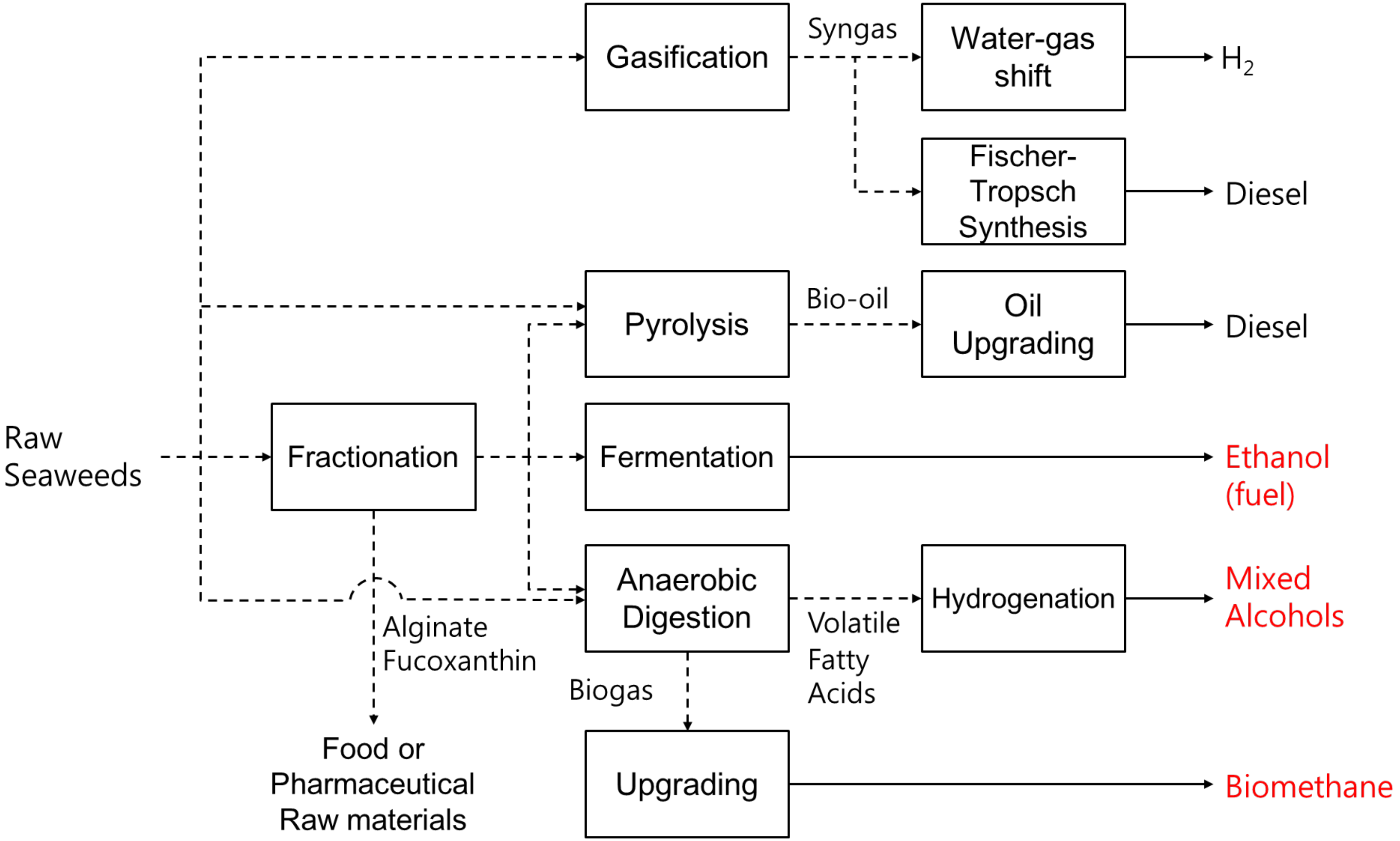
INTELLIGENT SYSTEMS LABORATORY

해조류 바이오연료 생산공정 설계 동향

- BIOCHEMICAL CONVESION 4 -

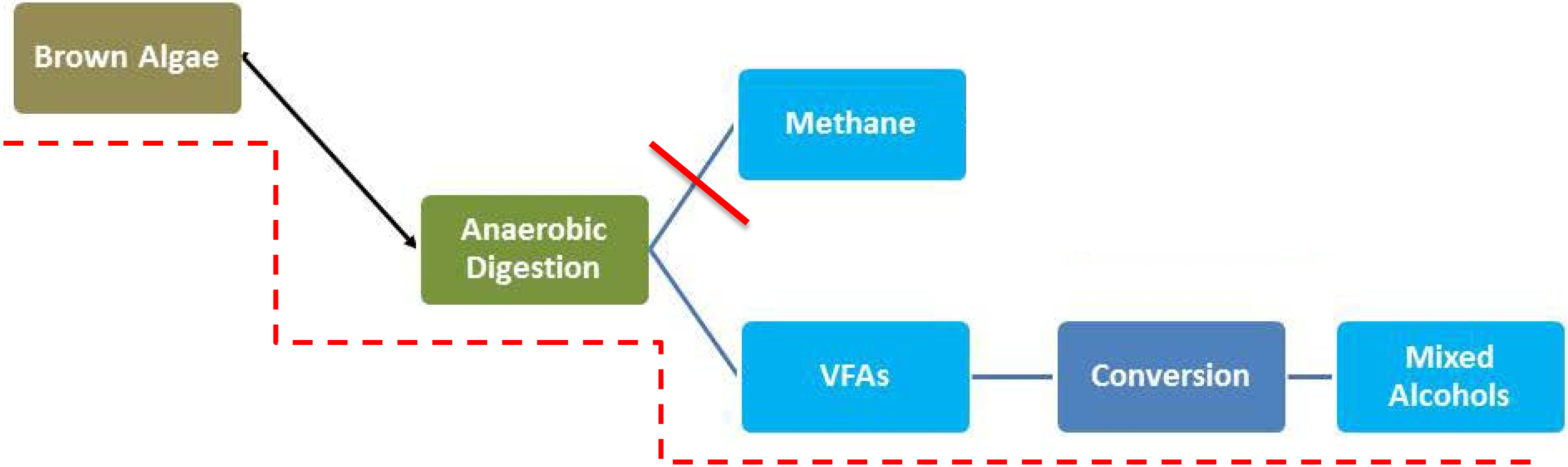
부경대학교 화학공학과 유준

(Possible) Biorefinery network for seaweed biomass



Biochemical Conversion of Biomass

3. *Volatile Fatty Acid (VFA) Platform*

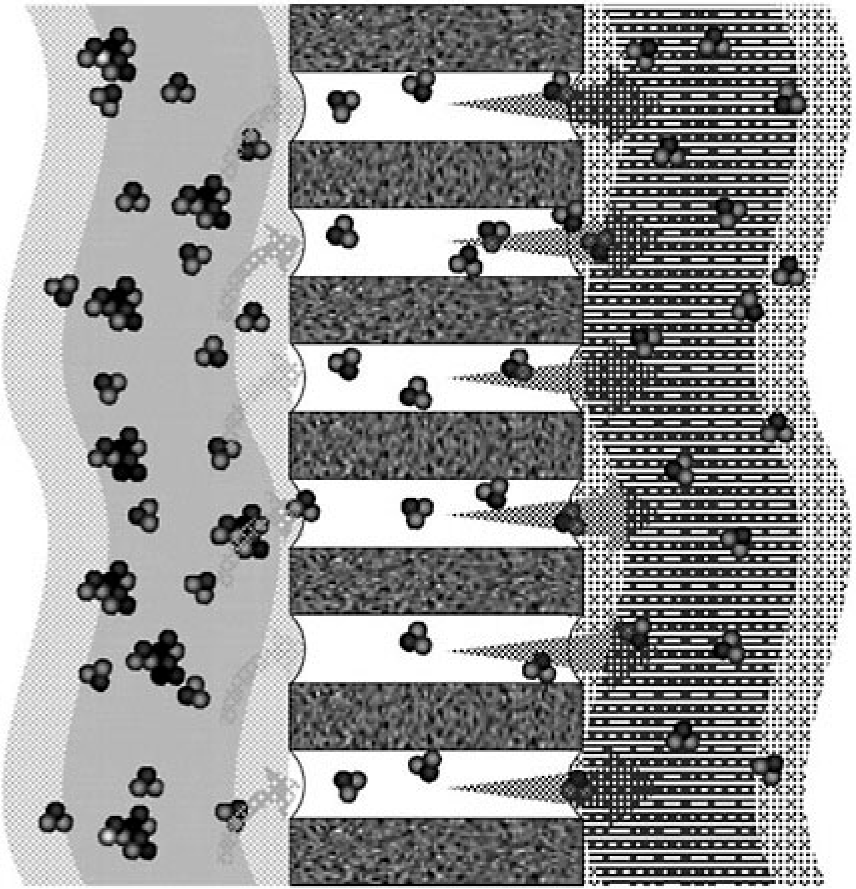


Energy Efficiency

- Molecular separation processes are responsible for an estimated 40% of the total energy consumption in the (petro)chemical industry worldwide.
- The main energy-consuming separation processes include dehydration of organic solvents, oxygen separation from air, olefin/paraffin separation, and hydrogen separation from several sources.
- These separations are currently performed using (cryogenic) distillation or adsorption-based techniques.
- The exergetic efficiency of these techniques is in general as low as 10% .
- Effective and energy-efficient separation technologies to dehydrate the wet fuels are a major hurdle to a large-scale application.
- Separation using membrane technology is widely accepted as an energy-efficient alternative.

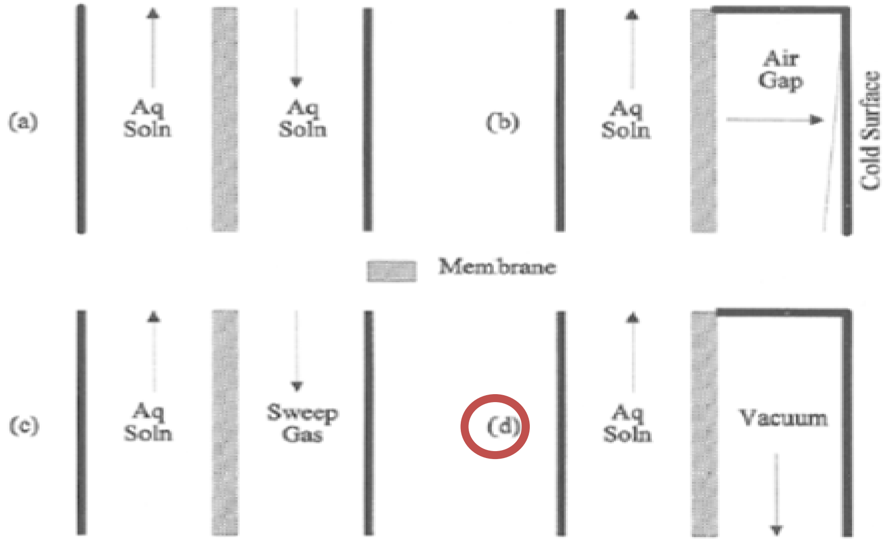
Membrane distillation

- Driving force in membrane distillation is a partial pressure gradient in the vapor phase.



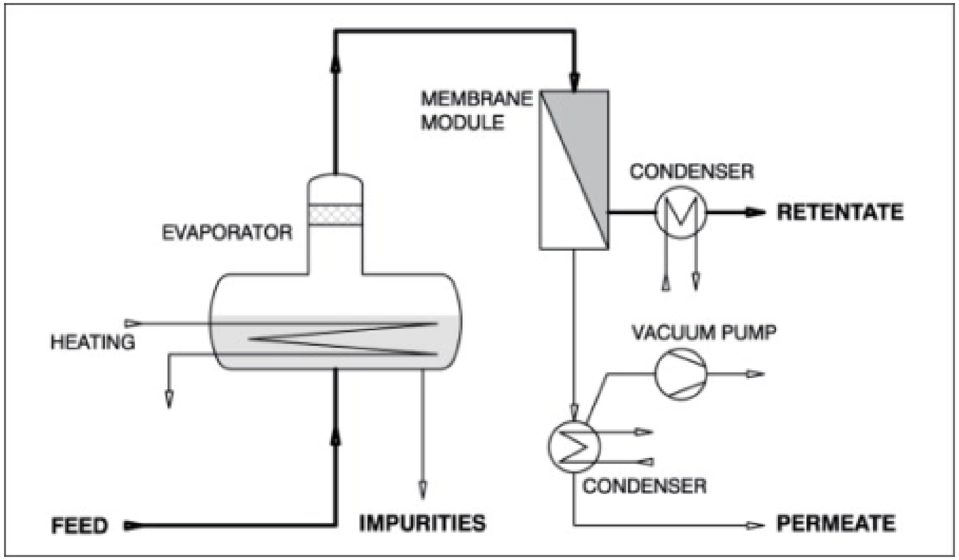
Membrane distillation

- A variety of methods may be employed to impose a vapor pressure difference across the membrane including:
  - a) Direct contact membrane distillation
  - b) Air gap membrane distillation
  - c) Sweep gas membrane distillation
  - d) Vacuum membrane distillation (VMD)

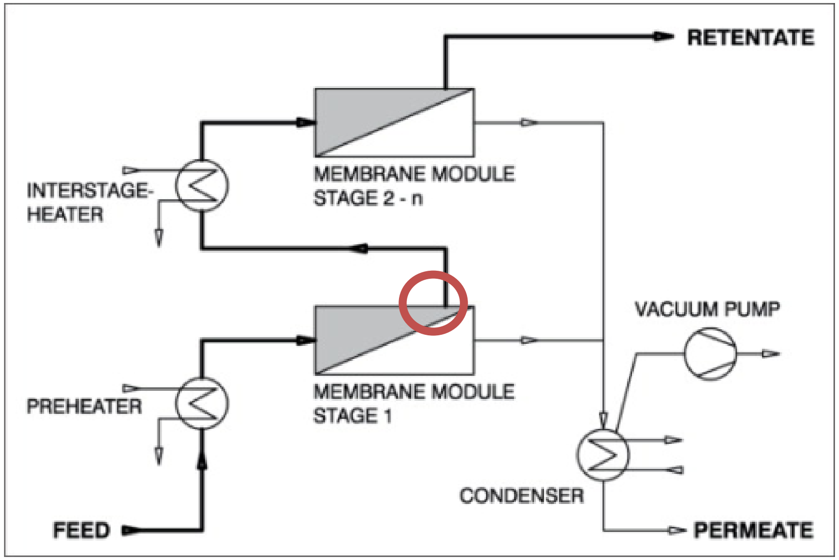


Membrane distillation

- A variety of methods may be employed to impose a vapor pressure difference across the membrane including:
  a) Direct contact membrane distillation
  b) Air gap membrane distillation
  c) Sweep gas membrane distillation
  d) Vacuum membrane distillation (VMD)



Vapor Permeation (VP)



Pervaporation (PV)

Membrane distillation

- Many experimental studies have been done so far on membrane development for vacuum membrane distillation.
- These membranes include:
  1. Inorganic membranes
  2. Mixed matrix membranes
  3. Polymeric membranes
  4. NaA zeolite membranes
  5. …
- In this study results of Sato et al. (2008) was considered for pervaporation and vapor permeation process:

Membrane distillation

- Many experimental studies have been done so far on membrane development for vacuum membrane distillation.
- These membranes include:
  1. **Inorganic membranes**
  2. **Mixed matrix membranes**

Type	Flux kg/m2h	Sep. fac. (α)	Temp ˚C	%water/%ethannol
Inorganic membranes				
ECN silica	2.33	60	70	10/90
Mitsui zeoliteA	1.12	18000	70	10/90
Zeolite X	0.89	360	75	10/90
CHA-type zeolite membrane increased stability	2.89	>100,000	40	28/72
CHA-type zeolite membrane	4.14	39500	75	10/90
Ceramic membrane	0.458	724	87	46/54
Ceramic membrane	0.1	1633	79	5/95
Mixed matrix membranes				
Hybsi®	1.70	139	70	5/95
PVA-KA zeolite mixed matrix	0.38	996	80	20/80
PVA-4A zeolite mixed matrix	1.50	530	80	20/80

Membrane distillation

3. Polymeric membranes

Polymeric membranes	Flux kg/m2h	Sep. fac. (α)	Temp ˚C	%water /%ethannol
Polyimide	1	900	60	5/95
P84 asymmetric membrane	0.40	1486	60	15/85
PAA/polyion complex	1.63	3500	60	5/95
PVA composite membrane	0.14	170	60	10/90
PERVAP®2201	0.1	100	60	10/90
PVAMMM membrane	0.5	1190	80	20/80
Sulfonated polysulfone membrane	0.87	500	35	10/90
Sodium alginate (Ca2+)-polymer	0.23	330	50	10/90
Matrimid® hollow fiber	0.16	130	45	15/85
Coated chitosan/cellulose acetate hollow fiber	0.23	23	25	10/90
Coated poly(vinyl alcohol)/poly sulfone hollow fiber	0.03	185	50	5/95
Grafted poly(acrylic acid)/polypropylene hollow fiber	0.20	11	24	30/70
Polyimide/Ultem® hollow fiber	0.49	124	60	15/85
Torlons – 4000T/Ultem® hollow fiber	0.66	50	60	15/85
Cellulose triacetate/Ultem® hollow fiber	1.28	466	50	15/85
PI/SPI/Ultem® (3 wt%SPI)	3.20	55	60	15/85
PI/SPI/Ultems (4.5 wt%SPI)	3.80	21	60	15/85
PI/SPI/Ultems (3 wt%SPI) – thermal treatment	2.60	130	60	15/85
PI/SPI/Ultems (3 wt%SPI) – PDMS coating	2.70	104	60	15/85
PI/SPI/Ultem® (3 wt%SPI) – POSS modification	2.00	237	60	15/85

Membrane distillation

4. NaA zeolite membranes

NaA zeolite membranes	Flux kg/m2h	Sep. fac. (α)	Temp ˚C	%water/%ethannol
α-Alumina (M-type)	2.2	10,000	75	10/90
Zeolite NaA	0.57	>10000	75	10/90
Mullite (M-type) (pervaporation)	2.1	42,000	75	10/90
Mullite (M-type) (Vapor permeation)	11		120	
TiO2/steel (AS-type)	0.86	54,000	45	5/95
α-Alumina (AS-type)	0.25	8,000	45	5/95
α-Alumina (M-type)	12.5	>5000	100	10/90
α-Alumina (M-type) (Vapor permeation)	10.5	>5000	125	10/90
α-Alumina (M-type) (Pervaporation)	5.6	10,000	75	10/90
α-Alumina (M-type) (Vapor permeation)	31	10,000	145	10/90
α-Alumina (AS-type) (Vapor permeation)	37	3900	145	10/90
α-Alumina (AS-type) (Vapor permeation)	20	4400	100	10/90
α-Alumina (AS-type) (Pervaporation)	8.5	10,000	75	10/90
NaA zeolite (Pervaporation)	5.9	9000	75	10/90
Zeolite NaA	2.1	2140	60	70/30
NaA	2.5	23000	75	10/90
NaA	3.80	3603	125	10/90

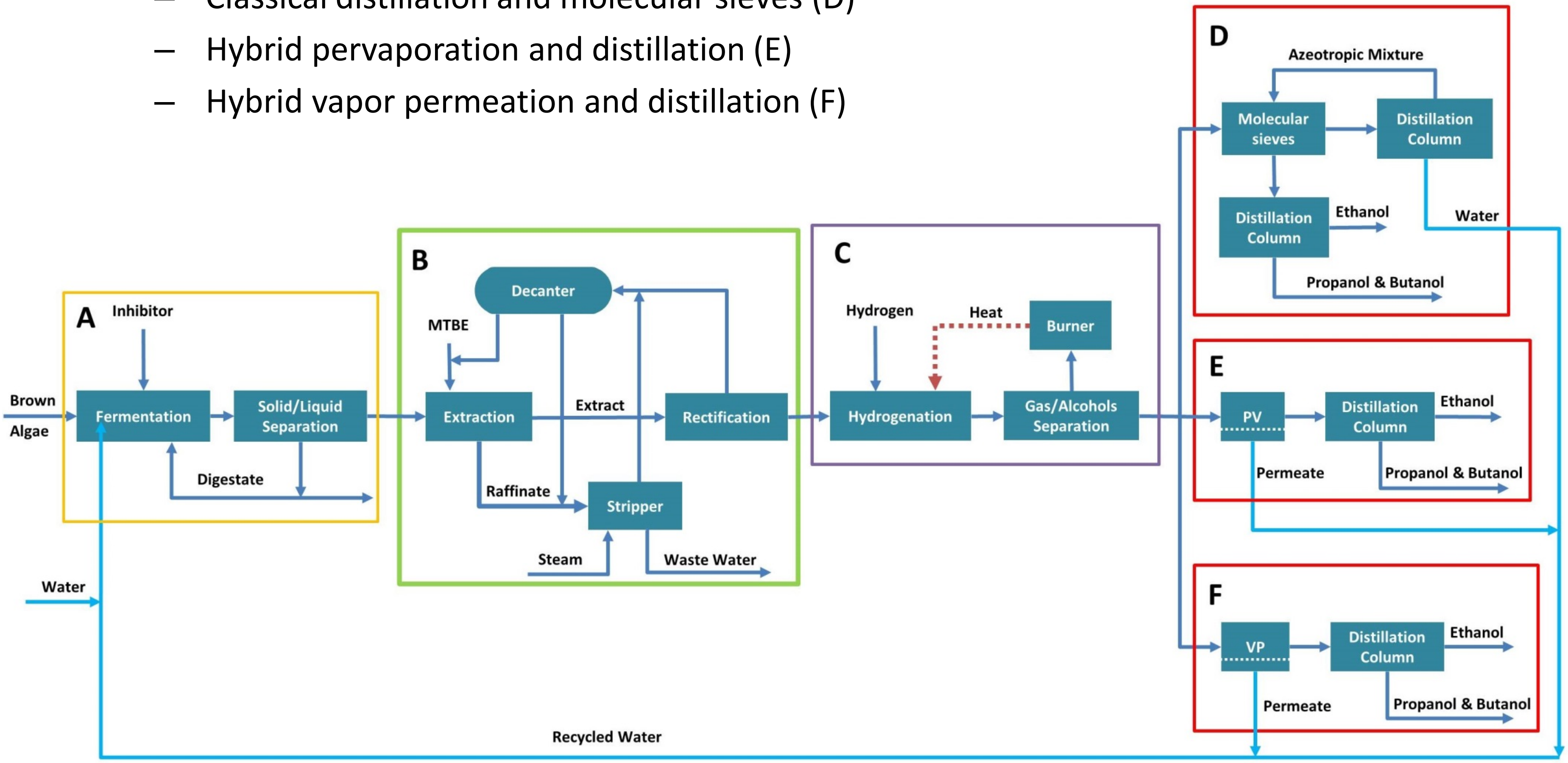
Membrane distillation

- In this study results of Sato et al. (2008) was considered for pervaporation and vapor permeation process:

NaA zeolite membranes	Flux kg/m2.h	Sep. fac. (α)	Temp ˚C	%water/%ethannol
α-Alumina (AS-type) (Vapor permeation)	37	3900	145	10/90
α-Alumina (AS-type) (Pervaporation)	8.5	10,000	75	10/90

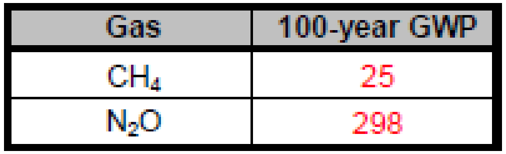
VFA platform (Impact of alcohols recovery)

- Two alternative VFA recovery methods were compared, including:
  - Classical distillation and molecular sieves (D)
  - Hybrid pervaporation and distillation (E)
  - Hybrid vapor permeation and distillation (F)



CO2 emissions

- CO2 emissions were calculated based on the methodology given by US Environmental Protection Agency (EPA). CO2 emissions were calculated only for alcohols recovery and dehydration unit.
- Natural gas was considered as fuel for provision of heat and steam.
- CO2 emissions due to electricity consumption were calculated based on US annual output emission rates for electricity production.
- 80% boiler efficiency were considered for steam production.
- Compression refrigeration with 38˚C condenser requires 1.31 kW/tonne at -18˚C.
- 0.254 KW energy is required for production of 1 m3/hr cooling water.
- Emission factors were converted to CO2 equivalent using 100 year global warming potential:



Gas	100-year GWP
CH_4	25
N_2O	298

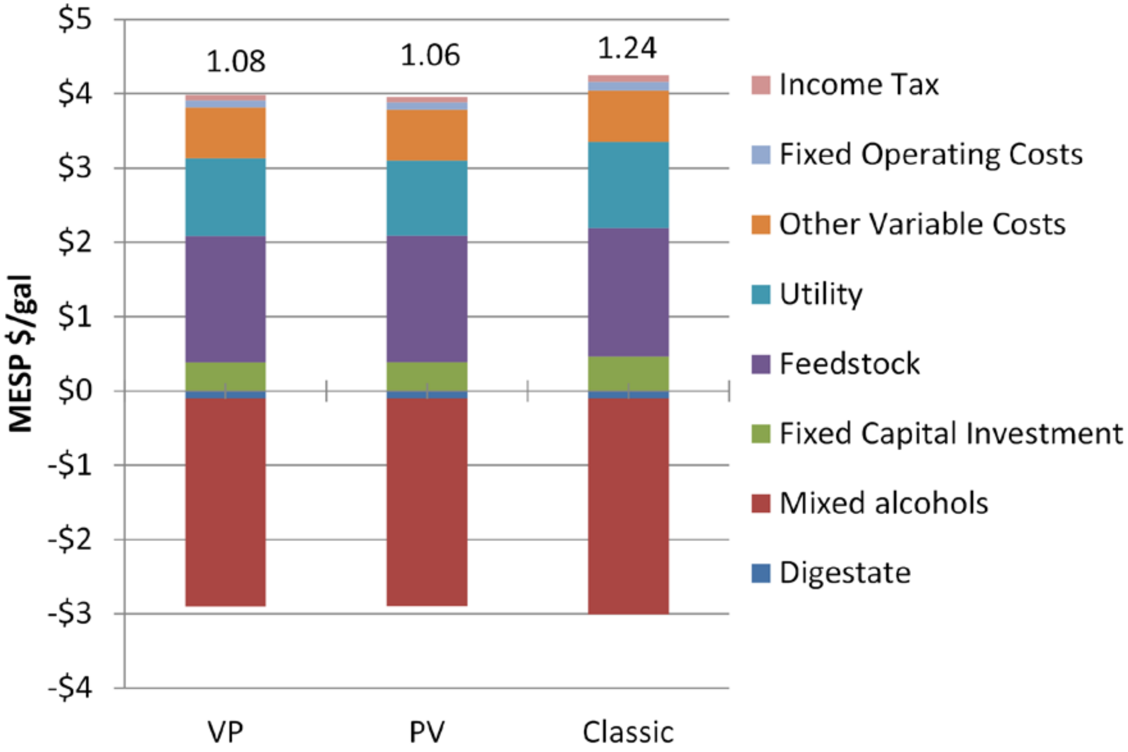
Results: Capital & Investments Costs

- Based on the techno-economic model presented before, the capital and investment costs of the process were calculated.
- PV and VP have similar capital costs.
- The capital costs of classic process is third times larger than PV and VP.
- This results in higher land, working capital and total capital investment for classical method.

	Classic (M$)	PV (M$)	VP (M$)
Fermentation	9.4	9.4	9.4
VFA recovery	16.2	16.2	16.2
Hydrogenation	4.1	4.1	4.1
Alcohols recovery	**8.0**	**2.7**	**2.4**
Total Installed Costs (TIC)	37.7	32.3	32
Total Direct Costs (TDC)	44.3	38.0	37.6
Total Indirect Costs	26.6	22.8	22.6
Fixed Capital Investment (FCI)	70.9	60.8	60.2
Land	2.3	1.9	1.9
Working Capital	3.5	3.0	3.0
Total Capital Investment (TCI)	**76.7**	**65.8**	**65.2**

Minimum Ethanol Selling Price: (MESP)

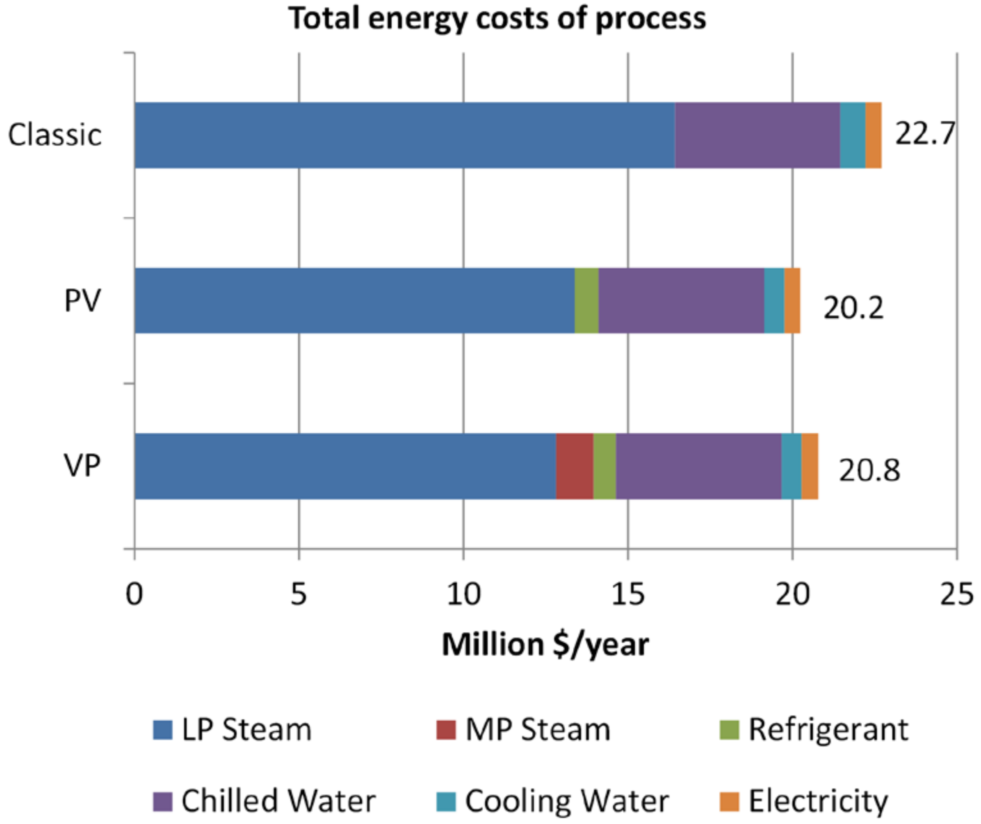
- The MESP for PV, VP, and classical cases were calculated to be 1.08, 1.06, and1.24 $/gal at scale of 400,000 ton/year, respectively.



Breakdown of minimum ethanol selling price ($/gal) for three process alternatives.

Results: Energy costs

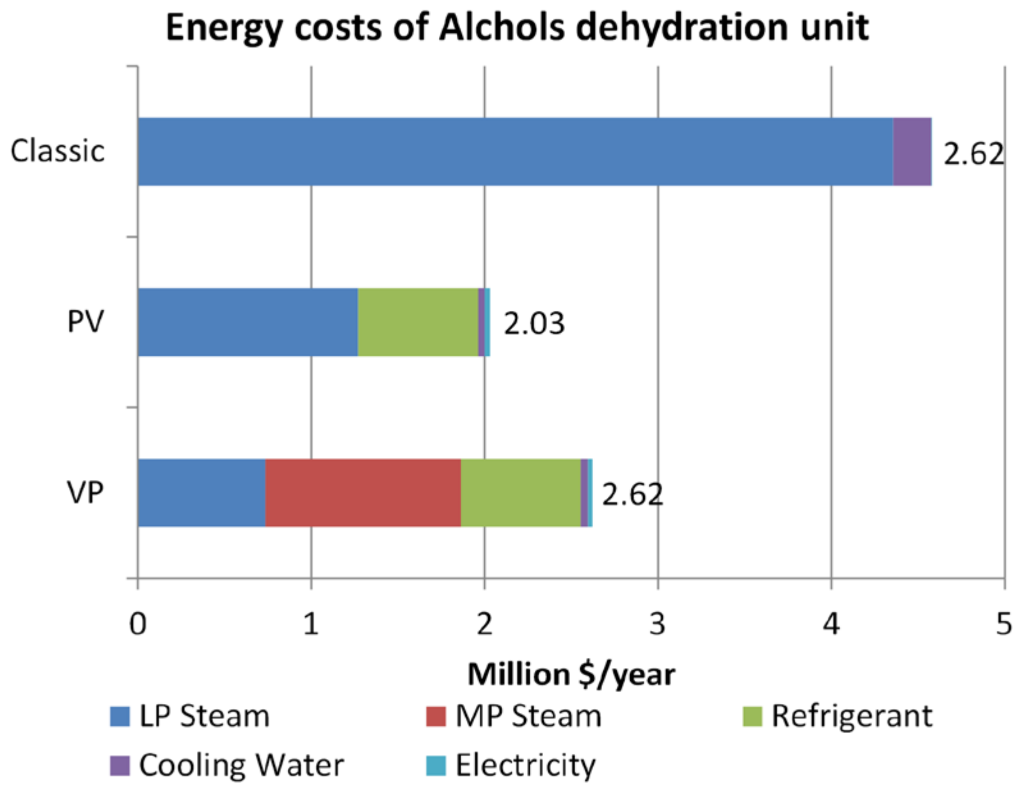
- Energy costs of each process were calculated and compared. Results showed that PV has the lowest energy requirement in comparison to other processes.



Total plant utility costs (Million$/year)

Results: Energy costs

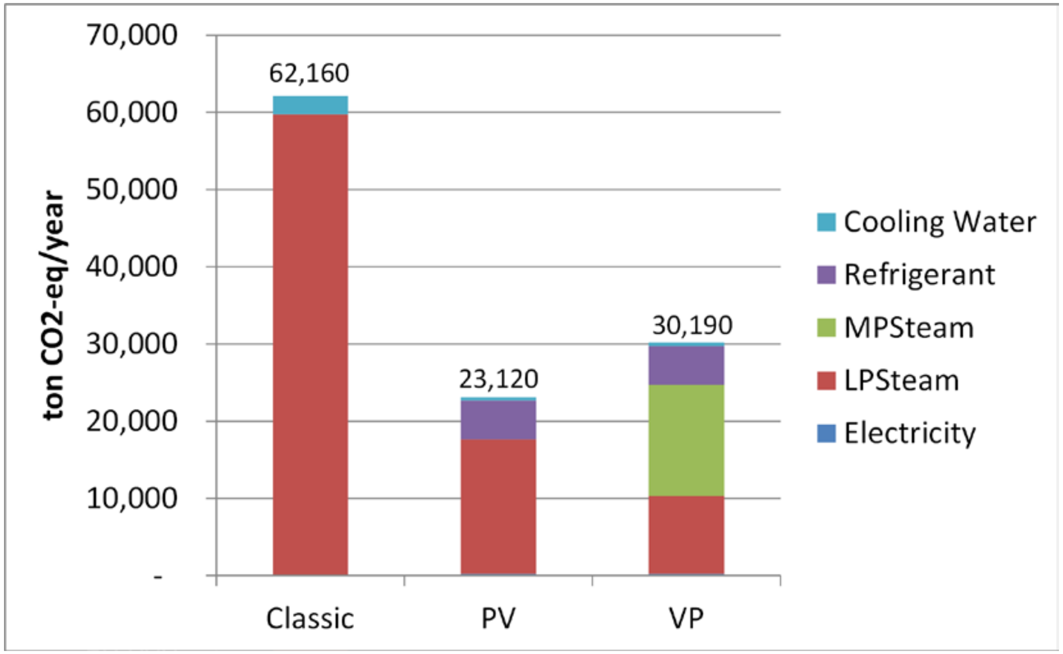
- Energy costs of each process were calculated and compared. Results showed that PV has the lowest energy requirement in comparison to other processes.



Energy costs of mixed alcohols recovery and ethanol dehydration unit

Results: CO2 emissions

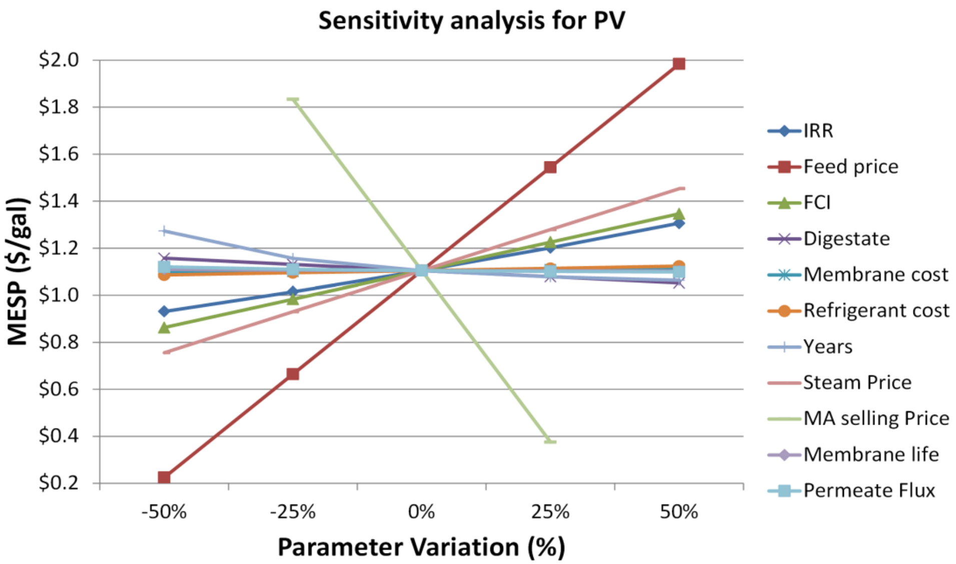
- The CO2 emissions of classic, PV, and VP processes were calculated to be 62, 23, and 30 kton CO2-eq/year.

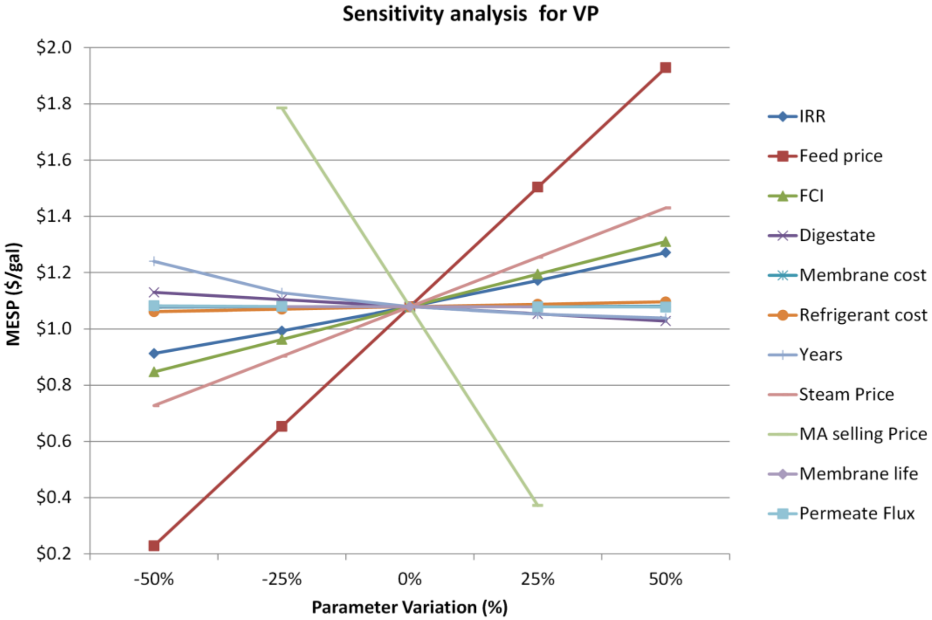


Annual CO2 equivalent emissions of alcohols dehydration and recovery unit

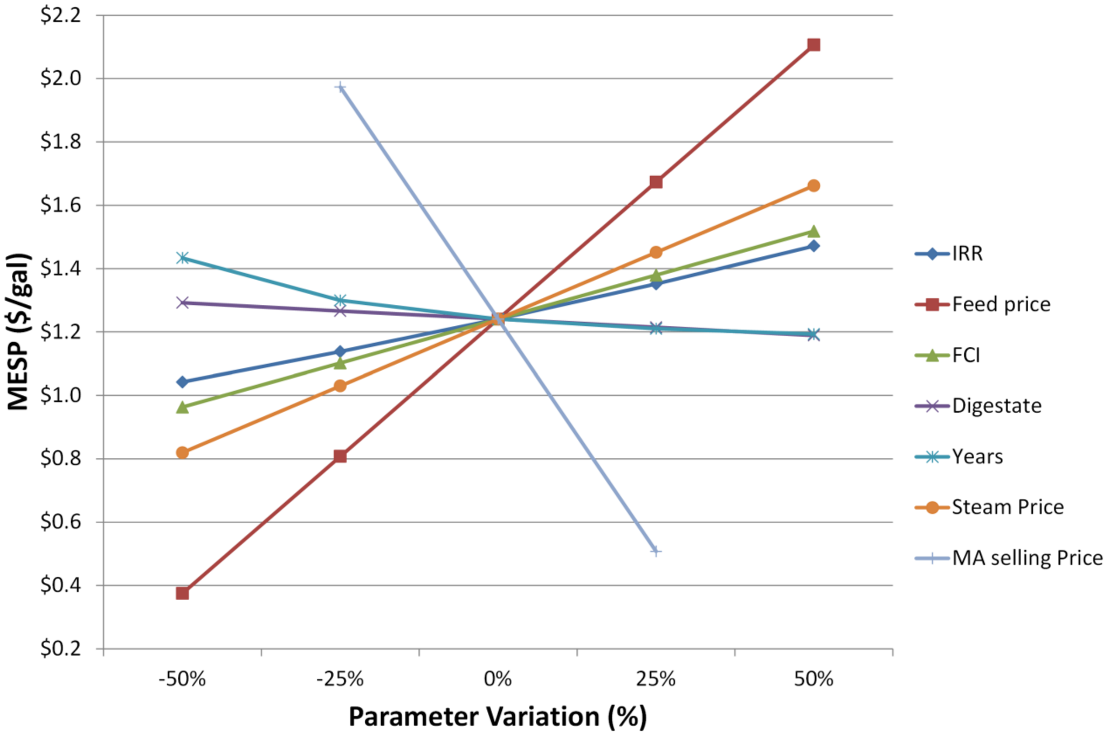
Sensitivity Analysis

- Single-point sensitivity results for PV.





Sensitivity Analysis



- ❖ Single-point sensitivity results for Classical case

- Results of the study showed that use of hybrid pervaporation/distillation and vapor permeation/distillation is superior over classical method for ethanol dehydration.
- Pervaporation has the lowest energy consumption and CO2 emissions compared to other processes.
- Higher permeate flux of VP process resulted in slightly lower capital costs compared to PV process. However, VP process requires more energy input compared to PV process.
- Sensitivity analysis showed that **coproduct selling price** and **seaweed price** has the highest impact on MESP. Therefore, A reduction in seaweed price can greatly contribute to plant economy, indicating the importance of developing high yield procedures for artificial seaweed cultivation.