Supporting Information

Tributyl Citrate Production via Reactive Distillation - Conceptual design and pilot scale validation

Miguel A. Santaella, Alvaro Orjuela*, Andrea Suaza, José L. Rivera, Andrés F. Martínez, Gerardo Rodríguez

Department of Chemical and Environmental Engineering, Universidad Nacional de Colombia, 111321 Bogotá D.C., Colombia.

*Corresponding author. Tel (+571) 3165000 x 14303. E-mail address: aorjuelal@unal.edu.co

Table S1. Characteristic of chemicals used in experiments and samples analysis.

Chemical	Grade	Purity wt. %	Supplier	Purpose
Anhydrous citric acid	Food	99.9	Sucroal S.A (Colombia)	Pilot Scale
Anhydrous Citric acid	Analysis	99.9	Sigma-Aldrich (USA)	HPLC-Calibration
1-Butanol	Analysis	99.5	Panreac (Spain)	GC Calibration
1-Butanol	Industrial	98	Sucroal S.A. (Colombia)	Pilot Scale
1-Butanol	Azeotropic	85	---	Pilot Scale
Tributyl Citrate	Analysis	98	Aldrich (USA)	HPLC-Calibration
Dibutyl Citrate	Analysis		Locally produced [11]	HPLC-Calibration
Amberlyst 70	N/A	N/A	Dow Chemical Company (USA)	Pilot Scale
Acetonitrile	HPLC	99.9	Panreac (Spain)	HPLC

Table S2. Detailed description of the distillation column sections

Section	HETP (m)	Height of section (m)	Approximated stage	Composition measurement	Temperature measurement
1	0.6	1	1		*
			2	*	
2	0.6	1	3	*	*
3	0.35	1.1	4		
			5		*
			6	*	
4	0.35	1.1	7		*
			8		
			9		
			10	*	*
5	0.35	1.1	11		
			12		
			13	*	*
6	0.35	1.1	14		
			15		*
			16	*	
7	0.18	1.1	17		
			18		
			19		
			20		*
			21		
			22		
Boiler	-	-	23	*	*

Table S3. Main characteristics of the pilot scale reactive distillation system.

Variable	Value
Diameter	76 mm
Total Height	7.5 m
Reactive Height	5.5 m
Rectifying Sections	2
Reactive Sections	4
Stripping Sections	1
Material	Stainless Steel 316L
Insulation	2.5mm Glass Fiber
Reactive Packing	Similar to Katapak-SP11*
Unreactive Packing	Stainless Steel 18mm Nutter Rings
Catalyst	Mesh 40 Amberlyst 70® 76kg/m^3
Reboiler liquid volume	7.5L
Agitated Prereactor	Glass 60L

*Procured from different vendor

Table S4. Kinetic model parameters for self-catalyzed and resin-catalyzed with Amberlyst 70 ® reactions [10].

Parameter	Units	Value
$k^o_{cat,1}$	$1/(\%wt_{cat}.s)$	1.543×10^5
$k^o_{cat,2}$		1.275×10^5
$k^o_{cat,3}$		8.255×10^4
$E_{a,cat,1}$	$kJ/kmol$	65582
$E_{a,cat,2}$		67529
$E_{a,cat,3}$		70561
$k^o_{self,1}$	$1/s$	3.207×10^6
$k^o_{self,2}$		8.873×10^6
$k^o_{self,3}$		1.166×10^7
$E_{a,self,1}$	$kJ/kmol$	71433
$E_{a,self,2}$		77346
$E_{a,self,3}$		80894
K_1	-	8.68
K_2		3.56
K_3		1.04

Table S5. UNIQUAC Interaction parameters for binary component pairs in the form $\tau = \exp(A_{ij} + B_{ij}/T)$. q=q'

Binary	A_{ij}	A_{ji}	B_{ij} (K)	B_{ji} (K)	Source
HCit-H_2O	-7.13	1.61	-1753.5	1.51	[18]
H_2O-BuOH	-5.86	2.23	794.1	-726.5	[12]
HCit-BuOH	-7.72	6.37	-1232	-1525.8	[12]
HCit-MBC			26.56	-40.54	UNIFAC
HCit-DBC			65.33	-154.12	UNIFAC
HCit-TBC	-14.4	0.369	-1700.3	163.2	[12]
BuOH-MBC			-40.66	-4.47	UNIFAC
BuOH-DBC			-37.16	-0.31	UNIFAC
BuOH-TBC	2.49	3.4	-582.2	-1957.7	[12]
MBC- H_2O			189.70	-339.13	UNIFAC
MBC-DBC			92.29	-116.94	UNIFAC
MBC-TBC			62.10	-105.48	UNIFAC
H_2O-DBC			-203.41	-9.43	UNIFAC
H_2O-TBC	1.33	-2.74	-310.3	-313.5	[12]
DBC-TBC			28.31	-32.74	UNIFAC

Table S6. Antoine parameters for vapor pressure calculation of pure components between 298K and 403K*.

Parameter	Component					
	CA	**BuOH**	**H_2O**	**MBC**	**DBC**	**TBC**
C_1	230.16	21.98	23.48	199.14	170.15	165.91
C_2	-29279	-3112.07	-3984.92	-24822.37	-20879.70	-18046.06
C_3	0	-93.34	-39.57	0.00	0.00	0.00
C_4	0	0	0	0.00	0.00	0.00
C_5	-26.80	0	0	-23.02	-19.44	-19.84
C_6	3.87E-18	0	0	4.14E-18	4.28E-18	5.77E-17
C_7	6	0	0	6	6	6

* $\ln(P) = C_1 + \frac{C_2}{T+C_3} + C_4 T + C_5 \ln(T) + C_6 T^{C_7}$ (P in N/m^2, T in K)

Table S7. Box-Behnken experimental design conditions

Run	Reflux Rate (kg/h) $\dot{F}_L$	Reactive mixture feed mass flow (kg/h) $\dot{F}_{rx}$	BuOH Feed (kg/h) $\dot{F}_{BuOH}$
1	0.1	3	0.6
2	0.1	5.1	0.6
3	1.2	3	0.6
4	1.2	5.1	0.6
5	0.1	4.05	0
6	0.1	4.05	1.2
7	1.2	4.05	0
8	1.2	4.05	1.2
9	0.65	3	0
10	0.65	3	1.2
11	0.65	5.1	0
12	0.65	5.1	1.2
13	0.65	4.05	0.6
14	0.65	4.05	0.6
15	0.65	4.05	0.6

Table S8. Experimental conditions during reactive distillation pilot scale experiments for TBC production

Run	$\dot{F}_{rx}$ (kg/h)	T_{rx} (K)	Feed Concentration (wt. %)						$\dot{F}_{BuOH}$ (kg/h)	$\dot{F}_L$ (kg/h)	$\dot{F}_V$ (kg/h)	RR	Steam Pressure (kPag)	$\dot{F}_B$ (kg/h)	Pre-reaction	Azeotropic BuOH
			w_{CA}	w_{BuOH}	w_{H_2O}	w_{MBC}	w_{DBC}	w_{TBC}								
1	2.30	364.1	0.028	0.498	0.047	0.141	0.208	0.078	1.54	0.67	1.96	0.34	137.9	2.55	no*	no
2	2.37	358.9	0.011	0.481	0.066	0.100	0.229	0.114	1.64	0.64	1.47	0.44	137.8	3.18	no*	no
3	4.31	312.0	0.132	0.821	0.019	0.026	0.002	0.000	0.00	1.38	2.59	0.53	124.1	3.10	no	no
4	0.61	296.4	0.136	0.828	0.018	0.018	0.000	0.000	1.19	1.38	2.96	0.47	128.9	0.22	no	no
5	4.13	297.8	0.137	0.818	0.019	0.024	0.002	0.001	0.00	0.09	2.56	0.03	199.9	1.66	no	no
6	5.11	298.9	0.180	0.765	0.019	0.033	0.003	0.000	0.48	0.10	3.63	0.03	206.8	2.06	no	no
7	4.87	300.4	0.131	0.752	0.026	0.025	0.066	0.000	0.45	1.32	4.56	0.29	220.6	2.08	no	no
8	1.52	315.9	0.150	0.806	0.019	0.024	0.001	0.000	0.00	0.76	1.04	0.74	220.6	1.24	no	no
9	4.88	301.6	0.149	0.789	0.020	0.039	0.003	0.000	0.92	0.84	4.81	0.17	220.6	1.82	no	no
10	5.72	302.5	0.146	0.821	0.018	0.013	0.001	0.000	0.46	0.81	4.31	0.19	202.8	2.68	no	no
11	2.13	301.6	0.149	0.818	0.018	0.014	0.001	0.000	0.45	0.11	1.00	0.11	199.9	1.69	no	no
12	4.54	299.6	0.118	0.821	0.021	0.029	0.005	0.007	0.90	1.06	4.50	0.24	168.9	2.00	no	no
13	2.14	299.5	0.130	0.824	0.019	0.020	0.003	0.005	0.00	0.51	1.61	0.32	202.0	1.04	no	no
14	0.74	302.5	0.128	0.831	0.019	0.013	0.002	0.005	0.98	0.16	1.45	0.11	211.6	0.42	no	no
15	3.30	301.3	0.125	0.821	0.020	0.021	0.012	0.000	0.00	0.67	2.66	0.25	211.6	1.31	no	no
16	4.65	297.9	0.127	0.686	0.176	0.006	0.005	0.000	0.51	0.37	3.60	0.10	211.6	1.94	no	yes
17	4.46	299.2	0.096	0.652	0.177	0.065	0.009	0.000	1.09	0.43	3.83	0.11	211.6	2.14	yes	yes
18	4.21	301.1	0.081	0.631	0.178	0.085	0.021	0.002	0.56	0.56	3.42	0.17	211.6	1.92	yes	yes

* Unexpected reaction took place while heating

Continues … Table S8. Experimental conditions during reactive distillation pilot scale experiments for TBC production

Run	Top Temperature (K)	Bottoms Temperature (K)	Top Concentration (wt. %)				Bottoms Concentration (wt. %)			
			w_{CA}	w_{MBC}	w_{DBC}	w_{TBC}	w_{CA}	w_{MBC}	w_{DBC}	w_{TBC}
1	373.5	383.7	0.000	0.000	0.000	0.000	0.002	0.033	0.164	0.302
2	363.6	383.5	0.000	0.000	0.002	0.000	0.001	0.024	0.138	0.227
3	372.0	383.4	0.000	0.000	0.000	0.000	0.021	0.073	0.125	0.133
4	376.2	383.4	0.001	0.000	0.000	0.000	0.007	0.052	0.165	0.215
5	376.4	383.1	0.001	0.000	0.000	0.001	0.006	0.045	0.228	0.414
6	376.3	383.6	0.000	0.000	0.000	0.000	0.010	0.057	0.269	0.368
7	376.6	383.7	0.024	0.000	0.068	0.000	0.011	0.054	0.236	0.284
8	375.3	383.2	0.000	0.000	0.001	0.002	0.004	0.049	0.262	0.460
9	377.5	383.6	0.000	0.000	0.001	0.002	0.007	0.069	0.241	0.429
10	377.2	383.8	0.000	0.000	0.000	0.000	0.005	0.044	0.214	0.479
11	377.9	383.4	0.000	0.000	0.001	0.004	0.011	0.063	0.155	0.256
12	377.7	383.7	0.000	0.000	0.000	0.000	0.014	0.076	0.216	0.243
13	376.2	383.4	0.000	0.006	0.002	0.007	0.000	0.031	0.219	0.416
14	379.3	383.3	0.000	0.005	0.002	0.005	0.000	0.019	0.171	0.471
15	376.6	383.4	0.000	0.000	0.006	0.000	0.004	0.047	0.187	0.401
16	370.8	383.5	0.000	0.000	0.006	0.003	0.011	0.071	0.215	0.337
17	370.3	383.6	0.000	0.000	0.000	0.000	0.000	0.063	0.226	0.337
18	376.7	383.5	0.000	0.000	0.005	0.001	0.001	0.054	0.217	0.354

Table S9. Mass and citrate species balance errors for experimental runs

Run	Mass Balance Error %	Citrate Species Balance Error %
1	8.46	4.42
2	4.88	4.18
3	3.86	6.72
4	0.03	43.32
5	6.88	3.62
6	0.31	20.05
7	6.90	23.94
8	N/A	N/A
9	0.13	9.67
10	N/A	N/A
11	N/A	N/A
12	13.52	2.28
13	N/A	N/A
14	3.95	39.65
15	16.63	0.70
16	11.43	16.16
17	21.87	15.70
18	13.46	3.72

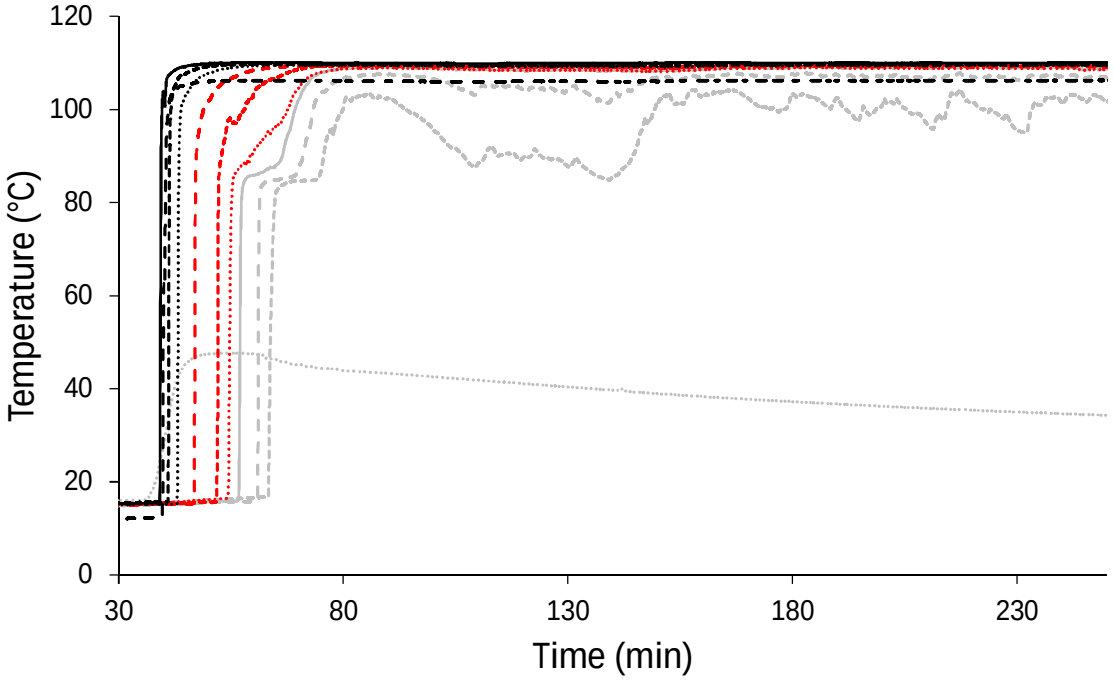


Figure S1. Dynamic temperature profiles for the different stages during stabilization of run 10. (⋯) Column Feed, (- -) Stage 1, (– –) Stage 3, (—) Stage 5, (⋯) Stage 7, (- -) Stage 8, (– –) Stage 10, (⋯) Stage 13, (- -) Stage 15, (– –) Stage 17, (—) Stage 20.

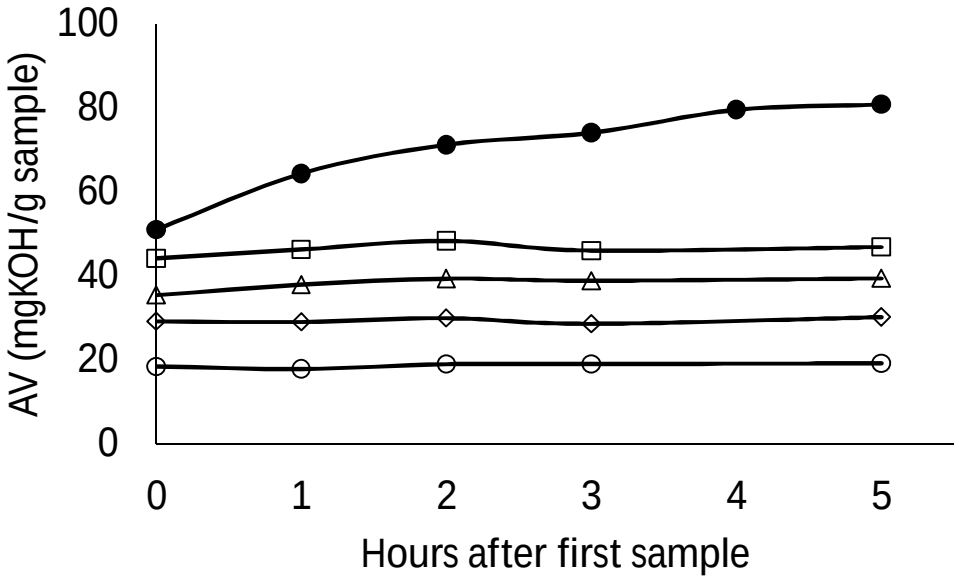


Figure S2. Dynamic acid value profiles at different stages in a reactive distillation column in the production of TBC during Run 10. (○) Stage 6 (◊) Stage 10, (Δ) Stage 13, (□) Stage 16, (•) Bottoms.

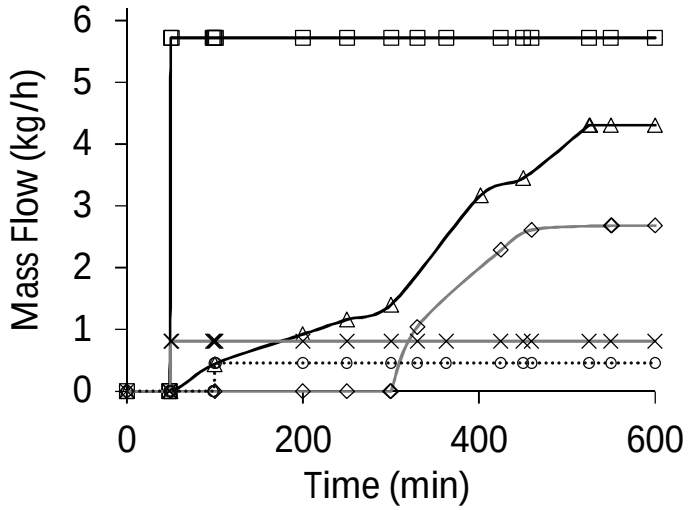
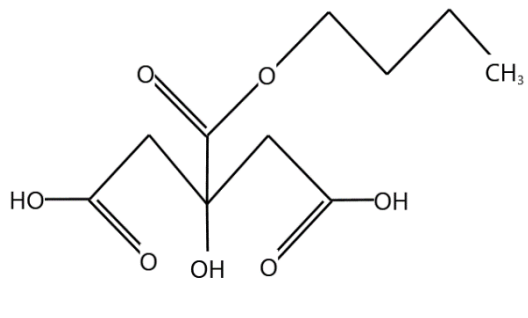
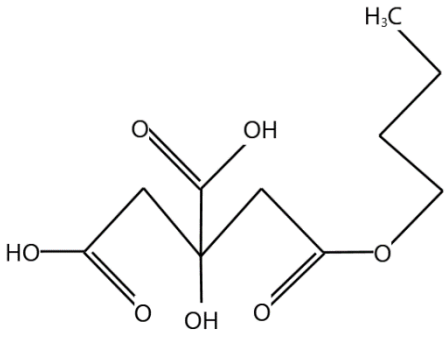


Figure S3. Dynamic mass flow rate profiles during stabilization of run 10. (-□-) F_{rx} flow rate of CA+BuOH feed, (-△-) $L + D$ flowrate at the condenser outlet, (-◇-) F_B Bottoms flow, (-×-) F_L reflux flow, (···○···) F_{BuOH} Butanol feed flow.

a

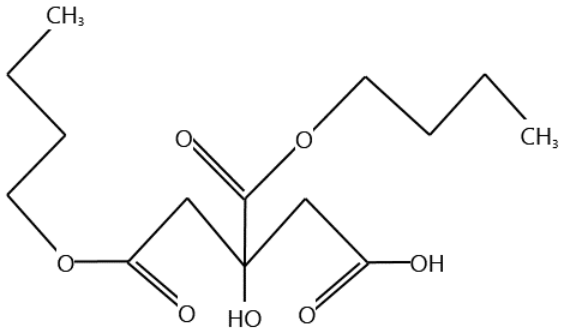


3-Butoxycarbonyl-3-hydroxyglutaric acid

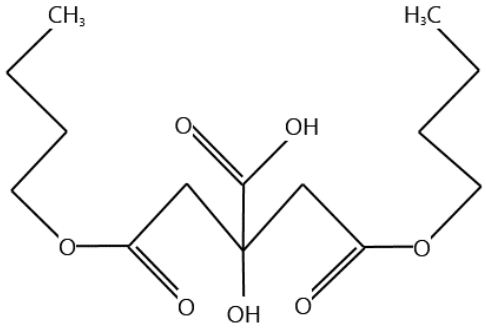


2-(Butoxycarbonylmethyl) malic acid

b



3,4-Dibutoxycarbonyl-3-hydroxybutyric acid



3-Butoxycarbonyl-2-(butoxycarbonylmethyl) lactic acid

Figure S4. Isomers during partial esterification of citric acid with butanol. a) Monobutyl Citrate isomers, b) Dibutyl citrate isomers.

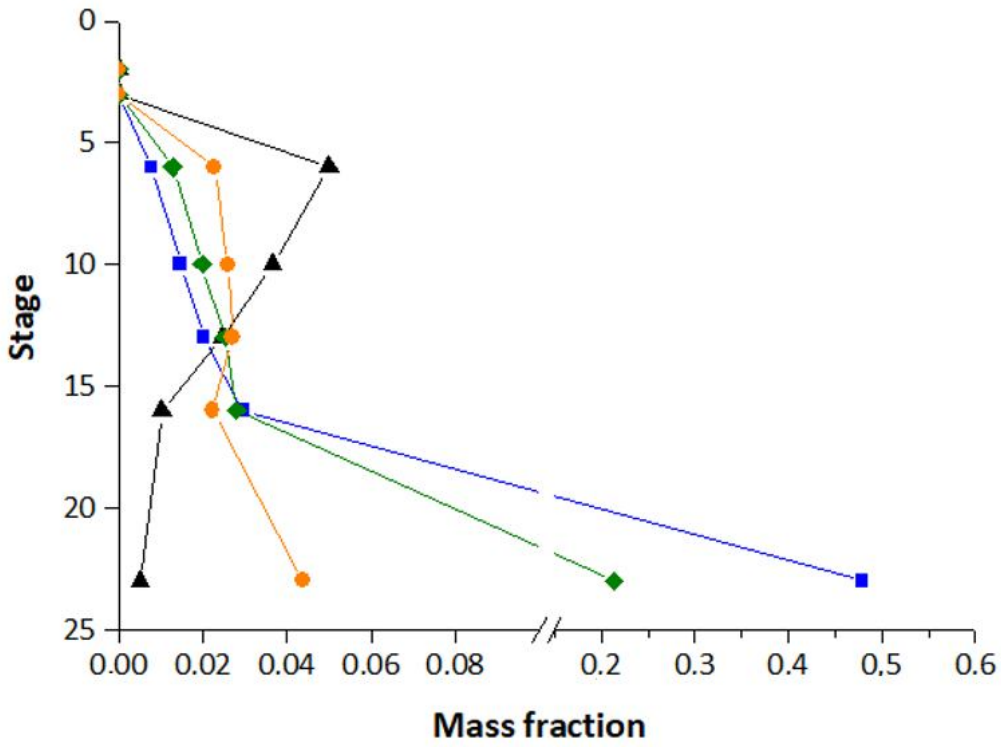


Figure S5. Composition profiles at stable state operation during run 10. (-▲-) CA, (-●-) MBC, (-◆-) DBC, (-■-) TBC.

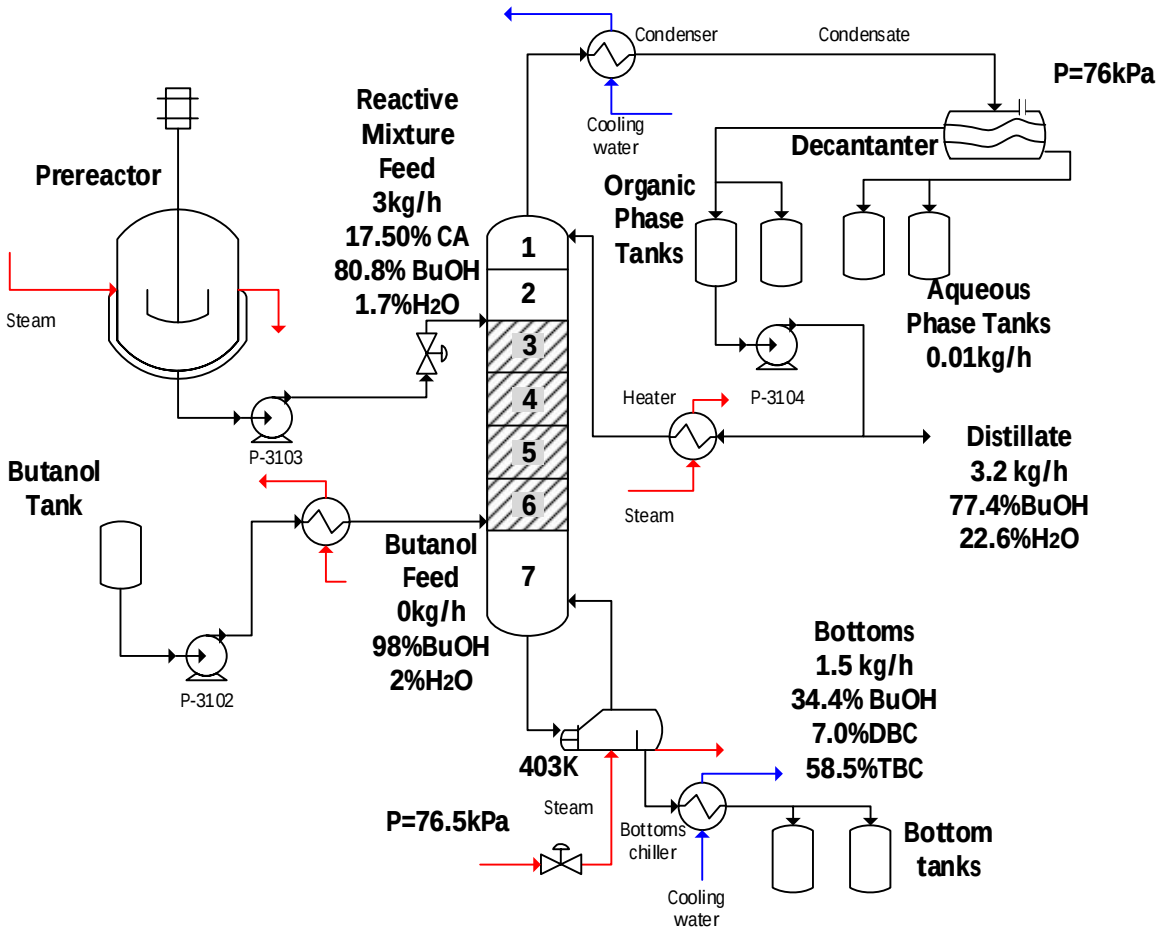


Figure S6. Aspen Simulated scheme of pilot scale reactive distillation column at limiting conditions for TBC production. CA:BuOH ratio of 1:12, a bottoms temperature of 403K and a reflux rate value of 0.01kg/h. SD results above 0.9