Retrofit with membrane the Paraffin/Olefin separation

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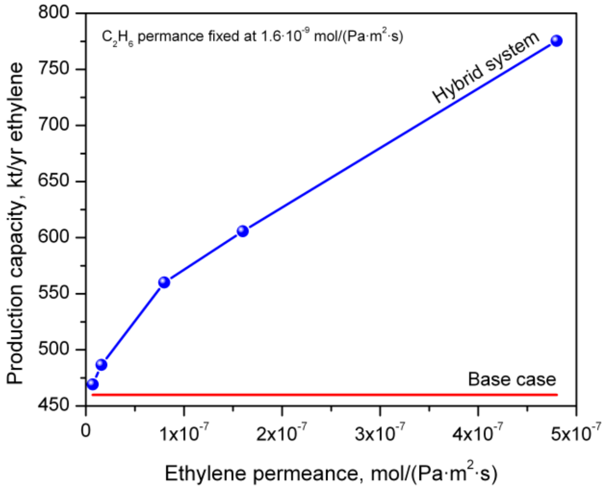
Abstract

Olefins, such as ethylene, propylene, and butadiene, are among the most produced intermediates in petrochemical industry. They are produced from a wide range of hydrocarbon feedstocks (ethane, propane, butane, naphtha, gas oil) via a cracking process. The last step in this process is the separation of olefins from other hydrocarbons, which is traditionally performed with distillation. As the physicochemical properties, such as volatility and boiling point, of the compounds are very similar, the purification becomes capital and energy intensive. For example, the top of an ethylene/ethane distillation column needs to be chilled to –30 oC and this requires large amount of electric energy consumption. The separation of butadiene from the C4-fraction is performed with the aid of an additional solvent. This solvent has to be regenerated at the cost of additional high temperature steam. To overcome these separation disadvantages of olefin/paraffin separation, different separation methods have been investigated and proposed in recent years. Suggested options are based on better heat integration of the overall process, or on novel separation systems such as Heat Integrated Distillation Columns, membrane separation, adsorption-desorption systems or on hybrid separation methods, for example, distillation combined with membrane separation.

The focus of the current presentation is on integration of membrane-based gas separation with conventional distillation. The aim is to find the minimum required membrane performance, like selectivity and permeability, for an economically attractive process. The separation of ethylene from ethane and butadiene from a C4-mixture are considered as the most representative separation cases. The case of propylene/propane separation is not considered due to mild temperatures (~30 oC) at which this column is typically operated. In addition, the option to debottleneck existing distillation columns for ethylene/ethane separation, with the aid of membrane, is presented as new possible application of membranes.

The results reveal that for a hybrid system, membrane-distillation, the energy saving potential for the separation of ethylene from ethane, if compared to the conventional distillation, is rather low due to required very high membrane selectivity. The savings in energy can be expected when the membrane selectivity for ethylene is > 60 (at this moment the best reported membrane selectivity for ethylene is 12). However, this study reveals that the possibility to debottleneck the column capacity in an existing ethylene plant by using membranes is very high (see Figure 1 below). This is economically attractive if the membrane has selectivity for ethylene ≥ 10. The reason for good economic perspectives is the high price of polymeric grade ethylene. In case of butadiene separation, the energy savings can be as high as 30% depending on membrane selectivity and selected process configuration. This high value can be reached when the membrane selectivity for butadiene relative to saturated hydrocarbons equals 15. Similar to ethylene separation case, an increase in the production capacity of butadiene can be achieved in an economic viable fashion.

Figure 1: Production capacity of a hybrid system (membrane + distillation) compared to the base case process (conventional distillation) for different ethylene permeances



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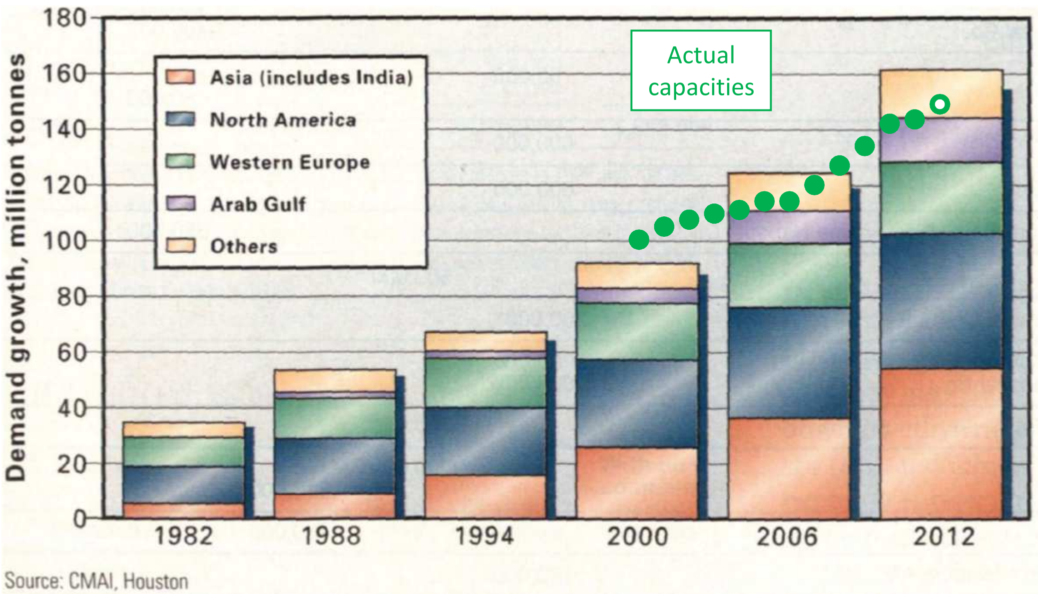
Retrofit with membrane Olefin/Paraffin Separation

Anatolie Motelica

Euromembrane 2012
London, 26 September 2012

Why retrofit Olefin/Paraffin?

Demand projections made in 2001 up to 2012



Global ethylene demand and capacity

Between 2000 – 2010

- an average increase with 4 mtpy
- or 4.3 % annually

147. 5 mtpy ethylene in 2012

Expectation beyond 2012

- an increase with 1 to 5 mtpy

Source: Oil & Gas Journal, Apr. 23 (2001)

Why Olefin/Paraffin separation?

- The most energy intensive processes
  Current global energy consumption[1]: 3000 – 4000 PJ/yr
  (1 PJ = 30 mln Nm^3 of Natural Gas) ~25 GJ/ton
  30% – is the theoretical minimum
  28% – Cracking process
  22% – Separation
  15% – Fractionation & Compression

- Difficult separation
  Close boiling components, Cryogenic Separation, Need for Compression

- The most capital intensive process
  Tall columns, Large compressors and Heat exchangers

Recent startup of the largest ethane cracker - **1.5 mtpy ethylene, $1.3 bn** (*Source:* Hydr. Proc. 2012).

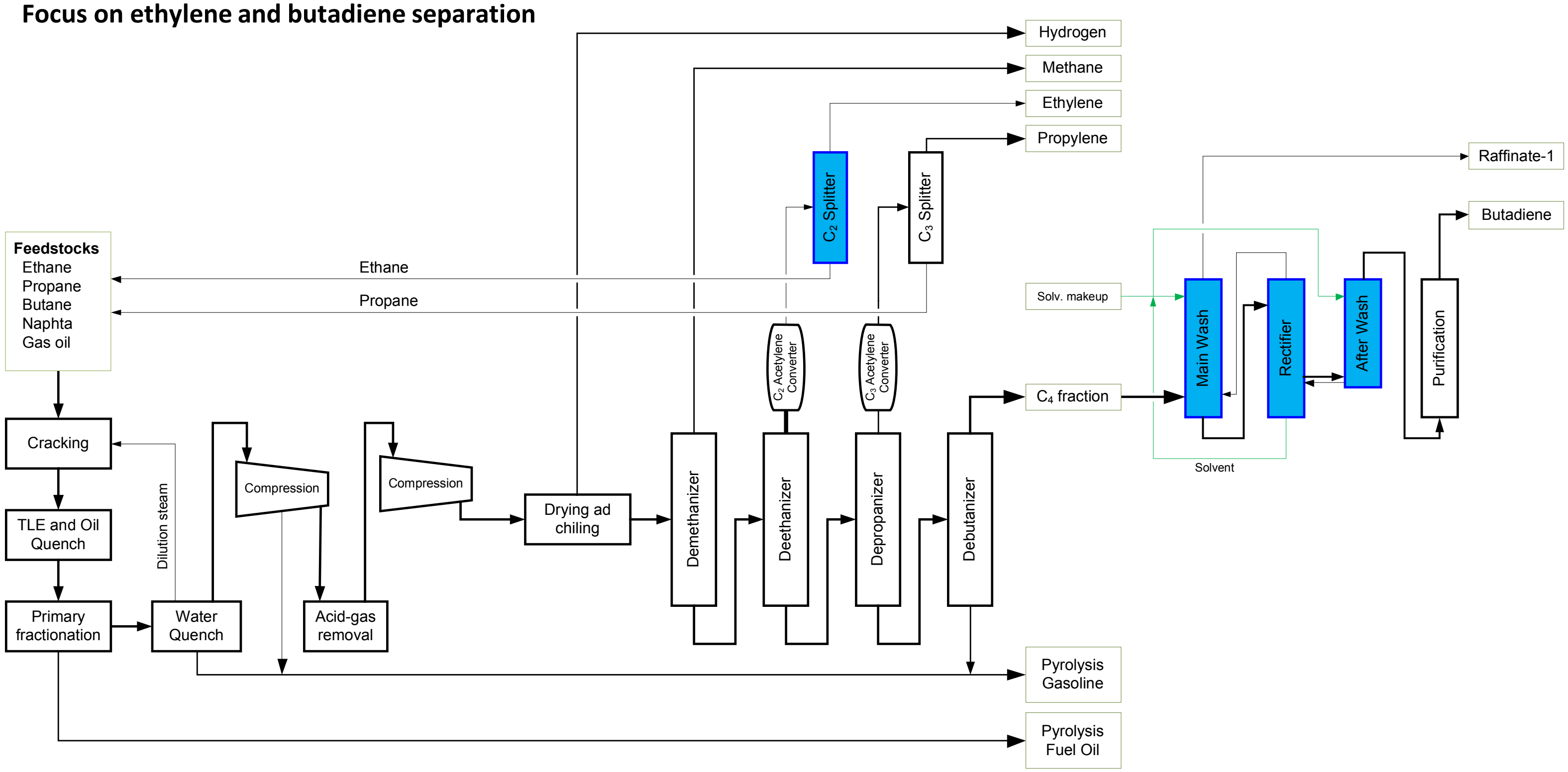
- The most produced chemicals
  in 2012 Ethylene: 147 mln tpy; Propylene: 77 mln. tpy; Butadiene: 14 mln. tpy

- Expected grow in demand in the next decades (2 to 4 % per year)
  driven by developing regions in Asia, Middle East and Latin America

[1] Ren et al., (2006), Energy, 31, p.425-451

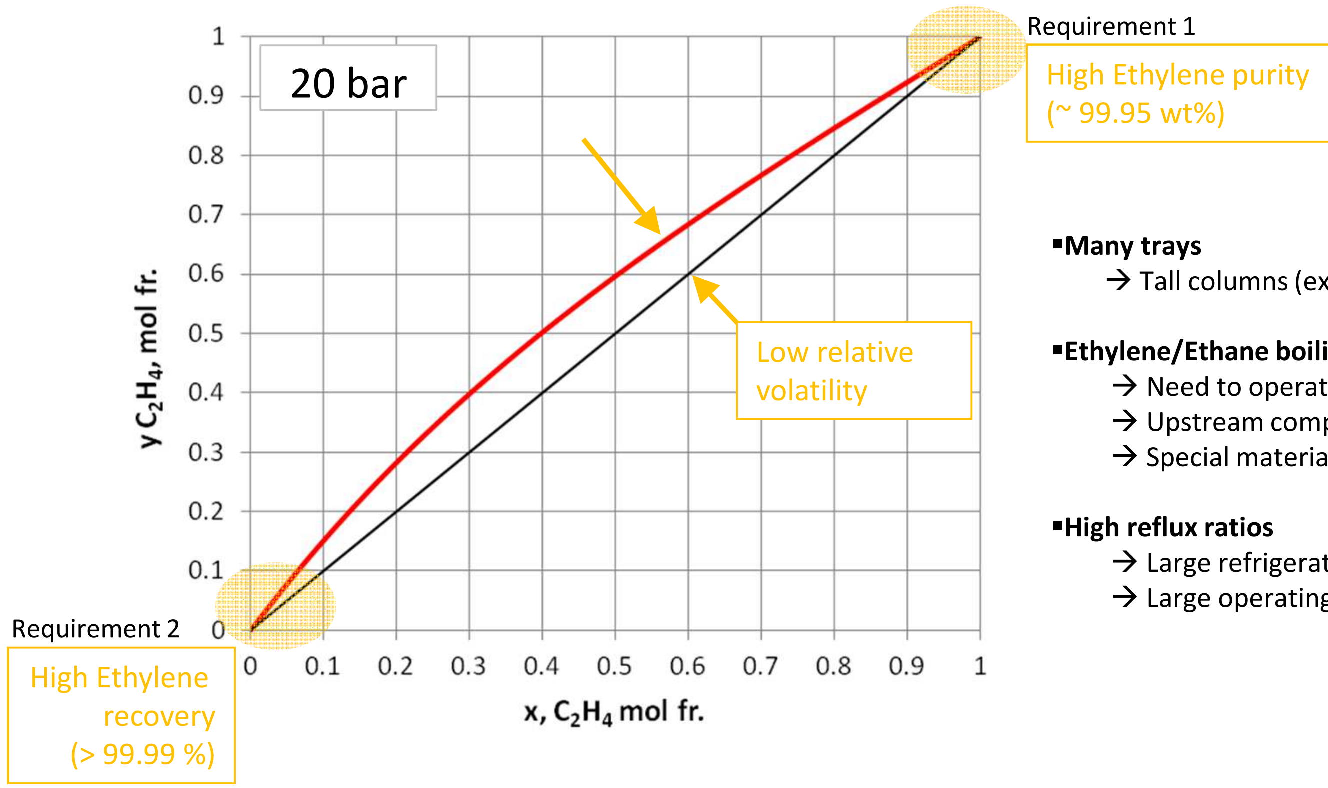
Olefin Plant

Focus on ethylene and butadiene separation



Ethylene separation

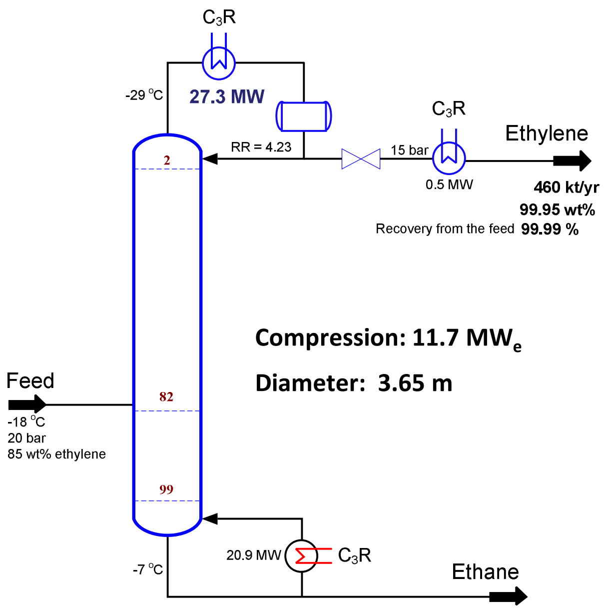
VLE diagram ethylene/ethane



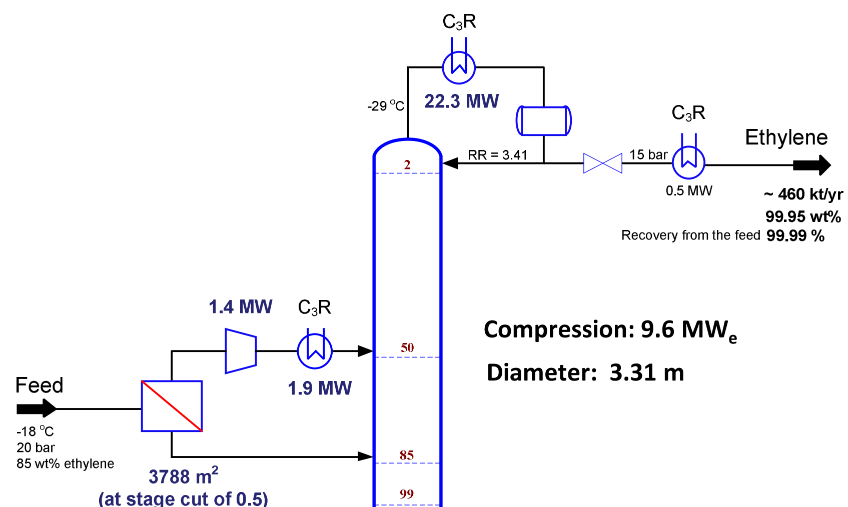
- **Many trays**
  - → Tall columns (expensive!)
- **Ethylene/Ethane boiling point at 1 atm (-103.6 °C/-89 °C)**
  - → Need to operate at high pressure (20 bar)
  - → Upstream compression
  - → Special materials needed
- **High reflux ratios**
  - → Large refrigeration duty (at -35 °C)
  - → Large operating cost (!)

Conventional vs Hybrid process

18 % Lower condenser duty !



Base case



Membrane data:

Permeance C_2H_6	$1.6 \cdot 10^{-9}$ mol·m^{-2}·Pa^{-1}·s^{-1}
Permeance C_2H_4	$80 \cdot 10^{-9}$ mol·m^{-2}·Pa^{-1}·s^{-1}
Selectivity C_2H_4/ C_2H_6	50

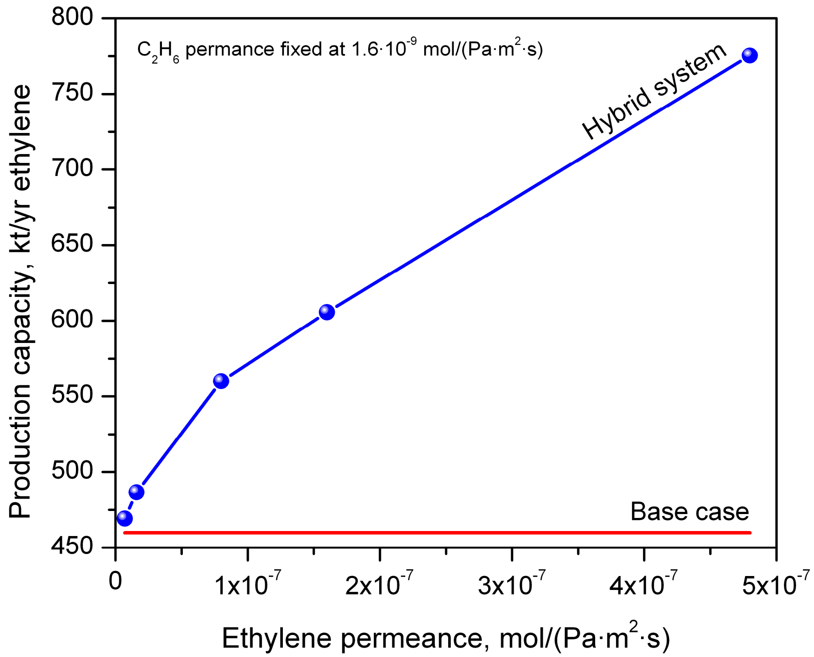
Hybrid process

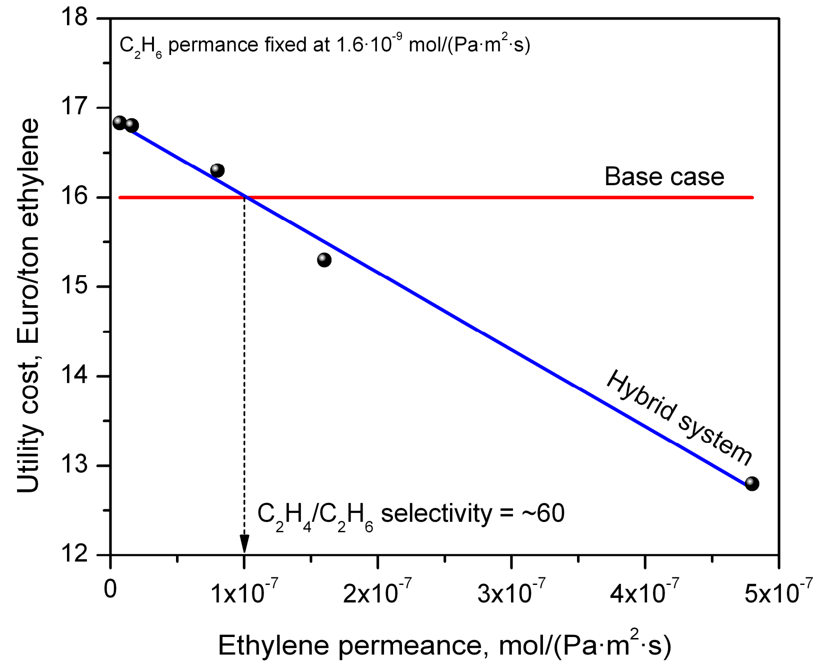
Simulation results

Electricity used	Base case (distillation)	Hybrid process (membrane + distillation)
Condenser column, MW	11.7	9.6
Compression, MW	0	1.4
Compressor cooler, MW	0	0.8
TOTAL	**11.7**	**11.8**
Reflux ratio, [-]	4.23	3.41
Column diameter, m	3.65	3.31 ⇨ **3.65**
Ethylene capacity, kt/yr	460	460 ⇨ **560**

An increase in ethylene production capacity with 22 %

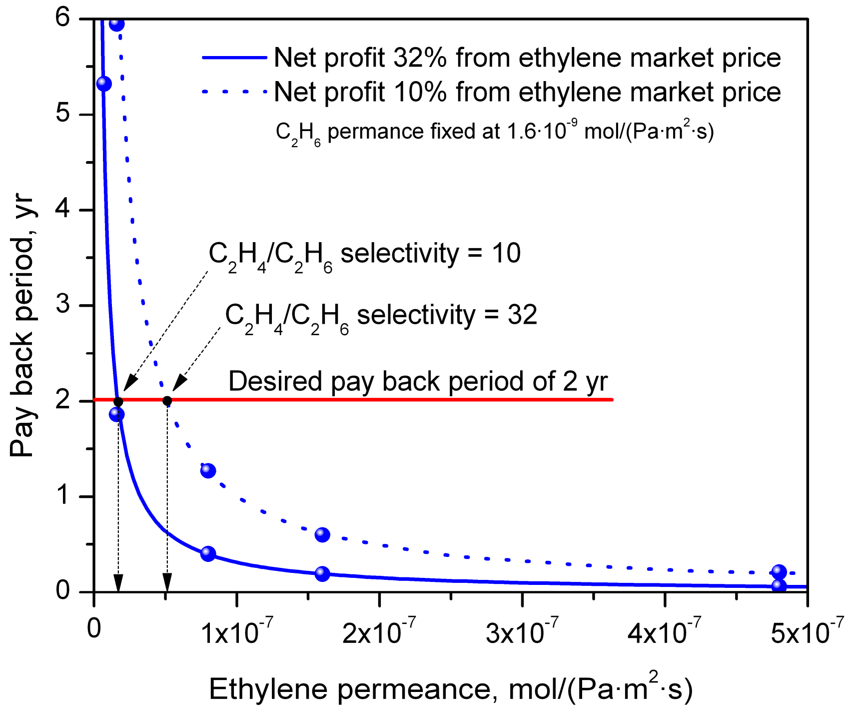
Sensitivity of membrane performance





The highest reported selectivity for a non facilitated membrane is 12.

Sensitivity of membrane performance



Assumptions:

Ethylene market price ~ 795 Euro/ton

Net profit 255 Euro/ton ethylene[1]

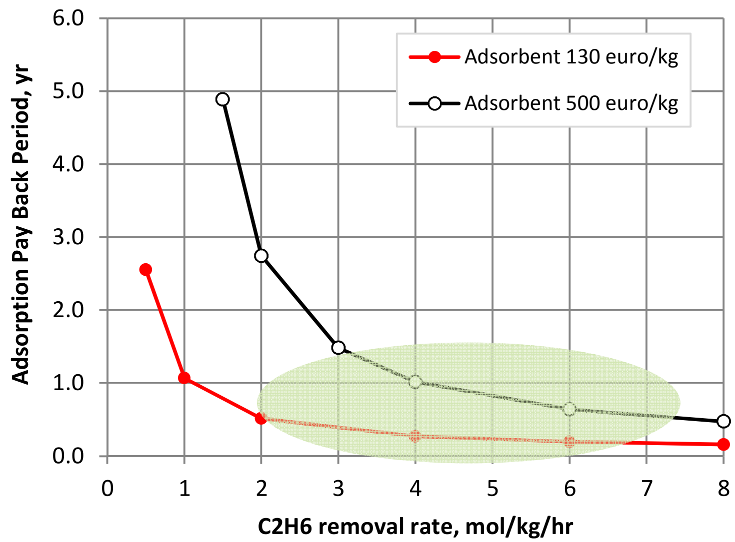
or 32 % from ethylene market price

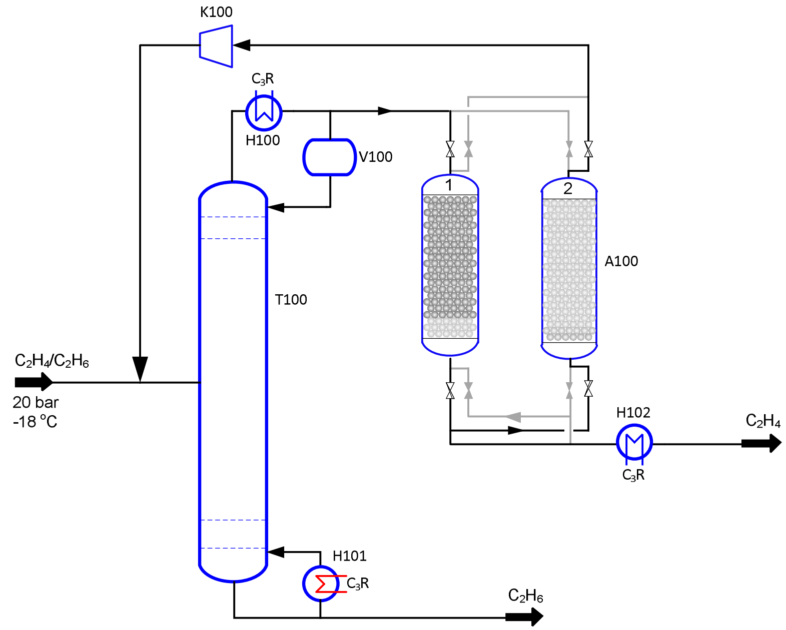
More details can be found in Motelica et.al., *Ind. Eng. Chem. Res.*, 2012, 51, p.6977

Summary EE Separation

- Growth in ethylene demand requires debottlenecking of C_2 splitter, which is a major issue in a olefin plant.
- Membrane technology is very promising in debottlenecking a C_2 splitter or lower the investments for green field plants.
- Membranes can bring energy savings in a C_2 splitter only if ethylene/ethane membrane selectivity is > 60.
- In retrofit applications the hybrid process is technically and economically feasible, when C_2H_4/C_2H_6 selectivity is > 10, and C_2H_6 permeance is ≥ $1.6 \cdot 10^{-9}$ $mol \cdot Pa^{-1} \cdot m^{-2} \cdot s^{-1}$

Alternative adsorption technology

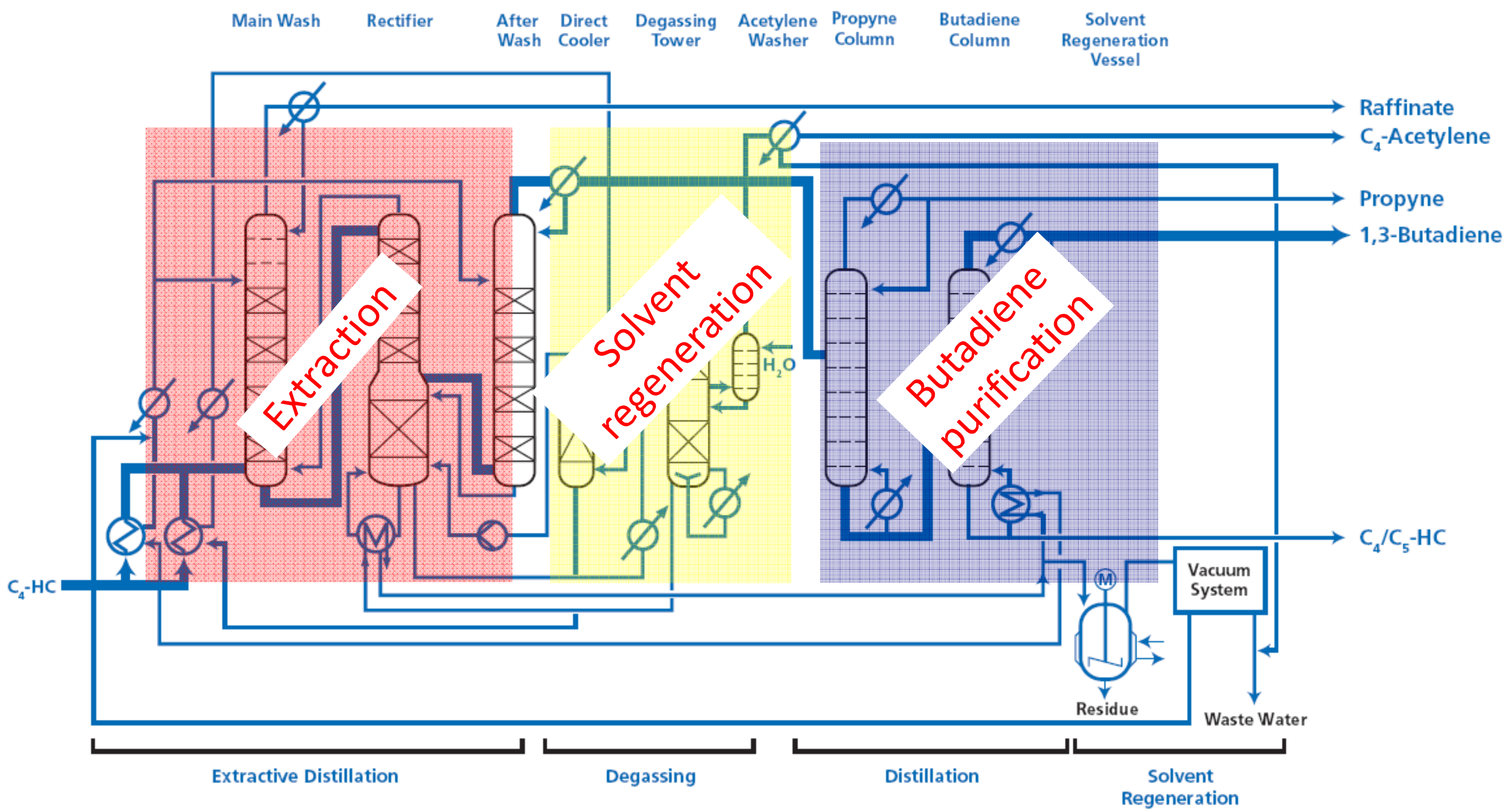




Boost in ethylene capacity with 15 %

Butadiene separation

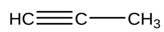
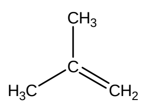
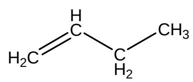
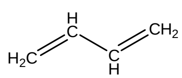
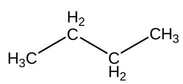
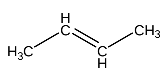
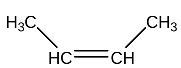
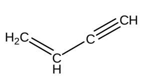
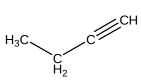
BASF NMP process (conventional)



Source: http://www.lurgi.info/website/index.php?id=55&L=1

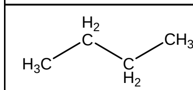
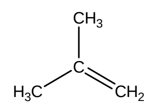
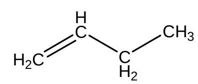
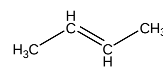
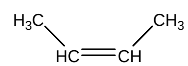
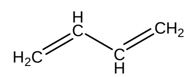
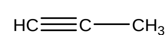
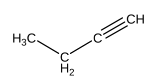
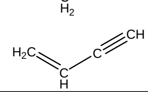
Feed composition

Distillation

Chemical structure	Name	Boiling point, °C	Composition, wt%
	Methyl Acetylene	-23.02	0.2
	*iso*-Butylene	-6.9	26.4
	1-Butene	-6.3	14.2
	**1,3-Butadiene**	**-4.4**	**45.7**
	n-Butane	-0.5	3.2
	*trans*-2-Butene	1	5.1
	*cis*-2-Butene	4	4.4
	Vinyl acetylene	5	0.7
	Ethyl acetylene	8.08	0.2

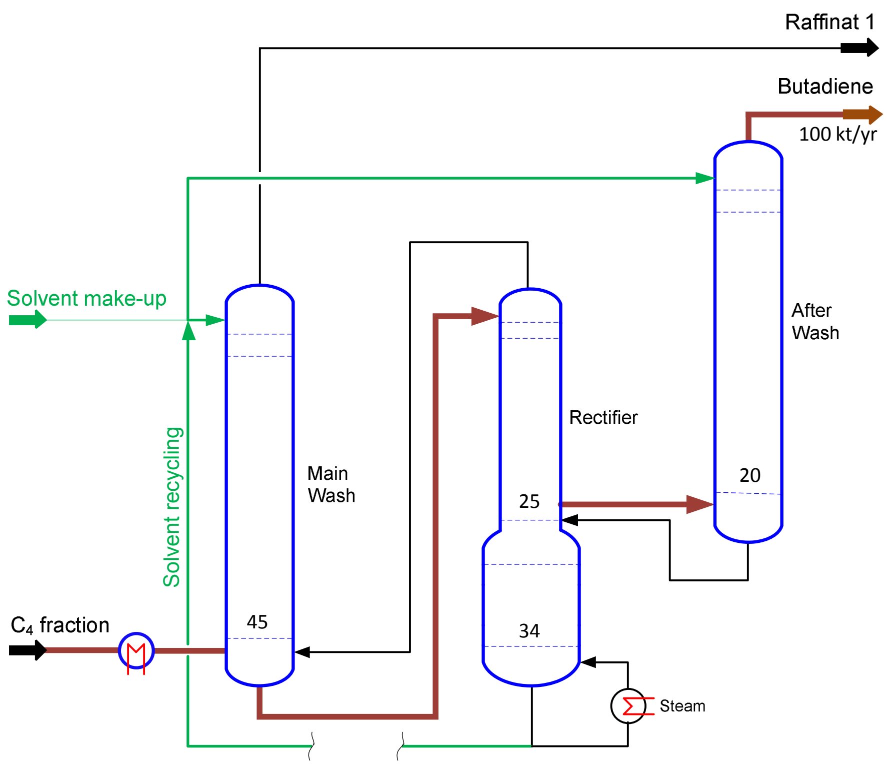
Data based on Bohner et al., (2007) and Lurgi brochure

Extractive Distillation

	Chemical structure	Component Name	Bunsen solubility, m^3_{gas}/m^3_{liq}	
			Experiment[1]	Calculated
Sat		n-Butane	9.5	10.8
Mono		*i*-Butylene	15.42	13.2
Mono		1-Butene	15.6	17.9
Mono		*trans*-2-Butene	20.4	23.4
Mono		*cis*-2-Butene	25.1	28.8
Di & Ace		**1,3-Butadiene**	**41.5**	**42.3**
Di & Ace		Methyl-Acetylene	43	49.2
Di & Ace		Ethyl acetylene	102	116.9
Di & Ace		Vinylacetylene	226	258.9

(1) Data from Wagner & Weitz (1970) ; Solubility is in pure NMP

Simplified process



Design Specifications:

- 2000 ppmw butadiene in Raffinat 1
- 97wt% butadiene in side stream of Rectifier
- 0.005 kg/kg butadiene recovery (Rectifier Bottom)
- 0.05 kg/kg of Vinyl Acetylene recovery (After Wash Bottom)

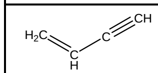
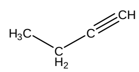
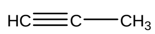
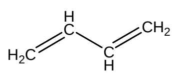
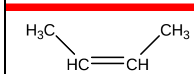
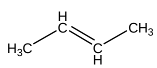
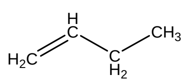
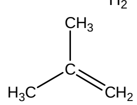
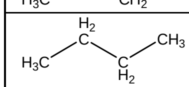
Results of simulations:

33.6 MW of steam at 190 °C

or 9.75 GJ/ton butadiene

or 4020 Nm^3/hr of natural gas

Component permeances

Chemical structure	Component name	Permeance, x 10^{-8} mol/(Pa·m^2·s)	
	Vinyl acetylene	**7.5**	**60**
	Ethyl acetylene		
	Methyl-Acetylene		
	**1,3-Butadiene**		
	*cis*-2-Butene	1	1
	*trans*-2-Butene		
	1-Butene		
	*i*-Butylene		
	**n-Butane**	**0.5**	**0.5**
Selectivity (Di-Olefins/Saturated C_4)		**15**	**120**

C4 Acetylenes & Di-olefins

C4 Mono-olefins

Saturated hydrocarbons

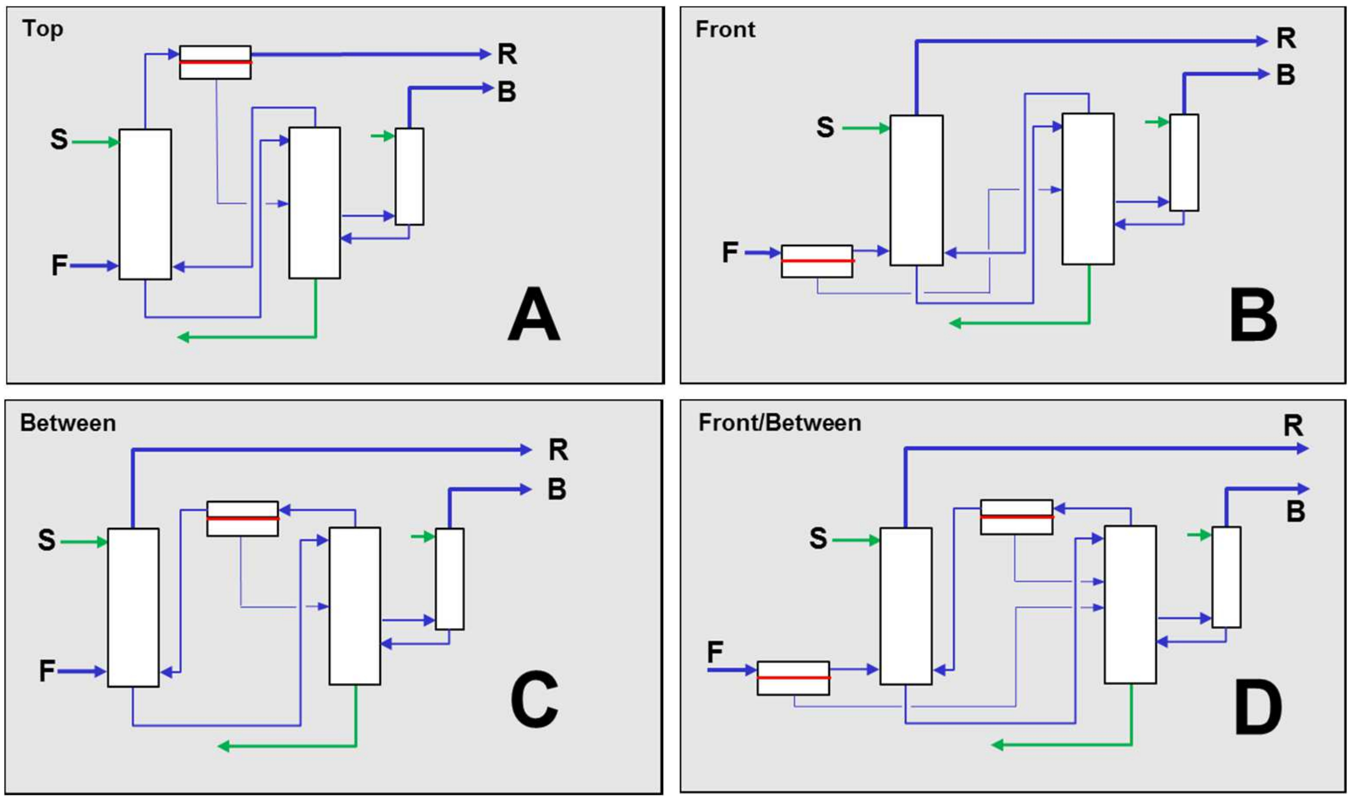
Permeate

Retentate

Separation challenge by membrane is di-olefins from mono-olefins

More details can be found in Motelica et.al., *Ind. Eng. Chem. Res*. 2012, 51, p.6977

Process Integration Options



Results process integration

Selectivity (Di-/Sat-)	15	60
Best process option from energy savings point of view	B	A
Energy savings (relative to base case)	23 %	30 %
Primary energy savings, GJ/ton butadiene	2.2	3.0
Potential savings in The Netherlands, PJ/yr	0.9	1.2

Summary Butadiene Separation

- Use of membranes with current extraction technology can lead up to 30% in energy savings .
- Required membrane selectivity:
  - Butadiene / Mono-olefins ≥ 7.5 or
  - Butadiene / Saturated hydrocarbons ≥ 15
- High membrane selectivity are beneficial, however depending on the process configuration, this does not lead always to significant benefits (upper limit of Butadiene/Mono-olefins is around 60).

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SEVENTH FRAMEWORK PROGRAMME

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