

Supporting Information

Manuscript Title: Reactive Distillation for the Production of Methoxy Propyl Acetate: Experiments and Simulation

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Supporting information S1

The plot of $\ln K_{eq}$ vs $(1/T)$

The slope of $\ln K_{eq}$ vs $(1/T)$ indicates the reaction to be endothermic. The Value of $\Delta H = 41.510$ kJ/mol

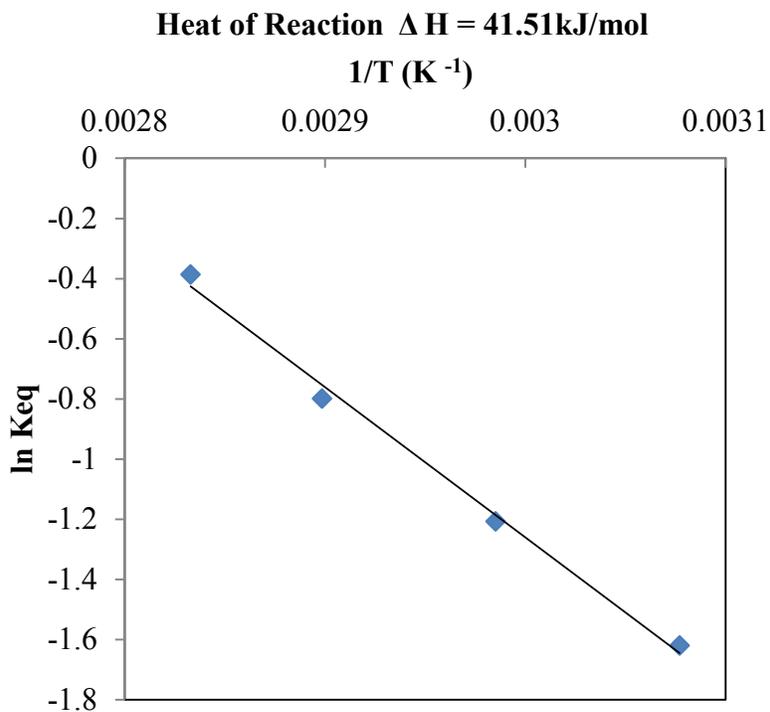


Figure S1. Van't Hoff plot for estimating heat of reaction

Supporting information S2

Comparison of experimental results and predictions by simulation for different feed and entrainer positions

1) Feed Position

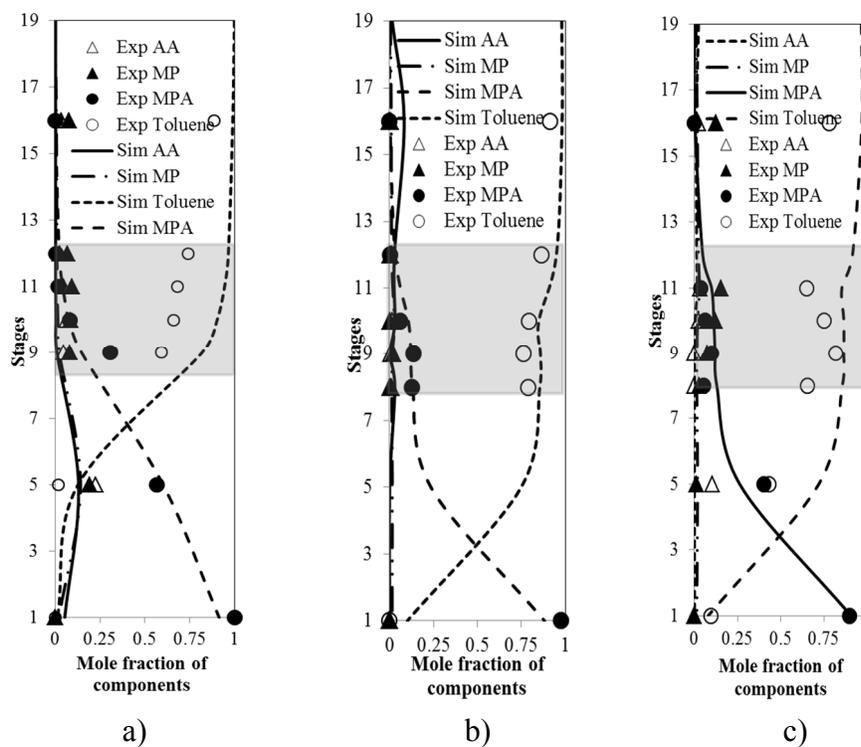


Figure S2. Comparison of experimental and simulation results for different feed positions a) stage-8 b) stage-11 c) stage-12. Column conditions: Reboiler duty = 400 Watt; Mole ratio AA: MP = 1; feed temperature = 30 °C; Operating pressure = 1 atm.

2) Entrainer position.

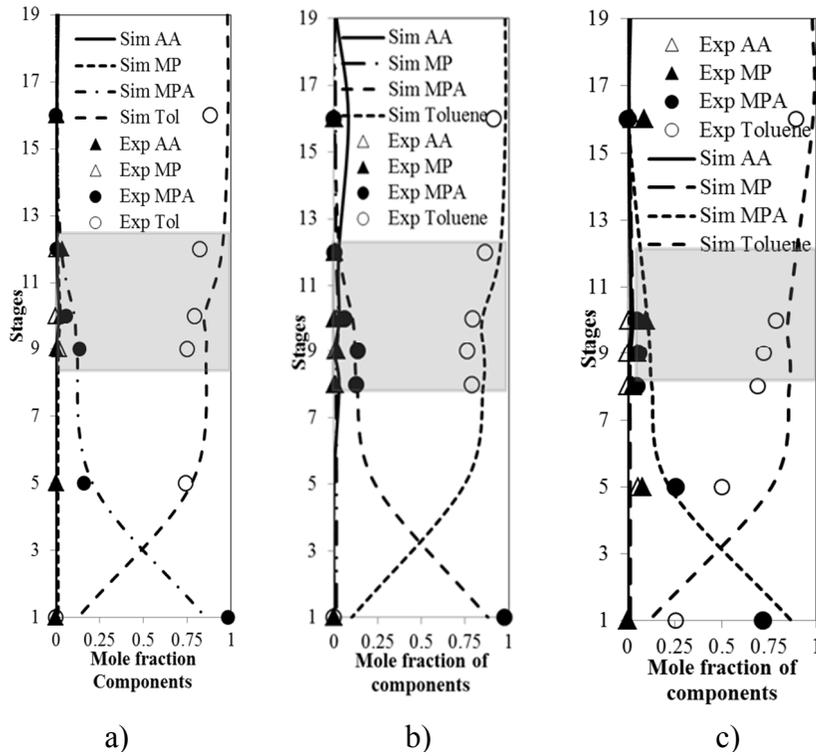


Figure S3. Comparison of experimental and simulation results for different entrainer positions a) stage-8 b) stage-11 c) stage-12. Column conditions: Reboiler duty = 400 Watt; Mole ratio AA: MP = 1; feed temperature = 30 °C; Operating pressure = 1 atm; feed AA: MP at stage 11.

Supporting Information S3

Table S1. The values of r and q parameters for UNIQUAC Model from Aspen

Component	Molecular volume r_i	Molecular area q_i
MP	3.97627	3.314
MPA	5.07053	4.432
Acetic acid	2.19512	2.072
Toluene	3.92287	2.968
Water	0.92	1.4

Supporting Information S4

Table S2. Mass balance for Experimental runs.

Mass balance for experimental Runs (Reboiler duty 400 W)					
Feed in the middle of reactive section					
Feed		Distillate		Bottom	
Flow rate	450 gm/h	Flow rate	57 gm/h	Flow rate	390 gm/h
Components	Wt fraction	Components	Wt fraction	Components	Wt fraction
Acetic acid	0.3857	Acetic acid	0.046	Acetic acid	-
MP	0.5781	MP	0.00565	MP	-
Toluene	0.036	Toluene	0.0005	Toluene	-
MPA	-	MPA	0	MPA	0.97
Water	-	Water	0.9476	Side product	0.03
Feed in the bottom of reactive section,					
Feed		Distillate		Bottom	
Flow rate	450 gm/h	Flow rate	54 gm/h	Flow rate	390 gm/h
Components	Wt fraction	Components	Wt fraction	Components	Wt fraction
Acetic acid	0.39	Acetic acid	0.138	Acetic acid	-
MP	0.58	MP	0.01	MP	-
Toluene	0.036	Toluene	0.0006	Toluene	-
MPA	-	MPA	0	MPA	0.999
Water	-	Water	0.85	Side product	0.0001
Feed at top of reactive section					
Feed		Distillate		Bottom	
Flow rate	450 gm/h	Flow rate	48 gm/h	Flow rate	420 gm/h
Components	Wt fraction	Components	Wt fraction	Components	Wt fraction
Acetic acid	0.39	Acetic acid	0.003	Acetic acid	-
MP	0.58	MP	0.0196	MP	-
Toluene	0.036	Toluene	0.0355	Toluene	0.03
MPA	-	MPA	0	MPA	0.93
Water	-	Water	0.9419	Side product	0.04
Entrainer at top of reactive section					
Feed		Distillate		Bottom	
Flow rate	450 gm/h	Flow rate	48 gm/h	Flow rate	432 gm/h
Components	Gm/hr	Components	Wt fraction	Components	Wt fraction
Acetic acid	0.39	Acetic acid	0.04	Acetic acid	-
MP	0.58	MP	0.06	MP	-
Toluene	0.036	Toluene	0.0038	Toluene	0.193
MPA	-	MPA	0	MPA	0.765
Water	-	Water	0.8962	Side product	0.042

Entrainer at bottom of reactive section					
Feed		Distillate		Bottom	
Flow rate	450 gm/h	Flow rate	48 gm/h	Flow rate	396 gm/h
Components	Wt fraction	Components		Components	Wt fraction
Acetic acid	0.39	Acetic acid	0.046	Acetic acid	0
MP	0.58	MP	0.018	MP	0
Toluene	0.036	Toluene	0.059	Toluene	0
MPA	-	MPA	0	MPA	0.99
Water	-	Water	0.877	Side product	0.01

Supporting Information S5

Conventional entrainer based batch process for esterification of higher alcohols

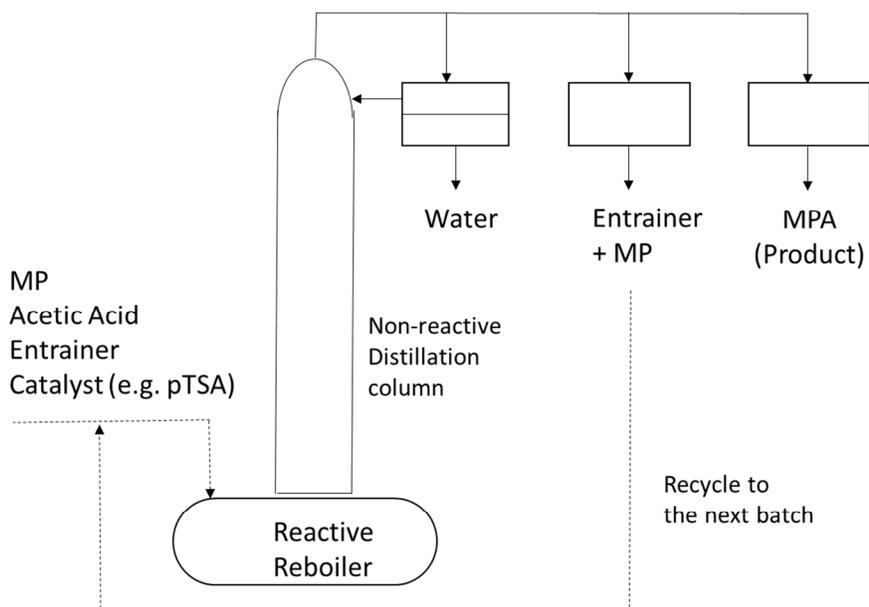


Figure S4. Conventional batch distillation process used for higher alcohols

Figure S4 shows the process flow diagram for a typical conventional batch process used for the synthesis of acetates of higher alcohol. The reboiler of the distillation column acts as a reactor, which is charged with acetic acid and alcohol (e.g. MP) along with entrainer (e.g. toluene) and homogeneous acid (e.g. pTSA: para-toluic sulphonic acid) as a catalyst. The reboiler duty is cleverly manipulated such that the water formed is azeotropically removed from the top through a decanter as the first cut. The organic phase that is rich in entrainer is recycled back to the column in the form of reflux. Generally alcohol is taken in excess because there are stringent specifications on the acidity of the product and hence it is desired to react acetic acid almost quantitatively. p-TSA being a heavy compound remains in the reboiler. The second cut is a

mixture of entrainer and excess alcohol, followed by the third cut of pure product. Here the reflux is generally kept high to avoid even traces of acids in the product. The energy consumption in this case is higher. Furthermore, scale-up of such process beyond a limit is not cost-effective. Use of heterogeneous catalyst such as ion exchange resin can bring home several benefits. One can perform reaction in a continuous reactive distillation column configuration as suggested in the main paper. The reactive zone in this configuration, is placed in the middle of the column and the lengths of rectifying and stripping sections can be manipulated conveniently to achieve desired purities at top and bottom. Reactive zone temperature can be adjusted and brought down (unlike that in the reactive reboiler in the batch process) to minimize the formation of side products. Obviously energy consumption is reduced significantly in the proposed RD configuration in this work.