Dividing Wall Columns Simulation

Done Easy

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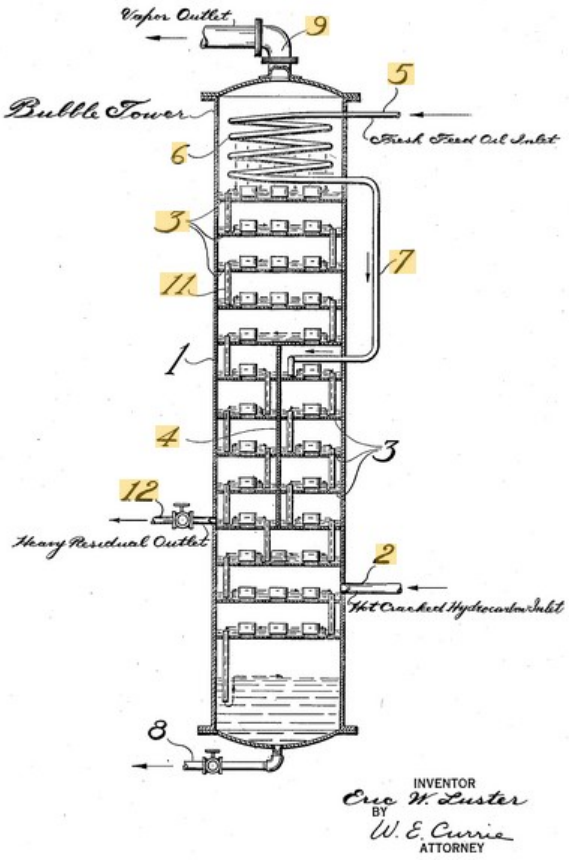
Overview

- Introduction: An incomplete history of Dividing Wall Columns
- Parallel Column Model for DWC in ChemSep
- Refinery application:
  - Reformate BenzOUT process
- Chemicals applications:
  - SHOP (Shell Higher Olefins Process)
  - Ethylene and Propylene Glycols
  - Ethanol-Amines
  - Oleo-Chemicals: Fatty Alcohols
- Summary

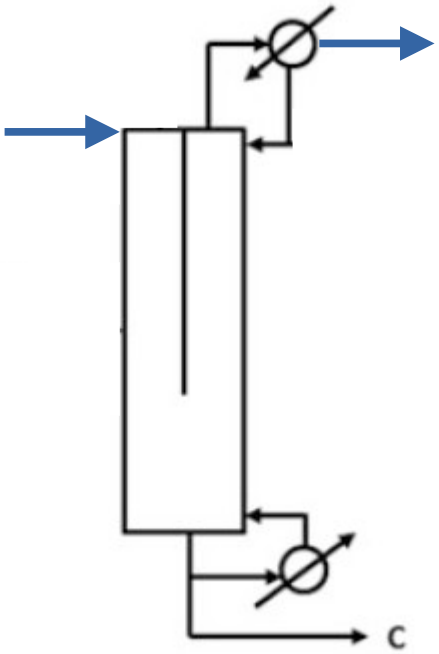
An Incomplete History of DWCs

A long road from concept to common-place:

- 1930: Luster, Standard Oil US 1,915,681 A



Equivalent to

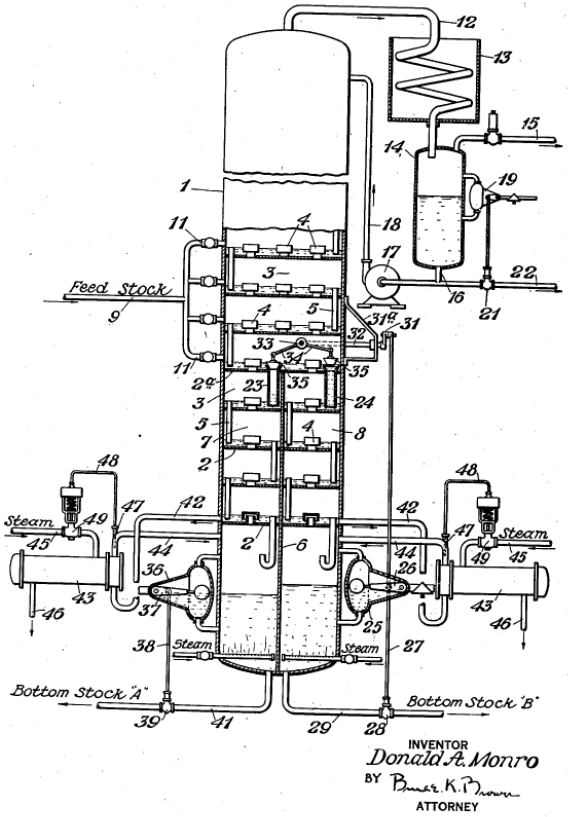


Top-split DWC
(with one condenser)

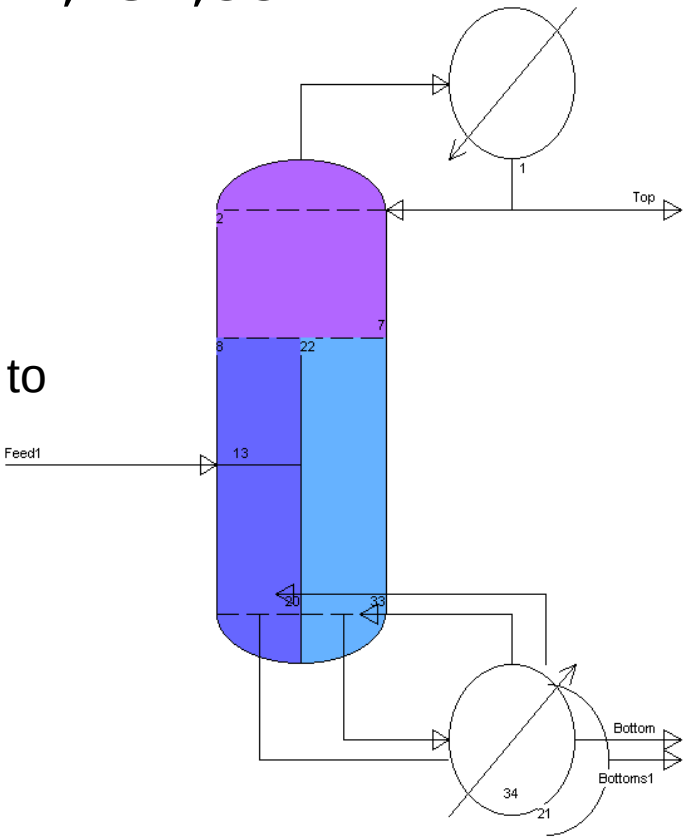
An Incomplete History of DWCs

A long road from concept to common-place:

- 1938: Monro*, Standard Oil, US 2,134,882



Equivalent to



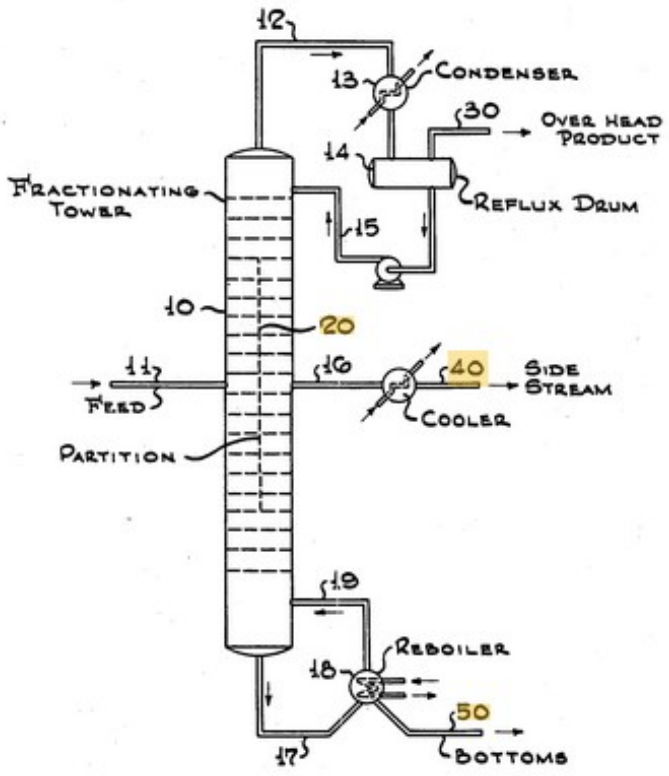
Bottom-split DWC

* Often cited as Monroe, but the patent has Monro in multiple locations

An Incomplete History of DWCs

A long road from concept to common-place:

- 1949: Wright, Standard Oil US 2,471,134 A



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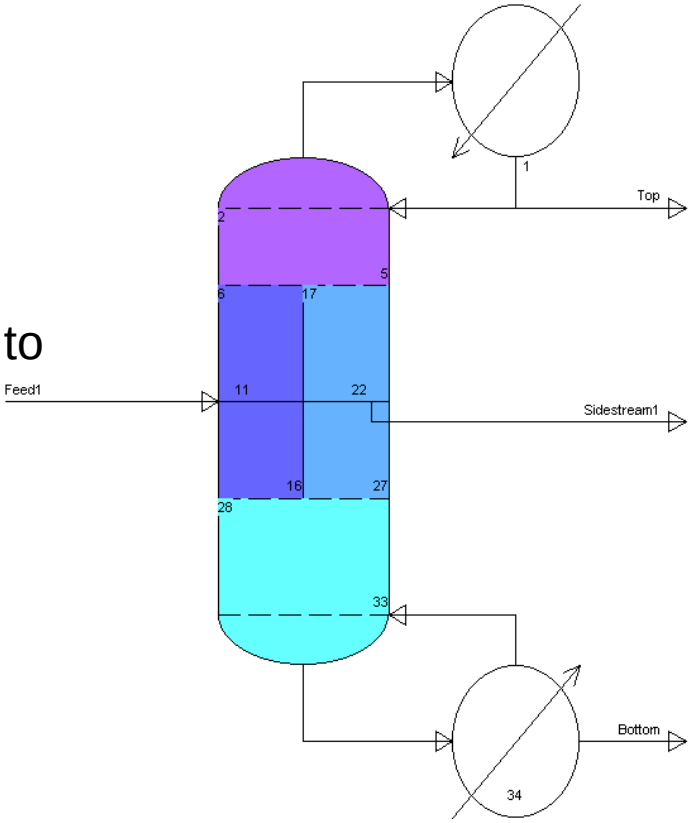
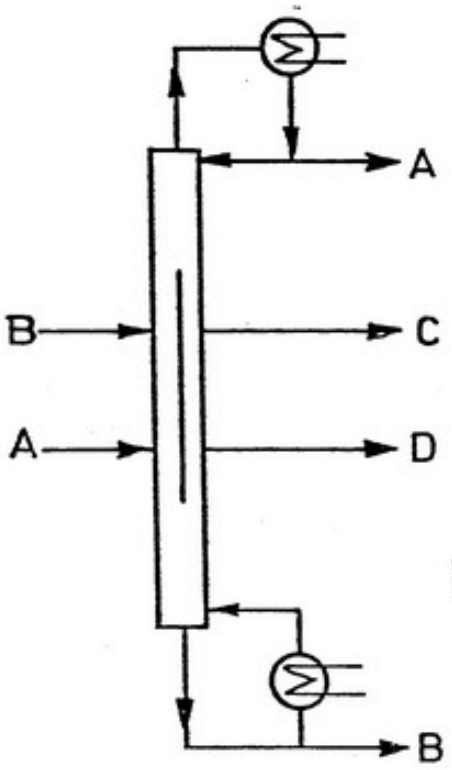


Simple DWC

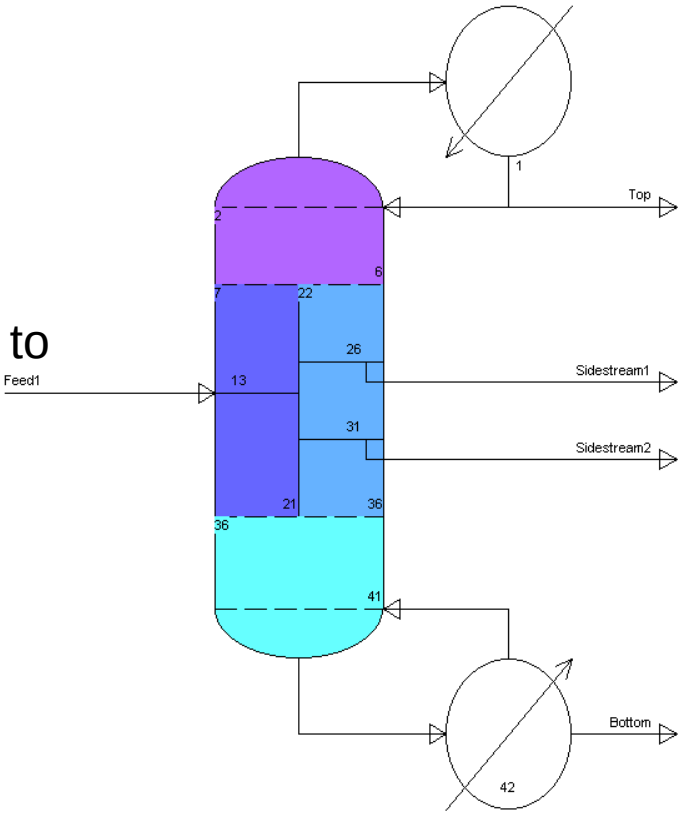
An Incomplete History of DWCs

A long road from concept to common-place:

- 1985: Kaibel, BASF EP 0,126,288 A2



Equivalent to

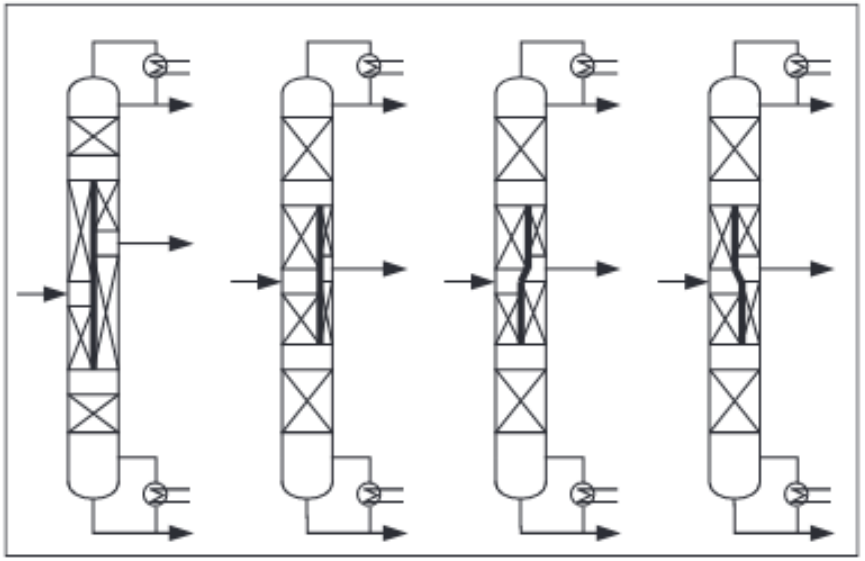


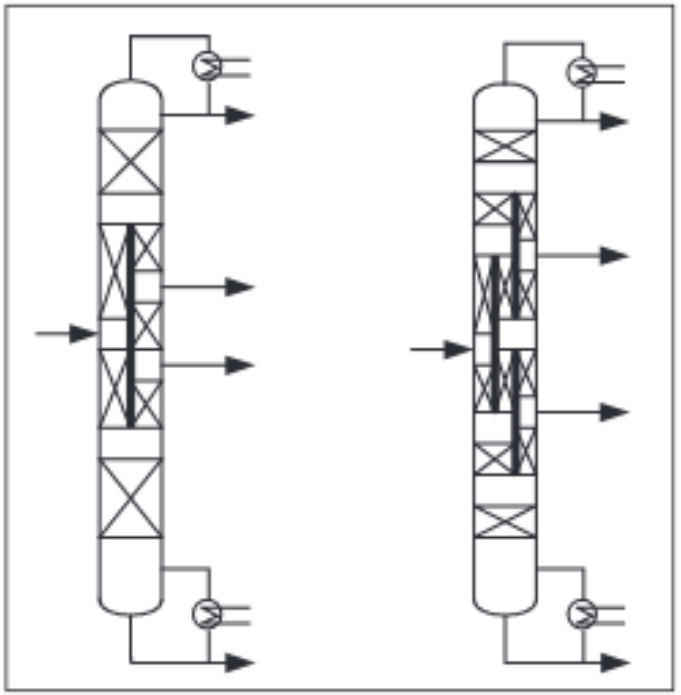
Kaibel DWC

An Incomplete History of DWCs

There is now, of course, MUCH more

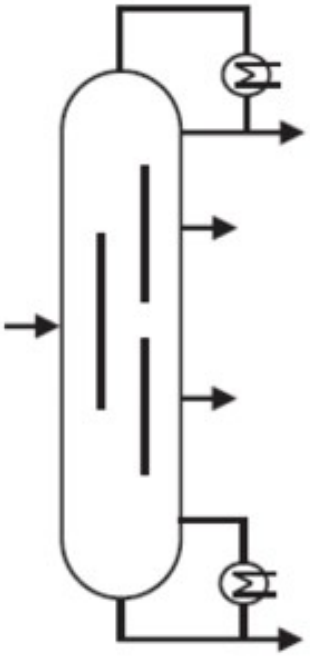
- ~1997: Montz unfixed walls technology & sloped walls
- **Multiple walls (up to 6 products)**
- **Linde DWC columns (heat integrated)**
- **Reactive DWCs**



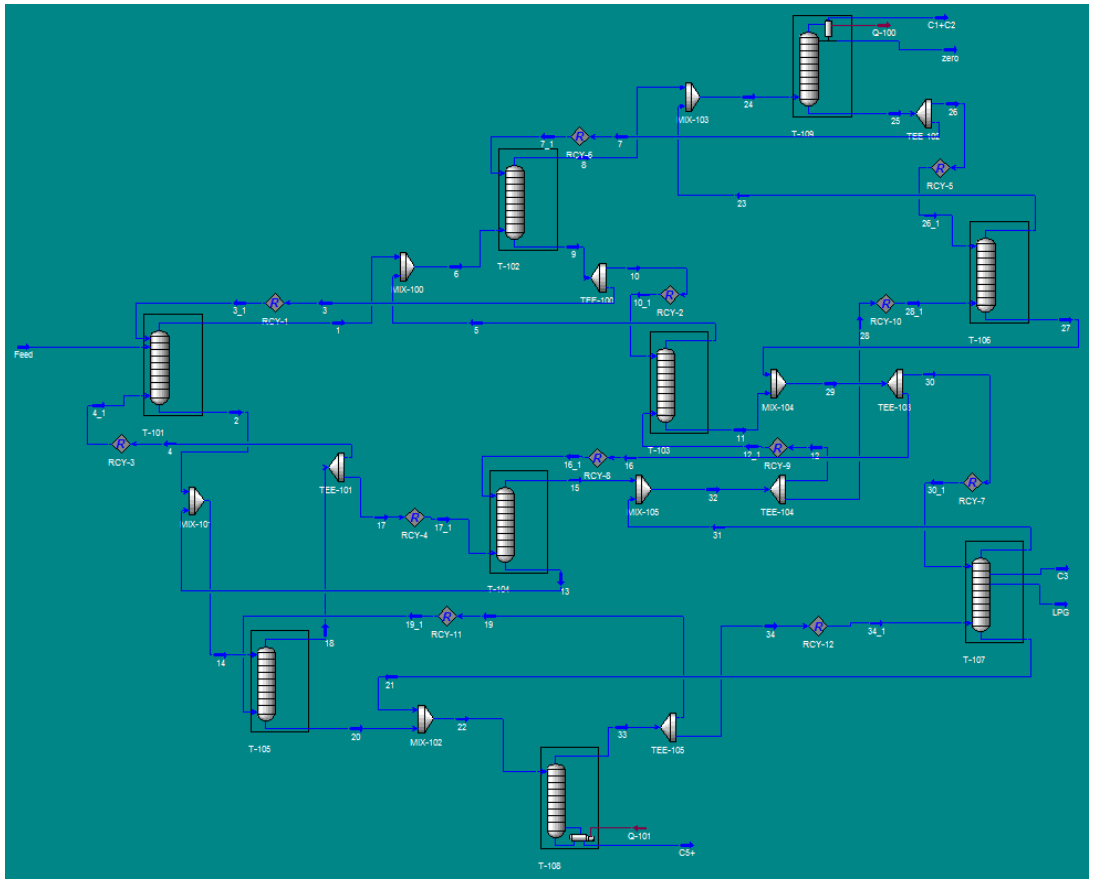


DWC Simulation: Old (and Hard) Way

Dividing Wall Column



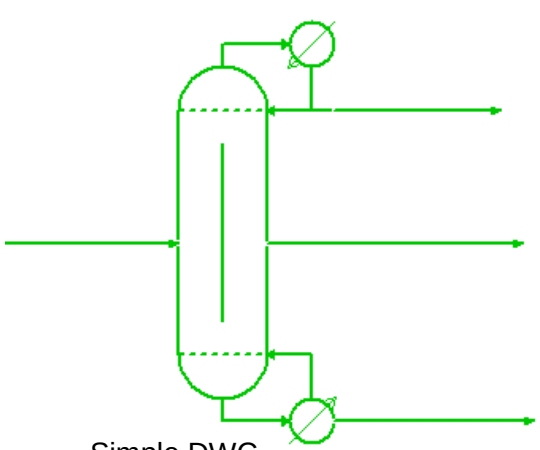
Simulated with multiple columns (here in UNISIM Design)



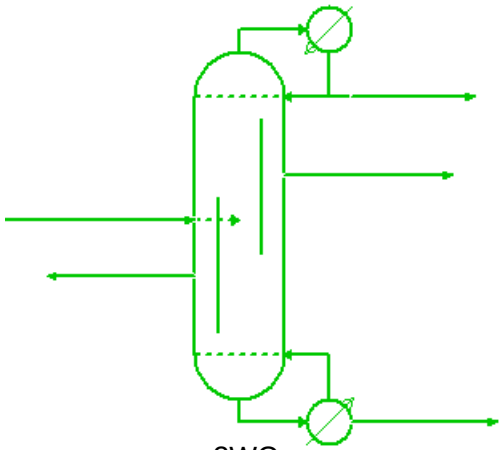
Ashrafian, R. (2014). *Using Dividing Wall Columns (DWC) in LNG Production: deviding wall column, double dividing wall column, prefractionator arrangement, Petlyuk column, NGL recovery, distillation* (Master's thesis, Institutt for energi-og prosessteknikk).

DWC Process Simulation in ChemSep

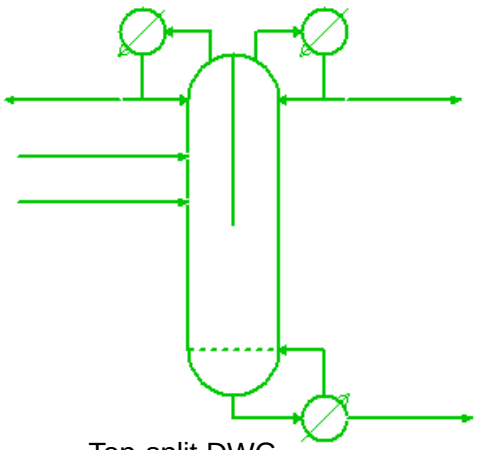
- Parallel Column Model for CAPE-OPEN compliant environments
- Does not require any guesses for streams
- Predefined configurations with single & multiple walls, selection from drop-down list
- Icons reflect actual configuration (in COCO via CAPE-OPEN)
- Rapid tray/packing internals design of each column section with selection of any modern type internal
- Column sizing include auxiliaries: CAPEX & OPEX
- Connection to vendor rating tools



Simple DWC



2WC

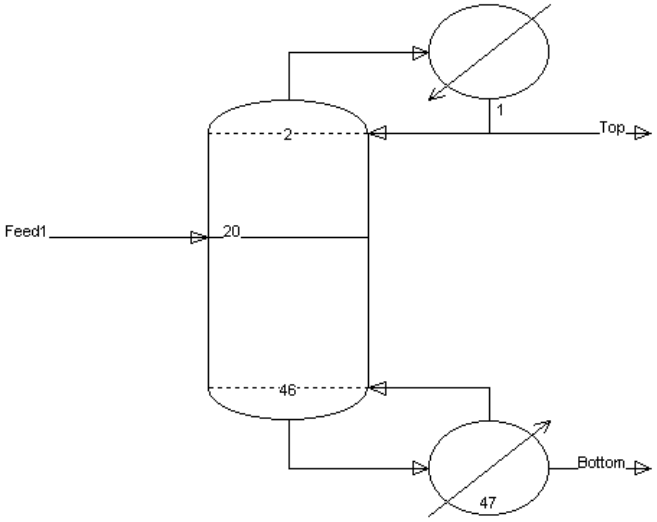


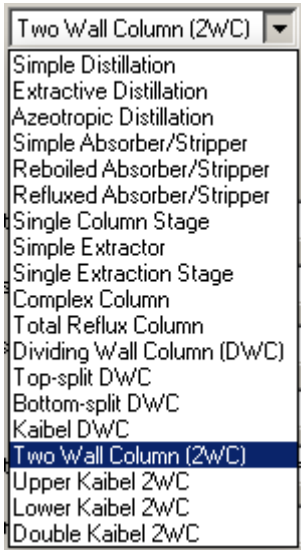
Top-split DWC

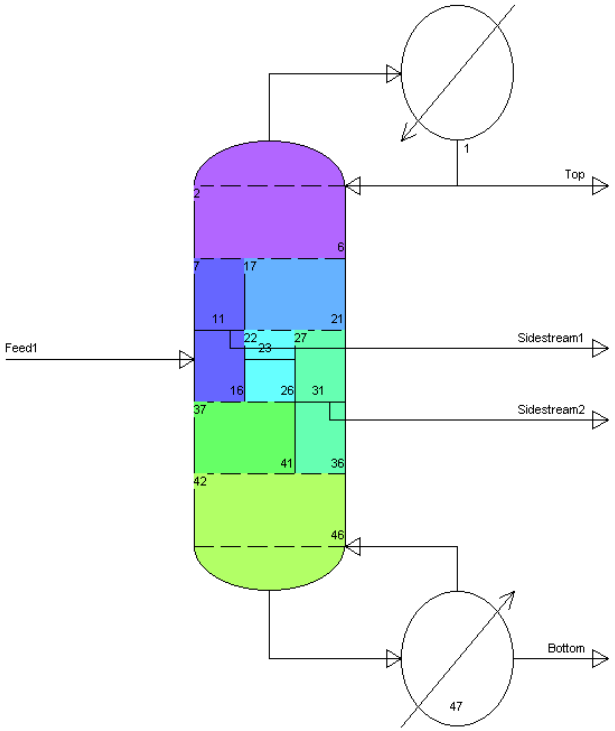
Icons in COCO (www.cocosimulator.com)

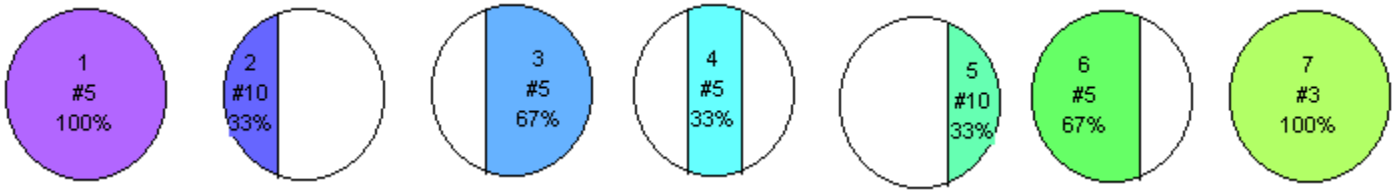
Parallel Column Model - ChemSep

Select DWC from predefined configurations





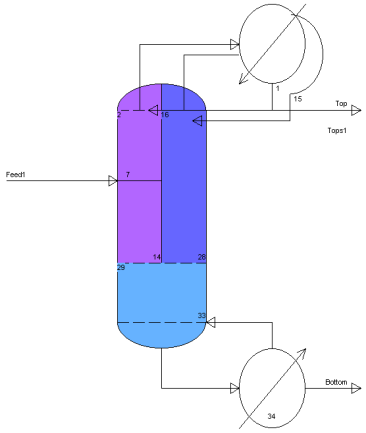




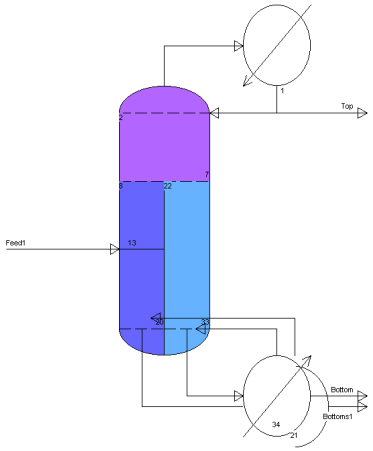
Predefined DWC / 2WC

Clarkson UNIVERSITY defy convention

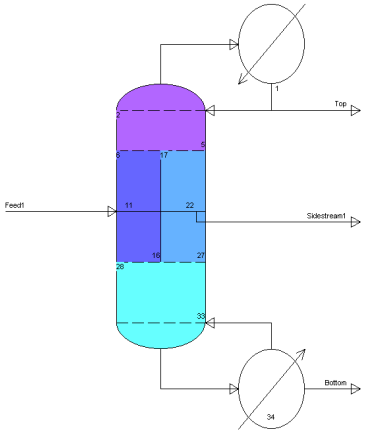
Top-Split DWC



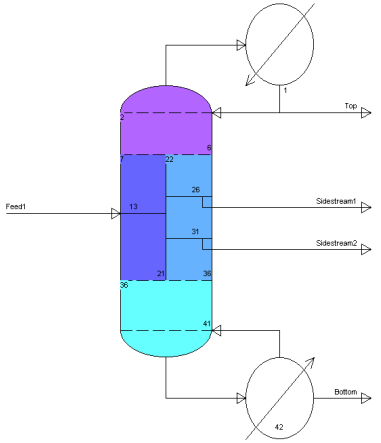
Bottom-Split DWC



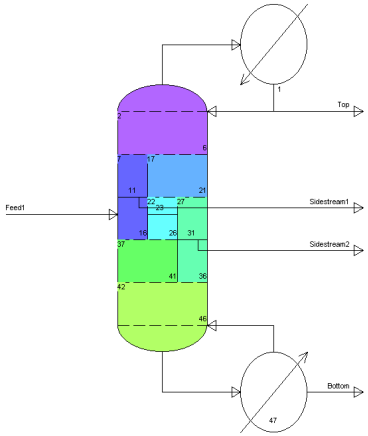
Regular DWC



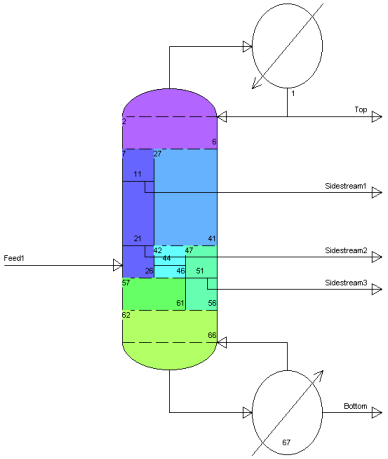
Kaibel DWC



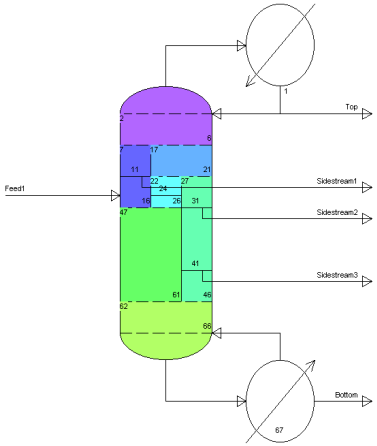
2WC



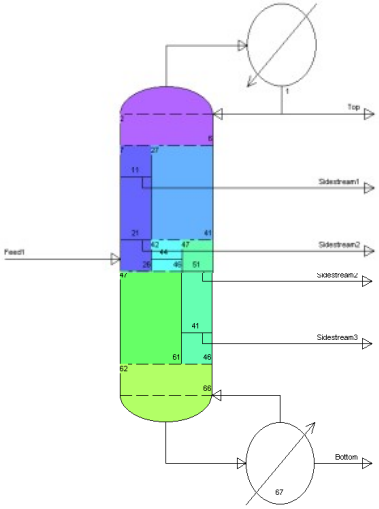
Upper-Kaibel 2WC



Lower-Kaibel 2WC



Double Kaibel 2WC

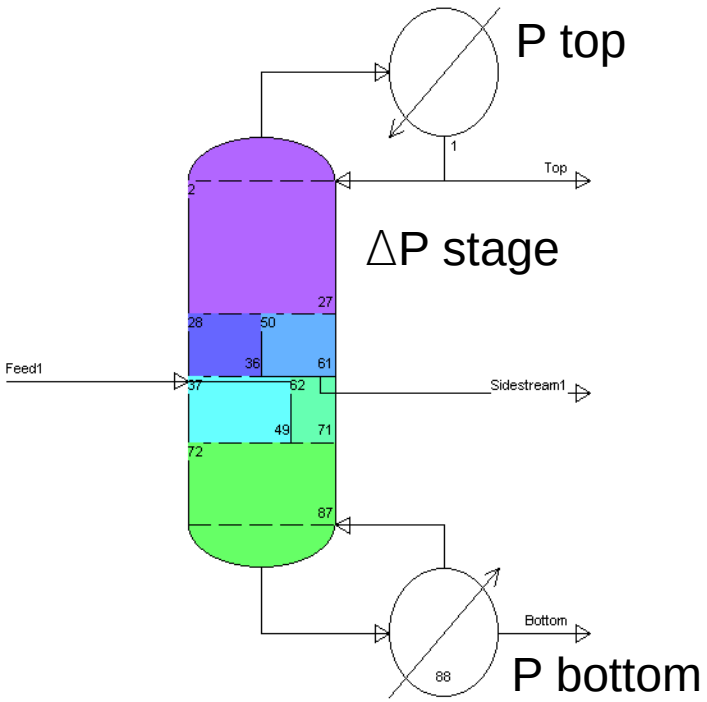


Parallel Column Model - ChemSep

Simplified pressure specification:

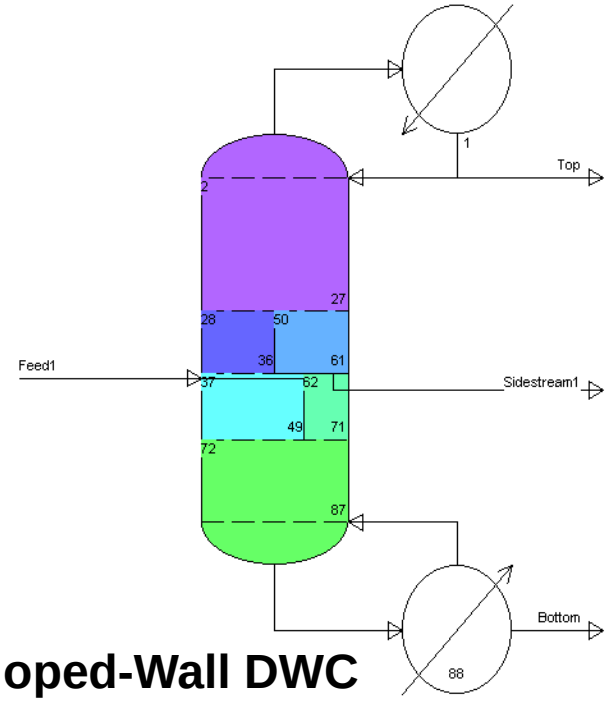
- Top and Bottom pressure
- Top and ∆P: makes switching configuration easy!

  Assume area ratio equalizes ∆P on either side of the wall

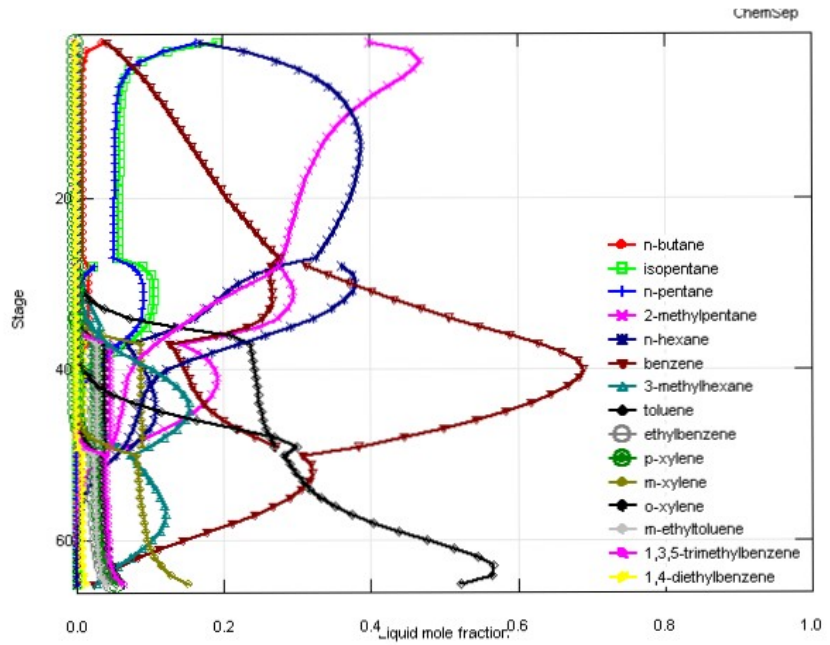


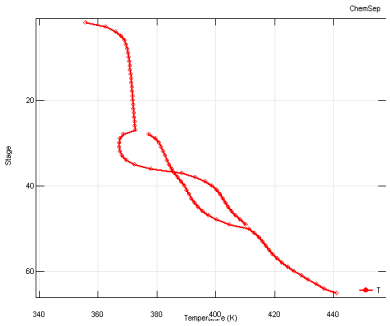
Parallel Column Model - Easy Results

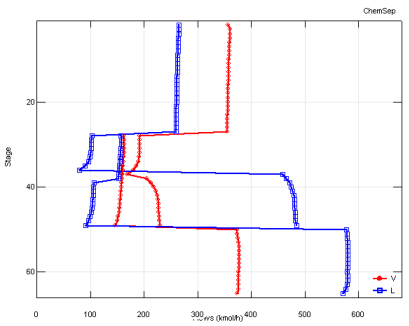
Profile plots with combined walls

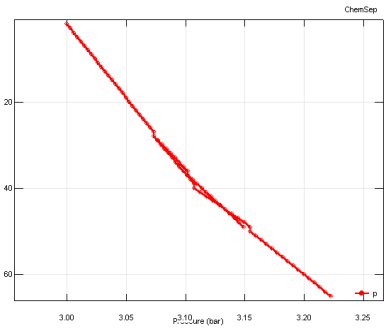


Sloped-Wall DWC



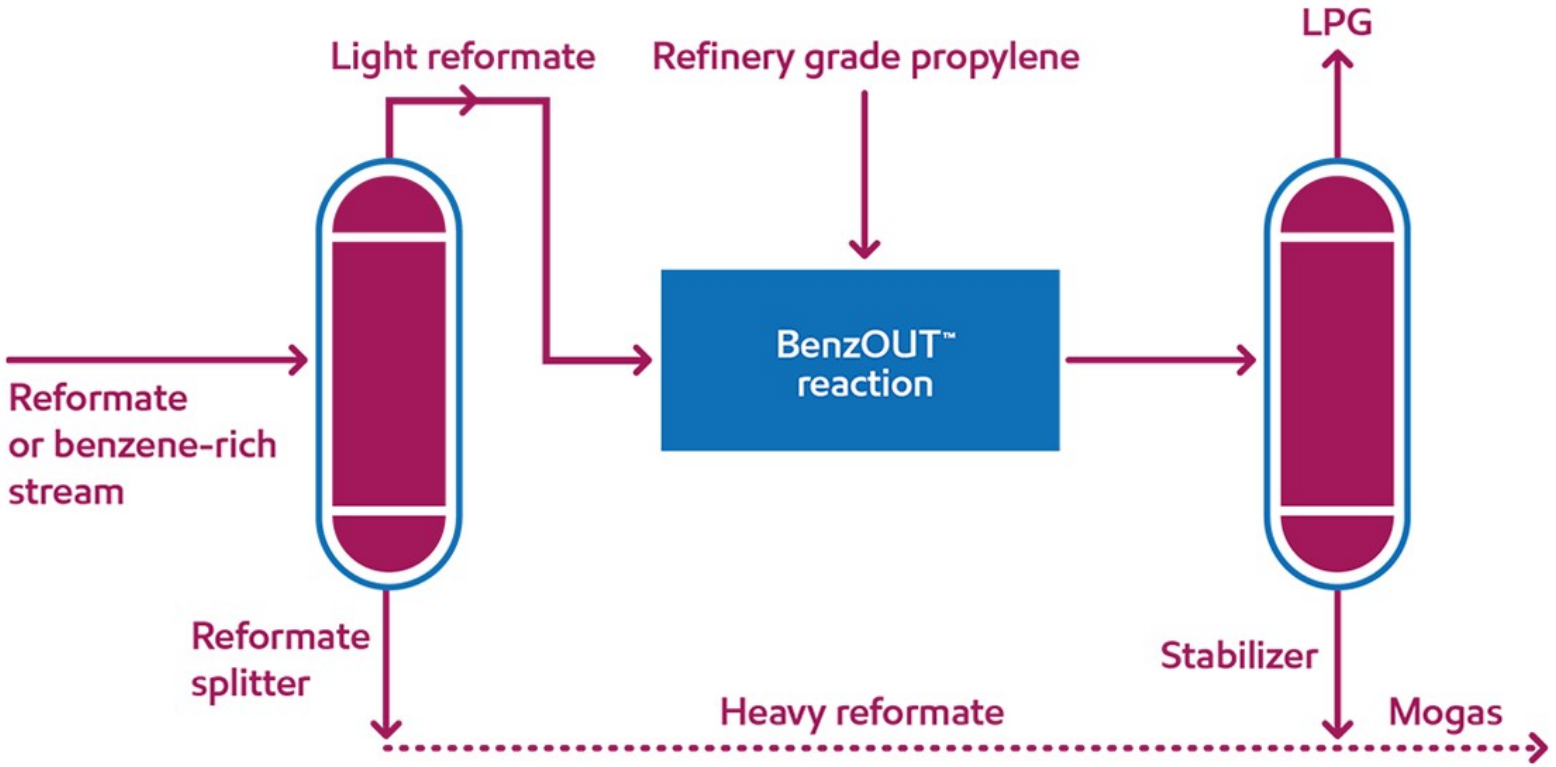






Refinery: Reformate Processing

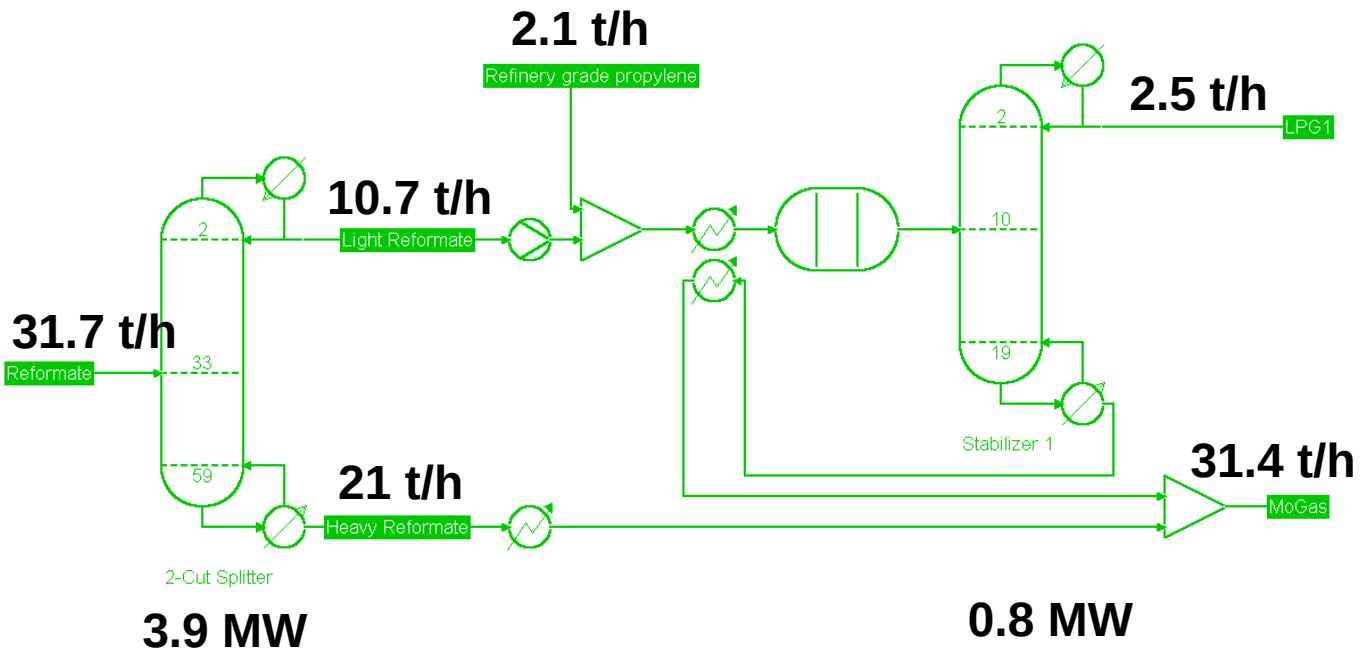
- Reduce Benzene in gazoline (Mogas) by reacting with Propylene without causing a loss in octane#
- Includes stabilizer to maintain low vapor pressure
- Patented US 8,395,006 B2 by EXXON-Mobile:



Refinery: EXXON-Mobil BenzOUT

- Process needs to fulfill petroleum properties specs:
  - Minimize drop in **Octane Number**
  - Maintain low **Reid Vapor Pressure**

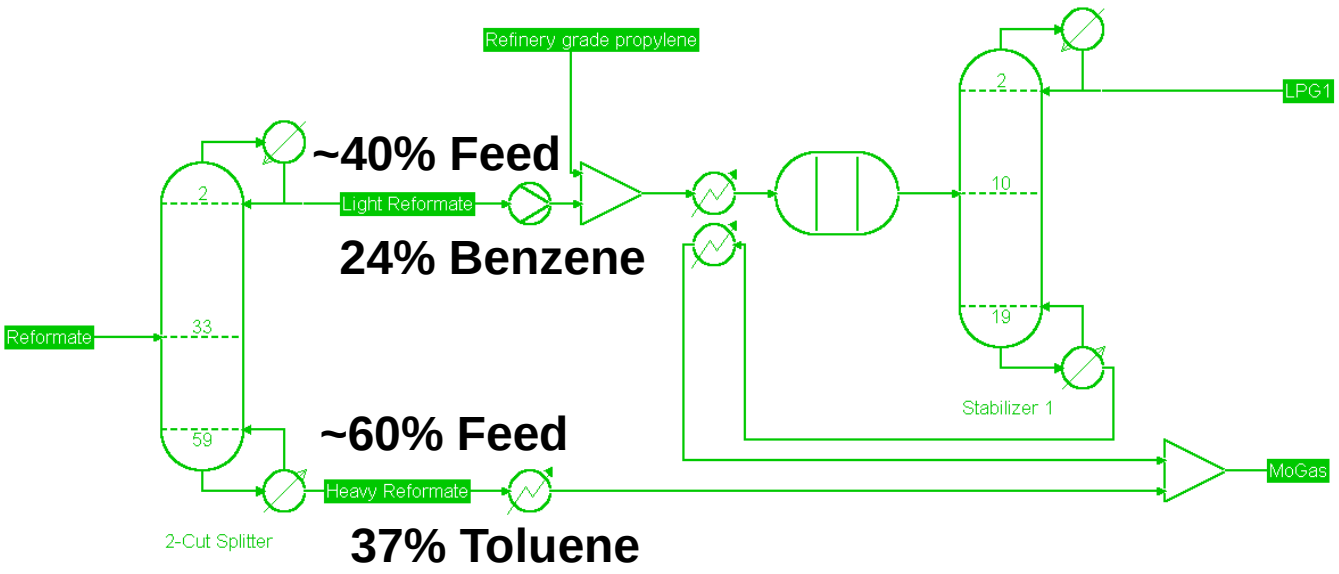
Need to monitor these extra properties



Stream	Reformate	MoGas	Unit
Pressure	3.5	2.5	bar
Temperature	100	71.0902	°C
Flow rate	343	335.349	kmol / h
Mole frac n-butane	0.0309038	0.00909843	
Mole frac isopentane	0.0819242	0.0835314	
Mole frac n-pentane	0.0580175	0.0592973	
Mole frac 2-methylpentane	0.0862974	0.0882657	
Mole frac n-hexane	0.045481	0.0465187	
Mole frac benzene	0.101458	0.0121412	
Mole frac 3-methylhexane	0.0186589	0.0190846	
Mole frac toluene	0.248397	0.254064	
Mole frac ethylbenzene	0.0306122	0.0313107	
Mole frac p-xylene	0.0370262	0.037871	
Mole frac m-xylene	0.106122	0.108544	
Mole frac o-xylene	0.0478134	0.0489043	
Mole frac m-ethyltoluene	0.0361516	0.0369765	
Mole frac 1,3,5-trimethylbenzene	0.0594752	0.0608322	
Mole frac 1,4-diethylbenzene	0.0116618	0.0119279	
Mole frac Propane	0	6.03384e-07	
Mole frac Propylene	0	6.69168e-07	
Mole frac Cumene	0	0.0595601	
Liquid phase			
OCTN	100.404	98.3165	-
RVP	0.414281	0.315115	bar
TVP100	0.427999	0.333599	bar

Refinery: EXXON-Mobil BenzOUT

- Process needs to fulfill petroleum properties specs:
  - Minimize drop in **Octane Number**
  - Maintain low **Reid Vapor Pressure**



Stream	Reformate	MoGas	Unit
Pressure	3.5	2.5	bar
Temperature	100	71.0902	°C
Flow rate	343	335.349	kmol / h
Mole frac n-butane	0.0309038	0.00909843	
Mole frac isopentane	0.0819242	0.0835314	
Mole frac n-pentane	0.0580175	0.0592973	
Mole frac 2-methylpentane	0.0862974	0.0882657	
Mole frac n-hexane	0.045481	0.0465187	
Mole frac benzene	0.101458	0.0121412	
Mole frac 3-methylhexane	0.0186589	0.0190846	
Mole frac toluene	0.248397	0.254064	
Mole frac ethylbenzene	0.0306122	0.0313107	
Mole frac p-xylene	0.0370262	0.037871	
Mole frac m-xylene	0.106122	0.108544	
Mole frac o-xylene	0.0478134	0.0489043	
Mole frac m-ethyltoluene	0.0361516	0.0369765	
Mole frac 1,3,5-trimethylbenzene	0.0594752	0.0608322	
Mole frac 1,4-diethylbenzene	0.0116618	0.0119279	
Mole frac Propane	0	6.03384e-07	
Mole frac Propylene	0	6.69168e-07	
Mole frac Cumene	0	0.0595601	
Mole frac P-diisopropylbenzene	0	0.0320708	
Liquid phase			
OCTN	100.404	98.3165	-
RVP	0.414281	0.315115	bar
TVP100	0.427999	0.333599	bar

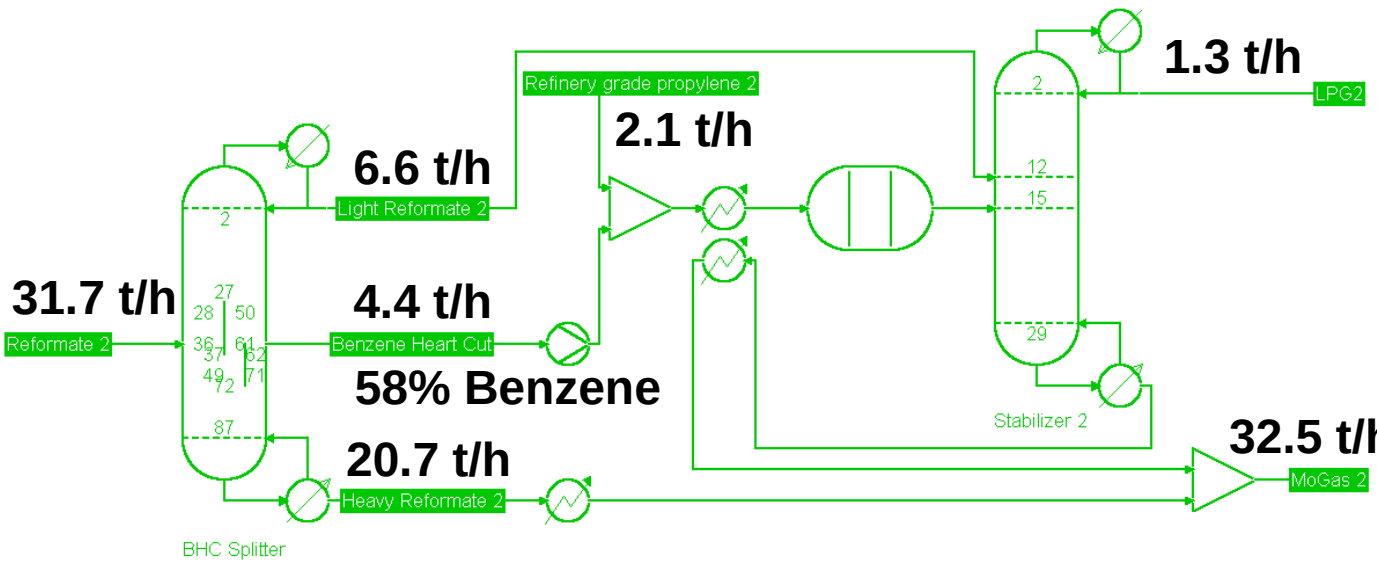
Refinery: EXXON-Mobil BenzOUT

Improve the economics of this process while maintaining OCTN & RVP:

- Only send Benzene-rich “heart-cut” to reactor: Reduce flow through reactor & stabilizer by 2x
- Can revamp existing reformate splitter to DWC

Refinery: EXXON-Mobil BenzOUT

- Advantages:
  - Smaller reactor + stabilizer: TAC -30%
  - No difference in OCTN or RVP
  - Slight lower overall duty (-5%)



Stream	Reformate 2	MoGas 2	Unit
Pressure	3.5	2.5	bar
Temperature	100	71.3644	°C
Flow rate	343	334.936	kmol / h
Mole frac n-butane	0.0309038	0.0115992	
Mole frac isopentane	0.0819242	0.0805443	
Mole frac n-pentane	0.0580175	0.0587449	
Mole frac 2-methylpentane	0.0862974	0.0883696	
Mole frac n-hexane	0.045481	0.0465759	
Mole frac benzene	0.101458	0.0120102	
Mole frac 3-methylhexane	0.0186589	0.0191081	
Mole frac toluene	0.248397	0.254377	
Mole frac ethylbenzene	0.0306122	0.0313493	
Mole frac p-xylene	0.0370262	0.0379177	
Mole frac m-xylene	0.106122	0.108678	
Mole frac o-xylene	0.0478134	0.0489646	
Mole frac m-ethyltoluene	0.0361516	0.037022	
Mole frac 1,3,5-trimethylbenzene	0.0594752	0.0609072	
Mole frac 1,4-diethylbenzene	0.0116618	0.0119426	
Mole frac Propane	0	2.02693e-06	
Mole frac Propylene	0	2.25938e-06	
Mole frac Cumene	0	0.0597255	
Liquid phase			
OCTN	100.404	98.3402	-
RVP	0.414281	0.318967	bar
TVP100	0.427999	0.337995	bar

Refinery: EXXON-Mobil BenzOUT

Other advantages:

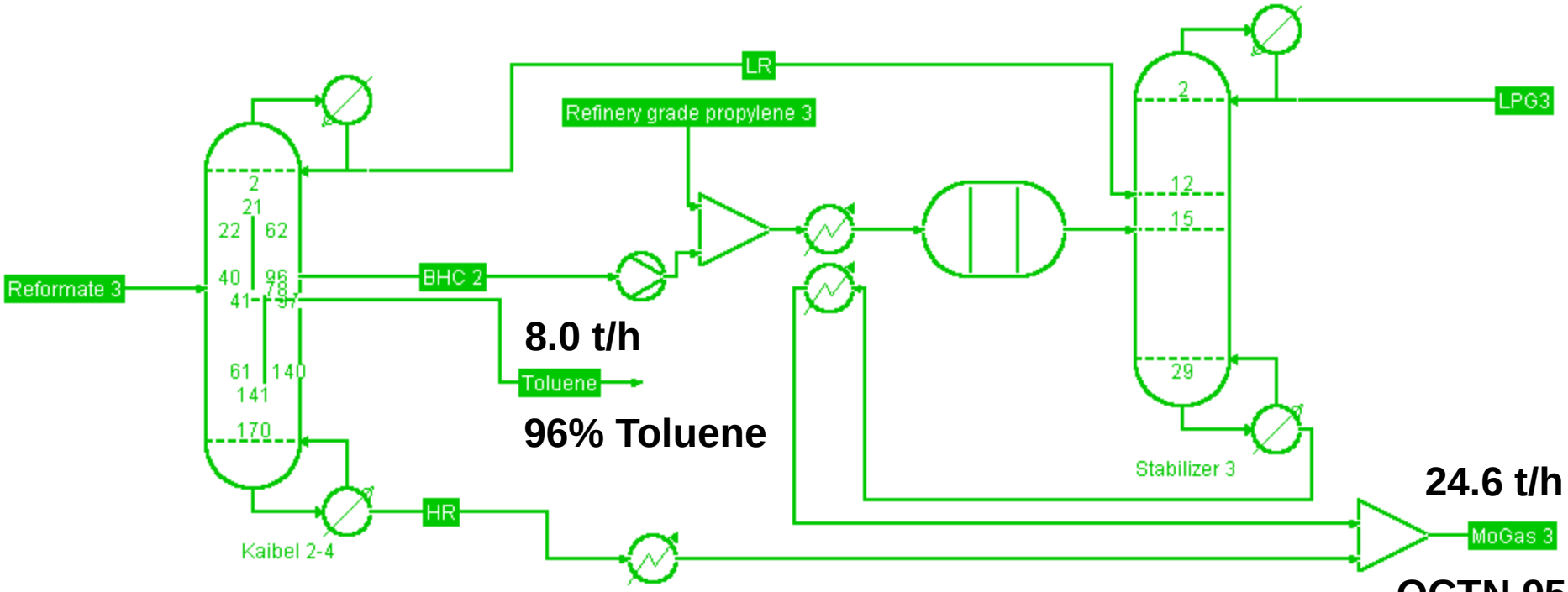
- Flexible co-production of Benzene-rich product

Can we further optimize?

- Kaibel configuration: enables co-production of >96% Toluene as separate product
- Maintaining OCTN 95 Mogas

Refinery: EXXON-Mobil BenzOUT

- Existing reformate splitters can be revamped using sloped-wall DWC designs, like Dejanovic *et al.**



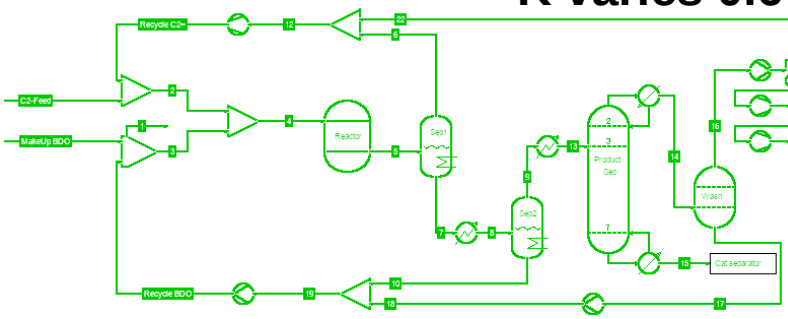
Slightly more energy if Toluene is produced

* **Dejanović, I.**, Matijašević, L., Jansen, H., **Olujić, Ž.**, 2011. Designing a Packed Dividing Wall Column for an Aromatics Processing Plant. Industrial & Engineering Chemistry Research 50, 5680–5692. https://doi.org/10.1021/ie1020206

Chemicals: SHOP

Shell Higher Olefins Process (linear α-olefins)

K varies 0.6 to 0.7



320 KTA

Stream	C4=	C6=	C8=	C10=	C12=	C14=	C16=, C18=
			1.1	0.1	0.1	0.1	0.15
Temperature, °C	56.70	65.88	124.06	97.52	135.16	169.26	221.49
Flowrate, ton/h	9.51	9.47	8.32		5.20	3.96	5.78
Mass composition:							
C2=	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
C4=	0.9985	0.0010	0.0000	0.0000	0.0000	0.0000	0.0000
C6= + b-C6=	0.0015	0.9990	0.0011	0.0000	0.0000	0.0000	0.0000
C8= + b-C8=	0.0000	0.0000	0.9985	0.0012	0.0000	0.0000	0.0000
C10= + b-C10=	0.0000	0.0000	0.0003	0.9986	0.0013	0.0000	0.0000
C12= + b-C12=	0.0000	0.0000	0.0000	0.0001	0.9987	0.0006	0.0000
C14= + b-C14=	0.0000	0.0000	0.0000	0.0000	0.0000	0.9991	0.0026
C16= + b-C16=	0.0000	0.0000	0.0000	0.0000	0.0000	0.0009	0.5189
C18= + b-C18=	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.3875
C20= + b-C20=	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0915

Columns	DeC6=	DeC8=	DeC10=	DeC12=	DeC14=
Condenser temperature, °C	65.88	124.06	97.52	135.16	169.26
Reboiler temperature, °C	178.46	227.39	183.49	214.43	221.49
Condenser duty, MW	-1.47	-1.65	-1.84	-1.47	-0.82
Reboiler duty, MW	3.41	2.13	0.73	1.51	0.72

K=0.65 Stoichiometric factors	
C2	36925
C4	3510
C6	2281
C8	1483
C10	964
C12	627
C14	407
C16	265
C18	172
C20	112
b-C6	53
b-C8	53
b-C10	12
b-C12	12
b-C14	12
b-C16	12
b-C18	12
b-C20	12

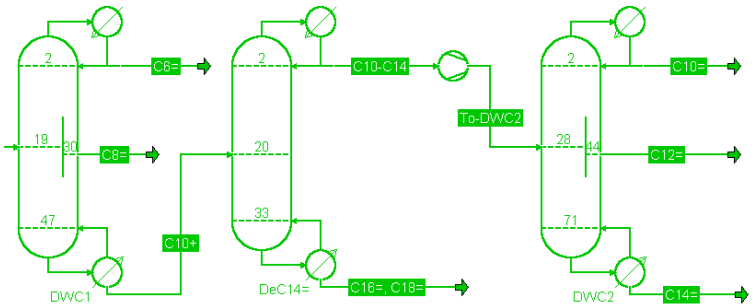
Stream	C2-Feed	5	9	C4+	C4=	C6=	C8=	C10=	C12=	C14=	C16=, C18=	Unit
Pressure	90	90	20	30	7	1.1	1.1	0.1	0.1		0.15	bar
Temperature	20	90	35	187.391	56.6957	65.884	124.058	97.5222	135.156	169.271	221.492	°C
Flow rate	50	501.071	51.2725	48.848	9.51108	9.46699	8.32323	5.60783	5.19476	3.96276	5.78139	ton/h
Mass frac ethylene	1	0.0249455	0.0118894	2.74822e-08	1.41146e-05	1.02364e-16	0	0	0	0	0	
Mass frac 1-butene	0	0.0968532	0.190414	0.194801	0.998451	0.00100411	1.41525e-13	0	0	0	0	
Mass frac 1-hexene	0	0.0475934	0.180724	0.189692	0.00149925	0.979292	0.00111156	2.19476e-14	0	0	0	
Mass frac 1-octene	0	0.0283196	0.155662	0.164438	2.94434e-09	1.90024e-05	0.96408	0.00121557	5.75434e-15	0	0	
Mass frac 1-decene	0	0.0183399	0.127295	0.133613	7.00812e-15	1.84848e-13	0.000310585	0.986348	0.00125591	5.72[illegible]e-13	0	
Mass frac 1-dodecene	0	0.0124623	0.0993534	0.104285	2.39491e-20	2.69345e-25	3.87106e-11	0.00011302[illegible]	0.979989	0.000[illegible]	8.88455e-13	
Mass frac 1-tetradecene	0	0.00867608	0.0752413	0.0789757	0	0	4.23952e-18	4.27453e-13	1.40539e-11	0.970[illegible]	0.00200184	
Mass frac 1-hexadecene	0	0.00614195	0.0559886	0.0587574	0	0	7.43385e-25	4.87163e-21	1.8518e-25	8.9038[illegible]	0.496478	
Mass frac 1-octadecene	0	0.00435499	0.0408822	0.0428705	4.97697e-21	0	0	0	0	5.1[illegible]	0.365221	
Mass frac 1-eicosene	0	0.00309758	0.0295789	0.0305757	0	0	2.08596e-21	1.88671e-23	5.67623e-25	5.35716e-23	0.231495	
Mass frac 2-methyl-1-pentene	0	0.00114203	0.00419921	0.00440756	3.51785e-05	0.0226837	2.64271e-05	5.89384e-16	1.51572e-21	0		
Mass frac 2-methyl-1-heptene	0	0.00104315	0.00559886	0.00587675	1.33961e-10	1.5186e-05	0.034462	3.29635e-05	4.51493e-17	0	0	
Mass frac 2-methyl-1-nonene	0	0.00023351	0.00158458	0.00166323	2.79407e-16	2.16372e-10	9.09699e-06	0.0122793	5.85167e-06	1.76898e-15	0	
Mass frac 2-methyl-1-undecene	0	0.00024168	0.0019013	0.00199588	8.97878e-22	0	1.42338e-12	1.0941e-05	0.0187496	5.67669e-08	4.46339e-06	
Mass frac 2-methyl-1-tridecene	0	0.00025722	0.00221842	0.00232852	0	0	1.92116e-19	6.32718e-14	5.93439e-12	0.0286527	2.77229e-05	
Mass frac 2-methyl-1-pentadecene	0	0.00027394	0.00253533	0.00266117	0	0	0	3.2109e-22	4.75007e-25	5.15376e-08	0.0225812	
Mass frac 2-methyl-1-heptadecene	0	0.00030468	0.00285225	0.00299163	0	0	0	0	0	1.34486e-13	0.0252769	
Mass frac 2-methyl-1-nonadecene	0	0.00033242	0.00316917	0.00217372	4.50834e-21	2.35795e-21	1.03944e-23	1.04229e-21	1.93204e-21	7.64807e-21	0.0183662	
Mass frac 1,4-butanediol	0	0.745273	0.00791098	0	0	0	0	0	0	0	0	

https://patentimages.storage.googleapis.com/calad9b/96b77a1003624e7/US4377499.pdf

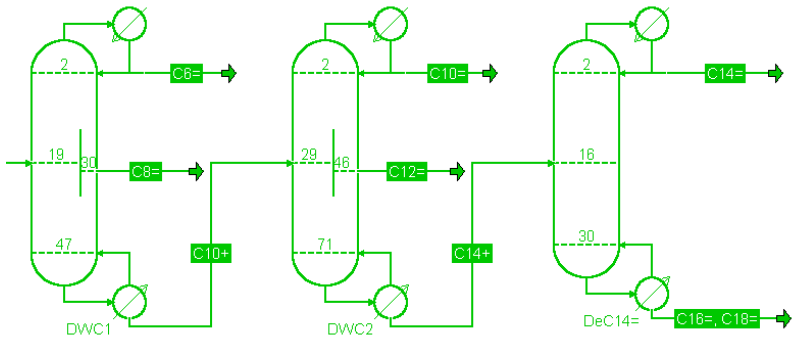
https://patentimages.storage.googleapis.com/7b/bb/1d/574d67c5899c79/US4020121.pdf

Catalysis Today, 14 (1992) pp. 1-124

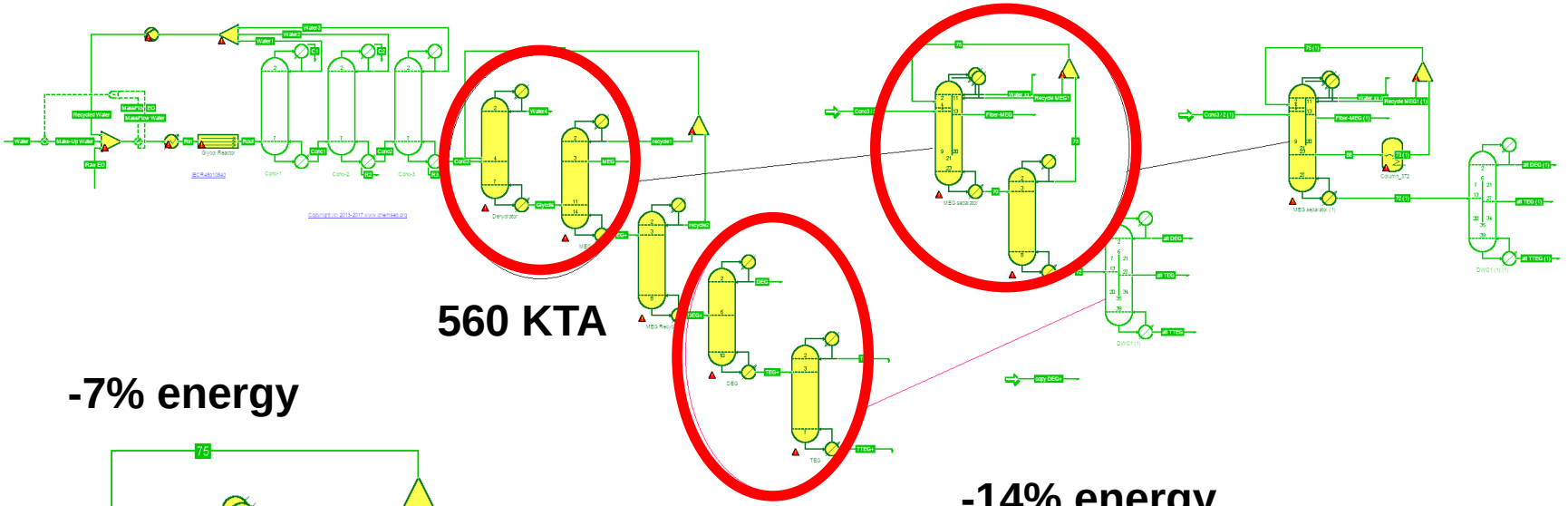
3,2,3: -12% energy



3,3,2: -22% energy

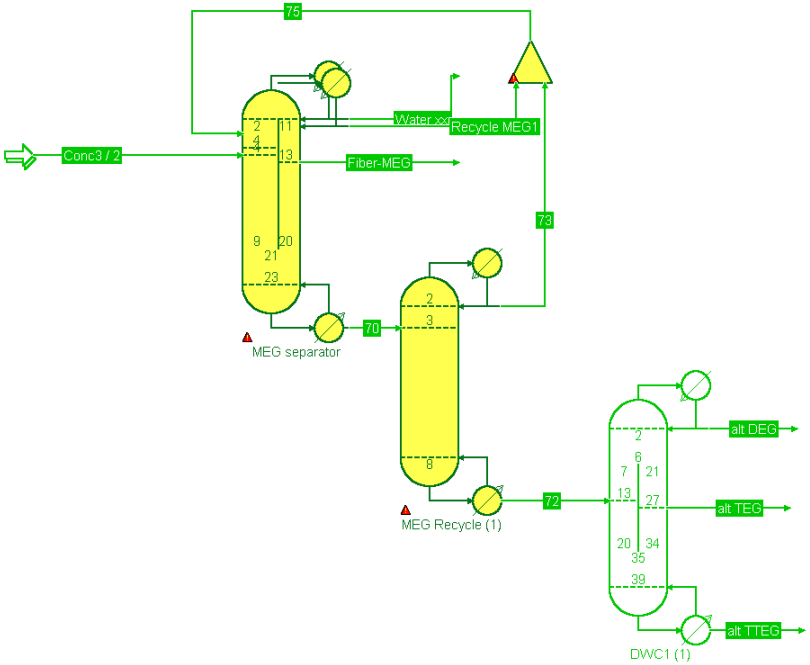


Chemicals: Ethylene Glycols (MEG)



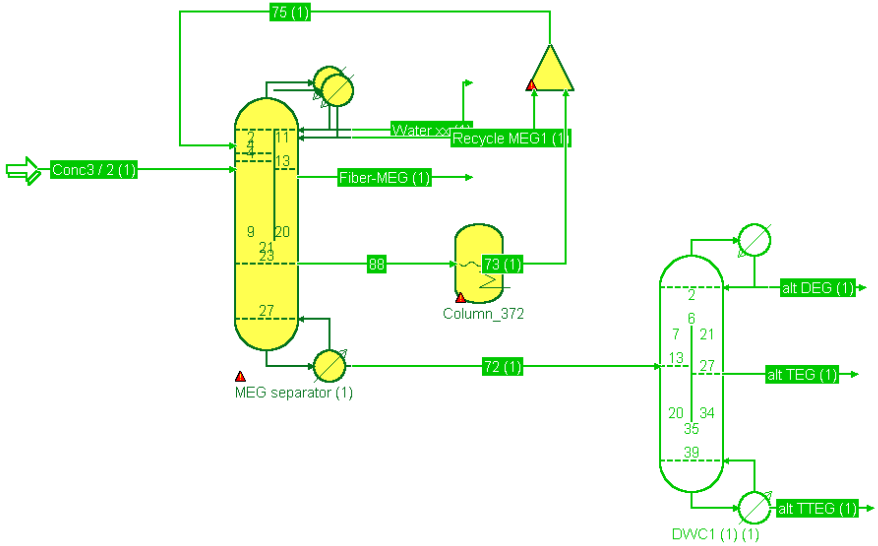
560 KTA

-7% energy

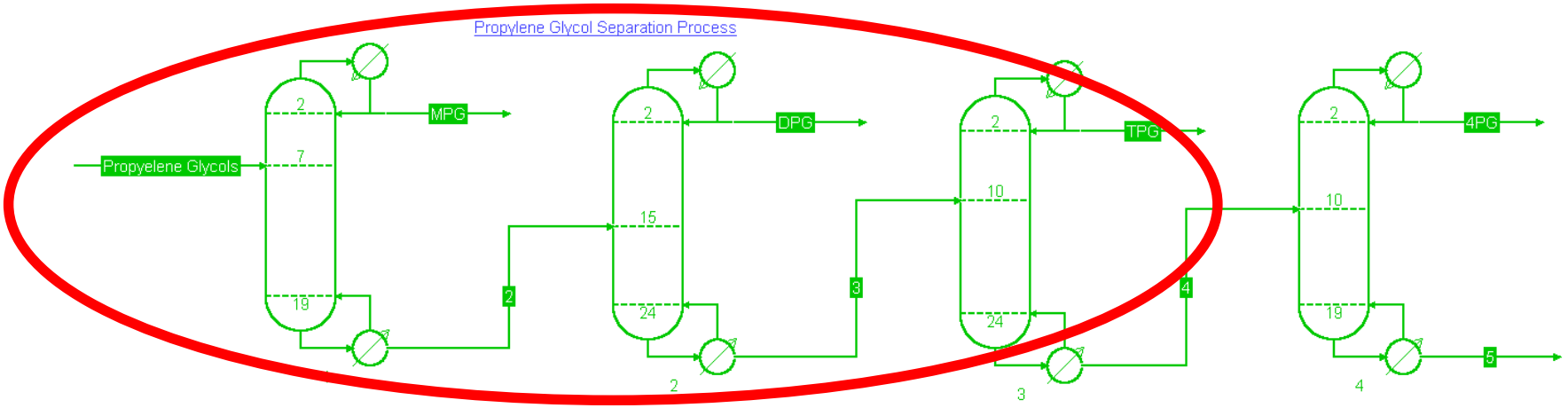


small savings

-14% energy



Chemicals: Propylene Glycol (MPG)



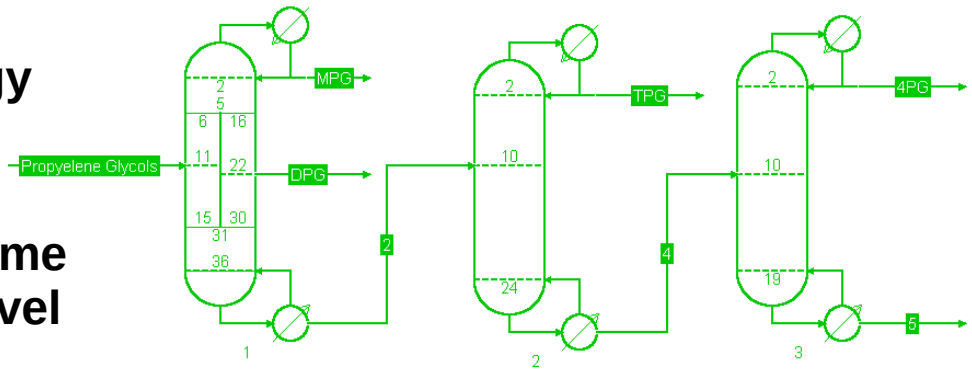
Shell MPG and DPG
Solventis MPG and DPG
BASF MPG, DPG, and TPG
Other routes to MPG
OltChim
Thyssen-Krupp

Stream	MPG	DPG	TPG	4PG	Unit
Pressure	0.1	0.1	0.05	0.02	bar
Temperature	124.656	161.651	170.525	192.629	°C
Flow rate	20	40	30	20	kmol / h
Mass frac MPG	0.996465	0.000565592	0	0	
Mass frac DPG	0.00348994	0.992301	0.00465464	0	
Mass frac TPG	4.46161e-05	0.0071331	0.992754	0.00228756	
Mass frac 4PG	0	0	0.00259103	0.991573	
Mass frac 5PG	0	0	0	0.00613969	
Mass frac HexaPropylene Glycol	0	0	0	0	

160 KTA

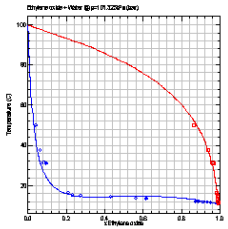
Large **energy savings**

DWC for same pressure level

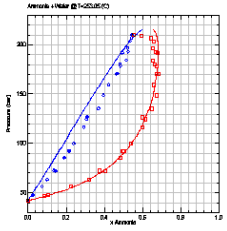


Chemicals: Ethanol-Amines

EO+Water, Coles K.F., Popper F., Ind.Eng.Chem., 42(7), pp. 1434-1438, (1950)



Syed S. H. Rizvi and Robert A. Heidemann, J.Chem.Eng.Data 32, pp. 183-191 (1987)



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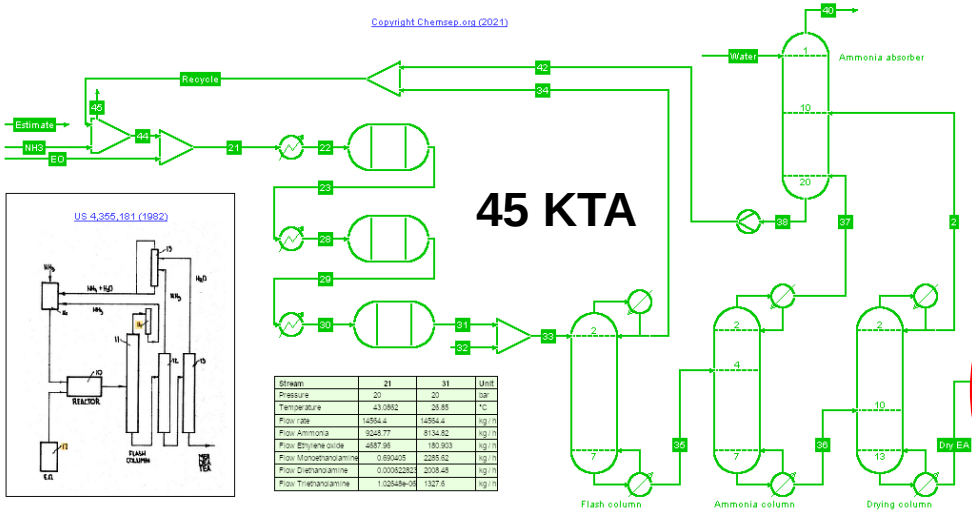
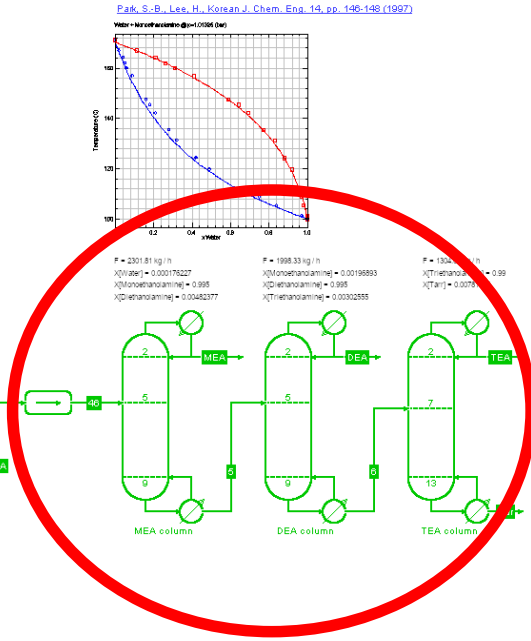


US 4,355,181 (1982)

Stream	21	31	Unit
Pressure	20	20	bar
Temperature	43.0862	26.85	°C
Flow rate	14554.4	14554.4	kg/h
Flow Ammonia	9248.77	8134.82	kg/h
Flow Ethylene oxide	4687.96	180.903	kg/h
Flow Monoethanolamine	0.690405	2285.62	kg/h
Flow Diethanolamine	0.000832823	2008.48	kg/h
Flow Triethanolamine	1.02648e-06	1327.6	kg/h

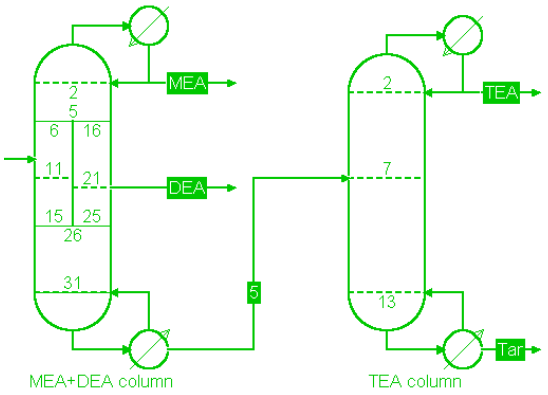
Park, S.-B., Lee, H., Korean J. Chem. Eng. 14, pp. 146-148 (1997)



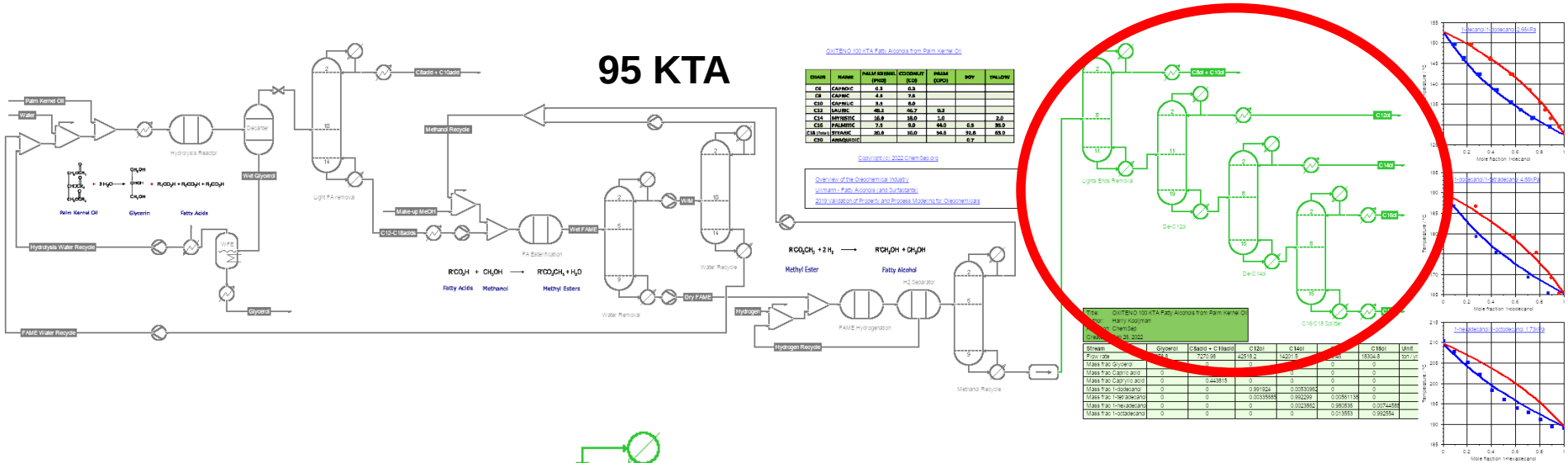
Simulation and optimization of ethanol amine production plant, Korean J. Chem.Eng. 26 (6) pp. 1504-1511 (2009)
Cost-efficient production of ethanolamines
Ullmann chapter on Ethanol-Amines
Catalysts for the production of ethanolamines, Ind.Eng.ChemProd.Res.Dev. (1985) 25 pp. 424-430
US 2,622,073 (1952) US 4,119,670 (1976)

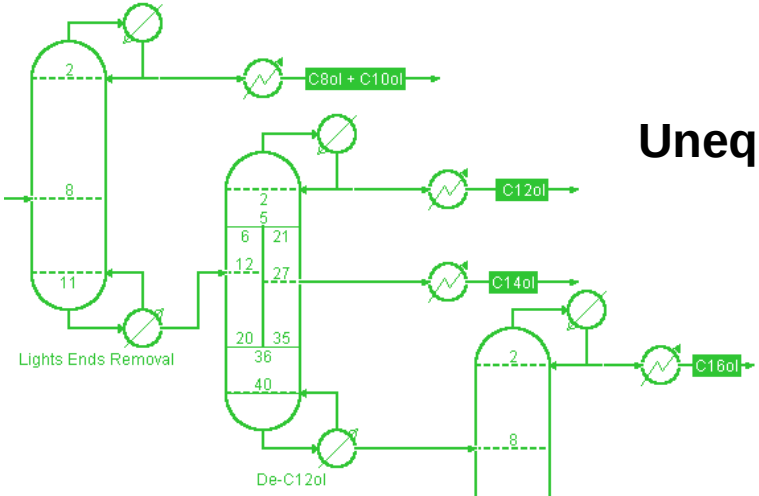
Stream	33	35	36	Dry EA	Unit
Pressure	20	20	8	1.01325	bar
Temperature	26.7941	139.076	175.184	190.137	°C
Flow rate	14814.3	7069.93	6859.05	5871.09	kg/h
Flow Ammonia	8134.82	417.134	21.5272	1.41325e-11	kg/h
Flow Water	629.945	624.603	624.603	0.119235	kg/h
Flow Monoethanolamine	2285.62	2284.93	2284.93	2284.93	kg/h
Flow Diethanolamine	2008.48	2008.48	2008.48	2008.48	kg/h
Flow Triethanolamine	1327.6	1327.6	1327.6	1327.6	kg/h

No energy savings
Savings from single C & R



Oleo-Chemicals: Fatty Alcohols

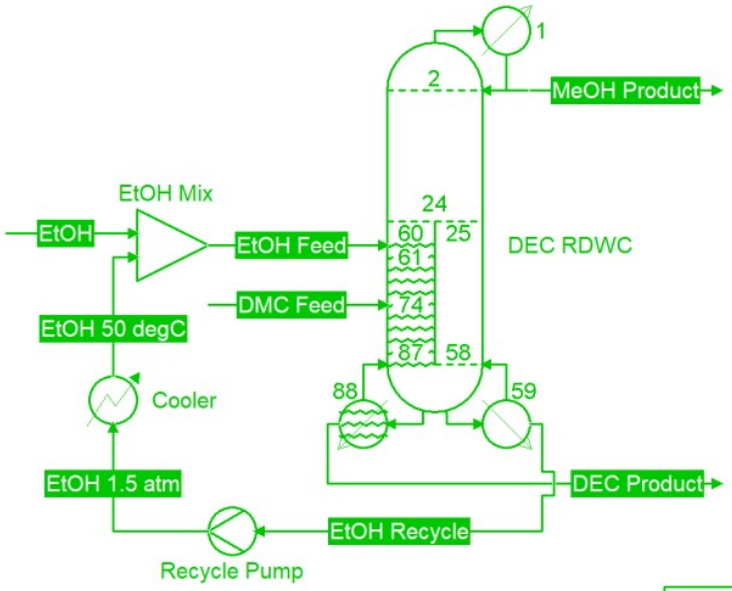


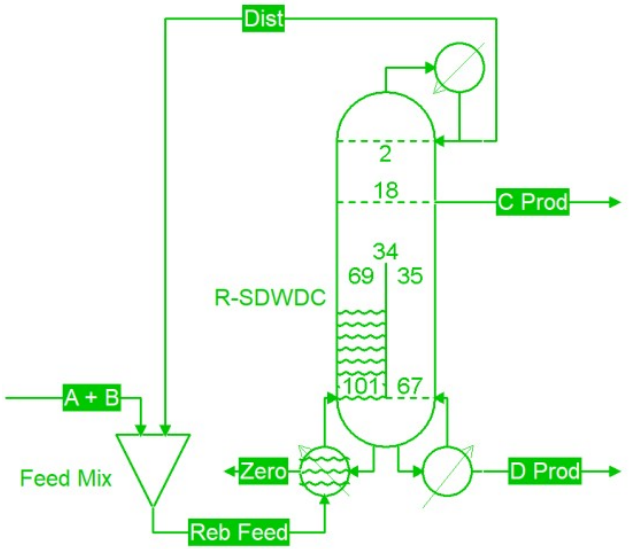


Unequal pressure levels

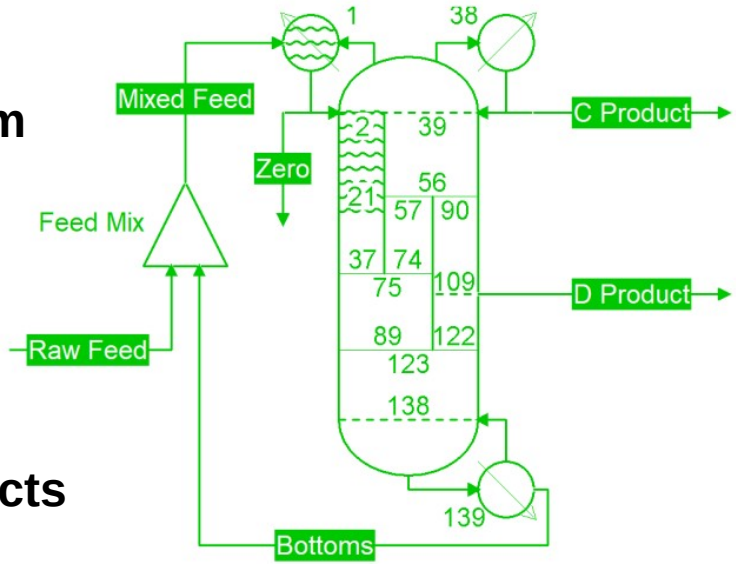
-30% energy

Reactive DWC





Capex savings from reactor integration



Big benefits from stripping of products

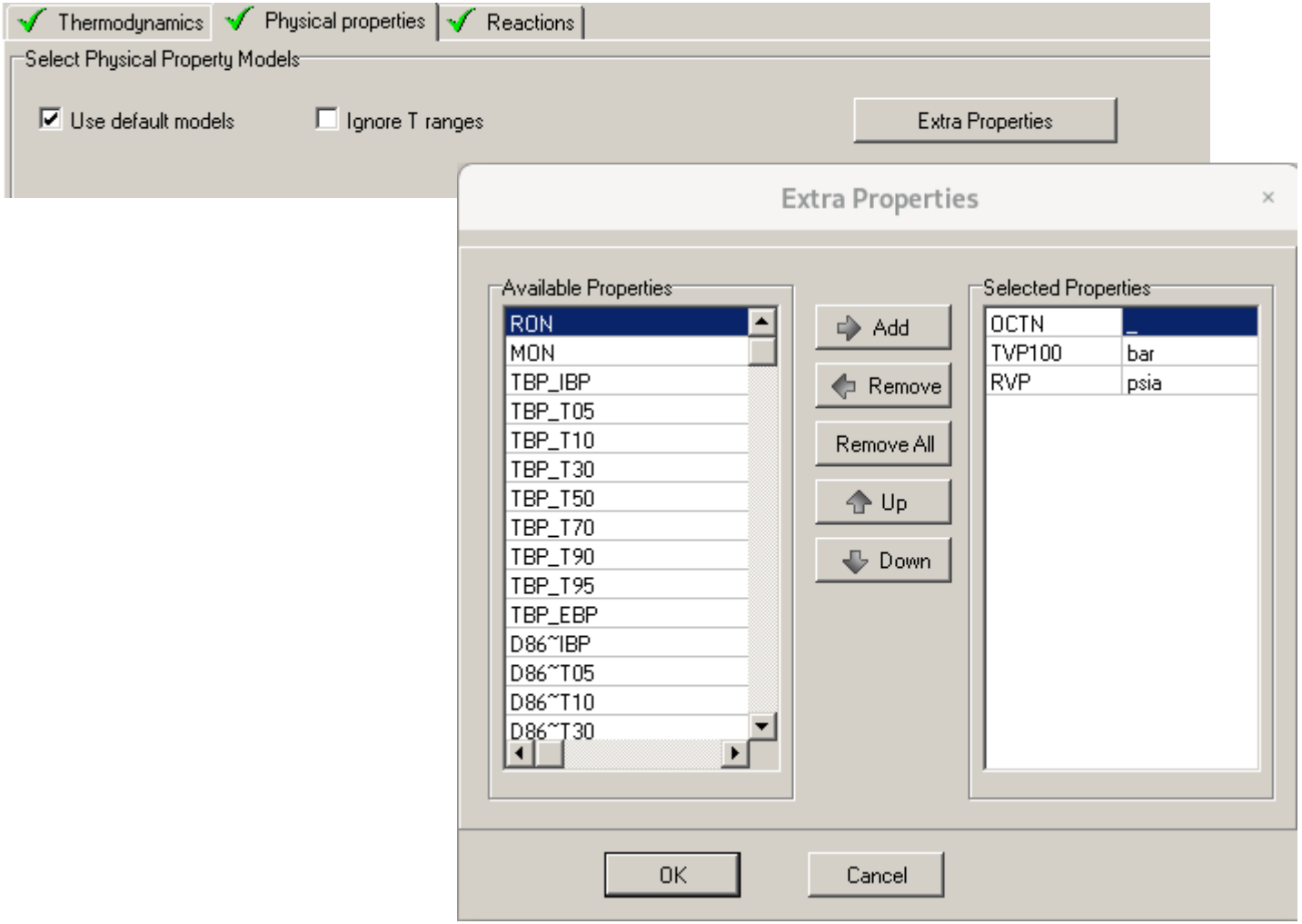
Summary

- Simulation ‘easily’ done in ChemSep by use of predefined configurations **with** pressure drops
- Can optimize DWC process on petroleum properties
- Not every DWC is physically feasible / lower in capex
- DWC selection & its integration in the process matter

Questions?

Selection of “Extra Properties”

Part of the physical properties models selection



Extra Properties Methods

RON & MON: Table values / Estimated from groups or Tb & SG

OCTN: Posted Octane Number = RON/2+MON/2

Flash Point: Riazi (eqn. 3.114/3.115)

TVP100: Antoine vapor pressure model at 100 F
(with Ambrose or Riedel as back-up)

RVP: Approximation using the TVP100, mixtures per Riazi p. 132

TBP: Spline interpolation

D86: Riazi-Daubert 1986 on TBP

API density

K Watson

More to come...

RON & MON Estimation

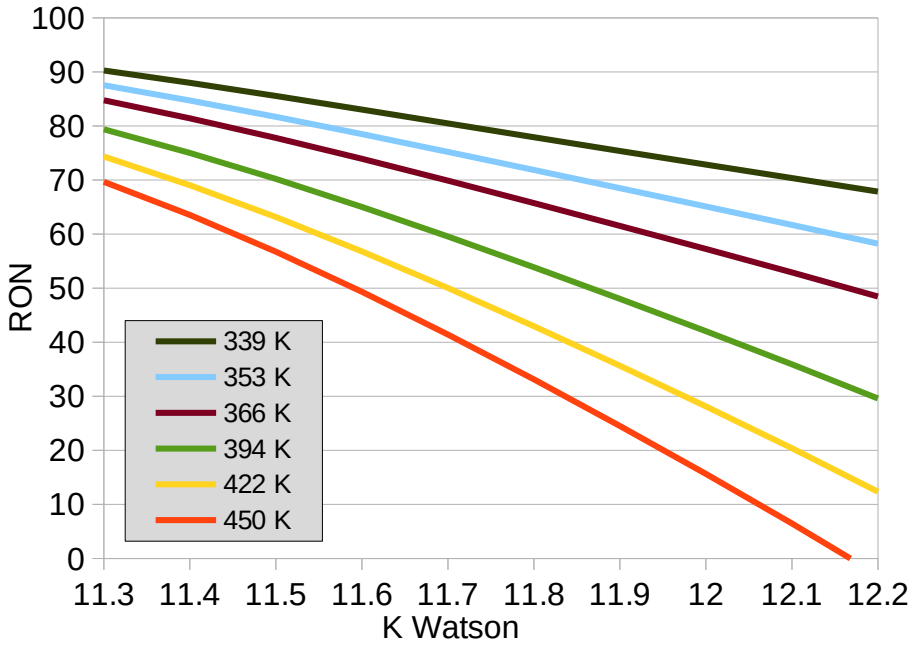
RON:

- UNIFAC groups: Albahri (*Ind.Eng.Chem.Res.* (2003) 42, pp. 657-662 + (2004) 43, p. 7964) and new -OH/=O/-O- groups average error 8.8%

- Pseudo's: Nelson (1969) as *f*(Kw,Tb) for Naphtha's

MON:

Jenkins (1968)
average error 8%

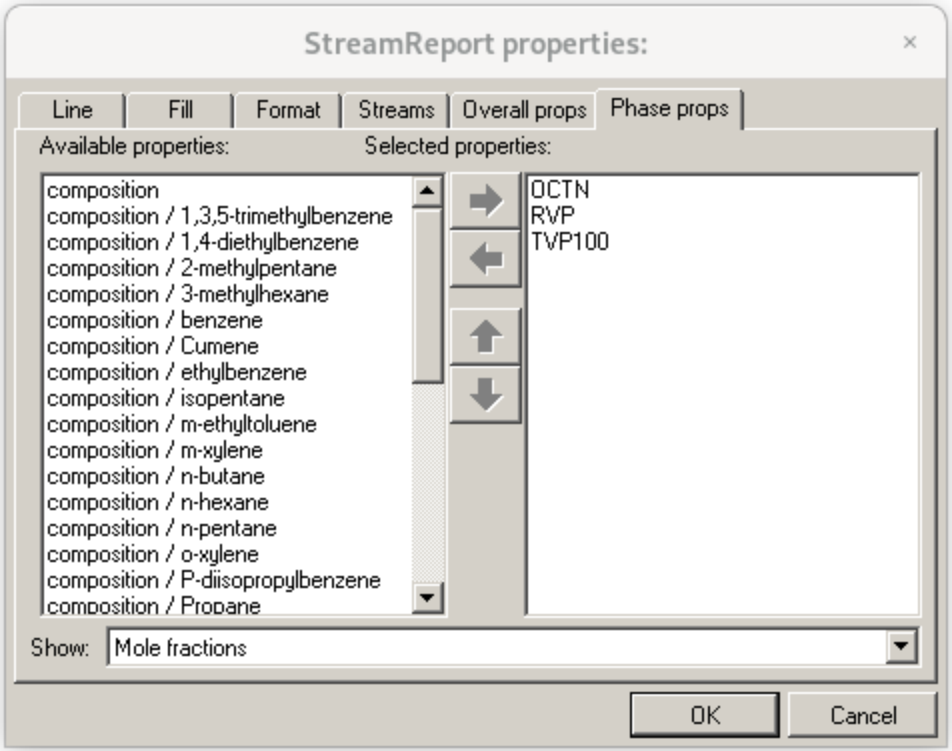


Extra Properties

Clarkson UNIVERSITY defy convention

Stream-tables with custom CAPE-OPEN properties

Stream	Reformate	MoGas	Unit
Pressure	3.5	2.5	bar
Temperature	100	71.0902	°C
Flow rate	343	335.349	kmol / h
Mole frac n-butane	0.0309038	0.00909843	
Mole frac isopentane	0.0819242	0.0835314	
Mole frac n-pentane	0.0580175	0.0592973	
Mole frac 2-methylpentane	0.0862974	0.0882657	
Mole frac n-hexane	0.045481	0.0465187	
Mole frac benzene	0.101458	0.0121412	
Mole frac 3-methylhexane	0.0186589	0.0190846	
Mole frac toluene	0.248397	0.254064	
Mole frac ethylbenzene	0.0306122	0.0313107	
Mole frac p-xylene	0.0370262	0.037871	
Mole frac m-xylene	0.106122	0.108544	
Mole frac o-xylene	0.0478134	0.0489043	
Mole frac m-ethyltoluene	0.0361516	0.0369765	
Mole frac 1,3,5-trimethylbenzene	0.0594752	0.0608322	
Mole frac 1,4-diethylbenzene	0.0116618	0.0119279	
Mole frac Propane	0	6.03384e-07	
Mole frac Propylene	0	6.69168e-07	
Mole frac Cumene	0	0.0595601	
Mole frac P-diisopropylbenzene	0	0.0320708	
Liquid phase			
OCTN	100.404	98.3165	-
RVP	0.414281	0.315115	bar
TVP100	0.427999	0.333599	bar



Liquid phase			
OCTN	100.404	98.3165	-
RVP	6.00864	4.57036	psi
TVP100	6.2076	4.83844	psi