DOE Bioenergy Technologies Office (BETO)

Hydrogen, Hydrocarbons, and Bioproduct Precursors from Wastewaters Workshop

Enhanced Anaerobic Digestion and Hydrocarbon Precursor Production

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Meltem Urgun-Demirtas, Ph. D.
Argonne National Laboratory

Total Potential Energy at Municipal WWTPs

Basis	Thermal energy (MMBtu/ year)	Electric power (kWh/year)	Total energy potential (MMBtu /year)	Reference
1 MGD wastewater equates 26 kW of electric capacity and 2.4 MMBtu/day of thermal energy	3.52×10^7	9.11×10^9	6.65×10^7	EPA, 2011
Sludge energy content = 8,000 Btu/dry lb CHP electric efficiency = 30% CHP thermal efficiency = 40%	4.59×10^7	1.01×10^{10}	9.86×10^7	NACWA, 2010 EPA, 2006
Available: 190 MW Electric power 18,000 MMBtu/day Thermal energy Potential: 400 MW Electric power 38,000 MMBtu/day Thermal energy	2.04×10^7	5.17×10^9	3.81×10^7	EPA, 2011

Project Objectives

- Ultimate Goal: Transform negative-value or low-value biosolids into high-energy-density, fungible hydrocarbon precursors
  - Enhance anaerobic digestion of biosolids to produce biogas with ~90% methane content and hydrogen sulfide at nondetectable level (Task 1)
  - Develop a Comprehensive Waste Utilization System (CWUS) for production of hydrocarbon precursors from the anaerobic digestion of biosolids (Task 2)
- Enables sustainable production of biogas that is considered as a cellulosic biofuel under new RFS2 (EPA, July 2014)
  - Biogas competes with conventional natural gas
  - Reduce greenhouse gas emissions relative to petroleum-derived fuels
  - Reduce U.S. dependence on foreign oil
  - Over 99% of D3 RINs generated from biogas
- Addresses DOE's goals of development of cost-competitive and sustainable biofuels by advancing efficient production strategies for drop-in biofuels

Enhanced Anaerobic Digestion

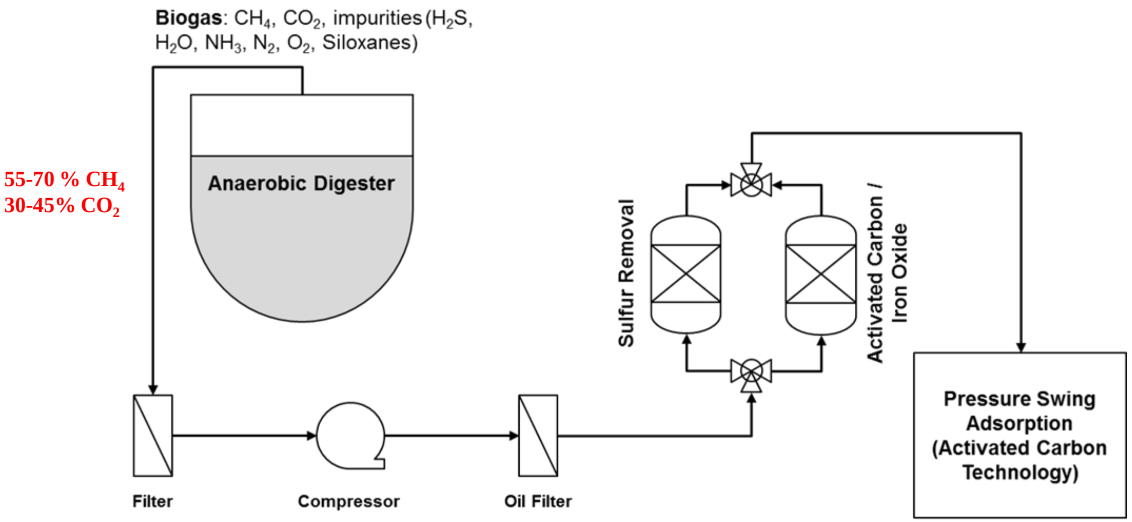
Waste-to-Energy: Why Biogas?

- Renewable sources for natural gas
  - Agricultural residues
  - Manure
  - Wastewater treatment
  - Landfill
  - Co-product in production of algal biofuels
- No competition with food and feed crops used for the production of other biofuels
- 7 days/24 hr production
- Low value materials
- It would displace the equivalent of 2.5 billion gallons of gasoline/year

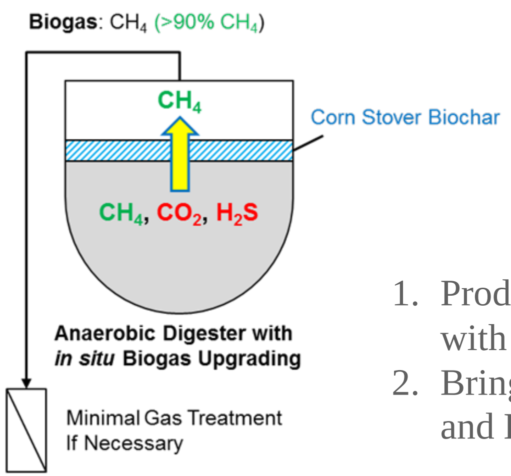
Deer Island WWTP (Boston, MA)

Project Overview

- Development and deployment of a novel AD process to produce biogas to qualify for D3 RINs (Task 1)



Conventional biogas upgrading: 20-72% of overall production cost



ANL's process
(U.S. Patent Serial No. 14/540,393)

1. Producing pipeline-quality biomethane via anaerobic digestion of sludge amended with corn stover biochar with in-situ CO_2 sequestration (*under review)*
2. Bringing It All Back to Nature: A New Process to Produce Renewable Natural Gas and High Fertilizer Value Products (*under review)*

Technical Approach

ANL's Patented Process
(US 8,247,009)
Accelerated weathering Ca/Mg rich rock sequester CO2 into carbonates

Bench-scale Testing
Serum bottles (FY14-15)

Biochemical Model TEA

Pilot-scale testing
14 liter Bioflo Fermenter (FY15-16)

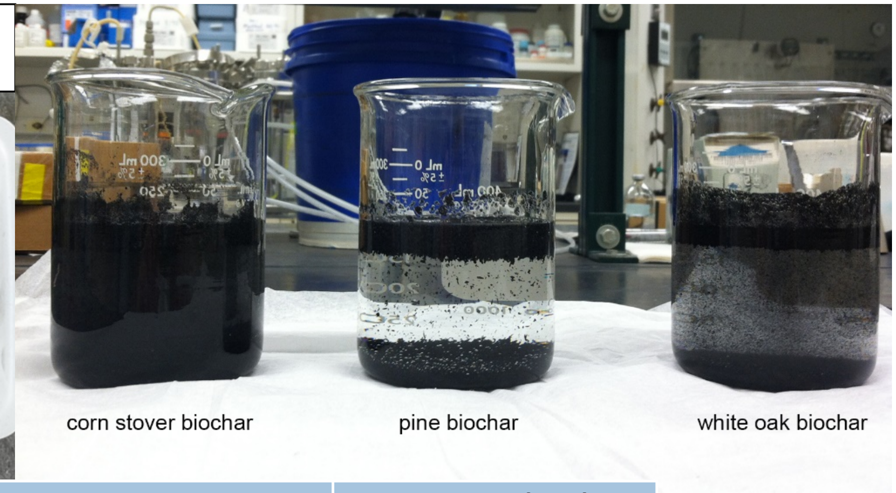
Biochemical Model TEA

Field-scale technology demonstration
Test at the field-scale digester (FY17)

Technology Deployment

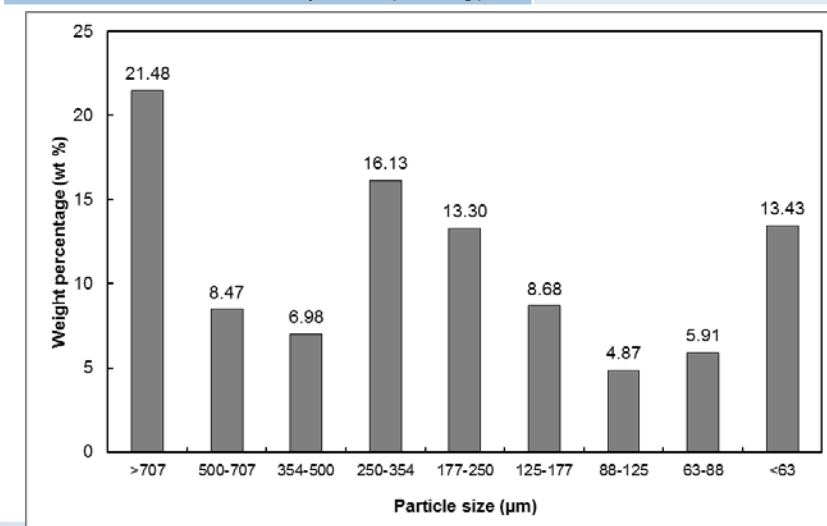
Not All Biochars are Equal!

Corn stover Pine White oak



Analysis	Content	Concentration
Proximate Analysis	Moisture	0.97 ± 0.05
	Ash	45.18 ± 0.40
	VM	7.18 ± 0.58
	FC	46.66 ± 086
Elemental Analysis of Ash	SiO_2	60.58 ± 0.58
	Al_2O_3	5.65 ± 0.10
	TiO_2	0.27 ± 0.01
	Fe_2O_3	1.93 ± 0.05
	CaO	3.87 ± 0.11
	MgO	4.23 ± 0.13
	Na_2O	0.74 ± 0.03
	K_2O	14.17 ± 0.15
	P_2O_5	2.19 ± 0.12
	SO_3	0.22 ± 0.06
	Cl	1.01 ± 0.02
	CO_2	1.17 ± 0.13

Property	Corn stover biochar
BET surface area (m^2/g)	105
Total volume of mesopores (cm^3/g)	0.02
Average diameter of mesopores (nm)	6.50
Total area of micropores (m^2/g)	315
Total volume of micropores (cm^3/g)	0.09



Summary

- Developed a novel process using biochar for producing biomethane at pipeline quality (>90% CH_4)
- A new paradigm of efficient and economical biomethane production for the AD industry
  - Both methane production and *in situ* sequestration of carbon dioxide and hydrogen sulfide take place in the same reactor
  - Facilitated CO_2 sequestration by up to 86.3% and H_2S removal (< 5 ppb), and boosted average CH_4 content in biogas by up to 30.1%
  - Enhanced AD performance
    - Methane yield, biomethanation rate and maximum methane production rate increased by up to 7.0%, 8% and 28%, respectively.
    - Increased alkalinity and mitigated ammonia inhibition, hence providing sustainable process stability
  - Increased fertilizer value of digestate
    - K, Ca, Fe and Mg in the biochar-amended digesters increased by 2000-4400% (corn stover), 122-273%, 60-134%, 43-95%, and 82-183%, respectively.

Hydrocarbon Precursor Production

Background

High cell density cultivation (Voss and Steinbuchel , 2001)

Fermentation	Batch	Fed-batch no. 1	Fed-batch no. 2	Fed-batch no. 3	Fed-batch no. 4	Fed-batch no. 5
Volume at the beginning[a] (l)	26	25	21	20	18	400
Volume at the end [b](l)	28	28	25	25	25	468
Media components added in total[c]						
Molasses[d] (g)	520	1,098	905	905	955	12,000
→Sucrose[e] (g)	→244	→516	→425	→425	→449	→5,640
Sucrose [f] (g)	–	781	1,867	2,311	2,820	14,648
$Na_2HPO_4 \cdot 12\ H_2O$ (g)	234	225	189	180	162	3,600
KH_2PO_4(g)	39	37	31	30	27	600
NH_4Cl (g)	52	92	192	215	286	2,000
$MgSO_4 \cdot 7\ H_2O$ (g)	5.2	5.0	11.5	12.5	18.0	80.0
$CaCl_2 \cdot 2H_2O$(g)	0.52	0.50	0.42	0.40	0.36	8.00
Fe(III)NH_4^+-citrate (g)	0.062	0.060	0.050	0.10	0.15	0.96
SL6 (ml)	2.6	2.5	2.1	4.5	6.8	40.0
Cell dry matter (g/l)	5.8	18.9	29.8	34.8	37.4	18.4
Σ Cell dry matter[g] (g)	162.4	529.2	745.0	870.0	935.0	8,611.0
Fatty acid content (% of CDM)	9.6	14.9	28.1	43.9	51.9	38.4
Σ Fatty acids[h] (g)	15.6	78.9	209.4	382.0	485.3	3,306.6
Yield (CDM $sucrose^{-1}$) (%)	66.6	40.8	32.5	31.8	28.6	42.4
Yield (fatty acid $sucrose^{-1}$) (%)	6.4	6.1	9.1	14.0	14.8	16.3

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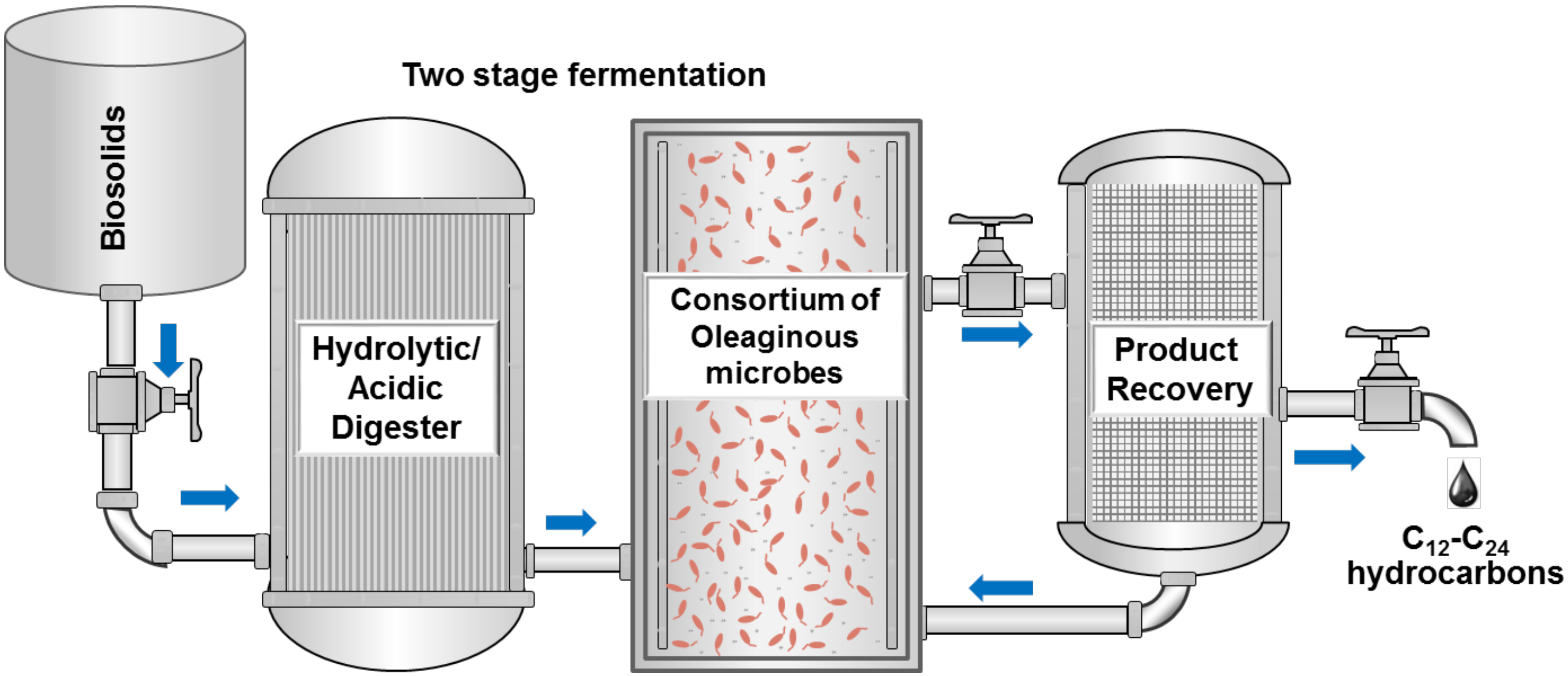
Introduction

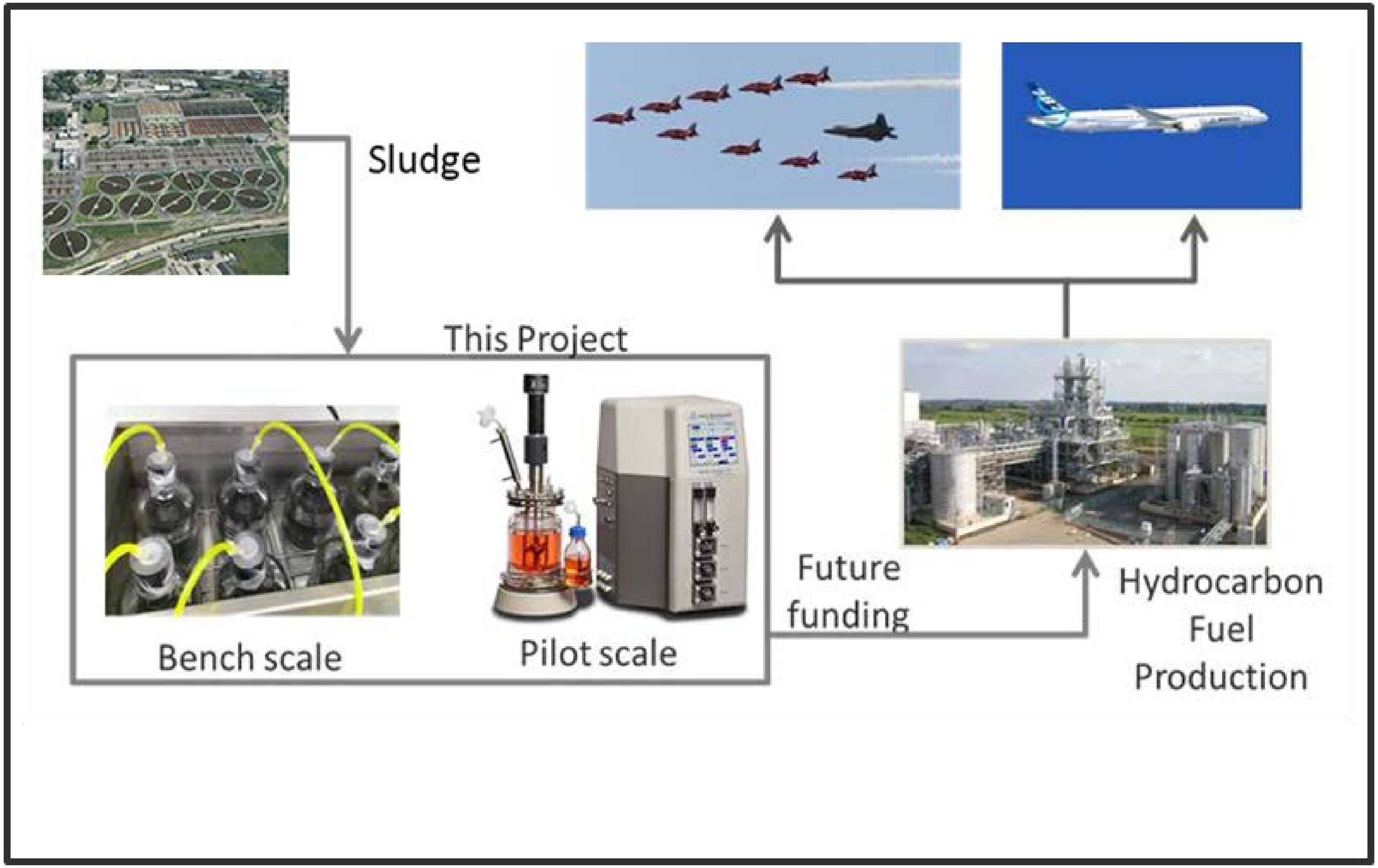
- Conversion of biosolids to hydrocarbon precursors would be
  - capable of displacing the equivalent of ~ 450 million gallons of gasoline per year
  - reduce US dependence on foreign oil, increasing energy security, and mitigating climate change.
- Such an integrated assessment and technology R&D project generating hydrocarbon precursors using CWUS has not been investigated before.

Project Overview

- Development of a low-cost process to produce hydrocarbon fuels



Technical Approach

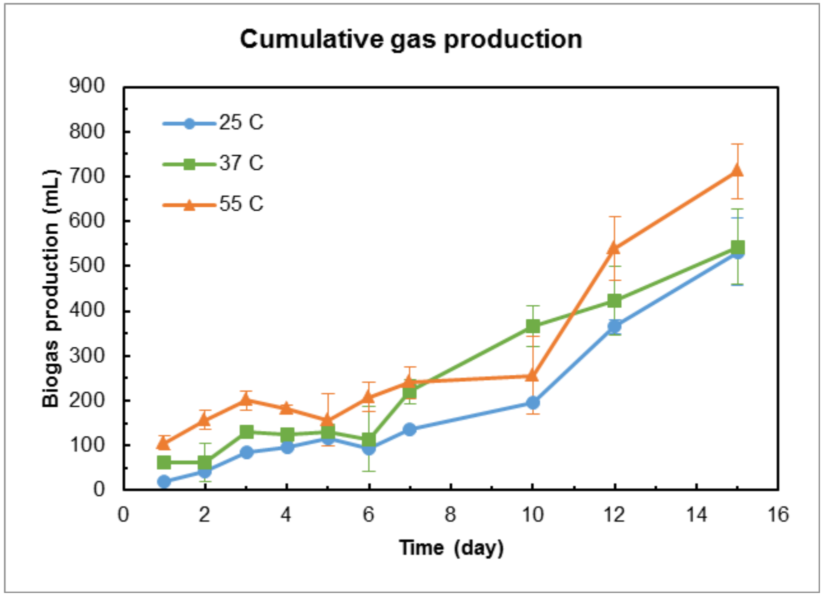


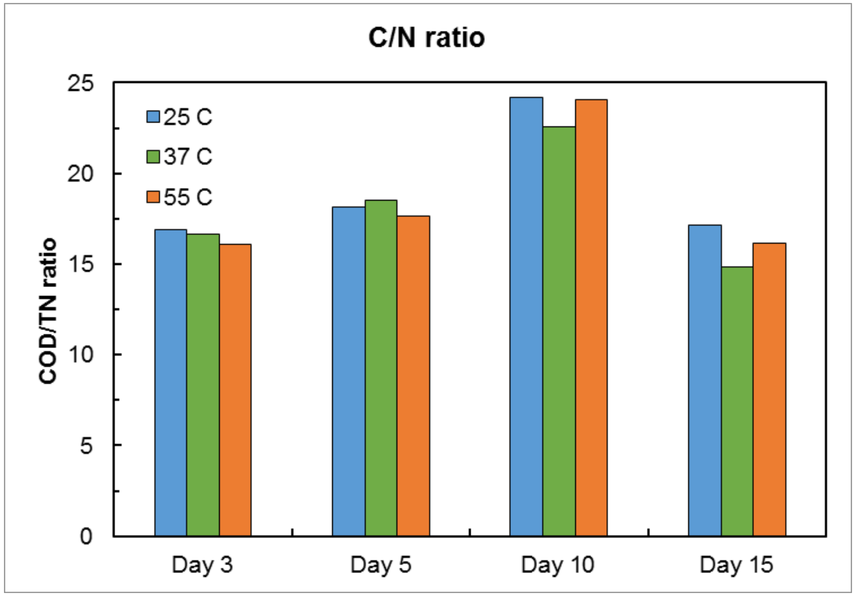
Results

- Identified and obtained most promising oleaginous microorganisms
- Completed initial short AD screening experiments
- Developed analytical methods for VFA (GC/FID) and FAME (GC/MS)
- Started testing of oleaginous microorganisms growth on digestate permeate

Strain	**Growth temp.**
***Apiotrichum curvatum* ATCC20509 (yeast)** ***Trichosporon oleaginosus* ATCC20509 (yeast)**	20°C to 25°C
***Lipomyces starkeyi* ATCC58680 (yeast)**	25.0°C
***Mortierella isabellina* ATCC38063 (fungus)**	24.0°C
***Mucor circinelloides* ATCC1216B (fungus)**	24.0°C
***Rhodosporidium toruloides* ATCC10788 (yeast)**	25.0°C
***Rhodotorula glutinis* ATCC204091 (yeast)**	25°C to 30°C
***Yarrowia lipolytica* ATCC20460 (yeast)**	20°C to 25°C
***Rhodococcus wratislaviensis* (bacteria)**	28^0 C
***Pseudomonas aeruginosa* (bacteria)**	37^0 C
***Rhodococcus opacus MITXM-61* (bacteria)**	28^0 C

Results





- First trial experiments showed that short AD operation should be less than 10 days.
  - Biogas productions starts to ramp up after 7 days
  - C/N ratio decreases after 10 days
- Second trial experiments needs to be conducted up to 7 days to minimize the biogas production.

Future Work

- Establish the links between feedstock characteristics, microbe community structure and environmental and economic impact on fuel production
- Develop the mathematical model to understand the complexities in the bioreactor environment
- Evaluate pathways to piloting and scale up the process.
- Complete techno-economic assessment of the process

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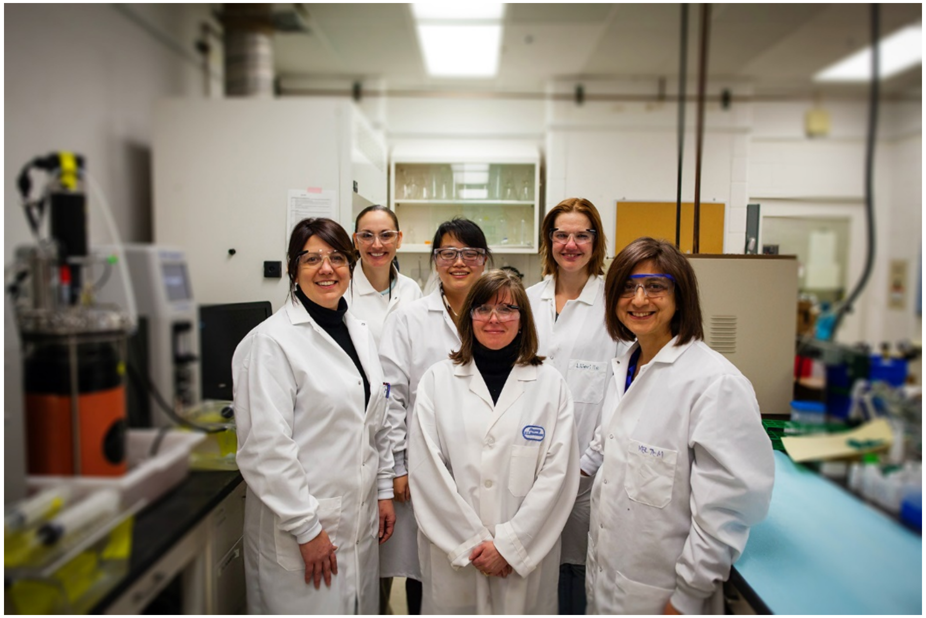

ANL Waste-to-Energy Group