MICHIGAN STATE UNIVERSITY

PHYCO2

A Combined Biological and Chemical Flue Gas Utilization System towards Carbon Dioxide Capture from Coal-fired Power Plants

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NETL CO_2 Capture Technology Project Review Meeting

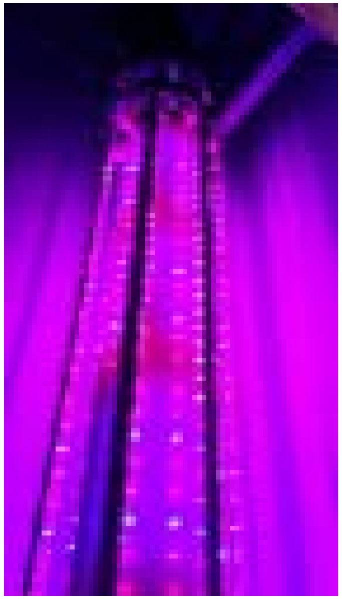
August 17, 2018

Outline

- Project Team
- Project Objectives
  - Current challenges related with biological CO_2 capture
  - Our strategy
  - Project goal and objectives
- Technical Approach
  - Optimizing the pilot-scale photobioreactor algal cultivation
  - Developing a cascade biomass conversion process
  - Conducting TEA and LCA on the studied system

90 MW T.B. Simon Power Plant, MSU

160 MW Erickson Power Plant, Lansing, MI



Algal cultivation on flue gas and wastewater from the power plant

Project Team

Dr. Yan (Susie) Liu

Biosystems and Agricultural Engineering, Michigan State University

Responsible for algal cultivation

Dr. Mitch Smith

Chemistry, Michigan State University

Responsible for catalysis of polymer synthesis

Dr. Angela Wilson

Chemistry, Michigan State University

Responsible for formulation of amino acid based absorbents

Dr. Wei Liao

Biosystems and Agricultural Engineering, Michigan State University

Responsible for system integration, TEA and LCA

Mr. Bill Clary, Mr. Dave Pavlik, Dr. Gary Allen, and Mr. Bob Morgan

$PHYCO_2$ LLC

Responsible for the reactor modification and pilot operation

Mr. Nate Verhanovitz and Mr. Bob Ellerhorst

The T.B. Simon Power Plant

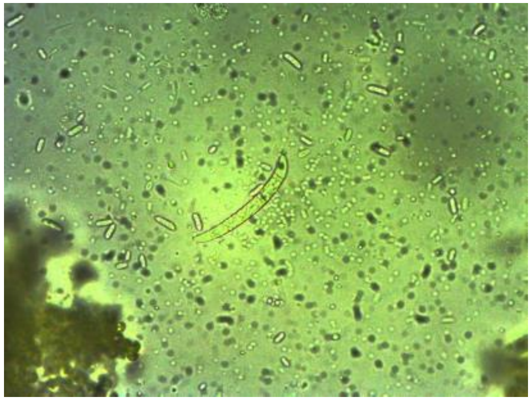
Responsible for the connection between the pilot unit and the power plant operation

Project Objectives

Current challenges related with biological CO_2 capture from flue gas

- Large algal cultivation systems required to completely capture CO_2 from a commercial coal-fired power plant (land and water demands)
  - Erickson Power Plant (150 MW): ~3,000 metric ton CO_2 per day requires ~150,000,000 m^2 area for the open pond reactor and ~45,000,000 m^3 volume for the photobioreactor (based on the algae biomass productivity of 20 $g/m^2/day$)
- Stability and robustness of algal strains for long-term cultivation on flue gas
  - Robust strains that can grow on flue gas for an extended period (months to years) without sterilization requirement are critical to sustain the algal cultivation systems
- Lack of comprehensive solutions to efficiently and completely utilize algal biomass
  - Algal composition: 10~20% Lipid; 30-50% Carbohydrate; 30-60% Protein

Large footprint of algal cultivation
From:
http://www.cyanotech.com/company/facility.html

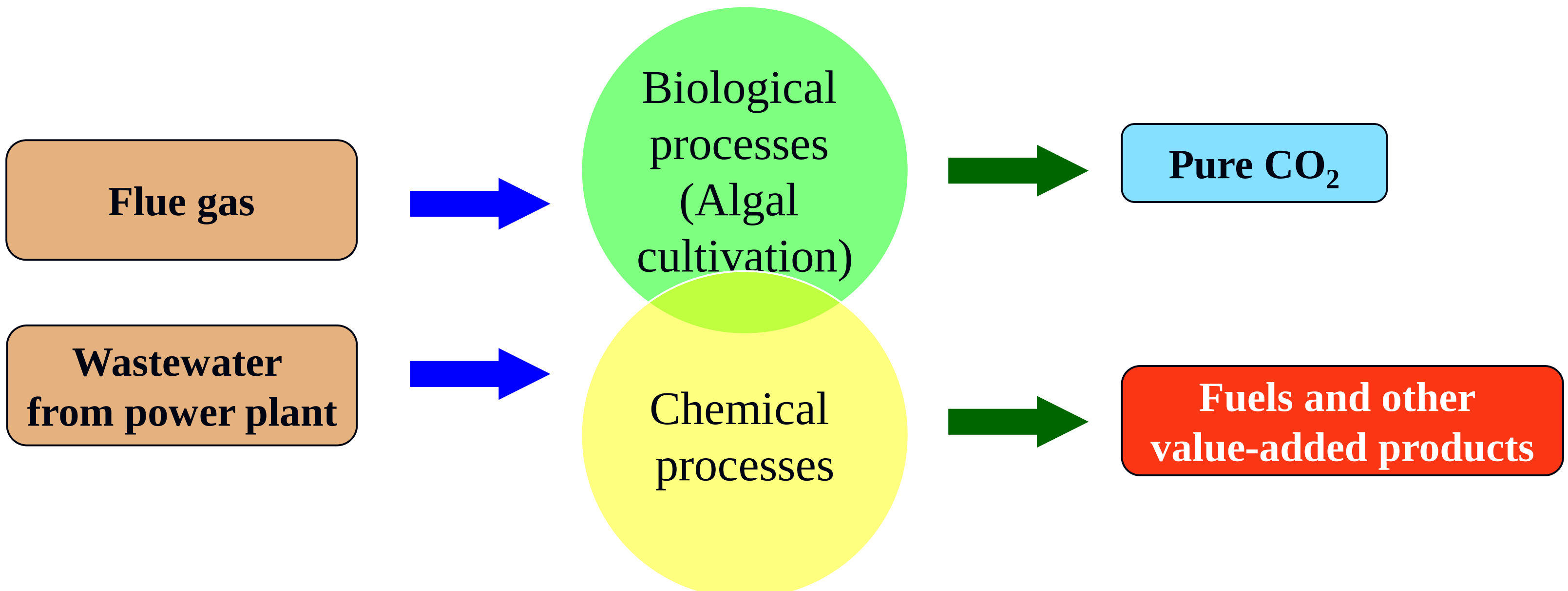


Contaminated algal cultivation
From:
https://www.youtube.com/watch?v=H4DQTeNamPE

Project Objectives

Our strategies

Synergistically integrating biological and chemical processes to efficiently capture CO_2 from flue gas and completely utilize the algal biomass for value-added chemical and fuel production



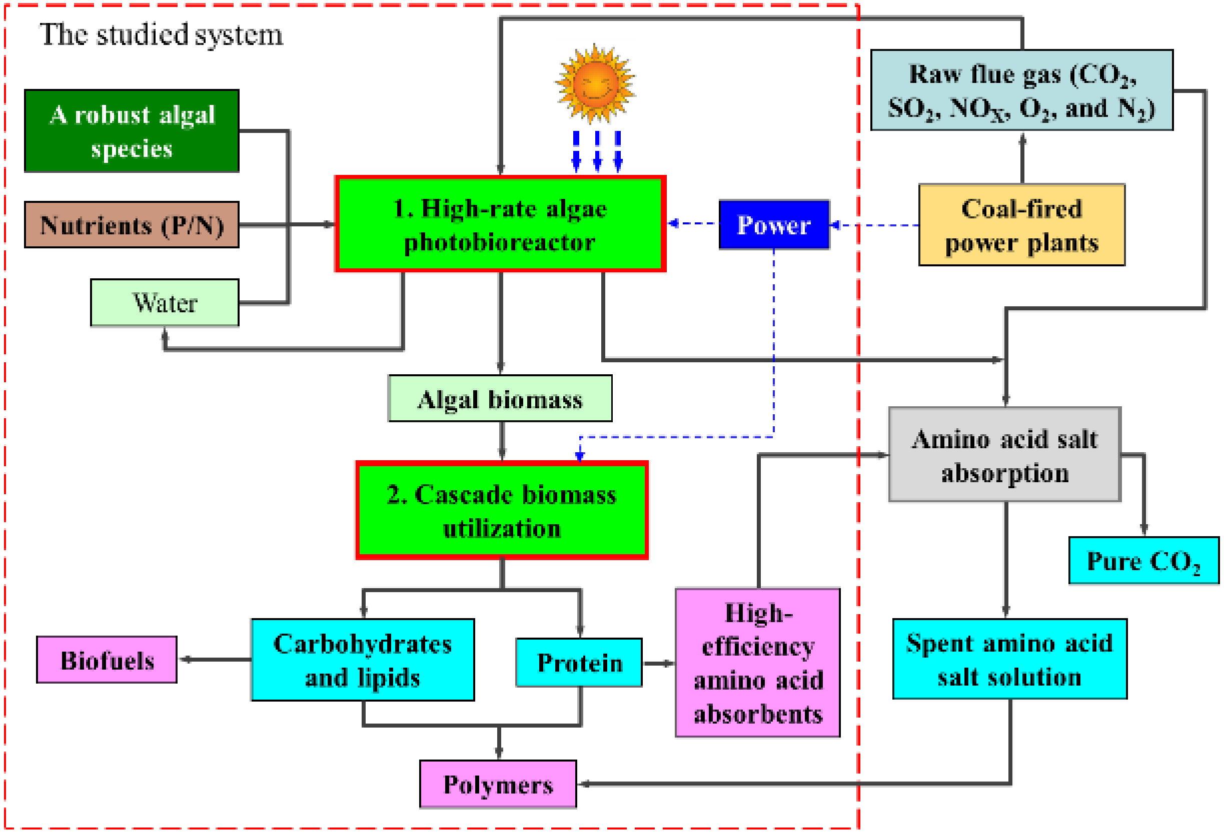
Project Objectives

The goal:

The goal of the proposed project is to develop a combined biological and chemical system for coal-fired power plants to generate bio-based CO_2 absorbent and other value-added products.

Project objectives:

1. Optimizing the growth of the selected algal strain to maximize biomass accumulation from the coal-fired flue gas
2. Developing a cascade biomass utilization to produce amino acid absorbents, polyurethanes, biodiesel, and methane
3. Conducting techno-economic analysis (TEA) and life cycle assessment (LCA) of the proposed process



The proposed biological and chemical algal cultivation system*

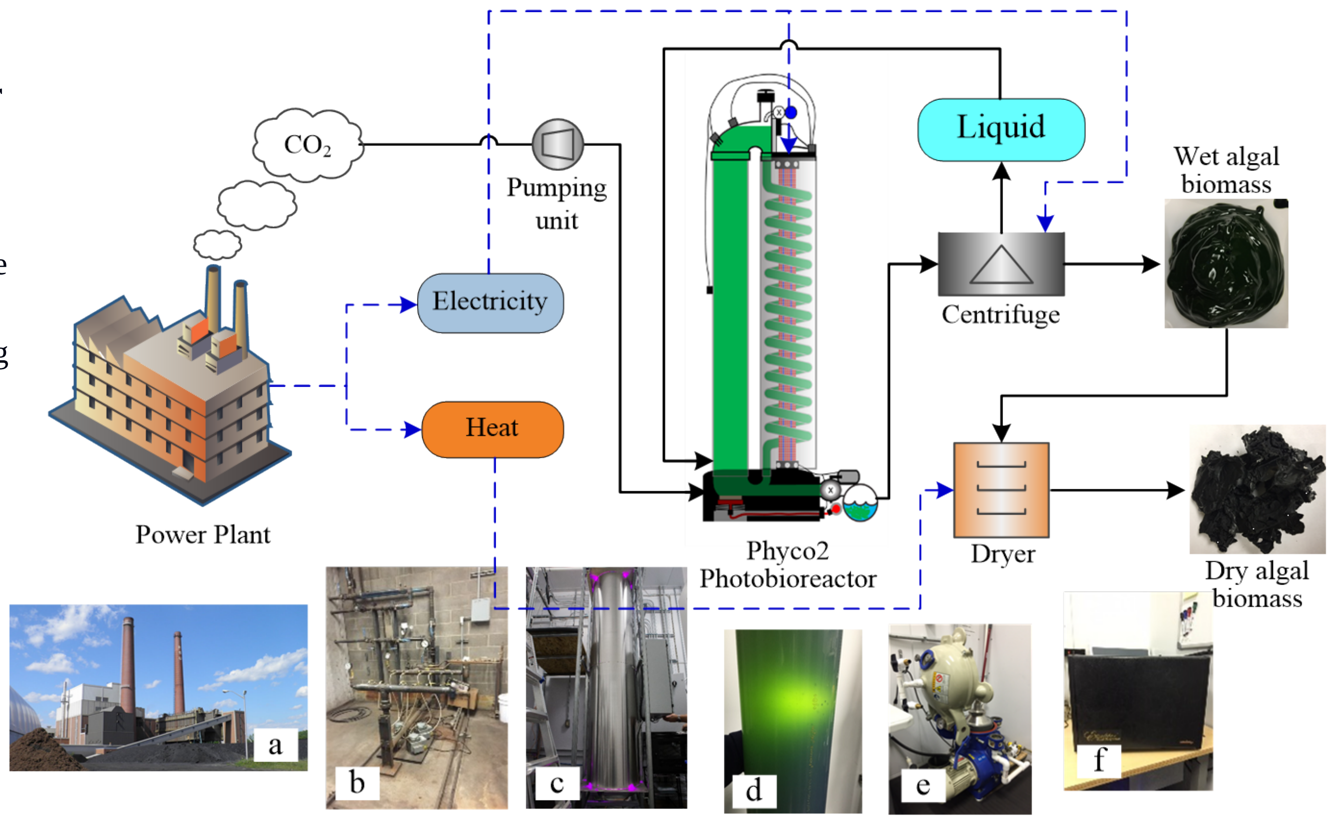
*: Solid black lines are the mass flow. Dashed blue lines are the energy flow. The red frame is the system that will be studied by this project.

Expected outcomes of the project

- Long-term culture stability of the selected algal strains will be achieved using flue gas as the carbon source.
- Algal biomass productivity reaches **0.5-0.8 g/L/day** at a biomass concentration of **1.0-1.2 g/L** from the pilot operation.
- The cascade utilization process will achieve **nearly 100%** utilization of the algal biomass.
- The combined biological and chemical flue gas utilization will lead to **a technically sound and economically feasible system** to efficiently capture CO_2 in the coal-fired flue gas.

The pilot photobioreactor system in the T.B. Simon power plant

a. T.B. Simon power plant; b. Flue gas pumping unit; c. Photobioreactor; d. Algae growing in the reactor; e. Centrifuge; f. Dryer

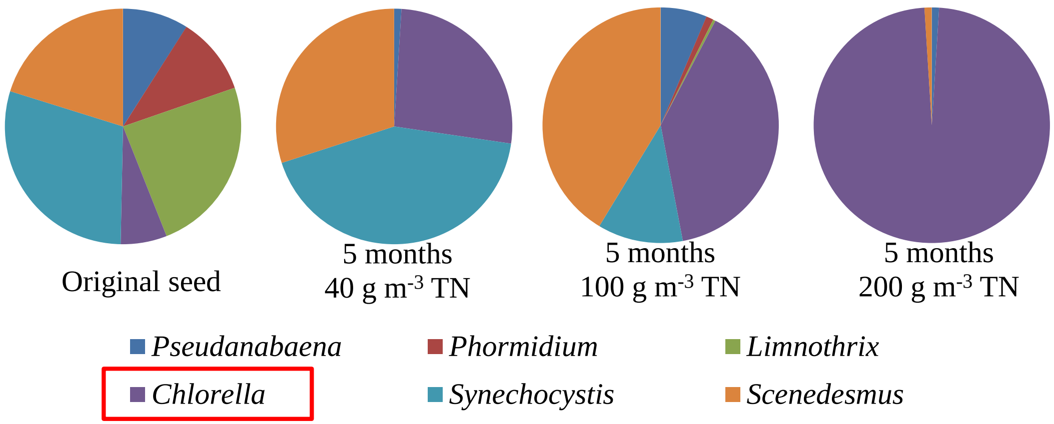


Technical Approach

1. Optimizing the pilot-scale photobioreactor algal cultivation

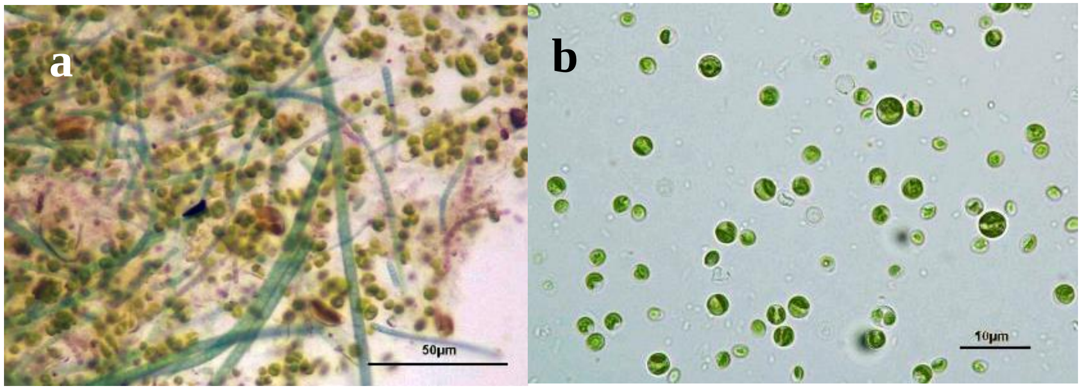
A. A robust algal strain from the Great Lakes Region

- A robust green alga, *Chlorella sorokiniana* MSU, has been selected from Great Lake region to capture algal biomass and produce algal biomass.

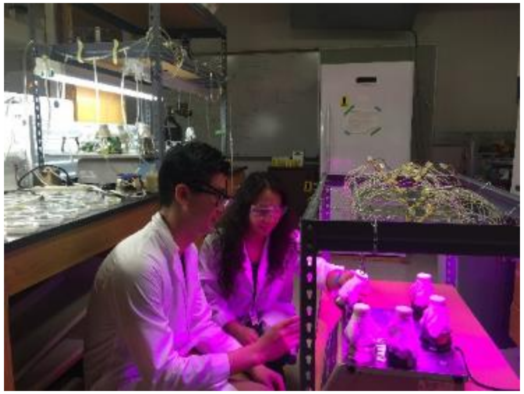


Changes of the algal assemblage during 5 months continuous culture

Flask culture (250 ml)



Algal community assemblages before (a) and after (b) cultured in AD effluent for 5 months



Effects of different wavelengths on algae

Technical Approach

1. Optimizing the pilot-scale photobioreactor algal cultivation

B. Pilot Operation

- This task optimizes and validates continuous algae cultivation using the pilot photobioreactors

- Pilot experiments
  - **The algal strain:**
    - The selected *Chlorella sorokiniana* MSU
  - **Culture system preparation:**
    - The **boiler water (12 mg/L TP)** is the water source for the culture.
    - The flue gas from the T.B. Simon power plant is the CO2 source.
    - Na2SO3 and NH4NO3 are used to mimic SO2 and NO2 in the flue gas.
  - **Operation of the algal cultivation:**
    - Flue gas flow rate: 12 L/min
    - Harvesting frequency: 12 hours and 24 hours
    - Harvesting amount: 30 L/harvesting, 50 L/harvesting, 60 L/harvesting, 70 L/harvesting
    - Key nutrients: NH4NO3, K2HPO4
    - Other flue gas component: Na2SO3
    - Trace nutrients: CaCO3, MgSO4, and FeCl2

100 L pilot unit

The culture started

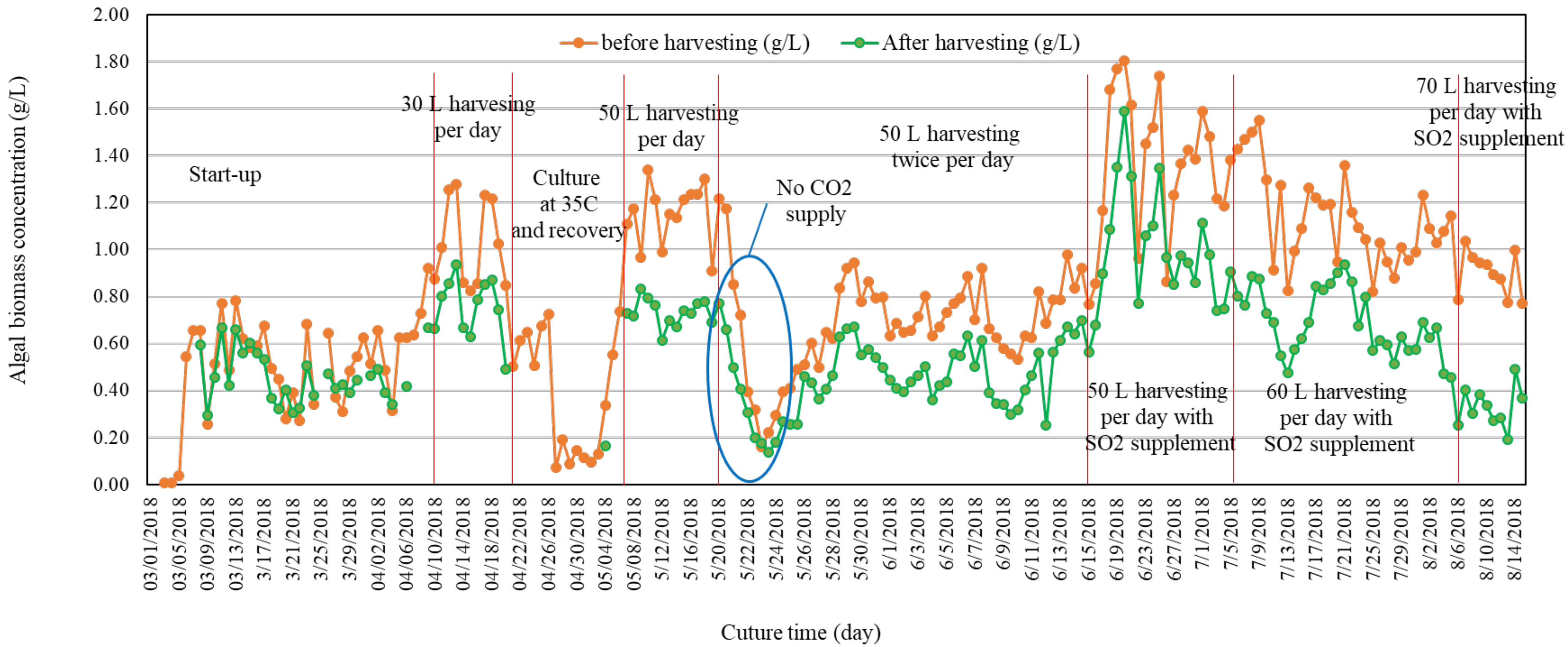
The normal growth

Technical Approach

1. Optimizing the pilot-scale photobioreactor algal cultivation

B. Pilot Operation

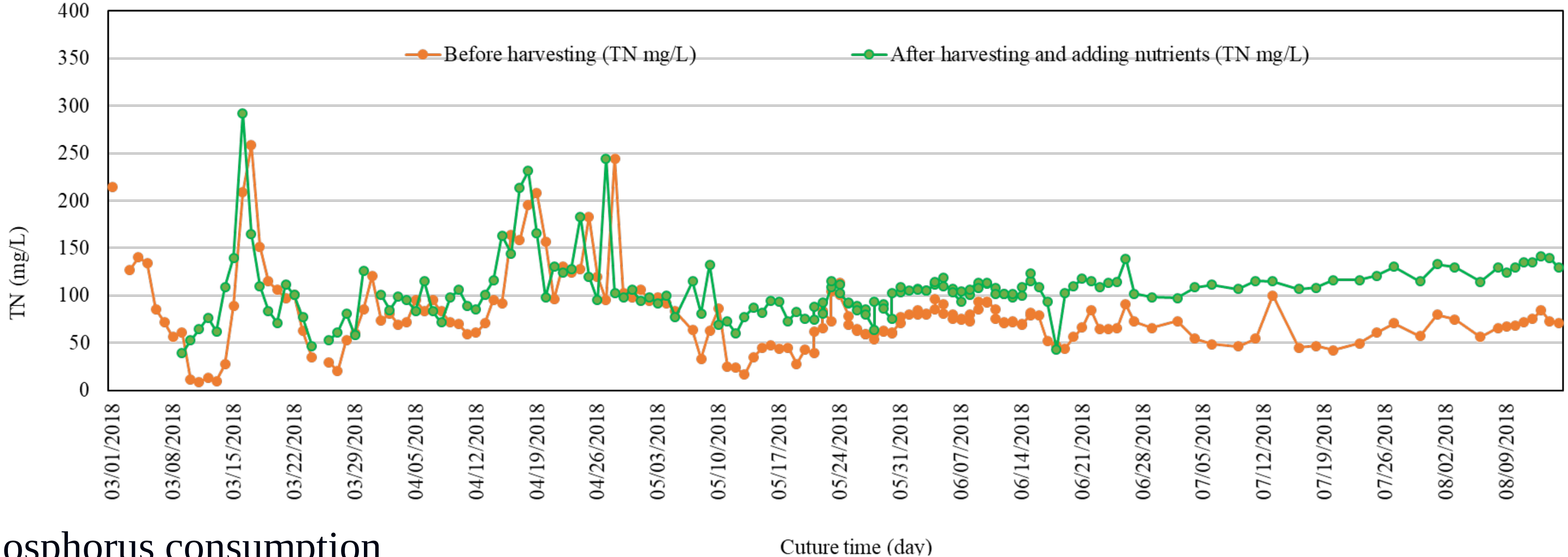
- Biomass concentration (from March to August, 2018)



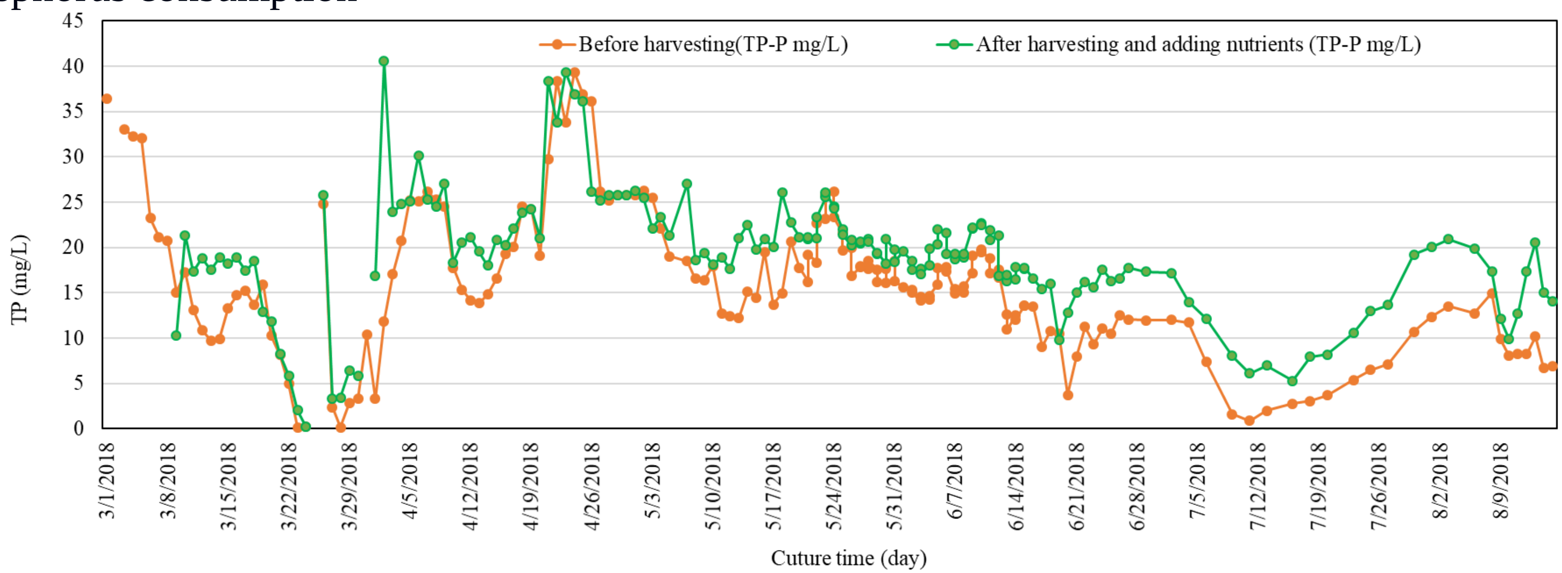
Technical Approach

1. Optimizing the pilot-scale photobioreactor algal cultivation
B. Pilot Operation

- Nitrogen consumption (from March to August, 2018)



- Phosphorus consumption

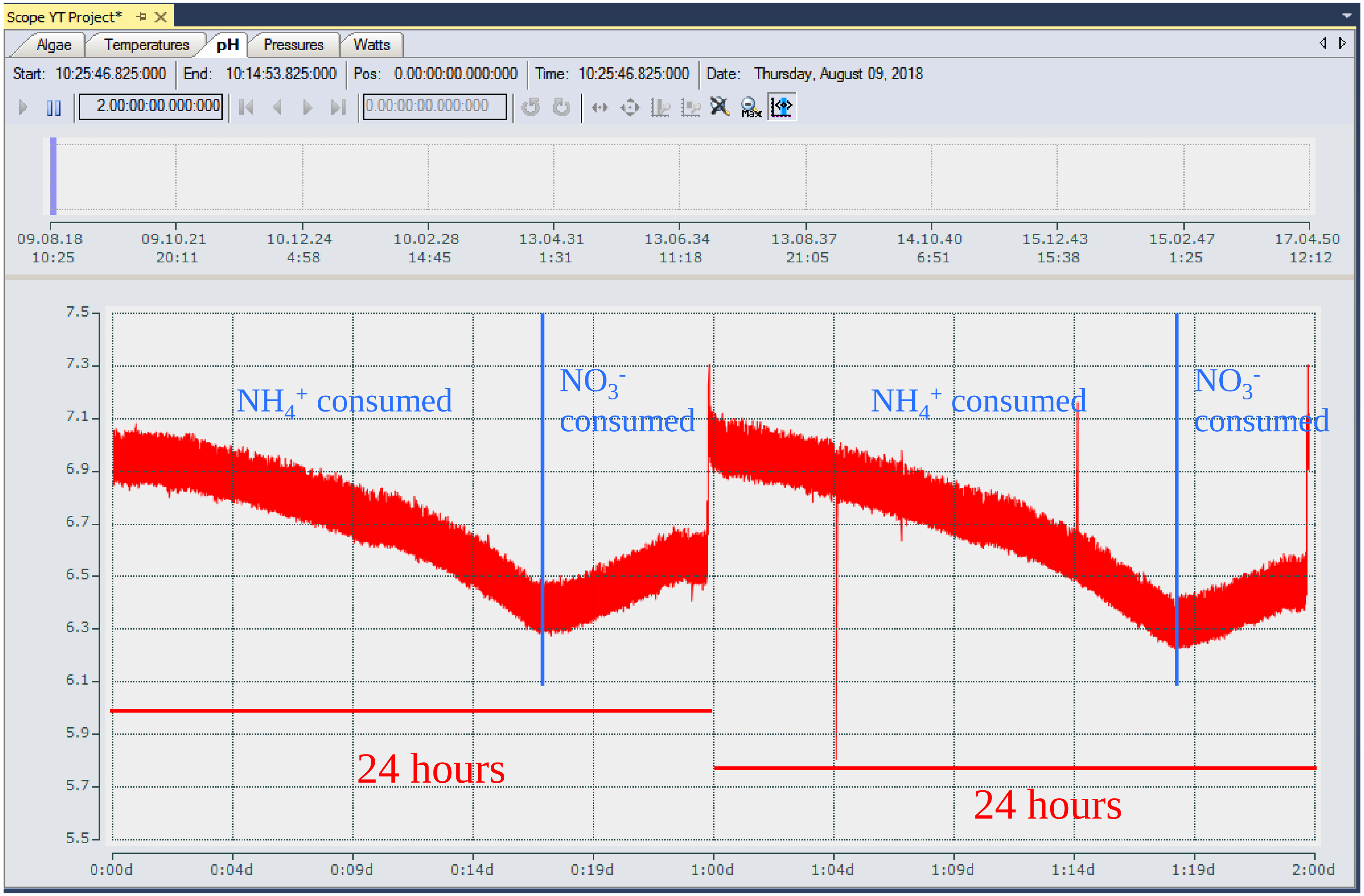


Technical Approach

1. Optimizing the pilot-scale photobioreactor algal cultivation

B. Pilot Operation

- pH change (without pH control)

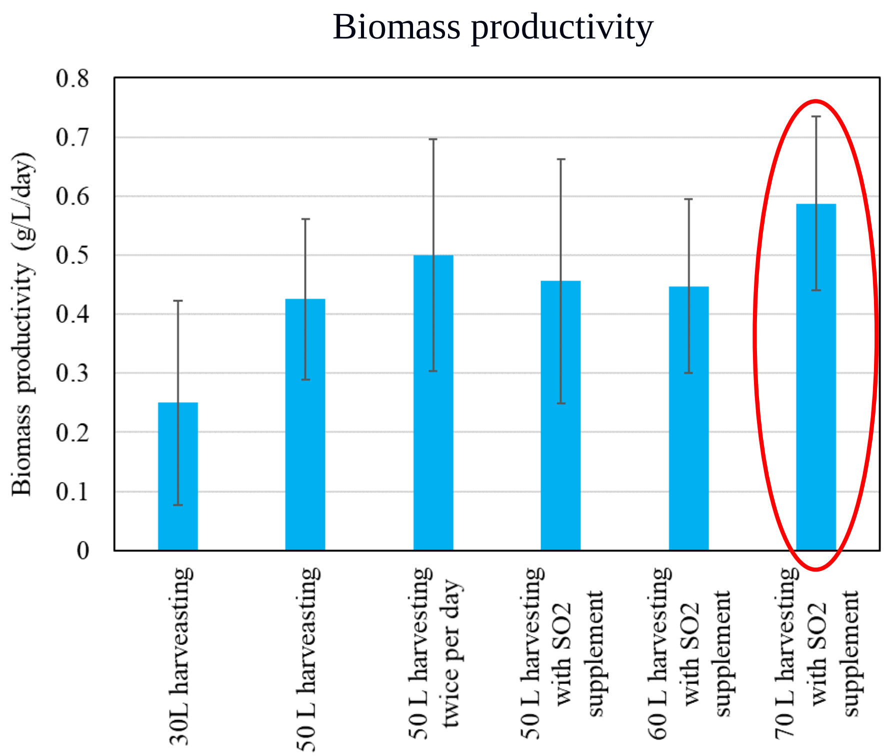


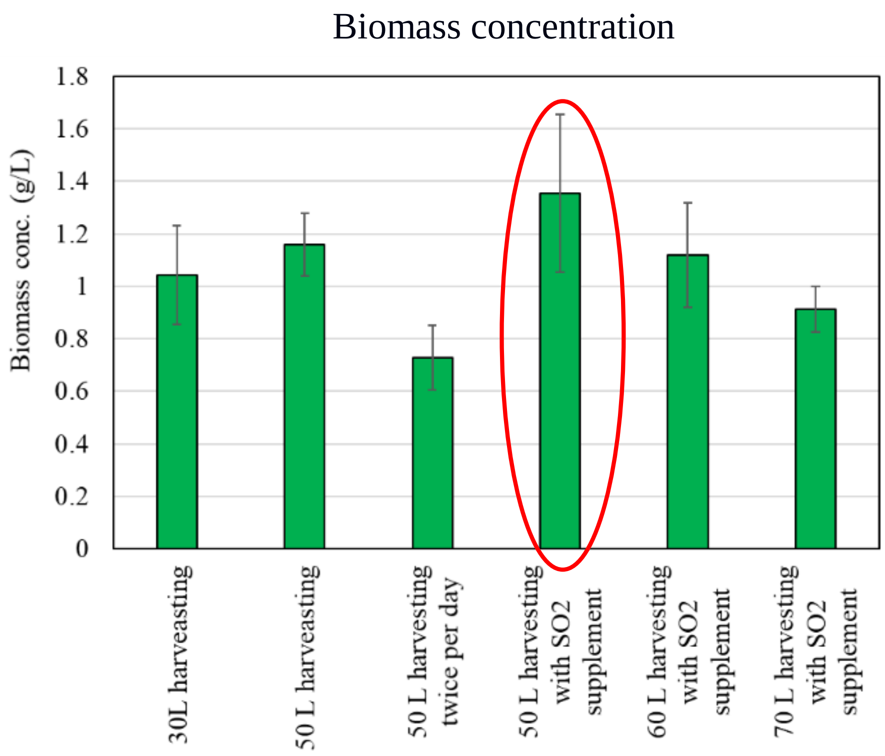
o N_xO in the flue gas could be beneficial for the pH control of the algal cultivation.

1. Optimizing the pilot-scale photobioreactor algal cultivation

B. Pilot Operation

- Biomass concentration and productivity





- 70 L harvesting with SO2 supplement had the highest ($P<0.05$) biomass productivity of 0.59 g/L/day.
- 50 L harvesting with SO2 supplement had the highest ($P<0.05$) biomass concentration of 1.36 g/L.

1. Optimizing the pilot-scale photobioreactor algal cultivation

C. Harvested biomass from the pilot Operation

- Characteristics of algal biomass from the pilot operation

Elements

Elements	value
Carbon (%, dry biomass)	48.2
Nitrogen (%, dry biomass)	9.1
Sulfur (%, dry biomass)	0.5

Components

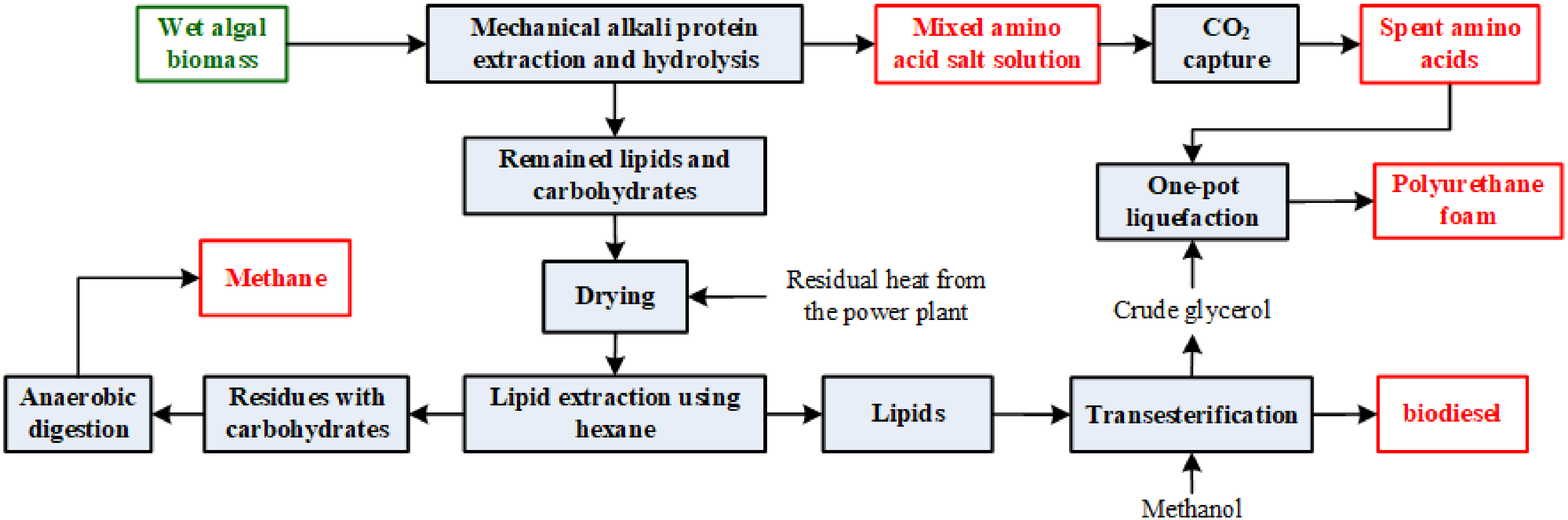
Components	value
Crude proteins (% dry biomass)	**56.8**
Lipids (% dry biomass)	6.8
Carbohydrates (% dry biomass)	30.4
Ash (% dry biomass)	6.0

Amino acids

Amino acids	Content (Mole %)
histidine	1.63
isoleucine	4.24
leucine	8.52
lysine	10.32
methionine	3.90
phenylalanine	3.58
threonine	3.62
tryptophan	-
valine	7.96
arginine	4.88
cysteine	1.43
glycine	11.04
proline	5.66
tyrosine	1.00
alanine	13.35
aspartic Acid	5.79
glutamic Acid	10.51
serine	2.53

2. Developing a cascade biomass conversion to produce amino acid absorbents, polyurethane, biodiesel, and methane

A. Flowchart



- Expected outcomes
  - The amino acid salt solutions have a high CO_2 absorption capacity of more than 0.5 mole CO_2/mole amino acids,
  - The cascade process can utilize all algal components (except ash) to fuels and polymers.

2. Developing a cascade biomass conversion to produce amino acid absorbents, polyurethane, biodiesel, and methane

B. High-efficiency protein extraction and hydrolysis

- Experimental design
  - **Ball milling:**
    - Ball material: Agate & Zirconia
    - Ball combination: 10 small balls (3 mm diameter), 10 medium balls (5 mm diameter), and 2 big balls (10 mm diameter)
    - Ball milling time: 0.5, 1, 2 hours
    - Temperature: 25 and 50ºC
  - **Alkali concentration:**
    - NaOH and KOH
    - Six concentrations: 0.05, 0.1, 0.2, 0.3, and 0.4 mole/L

2 L stirred ball mill

Planetary ball mill

Jars and balls of different ball mill materials used by the project (a). Agate; (b). Zirconia; (c). Stainless steel

Technical Approach

2. Developing a cascade biomass conversion to produce amino acid absorbents, polyurethane, biodiesel, and methane

B. High-efficiency protein extraction and hydrolysis

- Effects of NaOH on protein extraction efficiency of ball mill treated algal biomass

NaOH concentration (M)	Protein extraction efficiency (%)*
0	35.33
0.05	44.47
0.1	58.81
0.2	62.39
0.3	61.68
0.4	62.76

*: The extracted solution was centrifuged at 9,000 rpm for 5 minutes, the supernatant was used to analyze the extracted proteins.

- Effects of temperature on protein extraction efficiency

Temperature (°C)	Protein extraction efficiency (%)
25	63.47
50	**78.11**
25 without NaOH	37.65
50 without NaOH	36.15

*: The alkli concentration is 0.1 M.

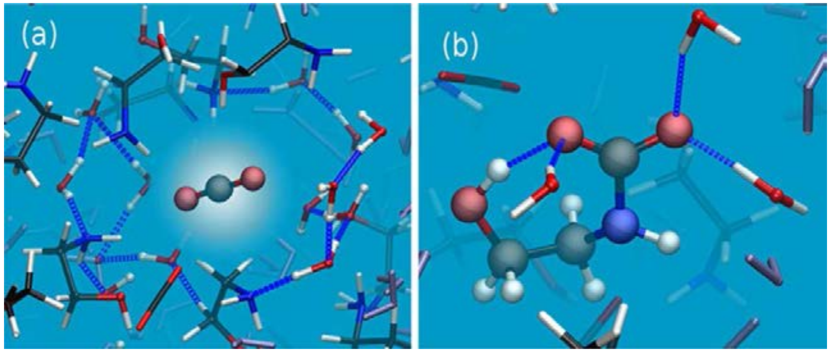
After mechano-chemical protein extraction

Technical Approach

2. Developing a cascade biomass conversion to produce amino acid absorbents, polyurethane, biodiesel, and methane

C. Optimization of mixed amino acid salt solution as a CO_2 absorbent (Under investigation)

- Molecular dynamic modeling of CO_2 absorption is being carried out based on the detailed amino acids and peptides information.



Molecular dynamic simulation (a) before and (b) after formation of carbamate. From: Ma, C et al. 2014. J. Phys. Chem. Lett. 5. 1672-1677

Chemical reactions of amino acid salt CO_2 absorption*

Amine formation: $\underbrace{{}^{-}OOC\text{-}R\text{-}NH_3^{+}}_{\text{amino acid}} + KOH \rightarrow K^{+} + \underbrace{{}^{-}OOC\text{-}R\text{-}NH_2}_{\text{amine}} + H_2O$

Carbamate formation: $CO_2 + 2\,{}^{-}OOC\text{-}R\text{-}NH_2 \leftrightarrow \underbrace{{}^{-}OOC\text{-}R\text{-}NH\text{-}COO^{-}}_{\text{carbamate}} + {}^{-}OOC\text{-}R\text{-}NH_3^{+}$

Carbamate hydrolysis: ${}^{-}OOC\text{-}R\text{-}NH\text{-}COO^{-} + H_2O \leftrightarrow {}^{-}OOC\text{-}R\text{-}NH_2 + \underbrace{HCO_3^{-}}_{\text{bicarbonate}}$

Biocarbonate formation: $CO_2 + {}^{-}OOC\text{-}R\text{-}NH_2 + H_2O \leftrightarrow {}^{-}OOC\text{-}R\text{-}NH_3^{+} + HCO_3^{-}$

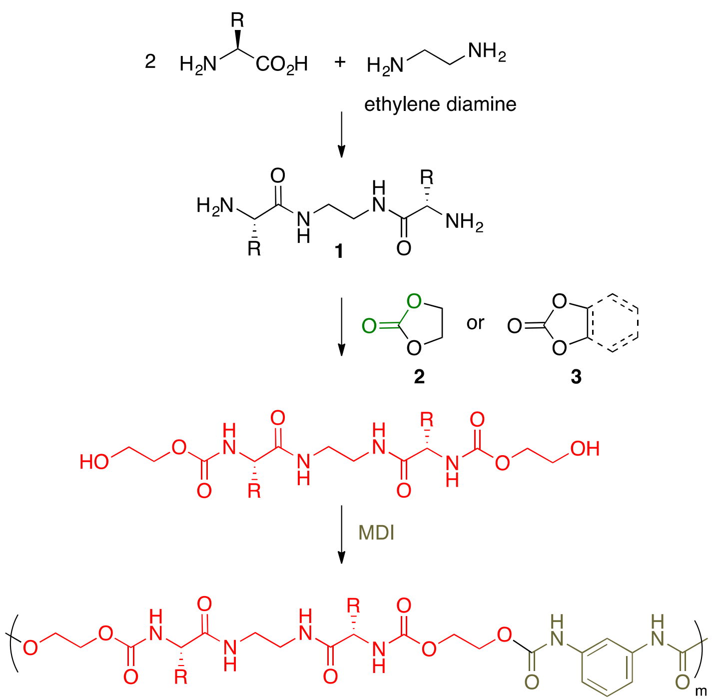
*: From: J.P. Brouwer, TNO Science & Industry, The Netherlands

Technical Approach

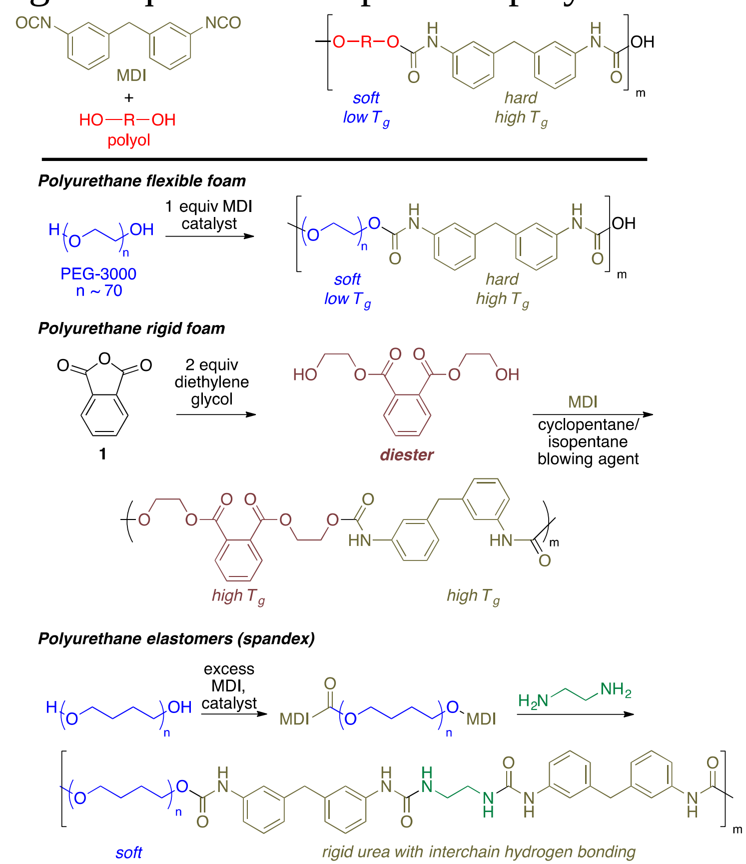
2. Developing a cascade biomass conversion to produce amino acid absorbents, polyurethane, biodiesel, and methane

D. One-pot synthesis of biopolyol for polyurethane production (Under investigation)

- The spent amino acids are mixed with ethylenediamine and then ethylene carbonate in a single reactor with different reaction conditions to produce hydroxyl-terminated polyols.
- The resulted polyol is blended with isocyannate by a high-torque mixer to produce polyurethane foam.



Amino-acid-based polyol formation



Synthesis of polyurethanes

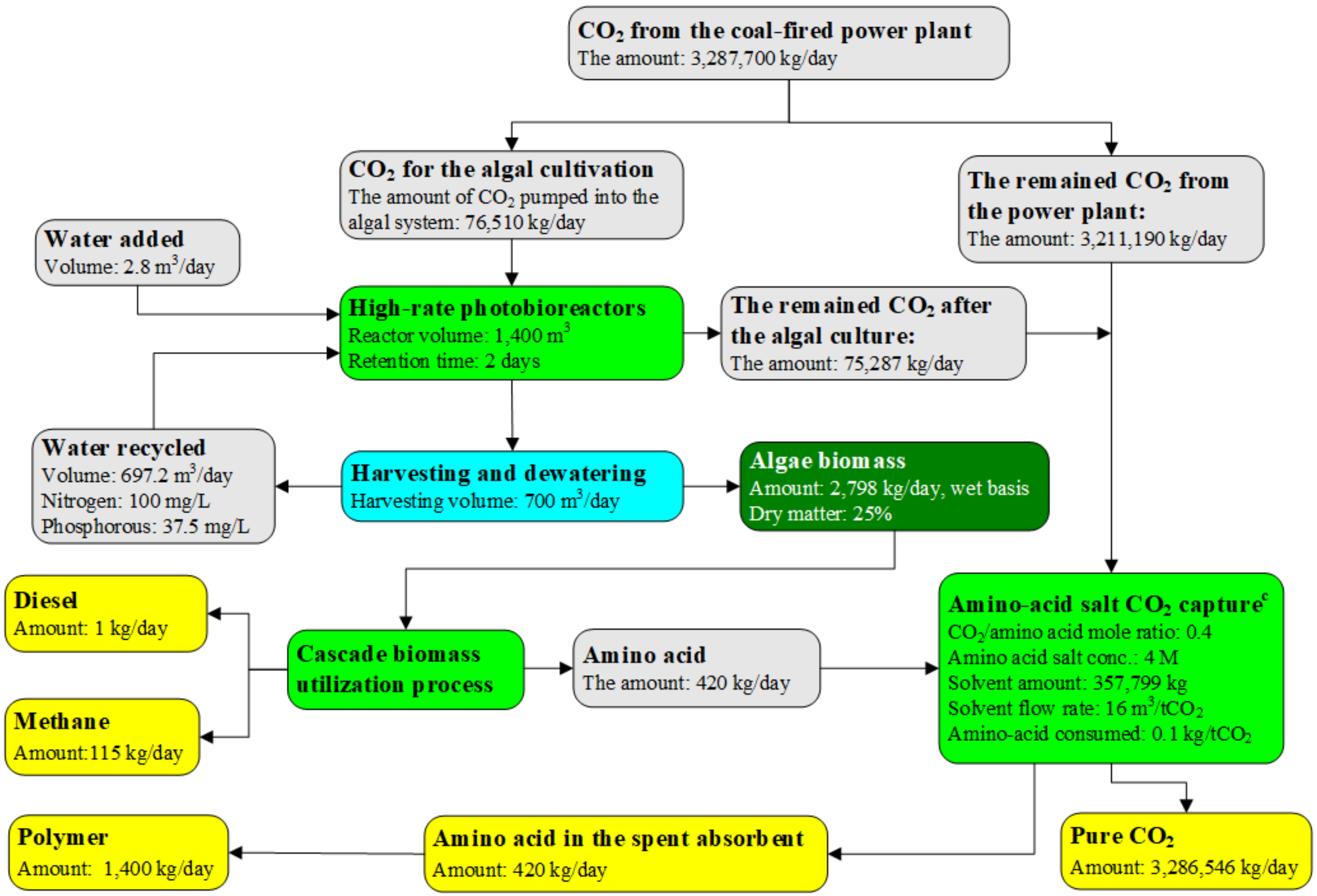
MDI: methylene diphenyl diisocyanate

Technical Approach

3. Conducting TEA and LCA on the studied system

A. Mass balance analysis (Under investigation)

- The preliminary mass balance analysis is based on the proposed system (not including the power plant operation) for a 150 MW coal-fired power plant.
- The power plant burns subbituminous coal and generates 1.2 million metric tons of CO_2, 6,000 metric tons of N_2O, and 3,000 metric tons of SO_2 per year.



Technical Approach

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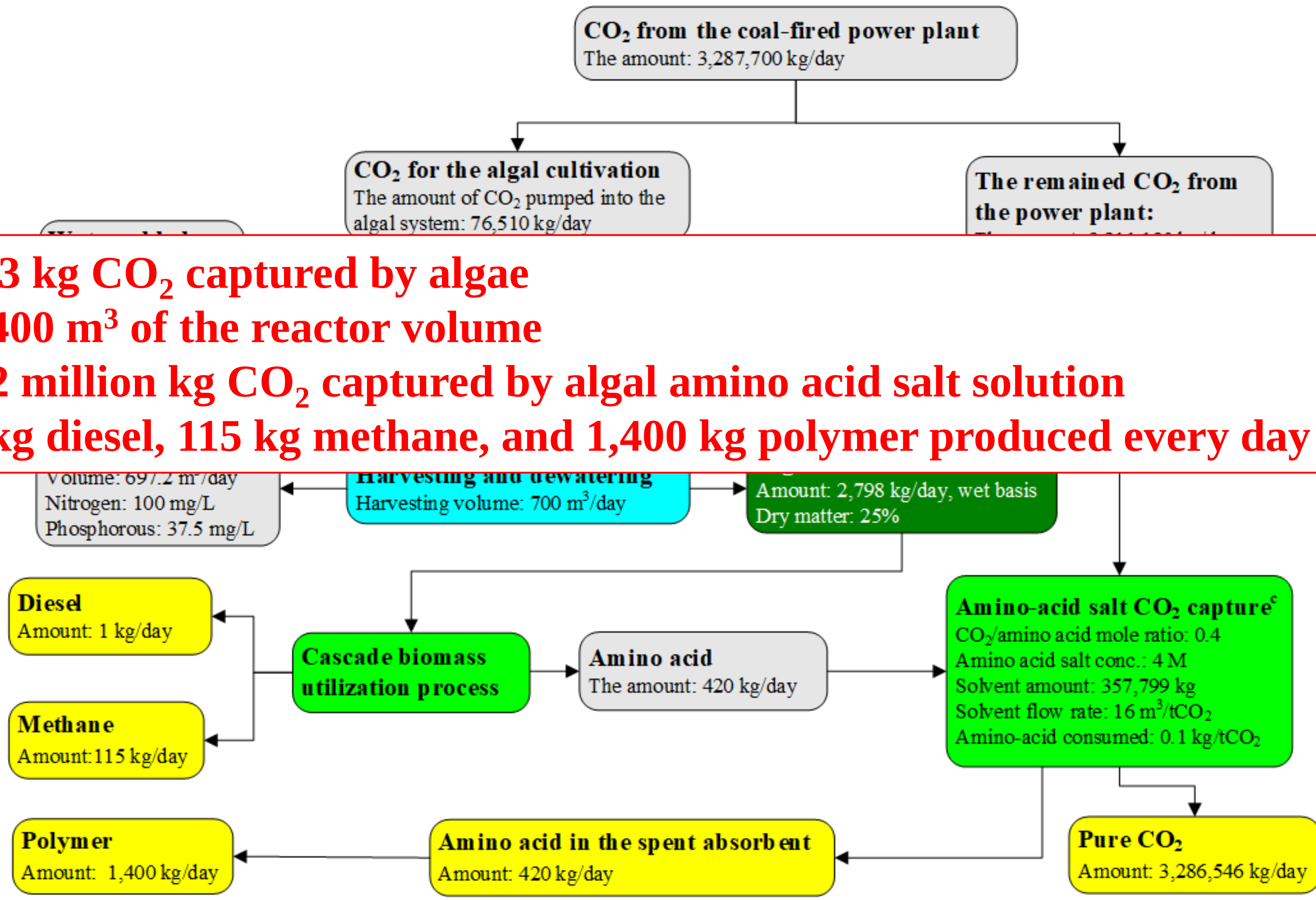


- 223 kg CO_2 captured by algae
- 1,400 m^3 of the reactor volume
- 3,2 million kg CO_2 captured by algal amino acid salt solution
- 1 kg diesel, 115 kg methane, and 1,400 kg polymer produced every day

3. Conducting TEA and LCA on the studied system

B. Energy balance analysis (Under investigation)

- The energy balance analysis is based on the previous mass balance.
- The 150 megawatts coal-fired power plant generates14,416,457 GJ/year for both electricity and heat.

System components	Energy value (GJ/year)		
	The proposed system [b]	The amino acid salt process [c]	MEA process [d]
Chemical production			
Energy input	-2,184	-52,805	-246
Energy output	2,920	-	-
CO_2 capture			
Energy input	-2,759,055	-2,759,055	-5,040,044
Energy output	-	-	-
Total energy input	-2,761,389	-	-5,040,290
Total energy output	1,920	-	-
Net energy	**-2,759,469**	**-2,811,860**	**-5,040,290**

a. Data used in the calculation are from the pilot scale algal cultivation and previous lab-scale utilization experiments. The energy input is assigned as negative. The energy out is assigned as positive.

b. The proposed system consists of algae photobioreactor cultivation, cascade biomass utilization, and CO_2 capture.

c. The single amino acid salt process includes both amino acid production and amino acid salt absorption.

d. The MEA process includes MEA production and MEA CO_2 capture.

3. Conducting TEA and LCA on the studied system

C. Economic analysis (Under investigation)

- The economic analysis is based on the previous mass balance and energy balance.
- The economic analysis does not include the capital cost.

Cost comparison between the proposed CO_2 capture system, commercial amino acid salt process, and MEA-based process [a]

System components	The proposed system [b]	The amino acid salt process [c]	MEA process [d]
Operational cost ($/year)	-400,000	-360,036	**-120,000**
Income ($/year)	849,018	0	**0**
Revenue ($/year)	**449,018**	**-360,036**	**-120,000**

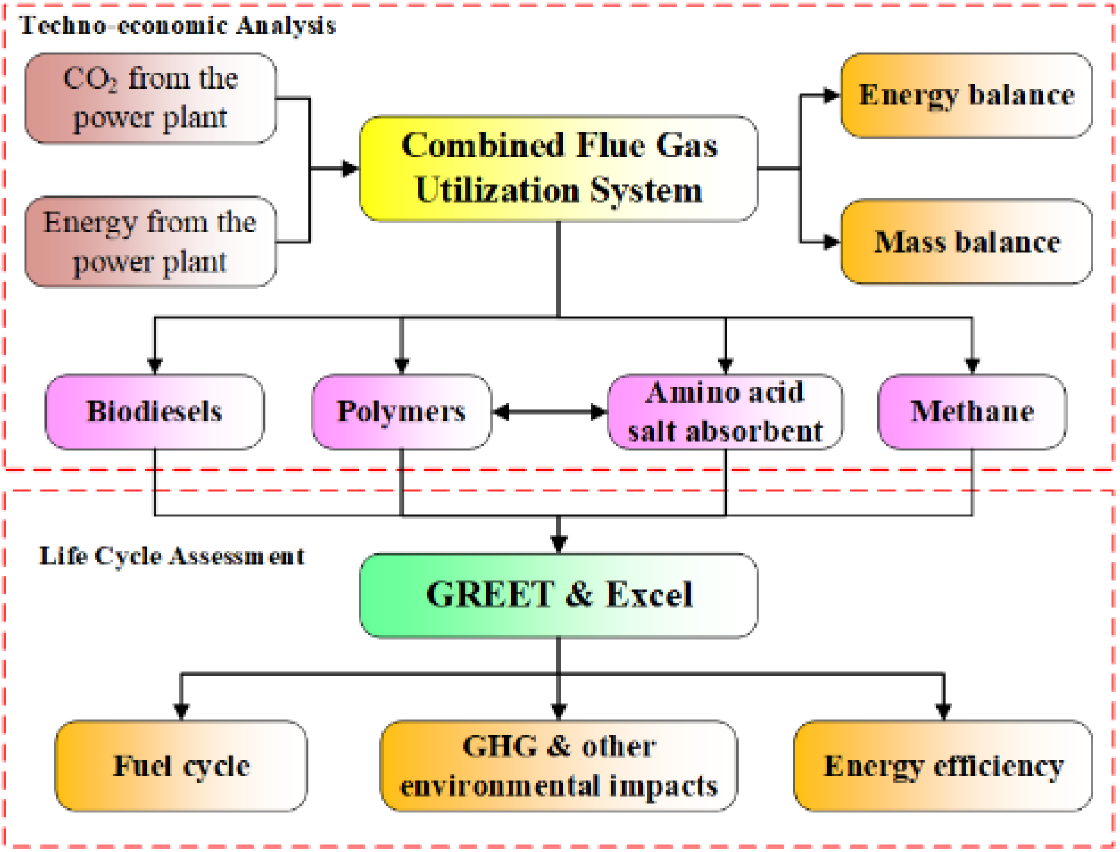
a. The cost is assigned as negative. The income is assigned as positive. The capital cost is not included in the analysis. It is assumed that the energy for CO_2 capture for all three processes are from residual energy. The cost of energy consumption is not included in the analysis.
b. The operation needs four operators ($60,000/operator/year). The cost of maintenance and other supplies is $160,000. With the current price of biodiesel ($1.25/kg), polyurethane ($2/kg), and methane ($0.42/kg), the annual income would be $849,018.
c. The amino acid cost (based on lysine) is $3/kg. The amount of amino acid required is 120,012 kg.
d. The MEA cost (Monoethanolamine) is $1/kg. The amount of MEA required to capture 1.2 million ton CO_2 is 120,000 kg.

3. Conducting TEA and LCA on the studied system

D. Life cycle assessment (LCA) (Under investigation)

- GREET and Excel are used as the tools to carry out LCA using the same boundary for TEA.
- Greenhouse gas emission and other environmental impact factors are targeted as the outputs of the LCA.

Procedure of TEA and LCA



Acknowledgements

- NETL FE0030977
- Erickson Power Plant

Go Green !!