

# Modeling and Simulation of Dual Reactive Distillation Column for Polyacrylate Synthesis: A Novel Approach

Chitragda Singh<sup>1</sup>, Sumint S. Trivedia<sup>2</sup>, Shriram Prasad<sup>3</sup>

<sup>1</sup>PG Scholar, Dept. of Chemical Engineering, Madhav Institute of Technology & Science, Madhya Pradesh, India

<sup>2</sup>Assistant Professor, Dept. of Chemical Engineering, Madhav Institute of Technology & Science, Madhya Pradesh, India

<sup>3</sup>Associate Professor, Dept. of Chemical Engineering, Madhav Institute of Technology & Science, Madhya Pradesh, India

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**Abstract** – Poly (methyl methacrylate), polymer of Polyacrylate group, is of great industrial interest due to its excellent optical and medical performance as plexiglass, optical fibers, fracture fixations and bone cement respectively. Conventionally, this polymer was synthesized using batch reactor with product purity not more than 80%. To solve this conversion problem, in this paper, we proposed an innovative Poly (methyl methacrylate) process based on dual reactive distillation unit which allows the production of high purity polymer latex with minimal cost. This study made a fair comparison between the conventional and optimally designed process based on reactive distillation. The process was optimized by simulating the Radfrac model in Aspen Polymer plus environment. The results clearly demonstrate that the polymer latex attained the maximum purity of more than 95% in reactive distillation column as compared to conventional method.

**Key Words:** Reactive Distillation, Aspen Polymer plus, Polyacrylate, Simulation, Radfrac model, Latex

## 1. INTRODUCTION

With the rapid development of industry, the size of polymer demand has been increased, so dealing with the intensified system of emulsion polymerization process can not only improve the product quality but may also reduce the energy consumption during reaction phase. The emulsion polymer latex obtained using batch and continuous reactors have been applied in many important areas [1]. Researchers have done lot of work in the synthesis of polymer latex and attained good results [2-4]. However, they keep the process condition and recipe confidential and have not achieved high product purity.

In emulsion polymerization, an aqueous dispersion of monomer is converted by free-radical polymerization into a stable dispersion of polymer particles, known as emulsion latex [5]. The main advantages of emulsion polymerization over solution and suspension polymerization includes: Low

viscosity of the reaction mixture, easy thermal control, higher conversions, high polymerization rates, final latex may be directly usable in paints.

Shimada et al. reported a process for the production of methyl methacrylate polymers, wherein the monomer were polymerized by bulk polymerization procedure at 150° & 180°C with a conversion of 50 to 80% and oligomers were separated from volatiles by conventional distillation process [6]. However, this method had the drawback of heat control and molecular weight distribution.

One of the promising ways to integrate different phenomena or operation together for process intensification is Reactive Distillation (RD) technology [7-10]. The advantages of RD include: increased yield because of overcoming chemical and thermodynamic equilibrium limitations, increased selectivity via suppression of undesired consecutive reactions, reduced energy consumption due to direct heat integration in the case of exothermic reactions, and ability to separate close boiling components [11].

In this work, we addressed an innovative system of dual RD column for PMMA latex synthesis where the simulation results for two different reaction schemes using Radfrac model in Aspen Polymer plus were compared with the conventional polymerization batch reactor existing literature and simulation data. The aim of this study was to improve the product purity at optimal operation of the proposed dual RD column. This paper combined the relative literature data and the correction in the actual simulation we had done, to get the better simulation effects. The predictive process design requires a detailed model considering both the dynamic character of batch processes and the influence of chemical reactions on the mass transfer. Therefore, a rigorous rate-based approach has been developed including heat and mass transfer, coupled with chemical reaction.

## 2. PROCESS MODEL

The model assumes adiabatic operation and the reaction takes place in the liquid phase. The vapour and liquid leaving any stage are in phase equilibrium with negligible heat of mixing of liquid and vapor mixtures. The vapor holdup on each stage is assumed to be negligible. The hydrodynamic effects are neglected to avoid the modeling complexities [12-14]. With reference to the column configuration given in Fig. 1, the model equations are presented in this section.

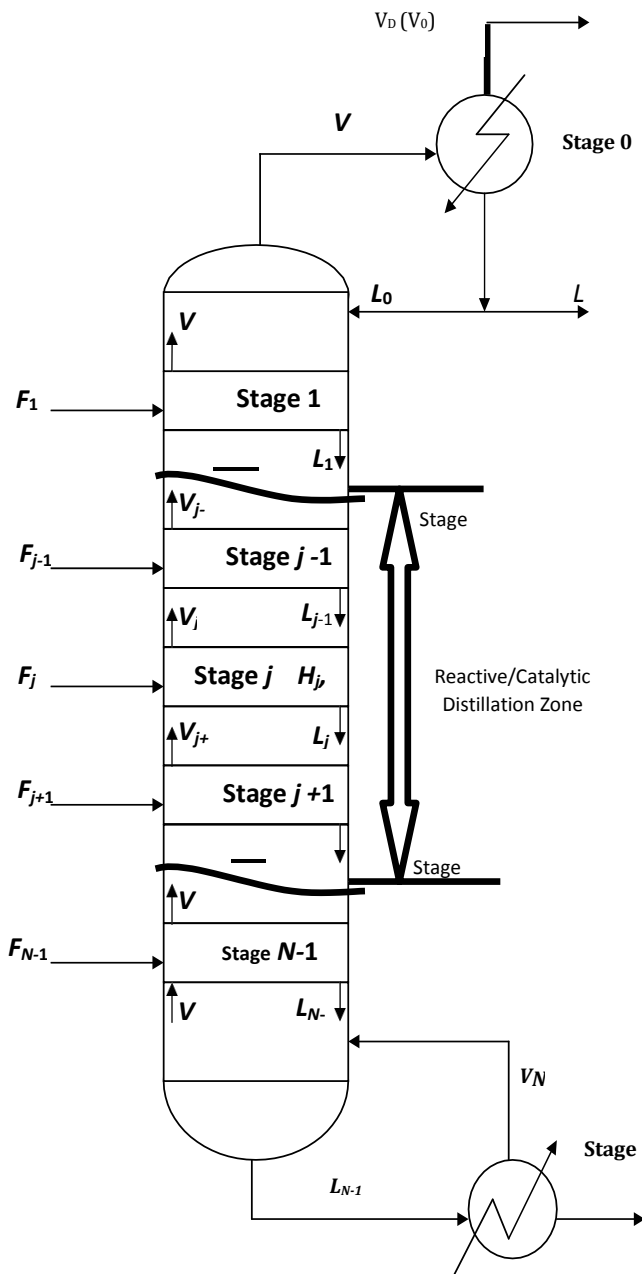


Fig. 1: Schematic Representation of Reactive Distillation Column

The overall material balance for equilibrium stage  $j$ :

$$F_j + L_{j-1} + V_{j+1} + \delta_j R_j = L_j + V_j \quad (\text{mol/s}) \quad (1)$$

Unsteady state component  $i$  material balance:

$$M_j \frac{dx_{i,j}}{dt} = (F_j z_{j,i} + L_{j-1} x_{j-1} + V_{j+1} y_{j+1}) - (L_j x_{j,i} + V_j y_{j,i}) + \delta_j \sum (v_{r,i} r_{j,r}) \quad (\text{mol/s}) \quad (2)$$

where  $j = 1, 2, \dots, N-1$ ;  $i = 1, 2, \dots, c$ ;  $r = 1, 2, \dots, R$

$j$  is the stage number,

$i$  is the component number,

$r$  is the specific reaction number.

The following definitions are useful in understanding and clarifying the derived material balance:

- Liquid hold-up on stage  $j$ ,  $H_j$  is defined as the molar quantity (or volumetric quantity) of liquid mixture that remains or held at certain level on stage  $j$ .
- $R_j$  is the total numbers of moles generated or disappear through reaction on stage  $j$ .
- $r_{j,r}$  is the rate of reaction  $r$  on stage  $j$  (mol/s). Parameter  $\alpha_j$  (0 or 1) refers to reaction occurrence on stage  $j$ . When reaction occurs on stage  $j$ ,  $\alpha_j$  is set to unity but when there is no reaction;  $\alpha_j$  is set to zero value.
- Symbols  $z_{j,i}$ ,  $x_{j,i}$ ,  $y_{j,i}$  are component  $i$  mole fractions of feed flow  $F_j$  (mol), liquid flow  $L_j$  (mol), and vapour flow  $V_j$  (mol) on stage  $j$  respectively.
- The  $v_{r,i}$  term is the stoichiometric coefficient of component  $i$  for reaction  $r$ .

The steady state energy balance for stages  $(j+1 \dots j-1)$ :

$$L_{j-1} C_{PL} (T_{j-1} - T_j) + V_{j+1} C_{PV} (T_{j+1} - T_j) = \sum_{j=1}^C V_{j+1} y_{i,j+1} H_{i,j+1}^V + \delta_j W \sum_{r=1}^R (\Delta H^R)_{j,r} r_{j,r} \quad (J/s) \quad (3)$$

where,

$C_{PL}$  = liquid mixture heat capacity,

$C_{PV}$  = vapor mixture heat capacity,

$H_{i,j+1}^V$  = heat of vaporization of component  $i$  on stage  $j+1$ ,

$\Delta H^R$  = heat of reaction in J/mol, and

W = weight of the catalyst (g).

Phase Equilibrium:

$$y = \gamma P^o x / \phi P \tag{4}$$

The vapor phase is assumed to be ideal so that the entire fugacity coefficients  $\phi$  for the system are equated to unity. The activity coefficients  $\gamma$  that characterize liquid phase non-ideality are calculated from the NRTL method. The saturated vapour pressure  $P^o$  is calculated from the Antoine equation and  $P$  is the total pressure.

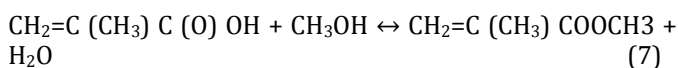
Summation (constraint) equations:

$$\sum_{i=1}^C x_{i,j} = 1.0 \text{ (liquid phase)} \tag{5}$$

$$\sum_{i=1}^C y_{i,j} = 1.0 \text{ (vapor phase)} \tag{6}$$

### 3. PROCESS SYNTHESIS

The process involves a reactor-column combination where methanol and methacrylic acid were introduced as feed stream to the first column and the esterification reaction proceeds as catalyzed according to the reaction at equilibrium given by equation (7) with the intermediate product, methyl methacrylate.



For the steady state study, an equilibrium reaction can be used. Thereafter, bottom of the first column was fed to the second column where methyl methacrylate undergoes free radical polymerization reaction to yield polymer latex, as desired product at the bottom stage. The kinetic data for polymerization was available from experiments and existing literature [15] as tabulated below:

**Table-1:** Reaction Type and Reaction Scheme

Reaction Type	Pre Exp. (1/sec)	Activation energy(J/kmol)	Initiator efficiency
INIT-DEC	1.13E+16	137000000	0.5
CHAIN- INI	3.26E+13	119710000	
PROPAGATION	12490000	17413760	
CHAT-MON	3320000	53020000	
TERM-COMB	1380000	13604500	

Table-2 illustrates the free radical emulsion polymerization mechanism and reaction scheme.

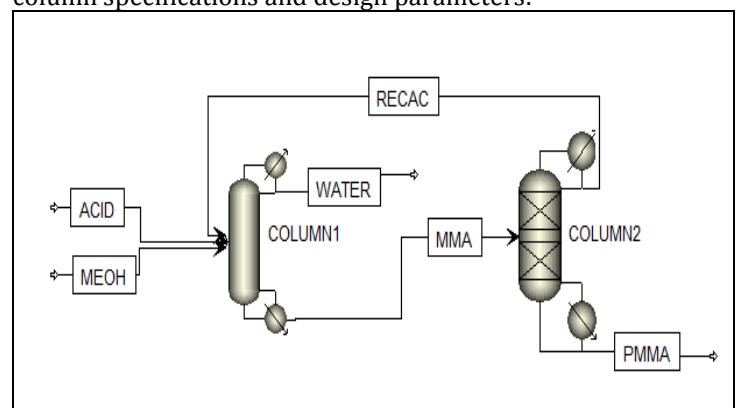
**Table-2:** Polymerization Mechanism and Reaction Scheme

Mechanism	Reaction Scheme
Initiator Decomposition	$I \rightarrow n.R^*$ Initiator $\rightarrow$ Radicals
Chain Initiation	$R^* + M \rightarrow P_1$ Primary radical + new monomer $\rightarrow$ Initial active segment
Propagation	$P_n + M \rightarrow P_{n+1}$ Active segment + Adding monomer $\rightarrow$ New active segment
Chain Transfer to monomer	$P_n + M \rightarrow D_n + P_1$ Active segment + Transfer monomer $\rightarrow$ Dead chain + Active segment
Termination by Combination	$P_n + P_m \rightarrow D_{n+m}$ Active segment + Active segment $\rightarrow$ Dead chain

### 4. PROCESS SIMULATION

Simulation for PMMA process was carried out in Aspen Polymer plus. The well-known MESH equations were governing the process. Note that MESH is an acronym referring to the type of equations: M- mass balance, E- equilibrium relationships, S - summation equations, H - enthalpy balance.

Poly NRTL (non-random two liquid) activity coefficient model was selected as the most adequate property method in Aspen Polymer plus and binary interaction parameter were estimated for the same [16, 17]. Fig. 2 presents the process flowsheet of Radfrac model. Table 3 depicts the column specifications and design parameters.



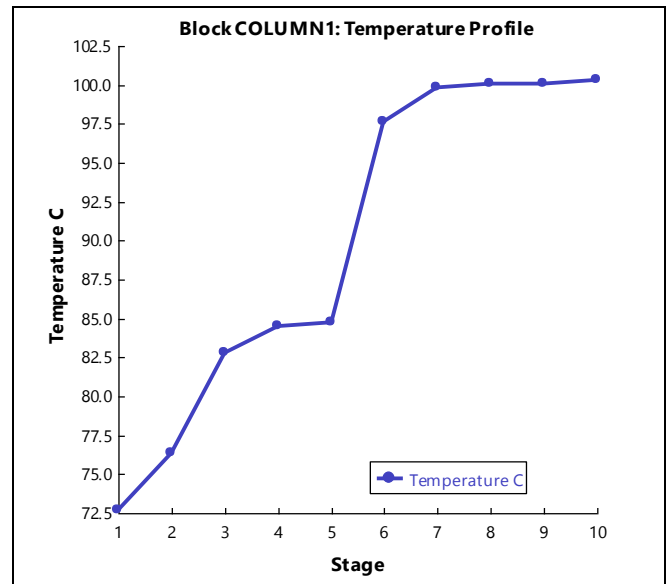
**Fig- 2:** Process Flowsheet of Dual RD column for PMMA synthesis in Aspen Polymer plus environment.

**Table-3:** Column Specification and Design parameters of Dual RD system for simulation in Aspen Polymer plus environment.

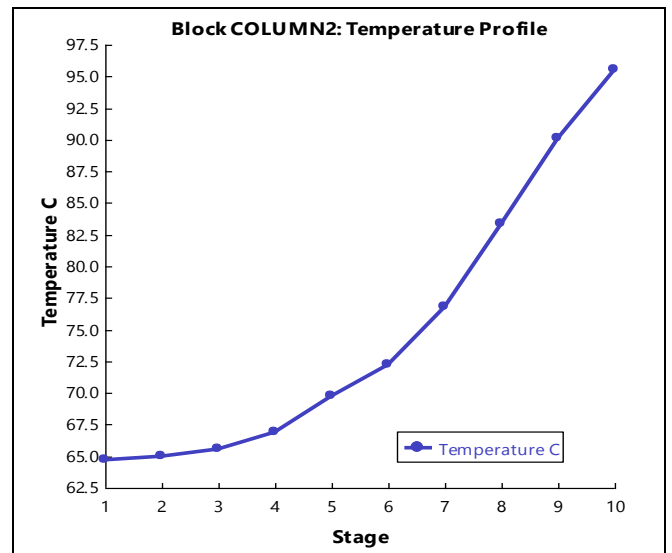
PARAMETERS	VALUE
Property Method	POLY-NRTL
<b>COLUMN 1 OPERATING CONDITIONS</b>	
Feed Temp. [Methacrylic Acid (Feed 1)]	70 °C
Feed Temp. [Methanol (FEED 2)]	55 °C
Feed 1 Feed Stage	3
Feed 2 Feed Stage	6
Feed 1 Flow Rate	0.04L/min
Feed 2 Flow Rate	0.035 L/min
Operating Pressure	Atmospheric
Reboiler Duty	1.5 kW
Reflux Ratio	3
Top Product	Water
Bottom Product	MMA(> 95% purity)
<b>COLUMN 2 OPERATING CONDITIONS</b>	
Feed Type	Mixed ( Bottom product of first column) fed at stage 5 to the column 2
Feed Temp	90 °C
Reflux Ratio	4
Reboiler Duty	1.5 KW
Operating Pressure	Atmospheric
Top Product	Recovered Acid
Bottom Product	PMMA (>95% purity)

### 5. RESULTS AND DISCUSSION

This section describes the results of process alternative considered in this work.



**Fig-3:** Temperature profile throughout the column 1.



**Fig-4:** Temperature profile throughout the column 2.

Fig 3 and 4 presents the temperature profiles for column 1 and column 2 respectively, obtained for esterification reaction based on equilibrium stage model in the first column and free radical emulsion polymerization reaction based on free radical kinetic model in the second column.

Fig. 5 and 6 shows the liquid composition profiles for reaction and product components at top and bottom of column 1 and 2 respectively. It can be seen from the results that the highest purity of intermediate product MMA (> 95%) and final desired polymer latex product (> 90%) was achieved. The complete conversion of MMA monomer was achieved in this proposed dual RD system which showed 10-20% rise in purity as compared to product purity restricted to approx 70% in conventional batch reactors, previously attained during experimental and simulation study conducted in emulsion batch reactors. The unreacted and recovered acid was recycled back to the first column and mixed with the fresh feed streams.

## 6. CONCLUSION

The novel integrated dual RD column presented in this paper clearly demonstrates the feasibility of PMMA latex synthesis (> 0.95 wt. fraction). The simulation study was performed in Aspen Polymer plus. Esterification in the first RD column and emulsion free radical polymerization in the second column was the model reaction for simulation studies in the proposed system. About 10-20% higher conversion was achieved in the RD column compared to the batch reactor process. Consequently, this synthesis route using dual RD column can be considered as a serious alternative in new plants as well as revamped industrial plants.

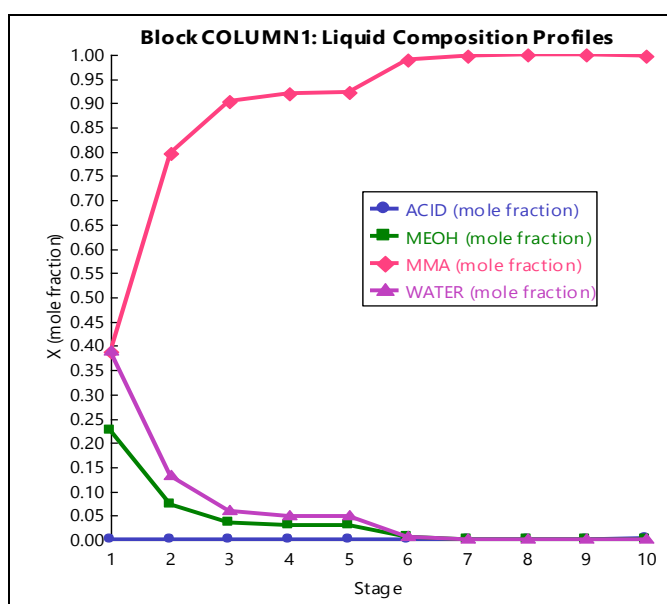


Fig-5: Liquid composition profiles for components along column 1.

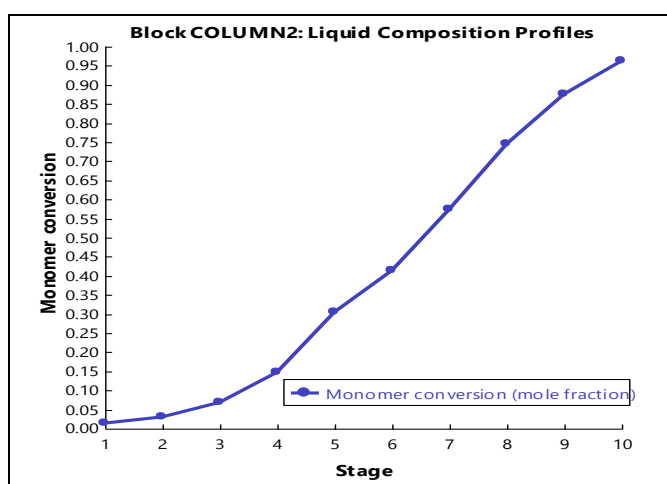


Fig-6: Monomer composition profile along the column 2.

## ACKNOWLEDGEMENT

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## NOMENCLATURE

C	Total number of components	
$F_j$	Feed flowrate of stage j	mol/s
$\Delta H_R$	Heat of Reaction	J/mol
N	Total number of stages	
P	Total pressure	Pa
$P^o$	Saturated vapor pressure	Pa
$r_j$	Rate of reaction on stage j	mol/s
T	Temperature	K
t	Time	s
x	Liquid composition	
y	Vapor composition	
z	Feed composition	
$V_j$	Vapor flowrate from stage j	mol/s
v	Stoichiometric coefficient	

### Greek letters

$\delta_j$	Parameter for reaction occurrence on stage j
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$\phi$  Fugacity coefficient

$\gamma$  Activity coefficient

#### Subscript

i Component number

j Stage number

r reaction number

#### Abbreviations

RD Reactive distillation

MMA Methyl methacrylate

PMMA Poly (methyl methacrylate)

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