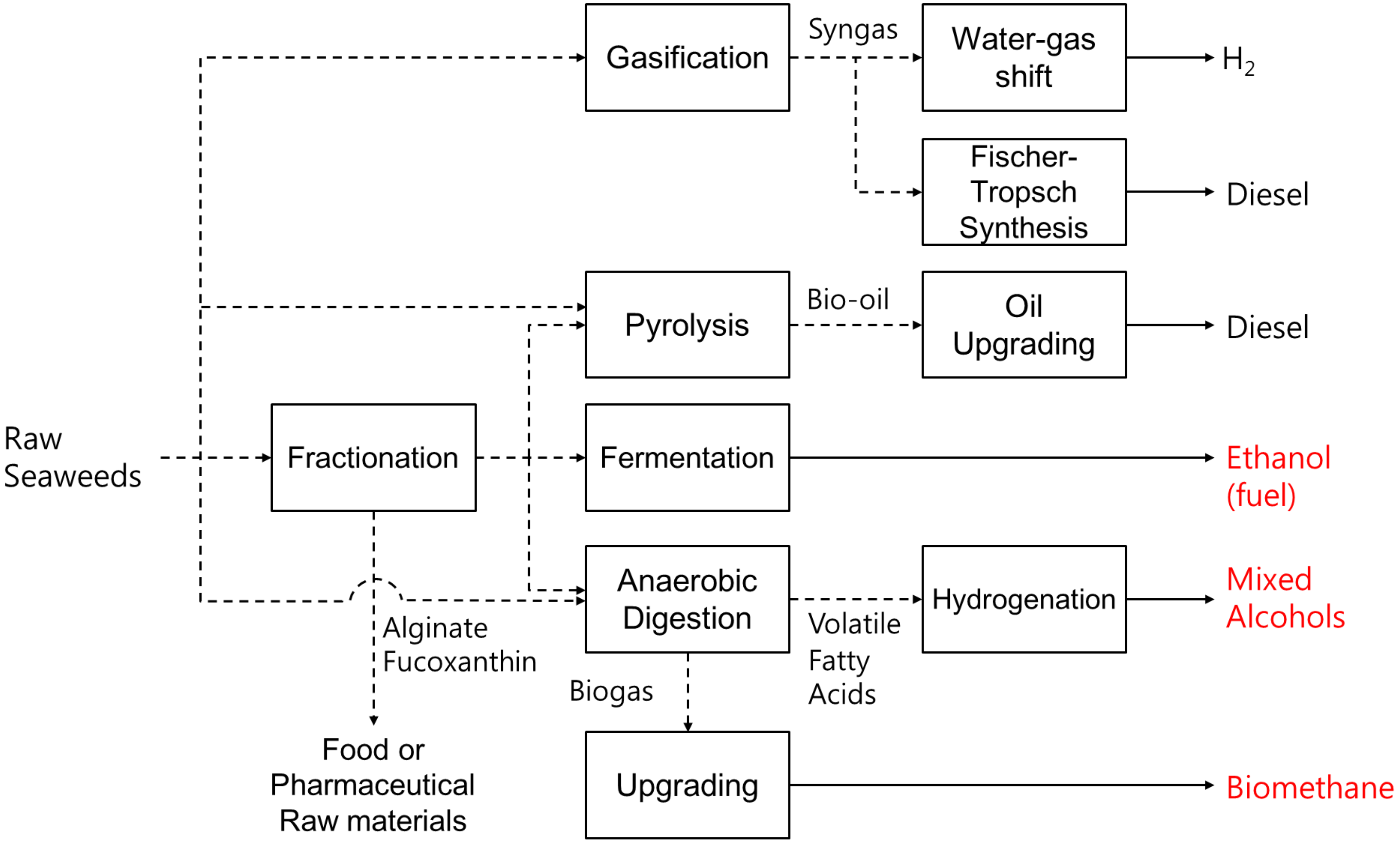
해조류 바이오연료 생산공정 설계 동향

- BIOCHEMICAL CONVESION 3 -

부경대학교 화학공학과 유준

(Possible) Biorefinery network for seaweed biomass



Raw Seaweeds

Fractionation

Gasification

Syngas

Water-gas shift

H_2

Fischer-Tropsch Synthesis

Diesel

Pyrolysis

Bio-oil

Oil Upgrading

Diesel

Fermentation

Ethanol (fuel)

Anaerobic Digestion

Volatile Fatty Acids

Hydrogenation

Mixed Alcohols

Biogas

Upgrading

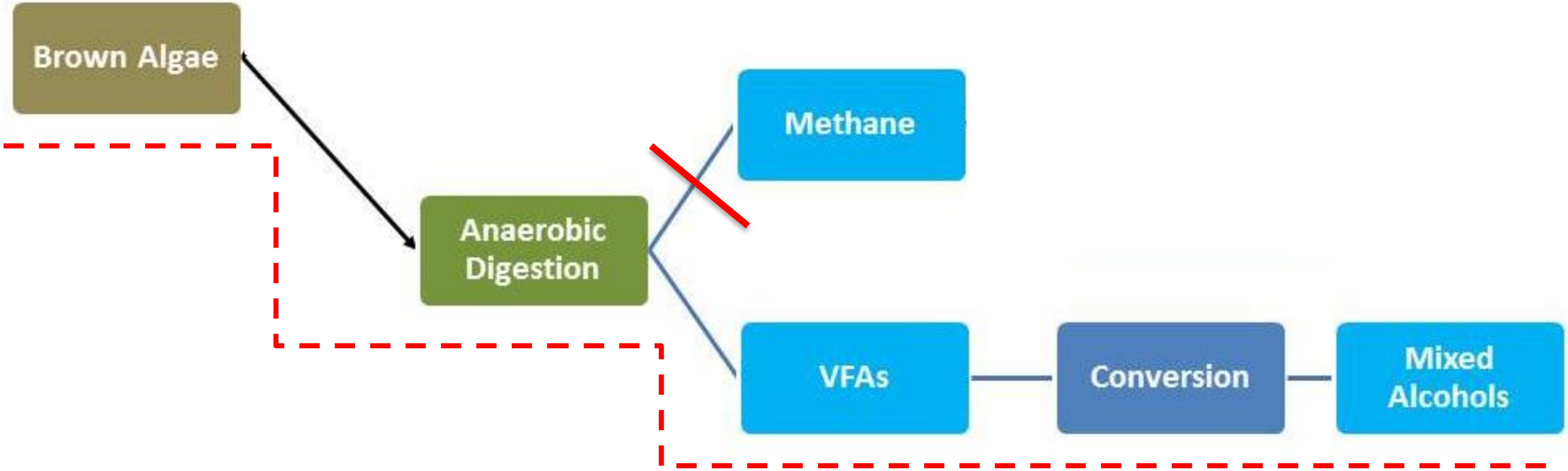
Biomethane

Alginate
Fucoxanthin

Food or Pharmaceutical Raw materials

Biochemical Conversion of Biomass

3. Volatile Fatty Acid (VFA) Platform

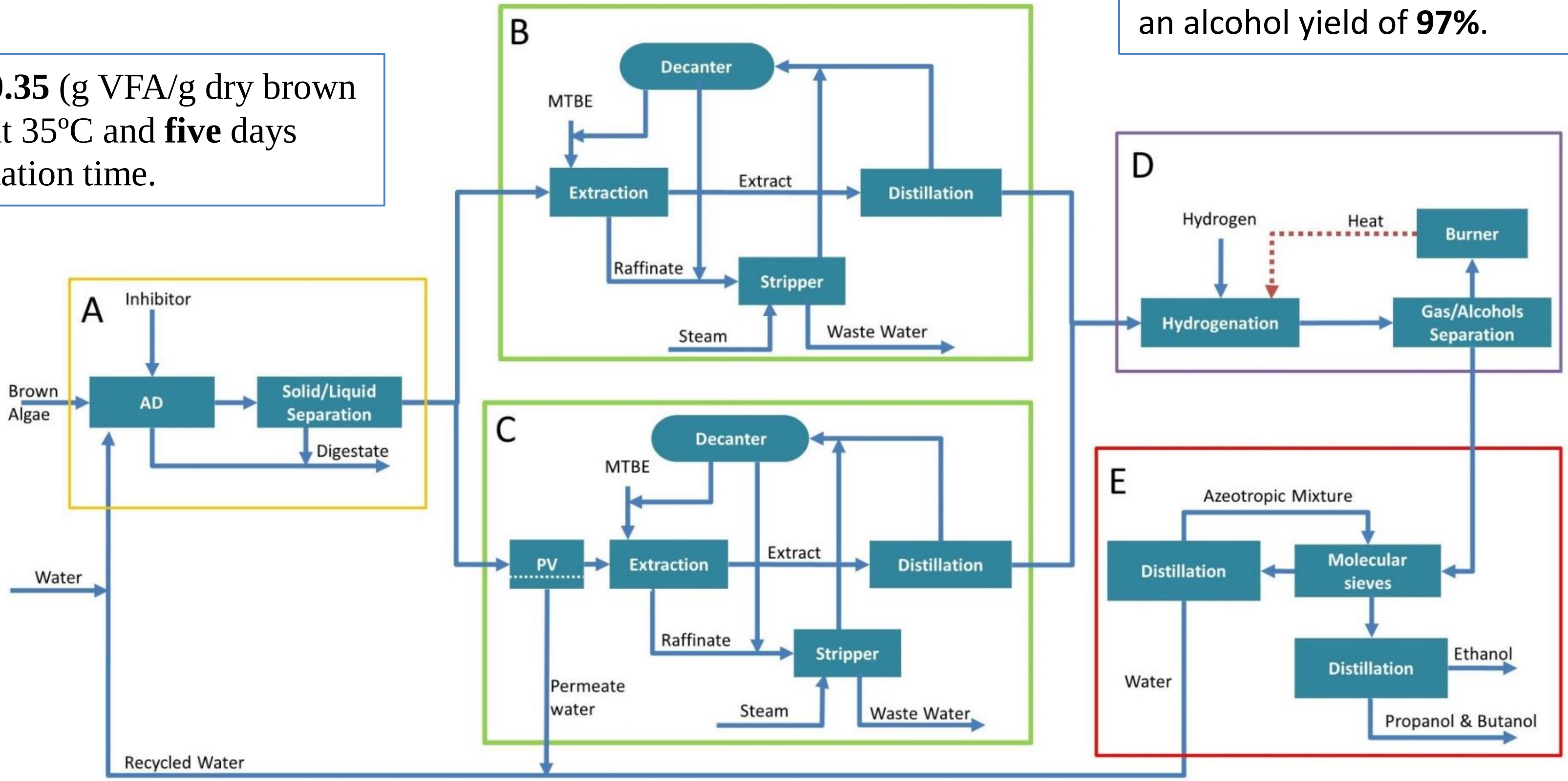


VFA platform (Impact of VFA recovery)

- Two alternative VFA recovery methods were compared, including:
  - B. classical extraction/distillation (**Case 1**)
  - C. hybrid PV and extraction/distillation (**Case 2**)

Gas-phase Hydrogenation with an alcohol yield of **97%**.

Yield: **0.35** (g VFA/g dry brown algae) at 35ºC and **five** days fermentation time.

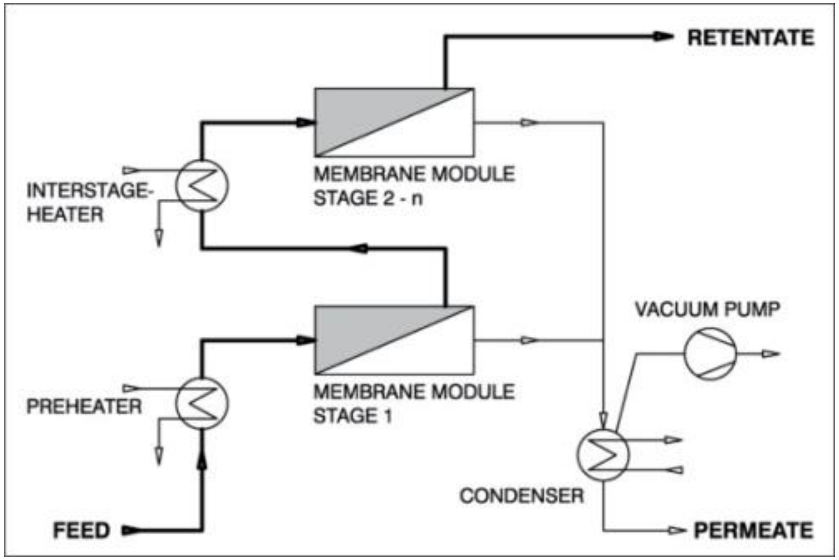


Process dsecription

Component	Reaction	Reference
Glucose	$5C_6H_{12}O_6 + 4H_2O \rightarrow 6C_2H_4O_2 + 2C_3H_6O_2 + C_4H_8O_2 + 8CO_2 + 12H_2$	Pham et al. 2012
Laminaran & cellulose	$5C_6H_{10}O_5 + 9H_2O \rightarrow 6C_2H_4O_2 + 2C_3H_6O_2 + C_4H_8O_2 + 8CO_2 + 12H_2$	
Mannitol	$5C_6H_{14}O_6 + 4H_2O \rightarrow 6C_2H_4O_2 + 2C_3H_6O_2 + C_4H_8O_2 + 8CO_2 + 17H_2$	
Alginate	$5C_6H_8O_6 + 12H_2O \rightarrow 6C_2H_4O_2 + 2C_3H_6O_2 + C_4H_8O_2 + 8CO_2 + 10H_2$	
Fucose	$5C_6H_{12}O_5 + 9H_2O \rightarrow 6C_2H_4O_2 + 2C_3H_6O_2 + C_4H_8O_2 + 8CO_2 + 17H_2$	
Protein	$C_{13}H_{25}O_7N_3S + 6H_2O \rightarrow 6.5CH_4 + 6.5CO_2 + 3NH_3 + H_2S$	Rajendran et al. 2014
Lipid	$C_{18}H_{34}O_2 + H_2O \rightarrow 12.75CH_4 + 5.25CO_2$	Humbird et al. 2011
Acetic acid	$CH_3COOH \rightarrow CH_4 + CO_2$	Wang et al. 1999
Propionic acid	$4CH_3CH_2COOH + 2H_2O \rightarrow 7CH_4 + 5CO_2$	Wang et al. 1999
Butyric acid	$CH_3CH_2CH_2COOH + 2H_2O \rightarrow 2CH_4 + 2CO_2 + 2H_2$	Wang et al. 1999
Protein	$23C_{13}H_{25}O_7N_3S + 99H_2O + 26H_2$ $\rightarrow 78C_2H_4O_2 + 26C_3H_6O_2 + 13C_4H_8O_2 + 13CO_2 + 69NH_3 + 23H_2S$	Wang et al. 1999
Lipid	$46C_{18}H_{34}O_2 + 294CO_2 + 238H_2O + 102H_2$ $\rightarrow 306C_2H_4O_2 + 102C_3H_6O_2 + 51C_4H_8O_2$	

Water-HAC pervaporation membranes

- Many experimental studies have been done so far on membrane development for water-HAC separation.
- In water-HAC pervaporation membranes **water** molecules (**kinetic diameter 2.96Å**) are separated from larger **acetic acid** (**4.36 Å**) and propionic acid molecules (5.5 Å).



Water-HAC pervaporation membranes

❖ These membranes include :

1. **Organic membranes**
2. **Modified PVA membrane**
3. **Charged membranes**
4. **PVC membrane**
5. Composite membrane
6. Inorganic membrane
7. …

Organic membrane	Flux kg/m2h	Sep. fac. (α)	Temp ˚C	%water/%HAC
25 wt.%PPSU	~0.24-1.48	2.5-6.1	30-80	20/80-10/90
27.5 wt.%PPSU	~0.12–0.83	5.0-11.4	30-80	20/80-10/90
30 wt.%PPSU	~0.09–0.48	2.8-12.0	30-80	20/80-10/90
Carbon	0.12	70	30	10/90

Charge membrane	Flux kg/m2h	Sep. fac. (α)	Temp ˚C	%water/%HAC
Nafion(C8H17)4N^{+}	0.18	243	25	10/90
PSF(SO3^{-})–H^{+}	0.02	9.4	-	10/90
AMV-CH3COO–	0.83	4.3	80	20/80
CMV-H+	0.33	4	80	20/80

Modified PVA membrane	Flux kg/m2h	Sep. fac. (α)	Temp ˚C	%water/%HAC
Modified PVA membrane with poly(acrylic acid)	0.03–0.6	34-3548	30-55	90-10
Modified PVA membrane with malic acid	0.05–0.29	121-670	40	90-20
Modified PVA membrane with amic acid	0.08–2.28	13-42	30-75	90-10
Modified PVA with glutaraldehyde	~0.0001–0.0003	4.0-9.0	30-60	90-10
Modified PVA with formaldehyde	~0.0001–0.0004	1.0-5.5	30-60	90-10
PVA-g-AN	0.18~1.17	2.3-14	25-50	90-10

PVC membrane	Flux kg/m2h	Sep. fac. (α)	Temp ˚C	%water/%HAC
Poly(vinyl chloride) Polyacrylonitrile	0.56–0.74	182-274	80	20/80
Poly(vinyl chloride)	6	45	40	50/50

Water-HAC pervaporation membranes

- ❖ These membranes include :

1. Organic membranes
2. Modified PVA membrane
3. Charged membranes
4. PVC membrane
5. **Composite membrane**
6. Inorganic membrane
7. …

Composite membrane	Flux kg/m2h	Sep. fac. (α)	Temp ˚C	%water/%HAC	Ref
Poly(4-methyl-1pentane)/ethylene-vinyl acetate copolymer TPX/P4-VP	0.215	606	25	16/84	Lee and Lai, 1994
NaAlg and PAN crosslinked with PVA	0.262	162	70	15/85	Wang, 2000
NaAlg and PAN cross-linked with HDM (ion: Na+)	0.037	38	40	10/90	Wang, 2000
	0.054	60	50	10/90	Wang, 2000
	0.092	98	60	10/90	Wang, 2000
	0.138	134	70	10/90	Wang, 2000
PAA/TPX	0.960	∞	25	97/3	Wang et al., 2002
PEK-C	0.59	90	50	10/90	Chen et al., 2008
NaAlg + 5%PVA + 10%PEG	0.0239	40	30	10/90	Toti and Aminabhavi, 2004
Polyelectrolytes complex PEC/PW11	0.440	144	50	10/90	Chen et al., 2013
MPPM Na-Alg cross-linked with Ca2$^+$	0.653	631	50	20/80	Zhang et al., 2014
MPPM Na-Alg cross-linked with Ca2$^+$	0.127	2078	40	10/90	Zhang et al., 2014

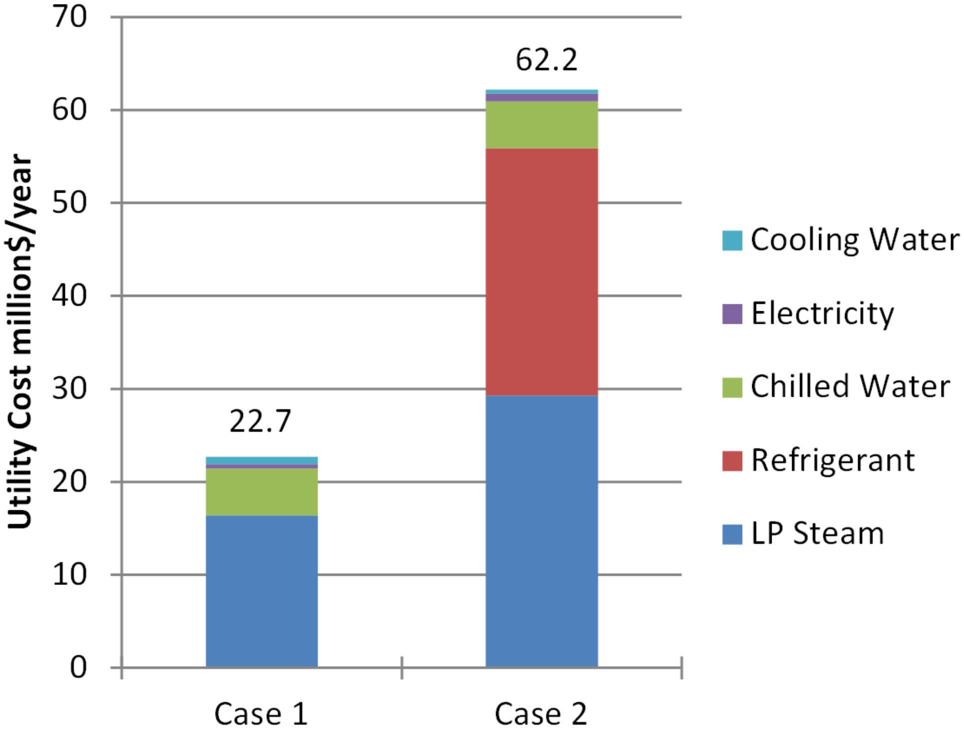
Water-HAC pervaporation membranes

- ❖ These membranes include :
  1. Organic membranes
  2. Modified PVA membrane
  3. Charged membranes
  4. PVC membrane
  5. Composite membrane
  6. **Inorganic membrane**
  7. …

Inorganic membrane	Flux kg/m2h	Sep. fac. (α)	Temp ˚C	%water/%HAC	Ref
Silicalite-1-zeolite	0.00045	∞	80	2/98	Masuda et al., 2003;
Zeolite T	0.95	780	75		Cui et al., 2004
NaAlg, 5wt%STA	0.66	120	70	10/90	Teli et al., 2007
NaAlg, 1wt%STA	0.35	820	70	10/90	Teli et al., 2007
Silica	5.9	530	100	10/90	Asaeda et al., 2005
Silica	3.1	800	100	10/90	Asaeda et al., 2005
Silica–titania	2.2	2100	100	10/90	Asaeda et al., 2005
Silica (ECN)	1.9	60	80	10/90	Sommer and Melin, 2005
Mordenite	10.9	500	130	50/50	Sato et al., 2011
	8.4	550	120	50/50	Sato et al., 2011
	6.4	-	110	50/50	Sato et al., 2011
	4.8	620	100	50/50	Sato et al., 2011
	2.25	630	80	50/50	Sato et al., 2011
	0.89	640	60	50/50	Sato et al., 2011
Zeolite MZM	0.33	>10,000	80	17/83	Chen et al., 2011
Zeolite MOR	1.2	840	90	50/50	Li et al., 2003
Zeolite MER	0.10	8000	40	10/90	Nagase et al., 2007
Poly(1-vinylimidazolo)/modernite	0.258	∞	80	17/83	Chen et al., 2009
Silica	5400	125	90	50/50	Kitao and Asaeda, 1990
Organosilica BTESE	2.0-4.0	200-500	75	10/90	Tsuru et al., 2012
NaAlg-4	0.15	2200	50	10/90	Kitson and Williams, 1991

Results: Energy costs

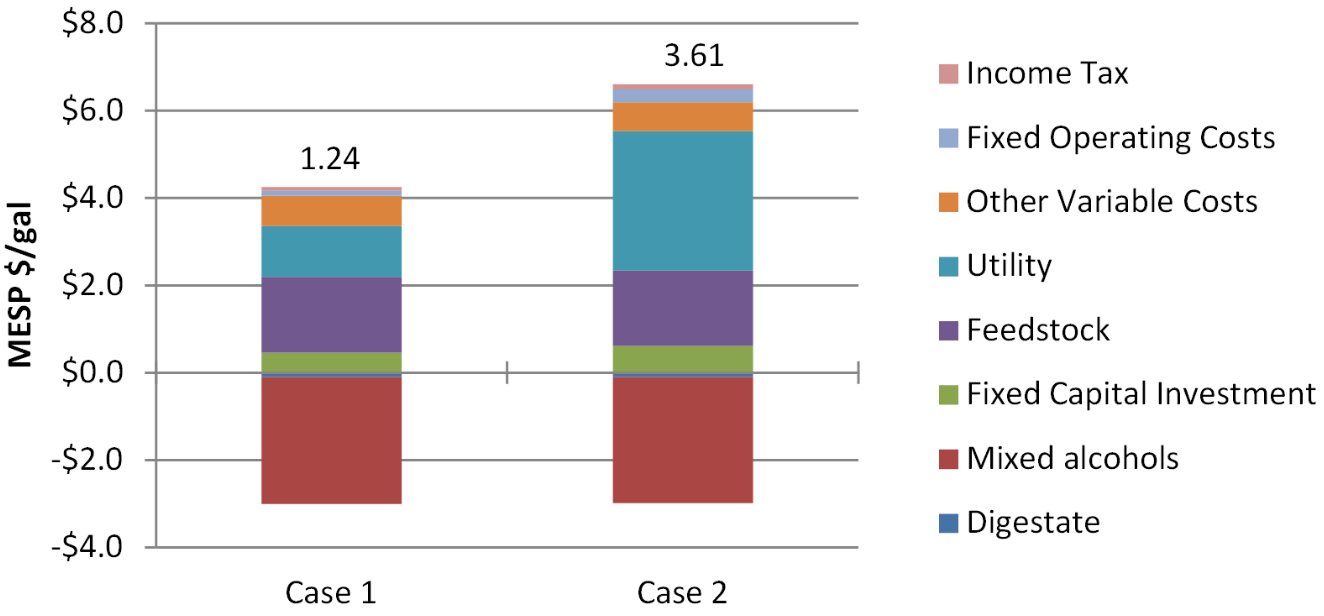
- ❖ Energy costs of each process were calculated and compared. Results showed that hybrid PV and extraction/distillation requires lots of energy in comparison to classical process.



Energy costs of Case1 (Ext/Dis) and Case 2 (PV and Ext/Dis)

Results: Minimum Ethanol Selling Price (MESP)

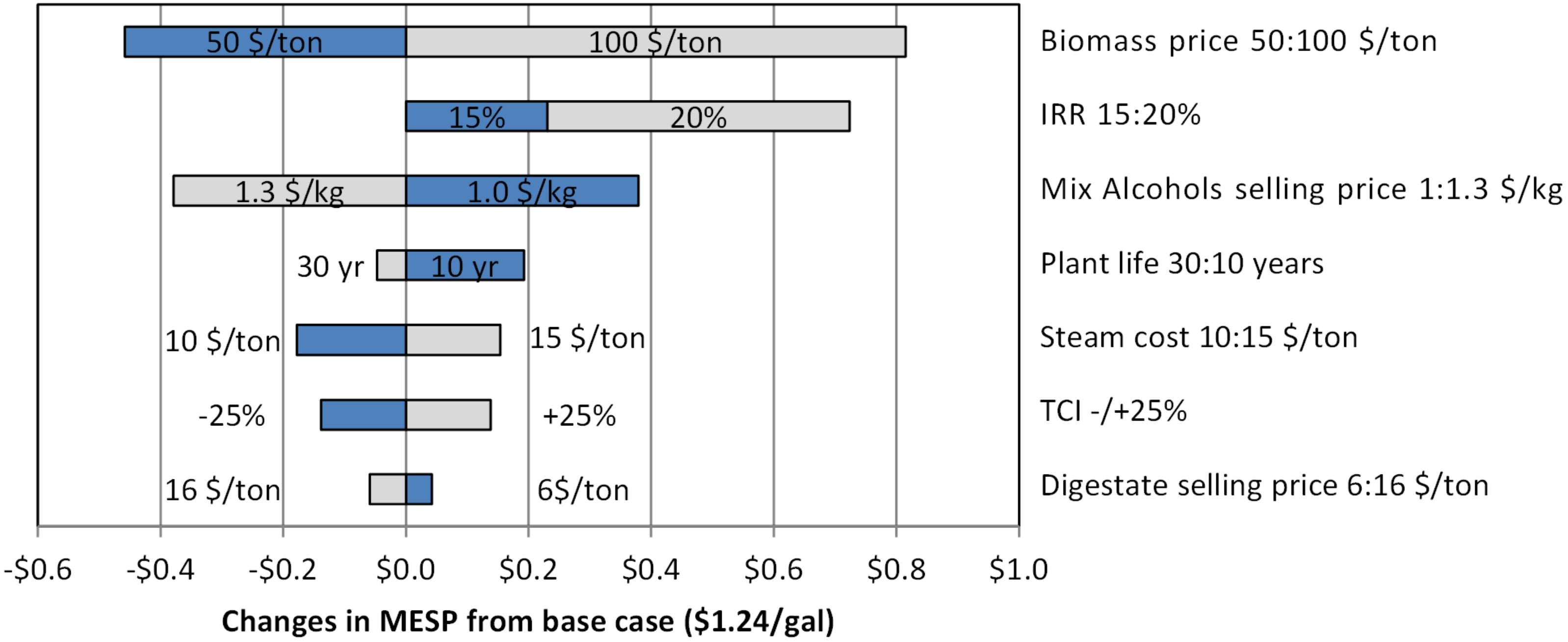
- The MESP is calculated to be 1.24 and 3.61 $/gal for case 1 and case 2, respectively, which is almost three times larger for case 2 in comparison to case 1.



Breakdown of minimum ethanol selling price ($/gal) for Case1 (Ext/Dis) and Case 2(PV and Ext/Dis)

Results: sensitivity analysis 1

- A sensitivity analysis were performed on economic and process parameters to find the bottle necks of the process.



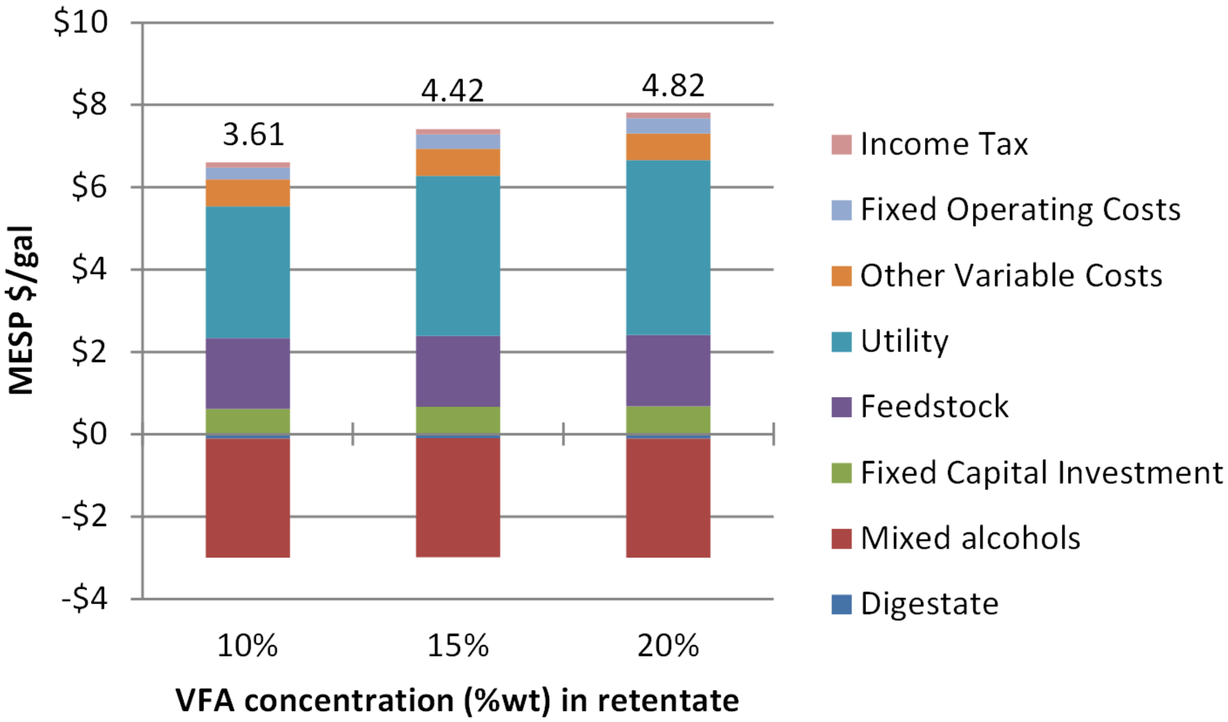
Results of sensitivity analysis on economic and process parameters for hybrid PV and Ext/Dis process.

Results: sensitivity analysis 2

- A sensitivity analysis were performed on economic and process parameters to find the bottle necks of the process.

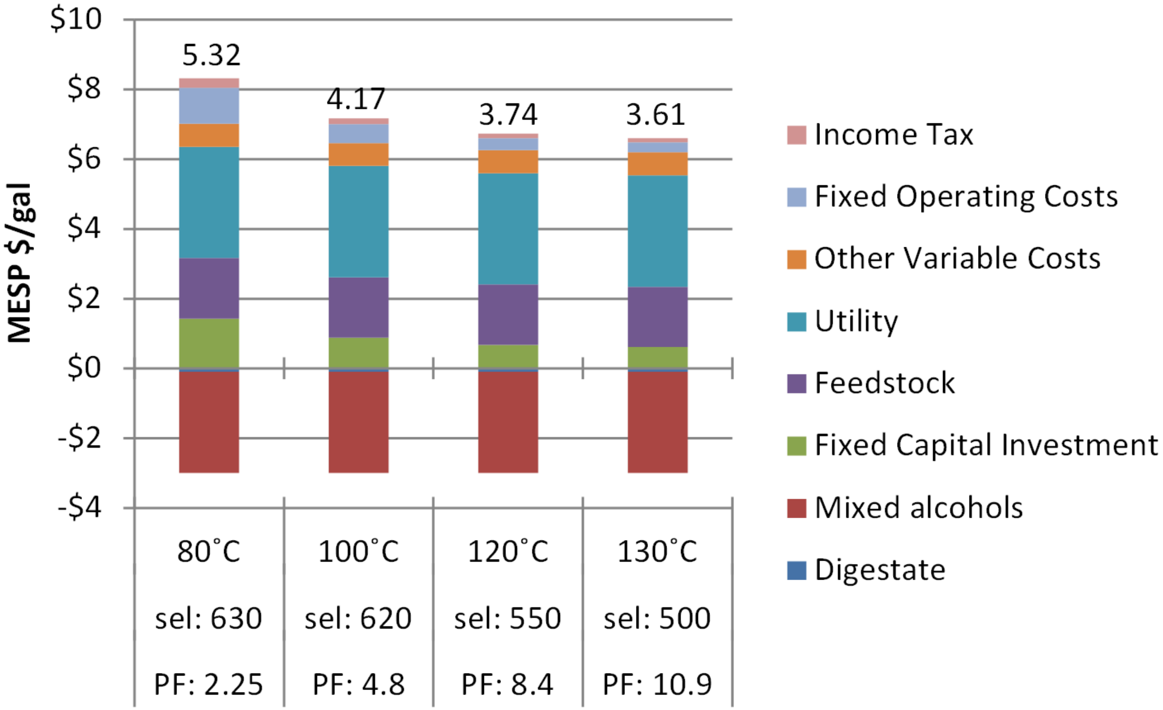
VFA concentration in retentate	10%	15%	20%
Membrane unit			
Capital costs (million$)	21.2	27.2	30.3
Steam (million$/year)	20.3	26.8	30.0
Refrigerant (million$/year)	26.6	35.7	40.2
Extraction and distillation unit			
Capital costs (million$)	7.4	5.8	3.9
Steam (million$/year)	5.2	3.4	2.5
Cooling water (million$/year)	0.198	0.097	0.052

Results: sensitivity analysis 3



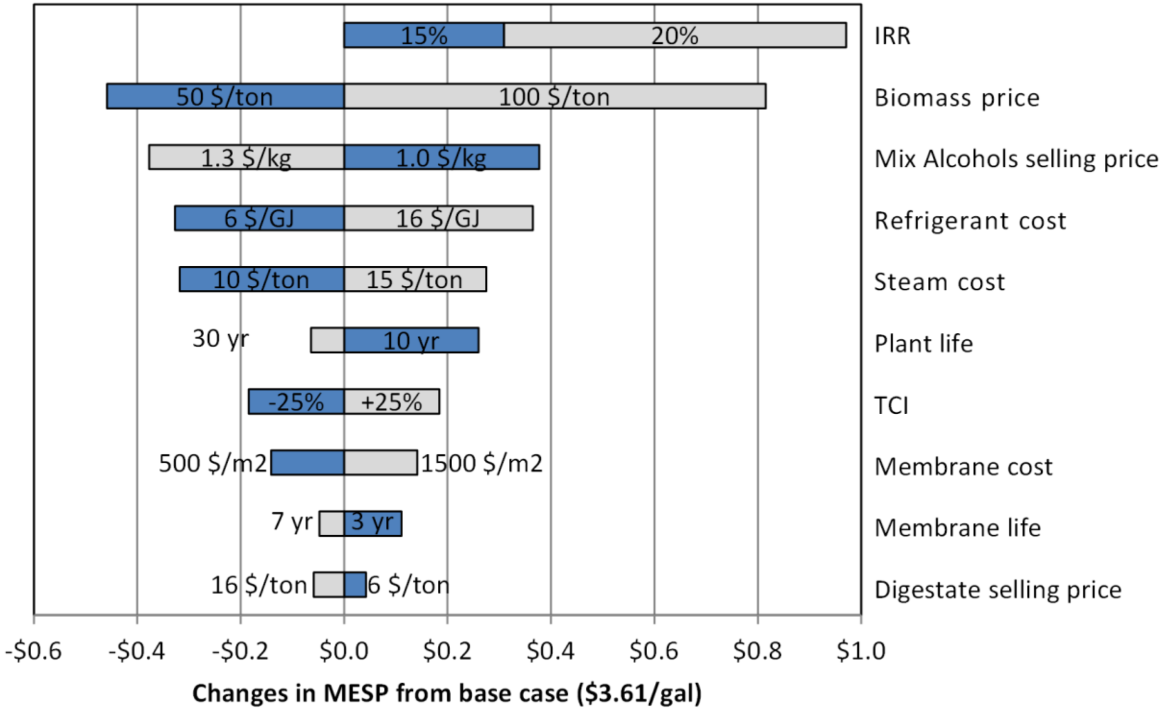
Impact of VFA concentration after PV unit on MESP

Results: sensitivity analysis 4



Impact of pervaporation temperature on MESP.

Results: sensitivity analysis 5



Results of sensitivity analysis on economic and process parameters for hybrid PV and Ext/Dis process.

Conclusions

- MESP values of 1.24 and 3.61 $/gal are calculated for two VFA recovery cases.
- VFA recovery from dilute fermentation products is the main bottleneck of the process.
- Pervaporation would be costly for recovery of dilute VFAs from fermentation broth.
- Higher solids loading can strongly reduce the VFA recovery costs.