Reactive Distillation
Esterification of Acetic Acid

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Outline

- Objectives
- Case Description
- FactSage Database creation and approach
- Results
  - Simulation
  - Optimization

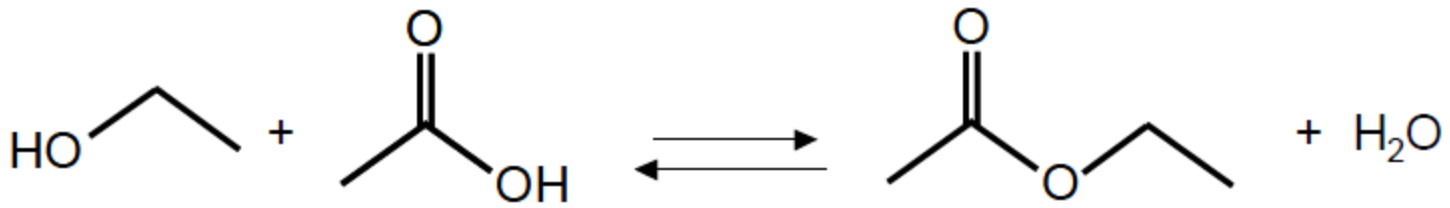
Objectives

- To simulate a reactive distillation column in FactSage
  - To estimate the temperature and concentration profiles in the distillation column
  - To estimate the extent of the reaction
- To optimize the reactive distillation column
  - Effect of condensation temperature, pressure and recirculation percentage

BACKGROUND

Esterification Reaction

$$\text{Ethanol (EtOH)} + \text{Acetic acid (HAc)} \overset{k_f,\ k_b}{\leftrightarrow} \text{Ethyl acetate (EtAc)} + \text{Water } (H_2O)$$

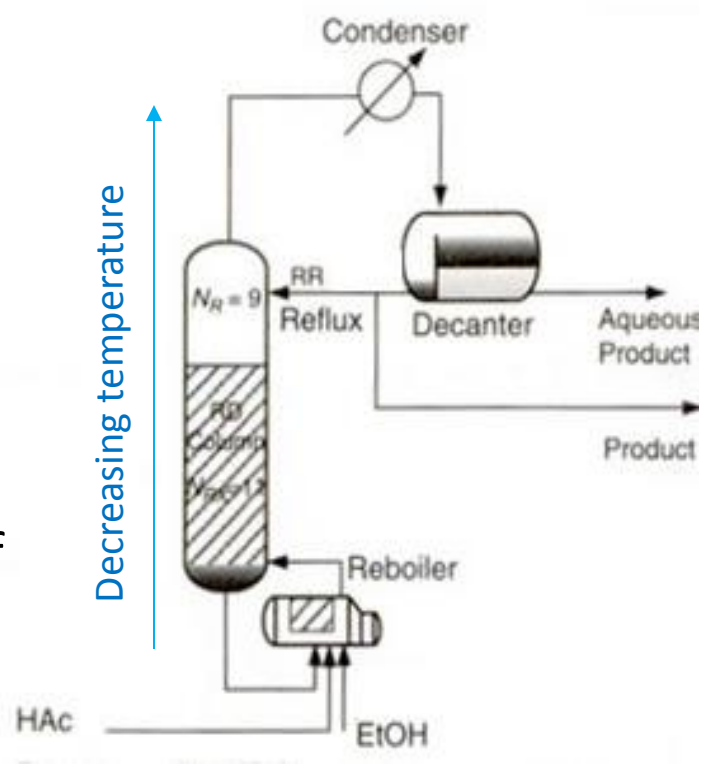


Tb=78°C Tb=118°C Tb=77°C Tb=100°C

If one or more of the products are removed, more of the product will be formed. This is the basis for using a reactive distillation column, where the products are removed as they are generated.

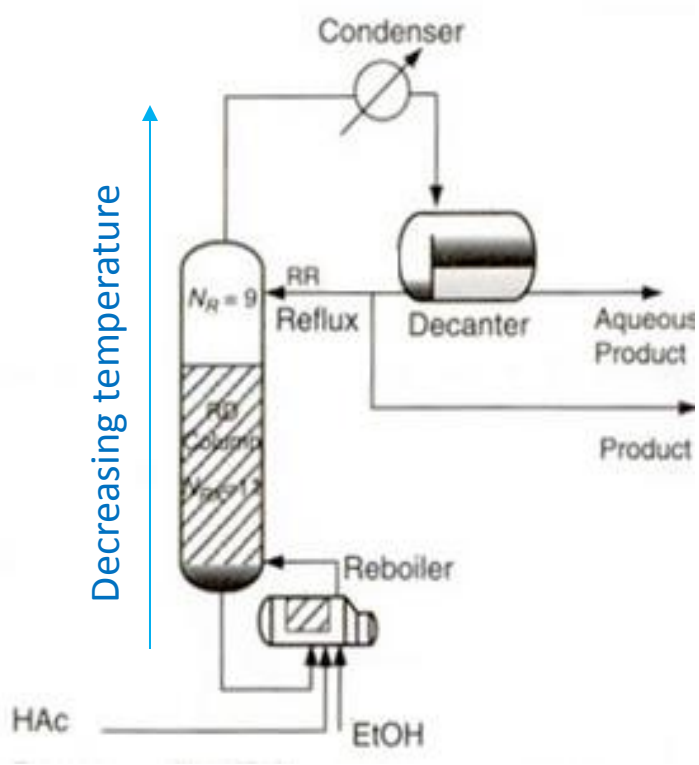
Process Description

- In the reactive distillation for generation of ethyl acetate both reactants (ethanol and acetic acid) are fed to the reboiler in the bottom of the column. Heat is added to the reboiler to promote the separation the volatile products.
- In the distillation column, the close contact between liquid and vapor phases facilitates the reaction and the recovery of ethyl acetate (main product).
- The temperature in the column decreases from bottom to top.

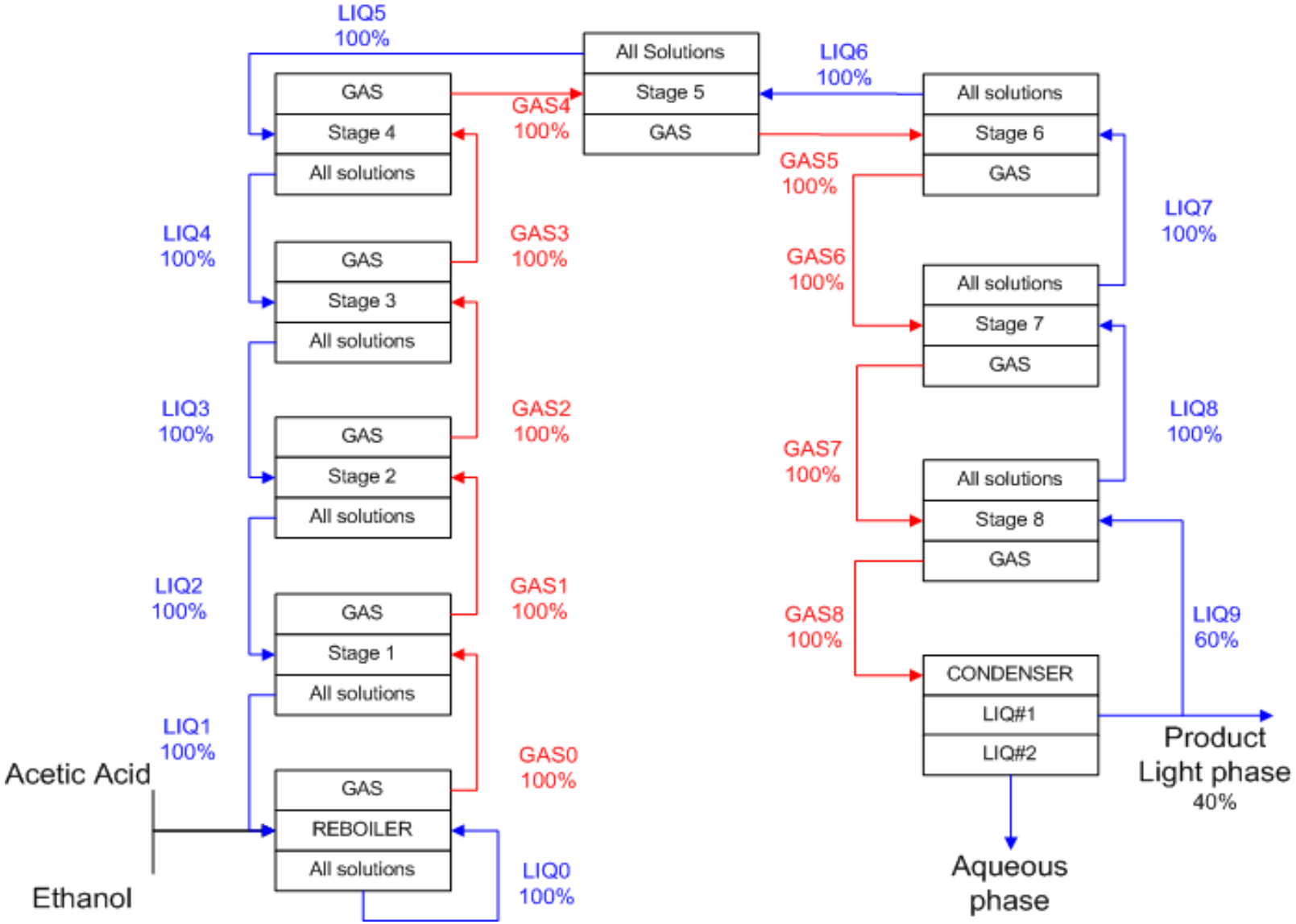


Process Description

- In the condenser, the vapor, which is rich in ethyl acetate, is liquefied and the aqueous and non-aqueous phases are separated in a decanter.
- The aqueous phase is sent to separation processes for the recovery of traces of ethyl acetate. This separation system is not part of the scope of this work.
- The product is recovered form the decanter (light phase).
- A portion of the product is recycled back to the column for further conversion of remaining reactants.



Reactive Distillation Flowsheet



Process Conditions (Luyben et al, 2009)

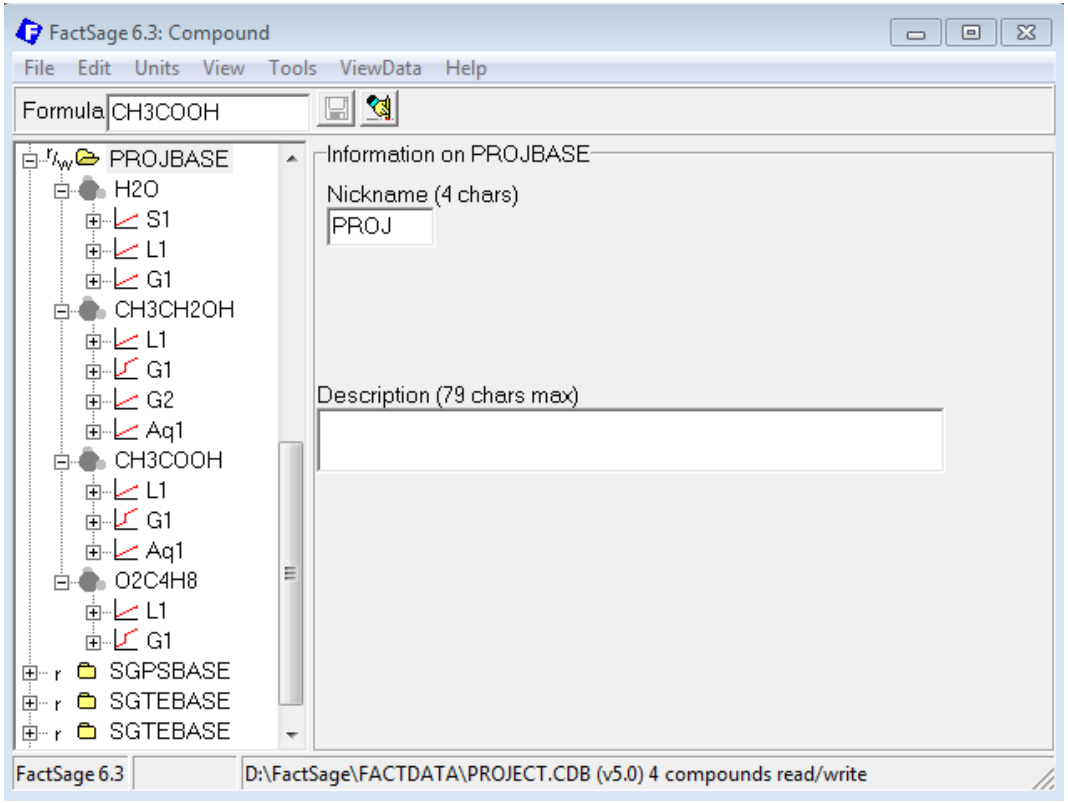
Condition	Value
Number of stages in the distillation column	8
Flow of Acetic acid (kg/h)	2000*
Quality of Acetic acid (Water wt%)	10%
Flow of Ethanol (kg/h)	100
Quality of Ethanol (Water wt%)	5%
Calculation basis (h)	1
Reboiler Temperature (C)	110
Condenser Temperature (C)	60 (See optimization section)
Column heat transfer (stages 1 to 8)	Adiabatic
Reflux percentage (%) (Percentage of the liquid from the condenser that is send back to the column)	60 (See optimization section)

* Acetic acid is feed in excess to improve the extent of the reaction (less expensive than ethanol)

COMPOUND AND SOLUTION DATABASES

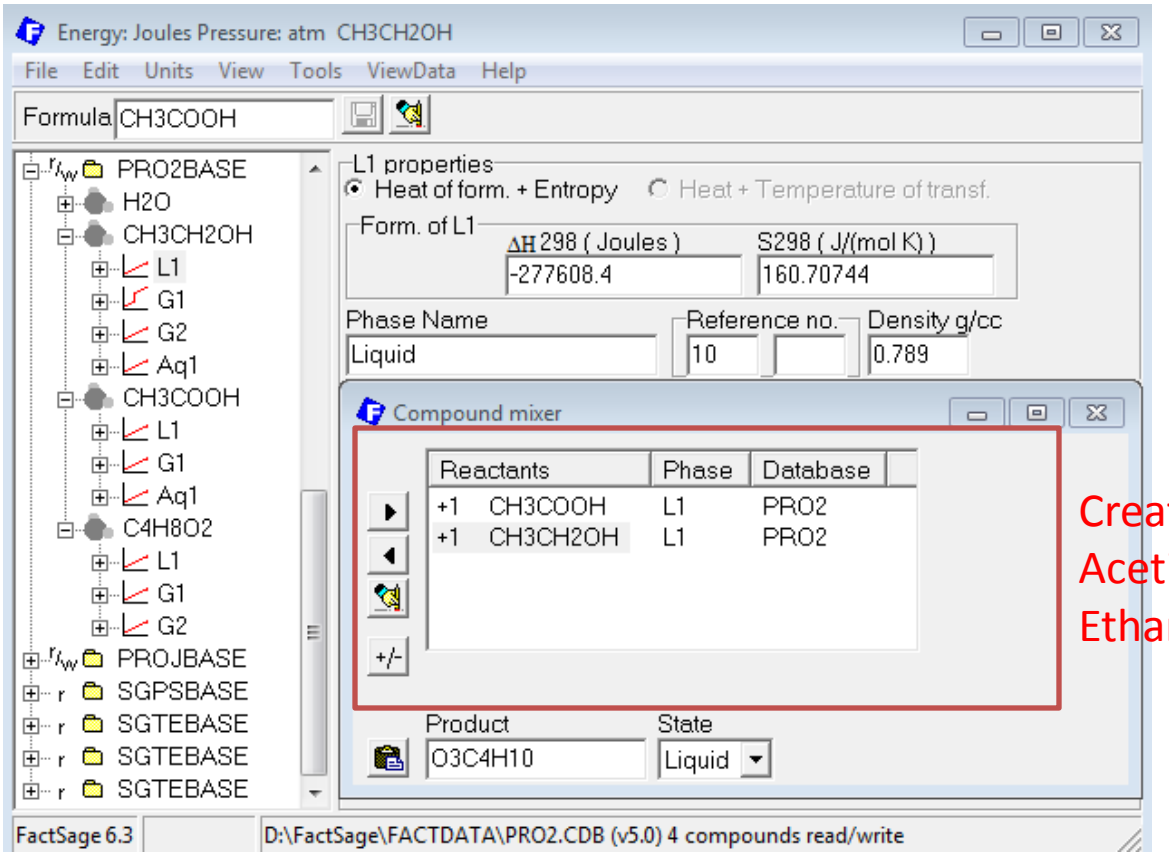
Compound Database Creation

- All the compounds were created in a new database.
- Water and Ethanol were taken from the FactIPS database
- The thermodynamic information for acetic acid was taken from the NIST Webbook (Linstrom et al, 2001).
- Ethyl acetate was created with the FactSage mixer tool



Compound Database Creation

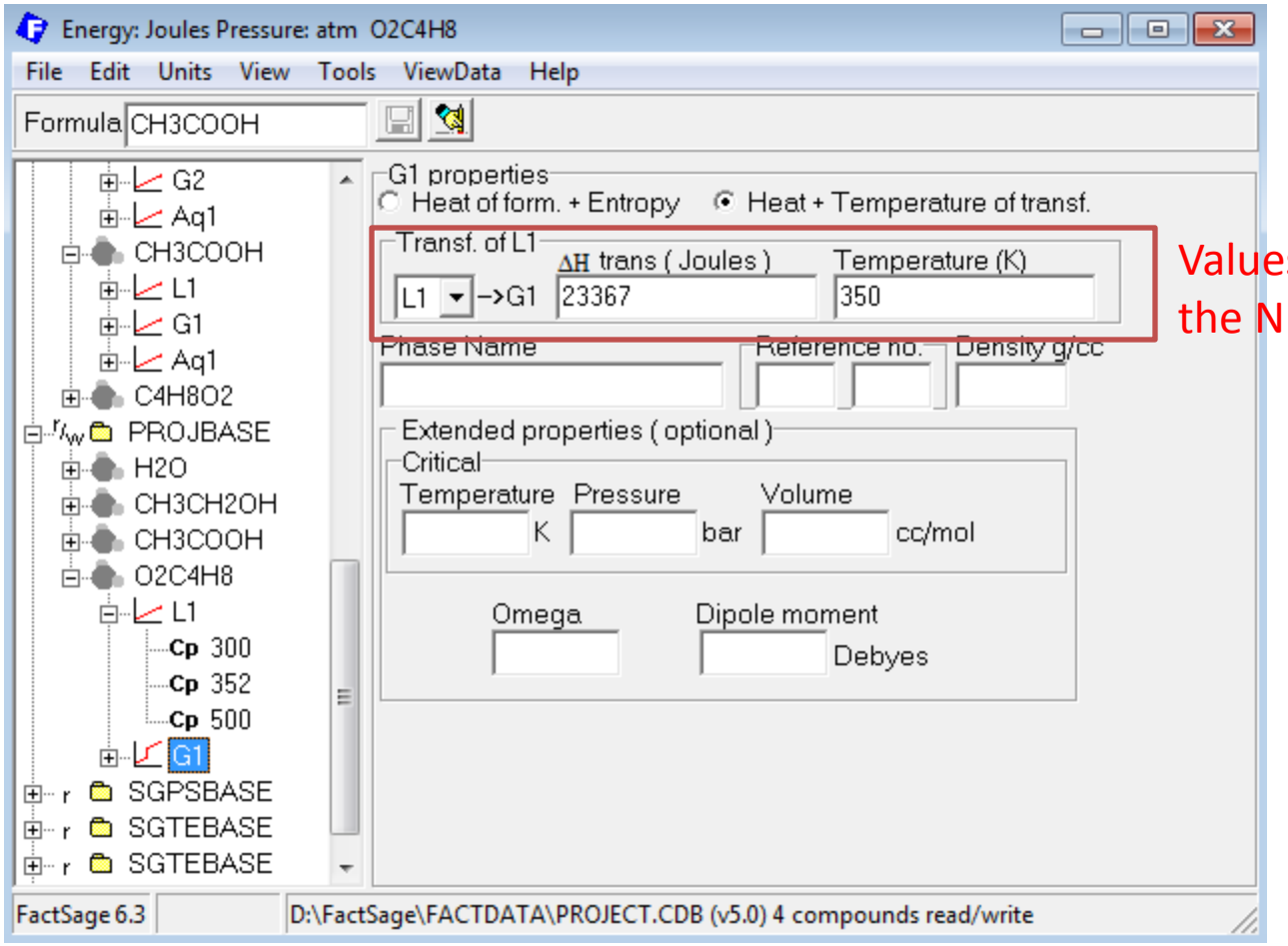
- Example: Creation of Ethyl acetate with the mixer tool



Created from Acetic acid and Ethanol

Compound Database Creation

- Example: Ethyl acetate. The boiling point was slightly modified to match the value in the NIST Webbook.



Values taken from the NIST Database

Solution Database

- A new solution file was generated for the six binary systems
- Binary interaction parameters were determined for each binary system by trial and error.
- Literature values for the vapor-liquid equilibrium and liquid-liquid equilibrium (activity) were used as reference for each binary system.
- Binary interaction parameters:

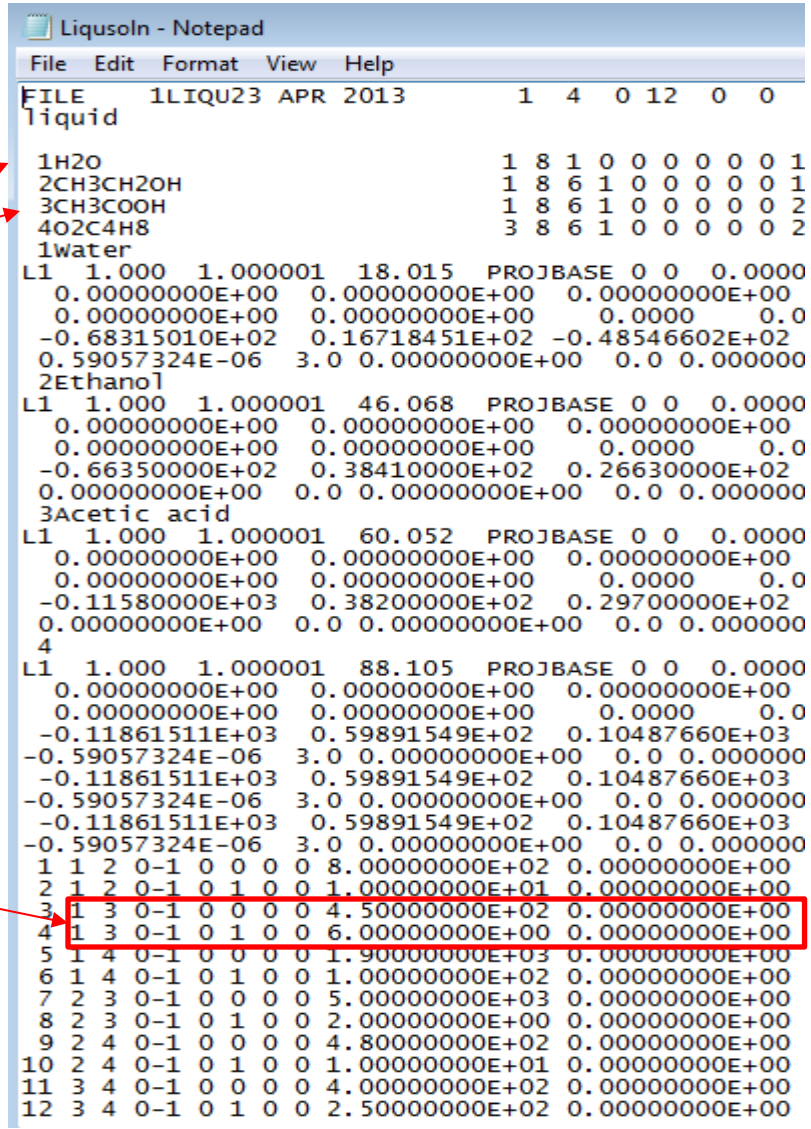
COMPONENT	CH3CH2OH		CH3COOH		O2C4H8	
H2O	8.00E+02	1.00E+01	4.50E+02	6.00E+00	1.90E+03	1.00E+02
CH3CH2OH			5.00E+03	2.00E+01	4.80E+02	1.00E+01
CH3COOH					4.00E+02	2.50E+02
O2C4H8						

Solution Database

Example: Acetic acid and water binary system

Number of components

Coefficients of the binary system to be adjusted

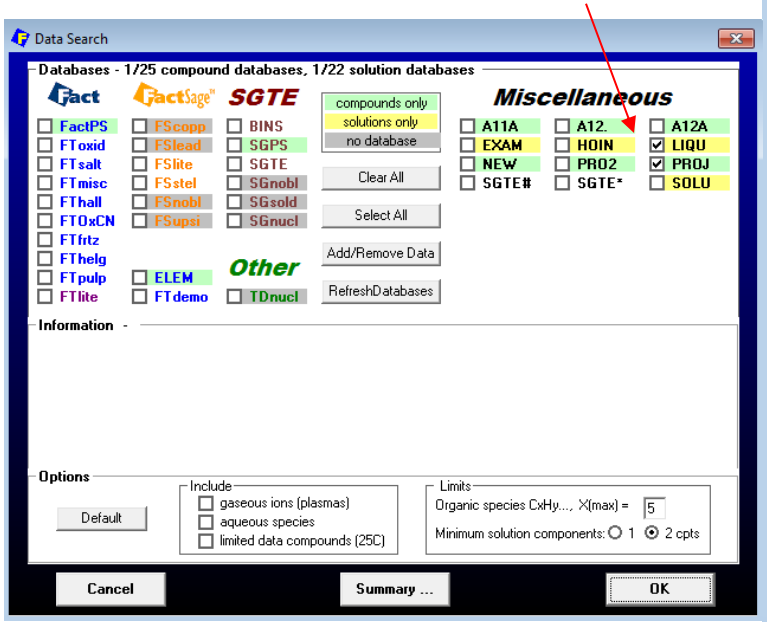


Solution Database

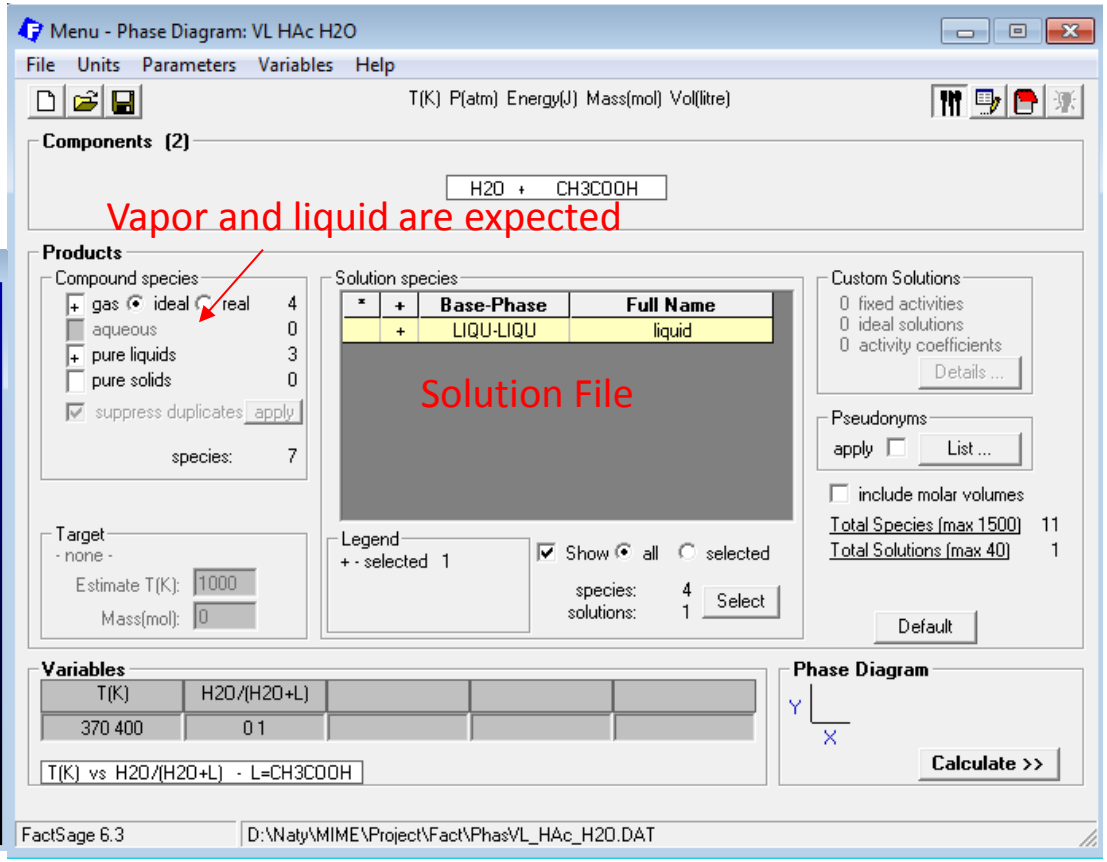
Example: Acetic acid and water binary system.

Generation of the VL Equilibrium Diagram with the phase Diagram Program

Solution and Pure Compound Databases



Vapor and liquid are expected

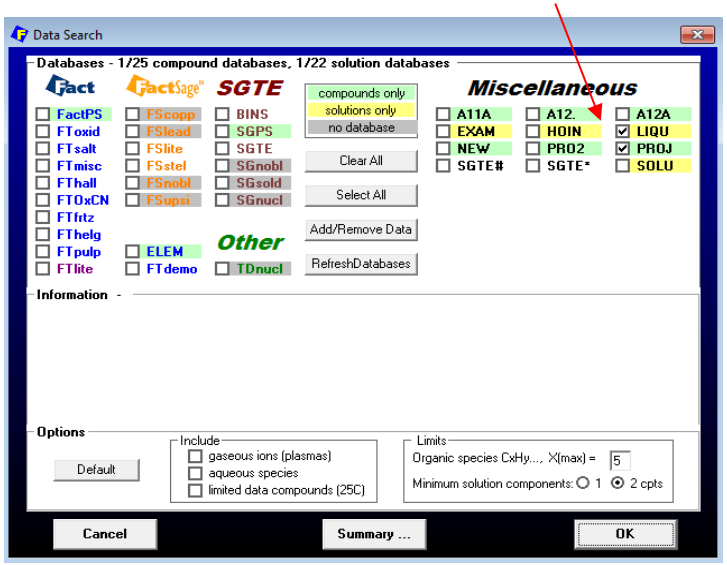


Solution Database

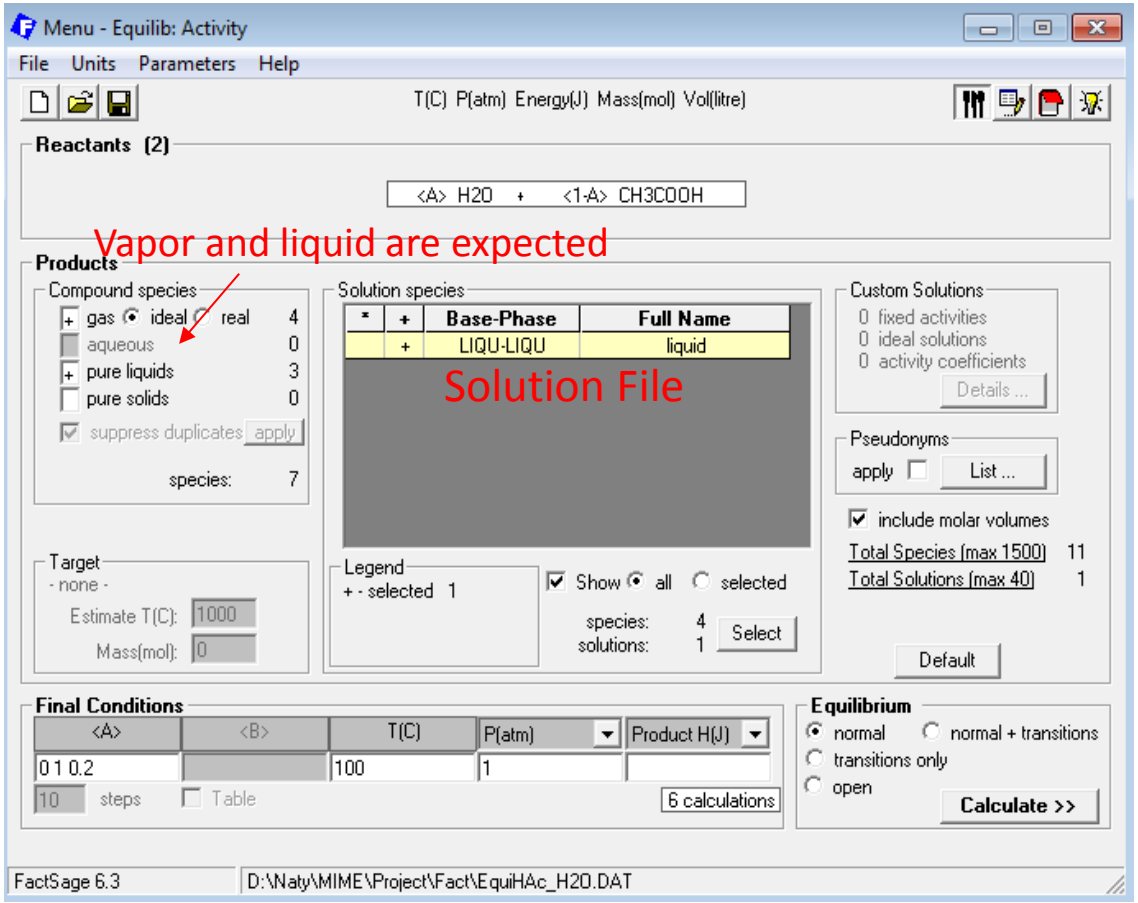
Example: Acetic acid and water binary system.

Generation of the Activity Diagram with the Equilib Program

Solution and Pure Compound Databases



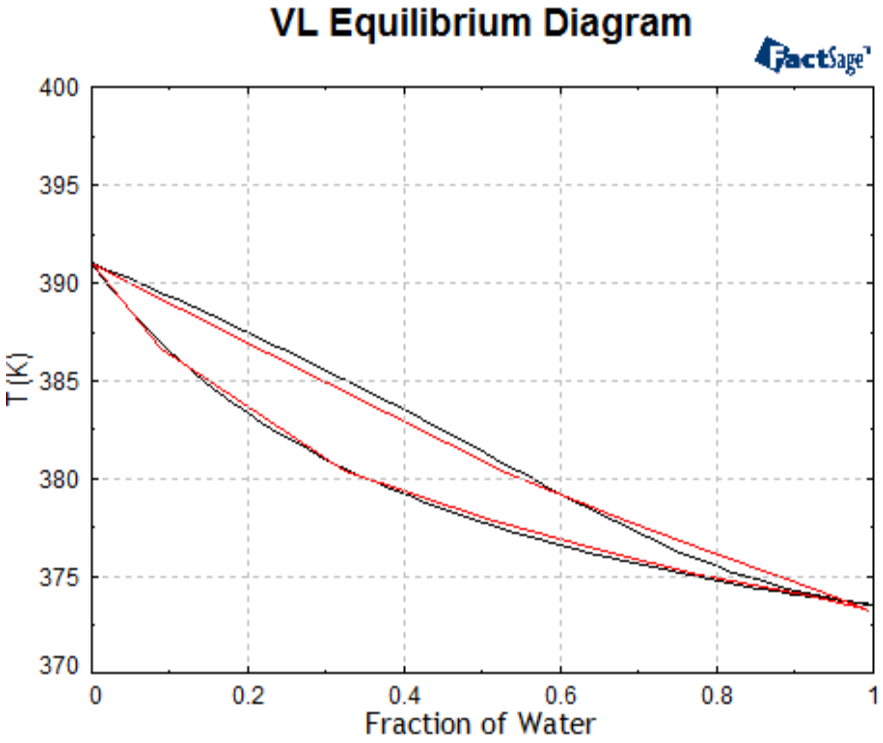
Vapor and liquid are expected

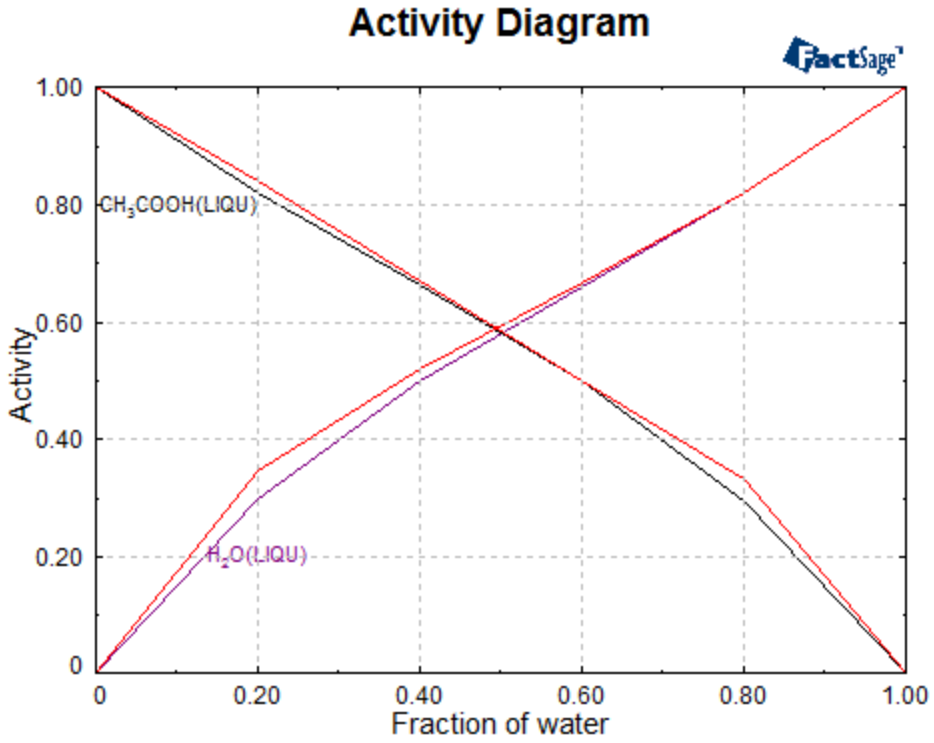


Solution Database

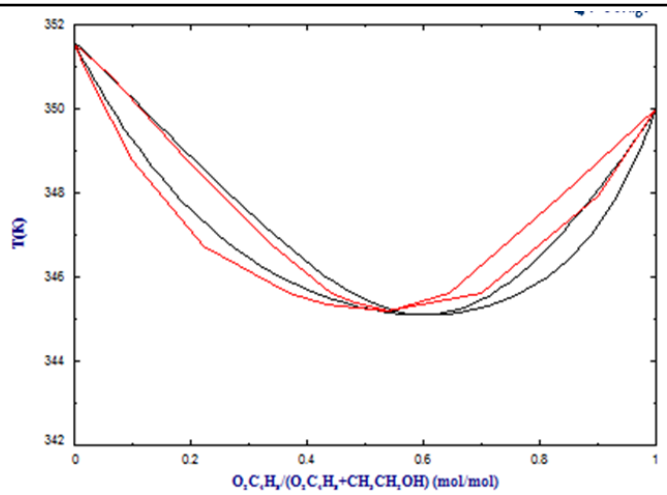
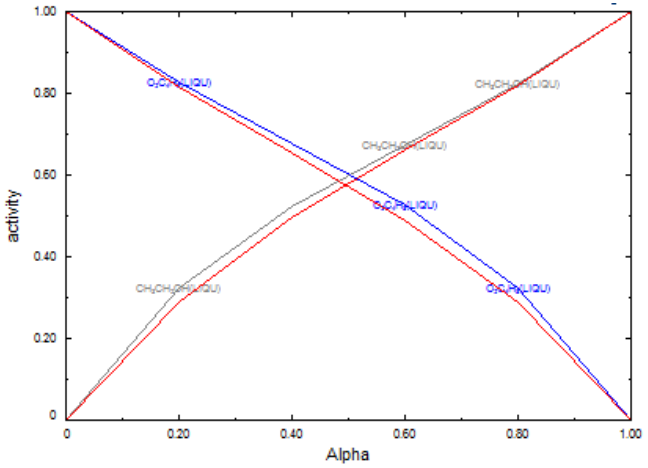
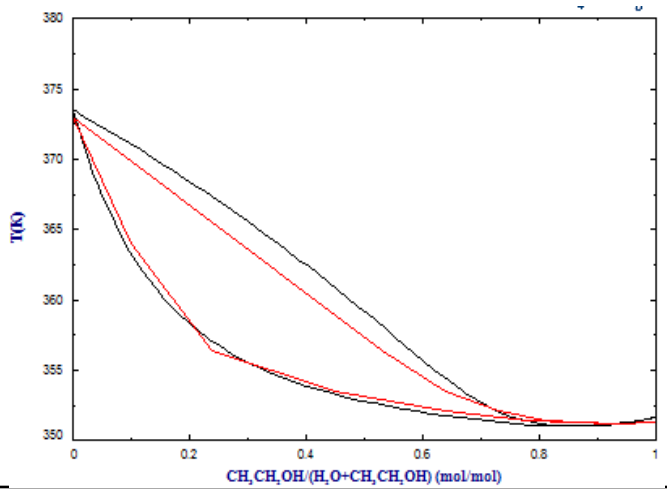
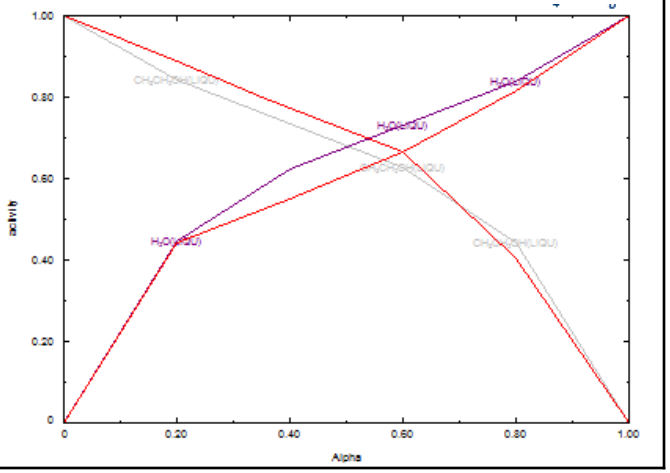
Example: Acetic acid and water binary system.

Fitted data (red lines are literature references)

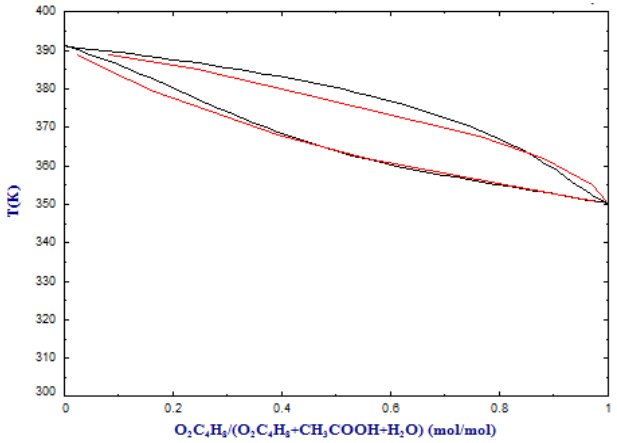
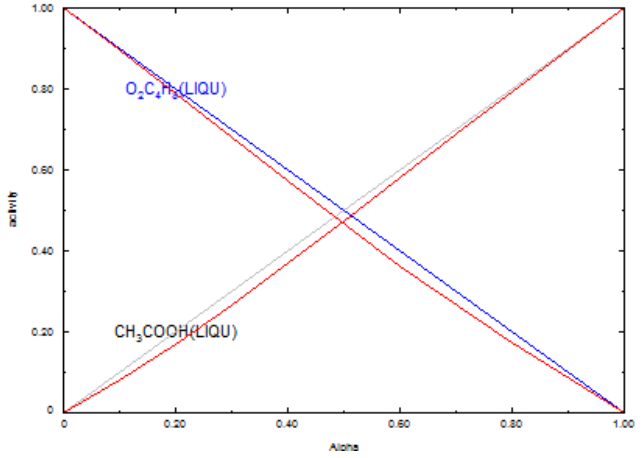
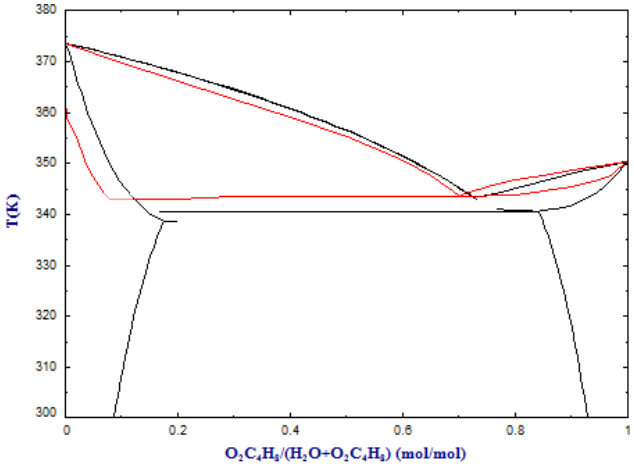
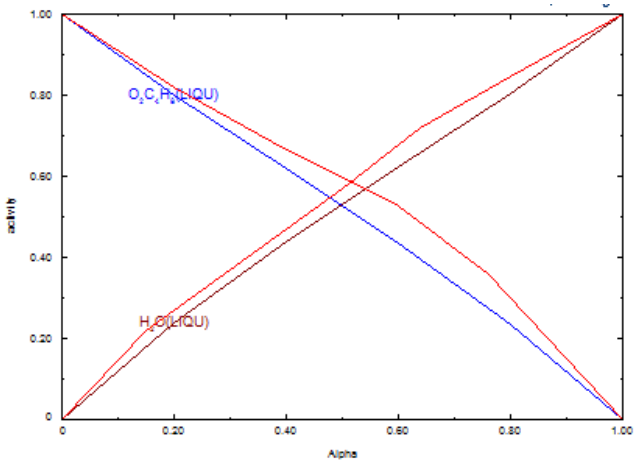




Solution Database

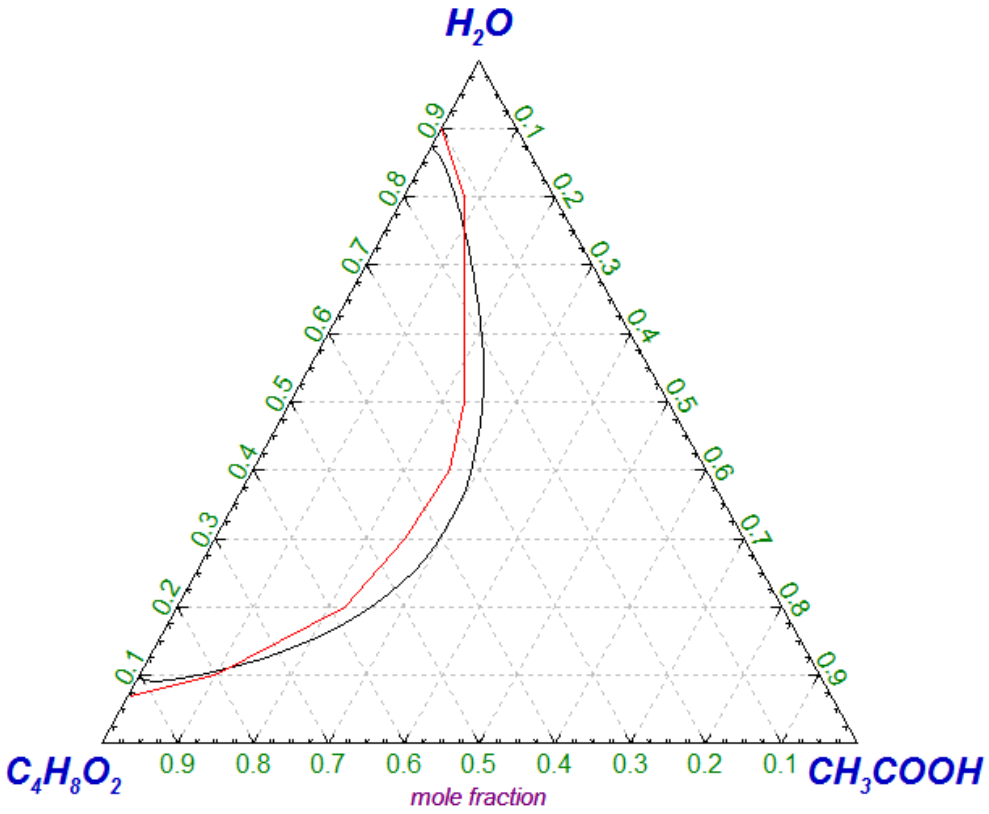
Binary system	VL Equilibrium	Activity
EtOH EtAc Red lines: (Calvar et al.,2005) (Griswold, 1949) (Luyben, 2009)		
EtOH H2O Red lines: (Calvar et al.,2005) (Griswold, 1949) (Luyben, 2009)		

Solution Database

Binary system	VL Equilibrium	Activity
HAc EtAc Red lines: (Calvar et al.,2005) (Griswold, 1949) (Luyben, 2009)		
EtAc H2O Red lines: (Calvar et al.,2005) (Griswold, 1949) (Luyben, 2009)		

Miscibility gap verification

- Binary and ternary miscibility gaps were verified. Example: Ternary system: Ethyl acetate- ethanol-water. Satisfactory prediction of the miscibility gap.
- The proper prediction of the miscibility gap is essential to adequately simulate the operation of the decanter (separation of the aqueous and non-aqueous phase)



Red line: (Luyben, 2009)

SOLVER APPROACH

Solver Approach

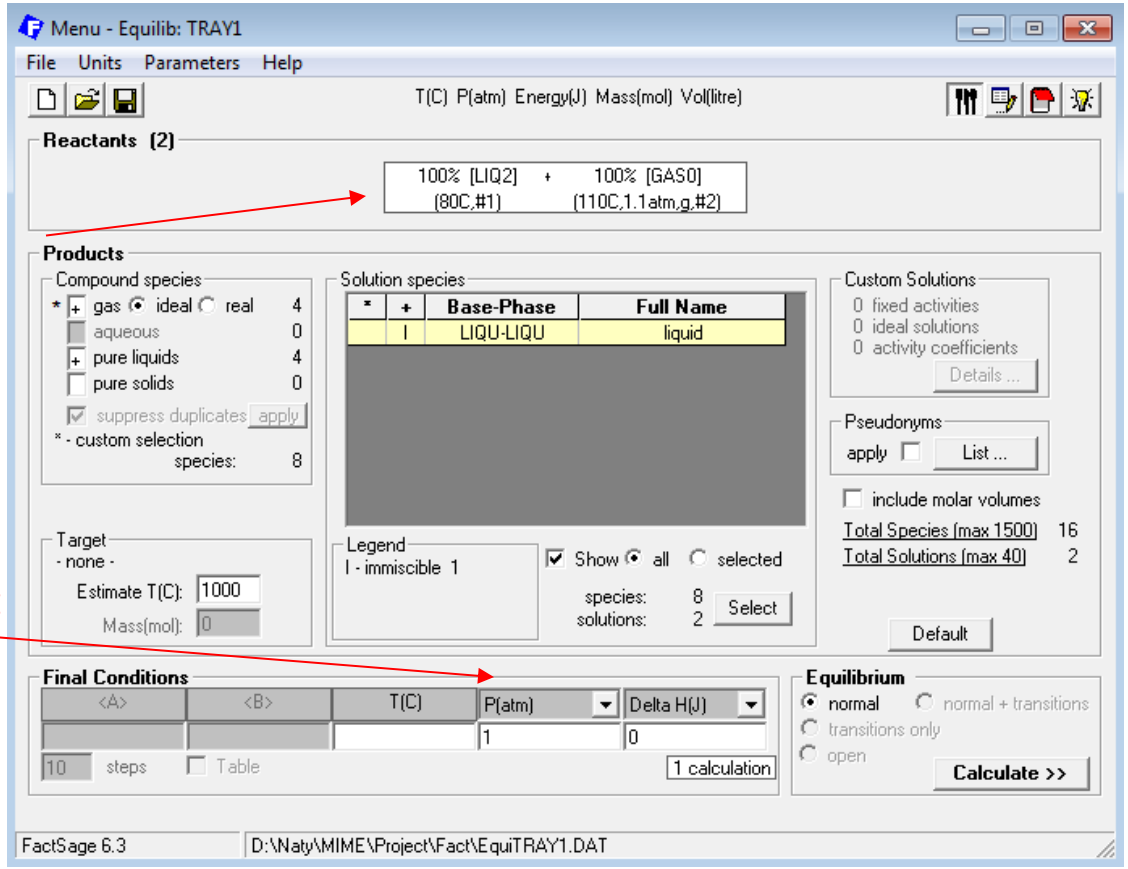
- Due to the great interaction among equilibrium stages, it is necessary to solve the system by trial and error to obtain convergence of all the temperature and concentration profiles across the column.
- The trial and error procedure involves the use of one Equilib file for each equilibrium stage (10 in total), 22 stream files (8 for gas and 14 for liquid), and one macro file
- The input values for the Equilib files are the flow of the reactants, the temperatures of the reboiler and the condenser, and the percentage of light condensed liquid recycled to the column

Approach: equilibrium stages

- Example of an Equilib File: Column Stage 1

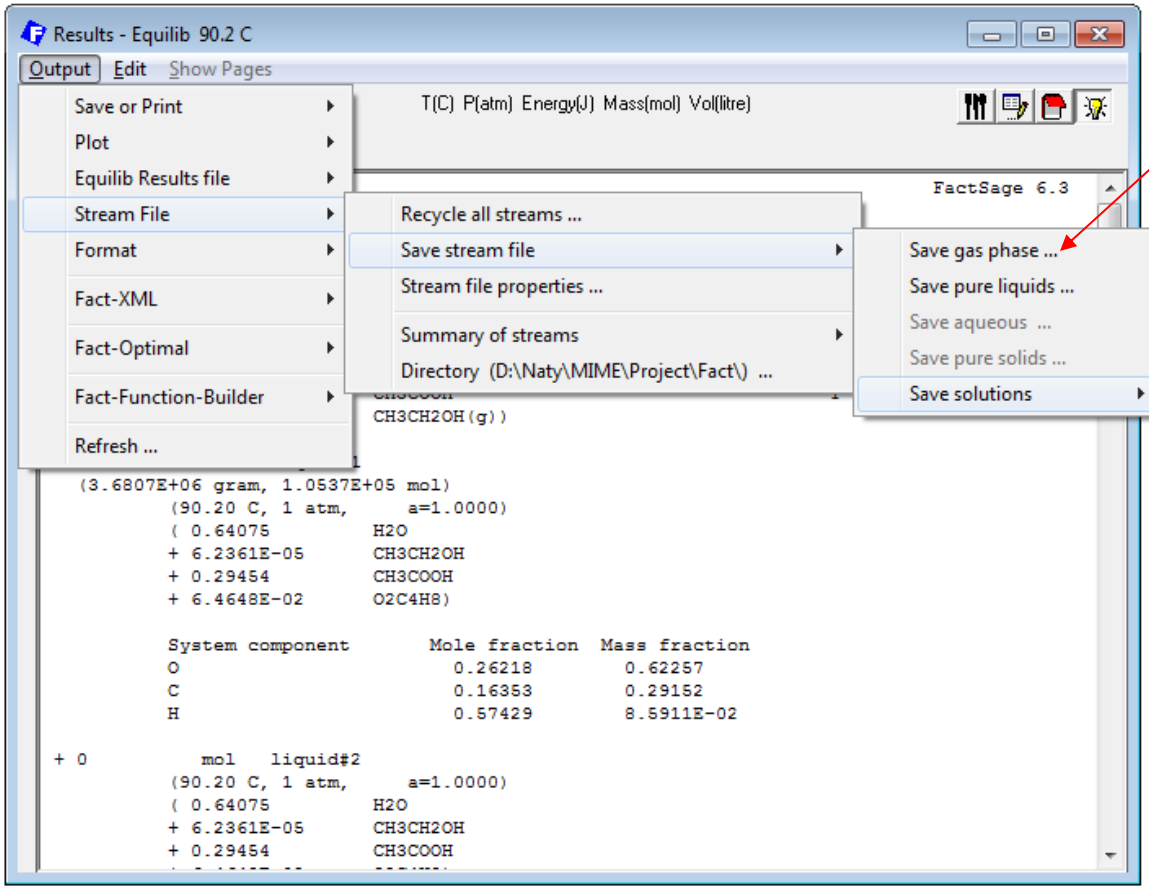
100% of Gas from the reboiler and 100% of Liquid from the equilibrium stage 2

Adiabatic operation at 1 atm



Approach: equilibrium stage

- Example of an Equilib File: Column Stage 1

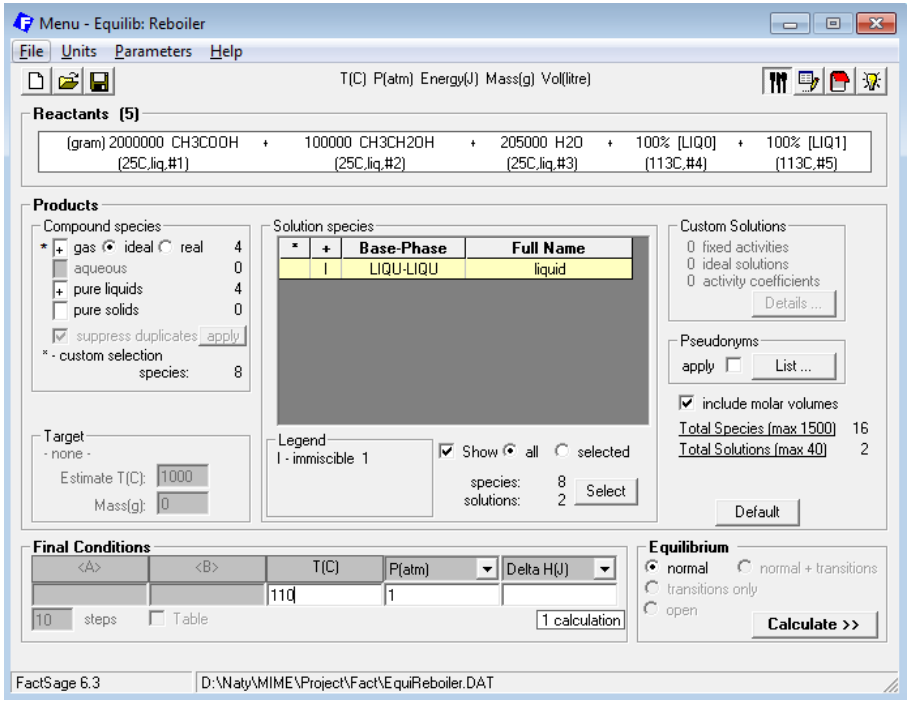


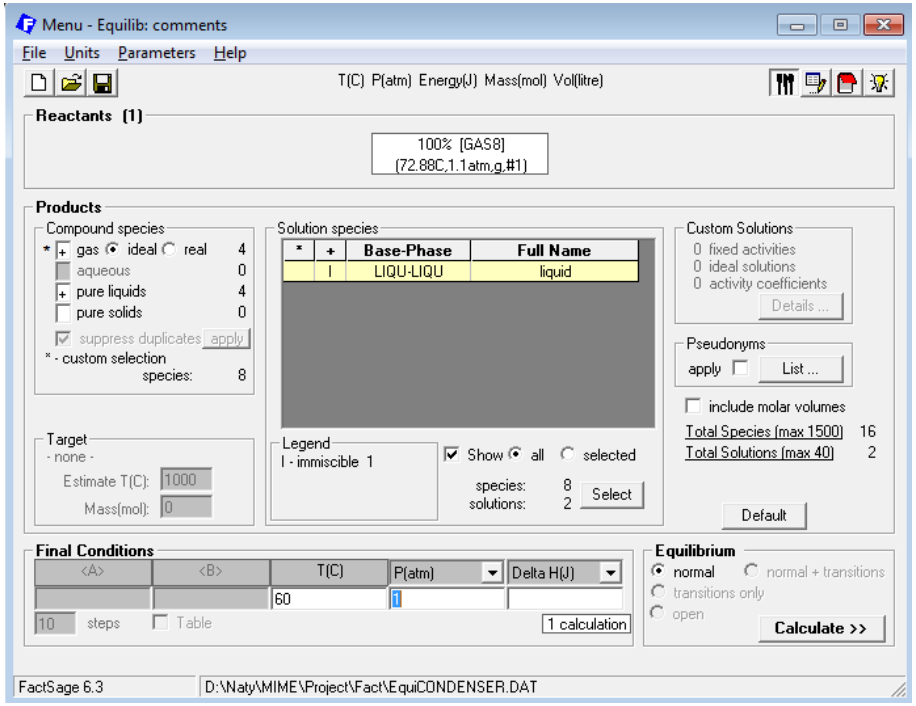
Gas phase is saved as GAS1. This stream is used as an input for the stage 2 in the column.

All solutions are saved as LIQ1. This stream is an input for the reboiler Equilib File. In the case of the condenser, the two liquid phases are saved independently. LIQU#1 is the one used for the recycle, while LIQU#2 is the aqueous phase .

Approach: equilibrium stage

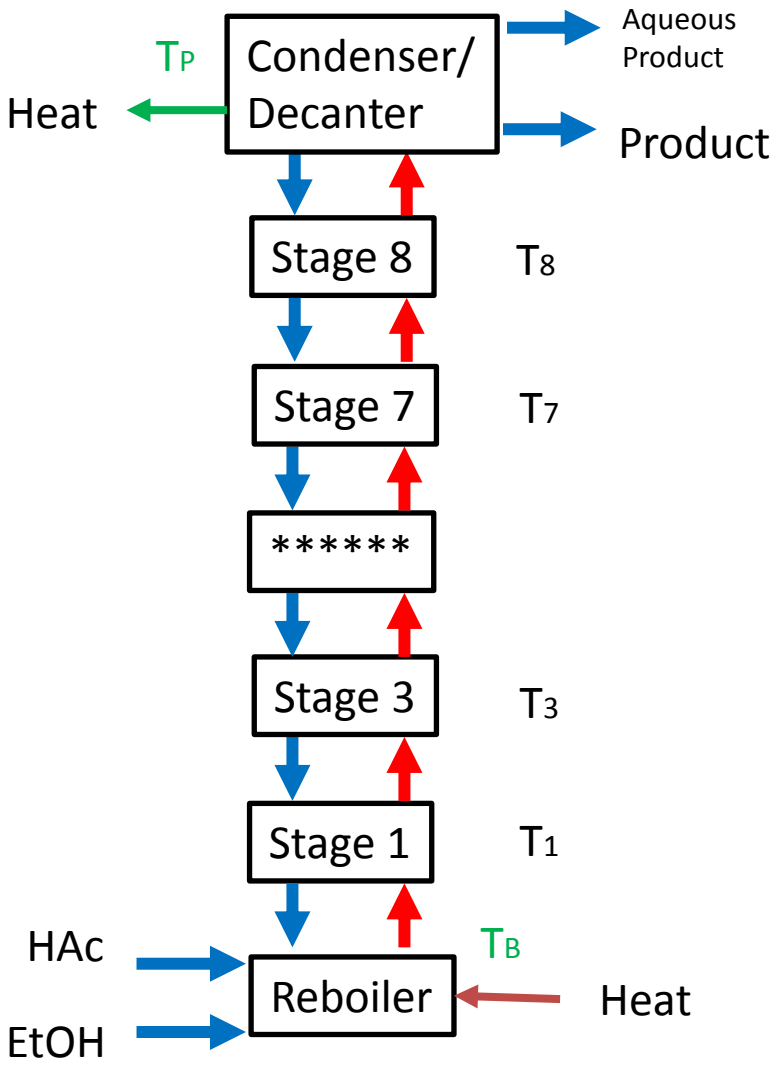
- Reboiler (Stae 0) and Condenser (Stage 9) Equilib Files





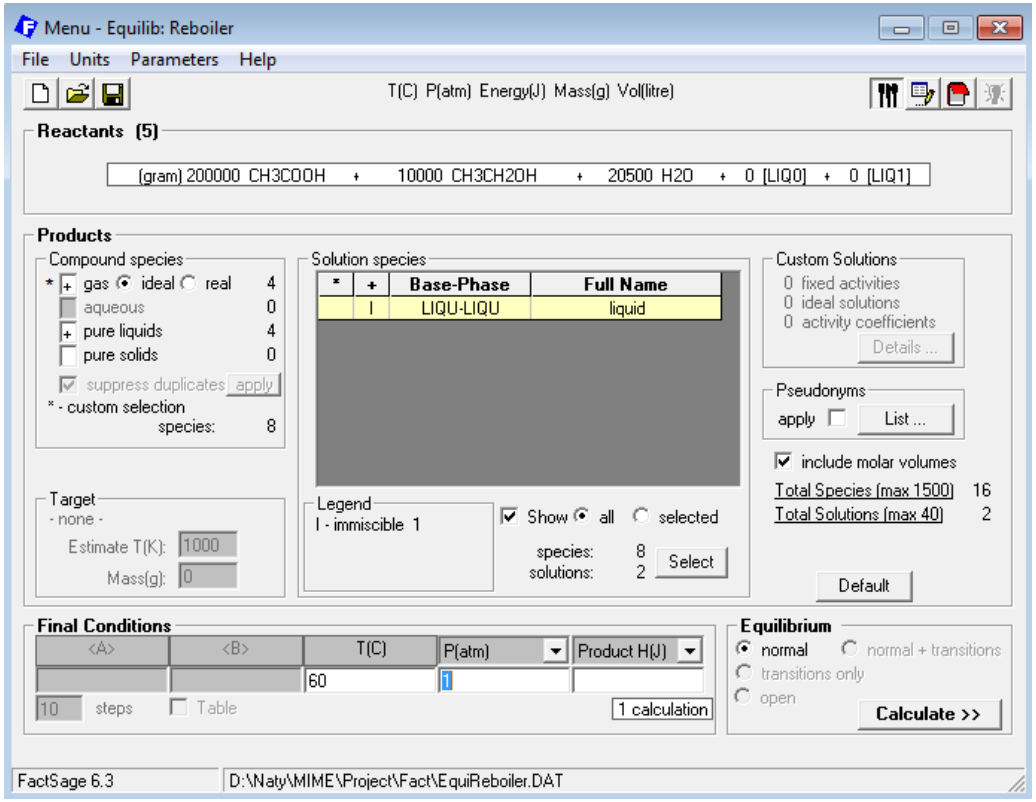
Solver Routine

1. Establish the reboiler and condenser temperatures
2. Initialize all the liquid streams
3. Solve each equilibrium stage from bottom to top
4. Repeat iterations until convergence



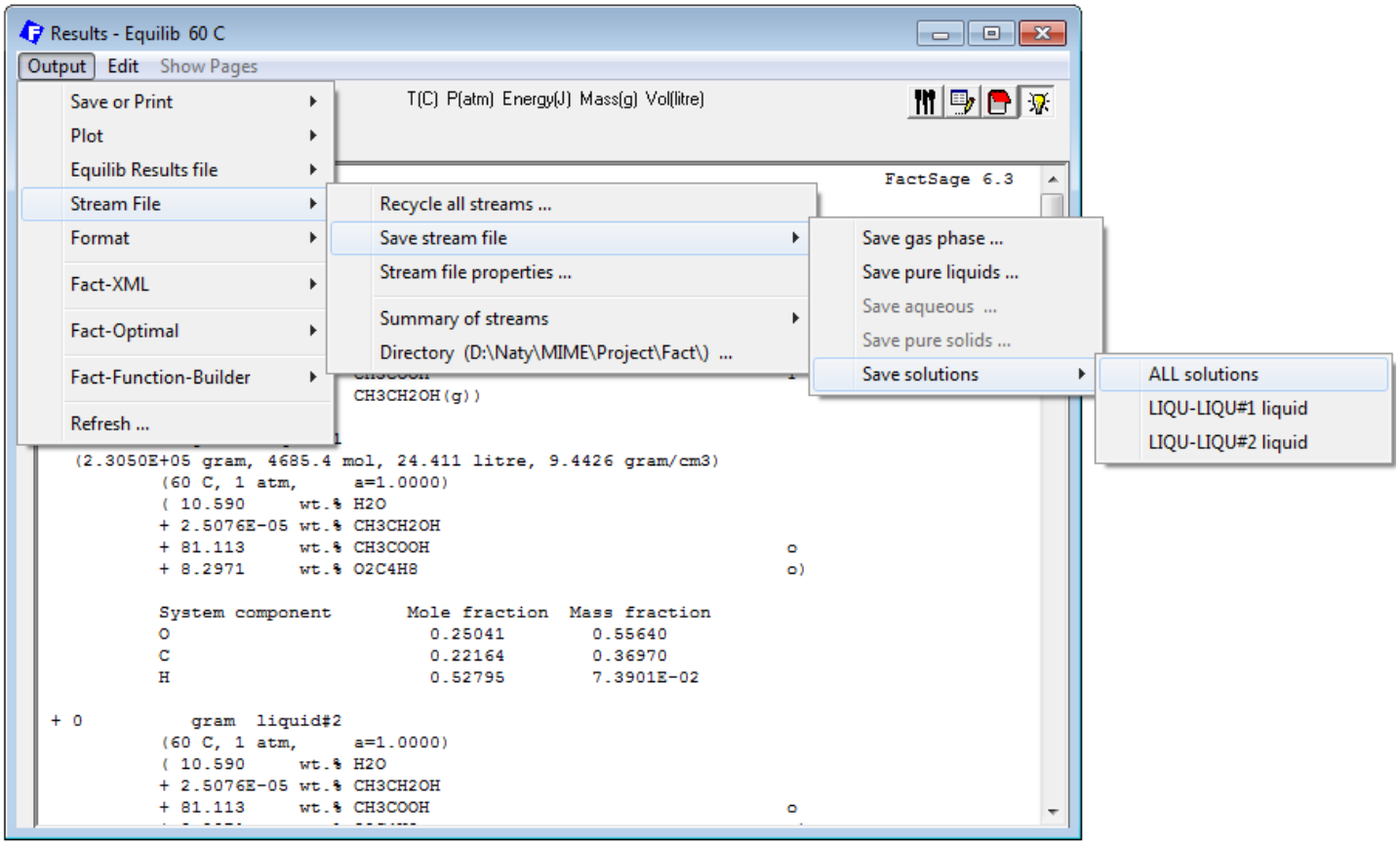
Approach: Initialization of liquid streams

- All the liquid streams are initialized with the liquid phase generated by the equilibrium of 10% of the total reactants mass at the condenser temperature.
- This condition is considered to be a good initial estimate since it represents the system as if there was only one equilibrium stage.



Approach: Initialization of liquid streams

- All solutions are saved as the streams LIQ1, LIQ2, LIQ3, LIQ4, LIQ5, LIQ6, LIQ7, LIQ8 and LIQ9 as initial estimates.



Approach: Macro File

Before using the macro file all the liquid streams are initialized as shown previously.

Sketch of the Macro File:

- Definition of Variables
- Reading input data (flows, temperatures and recycle percentage)
- For Loop from 1 to 15 (convergence is expected to be reached after 15 iterations)
  - Run Reboiler, print results and save streams
  - Run Stages 1 to 8, print results and save streams
  - Run Condenser, print results and save streams
- Repeat Loop

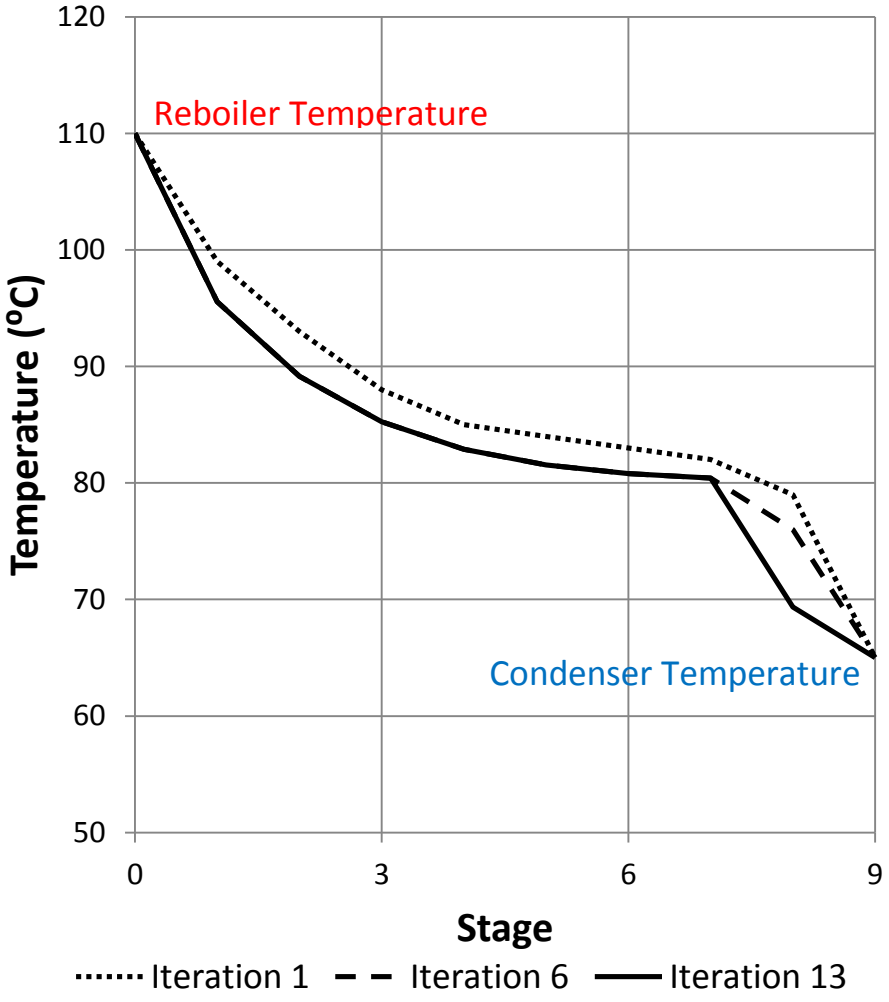
SIMULATION RESULTS

Summary

- The solver approach chosen leads to convergence of the temperature and composition profiles across the column after approximately 13 iterations.
- The composition of the product increases in both the liquid and gas phases, which causes a continuous increase in the overall composition profile.
- The extent of the reaction is significantly increased with the use of reactive distillation compared with a single reaction/separation stage.

Analysis: Temperature Profile

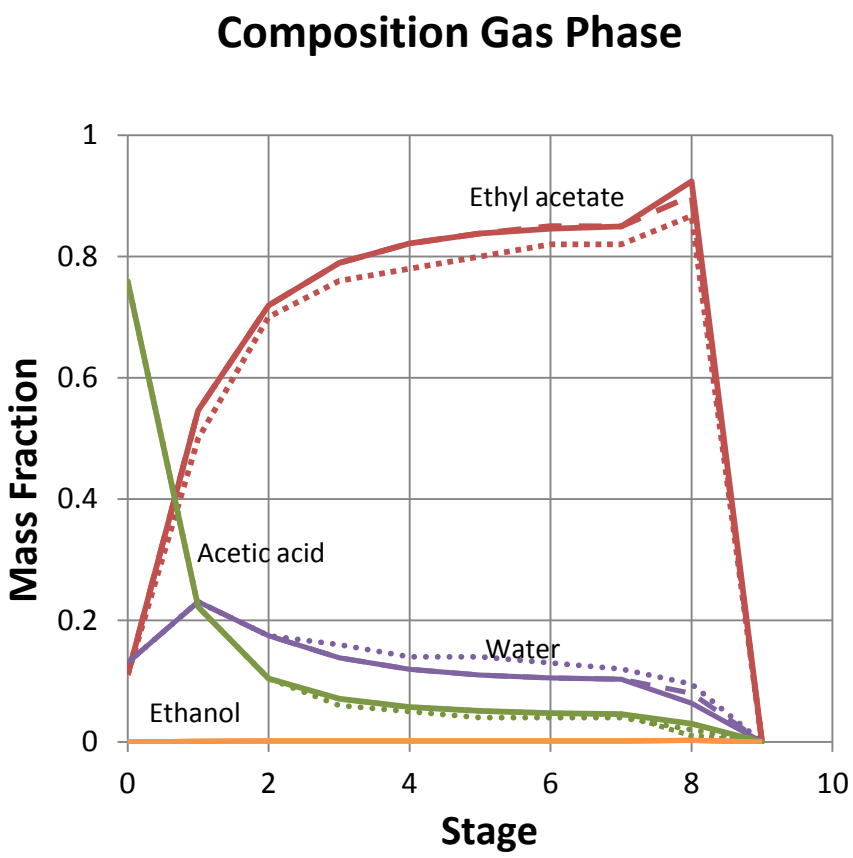
- The temperature across the column decreases as expected from the reboiler to the condenser temperatures.
- This temperature gradient ensures the proper separation of the mixture components according to their volatilities, as shown in the concentration profiles.
- The sharp decrease in temperature after stage 7 is caused by the recycling of condensed liquid to the column.

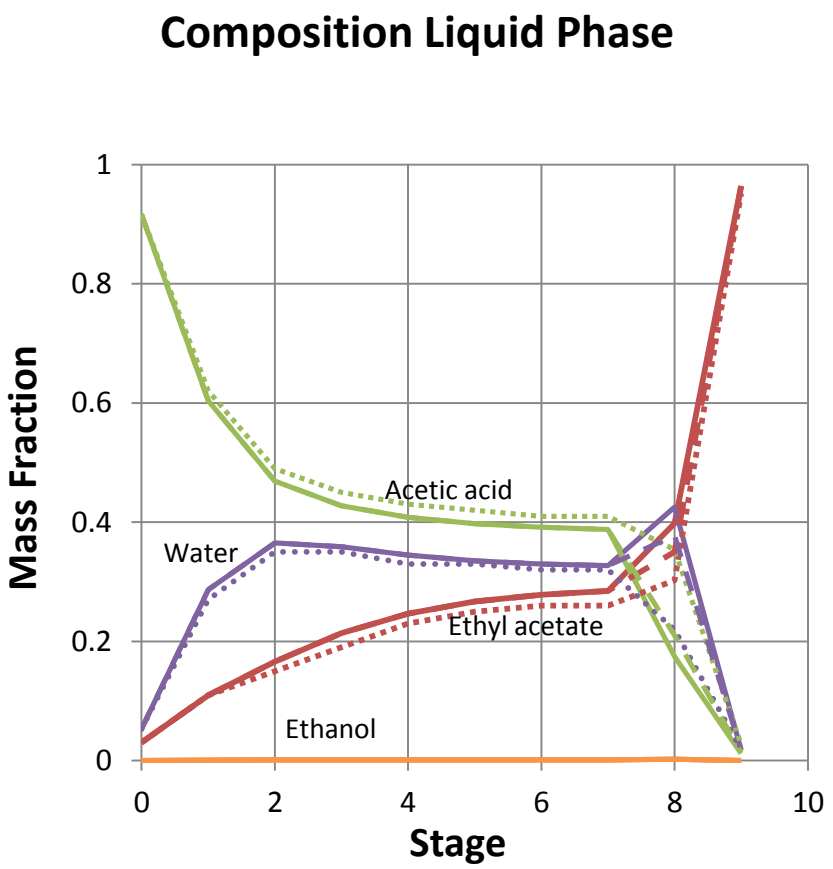


Analysis: Composition Profile

- Convergence was also reached for the concentration profiles in the liquid and the vapor phases.
- The concentration of ethyl acetate ($C_4H_8O_2$) increases in both the liquid and the vapor phase.
- The concentration of Ethanol (limiting reactant) is very small compared to the relative concentrations of the other components throughout the column. In despite of this, it is continuously consumed in the reaction as shown by the increase in the concentration of ethyl acetate.

Results: Composition profiles

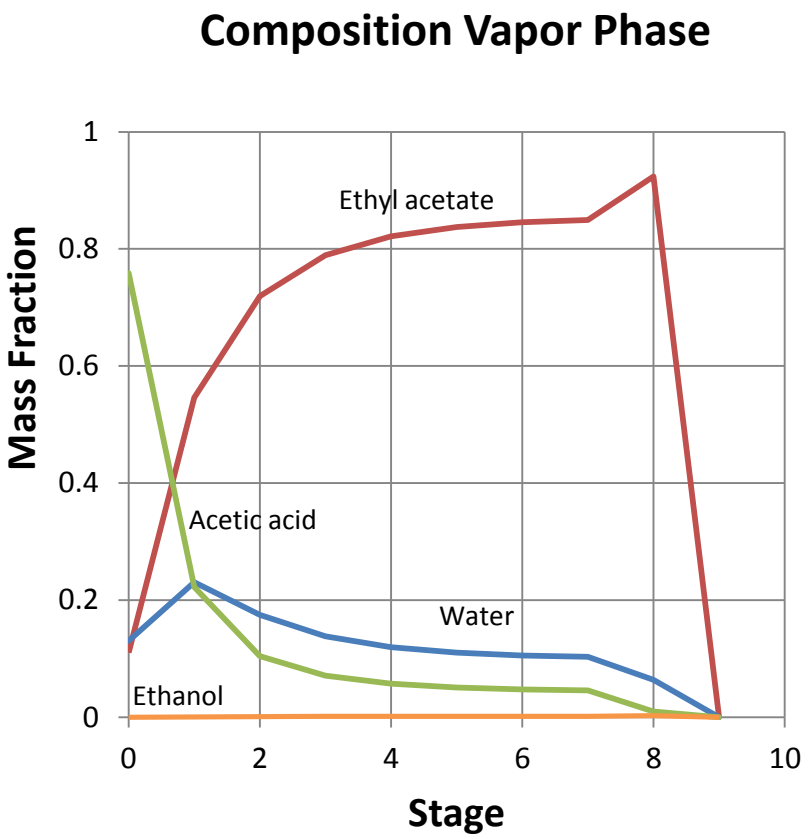




Iteration 1 — Iteration 6 — Iteration 13

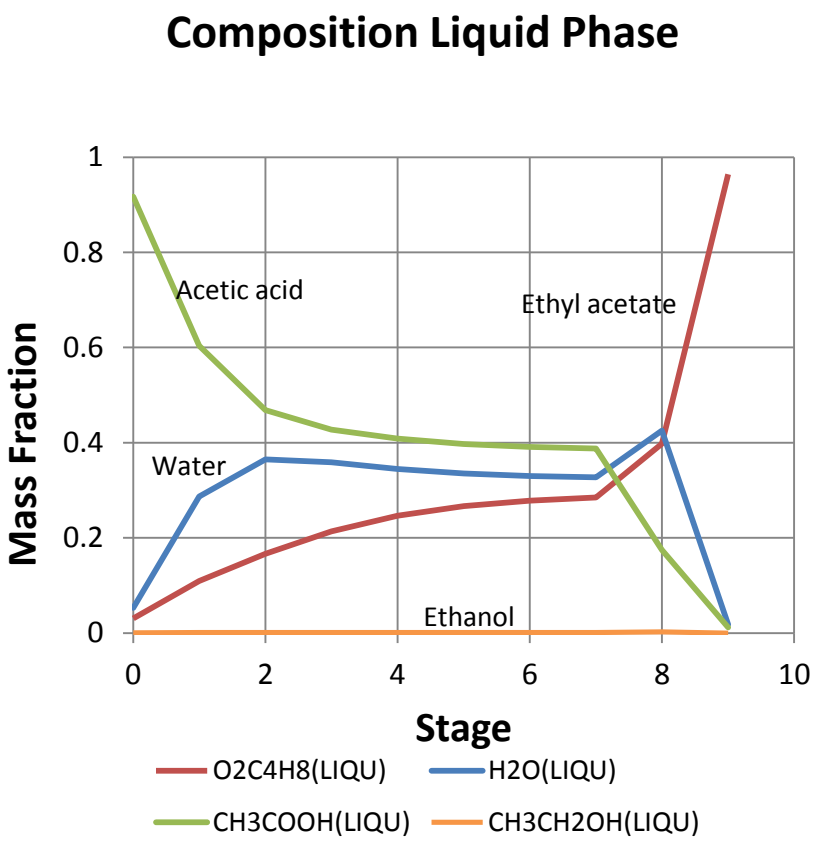
Analysis: vapor composition

- The concentration of ethyl acetate in the vapor phase throughout the column is significantly larger than the concentration of the other components due to its high volatility (Tb= 77°C).
- As expected, water is the second most abundant component in the gas phase because water is more volatile than acetic acid and ethanol concentration is very small.
- In the condenser (9th equilibrium stage), all the vapor phase is condensed as shown by the sharp decrease of all the concentrations to zero.



Analysis: liquid composition

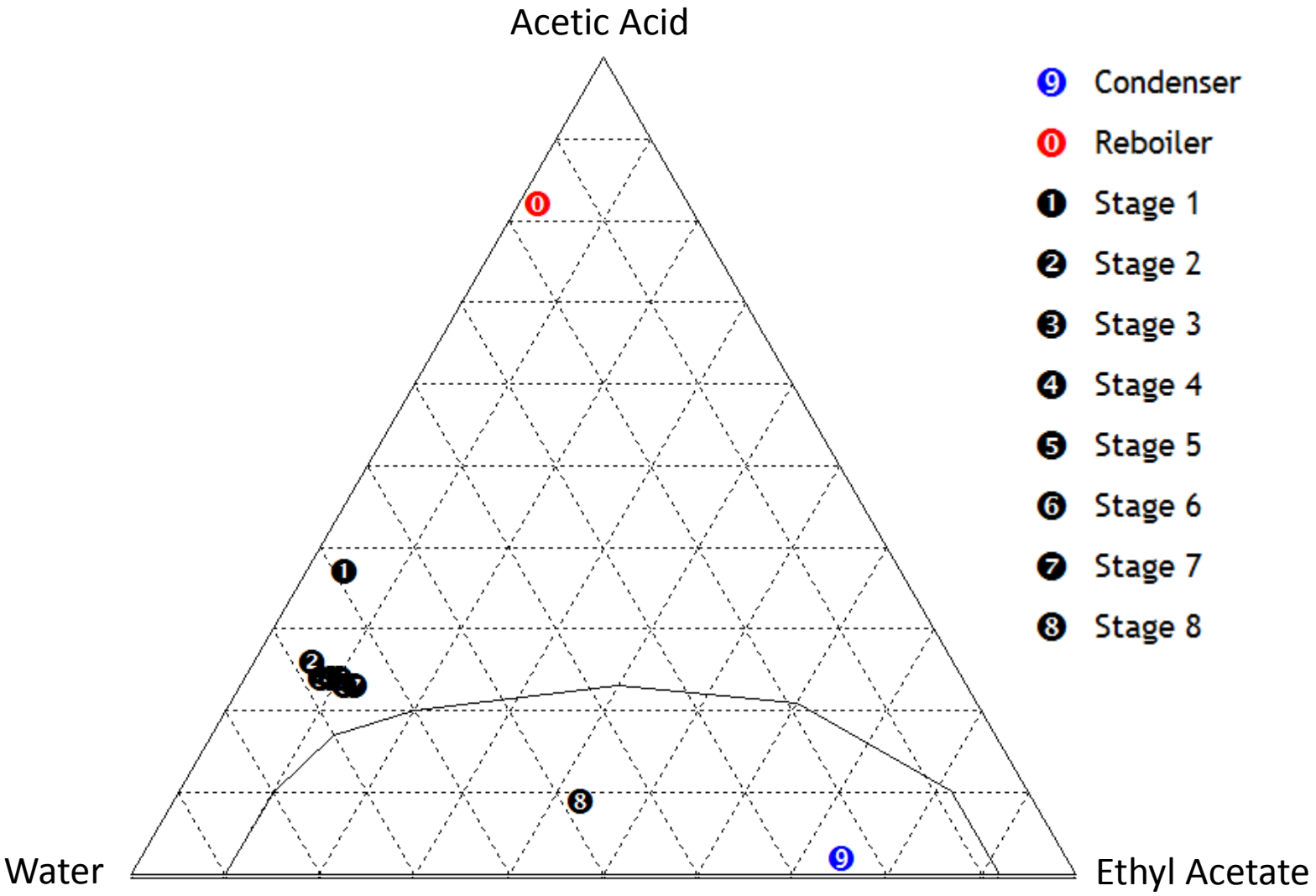
- The concentration shown in the graph to the right represents the concentration of the light liquid phase across the column.
- The aqueous (heavy) liquid phase is generated only after the condenser. Its composition is presented in the next slide.
- In this case, the opposite behavior of the vapor phase is observed. The less volatile compounds, acetic acid and water, are more abundant than ethyl acetate.
- A continuous increase in the concentration of the product C4H8O2 is observed, which indicates the progress of the reaction across the column.
- The sharp increase in the concentration of ethyl acetate in the last stage is caused by the condensation of the vapor.



Composition of the liquid products

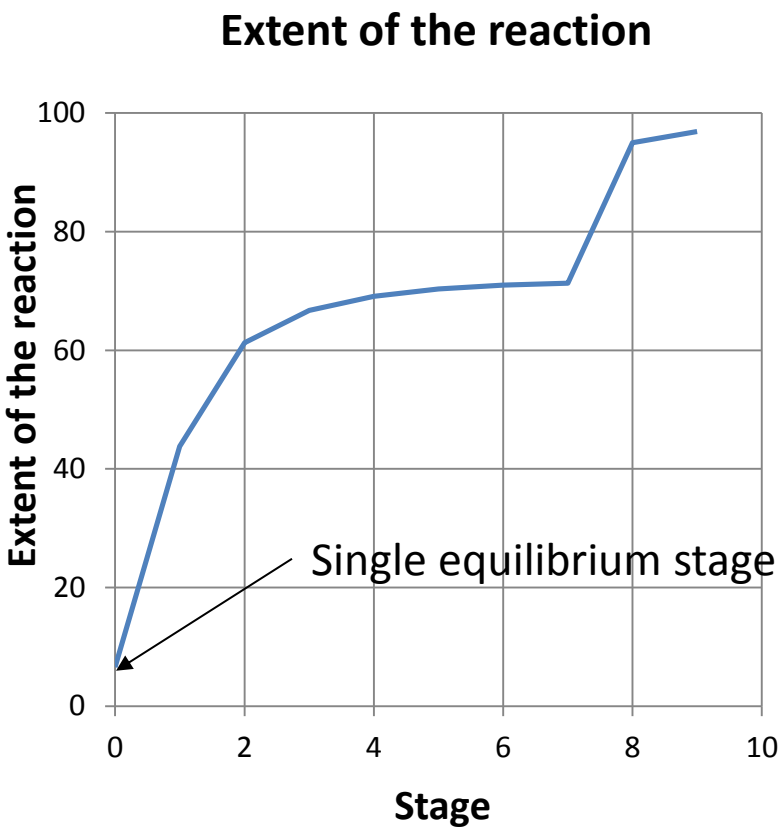
Component	Mass Composition in the light liquid phase (Product)	Mass Composition in the Aqueous (heavy) liquid phase
Water	1.8	57
Ethanol	0.6	1.3
Acetic Acid	1.2	4.9
Ethyl Acetate	96.4	36.8

Results: Liquid composition (mol)



The concentration of ethanol is very small compared to that of the other components

Results: Extent of the reaction



- The extent of the reaction is significantly increased with the use of reactive distillation compared with a single reaction/separation stage.
- The extent of the reaction per equilibrium stage is larger in the bottom of the column due to the removal of the product by evaporation.
- The additional increase in the extent in the top the column is due to the recycling of the condensed product, which promotes the reaction of the remaining reactants and the enrichment of the vapor phase.

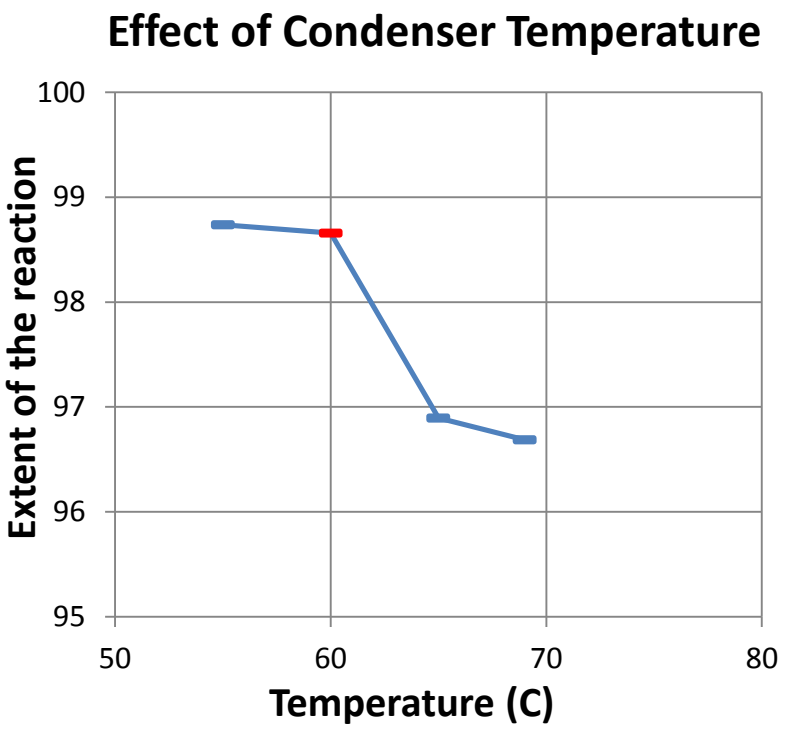
OPTIMIZATION RESULTS

Optimization

In order to optimize the operating conditions of the reactive distillation column, the effect of three essential parameters on product recovery was analyzed. These parameters are:

- Condensation temperature
- Pressure
- Reflux percentage: Mass of the condensed light phase that is send back to the column

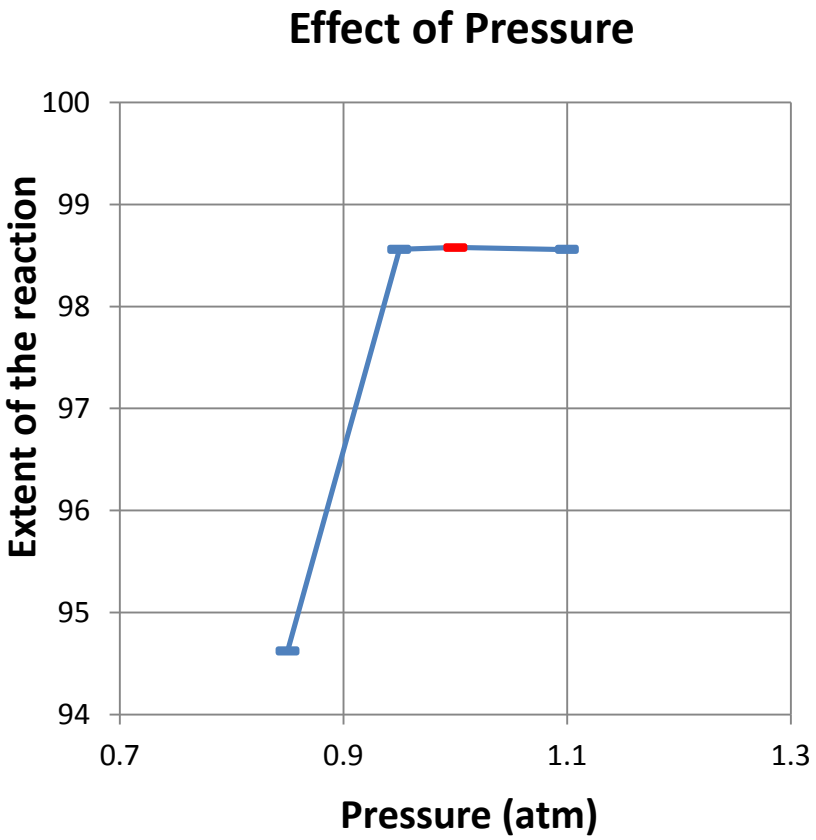
Optimization: Condensation Temperature



P= 1atm
Reflux= 60%

- Temperature has a significant effect on the overall extent of the reaction in the distillation column.
- Lower temperatures lead to greater recoveries because more of the residual reactants are condensed in the top of the column. This increases the extent of the reaction and also reduces the amount of impurities in the product.

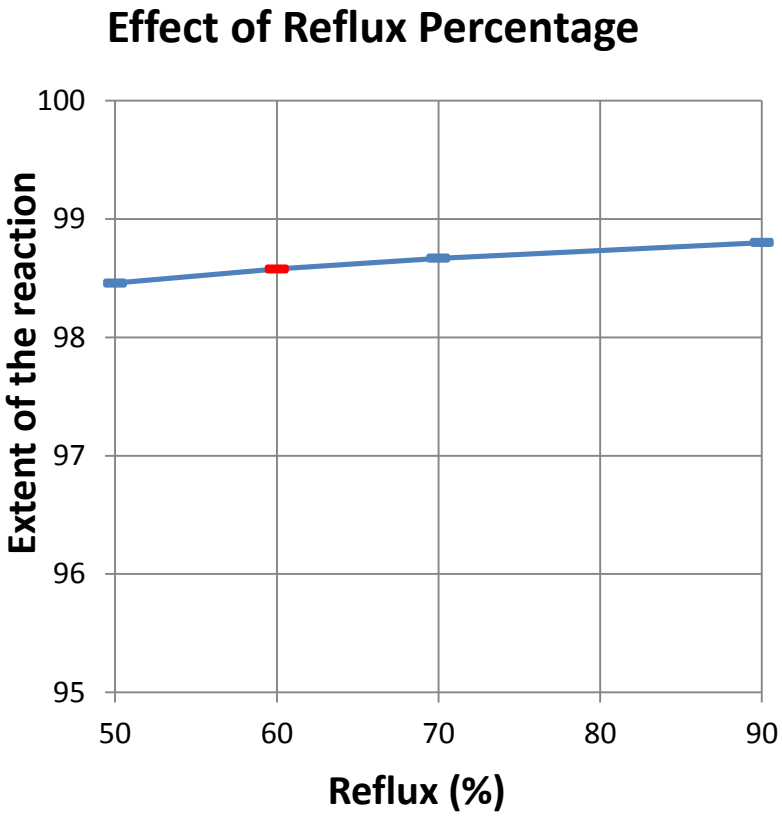
Optimization: Pressure



$T_{condenser}$= 60C
Reflux= 60%

- Pressure has a moderate effect on the overall extent of the reaction.
- Conversely to conventional distillation systems, the use of low pressure in this reactive system does not improve the extent of the reaction. This might be due to the intense volatilization of the reactants.

Optimization



$T_{condenser}$= 60C
P= 1 atm

- The reflux percentage has a minor effect on the overall extent of the reaction.
- Even tough the extent of the reaction is slightly increased at high reflux, the improvement does not give good reason for using high recirculation rates.

Optimization Results

According to the optimization analysis, the recommended operating conditions are:

- P= 1 atm
- $T_{condenser}$= 60 C
- Reflux= 60%

Conclusions: FactSage and solver approach

- FactSage has been proven to successfully simulate a reactive distillation column for esterification of acetic acid.
- The solver approach leads to convergence of the system after approximately 13 iterations.
- The use of a macro significantly simplifies the calculation effort for simulation and optimization of the distillation column.

Conclusions: Simulation

- The use of a distillation column significantly increases the extent and recovery of the esterification reaction when compared to a single stage reactor- separator.

- The decreasing temperature gradient across the column (from bottom to top) ensures the proper separation of the mixture components according to their volatilities.

- The composition profiles of the components in the vapor and liquid phases is consistent with their volatilities.

- The extent of the reaction per equilibrium stage is larger in the bottom of the column due to the removal of the product by evaporation.

Conclusions: Optimization

- The optimization analysis shows that condensation temperature has a significant effect on the extent of the reaction.
- Condensation temperatures below $60^{o}C$ are recommended for maximizing ethyl acetate production.
- Pressure and reflux percentage have a slight effect on the formation and recovery of ethyl acetate. Recommended values are 1 atm and 60%, respectively.

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