Introduction to UniSim

for Chemical & Petroleum Engineering students

UniSim Design
Academic Program

Honeywell

0. General remarks

This document is for your private use only. Do not distribute without permission from the Chemical Engineering group at the University of Aberdeen. Do not make the document available for download from the internet. This document makes no claim to be correct or complete.

1. Introduction

The UniSim® Design Suite software of Honeywell is a powerful tool for chemical, process and petroleum engineers. It is used to design chemical plant and to develop new processes. Behind a graphical user interface there is a huge data base containing (1) a library of the thermophysical properties of a large number of chemical species, (2) a set of equations of state and activity models to describe the behaviour of the different species and their mixtures as functions of thermodynamic parameters (p, T,...), and (3) a set of routines to describe the behaviour of different types of plant equipment.

In principle the use of UniSim® is very simple, but also dangerous in many respects for untrained users as the software delivers results in most cases. However, the user (this is YOU) defines the methods for determining any data and he must be able to select appropriate boundary conditions and a suitable equation of state, and eventually to judge the plausibility of the results. Basically the user describes his process as a flow chart inserting unit operations (pieces of equipment like reactors, heat exchangers, mixers, etc.) and interconnecting them by process steams (material and heat). The software solves mass balances, energy balances and equilibrium equations, and returns the results, for example, thermodynamic parameters, flow rates and mixture composition at any location in the process.

This document is a kind of tutorial that will explain you some basic features of UniSim® by providing a practical example process. In addition, a brief summary of the commonly used equations of state and activity models is given as a guide for their proper selection.

2. Selection of Fluid packages

A crucial point is the selection of an appropriate fluid package. This defines the methods and equations used for the calculations. The fluid package must be selected with respect to the species involved in the process to be simulated. This section gives a brief overview of the main fluid packages available in the academic version of UniSim. Details can be found in the literature or the internet.

a) Equations of state (EOS)

- **MBWR**
  Systems with select gases and light hydrocarbons.
- **Kabadi-Danner (KD)**
  The KD model is a modification of the SRK EOS, enhanced to improve the vapour-liquid-liquid equilibria calculations for H_2O-hydrocarbon systems, particularly in the dilute regions. The modification is based on an asymmetric mixing rule, whereby the interaction in the water phase (with its strong H_2 bonding) is calculated based on both the interaction

between the hydrocarbons and the H_2O, and on the perturbation by hydrocarbon on the H_2O-H_2O interaction (due to its structure).

- **Lee-Kesler-Plocker (LKP)**

  The Lee Kesler Plöcker equation is an accurate general method for nonpolar substances and mixtures. Plöcker et al. applied the Lee Kesler equation to mixtures, which itself was modified from the BWR equation.

- **Peng-Robinson (PR) and Soave-Redlich-Kwong (SRK)**

  For oil, gas and petrochemical applications, the Peng-Robinson (PR) or Soave-Redlich-Kwong (SKR) EOS are often the recommended property packages. They rigorously solve any single, two-phase or three-phase system with a high degree of efficiency and reliability, and are applicable over a wide range of conditions. Key components that require special treatment include He, H_2, N_2, CO_2, H_2S, H_2O, CH_3OH.

  Note: The PR or SRK EOS should not be used for nonideal chemicals such as alcohols, acids or other components. They are more accurately handled by the Activity Models (highly nonideal) or the PRSV EOS (moderately non-ideal).

- **Peng-Robinson Stryjek-Vera (PRSV)**

  The Peng-Robinson Stryjek-Vera (PRSV) equation of state is a two-fold modification of the PR equation of state that extends the application of the original PR method for moderately non-ideal systems. It has been shown to match vapour pressures curves of pure components and mixtures more accurately than the PR method, especially at low vapour pressures.

  It has been successfully extended to handle non-ideal systems giving results as good as those obtained using excess Gibbs energy functions like the Wilson, NRTL or UNIQUAC equations.

- **Sour SRK and Sour PR**

  The Sour option is available for both the PR and SRK equations of state. The Sour PR option combines the PR equation of state and Wilson's API-Sour Model for handling sour water systems, while Sour SRK utilizes the SRK equation of state with the Wilson model.

  The Sour options use the appropriate equation of state for calculating the fugacities of the vapour and liquid hydrocarbon phases as well as the enthalpy for all three phases. The K-values for the aqueous phase are calculated using Wilson's API-Sour method. This option uses Wilson's model to account for the ionization of the H2S, CO2 and NH3 in the aqueous water phase. The aqueous model employs a modification of Van Krevelen's original model with many of the key limitations removed.

- **Zudkevitch-Joffee**

  The Zudkevitch Joffee model is a modification of the Redlich Kwong equation of state. This model has been enhanced for better prediction of vapour liquid equilibria for hydrocarbon systems, and systems containing H_2. The major advantage of this model over the previous version of the RK equation is the improved capability of predicting pure component equilibria, and the simplification of the method for determining the required coefficients for the equation.

b) Activity models

Although equation of state models have proven to be very reliable in predicting properties of most hydrocarbon based fluids over a large range of operating conditions, their application has been limited to primarily non-polar or slightly polar components. Polar or non-ideal chemical systems have traditionally been handled using dual model approaches. In this approach, an equation of state

is used for predicting the vapour fugacity coefficients (normally ideal gas assumption or the Redlich Kwong, Peng-Robinson or SRK equations of state, although a Virial equation of state is available for specific applications) and an activity coefficient model is used for the liquid phase. Although there is considerable research being conducted to extend equation of state applications into the chemical arena (e.g., the PRSV equation), the state of the art of property predictions for chemical systems is still governed mainly by Activity Models.

Activity Models are much more empirical in nature when compared to the property predictions (equations of state) typically used in the hydrocarbon industry. For example, they cannot be used as reliably as the equations of state for generalized application or extrapolating into untested operating conditions. Their tuning parameters should be fitted against a representative sample of experimental data and their application should be limited to moderate pressures. Consequently, more caution should be exercised when selecting these models for your simulation.

- **Margules**

  The Margules equation was the first Gibbs excess energy representation developed. The equation does not have any theoretical basis, but is useful for quick estimates and data interpolation. The equation should not be used for extrapolation beyond the range over which the energy parameters have been fitted.

- **NRTL**

  The NRTL (Non-Random-Two-Liquid) equation, proposed by Renon and Prausnitz in 1968, is an extension of the original Wilson equation. It uses statistical mechanics and the liquid cell theory to represent the liquid structure. These concepts, combined with Wilson's local composition model, produce an equation capable of representing VLE, LLE and VLLE phase behaviour. Like the Wilson equation, the NRTL is thermodynamically consistent and can be applied to ternary and higher order systems using parameters regressed from binary equilibrium data. It has an accuracy comparable to the Wilson equation for VLE systems.

  Unlike the van Laar equation, NRTL can be used for dilute systems and hydrocarbonalcohol mixtures, although it may not be as good for alcohol-hydrocarbon systems as the Wilson equation.

- **UNIQUAC**

  The UNIQUAC (UNIversal QUAsi Chemical) equation proposed by Abrams and Prausnitz in 1975 uses statistical mechanics and the quasichemical theory of Guggenheim to represent the liquid structure. The equation is capable of representing LLE, VLE and VLLE with accuracy comparable to the NRTL equation, but without the need for a nonrandomness factor. The UNIQUAC equation is significantly more detailed and sophisticated than any of the other activity models. Its main advantage is that a good representation of both VLE and LLE can be obtained for a large range of non-electrolyte mixtures using only two adjustable parameters per binary. The fitted parameters usually exhibit a smaller temperature dependence which makes them more valid for extrapolation purposes.

  The UNIQUAC equation utilizes the concept of local composition as proposed by Wilson. Since the primary concentration variable is a surface fraction as opposed to a mole fraction, it is applicable to systems containing molecules of very different sizes and shape, such as polymer solutions. The UNIQUAC equation can be applied to a wide range of mixtures

containing H_2O, alcohols, nitriles, amines, esters, ketones, aldehydes, halogenated hydrocarbons and hydrocarbons.

- **Van Laar**

  The van Laar equation was the first Gibbs excess energy representation with physical significance. This equation fits many systems quite well, particularly for LLE component distributions. It can be used for systems that exhibit positive or negative deviations from Raoult's Law, however, it cannot predict maxima or minima in the activity coefficient. Therefore, it generally performs poorly for systems with halogenated hydrocarbons and alcohols. Due to the empirical nature of the equation, caution should be exercised in analyzing multi-component systems. It also has a tendency to predict two liquid phases when they do not exist. The van Laar equation also performs poorly for dilute systems and CANNOT represent many common systems, such as alcoholhydrocarbon mixtures, with acceptable accuracy.

  The van Laar equation has some advantages over the other activity models in that it requires less CPU time and can represent limited miscibility as well as three phase equilibrium.

- **Wilson**

  The Wilson equation, proposed by Grant M. Wilson in 1964, was the first activity coefficient equation that used the local composition model to derive the Gibbs Excess energy expression. It offers a thermodynamically consistent approach to predicting multicomponent behaviour from regressed binary equilibrium data. Our experience also shows that the Wilson equation can be extrapolated with reasonable confidence to other operating regions with the same set of regressed energy parameters.

  Although the Wilson equation is more complex and requires more CPU time than either the van Laar or Margules equations, it can represent almost all non-ideal liquid solutions satisfactorily except electrolytes and solutions exhibiting limited miscibility (LLE or VLLE). It performs an excellent job of predicting ternary equilibrium using parameters regressed from binary data only. The Wilson equation will give similar results as the Margules and van Laar equations for weak non-ideal systems, but consistently outperforms them for increasingly non-ideal systems.

  The Wilson equation CANNOT be used for problems involving liquid-liquid equilibrium.

- **Extended and General NRTL**

  The Extended and General NRTL models are variations of the NRTL model. More binary interaction parameters are used in defining the component activity coefficients. You may apply either model to systems:
  - with a wide boiling point range between components.
  - where you require simultaneous solution of VLE and LLE, and there exists a wide boiling point range or concentration range between components.

c) Acknowledgement

3. Exercise 1: Separation process

EG2570, UniSim Laboratory for Chemical Engineers
## Worked example: Ethanol/water separation process

Objectives: This section will guide you through a first simple example case in order to become familiar with the most common options implemented in UniSim and to learn how to avoid some 'famous' mistakes. A thermal separation process involving a binary mixture will be studied.

- Start the UniSim Design R380 program. Opening a new case will directly make you enter the 'Simulation Basis Manager'.
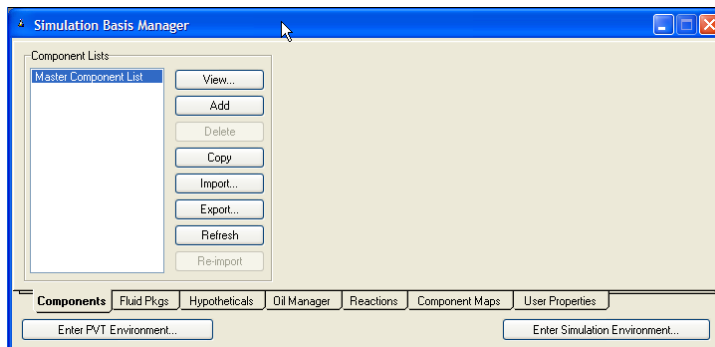
The main function of this interface is the selection of chemical components to be involved in your process and the fluid package to be used for the simulation.

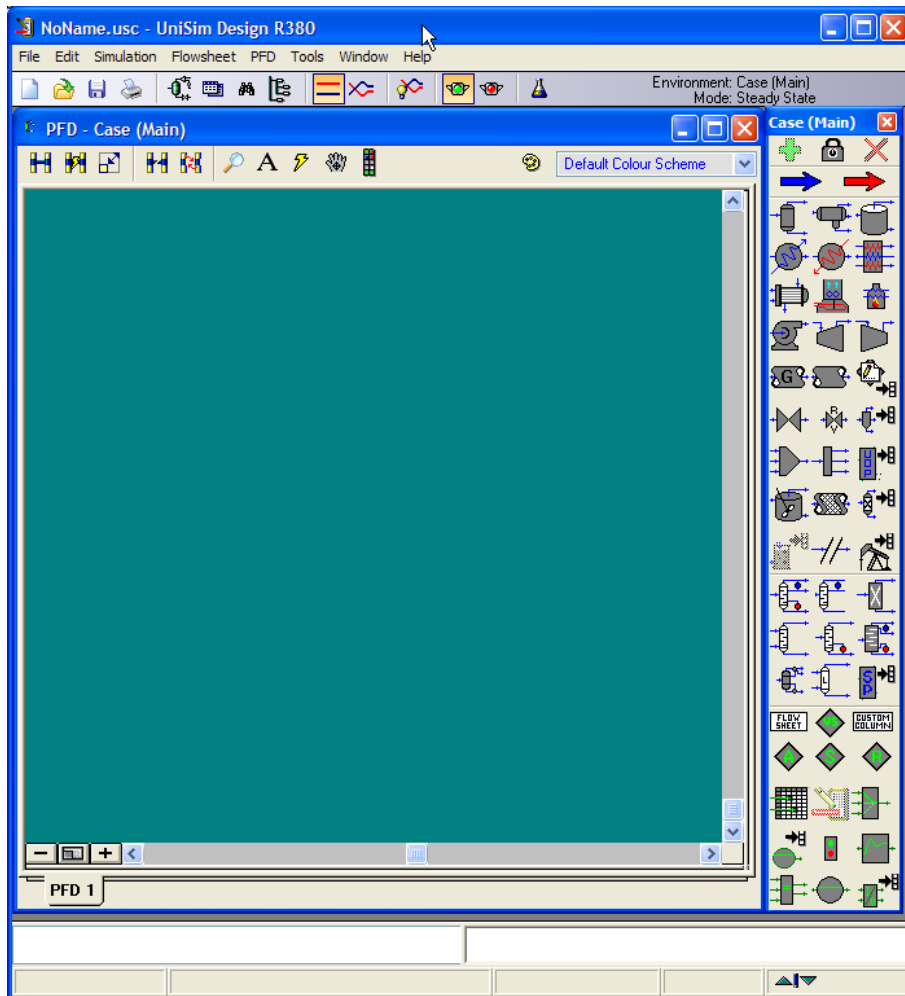- Click on *Components* and *Add*
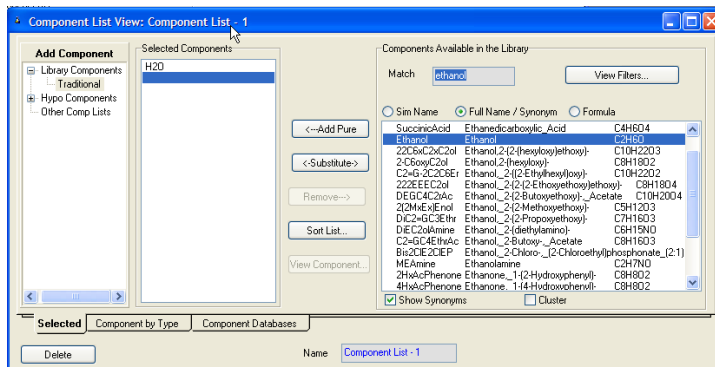
Add water and ethanol to your component list and close the selection interface again.

- Click on *Fluid Pkgs* and *Add*
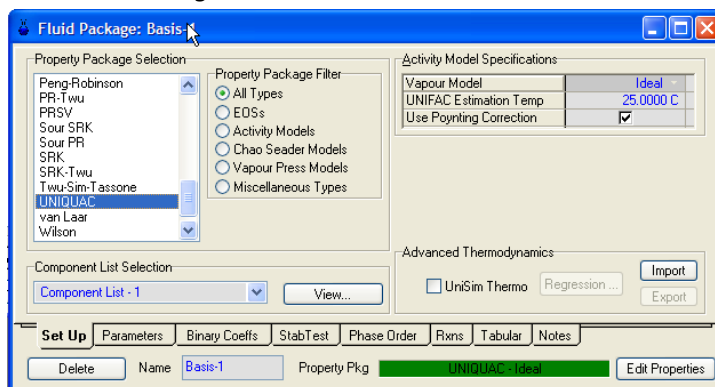
Select the UNIQUAC activity model and close the selection interface again.

- Click *Enter Simulation Environment*

- General remark: It is a good idea to safe the case from time to time in order to prevent data loss in case of a computer breakdown.
- It is important to know the main functions, buttons and features of UniSim in order make its use efficient:
   - General buttons (upper row; order from left to right)

        - Button 1: Displays the *Process Flow Diagram* (PFD) as foreground window.
        - Button 2: Displays the *Workbook* as foreground window. The workbook shows a summary of all streams and unit operations and allows them to be manipulated.
        - Buttons 3 and 4: *Object Navigator* and *Simulation Navigator* give an overview of streams and unit operations showing where data is missing or simulation problems occur.
        - Buttons 5-7: In most cases Button 5 (*Steady State Mode*) is activated as we are interested in processes that are not changing with time. Button 6 allows studying process *dynamics* e.g. to investigate the start-up of a process or the influences of changing feedstock.

- Buttons 8 and 9: The green Button 8 must be active in order to run the simulation. If you face the problem that the program is not reacting on changing parameters the solver is not running in 99% of all cases.
- Button 10: Clicking this button brings you back to the basic environment where you can modify component list and fluid package.
 - Specific buttons (in the PFD):

  - Button 1 and 2: *Attach mode* and *Auto attach mode* allow you connecting unit operation with energy and material streams
  - Button 3: Size mode allows you manipulating the displayed size of streams and unit operations.
  - Button 4: break connections between unit operations
  - Unit operations:
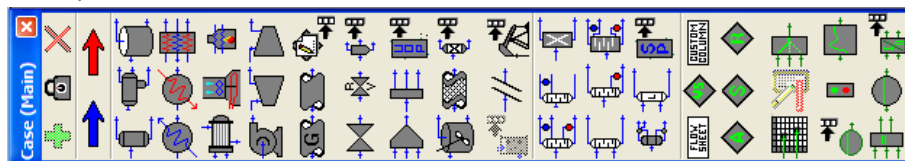
  All symbols can be added to the PFD by drag and drop.
- Add a mixer, a heater and a separator to your PFD. The mixer should have 2 feed streams; its output is then connected with the input of the heater and eventually enters the separator.
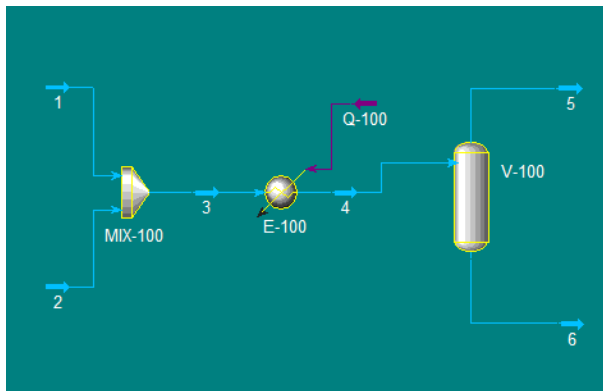
  Streams in pale blue and unit operation with yellow edges indicate missing data.
- Double clicking on streams or unit operation opens the interfaces to enter data.

- Enter the following parameters:
  - Stream 1: Pure water (mole fraction = 1), temperature 20 degC, pressure 1 bar, flow rate 1 kgmole/s.
  - Stream 2: Pure ethanol, temperature 20 degC, pressure 1 bar, flow rate 1 kgmole/s.
  - Heater: pressure drop = 0
  - Stream 4: set temperature = 20 degC
- Now all streams should be dark blue and the unit operations should show black lines. This means that you have successfully implemented your first process in UniSim.
  Open the workbook to see all data of your streams.

Tasks:

- Task 1: Vary the temperature after the heater in steps of 5 K from 20 to 100 degC and plot the ethanol mole fraction in the vapour and the liquid stream after the separator as a function of temperature using Excel. In addition, monitor the flow rates of the two product streams as a function of temperature.
- Task 2: Vary the temperature after the heater in steps of 1 K from 75 to 85 degC and plot the ethanol mole fraction in the vapour and the liquid stream after the separator as a function of temperature using Excel. In addition, monitor the flow rates of the product streams as a function of temperature.
- Task 3: Draw conclusions from you observations. What do the results mean for a technical separation process?

Deliverables:

Submission of worked example
Save your case with the file name EG2570_UNISIM_Lab1_XXX (XXX = initials) and send it as an email attachment to j.kiefer@abdn.ac.uk
In addition, include your results and findings along with concluding remarks in a one paragraph Word document and attach it to your email as well. The filename should be EG2570_UNISIM_Lab1_XXX.docx. Submit your work by Thursday, May 6, at the latest. Penalties for late or non-submission are as follows: for late submission, 1 CAS mark will be deducted for each day late (including weekends); submission later than 1 week after deadline will be considered as non-submission and a CAS mark of 0 will be awarded.

4. Exercise 2: Heat exchanger

EG2570, UniSim Laboratory for Chemical Engineers
Worked example: Heat exchange process

Objectives: In this exercise you will learn how to set up a heat exchanger in UniSim for heating a process fluid using the heat from a typical low pressure steam net. You will see how the efficiency of a heat exchange process can be increased by involving phase transitions. Furthermore, you will learn how to perform cases studies in UniSim.

The principle of a typical shell tube heat exchanger is illustrated in Fig. 1 involving two fluid streams: one that is heated up and a second one that delivers the heat required for this process. Open a new case in UniSim, add water and ethanol to your Component List and select UNIQUAC as Fluid Package. Enter the Simulation Environment.
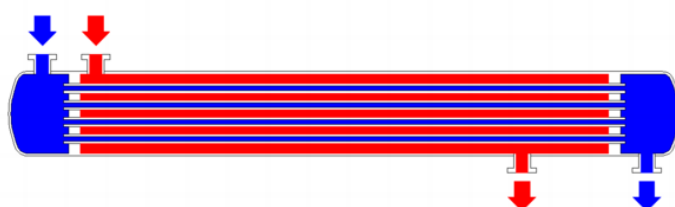
Scheme of a shell tube heat exchanger.

In most chemical plants there are several processes involved that require energy in terms of heat. Other processes deliver heat, e.g., from exothermic reactions. In order to allow transport of the heat from locations where it is produced to those where it is required, most plants have steam networks. Typical low pressure networks provide water steam at 4 bar pressure and 160 degC temperature.

Set up a heat exchanger in UniSim (the pressure drop can be neglected: $\Delta p = 0$). The heat from a low pressure steam network (specifications as given above) should be used to heat up 50 kg/s equimolar water/ethanol stream from 20 degC initial temperature to 80 degC target temperature at 1 bar constant pressure. The water/ethanol mixture is then delivered to a separator. For clarity reasons in the following we distinguish between the 'steam' and the 'mixture' streams without taking the actual state into account.
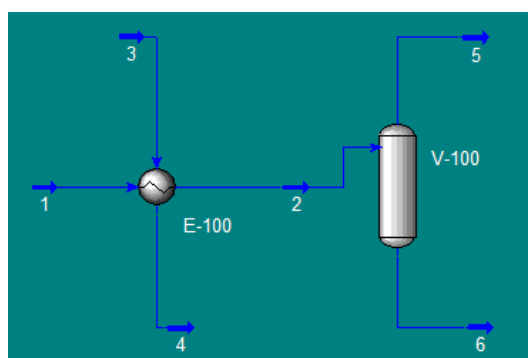
Tasks:

- Task 1: Determine the amount of steam that is required if the steam temperature must not drop below 145 degC. Why would a 145 degC lower limit make sense in a plant?

Chemical and Petroleum Engineers frequently require to analyze the effect of changing one process variable on another process variable. We will use our Heat Exchanger example to analyze the effect of changing the mixture flow rate on the final steam temperature and vapour fraction.

From the *Tools* menu, select the *Databook*. In the *Variables* tab, click on *Insert*… In the object list, highlight Stream 1, in the variable list highlight Mass Flow; click Add. Now highlight Stream 4 in the object list and in the variables list highlight Temperature and Vapour Fraction. Click on Add then click Close. In the Databook select the Case Studies tab. In the Available Case Studies area, click Add; UniSim will create Case Study 1. In the Case Studies Data Selection Area we will tell UniSim that we want to vary the mass flow rate of stream 1 and monitor its effect on the temperature and vapour fraction in stream 4. Check the tick-box for Stream 1 in the Ind (Independent Variable) list and check the tick-boxes for Stream 4 in the Dep (Dependent Variable) list. In the Available Case Studies area, click on View… Enter the lower range limit in the Low Bound field and upper range limit in the High Bound field and the appropriate number in the Step-Size field. UniSim should now tell you the number of states you are calculating. Click Start to undertake the analysis. Click Results… to view the results. You may view your results as a plot, a table or a 'transpose' table.

- Task 2: Before entering the Databook make the steam end temperature a dependent variable by deleting any set value. Set a constant steam flow rate of 200 kg/s. Vary the mixture flow rate
  i) from 1-100 kg/s in steps of 1 kg/s
  ii) from 1-700 kg/s in steps of 3 kg/s
  and monitor the steam end temperature and vapour fraction.
  Plot the data in a diagram (steam end temperature vs. mixture flow rate and vapour fraction vs. mixture flow rate). What conclusion can you draw from the data in view of heat exchanger design?
- Task 3: Determine the steam outlet temperature for 200 kg/s steam flow rate and 750 kg/s mixture flow rate. What may be a technical issue in this case?

Deliverables:

Submission of worked example:
Save your case with the file name EG2570_UNISIM_Lab2_XXX (XXX = initials) and send it as an email attachment to j.kiefer@abdn.ac.uk
In addition, include your results and findings along with concluding remarks in a one paragraph Word document and attach it to your email as well. The filename should be EG2570_UNISIM_Lab2_XXX.docx. Submit your work by Thursday, May 13, at the latest. Penalties for late or non-submission are as follows: for late submission, 1 CAS mark will be deducted for each day late (including weekends); submission later than 1 week after deadline will be considered as non-submission and a CAS mark of 0 will be awarded.

5. Exercise 3: Sugar concentration

EG2570, UniSim Laboratory for Chemical Engineers
Worked example: Sugar production

Objectives: In this exercise you will repeat performing case studies in UniSim and in addition learn how to create an adjust.

Example process: 22680 kg/h of a 10wt%, aqueous sugar (d-glucose) solution at 26.7°C and atmospheric pressure is to be concentrated to 50wt% using an evaporation process. Dry, saturated steam is available at 202.5 kPa.

Before beginning the laboratory, ensure that the Input Expert option is unchecked in the Preferences (Tools menu), General Options area.

Open a new case in UniSim, add **water** and **sugar** (d-glucose or Dextrose) to your **Component List** and select **NRTL** as your **Fluid Package**. Enter the **Simulation Environment**.

We will work through setting up a ***Single-Effect Evaporator*** operating at atmospheric pressure which will perform the concentration (Evaporation) process. An evaporator is essentially a partially filled vessel into which we feed a dilute liquid. At steady-state, we assume that the vessel is well mixed and that the liquid in the vessel has the same composition as the product. The evaporation is driven by a bank of submerged tubes within which we condense steam. We thus have condensation on the inside of the tubes and boiling on the outside of the tubes. For the system to operate we must ensure that the saturation temperature of the steam is greater than the boiling point of the liquid.

UniSim does not have a dedicated 'Evaporator' icon so our first task is to use the icons which are available to create an evaporator. To your **PFD** add a **Separator** from the **Palette**; this will be our evaporator vessel. Using the **Attach Mode**, create streams **1** (Feed Stream), **2** (Vapour Product) and **3** (Liquid Product). The feed stream is our dilute sugar solution (22680 kg/h, 26.7°C, 101.325 kPa, 0.1wt% d-glucose, 0.9wt% water); input the conditions of Stream 1.

We must now tell UniSim that we would like to condense saturated steam at 202.5 kPa and deliver the latent heat to the evaporator. From the **Palette**, add a **Cooler** to the sheet below and to the left of the vessel. Using the **Attach Mode**, create streams **4** (Feed) and **5** (Product). Attach the energy stream from the Cooler to the energy stream port of the separator icon.

Important Note: *The Vapour / Phase Fraction field in the Conditions window of the Worksheet Tab allows us to specify whether a stream is liquid (0), vapour (1) or two-phase $0<x_v<1$. For a pure fluid (e.g. water) the Gibbs Phase Rule tells us that we may only specify two of the variables Temperature, Pressure, Vapour Fraction.*

Specify stream 4 as having a vapour fraction of 1 (Vapour only), a pressure of 202.5 kPa, a mass fraction water of 1 and a flow rate of 10000 kg/h. We will assume that the condensation occurs at constant pressure (no pressure drop; idealized situation). In the Parameters window for the Cooler, input 0 in the Delta P field. UniSim now knows the flow rate, composition and pressure of the condensate stream (Stream 5) but does not know the temperature (it may be saturated liquid or

subcooled liquid). Input a vapour fraction of 0 in the Vapour / Phase Fraction (saturated liquid) field for Stream 5. The PFD should now have computed and you should have a liquid product (Stream 3) of 15887 kg/h. Your heat stream from the cooler to the separator should be 6109 kW and you should be generating 6793 kg/h of steam at 101.325 kPa with around 0.5°C of superheat (i.e. at a temperature of 100.5°C). The last stage in the completion of our single effect evaporator is to condense the steam which we have generated. Insert a cooler which accepts your superheated steam and condenses it at constant pressure (zero pressure drop) to yield saturated liquid (Vapour / Phase Fraction = 0).

Your PFD should look like this;
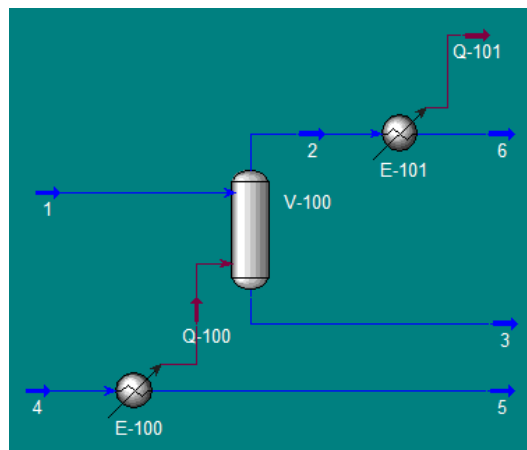
Case Study
We will use our Evaporator to analyze the effect of changing the Feed Steam flow rate on the product composition. More specifically, we will tell UniSim to test values of the flow rate of stream 4 of 10000 kg/h to 24000 kg/h in steps of 1000 kg/h and report the values of mass fraction d-glucose in the product (stream 3).

From the Tools menu, select the Databook. Add the variables of interest. We want to vary the mass flowrate of stream 4 and monitor its effect on the mass fraction of dextrose in stream 3. Create a new case study and enter 10000 in the Low Bound field 24000 in the High Bound field and 1000 in the Step-Size field. UniSim should now tell you that you are checking 15 states. Click Start to undertake the analysis and view your results as a plot.

- Task: Modify the lower bound, upper bound and step size fields to allow you to estimate the steam flow rate required to meet the specification (50wt% dextrose) to the nearest 100 kg/h.

Creating an Adjust (Specification)
Our goal in designing the evaporator is essentially determine the flow rate of steam required to yield a product of 50wt% dextrose. Ideally we would thus like to be able to specify the feed and product and have UniSim compute the steam flow rate. Unfortunately, most process simulators compute from feed to product (sequentially) which makes specifying the product impossible. Instead our approach must be to set up the PFD with a reasonable estimate and tell UniSim to iteratively converge to a specified value of a given variable. This is done using the Adjust function (found on the Palette).

On the same PFD as the evaporator used to perform the case Study, create another single effect evaporator identical to that used in the Case Study (Do not copy and paste as this will lead to problems!!). Use the Case Study you performed in the previous section to gain an estimate for the steam flow rate required to yield a 50wt% dextrose product (say 21500 kg/h).

From the Palette select an Adjust and place it on your PFD below the evaporator. Using the Attach Mode connect the Target Object port of the Adjust to the evaporator product stream (selecting Comp Mass Frac, Dextrose in the list menus) and connect the Adjusted Object port of the Adjust to the Feed Steam stream (selecting Mass Flow from the variable list). Double click on the Adjust Icon and in the Target Value area, specify a target value of 0.5 (50wt%). In the Parameters tab input 0 as the minimum and 24000 as the maximum (accept the default values for method, tolerance, step size and maximum iterations). The Adjust should solve and you will be able to view the iteration step results in the Monitor tab.

- Task: Plot the steam mass flow and the sugar concentration as function of the iteration step. Repeat setting up an adjust and choose a steam flow rate estimate of 2000 kg/h. Plot the steam mass flow and the sugar concentration as function of the iteration step again and compare the result with the previous one.

Deliverables

Submission of worked example:
Save your case containing the Case Study and Adjust Worked Examples with the file name EG2570_UNISIM_Lab3_XXX (XXX = initials) and send it as an email attachment to j.kiefer@abdn.ac.uk
In addition, include your results and findings along with concluding remarks in a one paragraph Word document and attach it to your email as well. The filename should be EG2570_UNISIM_Lab3_XXX.docx. Submit your work by Thursday, May 20, at the latest. Penalties for late or non-submission are as follows: for late submission, 1 CAS mark will be deducted for each day late (including weekends); submission later than 1 week after deadline will be considered as non-submission and a CAS mark of 0 will be awarded.