A Simulation Approach towards Material Balance of Methyl Acetate in Reactive Distillation Column Using Aspen plus

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Abstract: Reactive distillation is the combination of chemical reaction and distillation in a single unit operation. It has proven to be advantageous over conventional process systems consisting of separate reactor and distillation units. But the dynamic behavior of process is difficult to study. In this thesis, a reactive distillation column for Methyl acetate production has been created in ASPEN user interface. Steady state simulations are done in ASPEN user interface and the effect of reflux ratio on the composition of ethyl acetate in the distillate is studied. Simulation performed using a steady state RADFRAC model using NRTL Thermodynamics package for property estimation.

***Index Terms* – Reactive Distillation, Methyl Acetate, NRTL.**

I. INTRODUCTION

Methyl Acetate

Methyl acetate, also known as acetic acid methyl ester or methyl ethanoate is a carboxylate ester with the formula CH3COOCH3. It is a colorless flammable liquid with a characteristically pleasant smell. At elevated temperature, its solubility in water is much higher. Methyl acetate is also a byproduct in the industrial manufacturing process of poly vinyl alcohol. There is wide range of usage in adhesives, cement, lubricants, additives, paint additives, pigments and plasticizer industries. It is occasionally used as a solvent also, being weakly polar and lipophilic, even though its close relative, ethyl acetate, is a more common solvent being less toxic and less soluble in water. Methyl acetate is not stable in the presence of strong aqueous bases or aqueous acids. It is a volatile organic compound.

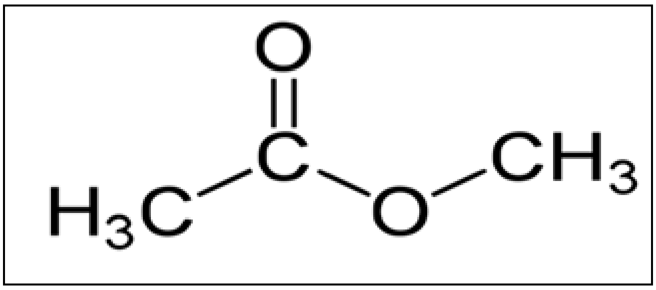

Figure No 1: Chemical Structure

Uses of Methyl Acetate

Methyl Acetate has the highest purity available in the market.High purity Methyl Acetate is used as an intermediate in a variety of synthesis applications, i.e. in production of pharmaceutical intermediates. Due to its high purity, Methyl Acetate can be used in numerous quality critical applications including as a solvent for polyurethane coatings and adhesives, blowing agent for polyurethane and other foams intermediates, process solvent for agricultural chemicals, general organic syntheses, etc. Other possible uses are paint strippers, fuel system cleaners and additives, battery electrolytes, polymerization solvents, cleaners for electronics, precision parts, photoresist strippers and inks: flexographic, gravure, marking and writing and for ink jet printers. Methyl acetate is a volatile solvent. It is therefore used in fast-drying paints and for the manufacture of celluloid adhesives from waste film. Methyl acetate is often used in lacquer solutions to lower the viscosity. Methyl acetate may also be used in perfumery and in dye manufacture.

Reactive Distillation

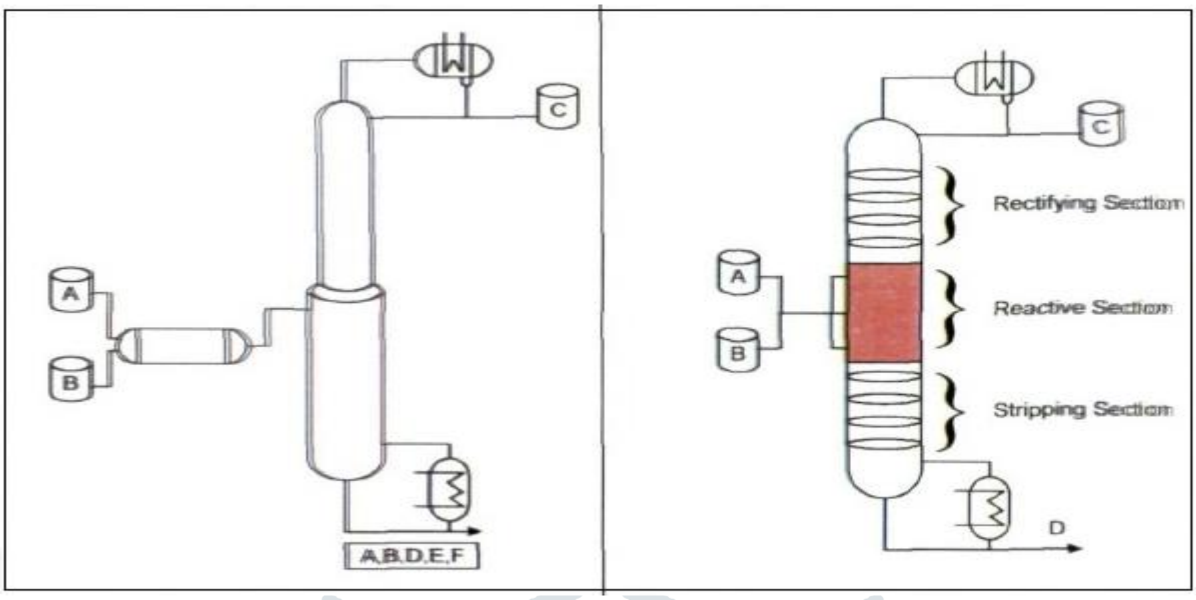

Figure No 2: Conventional and Reactive Distillation Processes [1]

Reactive distillation is an emerging technology that has considerable potential as an alternative process for carrying out equilibrium limited liquid phase chemical reactions. It is receiving increasing attention because of its high potential for process intensification.

It has proved to be an important process alternative to the conventional reactor - separator configuration, as it involves simultaneous chemical reaction and separation by distillation. The chemical reaction usually takes place in liquid or at solid catalyst surface. General application of reactive distillation is the separation of a close-boiling or azeotropic mixture. A second application of reactive distillation involves taking into account undesirable reaction that may occur during distillation but the most interesting application involves combining chemical reactions and separation by distillation in a single distillation apparatus. The technique offers a key opportunity for improving the structure of a process. It is a so-called hybrid process, i.e. it merges two different unit operations in a single apparatus, namely reaction and distillation.

The introduction of separation process in the reaction zone or vice versa leads to complex interactions between vapor–liquid equilibrium, mass transfer rates, diffusion and chemical kinetics, which poses a great challenge for design and synthesis of these systems. Reactive distillation being a relatively new field, research on various aspects such as modeling and simulation, process synthesis, column hardware design, non-linear dynamics and control is in progress. The suitability of reactive distillation for a particular reaction depends on various factors such as volatilities of reactants and products along with the feasible reaction and distillation temperature. Hence, the use of reactive distillation for every reaction may not be feasible. Exploring the candidate reactions for reactive distillations, an area that needs considerable attention to expand the domain of reactive distillation processes.

Advantages of Reactive Distillation [1]

- Simplification or elimination of the separation system can lead to significant capital savings.
- Improved conversion of reactant approaching 100%. This increase in conversion gives a benefit in reduced recycle costs.
- Improved selectivity. Removing one of the products from the reaction mixture or maintaining a low concentration of one of the reagents can lead to reduction of the rates of side reactions and hence improved selectivity for the desired products.
- Significantly reduced catalyst requirement for the same degree of conversion.
- Avoidance of azeotropes, it is particularly advantageous when the reactor product is a mixture of species that can form several azeotropes with each other. Reactive distillation conditions can allow the azeotropes to be reacted away in a single vessel.
- Reduces by-product formation.
- Heat integration benefits. If the reaction is exothermic, the heat of reaction can be used to provide the heat of vaporization and reduce the reboiler duty.
- Avoidance of hot spots and runaways using liquid vaporization as thermal fly wheel.

II. PROCESS MODELING

Continuous reactive distillation operation is analogous to that of continuous distillation operation. The equilibrium model equations are essentially mass and energy balances. In addition, it is assumed that the interfacial compositions are in equilibrium with each other, therefore they are related. HETPs of both reactive and non-reactive packing are chosen empirically, and the same is used in our simulation studies, as the number of theoretical stages. Figure No. 3 shows the schematic diagram of reactive distillation and equilibrium stage.

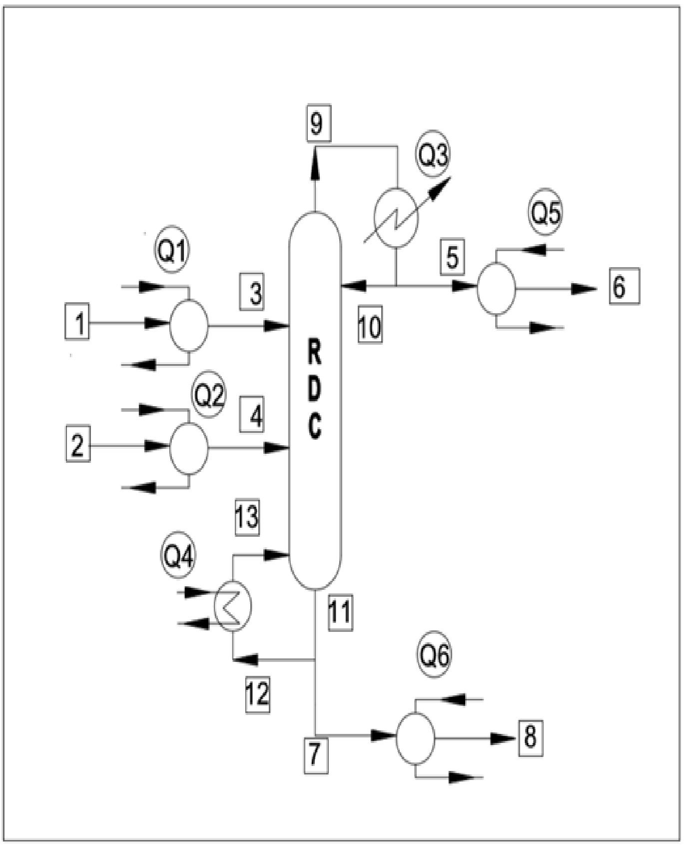

Figure No 3: The number of theoretical stages

Table No 1: Stream Data

Stream No	Description
1	Feed Acetic Acid
2	Feed Methanol
3	Pre Heated Acetic Acid
4	Pre Heated Methanol
5	Distillate Out (D)
6	Cooled Distillate
7	Bottoms Out (W)
8	Cooled Bottoms
9	Total Vapors Out
10	Reflux In (L)
11	Total Bottoms
12	Reboiler Feed
13	Sent Back to Distillation Column

Assumptions:

- The process has reached steady state.
- The liquid composition at each stage is homogeneous and equal to the composition of the liquid leaving the stage.
- The vapour and liquid leaving at any stage are in equilibrium.
- The mathematical equations describing the steady state equilibrium stage wise process are given

III. MATERIAL BALANCE

Material Balances are the basis of process design. A material balance taken over complete process will determine the quantities of raw materials required and products produced. The general conservation equation for any process can be written as:

Material In = Material Out + Accumulation + Disappearance

For a steady state process, accumulation is equal to zero.
Material In = Material Out + Disappearance

If a chemical reaction is taking place, a particular chemical species may be formed or consumed. But if there is no chemical reaction, the steady state balance reduces to:
Material In = Material Out

A balance equation can be written for each separately identifiable species present, elements.

$$CH_3COOH + CH_3OH \longrightarrow CH_3COOCH_3 + H_2O$$

Overall Material Balance:

Table No 2: Overall Material Balance

Components	IPUNT (Kg/hr)	OUTPUT Kg/hr
Acetic Acid	1000.00	2.000
Methanol	640.30	107.812
Methyl Acetate	--	1231.171
Water	--	299.317
Total	**1640.30**	**1640.30**

Feed Pre-Heater

Both Acetic Acid and Methanol are pre heated to50oC using feed pre-heater. Assuming of steady state conditions, there is no accumulation present. 1000Kg of Acetic Acid is fed to Pre-Heater 1 and 640.3Kg of Methanol is fed to Pre-Heater 2.

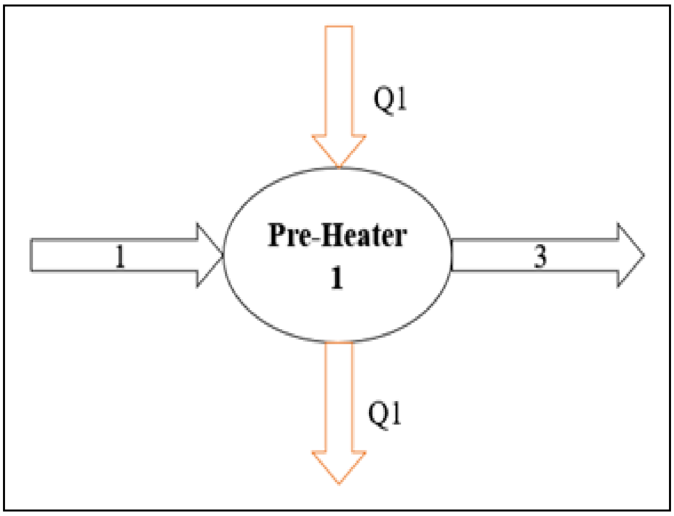

Figure No 3: Schematic Representation of Feed Pre-Heater 1

Table No 3: Material balance for Feed Pre-Heater 1

STREAM COMPONENT	INPUT (Kg/hr)	OUTPUT (Kg/hr)
	1	**3**
Acetic Acid	1000.00	1000.00
Methanol	--	--
Methyl Acetate	--	--
Water	--	--
Total	**1000.00**	**1000.00**

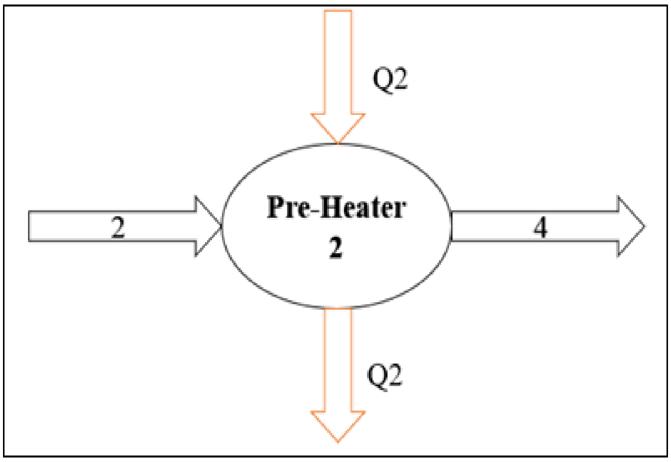

Figure No 4: Schematic Representation of Feed Pre-Heater 2

Table No 4: Material balances for Feed Pre-Heater 2

STREAM COMPONENT	INPUT (Kg/hr)	OUTPUT (Kg/hr)
	2	**4**
Acetic Acid	--	--
Methanol	640.30	640.30
Methyl Acetate	--	--
Water	--	--
Total	**640.30**	**640.30**

Reactive Distillation Column (RDC)

Feed Acetic Acid and Methanol is fed to column shown in Figure No9 from stream 3 and 4 respectively, and Methyl Acetate is withdrawn from the distillate (Stream 3). Remaining heavy ends(viz., Acetic Acid, Water, Methanol) are removed from bottom of column (Stream 4). Reflux Ratio kept for system is 2 (R=L/D). The outlet flow of Distillate is considered 1230 Kg/hr. The mass fraction data used is achieved from Aspen Plus v10.2 simulation.

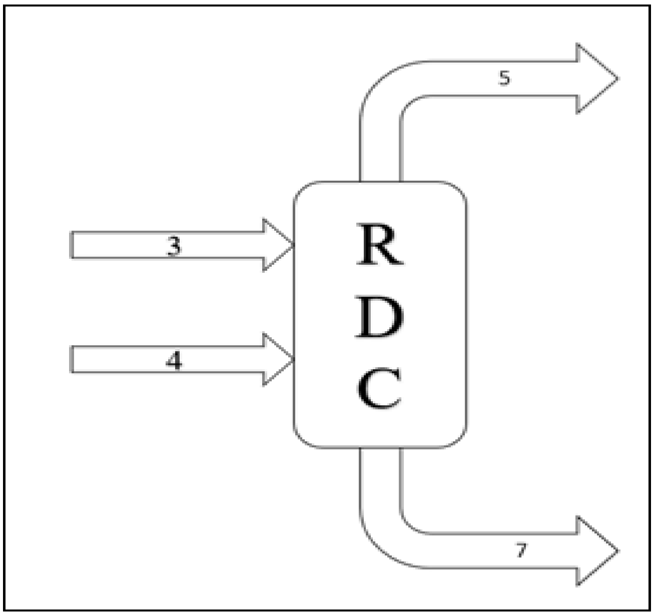

Figure No 5: Schematic Representation of Reactive Distillation Column

Table No 5: Overall Material Balance for RDC

STREAM / COMPONENT	INPUT		OUTPUT	
	3	**4**	**5**	**7**
Acetic Acid	1000	-	0.001	1.999
Methanol	-	640.3	0.400	107.412
Methyl Acetate	-	-	1227.488	3.684
Water	-	-	2.111	297.206
Total	**1000.00**	**640.30**	**1230.00**	**410.3**
	1640.30		**1640.30**	

Table No 6: Mass Fraction of Distillate

Chemical	Mass Fraction
Acetic Acid	$8.865e^{-07}$
Methanol	$3.251e^{-04}$
Methyl Acetate	0.9979
Water	$1.72\ e^{-03}$
Total	**1.000**

Table No 7: Mass Fraction of Bottoms

Chemical	Mass Fraction
Acetic Acid	0.005
Methanol	0.262
Methyl Acetate	0.009
Water	0.724
Total	**1.000**

Top Product Cooler

The distillate which is withdrawn from reactive distillation column's main condenser has to be further cooled to remove the sensible heat of mass and for maintaining proper storage conditions. Methyl Acetate can be stored at NTP conditions.

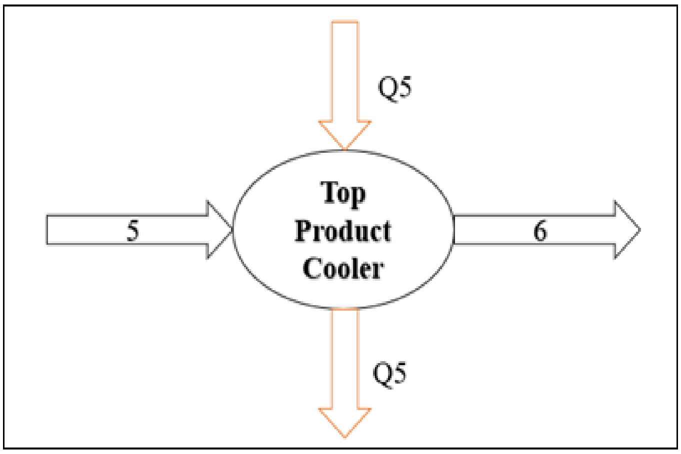

Figure No 6: Schematic Representation of Top Product Cooler

Table No 8: Material balance for Top Product Cooler

STREAM / COMPONENT	INPUT (Kg/hr)	OUTPUT (Kg/hr)
	5	**6**
Acetic Acid	0.001	0.001
Methanol	0.400	0.400
Methyl Acetate	1227.488	1227.488
Water	2.111	2.111
Total	**1230.000**	**1230.000**

Bottom Product Cooler

Residual which are taken out from reactive distillation column are cooled down to a temperature at which it can be stored.

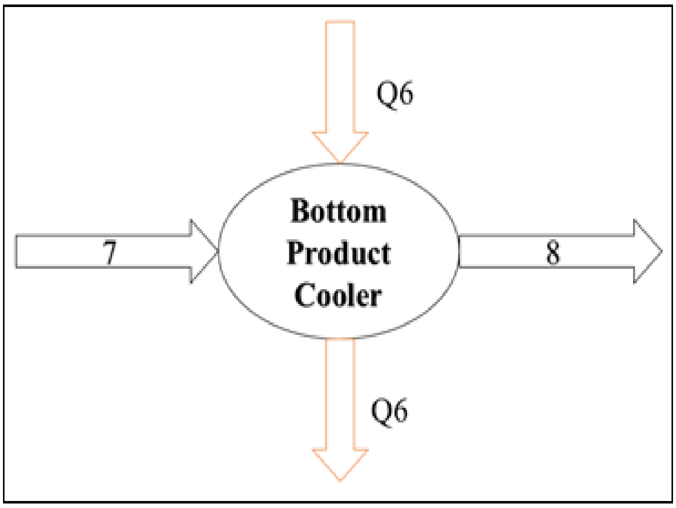

Figure No 7: Schematic Representation of Bottom Product Cooler

Table No 9: Material balance for Bottom Product Cooler

STREAM / COMPONENT	INPUT (Kg/hr)	OUTPUT (Kg/hr)
	7	**8**
Acetic Acid	1.999	1.999
Methanol	107.412	107.412
Methyl Acetate	3.684	3.684
Water	297.206	297.206
Total	**410.300**	**410.300**

IV. RESULTS AND DISCUSSION

Table No 10: Stream Summary by theoretical calculations in Kg/hr

Component	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**
Acetic Acid	1000	--	1000	--	0.001	0.001	1.999	1.999	0.003	0.002	5.997	3.998	3.998
Methanol	--	640.30	--	640.30	0.40	0.40	107.412	107.412	1.20	0.80	322.236	214.824	214.824
Methyl Acetate	--	--	--	--	1227.488	1227.488	3.684	3.684	3682.463	2454.975	11.051	7.367	7.367
Water	--	--	--	--	2.111	2.111	297.206	297.206	6.334	4.223	891.617	594.411	594.411
Total	1000	640.30	1000	640.30	1230.00	1230.00	410.30	410.30	3690.00	2460.00	1230.90	820.60	820.60

Molar Flow Rate

Given is molar flow rate of vapors and liquid throughout the column. In rectifying section vapor molar flow is highly observed and liquid flow rate is due to the reflux given to system which 2. In reaction section acetic acid, methanol fed to column is there and stripping section excess methanol and water which is formed in reaction is present.

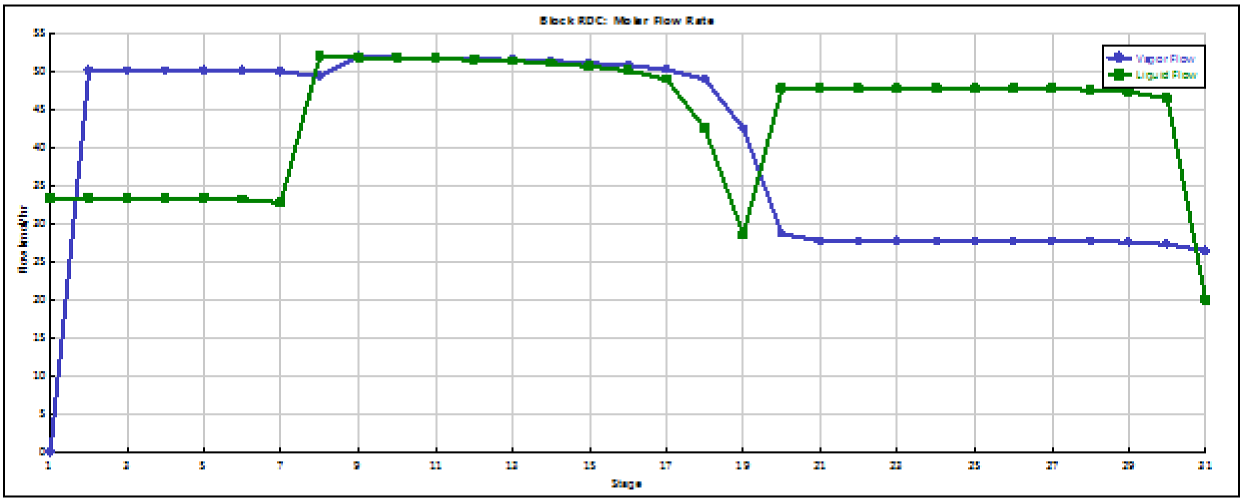

Figure No 8: Analysis for Molar Flow Rate

Composition Profiles

Figure 9 shows the variation of liquid phase composition of all the components, along the column height. The concentrations are shown in mole fractions. From Figure 9 it is clear that there is some amount of methyl alcohol present in the liquid phase below the stage 20. Acetic acid is present only in the reactive section, indicating reaction with methanol. Almost pure methyl acetate is observed in top stages while water formed in reaction and excess methanol fed to column is seen in bottoms.

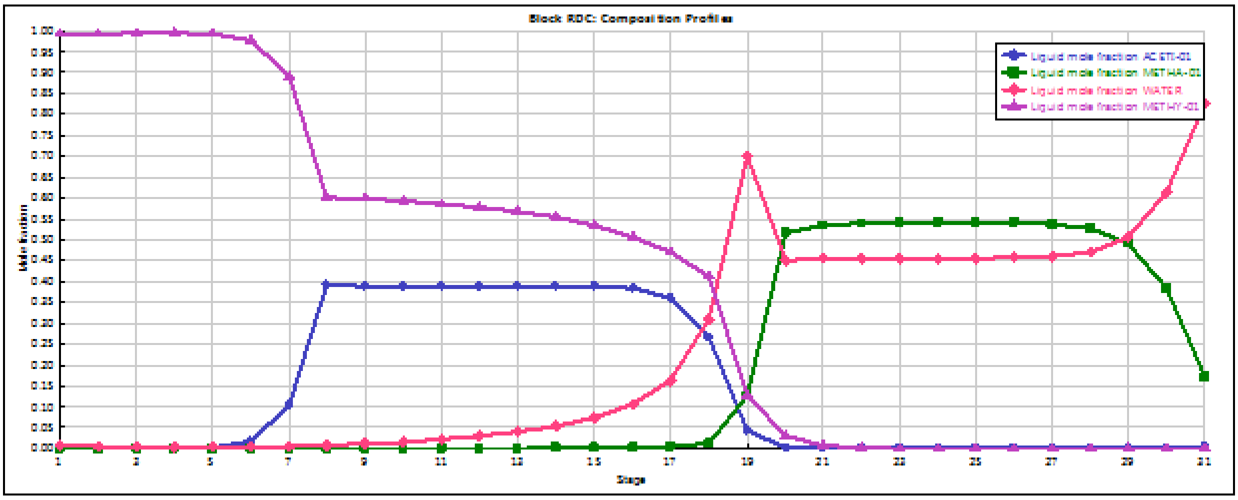

Figure No 9: Composition profiles in Liquid Phase

Figure 10 shows the variation of vapour phase composition of all the components, along the column height. The concentrations are shown in mole fractions. From Fig. 10 it is clear that there is considerable amount of methyl alcohol present in the vapour phase below the stage 20 as temperature at lower part is high. Acetic Acid is present only in the reactive section, indicating reaction with methanol. Pure Methyl Acetate is observed in vapour phase. Due to high boiling point of water the vapour phase composition is low at bottom side of column.

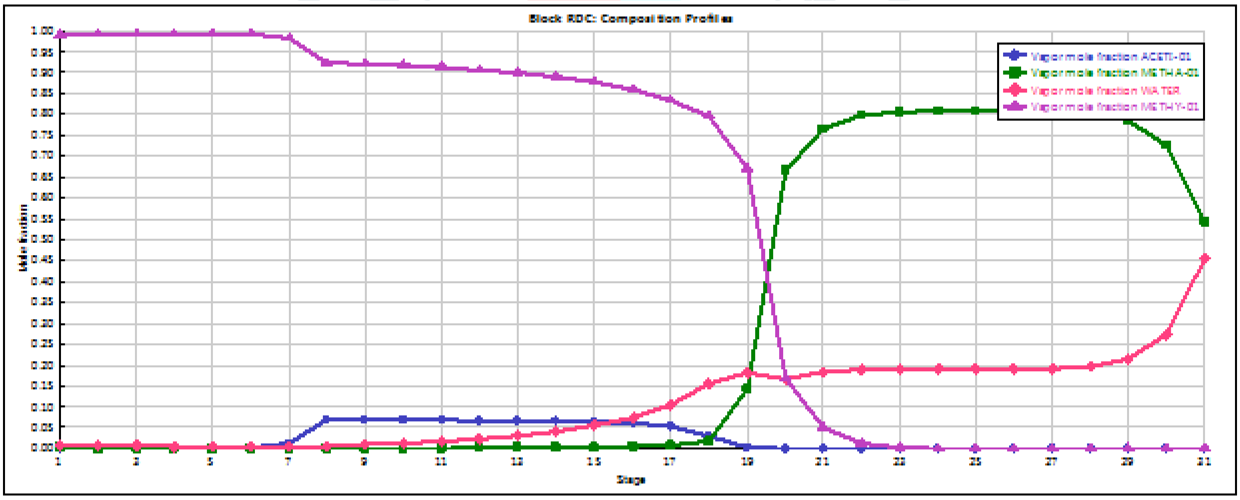

Figure No 10: Composition profiles in Vapor Phase

V. CONLUISON

The good convergence obtained from the simulation of the Aspen PLUS model developed for the reactive distillation esterification process used for the production of methyl acetate has shown the versatility of Aspen PLUS in successfully representing the behavior of the complex reactive distillation process. The attainment of the objective function given by the optimization when the estimated optimum values of reflux ratio and reboiler duty were used to run the model revealed that the optimum values obtained from Aspen PLUS.

The design of a methyl acetate reactive distillation column was modeled using a double- feed RadFrac column. A simulation of the column and a sensitivity analysis was conducted to determine the possibility of input multiplicity. The composition and temperature profiles versus stage number have been predicted. Temperature gradually falls from reboiler to condenser but the temperature remains constant in reactive section. The methyl acetate composition increased from reboiler position to condenser while the water composition decreased. The high purity of methyl acetate obtained in distillate.

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