DOE Bioenergy Technologies Office (BETO) 2023 Project Peer Review

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Synergistic Thermo-Microbial-Electrochemical (T-MEC) Approach for Drop-In Fuel Production from Wet Waste

April 7, 2023 Organic Waste Conversion

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This presentation does not contain any proprietary, confidential, or otherwise restricted information

Project Overview

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The post-hydrothermal liquefaction wastewater (PHW) is a burden (and opportunity) for hydrothermal liquefaction (HTL).



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1 – Approach

Project Goals:

Develop a synergistic thermo-microbial-electrochemical (T-MEC) process that converts food waste to jet fuel blendstocks and simultaneously treats HTL aqueous wastewater, thereby recovering H_2 and nutrients. The process targets include:

improve carbon yield by >50% compared to the anaerobic digestion baseline
 decrease waste processing cost by >25% compared to baseline

Proposed Budget Period	Tasks	Go/No-Go Decision
01/2021-03/2021	Initial verification	All baseline data will be verified successfully
04/2021-03/2023	Reactor development, product upgrading, and material innovation	Carbon conversion efficiency improves by >25% from AD baseline and/or Disposal costs are reduced by > 15%
03/2023-12/2024	Pilot reactor development and operation, system analyses	Carbon conversion efficiency improves by >50% from AD baseline and/or Disposal costs are reduced by > 25%



System Volumes	Length (in)	Diameter (in)	Volume (gal)
HP to HEX Hose	140	0.75	0.268
HEX to R Hose/Pipe	64	0.75	0.122
R to HEX Hose/Pipe	71	0.75	0.136
HEX to BPR Hose/Pipe	47	0.75	0.090
HEX Tubing	2550	0.742	4.773
Reactor	4076	0.742	7.630
Total			13.019

The team at UIUC developed and upgraded a plug-flow continuous HTL reactor:

Reactor: 7.63 gal (28.9 L)

Counterflow heat exchanger: 4.77 gal

Processing capacity: 1.5 ton/day wet feedstock



Food Waste Collection and Pretreatment



Combining HMFW





Homogenize HMFW





Diluted to 20% solids

Two food wastes:

- 1) Harvest Market food waste (HMFW)
- 2) Food processing plant: Salad dressing waste (SDW)







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2 – Progress and Outcomes – HTL tasks

Food Waste Collection and Pretreatment

Feedstock pretreatment process:

- Grade 16 mesh to sieve the shredded feedstock
- Semi-manual pressure-sieve
- Automated pretreatment is needed for large quantity feedstock – Future work



Proximate Analysis	HMFW	SDW
Moisture (wt%)	66.73	75.66
Dry matter (wt%)	33.27	24.34
Protein (wt%)	32.76	2.38
Fat (wt%)	29.10	62.45
Ash (wt%)	7.15	5.71
Carbohydrate* (wt%)	30.99	29.46

Elemental Analysis	HMFW	SDW
Carbon (wt%)	55.38	60.94
Hydrogen (wt%)	7.69	8.27
Nitrogen (wt%)	5.62	0.70
Oxygen (wt%)*	27.21	27.45
Sulfur (wt%)	0.33	<0.01
HHV(MJ/kg)**	25.74	28.04

*Calculated by difference

**HHV= $0.3516 \times C + 1.16225 \times H - 0.1109 \times O + 0.0628 \times N$

HTL System Performance

Runs with water and feedstock were performed to determine ideal system operating conditions and avoid HTL run disruptions from charring/plugging:

Q = f[P_{pump}, C, F, P_{bpr}, T, η] Q = flowrate in mL/min P_{pump}= pressure of HP pump P_{bpr} = nitrogen back pressure C = pump capacity F = frequency of pump motor T = temperature in reactor η = viscosity of the feedstock

Feed Carbon: 100.0



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Mass Flow

for HMFW:

HTL Pilot Reactor Products

20 gallons of each feedstock at 20 wt% solids content were successfully processed, producing biocrude oil (top) and post-HTL wastewater (PHW, bottom). Samples were collected in sequence during the run.



HTL operation conditions:

- Temperature: 280 ± 20°C
- Retention time: 30 min
- Pressure: 1,800 psi

S	•	Feed rate	: 1	L/min
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Biocrude	HMFW	SDW
Carbon (wt%)	78.74	75.64
Hydrogen (wt%)	11.31	11.42
Nitrogen (wt%)	3.36	0.76
Oxygen (wt%)	6.46	12.16
Sulfur (wt%)	0.12	0.01
HHV (MJ/kg)	40.32	38.57
Mass yield (wt%)	47.06	52.19
Energy yield (%)	68.17	70.77
Carbon yield (wt%)	66.91	64.78

PHW	HMFW	SDW
COD (mg/L)	101,850	42,380
рН	5.3	3.5
Total nitrogen (mg/L)	8,725	349
Ammonia nitrogen (mg/L)	2,330	14.8

HTL Biocrude Characterization, Treatment, and Upcoming Work

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Pretreatment: Biocrude dewatered (ASTM D2892 Annex X1) to remove residual moisture

Hydrotreating: required to further upgrade biocrude oil (hydrogenate, deoxygenate, denitrogenate)

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MEC (microbial electrolysis cell) recovers high purity H₂ while degrading the organic pollutants in **PHW** (Post-hydrothermal liquefaction wastewater)



- Two types of PHW feedstocks were tested in MECs
- Lab batch reactors delivered consistent good COD removal



- New alloy cathodes were provided by PNNL and tested in MECs for H₂ production during PHW treatment.
- High H₂ production rate was up to 2.69 L/L/day in batch with Pt/CF, higher than commercial Pt/Ti electrode, (1.81 L/L/day).
- All cathodes had FE > 90%
- MEC energy consumption was < 30 kWh/kg H₂ 25% lower than abiotic water electrolysis







DOE Hydrogen and Fuel Cells Program Record, 2020







2D HSQC NMR along with HPLC on PHW analysis indicates the organic degradation process:

- Many signals in the saturated alkane region;
- Multiple signals exhibit carbonyl group and alkene group;
- Strong presence of HCO structures, indicating alcohols, polyols and ethers



2D HSQC NMR along with HPLC on PHW analysis indicates the organic degradation process in MEC:

Many signals in the saturated alkane region;

Multiple signals exhibit carbonyl group and alkene group;

Strong presence of HCO structures, indicating

alcohols, polyols and ethers



- Most easily degradable organics (VFAs, alcohols) in PHW were removed within a day.
- Glycerol mainly went through fermentation process, and produced 1,3-propanediol (1,3-PDO), ethanol, propionate
- Ethanol and VFAs can be both produced (via fermentation) and consumed in the MEC anode.

Heteroaromatics

confirmed by GC-MS



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- Organic/aromatic N species generated during HTL are new to conventional wastewater treatment
- To characterize the composition, solution state ¹⁵N NMR was successfully applied to wastewater for the first time
- Results indicated the major org-N form was heteroaromatics with pyridine-like N



NH₂

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2 – Progress and Outcomes – MEC tasks

To develop scaled reactors, literature review and system $_{\mbox{A}}$ design analyses were carried out.

MEC pilot studies categorized by reactor operation volumes, configurations, and anode substrates.







Through extensive literature review, our takeaways on constructing pilot MEC reactors:

- Current density is the key metric to be improved for MEC;
- Good conductivity (which PHW has) is a prerequisite to high current density;
- Lessons from electrolysis industry the best design should be easy to modularize, and minimize the electrical resistance between electrodes: compact & modular;
- Lessons from TEA: material for MEC should be low in price.







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2 – Progress and Outcomes – MEC tasks



- Another acrylic pilot reactor was assembled and is in operation (~ 80 L)
- Inoculation took 2-3 weeks
- Waiting for more PHW supply



2 – Progress and Outcomes - TEC

The H₂ production performance of base-group metals (BGMs) is better than that of Platinum-group metals (PGMs)

Full-Recycle. Continuous Flow Configuration. Filtered and 5X diluted PHW derived from food waste. COD ≈ 17,000 ppm.



BGM outperforms PGM by 2-5X at a fraction of the metal cost (\$0.30/oz Cu, \$6.5/oz Ni, and \$2,321/oz Pd). Energy Efficiency is ≥100% at low current (densities).

2 – Progress and Outcomes – TEC

The power requirement in TEC for H₂ production and kg of H₂ per kg COD or TC removed decreases with current

Full-Recycle. Continuous-Flow Configuration. Filtered and 5X diluted Food Waste-derived PHW with 0.1 M Na₂HPO₄/ NaH₂PO₄. COD ≈ 17,000 ppm



The current TEC electrode composition (and reactor configuration) is limiting the performance. Future experiments will focus on optimizing cathode composition to lower energy requirement for H₂ production.

2 – Progress and Outcomes – TEC/MEC

Sufficient H₂ can be produced with MEC, but yield is tied with PHW COD and bio-crude carbon yield

PNNL-Derived PHW scaled for 5 dry ton/day, 68.2 kg COD/h and 6.71 kg H ₂ /h needed						h needed	
System	COD Removal	Energy Cost for H ₂ Production	H₂ produced per COD Removed	Energy Efficiency 39.4 kWh/kg H ₂	Power Requirement	H₂ Produced For 100% COD Removal	H₂ Produced For 90% COD Removal
-	kWh/kg COD	kWh/kg H ₂	kg H ₂ /kg COD	%	kW	kg/h	kg/h
H ₂ O Electrolyzer	-	45 - 54	-	73 - 86	302 – 362	-	-
MEC	2.3	22	0.104	179	148	7.12 (0.41 excess)	6.40 (0.30 deficit)
TEC	12 - 35	68 - 91	0.136	43 – 59	456 - 611	9.30 (2.59 excess)	8.37 (1.66 excess)



MEC is >3 times more energy efficient than TEC to generate H₂ from wasted organic carbon in PHW.
MEC and TEC can be integrated to 1) provide a more flexible H₂ supply via water electrolysis and 2) decompose recalcitrant organic molecules (if any).

2 – Progress and Outcomes – TEA

Carbon and Nitrogen Flows of Integrated HTL / MEC System



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- HTL can efficiently convert 60% of the feed carbon to finished oil (SAF, diesel, naphtha).
- MEC has the potential to efficiently decrease aqueous COD level by converting organics in aqueous to CO_2 .



- HTL transfers the majority of N to HTL aqueous (PHW) and biocrude. N in aqueous mainly present in the form of **NH**₃ and a small fraction in organic N.
- MEC can convert about 70% N in aqueous to N₂.

2 – Progress and Outcomes – TEA

Carbon and Nitrogen Flows of Integrated HTL / MEC System

Carbon Flow:



- HTL can efficiently convert 60% of the feed C to finished oil (SAF, diesel, naphtha) and ~23% of the feed C in PHW.
- MEC has the potential to efficiently decrease aqueous COD level by converting organics in aqueous to CO₂.

- HTL transfers ~52% of feed N to HTL aqueous (PHW), mainly in the form of NH₃ (~14% feed N) and organic N (~38% feed N), such as pyridine-, indole-like aromatics and short chain amines.
- MEC can convert about **70% N** in aqueous to N₂.



2 – Progress and Outcomes - TEA

Carbon Conversion Efficiency (CCE) for Integrated HTL vs. Benchmark AD



Food Waste to Natural Gas as Vehicle Fuel (NGV) via AD:

- Food waste to raw biogas CCE is 29%-57% (average 41%)
- Food waste to NGV CCE range is 23%-46% (average 33%)

Food Waste to Finished Fuel via HTL:

- Data source: 9 food waste or food waste/sludge co-feed PNNL's bench HTL runs and continuous biocrude hydrotreater runs
- Food waste to biocrude CCE range of 58%-74% (average 65%, JBLM to biocrude: 66%)
- Food waste to finished oil CCE range of 52%-67% (average of 58%, JBLM to finished fuel: 59%)

Carbon Conversion Efficiency (CCE)						
Feedstock	Product	AD	HTL/MEC	Change		
Different FW Jusing the average CCE)	Intermediate (biogas/biocrude)	41%	65%	+58%		
	Final fuel (NGV/ liquid fuel)	33%	58%	+76%		
JBLM FW Jusing heoretical AD correlation)	Intermediate (biogas/biocrude)	44%	66%	+50%		
	Final fuel (NGV/ liquid fuel)	35%	59%	+68%		

2 – Progress and Outcomes - TEC Levelized Cost of Disposal (LCOD) for Integrated HTL/MEC System vs. AD

HTL/Optimized MEC, (with \$3/gge fuel price LCOD)





The optimized HTL/MEC system begins to compete with AD (to raw biogas) > 50 TPD scale

Levelized Cost of Disposal (LCOD) Breakdown for IntegratedHTL/MEC System

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2 – Progress and Outcomes - LCA

AD: Sorbitol

AD: Glucose

- LCA models for three systems were developed:
 - 1. Anaerobic Digestion (AD)

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- 2. Hydrothermal Liquefaction (HTL) with Upgrading
- 3. Hydrothermal Liquefaction, Upgrading, and T-MEC
- ➢ TRACI 2.1 quantifies the environmental impact of each system.







HTL + Upgrading: Hydrogen

2 – Progress and Outcomes - System Level Analysis

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System level optimization model: Water, Organics, CO₂, Buffer, NH₃ Legend High level framework to evaluate distinct system NH₃ configurations Process Unit Accounts for material and energy balances Water ٠ MEC Organics, Buffer CO₂ NH Source Considers different requirements Water, Organics, Buffer, CO₂, NH₃ Buffer Sink System level analysis: \succ TEC CO, H **HO** K Water. Organics, CO₂, ▶0-Inlet Port \cap Calculate key economic/environmental outcomes Water Buffer, NH₃ ٠ Outlet Port Identify operational and economic drivers Food HTL Waste Perform sensitivity analyses H_2 Biochar **▶** → 15 CO, CO2 10 Vapors H₂, CH Profit (USD / gal Jet Fuel) Wastewate CH₄ 5 Gasoline Heat Natural 0 CB Gas HDO Jet fuel **>** Biocrude Products Catalytic **→** → Distillation Hydrodeoxygenation Utilities -5 Heavy Diese Heat Base Case H_2 Electricity TBG ► -10 Electricity Heavy oil **►** Electricity 2 6 8 10 0 4 Jet Fuel Selling Price (USD / gal)

3 – Impact

 The carbon conversion efficiency (CCE) of food waste to HTL biocrude is ~50% higher than the CCE of food waste to biogas via AD.

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- The CCE of integrated HTL and upgrading to produce finished fuel is ~68% higher than AD and gas cleaning to produce natural gas for vehicle fuel.
- The MEC can provide the required hydrogen for biocrude upgrading with a COD removal efficiency >90%.
- The integrated HTL/MEC process with optimization is cost-competitive with AD above about 50 TPD scale.
- When demonstrated successful, this project will provide an integrated approach to advance DOE's goal of scaling up new technologies to produce sustainable aviation fuels (SAF).

Summary

- We have successfully met the milestones of the project, passed the intermediate review, and now we focus on system analysis, pilot system development and integration.
- Pilot HTL systems were built and operated, converted two types of food wastes to biocrude. Hydrotreating is underway to produce jet fuel.
- Both MEC and TEC can produce H_2 from the PHW and meet H_2 demand for bio-crude upgrading.
- The integrated HTL/MEC process with optimization can be cost-competitive with AD above about 50 TPD scale.

Quad Chart Overview

Timeline

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- Oct. 1, 2020 (contract signed April, 2021) ۲
- Sept. 30, 2024 ٠

	FY22 Costed	Total Award	Aim to 50% o > 25%
DOE Funding	637,372 (PU+UIUC) 433,567 (PNNL)	2,499,732	Fun
Project Cost Share *	624,933		FOA-
TRL a TRL a	t Project Start: t Project End: 4	2-3 1-5	Proje

Project Goal

Integrated food waste to biofuel pathway with synergistic aqueous waste valorization.

End of Project Milestone

o improve carbon conversion efficiency by > or reduce disposal costs of the food waste by

ding Mechanism DE-EE0009269

ect Partners*

- UUC
- NNL

Publications, Patents, Presentations, Awards, and Commercialization

- 1. Summers, Sabrina, Amanda Valentine, Zixin Wang, Yuanhui Zhang. 2023. Pilot-Scale Continuous Plug-Flow Hydrothermal Liquefaction of Food Waste for Biocrude Production. Fuel: Under review.
- Summers, Sabrina, Siyu Yang, Jamison Watson, Yuanhui Zhang. 2022. Diesel blends produced via emulsification of hydrothermal liquefaction biocrude from food waste. Fuel: https://doi.org/10.1016/j.fuel.2022.124817
- 3. Zhang, Y. 2022. Toward a Circular Bioeconomy: Environment-Enhancing Food, Energy, and Water Systems (EE-FEWS). Resource Magazine 29 (3):11-15.
- 4. Jiang, J., et al., Scale-Up and Techno-Economic Analysis of Microbial Electrolysis Cells for Hydrogen Production from Wastewater, Water Research, in review

Publications, Patents, <u>Presentations</u>, Awards, and Commercialization

- 1. Summers, Sabrina. 2023. Pilot-scale hydrothermal liquefaction of wet biowaste. American Chemical Society. Energy and Fuels Division, Presidential Symposium: Biorefinery at the Crossroads, Sci-Mix
- 2. Jiang, J., et al., Molecular Transformation and Metabolic Insights during MEC treatment of post-hydrothermal liquefaction wastewater (PHW), 2022 AEESP Conference
- 3. Oral presentation at Organic Reactions Catalysis Society. Developing Electrocatalytic Processes for the Conversion of Biomass-Derived Molecules into Fuels and Chemicals at Normal Temperature and Pressure, PNNL
- 4. Presentation. Organic Reactions Catalysis Society Meeting. Jacksonville, FL. October 2022. "Developing Electrocatalytic Processes for the Conversion of Biomass-Derived Molecules into Fuels and Chemicals at Normal Temperature and Pressure"
- 5. Presentation*. 241st Electrochemical Society Meeting. May 2022. "Electrocatalytic Oxidation of Biomass-Derived Carboxylic Acids into Fuels and Chemicals"
- 6. Presentation*. TC Biomass 2022, April 2022. "Renewable Fuel Production via Electrocatalytic Co-processing of Biomass-Derived Aqueous Waste and Bio-oils at Normal Temperature and Pressure"
- 7. Winner of National Lab Accelerator Pitch Event. Palo Alto, CA. November 2022 with the pitched titled, "Cleaning Wastewater for Energy Production and a Sustainable Future."
- 8. Seminar at Iowa State University titled "Developing electrocatalytic processes for the conversion of biomass-derived feedstocks into renewable fuels and chemicals"
- 9. "Electrocatalytic bio-oil and wastewater treatment" with IPID 31994-E has been licensed to CogniTek Management Systems, Inc. ("CogniTek")

Publications, <u>Patents</u>, Presentations, <u>Awards</u>, and Commercialization

- Joint invention disclosure with Princeton University titled "Integrated microbial and electrocatalytic process to generate H2 from wastewater at 100% energy efficiency (iEdison No. 0685901-22-0216)"
- Lopez-Ruiz won an award for Basic Energy Sciences Reaching a New Energy Sciences Workforce (BES-RENEW) Program to increase participation of underrepresented groups in clean energy research. The topic is "Controlling reaction pathways under the non-ideal conditions of seawater electrolysis"
- 2. Lopez-Ruiz won the "National Lab Accelerator Pitch Event November 16 in Palo Alto, CA" with the pitched titled, "Cleaning Wastewater for Energy Production and a Sustainable Future."
- 3. Lopez-Ruiz was nominated for "2022 EP&M Innovation in Research Team" and "2022 EP&M Operational Excellence" awards
- 4. Jerry Jiang won the best poster award in the 2022 AEESP Conference.

Additional Slides

(Not a template slide – for information purposes only)

- The following slides are to be included in your submission for evaluation purposes, but <u>will **not**</u> <u>be part of your oral presentation</u> –
- You may refer to them during the Q&A period if they are helpful to you in explaining certain points.

2 – Progress and Outcomes

We evaluate the performance of different electrocatalysts in a continuousflow through cell in single pass and full recycle configuration



Anode reactions:

Oxygen evolution: $H_2 O \rightarrow 1/2 O_2 + 2H^+ + 2e^-$ Organic oxidation: $2C_x H_y O_z \rightarrow C_{2(x-1)} H_{2(y-2)} O_{2(z-2)} + CO_2 + 2H^+ + 2e^-$ (via decarboxylation) $e.g., 2C_2 H_4 O_2 \rightarrow C_2 H_6 + 2CO_2 + 2H^+ + 2e^-$ Ammonia oxidation: $2NH_3 \rightarrow N_2 + 6H^+ + 6e^-$ Cathode reaction: H_2 evolution (HER): $2H^+ + 2e^- \rightarrow H_2$

The TEC can produce H_2 from organics as well as water; hence, it can be used to close the gap between H_2 gen from organic molecules and H_2 needed in upgrading.

2 – Progress and Outcomes

We evaluate the performance of different electrocatalysts in a continuous-flow through cell in single pass and full recycle configuration



- We evaluate the electrocatalytic cell performance as a function of electrochemical conditions:
 - Metals
 - Morphology/ particle size
 - Electrolyte compositions (pH, species)
 - Electrochemical reaction conditions (A, V)

$$H_2 Production Rates \left(\frac{kWh \cdot g_{metal}}{kgH_2}\right) = \frac{V \cdot i_T}{kgH_2/(g_{metal} \cdot h)}$$

Energy Efficiency (FE, %) = $\frac{H_2 \text{ High Heating Value}}{V \cdot i_T \cdot h} \times 100$ V: Full cell voltage; i_T: total cell current; h: operation time

We will compare H₂ production rates and energy efficiencies to that of competitive technologies

2 – Progress and Outcomes Results: Carbon Conversion Estimation for Benchmark Anaerobic Digestion System



- · Food waste to biogas process data is collected from literature
- Food wastes are collected from university canteens/cafeteria or local community; batch or semicontinuous mesophilic AD process
- Methane recovery rate of 80% is assumed for purifying raw biogas to NGV based on literature
- The theoretical carbon efficiency of JBLM to biogas is 52% using the Buswell equation¹

	Carbon Conversion Efficiency	Assumption
JBLM food waste to Biogas	44%	85% theoretical biomethane yield ¹
JBLM food waste to RNGV	35%	80% methane recovery rate in gas cleaning ²
		(1) Browne, et al. Applied Energy (2013). (2) Byun, et al. Energy (2021).

Baseline AD LCOD Assumptions

Economic Assumptions for LCOD calculation

	Variables	Values	Ref	
	Discounted rate	10%	User defined	
	Loan interest rate	5%	User defined	
	Tax rate	21%	User defined	
	Capital cost financed percent	90%	User defined	
	Project lifetime, year	30	User defined	
	Electricity Price, \$/kWh	0.07	EIA historic data ⁽⁴⁾	
	biogas yield, m3/metric ton	200	EPA AD model ⁽⁵⁾	
calorific value of biogas, kWh/m3		6.5	EPA AD model ⁽⁵⁾	
	CHP efficiency	35%	EPA AD model ⁽⁵⁾	
	surplus electricity for sell	80%	Ullah (2017) ⁽⁶⁾	
	CAPEX	CAPEX= 5.5519(Capacity)0.4642 ⁽¹⁾		
		$CAPEX = 0.01(capacity)^{0.6}$		
	OPEX	$OPEX = 0.094 Capacity^{(1)}$		
Ref:	(1) Khan, et al. Waste Management 48: 548–64. (4) https://w	ΟΓΕΛ ww.eia.gov/electricity/an	- 0.0015(<i>cupucity</i>) ^{-/}	

(1) Initial, et al. Practice management for one one
 (2) Murphy, et al. Renewable Energy 29(7): 1043–57.
 (3) all price in 2019 dollars.

(5) https://www.epa.gov/anaerobic-digestion/anaerobic-digestion-tools-and-resources (6) Ullah. Master Thesis. University of Alberta.

Responses to Previous Reviewers' Comments

- If your project has been peer reviewed previously, address 1-3 significant questions/criticisms from the previous reviewers' comments which you have since addressed
- Also provide highlights from any Go/No-Go Reviews

Note: This slide is for the use of the Peer Reviewers only – it is not to be presented as part of your oral presentation. These Additional Slides will be included in the copy of your presentation that will be made available to the Reviewers.