Bioenergy II

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Biofuels Production from Volatile Fatty Acid Platform

Ho Nam Chang

Professor of Biochemical Engineering

Department of Chemical & Biomolecular Engineering, Korea Advanced Institute of Science and Technology（KAIST), 373-1, Guseong-dong, Yuseong-gu, Daejeon, 305-701, Republic of Korea

E-mail: hnchang@kaist.edu, Tel: +82-42-350-3912, Fax: +82-42-350-3910

Biofuel

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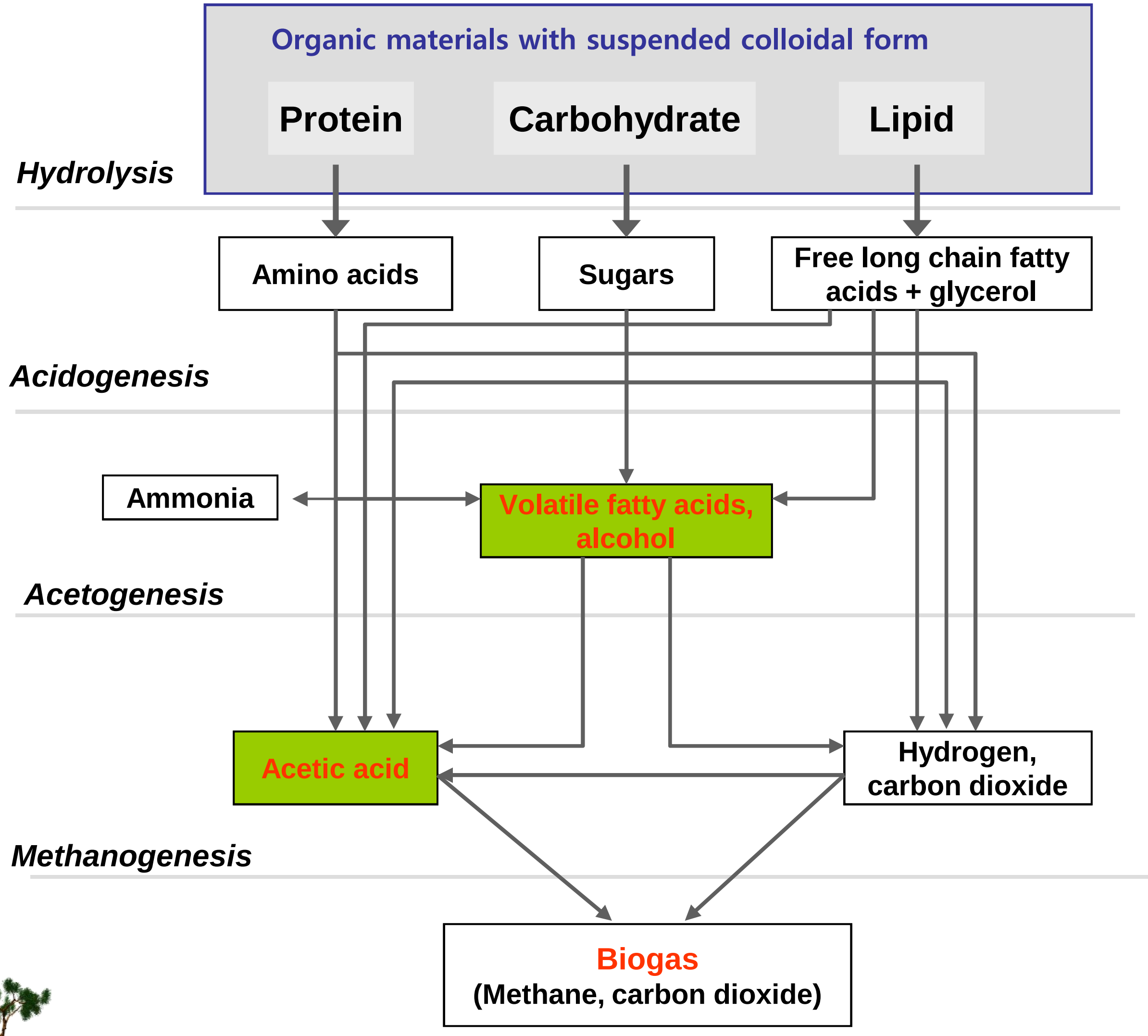
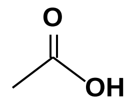
What are VFAs?

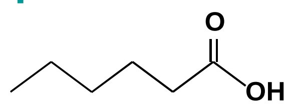
: Volatile Fatty Acid, carboxylic acid with less than C6



- No need sterilization
- No additional hydrolysis enzyme
- Mixed culture
- Acidogenesis : fast
- Methanogenesis : slow



Acetic acid	(C2)
Propionic acid	(C3)
Butyric acid	(C4)
Valeric acid	(C5)
Caproic acid	(C6)



Biofuel

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VFA-based Biofuels

1. Pretreatment (lignin: little, regular)
2. VFA (slow ➔high rate)
3. Concentration of VFAs (30g/L➔ 400g/L)
   - Evaporation (25kwh/m^3 ton of water)
   - Solvent extraction (efficiency ➔ durability)
4. Hydrogenation (catalytic, 200^oC, 20 atm)
   - $CH_3COOH + 2H_2$ ➔ $C_2H_5OH + H_2O$
   - Propionic acid + $2H_2$➔propanol + H_2O
   - Butyric acid + $2H_2$➔butanol +H_2O
5. Separation to ➔ ethanol, propanol, butanol

VFA Platform

Principle

Disintegration

↓

Hydrolysis
extracellular enzymatic process

↓

Fermentation
&
Anaerobic Oxidation

↓

Acetogenesis & Hydrogenesis

↓

VFAs

↓

Biological & thermochemical process

↓

Gas, Liquid Biofuels
Biochemicals

Biofuel

Application

Oct. 2008, presented in "International Workshop on Defining Issues in Biofuels R&D"

ECI

Engineering Conferences International
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www.engconfintl.org

Raw Materials

↓

Anaerobic digestion

↓

VFAs

C2	Acetate
C3	Propionate
C4	Butyrate
C5	Valerate
C6	Caproate

Biological and chemical processes

BioFuels

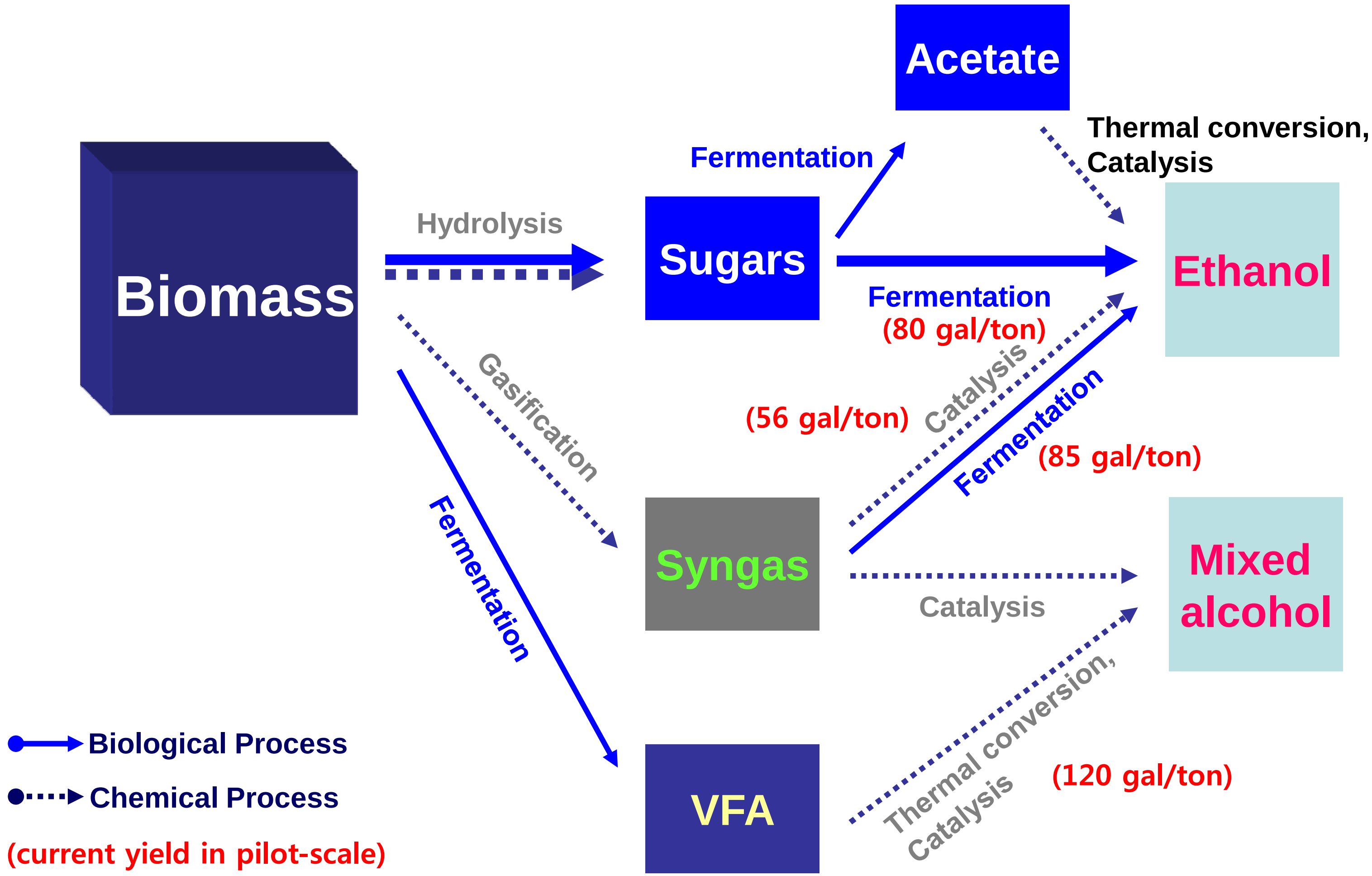
- Gas
  - Methane
  - BioHydrogen
- Liquid
  - Ethanol
  - Butanol
  - Microbial Biodiesel

BioChemicals

- Bioplastics
- Bulk chemicals(C3 ~C6)
- Pharmaceuticals
- Textiles
- Other value added chemicals

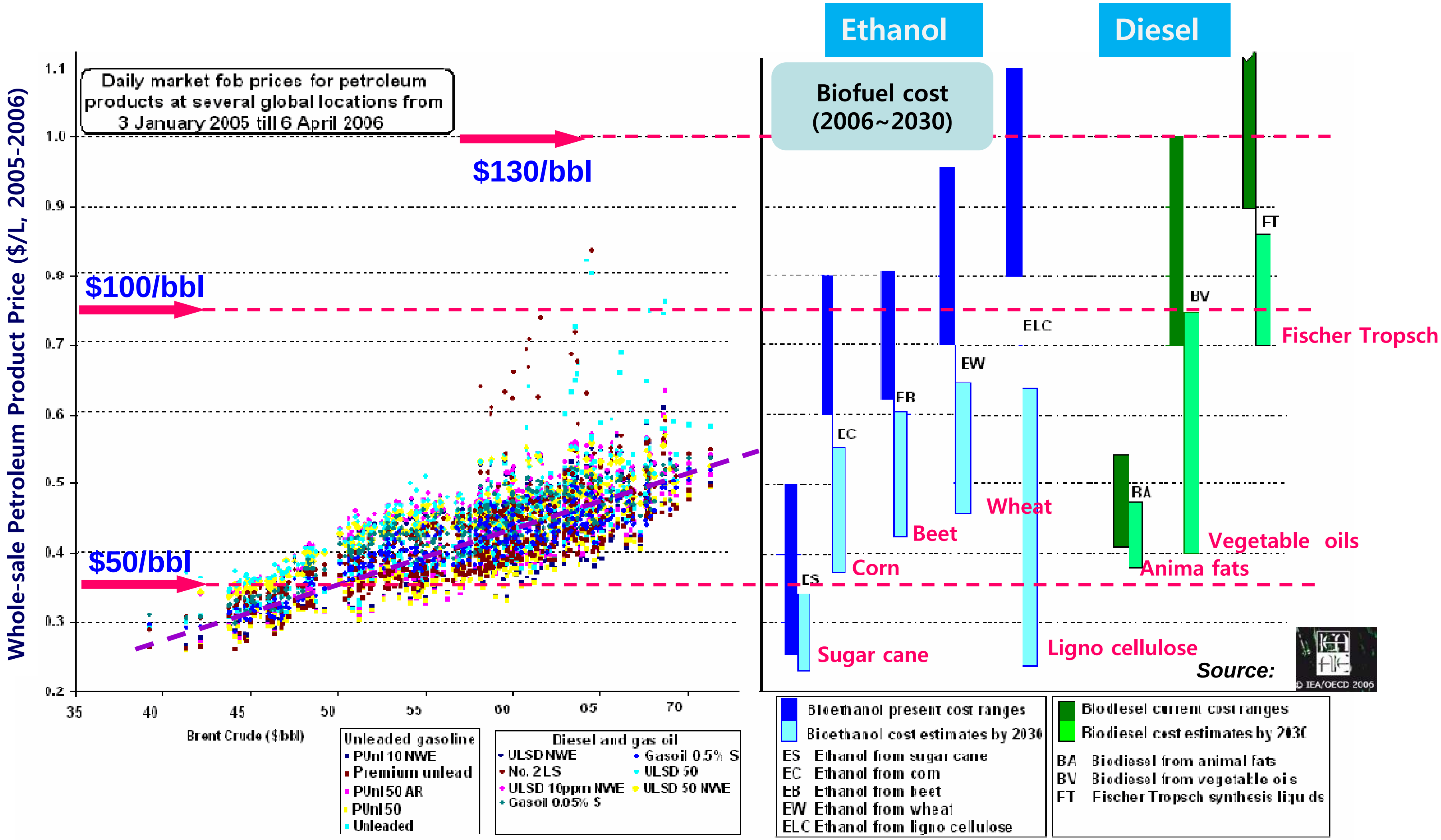
Production Routes of Fuel Alcohols

Fermentation : one of the key technologies in biological conversion

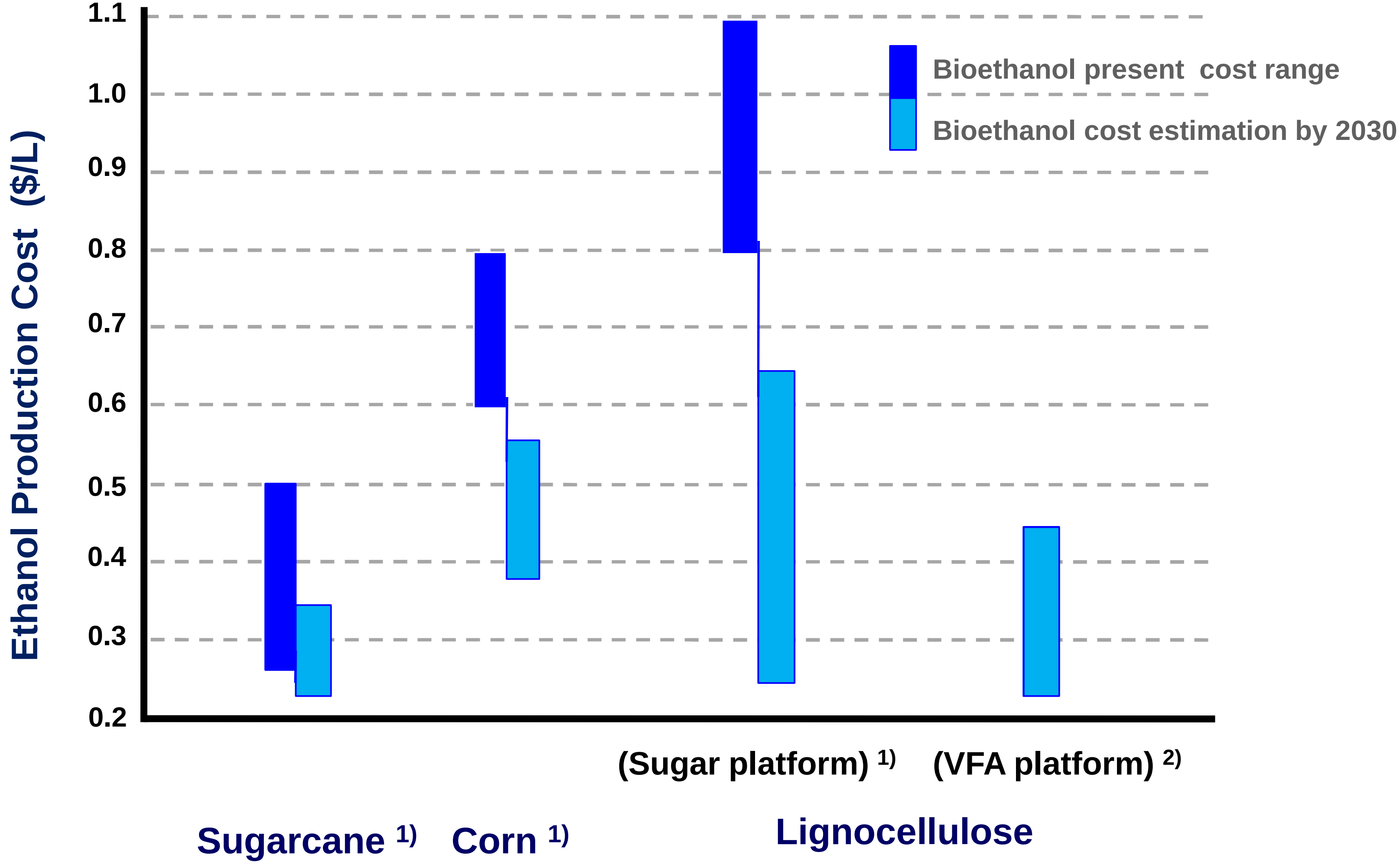


* VFA: volatile fatty acid

Liquid Biofuel Costs (2005~2030)



Cost Comparison



[1] Estimated by IEA/OECD, 2006

[2] Estimated by M. Holtzapple, 2009

Demand for New Process Development

Flexible application to various biomass

- Organic wastes
- Agricultural wastes
- Forest residues
- Energy crops
- Marine biomass
- MSW

Cost effective process

- No sterility
- No GMOs
- Adaptable
- No pure cultures
- Low capital
- No enzymes
- High product yields
- No vitamin addition
- Co-products not required

Requirement of new biorefinery platform less sensitive to species, composition, and water content of biomass

Search for New Biofuel Platform

1. Abundant Raw Materials in Korea and in other countries.

- Materials with negative cost: foodwaste, sewage sludge, fallen leaves and other biodegradable organic wastes

2. Do I have a good technology and experience ?

- Fermentation with high cell density culture (1982~)
- Foodwaste treatment since 1996

3. The cost of production should be competitive,

- vs. existing biofuels (sugar cane, grain-based; $100 bbl-oil)
- Even at a smaller scale, the product should be marketable so that technology development may go on.

My group started biofuel research in 2005.
We came to a conclusion. ⟹ VFA-platform

Mass

(Alcohol production from lignocellulosic biomass)

Cellulosic Ethanol

(Sugar platform)

Composition			Pretreat.	Hydrolysis	C6 ferment.	C5 ferment.	Recovery	Sum EtOH	Total EtOH
C6	38%	→	90%	90%	51%		95%	14.91%	25.51% (319 L/t)
C5	27%	→	90%	90%		51%	95%	10.60%	
Lignin	20%								
Ash	3%								
Others	12%								

Mixed Alcohol

(VFA platform)

Composition			Pretreat.	Anaerobic digestion	VFA recovery	Hydrogen Rxn	Sum Alcohol	Total Alcohol
C6	38%	→	90%	76%	95%	77%	19.01%	34.89% (436 L/t)
C5	27%	→	90%	76%	95%	77%	13.51%	
Lignin	20%							
Ash	3%							
Others	12%	→	90%	30%	95%	77%	2.37%	

Money

Cellulosic Ethanol Return $ = $0.3/kg(EtOH) * 0.2551/kg biomass = $ 0.0765/kg biomass (Biomass cost = 52.3%)

Mixed Alcohol Return $ = $0.3/kg(EtOH) * 0.3489/kg biomass = $0.105/kg biomass (Biomass cost = 38.1%)

* Biomass price = $40/tonne

Energy

Cellulosic Ethanol Y= 25.51% → 26.84 MJ/kg * 0.2749 kg/kg = 7.28 MJ/kg biomass

Mixed Alcohol Y= 34.89% → 30.2 MJ/kg[1] * 0.3489 kg/kg = 10.54 MJ/kg biomass (9.28 MJ/kg) [2]

[1] Ethanol:Propanol:Butanol = 6:1:3

[2] H_2 consumption = - 120 MJ/kg*0.3489*0.03 g H_2/g alcohol = - 1.256 MJ

Korean Foodwastes

Foodwastes Composition

Item	Content
Total Solid(TS), [%]	21
Volatile Solid(VS), [%]	83
Fibers in TS, [%]	7.05
Lipids in TS, [%]	15.5
Proteins in TS, [%]	17
Carbohydrates in TS, [%]	40

(Average values of Korean foodwastes)

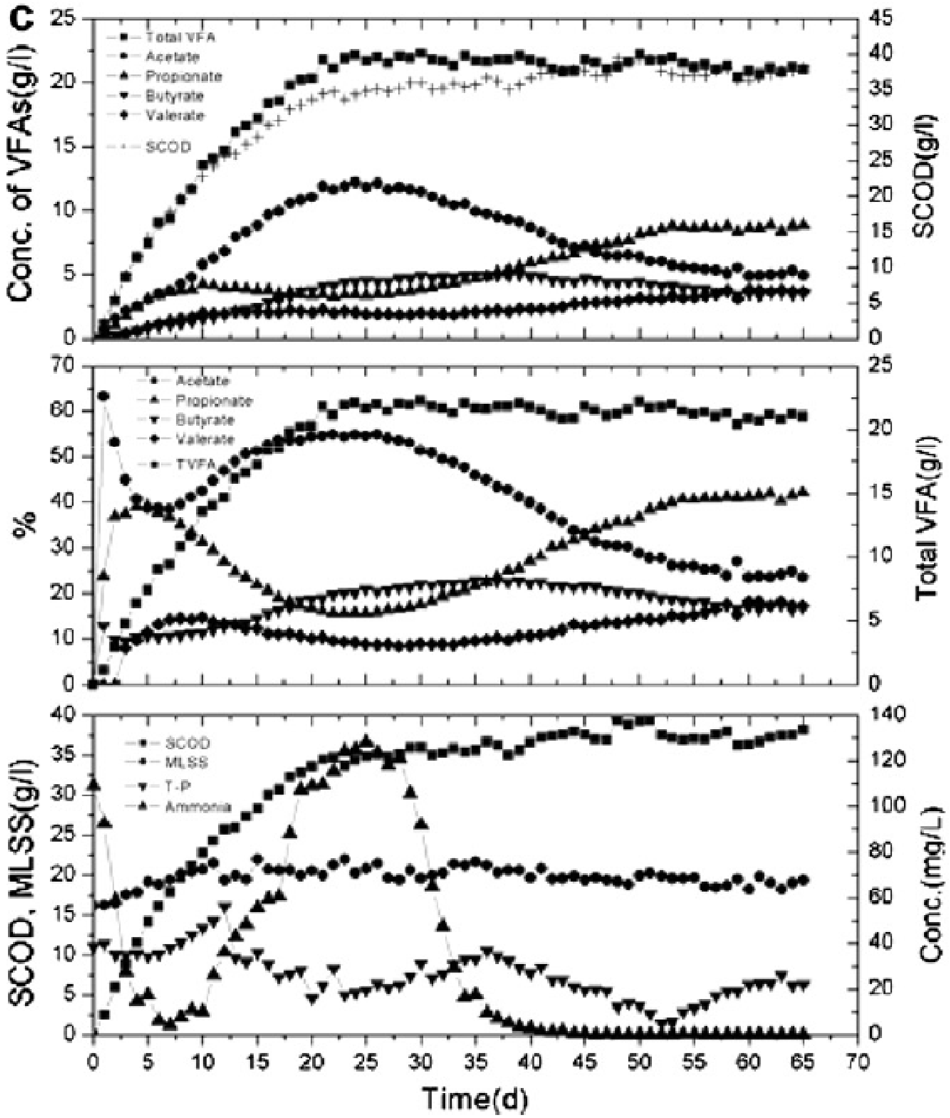
Amount of producible alcohols

	Sugar platform (% of TS)		VFA platform (% of TS)
Fibers →	3.5	→	4.0
Lipids		→	9.9
Proteins		→	6.4
Carbohydrates →	20	→	22.5
Sum :	23.5	<<	42.8

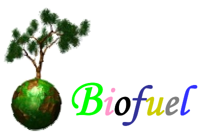
- Usually organic wastes have high protein and lipid content.
- Especially VFA platform is suitable for organic wastes.

VFA Fermentation

- **VFAs production from foodwates at HRT = 12 days**



Lim et al. ***Bioresource Technology***, **99 (16), 7866-7874 (2008)**



VFA Composition Control

Temperature

Effect of temperature on acidogenesis of food wastes

	Temperature (°C)		
	25	35	45
SCOD (mg/L)	30,500–32,500	37,000–38,000	35,000–36,500
TVFA (g/L)	16.5–17.5	23.0–24.0	19.3–20.3
Acetate (g/L, %)	3.00–3.50, 20.0–21.5	7.15–7.80, 30.0–33.0	9.50–9.90, 48.5–49.5
Propionate (g/L, %)	7.30–8.00, 44.0–46.0	5.88–6.74, 24.8–28.1	0.60–0.90, 3.2–4.2
Butyrate (g/L, %)	2.40–2.70, 14.5–16.0	4.72–5.10, 19.8–21.6	3.40–3.50, 17.0–18.0
Valerate (g/L, %)	3.00–3.20, 18.2–19.2	2.77–3.42, 11.7–14.3	0.90–1.50, 4.3–6.0
Caproate (g/L, %)	0, 0	0.52–0.97, 2.2–4.0	4.30–5.00, 23.0–25.0
Succinate (g/L, %)	0, 0	0.30–2.57, 1.3–10.9	0, 0
NH_4^+–N (mg/L)	1.0–4.0	7.2–20.2	20.0–30.0
PO_4^{3-}–P (mg/L)	40.0–50.0	74.0–88.0	75.0–95.0
Yield (VFA/VS_0)	0.24–0.26	0.34–0.35	0.28–0.30
Productivity (g VFA/L d)	2.06–2.19	2.88–3.00	2.41–2.54

pH

Effect of pH on acidogenesis of food wastes

	pH		
	5.0	5.5	6.0
SCOD (mg/L)	27,000–29,000	37,000–38,000	39,000–40,000
TVFA (g/L)	15.0–18.0	23.0–24.0	24.5–25.5
Acetate (g/L, %)	2.50–3.00, 16.3–18.2	7.15–7.80, 30.0–33.0	11.3–12.7, 48.1–50.9
Propionate (g/L, %)	0.50–0.70, 2.8–4.4	5.88–6.74, 24.8–28.1	5.40–6.50, 22.0–25.1
Butyrate (g/L, %)	2.60–3.20, 16.3–18.4	4.72–5.10, 19.8–21.6	5.00–5.50, 20.0–21.5
Valerate (g/L, %)	0, 0	2.77–3.42, 11.7–14.3	1.40–1.70, 5.5–7.0
Caproate (g/L, %)	1.70–2.00, 11.8–13.0	0.52–0.97, 2.2–4.0	0, 0
Succinate (g/L, %)	6.50–8.50, 44.0–48.0	0.30–2.57, 1.3–10.9	0, 0
NH_4^+–N (mg/L)	0	7.2–20.2	35.0–51.0
PO_4^{3-}–P (mg/L)	60.0–90.0	74.0–88.0	65.0–80.0
Yield (VFA/VS_0)	0.22–0.26	0.34–0.35	0.36–0.37
Productivity (g VFA/L d)	1.88–2.25	2.88–3.00	3.06–3.19

- High temperature: increase of acetate concentration and ratio
- High pH: increase of short chain VFA
- Controllability of VFA composition

Treatable Biomass

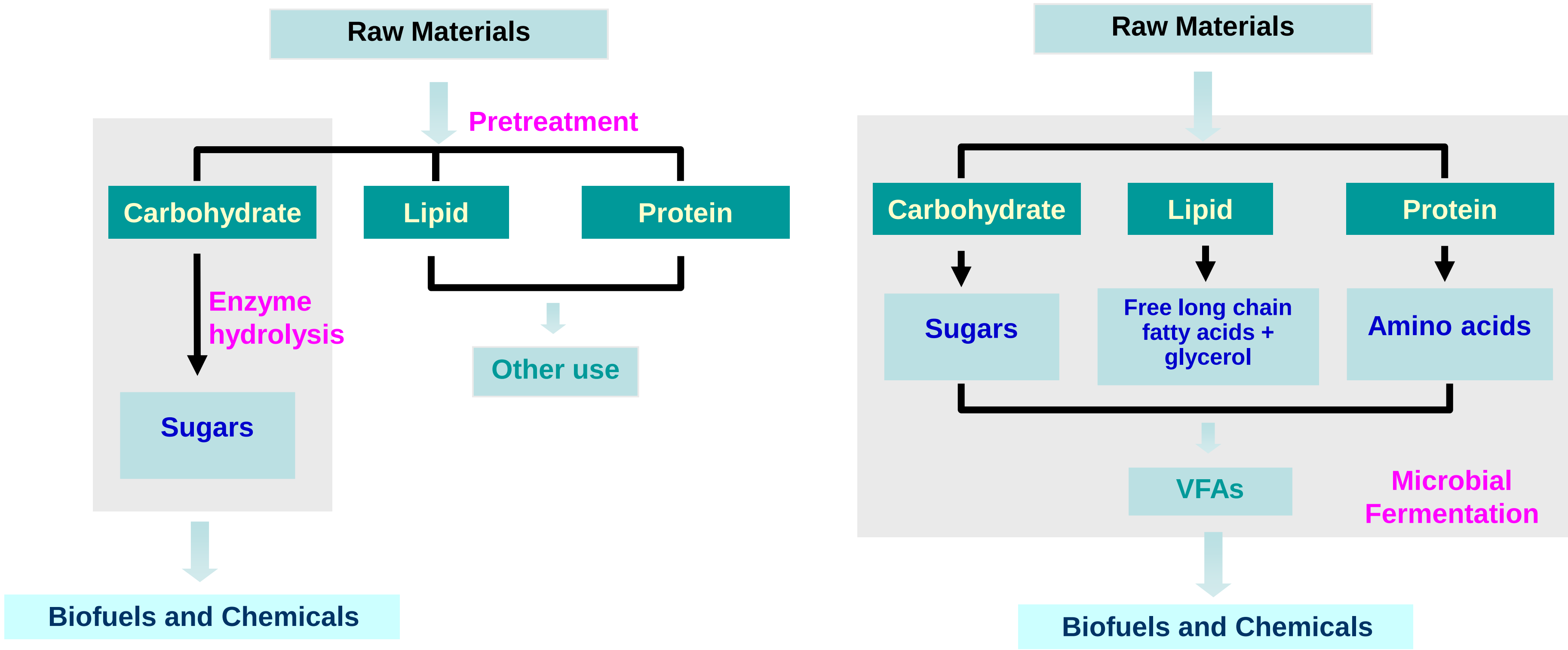
Low lignin biomass **(no pretreatment need)**

- Agricultural organic wastes
- Sludge
- Food wastes
- Manure
- Marine biomass
- All biodegradables

High lignin biomass **(need pretreatment)**

- Woods (forest wastes)
- Agricultural wastes
- Energy crops

Sugar Platform versus VFA Platform



Biomass is mainly composed of carbohydrates, lipids, and proteins. And many biomasses are the complex of biomass with various composition. Using the sugar part of biomass mixture, especially wetted organic wastes, is wasteful and needs the large wastewater treatment facilities. The VFA platform may be a modified form of biogas platform to diversify producible products, most part of biomass is converted to simple acids, and do not need additional enzymes.

Sugar Platform versus VFA Platform

	Advantage	Disadvantage
Sugar platform	Favorable substrate for microbes High energy potential High inhibitory concentration	Only use sugars part of biomass High sugar price High enzyme cost Sugar uptake specificity (C5 & C6)
VFA platform	Use all biomass (wastes) Low acids production cost No enzyme addition High VFA yield Hydrogen coproduction No sterilization Less CO_2 emission than sugar-P	Unfavorable substrate for microbes Low chemical energy level of VFA Relatively high inhibition to microbes

Major Bottlenecks in VFA Platform

VFA production

- Pretreatment of biomass (lignin removal)
- Low acid concentration (~ 30 g/L)
- Productivity enhancement (higher than 1 g/L/hr)
- VFA recovery from dilute fermentation broth
  - Distillation
  - Solvent extraction
- Inhibition of methane formation

Chemical route

- Catalysts (e.g. hydrogenation, hydrogenolysis)
- Catalysts life cycle

Biological route

- Strain development and fermentation
- Metabolic engineering for acid uptake and conversion (e.g. biohydrogenation)

MixAlco Process Plant

Terrabon Semi-Works Plant
Football field = 1.32 acres
Terrabon Semi-Works Plant = 1.43 acres

- **Capacity : five dry tons biomass/day**
- **Too large land area for pretreatment and fermentation**

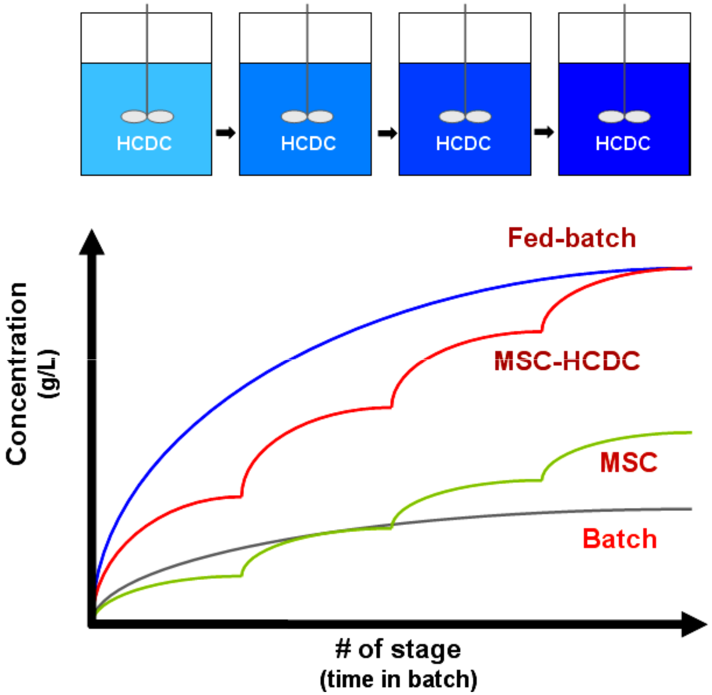
Fermentation Productivity

Q_p (g-product/L.h)

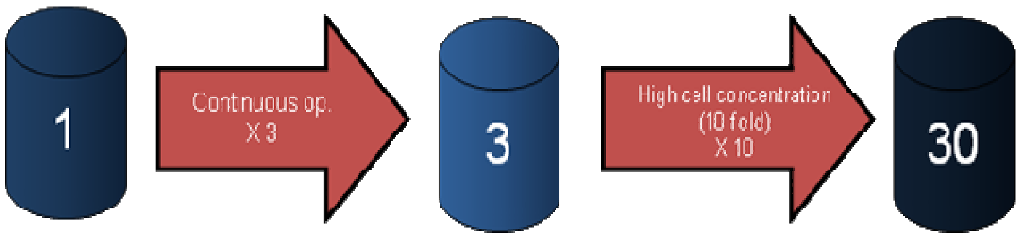
Specific cell productivity	Cell concentration	Substrate availability / Inhibitor removal
$q_{P/X}$: (g-product/g-cell•h)	**X (g-cell/L)**	$Y_{P/S}$ (g-p/g-s) / **K_I**
Strain Development	**HCDC**	**Feeding / Separation**
• **Mutation, Screening** • **Metabolic engineering** • **Directed Evolution**	• **Cell recycle** • **Immobilization** • **Perfusion**	• **Batch, fed-batch** • **Continuous** • **Air** • **Oxygen recycle** • ***in situ* separation**
Impact : variable	Impact : 4~40 fold	Impact : variable

High Efficiency Fermentation Technology

MSC-HCDC : Multistage Continuous High Cell Density Culture



Modes of Operation	Batch, Fed-batch	Continuous culture	Proposed MSC-HCDC
Cell conc.	10	10	100
Product titer	100	60	100
Productivity	1	3	30



Examples

- Monoclonal antibody
- Lactic acid
- Ethanol
- Ground food waste treatment

Methods of VFA Recovery

Concentration (water removal)

➢ Phase change

- Distillation (MSF, ME, VC, Solar) : heat energy
- Freezing (FD) : cold energy

➢ Membrane

- Reverse osmosis (RO, NF) : pressure difference (mechanical)
- Electro-dialysis (ED) : electrical energy

➢ Water extraction

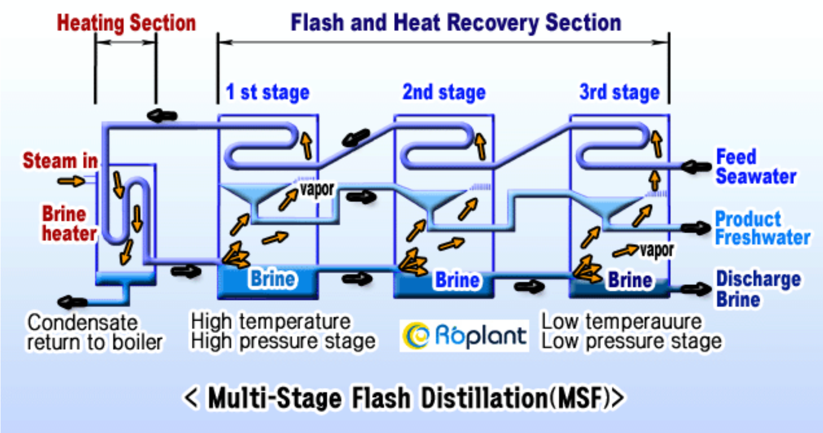
- Amine dewatering

VFA purification

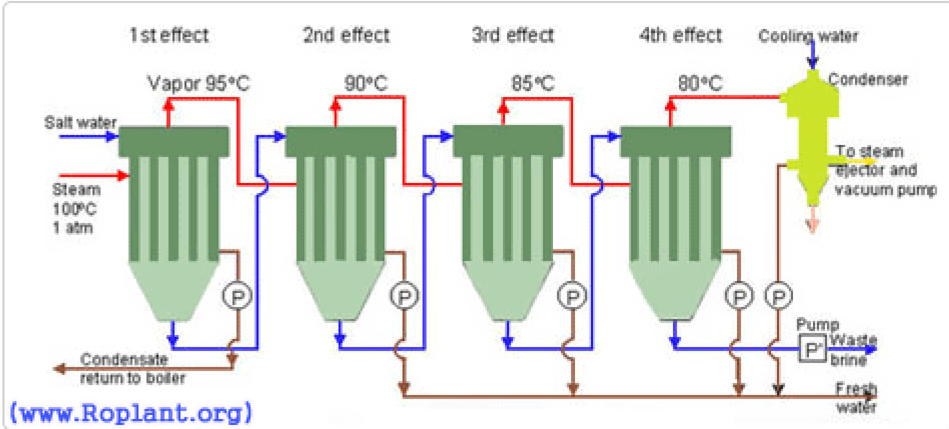
- Solvent extraction (amine solvent)
- Back-extraction
- Distillation (reactive distillation)

Efficient Water Distillation

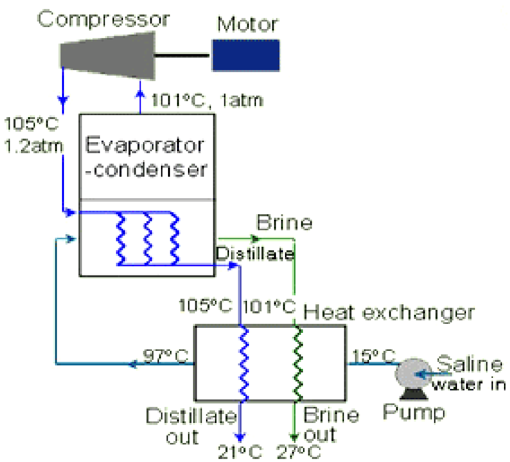
MSF: Multiple-Stage Flash Distillation



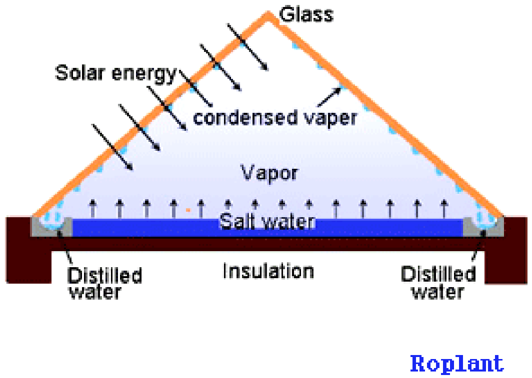
MED: Multi-Effect Distillation



VCD: Vapor Compression Distillation



(Mechanical VC)



(Direct vaporization using Solar energy)

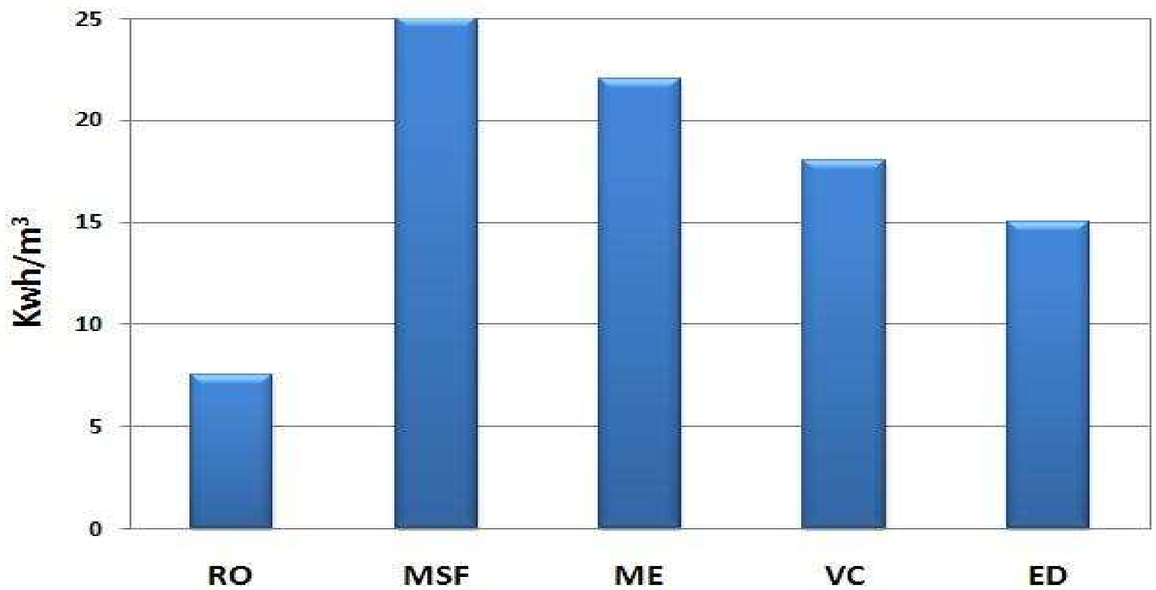
Source : www.roplant.org

Water Distillation Energy

Simple distillation

- Heat One kg Water to 100˚C = 418 kJ/kg
- 1 kWh = 3600 kW-sec = 3,600kJ
- One kWh Gives 3600/418 = 8.6 kg Water
- One kWh Gives 8.6 kg = 8.6 liter Water (116.3 kWh/m^3)
- Cost at 8 cents/kWh: 0.93 cents/liter ($9.3/$m^3$)
- Cost must be reduced (by one tenth).

Efficient Water Separation Methods



- ➢ **Distillation cost : < $2/$m^3$**

RO : Reverse Osmosis
ME : Multi-Effect Distillation
ED : Electro-Dialysis
MSF : Multi-Stage Flash
VC : Vapor Compression Distillation

Source : Park SJ, KIMM, 2007

Catalysts for Alcohol Synthesis

➢ Hydrogenolysis catalysts

: VFA ester conversion to alcohols

- **Copper chrmite**

  - high temperatures (> 200˚C)

  - high pressures (> 600 psi) (> 40.8 atm)

  - widely used in industry (e.g., for making detergent alcohols from fatty acids)

- **Reduced CuO-ZnO catalyst**

  - low temperature (~150˚C)

  - low pressure (<350 psi) (< 23.8 atm)

  - preferred


Thank you for your attention.
Question ?