Membrane separation processes in bioethanol production:

Developments and applications of inorganic microporous membranes

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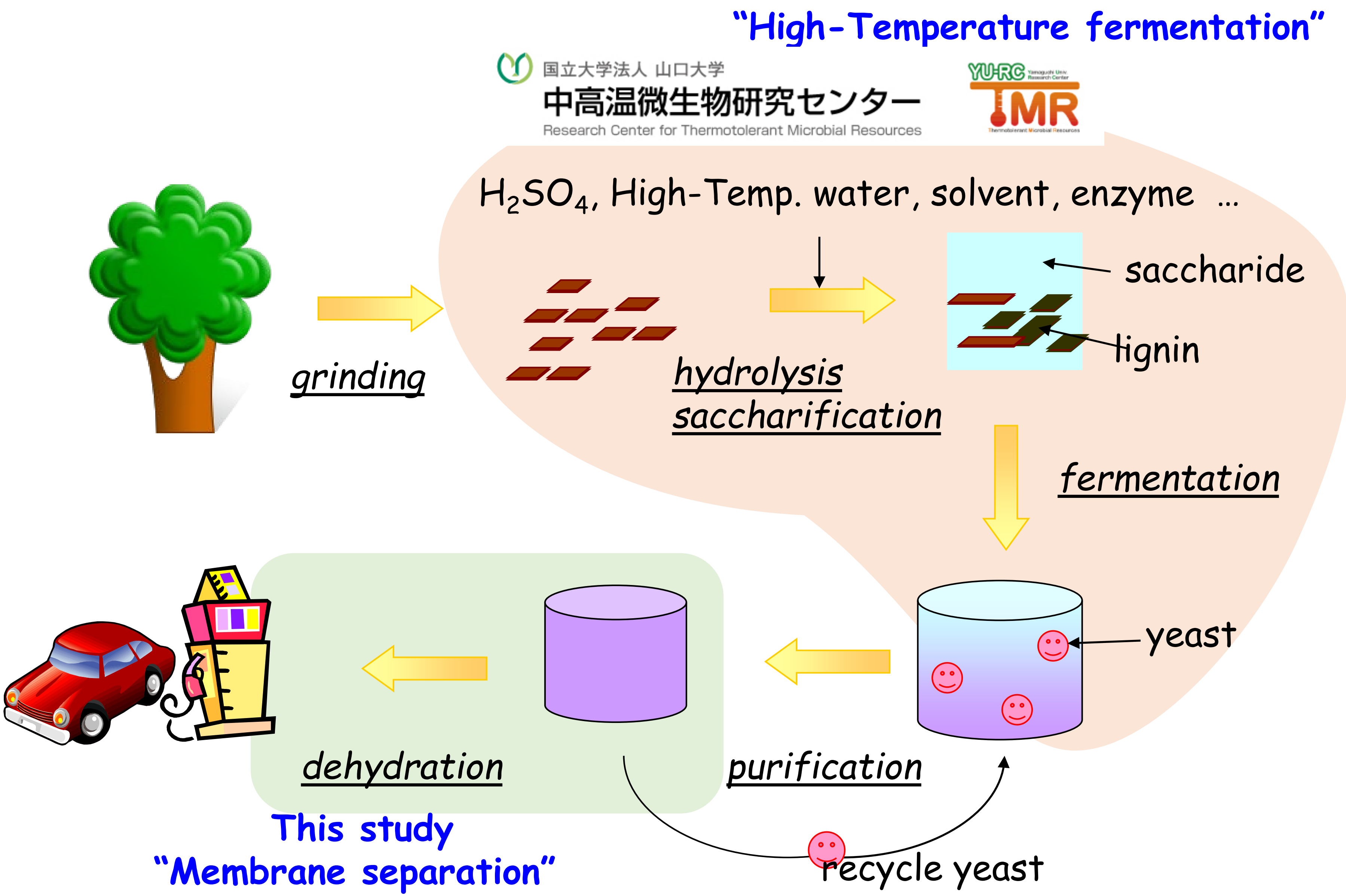
2024.01.17(Wed.) e-ASIA共同研究プログラム
代替エネルギー分野ワークショップ

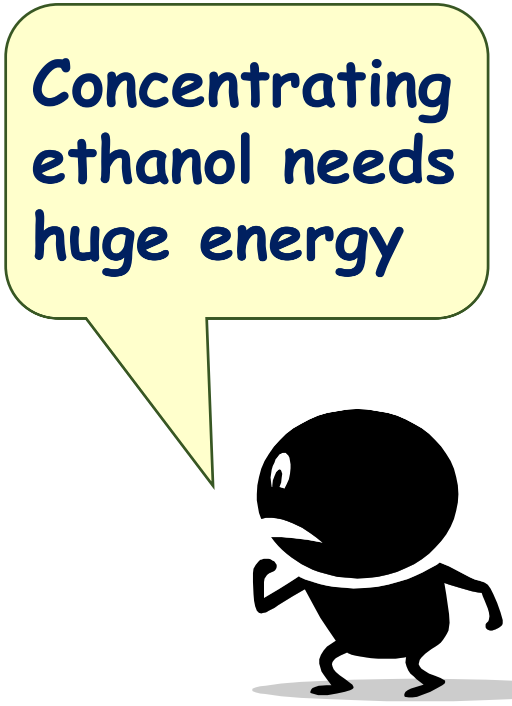
Bio-alcohol production



Energy balance

Process	Distribution (%)	
	McAloon et al (2004)	Kim and Dale (2005)
Milling	1.0	0.8
Cooking/liquefaction	19	29.6
Fermentation	1.0	3.5
Distillation/dehydration	45	56.5
DDGS recovery	34	9.6
Total	100	100

Ref.) FX Rongère,2007



Energy consumption
– distillation vs membrane -

Case I: Conventional distillation process:

Fermentation ‹ analyser › ‹ rectifier › ‹ distillation ›

7.3wt% (EtOH) ---→ 42wt% --→ 93wt% --→ 99.8wt%

980 kcal/L 350 kcal/L **1380 kcal/L**

< 10 % !

Case II: Combined membrane and fermentation

‹ **membrane separation** ›

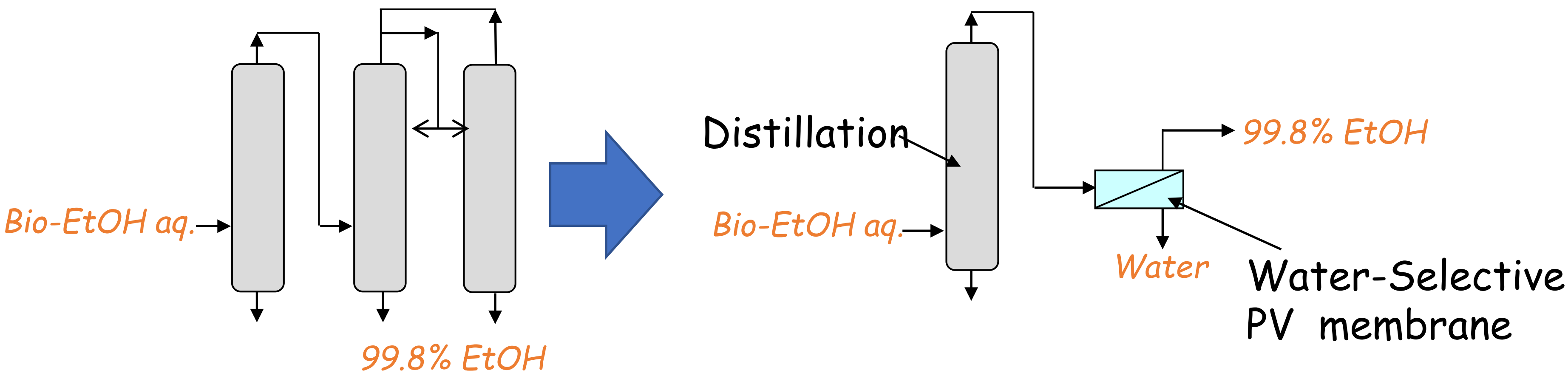
93wt% ----→ 99.8wt%

130 kcal/L

Water-selective PV membrane

Ref. BNRI, 67th Chem Eng. Japan Conf.

Separation of azeotropic and close-boiling mixtures



Conventional (azeotropic)
distillation process

Hybrid process

Less energy consumption
Lower CAPEX & OPEX

Ref.) V.V.Hoof et al., Sep. Purif. Tech. 37, 33-49 (2004)
A. Verhoef, et al., Comp. Chem. Eng. 32(6), 1136-1146 (2008)

Polymeric vs Zeolite Membranes

Membrane types	Temp.	Feed H_2O in EtOH (wt%)	Perm. H_2O wt%	Flux (kg m^{-2} h^{-1})	Selectivity (-)
Chitosan	60	10	99.9	0.1	6000
Polyimide	75	10	99.0	0.01	850
Polyimide (asymmetric)	60	10	96.9	0.22	280

Ref.) Kita *et al.*, J. Mater. Sci. Lett. 14, 206 (1995)

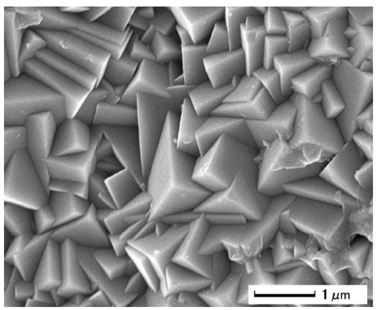
High performance

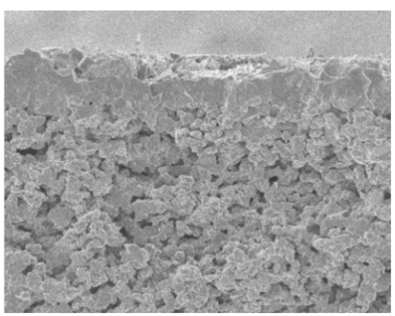
Higher flux & separation ability

Cost effective

1-step synthesis at <100°C, ca. 5h

Zeolite Membranes & Modules





MITSUI E&S

VP module for producing absolute ethanol from bioethanol (550 NaA membrane tubes, 1250kg/h of ethanol, Mitsui E. S., Japan)

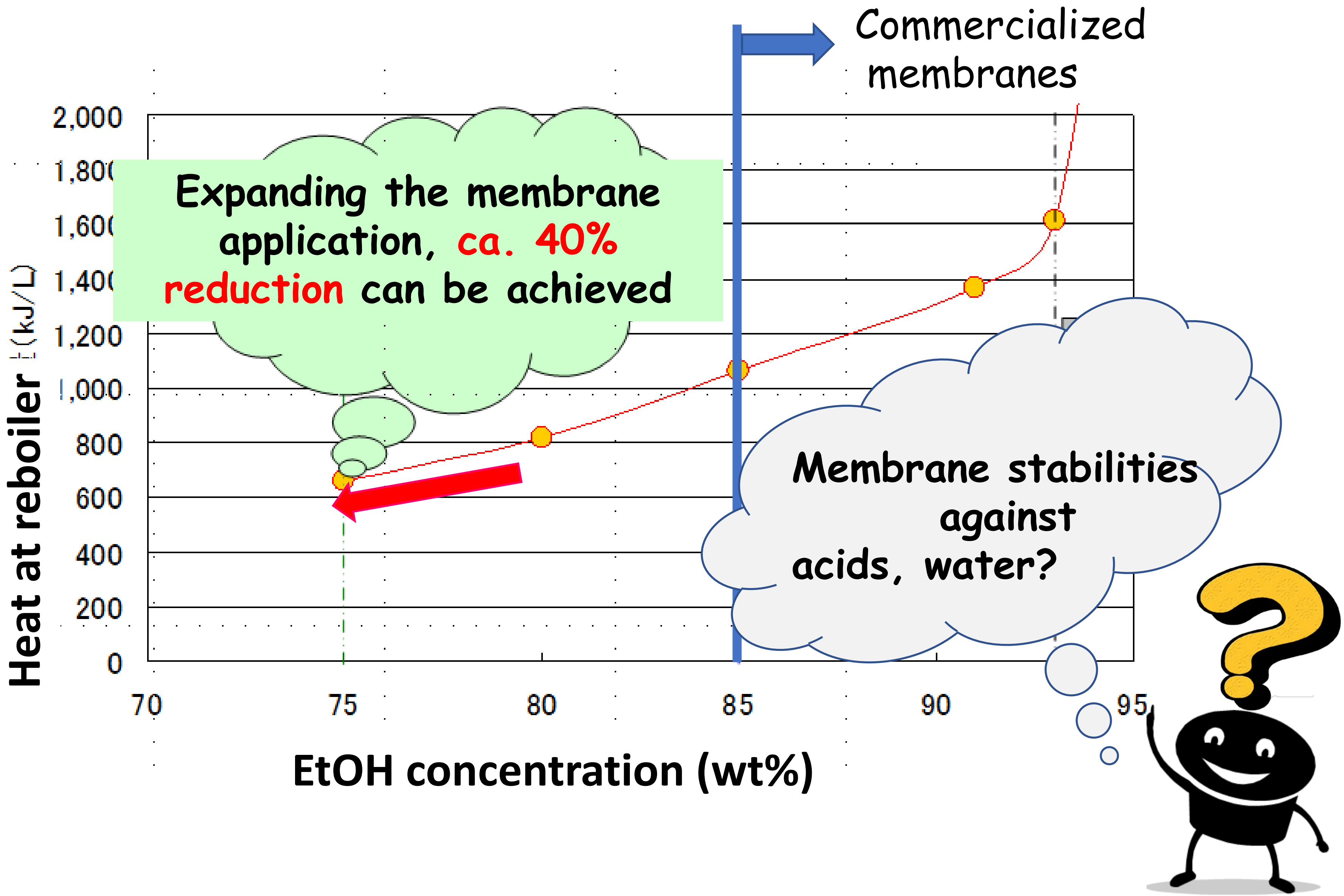
Since 1998, >500 membrane modules have been installed for drying solvents

Current interests

More efficient
bioethanol production?

- On-site/movable units?
- Circular economy?
- Simple operation/maintenance?

Reduction in separation energy



Dehydration performance (75°C)

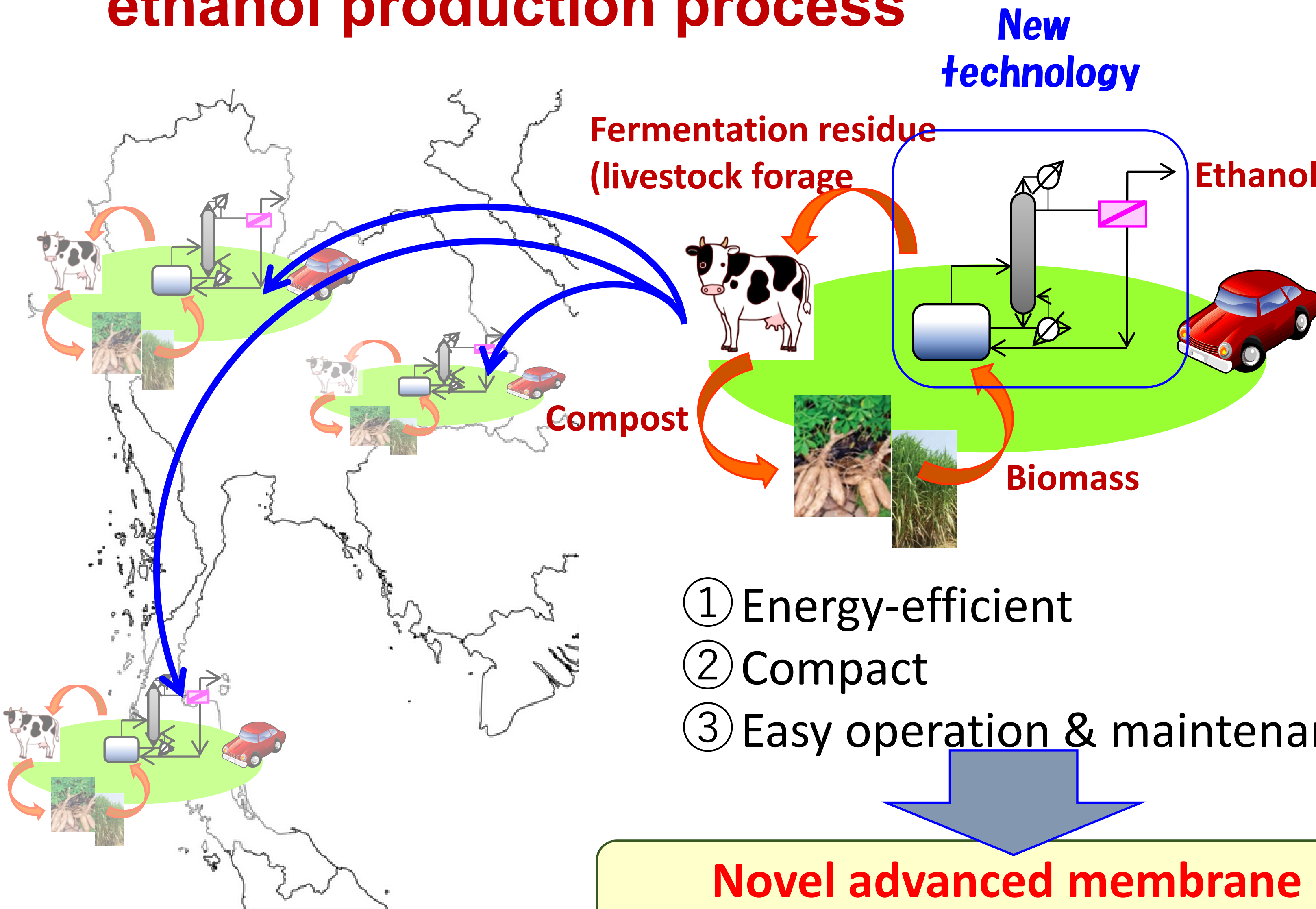
Feed composition [wt%]	Membr. type	Flux [kg·m^{-2}·h^{-1}]	H_2O in the permeate [wt%]	$\alpha_{w/o}$ [-]
50AA*/50H_2O	MOR	1.88	>99.99**	>90,000
	MFI	2.21	99.51	200
80AA/20H_2O	MOR	1.01	>99.99**	>90,000
90AA/10H_2O	MOR	0.50	99.65	2560
	MFI	0.25	94.82	165
90EtOH/10H_2O	MOR	1.10	99.88	7500
90IPA/10H_2O	MOR	1.45	99.93	13000

** AA: acetic acid, EtOH: ethanol, IPA: isopropyl alcohol*

*** AA concentration in the permeate was less than the detection limit*

Zhu, Mei-Hua, et al, *Microporous and mesoporous materials* 181, 47-53 2013

Ecological & economic on-site bio-ethanol production process

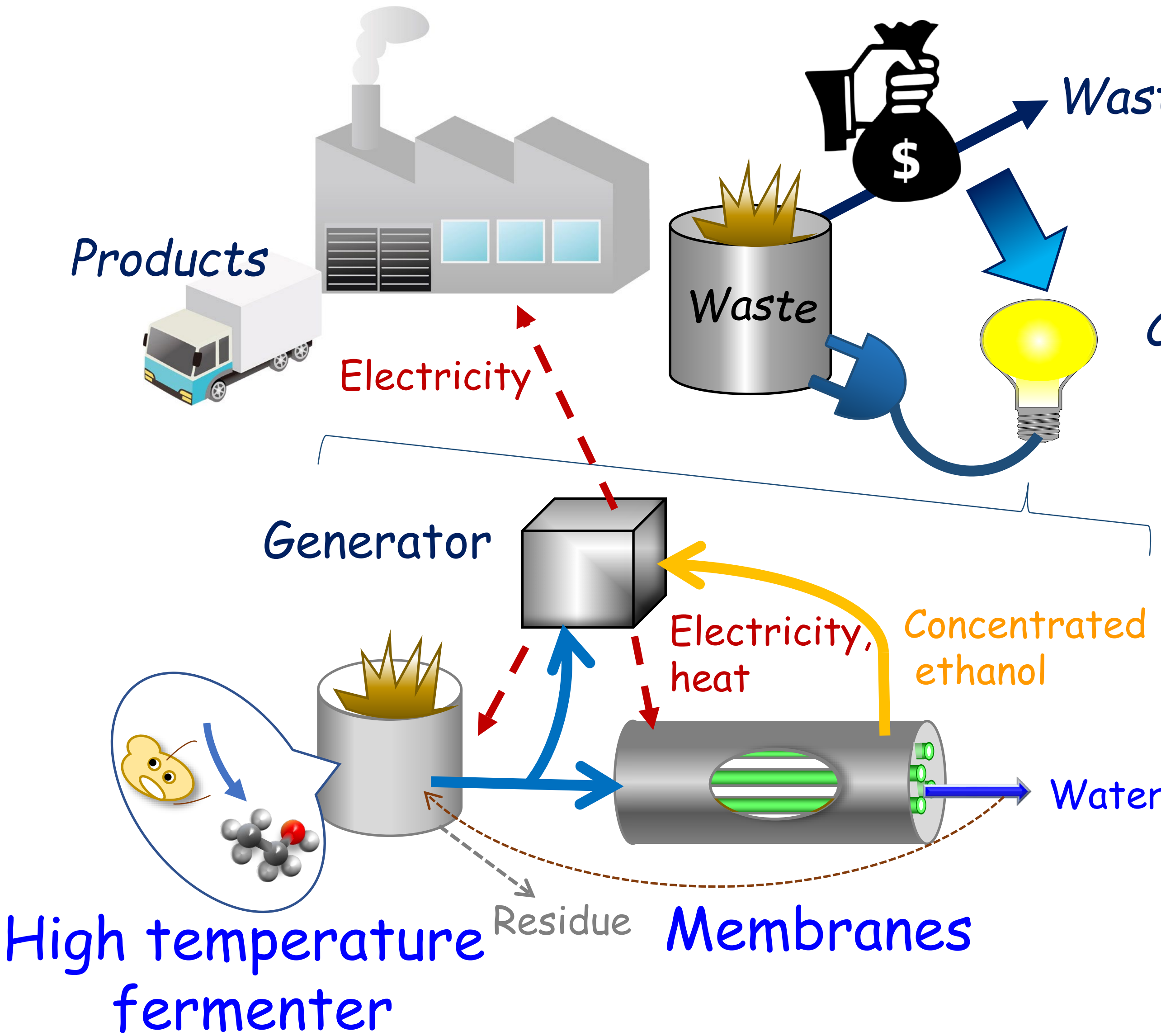


①Energy-efficient
②Compact
③Easy operation & maintenance

Novel advanced membrane technology system

Kumakiri I, et al, Fuels, 2(4):533 (2021).

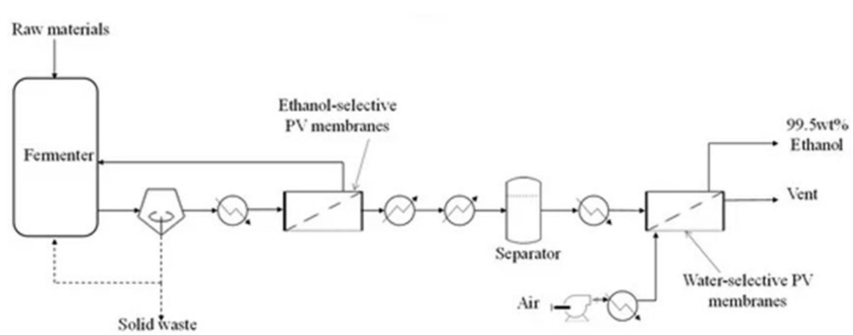
High-temperature fermentation + membrane separation



"On-site conversion"
Simple, small units
Easy maintenance

Proof of concept
through domestic projects

Various process configurations



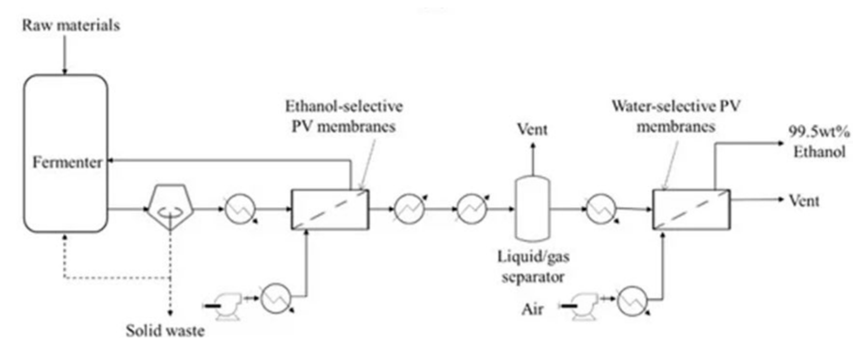


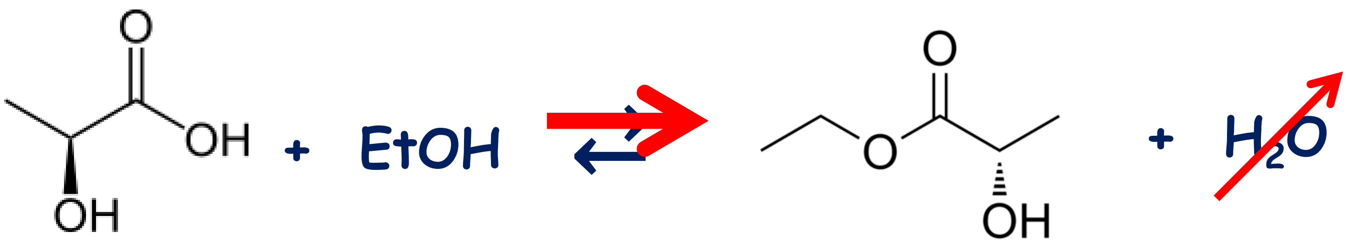
Table 4. Comparison of the energy demand to concentrate ethanol from 10 to 99.5 wt%.

Process Configuration	Energy Demand (W/kg-EtOH)			Ethanol Recovery (%)
	10 wt% Ethanol to 80 wt%	80 wt% Ethanol to 99.5 wt%	Total	
Distillation +azeotropic distillation	1804	2339	4142	99.95
Distillation + water-selective membrane #	1804	287	2091	99.95
Ethanol-selective membrane with vacuum at the permeate side + water-selective membrane #	1862	287	2149	99.5
Ethanol-selective membrane with 1ir sweep at the permeate side (×1.3 #) + water-selective membrane *	1199	277	1480	99.4
Ethanol-selective membrane with 1ir sweep at the permeate side (×2.2 #) + water-selective membrane *	1325	277	1602	99.0
Ethanol-selective membrane with 1ir sweep at the permeate side (×3.1 #) + water-selective membrane *	1450	278	[illegible]	[illegible]

* Sweep at the permeate side with flow rate 9.1 times higher than the membrane flux. # [illegible] a membrane.

Kumakiri I, et al., Process intensification in bio-ethanol production–Recent developments in membrane separation. Processes;9(6):1028., 2021

Reaction + separation = Membrane reactors

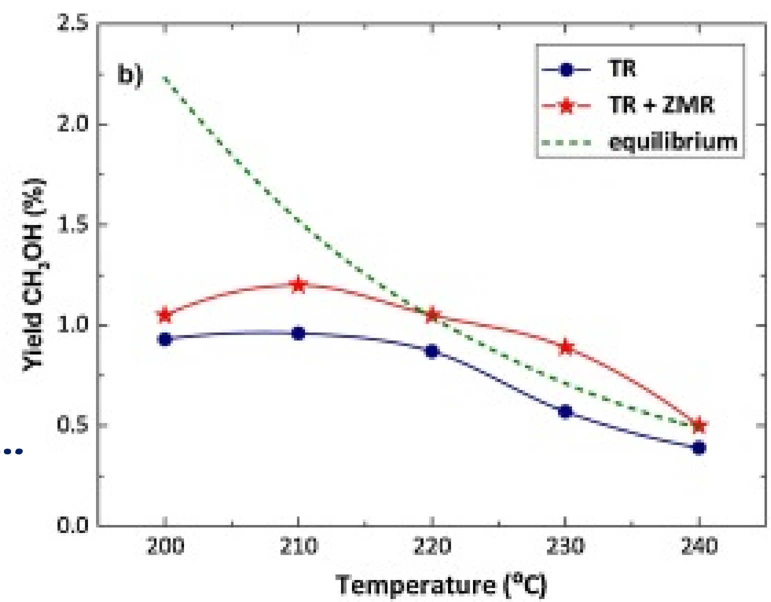


(Lactic acid) (Ethyl lactate)

$CO_2 + 3H_2 \rightleftarrows CH_3OH + H_2O$

$2\ CH_3OH \rightleftarrows CH_3OCH_3 + H_2O$

Higher conversation, Lower Pressure, …



Ref.s) J. Gorbe *et al.*, Sep. Purif. Technol, 200, 164-168 (201
R. Raso et al., *Catalysis Today*, 364, 270-275 (2021)

What we can offer

- **High temperature fermentation** (no need of cooling water)
- **Inorganic membranes** (dehydration & ethanol separation)
  - Reduction in separation energy = lower OPEX
  - Simple process, easy maintenance, modular design (easy scale-up)
  - Acid-stable new types of membranes

Current interests

- **On-site biorefinery** (fermentation + membrane separation)
  - Process configuration, circular economy, local environment impact
  - Influences of contaminants, fermentation variations, ...
- **Membrane reactors** (reaction + membrane separation)