Intelligent Systems Laboratory

# 해조류 바이오연료 생산공정 설계 동향

## - BIOCHEMICAL CONVERSION 5 -

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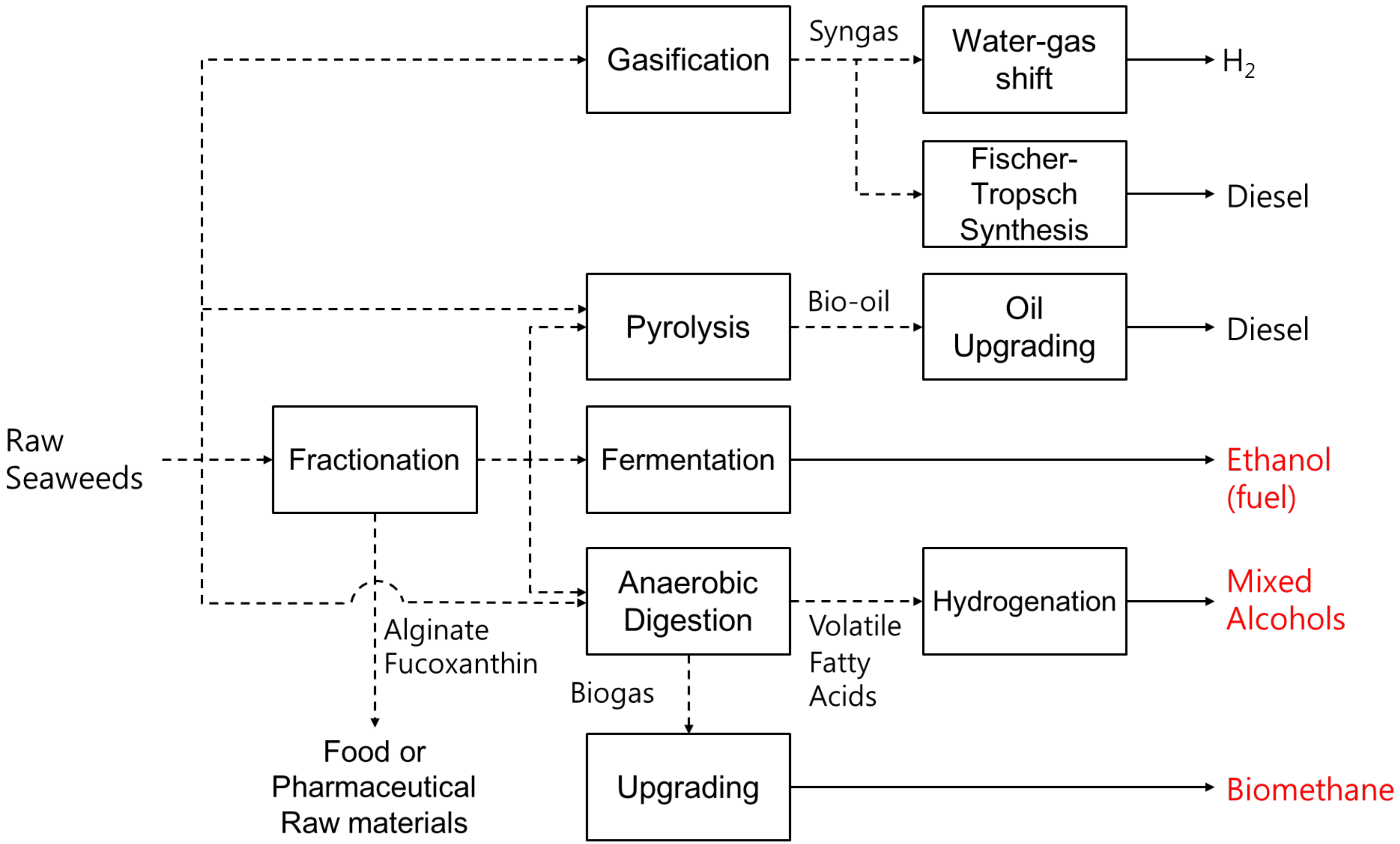
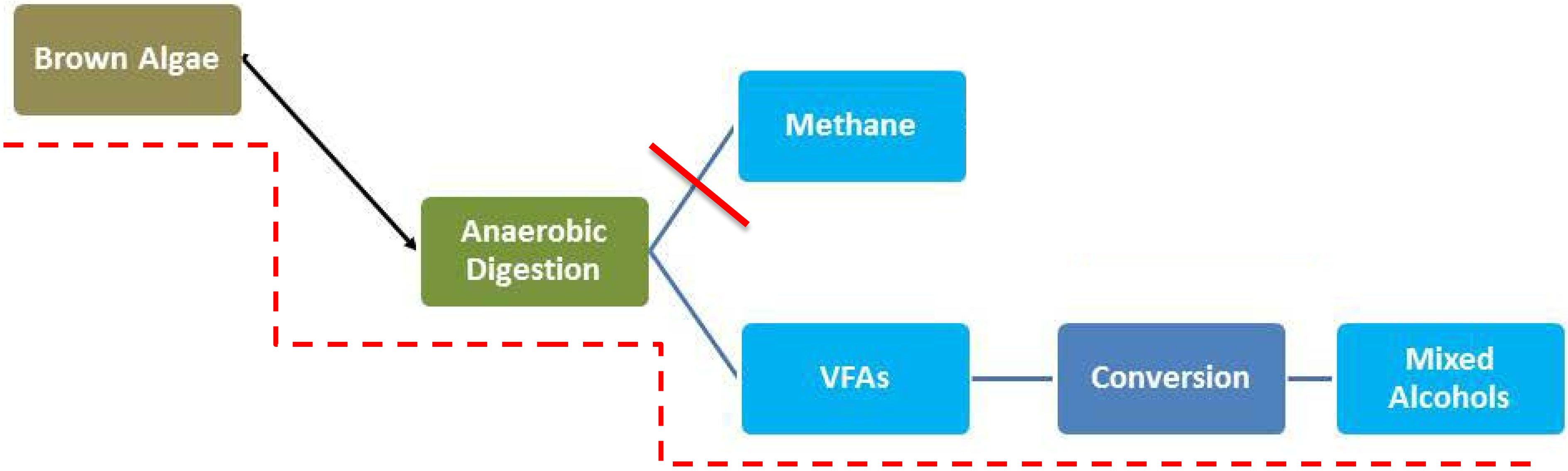
# (Possible) Biorefinery network for seaweed biomass



# Biochemical Conversion of Biomass

## *3. Volatile Fatty Acid (VFA) Platform*



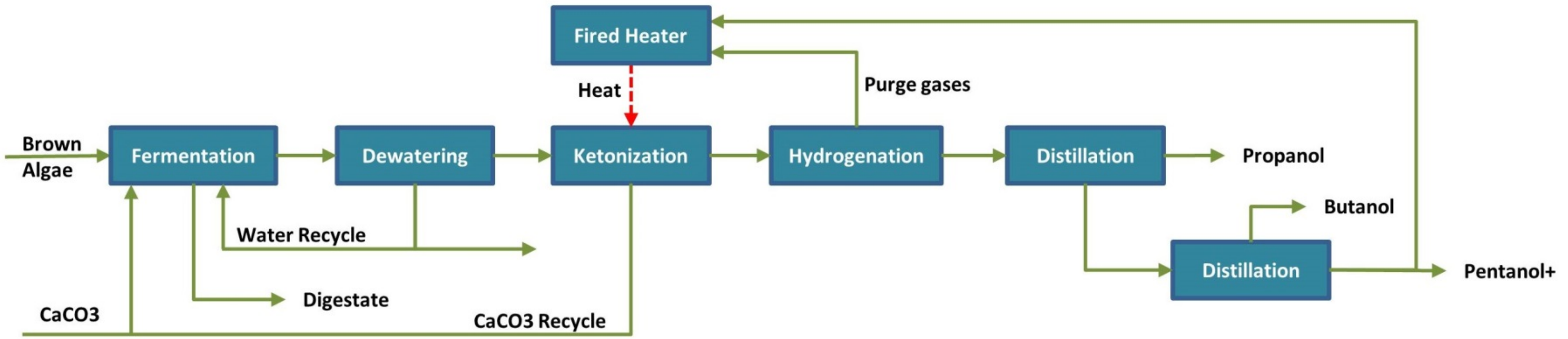
# MixAlco® Process

- The MixAlco process has been developed by **Dr. Holtzapple** and his team from the Department of Chemical Engineering at **Texas A&M University**.
- The process is a patented technology that converts any biodegradable material.
- **Terrabon Inc.** holds the licensing rights from Texas A&M for MixAlco process.
- In July 2010 Terrabon completed the construction and installation of a **50,000 gallon per year** downstream demonstration processing plant.

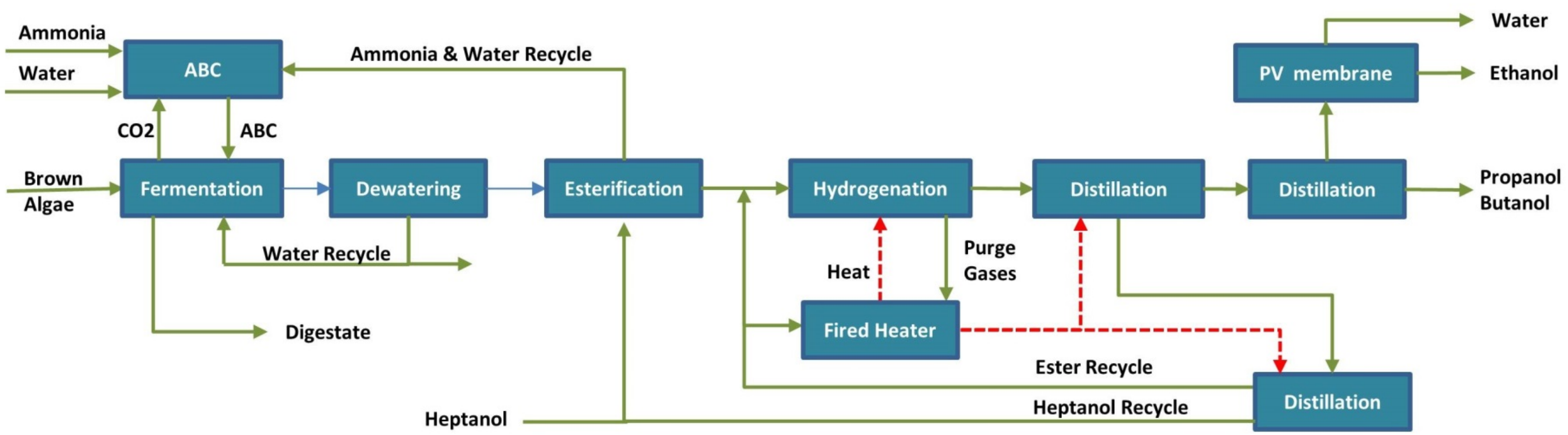
# MixAlco® Process

A. Mixed Alcohols production through **Ketonization Route (KR)**.

B




(A) Ketonization Route




(B) Esterification Route

# Conceptual design: Anaerobic digestion

- An average yield of **0.35** (g VFA/g dry brown algae) and **five** days fermentation time were considered.
- Iodoform is added to fermenters at a concentration of 30 ppm to inhibit methanogens.

**KR** $$2R - COOH + CaCO_3 \rightarrow (R - COO)_2Ca + H_2O + CO_2$$

**ER** $$R - COOH + NH_4HCO_3 \rightarrow R - COONH_4 + H_2O + CO_2$$

# Conceptual design: dewatering

- A **six stage evaporator** is used to evaporate the water and concentrate the salts.
- Vapors produced at each stage is used as a heat source at adjacent stage.
- The vapor from the last stage is compressed to a higher temperature and pressure in a **steam compressor** and is then saturated so it readily condenses and transfers heat to the first stage.
- **In the KR**, the multistage evaporator concentrates the dilute stream of salts to **50%** mass concentration. Later, the concentrated salts are dried in a **rotary drier**.
- **In the ER,** the concentration of ammonium carboxylate salts increase from **5 wt%** to **40 wt %**.

# Conceptual design

## Ketonization (KR) of calcium carboxylate salts

- Carboxylate salts are heated using a **fired heater** to reach **430°C** ketonization temperature. A low pressure of **30 mmHg** is maintained by vacuum pumps and condensation of produced vapor ketones.

## Esterification of ammonium carboxylate salts (ER)

- Concentrated ammonium carboxylate salts are reacted with **high molecular weight** alcohols (in this case **1-heptanol**) at **150°C** in the presence of solid acid catalyst to produce esters through the following reaction

$$R - COONH_4 + CH_3(CH_2)_6OH \rightarrow R - COOCH_2(CH_2)_5CH_3 + NH_3 + H_2O$$

# Conceptual design

## Hydrogenation of Ketones

- The reaction is performed at high pressure (**55 bar**) and isothermal (**130°C**) condition.
- The optimal design for hydrogenation of ketones reported to be three continually stirred tank reactors (CSTR) in series for a **98.4%** conversion of ketones into their alcohols.

$$R - CO - R' + H_2 \rightarrow R - CH(OH) - R'$$

## Hydrogenation of Esters

- **97%** of esters are hydrogenated to alcohols in the presence of heterogeneous catalysts such as **copper chromite** at **high temperature (200°C**) and **high pressure (200 atm)**.

$$R - COOCH_2(CH_2)_5CH_3 + \mathbf{2}H_2 \rightarrow R - COH + CH_3(CH_2)_6OH$$

# Conceptual design

## Recovery of secondary alcohols (KR)

- The alcohols recovery unit includes **two distillation columns**. The first column (D-501) separates propanol from alcohols mixture as top product of the column. The second column (D-502) separates butanol from top and C5~C7 alcohols from bottom.

## Recovery of primary alcohols (ER)

- The alcohols recovery unit contains **three distillation columns** to separate and recover alcohols.
- The first column separates ethanol, propanol, and butanol from top and heptanol and unreacted esters from the bottom. The vapors of light alcohols are distilled in second column to ethanol and mixture of propanol and butanol.
- Third column separates heptanol from the top and esters from the bottom.

# Conceptual design

## Ammonium BiCarbonate (ABC) Production (ER)

- ABC is produced as buffer for fermentation reactors. The ABC production process is similar to **ammonia based $CO_2$**. The absorber operates at **5°C.**
- The **electrolyte-NRTL** model is used for describing the chemical equilibrium among different molecules and ions.

| Type | Chemical equation |
|---|---|
| **Equilibrium** | $NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$ |
| **Equilibrium** | $2H_2O \leftrightarrow H_3O^+ + OH^-$ |
| **Equilibrium** | $HCO_3^- + H_2O \leftrightarrow CO_3^{2-} + H_3O^+$ |
| **Kinetic** | $CO_2 + OH^- \rightarrow HCO_3^-$ |
| **Kinetic** | $HCO_3^- \rightarrow CO_2 + OH^-$ |
| **Kinetic** | $NH_3 + CO_2 + H_2O \rightarrow NH_2COO^- + H_3O^+$ |
| **Kinetic** | $NH_2COO^- + H_3O^+ \rightarrow NH_3 + CO_2 + H_2O$ |
| **Salt** | $NH_4HCO_3(S) \leftrightarrow NH_4^+ + HCO_3^-$ |

# Conceptual design

- An **optimization** of the process is performed using Aspen plus for the **maximum production of ABC** and **minimum production of by products** such as $\mathbf{NH_4^+}$ and $\mathbf{NH_2COO^-}$ considering the cost of ammonia and cooling for the process.

# Results: Main stream (KR)

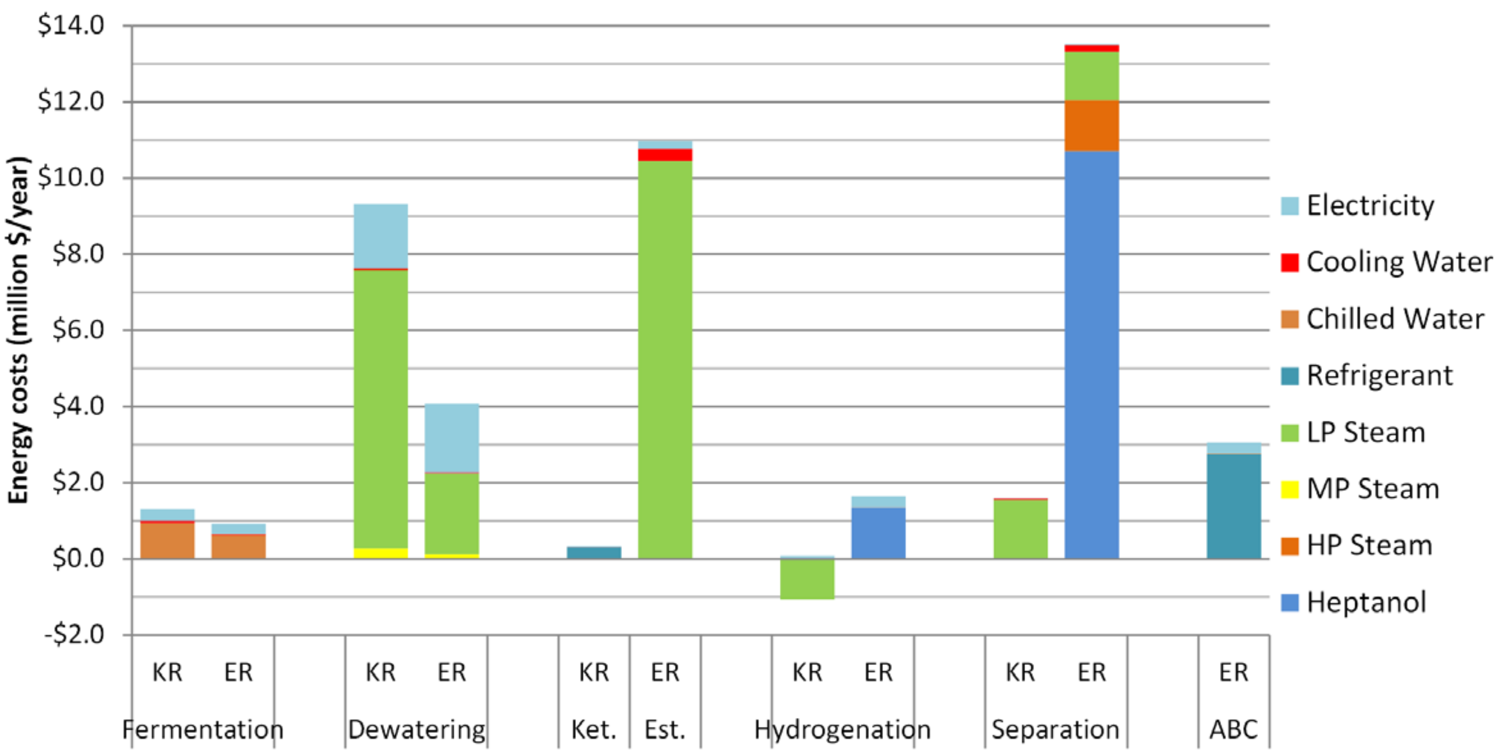
| Stream | Mass flow (kg/hr) |
| --- | --- |
| Brown algae | 62,500 |
| $CaCO_3$ | 13,268.3 |
| Digestate | 27,108.1 |
| Fresh water | 21,287.6 |
| Ketones | 9,313.7 |
| Mixed alcohols | 9,558.4 |
| Propanol | 2,965.5 |
| Butanol | 4,052.4 |
| Pentanol | 2,228.7 |

# Results: Main stream (ER)

| Stream | Mass flow (kg/hr) |
| --- | --- |
| Brown algae | 62,500 |
| Ammonium BiCarbonate | 79,997.3 |
| Digestate | 27,238.7 |
| Fresh water | 1,643.9 |
| Esters | 43,528.2 |
| Mixed alcohols | 44,715.9 |
| Ethanol | 7,785.7 |
| Propanol + Butanol | 5,725.3 |

# Results: Energy costs

- Total energy costs of the **KR** and **ER** are calculated to be **11.6** and **37.2** million$/y, respectively.
- The total energy requirement of the ER is more than three times of the KR.



# Results: (Total investment costs, NPV, and PVR)

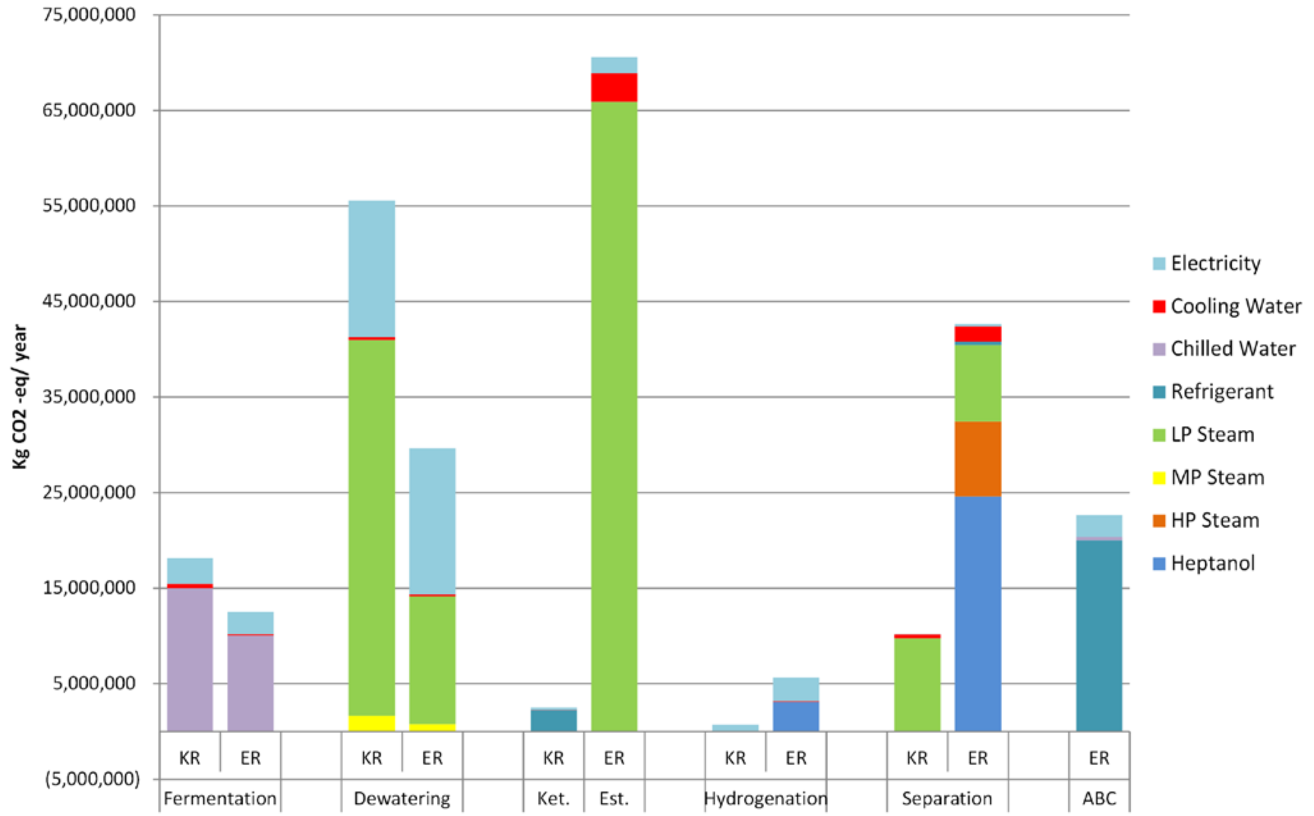
- The net present value (NPV) and the present value ratio (PVR) are calculated for profitability analysis of KR and ER over **20 years of plant** life.

| | KR (MM$) | ER (MM$) |
|---|---|---|
| Fermentation | 9.6 | 9.5 |
| Dewatering | 29.0 | 24.9 |
| Ketonization/Esterification | 6.7 | 4.7 |
| Hydrogenation | 5.1 | 5.1 |
| Separation | 1.7 | 8.7 |
| ABC production | - | 2.4 |
| Total Installed Costs (TIC) | **52.0** | **52.9** |
| Total Direct Costs (TDC) | 61.2 | 62.2 |
| Total Indirect Costs | 36.7 | 37.3 |
| Fixed Capital Investment | 97.8 | 99.5 |
| Land | 3.1 | 3.2 |
| Working Capital | 4.9 | 5.0 |
| Total Capital Investment | 105.9 | 107.6 |

| | KR MM$ | ER MM$ |
|---|---|---|
| Biomass cost (per year) | 34.0 | 34.0 |
| Utility cost (per year) | **11.6** | **37.2** |
| Total variable operating cost (per year) | **4.1** | **20.8** |
| Total fixed operating cost (per year) | 3.0 | 3.1 |
| NPV | **61.1** | **-55.1** |
| PVR | **1.57** | **0.48** |

# Results: $CO_2$ emissions

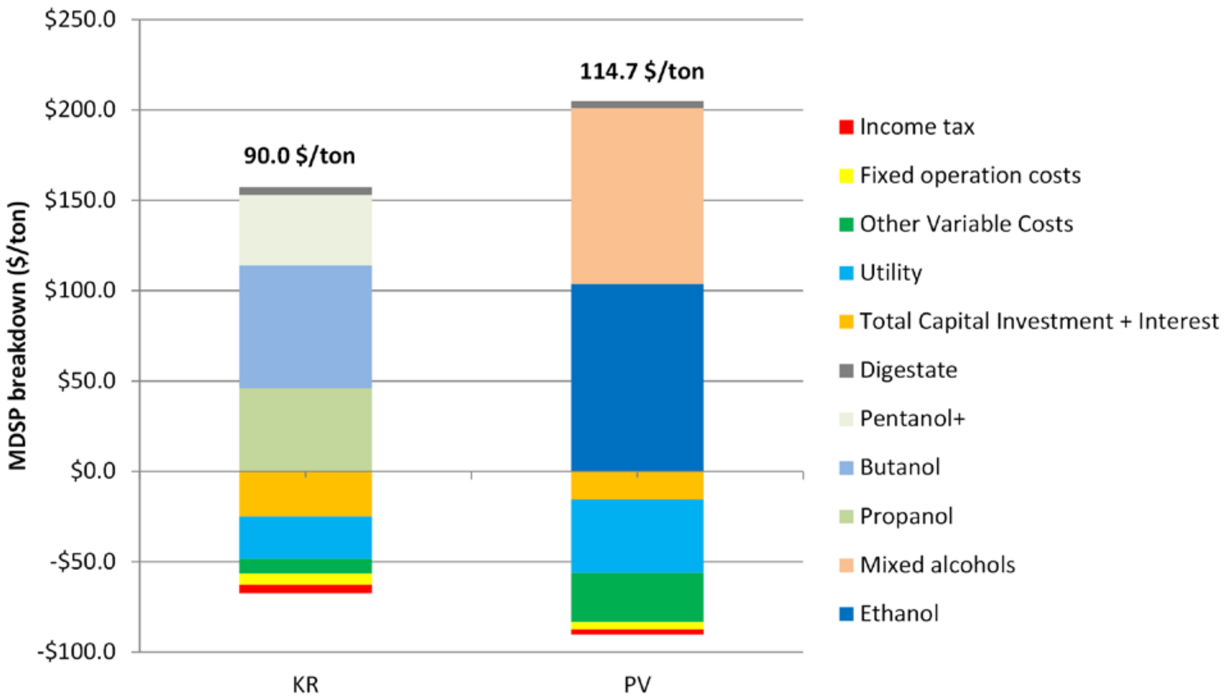
❖ The total $CO_2$-eq emissions are calculated to be **87.1** and **183.8 kton/year** for the **KR** and **ER**, respectively.




**$CO_2$ emissions of the KR and ER during plant operation**.

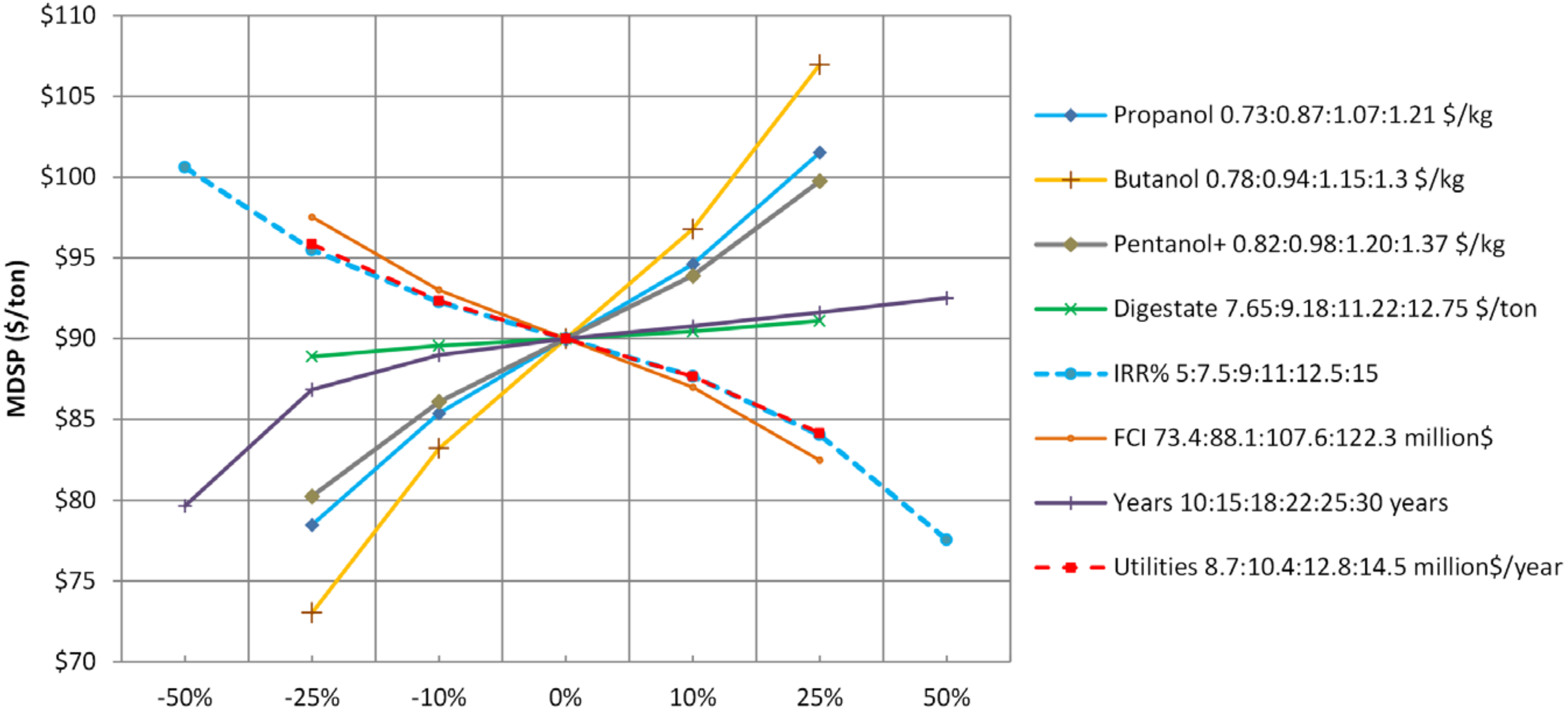
# Maximum Dry Seaweed Price (MDSP)

- The Techno-economic model is used to calculate the maximum dry seaweed price (**MDSP**) to have a Return On Investment break-even point after **20 years** of plant operation.
- The calculated MDSP is the price of the feedstock at the plant gates and includes the costs of cultivation, storage, and transportation.



# Sensitivity Analysis

❖ A sensitivity analysis on different economic parameters was performed to identify the main parameters affecting the plant economics for the KR.




**Impact of economic parameters on maximum dry seaweed price ($/ton) for KR.**

# Conclusions

- Application of MixAlco® routes for alcohol production from brown algae is assessed.
- KR is superior over ER in terms of energy efficiency, CO2 emissions, and economics.
- A NPV and PVR of 61.1 million dollars and 1.57 were calculated for the KR.
- A maximum dry seaweed price of 90.0 $/ton was calculated for the KR.