OTTO-VON-GUERICKE-UNIVERSITÄT MAGDEBURG

Faculty of Process & Systems Engineering

Simulation Lab WS 2018/19

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„ METHYL ACETATE PRODUCTION VIA REACTIVE COLUMN “

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1. INTRODUCTION

Methyl acetate, also commonly known as MeOAc, is a carboxylate easter, with the chemical formula CH_3COOCH_3. It is a flammable liquid, having a characteristic pleasant smell, used mostly in some glues or nail polish removers. At room temperature, methyl acetate has a solubility of 25% in water, and higher at elevated temperatures. It is not stable in the presence of strong aqueous bases or aqueous acids. It is a volatile organic compound (VOC) exempt [1]. Methyl acetate (MeOAc) is produced from the liquid phase reaction of acetic acid (HOAc) and methanol (MeOH) in the presence of an acid catalyst (e.g. sulphuric acid or sulphonic acid ion exchange resin) at a pressure of 1 atm [2].

Reactive distillation has a high potential for process intensification for various types of reactions, hence it has got severe attention in the last two decades. Important reactions among these are esterification, hydrolysis and etherifications, whose equilibrium limits its maximum conversion [3]. Reactive distillation combines both chemical reaction and separation in a single apparatus unit. This helps in minimizing the operating costs. For a better product, the volatilities of the components must be such that reactants can be retained inside and products can be removed out. Some other advantages of reactive distillation are (i) increases yield, (ii) improved selectivity (iii) reduced energy consumption (iv) availability to separate close boiling components [1]. Production of methyl acetate via a reactive column is a classic example of successful reactive distillation technology [2].

1.1 INTRODUCTION TO ASPEN

In 1970, a prototype of a process simulation was developed at the MIT energy lab, which was later known as Advanced System for Process Engineering (ASPEN). Since 2007, aspentech provides to various universities, a closed single software package, joining two process simulators: Aspen plus and HYSIS. It has a built-in library models for components like columns, separators, mixers, etc. Aspen plus can solve problems related to polymerization reactions, solids separation, reactive distillation, dynamic simulations more efficiently than other present softwares [4]. Specifications like the feed conditions, operating conditions, other flowsheet

configurations can be easily added or modified in aspen. It performs numerous tasks such as regressions, graph estimations, convergence, energy and cost estimations, etc.

1.2 INTRODUCTION TO THE REACTION

Methyl acetate (MeOAc) can be made by the liquid phase reaction of acetic acid (HOAc) and methanol (MeOH), catalysed by sulphuric acid in the temperature range of 310-325K, at a pressure of 1 atm. A new activity-based model utilising the Langmuir-Hinshelwood/ Hougen-Watson isotherm was developed due to the high polarity of water and methanol compared to methyl acetate, leading to a strongly nonideal solution behaviour [5].

The reaction of methyl acetate production is as follows [2]:

HOAc + MeOH ↔ MeOAc + H_2O

According to Muhammad et al. [5], the reaction kinetics for production of methyl acetate are as follows:

$$R_{MeOAc} = \frac{M_{cat} k_1 \left(a_{HOAc} a_{MeOH} - \frac{a_{MeOAC} a_{H2O}}{K_{eq}}\right)}{\left(1 + K_{HOAc} a_{HOAc} + K_{MeOH} a_{MeOH} + K_{MeOAc} a_{MeOAc} + K_{H2O} a_{H2O}\right)^2}$$

k_1 = 6.942 x 10^9 exp $\left(\frac{-6287.7}{T}\right)$

K_{eq} = 2.32 exp $\left(\frac{782.98}{T}\right)$

K_{HOAc} = 3.18

K_{MeOH} = 4.95

K_{MeOAc} = 0.82

K_{H2O} = 10.5

$a_i = \gamma_i x_i$

where,

a_i is the activity, γ_i is the liquid activity coefficient, x_i is the liquid mole fraction

k_i is the reaction rate constant (mol/ (g cat h))

M_{cat} is the mass of the catalyst (g)

T is the temperature (K)

2. METHODS AND MATERIALS

2.1 MODELLING

The model of the reactive distillation column used for the easterification process of methyl acetate, i.e. reaction of acetic acid and methanol to form methyl acetate developed in ASPEN Plus, is shown in Figure 1 below. A RadFrac Packed column and Non-Random two liquid (NRTL) property method was used. RadFrac column is mostly used for extractive distillation, azeotropic distillation, highly non-ideal liquids and distillation with ongoing chemical reactions. The rectification and the stripping section of the column were filled with Raschig type packing of ceramic materials of dimension 25mm. The packaging adds to the surface area of the column and the number of vaporisation/condensation cycles that the feeds goes through are enhanced. This increases the separation efficiency of the lower and higher boiling point components in the feed. The RadFrac column used in the modelling and its details are shown in the Figure 1. The phase of the reaction was liquid and the equilibrium constant (K_{eq}) was calculated from the Gibbs free energies. The reaction was allowed to take place between the stages 2-23.

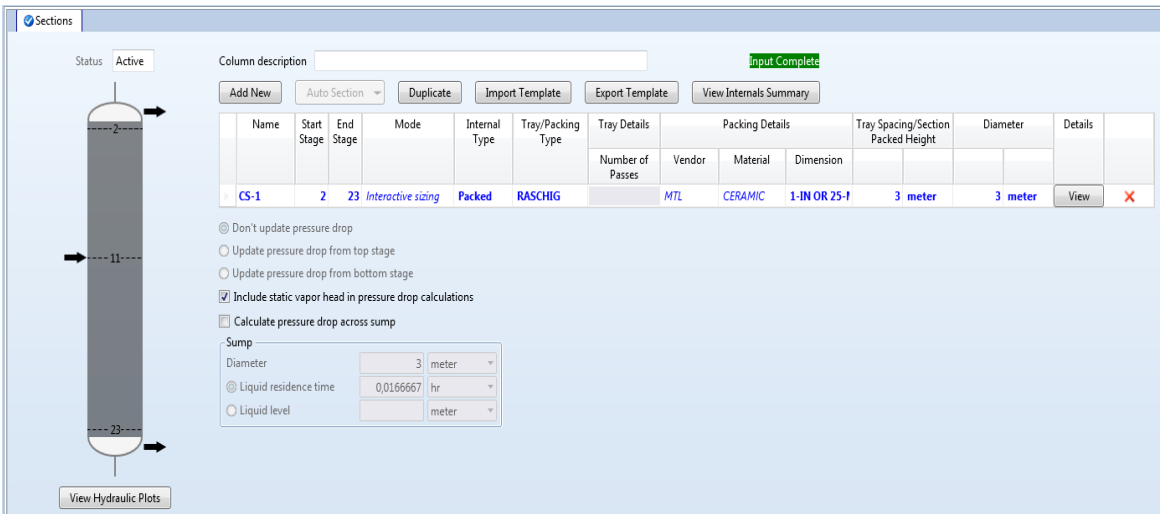


Figure 1: RadFrac column details

2.2 SIMULATION

A property method defines the method and models used for the calculation of the thermodynamic and the transport properties used in the simulation. Non-Random Two Liquid (NRTL) method is generally used in the simulation of the reactive distillation columns. Wilson method and Vaanlaar method are other commonly used methods in distillation simulations.

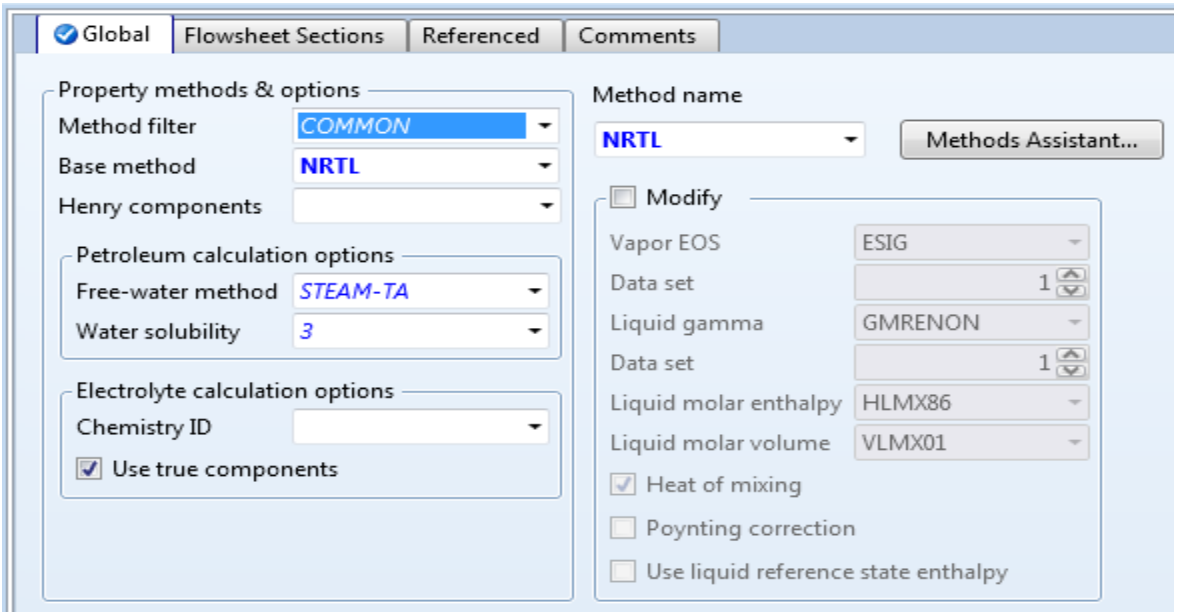


Figure 2: Selection of base method for simulation.

A RadFrac distillation column of Type1 was setup. A mixed single flow feed of acetic acid and methanol was given to the RadFrac column. Methyl acetate as the main product, was collected from the top stage i.e. the condenser. Water was given out as a side product in the bottom stage, i.e. the reboiler. Figure 3 shows the simulation flow chart of the RadFrac column with mixed single flow feed.

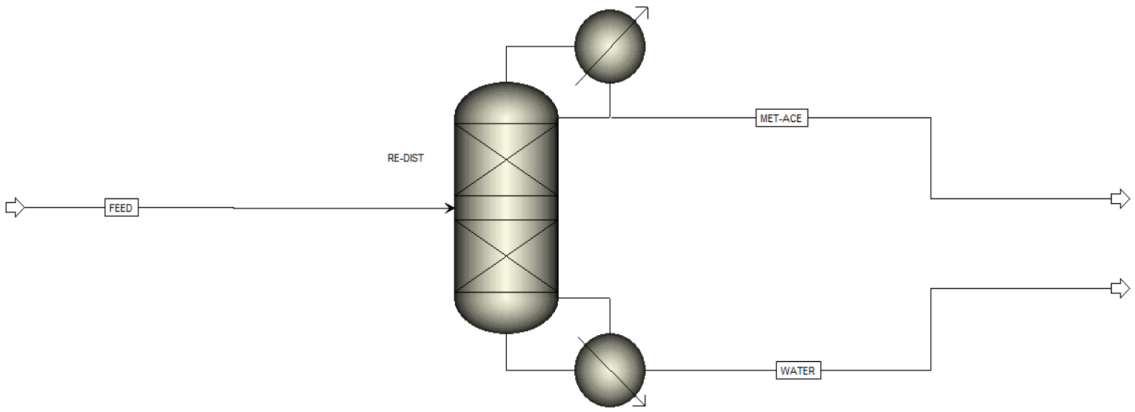


Figure 3: Simulation flow chart of the RadFrac column with mixed single flow feed.

Temperature and pressure of 25°C and 1 bar respectively, was selected because at higher pressure (pressure above 1.3 bar) it becomes difficult to achieve the desired separation. Reaction equilibrium is a very important factor in reactive distillation, hence to maintain the equilibrium these conditions were chosen. At pressure of 1 bar, there is a minimum reflux ratio of r=1.3 and maximum r=2.8. Outside these ranges, even infinite number of equilibrium stages will not fulfil the desired separation. By increasing the pressure, the number of stages also increase. On increasing the temperature, equilibrium constant decreases with lead to other side reactions. Hence, and optimum value of reflux ratio r=1.7 is chosen at given temperature and pressure. The reactive distillation of methyl acetate was simulated with the following conditions:

Temperature	25°C
Pressure	1 bar
Total feed flow rate	2072 kg/hr
Molar composition of feed	
Methanol	0.5
Acetic acid	0.5
Water	0
Methyl acetate	0

Table 1: Feed conditions.

Table 2: Reactive column specifications.

Number of trays	24
Feed stage	11
Distillate rate	20 kmol/hr
Reflux ratio	1.7
Condensation	Total
Valid phases	Vapour-liquid
Top column pressure	0.9 bar

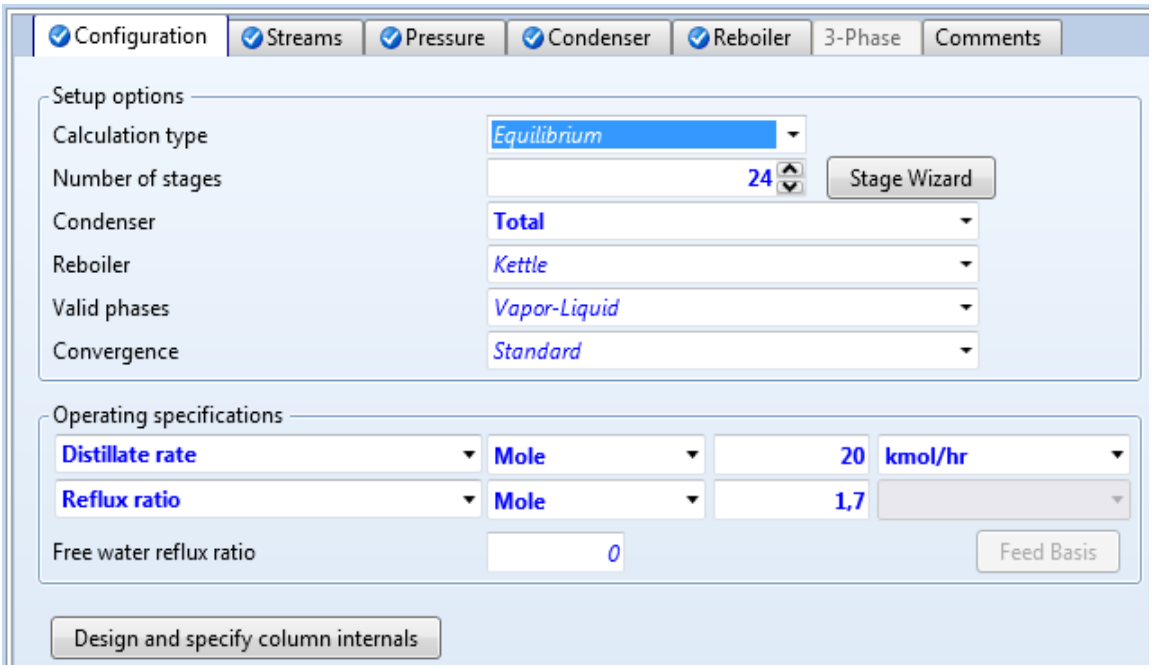


Figure 4: Configuration of reactive column.

It is important to setup the reaction according to its stoichiometry and its eligible range for the column. Unless the reaction is not added to the column block configurations separately, the feed that goes in will not react even if the reaction conditions are specified and the desired product reaction and separation will not be achieved. This will result in the failure of the simulation and wrong calculations will be displayed. A value of 100-150 iterations for the calculation of the convergence should be set so as to achieve more accurate values of the output products. Figure 5 shows the reaction added to the column simulation.

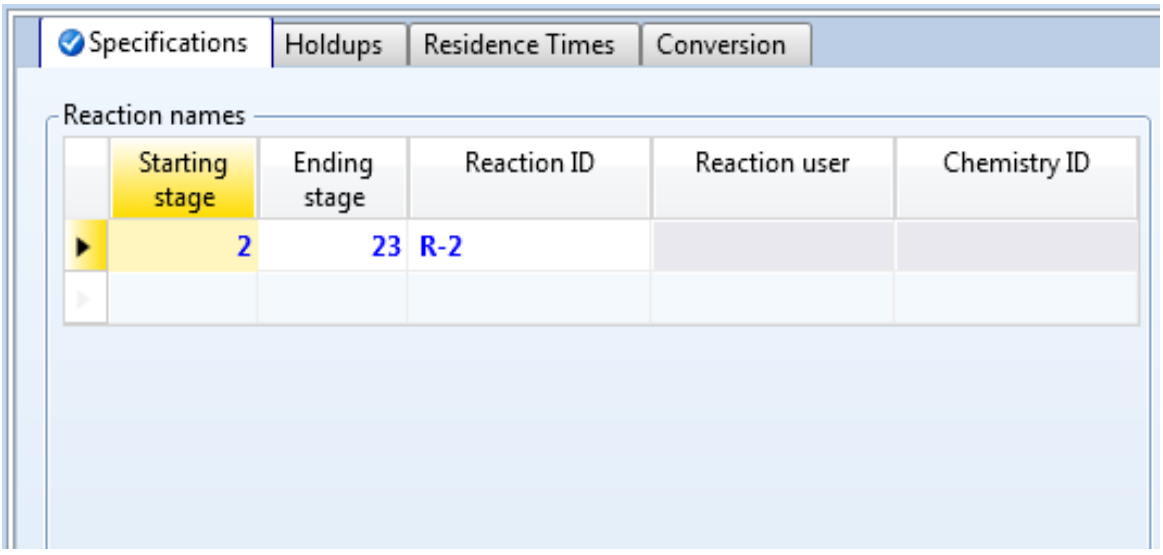


Figure 5: Specifying reaction and its range in the column.

3. RESULTS AND DISCUSSIONS

After running the simulation when no errors were displayed, the following results were achieved. With a single feed flow of acetic acid and methanol mixed together at a mass flow rate of 2072 kg/hr (or 45 kmol/hr), methyl acetate with a molar fraction of almost 0.81 was produced and collected in the output stream of the condenser. Water was extracted from the reboiler in the bottom with a molar fraction of 0.70.

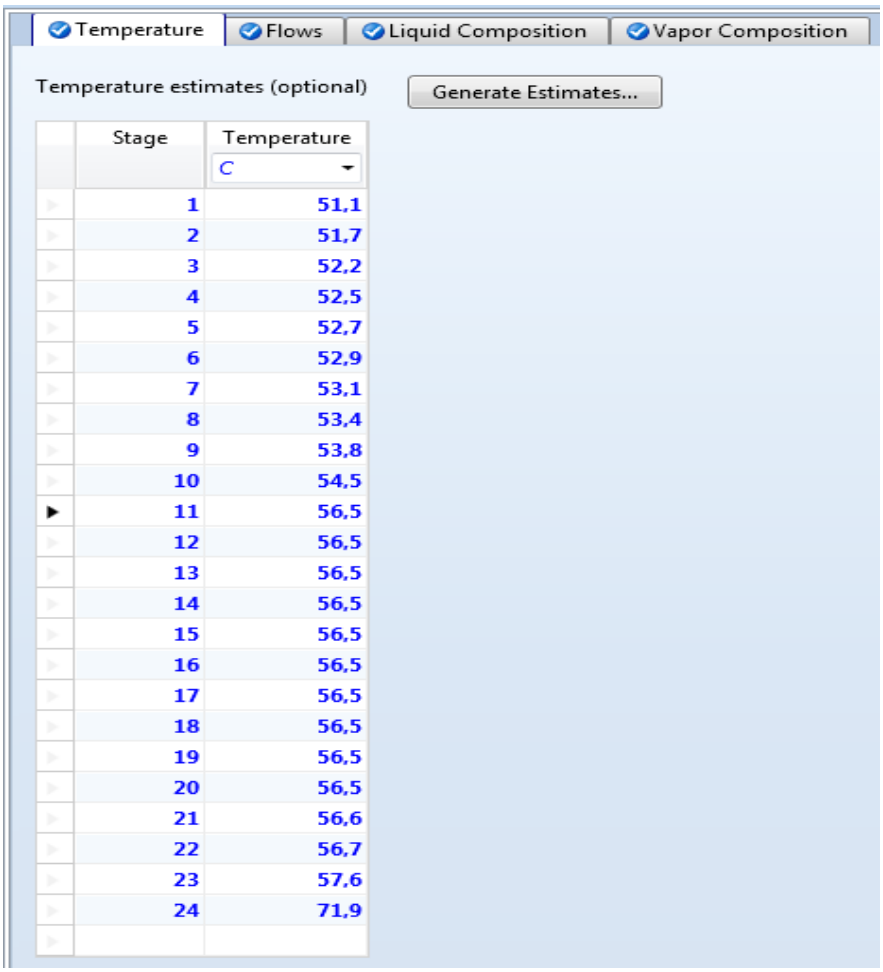
Figure 6 below, shows the stream results generated for the reactive distillation for producing methyl acetate.

Material | Heat | Load | Work | Vol.% Curves | Wt. % Curves | Petroleum | Polymers | Solids

	Units	FEED	MET-ACE	WATER	
Phase		Liquid Phase	Liquid Phase	Liquid Phase	
Temperature	C	25	51,1479	71,9273	
Pressure	bar	1	0,9	0,9	
Molar Vapor Fraction		0	0	0	
Molar Liquid Fraction		1	1	1	
Molar Solid Fraction		0	0	0	
Mass Vapor Fraction		0	0	0	
Mass Liquid Fraction		1	1	1	
Mass Solid Fraction		0	0	0	
Molar Enthalpy	cal/mol	-83204,2	-96224,7	-76724,1	
Mass Enthalpy	cal/gm	-1806,93	-1457,74	-2551,02	
Molar Entropy	cal/mol-K	-56,6308	-82,8003	-42,9456	
Mass Entropy	cal/gm-K	-1,22984	-1,25437	-1,42791	
Molar Density	mol/cc	0,0205518	0,0134881	0,0304451	
Mass Density	gm/cc	0,946356	0,890342	0,915662	
Enthalpy Flow	cal/sec	-1,03999e+06	-534582	-532746	
Average MW		46,0474	66,0095	30,0758	
+ Mole Flows	**kmol/hr**	**44,9972**	**20**	**24,9972**	
− Mole Fractions					
METHA-01		0,5	0,166918	0,046302	
ACETI-01		0,5	0,000294328	0,179616	
WATER		0	0,0187105	0,705224	
METHY-01		0	0,814077	0,068858	
+ Mass Flows	**kg/hr**	**2072**	**1320,19**	**751,809**	

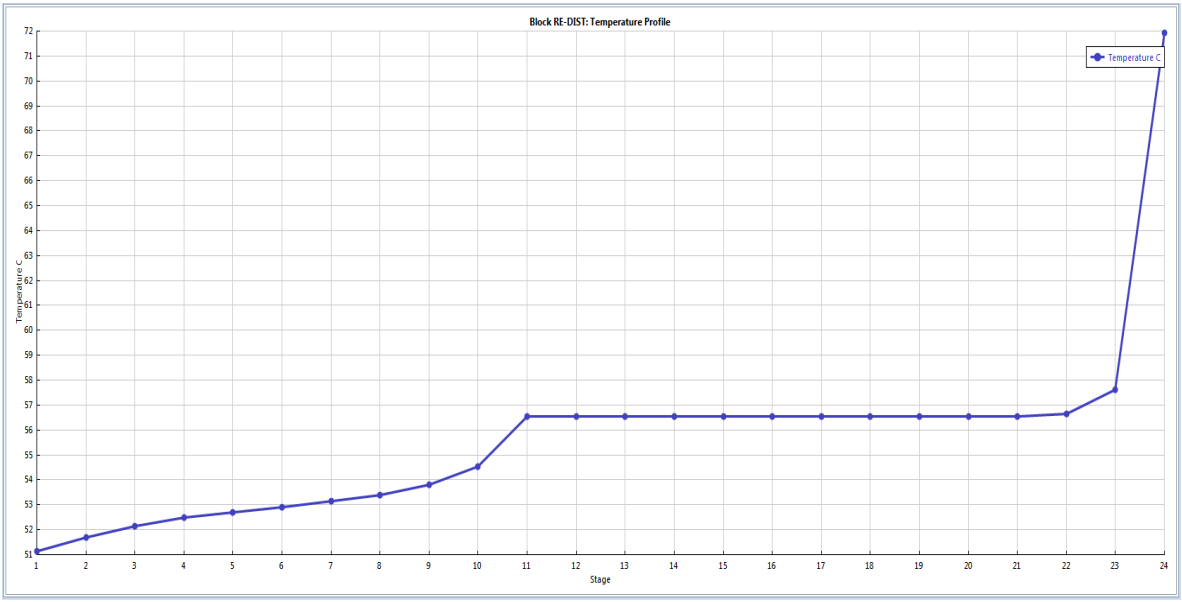
Figure 6: Stream results of the reactive distillation for producing methyl acetate.

Figure 7 shows the stage-wise temperature gradient estimates and graph 1 shows the stage wise temperature profile as the distillation proceeded.



Stage	Temperature C
1	51,1
2	51,7
3	52,2
4	52,5
5	52,7
6	52,9
7	53,1
8	53,4
9	53,8
10	54,5
11	56,5
12	56,5
13	56,5
14	56,5
15	56,5
16	56,5
17	56,5
18	56,5
19	56,5
20	56,5
21	56,6
22	56,7
23	57,6
24	71,9

Figure 7: Stage-wise temperature gradient estimates.



Graph 1: Stage-wise temperature profile.

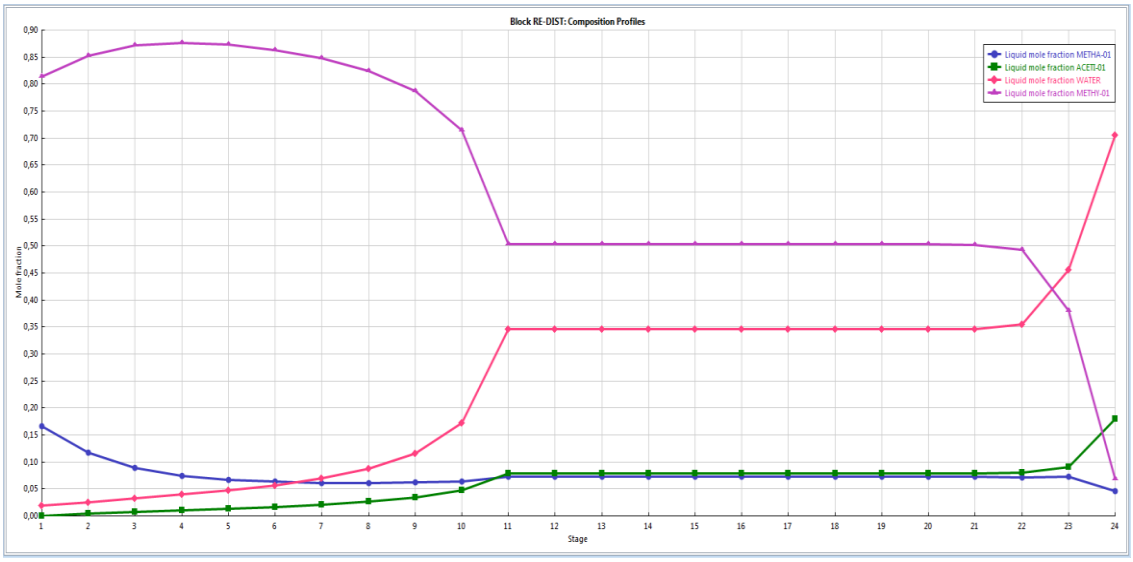
Figure 8 shows the stage-wise liquid compositions of all the components and graph 2 shows the liquid composition profiles of the components.

Temperature | Flows | Liquid Composition | Vapor Composition

Liquid mole fraction estimates (optional) Generate Estimates...

Stage	METHA-01	ACETI-01	WATER	METHY-01	
1	0,1669	0,0002944	0,01871	0,8141	
2	0,1179	0,004124	0,02548	0,8525	
3	0,08932	0,006867	0,03252	0,8713	
4	0,07438	0,00993	0,03947	0,8762	
5	0,06683	0,0132	0,04735	0,8726	
6	0,06312	0,01678	0,05707	0,863	
7	0,06148	0,02102	0,06981	0,8477	
8	0,06113	0,02652	0,08785	0,8245	
9	0,06192	0,03454	0,1165	0,787	
10	0,06454	0,04826	0,1723	0,7149	
11	0,0726	0,07807	0,3461	0,5032	
12	0,0726	0,07807	0,3461	0,5032	
13	0,0726	0,07807	0,3461	0,5032	
14	0,0726	0,07807	0,3461	0,5032	
15	0,0726	0,07807	0,3461	0,5032	
16	0,0726	0,07807	0,3461	0,5032	
17	0,0726	0,07807	0,3461	0,5032	
18	0,07259	0,07808	0,3461	0,5032	
19	0,07256	0,0781	0,3461	0,5032	
20	0,07247	0,07819	0,3461	0,5032	
21	0,07221	0,07854	0,3468	0,5025	
22	0,07172	0,08022	0,3548	0,4932	
23	0,07271	0,09056	0,456	0,3808	
24	0,0463	0,1796	0,7052	0,06886	

Figure 8: Stage-wise liquid compositions of all components.



Graph 2: Stage-wise liquid composition profiles of all components.

Overall results summary is shown in figure 9 below.

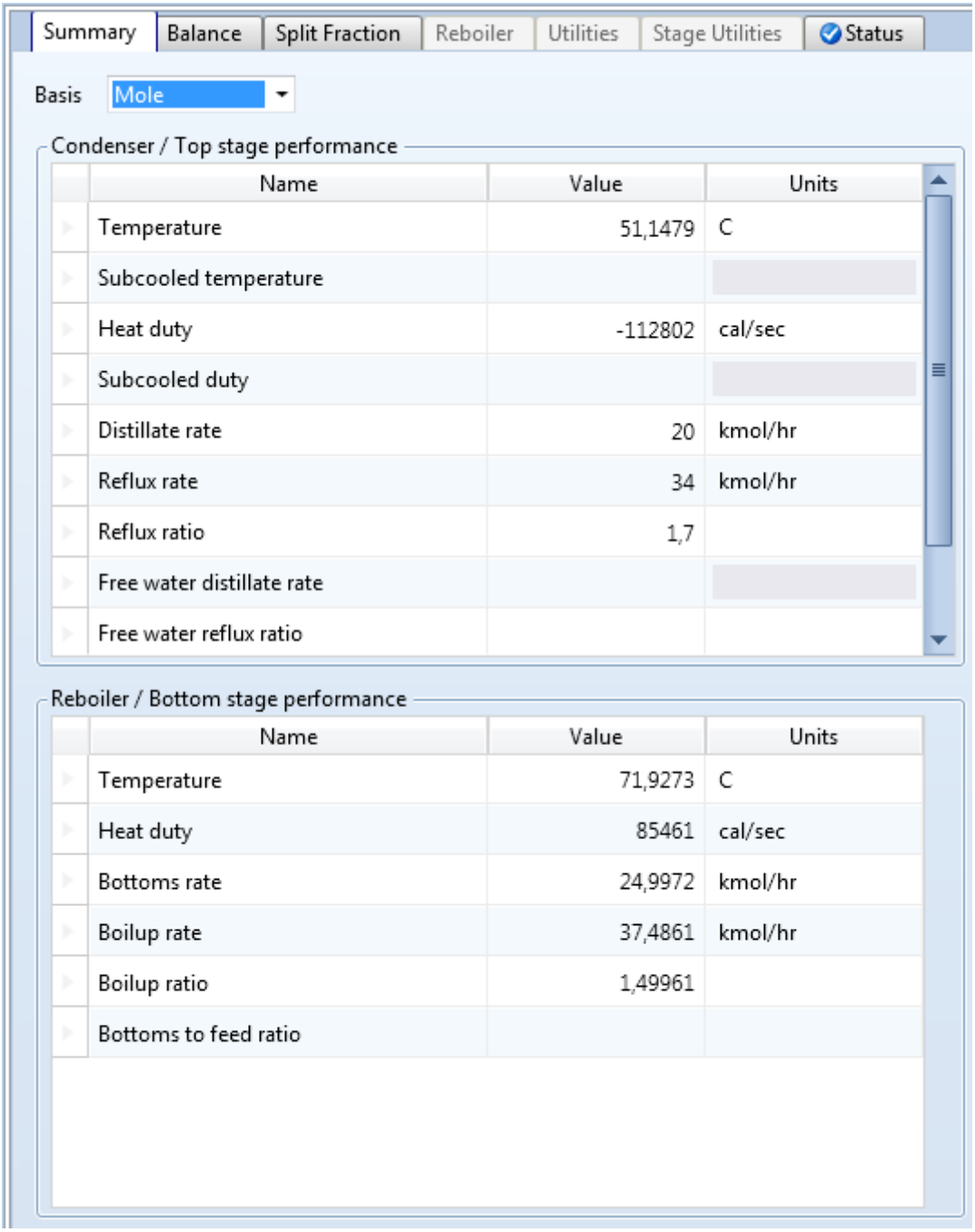


Figure 9: Overall result summary of the reactive distillation simulation.

4. CONCLUSION

Successful simulation for the methyl acetate production through a reactive distillation packed column was carried out. An output of methyl acetate with molar fraction of 0.81 was produced in the condenser along with water as a waste product in the reboiler for the reflux ratio of r=1.7 at 25°C and 1 atm. The product quality depends upon the reflux ratio, number of equilibrium stages, the pressure drop across the column. More improved results can be expected if the feed components are supplied separately in two different stages, with increased number of stages and reflux ratio.

5. FUTURE WORK

Future work can be carried out with an aim of enriching the achieved product quality. A simulation with different feed and working conditions can be carried out, also the feed can be provided in two different stages and the results can be compared. A regular distillation column can also be placed in series with the RadFrac column to attain the desired enrichment of methyl acetate.

6. REFERENCES

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[4] A. D. C. Júlio, “Comparison of Chemical Process Simulators: Aspen vs. HYSYS.”

[5] M. A. Al-Arfaj and W. L. Luyben, “Comparative control study of ideal and methyl acetate reactive distillation,” *Chem. Eng. Sci.*, vol. 57, no. 24, pp. 5039–5050, Dec. 2002.

Appendix

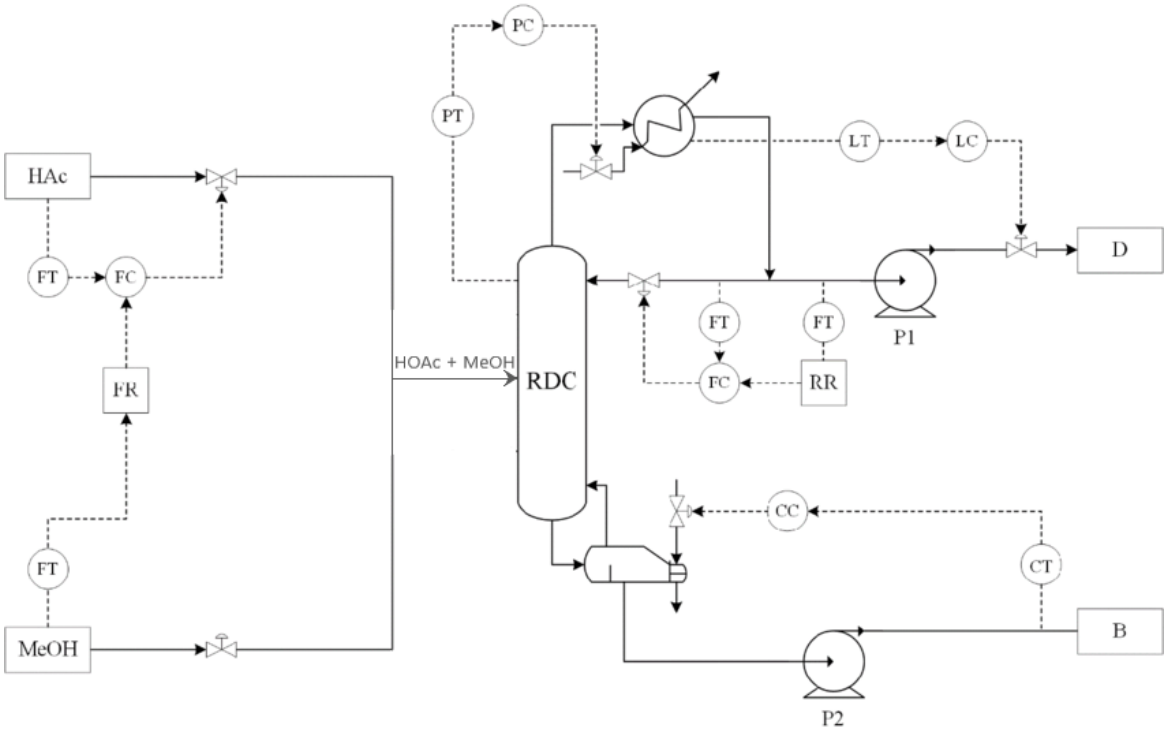

Figure I: Process flow diagram of a methyl acetate plant.

Select components

Component ID	Type	Component name	Alias
METHA-01	Conventional	METHANOL	CH4O
ACETI-01	Conventional	ACETIC-ACID	C2H4O2-1
WATER	Conventional	WATER	H2O
METHY-01	Conventional	METHYL-ACETATE	C3H6O2-3

Find | Elec Wizard | SFE Assistant | User Defined | Reorder | Review

Figure II: Specifying components in the simulation.

Stoichiometry | Kinetic | Equilibrium | Conversion | Salt | Subroutine | Comments

New | Edit

Rxn No.	Reaction type	Stoichiometry	Delete
1	EQUIL	METHA-01 + ACETI-01 <--> METHY-01 + WATER	✕

Figure III: Specifying stoichiometric reaction in the simulation.

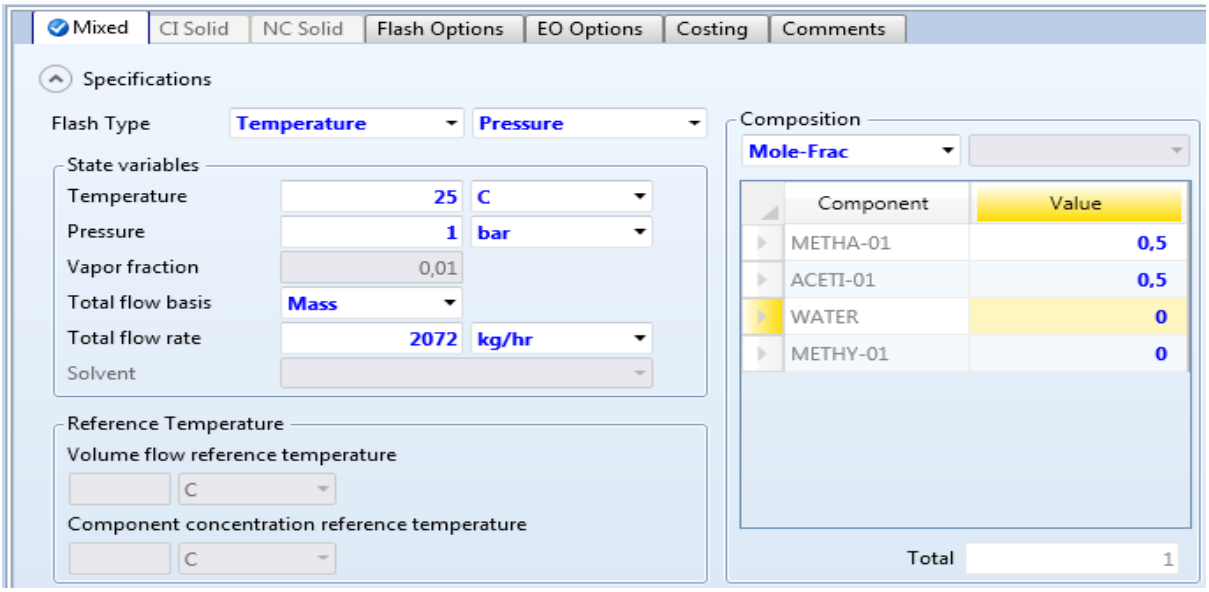

Figure IV: Specifications for mixed flow single stage feed.

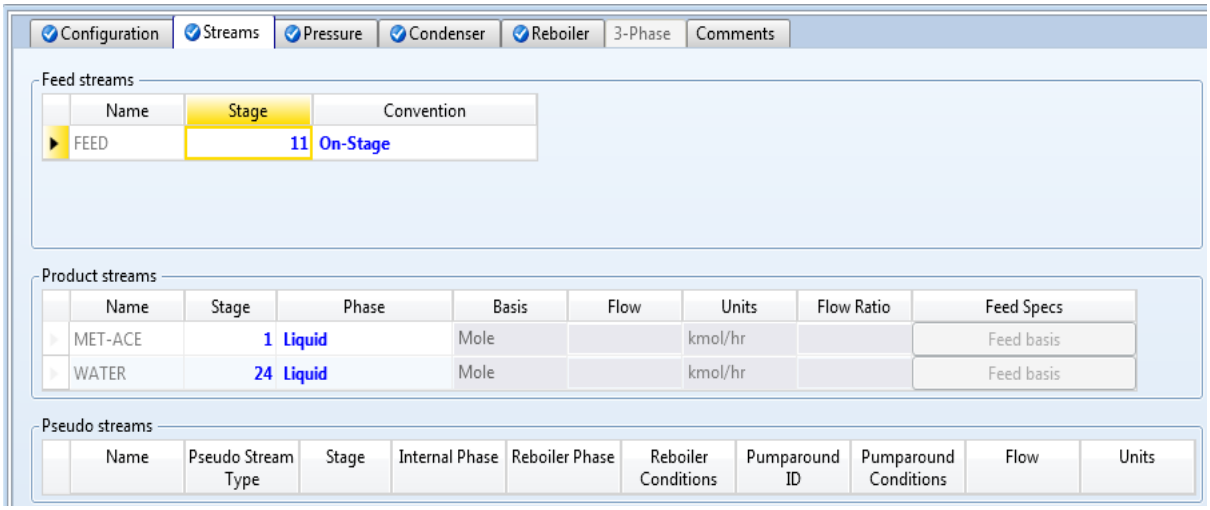

Figure V: Streams and Feed specifications.

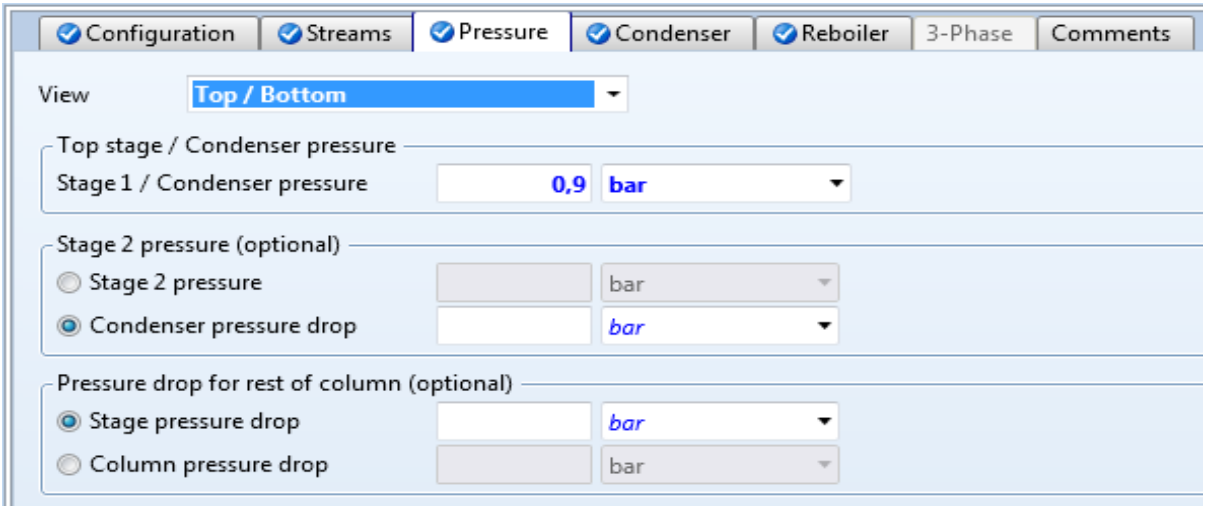

Figure VI: Specifying column pressure.