = (a_1^i + \frac{1}{2} a_2^i T + \frac{1}{3} a_3^i T^2 + \frac{1}{4} a_4^i T^3 + \frac{1}{5} a_5^i T^4 + \frac{b_1^i}{T}) RT \quad J/mol$$

$i = H_2O, N_2, Ar, CO_2, O_2, SiO_2, C$

$k = 110, 112, 151, 165, 166, 200, 201$

$$H^{(P_2O_5)} = (-1278.437)(1000) + 106.014(T - 298.15) J/mol$$

Source: Lide (1982)

$$H^{(CaSiO_3)}(T) = -1584000 + 93(T - 298.15) J/mol$$

Source: Felder and Roussleu (1986)

$$H^{(CaF_2)}(T) = ((-291.5)(1000) + 16.02(T - 298.15))(4.182) J/mol$$

Source: Lide (1982)

$$H^{(ROCK)}(T) = (((-291.5)(1000) + (3)(-984.9)(1000)) + (16.02 + (3)(54.45))$$
$$(T - 298.15))(4.182) \quad J/mol$$

Source: Lide (1982)

In Table 7-50, the overall material balance for the whole process is given with the mixture stream expressions. For the species material balance obtained using the reaction equations (7-48, 7-49, 7-50 and 7-51), the first equation is for the P_2O_5 balance; the second one is for the CO_2 generated from C balance; the third one is for the sand (SiO_2) balance; the fourth one is for the C balance; the fifth one is for the $CaSiO_3$ balance; the sixth one is for the oxygen balance; the seventh one is for the nitrogen balance; the eighth one is for the argon balance; the ninth one is for the carbon dioxide balance from the air input and output part; the tenth one is for the water balance; the eleventh one is for the CaF_2 balance, which is assumed to be inert in the whole process; the last one is for the impurity balance in the phosphate ore, which is assume as an inert in the whole process.

In the overall energy balance, Q_{EF} is the heat input for the electric furnace process in the form of steam and electrictiy, which is calculated from the energy balance. Q_{out} is the heat output removed by cooling water in heat exchangers in the electric furnace based on unit product output, i.e. 10.2 MJ per lb of P_2O_5 (Austin, 1984). In enthalpy functions, the coefficients a_1, a_2, a_3, a_4, a_5, and b_1 for different species are given in Table A-1 in Appendix A in (Xu, 2004).

In the material balance part, there are 20 variables and 20 equations including one dependent equation (overall material balance), so the number of degrees of

freedom is 1. For the material and energy balance, there are 47 variables and 37 equations including the dependent overall material balance, so the number of degrees of freedom is 11.

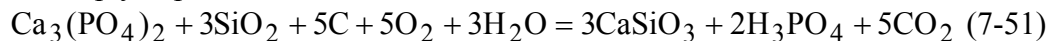B-16. HCl Digestion (Haifa Process) to Produce Phosphoric Acid (Slack, 1968; Baniel, et al., 1962; Baniel and Blumberg, 1959; Austin, 1984)

The capacity of Haifa process is set as the same as the wet process for phosphoric acid production, 3,833 TPD. This process use hydrochloric acid instead of sulfuric acid. The calcium chloride is soluble in phosphoric acid rather than precipitating as calcium sulfate (gypsum) does.

B-16-1. Process Description

The Israel Mining Industries (IMI) first developed the hydrochloric acid process for phosphoric acid production and has operated a demonstration plant in Haifa since 1962 (Slack, 1968). This process has the advantage of using waste or by-product hydrochloric acid, where its disposal is often mandatory for expansion of the parent industry and for which sometimes it is very hard to find an outlet (Baniel, et al., 1962; Baniel and Blumberg, 1959).

Although the digestion of phosphate rock with hydrochloric acid produces phosphoric acid, the product acid includes the soluble byproducts, represented by calcium chloride, fluorine compounds and other impurities. The success of the process is determined by the ease that phosphoric acid can be separated from the highly soluble calcium chloride (Baniel, et al., 1962). Following the separation of solid impurities, the solution is contacted with butyl alcohol or isoamyl alcohol to selectively extract the phosphoric acid and hydrochloric acid, and leave the calcium chloride in the water layer, which is calcium chloride brine treated as a waste. Then, the acids enter the aqueous phase upon contact with demineralized water and separate as a solution of P_2O_5 and HCl. The mixture is then concentrated to phosphoric acid, and HCl in the exhaust vapor from the concentrator is recycled to the system (Slack, 1968). If the phosphate contains fluoride, hydrogen fluoride is either removed from the acid aqueous decomposition mixture prior to the solvent extraction, or extracted into the solvent together with the excess HCl and accompanies the latter when it is being separated from the phosphoric acid (Baniel and Blumberg, 1959).

The main reaction is as Equation 7-52. The block diagram is in Figure 7.17 with stream descriptions from Table 7-51.

$$CaF_2 \cdot 3Ca_3(PO_4)_2 + 20HCl = 10CaCl_2 + 6H_3PO_4 + 2HF \qquad (7\text{-}52)$$
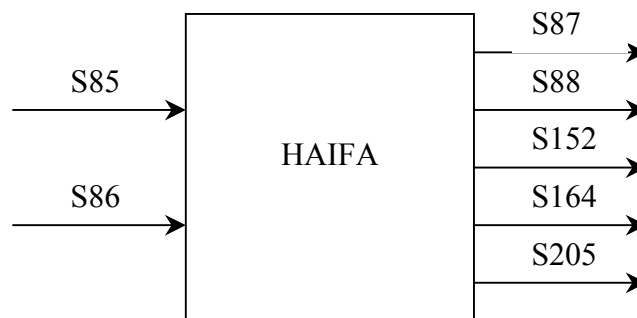
Figure 7.17 Block Diagram of Haifa Process

Table 7-51 Description of Haifa Process Streams

Name of Streams	Description
Input Streams	
S85	Phosphate rock to Haifa process
S86	HCl solution to Haifa process
Output Streams	
S87	Product H_3PO_4 from Haifa process
S88	Production of $CaCl_2$ in Haifa process
S152	Production of inert impurities from Haifa process
S164	Production of HF from Haifa process
S205	Production of water from Haifa process

B-16-2. Material Balance and Energy Balance

The parameters used in the material and energy balance of the Haifa Process are shown in Table 7-52 and the constraint equations are given in Table 7-53.

Table 7-52 Parameters in Haifa Proces, from Slack (1968) and Austin (1984)

Name	Meaning	Value
CONCPHCL	P_2O_5 concentration produced from Haifa process	0.54
CONCHCL	HCl concentration(weight fraction) to Haifa process	0.34
	Overall HCl conversion in Haifa process	1
	$CaF_2 \cdot 3Ca_3(PO_4)_2$ concentration in Haifa process	0.88

In Table 7-53, the overall material balance for the whole process is given with the mixture stream expressions. For the species material balance obtained using the

Table 7-53 Constraint Equations for Haifa Process

Material Balance	

Overall

$(F_{85} + F_{86}) - (F_{87} + F_{88} + F_{152} + F_{164} + F_{205}) = 0$

where $F_{86} = F_{86}^{(HCl)} + F_{86}^{(H_2O)}$

$F_{87} = F_{87}^{(P_2O_5)} + F_{87}^{(H_2O)}$

Species

HCl : $\dfrac{6}{(20)(36.46)} F_{86}^{(HCl)} - \dfrac{2}{141.94} F_{87}^{(P_2O_5)} = 0$

CaCl$_2$: $\dfrac{1}{(20)(36.46)} F_{86}^{(HCl)} - \dfrac{1}{(10)(110.98)} F_{88} = 0$

HF: $\dfrac{1}{(10)(110.98)} F_{88} - \dfrac{1}{(2)(20.01)} F_{164} = 0$

P$_2$O$_5$: $\dfrac{0.88}{1008.62} F_{85} - \dfrac{2}{(141.94)(6)} F_{87}^{(P_2O_5)} = 0$

H$_2$O: $F_{86}^{(H_2O)} - (F_{205} + F_{87}^{(H_2O)} - \dfrac{(3)(18.02)}{141.94} F_{87}^{(P\ O_5)}) = 0$

Energy Balance

Overall

$((F_{164}^{(HF)} / M^{(HF)} H_{164}^{(HF)} + F_{88}^{(CaCl_2)} / M^{(CaCl_2)} H_{88}^{(CaCl_2)} + \Sigma F_{87}^{(i)} / M^{(i)} H_{87}^{(i)}$

$+ F_{205} / M^{(H_2O)} H_{205}^{(H_2O)}) - (F_{86}^{(HCl)} / M^{(HCl)} H_{86}^{(HCl)} + F_{86}^{(H_2O)} / M^{(H_2O)} H_{86}^{(H_2O)}$

$+ 0.88 F_{85} / M^{(ROCK)} H_{85}^{(ROCK)})) - Q_{CH} = 0$

where i = H$_2$O, P$_2$O$_5$

Enthalpy Function

$H_k^i (T) = (a_1^i + \dfrac{1}{2} a_2^i T + \dfrac{1}{3} a_3^i T^2 + \dfrac{1}{4} a_4^i T^3 + \dfrac{1}{5} a_5^i T^4 + \dfrac{b_1^i}{T}) RT$ J/mol

i = H$_2$O, CaCl$_2$, HF

k = 86, 87, 88, 164, 205

$H^{(P_2O_5)} = (-1278.437)(1000) + 106.014(T - 298.15) J / mol$

Source: Lide (1982)

$H^{(ROCK)} (T) = (((-291.5)(1000) + (3)(-984.9)(1000)) + (16.02 + (3)(54.45))$

$(T - 298.15))(4.182)$ J / mol

Source: Lide (1982)

$H^{(HCl)} = (-98.34)(1000) + 73.993(T - 298.15) + \dfrac{1}{2}(-12946E - 01)$

$(T^2 - 298.15^2) + \dfrac{1}{3}(-7.8980E - 05)(T^3 - 298.15^3) + \dfrac{1}{4}(2.6409E - 06)$

$(T^4 - 298.15^4)$

Source: Yaws (1999)

reaction equations (7-52), the first equation is for the HCl balance; the second one is for the $CaCl_2$ balance; the third one is for the HF balance; the fourth one is for the P_2O_5 balance; the last one is for the H_2O balance.

In the overall energy balance, Q_{CH} is the heat input for Haifa process in the form of steam in the heat exchanger, which is calculated from the energy balance. In enthalpy functions, the coefficients a_1, a_2, a_3, a_4, a_5, and b_1 for different species are given in Table A-1 in Appendix A in (Xu, 2004).

In the material balance part, there are 11 variables and 10 equations, so the number of degrees of freedom is 1. For the material and energy balance, there are 26 variables and 19 equations, so the number of degrees of freedom is 7.

B-17. Gypsum Reuse - Sulfur and Sulfur Dioxide Recovery (Paisley, 2000; Kosyl'kov and Rogachev, 1983; Campbell and Fisher, 1971)

The gypsum produced from wet process for phosphoric acid production can be reused to recover sulfur and sulfur dioxide. There are two processes, one is sulfur dioxide recovery; and the other is sulfur and sulfur dioxide recovery. Neither process is commercialized now because of sulfur from other sources and process energy requirements. These two processes are incorporated in the chemical complex, and they may become important in the future.

B-17-1. Sulfur Dioxide Recovery from Gypsum (Paisley, 2000; Kosyl'kov and Rogachev, 1983)

The capacity of this process was set to be 1,970,000 metric tons per year of SO_2, which is based on the consuming all of gypsum produced from the wet process for phosphoric acid.

B-17-1-1. Process Description

Crushed waste gypsum is dried and dehydrated to anhydride in a dryer or calciner (Equation 7-53). Then the anhydride is reduced to CaS by means of a reducing agent such as a medium BTU wood gas whose composition is in Table 7-54. The reactions of CO, H_2 and CH_4 are shown in Equation 7-54, 7-55 and 7-56. The preferred temperature for reducing the calcium sulfate is about $1,500\,°F$ to about $1,600\,°F$. CH_4 conversion is 56%.

After separating CaS from the gaseous by-products of the reactions, CaS is oxidized with air to produce calcium oxide and sulfur dioxide that is the feed to the sulfuric acid plant (Equation 7-57) (Paisley, 2000). The block diagram is Figure 7.18 with stream description in Table 7-55.

$$CaSO_4 \cdot 2H_2O \rightarrow CaSO_4 + 2H_2O \qquad \text{Dehydration} \quad (7\text{-}53)$$
$$CaSO_4 + 4CO \rightarrow CaS + 4CO_2 \qquad \text{Reduction} \quad (7\text{-}54)$$
$$CaSO_4 + 4H_2 \rightarrow CaS + 4H_2O \qquad \text{Reduction} \quad (7\text{-}55)$$
$$CaSO_4 + CH_4 \rightarrow CaS + CO_2 + 2H_2O \qquad \text{Reduction} \quad (7\text{-}56)$$
$$CaS + O_2 + CaSO_4 \rightarrow 2CaO + 2SO_2 \qquad \text{Oxidation} \quad (7\text{-}57)$$
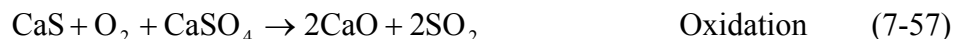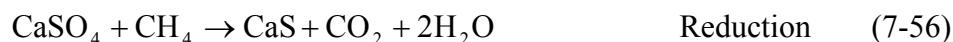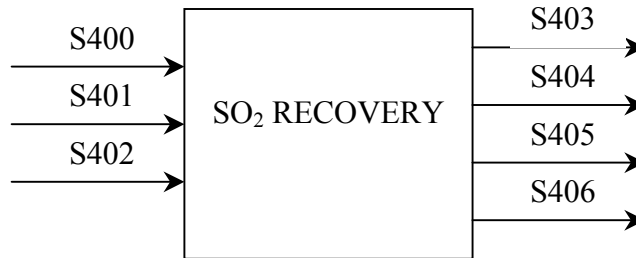
Figure 7.18 Block Diagram of SO₂ Recovery Plant

Table 7-54 Parameters in Sulfur Dioxide Recovery from Gypsum, from Paisley (2000)

Parameters	
CH$_4$ conversion	0.56
CO conversion	1
H$_2$ conversion	1
Wood gas composition (Volume %)	
H$_2$	17.76
CO	50.09
CO$_2$	9.88
CH$_4$	16.76
C$_2$H$_6$	5.51

Table 7-55 Description of Process Streams in SO₂ Recovery Plant

Name of Streams	Description
Input Streams	
S400	Gypsum to sulfur dioxide recovery plant
S401	Wood gas to sulfur dioxide recovery plant
S402	Air to sulfur dioxide recovery plant
Output Streams	
S403	Vent gas from sulfur dioxide recovery plant
S404	Cao produced from sulfur dioxide recovery plant
S405	SO$_2$ produced from sulfur dioxide recovery plant
S406	Water produced from sulfur dioxide recovery plant

B-17-1-2. Material Balance and Energy Balance

Using the parameters in Table 7-54 the material balance and energy balance of the SO₂ recovery plant are given in Table 7-56.

In Table 7-56, the overall material balance for the whole process is given with the mixture stream expressions. For the species material balance obtained using the reaction equations (7-53, 7-54, 7-55, 7-56 and 7-57), the first equation is for the crystal water balance from the gypsum; the second one is for the water balance produced from the reactions; the third one is for the gypsum balance; the fourth one is for the CaO balance; the fifth one is for the SO_2 balance; the sixth one is for the O_2 balance; the seventh one is for CH_4 balance; the eighth one is for the Ar balance; the ninth one is for CO_2 balance; the tenth one is for the N_2 balance; the last one is for the C_2H_6 balance.

Table 7-56 Constraint Equations for Sulfur Dioxide Recovery from Gypsum

Material Balance

Overall
$$(F_{400} + F_{401} + F_{402}) - (F_{403} + F_{404} + F_{405} + F_{406}) = 0$$

where
$$F_{401} = F_{401}^{(H_2)} + F_{401}^{(CO)} + F_{401}^{(CO_2)} + F_{401}^{(CH_4)} + F_{401}^{(C_2H_6)}$$

$$F_{402} = F_{402}^{(O_2)} + F_{402}^{(N_2)} + F_{402}^{(CO_2)} + F_{402}^{(Ar)}$$

$$F_{403} = F_{403}^{(N_2)} + F_{403}^{(Ar)} + F_{403}^{(CO_2)} + F_{403}^{(CH_4)} + F_{403}^{(C_2H_6)} + F_{403}^{(H_2O)}$$

Species

H_2O-1:
$$\frac{(2)(18.02)}{172.18} F_{400} - F_{406} = 0$$

H_2O-2:
$$\frac{(2)(0.56)}{16.05} F_{401}^{(CH_4)} + \frac{1}{2.02} F_{401}^{(H_2)} - \frac{1}{18.02} F_{403}^{(H_2O)} = 0$$

Gypsum:
$$\frac{1}{172.18} F_{400} - \frac{0.5}{56.08} F_{404} - (\frac{1}{(28.01)(4)} F_{401}^{(CO)} + \frac{1}{(2.02)(4)} F_{401}^{(H_2)}$$
$$+ \frac{0.56}{16.05} F_{401}^{(CH_4)}) = 0$$

CaO:
$$\frac{1}{56.08} F_{404} - \frac{1}{172.18} F_{400} = 0$$

SO_2:
$$\frac{1}{172.08} F_{400} - \frac{1}{64.06} F_{405} = 0$$

O_2:
$$\frac{1}{32} F_{402}^{(O_2)} - \frac{0.5}{56.08} F_{404} = 0$$

CH_4:
$$(1 - 0.56)F_{401}^{(CH_4)} - F_{403}^{(CH_4)} = 0$$

Ar:
$$F_{403}^{(Ar)} - F_{402}^{(Ar)} = 0$$

CO_2:
$$F_{403}^{(CO_2)} - (\frac{44.01}{28.01} F_{401}^{(CO)} + \frac{(0.56)(44.01)}{16.05} F_{401}^{(CH_4)} + F_{402}^{(CO_2)} + F_{401}^{(CO_2)}) = 0$$

N_2:
$$F_{403}^{(N_2)} - F_{402}^{(N_2)} = 0$$

C_2H_6:
$$F_{403}^{(C_2H_6)} - F_{401}^{(C_2H_6)} = 0$$

Energy Balance

Overall	$(\Sigma F_{403}^{(i)} / M^{(i)} H_{403}^{(i)} + F_{404} / M^{(CaO)} H_{404}^{(CaO)} + F_{405} / M^{(SO_2)} H_{405}^{(SO_2)}$
	$+ F_{406} / M^{(H_2O)} H_{406}^{(H_2O)}) - (F_{400} / M^{(GYP)} H_{400}^{(GYP)} + \Sigma F_{401}^{(j)} / M^{(j)} H_{401}^{(j)}$
	$+ \Sigma F_{402}^{k} / M^{(k)} H_{402}^{(k)}) + Q_{out} F_{400} - Q_{SR} = 0$

Table 7-56 Continued

Energy Balance (Continued)	
Overall	$i = CO_2, N_2, Ar, H_2O, CH_4, C_2H_6$; $j = CO_2, CH_4, C_2H_6, H_2, CO$; $k = CO_2, N_2, Ar, O_2$
Enthalpy Function	$H_k^i(T) = (a_1^i + \frac{1}{2} a_2^i T + \frac{1}{3} a_3^i T^2 + \frac{1}{4} a_4^i T^3 + \frac{1}{5} a_5^i T^4 + \frac{b_1^i}{T}) RT$ J/mol
	$\quad i = CO_2, N_2, Ar, H_2O, CH_4, C_2H_6, H_2, CO, O_2, CaO, SO_2,$
	$\quad\ k = 401, 402, 403, 404, 405, 406$
	$H_k^{(GYP)}(T) = ((-483.42)(1000) + (44.46)(T - 298.15))(4.182)$ J/mol
	k=400
	Source: Lide (1982).

In the overall energy balance, Q_{SR} is heat input of the SO_2 recovery from gypsum plant in the form of steam in heat exchanger, heater and dryer, which is calculated from the energy balance. Q_{out} is heat output removed by cooling water in heat exchanger and condenser in the SO_2 recovery from gypsum plant based on the unit of gypsum feedstock, 2.2 MJ per lb of gypsum (Kosyl'kov and Rogachev, 1983). In enthalpy functions, the coefficients a_1, a_2, a_3, a_4, a_5, and b_1 for different species are given in Table A-1 in Appendix A in (Xu, 2004).

In the material balance part, there are 22 variables and 22 equations including the dependent overall mass balance, so the number of degrees of freedom is 1. For the material and energy balance, there are 49 variables and 42 equations including the dependent overall mass balance, so the number of degrees of freedom is 8.

B-17-2. Sulfur and Sulfur Dioxide Recovery from Gypsum (Campbell and Fisher, 1971; Kosyl'kov and Rogachev, 1983)

The capacity of this process was set to be 988,000 metric tons per year of S, which is based on the consuming all of gypsum produced from the wet process for phosphoric acid.

B-17-2-1. Process Description

Crushed gypsum, having particle sizes within the approximately range of 0.25-1.50 inch, is first dehydrated by heating (Equation 7-58) (Campbell and Fisher, 1971).

$$CaSO_4 \cdot 2H_2O \rightarrow CaSO_4 + 2H_2O \qquad (7\text{-}58)$$
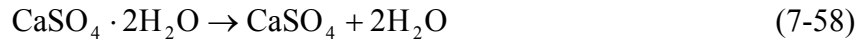
Secondly, the dehydrated calcium sulfate is reacted with the reducing gas (Equation 7-59, 7-60, 7-61 and 7-62).

$$CaSO_4 + 4CO \rightarrow CaS + 4CO_2 \qquad (7\text{-}59)$$

$$CaSO_4 + 4H_2 \rightarrow CaS + 4H_2O \qquad (7\text{-}60)$$

$$CaSO_4 + H_2 \rightarrow CaO + SO_2 + H_2O \qquad (7\text{-}61)$$

$$CaSO_4 + CO \rightarrow CaO + SO_2 + CO_2 \qquad (7\text{-}62)$$
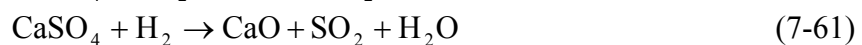
Then the gas product contains SO_2, CO_2 and H_2O. The SO_2 is separated and becomes the feed to sulfuric acid plant. The reactor product CaO and CaS are quenched in water, ground to a fine slurry and carried to a gas-liquid reactor where it reacts with CO_2 supplied by the recover gas stream from a later stage in the process, and the reactions are the following Equations (7-63, 7-64 and 7-65).

$$CaO + H_2O \rightarrow Ca(OH)_2 \qquad (7\text{-}63)$$

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 \qquad (7\text{-}64)$$

$$CaS + H_2O + CO_2 \rightarrow CaCO_3 + H_2S \qquad (7\text{-}65)$$

To convert the gaseous product H_2S to elemental sulfur, the conventional Claus process is employed with additional air input according to the following Equations (7-7 and 7-8).

$$H_2S + 1.5O_2 \rightarrow SO_2 + H_2O \qquad (7\text{-}7)$$

$$2H_2S + SO_2 \rightarrow 3S + 2H_2O \qquad (7\text{-}8)$$

The block diagram is Figure 7.19 with stream description in Table 7-57.
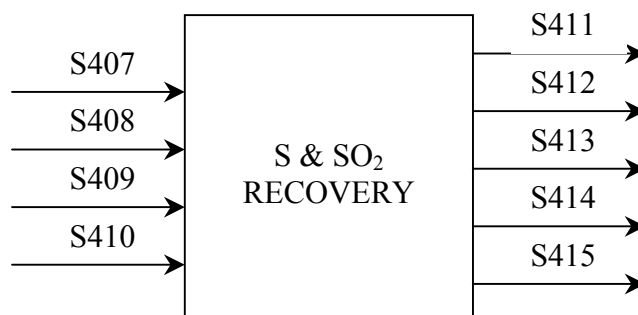
Figure 7.19 Block Diagram of S and SO_2 Recovery Plant

Table 7-57 Description of Process Streams in S and SO_2 recovery Plant

Name of Streams	Description
Input Streams	
S407	Reducing gas to sulfur and sulfur dioxide recovery plant
S408	Gypsum to sulfur and sulfur dioxide recovery plant
S409	H_2O to sulfur and sulfur dioxide recovery plant
S410	Air to sulfur and sulfur dioxide recovery plant
Output Streams	
S411	SO_2 generated from sulfur and sulfur dioxide recovery plant
S412	Sulfur generated from sulfur and sulfur dioxide recovery plant
S413	Vent generated from sulfur and sulfur dioxide recovery plant
S414	$CaCO_3$ generated from sulfur and sulfur dioxide recovery plant
S415	H_2O generated from sulfur and sulfur dioxide recovery plant

B-17-2-2. Material Balance and Energy Balance

Using the parameters in Table 7-58 the material balance and energy balance of the S and SO_2 recovery plant are given in Table 7-59.

In Table 7-59, the overall material balance for the whole process is given with the mixture stream expressions. For the species material balance obtained using the reaction equations (7-7, 7-8, 7-58, 7-59, 7-60, 7-61, 7-62, 7-63, 7-64 and 7-65), the first equation is for the $CaCO_3$ balance; the second one is for the SO_2 balance; the third one is for the H_2 balance; the fourth one is for the S balance; the fifth one is for the gypsum balance; the sixth one is for the H_2O balance; the seventh one is for the CO_2 balance; the eighth one is for the O_2 balance; the ninth one is for N_2 balance; the last one is for the Ar balance.

Table 7-58 Parameters in S and SO_2 Recovery from Gypsum Plant, from Campbell and Fisher (1971)

Parameters	
Ratio of Slurry water to gypsum	420:100
Ratio of H_2 and CO for CaO to those for CaS	1:8
Reduce gas composition (Volume %)	
H_2	39.5
CO	39.5
H_2O	13.2
CO_2	7.8

In the overall energy balance, Q_{SSR} is heat input of the S and SO_2 recovery from gypsum plant in the form of steam in heat exchanger and heater, which is calculated from the energy balance. Q_{out1} is one part of heat output removed by cooling water in heat exchanger and condenser in the S and SO_2 recovery plant based on the unit of SO_2 product, 6 MJ per lb of SO_2 (Kosyl'kov and Rogachev, 1983). Q_{out2} is another part of heat output removed by cooling water in heat exchanger and condenser in the S and SO_2 recovery plant based on the unit of S product, 8.6 MJ per lb of S (Kosyl'kov and Rogachev, 1983). In enthalpy functions, the coefficients a_1, a_2, a_3, a_4, a_5, and b_1 for different species are given in Table A-1 in Appendix A in (Xu, 2004).

In the material balance part, there are 20 variables and 20 equations including the dependent overall mass balance, so the number of degrees of freedom is 1. For the

Table 7-59 Constraint Equations for S and SO_2 Recovery from Gypsum Plant

Material Balance	
Overall	$(F_{407} + F_{408} + F_{409} + F_{410}) - (F_{411} + F_{412} + F_{413} + F_{414} + F_{415}) = 0$
	where $F_{407} = F_{407}^{(H_2)} + F_{407}^{(CO)} + F_{407}^{(CO_2)} + F_{407}^{(H_2O)}$

$$F_{410} = F_{410}^{(O_2)} + F_{410}^{(N_2)} + F_{410}^{(CO_2)} + F_{410}^{(Ar)}$$

$$F_{413} = F_{413}^{(N_2)} + F_{413}^{(Ar)} + F_{413}^{(CO_2)}$$

Species

CaCO$_3$: $\dfrac{1}{172.18}F_{408} - \dfrac{1}{100.09}F_{414} = 0$

SO$_2$: $\dfrac{1}{(2.02)(9)}F_{407}^{(H_2)} + \dfrac{1}{(28.01)(9)}F_{407}^{(CO)} - \dfrac{1}{64.06}F_{411} = 0$

H$_2$: $\dfrac{8}{(2.02)(9)(4)}F_{407}^{(H_2)} + \dfrac{8}{(28.01)(9)(4)}F_{407}^{(CO)} - \dfrac{1}{32.06}F_{412} = 0$

S: $\dfrac{1}{172.18}F_{408} - (\dfrac{1}{64.06}F_{411} + \dfrac{1}{32.06}F_{412}) = 0$

Gypsum: $\dfrac{100}{18.02}F_{409} - \dfrac{420}{172.18}F_{408} = 0$

H$_2$O: $F_{407}^{(H_2O)} + \dfrac{(18.02)(2)}{172.18}F_{408} + \dfrac{18.02}{2.02}F_{407}^{(H_2)} + F_{409} - F_{415} = 0$

CO$_2$: $F_{407}^{(CO_2)} + \dfrac{44.01}{28.01}F_{407}^{(CO)} - \dfrac{44.01}{100.09}F_{414} + F_{410}^{(CO_2)} - F_{413}^{(CO_2)} = 0$

O$_2$: $\dfrac{1}{32}F_{410}^{(O_2)} - \dfrac{0.5}{32.06}F_{412} = 0$

N$_2$: $F_{413}^{(N_2)} - F_{410}^{(N_2)} = 0$

Ar: $F_{413}^{(Ar)} - F_{410}^{(Ar)} = 0$

Energy Balance

Overall

$(F_{411}/M^{(SO_2)}H_{411}^{(SO_2)} + F_{412}/M^{(S)}H_{412}^{(S)} + \Sigma F_{413}^{(i)}/M^{(i)}H_{413}^{(i)}$

$+ F_{414}/M^{(CaCO_3)}H_{414}^{(CaCO_3)} + F_{415}/M^{(H_2O)}H_{415}^{(H_2O)}) - (\Sigma F_{407}^{(j)}/M^{(j)}H_{407}^{(j)}$

$+ F_{408}/M^{(GYP)}H_{408}^{(GYP)} + F_{409}/M^{(H_2O)}H_{409}^{(H_2O)} + \Sigma F_{410}^{(k)}/M^{(k)}H_{410}^{(k)}) + Q_{out1}F_{411}$

$+ Q_{out2}F_{412} - Q_{SSR} = 0$

i = N$_2$, CO$_2$, Ar; j = CO$_2$, H$_2$, CO, H$_2$O; k = N$_2$, CO$_2$, Ar, O$_2$

Enthalpy Function

$H_k^i(T) = (a_1^i + \dfrac{1}{2}a_2^i T + \dfrac{1}{3}a_3^i T^2 + \dfrac{1}{4}a_4^i T^3 + \dfrac{1}{5}a_5^i T^4 + \dfrac{b_1^i}{T})RT$ J/mol

i = CO$_2$, N$_2$, Ar, H$_2$O, H$_2$, CO, O$_2$, SO$_2$, S, CaCO$_3$

k = 407, 409, 410, 411, 412, 413, 414, 415

$H_k^{(GYP)}(T) = ((-483.42)(1000) + (44.46)(T - 298.15))(4.182)$ J/mol

k=408; Source: Lide (1982).

material and energy balance, there are 47 variables and 38 equations including the dependent overall mass balance, so the number of degrees of freedom is 10.

B-18. Acetic Acid (New Process) (Taniguchi, et al., 1998; Zerella, et al., 2003; Indala, 2004; Louisiana Chemical & Petroleum Products List, 1998)

There are two acetic acid processes in the chemical complex superstructure, one is conventional acetic acid plant where acetic acid produced from methanol and carbon monoxide in the base case; and the other is a potentially new acetic acid plant which uses methane and carbon dioxide as feedstock. The detailed description of the new process is given below.

The production capacity of this process was selected to be 8,180 metric tons per year (Indala, 2004). This is based on the Dow Chemical Company, an acetic acid plant located in Hahnville, LA, with the production capacity of 18 million pouns per year (8,160 metric tons per year) (Louisiana Chemical & Petroleum Products List, 1998).

B-18-1. Process Description

Acetic acid can be made by direct conversion of carbon dioxide and methane to acetic acid (Equation 7-66) (Taniguchi, et al., 1998; Zerella, et al., 2003). The block diagram is shown in Figure 7.20 with the stream definitions in Table 7-60.

$$CO_2 + CH_4 = CH_3COOH \qquad \Delta H° = 36 \text{ KJ/mol} \qquad (7\text{-}66)$$

Figure 7.20 Block Diagram of New Acetic Acid Plant

Table 7-60 Description of Process Streams in New Acetic Acid Plant

Name of Streams	Description
Input Streams	
S700	CO_2 to new acetic acid plant
S701	Natural gas to new acetic acid plant
Output Streams	
S702	Production of acetic acid from new acetic acid plant

B-18-2. Material Balance and Energy Balance

Using the parameters in Table 7-61 the material balance and energy balance of new acetic acid plant are shown in Table 7-62.

In Table 7-62, the overall material balance for the whole process is given first. For the species material balance obtained using the reaction equation (7-66), the first equation is for the CO_2 balance; and the second one is for the CH_4 balance.

In the overall energy balance, Q_{AA2} is heat input of the new acetic acid plant in the form of steam in heat exchanger to supply the heat needed for the endothermic reaction (Equation 7-66) and distillation column reboiler for heating reactants and product separation, which is calculated from the energy balance. Q_{out} is heat output removed by cooling water in heat exchanger and distillation column condenser for

cooling reactants and product separation in the new acetic acid plant, based on the unit of acetic acid product, 558 KJ per lb of acetic acid (Indala, 2004). In enthalpy functions, the coefficients a_1, a_2, a_3, a_4, a_5, and b_1 for different species are given in Table A-1 in Appendix A in (Xu, 2004).

In the material balance part, there are 3 variables and 3 equations including the dependent overall mass balance, so the number of degrees of freedom is 1. For the material and energy balance, there are 10 variables and 7 equations including the dependent overall mass balance, so the number of degrees of freedom is 4.

Table 7-61 Parameters in New Acetic Acid Production

Name	Meaning	Value
	CO_2 utilization	1.0
	CH_4 utilization	1.0

Table 7-62 Constraint Equations for New Acetic Acid Production

Material Balance	
Overall	$F_{700} + F_{701} - F_{702} = 0$
Species	CO_2: $\dfrac{1}{44.01}F_{700} - \dfrac{1}{60.06}F_{702} = 0$
	CH_4: $\dfrac{1}{16.05}F_{701} - \dfrac{1}{60.06}F_{702} = 0$
Energy Balance	
Overall	$F_{702}^{(aceticacid)}/M^{(aceticacid)}H_{702}^{(aceticacid)} - (F_{700}^{(CO_2)}/M^{(CO_2)}H_{700}^{(CO_2)}$
	$+ F_{701}^{(CH_4)}/M^{(CH_4)}H_{702}^{(CH_4)}) + Q_{out}F_{702}^{(aceticacid)} - Q_{AA2} = 0$
Enthalpy Function	$H_k^i(T) = (a_1^i + \dfrac{1}{2}a_2^i T + \dfrac{1}{3}a_3^i T^2 + \dfrac{1}{4}a_4^i T^3 + \dfrac{1}{5}a_5^i T^4 + \dfrac{b_1^i}{T})RT$ J/mol
	$i = CO_2, CH_4; k = 700, 701$
	$H_k^{(aceticacid)}(T) = ((-115.8)(1000) + (29.7)(T - 298.15))(4.185)$ J/mol
	k=702
	Source: Lide (1982).

C-5. Ethylbenzene (EB) Dehydrogenation with CO_2 to Styrene (New Styrene Process) (Sakurai, et al., 2000; Chang, et al., 1998; Indala, 2004; Mimura, et al., 1998; Louisiana Chemical & Petroleum Products List, 1998)

There are several potentially new processes that use CO_2 for the production of styrene available (Sakurai, et al., 2000; Chang, et al., 1998; Mimura, et al., 1998). After detailed comparison using HYSYS simulation and economic evaluation (Indala,

2004), a potentially new styrene process by Mimura, et al. (1998) was integrated into the chemical complex. The capacity of this process is set to be 362,000 metric tons per year. For styrene production, the production rate of Deltech Corporation in Baton Rouge plant, 800 million pounds per year (362,000 metric tons per year), was used in the superstructure (Louisiana Chemical & Petroleum Products List, 1998).

B-18-1. Process Description

A new method for the production of styrene through dehydrogenation of ethylbenzene in the presence of carbon dioxide was described by Mimura, et al. (1998). The Fe/Ca/Al oxides catalyst exhibited high activity in the presence of CO_2. The reactor operated at 580°C and 1 atm pressure. The ratio of CO_2 to EB in the feedstock input is 9:1. The observed yield of styrene was 70%, and the selectivity to styrene was 100%. The following reaction occurs in the reactor.

$$C_6H_5\text{-}C_2H_5 + CO_2 \rightarrow C_6H_5\text{-}C_2H_3 + CO + H_2O \qquad (7\text{-}67)$$
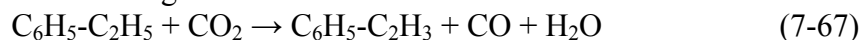
The block diagram of new styrene process is in Figure 7.21 with the stream description in Table 7-63.
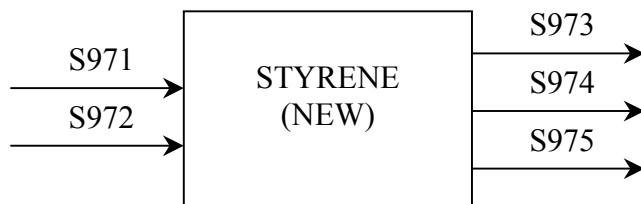
Figure 7.21 Block Diagram of New Styrene Process

B-18-2. Material Balance and Energy Balance

Using the parameters in Table 7-64, the material and energy balances of new styrene process are given in Table 7-65.

In Table 7-65, the overall material balance for the whole process is given first. For the species material balance obtained using the reaction equations (7-67), the first equation is for the CO balance; and the second one is for the H_2O balance; the third one is for the CO_2 balance; the last one is for the EB balance.

Table 7-63 Description of the Streams in New Styrene Process

Stream Name	Stream Description
Input Streams	
S971	Ethylbenzene to new styrene process
S972	Carbon dioxide to new styrene process
Output Streams	
S973	Carbon monoxide produced from new styrene process
S974	Styrene produced from new styrene process
S975	Water produced from new styrene plant

In the overall energy balance, Q_{NSTYB} is heat input in the form of steam in heat exchanger to supply the heat for the endothermic reaction and product separation of the new styrene process, which is calculated from the energy balance. Q_{out} is the heat output removed by cooling water in heat exchanger and condenser for product separation in the new styrene process based on the unit of styrene product, 3 MJ per lb of styrene (Indala, 2004). In enthalpy functions, the coefficients a_1, a_2, a_3, a_4, a_5, and b_1 for different species are given in Table A-1 in Appendix A in (Xu, 2004).

In the material balance part, there are 5 variables and 5 equations including one dependent one (overall material balance), so the number of degrees of freedom is 1. For the material and energy balances, there are 16 variables and 11 equations including one dependent one (overall material balance), so the number of degrees of freedom is 6.

Table 7-64 Parameters in New Styrene Process

Name	Meaning	Value
	Conversion of EB in new styrene process	100%
	Selectivity of EB to styrene in new styrene process	100%

Table 7-65 Constraint Equations for New Styrene Process

Material Balance	
Overall	$(F_{971} + F_{972}) - (F_{973} + F_{974} + F_{975}) = 0$
Species	CO: $\dfrac{F_{973}}{mw(CO)} - \dfrac{F_{974}}{mw(styrene)} = 0$
	H_2O: $\dfrac{F_{975}}{mw(H_2O)} - \dfrac{F_{974}}{mw(styrene)} = 0$
	CO_2: $\dfrac{F_{974}}{mw(styrene)} - \dfrac{F_{972}}{mw(CO_2)} = 0$
	EB: $\dfrac{F_{974}}{mw(styrene)} - \dfrac{F_{971}}{mw(EB)} = 0$
Energy Balance	
Overall	$(F_{973}^{(CO)} / M^{(CO)} H_{973}^{(CO)} + F_{974}^{(STYRENE)} / M^{(STYRENE)} H_{974}^{(STYRENE)}$
	$+ F_{975}^{(H_2O)} / M^{(H_2O)} H_{975}^{(H_2O)}) - (F_{971}^{(EB)} / M^{(EB)} H_{971}^{(EB)} + F_{972}^{(CO_2)} / M^{(CO_2)} H_{972}^{(CO_2)})$
	$+ Q_{out} F_{974}^{(STYRENE)} - Q_{NSTYB} = 0$
Enthalpy Function	$H_k^i(T) = (a_1^i + \dfrac{1}{2} a_2^i T + \dfrac{1}{3} a_3^i T^2 + \dfrac{1}{4} a_4^i T^3 + \dfrac{1}{5} a_5^i T^4 + \dfrac{b_1^i}{T})RT$ J/mol
	$i = CO_2, CO, H_2O$

$$k = 972, 973, 975$$

$$H_{1071}^{(EB)} = -12300 + 185.572(T - 298.15) \text{ J/mol}$$

Source: Lide (1990) and NIST (2002)

$$H_{1072}^{(STYRENE)} = 103400 + 183.2(T - 298.15) \text{ J/mol}$$

Source: NIST (2002)

B-18-3. Comparison between Conventional and New Styrene Processes

Mimura, et al. (1998) gave a detailed comparison between the conventional and potentially new styrene processes. On one hand the potentially new process would operate at 580°C whereas the conventional process operates at over 630°C. On the other hand, the energy requirement in the new styrene process (about 6.3×10^8 cal/t-styrene) could be much lower than that for the conventional process (about 1.5×10^9 cal/t-styrene), mainly because a large quantity of latent heat of water condensation cannot be recovered in the conventional process. In general, the potentially new styrene process using CO_2 with lower reaction temperature would have lower energy requirement compared to the existing conventional process.

B-19. Methanol (New Processes) (Pellegrino, 2000; Inui, 2002; Nerlov and Chorkendorff, 1999; Omata, et al., 2002; Toyir, et al., 1998; Sahibzada, et al., 1998; Ushikoshi, et al., 1998; Nomura, et al., 1998; Jun, et al., 1998; Mabuse, et al., 1998; Fukui, et al., 1998; Hara, et al., 1998a; Bill, et al., 1998; Bonivardi, et al., 1998; Hirano, et al., 1998; Indala, 2004; Louisiana Chemical & Petroleum Products List, 1998)

Pellegrino (2000) reported that methanol is in the list developed by Pacific Northwest National Laboratory (PNNL) with a potential energy savings of 37 trillion BTUs per year through improved catalysts. The conventional processes for methanol include production from synthesis gas. Following is a summary of experimental studies that use carbon dioxide to produce methanol.

Inui (2002) described four ways for the synthesis of methanol by CO_2 hydrogenation using multifunctional catalysts (Cu-Zn-Cr-Al mixed oxide) at different temperature and pressure (Equation 7-68). However, the conversions and selectivities are low in the experimental studies, and they require more hydrogen than that required in the conventional process. The catalysts used in these studies were not commercial catalysts (Cu-Zn-Cr mixed oxide) for methanol production.

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \qquad \Delta H^o = \text{-49 KJ/mol}, \Delta G^o = 3 \text{ KJ/mol} \quad (7\text{-}68)$$

Nerlov and Chorkendorff (1999) described a laboratory scale process for the synthesis of methanol from CO_2 and H_2 over Cu(100) catalysts at 543K and 1.5 atm (Equation 7-68). They also reported the use of Ni/Cu(100) catalyst operated at the same temperature and pressure but the reaction mixture contained CO, CO_2 and H_2 (Equation 7-68 and 7-22).

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta H^o = \text{-41 KJ/mol}, \Delta G^o = \text{-29 KJ/mol} \quad (7\text{-}22)$$
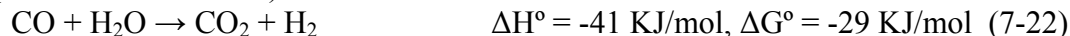
Omata, et al. (2002) described methanol synthesis from CO_2-containing synthesis gas over Cu-Mn catalysts supported on $ZnrO_2$ and TiO_2 in a flow type fixed bed reactor at 250°C and 10 atm (Equation 7-68 and 7-22).

Toyir, et al. (1998) gave the methanol synthesis method from CO_2 hydrogenation over Raney Cu-Zr catalyst leached with aqueous solution of zincate (NaOH + ZnO) in a flow reactor at a temperature of 523K and at a pressure of 50 atm (Equation 7-68 and 7-32). The ratio of hydrogen to carbon dioxide in the feed was 3:1 and the space velocity was 18000 h^{-1}.

$$CO_2 + H_2 \rightarrow CO + H_2O \qquad \Delta H^o = 41 \text{ KJ/mol}, \Delta G^o = 29 \text{ KJ/mol} \quad (7\text{-}32)$$

Sahibzada, et al. (1998) described a laboratory methanol process from CO_2 and H_2 over Pd promoted $Cu/ZnO/Al_2O_3$ catalysts in an internal recycle reactor (300 cm^3 volume, 100cm^3 catalyst basket) at 250°C and 5 MPa (Equation 7-68 and 7-32). The ratio of hydrogen to carbon dioxide in the feed gas was 4:1.

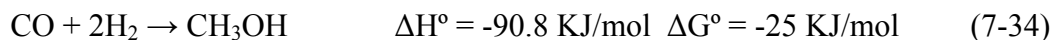Ushikoshi, et al. (1998) reported a pilot methanol plant from CO_2 and H_2 over a multi-component catalyst ($Cu/ZnO/ZrO_2/Al_2O_3/Ga_2O_3$) at 523 K and 5 MPa (Equation 7-68, 7-32 and 7-34). The ratio of hydrogen to carbon dioxide in the feed gas was 3:1.

$$CO + 2H_2 \rightarrow CH_3OH \qquad \Delta H^o = -90.8 \text{ KJ/mol} \quad \Delta G^o = -25 \text{ KJ/mol} \qquad (7\text{-}34)$$

Nomura, et al. (1998) described the hydrogenation of carbon dioxide over Fe promoted Cu based catalysts. $Fe\text{-}CuO\text{-}ZnO/TiO_2$ catalyst was used in this research. The reaction was carried out at 553 K, 1 MPa (10 atm), and W/F_{CO2} = 570 kg-cat-s/mol. The ratio of hydrogen to CO_2 in the feed gas was 4:1.

Jun, et al. (1998) reported hydrogenation of CO_2 for methanol and dimethyl ether over hybrid catalyst of $Cu/ZnO/Cr_2O_3$ and CuNaY zeolite at 523K and 30atm (Equation 7-68, 7-34 and 7-69). The feed gas composition of H_2 to CO_2 was 3:1.

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O \qquad \Delta H^o = -24 \text{ KJ/mol} \quad \Delta G^o = -17 \text{ KJ/mol} \quad (7\text{-}69)$$

Mabuse, et al. (1998) described the liquid-phase methanol synthesis from CO_2 and H_2 over Cu/ZnO-based multicomponent catalyst ($Cu/ZnO/ZrO_2/Al_2O_3$) modified with special silicone oil (5 wt%) at 523K and 15 MPa (Equation 7-68). The ratio of hydrogen to carbon dioxide in the feed gas was 3:1.

Fukui, et al. (1998) described methanol production from hydrogenation of carbon dioxide over Cu/ZnO catalysts at 250°C and 5 MPa (Equation 7-68).

Hara, et al. (1998a) presented a laboratory process for the synthesis of gasoline from carbon dioxide via methanol as an intermediate over a Pd-modified composite catalyst (38.1% Cu, 29.4% ZnO, 1.6% Cr_2O_3, 13.1% Al_2O_3, 17.8% Ga_2O_3) at 270°C and 80 atm. The feed gas was a CO_2 rich gas with composition $CO_2/CO/H_2$ equal to 22/3/75.

Bill, et al. (1998) described two different methods of CO_2 hydrogenation for methanol production. The first one was in a conventional tubular packed-bed reactor filled with copper based catalyst ($CuO/ZnO/Al_2O_3$) at 220°C and 20 bar with the feed gas composition H_2/CO_2 = 3:1. The second one uses a dielectric-barrier discharge (DBD) with the aid of a catalyst inside the discharge space at less than 100°C.

Bonivardi, et al. (1998) described a new methanol production method from CO_2 hydrogenation over Ca promoted Pd/SiO_2 catalyst in a copper-plated differential microreactor at 523 K and 3 MPa. The ratio of H_2 to CO_2 in the feed gas was 3:1. The selectivity to methanol was more than 95% (Equation 7-32 and 7-34).

$$CO_2 +\ H_2 \rightarrow CO + H_2O \qquad \Delta H^\circ = 41\ KJ/mol,\ \Delta G^\circ = 29\ KJ/mol \qquad (7\text{-}32)$$

$$CO + 2H_2 \rightarrow CH_3OH \qquad \Delta H^\circ = -90.8\ KJ/mol,\ \Delta G^\circ = -25\ KJ/mol \qquad (7\text{-}34)$$
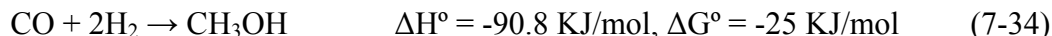
Hirano, et al. (1998) described a laboratory process of carbon dioxide hydrogenation for methanol production over $CuO\text{-}ZnO\text{-}Al_2O_3$ catalyst (Al_2O_3 5 wt%) at 513-521 K and 9 MPa with a feed gas composition of $H_2/CO_2 = 3/1$.

However, not all of the above experimental studies for methanol from carbon dioxide hydrogenation are competitive with the conventional process. Only four new methanol processes (Bonivardi, et al., 1998; Jun, et al., 1998; Nerlov and Chorkendorff, 1999; Ushikoshi, et al., 1998) were selected for process design using HYSYS which is discussed in the next section (Indala, 2004).
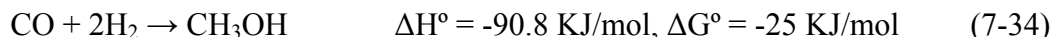
The production capacity of these four processes was based on a methanol plant of Ashland Chemical Inc., located in Plaquemine, LA, with the production rate of 160 million gallons per year (480,000 metric tons per year) (Louisiana Chemical & Petroleum Products List, 1998).

B-18-1. New Methanol (Bonivardi) Process (Bonivardi, et al., 1998; Indala, 2004; Louisiana Chemical & Petroleum Products List, 1998)

B-18-1-1. Process Description

Bonivardi, et al. (1998) described a new methanol production method from CO_2 hydrogenation over Ca promoted Pd/SiO_2 catalyst. The reaction was carried out in a copper-plated differential microreactor at 523 K and 3 MPa with a space velocity of 10000 h^{-1}. The ratio of H_2 to CO_2 in the feed gas was 3:1. The observed rate of synthesis of methanol was 50 x 10^{-8} mol/gPd-s. The selectivity to methanol was more than 95%.

The reaction mechanism was given that methanol was not directly formed through the CO_2 reaction, but it was produced through formation of CO and its consecutive hydrogenation to methanol (Equation 7-32 and 7-34) (Bonivardi, et al., 1998). Large recycle ratios were employed to maintain the selectivity to methanol if the process is commercialized (Bonivardi, et al., 1998). The reactions occurring in this study are:

$$CO_2 + H_2 \rightarrow CO + H_2O \qquad \Delta H^o = 41 \text{ KJ/mol}, \Delta G^o = 29 \text{ KJ/mol} \qquad (7\text{-}32)$$

$$CO + 2H_2 \rightarrow CH_3OH \qquad \Delta H^o = -90.8 \text{ KJ/mol}, \Delta G^o = -25 \text{ KJ/mol} \qquad (7\text{-}34)$$

The operating temperature of this new method (523K) is in the same range as that of the conventional process (250-260°C). This study was conducted at 3MPa pressure where as the conventional process operates at 5-8 MPa pressure. Thus, this potential process would operate at a pressure less than the conventional process. The selectivity to methanol in this study is comparable to that of the conventional process. Hence, this potentially new process is selected for HYSYS simulation (Indala, 2004). The block flow diagram is given in Figure 7.22 with stream definitions in Table 7-66.
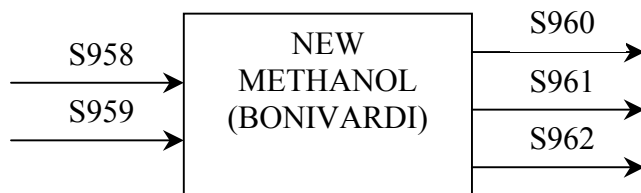

Figure 7.22 Block Diagram of New Methanol (Bonivardi) Process

Table 7-66 Description of Process Streams in New Methanol (Bonivardi) Process

Name of Streams	Description
Input Steams	
S958	CO_2 to new methanol (Bonivardi) process
S959	H_2 to new methanol (Bonivardi) process
Output Streams	
S960	CO produced from new methanol (Bonivardi) process
S961	Methanol produced from new methanol (Bonivardi) process
S962	Water produced from new methanol (Bonivardi) process

B-18-1-2. Material Balance and Energy Balance

Using the parameters in Table 7-67, the material balance and energy balance of new methanol (Bonivardi) process are given in Table 7-68.

In Table 7-68, the overall material balance for the whole process is given first. For the species material balance obtained using the reaction equations (7-32 and 7-33), the first equation is for the CO_2 balance; the second one is for the H_2 balance; the third one is for the H_2O balance; the last one is for the CO balance.

In the overall energy balance, Q_{NMEB} is heat input in the form of steam in heat exchanger and distillation column reboilers for heating reactants and product separation of the new methanol (Bonivardi) process, which is calculated from the energy balance. Q_{out} is the heat released removed by cooling water in heat exchanger and distillation column condensers for product separation in the new methanol (Bonivardi) process based on the unit of methanol product, 9.2 MJ per lb of methanol (Indala, 2004). In enthalpy functions, the coefficients a_1, a_2, a_3, a_4, a_5, and b_1 for different species are given in Table A-1 in Appendix A in (Xu, 2004).

Table 7-67 Parameters in New Methanol (Bonivardi) Production, from Bonivardi, et al. (1998) and Indala (2004)

Name	Meaning	Value
COMe	Overall conversion of CO in new methanol (Bonivardi) process	0.9497
	Overall H_2 utilization in new methanol (Bonivardi) process	1

Table 7-68 Constraint Equations for New Methanol (Bonivardi) Production

Material Balance	
Overall	$(F_{958} + F_{959}) - (F_{960} + F_{961} + F_{962}) = 0$
Species	$CO_2: \dfrac{F_{960}}{mw(CO)} + \dfrac{F_{961}}{mw(MeOH)} - \dfrac{F_{958}}{mw(CO_2)} = 0$

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$$H_2: \frac{F_{960}}{mw(CO)} + \frac{3F_{961}}{mw(MeOH)} - \frac{F_{959}}{mw(H_2)} = 0$$

$$H_2O: F_{962} - \frac{F_{958}(mw(H_2O))}{mw(CO_2)} = 0$$

$$CO: F_{960} - \frac{F_{958}(mw(CO))(1 - COMe)}{mw(CO_2)} = 0$$

Energy Balance
Overall

$$(F_{960}^{(CO)}/M^{(CO)}H_{960}^{(CO)} + F_{961}^{(MeOH)}/M^{(MeOH)}H_{961}^{(MeOH)} + F_{962}^{(H_2O)}/M^{(H_2O)}H_{962}^{(H_2O)})$$

$$- (F_{958}^{(CO_2)}/M^{(CO_2)}H_{958}^{(CO_2)} + F_{959}^{(H_2)}/M^{(H_2)}H_{959}^{(H_2)}) + Q_{out}F_{961}^{(MeOH)} - Q_{NMEB} = 0$$

Enthalpy
Function

$$H_k^i(T) = (a_1^i + \frac{1}{2}a_2^iT + \frac{1}{3}a_3^iT^2 + \frac{1}{4}a_4^iT^3 + \frac{1}{5}a_5^iT^4 + \frac{b_1^i}{T})RT \quad J/mol$$

$$i = CO_2, H_2, CO, H_2O$$
$$k = 958, 959, 960, 962$$
$$H_k^{(MeOH)}(T) = (-238.54)(1000) + (79.225)(T - 298.15) \quad J/mol \; k=961$$

Source: Felder and Roussleu (1986)

In the material balance part, there are 5 variables and 5 equations including one dependent equation (overall material balance), so the number of degrees of freedom is 1. For the material and energy balance, there are 16 variables and 11 equations including the dependent overall material balance, so the number of degrees of freedom is 6.

B-18-2. New Methanol (Jun) Process (Jun, et al., 1998; Indala, 2004; Louisiana Chemical & Petroleum Products List, 1998)

B-18-2-1. Process Description

Jun, et al. (1998) described catalytic hydrogenation of CO_2 for the synthesis of methanol and dimethyl ether (DME) (oxygenates). The catalysts were hybrid catalyst of $Cu/ZnO/Cr_2O_3$ and CuNaY zeolite. The ratio of H_2 to CO_2 in the feed gas was 3:1. The reaction was carried out in a fixed bed micro-reactor at 523 K and 3MPa, and at a flow rate of 30 ml/min. The conversion of CO_2 to CO was 10.21% and to oxygenates was 9.37%. The selectivity of dimethyl ether in oxygenates was 36.7%. The reaction mechanism was provided as Equation (7-32, 7-34 and 7-69) (Jun, et al., 1998).
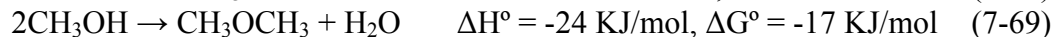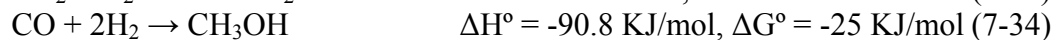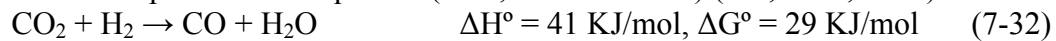
$CO_2 + H_2 \rightarrow CO + H_2O$ ΔH° = 41 KJ/mol, ΔG° = 29 KJ/mol   (7-32)
$CO + 2H_2 \rightarrow CH_3OH$ ΔH° = -90.8 KJ/mol, ΔG° = -25 KJ/mol (7-34)
$2CH_3OH \rightarrow CH_3OCH_3 + H_2O$ ΔH° = -24 KJ/mol, ΔG° = -17 KJ/mol (7-69)

The operating temperature of this new method (523K) is in the same range as that of the conventional process (250-260 ^{o}C). This study was conducted at 3MPa pressure where as the conventional process operates at 5-8 MPa pressure. Thus, this potential process would operate at a pressure less than the conventional process. DME is also produced as a by-product. Though the conversion of CO_2 to CO is less, through

large recycle volumes, the total yield can be increased. Hence, this potentially new process was selected for HYSYS simulation (Indala, 2004).

The block flow diagram is given in Figure 7.23 with stream definitions from Table 7-69.
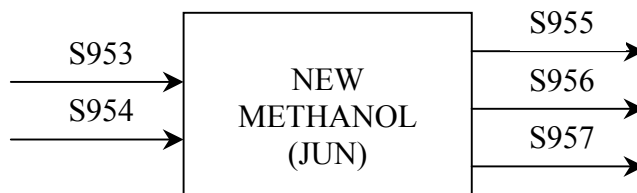
Figure 7.23 Block Diagram of New Methanol (Jun) Process

Table 7-69 Description of Process Streams in New Methanol (Jun) Process

Name of Streams	Description
Input Steams	
S953	CO_2 to new methanol (Jun) process
S954	H_2 to new methanol (Jun) process
Output Streams	
S955	Methanol produced from new methanol (Jun) process
S956	DME produced from new methanol (Jun) process
S957	Water produced from new methanol (Jun) process

B-18-2-2. Material Balance and Energy Balance

Using the parameters in Table 7-70, the material balance and energy balance of new methanol (Jun) process are given in Table 7-71.

Table 7-70 Parameters in New Methanol (Jun) Production, from Jun, et al. (1998) and Indala (2004)

Name	Meaning	Value
MeDME	Overall conversion of methanol to DME in new methanol (Jun) process	0.0519
	Overall CO_2 utilization in new methanol (Jun) process	1
	Overall H_2 utilization in new methanol (Jun) process	1

In Table 7-71, the overall material balance for the whole process is given first. For the species material balance obtained using the reaction equations (7-32, 7-34 and 7-69), the first equation is for the CO_2 balance; the second one is for the H_2 balance; the third one is for the H_2O balance; the fourth one is for the DME balance; the last one is for the methanol balance.

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Table 7-71 Constraint Equations for New Methanol (Jun) Production

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Material Balance

Overall $(F_{953} + F_{954}) - (F_{955} + F_{956} + F_{957}) = 0$

Species

CO_2: $F_{953} - (\dfrac{F_{955}}{mw(MeOH)} + \dfrac{F_{956}}{mw(DME)})mw(CO_2) = 0$

H_2: $F_{954} - (\dfrac{3F_{955}}{mw(MeOH)} + \dfrac{6F_{956}}{mw(DME)})mw(H_2) = 0$

H_2O: $(\dfrac{F_{953}}{mw(CO_2)} + \dfrac{F_{956}}{mw(DME)})mw(H_2O) - F_{957} = 0$

DME: $\dfrac{F_{953}(mw(DME))(MeDME)}{2mw(CO_2)} - F_{956} = 0$

MeOH: $\dfrac{F_{953}(mw(MeOH))(1 - MeDME)}{mw(CO_2)} - F_{955} = 0$

Energy Balance

Overall

$(F_{955}^{(MeOH)} / M^{(MeOH)} H_{955}^{(MeOH)} + F_{956}^{(DME)} / M^{(DME)} H_{956}^{(DME)} + F_{957}^{(H_2O)} / M^{(H_2O)} H_{957}^{(H_2O)}$

$) - (F_{953}^{(CO_2)} / M^{(CO_2)} H_{953}^{(CO_2)} + F_{954}^{(H_2)} / M^{(H_2)} H_{954}^{(H_2)}) + Q_{out} F_{955}^{(MeOH)} - Q_{NMEA} = 0$

Enthalpy Function

$H_k^i(T) = (a_1^i + \dfrac{1}{2}a_2^i T + \dfrac{1}{3}a_3^i T^2 + \dfrac{1}{4}a_4^i T^3 + \dfrac{1}{5}a_5^i T^4 + \dfrac{b_1^i}{T})RT$ J/mol

$i = CO_2, H_2, DME, H_2O$

$k = 953, 954, 956, 957$

$H_k^{(MeOH)}(T) = (-238.54)(1000) + (79.225)(T - 298.15)$ J/mol k=955

Source: Felder and Roussleu (1986)

In the overall energy balance, Q_{NMEA} is heat input of the new methanol (Jun) process in the form of steam in heat exchanger and distillation column reboilers for heating reactants and product separation, which is calculated from the energy balance. Q_{out} is the heat released removed by cooling water in heat exchanger and distillation column condensers for product separation in the new methanol (Jun) process based on the unit of methanol product, 10.3 MJ per lb of methanol (Indala, 2004). In enthalpy functions, the coefficients a_1, a_2, a_3, a_4, a_5, and b_1 for different species are given in Table A-1 in Appendix A in (Xu, 2004).

In the material balance part, there are 5 variables and 6 equations including two dependent equations (overall material balance and CO_2 balance), so the number of degrees of freedom is 1. For the material and energy balance, there are 16 variables and 12 equations including the dependent overall material balance and CO_2 balance, so the number of degrees of freedom is 6.

B-18-3. New Methanol (Nerlov) (Nerlov and Chorkendorff, 1999; Indala, 2004; Louisiana Chemical & Petroleum Products List, 1998)

B-18-3-1. Process Description

Nerlov and Chorkendorff (1999) described a laboratory scale process for the synthesis of methanol from CO_2 and H_2 over Cu(100) catalyst in a high-pressure cell at a temperature of 543 K and a pressure of 0.15 MPa. The average volume ratio of CO_2 to H_2 is about 2:3 in the feed gas. The rate of formation of methanol was 60 x 10^{-6} TurnOver Frequency (TOF) /site·s. The reaction mechanism (Equation 6-68) was provided without the CO_2 conversion rate.

$$CO_2 + 3\ H_2 \rightarrow CH_3OH + H_2O \qquad \Delta H^o = -49\ KJ/mol,\ \Delta G^o = 3\ KJ/mol \quad (7\text{-}68)$$

The operating temperature in this new method (543K) is in the same range as that of the conventional process (250-260 ^{o}C). The operating pressure in this method (0.15 MPa) is less than that of conventional process (5-8 MPa). Hence, this new methanol synthesis process was selected for HYSYS simulation (Indala, 2004).

The block flow diagram is given in Figure 7.24 with stream definitions from Table 7-72.

Figure 7.24 Block Diagram of New Methanol (Nerlov) Process

Table 7-72 Description of Process Streams in New Methanol (Nerlov) Process

Name of Streams	Description
Input Steams	
S963	CO_2 to new methanol (Nerlov) process
S964	H_2 to new methanol (Nerlov) process
Output Streams	
S965	Methanol produced from new methanol (Nerlov) process
S966	Water produced from new methanol (Nerlov) process

B-18-3-2. Material Balance and Energy Balance

Using the parameters in Table 7-73, the material balance and energy balance of new methanol (Nerlov) process are given in Table 7-74.

In Table 7-74, the overall material balance for the whole process is given first. For the species material balance obtained using the reaction equations (7-65), the first equation is for the CO_2 balance; the second one is for the H_2 balance; the last one is for the H_2O balance.

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In the overall energy balance, Q_{NMEC} is heat input of the new methanol (Nerlov) process in the form of steam in heat exchanger and distillation column reboilers for heating reactants and product separation, which is calculated from the energy balance. Q_{out} is the heat ouput removed by cooling water in heat exchanger and distillation column condensers for cooling reactants and product separation in the new methanol (Nerlov) process based on the unit of methanol product, 12.6 MJ per lb of methanol (Indala, 2004). In enthalpy functions, the coefficients a_1, a_2, a_3, a_4, a_5, and b_1 for different species are given in Table A-1 in Appendix A in (Xu, 2004).

In the material balance part, there are 4 variables and 4 equations including one dependent equation (overall material balance), so the number of degrees of freedom is 1. For the material and energy balance, there are 13 variables and 9 equations including the dependent overall material balance, so the number of degrees of freedom is 5.

Table 7-73 Parameters in New Methanol (Nerlov) Production,

from Nerlov and Chorkendorff (1999) and Indala (2004)

Name	Meaning	Value
	Overall CO_2 utilization in new methanol (Jun) process	1
	Overall H_2 utilization in new methanol (Jun) process	1

Table 7-74 Constraint Equations for New Methanol (Nerlov) Production

Material Balance

Overall
$$(F_{963} + F_{964}) - (F_{965} + F_{966}) = 0$$

Species
$$CO_2: \frac{F_{963}}{mw(CO_2)} - \frac{F_{965}}{mw(MeOH)} = 0$$

$$H_2: \frac{F_{964}}{mw(H_2)} - \frac{3F_{965}}{mw(MeOH)} = 0$$

$$H_2O: \frac{F_{965}}{mw(MeOH)} - \frac{F_{966}}{mw(H_2O)} = 0$$

Energy Balance

Overall
$$(F_{965}^{(MeOH)} / M^{(MeOH)} H_{965}^{(MeOH)} + F_{966}^{(H_2O)} / M^{(H_2O)} H_{966}^{(H_2O)})$$
$$- (F_{963}^{(CO_2)} / M^{(CO_2)} H_{963}^{(CO_2)} + F_{964}^{(H_2)} / M^{(H_2)} H_{964}^{(H_2)}) + Q_{out} F_{965}^{(MeOH)} - Q_{NMEC} = 0$$

Enthalpy Function
$$H_k^i (T) = (a_1^i + \frac{1}{2} a_2^i T + \frac{1}{3} a_3^i T^2 + \frac{1}{4} a_4^i T^3 + \frac{1}{5} a_5^i T^4 + \frac{b_1^i}{T}) RT \quad J/mol$$
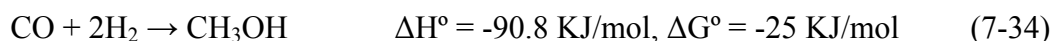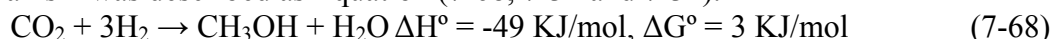$$i = CO_2, H_2, H_2O$$
$$k = 963, 964, 966$$

$$H_k^{(MeOH)}(T) = (-238.54)(1000) + (79.225)(T - 298.15) \ \text{J/mol} \ k=965$$

Source: Felder and Rousslen (1986)

B-18-4. New Methanol (Ushikoshi) (Ushikoshi, et al., 1998; Indala, 2004; Louisiana Chemical & Petroleum Products List, 1998)

B-18-4-. Process Description

Ushikoshi, et al. (1998) described a pilot plant for methanol synthesis from CO_2 and H_2 with a production capacity of 50 kg/day over a multicomponent catalyst ($Cu/ZnO/ZrO_2/Al_2O_3/Ga_2O_3$) under reaction condition of 523 K, 5 MPa and space velocity = 10000 h^{-1}. The ratio of H_2 to CO_2 in the feed gas was 3:1. The reaction mechanism was described as Equation (7-68, 7-32 and 7-34).

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \ \Delta H^o = \text{-49 KJ/mol}, \ \Delta G^o = \text{3 KJ/mol} \qquad (7\text{-}68)$$

$$CO_2 + H_2 \rightarrow CO + H_2O \qquad \Delta H^o = \text{41 KJ/mol}, \ \Delta G^o = \text{29 KJ/mol} \qquad (7\text{-}32)$$

$$CO + 2H_2 \rightarrow CH_3OH \qquad \Delta H^o = \text{-90.8 KJ/mol}, \ \Delta G^o = \text{-25 KJ/mol} \qquad (7\text{-}34)$$

Carbon dioxide and hydrogen supplied from gas cylinders were mixed and compressed along with recycled gases, and then fed into the reaction tube through a pre-heater (Ushikoshi, et al., 1998). The reaction products were cooled and the mixture of methanol and water was separated in a gas-liquid separator from unreacted gases and stored in a container ready for further separation (Ushikoshi, et al., 1998). The space-time yield of methanol was 700 g-CH_3OH/l-cat-h with the purity of 99.9% (Ushikoshi, et al., 1998). Since the conversion of CO_2 at 523 K and 5 MPa was 17%, the unreacted gases and gaseous products like CO were recycled back to the reactor (Ushikoshi, et al., 1998).

Ushikoshi, et al. (1998) compared the new catalyst ($Cu/ZnO/ZrO_2/Al_2O_3/Ga_2O_3$) performance with a commercial $Cu/ZnO/Al_2O_3$ catalyst and concluded that the new catalyst exhibited a higher activity of over 700 g-CH_3OH/l-cat-h whereas the commercial catalyst exhibited an activity of 550 g-CH_3OH/l-cat-h. But they did not report an exact time period for catalyst deactivation. On the other hand, the operating temperature and pressure of the new process (523K and 5 MPa) were in the same range as that of the conventional process (250-260°C and 5MPa). The purity of methanol produced was 99.9%. Hence, this potentially new process was selected for HYSYS simulation (Indala, 2004).

The block flow diagram is given in Figure 7.25 with stream definitions from Table 7-75.
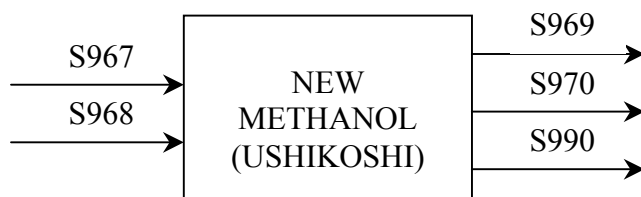
Figure 7.25 Block Diagram of New Methanol (Ushikoshi) Process

Table 7-75 Description of Process Streams in New Methanol (Ushikoshi) Process

Name of Streams	Description
Input Steams	
S967	CO_2 to new methanol (Ushikoshi) process
S968	H_2 to new methanol (Ushikoshi) process
Output Streams	
S969	Methanol produced from new methanol (Ushikoshi) process
S970	Water produced from new methanol (Ushikoshi) process
S990	CO produced from new methanol (Ushikoshi) process

B-18-4-2. Material Balance and Energy Balance

Using the parameters in Table 7-76, the material balance and energy balance of new methanol (Ushikoshi) process are given in Table 7-77.

In Table 7-77, the overall material balance for the whole process is given first. For the species material balance obtained using the reaction equations (7-32, 7-34 and 7-68), the first equation is for the CO_2 balance; the second one is for the H_2 balance; the third one is for the H_2O balance; the last one is for the CO balance.

Table 7-76 Parameters in New Methanol (Ushikoshi) Production, from Ushikoshi, et al. (1998) and Indala (2004)

Name	Meaning	Value
CIDMe	CO_2 indirect conversion to CO in new methanol (Ushikoshi) process	0.1176
CODCMe	CO conversion to methanol in new methanol (Ushikoshi) process	0.90
	Overall H_2 utilization in new methanol (Ushikoshi) process	1
	Overall CO_2 utilization in new methanol (Ushikoshi) process	1

Table 7-77 Constraint Equations for New Methanol (Ushikoshi) Production

Material Balance	
Overall	$(F_{967} + F_{968}) - (F_{969} + F_{970} + F_{990}) = 0$
Species	$CO_2: F_{967} - (\dfrac{F_{969}}{mw(MeOH)} + \dfrac{F_{990}}{mw(CO)})mw(CO_2) = 0$
	$H_2: F_{968} - (\dfrac{3F_{969}}{mw(MeOH)} + \dfrac{F_{990}}{mw(CO)})mw(H_2) = 0$

$$\text{H}_2\text{O: } \left(\frac{F_{969}}{\text{mw(MeOH)}} + \frac{F_{990}}{\text{mw(CO)}}\right)\text{mw(H}_2\text{O)} - F_{970} = 0$$

$$\text{CO: } \frac{F_{967}(\text{mw(CO)})(\text{CIDMe})(1 - \text{CODCMe})}{\text{mw(CO}_2)} - F_{990} = 0$$

Energy Balance

Overall
$$\left(F_{969}^{(\text{MeOH})}/M^{(\text{MeOH})}H_{969}^{(\text{MeOH})} + F_{970}^{(\text{H}_2\text{O})}/M^{(\text{H}_2\text{O})}H_{970}^{(\text{H}_2\text{O})} + F_{990}^{(\text{CO})}/M^{(\text{CO})}H_{990}^{(\text{CO})}\right)$$

$$-\left(F_{967}^{(\text{CO}_2)}/M^{(\text{CO}_2)}H_{967}^{(\text{CO}_2)} + F_{968}^{(\text{H}_2)}/M^{(\text{H}_2)}H_{968}^{(\text{H}_2)}\right) + Q_{\text{out}}F_{969}^{(\text{MeOH})} - Q_{\text{NMED}} = 0$$

Enthalpy
Function
$$H_k^i(T) = \left(a_1^i + \frac{1}{2}a_2^i T + \frac{1}{3}a_3^i T^2 + \frac{1}{4}a_4^i T^3 + \frac{1}{5}a_5^i T^4 + \frac{b_1^i}{T}\right)RT \text{ J/mol}$$

$$i = \text{CO}_2,\ \text{H}_2,\ \text{H}_2\text{O},\ \text{CO};\ k = 967,\ 968,\ 970,\ 990$$

$$H_k^{(\text{MeOH})}(T) = (-238.54)(1000) + (79.225)(T - 298.15) \text{ J/mol k=969}$$

Source: Felder and Roussleu (1986)

In the overall energy balance, Q_{NMED} is heat input of the new methanol (Ushikoshi) process in the form of steam in heat exchanger and distillation column reboilers for heating reactants and product separation, which is calculated from the energy balance. Q_{out} is the heat ouput removed by cooling water in heat exchanger and distillation column condensers for cooling reactants and product separation in the new methanol (Ushikoshi) process based on the unit of methanol product, 11.5 MJ per lb of methanol (Indala, 2004). In enthalpy functions, the coefficients a_1, a_2, a_3, a_4, a_5, and b_1 for different species are given in Table A-1 in Appendix A in (Xu, 2004).

In the material balance part, there are 5 variables and 5 equations including one dependent equation (overall material balance), so the number of degrees of freedom is 1. For the material and energy balance, there are 16 variables and 11 equations including the dependent overall material balance, so the number of degrees of freedom is 6.

B-19. Formic Acid (New Process) (Wells, 1999; Thomas, et al., 2001; Dinjus, 1998; Indala, 2004)

Currently, there are four commercial formic acid processes: hydrolysis of formamide; hydrolysis of methyl formate; acidolysis of formate salts; and oxidation of n-butane or naphtha where it is a by-product. Over half of formic acid production worldwide comes from hydrolysis of methyl formate because of the lower raw material cost (Wells, 1999). The formation of by-product ammonium sulfate made hydrolysis of formamide unattractive. The production as a by-product from oxidation of n-butane and naphtha to acetic acid has declined due to the commercial acetic acid process without the formic acid by-product.

Wells (1999) gave a brief description of the production of formic acid by hydrolysis of methyl formate. Methanol is reacted with dilute or impure anhydrous CO in the liquid phase at 80ºC and 4.5 MPa over sodium methoxide catalyst with 2.5% concentration. Methyl formate is the reaction product and unreacted CO is recycled with the conversion of 64% per pass (Equation 7-70). Methyl formate is degassed and

hydrolyzed with excess water to overcome the unfavorable equilibrium constant at 80ºC and under increased pressure (Equation 7-71). The reactor effluent contains unreacted water and methyl formate, and produced formic acid and methanol. Methanol and methyl formate are recovered overhead and recycled. The remaining formic acid-water mixture is distilled and excess water is removed in an extraction tower using secondary amide to extract. The product obtained is a 90% solution of formic acid

$$CH_3OH + CO \rightarrow HCOOCH_3 \qquad \Delta H^o = -46 \text{ KJ/mol}, \Delta G^o = 2 \text{ KJ/mol} \quad (7-70)$$

$$HCOOCH_3 + H_2O \rightarrow HCOOH + CH_3OH \quad \Delta H^o = 20 \text{ KJ/mol}, \Delta G^o = 13 \text{ KJ/mol} \quad (7-71)$$

Compared to the conventional formic acid process, there are two potentially new processes that use carbon dioxide for the production of formic acid. Thomas, et al. (2001) described a laboratory process for the synthesis of formic acid through CO_2 hydrogenation in liquid triethylamine over $RuCl(O_2CMe)(PMe_3)_4$ catalyst at 50°C and 10MPa (Equation 7-72). The volume ratio of H_2 to CO_2 was 2:3. However, no separation techniques for the formic acid-triethylamine mixture were provided, and conversion of the reactants in the reaction was also not mentioned. The new process described by Dinjus (1998) will be discussed in detail in the next section.

$$CO_2 + H_2 + \tfrac{1}{2} N(C_2H_5)_3 \rightarrow \tfrac{1}{2} [HCOOH]_2N(C_2H_5)_3 \qquad (7-72)$$

Since a production capacity of formic acid was not available in Louisiana Chemical & Petroleum Products List (1998) and Wells (1999) gave the typical production capacities of formic acid ranged from 6,000 to 150,000 metric tons per year. Hence, an average of production capacity of 78,000 metric tons per year was used for this potentially new process.

B-19-1. Process Description

Dinjus (1998) described an experimental study for the production of formic acid through hydrogenation of carbon dioxide in aqueous solution over Wilkinson's catalyst $[ClRh(TPPTS)_3]$ at 25°C and 4 MPa (Equation 7-73). The synthesis rate of formic acid was 3,440 mol formic acid per mol of catalyst. This new method (25°C and 4MPa) has mild reaction condition than the conventional one (50°C and 4.5 MPa). On the other hand, the purification costs for the raw material CO_2 can be eliminated due to the aqueous solution reaction media since industrial CO_2 removal from process waste streams is predominantly carried out in water (Dinjus, 1998). Hence, this new potential process is selected for HYSYS simulation (Indala, 2004). The block flow diagram is given in Figure 7.26 with stream definitions from Table 7-78.

$$CO_2 (g) + H_2 (g) \rightarrow HCOOH (l) \qquad \Delta H^o = -31 \text{ KJ/mol}, \Delta G^o = 33 \text{ KJ/mol} \quad (7-73)$$

Figure 7.26 Block Diagram of New Formic Acid Process

Table 7-78 Description of Process Streams in New Formic Acid Process

Name of Streams	Description
Input Steams	
S942	CO_2 to new formic acid process
S943	H_2 to new formic acid process
Output Streams	
S944	Formic acid produced from new formic acid process

B-19-2. Material Balance and Energy Balance

Using the parameters in Table 7-79, the material balance and energy balance of new formic acid process are given in Table 7-80.

In Table 7-80, the overall material balance for the whole process is given first. For the species material balance obtained using the reaction equations (7-73), the first equation is for the HCOOH balance; the second one is for the CO_2 balance.

In the overall energy balance, Q_{FA} is heat input of the new formic acid process in the form of steam in heat exchanger and distillation column reboilers for heating reactants and product separation, which is calculated from the energy balance. Q_{out} is the heat output removed by cooling water in heat exchanger and distillation column condensers for cooling reactants and product separation in the new formic acid process based on the unit of methanol product, 389 KJ per lb of formic acid (Indala, 2004). In enthalpy functions, the coefficients a_1, a_2, a_3, a_4, a_5, and b_1 for different species are given in Table A-1 in Appendix A in (Xu, 2004).

In the material balance part, there are 3 variables and 3 equations including one dependent equation (overall material balance), so the number of degrees of freedom is 1. For the material and energy balance, there are 10 variables and 7 equations including the dependent overall material balance, so the number of degrees of freedom is 4.

Table 7-79 Parameters in New Formic Acid Production, from Dinjus (1998) and Indala (2004)

Name	Meaning	Value
	Overall H_2 utilization in new formic acid process	1
	Overall CO_2 utilization in new formic acid process	1

Table 7-80 Constraint Equations for New Formic Acid Production

Material Balance	
Overall	$(F_{942} + F_{943}) - F_{944} = 0$

Species	
	HCOOH: $\dfrac{F_{943}}{mw(H_2)} mw(HCOOH) - F_{944} = 0$
	CO$_2$: $F_{942} - \dfrac{F_{943}}{mw(H_2)} mw(CO_2) = 0$

Energy Balance

Overall $\quad F_{944}^{(HCOOH)} / M^{(HCOOH)} H_{944}^{(HCOOH)} - (F_{942}^{(CO_2)} / M^{(CO_2)} H_{942}^{(CO_2)} + F_{943}^{(H_2)} / M^{(H_2)} H_{943}^{(H_2)})$

$\qquad + Q_{out} F_{944}^{(HCOOH)} - Q_{FA} = 0$

Enthalpy Function

$$H_k^i(T) = (a_1^i + \frac{1}{2} a_2^i T + \frac{1}{3} a_3^i T^2 + \frac{1}{4} a_4^i T^3 + \frac{1}{5} a_5^i T^4 + \frac{b_1^i}{T}) RT \ \text{J/mol}$$

$\qquad i = CO_2, H_2$

$\qquad k = 942, 943$

$H_k^{(HCOOH)}(T) = (-424.7)(1000) + (99.5)(T - 298.15) \ \text{J/mol} \ k=944$

Source: Knovel (2003)

B-20. Methylamines (New Process) (Wells, 1999; Arakawa, 1998; Indala, 2004)

Currently, all three methylamines (mono-, di-, and tri-methylamine, i.e., MMA, DMA, TMA) are produced by catalytic alkylation of anhydrous ammonia with methanol. It is not economic to produce only one of the amines even though DMA is the most desired isomer (Wells, 1999). Another process for methylamines production uses formaldehyde instead of methanol. The choice of route is determined by the cost of raw materials (Wells, 1999).

In the conventional process that uses methanol, vaporized methanol and ammonia with a molar ratio of 1:2 react at 390-450°C and 1.4 MPa over amorphous silica-aluminum oxides as catalyst (Equation 7-74, 7-75 and 7-76). The unreacted methanol and ammonia are separated and recycled back. The methylamine mixture is extractively distilled under pressure with water. Because the market demand is mainly for MMA and DMA, most of the formed TMA is recycled back. A total yield of 95% is obtained in this process (Wells, 1999).

$CH_3OH + NH_3 \rightarrow CH_3NH_2 + H_2O \qquad \Delta H° = $ -17 KJ/mol, $\Delta G° = $ -17 KJ/mol (7-74)

$CH_3OH + CH_3NH_2 \rightarrow (CH_3)_2NH + H_2O \ \ \Delta H° = $ -37 KJ/mol, $\Delta G° = $ -30 KJ/mol (7-75)

$CH_3OH + (CH_3)_2NH \rightarrow (CH_3)_3N + H_2O \ \ \Delta H° = $ -46 KJ/mol, $\Delta G° = $ -36 KJ/mol (7-76)

A potentially new process that uses CO$_2$ for methylamines production is given by Arakawa (1998). This potential process selected for HYSYS simulation is discussed in detail in the next section (Indala, 2004).

Since a production capacity of methylamines was not available in Louisiana Chemical & Petroleum Products List (1998) and Wells (1999) gave the typical production capacities of methylamines ranged from 10,000 to 100,000 metric tons per year. Hence, an average of production capacity of 55,000 metric tons per year was used as a basis. The production capacity for MMA of this process was set to be 26,400 metric tons per year.

B-20-1. Process Description

Arakawa (1998) described an experimental process for the production of methylamines from a mixture of CO_2, H_2, and NH_3 over Cu/Al_2O_3 catalyst at 277°C and 0.6 MPa with feed gas composition $H_2/CO_2/NH_3$ = 3/1/1 (Equation 7-32, 7-34, 7-74 and 7-75). MMA and DMA were produced effectively with by-product CO (Arakawa, 1998). Because this new experimental process (277°C and 0.6MPa) operates at a lesser temperature and pressure than the conventional process (390-450°C and 1.4MPa), it is competitive with the conventional process.

$$CO_2 + H_2 \rightarrow CO + H_2O \qquad \Delta H°= 41 \text{ KJ/mol}, \Delta G° = 29 \text{ KJ/mol (7-32)}$$
$$CO + 2H_2 \rightarrow CH_3OH \qquad \Delta H°= -90.5 \text{ KJ/mol}, \Delta G°= -25 \text{ KJ/mol (7-34)}$$
$$CH_3OH + NH_3 \rightarrow CH_3NH_2 + H_2O \quad \Delta H°= -17 \text{ KJ/mol}, \Delta G° = -17 \text{ KJ/mol (7-74)}$$
$$CH_3OH + CH_3NH_2 \rightarrow (CH_3)_2NH + H_2O \quad \Delta H°= -37 \text{ KJ/mol}, \Delta G°= -30 \text{ KJ/mol (7-75)}$$
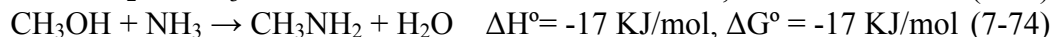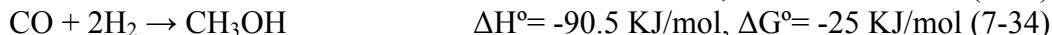
The block flow diagram is given in Figure 7.27 with stream definitions from Table 7-81.
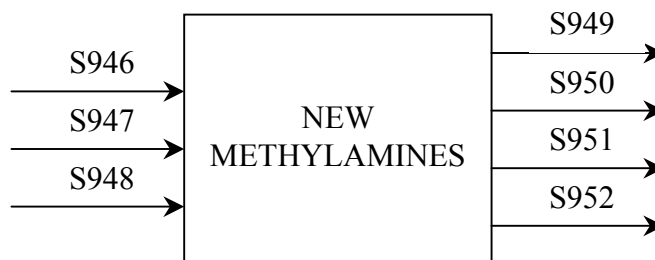

Figure 7.27 Block Diagram of New Methylamines Process

B-20-2. Material Balance and Energy Balance

Using the parameters in Table 7-82, the material balance and energy balance of new methylamines process are given in Table 7-83.

Table 7-81 Description of Process Streams in New Methylamines Process

Name of Streams	Description
Input Steams	
S946	CO_2 to new methylamines process
S947	H_2 to new methylamines process
S948	NH_3 to new methylamines process
Output Streams	
S949	CO and CO_2 mixture gas produced from new methylamines process
S950	MMA produced from new methylamines process
S951	DMA produced from new methylamines process
S952	Water produced from new methylamines process

Table 7-82 Parameters in New Methylamines Production, from Arakawa (1998) and Indala (2004)

Name	Meaning	Value
CDCONV	CO_2 conversion in new methylamines process	0.9978
COCONV	CO conversion in new methylamines process	0.90
MMASE	MMA final selectivity based on methanol in new methylamines process	0.40
DMASE	DMA final selectivity based on methanol in new methylamines process	0.60
	Methanol conversion in new methylamines process	1

In Table 7-83, the overall material balance for the whole process is given with the mixture stream expression. For the species material balance obtained using the reaction equations (7-32, 7-34, 7-74 and 7-75), the first equation is for the CO_2 balance; the second one is for the H_2 balance; the third one is for the NH_3 balance; the fourth one is for the CO balance; the fifth one is for the MMA balance; the sixth one is for the DMA balance; the last one is for the water balance.

In the overall energy balance, Q_{MA} is heat input of the new methylamines process in the form of steam in heat exchanger and distillation column reboilers for heating reactants and product separation, which is calculated from the energy balance.

Table 7-83 Constraint Equations for New Methylamines Production

Material Balance	
Overall	$(F_{946} + F_{947} + F_{948}) - (F_{949} + F_{950} + F_{951} + F_{952}) = 0$
	$F_{949} = F_{949}^{(CO)} + F_{949}^{(CO_2)}$
Species	CO_2: $F_{946} - (F_{949}^{(CO_2)} + F_{946}(CDCONV)) = 0$
	H_2: $F_{947} - (\dfrac{3F_{950}}{mw(MMA)} + \dfrac{6F_{951}}{mw(DMA)} + \dfrac{F_{949}^{(CO)}}{mw(CO)})mw(H_2) = 0$
	NH_3: $F_{948} - (\dfrac{F_{950}}{mw(MMA)} + \dfrac{F_{951}}{mw(DMA)})mw(NH_3) = 0$
	CO: $\dfrac{F_{946}(mw(CO))(CDCONV)(1-COCONV)}{mw(CO_2)} - F_{949}^{(CO)} = 0$
	MMA: $\dfrac{F_{946}(mw(MMA))(CDCONV)(COCONV)(MMASE)}{mw(CO_2)} - F_{950} = 0$
	DMA: $\dfrac{F_{946}(mw(DMA))(CDCONV)(COCONV)(DMASE)}{(2)mw(CO_2)} - F_{951} = 0$
	H_2O:

$$\left(\frac{F_{946}(\text{CDCONV})}{\text{mw}(CO_2)} + \frac{F_{950}}{\text{mw}(MMA)} + \frac{2F_{951}}{\text{mw}(DMA)}\right)\text{mw}(H_2O) - F_{952} = 0$$

Energy Balance

Overall

$$(\Sigma F_{949}^{(i)} / M^{(i)} H_{949}^{(i)} + F_{950}^{(MMA)} / M^{(MMA)} H_{950}^{(MMA)} + F_{951}^{(DMA)} / M^{(DMA)} H_{951}^{(DMA)}$$

$$+ F_{952}^{(H_2O)} / M^{(H_2O)} H_{952}^{(H_2O)}) - (F_{946}^{(CO_2)} / M^{(CO_2)} H_{946}^{(CO_2)} + F_{947}^{(H_2)} / M^{(H_2)} H_{947}^{(H_2)}$$

$$+ F_{948}^{(NH_3)} / M^{(NH_3)} H_{948}^{(NH_3)}) + Q_{out}(F_{950}^{(MMA)} + F_{951}^{(DMA)}) - Q_{MA} = 0$$

where i = CO, CO_2

Enthalpy Function

$$H_k^i(T) = (a_1^i + \frac{1}{2}a_2^i T + \frac{1}{3}a_3^i T^2 + \frac{1}{4}a_4^i T^3 + \frac{1}{5}a_5^i T^4 + \frac{b_1^i}{T})RT \quad \text{J/mol}$$

$\quad$ i = CO_2, H_2, NH_3, CO, H_2O

$\quad$ k = 946, 947, 948, 949, 952

$H_k^{(MMA)}(T) = (-22.5)(1000) + (50.1)(T - 298.15)$ J/mol k=950

Source: Knovel (2003)

$H_k^{(DMA)}(T) = (-18.5)(1000) + (70.7)(T - 298.15)$ J/mol k=951
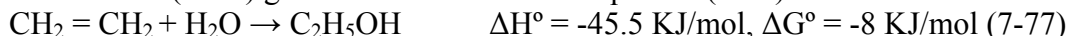
Source: Knovel (2003)

Q_{out} is the heat ouput removed by cooling water in heat exchanger and distillation column condensers for cooling reactants and product separation in the new methylamines process based on the unit of methylamines product, 11.7 MJ per lb of methylamines (Indala, 2004). In enthalpy functions, the coefficients a_1, a_2, a_3, a_4, a_5, and b_1 for different species are given in Table A-1 in Appendix A in (Xu, 2004).

In the material balance part, there are 9 variables and 9 equations including one dependent equation (overall material balance), so the number of degrees of freedom is 1. For the material and energy balance, there are 25 variables and 18 equations including the dependent overall material balance, so the number of degrees of freedom is 8.
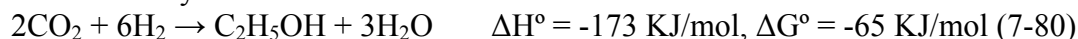
B-21. Ethanol (EtOH) (New Process) (Wells, 1999; Speight, 2002; Inui, 2002; Kusama, et al., 1998; Bando, et al., 1998; Yamamoto and Inui, 1998; Takagawa, et al., 1998; Izumi, et al., 1998; Higuchi, et al., 1998; Indala, 2004; Louisiana Chemical & Petroleum Products List, 1998)

There are three commercial processes for ethanol production (Wells, 1999). The first one is the indirect catalytic hydration of ethylene with disadvantages such as handling large volumes of dilute sulfuric acid, energy required for its concentration, and corrosion caused by the acid. The second one is direct catalytic hydration of ethylene over phosphoric acid absorbed onto silica gel catalyst at 230-300°C and 6-8 MPa (Equation 7-77). The molar ratio of ethylene to water is 1:0.3-0.8 (Wells, 1999). The conversion of ethylene to ethanol is about 4% per pass with a net yield of 97% due to large recycle volume of unconverted ethylene and diethyl ether (Equation 7-78) (Speight, 2002). The third new process for ethanol synthesis has three steps: carbonylation of methanol with carbon monoxide to acetic acid; acetic acid esterified

with methanol to methyl acetate; and methyl acetate hydrogenolysis to ethanol and methanol. Wells (1999) gave the overall reaction equation (7-79).

$$CH_2 = CH_2 + H_2O \rightarrow C_2H_5OH \qquad \Delta H^\circ = -45.5 \text{ KJ/mol}, \Delta G^\circ = -8 \text{ KJ/mol} \quad (7\text{-}77)$$

$$2C_2H_5OH \leftrightarrow (C_2H_5)_2O + H_2O \qquad \Delta H^\circ = -24 \text{ KJ/mol}, \Delta G^\circ = -15 \text{ KJ/mol} \quad (7\text{-}78)$$

$$CH_3OH + CO + 2H_2 \rightarrow C_2H_5OH + H_2O \quad \Delta H^\circ = -165 \text{ KJ/mol}, \Delta G^\circ = -97 \text{ KJ/mol} \quad (7\text{-}79)$$

For potentially new processes for ethanol from carbon dioxide, Inui (2002) reviewed five experimental processes for synthesis of ethyl alcohol from the hydrogenation of carbon dioxide with the same ratio of H_2 to CO_2 = 3:1 (Equation 7-80). In the first case, the reaction condition was 573 K and 6.9 MPa over Rh-Li-Fe/SiO_2 catalyst with 10.5% both of the conversion of carbon dioxide to ethanol and the selectivity to ethanol. In the second case, the reaction condition was 513-533K and 4.9 MPa over Cu-Zn-Fe-K catalyst with 21.2% both of the conversion of carbon dioxide to ethanol and the selectivity to ethanol. In the third case, the reaction condition was 583 K and 8 MPa over Fe-Cu-Zn-Al-K catalyst with 28.5% both of the conversion of carbon dioxide and the selectivity to ethanol. In the fourth case, the reaction condition was 623 K and 8 MPa over (Rh/MFI-silicate)-(Fe-Cu-Zn-Al-K) catalyst with 12.8% both of the conversion of carbon dioxide and the selectivity to ethanol. In the fifth case, the reaction condition was 603 K and 8 MPa over (Fe-Cu-Al-K)-(Cu-Zn-Al-K.Ga.Pd) catalyst with 25.1% both of the conversion of carbon dioxide and the selectivity to ethanol.

$$2CO_2 + 6H_2 \rightarrow C_2H_5OH + 3H_2O \qquad \Delta H^\circ = -173 \text{ KJ/mol}, \Delta G^\circ = -65 \text{ KJ/mol} \quad (7\text{-}80)$$

Kusama, et al. (1998) described a laboratory process for ethanol synthesis through hydrogenation of carbon dioxide over Rh/SiO_2 catalyst at 533K and 5 MPa with the feed gas composition H_2:CO_2 = 3:1 and 2% of the selectivity to ethanol (Equation 7-80).

Bando, et al. (1998) gave an experimental process for the hydrogenation of carbon dioxide over Rh ion exchanged zeolite catalysts at 523 K and 3 MPa with the feed gas contains hydrogen and carbon dioxide with a composition of 3:1, along with 1.8% CO. No reaction mechanism was provided. Main products were methane, carbon monoxide, and ethyl alcohol with 7% of conversion of carbon dioxide and 16%, 40%, 38% of selectivity to ethanol, methane and carbon monoxide, respectively.

Yamamoto and Inui (1998) provided a method for the synthesis of ethanol over Cu-Zn-Al-K and Fe-Cu-Al-K mixed oxide catalyst at 603K and 8 MPa with the feed gas composition H_2/CO_2 = 3/1. No reaction mechanism was provided. The products were ethyl alcohol, methanol, hydrocarbons, and carbon monoxide. The CO_2 overall conversion was 54.5% with 5% to ethanol.

Takagawa, et al. (1998) described hydrogenation of carbon dioxide for the synthesis of ethanol over K/Cu-Zn-Fe oxide catalyst at 573K and 7MPa with 3:1of the ratio of H_2 to CO_2. CO_2 conversion was 44% and selectivity to ethanol was 20%.

Izumi, et al. (1998) gave an experimental process for ethanol from carbon dioxide and hydrogen over [$Rh_{10}Se$]/TiO_2 catalyst at 623K and 47 kPa with the ratio of 2:1 H_2 to CO_2. The reaction path for the formation of ethanol was described as CH_x (a) + CO_y (a) $\rightarrow$ acetate (a) $\rightarrow$ ethanol. CO_2 conversion was 83% and ethanol selectivity was 80%.

In general, the above potentially new processes for ethanol synthesis from CO_2 and hydrogen are not as profitable as the new process described by Higuchi, et al. (1998) which is discussed in detail in the next section (Indala, 2004).

The capacity of this process is set to be 104,000 metric tons per year of ethanol. This was based on an ethanol plant of Shepherd Oil, located in Jennings, LA, with the capacity of 300 million gallons of ethanol per year (108,000 metric tons per year) (Louisiana Chemical & Petroleum Products List, 1998).

B-21-1. Process Description

Higuchi, et al. (1998) described an experimental process for the ethanol synthesis from CO_2 hydrogenation over K/Cu-Zn-Fe-Cr oxide catalyst in a conventional flow reactor at 300°C and 7 MPa (Equation 7-80). The catalyst exhibited a long catalytic life because of its slow segregation rate. The conversion rate of CO_2 was 35% and selectivity to ethanol was 16%.

$$2CO_2 + 6H_2 \rightarrow C_2H_5OH + 3H_2O \qquad \Delta H^o = -173 \text{ KJ/mol}, \Delta G^o = -65 \text{ KJ/mol (7-80)}$$
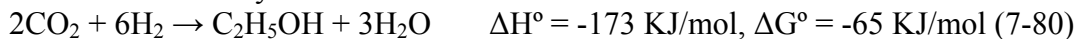
Compared with the conventional process, the operating temperature and pressure of the new process (300°C and 7 MPa) are in the same range as those of conventional process (230-300°C and 6-8 MPa). The 35% conversion of CO_2 is higher than the 4% conversion of ethylene to ethanol per pass in conventional process. Meanwhile, the catalyst used in the new process had a long life without deactivation. Hence, this new process was selected for HYSYS simulation and incorporated into the chemical complex.

The block flow diagram is given in Figure 7.28 with stream definitions from Table 7-84.

Figure 7.28 Block Diagram of New Ethanol Process

Table 7-84 Description of Process Streams in New Ethanol Process

Name of Streams	Description
Input Steams	
S980	CO_2 to new ethanol process
S981	H_2 to new ethanol process
Output Streams	
S982	Ethanol solution produced from new ethanol process
S983	Water produced from new ethanol process

B-21-2. Material Balance and Energy Balance

Using the parameters in Table 7-85, the material balance and energy balance of new ethanol process are given in Table 7-86.

Table 7-85 Parameters in New Ethanol Production, from Higuchi, et al. (1998) and Indala (2004)

Name	Meaning	Value
WTEtB	Weight fraction of ethanol solute in ethanol solution in new ethanol process	0.88
	Overall CO_2 utilization in new ethanol process	1
	Overall H_2 utilization in new ethanol process	1

In Table 7-86, the overall material balance for the whole process is given with the mixture stream expression. For the species material balance obtained using the reaction equations (7-80), the first equation is for the CO_2 balance; the second one is for the H_2 balance; the last one is for the water balance.

Table 7-86 Constraint Equations for New Ethanol Production

Material Balance	
Overall	$(F_{980} + F_{981}) - (F_{982} + F_{983}) = 0$
	$F_{982} = F_{982}^{(EtOH)} + F_{982}^{(H_2O)}$
Species	CO_2: $F_{980} - \dfrac{2F_{982}^{(EtOH)}}{mw(EtOH)} mw(CO_2) = 0$
	H_2: $F_{981} - \dfrac{6F_{982}^{(EtOH)}}{mw(EtOH)} mw(H_2) = 0$
	H_2O: $\dfrac{3F_{982}^{(EtOH)}}{mw(EtOH)} mw(H_2O) - (F_{983} + F_{982}^{(H_2O)}) = 0$
Energy Balance	
Overall	$(\Sigma F_{982}^{(i)} / M^{(i)} H_{982}^{(i)} + F_{983}^{(H_2O)} / M^{(H_2O)} H_{983}^{(H_2O)}) - (F_{980}^{(CO_2)} / M^{(CO_2)} H_{980}^{(CO_2)}$
	$+ F_{981}^{(H_2)} / M^{(H_2)} H_{981}^{(H_2)}) + Q_{out} F_{982} - Q_{ETB} = 0$
	where i = EtOH, H_2O
Enthalpy Function	$H_k^i(T) = (a_1^i + \dfrac{1}{2} a_2^i T + \dfrac{1}{3} a_3^i T^2 + \dfrac{1}{4} a_4^i T^3 + \dfrac{1}{5} a_5^i T^4 + \dfrac{b_1^i}{T})RT$ J/mol
	i = CO_2, H_2, H_2O
	k = 980, 981, 982, 983
	$H_k^{(EtOH)}(T) = (-277.6)(1000) + (112.3)(T - 298.15)$ J/mol k=982
	Source: Knovel (2003)

In the overall energy balance, Q_{ETB} is heat input of the new ethanol process in the form of steam in heat exchanger and distillation column reboilers for heating reactants and product separation, which is calculated from the energy balance. Q_{out} is the heat output removed by cooling water in heat exchanger and distillation column condensers for cooling reactants and product separation in the new ethanol process based on the unit of ethanol solution product, 13.5 MJ per lb of ethanol solution (Indala, 2004). In enthalpy functions, the coefficients a_1, a_2, a_3, a_4, a_5, and b_1 for different species are given in Table A-1 in Appendix A in (Xu, 2004).

In the material balance part, there are 6 variables and 6 equations including one dependent equation (overall material balance), so the number of degrees of freedom is 1. For the material and energy balance, there are 16 variables and 12 equations including the dependent overall material balance, so the number of degrees of freedom is 5.
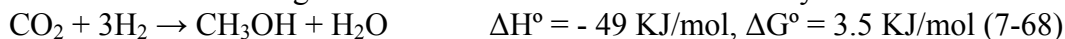
B-22. Dimethyl Ether (DME) (New process) (Turton, et al., 1998; Tao, et al., 2001; Jun, et al., 1998; Romani, et al., 2000; Jun, et al., 2002; Indala, 2004)

Dimethyl ether (DME) is produced commercially by catalytic dehydration of methanol over an amorphous alumina catalyst treated with 10.2% silica at 250-368ºC and 1.5 MPa (Equation 7-69) (Turton, et al., 1998). The single-pass conversion of methanol is about 80%.

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O \qquad \Delta H^\circ = -24 \text{ KJ/mol}, \Delta G^\circ = -17 \text{ KJ/mol} \quad (7\text{-}69)$$

There are four new experimental studies for the production of DME where three use CO_2 as a raw material and the other one uses natural gas as a feedstock. These are described below.

Tao, et al. (2001) reported a laboratory process for the production of methanol and DME from CO_2 hydrogenation over the mixture catalysts of Cu-Zn-Al-Cr mixed oxide catalyst and HZSM catalyst (Cu-ZnO-Al$_2$O$_3$-Cr$_2$O$_3$ + H-ZSM-5 (SiO$_2$/Al$_2$O$_3$=80)) at 523 K and 3 MPa (Equation 7-68 and 7-69). The total yield of DME and methanol was higher than 26% with over 90% selectivity to DME.

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \qquad \Delta H^\circ = -49 \text{ KJ/mol}, \Delta G^\circ = 3.5 \text{ KJ/mol} \quad (7\text{-}68)$$
$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O \qquad \Delta H^\circ = -24 \text{ KJ/mol}, \Delta G^\circ = -17 \text{ KJ/mol} \quad (7\text{-}69)$$

Jun, et al. (1998) described a process for production of methanol and DME by CO_2 hydrogenation over a hybrid catalyst of Cu/ZnO/Cr$_2$O$_3$ and CuNaY zeolite, which was discussed in the new methanol production section.

Romani, et al. (2000) described a three-step large-scale process for the production of DME from natural gas, synthesis gas preparation, synthesis of methanol and DME, and product separation and purification. Since the research interest is the processes consume CO_2, this process is not considered.
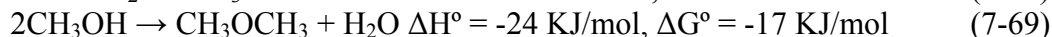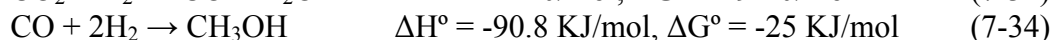
Above three processes are not included in the chemical complex because they were not competitive with the potentially new process described by Jun, et al. (2002) which is discussed in detail in the following section.

Since there was no available production capacity for DME in Louisiana Chemical & Petroleum Products List (1998), a typical production capacity of 100

million pounds per year was taken as a basis. Hence, the capacity of the new process for DME was set to be 45,800 metric tons per year (Indala, 2004).

B-22-1. Process Description

Jun, et al. (2002) gave a potentially new process for the synthesis of DME from CO_2 hydrogenation over the γ-Al_2O_3 modified with 1% silica catalyst in a fixed-bed reactor at 523 K and 0.053 MPa (Equation 7-32, 7-34 and 7-69). The conversion of intermediate methanol to DME was 70%.

$$CO_2 + H_2 \rightarrow CO + H_2O \qquad \Delta H^o = 41 \text{ KJ/mol}, \Delta G^o = 29 \text{ KJ/mol} \qquad (7\text{-}32)$$
$$CO + 2H_2 \rightarrow CH_3OH \qquad \Delta H^o = -90.8 \text{ KJ/mol}, \Delta G^o = -25 \text{ KJ/mol} \qquad (7\text{-}34)$$
$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O \quad \Delta H^o = -24 \text{ KJ/mol}, \Delta G^o = -17 \text{ KJ/mol} \qquad (7\text{-}69)$$

Compared to the conventional process, the operating condition of the new process (523 K and 0.053 MPa) is milder than that of the conventional process (523-641 K and 1.5 MPa). The intermediate methanol conversion to DME in the new process is 70% closer to the 80% conversion in the conventional process.

The block flow diagram is given in Figure 7.29 with stream definitions from Table 7-87.
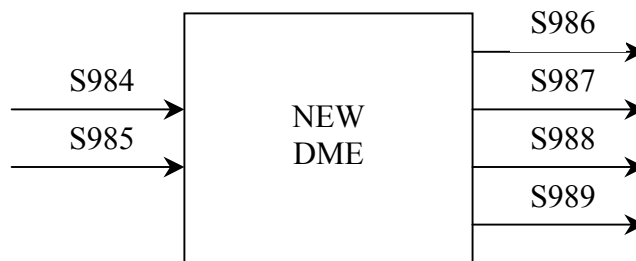

Figure 7.29 Block Diagram of New DME Process

Table 7-87 Description of Process Streams in New DME Process

Name of Streams	Description
Input Steams	
S984	CO_2 to new DME process
S985	H_2 to new DME process
Output Streams	
S986	CO produced from new DME process
S987	DME produced from new DME process
S988	Methanol produced from new DME process
S989	Water produced from new DME process

B-22-2. Material Balance and Energy Balance

Using the parameters in Table 7-88, the material balance and energy balance of new DME process are given in Table 7-89.

In Table 7-89, the overall material balance for the whole process is given first. For the species material balance obtained using the reaction equations (7-32, 7-34 and

Table 7-88 Parameters in New DME Production, from Jun, et al. (2002) and Indala (2004)

Name	Meaning	Value
COMeD	CO conversion rate to methanol in new DME process	0.63
MeDMED	Methanol conversion rate to DME in new DME process	0.89
	Overall CO_2 conversion rate in new DME process	1

Table 7-89 Constraint Equations for New DME Production

Material Balance

Overall
$$(F_{984} + F_{985}) - (F_{986} + F_{987} + F_{988} + F_{989}) = 0$$

Species
$$CO_2: \ F_{984} - (\frac{F_{986}}{mw(CO)} + \frac{2F_{987}}{mw(DME)} + \frac{F_{988}}{mw(MeOH)})mw(CO_2) = 0$$

$$H_2: \ F_{985} - (\frac{F_{986}}{mw(CO)} + \frac{6F_{987}}{mw(DME)} + \frac{3F_{988}}{mw(MeOH)})mw(H_2) = 0$$

$$CO: \ \frac{F_{984}(1 - COMeD)}{mw(CO_2)}mw(CO) - F_{986} = 0$$

$$DME: \ \frac{F_{984}(COMeD)(MeDME)}{(2)mw(CO_2)}mw(DME) - F_{987} = 0$$

$$MeOH: \ \frac{F_{984}(COMeD)(1 - MeDMED)}{mw(CO_2)}mw(MeOH) - F_{988} = 0$$

$$H_2O: \ (\frac{F_{984}}{mw(CO_2)} + \frac{F_{987}}{mw(DME)})mw(H_2O) - F_{989} = 0$$

Energy Balance

Overall
$$(F_{986}^{(CO)}/M^{(CO)}H_{986}^{(CO)} + F_{987}^{(DME)}/M^{(DME)}H_{987}^{(DME)} + F_{988}^{(MeOH)}/M^{(MeOH)}H_{988}^{(MeOH)}$$

$$+ F_{989}^{(H_2O)}/M^{(H_2O)}H_{989}^{(H_2O)}) - (F_{984}^{(CO_2)}/M^{(CO_2)}H_{984}^{(CO_2)} + F_{985}^{(H_2)}/M^{(H_2)}H_{985}^{(H_2)})$$

$$+ Q_{out}F_{987}^{(DME)} - Q_{DME} = 0$$

Enthalpy Function
$$H_k^i(T) = (a_1^i + \frac{1}{2}a_2^i T + \frac{1}{3}a_3^i T^2 + \frac{1}{4}a_4^i T^3 + \frac{1}{5}a_5^i T^4 + \frac{b_1^i}{T})RT \quad J/mol$$

$\quad i = CO_2, H_2, CO, DME, H_2O$
$\quad k = 984, 985, 986, 987, 989$

$$H_k^{(MeOH)}(T) = (-238.54)(1000) + (79.225)(T - 298.15) \ J/mol \ k=988$$

Source: Felder and Roussleu (1986)

7-69), the first equation is for the CO_2 balance; the second one is for the H_2 balance; the third one is for the CO balance; the fourth one is for the DME balance; the fifth one is for the methanol balance; the last one is for the H_2O balance.

In the overall energy balance, Q_{DME} is heat input of the new DME process in the form of steam in heat exchanger and distillation column reboilers for heating reactants and product separation, which is calculated from the energy balance. Q_{out} is the heat output removed by cooling water in heat exchanger and distillation column condensers for cooling reactants and product separation in the new DME process based on the unit of DME product, 5.9 MJ per lb of DME (Indala, 2004). In enthalpy functions, the coefficients a_1, a_2, a_3, a_4, a_5, and b_1 for different species are given in Table A-1 in Appendix A in (Xu, 2004).

In the material balance part, there are 6 variables and 7 equations including two dependent equations (overall material balance and CO_2 balance), so the number of degrees of freedom is 1. For the material and energy balance, there are 19 variables and 14 equations including the dependent overall material balance and CO_2 balance, so the number of degrees of freedom is 7.

B-23. Graphite and Hydrogen (New process) (Speight, 2002; Arakawa, 1998; Motiei, et al., 2001; Nishiguchi, et al., 1998; Indala, 2004)

Graphite is a soft crystalline form of carbon different from amorphous carbon and diamond. Currently, graphite is produced from retort or petroleum coke at about 2,700ºC where the amorphous carbon is processed into graphite (Speight, 2002). Meanwhile, there are some new experimental methods consuming CO_2 for the production of graphite.

Arakawa (1998) described an experimental process for graphite production from carbon dioxide CO by direct hydrogenation over a WO_3 or Y_2O_3 catalyst at 700ºC and 0.1 MPa. The feed gas composition was $H_2/CO_2/N_2 = 2/1/5$. The conversion of carbon dioxide was 60% and the selectivity to graphite was 40%.

Motiei, et al. (2001) reported a laboratory process for synthesizing carbon nanotubes and nested fullerenes, along with graphite, from supercritical CO_2 at 1,000°C and 1,000 MPa with 16% yield of carbonaceous materials. But 59% of the gases leaked out during the reaction because of the high pressure involved.
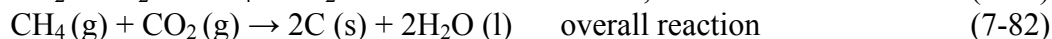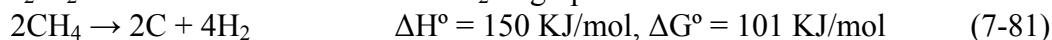
The above two new methods can not compete with the potentially new process described by Nishiguchi, et al. (1998) based on process ecomomic evaluation, which is discussed in detail in the following section (Indala, 2004).

Since there was no available production capacity for graphite in Louisiana Chemical & Petroleum Products List (1998), a typical production capacity of 100 million pounds per year was taken as a basis. Hence, the capacity of the new process for graphite was set to be 46,000 metric tons per year (Indala, 2004).

B-23-1. Process Description

Nishiguchi, et al. (1998) described an experimental process for the production of graphite by catalytic reduction of carbon dioxide with methane as an intermediate over Ni supported on SiO_2 catalyst. Two-stage reaction mechanism was provided: recycled methane decomposed into graphite carbon and hydrogen, and hydrogen

treated with CO_2 to produce methane and water (Equation 7-81, 7-25 and 7-82). The operating condition was 500ºC, atmospheric pressure, and the feed gas composition $H_2/CO_2/N_2 = 4/1/3$. The conversion of CO_2 to graphite carbon was 70%.

$$2CH_4 \rightarrow 2C + 4H_2 \qquad \Delta H^\circ = 150 \text{ KJ/mol, } \Delta G^\circ = 101 \text{ KJ/mol} \qquad (7\text{-}81)$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad \Delta H^\circ = \text{-}165 \text{ KJ/mol, } \Delta G^\circ = \text{-}113 \text{ KJ/mol} \qquad (7\text{-}25)$$

$$CH_4\,(g) + CO_2\,(g) \rightarrow 2C\,(s) + 2H_2O\,(l) \qquad \text{overall reaction} \qquad (7\text{-}82)$$

Compared with the convention process, the new process (500ºC) has much lower temperature than the conventional process (2,700ºC). High CO_2 conversion (70%) and the stable catalyst activity makes the new process competitive with the conventional process and included in the chemical complex.

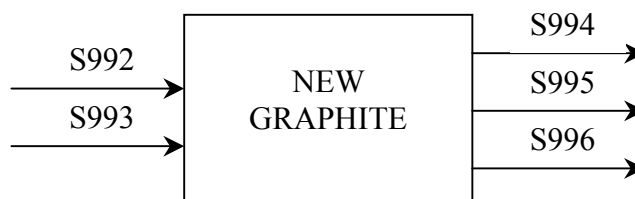The block flow diagram is given in Figure 7.30 with stream definitions from Table 7-90.

Figure 7.30 Block Diagram of New Graphite Process

Table 7-90 Description of Process Streams in New Graphite Process

Name of Streams	Description
Input Steams	
S992	CH_4 to new graphite process
S993	CO_2 to new graphite process
Output Streams	
S994	H_2 produced from new graphite process
S995	Graphite produced from new graphite process
S996	Water produced from new graphite process

B-23-2. Material Balance and Energy Balance

Using the parameters in Table 7-91, the material balance and energy balance of new graphite process are given in Table 7-92.

Table 7-91 Parameters in New Graphite Production, from Nishiguchi, et al. (1998) and Indala (2004)

Name	Meaning	Value

MCR	Weight ratio of CH_4 to CO_2 in the feedstock in the new graphite process	0.54
	Overall CH_4 conversion rate in new graphite process	1
	Overall CO_2 conversion rate in new graphite process	1

Table 7-92 Constraint Equations for New Graphite Production

Material Balance

Overall
$$(F_{992} + F_{993}) - (F_{994} + F_{995} + F_{996}) = 0$$

Species
$$C: \left(\frac{F_{992}}{mw(CH_4)} + \frac{F_{993}}{mw(CO_2)}\right)mw(C) - F_{995} = 0$$

$$H_2: F_{994} - \left(\frac{2F_{995}}{mw(C)} - \frac{4F_{993}}{mw(CO_2)}\right)mw(H_2) = 0$$

$$H_2O: \frac{2F_{993}}{mw(CO_2)}mw(H_2O) - F_{996} = 0$$

$$CO_2: F_{992} - F_{993}(MCR) = 0$$

Energy Balance

Overall
$$(F_{994}^{(H_2)} / M^{(H_2)}H_{994}^{(H_2)} + F_{995}^{(C)} / M^{(C)}H_{995}^{(C)} + F_{996}^{(H_2O)} / M^{(H_2O)}H_{996}^{(H_2O)})$$
$$- (F_{992}^{(CH_4)} / M^{(CH_4)}H_{992}^{(CH_4)} + F_{993}^{(CO_2)} / M^{(CO_2)}H_{993}^{(CO_2)}) + Q_{out}F_{995}^{(C)} - Q_{GH} = 0$$

Enthalpy Function
$$H_k^i(T) = (a_1^i + \frac{1}{2}a_2^i T + \frac{1}{3}a_3^i T^2 + \frac{1}{4}a_4^i T^3 + \frac{1}{5}a_5^i T^4 + \frac{b_1^i}{T})RT \quad J/mol$$
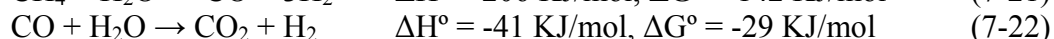$$i = CH_4, CO_2, H_2, C, H_2O$$
$$k = 992, 993, 994, 995, 996$$

In Table 7-92, the overall material balance for the whole process is given first. For the species material balance obtained using the reaction equations (7-81, 7-25 and 7-82), the first equation is for the graphite balance; the second one is for the H_2 balance; the third one is for the H_2O balance; the last one is for the CO_2 balance.

In the overall energy balance, Q_{GH} is heat input of the new graphite process in the form of steam in heat exchanger and distillation column reboilers for heating reactants and product separation, which is calculated from the energy balance. Q_{out} is the heat output removed by cooling water in heat exchanger and distillation column condensers for cooling reactants and product separation in the new graphite process based on the unit of graphite product, 11.4 MJ per lb of graphite (Indala, 2004). In enthalpy functions, the coefficients a_1, a_2, a_3, a_4, a_5, and b_1 for different species are given in Table A-1 in Appendix A in (Xu, 2004).

In the material balance part, there are 5 variables and 5 equations including one dependent equation (overall material balance), so the number of degrees of freedom is 1. For the material and energy balance, there are 16 variables and 11 equations including the dependent overall material balance, so the number of degrees of freedom is 6.

B-24. Hydrogen (New Process) (Speight, 2002; Song, et al., 2002; Inui, 2002; Wei, et al., 2002; Nakagawa, et al., 2002; Effendi, et al., 2002; Tomishige, et al., 1998; Shamsi, 2002; Indala, 2004; Louisiana Chemical & Petroleum Products List, 1998)

To provide H_2 needed in the potentially new processes consuming CO_2 in the previous sections, the H_2 sources will be discussed here. The commercial process for hydrogen production is steam reforming of natural gas involving reforming and shift conversion (Equation 7-21 and 7-22). Desulfurized natural gas is mixed with steam over a nickel catalyst in a reforming furnace at 760-980ºC and 4.1 MPa (Speight, 2002). Formed gas mixture of CO and H_2 enters a shift converter where carbon monoxide reacts with more steam to produce hydrogen and CO_2 over iron or chromic oxide catalysts at 425ºC. The product mixture gas of CO_2 and H_2 are separated using monoethanolamine absorbing and desorbing CO_2 (Speight, 2002).

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad \Delta H^o = 206 \text{ KJ/mol, } \Delta G^o = 142 \text{ KJ/mol} \qquad (7\text{-}21)$$
$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta H^o = -41 \text{ KJ/mol, } \Delta G^o = -29 \text{ KJ/mol} \qquad (7\text{-}22)$$

There are many experimental processes consuming CO_2 to produce either pure H_2 or synthesis gas through reforming of methane, which is a good source of H_2 for the chemical complex. Some of these potentially new processes are reviewed here.

Song, et al. (2002) gave the new process to produce CO rich synthesis gas from CO_2 reforming of methane over Ni/Al_2O_3 catalyst at 750ºC and 1 atm with equimolar methane and CO_2 input (Equation 7-83). The results were 91.8% CO_2 conversions, 95.3% CH_4 conversion, 82% CO yield, 66% H_2 yield, and product composition of $H_2/CO = 0.81$.

$$CH_4 + CO_2 \rightarrow 2H_2 + 2CO \qquad \Delta H^o = 247 \text{ KJ/mol, } \Delta G^o = 171 \text{ KJ/mol (7-83)}$$
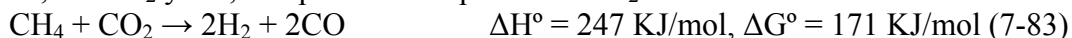
Inui (2002) discussed the catalyst role in the production of synthesis gas through CO_2 reforming of methane. The highest CH_4 conversion rate was 82.2% over a Rh-modified four-component catalyst at 700ºC and 1 atm. The observed conversion of methane was 80.8%.

Wei, et al. (2002) described an experimental process of reforming methane to synthesis gas through over Ni supported ultra fine ZrO_2 catalyst at 757°C and 1atm with equimolar CH_4 and CO_2 input (Equation 7-83). There was no deactivation of the catalyst for over 600 hours. The results were 88.3% CO_2 conversions, 86.2% CH_4 conversion, 95.4% CO selectivity, 66% H_2 selectivity, and product composition of $H_2/CO = 0.83$.

Nakagawa, et al. (2002) reported a new process for synthesis gas production by reforming methane over a Ru loaded Y_2O_3 catalyst at 600°C and 1 atm with equimolar CH_4 and CO_2 input (Equation 7-83). The results were 35.5% CO_2 conversions, 30% CH_4 conversion, 32.7% CO yield, 27% H_2 yield, and product composition of $H_2/CO = 0.83$.

Effendi, et al. (2002) described an experimental process for reforming methane to synthesis gas over Ni/SiO$_2$-MgO catalyst at 700°C and 1 atm with the feed gas composition CO$_2$/CH$_4$ = 0.84 (Equation 7-83). The conversions of CH$_4$ and CO$_2$ were 37.7% and 52.7%, respectively, and synthesis gas composition was H$_2$/CO = 0.69.

Tomishige, et al. (1998) described a laboratory process by reforming methane for the production of synthesis gas over a nickel-magnesia solid solution catalyst at 850°C and 0.1 MPa with equimolar of CH$_4$ and CO$_2$ input (Equation 7-83). The conversion of methane was 80%. Meanwhile, the catalyst was inexpensive compared to the other commercial catalysts, and was effective in preventing the coke deposition inside the reactor (Tomishige, et al., 1998).

According process evaluation by Indala (2004), the above new processes for the production of synthesis gas could not compete with the potentially new process described by Shamsi (2002) which is discussed in the following section and included in the chemical complex as a H$_2$ source.

The process production capacity was set to be 13,400 metric tons of H$_2$ per year. This was based on a hydrogen plant of Air Products and Chemicals Inc., located in Geismar, LA, with the capacity of 15 million cubic feet per day (Louisiana Chemical & Petroleum Products List, 1998).

B-27-1. Process Description

Shamsi (2002) reported three laboratory processes of CO$_2$ reforming methane to produce synthesis gas over three different catalysts. The best reaction condition was at 850°C and 1 atm over a noble metal catalyst of 1% rhodium supported on alumina in a fixed bed reactor (Equation 7-83). The conversions of methane and CO$_2$ were both 97%. The reported yield of CO was 96% with equimolar products of CO and H$_2$.

$$CH_4 + CO_2 \rightarrow 2H_2 + 2CO \qquad \Delta H° = 247 \text{ KJ/mol}, \Delta G° = 171 \text{ KJ/mol} \quad (7\text{-}83)$$
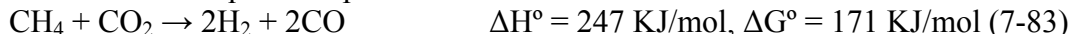
Compared with the conventional process, the new process (850°C) operates in the same temperature range as the conventional process (760-980°C). But, the new one (0.1 MPa) operates very lower pressure than the conventional process (4.1 MPa). On the other hand, the new process had the competitive high yields of the products with better performance catalysts. Hence, the potentially new process was selected for the HYSYS simulation and included in the chemical complex.

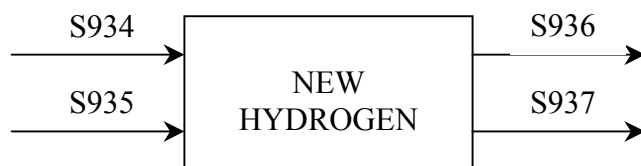The block flow diagram is given in Figure 7.31 with stream definitions from Table 7-93.

Figure 7.31 Block Diagram of New Hydrogen Process

Table 7-93 Description of Process Streams in New Hydrogen Process

Name of Streams	Description
Input Steams	
S934	CH_4 to new hydrogen process
S935	CO_2 to new hydrogen process
Output Streams	
S936	H_2 produced from new hydrogen process
S937	CO produced from new hydrogen process

B-24-2. Material Balance and Energy Balance

Using the parameters in Table 7-94, the material balance and energy balance of new hydrogen process are given in Table 7-95.

In Table 7-95, the overall material balance for the whole process is given first. For the species material balance obtained using the reaction equations (7-83), the first equation is for the CH_4 balance; the second one is for the CO_2 balance; the last one is for the CO balance.

In the overall energy balance, Q_{SYNGC} is heat input of the new hydrogen process in the form of steam in heat exchanger and distillation column reboilers for heat supply of the endothermic reaction and product separation, which is calculated from the energy balance. Q_{out} is the heat output removed by cooling water in distillation column condensers for product separation in the new hydrogen process based on the unit of hydrogen product, 1.4 MJ per lb of hydrogen (Indala, 2004). In enthalpy functions, the coefficients a_1, a_2, a_3, a_4, a_5, and b_1 for different species are given in Table A-1 in Appendix A in (Xu, 2004).

In the material balance part, there are 4 variables and 4 equations including one dependent equation (overall material balance), so the number of degrees of freedom is 1. For the material and energy balance, there are 13 variables and 9 equations including the dependent overall material balance, so the number of degrees of freedom is 5.

Table 7-94 Parameters in New Hydrogen Production, from Shamsi (2002) and Indala (2004)

Name	Meaning	Value
	Overall CH_4 conversion rate in new graphite process	1
	Overall CO_2 conversion rate in new graphite process	1
	H_2 selectivity in new hydrogen process	1

Table 7-95 Constraint Equations for New Hydrogen Production

Material Balance	
Overall	$(F_{934} + F_{935}) - (F_{936} + F_{937}) = 0$
Species	CH_4: $F_{934} - \dfrac{F_{936}}{2mw(H_2)} mw(CH_4) = 0$
	CO_2: $F_{935} - \dfrac{F_{936}}{2mw(H_2)} mw(CO_2) = 0$

$$\text{CO:} \quad \frac{F_{936}}{mw(H_2)} mw(CO) - F_{937} = 0$$

Energy Balance

Overall

$$(F_{936}^{(H_2)} / M^{(H_2)} H_{936}^{(H_2)} + F_{937}^{(CO)} / M^{(CO)} H_{937}^{(CO)}) - (F_{934}^{(CH_4)} / M^{(CH_4)} H_{934}^{(CH_4)}$$

$$+ F_{935}^{(CO_2)} / M^{(CO_2)} H_{935}^{(CO_2)}) + Q_{out} F_{936}^{(H_2)} - Q_{SYNGC} = 0$$

Enthalpy Function

$$H_k^i(T) = (a_1^i + \frac{1}{2} a_2^i T + \frac{1}{3} a_3^i T^2 + \frac{1}{4} a_4^i T^3 + \frac{1}{5} a_5^i T^4 + \frac{b_1^i}{T}) RT \quad \text{J/mol}$$

$$i = CH_4, CO_2, H_2, CO$$

$$k = 934, 935, 936, 937$$

B-25. Propylene (New Processes) (Pellegrino, 2000; Speight, 2002; Wells, 1999; Takahara, et al., 1998; Indala, 2004; C & EN, 2003; Louisiana Chemical & Petroleum Products List, 1998)

Propylene has a potential energy savings of 98 trillion BTUs per year though improved catalysts (Pellegrino, 2000). The conventional production of propylene is the steam cracking of hydrocarbons. Propane, naphtha, or gas oil is used as a feedstock and propylene and ethylene are co-products (Speight, 2002). 70% of world propylene production is obtained as co-product from naphtha cracking, with 2% from propane and the remainder from refinery operations and dehydrogenation (Wells, 1999). The overall chemical reaction using propane as feedstock (Equation 7-84) takes place at a temperature of 750-870°C and 31-37 atm, with the propylene yield 14-18% and the ethylene yield 42-45% (Wells, 1999).

$$2C_3H_8 \rightarrow C_3H_6 + C_2H_4 + CH_4 + H_2 \quad \Delta H° = 205.5 \text{ KJ/mol}, \Delta G° = 127.5 \text{ KJ/mol} \quad (7-84)$$
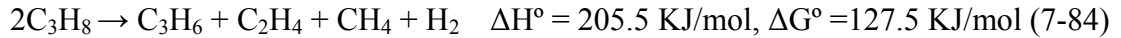
Two new processes for propylene production are discussed and included in the chemical complex after HYSYS simulation, one from dehydrogenation of propane using CO_2, and the other from dehydrogenation of propane. The first one consumes carbon dioxide and the other is a source of hydrogen for hydrogenation of carbon dioxide.

B-25-1. Propane Dehydrogenation by CO_2 (New Propylene by CO_2) (Takahara, et al., 1998; Indala, 2004; Louisiana Chemical & Petroleum Products List, 1998)

The process production capacity was set to be 41,900 metric tons of propylene per year. This was based on a plant of Union Texas Ethylene Corporation, located in Geismar, LA, with the capacity of 92 million pounds propylene per year (Louisiana Chemical & Petroleum Products List, 1998).

B-25-1-1. Process Description

Takahara, et al. (1998) described a new laboratory process by dehydrogenation of propane using carbon dioxide for the synthesis of propylene over Cr_2O_3/SiO_2 catalyst at 550°C and 1 atm (Equation 7-85). The major by-products were CO and H_2. The conversion of propane was 45% and the yield to propylene was 10 %.

$$2C_3H_8 + CO_2 \rightarrow 2C_3H_6 + CO + H_2O + H_2 \quad \Delta H° = 289 \text{ kJ/mol}, \Delta G° = 201 \text{ kJ/mol} \quad (7-85)$$

Compared with the conventional process, the reaction condition of the new process (550°C and 1 atm) is much milder than that of the conventional process (750-870°C and 31-37 atm). The yield of propylene in the new process (10%) is comparable with that of the conventional process (14-18%). On the other hand, CO_2 feedstock from other process emissions can suppresses catalyst deactivation in the new process. Hence, this new process

was simulated with HYSYS and included in the chemical complex. The block flow diagram is given in Figure 7.32 with stream definitions from Table 7-96.
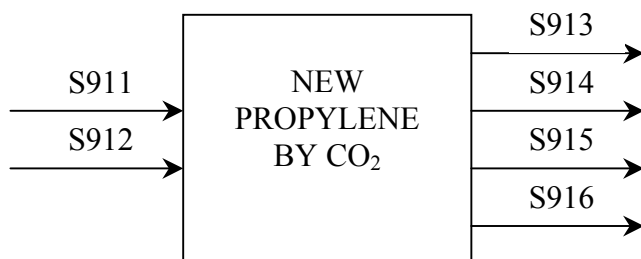

Figure 7.32 Block Diagram of New Propylene by CO_2 Process

Table 7-96 Description of Process Streams in New Propylene by CO_2 Process

Name of Streams	Description
Input Steams	
S911	Propane to new propylene by CO_2 process
S912	CO_2 to new propylene by CO_2 process
Output Streams	
S913	CO produced new propylene by CO_2 process
S914	Propylene produced from new propylene by CO_2 process
S915	Water produced from new propylene by CO_2 process
S916	H_2 produced from new propylene by CO_2 process

B-25-1-2. Material Balance and Energy Balance
        Using the parameters in Table 7-97, the material balance and energy balance of new propylene by CO_2 process are given in Table 7-98.

Table 7-97 Parameters in New Propylene Production by CO_2, from Takahara, et al. (1998) and Indala (2004)

Name	Meaning	Value
	Overall propane conversion rate in new propylene by CO_2 process	1
	Propylene selectivity in new propylene by CO_2 process	1

Table 7-98 Constraint Equations for New Propylene Production by CO_2

Material Balance	
Overall	$(F_{911} + F_{912}) - (F_{913} + F_{914} + F_{915} + F_{916}) = 0$

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Species	
	C_3H_8: $F_{911} - \dfrac{F_{914}}{mw(C_3H_6)} mw(C_3H_8) = 0$
	CO_2: $\dfrac{F_{914}}{2mw(C_3H_6)} mw(CO_2) - F_{912} = 0$
	H_2: $\dfrac{F_{914}}{2mw(C_3H_6)} mw(H_2) - F_{916} = 0$
	CO: $\dfrac{F_{914}}{2mw(C_3H_6)} mw(CO) - F_{913} = 0$
	H_2O: $\dfrac{F_{914}}{2mw(C_3H_6)} mw(H_2O) - F_{915} = 0$

Energy Balance

Overall

$$(F_{913}^{(CO)} / M^{(CO)} H_{913}^{(CO)} + F_{914}^{(C_3H_6)} / M^{(C_3H_6)} H_{914}^{(C_3H_6)} + F_{915}^{(H_2O)} / M^{(H_2O)} H_{915}^{(H_2O)}$$

$$+ F_{916}^{(H_2)} / M^{(H_2)} H_{916}^{(H_2)}) - (F_{911}^{(C_3H_8)} / M^{(C_3H_8)} H_{911}^{(C_3H_8)} + F_{912}^{(CO_2)} / M^{(CO_2)} H_{912}^{(CO_2)})$$

$$+ Q_{out} F_{914}^{(C_3H_6)} - Q_{PPEN} = 0$$

Enthalpy Function

$$H_k^i(T) = (a_1^i + \frac{1}{2} a_2^i T + \frac{1}{3} a_3^i T^2 + \frac{1}{4} a_4^i T^3 + \frac{1}{5} a_5^i T^4 + \frac{b_1^i}{T})RT \quad J/mol$$

$i = C_3H_8, CO_2, CO, C_3H_6, H_2O, H_2$
$k = 911, 912, 913, 914, 915, 916$

In Table 7-98, the overall material balance for the whole process is given first. For the species material balance obtained using the reaction equations (7-85), the first equation is for the C_3H_8 balance; the second one is for the CO_2 balance; the third one is for the H_2 balance; the fourth one is for the CO balance; the last one is for the H_2O balance.

In the overall energy balance, Q_{PPEN} is heat input of the new propylene by CO_2 process in the form of steam in heat exchanger and distillation column reboilers for heat supply of the endothermic reaction and product separation, which is calculated from the energy balance. Q_{out} is the heat output removed by cooling water in heat exchanger and distillation column condensers for product separation in the new propylene by CO_2 process based on the unit of propylene product, 3.2 MJ per lb of propylene (Indala, 2004). In enthalpy functions, the coefficients a_1, a_2, a_3, a_4, a_5, and b_1 for different species are given in Table A-1 in Appendix A in (Xu, 2004).

In the material balance part, there are 6 variables and 6 equations including one dependent equation (overall material balance), so the number of degrees of freedom is 1. For the material and energy balance, there are 19 variables and 13 equations including the dependent overall material balance, so the number of degrees of freedom is 7.

B-25-2. Propane Dehydrogenation (C & EN, 2003; Indala, 2004; Louisiana Chemical & Petroleum Products List, 1998)

The process production capacity was set to be 41,800 metric tons of propylene per year. This was based on a plant of Union Texas Ethylene Corporation, located in Geismar, LA, with the capacity of 92 million pounds propylene per year (Louisiana Chemical & Petroleum Products List, 1998).

B-25-2-1. Process Description

The world largest propane dehydrogenation plant for propylene production, which was built and operated by BASF Sonatrac PropanChem S.A., has started its trial operations at Tarragona, Spain (Equation 7-86) (C & EN, 2003). It is the first plant in Europe to use UOP LLC's C_3 Oleflex technology to only produce propylene from propane with the capacity of 350,000 metric tons per year of propylene. The reaction condition is 600°C and 1 atm over a proprietary platinum catalyst from UOP (called DeH-14) with 85% selectivity to propylene and 407% propane conversion per pass (C & EN, 2003).

$$C_3H_8 \rightarrow C_3H_6 + H_2 \qquad \Delta H° = 124 \text{ kJ/mol}, \Delta G° = 86 \text{ kJ/mol} \quad (7-86)$$
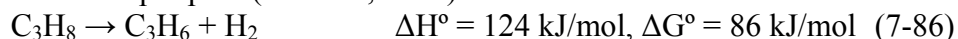
Compared with the conventional process (steam cracking), the new process has much milder reaction condition (600°C and 1 atm) than the conventional process (750-870°C and 31-37 atm). No by-product ethylene is produced in the new process with the by-product H_2 that can be used as a feedstock in other CO_2 hydrogenation processes. It is more economical to use the propane dehydrogenation process than the conventional process because only propylene is needed at the Tarragona site and the production cost is at most one fourth of the conventional process (C & EN, 2003). On the other hand, since this new process has already started trial operation with industrial production scale at Tarragona, Spain, this process is more realistic than laboratory scale processes. Meanwhile, there are no such plants in the lower Mississippi River corridor that uses this new process, so this process is simulated with HYSYS and incorporated into the chemical complex.

The block flow diagram is given in Figure 7.33 with stream definitions from Table 7-99.

Figure 7.33 Block Diagram of New Propylene Process

Table 7-99 Description of Process Streams in New Propylene Process

Name of Streams	Description
Input Steams	
S917	Propane to new propylene process
Output Streams	
S918	H_2 produced from new propylene process
S919	Propylene produced from new propylene process

B-25-2-2. Material Balance and Energy Balance

Using the parameters in Table 7-100, the material balance and energy balance of new propylene process are given in Table 7-101.

In Table 7-101, the overall material balance for the whole process is given first. For the species material balance obtained using the reaction equations (7-86), the first equation is for the C_3H_8 balance; the second one is for the H_2 balance.

In the overall energy balance, Q_{PPEND} is heat input of the new propylene process in the form of steam in heat exchanger and distillation column reboilers for the heat supply for the endothermic reaction and product separation, which is calculated from the energy balance. Q_{out} is the heat output removed by cooling water in heat exchanger and distillation column condensers for product separation in the new propylene process based on the unit of propylene product, 5.8 MJ per lb of propylene (Indala, 2004). In enthalpy functions, the coefficients a_1, a_2, a_3, a_4, a_5, and b_1 for different species are given in Table A-1 in Appendix A in (Xu, 2004).

In the material balance part, there are 3 variables and 3 equations including one dependent equation (overall material balance), so the number of degrees of freedom is 1. For the material and energy balance, there are 10 variables and 7 equations including the dependent overall material balance, so the number of degrees of freedom is 4.

Table 7-100 Parameters in New Propylene Production, from C & EN (2003) and Indala (2004)

Name	Meaning	Value
	Overall propane conversion rate in new propylene process	1
	Propylene selectivity in new propylene process	1

Table 7-101 Constraint Equations for New Propylene Production

Material Balance	
Overall	$F_{917} - (F_{918} + F_{919}) = 0$
Species	$C_3H_8:\ F_{917} - \dfrac{F_{919}}{mw(C_3H_6)} mw(C_3H_8) = 0$
	$H_2:\ \dfrac{F_{919}}{mw(C_3H_6)} mw(H_2) - F_{918} = 0$
Energy Balance	
Overall	$(F_{918}^{(H_2)} / M^{(H_2)} H_{918}^{(H_2)} + F_{919}^{(C_3H_6)} / M^{(C_3H_6)} H_{919}^{(C_3H_6)}) - F_{917}^{(C_3H_8)} / M^{(C_3H_8)} H_{917}^{(C_3H_8)}$
	$+ Q_{out} F_{919}^{(C_3H_6)} - Q_{PPEND} = 0$
Enthalpy Function	$H_k^i(T) = (a_1^i + \dfrac{1}{2} a_2^i T + \dfrac{1}{3} a_3^i T^2 + \dfrac{1}{4} a_4^i T^3 + \dfrac{1}{5} a_5^i T^4 + \dfrac{b_1^i}{T}) RT$ J/mol
	$i = C_3H_8,\ H_2,\ C_3H_6$
	$k = 917,\ 918,\ 919$

B-26. Sulfuric Acid (Superstructure) (Hertwig, 2004)

Because there were S and SO_2 from two gypsum reuse processes (Process C-3-1 and C-3-2) as feedstocks to sulfuric acid plant in the superstructure, these streams were added as

input streams compared to the process in the base case with the corresponding mass and energy balance changes given in this section.

B-26-1. Process Description of Contact Process for Sulfuric Acid

The block diagram is shown in Figure 7.34 with the stream definitions in Table 7-102.

Figure 7.34 Block Diagram of Contact Process to Produce Sulfuric Acid (Superstructure)
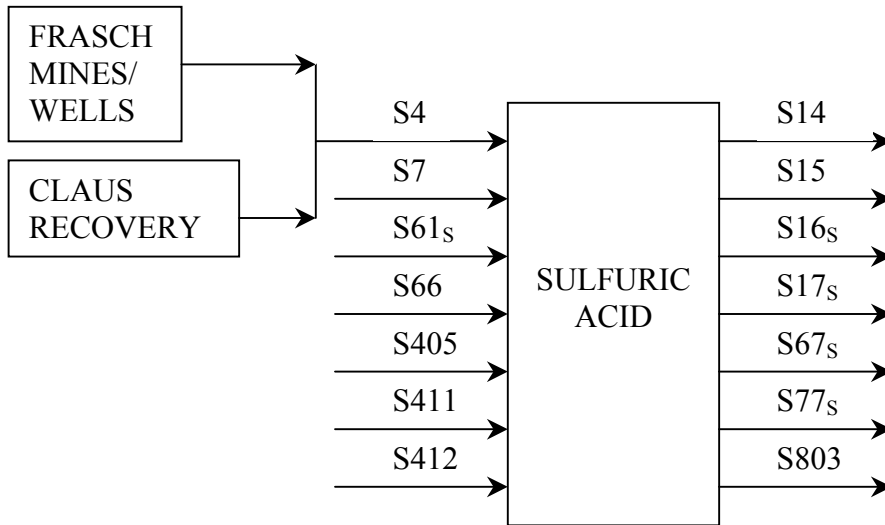
B-26-2. Material Balance and Energy Balance

The material balance and energy balance equations for this process are given in Table 7-103. The only changes compared with the one in base case are the input of S and SO_2 from two gypsum reuse process.

In the material balance part, there are 26 variables and 23 equations including one dependent one (overall material balance). So the number of degrees of freedom is 4 for the material balance part. For the material and energy balance, there are 38 variables and 29 equations including the dependent overall material balance. The number of degrees of freedom is 10.

Table 7-102 Description of Process Streams in Contact Sulfuric Acid Production (Superstructure)

Name of Streams	Description
Input Streams	
S2	S from Frasch mines/wells to sulfuric acid process (SAP)
S3	S from Claus recovery to SAP
S4	Total S to SAP
S7	Dry air to SAP
S61$_S$	boiler feed water (BFW) to SAP
S66	Process water to SAP
S405	SO_2 from sulfuric dioxide recovery process
S411	SO_2 from sulfur and sulfur dioxide recovery process

S412	S from sulfur and sulfur dioxide recovery process
Output Streams	
S14	H_2SO_4 solution produced from SAP
S15	Vent gases exiting from SAP
S16$_S$	Low pressure steam (LP) (40 psig) exiting from SAP
S17$_S$	High pressure steam (HP) (600 psig) exiting from SAP
S67$_S$	Boiler blowdown H_2O from SAP
S77$_S$	Intermediate pressure steam (IP) (150 psig) exiting from SAP
S803	Impurity of sulfur from SAP

Table 7-103 Constraint Equations for Contact Sulfuric Acid Production (Superstructure)

Material Balances

Overall

$$(F_4 + F_7 + F_{S61} + F_{66} + F_{405} + F_{411} + F_{412})$$
$$-(F_{14} + F_{15} + F_{S16} + F_{S17} + F_{S67} + F_{S77} + F_{803}) = 0$$
$$\text{where } F_7 = F_7^{(O_2)} + F_7^{(N_2)} + F_7^{(CO_2)} + F_7^{(Ar)}$$
$$F_{14} = F_{14}^{(H_2SO_4)} + F_{14}^{(H_2O)}$$
$$F_{15} = F_{15}^{(N_2)} + F_{15}^{(Ar)} + F_{15}^{(CO_2)} + F_{15}^{(SO_2)}$$

Table 7-103 Continued

Material Balance (Continued)

Heat Exchange (boiler feed water and steam balance)

$$(F_{S16} + F_{S17} + F_{S67} + F_{S77}) - F_{S61} = 0$$
$$F_{S61} = F_{S61}^{(a)} + F_{S61}^{(b)}$$

Species

$$S: \quad (F_4(1-\text{SIPSA}) + F_{412} + \frac{32.06}{64.06}(F_{405} + F_{411})) - \frac{32.06}{98.08}F_{14}^{(H_2SO_4)}$$
$$-\frac{32.06}{64.06}F_{15}^{(SO_2)} = 0$$

$$H_2O(\text{process water}): \quad F_{66} - \frac{18.02}{98.08}F_{14}^{(H_2SO_4)} - F_{14}^{(H_2O)} = 0$$

$$O_2: \quad F_7^{(O_2)} + \frac{32}{64.06}(F_{405} + F_{411}) - (1.5)\frac{32}{98.08}F_{14}^{(H_2SO_4)} - \frac{32}{64.06}F_{15}^{(SO_2)} = 0$$

$$N_2: \quad F_{15}^{(N_2)} - F_7^{(N_2)} = 0$$

$$Ar: \quad F_{15}^{(Ar)} - F_7^{(Ar)} = 0$$

$$CO_2: \quad F_{15}^{(CO_2)} - F_7^{(CO_2)} = 0$$

$$SO_2: \quad \frac{\text{SO2EMSA}}{2000}F_{14}^{(H_2SO_4)} - F_{15}^{(SO_2)} = 0$$

$$\text{Impurity: } F_{803} = F_4 \times \text{SIPSA}$$

Heat Exchange	BFW: $F_{S61}^{(a)} - \dfrac{(F_{S16} + F_{S17})}{(1 - BBLSA)} = 0$
	HP: $F_{S17} - \dfrac{(12)(1 - HPBTSA)}{SHPSA} F_{14}^{(H_2SO_4)} = 0$
	IP: $F_{S77} - \dfrac{IPCAPSA \times IPHRSSA(12)}{(3400)} F_{14}^{(H_2SO_4)} = 0$
	LP: $F_{S16} - \dfrac{(12)HPBTSA}{SHPSA} F_{14}^{(H_2SO_4)} = 0$
	Blowdown H_2O: $F_{S67} = BBLSA \times F_{S61}^{(a)}$
Energy Balance Overall	$(\dfrac{1}{M^{(H_2O)}} F_{S61}^{(H_2O)} H_{S61}^{(H_2O)} - (F_{S16} H^{(LP)} + F_{S17} H^{(HP)} + F_{S77} H^{(IP)}$
	$+ \dfrac{1}{M^{(H_2O)}} F_{S67}^{(H_2O)} H_{S67}^{(H_2O)})) - Q_{SACID} = 0$
	where M^i is molecule weight, $i = H_2O$

Table 7-103 Continued

Energy Balance (Continued)	
Enthalpy Function	$H_k^i(T) = (a_1^i + \dfrac{1}{2}a_2^i T + \dfrac{1}{3}a_3^i T^2 + \dfrac{1}{4}a_4^i T^3 + \dfrac{1}{5}a_5^i T^4 + \dfrac{b_1^i}{T})RT$ J/mol
	where R is gas constant
	T is temperature
	$i = H_2O$
	$k = 61, 67$
	$H^{(LP)}(T) = ((72.558 + (0.5)(-0.66244)T + (\dfrac{1}{3})(0.002562)T^2 +$
	$(0.25)(-4.3659E - 06)T^3 + (0.2)(2.7818E - 09)T^4 + \dfrac{(-41886)}{T})(8.3145)T$
	$-1893)\dfrac{1}{18.02} + ((-0.007)T^2 + (2.7838)T + 2292.0563)$
	J/g
	$H^{(IP)}(T) = ((72.558 + (0.5)(-0.66244)T + (\dfrac{1}{3})(0.002562)T^2 +$
	$(0.25)(-4.3659E - 06)T^3 + (0.2)(2.7818E - 09)T^4 + \dfrac{(-41886)}{T})(8.3145)T$
	$-1893)\dfrac{1}{18.02} + ((-0.007)T^2 + (2.7838)T + 2292.0563)$
	J/g

$$H^{(HP)}(P,T) = 2.326((5.32661)((T-273.15)(1.8)+32) - 0.2839015P$$

$$-(7.352389E-03)((T-273.15)(1.8)+32)^2 + (3.581547E-06)$$

$$((T-273.15)(1.8)+32)^3 - (7.289244E-05)P^2 + (4.595405E-04)$$

$$((T-273.15)(1.8)+32)P) - 15861.82$$

J/g, P:psia

Note: LP and IP have no super heat, from Meyer, et al. (1977) and McBride, et al. (1993); HP has super heat, from Chen (1998).

B-27. Granular Triple Super Phosphate (GTSP) (Superstructure) (Hertwig, 2004; Brown, et al., 1985)

B-27-1. Process Description

Because there were phosphoric acid from electric furnace (Process C-1) and Haifa (Process C-2) processes as feedstock to the GTSP process in the superstructure, these streams were added as input streams compared to the process in the base case with the corresponding mass and energy balance changes given in this section. The block diagram is given in Figure 7.35 with the stream descriptions from Table 7-104.
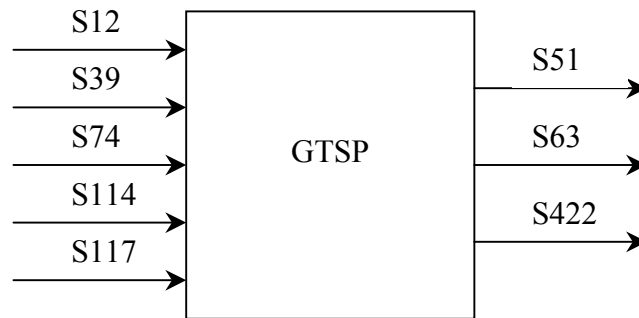
Figure 7.35 Block Diagram of GTSP Plant (Superstructure)

Table 7-104 Description of Process Streams in GTSP Plant (Superstructure)

Name of Stream	Description
Input Streams	
S12	Phosphate rock to GTSP
S39	Wet process phosphorous acid to GTSP
S74	Inert impurity to GTSP
S114	Electric furnace H_3PO_4 to GTSP
S117	Haifa H_3PO_4 to GTSP
Output Streams	
S51	GTSP produced from GTSP
S63	HF produced from GTSP
S422	Water evaporated from GTSP

B-27-2. Material Balance and Energy Balance

The material balance and energy balance equations for this process are given in Table 7-105. The only changes compared with the one in base case are the input of phosphoric acid from electric furnace and Haifa processes.

Table 7-105 Constraint Equations for GTSP Production (Superstructure)

Material Balance	
Overall	$(F_{12} + F_{39} + F_{74} + F_{114} + F_{117}) - (F_{51} + F_{63} + F_{422}) = 0$

where

$$F_{12} = F_{12}^{(ROCK)}$$

$$F_{39} = F_{39}^{(P_2O_5)} + F_{39}^{(H_2O)}$$

$$F_{114} = F_{114}^{(P_2O_5)} + F_{114}^{(H_2O)}$$

$$F_{117} = F_{117}^{(P_2O_5)} + F_{117}^{(H_2O)}$$

Species

P_2O_5:
$$\dfrac{UPAGTSP}{\dfrac{141.94}{(2)(98)}}(F_{39}^{(P_2O_5)} + F_{114}^{(P_2O_5)} + F_{117}^{(P_2O_5)}) - \dfrac{(PGTSP)(14)(98)}{\dfrac{141.94}{234.06}(10)(234.06)} F_{51} = 0$$

ROCK:
$$F_{12}^{(ROCK)} - \dfrac{(UPAGTSP)(2)(98)(1008.62)(100)(3)(310.18)}{(141.94)(14)(98)(BPLGTSP)(1008.62)(URGTSP)}(F_{39}^{(P_2O_5)} + F_{114}^{(P_2O_5)}$$
$$+ F_{117}^{(P_2O_5)}) = 0$$

HF:
$$\dfrac{(UPAGTSP)(2)(98)(2)(20.01)}{(141.94)(14)(98)}(F_{39}^{(P_2O_5)} + F_{114}^{(P_2O_5)} + F_{117}^{(P_2O_5)}) - F_{63} = 0$$

H_2O:
$$F_{422} - ((F_{39}^{(H_2O)} + F_{114}^{(H_2O)} + F_{117}^{(H_2O)}) - \dfrac{(3)(18.02)}{141.94}(F_{39}^{(P_2O_5)} + F_{114}^{(P_2O_5)} + F_{117}^{(P_2O_5)}) = 0$$

Energy Balance	
Overall	

$$((PGTSP)F_{51}^{(GTSP)} / M^{(P_2O_5)}H^{(GTSP)} + F_{63}^{(HF)} / M^{(HF)}H_{63}^{(HF)} + F_{422}^{(H_2O)} / M^{(H_2O)}H_{422}^{(H_2O)})$$

$$- ((BPLGTSP)/(100)F_{12}^{(ROCK)} /((3)M^{(Ca_3(PO_4))})H^{(ROCK)} +$$

$$\Sigma(F_{39}^{(i)} + F_{114}^{(i)} + F_{117}^{(i)}) / M^{(i)}H^{(i)}) + F_{51}Q_{out} - Q_{GTSP} = 0$$

$$i = P_2O_5, H_2O$$

Enthalpy Function
$$H_k^i(T) = (a_1^i + \dfrac{1}{2}a_2^i T + \dfrac{1}{3}a_3^i T^2 + \dfrac{1}{4}a_4^i T^3 + \dfrac{1}{5}a_5^i T^4 + \dfrac{b_1^i}{T})RT \quad J/mol$$

$$i = H_2O, HF$$
$$k = 39, 63, 114, 117, 422$$

$$H^{(ROCK)}(T) = (((-291.5)(1000) + (3)(-984.9)(1000)) + (16.02 + (3)(54.45))$$

$$(T - 298.15))(4.182)J/mol$$

Source: Lide (1982)

$$H^{(P_2O_5)} = (-1278.437)(1000) + (106.014)(T - 298.15) J / mol$$

Source: Lide (1982)

$$H^{(GTSP)}(T) = (-742.04)(1000)(4.182) + (246.4)(T - 298.15) J / mol$$

Source: Felder and Roussleu (1986)

In the material balance part, there are 15 variables and 12 equations, so the number of degrees of freedom is 3. For the material and energy balance, there are 27 variables and 19 equations, so the number of degrees of freedom is 8.

B-28. Mono-/Di-Ammonium Phosphates (MAP/DAP) (Superstructure) (Hertwig, 2004; Brown, et al., 1985; Louisiana Chemical & Petroleum Products List, 1998)

B-28-1. Process Description

Because there were phosphoric acid from electric furnace (Process C-1) and Haifa (Process C-2) processes as feedstock to the MAP and DAP process in the superstructure, these streams were added as input streams compared to the process in the base case with the corresponding mass and energy balance changes given in this section. The block diagram is illustrated in Figure 7.36 with the stream definitions in Table 7-106.
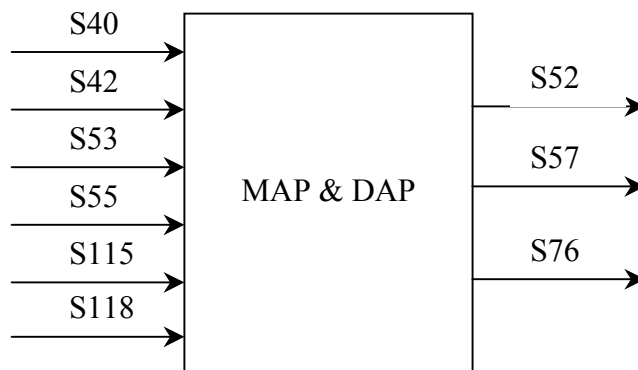
Figure 7.36 Block Diagram of MAP & DAP Plant (Superstructure)

B-28-2. Material Balance and Energy Balance

The material balance and energy balance equations for this process are given in Table 7-107. The only changes compared with the one in base case are the input of phosphoric acid from electric furnace and Haifa processes.

Table 7-106 Description of Process Streams in MAP & DAP Plant (Superstructure)

Name of Streams	Description
Input Streams	
S40	Wet process phosphoric acid to MAP & DAP plant
S42	Ammonia to MAP & DAP plant
S53	Urea produced from urea plant as N-boosters to MAP & DAP plant
S55	Inert impurity to MAP & DAP plant
S115	Electric furnace H_3PO_4 to MAP & DAP plant
S118	H_3PO_4 produced from Haifa process to MAP & DAP plant
Output Streams	
S52	MAP produced from MAP & DAP plant
S57	DAP produced from MAP & DAP plant
S76	Water vapor from MAP & DAP plant

Table 7-107 Constraint Equations for MAP & DAP Production (Superstructure)

Material Balance	
Overall	$(F_{40} + F_{42} + F_{53} + F_{55} + F_{115} + F_{118}) - (F_{52} + F_{57} + F_{76}) = 0$

where

$$F_{40} = F_{40}^{(P_2O_5)} + F_{40}^{(H_2O)}$$

$$F_{53} = F_{53}^{(UREA)}$$

$$F_{115} = F_{115}^{(P_2O_5)} + F_{115}^{(H_2O)}$$

$$F_{118} = F_{118}^{(P_2O_5)} + F_{118}^{(H_2O)}$$

Species

P_2O_5: $(F_{40}^{(P_2O_5)} + F_{115}^{(P_2O_5)} + F_{118}^{(P_2O_5)}) - (\dfrac{P2O5MAP}{100} F_{52} + \dfrac{P2O5DAP}{100} F_{57}) = 0$

NH_3:

$$\frac{1}{17.04} F_{42} - \frac{(RPDAP)(NDAP)}{(RPDAP + RPMAP)(P2O5DAP)(14.01)} (F_{40}^{(P_2O_5)} + F_{115}^{(P_2O_5)}$$

$$+ F_{118}^{(P_2O_5)}) - \frac{(RPMAP)(NMAP)}{(RPDAP + RPMAP)(P2O5MAP)(14.01)} (F_{40}^{(P_2O_5)} + F_{115}^{(P_2O_5)}$$

$$+ F_{118}^{(P_2O_5)}) = 0$$

UREA: $F_{53}^{(UREA)} - (NBRDAP)F_{57} = 0$

H_2O:

$$F_{76} - ((F_{40}^{(H_2O)} + F_{115}^{(H_2O)} + F_{118}^{(H_2O)}) - \frac{(3)(18.02)}{141.94} (F_{40}^{(P_2O_5)} + F_{115}^{(P_2O_5)} + F_{118}^{(P_2O_5)})) = 0$$

Table 7-107 Continued

Material Balance (Continued)	
Species	MAP:

$$F_{52} - \frac{(RPMAP)(100)}{(RPDAP + RPMAP)(P2O5MAP)}(F_{40}^{(P_2O_5)} + F_{115}^{(P_2O_5)} + F_{118}^{(P_2O_5)}) = 0$$

Energy Balance

Overall

$$((PURMAP)F_{52}^{(MAP)} / M^{(MAP)}H_{52}^{(MAP)} + (PURDAP)F_{57}^{(DAP)} / M^{(DAP)}H_{57}^{(DAP)} +$$

$$F_{76}^{(H_2O)} / M^{(H_2O)}H_{76}^{(H_2O)}) - (\Sigma F_{40}^{(i)} / M^{(i)}H_{40}^{(i)} + \Sigma F_{115}^{(i)} / M^{(i)}H_{115}^{(i)}$$

$$+ \Sigma F_{118}^{(i)} / M^{(i)}H_{118}^{(i)} + F_{42}^{(NH_3)} / M^{(NH_3)}H_{42}^{(NH_3)}) + Q_{out}(F_{52} + F_{57}) - Q_{APG} = 0$$

$$i = P_2O_5, H_2O$$

Enthalpy Function

$$H_k^i(T) = (a_1^i + \frac{1}{2}a_2^i T + \frac{1}{3}a_3^i T^2 + \frac{1}{4}a_4^i T^3 + \frac{1}{5}a_5^i T^4 + \frac{b_1^i}{T})RT \quad J/mol$$

$$i = H_2O, NH_3$$

$$k = 40, 42, 76, 115, 118$$

$$H^{(P_2O_5)} = (-1278.437)(1000) + 106.014(T - 298.15)J / mol$$

Source: Lide (1982)

$$H_k^{(MAP)} = ((-345.38)(1000) + 34.00(T - 298.15))4.182 \quad J/mol \ k=52$$

Source: Lide (1982)

$$H_k^{(DAP)} = ((-374.50)(1000) + 45.00(T - 298.15))4.182 \quad J/mol \ k=57$$

Source: Lide (1982)

In the material balance part, there are 15 variables and 12 equations, so the number of degrees of freedom is 3. For the material and energy balance, there are 27 variables and 19 equations, so the number of degrees of freedom is 8.

B-29. Relations of Chemical Production Complex in the Superstructure

The streams not defined in the above plant models are described in Table 7-108. The stream relationship for mass balance in the superstructure of chemical production complex is given in Table 7-109, and for energy balance is given in Table 7-110.

Table 7-108 Description of Process Streams in the Superstructure

Name of Streams	Description
S5	Total air input to the superstructure
S6	Total natural gas input to the superstructure
Sapply	Steam available for the superstructure
S30	NH_3 from NH_3 plant to ammonium nitrate plant and for sale
S43	NH_3 for sale
SCDEM	Total impure CO_2 emissions from the superstructure
S59	Urea for sale
S423	Methanol for sale

Table 7-109 Stream Relationship for Mass Balance in the Superstructure

Relationship	Description
$F_2 + F_3 = F_4$	Sulfur from Frasch mines/wells and Claus recovery to sulfuric acid plant
$F_5 = F_7 + F_8 + F_9$ $+ F_{200} + F_{402} + F_{410}$	Air to sulfuric acid, nitric acid, ammonia, electric furnace, SO_2 recovery, and S and SO_2 recovery plant
$F_6 = F_{10} + F_{11} + F_{300}$ $+ F_{83} + F_{701} + F_{924}$	Natural gas to ammonia, methanol, power plant, acetic acid, new acetic acid plant, and other CO_2 consuming plants
$F_{16} + F_{18}$ $= F_{24} + F_{27} + F_{28} + F_{apply}$	LP steam from sulfuric acid and power plant to phosphoric acid, urea and other plants as heat input
$F_{19} = F_{29} + F_{30} + F_{31}$ $+ F_{42} + F_{948}$	Ammonia from ammonia plant to nitric acid, ammonium nitrate, ammonium phosphate, urea plant, for sale, and methylamines plant
$F_{20} = F_{32} + F_{33} + F_{64}$ $+ F_{82} + F_{700} + F_{922}$	CO_2 from ammonia plant to urea, methanol, acetic acid, emission to atmosphere, new acetic acid, and other CO_2 consuming processes
$F_{30} = F_{43} + F_{44}$	Ammonia to ammonium phosphate plant and for sale
$F_{46} = F_{54} + F_{59}$	Urea from urea plant to UAN plant and for sale
$F_{60} = F_{39} + F_{40} + F_{41}$	Phosphoric acid from phosphoric acid plant to GTSP, ammonium phosphate plant and for sale
$F_{47} + F_{991} = F_{423} + F_{424}$	Methanol from methanol plant and other methanol production plants to acetic acid plant and for sale
$F_{1069} = F_{1070} + F_{1071} + F_{971}$	Ethylbenzene from ethylbenzene plant to styrene plant, for sale, and new styrene process
Relationship	Description
$F_{CDEM} = F_{301} + F_{801}$ $+ F_{81}^{(CO_2)} + F_{15}^{(CO_2)} + F_{802}^{(CO_2)}$ $+ F_{166} + F_{151}^{(CO_2)} + F_{403}^{(CO_2)}$ $+ F_{413}^{(CO_2)} + F_{949}^{(CO_2)}$	Impure CO_2 emissions from power plant, urea, nitric acid, sulfuric acid, methanol, electric furnace, SO_2 recovery, S and SO_2 recovery, and methylamines plants
$F_{22} = F_{408} + F_{400} + F_{416}$	Gypsum from wet process for phosphoric acid to electric furnace and Haifa processes, and to the gypsum stack
$F_{112} = F_{114} + F_{115}$	Phosphoric acid from electric furnace to GTSP, MAP and DAP plants
$F_{87} = F_{117} + F_{118}$	Phosphoric acid from Haifa process to GTSP, MAP and DAP plants
$F_{922} = F_{912} + F_{935} + F_{942}$ $+ F_{946} + F_{953} + F_{958} + F_{963}$ $+ F_{967} + F_{972} + F_{980} + F_{984}$ $+ F_{993}$	CO_2 from ammonia plant to new CO_2 consuming processes, such as propane degydrogenation with CO_2, H_2, formic acid, methylamines, methanol (Jun), methanol (Bonivardi), methanol (Nerlov), methanol (Ushikoshi), new styrene, ethanol, DME, and graphite processes

$F_{924} = F_{934} + F_{992}$	Natural gas to new processes, such as graphite and H_2
$F_{936} + F_{918} + F_{916} + F_{994} =$ $F_{903} + F_{943} + F_{947} + F_{981}$ $+ F_{985} + F_{954} + F_{959} + F_{964}$ $+ F_{968}$	H_2 produced from H_2, propane dehydrogenation, propane dehydrogenation with CO_2 and graphite processes to for sales, formic acid, methylamines, ethanol, DME, methanol (Jun), methanol (Bonivardi), methanol (Nerlov), and methanol (Ushikoshi) processes
$F_{955} + F_{961} + F_{965}$ $+ F_{969} = F_{991}$	Methanol produced from methanol (Jun), methanol (Bonivardi), methanol (Nerlov), and methanol (Ushikoshi) processes

Table 7-110 Stream Relationship for Energy Balance in the Superstructure

Relationship	Description
Tlp = Ts24	LP from sulfuric acid plant (S16$_S$) and LP to phosphoric acid plant (S24$_S$) have same temperature.
Tlp = Tlpp	LP from sulfuric acid plant (SS16) and LP from power plant (S18$_S$) have same temperature.
TO2b = TO2a	Air to nitric acid plant (S8) and air to ammonia plant (S9) have same temperature.
TNH3a = TNH3b	NH_3 from NH_3 plant (S19) and NH_3 to nitric acid plant (S29) have same temperature.
TNH3a = TNH3i	NH_3 from NH_3 plant (S19) and NH_3 to urea plant (S31) have same temperature.
Relationship	Description
TNH3a = TNH3k	NH_3 from NH_3 plant (S19) and NH_3 to MAP and DAP plant (S42) have same temperature.
TNH3a = TNH3j	NH_3 from NH_3 plant (S19) and NH_3 to ammonium nitrate plant (S29) have same temperature.
TCO2c = TCO2i	CO_2 from NH_3 plant (S20) and CO_2 to urea plant (S32) have same temperature.
TCO2c = TCO2h	CO_2 from NH_3 plant (S20) and CO_2 to methanol plant (S33) have same temperature.
Taq = Ta	Nitric acid from nitric acid plant (S45) and nitric acid to ammonium nitrate plant (S45) have same temperature.
TCH4a = TCH4h	CH_4 to NH_3 plant (S10) and CH_4 to methanol plant (S11) have same temperature.
Thp39 = Thp40	Phosphoric acid to GTSP plant (S39) and phosphoric acid to MAP and DAP plant (S40) have same temperature.
TCO2c = Ts82	CO_2 from NH_3 plant (S20) and CO_2 to acetic acid plant (S82) have same temperature.
TCH4a = Ts83	CH_4 to NH_3 plant (S10) and CH_4 to acetic acid plant (S83) have same temperature.
Tmet = Ts424	Methanol from methanol plant (S47) and methanol to acetic acid plant (S424) have same temperature.

Relationship	Description
T('1069') = T('1071')	Ethylbenzene from ethylbenzene plant (S1069) and ethylbenzene to styrene plant (S1071) have same temperature.
TO2a = Ts402	Air to ammonia plant (S9) and air to SO_2 recovery plant have same temperature.
TO2a = Ts410	Air to ammonia plant (S9) and air to S and SO_2 recovery plant (S410) have same temperature.
TO2a = Ts200	Air to ammonia plant (S9) and air to electric furnace plant (S200) have same temperature.
Thp39 = Thp112	Phosphoric acid from wet process to GTSP plant (S39) and phosphoric acid from electric furnace plant (S112) have same temperature.
Thp39 = Ts87	Phosphoric acid from wet process to GTSP plant (S39) and phosphoric acid from Haifa process (S87) have same temperature.
Ts22 = Ts400	Gypsum from wet process (S22) and gypsum to SO_2 recovery plant (S400) have same temperature.
Ts22 = Ts408	Gypsum from wet process (S22) and gypsum to S and SO_2 recovery plant (S408) have same temperature.
TCH4a = Ts701	CH_4 to NH_3 plant (S10) and CH_4 to new acetic acid plant (S701) have same temperature.

Table 7-110 Continued

Relationship	Description
TCO2c = Ts700	CO_2 from NH_3 plant (S20) and CO_2 to new acetic acid plant (S700) have same temperature.
TCH4a = T('924')	CH_4 to NH_3 plant (S10) and CH_4 to new processes added in the superstructure (S924) have same temperature.
TCO2c = T('922')	CO_2 from NH_3 plant (S20) and CO_2 to new CO2 consuming processes (S922) have same temperature.
TNH3a = T('948')	NH_3 from NH_3 plant (S19) and NH_3 to methylamines plant (S948) have same temperature.
Ts424 = T('991')	Methanol from methanol plant (S47) and methanol from the new methanol processes (S991) have same temperature.
T('994') = T('959')	H_2 from graphite plant (S994) and H_2 to methanol (Bonivardi) plant (S959) have same temperature.
T('912') = T('953')	CO_2 to propane dehydrogenation with CO_2 plant (S912) and CO_2 to methanol (Jun) plant (S953) have same temperature.
T('994') = T('918')	H_2 from graphite plant (S994) and H_2 from propane dehydrogenation plant (S918) have same temperature.
T('994') = T('916')	H_2 from graphite plant (S994) and H_2 from propane dehydrogenation with CO_2 plant (S916) have same temperature.
T('994') = T('903')	H_2 from graphite plant (S994) and H_2 for sale (S903) have

Relationship	Description
	same temperature.
T('994') = T('943')	H_2 from graphite plant (S994) and H_2 to formic acid plant (S943) have same temperature.
T('912') = T('935')	CO_2 to propane dehydrogenation with CO_2 plant (S912) and CO_2 to H_2 plant (S935) have same temperature.
T('994') = T('981')	H_2 from graphite plant (S994) and H_2 to ethanol plant (S981) have same temperature.
T('994') = T('985')	H_2 from graphite plant (S994) and H_2 to DME plant (S985) have same temperature.
T('912') = T('942')	CO_2 to propane dehydrogenation with CO_2 plant (S912) and CO_2 to formic acid plant (S942) have same temperature.
T('912') = T('972')	CO_2 to propane dehydrogenation with CO_2 plant (S912) and CO_2 to new styrene plant (S972) have same temperature.
T('994') = T('947')	H_2 from graphite plant (S994) and H_2 to methylamines plant (S947) have same temperature.
T('994') = T('968')	H_2 from graphite plant (S994) and H_2 to methanol (Ushikoshi) plant (S968) have same temperature.

Table 7-110 Continued

Relationship	Description
T('994') = T('964')	H_2 from graphite plant (S994) and H_2 to methanol (Nerlov) plant (S964) have same temperature.
T('994') = T('954')	H_2 from graphite plant (S994) and H_2 to methanol (Jun) plant (S954) have same temperature.
T('912') = T('967')	CO_2 to propane dehydrogenation with CO_2 plant (S912) and CO_2 to methanol (Ushikoshi) plant (S967) have same temperature.
T('912') = T('963')	CO_2 to propane dehydrogenation with CO_2 plant (S912) and CO_2 to methanol (Nerlov) plant (S963) have same temperature.
T('924') = T('934')	CH_4 to the new processes added in the superstructure (S924) and CH_4 to H_2 plant (S992) have same temperature.
T('912') = T('958')	CO_2 to propane dehydrogenation with CO_2 plant (S912) and CO_2 to methanol (Bonivardi) plant (S958) have same temperature.
T('912') = T('946')	CO_2 to propane dehydrogenation with CO_2 plant (S912) and CO_2 to methylamines plant (S946) have same temperature.
T('924') = T('992')	CH_4 to the new processes added in the superstructure (S924) and CH_4 to graphite plant (S992) have same temperature.
T('912') = T('980')	CO_2 to propane dehydrogenation with CO_2 plant (S912) and CO_2 to ethanol plant (S980) have same temperature.

T('912') = T('984')	CO_2 to propane dehydrogenation with CO_2 plant (S912) and CO_2 to DME plant (S984) have same temperature.
T('912') = T('993')	CO_2 to propane dehydrogenation with CO_2 plant (S912) and CO_2 to graphite plant (S993) have same temperature.
T('1069') = T('971')	Ethylbenzene from ethylbenzene plant (S1069) and ethylbenzene to new styrene plant (S971) have same temperature.
T('912') = T('922')	CO_2 to propane dehydrogenation with CO_2 plant (S912) and CO_2 from ammonia plant to CO_2 consuming processes (S992) have same temperature.
T('991') = T('965')	Methanol from the new methanol processes (S991) and methanol from methanol (Nerlov) plant (S965) and have same temperature.
T('991') = T('955')	Methanol from the new methanol processes (S991) and methanol from methanol (Jun) plant (S955) and have same temperature.

Table 7-110 Continued

Relationship	Description
T('991') = T('961')	Methanol from the new methanol processes (S991) and methanol from methanol (Bonivardi) plant (S965) and have same temperature.
T('991') = T('969')	Methanol from the new methanol processes (S991) and methanol from methanol (Ushikoshi) plant (S969) and have same temperature.

The model of the superstructure of chemical production complex is a mixed integer nonlinear programming problem. For mixed integer optimization, binary variables are associated with the production capacities of each plant. If the binary variable for a process is one, then the plant operates at least at its lower bound on the production capacity. If the binary variable of a process is zero, then the production capacity of that process is zero, and the plant is not in the optimal structure. Relations among the binary variables and the logic constraints used in the System are given in Table 7-111, and the binary variables associated the plants are:

acetic acid (Y_{11})   acetic acid-new process (Y_{12})
SO_2 recovery from gypsum (Y_{13})   S and SO_2 recovery from gypsum (Y_{14})
phosphoric acid, electric furnace (Y_1)   phosphoric acid, Haifa process (Y_2)
phosphoric acid, wet process (Y_3)   methanol (Y_{16})
methanol – Jun, et al., 1998 (Y_{31})   methanol - Bonivardi, et al., 1998 (Y_{32})
methanol – Nerlov and Chorkendorff, 1999 (Y_{33})
methanol – Ushikoshi, et al., 1998 (Y_{34})
styrene-new process (Y_{35})   styrene (Y_{40})
ethyl benzene (Y_{41})   formic acid (Y_{29})
methylamines (Y_{30})   ethanol (Y_{37})
dimethyl ether (Y_{38})   propylene from CO_2 (Y_{23})

propylene from propane dehydrogenation (Y_{24})

synthesis gas (Y_{27})   graphite (Y_{39})

Table 7-111 Logical Relations Used to Select the Optimal Structure

Logic Expression	Logic Meaning
$Y_{11} + Y_{12} \leq 1$	At most one of these two acetic acid plants is selected.
$Y_{13} + Y_{14} \leq Y_3$	At most one of these two S and SO_2 recovery plants is selected only if phosphoric acid (wet process) is selected.
$Y_{16} + Y_{31} + Y_{32} + Y_{33} + Y_{34} \leq 1$	At most one of the five methanol plants is selected, the existing one or one of the four proposed plants.
$Y_{11} \leq Y_{16} + Y_{31} + Y_{32} + Y_{33} + Y_{34}$	Only if at least one of these five methanol plants is selected, the conventional acetic acid may be selected.
$Y_{35} + Y_{40} \leq Y_{41}$	At most one of these two styrene plants is selected only if ethylbenzene plant is selected.
$Y_{29} \leq Y_{23} + Y_{24} + Y_{27} + Y_{39}$	Only if at least one of the four plants that produce H_2 is selected, the formic acid plant may be selected.
$Y_{30} \leq Y_{23} + Y_{24} + Y_{27} + Y_{39}$	Only if at least one of the four plants that produce H_2 is selected, the methylamines plant may be selected.
$Y_{31} \leq Y_{23} + Y_{24} + Y_{27} + Y_{39}$	Only if at least one of the four plants that produce H_2 is selected, the new methanol plant may be selected.
$Y_{32} \leq Y_{23} + Y_{24} + Y_{27} + Y_{39}$	Only if at least one of the four plants that produce H_2 is selected, the new methanol plant may be selected.
$Y_{33} \leq Y_{23} + Y_{24} + Y_{27} + Y_{39}$	Only if at least one of the four plants that produce H_2 is selected, the new methanol plant may be selected.
$Y_{34} \leq Y_{23} + Y_{24} + Y_{27} + Y_{39}$	Only if at least one of the four plants that produce H_2 is selected, the new methanol plant may be selected.
$Y_{37} \leq Y_{23} + Y_{24} + Y_{27} + Y_{39}$	Only if at least one of the four plants that produce H_2 is selected, the ethanol plant may be selected.
$Y_{38} \leq Y_{23} + Y_{24} + Y_{27} + Y_{39}$	Only if at least one of the four plants that produce H_2 is selected, the dimethyl ether plant may be selected.

Referring to Table 7-111, the conventional processes and the corresponding potentially new processes were compared to each other for acetic acid, S and SO_2 recovery, methanol and styrene; and the best processes were selected. Also, hydrogen must be available for plants that require hydrogen for them to be included in the complex.

For optimization, upper and lower bounds of the production capacities of plants in the complex are required. The upper bounds for the potentially new processes were from the HYSYS simulations that were based on actual plants. For convenience, the lower bound for the production capacity was selected as half the value of upper bound. If a process is selected, it has to operate at least at the lower bound of its production capacity. The upper bounds and lower bounds of the production capacities of all the plants in the chemical complex are shown in Table 7-112.

Table 7-112 Plant Capacities of the Chemical Production Complex

Plant Names	Capacity Constraints (metric tons per year)
Ammonia	$329,000 \leq F_{19} \leq 658,000$
Nitric acid	$89,000 \leq F_{45}^{(HNO_3)} \leq 178,000$
Ammonium nitrate	$113,000 \leq F_{56} + F_{62}^{(AN)} \leq 227,000$
Urea	$49,900 \leq F_{46} + F_{53}^{(UREA)} \leq 99,800$
Methanol	$91,000 \leq F_{47} \leq 181,000$
UAN	$30,000 \leq F_{58} \leq 60,000$
MAP	$146,000 \leq F_{52} \leq 293,000$
DAP	$939,000 \leq F_{57} \leq 1,880,000$
GTSP	$374,000 \leq F_{51} \leq 749,000$
Contact process sulfuric acid	$1,810,000 \leq F_{14}^{(H_2SO_4)} \leq 3,620,000$
Wet process phosphoric acid	$635,000 \leq F_{60}^{(P_2O_5)} \leq 1,270,000$
Electric furnace phosphoric acid	$635,000 \leq F_{112}^{(P_2O_5)} \leq 1,270,000$
Haifa phosphoric acid	$635,000 \leq F_{87}^{(P_2O_5)} \leq 1,270,000$
Acetic acid (conventional)	$4,080 \leq F_{84} \leq 8,160$
Acetic acid (new)	$4,090 \leq F_{702} \leq 8,180$
SO$_2$ recovery from gypsum	$987,000 \leq F_{405} \leq 1,970,000$

Table 7-112 Continued

Plant Names	Capacity Constraints (metric tons per year)
S and SO$_2$ recovery from gypsum	$494,000 \leq \dfrac{32.06}{64.06} F_{411} + F_{412} \leq 988,000$
Ethylbenzene	$431,000 \leq F_{1069} \leq 862,000$
Styrene	$386,000 \leq F_{1072} \leq 771,000$
New Styrene	$181,000 \leq F_{974} \leq 362,000$
New Methanol (Bonivardi)	$240,000 \leq F_{961} \leq 480,000$
New Methanol (Jun)	$240,000 \leq F_{955} \leq 480,000$
New Methanol (Nerlov)	$240,000 \leq F_{965} \leq 480,000$
New Methanol (Ushikoshi)	$240,000 \leq F_{969} \leq 480,000$
New Formic Acid	$39,000 \leq F_{944} \leq 78,000$
New Methylamines	$13,200 \leq F_{950} \leq 26,400$

New Ethanol	$52,000 \le F_{982} \le 104,000$
New DiMethyl Ether (DME)	$22,900 \le F_{987} \le 45,800$
New Graphite	$23,000 \le F_{995} \le 46,000$
New Hydrogen	$6,700 \le F_{936} \le 13,400$
New Propylene by CO_2	$21,000 \le F_{914} \le 41,900$
New Propylene	$20,900 \le F_{919} \le 41,800$

C. Summary

This chapter describes the detail process model for the chemical production complex in the lower Mississippi River corridor. The simulation of chemical production complex of existing plants in the Chemical Complex Analysis System has been validated using results from the industrial advisory group.

VII. GETTING STARTED WITH THE CHEMICAL COMPLEX ANALYSIS SYSTEM
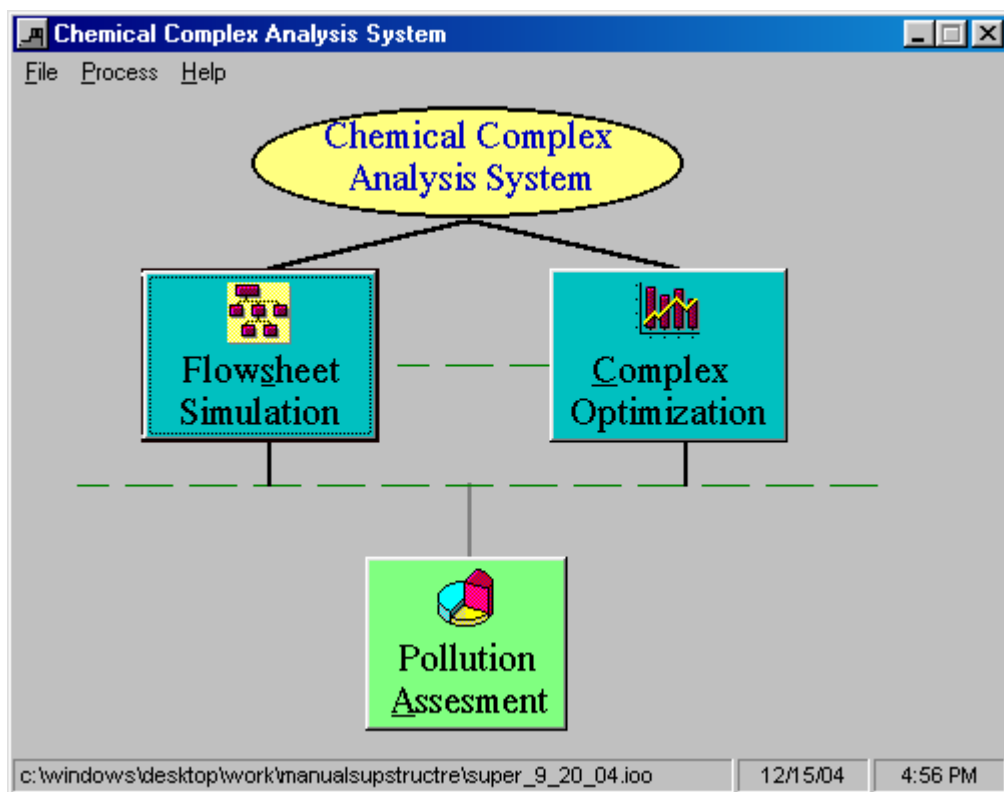
Figure 44: Chemical Complex Analysis Desk
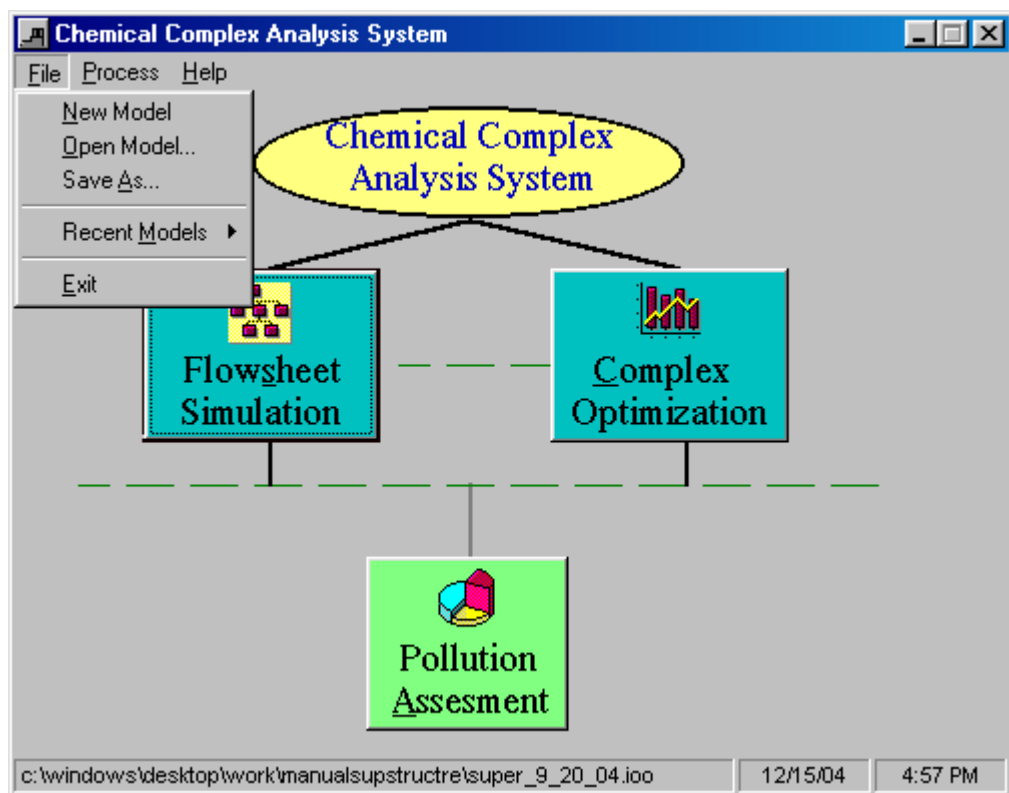
Figure 45: The File Menu of the Chemical Complex Analysis Desk
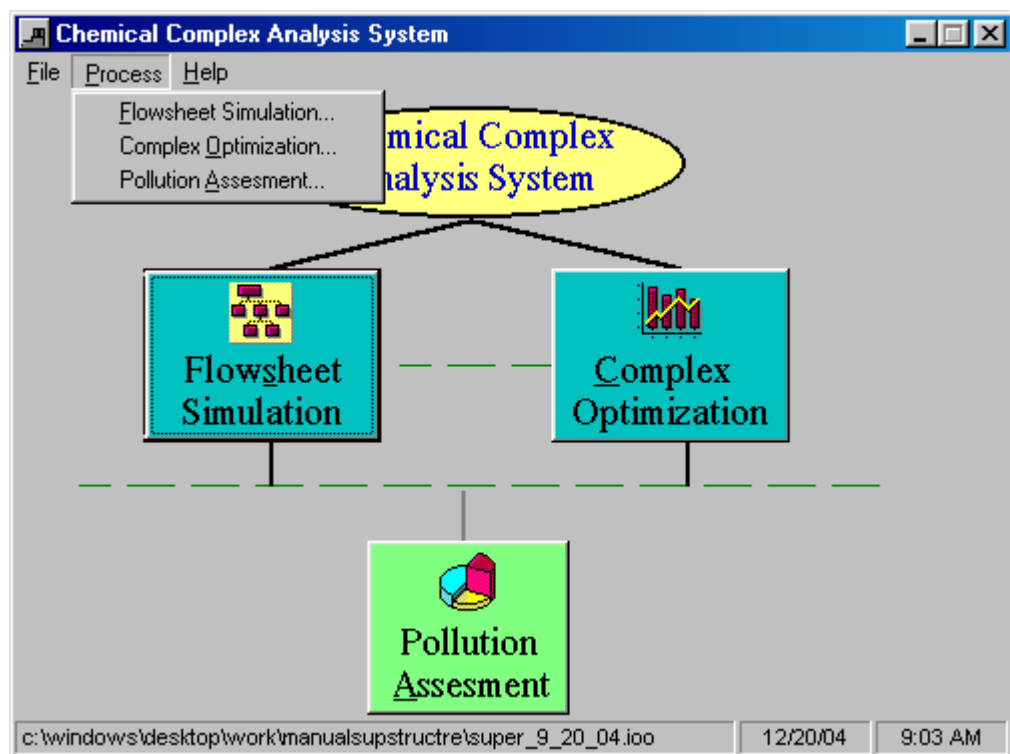
Figure 46: The Process Menu of the Chemical Complex Analysis Desk

Upon running the Chemical Complex Analysis System, the first window presented to the user is the 'Chemical Complex Analysis Desk'. This is shown in Figure 44.

By default, the Chemical Complex Analysis System opens a new model named 'untitled.ioo' in the program directory. The complete filename for this new model is shown in the bottom left corner of the window. The bottom right corner shows the date and the time the program was started. The file menu provides various options such as opening a new or an existing model. This is shown in Figure 45. The 'Recent Models' item in the file menu maintains a list of last four recently used models for easy access.

The Chemical Complex Analysis Desk has five buttons leading to the five component programs, which were described in earlier sections. All of these can also be called using the process menu at the top. This is shown in Figure 46.

When a new model is opened, only the 'Flowsheet Simulation' button is available. This is because the development of the process model using Flowsim is the first step in the implementation of the Chemical Complex Analysis System. Until the flowsheet simulation part is completed, buttons for the other four programs remain dimmed and unavailable.

To implement the Chemical Complex Analysis System for the Chemical Complex process described in earlier section, the first step is to develop the process model using the Flowsim program. The 'Flowsheet Simulation' button should be now clicked to open the Flowsim program.

VII A. USING FLOWSIM

Upon clicking the 'Flowsheet Simulation' button in Figure 46, the FlowSim window is displayed with the 'General Information' box. In the space for model name, let us enter 'complexfinal'. In the process description box, let us enter "Fertilizer Production Complex". The 'General Information' box with this information is shown in Figure 47.

By clicking the 'OK' button, the main screen of 'FlowSim' is displayed. This is the screen where the user draws the flowsheet diagram. The 'Model' menu shown in Figure 48 provides the various commands used to draw the flowsheet diagram. The menu commands are divided into two groups. The first group has commands for drawing the flowsheet diagram whereas the second group has commands for entering various kinds of process information.

The 'Add Unit' command should be used to draw a process unit. The 'Add Stream' command should be used to draw a process stream between two process units. The program requires that every stream be drawn between two units. However, the input and output streams of a process only have one unit associated with them. To solve this problem, the FlowSim program provides an additional type of unit called 'Environment I/O'. This can be drawn using the command 'Add Environment I/O' in Figure 48. The 'Lock' option makes the diagram read-only and does not allow any changes. The diagram can be unlocked by clicking on the command again.
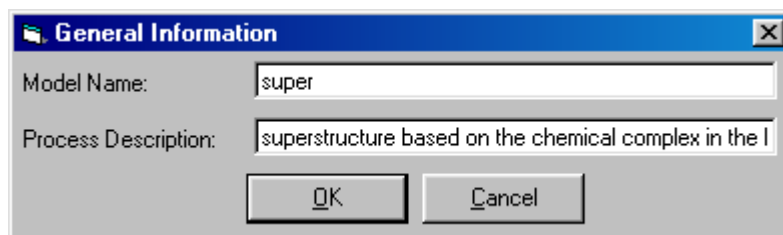
Figure 47: General Information Box
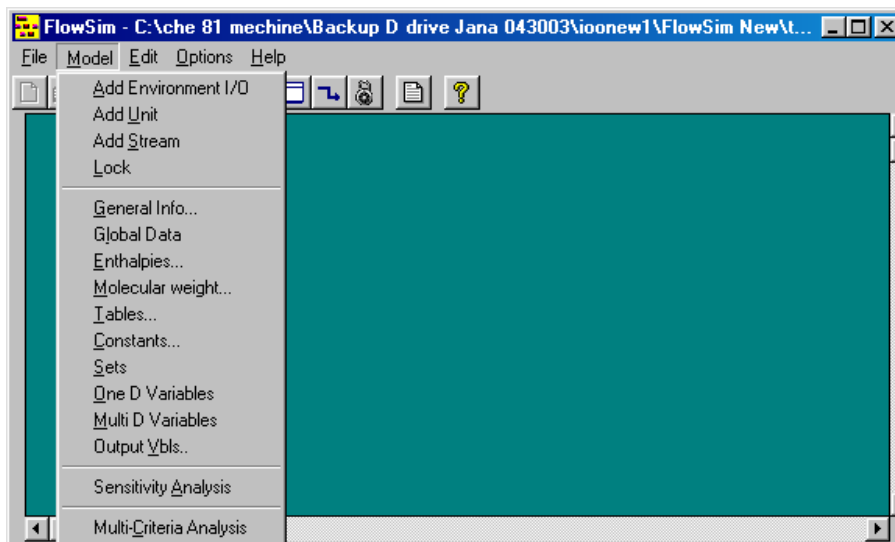
Figure 48: The Model Menu

Now, let us use these commands to draw the flowsheet diagram for the complexfinal process. Although FlowSim allows the units and streams to be drawn in any order, it is recommended that while drawing a process model, one should start with the feed and then add units and streams in order. Let us draw the mixer, which is the unit with the two feed streams and the two recycle streams as inputs. Select the 'Add Unit' command from the 'Model' menu. The mouse cursor changes to a hand. The cursor can now be dragged to draw a rectangle. Once, the mouse button is released, a small input window appears on the screen as shown in Figure 49. For every process unit that is drawn in FlowSim, the user is required to enter a unique Unit ID and description. let us enter 'U12' as the unit ID and 'nitric acid' as the description.
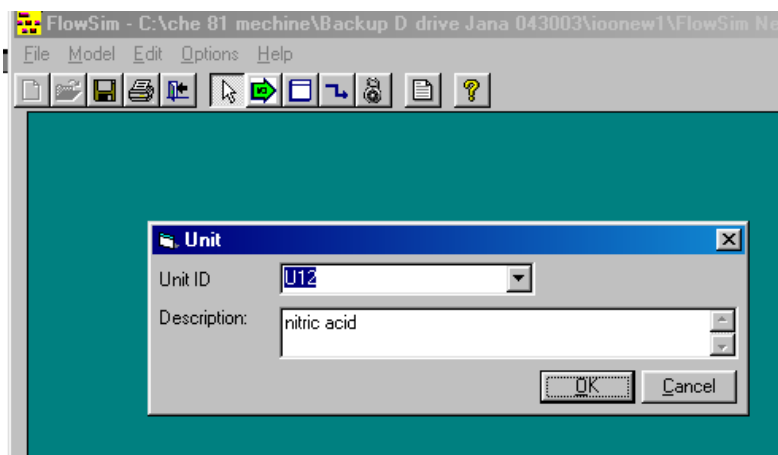
Figure 49: The Unit Window

Now, let us draw the cross heat exchanger in the flowsheet diagram. Let us enter the Unit ID 'U20' and description 'Ammonium Nitrate'. With these two units, the screen looks like in Figure 50.Now, let us add the stream that leaves the mixer and enters the cross heat

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exchanger. To do this, select the 'Add stream' command from the 'Model' menu. The cursor changes to a small circle. Position the cursor on the U12 unit and drag the cursor to the U20 unit. The program now displays a small box shown in Figure 51. Let us enter the stream ID 'S45' and the description 'Mixed stream'. With units U12 and U20 and stream S45, the FlowSim screen looks as shown in Figure 52. In this way, the entire process flow diagram for the sulfuric acid process can be drawn using the Model menu commands. After drawing the complete diagram, the FlowSim Screen Looks like as shown in Figure 53.
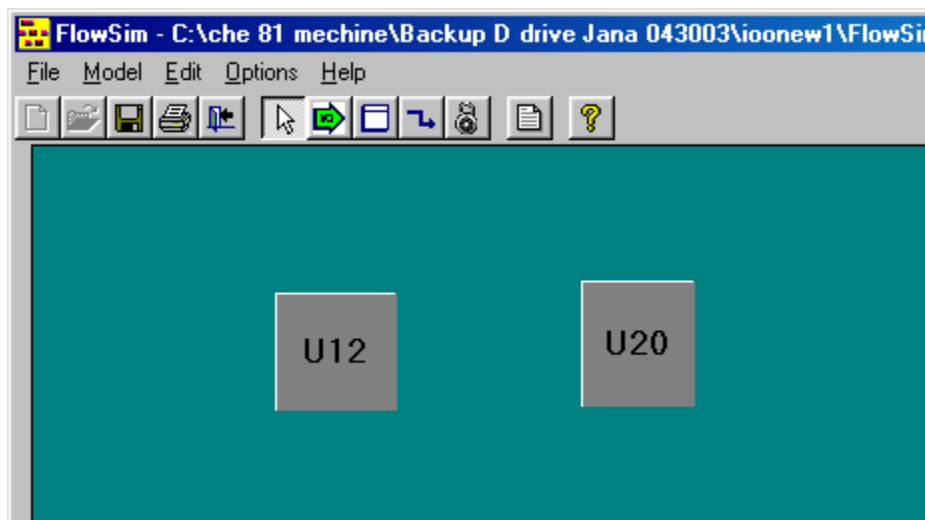
Figure 50: Flowsheet Screen with two Units.
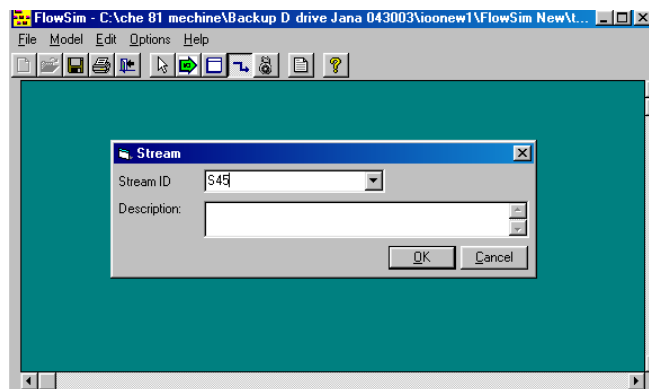
Figure 51: The Stream Window
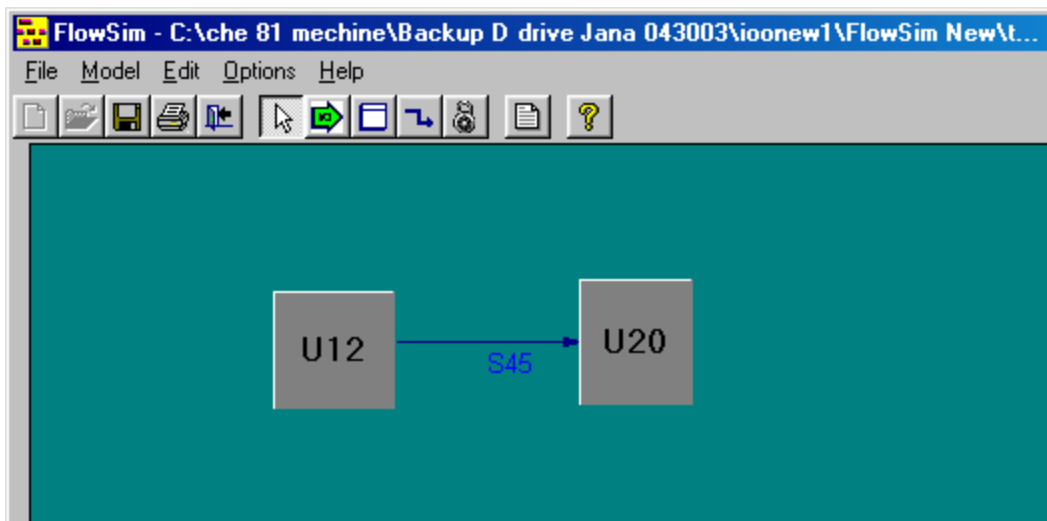
Figure 52: FlowSim Screen with two Units and a Stream
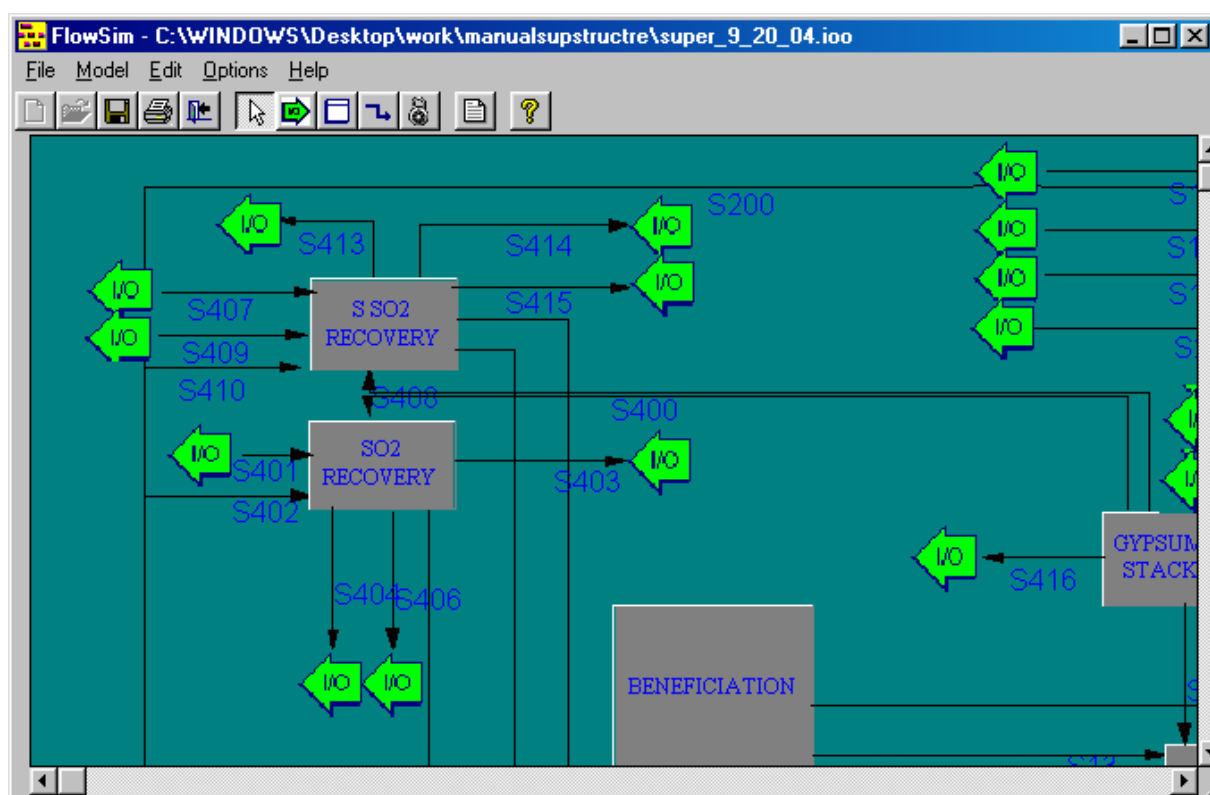
Figure 53: The Flowsim Screen with the Complete Process Diagram for Complexfinal Process Model

The 'Edit' menu at the top of the FlowSim screen provides various options for editing the diagram. It is shown in Figure 54. To use the Edit commands, a unit in the flowsheet

diagram has to be selected first by clicking on it. The cut, copy and paste commands can be used for both units as well as streams. The 'Delete' command can be used to permanently remove a unit or a stream from the diagram. The 'Rename' command can be used to change the unit ID for a unit or to change the stream ID for a stream. The 'Properties' command can be used to change the appearance of a unit or a stream.
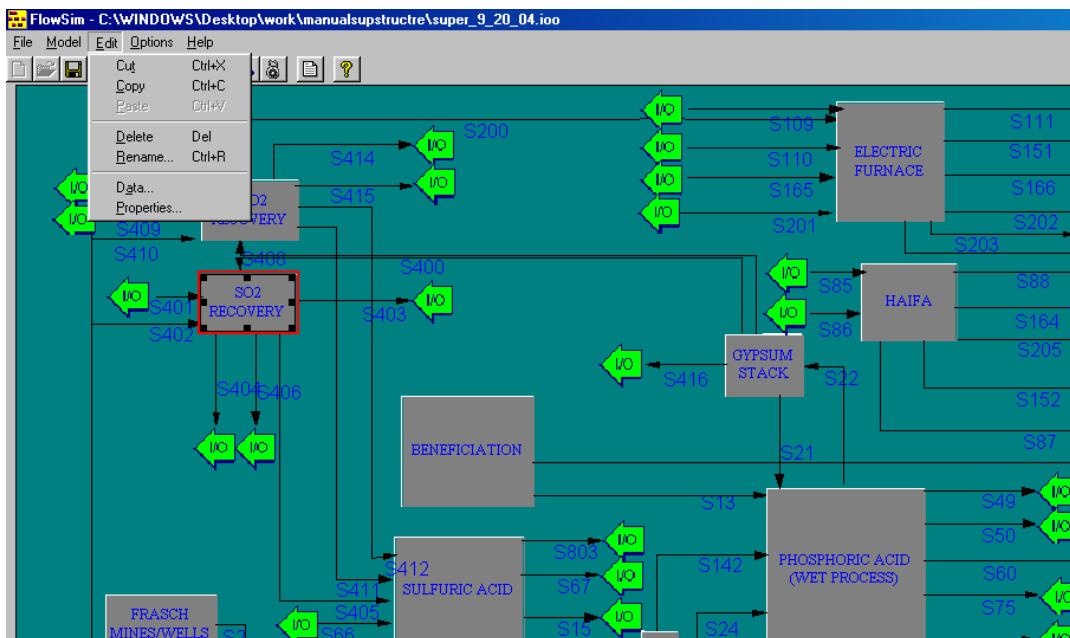
Figure 54: The Edit Menu

The 'Options' menu in the FlowSim screen is shown in Figure 55. The zoom option can be used to change the magnification by zooming in and out. The 'zoom to fit' option will automatically select the appropriate magnification so that the diagram occupies the entire screen. The 'Grid Lines' command can be used to display grid lines on the FlowSim screen, to change the spacing between the grid lines and to change the grid line and background colors. The 'Object settings' command is useful to change the appearance of all the units and streams in the FlowSim screen. The object settings window is shown in Figure 56. To change settings for all the streams, click on the streams tab. To change settings for all the environment I/O units, click on the 'Environment I/O' tab. If you want the changes to remain effective even after you close the application, you must select 'Save the palette for future users' box.
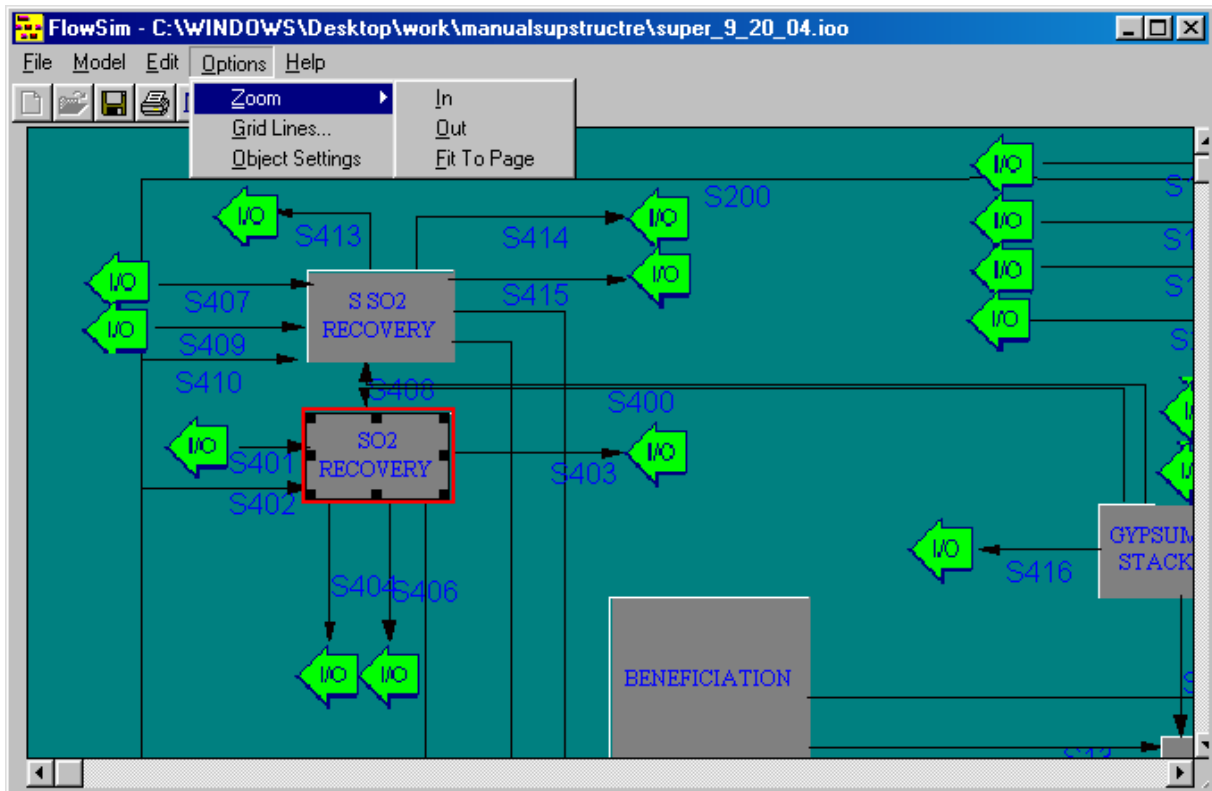
Figure 55: The Options Menu
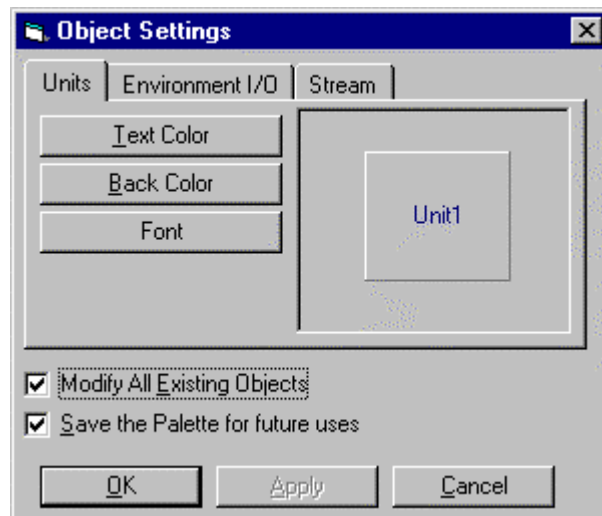
Figure 56: Object Settings Window

Once you have drawn a stream, the data associated with the stream can be entered by clicking on the data option in the edit menu or by double clicking on the stream. Let us enter the data associated with the stream S45. When you double click on this stream, a data form is opened. This is shown in Figure 57.

To enter the continuous variables associated with the stream, the 'add' button should be clicked. When the 'add' button is clicked, the caption of the 'Refresh' button changes to 'Cancel'. Then the information about the variable such as the name of the variable, the plant data, the standard deviation of the plant data should be entered. The description, initial point, scaling factor, lower and upper bounds and the unit of the variable are optional.

The changes can be recorded to the model by clicking on the 'Update' button or can be cancelled by clicking on the 'Cancel' button. When the update button is clicked, the caption of the cancel button reverts back to 'Refresh'. The Stream Data Window with the information appears as shown in Figure 57. In this way, all the other continuous variables associated with the stream 'S45' can be entered

To enter the Integer variables associated with the stream, click on the 'Integer Vars' tab. As explained above for the continuous variables, click on the add button in the stream data window. Enter the name, initial point of the Integer variable. The bounds, scaling factor, description and unit of the variable are optional. The Stream Data window with the Integer variable data is shown in Figure 58.

Figure 57: Stream Data Window

Figure 58: Integer Variables Tab in the Unit Data Window

To move to a particular variable, enter the record number in the box adjacent to 'Go to Record' button. Then press 'enter' or click on the 'Go to Record' button to move to that variable. To delete a variable, first move to that variable and then click 'Delete'. To return to the main screen, click on the 'close' button.

To enter the data associated with a unit, double click on the unit. When you double click on the unit, a data form similar to the one shown in Figure 57 is opened as shown in figure 58. The continuous variables, Integer variables are entered in the same way as for the streams.

Let us proceed to enter the equality constraints for the Ammonium Nitrate unit. Click on the Equalities tab in the Unit Data window to enter the equality constraints.

Let us enter the material balance equation for the Ammonium Nitrate unit. Click on the add button on the Unit Data window. Enter the equation in the box provided and click 'Update'. Note the use of '=e=' in place of '=' as required by the GAMS programming language. The screen now looks as shown in Figure 59-a.

Let us enter the heat transfer equation for the Ammonium Nitrate unit. The Equality constraints tab in the Unit Data window for the Ammonium Nitrate unit with this equation is shown in Figure 59-b.

Figure 59-a: Equality Constraints Tab in the Unit Data Window

Figure 59-b: Equality Constraints Tab in the Unit Data Window

D. Global Data

If there are variables, parameters and equations that do not belong to either a unit or a stream, then they can be entered in the Global Data window. This includes the economic model and the equations to evaluate emissions and energy use. To enter this global data, double click on the background of the flowsheet diagram or click on the 'Global Data' option in the Model menu.

The Global Data window in Figure 60-a shows the equality constraints in the Global Data section for the chemical complex process model . There are no equality constraints in the Global Data section for an chemical complex process so the window in figure 60-a shows empty in the equality constraint section .
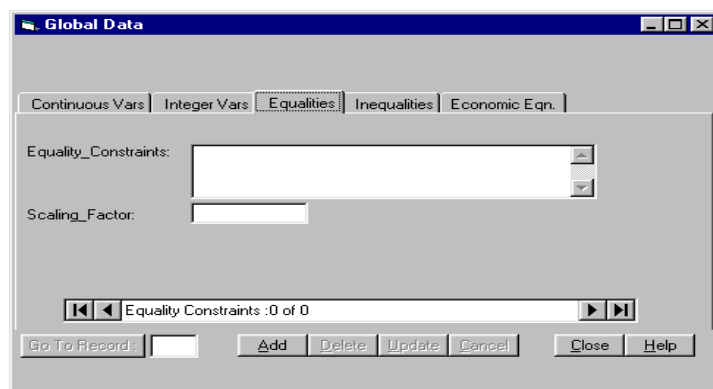
Figure 60-a: Equalities Tab in the Global Data Window
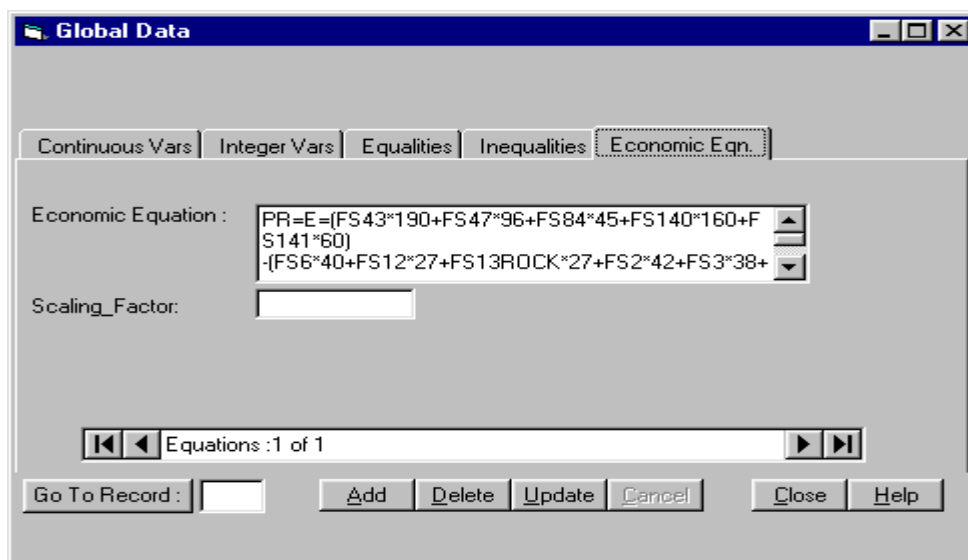
Figure 60-b: The Economic Equations Tab of Global Data

The last tab in the Global Data window is for the Economic Equations. These are equations, which can be used as the economic model and the left-hand side of one of these

equations is specified in optimization. For the agriculture complex process, let us enter the equation that defines the profit function for the whole process. Click on the 'Add' button and enter the equation shown in Figure 60-b. The variable 'profit' will be used later to specify the objective function for economic optimization. As seen in Figure 60-b, the profit function is equal to the product stream flowrates (lb/hr) multiplied by their sales coefficients ($/lb) subtracted by the input stream flowrates (lb/hr) multiplied by their cost coefficients ($/lb).

E. Constant Properties

The Constant Property window is where a list of constants is stored. Clicking on the 'Constants' option in the model menu opens the Constant Property window as shown in Figure 61. To create a set of constant properties, click on the 'Add New' button in Constant Property window to activate the window. As soon as the 'Add New' button is clicked, the caption of the 'Add New' button changes to 'Save' and that of 'Delete' changes to 'Cancel'. Then the general information of a constant property - the name and an optional description - must be entered in the Constant Property window.
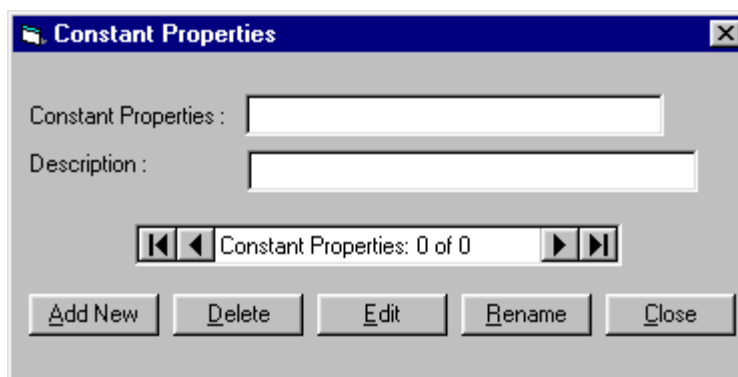
Figure 61: Constant Properties Window

After entering the constant property information, the 'Save' button should be clicked to save the changes. To enter the data in the constant property window, click on the 'Edit' button. The Edit Constant Property window is opened for entering the name of the constant, the corresponding numerical value and an optional description.

After entering all of the above information, the model is complete. Save the changes by clicking on the 'Save' option in the File menu. If you click 'Exit' without saving the model, a message is displayed asking whether you want to save the changes or not. The 'Print' option in the File menu when clicked, prints the flowsheet diagram. When the 'Exit' button is clicked, the FlowSim window is closed and the user is taken back to the Chemical Complex Analysis Desk.

The development of the process model using FlowSim has been completed. The equations, parameters and constants have been stored in the database as shown in Figure 45.

Save the model using the 'Save As' option in the File menu. Save the model as 'complexfinal.ioo' in the 'Examples' subdirectory of the program folder.

The process model developed above needs to be validated to make sure that it is representing the actual process accurately and it does not have any mistakes. This can be done by using the model to carry out a simulation and then comparing the results with the design data for the process.

The next step of the Chemical Complex Analysis System is optimization. The ' Optimization' button in Figure 44 should be now clicked to open the Optimization program.

VII B. USING OPTIMIZATION PROGRAM

Upon clicking the ' Optimization' button, the Optimization main window is displayed with the Optimization Algorithm window as shown in Figure 62. This window includes the Objective function for Economic Optimization, the Optimization direction and the Economic Model type. In the Economic Optimization for the complexfinal process, the objective function is 'profit' as defined in Section V for the global economic equation (Figure 60-b). Let us choose the optimization direction to be 'Maximizing' and the Economic Model type to be 'Non-Linear'.

When you click on the View menu in the Optimization Algorithm window, a pull-down menu is displayed as shown in Figure 63. The View menu includes commands for the Optimization Algorithm mode, the All Information mode and Flowsheet diagram. The 'Optimization Algorithm' mode displays the model description window. The 'All Information' mode contains the different windows combined together into one switchable window. The Flowsheet diagram option is used to view the flowsheet diagram, which is drawn using the flowsheet simulation program.
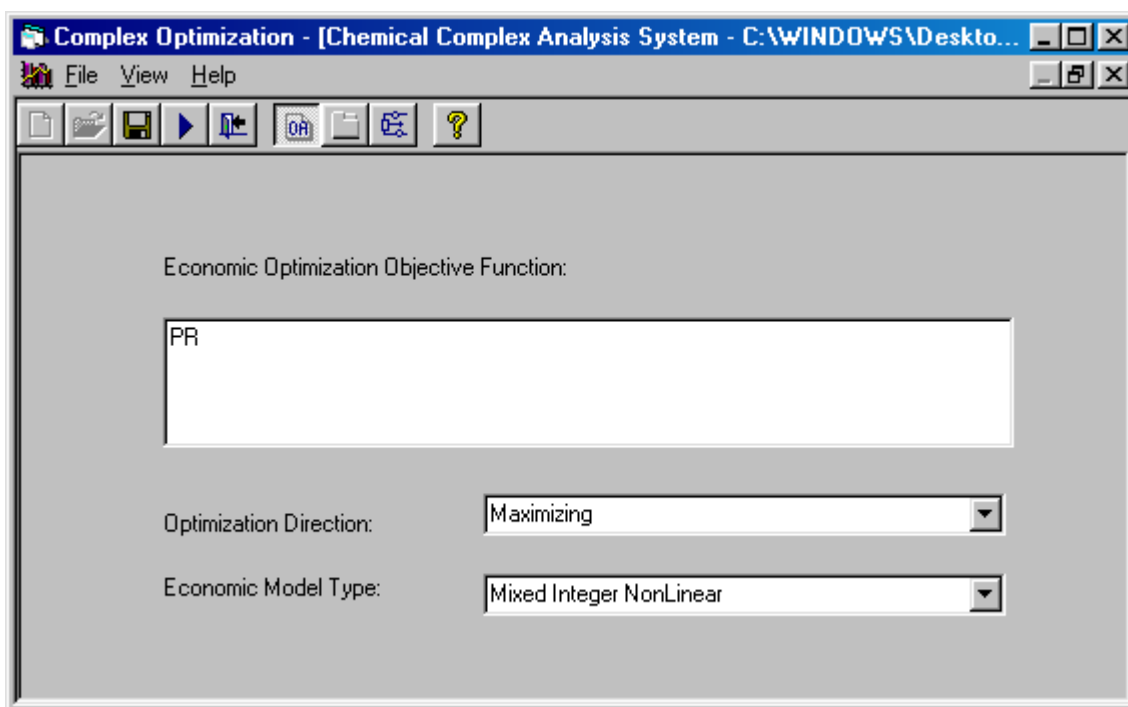

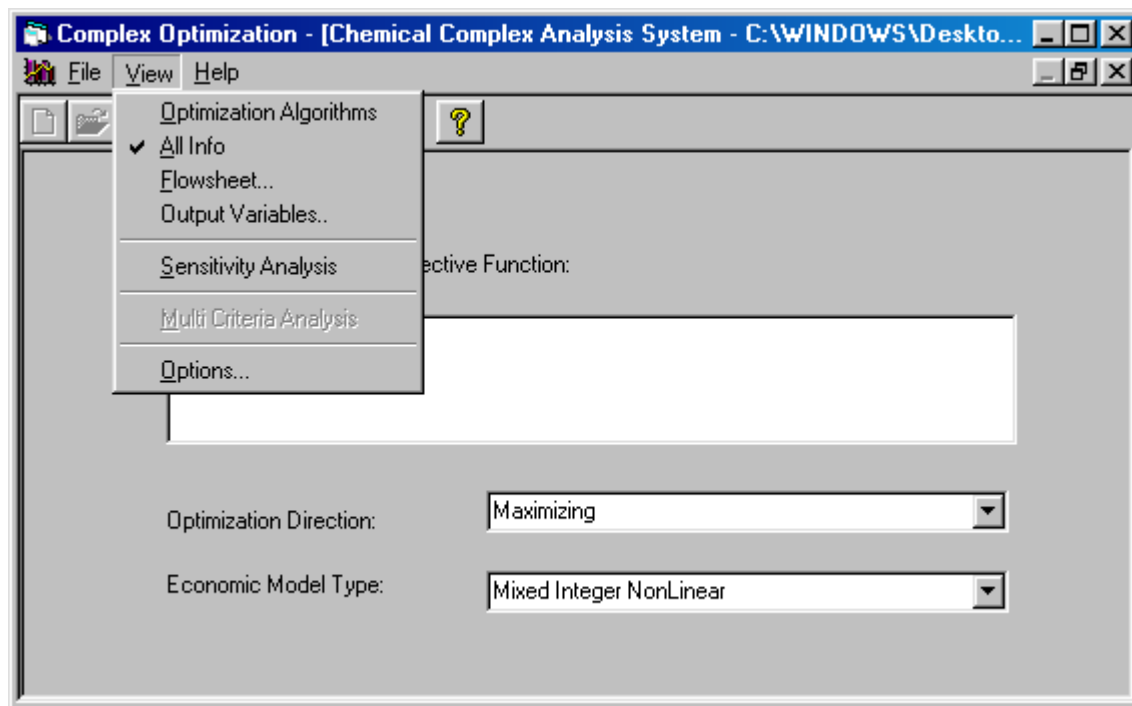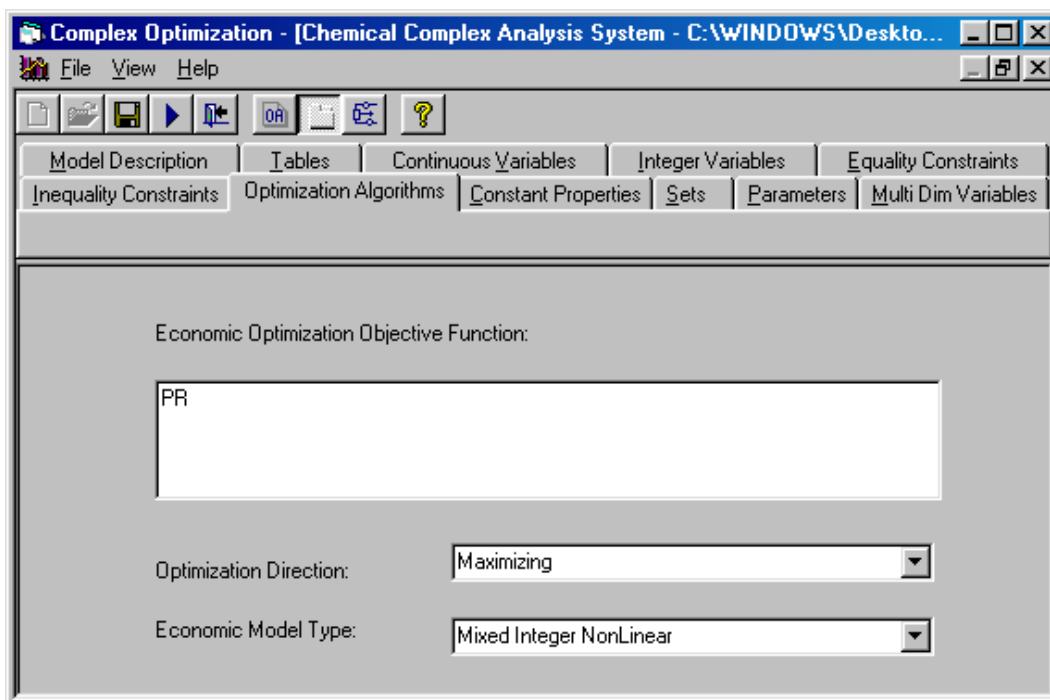Figure 62:Optimization Algorithm Window

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Figure 63: View Menu

Figure 64: Model Description Window

To view the other windows used by the Optimization program click on the 'All Information' option in the view menu which is shown in Figure 63. The Model Description window is shown in Figure 64.

For the Model Description window, the model name and the description were entered in the Flowsim program. This window includes the Optimization Objective and Model Type. The optimization objective has only one selection that can be selected from the drop-down list of 'Optimization Objective'. The selection is 'Economic Optimization'. Let us choose the 'Economic Optimization' option for the optimization objective. The model type of the plant model must be specified as either 'Linear' or 'Nonlinear' from the drop-down list. Let us choose 'Nonlinear' as the model type for the complexfinal model.

When the information for the Model Description window is completed, you can proceed to the next window by clicking on the tab to move to any other window. Let us proceed to the Tables window by clicking on the 'Tables' tab. The Tables window is shown in Figure 65. It contains information about the tables that were entered in the FlowSim program.

Let us proceed to the Continuous Variables window by clicking the 'Continuous Variables' tab. The Continuous Variables window has a table with twelve columns which display the name, initial point, scaling factor, lower and upper bounds, stream number, process unit-ID, the unit and a short description of the continuous variables. The Continuous Variables window lists all the continuous variables that are associated with all the units and streams in the process model and the global continuous variables if any that were entered in the FlowSim program. The column 'Process Unit-ID' has the name of the process unit and the column 'Stream Number' has the name of the stream with which the variable is associated. The Continuous Variables window is shown in Figure 66. In this window, information can only be viewed. All of the data entered in FlowSim can only be viewed using the screens of optimization. To change the data, the user has to go back to the FlowSim program.

Then proceed to the Integer Variables window by clicking on the 'Integer Variables' tab. The Integer Variables window has nine columns for displaying the name, initial point, scaling factor, lower and upper bounds, stream number, process unitID, unit and description of the Integer variables. The Integer Variables window lists all the Integer variables, which were entered in the FlowSim program. The Integer Variables window is shown in Figure 67.
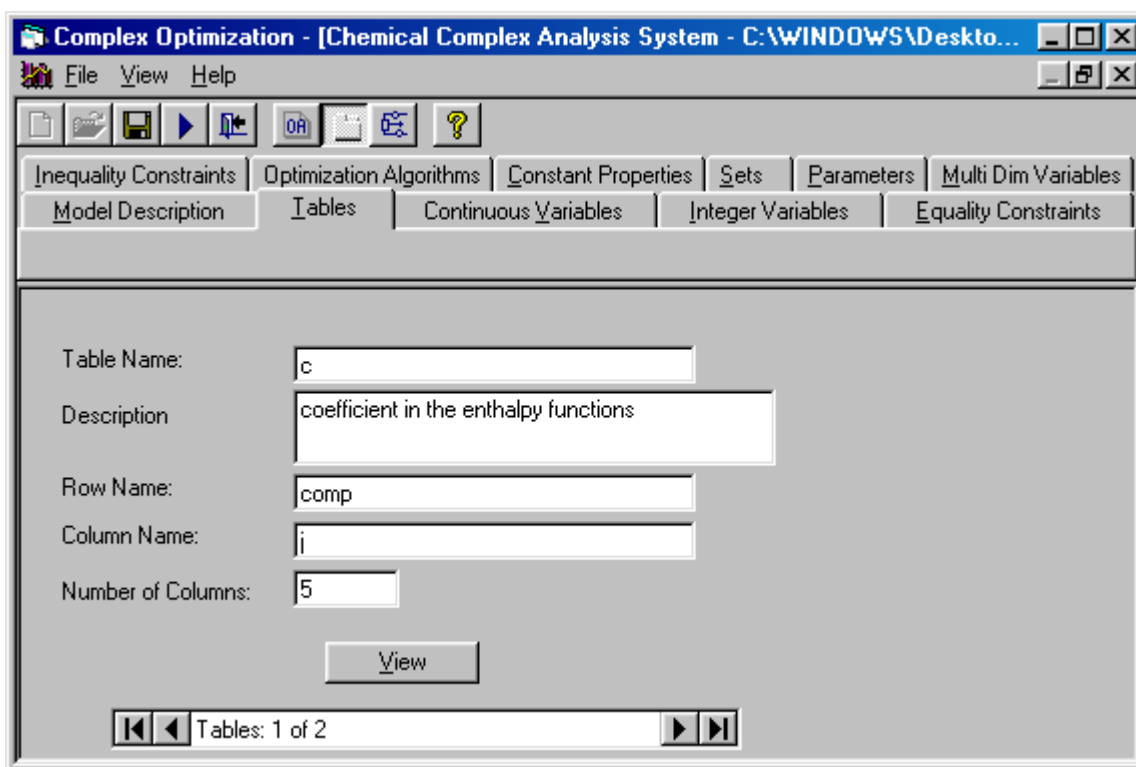
Figure 65. Tables window
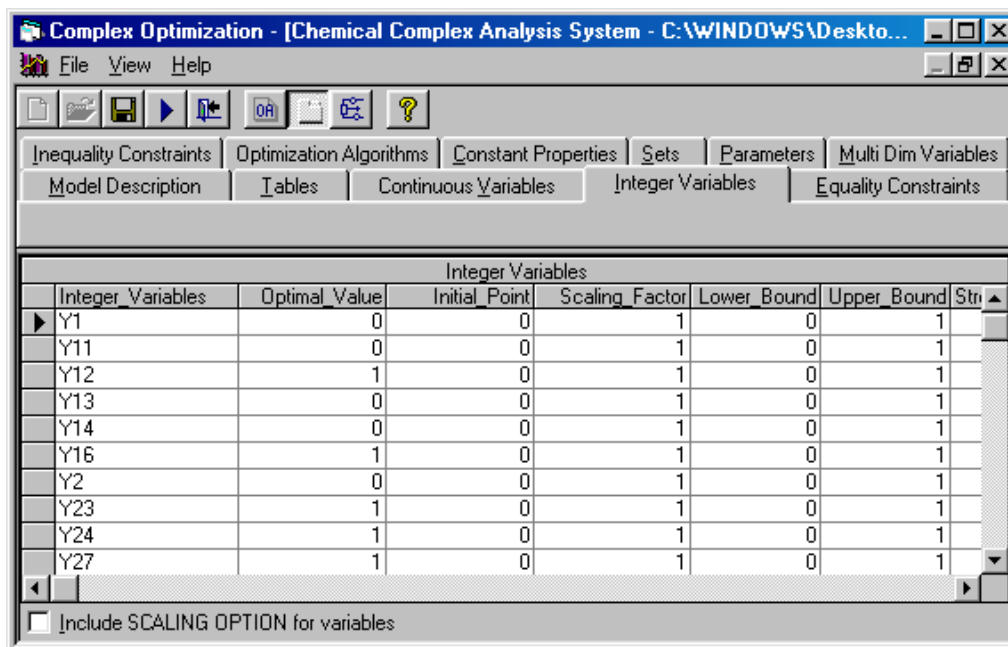

Figure 66: Continuous Variables Window

Figure 67: Integer Variables Window

Then proceed to the Equality Constraints window. This window has four columns for displaying the constraints, scaling factor, process unitID and stream number. All of the equality constraints entered in the FlowSim program are listed in this window. The Equality Constraints window is shown in Figure 68. The next step is the Inequality Constraints window, which is similar to the Equality Constraints window. The Inequality Constraints window has three columns for displaying the constraints, process unitID and stream number. Scaling factors are not available for inequality constraints. The Inequality Constraints window is shown in Figure 69.
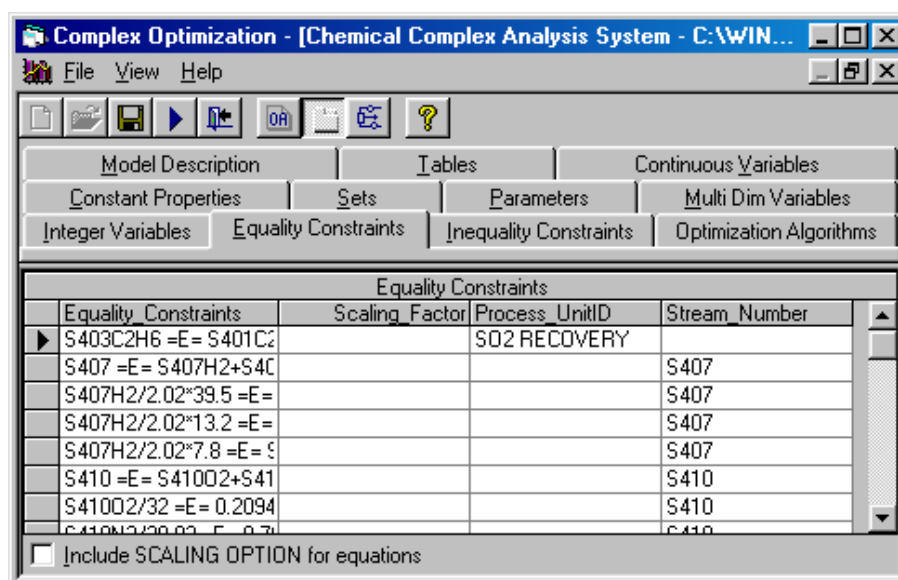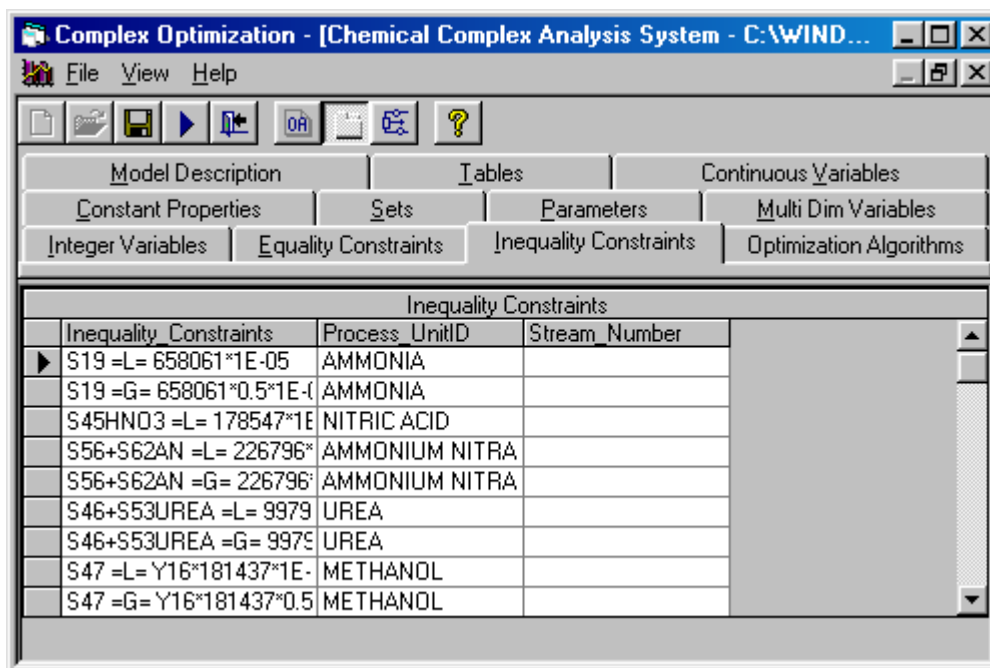

Figure 68:Equality Constraints Window

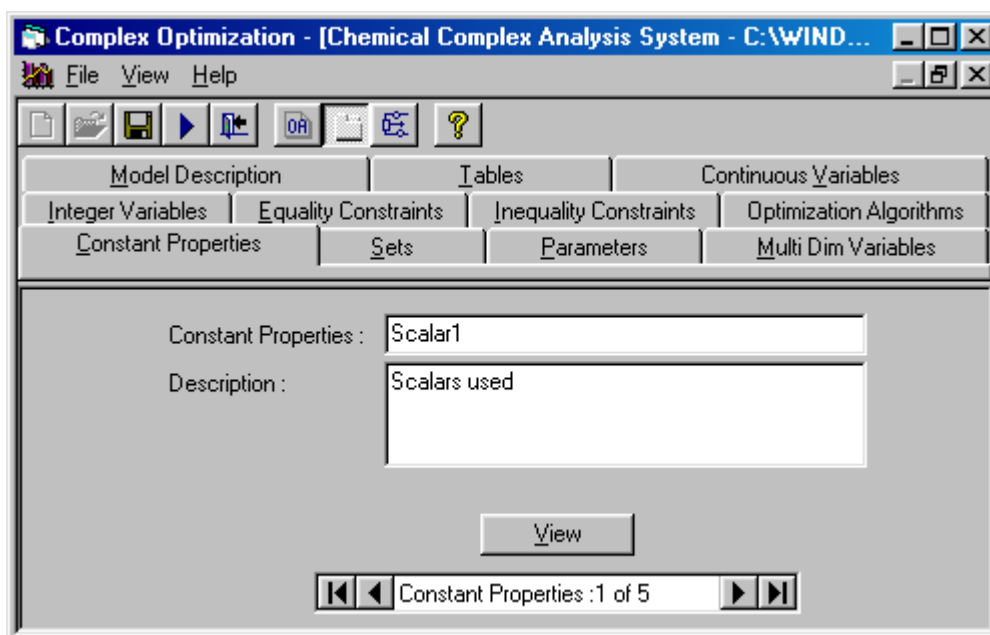Figure 69 : Inequality Constraints Window

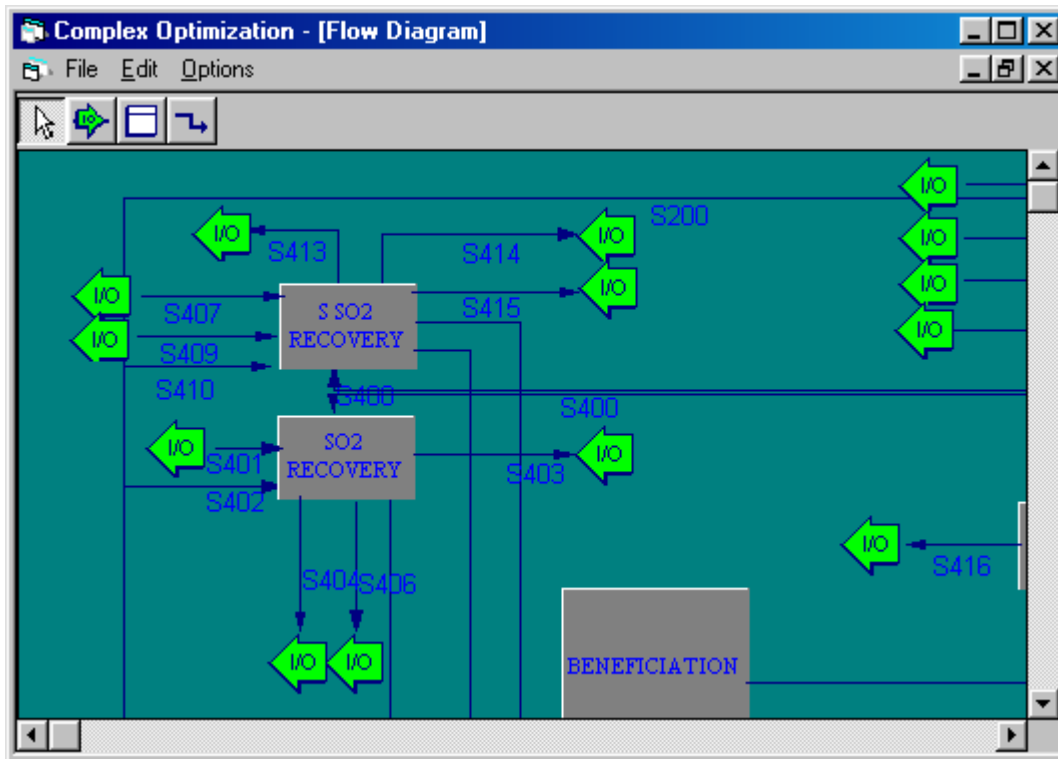Figure 70: Constant Properties Window

Figure 71: Flowsheet Diagram Window

The next step is the Constant Properties window. The constant properties window is shown in Figure 70. The flowsheet diagram can be viewed by clicking on the 'FlowSheet Diagram' option in the view menu as shown in Figure 63. The flowsheet cannot be edited in the Optimization program. The flowsheet diagram is shown in Figure 71. Double clicking on a unit opens a data form which displays all the continuous variables, Integer variables and plant parameters that are associated with that unit. Similarly, double clicking on a stream opens a data form which displays the continuous and Integer variables, associated with the stream. The global data can be viewed by double clicking on the background of the flowsheet
Figure 72: Options With **GAMS** process tab

Clicking on the 'Options' item in 'View' menu, opens the Options window as shown in Figure 72. General GAMS Process options are set in the 'GAMS Process' tab as shown in the first window of Figure 72. The format for the GAMS output can be specified in the 'Output Format' tab as shown in second window of Figure 72. LP and NLP values for the Solver can be set in the 'Solver' tab as shown in the third window of Figure 72. The default values are OSL2 for both LP and NLP. These default values can be restored by clicking on the 'Use Defaults…' button. Solver Parameters like Number of Iterations, Number of Domain Errors and Amount of Time Used can be specified in the 'Solver Parameters' tab as shown in the fourth window of Figure 72. The recommended values for the 'Solver Parameters' of the complexfinal process are Number of iterations 100, Domain Errors 0, and Amount of time Used 1000 sec. The default values for Number of iterations 1000, Number of Domain Errors 0, and Amount of time used 1000 sec can be restored by clicking on the 'Use Defaults…' button.   Other advanced options can be set by clicking on the 'Advanced Options' button, which brings up the window shown in Figure 73.
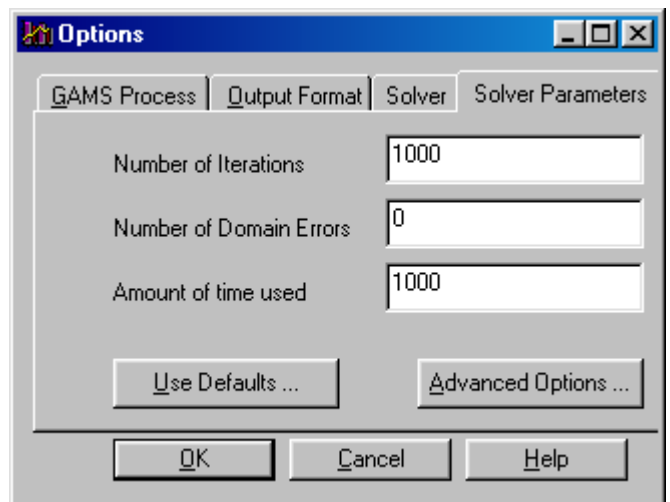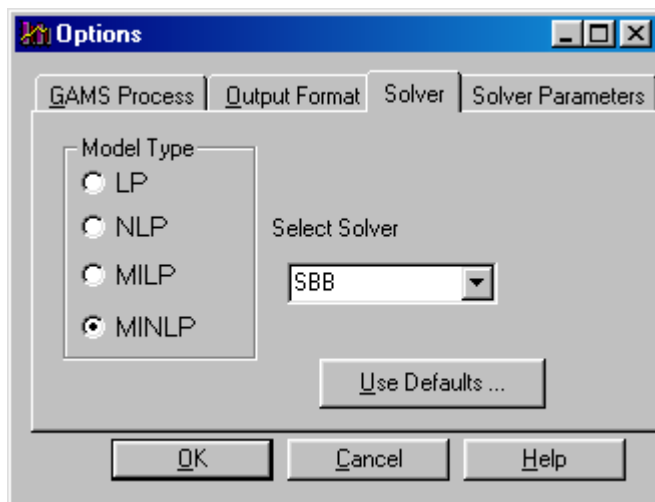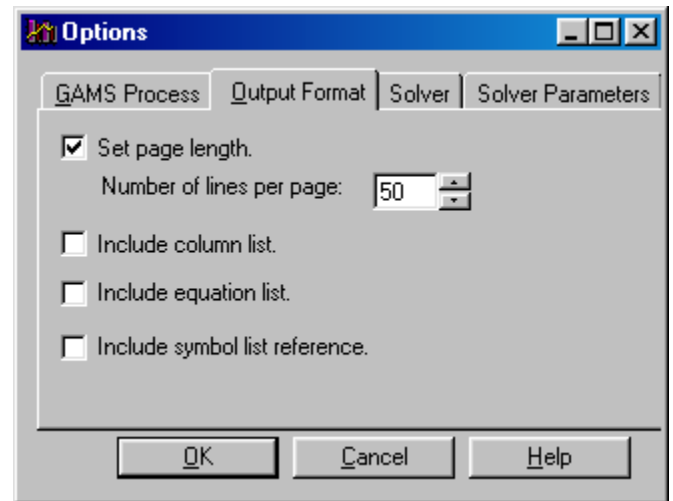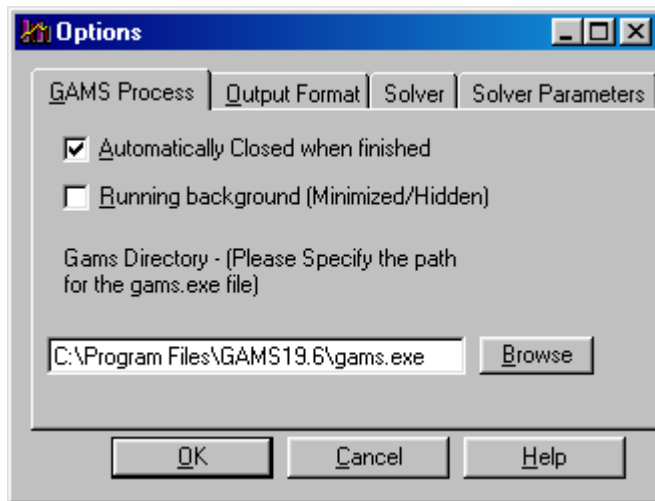
Figure 44. Options with **GAMS** process tab
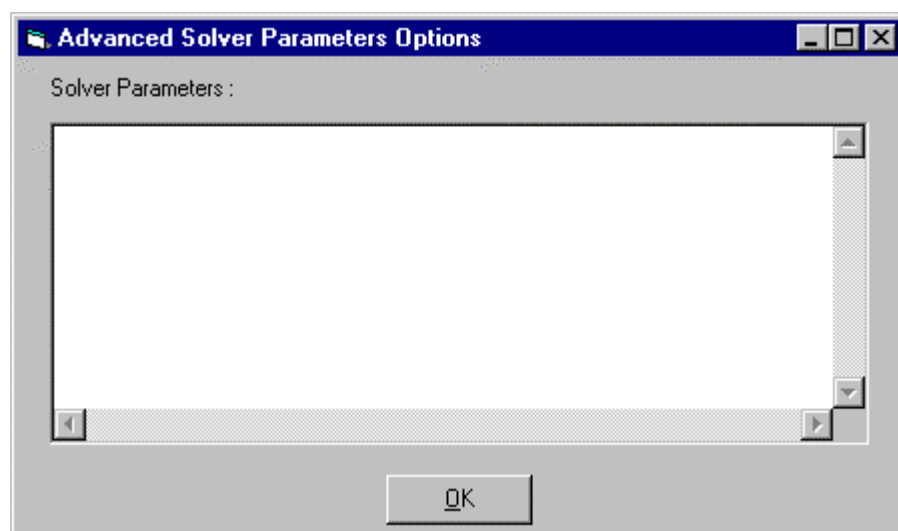
Figure 73: Advanced Parameters Options Window

After entering the required information, let us proceed to execute the model. To execute the model, click on the 'Execute' option in the File menu or click on the 'Execute' button (the button with the triangle) in the toolbar. Once the 'Execute' option is clicked the Model Summary and Execute window as shown in Figure 74 is opened. This window gives the summary of the agriculture complex process.

When the 'Execute' button in the 'Model Execute and Summary' window is clicked, the program first extracts the model information from the database. Based on this information, it generates the GAMS input files and calls the GAMS solver. The progress of the GAMS program execution is shown in Figure 75. This window is automatically closed as soon as the execution is over. When the execution of the program is completed, it displays the results of the optimization in the Output window.

Figure 74. Model Execution Summary Window

Figure 75.**GAMS** Program Execution Window

Figure 76: Final Report in the Output Window

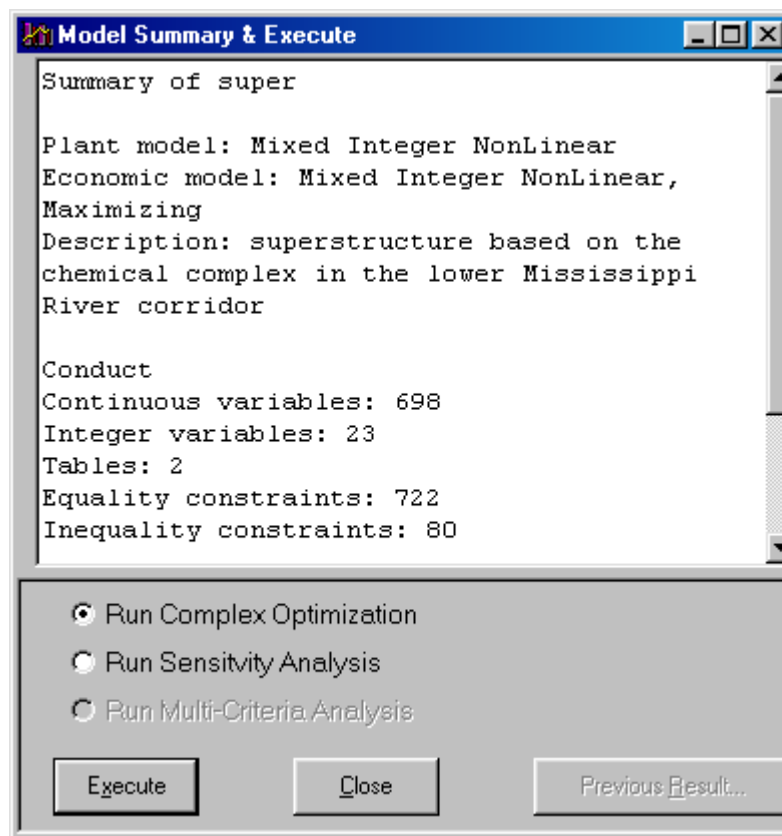After the three programs have been executed, three detailed GAMS output files will be generated by GAMS for the three optimization problems. This file gives detailed solutions of the optimization problems for Economic Optimization. Also, a final report is generated by the Interactive Optimization system. In the final report, the optimal set points and the profit from Economic Optimization are shown. The Output Window with the Final Report is shown in Figure 76. The View menu in the Output window has three options named Final Report, Full Output and Flowsheet.

The Final Report option has four options namely the Economic Objective, the Continuous Variables, the Integer Variables and the Stream Number as shown in Figure 77. The Economic Objective value is shown in Figure 76.
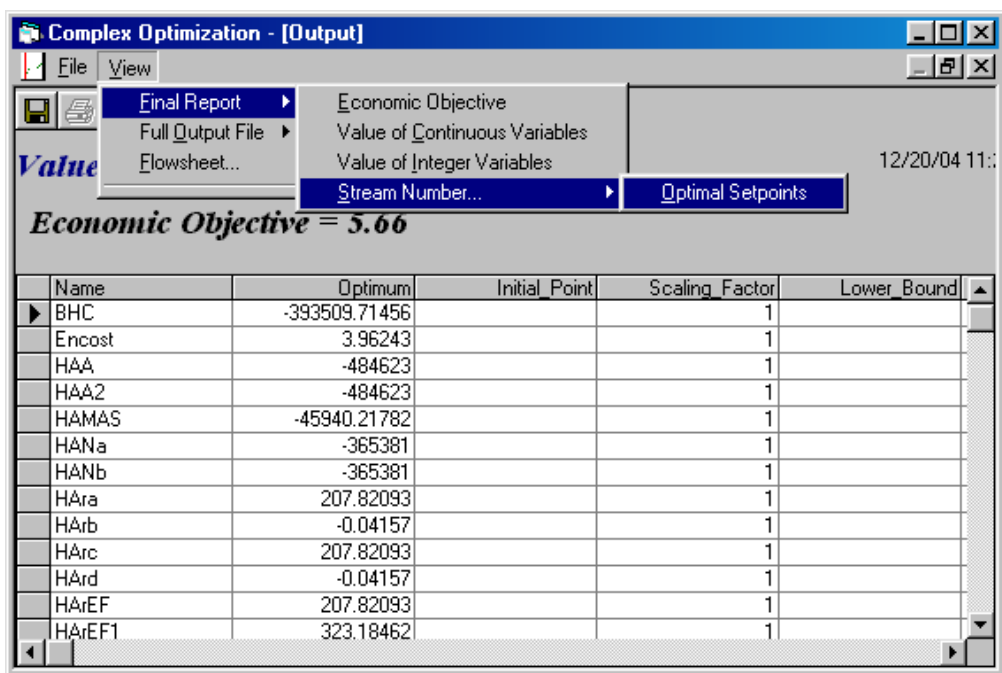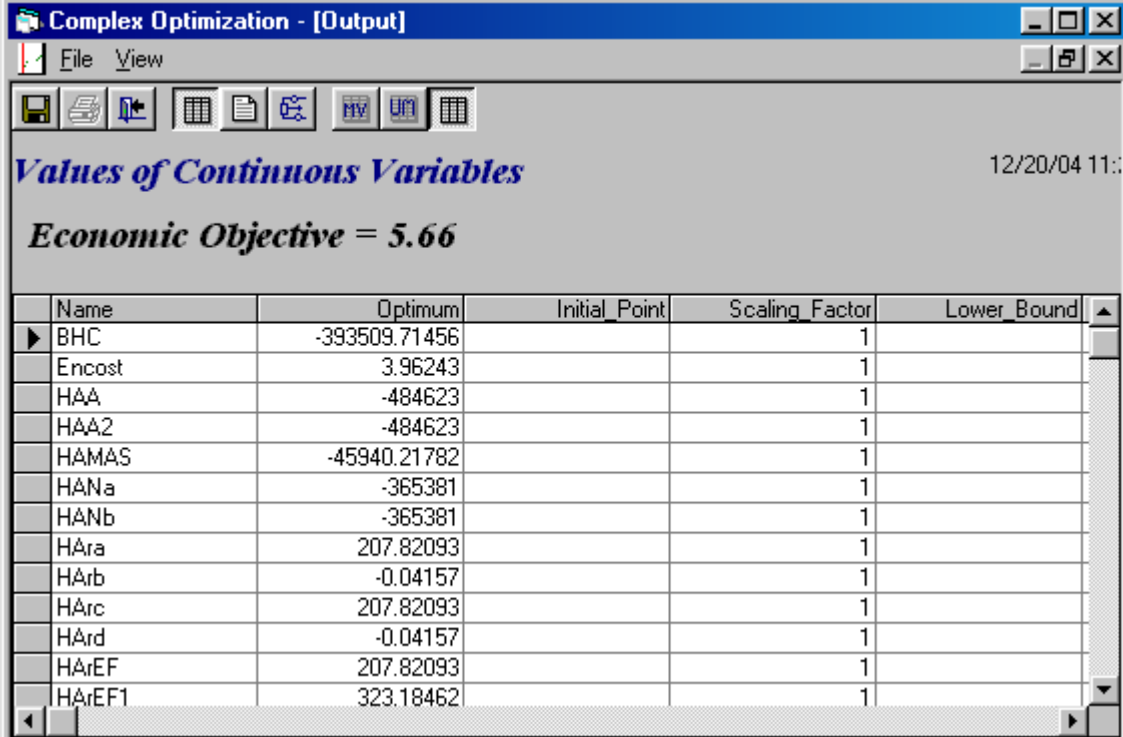
Figure 77: View Menu in the output Window

When the option 'Continuous Variables' in the Final Report menu is clicked, the system opens a spreadsheet data form which includes the optimum values from economic optimization as shown in Figure 78.

Clicking on the 'Integer Variables', the system opens a spreadsheet data form which includes the Integer variables and their optimal values as shown in Figure 79. In the 'Stream Number' menu as shown in Figure 77, we see the Optimum Values. Let us click the 'Optimum Values' option. An input box appears. Let us enter 'S5' and click 'OK'. The Continuous Variables and Integer variables which are associated with the stream 'S5' with their optimum values from Economic Optimization are displayed as shown in Figure 80.
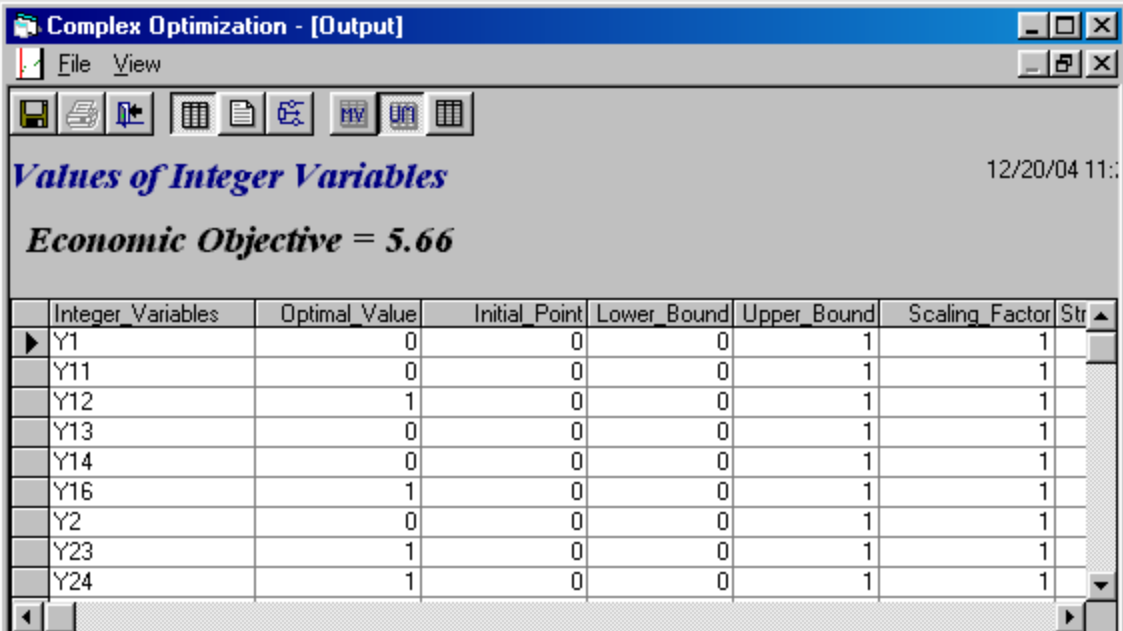
Figure 78: Optimum Values in Final Report for Continuous Variables

Figure 79: Optimal Values for Integer Variables

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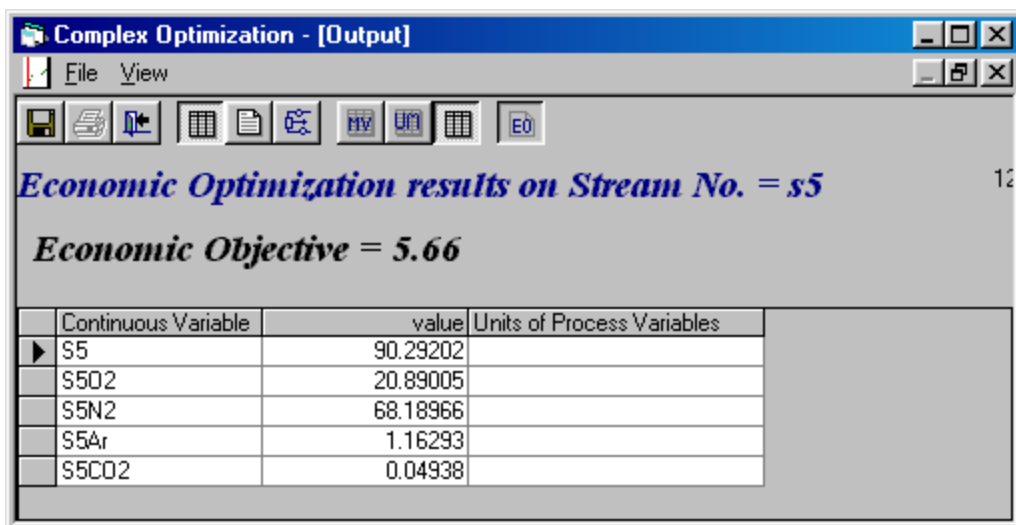
Figure 80: Information based on Stream Number
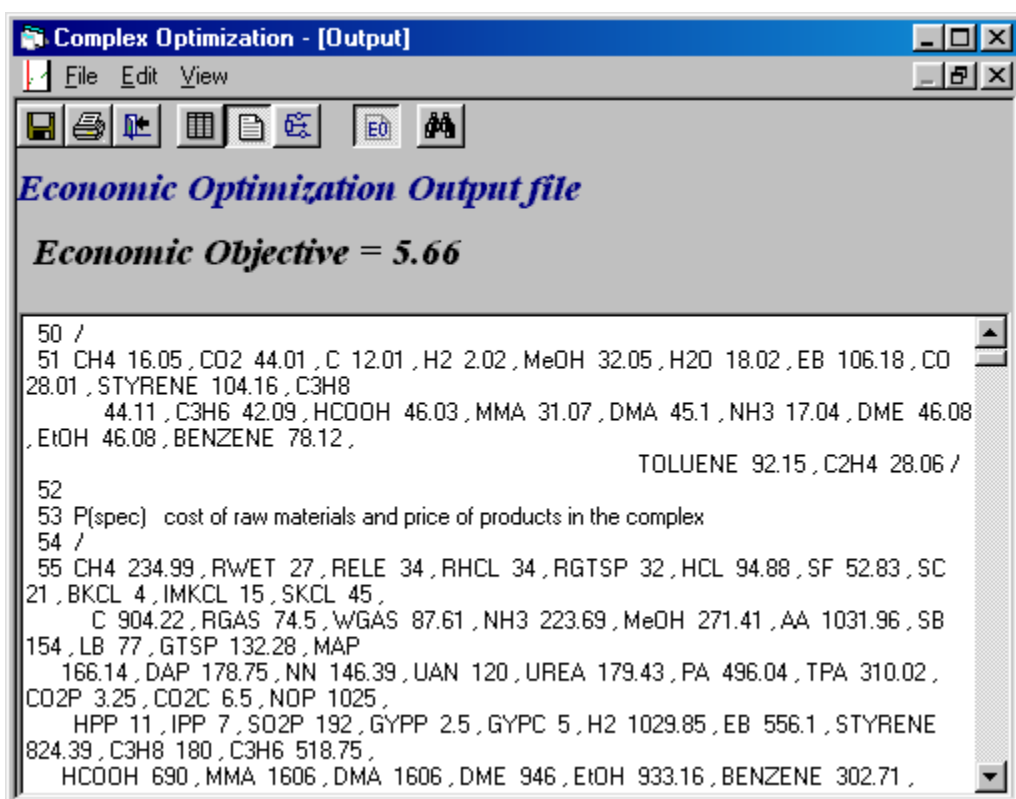
Figure 81: Full Output File of GAMS Programs

When the 'Full Output File' option in the view menu is selected, the output file of the Economic Optimization is shown. The full output file is shown in Figure 81.

The user can use the 'Find' and 'Goto' options in the Edit menu to search for a particular phrase or go to a particular section in the Full Output file. The Final Report can be exported as an Excel file using the 'Export' option in the file menu. The Full Output files can also be exported as a text file using the 'Export' option.

The results can also be viewed as a flowsheet in a window similar to the one shown in Figure 71. Double clicking on a stream or unit opens the corresponding data window. The Data window for stream 'S12' is shown in Figure 82. As seen in this figure, the values of the continuous variables obtained as a result of optimization are displayed in the data window.

Figure 82: Stream Data Window

Clicking the 'Close' option in the file menu of the Output window returns the user to the main screen, which was shown in Figure 62. The model information can be exported as an Excel file using the 'Export' option in the file menu of the main window. Save the optimization results using the 'Save' option in the file menu. The results including the full output files are stored along with the model. When the 'Exit' button is clicked, the Interactive Optimization main window is closed and the user is taken back to the Chemical Complex Analysis Desk.

VIII. OPTIMIZATION SOLVER-GAMS

A. Compilation Output (Brooke, et al., 1996)

The compilation output is produced during the initial check of the program, and it is often referred to as a compilation. It includes two or three parts: the echo print of the program, an explanation of any errors detected, and the symbol reference maps. The echo print of the program is always the first part of the output file. If errors had been detected, the explanatory messages would be found at the end of the echo print. The echo print of the GAMS program for the economic optimization of the contact process is included in the GAMS output file in Section X.

The symbol reference maps follow the echo print, and they include the symbol cross-reference and the symbol-listing map. These are extremely useful if one is looking into a model written by someone else, or if one is trying to make some changes in their own model after spending time away from it. The symbol cross reference lists the identifiers (symbols) in the model in alphabetical order, identifies their type, shows the line numbers where the symbols appear, and classifies each appearance. The complete list of data types is given in Table 8. Next in the listing is a list of references to the symbols, grouped by reference type and identified by the line number in the output file. The actual references can then be found by referring to the echo print of the program, which has line numbers on it. The complete list of reference types is given in Table 9. The symbol reference maps do not appear in the output files by default. However, it can be included in the output files by changing the default setting in Output File Format Specification window.

Table 8 A List of Data Types

Entry in symbol reference table	GAMS data type
SET	set
PARAM	parameter
VAR	variable
EQU	equation
MODEL	model

B. Execution Output

The execution output follows the compilation output and is also found in the GAMS output file. If a display statement is present in the GAMS program, then data requested by the display statement is produced in the execution output while GAMS performs data manipulations. Also, if errors are detected because of illegal data operations, a brief message indicating the cause and the line number of the offending statement, will appear in the execution output. The execution output will be shown in the GAMS output file if a display statement is present in the GAMS program (which requests the display of the value of a variable) or if an execution error is encountered.

Table 9 A List of Reference Types

Reference	Description
DECLARED	This is where the identifier is declared as to type. This must be the first appearance of the identifier.
DEFINED	This is the line number where an initialization (a table or a data list between slashes) or symbol definition (equation) starts for the symbol.
ASSIGNED	This is when values are replaced because the identifier appears on the left of an assignment statement.
IMPL-ASN	This is an "implicit assignment": an equation or variable will be updated as a result of being referred to implicitly in a solve statement.
CONTROL	This refers to the use of a set as the driving index in an assignment, equation, loop or other indexed operation (sum, prod, smin or smax).
REF	This is a reference: the symbol has been referenced on the right of an assignment in a display, in an equation, or in a model or solve statement.

C. Output produced by a Solve Statement (Brooke, et al., 1996)

The output triggered by a solve statement includes the equation listing, the column listing, the model statistics, solver report, the solution listing, report summary, and file summary as shown in the GAMS output file in Section X. All of the output produced as a result of a SOLVE statement is labeled with a subtitle identifying the model, its type, and the line number of the solve statement.

The first list in the output produced by the SOLVE statement is the Equation Listing, which is marked with that subtitle in the output file. The Equation Listing is an extremely useful debugging aid. It shows the variables that appear in each constraint, and what the individual coefficients and right-hand-side value evaluate to after the data manipulations have been made. Normally, the first three equations in every block are listed. Most of the listing is self-explanatory. The name, text, and type of constraints are shown. The four dashes are useful for mechanical searching. All terms that depend on variables are collected on the left, and all the constant terms are combined into one number on the right, with any necessary sign changes made. For example, a equation "x + 5y - 10z +20 =e= 0" is rearranged as: "x + 5y - 10z =e= -20". Four places of decimals are shown if necessary, but trailing zeroes following the decimal point are suppressed. E-format is used to prevent small numbers being displayed as zero. By default, the equation listing will not appear in the output file unless specified by the user in the Output File Format Specification Window.

The general format in the equation listing was described above. However, the nonlinear terms in an equation are treated differently from the linear terms. If the coefficient

of a variable in the Equation Listing is enclosed in parentheses, then the variable corresponding to this coefficient is nonlinear in the constraint equation, and the value of the coefficient depends on the activity levels of one or more of the variables. This coefficient is not algebraic, but it is the partial derivative of each variable evaluated at their current level values (initial points).

For an equation: $x + 2y^3 + 10$ =e= 0 with current level values $x = 2$ and $y = 1$, this equation is listed in the equation listing as: $x + (6) y$ =e= -12, where the coefficient of y is the partial derivative of the equation with respect to y evaluated at y=1, i.e., $6y^2 = 6$. The right hand side coefficient, -12, is the sum of constant in the equation, 10, and the constant, 2, from the linearization of the nonlinear term $2y^3$ using Taylor expansion evaluated at $y = 1$. x in this equation is linear, and its coefficient is shown as 1 without the parentheses.

Next, the column listing gives the individual coefficients sorted by column rather than by row. The default shows the first three entries for each variable, along with their bound and level values. The format for the coefficients is the same as in the equation listing, with the nonlinear ones enclosed in parentheses and the trailing zeroes dropped. The order in which the variables appear is the order in which they were declared.

The final information generated while a model is being prepared for solution is the statistics block to provide details on the size and nonlinearity of the model. The status for the solver (the state of the program) and the model (what the solution looks like) are characterized in solver status and model status. The model status and solver status are listed in Table 10 and Table 11, respectively.

The next section is the solver report, which is the solve summary particular to the solver program that has been used. Also, there will be diagnostic messages in plain language if anything unusual was detected, and specific performance details as well. In case of serious trouble, the GAMS listing file will contain additional messages printed by the solver, which may help, identify the cause of the difficulty.

Solution listing is a row-by-row then column-by-column listing of the solutions returned to GAMS by the solver program. Each individual equation and variable is listed with four pieces of information. The four columns associated with each entry are listed in Table 12. For variables, the values in the LOWER and UPPER columns refer to the lower and upper bounds. For equations, they are obtained from the (constant) right-hand-side value and from the relational type of the equation. EPS means very small or close to zero. It is used with non-basic variables whose marginal values are very close to, or actually, zero, or in nonlinear problems with super-basic variables whose marginal values are zero or very close to it. A superbasic variable is the one between its bounds at the final point but not in the basis.

For models that do not reach an optimal solution, some constraints may be marked with the flags shown in Table 13. The final part of solution listing is the report summary marked with four asterisks. It shows the count of rows or columns that have been marked INFES, NOPT, UNBND. The sum of infeasibilities will be shown if the reported solution is infeasible. The error count is only shown if the problem is nonlinear. The last piece of the output file is the file summary, which gives the names of the input and output disk files. If work files have been used, they will be named here as well.

D. Error Reporting

The last part in the output file is error reporting. All the comments and descriptions about errors have been collected into this section for easy reference. Errors are grouped into the three phases of GAMS modeling in the optimization system: compilation, execution and model generation (which includes the solution that follows). They will be illustrated in the section, "Error Reporting".

Table 10 A List of Model Status in GAMS Output Files

Model status	Meaning
1. Optimal	This means that the solution is optimal. It only applies to linear problems or relaxed mixed integer problems (RMIP).
2. Locally Optimal	This message means that a local optimal for nonlinear problems, since all that can guarantee for general nonlinear problems is a local optimum.
3. Unbounded	That means that the solution is unbounded. It is reliable if the problem is linear, but occasionally it appears for difficult nonlinear problem that lack some strategically paced bounds to limit the variables to sensible values.
4. Infeasible	This means that he linear problem is infeasible.
5. Locally Infeasible	This message means that no feasible point could be found for the nonlinear problem from the given starting point. It does not necessarily mean that no feasible point exists.
6. Intermediate Infeasible	The current solution is not feasible, the solver program stopped, either because of a limit (iteration or resource), or some sort of difficulty.
7. Intermediate Nonoptimal	This is again an incomplete solution, but it appears to be feasible.
8. Integer Solution	An integer solution has been found to a MIP (mixed integer problem).
9. Intermediate Noninteger	This is an incomplete solution to a MIP. An integer solution has not yet been found.
10. Integer	There is no integer solution to a MIP. This message should be reliable.
11.Error Unknown, Error no Solution	There is no solution in either of these cases.

Table 11 A List of Solver Status in GAMS Output Files

Solver status	Meaning
1. Normal Completion	This means that the solver terminated in a normal way: i.e., it was not interrupted by an iteration or resource limit or by internal difficulties. The model status describes the characteristics of the accompanying solution.

2. Iteration Interrupt	This means that the solver was interrupted because it used too many iterations. Use option iterlim to increase the iteration limit if everything seems normal.
3. Resource Interrupt	This means that the solver was interrupted because it used too much time. Use option reslim to increase the time limit if everything seems normal.
4. Terminated by Solver	This means that the solver encountered difficulty and was unable to continue. More detail will appear following the message.
5. Evaluation Error Limit	Too many evaluations of nonlinear terms at undefined values. You should use bounds to prevent forbidden operations, such as division by zero. The rows in which the errors occur are listed just before the solution.
6. Unknown Error Preprocessor(s) Error Setup Failure Error Solver Failure Error Internal Solver Error Error Post-Processor	All these messages announce some sort of unanticipated failure of GAMS, a solver, or between the two. Check the output thoroughly for hints as to what might have gone wrong.

Table 12 A List of Solution Listing Types

Heading in listing file	Description
LOWER	Lower Bound (.lo)
LEVEL	Level Value (.l)
UPPER	Upper Bound (.up)
MARGINAL	Marginal (.m)

Table 13 A List of Constraint Flags

Flag	Description
INFES	The row or column is infeasible. This mark is make for any entry whose LEVEL value is not between the UPPER and LOWER bounds.
NOPT	The row or column is non-optimal. This mark is made for any non-basic entries for which the marginal sign is incorrect, or superbasic ones for which the marginal value is too large.
UNBND	The row or column that appears to cause the problem to be unbounded.

E. GAMS Input Model (Brooke et al., 1996)

The basic components of a GAMS input model include:
- Sets
- Data (Parameters, Tables, Scalar)
- Variables
- Assignment of bounds and/or initial values
- Equations
- Model and Solve statements
- Display/Put statement

The overall content of GAMS output file is:
- Echo Print
- Reference Maps
- Equation Listings
- Status Reports
- Results

E-1. Format for Entering System Information

The GAMS input code generated by the interactive optimization system is based on the information provided by the user. Although the user usually does not need to consider the format of the GAMS program, there are some regulations about the format related to GAMS that must be followed to properly enter information about the plant. The input must be in correct format for an accurate GAMS input file to be generated automatically by the optimization system.

Most of the characters and words are allowable for the input information, however, the letters in the input information are case insensitive. A few characters are not allowed for the input because they are illegal or ambiguous on some machines. Generally, all unprintable and control characters are illegal. Most of the uncommon punctuation characters are not part of the language, but can be used freely. In Table 14, a full list of legal characters is given.

Besides characters, there are some reserved words and non-alphanumeric symbols with predefined meanings in GAMS, which can not be used, in input information. The reserved words and non-alphanumeric symbols are listed in Table 15 and Table 16, respectively.

Table 14 A List of Full Set of Legal Characters for GAMS

A to Z	alphabet	a to z	alphabet	0 to 9	Numerals
&	ampersand	" "	double quote	#	pound sign
*	asterisk	=	equals	?	question mark
@	at	>	greater than	;	semicolon

\	back slash	<	less than		'	single quote
:	Colon		minus		/	slash
,	comma	( )	parenthesis			space
$	Dollar	[ ]	square brackets		_	underscore
.	Dot	{ }	braces		!	exclamation mark
+	Plus	%	percent		^	circumflex

Table 15 A List of All Reserved Words for GAMS

abort	ge	Not	smin	if
acronym	gt	Option	sos1	then
acronyms	inf	Options	sos2	else
alias	integer	Or	sum	semicont
all	le	Ord	system	semiint
and	loop	Parameter	table	file
assign	lt	Parameters	using	files
binary	maximizing	Positive	variable	putpage
card	minimizing	Prod	variables	puttl
display	model	Scalar	xor	free
eps	models	Scalars	yes	no
eq	na	Set	repeat	solve
equation	ne	Sets	until	for
equations	Negative	Smax	while	

In the optimization system, numeric values are entered in a style similar to that used in other computer languages. Blanks cannot be used in a number because the system treats a blank as a separator. The common distinction between real and integer data types does not exist. If a number is entered without a decimal point, it is still stored as a real number. In addition, the system uses an extended range arithmetic that contains special symbols for infinity (INF), negative infinity (-INF), undefined (UNDF), epsilon (EPS), and not available (NA) as shown in Table 17. One cannot enter UNDF; it is only produced by an operation that does not have a proper result, such as division by zero. All other special symbols can be entered and used as if they were ordinary numbers.

Table 16 A List of Non-alphanumeric Symbols for GAMS

=l=	--
=g=	++
=e=	**
=n=	

GAMS uses a small range of numbers to ensure that the system will behave in the same way on a wide variety of machines. A general rule is to avoid using or creating numbers with absolute values greater than 1.0e+20. A number up to 10 significant digits can be entered on all machines, and some machines can even support more than that. However, if a number is too large, it may be treated by the system as undefined (UNDF), and all values derived from it in a model may be unusable. It is recommended to always use INF (or -INF) explicitly for arbitrarily large numbers. When an attempted arithmetic operation is illegal or has undefined results because of the value of arguments (division by zero is the normal example), an error is reported and the result is set to undefined (UNDF). Afterwards, UNDF is treated as a proper data value and does not trigger any additional error messages. Thus, the system will not solve a model if an error has been detected, but it will terminate with an error condition.

The string definition such as the variable's name in the system has to start with a letter followed by more letters or digits. It can only contain alphanumeric characters and up to 10 characters long. The comment to describe the set or element must not exceed 80 characters. Basically, there are five possible types of variables that may be used which are listed in Table 18.

The type of mathematical programming problem must be known before the problem is solved. The optimization system can only solve linear and nonlinear optimization problems. However, GAMS can solve a large number of optimization problems, which are summarized in Table 19.

As the interactive optimization system writes all the required GAMS input files for the user, most of the components in the GAMS input model are automatically formulated from the information provided in the input windows. If the user can follow the explicit rules introduced above, the GAMS input file can be generated automatically. After the user enters all the plant information through the input windows, the GAMS source codes will be generated.

Table 17 A List of Special Symbols for GAMS

Special symbol	Description
INF	Plus infinity. A very large positive number
-INF	Minus infinity. A very large negative number
NA	Not available. Used for missing data. Any operation that uses the value NA will produce the result NA

UNDF	Undefined. The result of an undefined or illegal operation. The user cannot directly set a value to UNDF	
EPS	Very close to zero, but different from zero.	

Table 18 A List of Types of Variables for GAMS

Keyword	Default Lower Bound	Default Upper Bound	Description
Free (default)	-inf	+inf	No bounds on variables. Both bounds can be changed from the default values by the user
Positive	0	+inf	No negative values are allowed for variables. The upper bound can be changed from the default value by the user
Negative	-inf	0	No positive values are allowed for variables. The user can change the lower bound from the default value.
Binary	0	1	Discrete variable that can only take values of 0 or 1
Integer	0	100	D Discrete variable that can only take integer values between the bounds. Bounds can be changed from the default value by the user

The optimization system will then forward these source codes to the GAMS software. This initiates the execution of GAMS and also creates output files so the user can view the execution in the output window. The execution and the output has been discussed in the previous sections.

Table 19 A List of Types of Models for GAMS

Model Type	Description
LP	Linear programming. No nonlinear terms or discrete (binary or integer) variables.
NLP	Nonlinear programming. There are general nonlinear terms involving only "smooth" functions in the model, but no discrete variables.
DNLP	Nonlinear programming with discontinuous derivatives. Same as NLP, but "non-smooth" functions can appear as well. More difficult to solve than NLP. Not recommended to use.
RMIP	Relaxed mixed integer programming. Can contain discrete variables but the integer and binary variables can be any values between their bounds.
MIP	Mixed integer programming. Like RMIP but the discrete requirements are enforced: the discrete variables must assume integer values between their bounds.
RMINLP	Relaxed mixed integer nonlinear programming. Can contain both discrete variables and general nonlinear terms. The discrete requirements are relaxed. Same difficulty as NLP.
MINLP	Mixed integer nonlinear programming. Characteristics are the same as for RMINLP, but the discrete requirements are enforced.
MCP	Mixed Complementarily Problem
CNS	Constrained Nonlinear System

E-2. Equation Formulation

Besides the rules introduced above, the equations as the main part of the input information have their own specific requirements. The mathematical definitions of equations can be written in one or multiple lines. Blanks can be inserted to improve readability, and expressions can be arbitrarily complicated. The standard arithmetic operations for the equations are listed in Table 20. The arithmetic operations listed in Table 20 are in order of precedence, which determines the order of evaluation in an equation without parentheses. The relational operators in the equations are:

=L=   Less than: left hand side (lhs) must be less than or equal to right hand side (rhs)
=G=   Greater than: lhs must be greater than or equal to rhs
=E=   Equality: lhs must equal to rhs
=N=   No relationships enforced between lhs and rhs. This type is rarely used.

Additionally, GAMS provides the numerical relationships and logical operators used to generate logical conditions for evaluating values of True or False. A result of zero is treated as a logical value of False, while a non-zero result is treated as a logical value of True.

A complete numerical relationship operators and logical operators are listed in the Table 21 and Table 22, respectively.

Table 20 A List of Standard Arithmetic Operators

Operator	Description
**	Exponentiation
*, /	Multiplication and division
+, -	Addition and subtraction (unary and binary)

Table 21 A List of Numerical Relationship Operators

Operator	Description
lt, <	Strictly less than
le, <=	Less than or equal to
eq, =	Equal to
ne, <>	Not equal to
ge, >=	Greater than or equal to
gt, >	Strictly greater than

Table 22 A List of Logical Operators

Operator	Description
not	Not
And	And
Or	Inclusive or
Xor	Exclusive or

Table 23 The Truth Table Generated by the Logical Operators

Operands		Results			
A	b	a and b	a or b	a xor b	not a
0	0	0	0	0	1
0	non-zero	0	1	1	1
Non-zero	0	0	1	1	0
Non-zero	non-zero	1	1	0	0

Table 24 The Operator Precedence Order in case of Mixed Logical Conditions

Operation	Operator
Exponentiation	**
Numerical Operators	
Multiplication, Division	*, /
Unary operators - Plus, Minus	+, -
Binary operators - Addition, Subtraction	+, -
Numerical Relationship Operators	<, <=, =, <>, >=, >
Logical Operators	
Not	not
And	and
Or, xor	or, xor

The functions of the logical operators are expressed in Table 23. For the mixed logical conditions, the default operator precedence order used by GAMS in the absence of parenthesis is shown in Table 24 in decreasing order. For the formulation of equations, variables can appear on the left or right-hand side of an equation or on both sides. The system can automatically convert the equation to its standard form (variables on the left, no duplicate appearances) before calling the GAMS solver. For the convenience of input, the system also provides several special notations, such as summation (sum) and product (prod), minimum value (smin), maximum value (smax).

E-3. Functions Predefined in the System

There are two types of functions based on the type of argument: exogenous or endogenous. For exogenous arguments, the arguments are known, and examples are parameters and variable attributes. The expression is evaluated once when the model is set up. All functions except the random distribution functions, uniform and normal, are allowed. With endogenous arguments, the arguments are variables, and are, therefore, unknown. The function will be evaluated many times at intermediate points while the model is being solved. The occurrence of any function with endogenous arguments implies that the model is not linear and the use of the functions of "uniform" and "normal" are forbidden in an equation definition. Some built-in functions are listed in Table 25.

E-4. Scaling Option for Variables and Equations

To facilitate the translation between a natural model (no scaling) to a well scaled model, GAMS introduces the concept of a scale factor for variables and equations with a

scaling option. This feature is incorporated in the interactive optimization system to provide a well-scaled optimization problem for GAMS to solve. To use the scaling option in the interactive optimization, the user must highlight the scaling option in the variable declaration and the equations declaration windows. Then, the user must enter the values of the scale factors for the variables and equations that need to be scaled. The following describes how the scale factor is incorporated in the GAMS program and how to determine the value of a scale factor.

The scale factor on a variable V^s is used to relate the variable as seen by user (in natural model) V^u to the variable as seen by the optimization algorithm (in well scaled model) V^a as follows:

$$V^u = V^a \ V^s$$

This means that the scaled variable V^a will become around 1 if the scale factor V^s is chosen to represent the order of magnitude of the user variable V^u.

If the approximate expected value for a variable in the model is known, then the magnitude of this variable value is used as the scale factor of the variable. The scale factor can be specified by users through the Continuous or Integer Variables window. If the approximate expected values for some of the variables in the model are not available, these values can be found in the column list of the corresponding GAMS output file. The scale factor will not change the values of variables in the solution seen by users. GAMS uses the scale factor to scale variables and transfer the model into a well scaled model for optimization algorithm. When the optimal solution is found, GAMS will rescale the variables and transfer them back to user's notation. The effect of scaling can only be viewed in the Column and Equation lists of the GAMS output files.

The scale factor for an equation is dependent on the order of magnitude of the equation coefficients. It is slightly different from the determination of scale factor for a variable that is dependent on the magnitude of the variable. An equation usually contains several terms, and it has several coefficients that may not be in the same order.

If the equation is linear, the coefficients of this equation is known. If the equation is nonlinear, then the equation is linearized first using the initial values. However, the linearized coefficients must be obtained from the equation list. Users can obtain the values of the linearized equation coefficients for nonlinear constraints from the equation list of the corresponding GAMS output file. To appropriately assign the scale factor for an equation, users need to carefully select the value of the scale factor based on the coefficients shown in equation list of the GAMS output file so that all coefficients will be in the range of 0.01 to 100 after scaling.

The column (variables) and equation lists are very important for nonlinear problems when scaling the variables and equations. It provides initial values of all variables and linearized constraint coefficients, which can be used to determine the scale factors for both variables and equations. It is suggested that the user turn off the scaling option for both variables and equations before GAMS is initiated.

Table 25 A List of Functions Predefined in the Optimization System

Function	Description	Classification	Exogenous Classification	Endogenous model type
Abs	Absolute value	Non-smooth	Legal	DNLP
Arctan	Arctangent	Smooth	Legal	NLP
Ceil	Ceiling	Smooth	Legal	Illegal
Cos	Cosine	Discontinuous	Legal	NLP
Errorf	Error function	Smooth	Legal	NLP
Exp	Exponential	Smooth	Legal	NLP
Floor	Floor	Discontinuous	Legal	Illegal
Log	Natural log	Smooth	Legal	NLP
Log10	Common log	Smooth	Legal	NLP
Mapval	Mapping function	Discontinuous	Legal	Illegal
Max	Largest value	Non-smooth	Legal	DNLP
Min	Smallest value	Non-smooth	Legal	DNLP
Mod	Remainder	Discontinuous	Legal	Illegal
Normal	Normal random	Illegal	Illegal	Illegal
Power	Integer power	Smooth	Legal	NLP
Round	Rounding	Discontinuous	Legal	Illegal
Sign	Sign	Discontinuous	Legal	Illegal
Sin	Sine	Smooth	Legal	NLP
Sqr	Square	Smooth	Legal	NLP
Sqrt	Square root	Smooth	Legal	NLP
Trunc	Truncation	Discontinuous	Legal	Illegal
Uniform	Uniform random	Illegal	Illegal	Illegal

After the program ends, if the solution is correct and there was no difficulty in searching for an optimal solution, then the scaling option is not necessary. If the solution is not correct or some difficulty was encountered while searching for an optimal solution, then the scaling option must be incorporated in the program. In this case, users may instruct the system to include the column and equation lists in the output file. To do this, the user must change the default setting for the output files in window 12, the Output File Format Specification window. This will run the optimization program without the scaling option. Based on the values of variables in column list without scaling, users can decide the values of

scale factors for variables, enter them in the Continuous Variables and Integer variables windows, and highlight the icon "Include Scaling Option for variables" to scale the variables first. After the system executes the program, a new equation list, which incorporates the scale information of variables, is generated and can be used for equation scaling. Based on the linearized coefficients in this new equation list, users can determine the scale factors for the equations and enter them in the Equality Constraints and Inequality Constraints windows. Also, users must highlight the icon "Include Scaling Option for Equations" to add the Scaling Option in the programs.

E-5. Error Reporting

During compiling, executing, and solving the optimization problem, GAMS checks the input source code for program syntax, rearranges the information in the source code, and solves the optimization problem. At every step, GAMS records any error encountered and reports it in the GAMS output file. The following describes error reporting during solving the optimization problems.

Compilation Errors

The first type of error is a compilation error. When the GAMS compiler encounters an error in the input file, it inserts a coded error message inside the echo print on the line immediately following the scene of the offense. The message includes a $-symbol and an error number printed below the offending symbol (usually to the right). This error number is printed on a separate line starting with four asterisks (****). If more than one error occurs on a line, the $-signs may be suppressed and the error number is squeezed. GAMS programs are generated by the system, and no serious compilation errors are expected to appear. The most common error will be a spelling error, i.e., the variables defined in the equations may be mistyped and mismatch while declaring the variables. This will result in "variable undefined error". GAMS will not list more than 10 errors on any single line. At the end of the echo print, a list of all error numbers encountered, together with a description of the probable cause of each error, will be printed. The error messages are self-explanatory and will not be listed here. Checking the first error is recommended because it has the highest priority.

Execution Errors

The second type of error is an execution error. Execution errors are usually caused by illegal arithmetic operations such as division by zero or taking the log of a negative number. GAMS prints a message on the output file with the line number of the offending statement and continues execution. A GAMS program should never abort with an unintelligible message from the computer's operating system if an invalid operation is attempted. GAMS has rigorously defined an extended algebra that contains all operations including illegal ones. The model library problem [CRAZY] contains all non-standard operations and should be executed to study its exceptions. GAMS arithmetic is defined over the closed interval [-INF, INF] and contains values EPS (small but not zero), NA (not available), and UNDF (the result of an illegal operation). The results of illegal operations are propagated through the entire

system and can be displayed with standard display statements. The model cannot be solved if errors have been detected previously.

Solve Errors

The last type of error is a solve error. The execution of a solve statement can trigger additional errors called MATRIX errors, which report on problems encountered during transformation of the model into a format required by the solver. Problems are most often caused by illegal or inconsistent bounds, or an extended range value being used as a matrix coefficient. Some solve statement require the evaluation of nonlinear functions and the computation of derivatives. Since these calculations are not carried out by the system but by other subsystems not under its direct control, errors associated with these calculations are reported in the solution report.

If the solver returns an intermediate solution because of evaluation errors, then a solution will still be attempted. The only fatal error in the system that can be caused by a solver program is the failure to return any solution at all. If this happens as mentioned above, all possible information is listed on the GAMS output file, but the solution will not be given.

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