해조류 바이오연료 생산공정 설계 동향

- BIOCHEMICAL CONVESION 1 -

부경대학교 화학공학과 유준

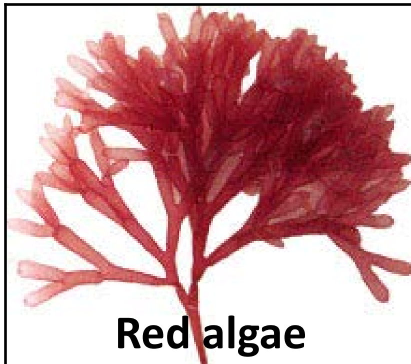
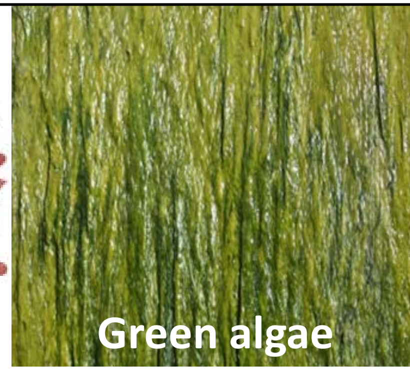
Biomass ?

IUPAC definition

Living systems and collection of organic substances produced by living systems that are exploitable as materials, including recent postmortem residues.

First Generation (sugar cane, sugar beet, maize…)	
Second generation (lignocellulosic agriculture and forest residues)	
Third generation (microalgae, **macroalgae**)	

Seaweed

 Red algae	 Green algae	 Brown algae
Carrageenan	Starch	Laminaran
Agar	Cellulose	Mannitol
Cellulose		Alginate
Lignin		Fucoidan
		Cellulose

Why seaweeds?

	Wheat	Corn	Sugar beet	Sugarcane	Macroalgae
Average world yield (kg ha^{-1} $year^{-1}$)	2,800	4,815	47,070	68,260	730,000
DW of hydrolysable Carbohydrates (kg ha^{-1} $year^{-1}$)	1,560	3,100	8,825	11,600	40,150
Potential volume of Bioethanol (L ha^{-1} $year^{-1}$)	1,010	2,010	5,150	6,756	23,400

Why seaweeds?

Very low terrestrial biomass density in Korea

Why seaweeds?

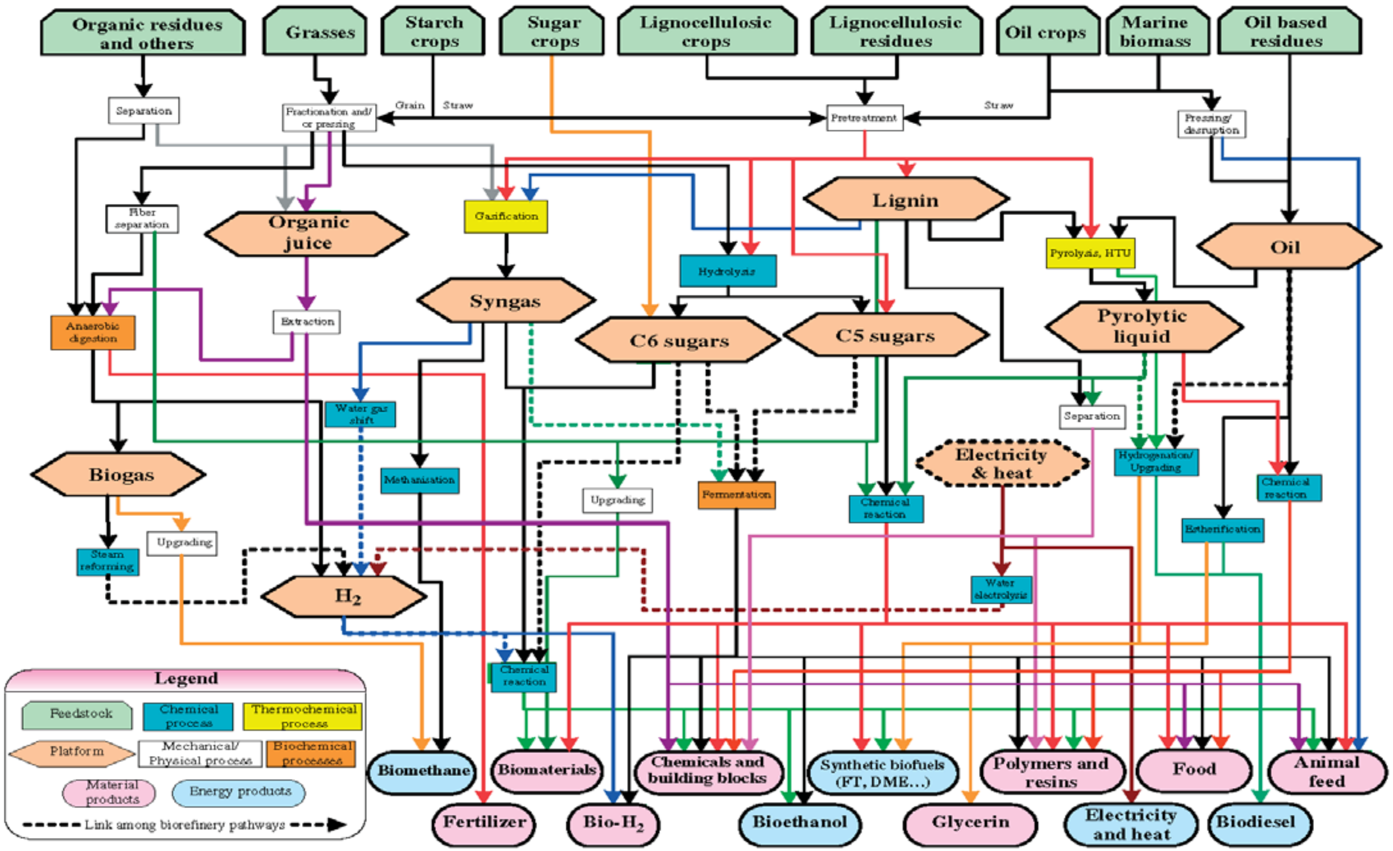

Korea is **among top three** in terms of production amount and production technology.

What is biorefinery ?

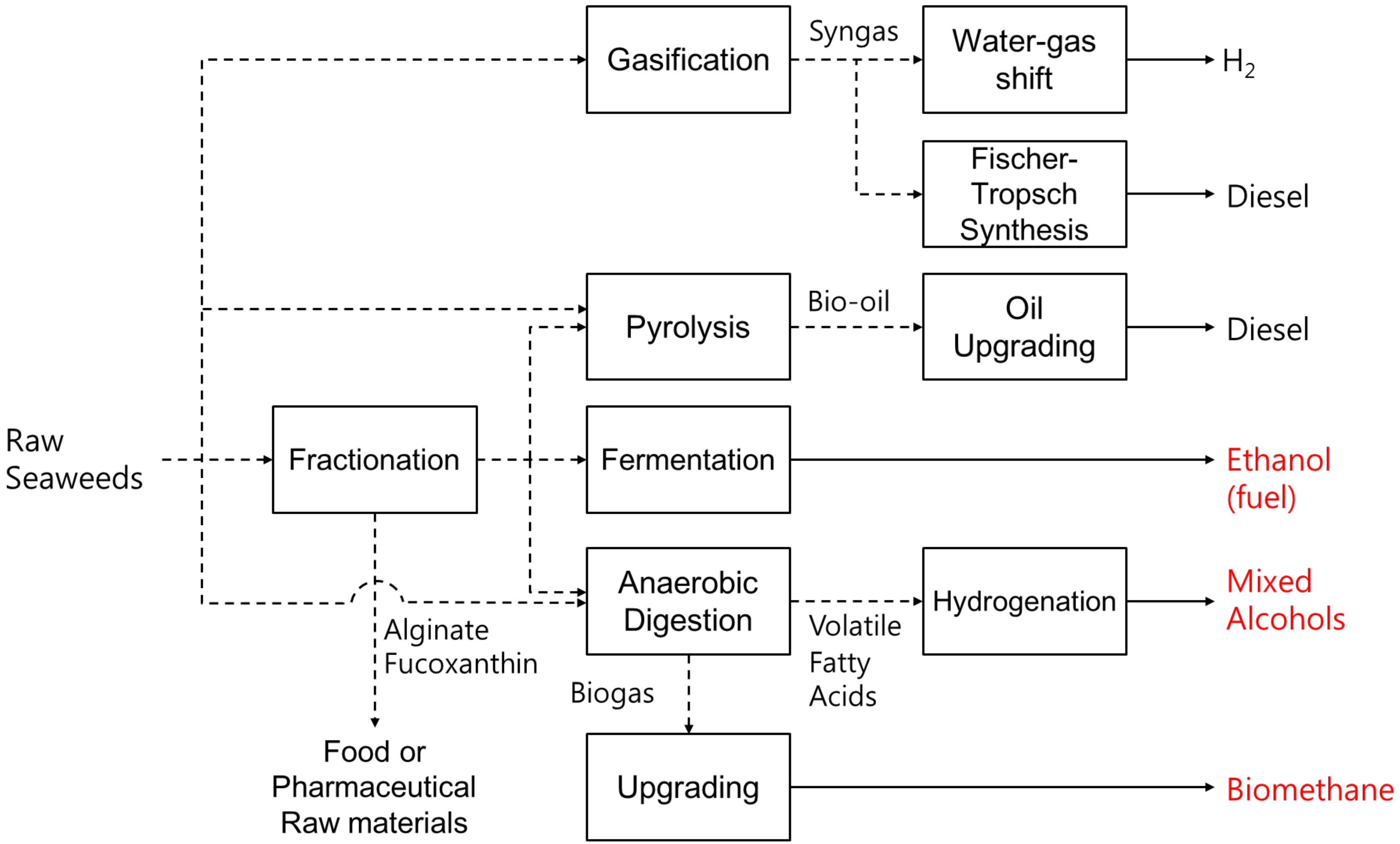
“Biorefining is the sustainable processing of biomass into a *spectrum* of marketable Biobased Products and Bioenergy.” Biobased Products are chemicals & materials, but also human food & animal feed. Bioenergy includes fuels, power and/or heat. In general, both Energy-driven and Product-driven Biorefineries can be distinguished.

(http://www.ieabioenergy.com/ & http://www.iea-bioenergy.task42-biorefineries.com/en/ieabiorefinery.htm)

Biorefinery network by IEA Bioenergy task 42

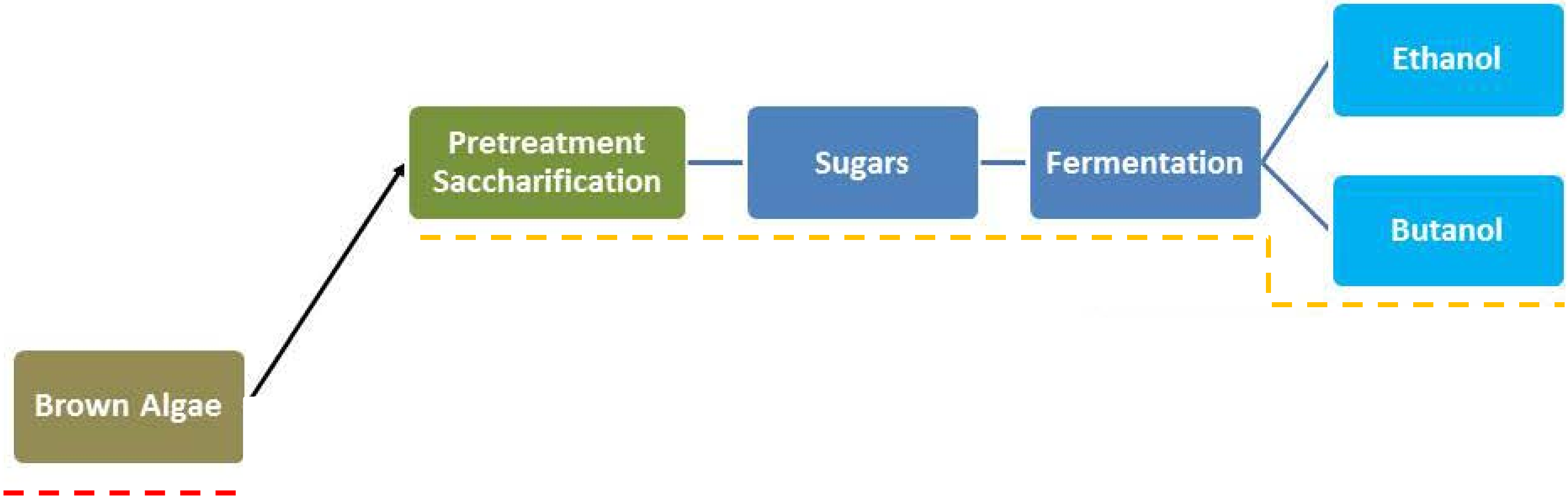


(Possible) Biorefinery network for seaweed biomass



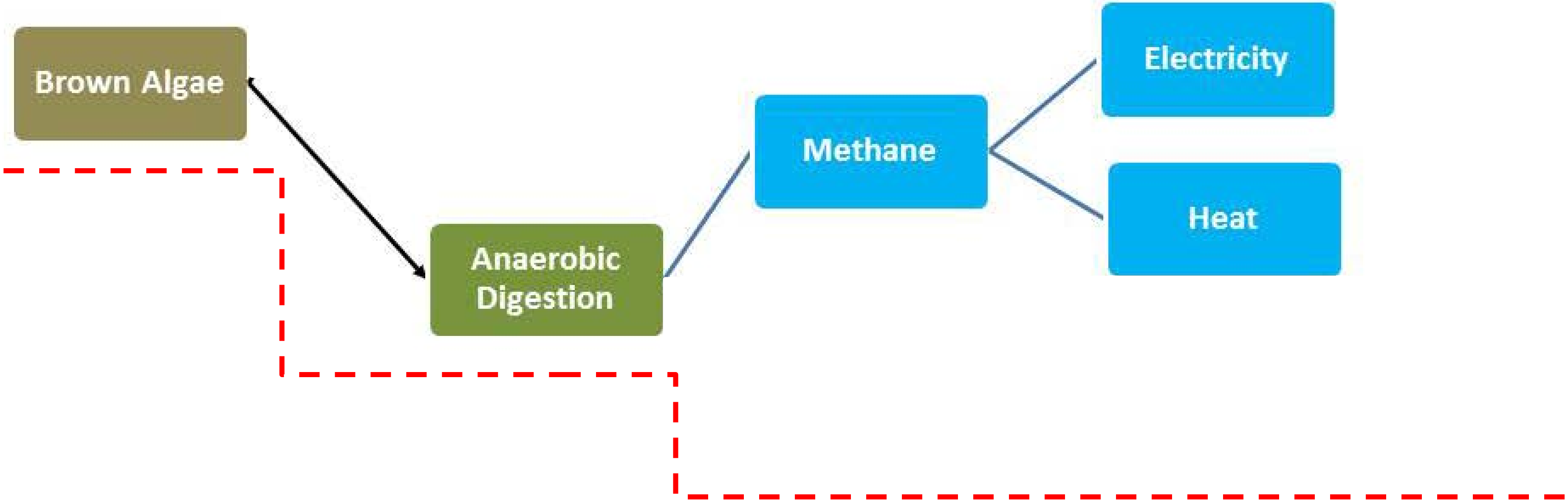
Biochemical Conversion of Biomass

1. Sugar Platform



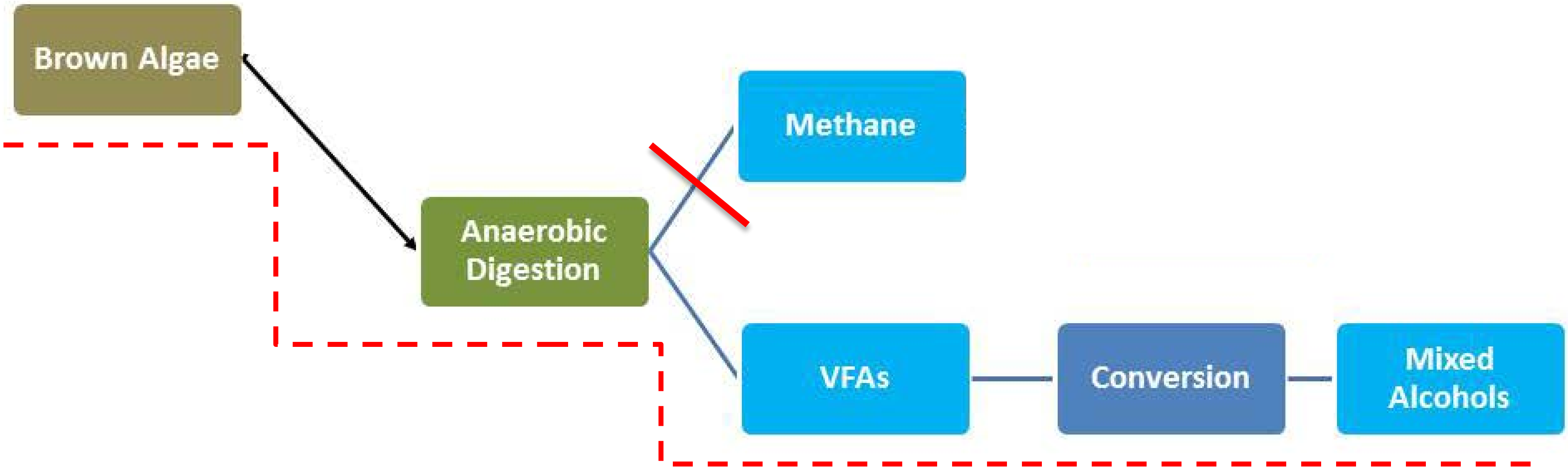
Biochemical Conversion of Biomass

2. Methane Production



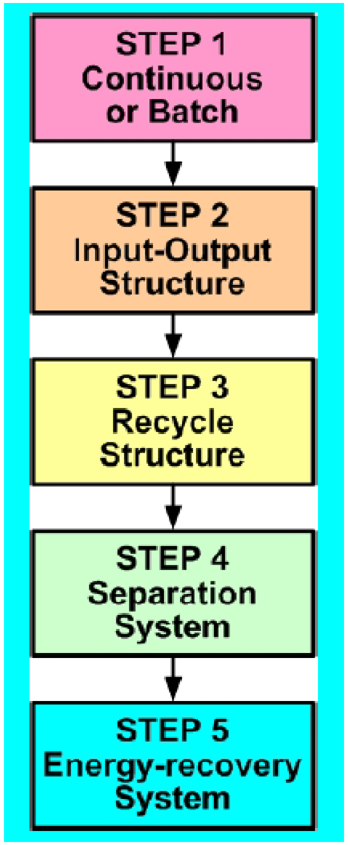
Biochemical Conversion of Biomass

2. Methane Production

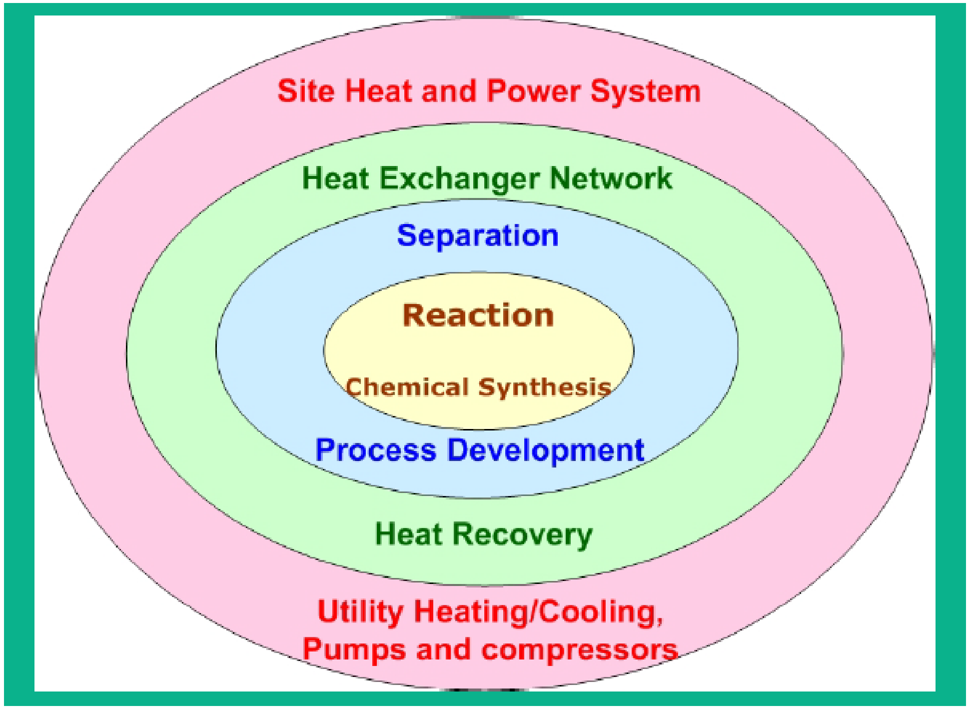


Conceptual process design

Hierarchical design



Onion model



Fermentation vs. anaerobic digestion

1. Acetic acid is biologically produced from simple sugars without the production of carbon dioxide:

$$C_6H_{12}O_6 \rightarrow 2\ CH_3CH_2OH + 2\ CO_2$$

(Biological production of ethanol from glucose)

$$C_6H_{12}O_6 \rightarrow 3\ CH_3COOH$$

(Biological production of acetic acid from glucose)

Hence, on a Mass basis, the yield is higher for acetic acid compared to ethanol fermentation.

Fermentation vs. anaerobic digestion

2. $C_6H_{12}O_6 \rightarrow 2C_2H_5OH + CO2$ G = - 48.56 kcal/mol
glucose ethanol

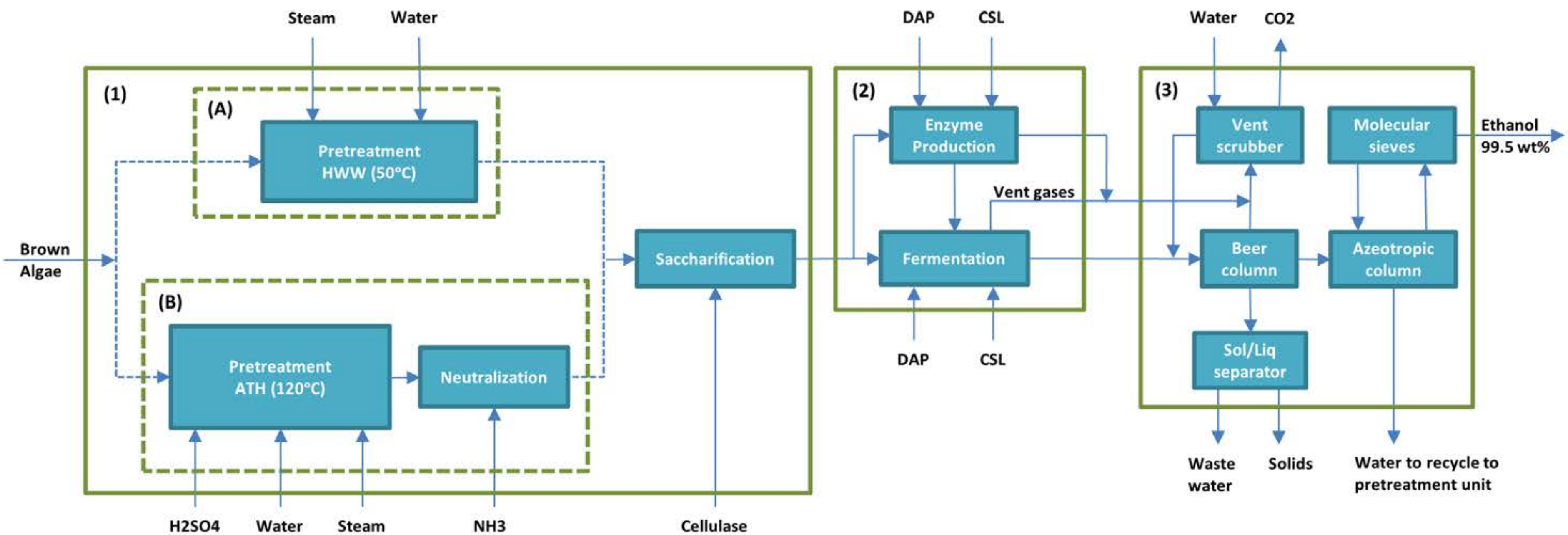
$C_6H_{12}O_6 \rightarrow 3\ C_2H_3OOH$ G = - 61.8 kcal/mol
glucose acetic acid

The actual stoichiometry is more complex

$C_6H_{12}O_6 \rightarrow$ 6 acetate + 2 propionate + butyrate + $5CO_2$ + 3 CH_4 + $6H_2O$
(67 mol%) (22 mol%) (11mol%)

Conceptual design of ethanol production

- In sugar platform, the brown algae is pretreated, saccharified, and fermented to ethanol.
- Two possible pretreatment processes i.e. **simple process** and **combined process** were identified from literature.
- All the data for operating conditions and conversions are extracted from literature and are based on experimental studies.



Required information for design

- Feedstock compositions & thermodynamic properties
- Reaction information
  - Stoichiometric equations & conversions of saccharification
  - Stoichiometric equations & conversions of fermentation & anaerobic digestion
  - Reaction conditions (time, temp., …)
- …

Feedstock compositions (Required information)

- **Alginate:** Major structural component made of β-D-Mannuronic acid and α-L-Guluronic acid.
- **Laminaran**: Linear polysaccharide of β-(1,3)-D-glucose
- **Cellulose:** Linear chain of several hundred to over ten thousand β(1→4) linked D-glucose
- **Mannitol**: Sugar alcohol derived from mannose
- **Fucoidan**: Sulphated polysaccharide containing l-fucose and sulphate ester groups

Laminaria Japonica at harvest		
Component	%of dry matter	
	Min.	Max.
Ash	22	28
protein	6	19
Lipids	1	3.5
Cellulose	3	9
Alginate	17	19
Laminaran (D-Glucose)	12	16
Fucoidan (Fucose)	11	23
Mannitol	8.5	28

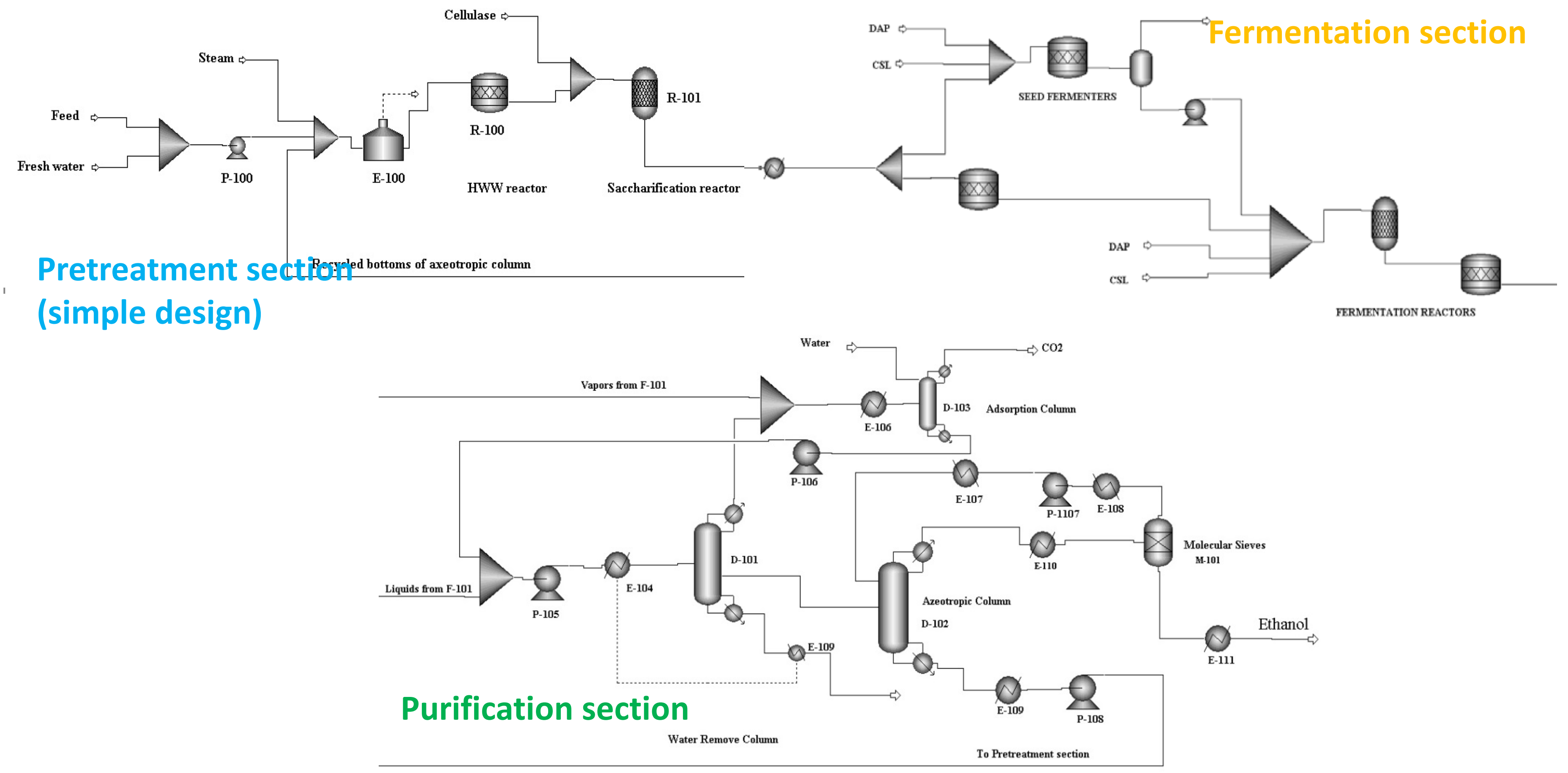
Conversions (Required information)

Material	Fermentation Yield	Ref.
Laminaria japonica	0.281 kg/kg dry seaweed	Wargacki et al. 2012
Glucose and mannitol	0.4 g/g (glucose + mannitol)	Horn et al., 2000c
Mannitol	0.41 g/g	Kim et al. 2011
Glucose	0.395 g/g	Kim et al. 2011
Laminaria hyperborea extracts	0.43 g/g substrate	Horn et al., 2000b

Material	Saccharification Yield	Fermentation Yield	Ref.
Laminaria japonica	69.1%	33.3% theoretical yield	Jang et al., 2011
Laminaran & Mannitol	277.5 mg/g	41.2% theoretical yield	Ge et al., 2011
Alginate	50-87% of alginate		Moen et al., 1997a
Cellulose	91 %	95%	Humbird et al., 2011
synthetic mannitol medium		0.38 g ethanol/g Mannitol	Horn et al., 2000c

Simulation results (ethanol production)

PFD by Aspen plus



Simulation results (ethanol production)

- Simple design : 24.8% kg ethanol/kg dry seaweed.
- Combined design: 26.1% kg ethanol/kg dry seaweed.

Material	Simple design (Kg/hr)	Combined design (Kg/hr)
Feed	11,408	11,408
Ethanol	2,831	2,978
CO_2	2,798	2,944
Steam	4,954	18,494
H_2SO_4	-	220
Cellulase	40	36
Corn Steep liquor	135	139
Diammonium phosphate	18	18

Techno-economic comparison

Tools

- MSP (Maximum allowable seaweed price) – higher the better
  - Maximum value of seaweed purchase cost that reaches a return-on-investment (ROI) break-even point after 10 years of plant operation.
- MESP (Minimum Ethanol Selling Price) – lower the better
  - Minimum value of ethanol selling price that produces a net present value (NPV) of zero for a 15 % internal rate of return (IRR) after 10 years of plant operation.

Techno-economic comparison

	Simple design	Combined design
Total Project Cost ($MM)	28.6	37.9
Total operating labor & maintenance cost ($MM) per year	1.5	1.9
Total product sales ($MM) per year	21.1	22.1
Max. Seaweed Price ($/ton)	75	19.7
Min. Ethanol Selling Price(*) ($/gal)	2.28	2.77

(*) assuming $112/ton as seaweed price

Conclusions

- Industrial-scale biofuel production from seaweeds was investigated and a techno-economic model were developed to assess the plant economy.
- For ethanol production, simple pretreatment (hot water wash + enzymatic saccharification) is economically preferable to combined pretreatment (acid thermal hydrolysis + enzymatic saccharification) in terms of both MSP & MESP.