INTRODUCTION TO PROCESS OPTIMIZATION

Most things can be improved, so engineers and scientists optimize. While designing systems and products requires a deep understanding of influences that achieve desirable performance, the need for an efficient and systematic decision-making approach drives the need for optimization strategies. This introductory chapter provides the motivation for this topic as well as a description of applications in chemical engineering. Optimization applications can be found in almost all areas of engineering. Typical problems in chemical engineering arise in process design, process control, model development, process identification, and real-time optimization. The chapter provides an overall description of optimization problem classes with a focus on problems with continuous variables. It then describes where these problems arise in chemical engineering, along with illustrative examples.

5.1 SCOPE OF OPTIMIZATION PROBLEMS

From a practical standpoint, we define the optimization task as follows: given a system or process, find the best solution to this process within constraints. This task requires the following elements:

- An objective function is needed that provides a scalar quantitative performance measure that needs to be minimized or maximized. This can be the system's cost, yield, profit, etc.

- A predictive model is required that describes the behavior of the system. For the optimization problem this translates into a set of equations and inequalities that we term constraints. These constraints comprise a feasible region that defines limits of performance for the system.

- Variables that appear in the predictive model must be adjusted to satisfy the constraints. This can usually be accomplished with multiple instances of variable values, leading to a feasible region that is determined by a subspace of these variables. In many engineering problems, this subspace can be characterized by a set of decision variables that can be interpreted as degrees of freedom in the process.

Optimization is a fundamental and frequently applied task for most engineering activities. However, in many cases, this task is done by trial and error (through case study). To avoid such tedious activities, we take a systematic approach to this task, which is as efficient as possible and also provides some guarantee that a better solution cannot be found. The systematic determination of optimal solutions leads to a large family of methods and algorithms. Moreover, the literature for optimization is dynamic, with hundreds of papers published every month in dozens of journals. Moreover, research in optimization can be observed at a number of different levels that necessarily need to overlap but are often considered by separate communities:

- At the mathematical programming level, research focuses on understanding fundamental properties of optimization problems and algorithms. Key issues include existence of solutions, convergence of algorithms, and related issues such as stability and convergence rates.
- The scientific computing level is strongly influenced by mathematical properties as well as the implementation of the optimization method for efficient and "practical" use. Here research questions include numerical stability, ill-conditioning of algorithmic steps, and computational complexity and performance.
- At the level of operations research, attention is focused on formulation of the optimization problem and development of solution strategies, often by using well-established solution methods. Many of the problems encountered at this level consider well structured models with linear and discrete elements.
- At the engineering level, optimization strategies are applied to challenging, and often poorly defined, real-world problems. Knowledge of optimization at this level is engaged with the efficiency and reliability of applicable methods, analysis of the solution, and diagnosis and recovery from failure of the solution method.

From the above description of optimization research, it is clear that successful development of an optimization strategy within a given level requires a working knowledge of the preceding levels. For instance, while it is important at the mathematical programming level to develop the "right" optimization algorithm, at the engineering level it is even more important to solve the "right" optimization problem formulation. On the other hand, as engineers need to consider optimization tasks on a regular basis, a systematic approach with a fundamental knowledge of optimization formulations and algorithms is essential. It should be noted that this requires not only knowledge of existing software, which may have limited application to particularly difficult problems, but also knowledge of the underlying algorithmic principles that allow challenging applications to be addressed.

CLASSIFICATION OF OPTIMIZATION PROBLEMS

Optimization is a key enabling tool for decision making in chemical engineering. It has evolved from a methodology of academic interest into a technology that continues to significant impact in engineering research and practice. Optimization algorithms form the core tools for (a) experimental design, parameter estimation, model development, and statistical analysis; (b) process synthesis, analysis, design, and retrofit; (c) model predictive control and real-time optimization; and (d) planning, scheduling, and the integration of process operations into the supply chain for manufacturing and distribution.

As shown in Figure 5.1, optimization problems that arise in chemical engineering can be classified in terms of continuous and discrete variables. When represented in algebraic form, the formulation of discrete/continuous optimization problems can be written as mixed integer optimization problems. The most general of these is the mixed integer nonlinear program (MINLP) of the form

Problem:5.1

$$\begin{aligned} \min_{x,y} \quad & f(x,y) \\ \text{s.t.} \quad & h(x,y) = 0, \\ & g(x,y) \leq 0, \\ & x \in \mathbb{R}^n, \quad y \in \{0,1\}^t, \end{aligned}$$

where $f(x,y)$ is the objective function (e.g., cost, energy consumption, etc.), $h(x,y) = 0$ are the equations that describe the performance of the system (e.g., material balances, production rates), and the inequality constraints $g(x,y) \leq 0$ can define process specifications or constraints for feasible plans and schedules. Note that the operator max $f(x,y)$ is equivalent to min $-f(x,y)$. We define the real n-vector x to represent the continuous variables while the t-vector y represents the discrete variables, which, without loss of generality, are often restricted to take 0/1 values to define logical or discrete decisions, such as assignment of equipment and sequencing of tasks. (These variables can also be formulated to take on other integer values as well.) Problem (5.1) corresponds to an MINLP when any of the functions involved are nonlinear. If the functions $f(x,y)$, $g(x,y)$, and $h(x,y)$ are linear (or vacuous), then (5.1) corresponds to a mixed integer linear program (MILP). Further, for MILPs, an important case occurs when all the variables are integer; this gives rise to an integer programming (IP) problem. IP problems can be further classified into a number of specific problems (e.g., assignment, traveling salesman, etc.), not shown in Figure 5.1. If there are no 0/1 variables, then problem (5.1) reduces to the nonlinear program (5.2) given by

$$\begin{aligned} \min_{x \in \mathbb{R}^n} \quad & f(x) \\ \text{s.t.} \quad & h(x) = 0, \\ & g(x) \leq 0. \end{aligned}$$

This general problem can be further classified. First, an important distinction is whether the problem is assumed to be differentiable or not. In this text, we will assume that the functions $f(x)$, $h(x)$, and $g(x)$ have continuous first and second derivatives. (In many cases, non smooth problems can be reformulated into a smooth form of (5.2).

Second, a key characteristic of (5.2) is whether it is convex or not, i.e., whether it has a convex objective function, $f(x)$, and a convex feasible region. This can be defined as follows.

- Aset $S \in$ Rn is convex if and only if all points on the straight line connecting any two points in this set are also within this set. This can be stated as

$$x(\alpha) = \alpha x_1 + (1-\alpha)x_2 \in S \quad \text{for all } \alpha \in (0,1) \text{ and } x_1, x_2 \in S.$$

- A function $\varphi(x)$ is convex if its domain X is convex and

$$\alpha\phi(x_1) + (1-\alpha)\phi(x_2) \geq \phi(x(\alpha))$$

holds for all $\alpha \in (0,1)$ and all points $x1,x2 \in X$.
- Convex feasible regions require $g(x)$ to be a convex function and $h(x)$ to be *linear*.
- A function $\varphi(x)$ is (strictly) concave if the function $-\varphi(x)$ is (strictly) convex.

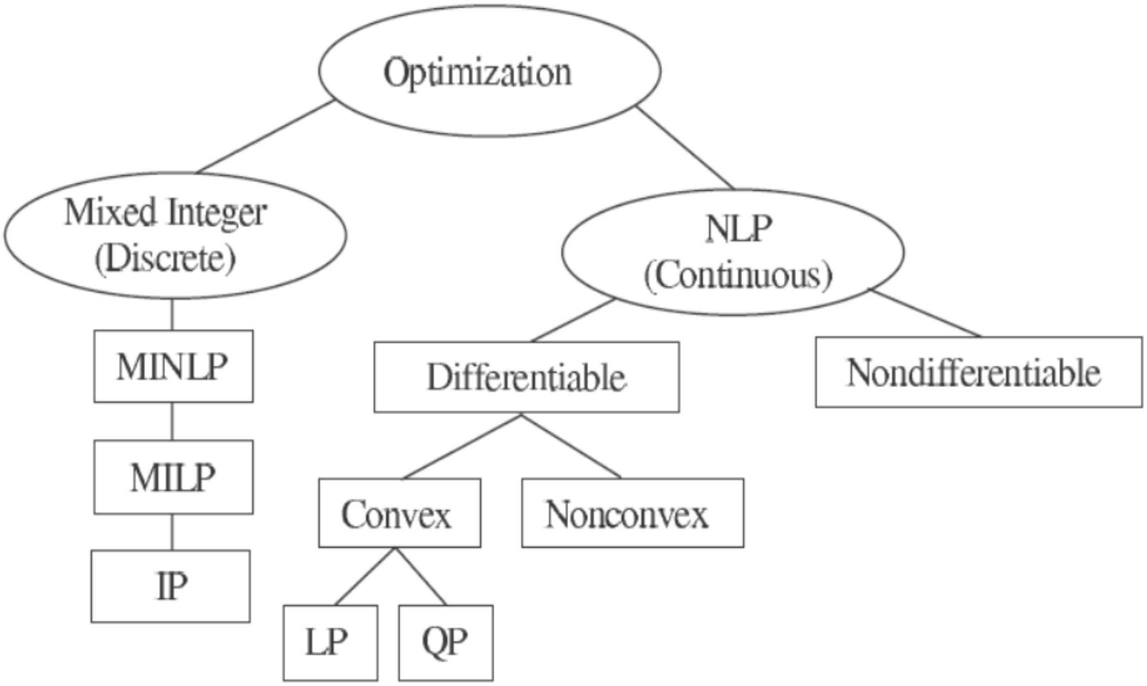


Figure 5.1. *Classes of optimization problems.*

If (5.2) is a convex problem, then any local solution (for which a better, feasible solution cannot be found in a neighborhood around this solution) is guaranteed to be a global solution to (5.2); i.e., no better solution exists. On the other hand, nonconvex problems may have multiple local solutions, i.e., feasible solutions that minimize the objective function only within some neighborhood about the solution.

Further specializations of problem (5.2) can be made if the constraint and objective functions satisfy certain properties, and specialized algorithms can be constructed for these cases. In particular, if the objective and constraint functions in (5.2) are linear, then the resulting linear program (LP) can be solved in a finite number of steps. Methods to solve LPs are widespread and well implemented. Currently, state-of-the-art LP solvers can handle millions of variables and constraints, and the application of further decomposition methods leads to the solution of problems that are two or three orders of magnitude larger than this. Quadratic programs (QPs) represent a slight modification of LPs through the addition of a quadratic term in the objective function. If the objective function is convex, then the resulting convex QP can also be solved in a finite number of steps. While QP models are generally not as large or widely applied as LP models, a number of solution strategies have been created to solve large-scale QPs very efficiently.

Optimization Applications in Chemical Engineering

Optimization has found widespread use in chemical engineering applications, especially in the engineering of process systems. Problems in this domain often have many alternative solutions with complex economic and performance interactions, so it is often not easy to identify the optimal solution through intuitive reasoning. Moreover, the economics of the system often indicate that finding the optimum solution translates into large savings, along with a large economic penalty for sticking to suboptimal solutions. Therefore, optimization has become a major technology that helps the chemical industry to remain competitive.

As summarized in Table 5.1, optimization problems are encountered in all facets of chemical engineering, from model and process development to process synthesis and design, and finally to process operations, control, scheduling, and planning.
Process development and modeling is concerned with transforming experimental data and fundamental chemical and physical relationships into a predictive process model. Incorporating the tasks of experimental design, parameter estimation, and discrimination of competing models, this step gives rise to NLP and MINLP problems.

At the next level, process synthesis and design incorporates these predictive models to devise a process that is both technically and economically feasible. The synthesis step is largely focused on establishing the structure of the process flow sheet (usually with simplified models) and systematic strategies have been developed for particular subsystems that involve reaction, separation, energy management, and waste reduction. On the other hand, the design step is concerned with establishing equipment parameters and nominal operating conditions for the flow sheet. As a result, synthesis problems can be addressed with a wide range of optimization formulations, while the design step requires more detailed models that give rise to NLP and MINLP problems.

In the operation of chemical processes, there is widespread interest in improving the scheduling and planning of these operations. These tasks are usually formulated as LP and MILP problems which are less detailed, as most operations are described through time requirements and activities. On the other hand, the development of large-scale NLP tools has led to the application of real-time optimization which interacts with the process and responds to changes in the production schedule and from other inputs. The results of the real-time optimization also feed operating conditions or *set points* to the control system. The distinction between these two levels is that real-time optimization describes steady state behavior, while the control system responds essentially to the process dynamics. The control task addresses maintenance of optimal production levels and rejection of disturbances. For multivariable, constrained systems, model predictive control (MPC) is now accepted as a widely used optimization-based strategy. MPC models allow various levels of detail to handle linear and nonlinear dynamics as well as discontinuities that occur in hybrid systems.

Table 5.1. *Mathematical programming in process systems engineering.*

	LP	MILP	QP	NLP	MINLP
Process Model Building				X	X
Process Design & Synthesis					
Heat Exchangers	X	X		X	X
Mass Exchangers	X	X		X	X
Separations		X		X	X
Reactors	X			X	X
Flowsheeting				X	X
Process Operations					
Scheduling	X	X			X
Supply Chain	X	X			X
Real-Time Optimization	X		X	X	
Process Control					
Model Predictive Control	X		X		
Nonlinear MPC			X	X	
Hybrid MPC		X			

Table 5.1 summarizes model types that have been formulated for process engineering applications. Design is dominated by NLP and MINLP models due to the need for the explicit handling of performance equations, although simpler targeting models for synthesis give rise to LP and MILP problems. Operations problems, in contrast, tend to be dominated by linear models, LPs and MILPs, for planning, scheduling, and supply chain problems. Nonlinear Programming, however, plays a crucial role at the level of real-time optimization. Finally, process control has traditionally relied on LP and NLP models, although MILPs are being increasingly used for hybrid systems. It is also worth noting that the applications listed in Table 5.1 have been facilitated not only by progress in optimization algorithms, but also by modeling environments such as GAMS and AMPL.

This book focuses on the nonlinear programming problem (5.2) and explores methods that locate local solutions efficiently. While this approach might first appear as a restricted form of optimization, NLPs have broad applications, particularly for large-scale engineering models. Moreover, while the study of NLP algorithms is important on its own, these algorithms also form important components of strategies for MINLP problems and for finding the global optimum of nonconvex problems.

GENERAL PROCEDURE FOR SOLVING OPTIMIZATION PROBLEMS.

1.Analyze the process itself so that the process variables and specific characteristics of interest are defined, i.e., make a list of all of the variables.

2. Determine the criterion for optimization and specify the objective function in terms of the above variables together with coefficients. This step provides the performance model (sometimes called the economic model when appropriate).

3. Develop via mathematical expressions a valid process or equipment model that relates the input-output variables of the process and associated coefficients. Include both equality and inequality constraints. Use well-known physical principles (mass balances, energy balances), empirical relations, implicit concepts, and external restrictions. Identify the independent and dependent variables (number of degrees of freedom).

4. If the problem formulation is too large in scope:

(A) Break it up into manageable parts and/or

(B) Simplify the objective function

5. Apply a suitable optimization technique to the mathematical statement of the problem.

6. Check the answers and examine the sensitivity of the result to changes in the coefficients in the problem and the assumptions.

SIMULATION

Process simulation is used to determine the size of equipment in a chemical plant, the amount of energy needed, the overall yield, and the magnitude of the waste streams. Because the results of process simulation depend upon thermodynamics and transport processes, the mathematical models are complicated and would be time-consuming to solve without a computer. In this chapter some of the problems are solved by using **chemcad**

Examples

A gas mixture of air (4 kmol/hr) and hydrogen sulfide (2 kmol/hr) is to be absorbed by water so that 99% of hydrogen sulfide is recovered from the bottom stream. The absorber has 10 trays. Water enters the absorber from 1st tray at 298 K and 1 atm and gas feed enters from 10th tray at the same temperature and pressure as those of water. Simulate this absorber in

CHEMCAD to determine the mole rate of water needed to recover 99% of hydrogen sulfide in the bottom stream.

Procedure:

Step 1: Creating the flow sheet

Step 2: Entering the components and formatting engineering units

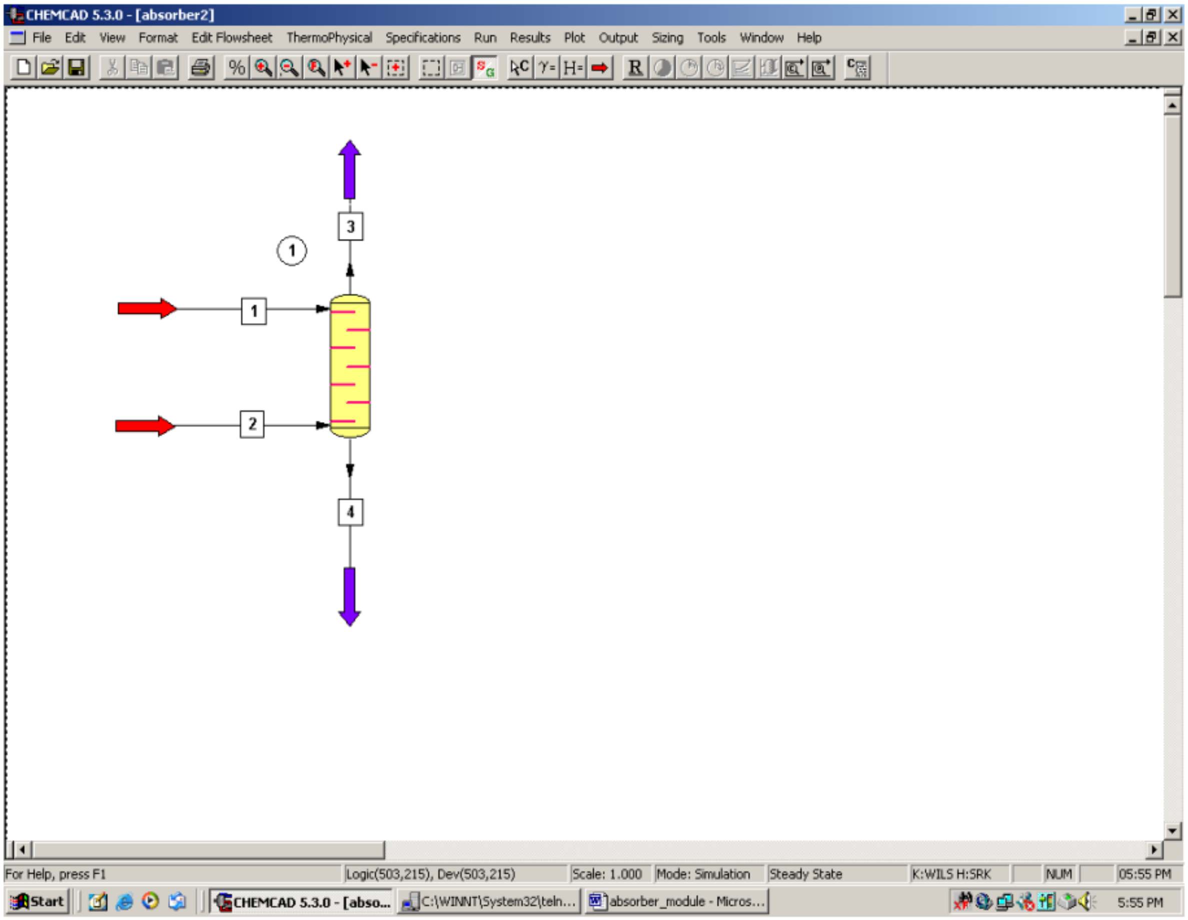
Step 3: Entering the feed stream composition

Step 4: Entering the absorber specs

Step 5: Running the simulation and retrieving the results

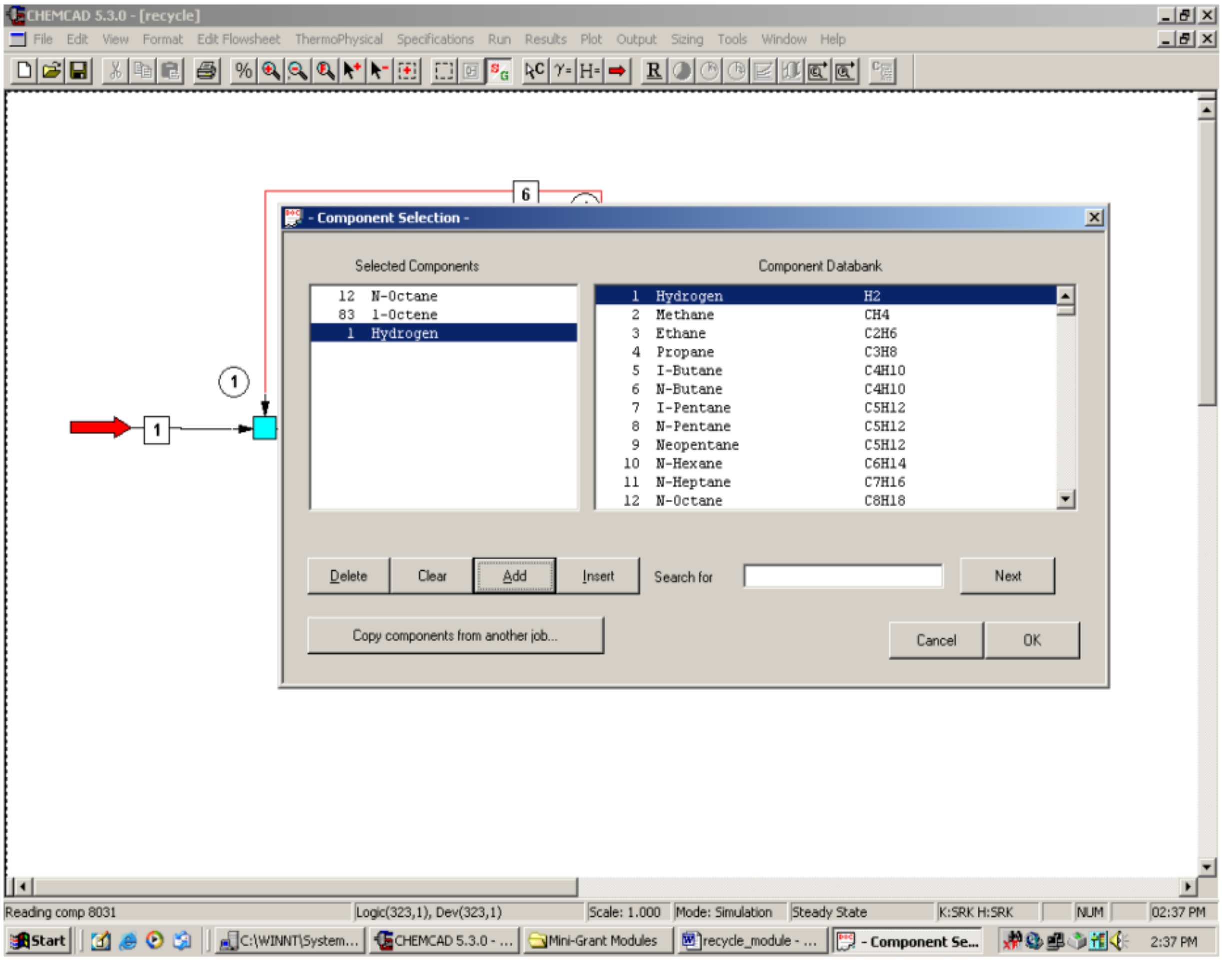
Step 1: Creating the flow sheet

Select and click *feed (2), SCDS column* #3 (right click on the regular SCDS icon to find the icon representing absorber mode) and *product(2)* icons on the workspace. Connect the icons appropriately using *Stream*. Click once on the **S**/**G** icon on the menu bar to switch the simulation mode from *Edit Simulation* to *Run Simulation*.



Step 2: Entering the components and formatting engineering units

Go to the *Thermophysical* on the menu bar and click on *Components List*. Find air, hydrogen sulfide and water from the CHEMCAD components list and add them to the component list. Go to the *Format* menu and click on *Engineering Units* and select the desired units for such properties as temperature, pressure etc. Click OK to continue.



Selected Components

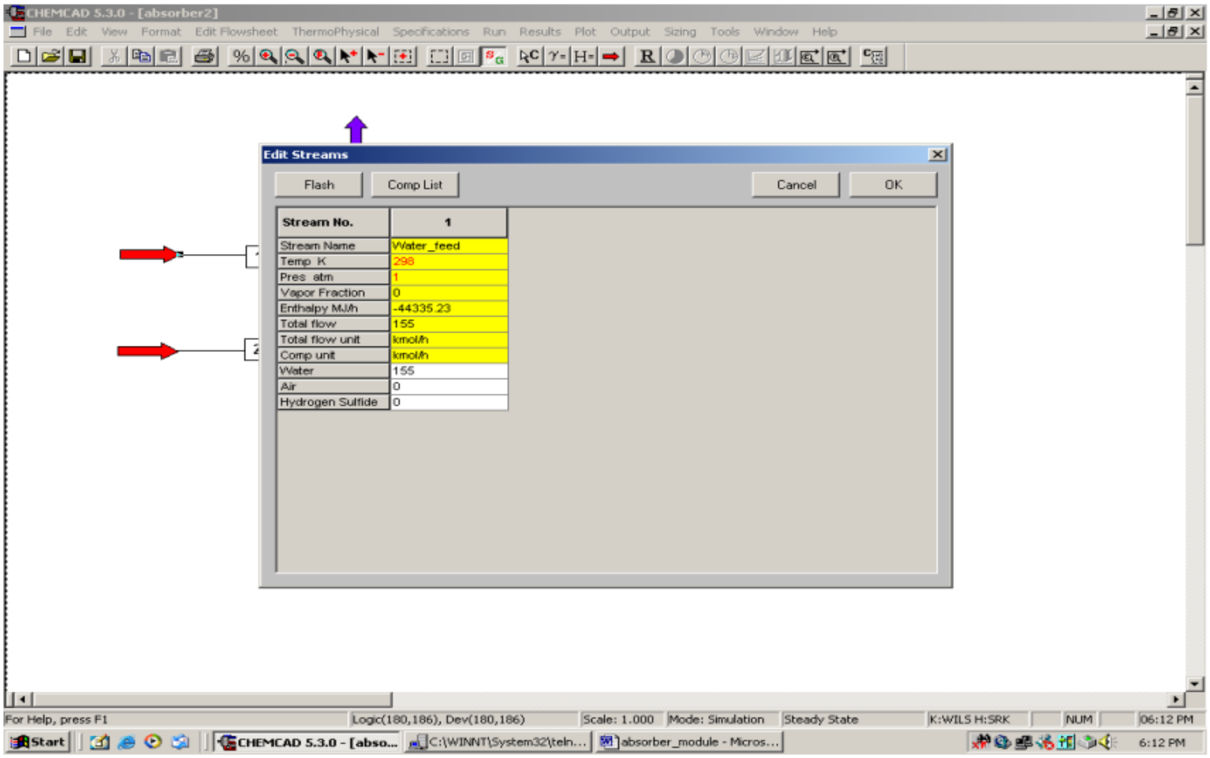
12	N-Octane
83	1-Octene
1	Hydrogen

Component Databank

1	Hydrogen	H_2
2	Methane	CH_4
3	Ethane	C_2H_6
4	Propane	C_3H_8
5	I-Butane	C_4H_{10}
6	N-Butane	C_4H_{10}
7	I-Pentane	C_5H_{12}
8	N-Pentane	C_5H_{12}
9	Neopentane	C_5H_{12}
10	N-Hexane	C_6H_{14}
11	N-Heptane	C_7H_{16}
12	N-Octane	C_8H_{18}

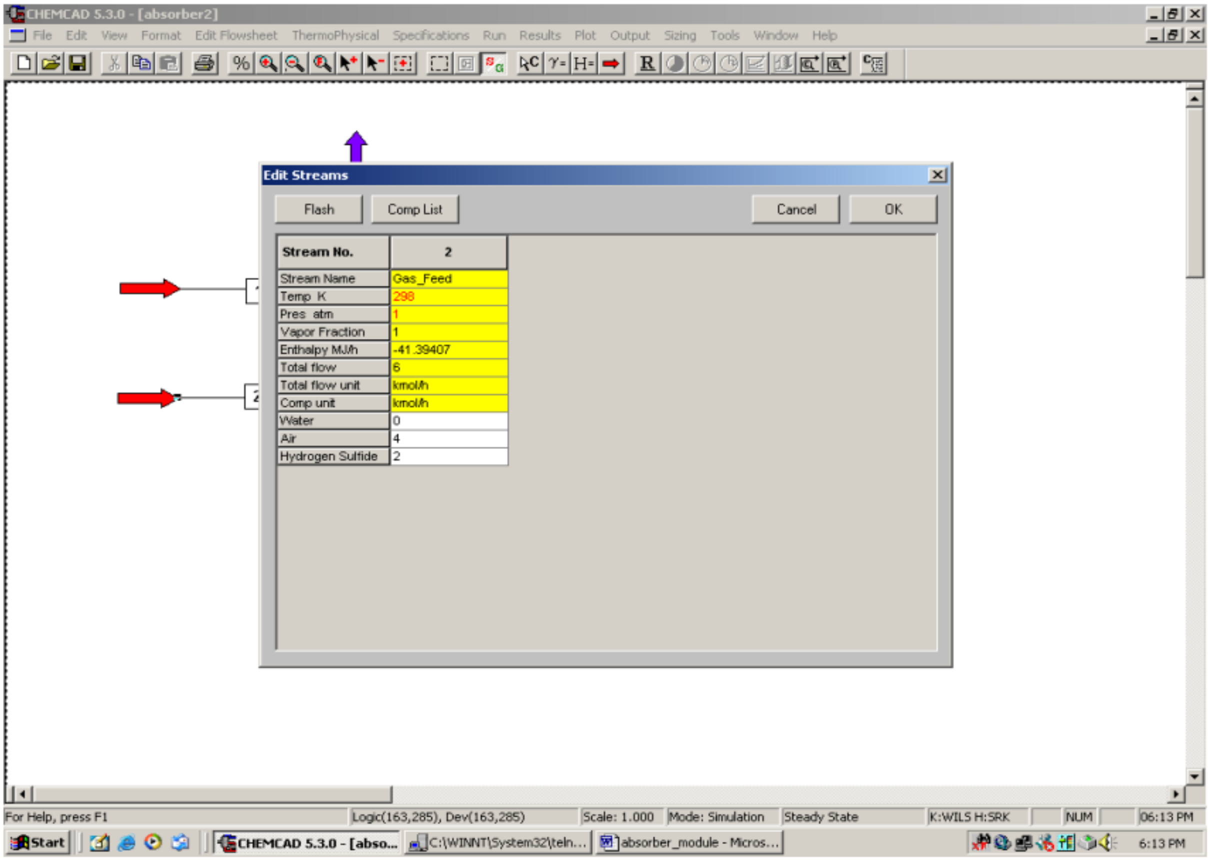
Step 3: Entering the feed stream composition

Double click on the first feed stream (water stream). Enter the feed information (temperature, pressure, and an initial guess, say 100 kmol/hr for flow rate of water) given in the problem statement. Click once on *Flash* to get the feed stream enthalpy and vapor fraction in feed at the feed conditions.



Stream No.	1
Stream Name	Water_feed
Temp K	298
Pres atm	1
Vapor Fraction	0
Enthalpy MJ/h	-44335.23
Total flow	155
Total flow unit	kmol/h
Comp unit	kmol/h
Water	155
Air	0
Hydrogen Sulfide	0

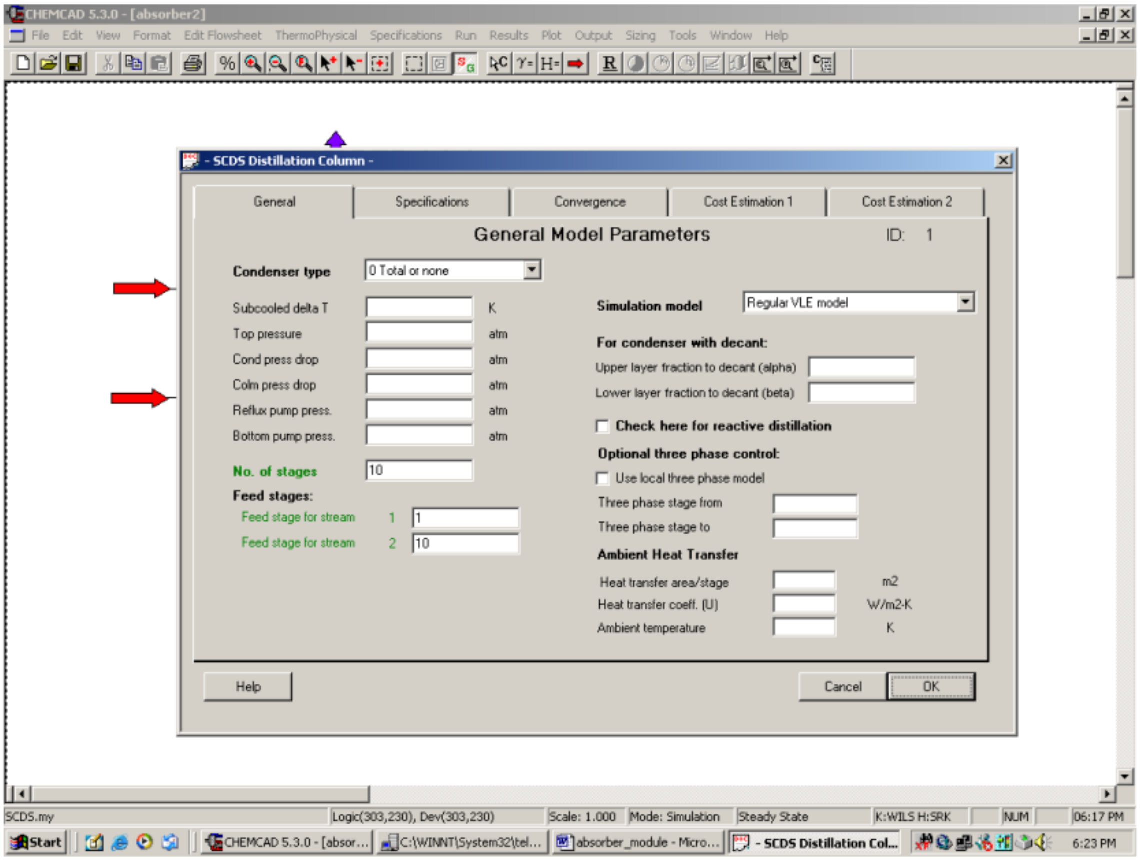
Similarly, enter the feed conditions for the second stream (gas stream).



Stream No.	2
Stream Name	Gas_Feed
Temp K	298
Pres atm	1
Vapor Fraction	1
Enthalpy MJ/h	-41.39407
Total flow	6
Total flow unit	kmol/h
Comp unit	kmol/h
Water	0
Air	4
Hydrogen Sulfide	2

Step 4: Entering the absorber specs

Double click on the SCDS column. This can be used as an absorber.



General Model Parameters ID: 1

Condenser type: 0 Total or none

Subcooled delta T: K

Top pressure: atm

Cond press drop: atm

Colm press drop: atm

Reflux pump press.: atm

Bottom pump press.: atm

No. of stages: 10

Feed stages:

Feed stage for stream 1: 1

Feed stage for stream 2: 10

Simulation model: Regular VLE model

For condenser with decant:

Upper layer fraction to decant (alpha):

Lower layer fraction to decant (beta):

☐ Check here for reactive distillation

Optional three phase control:

☐ Use local three phase model

Three phase stage from:

Three phase stage to:

Ambient Heat Transfer

Heat transfer area/stage: m2

Heat transfer coeff. (U): W/m2-K

Ambient temperature: K

The required inputs in this page are the same as those for a distillation column and are described below:

No. of stages: Enter the number of stages (10)

Feed stage for stream 1: Enter the stage number at which water enters the column (1)

Feed stage for stream 2: Enter the stage number at which gas mixture enters the column (10)

The other inputs on this page are optional and can be neglected.

Don't click *OK* yet!

Click on the *Specifications* tab. Note that the default options for *Condenser mode* and *Reboiler mode* are *No Condenser* and *No Reboiler* respectively. These options are always left to default when simulating for an absorber using an SCDS column.

Click *OK* to continue.

Step 5: Running the simulation and retrieving the results:

Now the simulation is ready to be run. Click once on ***R*** to run the simulation. Alternatively, one can run the simulation by clicking on *Run* on the menu bar and selecting *Run all.* The status of the simulation can be found at the bottom left hand corner of the screen. The message, *Run Finished,* appears if the run is successfully completed. The product stream properties can be found by double clicking the product streams. At this point, a check is made to see the mole rate of hydrogen sulfide in the bottom stream. If this is more than 1.98 kmol/hr (99% of hydrogen sulfide in feed, as per the problem statement), the guessed flow rate of water is too high. Decrease the flow rate of water in feed stream and repeat the above steps. Conversely, if the mole rate of hydrogen sulfide exiting from the bottom is less than 1.98 kmol/hr, increase the flow rate of water in the feed stream and repeat the above steps until the flow rate of hydrogen sulfide from the bottom is approximately 1.98 kmol/hr.

Alternatively, a sensitivity analysis can made with water feed flow rate as the independent variable and the hydrogen sulfide product flow rate in the bottom as the dependent variable. The plot obtained after running the sensitivity analysis can be used to read the water flow rate at which the flow rate of hydrogen sulfide from the bottom is 1.98 kmol/hr.

It can be verified that the water flow rate to meet the specifications in problem staement is 145 kmol/hr

The Problem Statement:

5.4.2 Reaction:

Decomposition of di-t-butyl peroxide (DTBP) to acetone and ethane

$$(CH_3)_3COOC(CH_3)_3 \rightarrow 2(CH_3)_2CO + C_2H_6$$

Reaction kinetics:

$$k_c = 2.095*10^{-2} \min^{-1}$$
$$-r_A = k_c C_A$$

Reaction conditions:

Temperature 154.6 °C

Pressure 491.8 mmHg

Feed and initial conditions:

100 kmol/h of (DTBP) at 110 °C and 760 mmHg

Information for steady state:

1. Reaction is isothermal
2. Conversion with respect to DTBP is 85%
3. Reference temperature for heat of reaction is 25 °C

Perform a simulation to determine the volume of the reactor at steady state to achieve the desired conversion, the steady state heat duty and the steady-state mole rates of components in the product stream.

Procedure:

Step 1: Creating the Flow sheet

Step 2: Formatting Engineering Units and Selecting Components

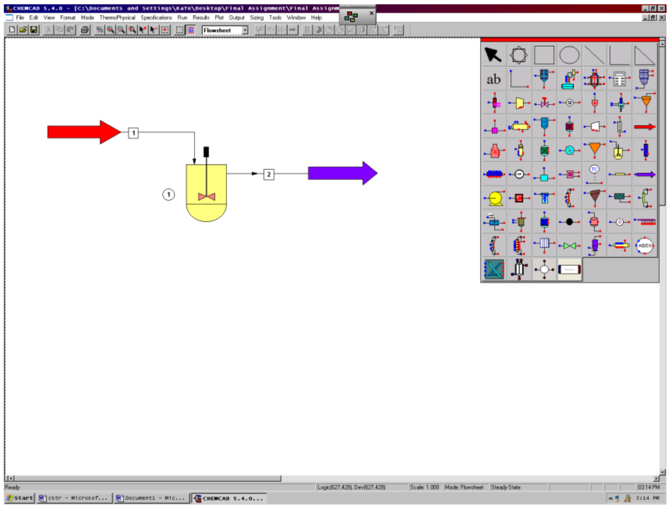
Step 3: Entering the feed stream composition

Step 4: Entering the reactor specs

Step 5: Running the simulation and retrieving the results

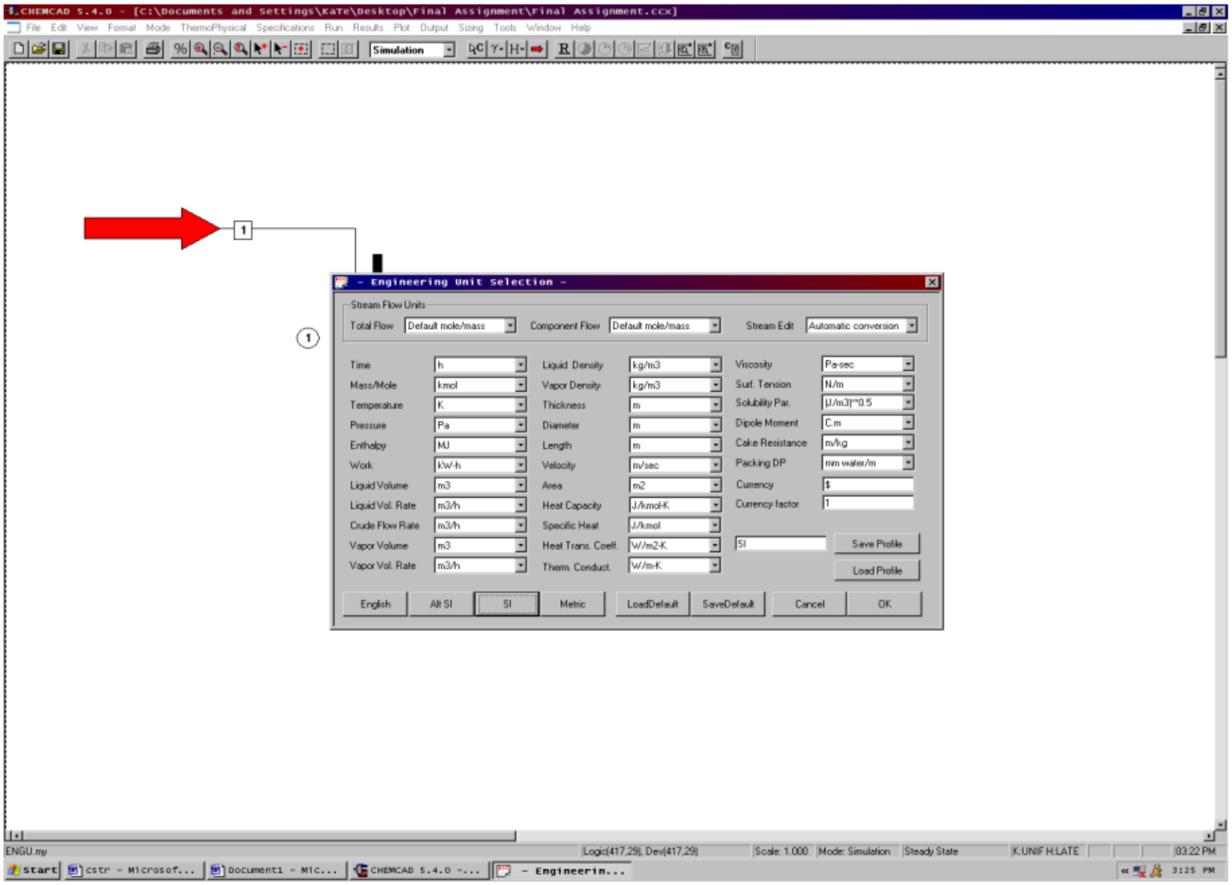
Step 1: Creating the flow sheet

From the File menu select New, save to desired directory. Select and click the *kinetic reactor, feed* and *product* icons on the workspace. Connect the three using the *stream icon*.



Step 2: Formatting Engineering Units and Selecting Components

At the top of the screen change the scroll down menu from Flowsheet to Simulation. Go to the *Format* menu and select *Engineering Units.* Use the *SI* option at the bottom to convert all units at the same time. The desired units for each category may also be selected individually. Click OK to continue.

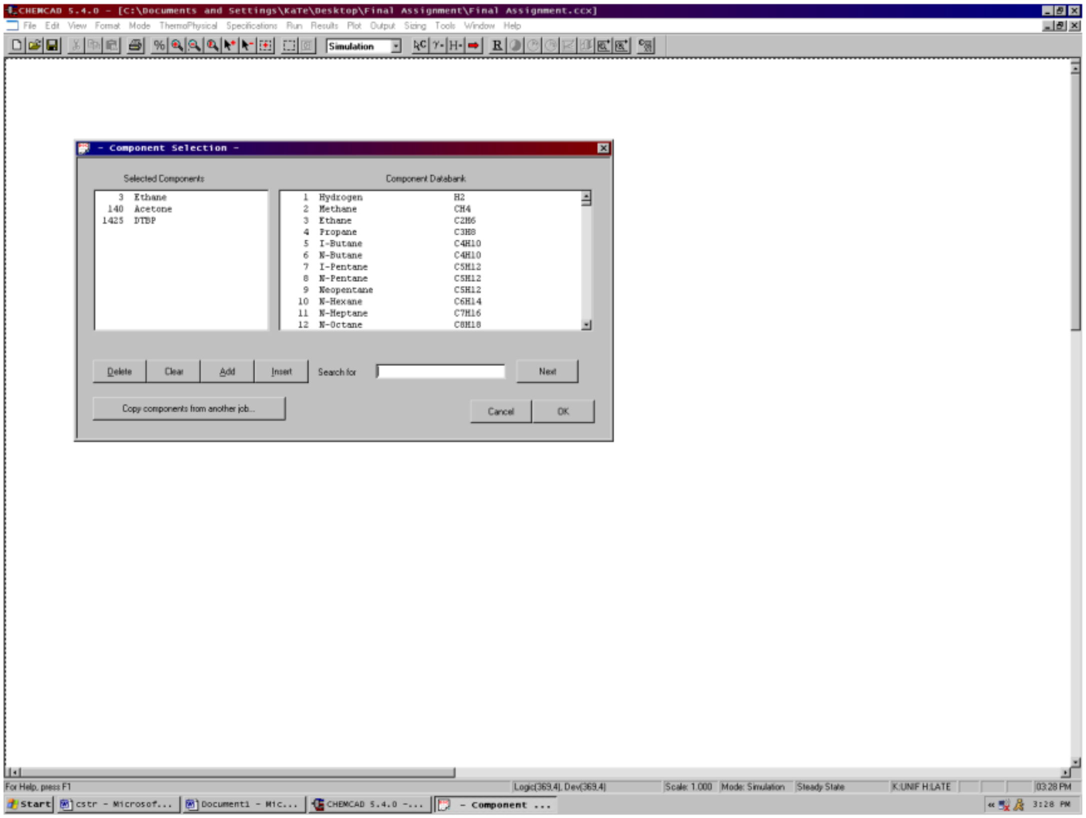


Stream Flow Units

Total Flow	Default mole/mass	Component Flow	Default mole/mass	Stream Edit	Automatic conversion

Time	h	Liquid Density	kg/m3	Viscosity	Pa-sec
Mass/Mole	kmol	Vapor Density	kg/m3	Surf. Tension	N/m
Temperature	K	Thickness	m	Solubility Par.	(J/m3)^0.5
Pressure	Pa	Diameter	m	Dipole Moment	C.m
Enthalpy	MJ	Length	m	Cake Resistance	m/kg
Work	kW-h	Velocity	m/sec	Packing DP	mm water/m
Liquid Volume	m3	Area	m2	Currency	$
Liquid Vol. Rate	m3/h	Heat Capacity	J/kmol-K	Currency factor	1
Crude Flow Rate	m3/h	Specific Heat	J/kmol		
Vapor Volume	m3	Heat Trans. Coeff.	W/m2-K		SI
Vapor Vol. Rate	m3/h	Therm. Conduct.	W/m-K		

Next Go to *Thermophysical* on the menu bar and click on *Components List*. Find DTBP (Di tertiary butyl peroxide), acetone, and ethane from the CHEMCAD components list and add them to the component list. Click OK to continue.



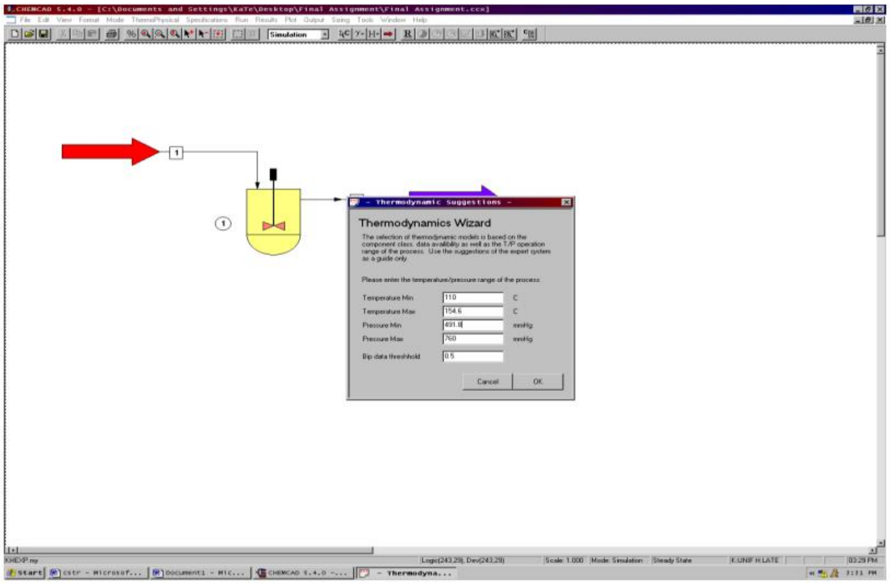
Selected Components

3	Ethane
140	Acetone
1425	DTBP

Component Databank

1	Hydrogen	H2
2	Methane	CH4
3	Ethane	C2H6
4	Propane	C3H8
5	I-Butane	C4H10
6	N-Butane	C4H10
7	I-Pentane	C5H12
8	N-Pentane	C5H12
9	Neopentane	C5H12
10	N-Hexane	C6H14
11	N-Heptane	C7H16
12	N-Octane	C8H18

The Thermodynamics Wizard will then appear, enter the desired information. Click OK to Continue. The K-Value Wizard can be accessed any time by clicking on the *Thermo physical menu* and then scrolling down to K-Value Wizard. Click OK. On the second screen select the SRK equation of state if the UNIFAC equation of state does not work. Click OK.



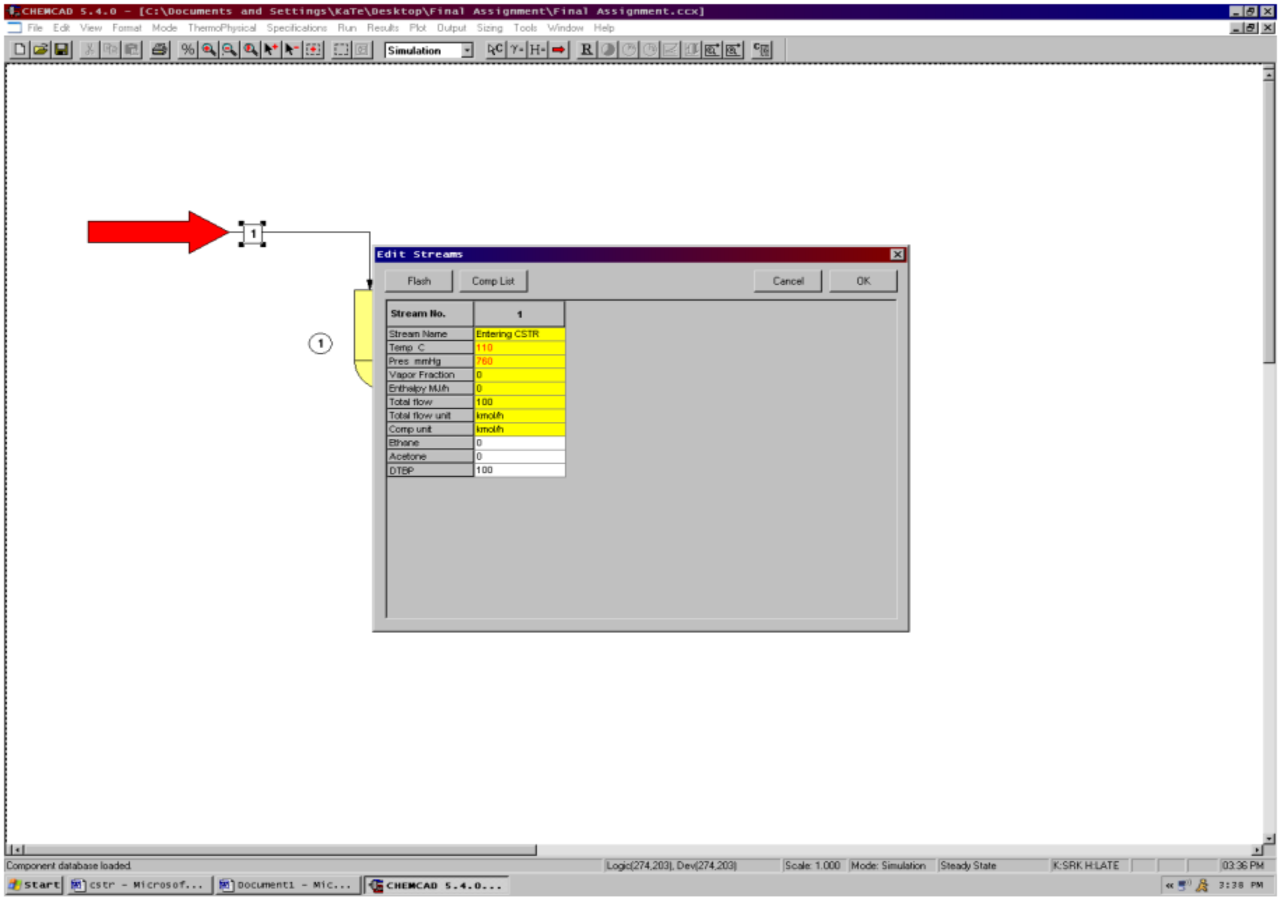
The selection of thermodynamic models is based on the component class, data availability as well as the T/P operation range of the process. Use the suggestions of the expert system as a guide only.

Please enter the temperature/pressure range of the process:

Temperature Min	110	C
Temperature Max	154.6	C
Pressure Min	491.8	mmHg
Pressure Max	760	mmHg
Bip data threshhold	0.5	

Step 3: Entering the feed stream composition

Double click on the feed stream and enter the feed information (temperature, pressure, total flow rate and component mole fractions) given in the problem statement. Click once on *Flash* to get the feed stream enthalpy and vapor fraction in feed at the feed conditions. Click OK. Click on the Exit stream and input the isothermal temperature and pressure. Click Flash. Click OK.



Stream No.	1
Stream Name	Entering CSTR
Temp C	110
Pres mmHg	760
Vapor Fraction	0
Enthalpy MJ/h	0
Total flow	100
Total flow unit	kmol/h
Comp unit	kmol/h
Ethane	0
Acetone	0
DTBP	100

Step 4: Entering the reactor specs

Double click on the reactor.

General Specifications Page:

Number of reactions: As there is only one reaction in the problem statement, enter '1'

Reactor Pressure: Enter the reactor pressure as given in the problem statement (491.8 mmHg)

Pressure Drop: As there is no pressure drop specified within the reactor. Leave this blank.

Kinetic Rate Expression*:* There are two options for this. The default option *(Standard)* is used when the rate equation is in standard Arrhenius form. The other option *(User Specified)* is used when the rate law is not in its standard form and the user needs to enter this manually. For more information on this, the user can always click on the *help* button that appears at the bottom left corner on this page. For this problem, the kinetic rate expression is given to the user. So, the *User Specified* option should be selected.

Reaction Phase*:* As the reactant, DTBP and one product, ethane, are in vapor phase at reaction pressure and temperature and the other product, acetone is in liquid phase, *Vapor Reaction, Mixed Phase* radio button should be selected.

Specify Reactor Type*:* As the reactor described in the problem statement is a CSTR, *CSTR* should be selected form the drop box.

Thermal Mode*:* As the temperature of the reaction is given as 154.6 °C, *Isothermal* option should be selected.

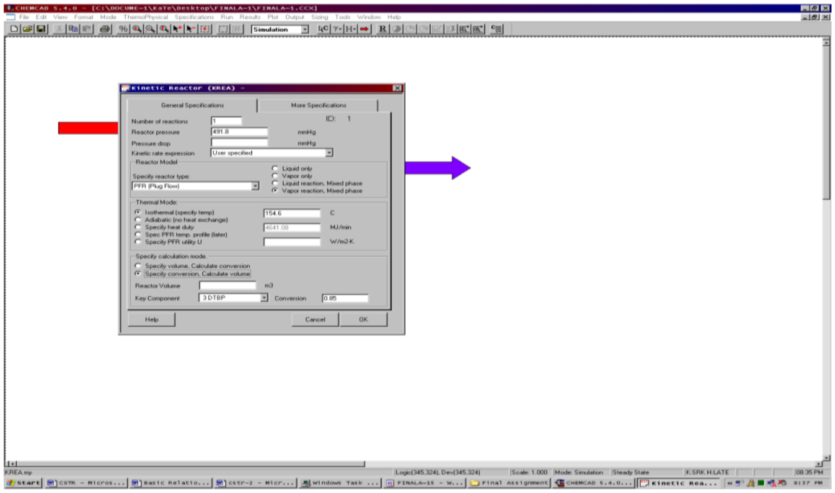
Specify Calculation Mode*:* As the desired conversion is given in the problem statement, *Specify Conversion, Calculate Volume* option should be selected.

Reactor Volume*:* This needs to left blank as this is the value that is required to be calculated in the simulation.

Key Component*:* The key component to specify conversion is DTBP and this is selected from the drop box.

Conversion*:* The conversion with respect to the key component, DTBP is given as 85% and this conversion (0.85) is entered in this field.

Don't Click *OK* yet! There is more to complete in the *More Specifications* page!



ID: 1
Number of reactions: 1
Reactor pressure: 491.8 mmHg
Pressure drop: mmHg
Kinetic rate expression: User specified

Reactor Model
Specify reactor type: PFR (Plug Flow)
○ Liquid only
○ Vapor only
○ Liquid reaction, Mixed phase
● Vapor reaction, Mixed phase

Thermal Mode:
● Isothermal (specify temp) 154.6 C
○ Adiabatic (no heat exchange)
○ Specify heat duty 4641.08 MJ/min
○ Spec PFR temp. profile (later)
○ Specify PFR utility U W/m2-K

Specify calculation mode:
○ Specify volume, Calculate conversion
● Specify conversion, Calculate volume
Reactor Volume: m3
Key Component: 3 DTBP
Conversion: 0.85

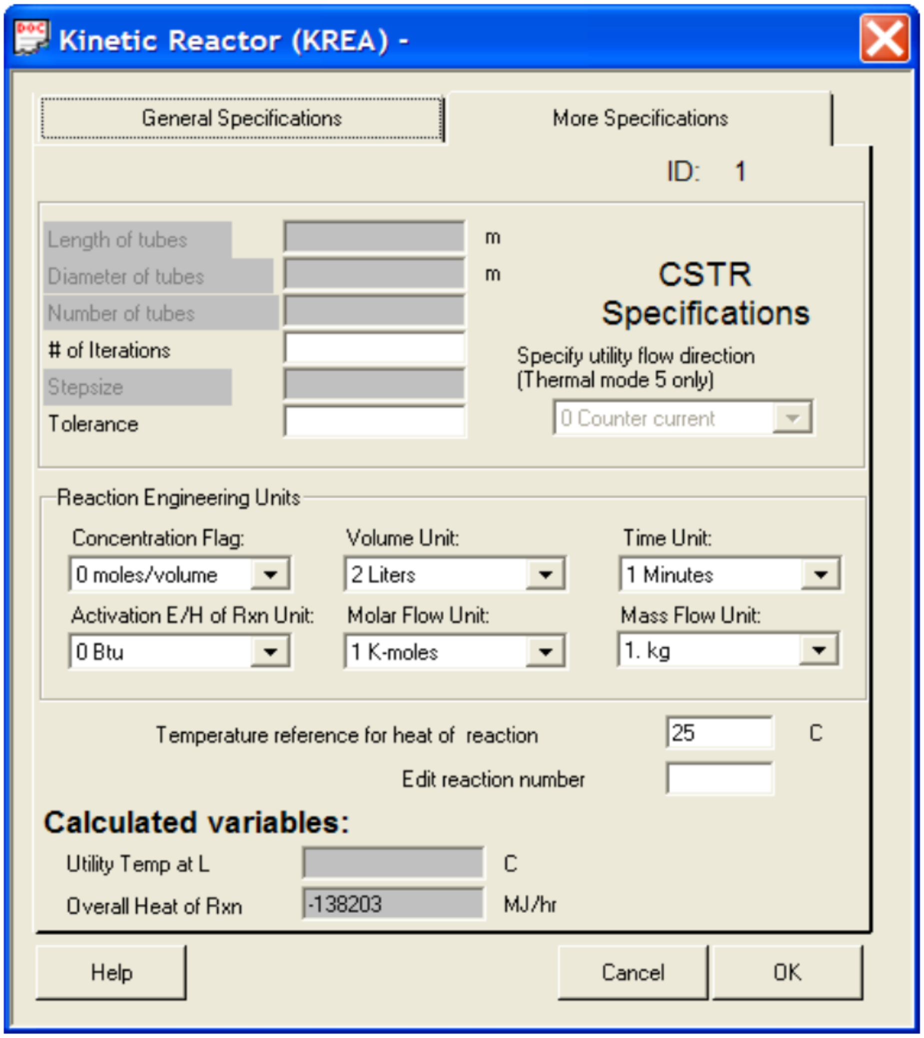
More Specifications:

# of Iterations and ***Tolerance*** can be left blank as these are optional fields.

Reaction Engineering Units: Change the units so that the units are consistent with the rate law (Change *time* units to *min*)

Temperature reference for heat of reaction: Enter 25 °C in this field.

Edit reaction number: Can be left blank.



ID: 1

Length of tubes m

Diameter of tubes m

Number of tubes

# of Iterations

Stepsize

Tolerance

CSTR Specifications

Specify utility flow direction (Thermal mode 5 only): 0 Counter current

Reaction Engineering Units

Concentration Flag: 0 moles/volume

Volume Unit: 2 Liters

Time Unit: 1 Minutes

Activation E/H of Rxn Unit: 0 Btu

Molar Flow Unit: 1 K-moles

Mass Flow Unit: 1. kg

Temperature reference for heat of reaction 25 C

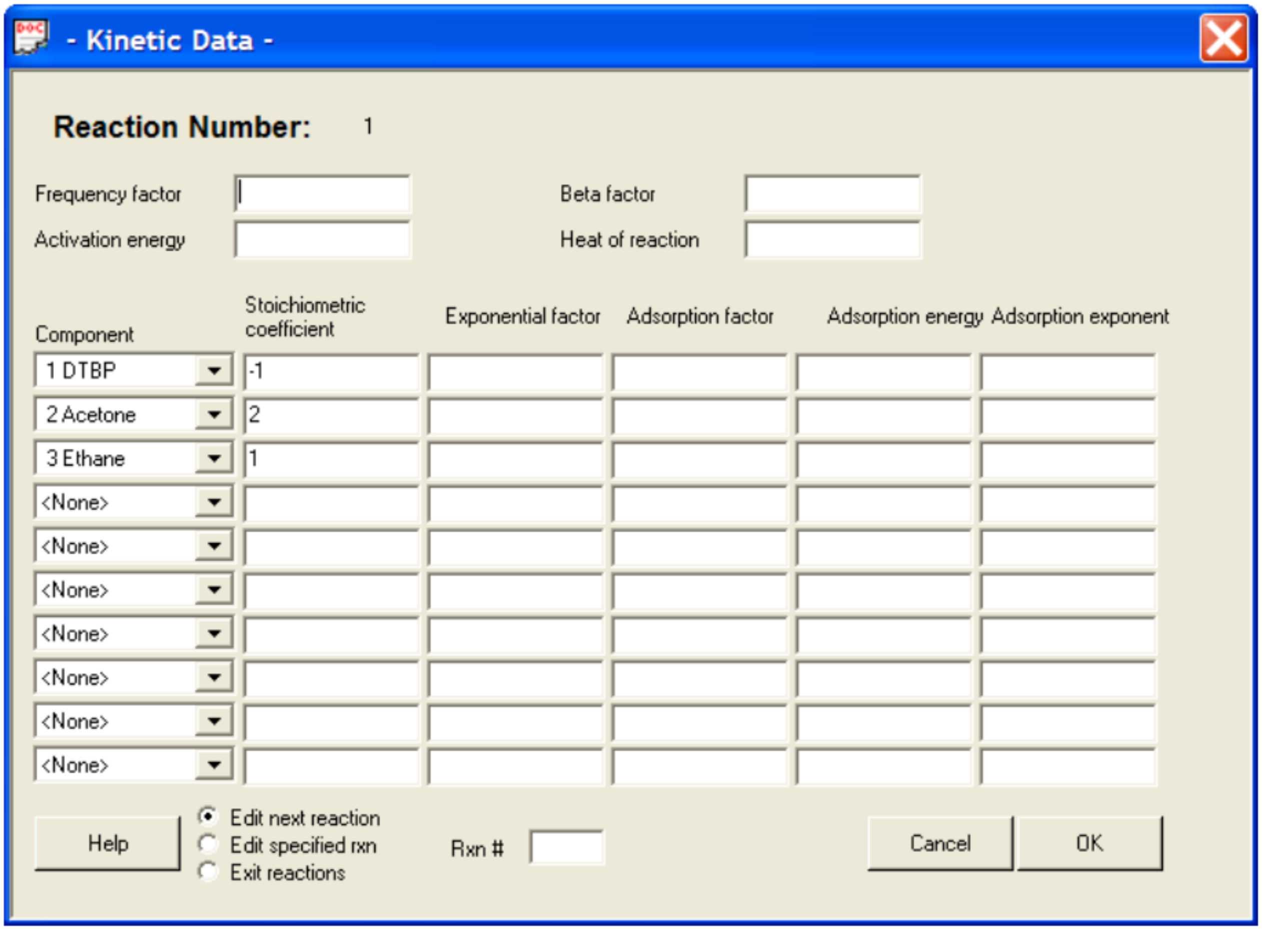
Edit reaction number

Calculated variables:

Utility Temp at L C

Overall Heat of Rxn -138203 MJ/hr

Click *OK* after completing the specifications page. A new window will appear and the stoichiometric coefficients should be entered in this window. Remember Reactants are negative (-), while products are positive (+). Click *OK* after entering the coefficients.



Reaction Number: 1

Frequency factor		Beta factor	
Activation energy		Heat of reaction	

Component	Stoichiometric coefficient	Exponential factor	Adsorption factor	Adsorption energy	Adsorption exponent
1 DTBP	-1				
2 Acetone	2				
3 Ethane	1				
<None>					
<None>					
<None>					
<None>					
<None>					
<None>					
<None>					

● Edit next reaction
○ Edit specified rxn
○ Exit reactions

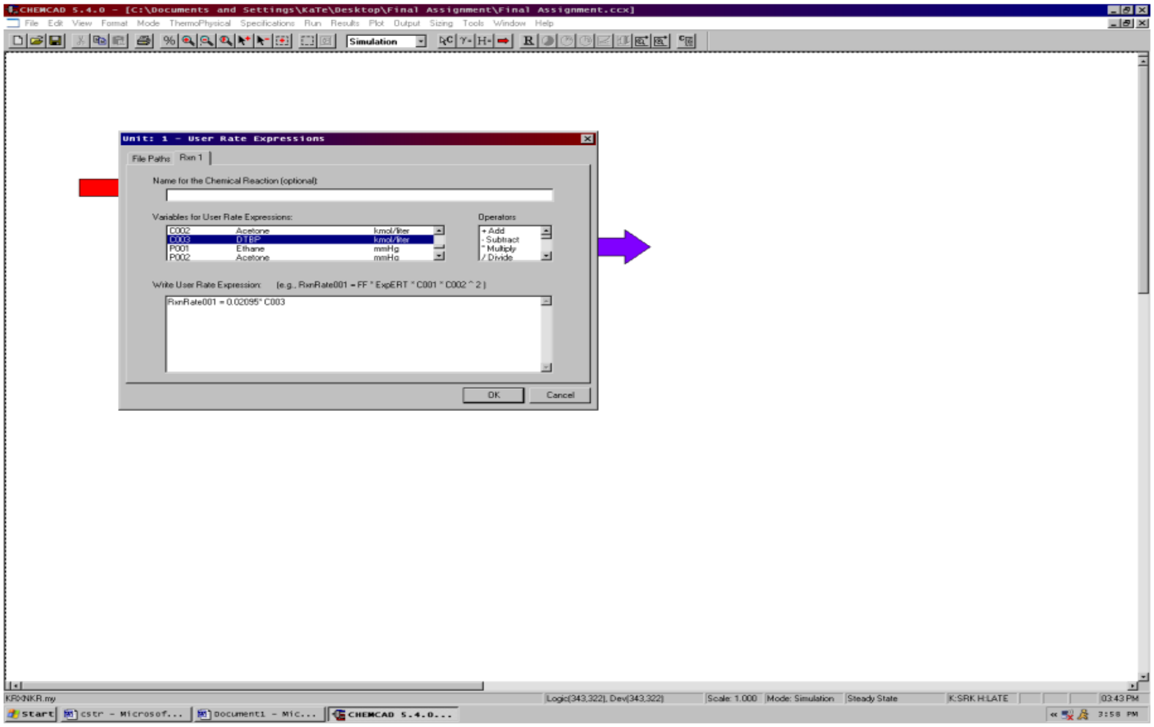
Rxn #

Because the *User Specified* option is selected for kinetic rate expression, another window with the title *Unit: 1-User Rate Expressions* appears. If a separate Visual Basic code is available, the user can browse those files using options available on *File path* tab. For most practical purposes, the user can go directly to the *Rxn1* tab and complete the information as follows:

Name for the Chemical Reaction: DTBP decomposition

Variables for User Rate Expressions: CHEMCAD supplies the user with the variables described in this section to be used for user rate expressions.

Write User Rate Expression: 0.02095*C003

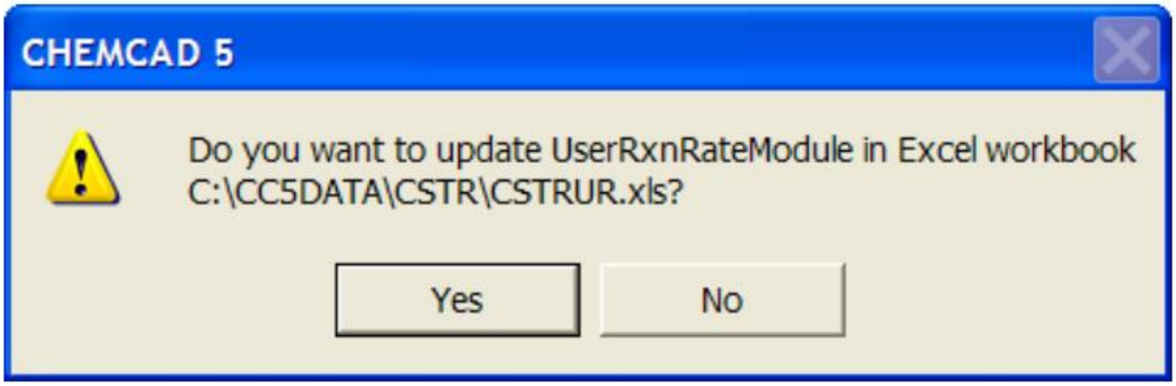


C002	Acetone	kmol/liter
C003	DTBP	kmol/liter
P001	Ethane	mmHg
P002	Acetone	mmHg

(e.g., RxnRate001 = FF * ExpERT * C001 * C002 ^ 2)

```
RxnRate001 = 0.02095* C003
```

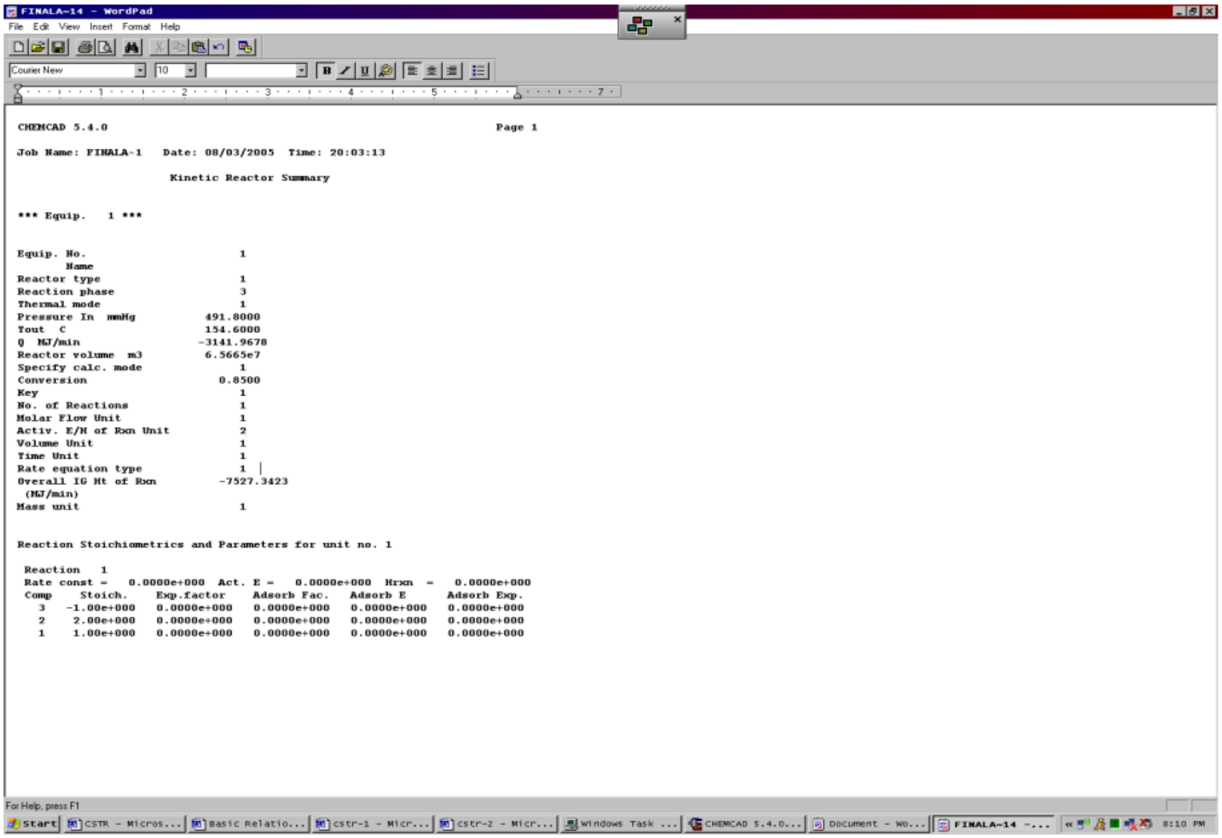
Click *OK* when finished. The following window will appear to confirm that we are allowing the cookies from an existing excel file so that the Visual Basic program accesses the rate expression specified by us. Click on *Yes* to continue.



Do you want to update UserRxnRateModule in Excel workbook C:\CC5DATA\CSTR\CSTRUR.xls?

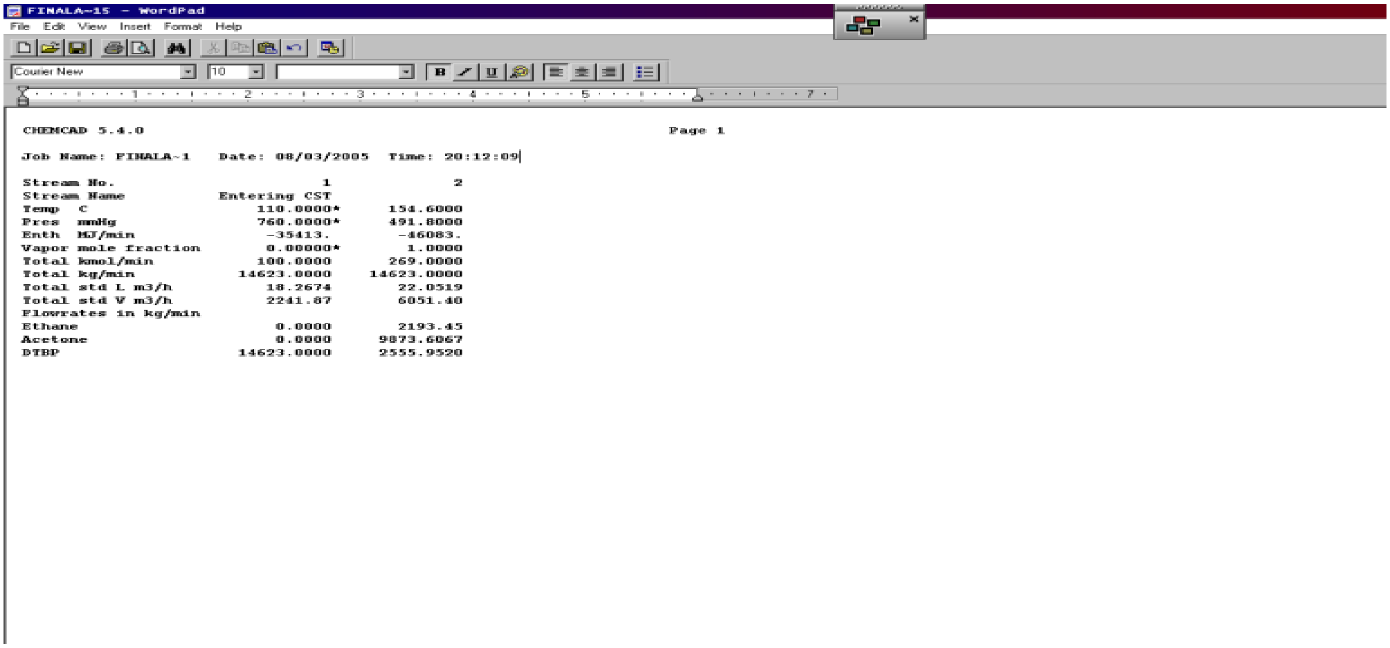
Step 5: Running the simulation and retrieving the results:

Now the simulation is ready to run. Click once on R at the top of the screen to run the simulation. Alternatively, one can run the simulation by clicking on *Run* on the menu bar and selecting *Run all.* The status of the simulation can be found at the bottom left hand corner of the screen. The message, *Run Finished* appears in this place if the run is successfully completed. The volume of the reactor for the desired conversion can be found from the *General specifications page* (double click on the reactor for this screen) to be 6.53e4 m^3. Alternatively, all the results associated with the Unit operation, CSTR can be found by clicking *Results* on the menu and selecting *Unit Op's* and entering the number the CSTR is associated with ('1' in this case) on the flow sheet. The CSTR results will then be available in a WordPad file.



```
CHEMCAD 5.4.0                                              Page 1

Job Name: FINALA-1   Date: 08/03/2005  Time: 20:03:13

                      Kinetic Reactor Summary


*** Equip.   1 ***


Equip. No.                        1
       Name
Reactor type                      1
Reaction phase                    3
Thermal mode                      1
Pressure In  mmHg            491.8000
Tout  C                      154.6000
Q  MJ/min                   -3141.9678
Reactor volume  m3           6.5665e7
Specify calc. mode                1
Conversion                     0.8500
Key                               1
No. of Reactions                  1
Molar Flow Unit                   1
Activ. E/H of Rxn Unit            2
Volume Unit                       1
Time Unit                         1
Rate equation type                1
Overall IG Ht of Rxn           -7527.3423
 (MJ/min)
Mass unit                         1


Reaction Stoichiometrics and Parameters for unit no. 1

 Reaction   1
 Rate const =   0.0000e+000  Act. E =   0.0000e+000  Hrxn  =   0.0000e+000
 Comp     Stoich.     Exp.factor    Adsorb Fac.   Adsorb E      Adsorb Exp.
   3   -1.00e+000   0.0000e+000   0.0000e+000   0.0000e+000   0.0000e+000
   2    2.00e+000   0.0000e+000   0.0000e+000   0.0000e+000   0.0000e+000
   1    1.00e+000   0.0000e+000   0.0000e+000   0.0000e+000   0.0000e+000
```

Similarly, the product stream properties can found either by clicking once on the product stream or by clicking once on *Results* on the menu, selecting *Stream Composition* and then clicking on *All Streams.* The results will again be available in a WordPad file.



```
CHEMCAD 5.4.0                                                         Page 1

Job Name: FINALA~1   Date: 08/03/2005   Time: 20:12:09

Stream No.                          1             2
Stream Name                Entering CST
Temp  C                      110.0000*     154.6000
Pres  mmHg                   760.0000*     491.8000
Enth  MJ/min                  -35413.       -46083.
Vapor mole fraction          0.00000*       1.0000
Total kmol/min               100.0000      269.0000
Total kg/min               14623.0000    14623.0000
Total std L m3/h              18.2674       22.0519
Total std V m3/h              2241.87       6051.40
Flowrates in kg/min
Ethane                         0.0000       2193.45
Acetone                        0.0000     9873.6067
DTBP                       14623.0000     2555.9520
```

You Are Done!

A few hints:

If CHEMCAD gives you a 0 slope error, you need to make sure your More Specifications have been typed in correctly.

You may have to run the reactor as a PFR then as a CSTR.

If you get a mass balance error make sure your reaction rate and stoichiometric coefficients are typed in correctly.

If you have checked all of the above and you are still getting an error, you may want to close CHEMCAD and try again. Sometimes the program stops taking your corrections. You may actually have to close the program several times before you get it to run.