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Introduction

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Course on

MEMBRANE TECHNOLOGY

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MAIN FUTURE CHALLENGES
OF CHEMICAL AND PROCESS ENGINEERING

Increasing productivity and selectivity via intensification and multi-scale control of processes

Designing innovative equipment and implementing more efficient production methods

Driving chemical engineering methodology to fit end-use properties required by the customer

Realizing multi-scale applications of computational chemical engineering from molecular scale to complex production scale

Process Intensification: strategy aiming to *produce much more with much less**

by replacing processes and equipments

- ✓ large
- ✓ expensive
- ✓ energy intensive
- ✓ polluting

with avant-garde versions

- ✓ smaller
- ✓ less costly
- ✓ more efficient
- ✓ less polluting
- ✓ highly safe
- ✓ automatized
- ✓ compact

One vision of how a future plant employing process intensification may look (right) vs. a conventional plant (left).

OPERATING with NON POLLUTING PROCESSES involving PROCESS INTENSIFICATION

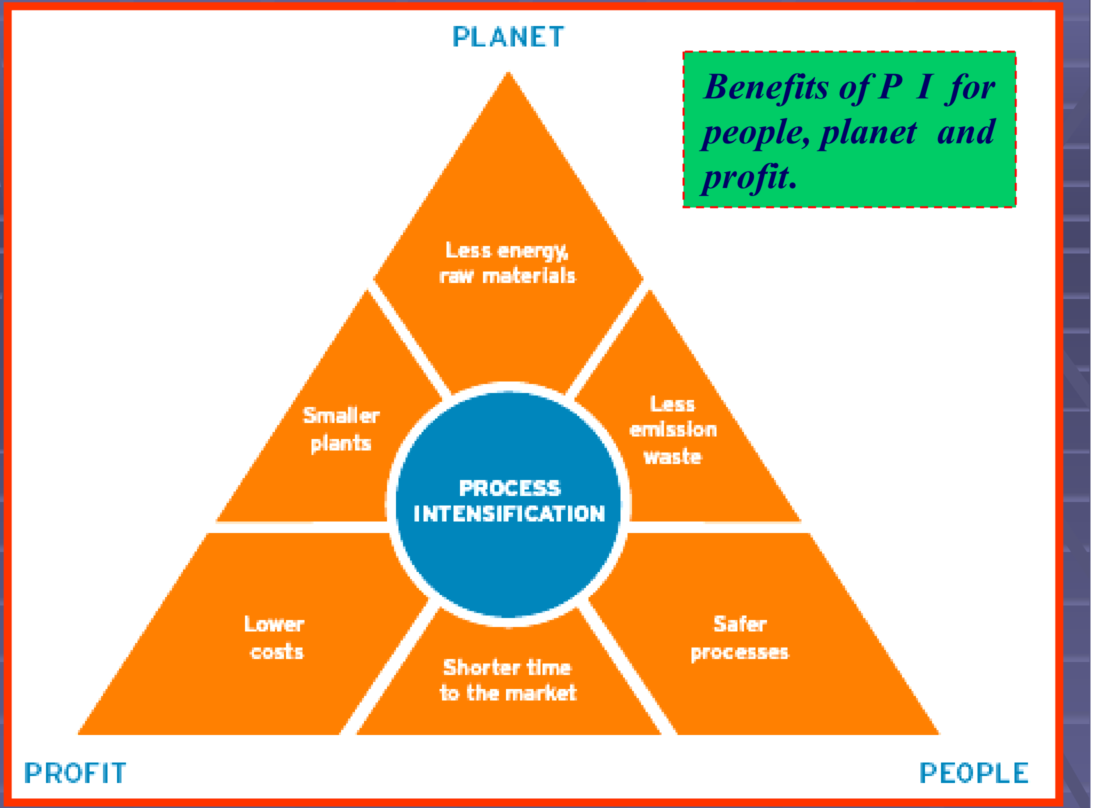
SAVINGS ABOUT 30 % (RAW MATERIALS + ENERGY + OPERATING COSTS)

* Jean-Claude Charpentier, *Ind. Eng. Chem. Res.* 2007, *46,* 3465-3485.

Process Intensification (PI) addresses several needs of the process industry: energy savings, CO_2 emission reduction and enhanced cost competitiveness.

The potential benefits of PI that have been identified are significant.

The needs vary somewhat between sectors but the benefits promised by PI impact each sector in one way or another.



Benefits of PI for people, planet and profit.

Process Intensification provides radically innovative principles ("paradigm shift") in process and equipment design which can benefit (often with more than a factor of two) process and chain efficiency, capital and operating expenses, quality, wastes, process safety and more.

Action Plan Process Intensification, **www.creative-energy.org.**

Process Intensification principles and explicit goals

Optimize the Driving Forces at Every Scale and Maximize the Specific Surface Area to Which These Forces Apply (principle which refers to the maximization of the driving force effects and not to the simply driving forces).

Give Each Molecule the Same Processing Experience (which means to take into account that processes deliver ideally uniform products with minimum waste when all molecules undergo the same history).

Maximize the Effectiveness of Intra- and Intermolecular Events (principle which looks for the *engineering* methods to better control, improve and, therefore, change the inherent kinetics of chemical reactions – i.e. number/frequency of collisions, mutual orientation of molecules and their energy)

Maximize the Synergistic Effects from Partial Processes at all possible scales.

T. Van Gerven, A. Stankiewicz, Ind. Eng. Chem. Res., 48 (2009), 2464-2474.

Approaches for reaching Process Intensification goals

Structure: **how** a structure can be introduced to avoid spatial randomness.

Energy: how energy can be transferred from source to recipient
- in the required form,
- in the required amount,
- on the required moment,
- at the required position.

Time: symbolize the PI approaches in the temporal damain which are basically twofold and involve either manipulations of the time scales at which different process steps procced, or the itroduction of dynamic states into a process, usually in form of periodicity.

Sinergy: how maximizing the synergistic effects from partial processes

T. Van Gerven, A. Stankiewicz, Ind. Eng. Chem. Res., 48 (2009), 2464-2474.

Nanostructured artificial membranes: technologies addressed towards the *Process Intensification Strategy.*

Membrane technologies respond efficiently to the requirements of the "Process Intensification Strategy", because they permit <u>improvements in manufacturing and processing</u>, substantially <u>decreasing the equipment-size/production-capacity ratio, energy consumption, and/or waste production</u> and resulting in cheaper, sustainable technical solutions.

Some examples:

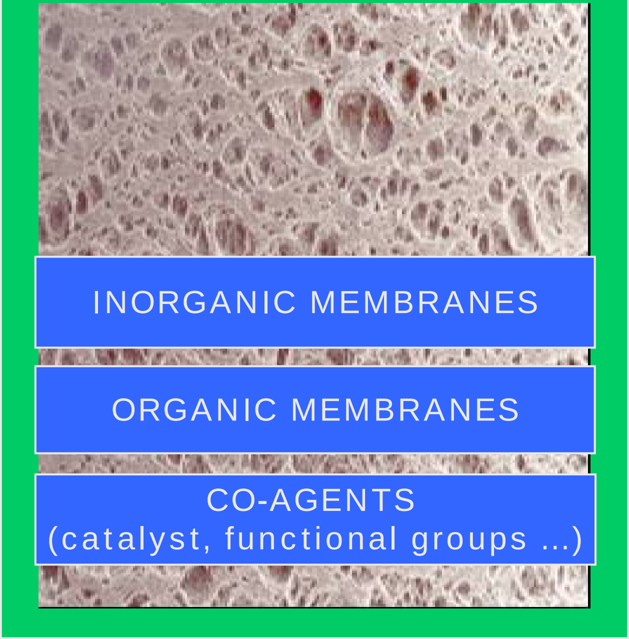
Process	Problem	Advantages
Separation processes	Around 40-50% of the energy use in industries is consumed in separation processes	In membrane operations over *an order* of magnitude reduction in energy use can be obtained in comparison with thermal driven separation
Seawater desalination	An optimized thermal distillation plant producing 100 million gallons per day requires 73 kw hr/m^3	A seawater RO system (with an energy consumption of only 2.2 (kw hr)/m^3) is over *10 fold more efficient* than the thermal approach.
Power	Electrochemical oxidation of a fuel to extract power can be performed in a fuel cell or via a heat cycle. Current fuel cells have efficiencies in the range of 50-60% (higher than the 33% efficiency for optimized thermal systems).	Using a 50% efficiency limit, a fuel cell coupled to a RO unit would show an improvement of *16 fold* better than the thermal alternative!

W.J. Koros, Journal of Membrane Science, 300 (2007) 1.

MEMBRANE TECHNOLOGY

- High efficiency and operational simplicity
- High selectivity and compatibility
- Low energy and chemicals consumption
- Good stability and modularity
- Easy control and scale-up

HARDWARE (MATERIALS)

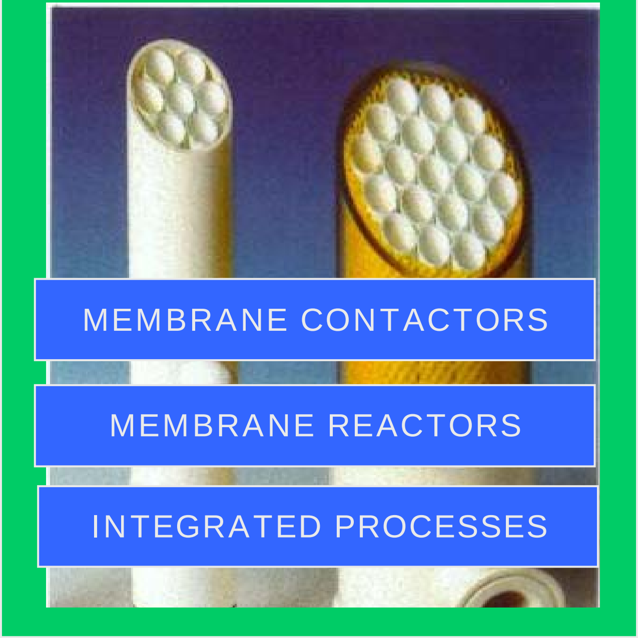


INORGANIC MEMBRANES

ORGANIC MEMBRANES

CO-AGENTS
(catalyst, functional groups ...)

SOFTWARE (METHODS)

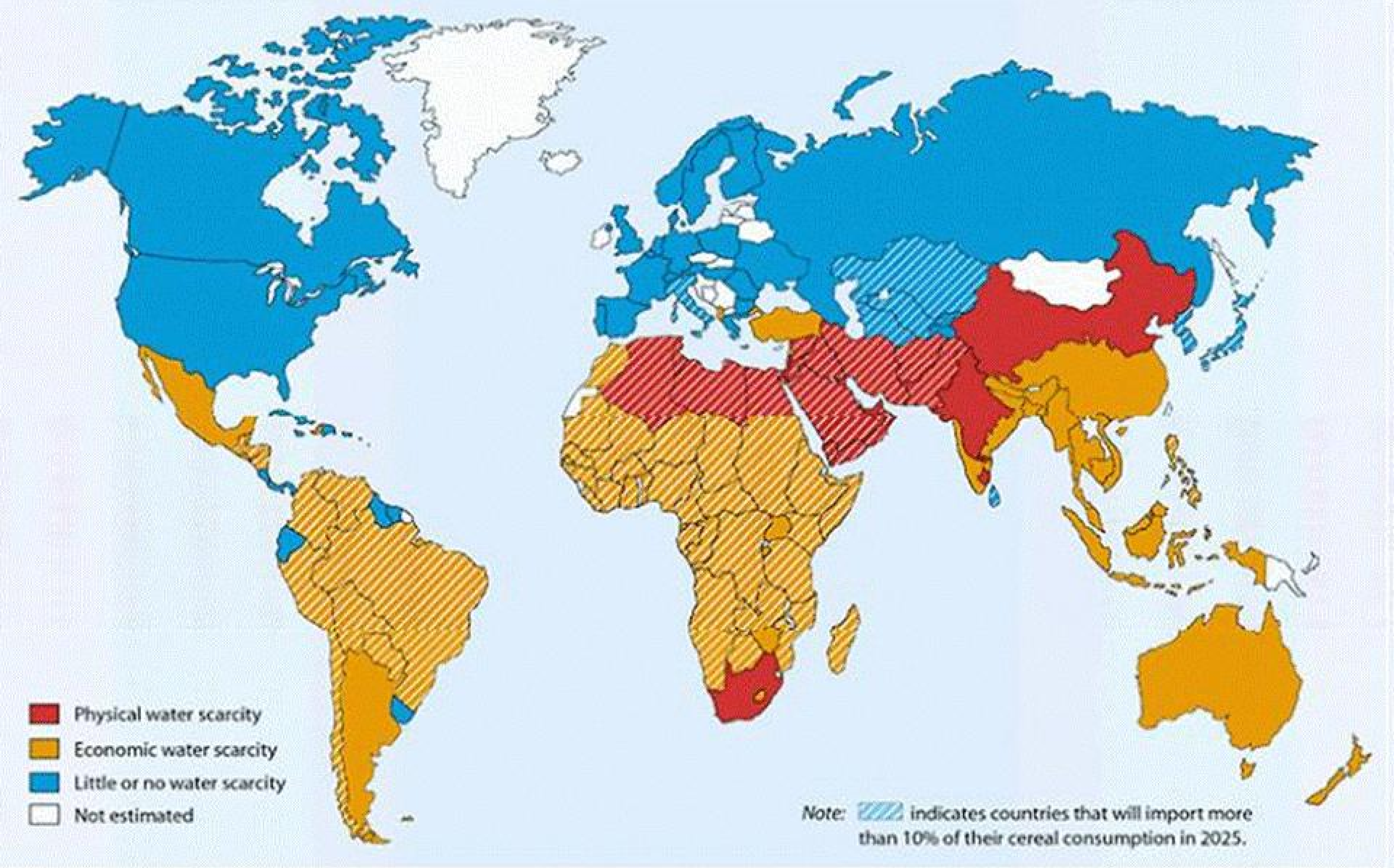


MEMBRANE CONTACTORS

MEMBRANE REACTORS

INTEGRATED PROCESSES

WATER STRESS



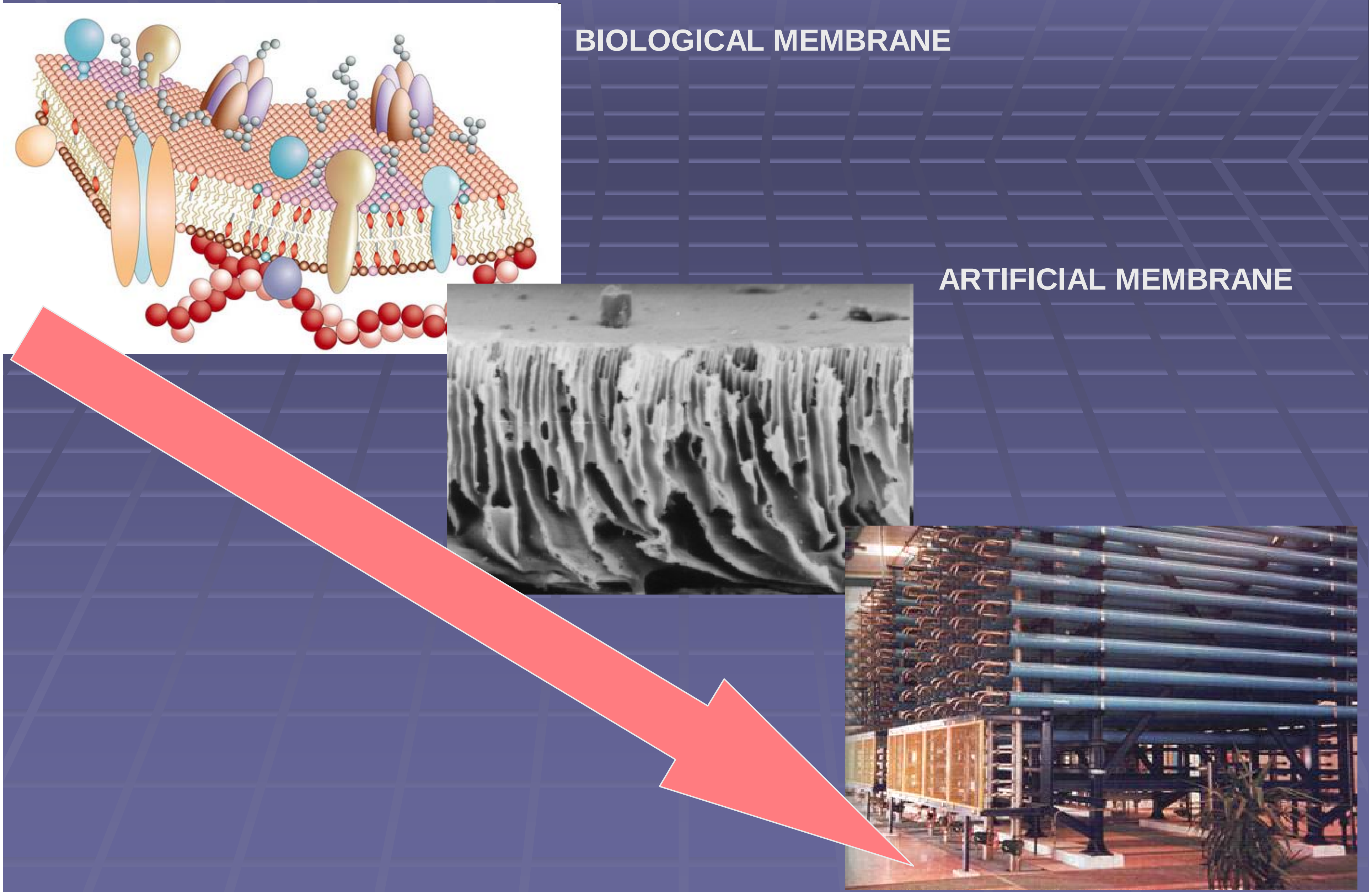
CONVENTIONAL SEAWATER DISTILLATION

Arabic manuscript, Jabir ibn Hayyan (722-815)

From: J. Rate “Mysteries of Nature and Art” 1634

MULTI-EFFECT DISTILLATION

MEMBRANE DESALINATION TECHNOLOGY: LEARNING FROM NATURE

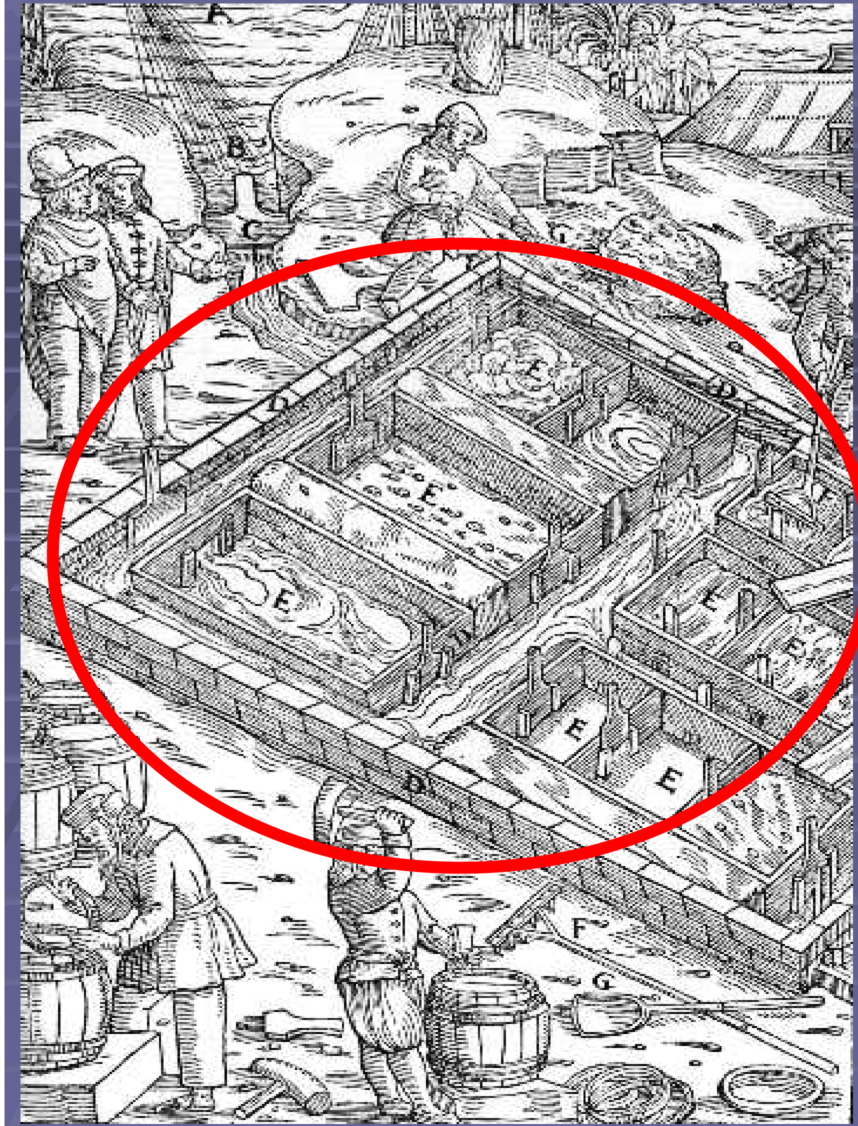


BIOLOGICAL MEMBRANE

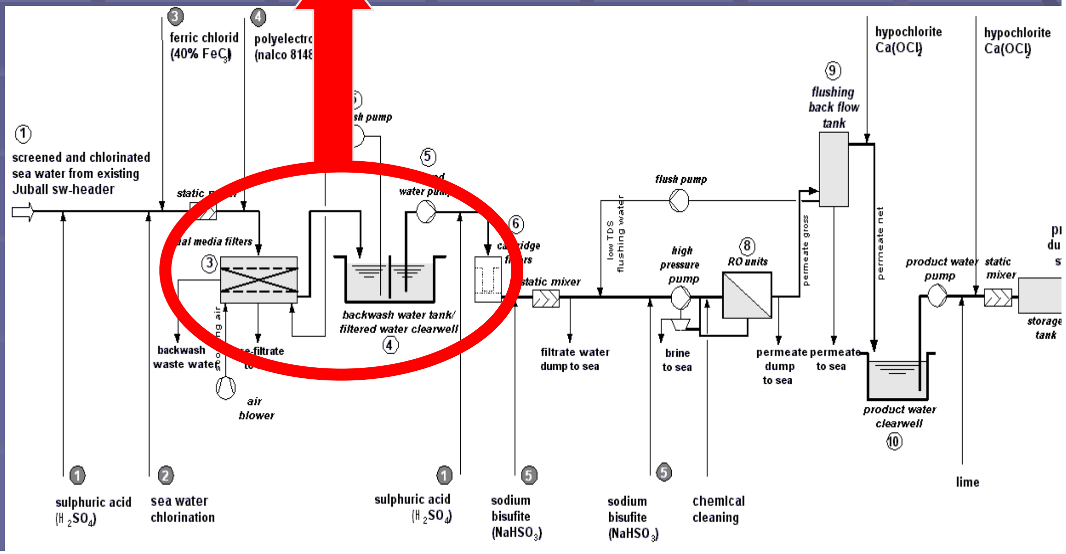
ARTIFICIAL MEMBRANE

REVERSE OSMOSIS

CONVENTIONAL WATER PRETREATMENT: SEDIMENTATION STAGE

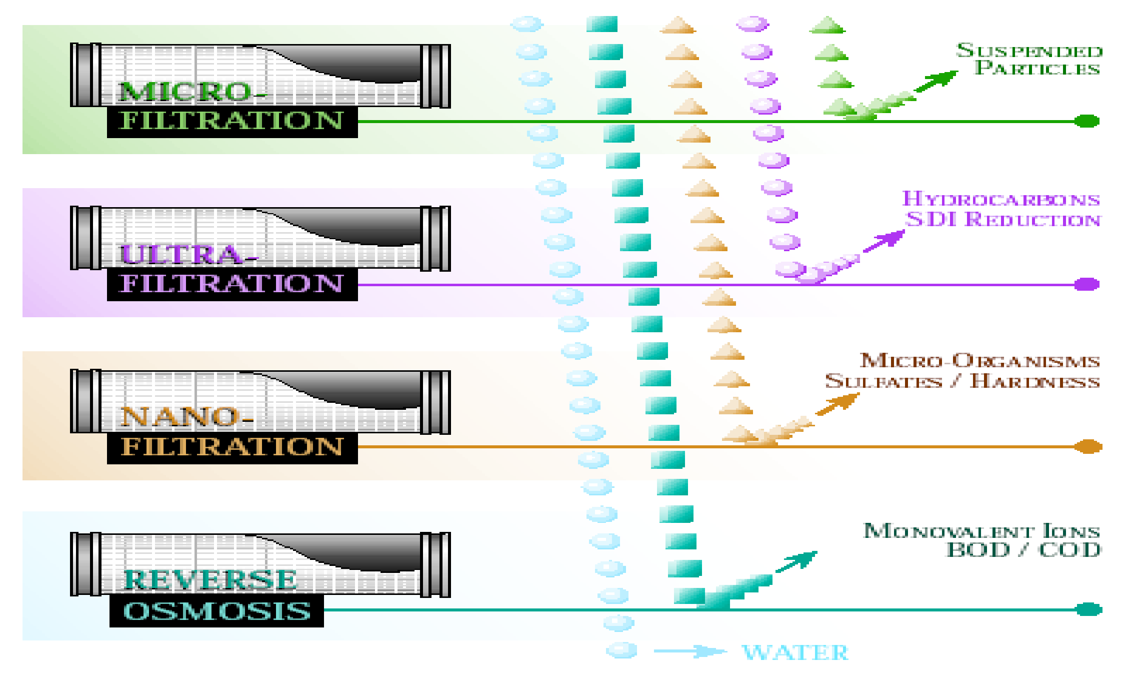


Agricola, *De Re Metallica*, 1556

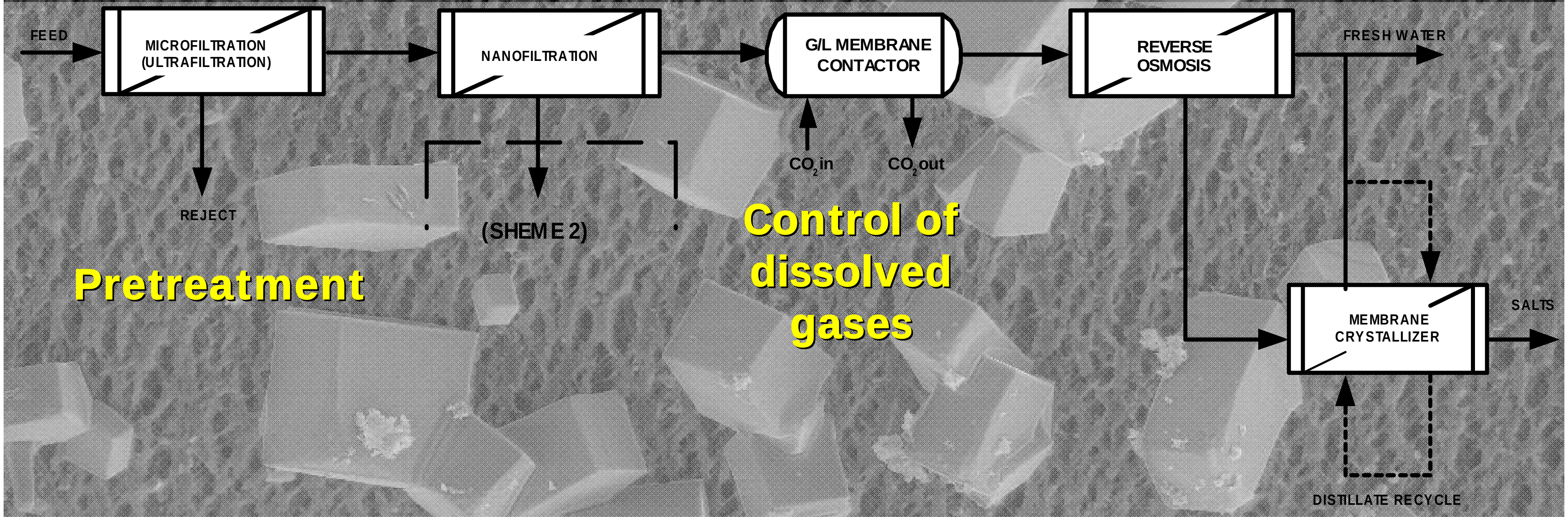


INTEGRATED MEMBRANE DESALINATION SYSTEMS

- Recovery of salts from NF & RO concentrates
- Improvement of the water production
- Reduction of the impact of discharghing brines on marine environment



INTEGRATED MEMBRANE DESALINATION SYSTEM



FEED

MICROFILTRATION (ULTRAFILTRATION)

REJECT

NANOFILTRATION

(SHEME 2)

G/L MEMBRANE CONTACTOR

CO_2 in

CO_2 out

REVERSE OSMOSIS

FRESH WATER

MEMBRANE CRYSTALLIZER

SALTS

DISTILLATE RECYCLE

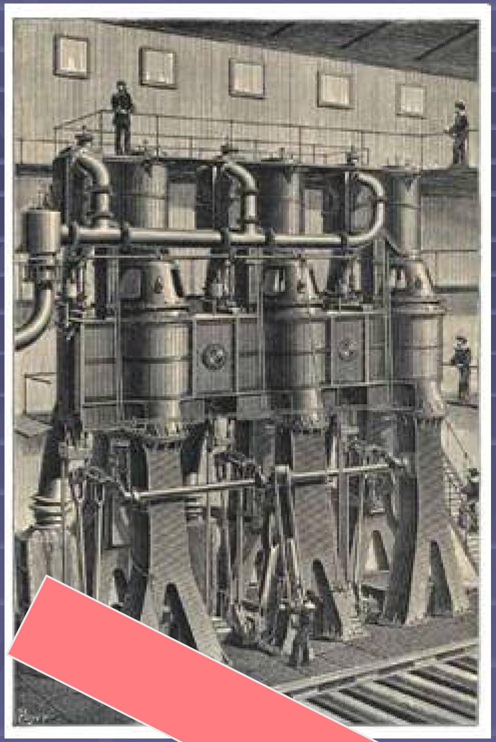
Pretreatment

Control of dissolved gases

Crystallization of NaCl and $MgSO_4 \cdot 7H_2O$

ENERGY

CONVENTIONAL ENERGY SYSTEMS

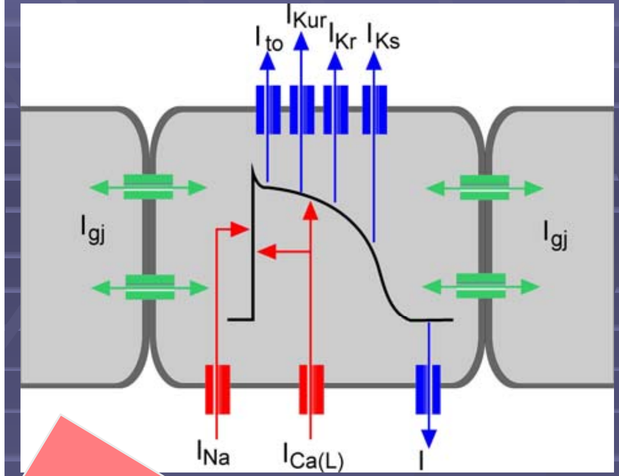


VAPOUR MACHINE (1800 c.a)

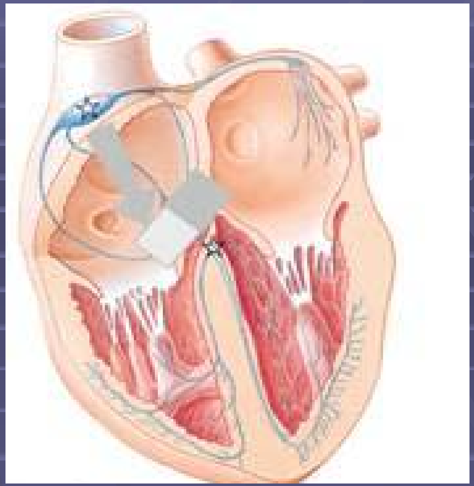
INTERNAL COMBUSTION ENGINE
(efficiency: 30%)

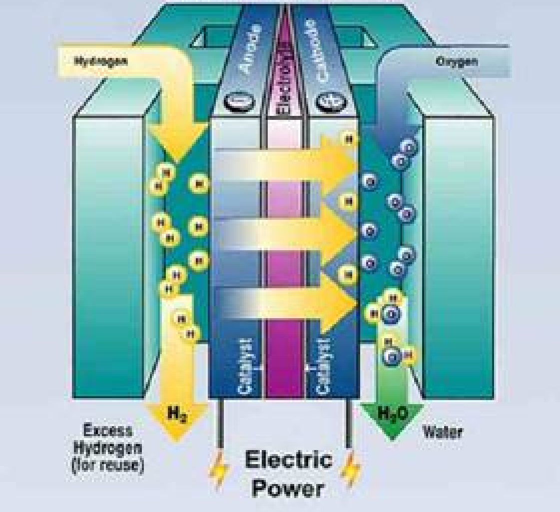
**CONVENTIONAL
AUTOMOTIVE SYSTEM**

MEMBRANE TECHNOLOGY: LEARNING FROM NATURE



BIOELETTRYCITY:
MEMBRANE PROTEIN
CHANNELS IN BIOLOGICAL
MEMBRANES





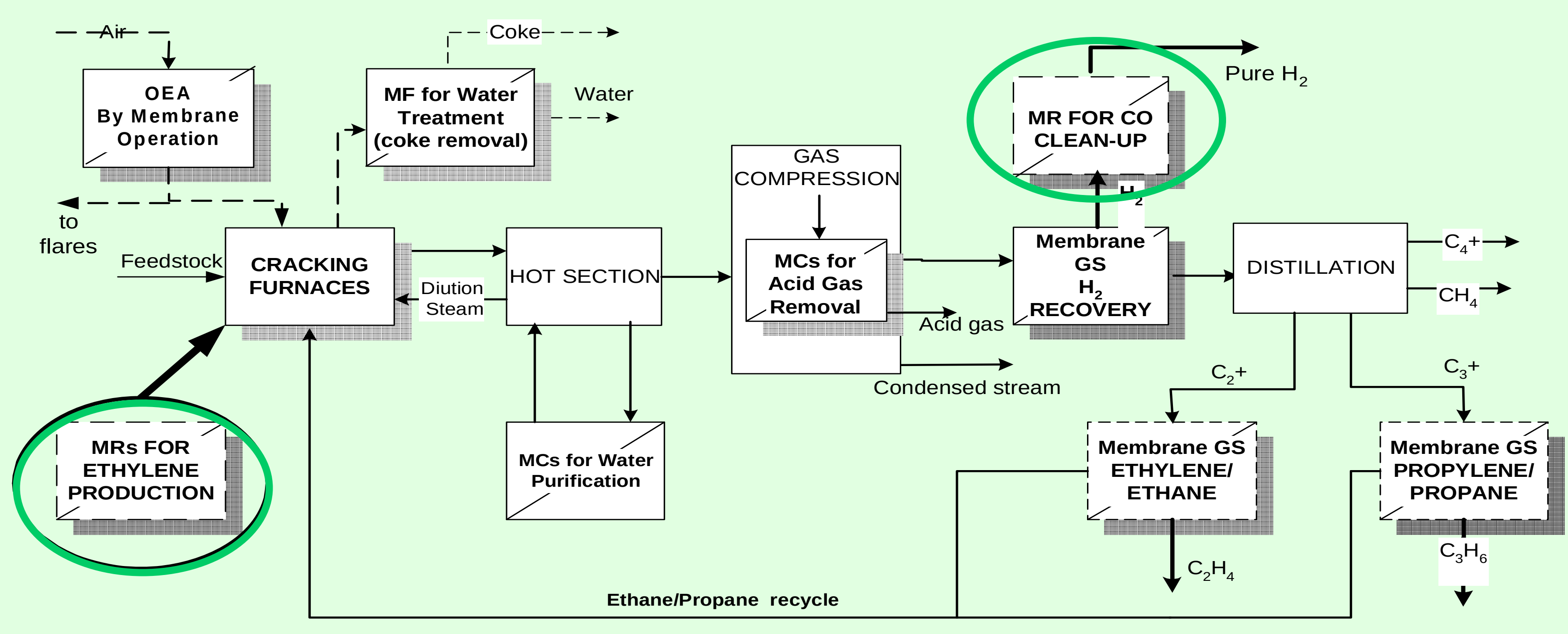
PEM FUEL CELLS
(efficiency: 70%)

“ZERO EMISSION”
AUTOMOTIVE SYSTEM

Membrane unit operations integrated in a steam cracking ethylene plant

Membrane operation can easily be combined in a whole variety of hybrid processes.

In particular, catalytic membrane reactors (MRs) offer new opportunities in the petrochemical field, e.g. for ethylene production.



P. Bernardo, C. Algieri, G. Barbieri, E. Drioli, Catalytic (Pt-Y) membranes for the purification of H_2–rich streams, *Catalysis Today, 2005, submitted.*

Ethane oxidative dehydrogenation

$C_2H_6 + 1/2\,O_2 \rightarrow C_2H_4 + H_2O$ Exothermic and not equilibrium limited

The presence of oxygen limits coke formation ➔ Long-term stable operation, no need for steam in the feed

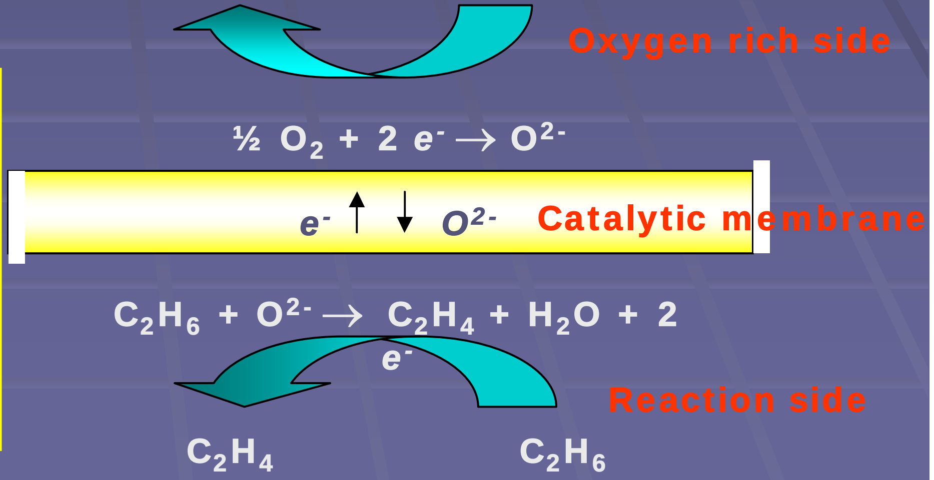
Control of the contact mode of reactants is necessary to control the ethane conversion.

MR with segregated feeding:

the complete oxidation of valuable intermediate products (olefins) can be prevented.

Ethane oxidative dehydrogenation was studied in a dense tubular ceramic MR made of **perovskite** (oxygen ion conducting fluorite structured $Bi_{1.5}Y_{0.3}Sm_{0.2}O_3$) at 825–875°C.

F.T. Akin, Y.S. Lin Journal of Membrane Science 209 (2002) 457.



Oxygen rich side

$\frac{1}{2}\,O_2 + 2\,e^- \rightarrow O^{2-}$

e^- ↑ ↓ O^{2-} Catalytic membrane

$C_2H_6 + O^{2-} \rightarrow C_2H_4 + H_2O + 2\,e^-$

Reaction side

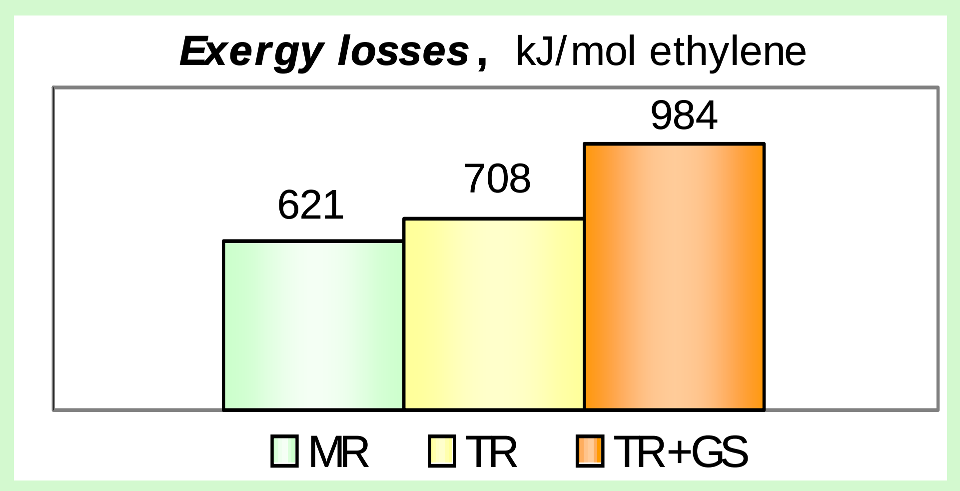
C_2H_4 C_2H_6

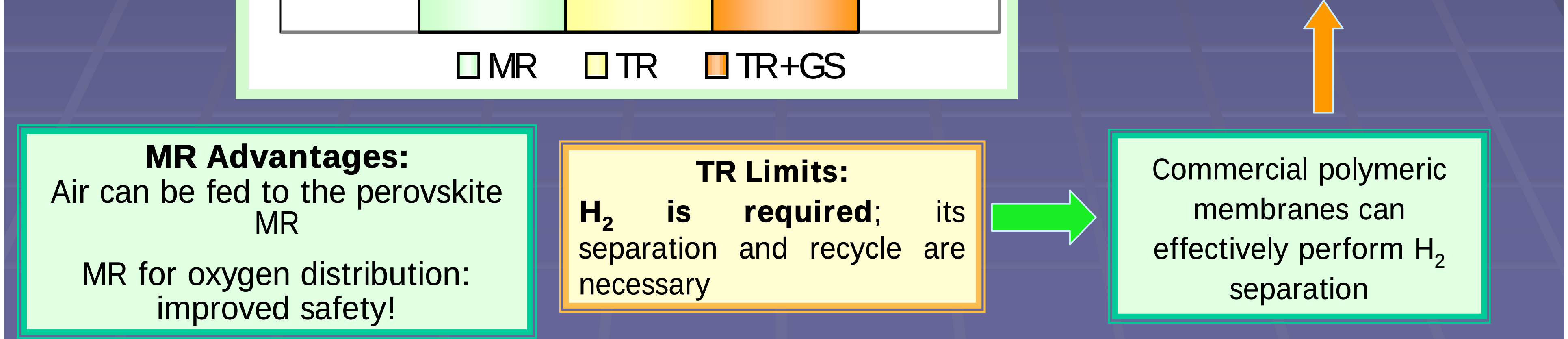
Exergetic analysis

Exergy balance

$$R_s T_0 = W_u + W_u' - \Delta Ex$$

$R_s T_0$: entropy production (irreversible),
W_u : electrical exergy supplied to the cycle,
W_u' : thermal exergy supplied to the cycle,
ΔEx : exergy variation between inlet and outlet streams.





TR+GS:
TR integrated with *gas separation* (GS) membranes for H2 separation

MR Advantages:
Air can be fed to the perovskite MR

MR for oxygen distribution: improved safety!

TR Limits:
H_2 is required; its separation and recycle are necessary

Commercial polymeric membranes can effectively perform H_2 separation

E. Drioli , P. Bernardo, G. Barbieri, An exergetic analysis of membrane unit operations integrated in the Ethylene Production cycle, *6th International Conference on Process Intensification for the Chemical Industry* , Delft (The Netherlands), 27 - 29 September 2005.

METRICS

CATEGORY	METRIC	UNIT
Mass	$MASS\ INTENSITY = \frac{TOTAL\ MASS}{MASS\ OF\ PRODUCT}$	kg/kg
Energy	$ENERGY\ EFFICIENCY = \frac{TOTAL\ PROCESS\ ENERGY}{MASS\ OF\ PRODUCT}$	MJ/kg
Ecotoxicity	$ECOTOXICITY = \frac{TOTAL\,(MASS\ PERSISTENT + BIOACCUMULATIVE)}{EC_{50}MATERIAL\,/\,EC_{50}DDT\ CONTROL}$ $WASTE\ INTENSITY = \frac{TOTAL\ WASTE}{MASS\ OF\ PRODUCT\,(FRESH\ WATER + SALTS)}$	kg Kg
Safety	$THERMAL\ HAZARD,\ REAGENT\ HAZARD,\ PRESSURE$ $HAZARDOUS\ BY-PRODUCTS$	
Economic	$COST$	$\$$

NEW METRICS

NAME	METRIC
PS	$\frac{\textit{PRODUCTIVITY}}{\textit{SIZE (MEMBRANES)}}$
PW	$\frac{\textit{PRODUCTIVITY}}{\textit{WEIGHT (MEMBRANES)}}$
EI	$\frac{\textit{PRODUCTIVITY}}{\textit{LOAD OF POLLUTANT EMISSIONS}}$
FLEXIBILITY	*VARIATIONS HANDLED*