

ChemSep Tutorial: Reactive Distillation

Ross Taylor and Harry Kooijman

In this document we demonstrate how to create a model of a reactive distillation column to make methyl acetate from acetic acid and methanol. We will be recreating an example described in some detail in a book by Luyben and Yu (Luyben, W.L., Yu, C.-C., 2008. *Reactive distillation design and control*. Wiley: AIChE, Hoboken, NJ). We will highlight the ways that the set-up of the ChemSep model differs from that of Luyben and Yu.

(We do assume some familiarity with ChemSep; in other words, this is not your first ChemSep simulation.)

The results with ChemSep are very close to those of Luyben and Yu (we will refer to them as L+Y to save space). There are some minor differences that are more or less inevitable when different simulation tools are used. These differences arise due to small discrepancies in things like the vapor pressure, heat of vaporization, ideal gas heat capacity and so on. Simulation software users have limited scope to change these things. (What matters more are activity coefficient model parameters and reaction rate coefficients and we will write more about those in what follows).

Component Selection

The components involved in this case are shown here:

The screenshot shows the 'Select Components' dialog box in ChemSep. At the top, there is a 'Component databank' field containing 'c:\chemsep845\pcd*.pcd', a 'Browse' button, and an 'Advanced search' checkbox. Below this is a 'Find' text box and a 'Sort' button. The main area is divided into two sections: 'Components in Databank' on the left and 'Selected components for simulation' on the right. The 'Components in Databank' list includes Air, Argon, Bromine, Carbon tetrachloride, and Carbon monoxide. The 'Selected components for simulation' table lists Methanol, Acetic acid, Methyl acetate, and Water with their respective L#, Trnb, Cl, File, Loc., CAS, and SMILES values.

Identifier	L#	Trnb	Cl	File	Loc.	CAS	SMILES
Methanol	1101	64.5401	c:\chemsep845\pcd\32		67-56-1	CO	
Acetic acid	1252	117.891	c:\chemsep845\pcd\48		64-19-7	CC(=O)O	
Methyl acetate	1312	56.9401	c:\chemsep845\pcd\64		79-20-9	CC(=O)OC	
Water	1921	100.001	c:\chemsep845\pcd\14		7732-18-5	O	

Methanol and acetic acid are the reactants; methyl acetate and water are the products.

Column Configuration

The column configuration is shown below:

✓ Operation

Select Type of Simulation

Flash

Equilibrium column

Nonequilibrium column

Configuration

Operation: Simple Distillation

Condenser: Total (Liquid product)

Reboiler: Partial (Liquid product)

Number of stages (e.g. 10): 40

Feed stage(s) (e.g. 5,7): 5,28

Sidestream stage(s) (e.g. 2,9):

Pumparound(s) (e.g. 6>8, 9>1):

Interconnections:

Extra condensers:

Extra reboilers:

Drawing:

L+Y count stages starting at the bottom of the column and do not include the condenser. In ChemSep, stages are counted starting from the top and the total number does include the condenser. This is the reason why the feed stage locations are slightly different from those in L+Y.

Vapor-Liquid Equilibrium Model

The key to any successful column model is, of course, the thermodynamic models. Following L+Y we use the UNIQUAC model for the activity coefficients with the temperature dependent BIPs shown in the screen image below. These BIPs are from Pöpkén et al. (2000).

Thermodynamics
 Physical properties
 Reactions

Select Thermodynamic Models

K-value:
 Reference state: (K)
 Henry's law components

Equation of state:
 Heat of formation:

Activity coefficient:
 Surroundings T: (K)

Vapour pressure:
 Heat Capacity IG:

Enthalpy:
 Heat Capacity L:

Select Thermodynamic Model parameters (when required)

UNIQUAC |

Units:
 BIP estimation
 BIP T est. (K):
 T dependence:

i - j	A-ij	A-ji	B-ij	B-ji	D-ij	D-ji
Methanol - Acetic acid	-2.03460	0.970390	62.2450	390.260	0.00315700	-3.061E-03
Methanol - Methyl acetate	-0.710110	0.724760	62.9720	326.200	0.00116700	-2.354E-03
Methanol - Water	3.14530	-2.05850	-575.680	219.040	-6.071E-03	0.00701400
Acetic acid - Methyl acetate	-0.436370	1.11620	-62.1860	81.8480	2.7230E-04	-1.333E-03
Acetic acid - Water	-0.0510070	-0.293550	422.380	-98.1200	-2.401E-04	-7.674E-05
Methyl acetate - Water	0.0101430	0.962950	593.700	-265.830	-2.160E-03	2.0130E-04

The temperature dependent binary interaction parameters (BIPs) are given by Y+L. Note however, that Y+L defines them differently than the implementation in ChemSep; for our use it is necessary to negate all of the BIPs in L+Y.

We use the ChemSep correlation for the vapor pressure (L+Y do not say what they use). Chemical Theory (The Hayden-O'Connell equation of state) is used for the vapor phase fugacity coefficients. This is to account for vapor-phase dimerization of acetic acid (Y+L use the same equation of state and, although, they do not specify the BIPs for this model, it is likely that they are from the same source used by ChemSep; the book of Anderson et al. See the list of references).

As noted, our simulation is based on that of Luyben and Yu, who state that the binary interaction parameters for the UNIQUAC activity coefficient model come from Pöpken et al. (2000). The parameters can be found in Table 3 of their paper and, per Pöpken et al., are used in the calculation of the interaction energy term:

$$\Delta(u_{ij})(K) = a_{ij} + b_{ij}T + c_{ij}T^2$$

Pöpken et al. (2000) cite the original paper of Abrams and Prausnitz (1975) where we find:

$$\tau_{ij} = \exp(-\Delta u_{ij}/RT)$$

The stated units of Kelvin for $\Delta(u_{ij})$ means mean that the gas constant in the above equation should take the value of 1. What it means is that the BIP in the first equation above is really divided by R to get it to have the units of K. (This is not a particularly unusual thing to do.)

By their use of the symbol q' in Table 7.2. of their book, Luyben and Yu imply that they are using a modified form of UNIQUAC due to Anderson and Prausnitz (1978). It is highly unlikely that the paper of Pöpken et al. (2000) is using this modified version of UNIQUAC since they do not provide values of q' whereas they do list values of r and q . This means that $q' = q$.

Luyben and Yu state that the τ_{ij} are calculated from

$$\tau_{ij} = A_{ij} + B_{ij}/T + C_{ij}T$$

Luyben's formula for τ_{ij} must be wrong; the equation should read:

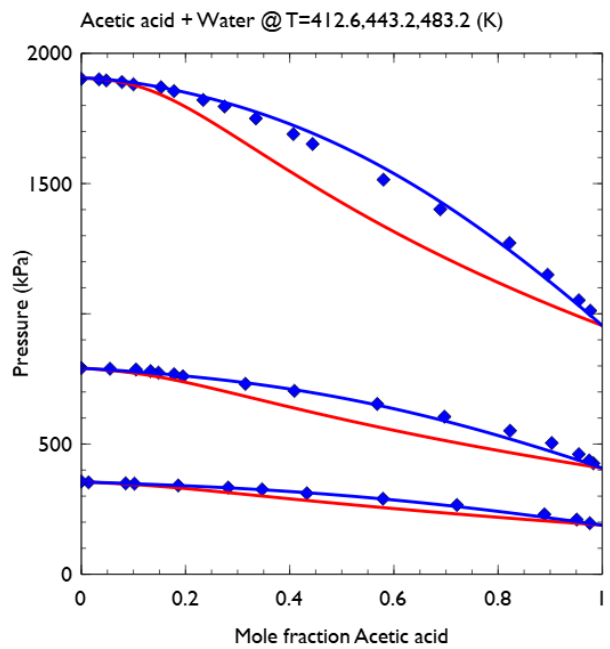
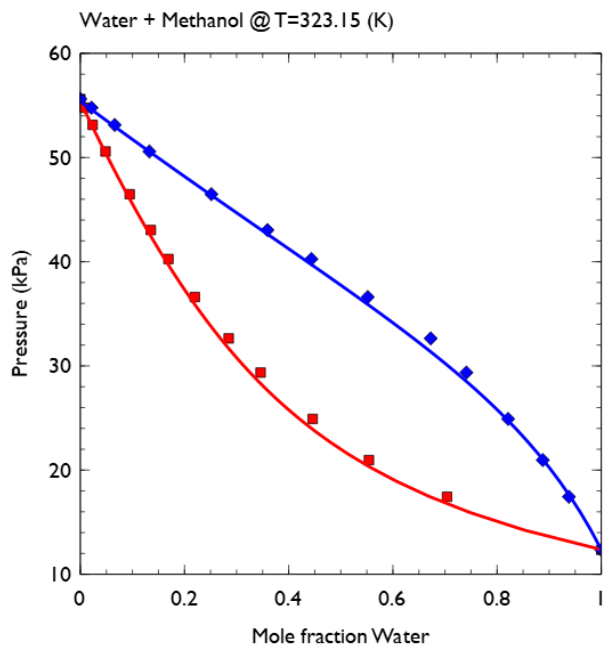
$$\ln(\tau_{ij}) = A_{ij} + B_{ij}/T + C_{ij}T$$

Thus, in order to align with the BIPs in Pöpken et al. (2000), the following must be true:

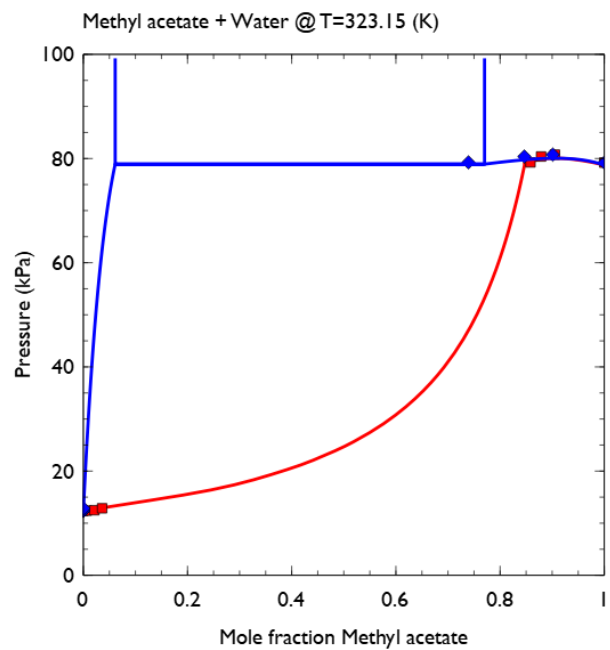
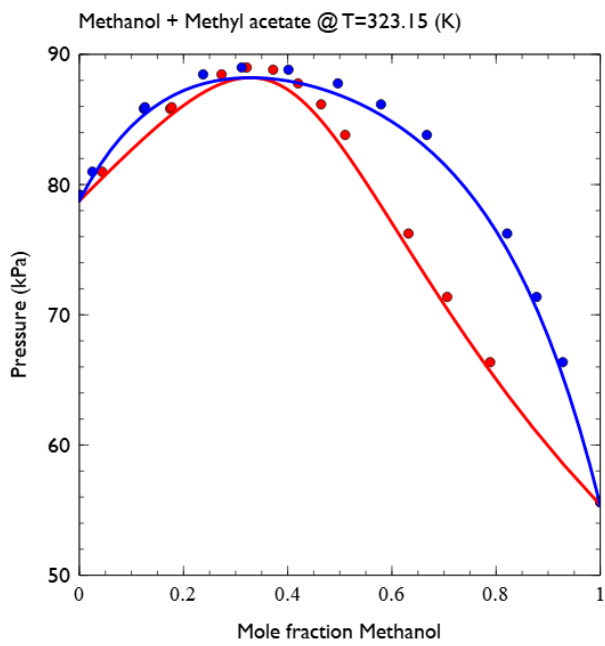
$$A_{ij} = -b_{ij}; B_{ij} = -a_{ij}; C_{ij} = -c_{ij}.$$

Note that all of the BIPs in Luyben and Yu require negation in order to match those in Pöpken et al. (see screenshot above).

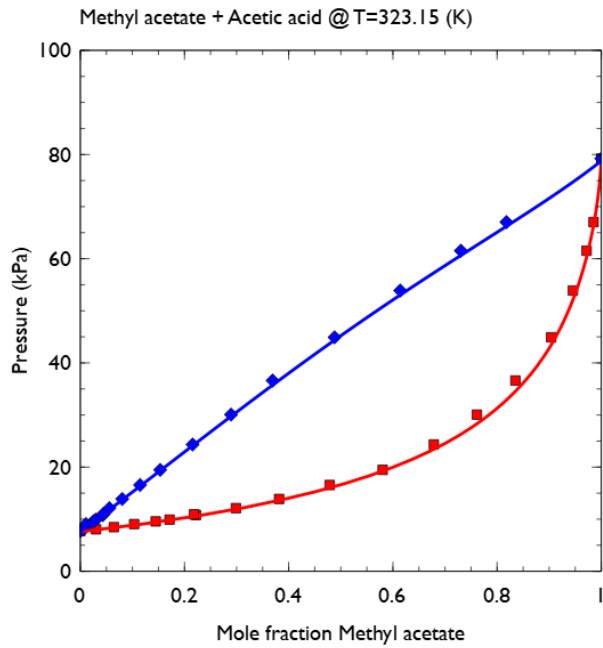
To ensure that the BIPs in these sources (after allowing for corrections as described) we compared the predictions of the model to experimental data. The VLE data for three binary pairs is from Bernatová et al. (2006); the data for acetic acid and water from Román-Ramírez and Leeke (2016). It is worth noting that none of these data sets were available when the paper by Pöpken et al. was published.



Phase diagrams for methanol – water (left) and acetic acid – water (right)



Phase diagrams for methanol – methyl-acetate (left) and methyl-acetate – water (right)



Phase diagram for methyl-acetate – acetic acid

Reaction Rate Model

We turn now to the reaction kinetics. The models are specified in ChemSep as shown below:

Thermodynamics Physical properties Reactions

Define Reactions

Insert Remove Library Save

Reaction
1 MeAc

Reaction 1: MeAc

Reversible reaction

Reaction type: Pseudo-homogeneous

Kinetics basis: activities

Reactive zones:

Reactive zone	1
Begin stage	4
End stage	36
Stage volume (m3)	32.6000
Catalyst activity	1.00000

Component	Methanol	Acetic acid	Methyl ac	Water
Stoichiometric coeff.	-1	-1	1	1
Forward orders	1	1	0	0
Backward orders	0	0	1	1

Reaction rate	Eqn #	A	B	C	D	E
k-forward	119	-5916.53	10.2959	0	0	0
k-backward	119	-8326.92	14.1141	0	0	0

L+Y use a reaction kinetic model from Pöpken et al. (2000):

$$r = m_{cat} (k_F a_{HAc} a_{MeOH} - k_B a_{MeAc} a_{H_2O})$$

where m_{cat} is the mass of the catalyst (more on this below), a_i are the activities of the various species, and k_F and k_B are the forward and backward rate coefficients respectively. L+Y use the following model for both of the rate coefficients:

$$k = A \exp(-B/RT)$$

The screen shot above shows that we are using Eqn 119 in ChemSep; this is:

$$\ln(k) = a/T + b + cT + dT^2 + e \ln(T)$$

The ChemSep model and the L+Y model are identical when:

$$a = -B/R, b = \ln(A), c = d = e = 0$$

and the gas constant R has units of $J/kmol.K$.

The numbers in the screen shot above reflect these conversions.

The units of the rate coefficients in L+Y are $kmol/kg_{cat}s$. Thus, to get the reaction rate in $kmol/s$ requires us to multiply by the mass of the catalyst on a stage. This is why the rate equation from L+Y includes the mass of catalyst as a multiplier. However, ChemSep looks for the reaction rate to be given in $kmol/m^3s$. This is why we have a place for the stage volume (look to the mid-right of the screen shot above). We can use this same slot as a surrogate for the catalyst mass. L+Y tell us that they assume a weir height of 10.16 cm, a tray diameter of 1.03 m and that 50% of the tray holdup is catalyst. Thus, the "stage volume" (in ChemSep terms) is

$$m_{cat} = 0.5 \rho_{cat} \pi r^2 h_w$$

With the tray radius at 0.5015 m, the weir height equal to 0.1016 m, the catalyst density $770 kg/m^3$ we find that the mass of catalyst is 32.6 kg (per stage). This is the number entered in the stage volume cell in ChemSep to give the reaction rate in the required units of $kmol/m^3s$.

The Remaining Specifications

The column is assumed to be at a pressure of 1 atm throughout.

The column is assumed to be adiabatic (no heat losses).

The stage efficiency is assumed to be 100%.

The feeds are specified as shown in the screen shot below.

✓ Feeds

Feed Stream(s) Specifications

Insert Remove Molar flows ▼

Feed:	1	2
Name	Acetic Acid	Methanol
Stage	5	28
Two-phase feed	Split	Split
State	T & p	T & p
Pressure (atm)	1.00000	1.00000
Vapour fraction (-)		
Temperature (C)	24.8500	24.8500
Flowrates (kmol/h):		
Methanol	0.000000	50.0000
Acetic acid	50.0000	0.000000
Methyl acetate	0.000000	0.000000
Water	0.000000	0.000000
Total flowrate	50.0000	50.0000

The two remaining column specifications are as shown below:

Column Product Specifications

Top product name: Top Condenser duty name: Qcondenser

Top specification: Reflux ratio = 1.96600 (-)

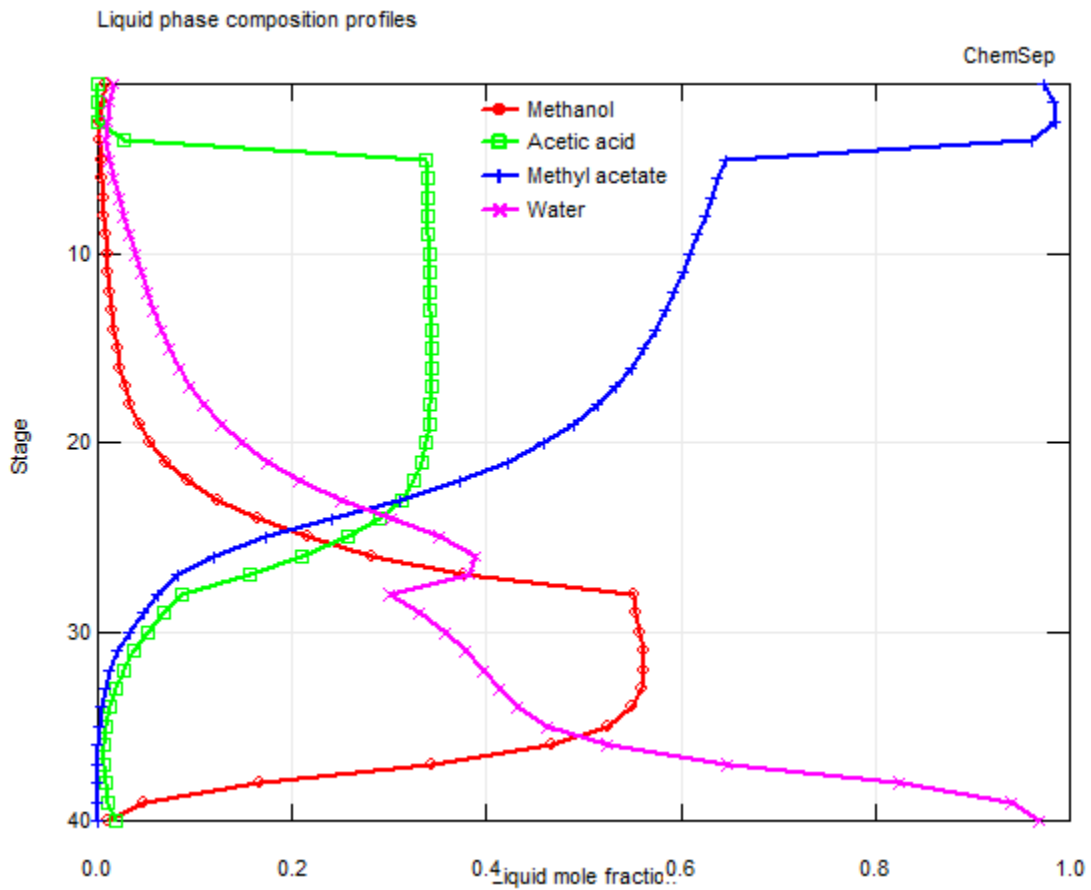
Bottom product name: Bottom Reboiler duty name: Qreboiler

Bottom specification: Bottom product flow rate = 49.6501 (kmol/h)

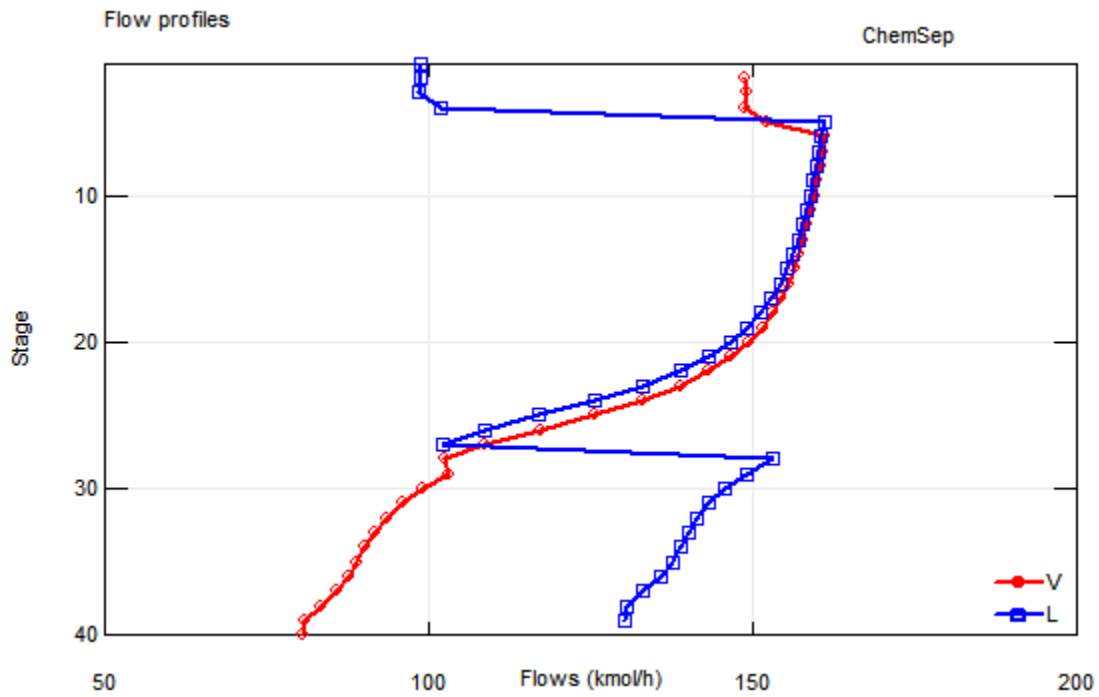
The specifications are now complete.

Results

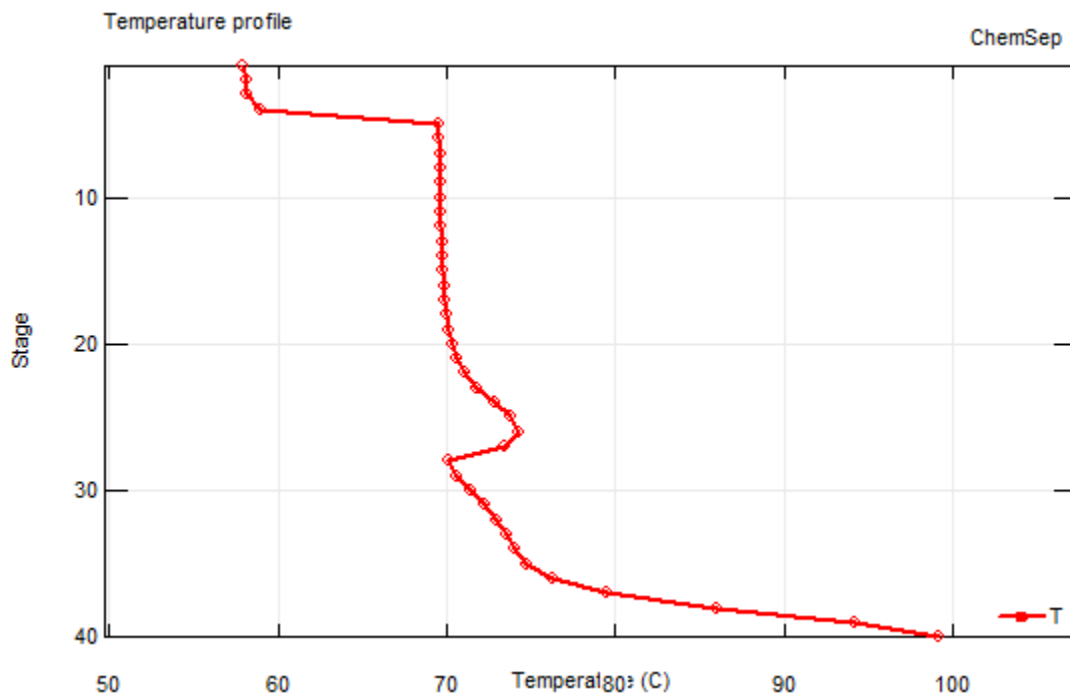
Here is the composition profile in the liquid phase:



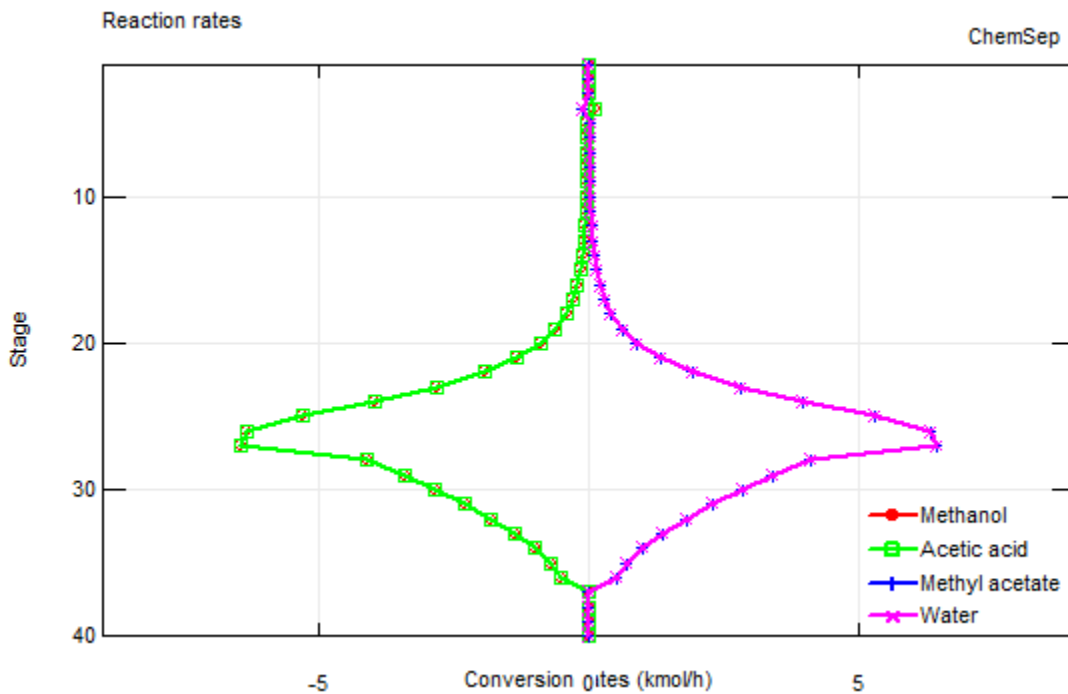
The flow profiles:



The temperature profile:



Reaction rate profile:



Multiple Steady State Solutions

It has been known for many decades that column models for non-ideal and reactive distillation can possess multiple steady-state solutions (MSS). (The ethanol-benzene-water system is another case in point that is available on the ChemSep downloads page.)

Here (next page) we show two alternative solutions for this methyl acetate reactive distillation column. To obtain the first of these it suffices to remove the initial estimates of the reflux ratio and bottoms flow rate that were used to obtain the solution shown above. The second alternative solution is obtained by removing the initial estimates *and* changing the convergence method to *2-pass, constant H first*. These alternative solutions are similar in many ways, but both are quite different from the result shown above.

Huss et al. (2003) reported multiple steady state solutions for the methyl acetate reactive distillation. Their solutions differ from those shown here but, since their kinetic model, VLE model, column configuration, and column specifications differ from those used here, that should not be a surprise. The important point is that the existence of MSS for this case is confirmed.

References

Abrams, D.S., Prausnitz, J.M., 1975. Statistical thermodynamics of liquid mixtures: A new expression for the excess Gibbs energy of partly or completely miscible systems. *AIChE J.* 21, 116–128. <https://doi.org/10.1002/aic.690210115>

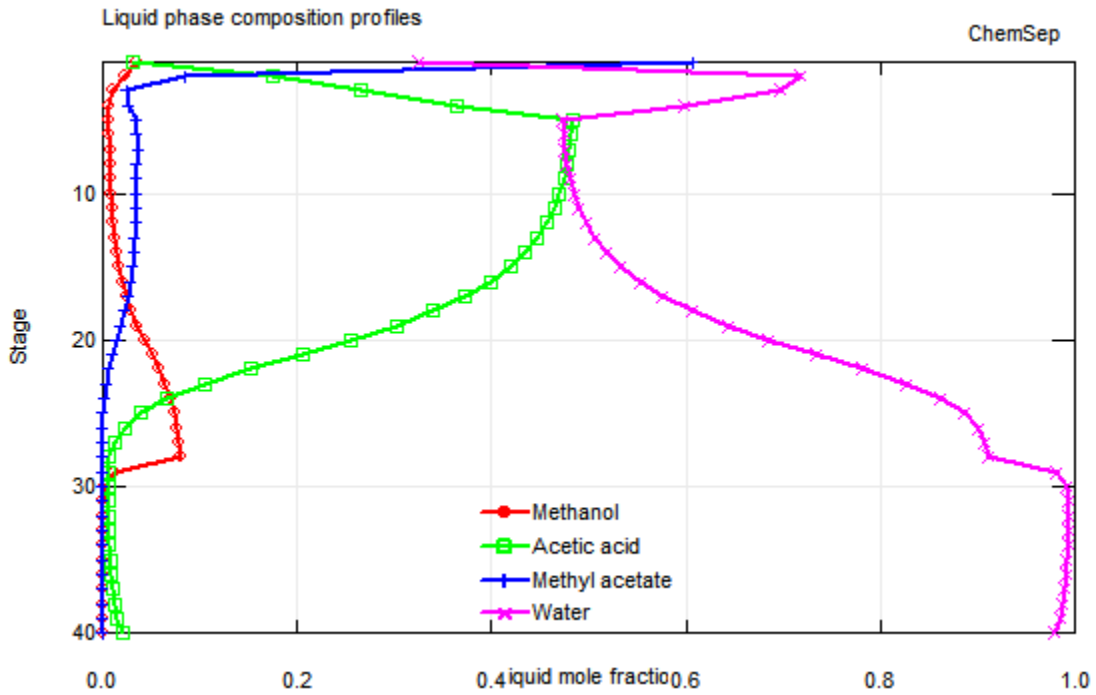
Anderson, T.F., Prausnitz, J.M., 1978. Application of the UNIQUAC Equation to Calculation of Multicomponent Phase Equilibria. 1. Vapor-Liquid Equilibria. *Industrial & Engineering Chemistry Process Design and Development* 17, 552–561. <https://doi.org/10.1021/i260068a028>

Bernatová, S., Aim, K., Wichterle, I., 2006. Isothermal vapour–liquid equilibrium with chemical reaction in the quaternary water+methanol+acetic acid+methyl acetate system, and in five binary subsystems. *Fluid Phase Equilibria* 247, 96–101. <https://doi.org/10.1016/j.fluid.2006.06.005>

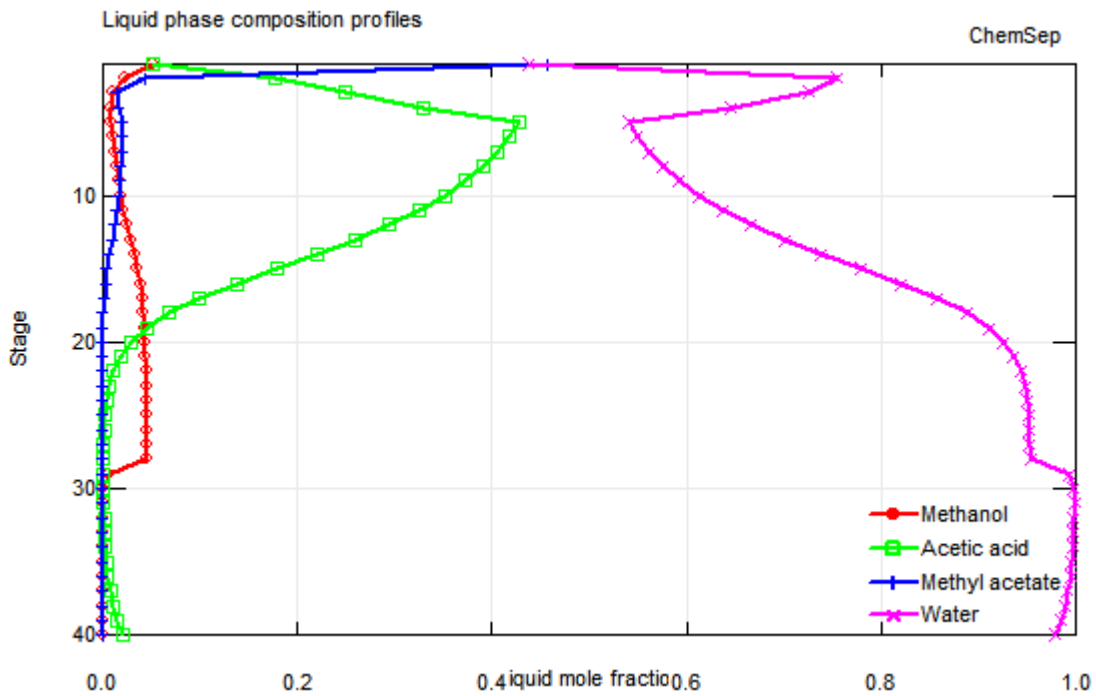
Huss, R.S., Chen, F., Malone, M.F., Doherty, M.F., 2003. Reactive distillation for methyl acetate production. *Computers & Chemical Engineering* 27, 1855–1866. [https://doi.org/10.1016/S0098-1354\(03\)00156-X](https://doi.org/10.1016/S0098-1354(03)00156-X)

Pöpken, T., Götze, L., Gmehling, J., 2000. Reaction Kinetics and Chemical Equilibrium of Homogeneously and Heterogeneously Catalyzed Acetic Acid Esterification with Methanol and Methyl Acetate Hydrolysis. *Industrial & Engineering Chemistry Research* 39, 2601–2611. <https://doi.org/10.1021/ie000063q>

Román-Ramírez, L.A., Leeke, G.A., 2016. p_x Data of (Acetic Acid + Water) at $T = (412.6, 443.2, 483.2)$ K. *Journal of Chemical & Engineering Data* 61, 2078–2082. <https://doi.org/10.1021/acs.jced.5b01104>



Liquid phase mole fraction profiles for methyl acetate reactive distillation: Alternative 1



Liquid phase mole fraction profiles for methyl acetate reactive distillation: Alternative 2