해조류 바이오연료 생산공정 설계 동향

- THERMOCHEMICAL CONVERSION (GASIFICATION) -

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2nd and 3rd Gen Biobutanol Big Picture

Option 1 – Thermochemical Route: Gasification → Reaction → Separation

- Gasification – Advantage: Biomass, including lignin converted to syngas efficiently
- Reaction – Disadvantage: Reaction conversion is low
- Separation – Advantage: Easier separation. High butanol concentration.

Switchgrass, Macroalgae (Seaweed), Wood, etc.

Option 2 – Biological Route: Saccharification ABE Fermentation → Separation → Wastewater Treatment

- Saccharification ABE Fermentation – Advantage: More experience and knowledge. Disadvantage: Poor lignin conversion (thus poor carbon conversion)
- Separation – Disadvantage: Poor butanol concentration, lots of water. Difficult separation.
- Wastewater Treatment – Disadvantage: Can be very significant.

Prior Work in 2nd Gen Biobutanol

1 Key Finding: Thermochemical route with wood is promising.

Minimum Butanol Selling Price (MBSP): $0.83 to 1.12/L
LCA Cost of CO_2 Avoided (CCA): $132/tonne

Gasification → Reaction → Separation

Option 1
Thermochemical Route

Saccharification ABE Fermentation → Separation → Wastewater Treatment

Option 2
Biological Route

2 Key Finding: Biological route with switchgrass requires a very particular separation strategy, still not very competitive.

Minimum Butanol Selling Price (MBSP): $1.56 to $1.80/L
LCA Cost of CO_2 Avoided (CCA): $472/tonne

Why Butanol? Property

Next generation alcohol fuel with life cycle advantages over ethanol.

Higher energy density compared to ethanol. Much closer to gasoline.

Property	Ethanol	i-Butanol	n-Butanol	Gasoline
Density at 20 °C (g/cm^3)	0.794	0.802	0.810	0.791
Research Octane number	112 – 122	102 – 105	94 – 96	85 - 87
Energy density (% of gasoline)	65	82	82.3	100
Water solubility (wt.%)	100.0	8.5	7.7	–

Low water solubility
(Can pipeline it, blend at refinery)

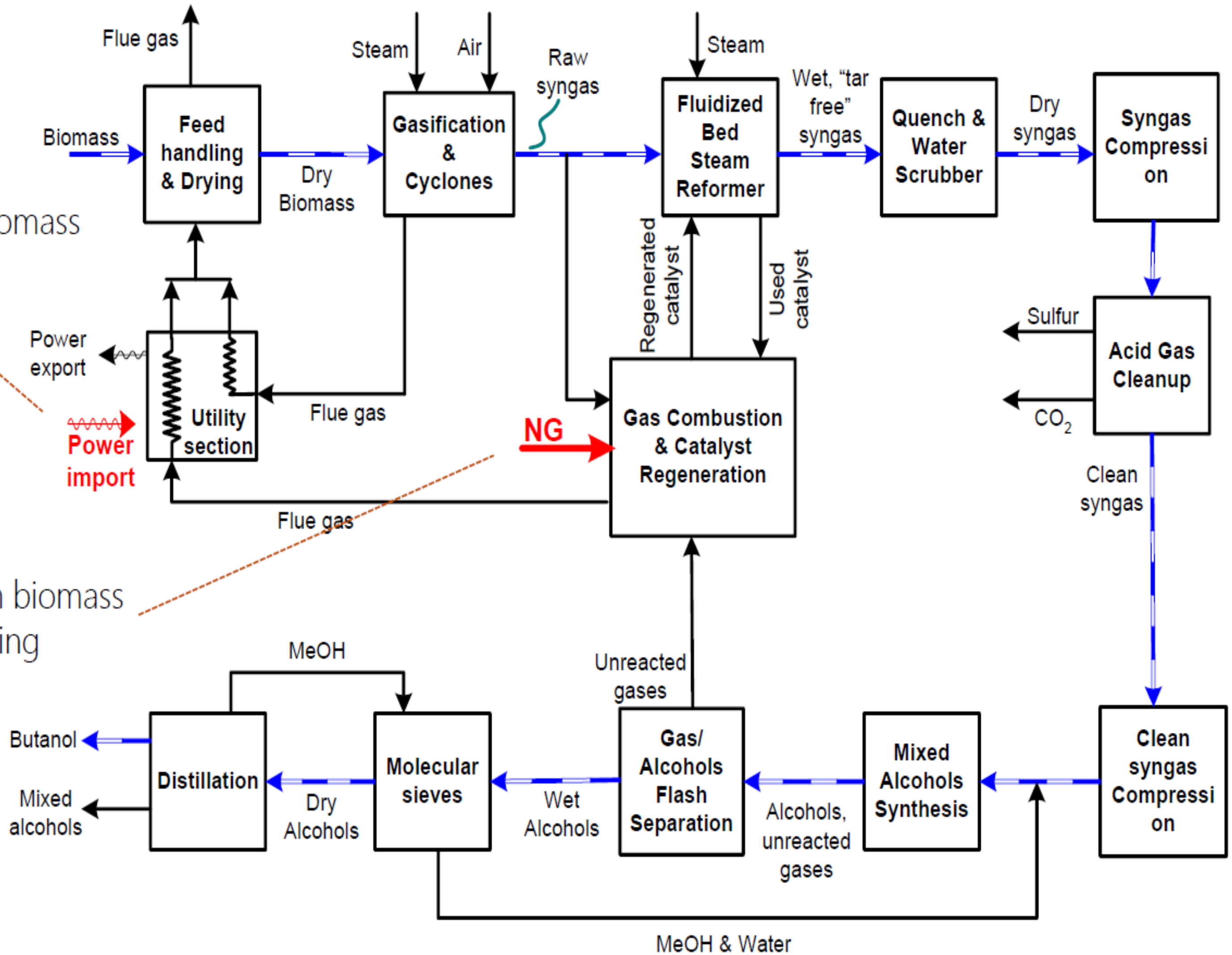
Had not been explored for macroalgae prior to this work.

Why Macroalgae (seaweed?)

- 25 Mt/yr produced worldwide
- Korean Ministry of Oceans and Fisheries goals:
  - Increase aquaculture yields
  - Convert into renewable energy products
- Idea: Can greatly increase production since grown on oceans instead of land
  - Less impact on food-vs-fuel problem
- Our big picture question: Will thermochemical conversion be a promising path? Does this make sense at all?
  - Economics and Business Case
  - Wells-to-wheels CO_2 Emissions and Policy Case

Lamanaria Japonica
A brown macroalgae

Simplified Block Flow Diagram

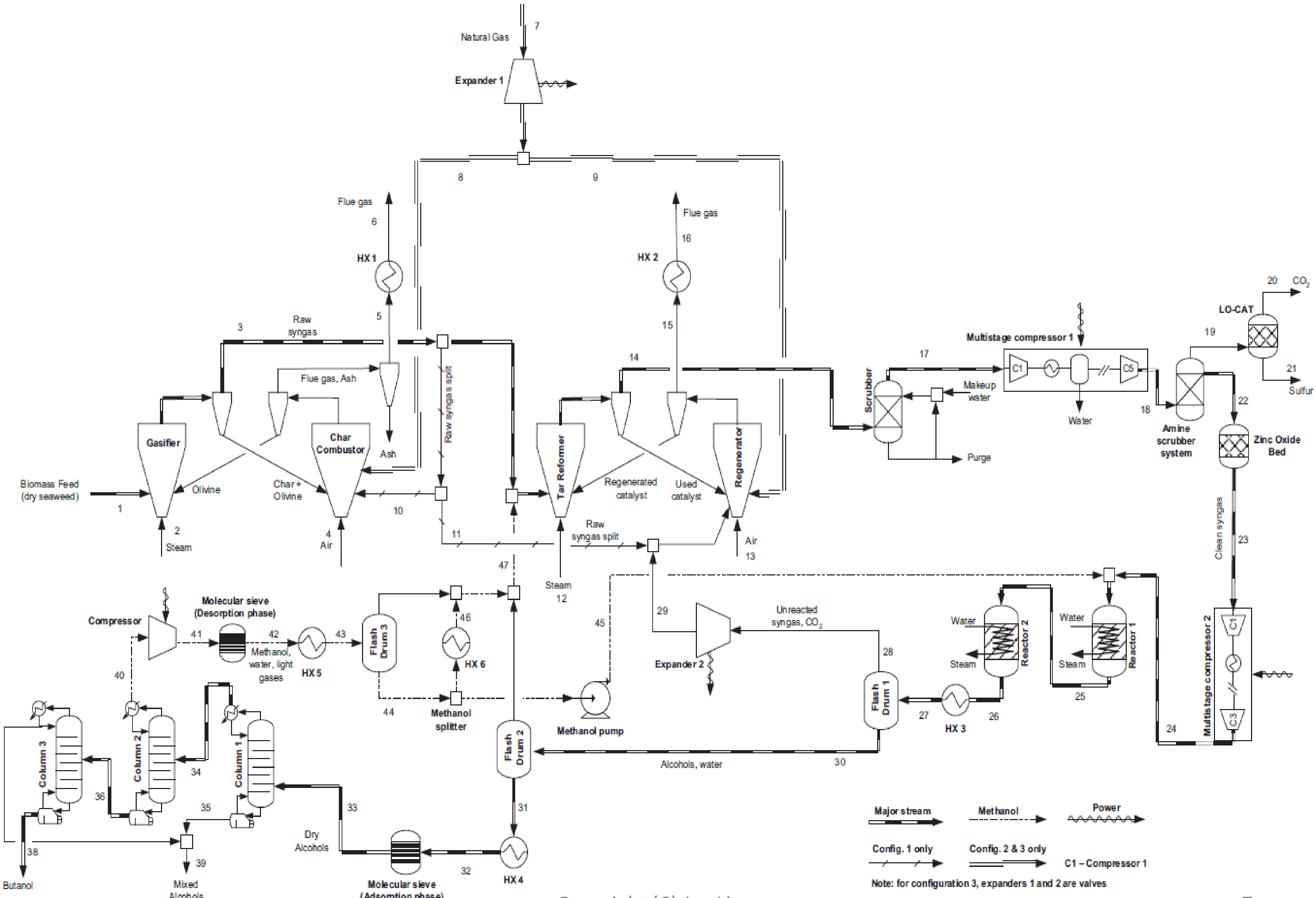


Choice 1

- Generate own power from biomass
- Purchase power from grid

Choice 2

- Generate our utility heat from biomass
- Purchase natural gas for heating



Natural Gas
7
Expander 1
8
9
Flue gas
6
HX 1
Flue gas
16
HX 2
20 CO2
LO-CAT
19
21
Sulfur
Multistage compressor 1
17
Makeup water
Water
18
Amine scrubber system
22
Zinc Oxide Bed
Scrubber
Purge
3
Raw syngas
5
15
14
Flue gas, Ash
Raw syngas split
Gasifier
Char Combustor
Ash
Tar Reformer
Regenerator
Biomass Feed (dry seaweed)
1
Olivine
Char + Olivine
10
Regenerated catalyst
Used catalyst
2
Steam
4
Air
11
Raw syngas split
Air
13
Clean syngas
23
47
Steam
12
Compressor
Molecular sieve (Desorption phase)
41
42
43
Methanol, water, light gases
HX 5
Flash Drum 3
46
HX 6
45
29
Unreacted syngas, CO2
Expander 2
28
Water
Steam
Reactor 2
Reactor 1
Multistage compressor 2
40
44
Methanol splitter
Methanol pump
Flash Drum 1
27
HX 3
26
25
24
Column 3
Column 2
Column 1
34
37
36
35
Flash Drum 2
Alcohols, water
30
33
31
Dry Alcohols
38
Butanol
39
Mixed Alcohols
Molecular sieve (Adsorption phase)
32
HX 4
Major stream
Methanol
Power
Config. 1 only
Config. 2 & 3 only
C1 – Compressor 1
Note: for configuration 3, expanders 1 and 2 are valves

Gasification Step: Experimental Data

Ultimate analysis of L. Japonica used in this study provided by collaborators at Pukyong National University

(Small changes based on season)

Ultimate analysis	wt % dry basis	Proximate analysis	wt %
Carbon	32.41	Moisture	2.79
Hydrogen	3.37	Volatile matter	70.9
Nitrogen	1.18	Fixed Carbon	3.32
Sulphur	0.31	Ash	22.99
Oxygen	39.74		
Ash	22.99		
HHV (MJ/kg)	14.05		

The seaweed is dried before it is gasified

(Drying process factored into costs and life cycle CO_2 emissions study)

Note high ash content (disadvantage).

Have to lug that dead weight around the whole supply chain.

Simulation Methodolgy

- Aspen Plus Simulations
  - Built-in unit operation models where available
  - Batelle Columbus Laboratory model to predict gasifier outputs
  - Monoethanolamine (MEA) / LO-CAT / ZnO for CO_2/H_2S removal
  - Modifed Cs/Cu/ZnO/Cr_2O_3-based low-pressure methanol synthesis catalyst products mixed alcohols from methanol to pentanol^{+}.
  - Molecular sieve and distillation used for product purification
  - Iso-butanol meets ASTM standards.
  - NRTL-RK activity coefficient model for alcohol separation sections, RK-BM & ASME Steam Tables for the rest as appropriate (matches literature data)
  - Heat Exchanger Networks optimized with Aspen Energy Analyzer
  - Capital Costs from Aspen Capital Cost Estimator and US NREL correlations

Key Market Parameters

The prices differ depending on whether we are building this in the USA or Korea.

Considers replenishment of catalysts and waste treatment

Commodity prices in 2014 U.S. dollars	U.S.	South Korea
Seaweed cost ($/dry tonne)	71.42	67.9
Olivine ($/tonne)	304.75	237.71
MgO ($/tonne)	604.33	471.38
Tar reformer catalyst ($/kg)	53.16	41.46
Alcohol synthesis catalyst ($/kg)	28.58	22.29
Solids disposal (Ash) ($/tonne)	81.28	63.40
Water makeup ($/tonne)	0.47	0.37
Boiler feed water chemicals ($/kg)	6.79	5.30
Cooling tower chemicals ($/kg)	4.08	3.18
LO-CAT chemicals ($/tonne sulphur produced)	555.5	433.29
Amine makeup ($/ million kg acid gas removed)	44.15	34.44
Waste water treatment ($/tonne)	1.12	0.87
Electricity (cents/kWh)	6.63	9.98
Gasoline ($/L)	0.91	1.53
NG ($/tonne)	397	1,221

Key Business Parameters

Uses US DOE/NREL recommended numbers for high risk liquid fuel plants

Different inflation rates by country.

Economic parameter	Basis
Cost year for analysis	2014
Plant financing by equity/debt	50%/50%
Internal rate of return (IRR)	10% after tax
Term for debt financing	10 years
Interest rate for debt financing	8%
Plant life/analysis period	30 years
Depreciation method	Straight Line depreciation 10 years for general plant and utilities
Income tax rate	35%
Plant construction cost schedule	3 years (20% Y1, 45% Y2, 35% Y3)
Plant decommissioning costs	$0
Plant salvage value	$0
Start-up period	3 months
Revenue and costs during start-up	Revenue = 50% of normal. Variable costs = 75% of normal. Fixed costs = 100% of normal
Inflation rate	1.75% U.S. , 1.10% South Korea
On-stream percentage	90% (7884 h/year)
Land	6.5% of Total Purchased Equipment Cost (TPEC)
Royalties	6.5% of TPEC
Working capital	5% of Fixed Capital Investment (excluding land)
Indirect costs	
Engineering and supervision	32% of TPEC
Construction expenses	34% of TPEC
Contractor's fee and legal expenses	23% of TPEC
Contingencies	20.4% of TPEC

MB & EB Results

Uses 100% of L. Japonica made in Korea today

Not burning seaweed for heat lets us make more.

But just 13-21% of the biomass ends up as product!

Not building a power plant greatly reduces capital cost.

Net HHV efficiency is 33-38% Not particularly wonderful.

	Case 1 - self-sufficient	Case 2 - NG import	Case 3 - NG & power import
Seaweed flow rate (kg/h)	45,631	45,631	45,631
NG requirement (kg/h)	–	5024	5024
Total product yields (kg/h)	5921	9730	9730
Butanol	2782	4572	4572
Mixed alcohols	3139	5158	5158
% products yield per feed (mass basis)	13.0	21.3	21.3
Net electric power exported (MW)	3.24	5.04	−20.4
Power generation	16.04	24.79	–
Power consumption	12.8	19.75	20.4
Biomass HHV (MW)	178.09	178.09	178.09
NG HHV (MW)	–	90.17	90.17
Butanol HHV (MW)	28.85	47.41	47.41
Mixed alcohols HHV (MW)	29.07	47.77	47.77
Total input HHV + electricity import	178.09	268.26	288.66
Total output HHV + electricity export	61.16	100.23	95.19
Plant energy efficiency (% HHV basis)	34.34	37.36	32.98

Key Economic Results

Plant design	U.S. Self-sufficient plant	U.S. NG import	U.S. NG & power import	South Korea Self-sufficient plant	South Korea NG import	South Korea NG & power import
Total capital investment ($'000)	243,852	291,511	193,951	190,205	227,379	151,282
Total operating costs *($'000/year)*	81,252	98,585	99,422	69,999	117,233	123,988
Total co-prod. revenue *($'000/year)*	21,149	34,612	31,980	35,392	57,947	53,986
MBSP ($/l)	3.33	2.25	2.07	2.15	1.97	2.01
Butanol revenue at MBSP ($'000/year)	89,816	99,618	91,657	57,835	87,326	89,199

It gets cheaper to make the more fossil fuels you use to power your plant (but it gets less green)

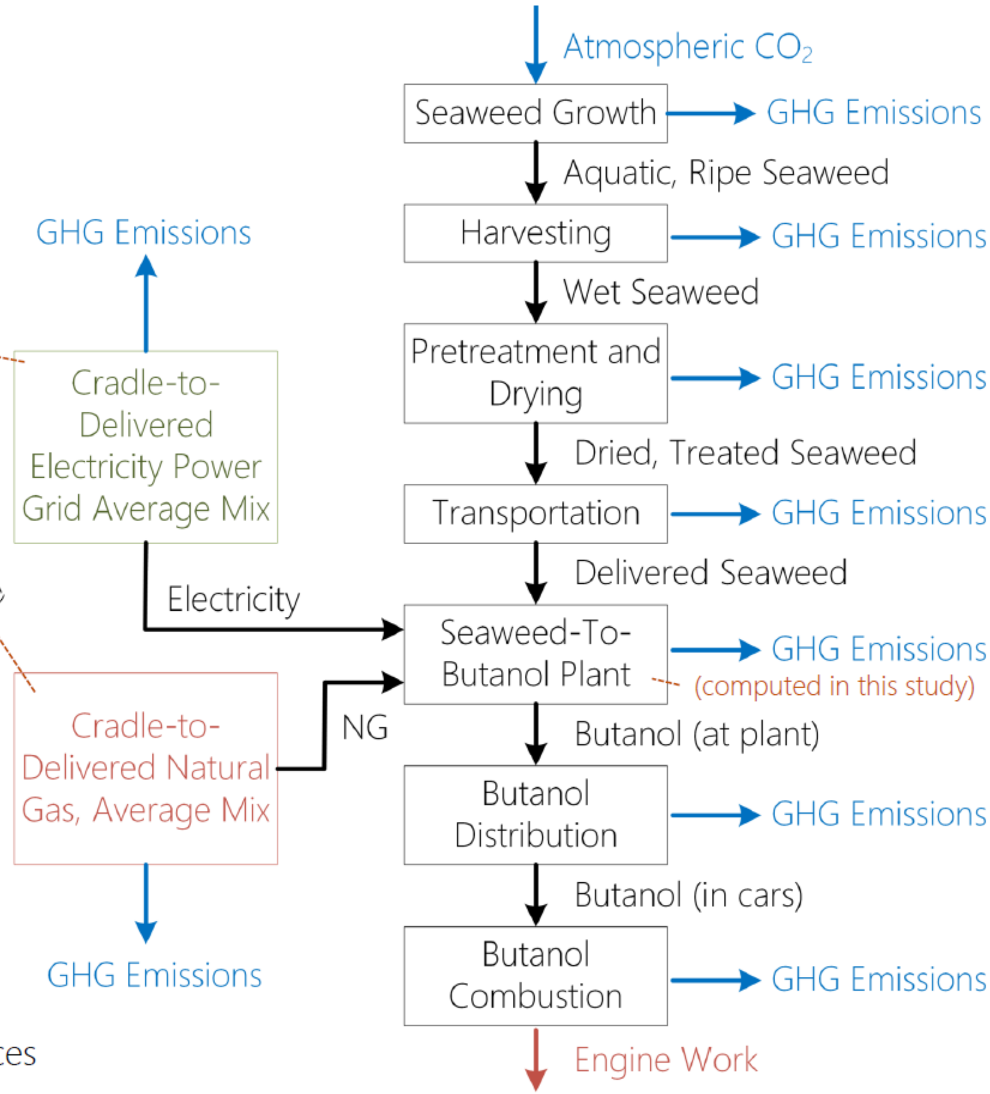
Lower seaweed, lower capital costs, and higher co-product revenues in Korea have major effect on final price.

Higher electricity costs in Korea means it is better to use seaweed-syngas to make electricity

Wells-to-Wheels CO2

Emissions (kgCO_2e/GJ)	U.S.	South Korea
Indirect electricity emissions	21.26	18.79
Indirect NG emissions	8.4	26.63
Indirect seaweed emissions (harvesting, pre-treatment and transportation)	12.53	12.53
Indirect gasoline emissions	17.36	17.36
Direct gasoline emissions	67.87	67.87

Much higher in Korea (LNG)



Only greenhouse gas emissions were tracked in this life cycle analysis.

Utility boxes include entire life cycle of the power grid and natural gas grid, including resource harvesting, transport, commissioning, etc.

Data: Variety of literature sources

LCA and Cost of CO2e Avoided (CCA)

Plant		U.S.			South Korea		
		Self-sufficient	NG import	NG + power import	Self-sufficient	NG import	NG + power import
Seaweed growth	($kgCO_2e/GJ$)	−1189	−1189	−1189	−1189	−1189	−1189
Seaweed supply chain	($kgCO_2e/GJ$)	176	176	176	176	176	176
Seaweed to butanol process	($kgCO_2e/GJ$)	880	981	981	880	981	981
Indirect emissions from natural gas	($kgCO_2e/GJ$)	–	61.47	61.47	–	194.88	194.88
Indirect emissions from electricity	($kgCO_2e/GJ$)	–	–	35.20	–	–	31.11
Direct emissions from butanol use	($kgCO_2e/GJ$)	63.32	63.32	63.32	63.32	63.32	63.32
Well to wheel emission for butanol	($kgCO_2e/GJ$)	36.36	66.85	71.61	36.36	83.25	88.34
CO_2e avoided	($kgCO_2e$ avoided/GJ)	48.87	18.38	13.62	48.87	1.98	−3.11
MBSP	($/L)	3.33	2.25	2.07	2.15	1.97	2.01
CO_2e avoided cost	($/t$CO_2e$ avoided)	1756	2724	3239	616	12,170	N/A

The best case in US
(is not worth doing)

The best case in Korea
(is competitive with other biofuels)

This is worse than gasoline.

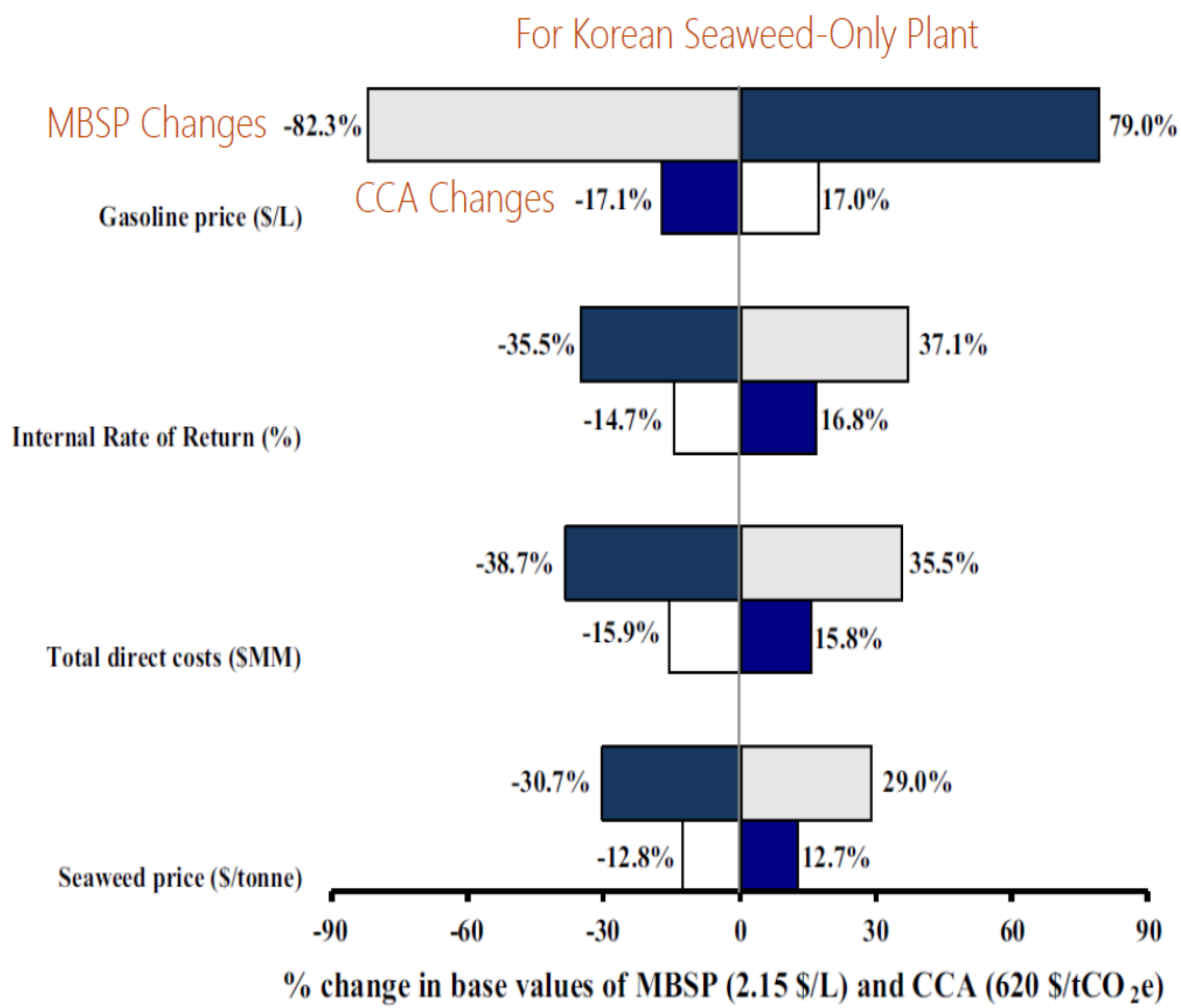
$$CO_2e\ avoidance\ cost = \frac{MBSP\left(\frac{\$}{MJ}\right) - wholesale\ gasoline\ price\ \left(\frac{\$}{MJ}\right)}{Carbon\ intensity\ of\ gasoline\ \left(\frac{kgCO_2e}{MJ}\right) - carbon\ intensity\ of\ biobutanol\ \left(\frac{kgCO_2e}{MJ}\right)}$$

Sensitivity Analysis (Brief)

+/30% Change in parameters

Changes in energy price have a huge impact on MBSP in Korea.

(Due to assumed impact on price of co-products)



Conclusions

			USA	USA	USA	Korea
			Thermochemical Wood	*Biological Switchgrass*	*Thermo. Seaweed*	*Thermo. Seaweed*
Best Minimum Butanol Selling Price	(MBSP):	\$/L	0.92	1.56	2.07	1.97
Best Cost of CO_2 Avoided	(CCA):	\$/tonne	132	472	1756	616

This is a very promising US option.
It is the best because gasification converts the lignin into syngas too, and has lower ash content.

The USA should not use this to avoid CO_2 emissions, the money is better spent elsewhere.

Too much ash.

This may make sense for price in Korea, but likely there are better options for investing money for GHG reduction purposes.

(Should probably just eat the seaweed)

Future Work:
Process improvements and optimization
Complete LCA on these studies (more than just GHGs)
Other biomass combinations