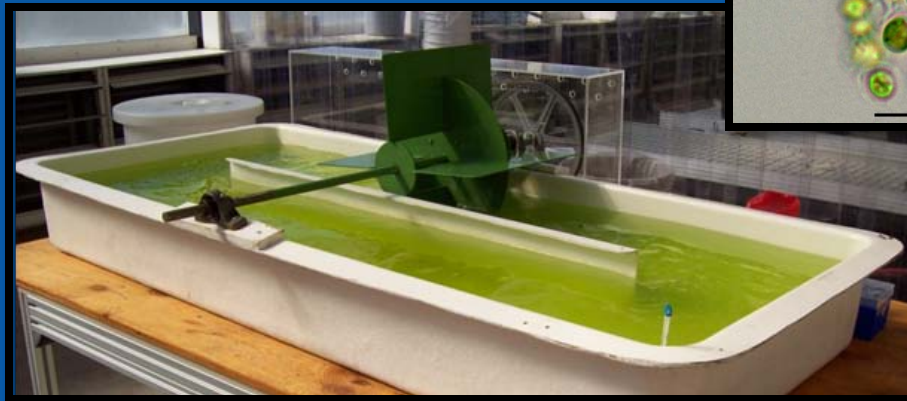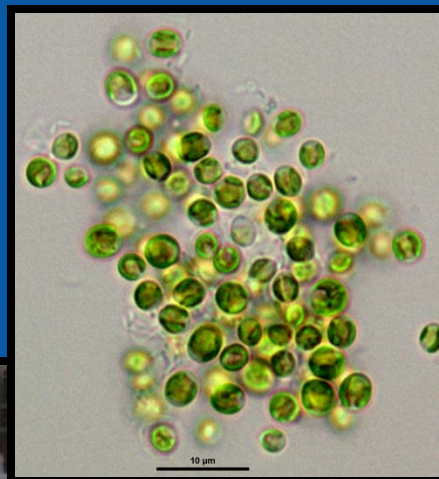# Efficient Use of Algal Biomass Residues for Biopower Production with Nutrient Recycle

May 20, 2013
Algae Peer Review

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Goal Statement

- The goal of this project is to advance the economic viability of algal biofuels by filling knowledge gaps on the conversion of algal residues to biogas/biopower *via* Anaerobic Digestion (AD)

- Specific objectives include:

  - *Optimize biogas production from spent microalgae to increase potential levels of biopower production.*

  - *Understand fate of nitrogen and phosphorous and test nutrient recycle to support algal growth.*

  - *Generate meaningful yield/retention time data using scaled-up reactors and assess the impacts on the process economics and life cycle analysis.*

Overview

Timeline

Start: Oct. 1, 2010
End: June 30, 2013
95% Complete

Barriers

- Im-F. Cost of Production
- Bt-K. Biological Process Integration
- Ft-B. Sustainable Production
- Ft-N. Algal Feedstock Processing

Budget

Total: $900,000
FY11: $219,000
FY12: $447,000
FY13: $234,000
No ARRA Funding

Partners

Collaboration (subcontract) with
        Washington State University --
        Dr. Shulin Chen and
        Dr. Craig Frear
Interactions with Dr. Ed Frank,
        Argonne National Laboratory

Project Overview

- Concept of using AD to produce biogas/biopower from whole algae or algal residues has been around since the 1950's (Golueke, Oswald, Benemann)

- For lipid pathway, need to gain value from 50%+ of biomass remaining after extraction

- AD provides opportunity to convert most of remaining fixed carbon to biogas (mostly methane and CO_2) for power generation

- Potentially allows recycle of carbon and inorganic nutrients (N and P)

- The purpose of this project is to provide real-world data on the feasibility of this concept (yields, loading rates, retention times, inhibitors, N and P recycle)
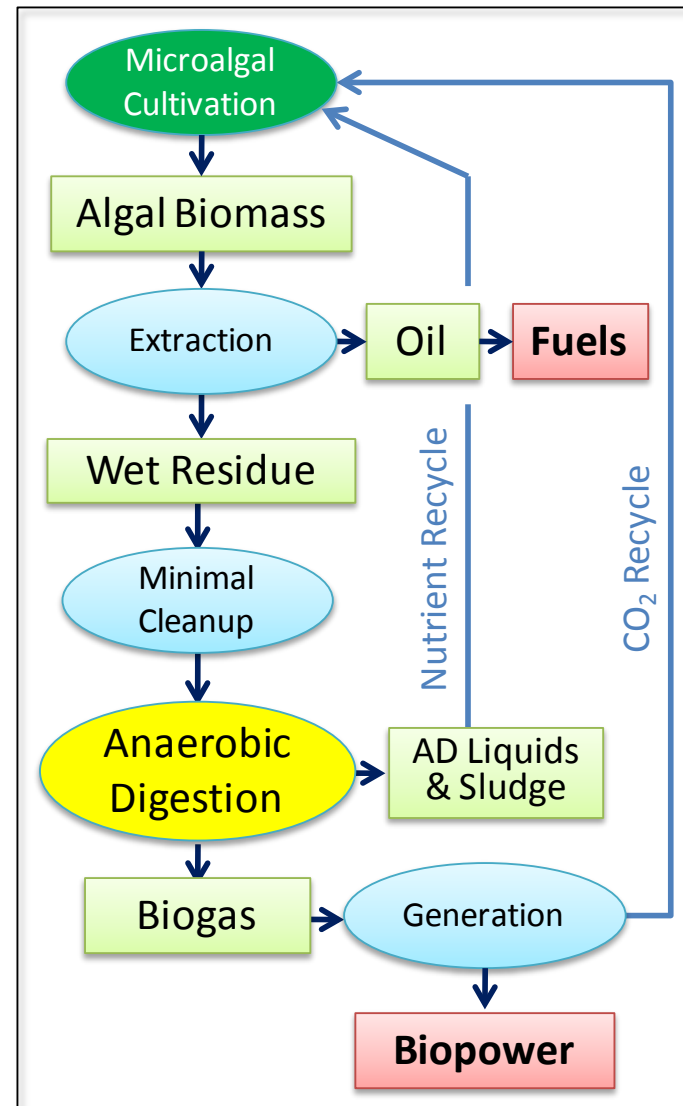
1 - Approach

Project organized into five tasks:

A. Generation/acquisition of microalgal biomass and lipid extraction

B. High-throughput testing for biogas optimization (WSU)
   - Biochemical Methane Potential (BMP) experiments
   - Explore species, AD inoculum, organic loading rate, etc.

C. Scale-up to multi-liter AD reactors (WSU)

D. Characterize AD effluent (N and P), explore pre-treatments, test ability to recycle nutrients for phototrophic algal growth

E. Test impacts of AD data on algal biofuels techno-economic (TE) and life cycle analyses (LCA)

Six Milestones, including key metrics such as:

- Continuous-flow AD reactor runs demonstrating stable biogas production over ≥30 days with ≥50% conversion of incoming volatile organic carbon

- Demonstrate ≥20% replacement of chemical nitrogen with <10% impact on growth rate

2 - Technical Accomplishments

Task A: Feedstock Development

- Goal to test genetically diverse species to ensure broadly applicable conclusions

  - Eustigmatophyte: *Nannochloropsis* sp. (Seambiotic)

  - Green alga: *Chlorella vulgaris* UTEX 395 (NREL hanging bags)

  - Diatom: *Phaeodactylum tricornutum* CCMP632 (NREL greenhouse ponds)

- Based on feedback from previous Peer Review, expanded to two additional industrial strains available in large quantity (extracted and non-extracted)

  - *Nannochloropsis salina* from Solix Biosystems Coyote Gulch facility (CO)

  - *Nannofrustulum* sp. from Cellana (HI)

Credit: Solix (Coyote Gulch facility)

2 - Technical Accomplishments

Task A … Feedstocks Studied

- Extracted oil to mimic process-derived algal residues (LEA)
- All algal biomass characterized for:
  - Elemental analysis
  - Total solids, volatile solids, fixed solids
  - Macromolecular components—lipid, protein, carbohydrate

Species	Source	Scale	Extraction	Lipid	Protein	Carbs
Nannochloropsis sp.	Seambiotic	kg	N1 – Whole cells	10.6	34.0	7.6
			N2 – Hexane:IPA	3.0	32.7	9.6
Chlorella vulgaris	NREL	100 g	C1 – Whole cells	9.8	35.1	16.9
			C2 – Hexane:IPA	2.8	39.0	12.2
Phaeodactylum tricornutum	NREL	100 g	P1 – Whole cells	7.6	26.5	19.0
			P2 – Hexane:IPA	6.1	32.5	16.1
Nanofrustulum sp.	Cellana	kg	NF1 – Whole cells	13.0	12.5	9.0
			NF2 – Methyl pentane	2.6	8.7	11.0
Nannochloropsis salina	Solix	kg	NS1 – Whole cells	37.2	17.2	11.5
			NS2 – Hexane	11.8	26.7	17.0

2 - Technical Accomplishments

Task B: AD Optimization (BMP Assays)

- Biochemical Methane Potential (BMP) assays conducted in16-cell automated system, 250 mL flasks, 35°C, 100 rpm mixing, online gas monitoring, ~3 week runs, triplicates

- Inoculum from anaerobic sludge from a waste water treatment plant or a dairy manure digester (preferred)

- Tested many parameters including:

  - Algal species

  - Lipid extracted *vs*. whole cells

  - Extraction solvent type

  - Pretreatments

  - Inoculum source

  - Solids loading
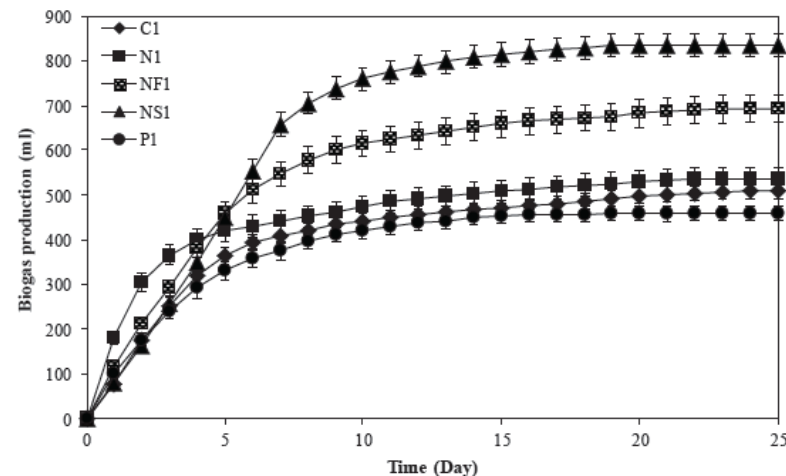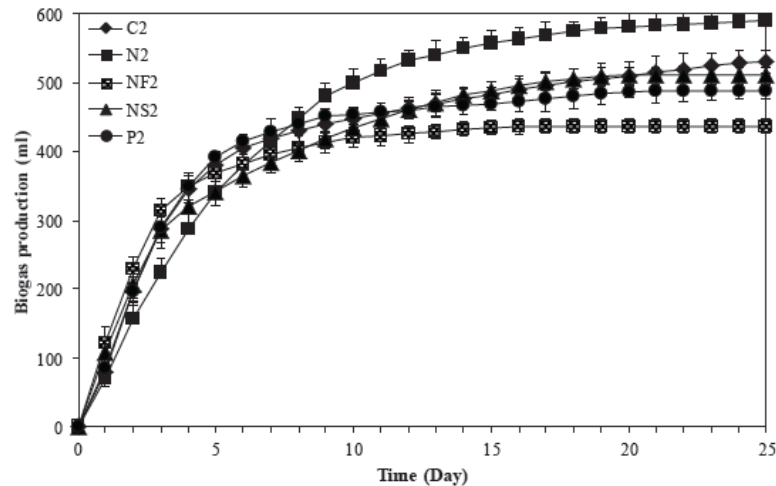
  - Inoculum:substrate ratio

2 - Technical Accomplishments

Task B … Highlights of BMP Studies

- Conditions were found under which all ten feedstocks digested well
- Lower loadings (higher Inoculum:Substrate ratio) gave better results

- Overall yields were good, ranging from 0.3-0.6 L CH_4/g VS fed (consistent with literature numbers)
- Best yields were with whole biomass (*e.g.*, 0.38 *vs.* 0.56 L/g for *N. salina*)
- Yields correlated to lipid content
- Volatile solids reduction 60-78%
- Max rates (initial slopes) quite good
- 60-75% of biogas consisted of methane
- 6-14 days to 95% digestion
- **No serious issues of ammonia toxicity, C/N ratios, or cell wall recalcitrance**

2 - Technical Accomplishments

Task B … Other Findings

- Methanogenesis was inhibited in Bligh-Dyer extracted material (chloroform carryover even after extensive drying)
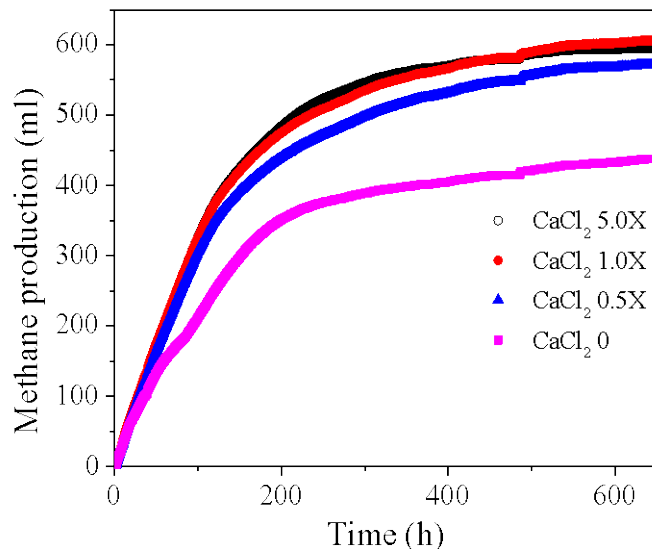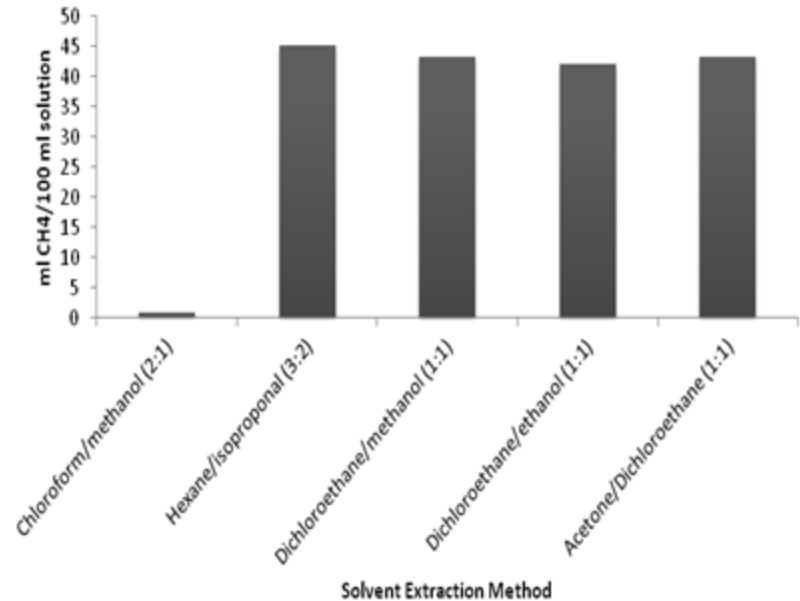
- Calcium dosing enabled higher methane productivity
- Thought to be due to prevention of Long Chain Fatty Acid (LCFA) inhibition on cell surfaces

2 - Technical Accomplishments

Task C: AD Scale-Up

- Critical for industrial relevancy; continuous reactor conditions quite different from BMPs

- Sequencing Batch Reactors (WSU)

- 5 L scale, 35°C, 20 day retention time, 0.2 L/day flow rate, mixed 10/120 min, OLR 0.5-5 g VS/L/day

- Used *N. salina* feedstock from Solix, compared extracted and non-extracted (NS1, NS2)

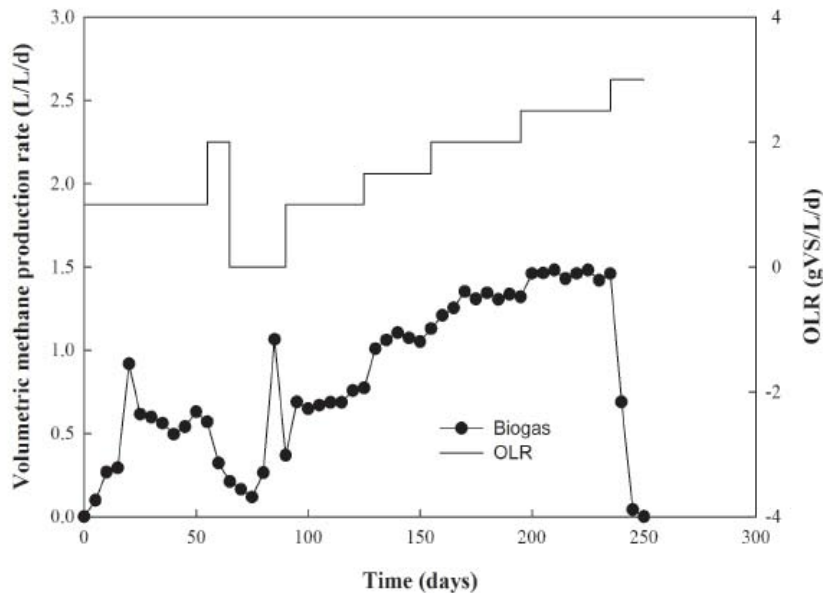- Following initial failures, success with slow ramp-up of OLR

2 - Technical Accomplishments

Task C … Scale-Up Results
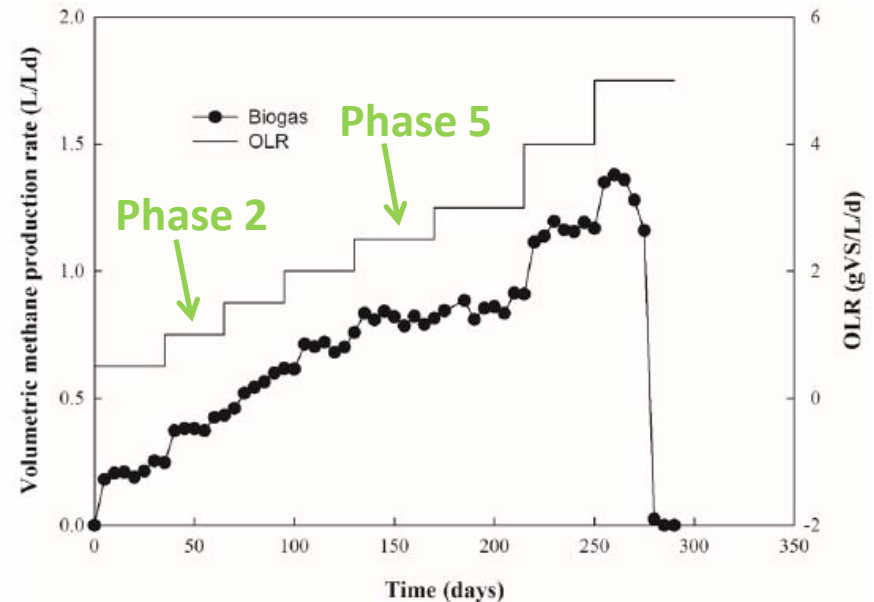
NS1 (whole *N. salina*):
OLR 1.0 -> 2.5 g VS/L/d
Yields 0.65 -> 0.59 L/g VS
VS destruction 75 -> 76%

NS2 (extracted *N. salina*):
OLR 0.5 -> 5.0 g VS/L/d
Yields 0.42 -> 0.28 L/g VS
VS destruction 73 -> 68%

- Long periods of stable performance
- Biogas yields and solids reduction consistent with BMPs
- Destruction of volatile solids exceeded Milestone target of >50%

2 - Technical Accomplishments

Task D: Nutrient Recycle Testing

Effluent Characterization

- Utilizing Phase 2 and Phase 5 from NS2 (Solix's lipid-extracted *N. salina*) continuous digester

- Separated into liquid and solid fractions by centrifugation

- Full elemental, Total Ammonia Nitrogen (TAN) and Total Kjeldahl Nitrogen (TKN) analyses

	Feed Solids Content g/L	Feed Nitrogen Content g/L	Feed Phosphorus Content g/L	Input N Recovered in Liquid Effluent as TAN %	Input N Recovered in Liquid Effluent as TKN %	Input P Recovered In Liquid Effluent as TP %
Phase 2	22	1.2	0.24	32	57	40
Phase 5	56	3.1	0.62	30	81	26

2 - Technical Accomplishments

Task D: Nutrient Recycle Testing

Growth Assays for Nutrient Recycle

- *N. salina* CCMP1776 used for studies (same strain grown by Solix)
- Strain utilizes NH_4 well, but higher than 1.5-2.0 mM inhibitory
- Growth studies in shake flasks, some 1 L Roux bottle studies

- Toxicity of liquid effluent not a problem
- Opacity not a problem
- Able to completely replace chemical NH_4 with effluent with no negative impact on growth (surpassing Milestone target of ≥20% replacement with <10% growth impact)
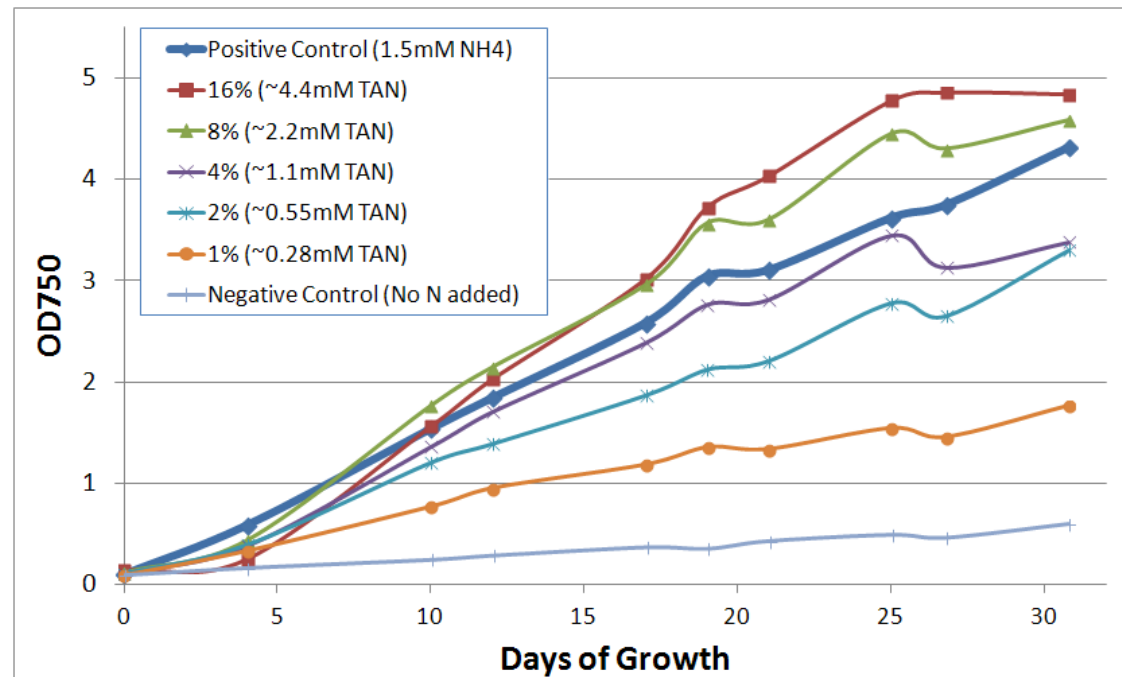
2 - Technical Accomplishments

Task E: Techno-Economic and Life Cycle Analysis
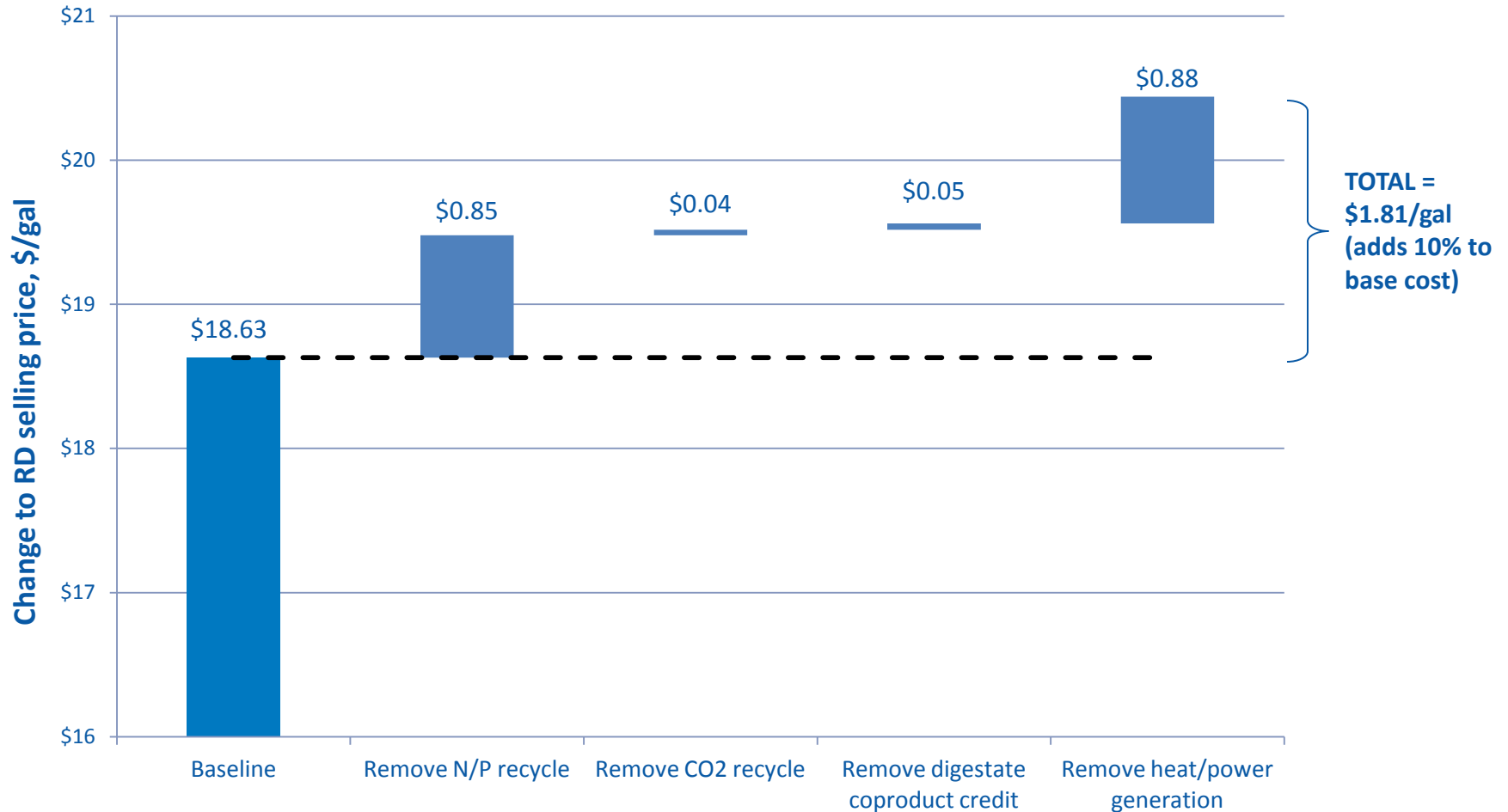
TOTAL = $1.81/gal (adds 10% to base cost)

*Basis = NREL TEA model, 13 g/m²/d, 25% oil content (http://www.nrel.gov/docs/fy12osti/55431.pdf)

2 - Technical Accomplishments

Base case AD assumptions:
- 0.3 L CH_4/g TS
- 75% N recycle
- 50% P recycle
- 100% flue gas recycle
- Power coproduct reduces total electricity demand/ heat integration negates need for external heat

Change to RD selling price, $/gal (base = $18.63/gal)

Basis = NREL TEA model, 13 g/m^2/d, 25% oil content (http://www.nrel.gov/docs/fy12osti/55431.pdf)
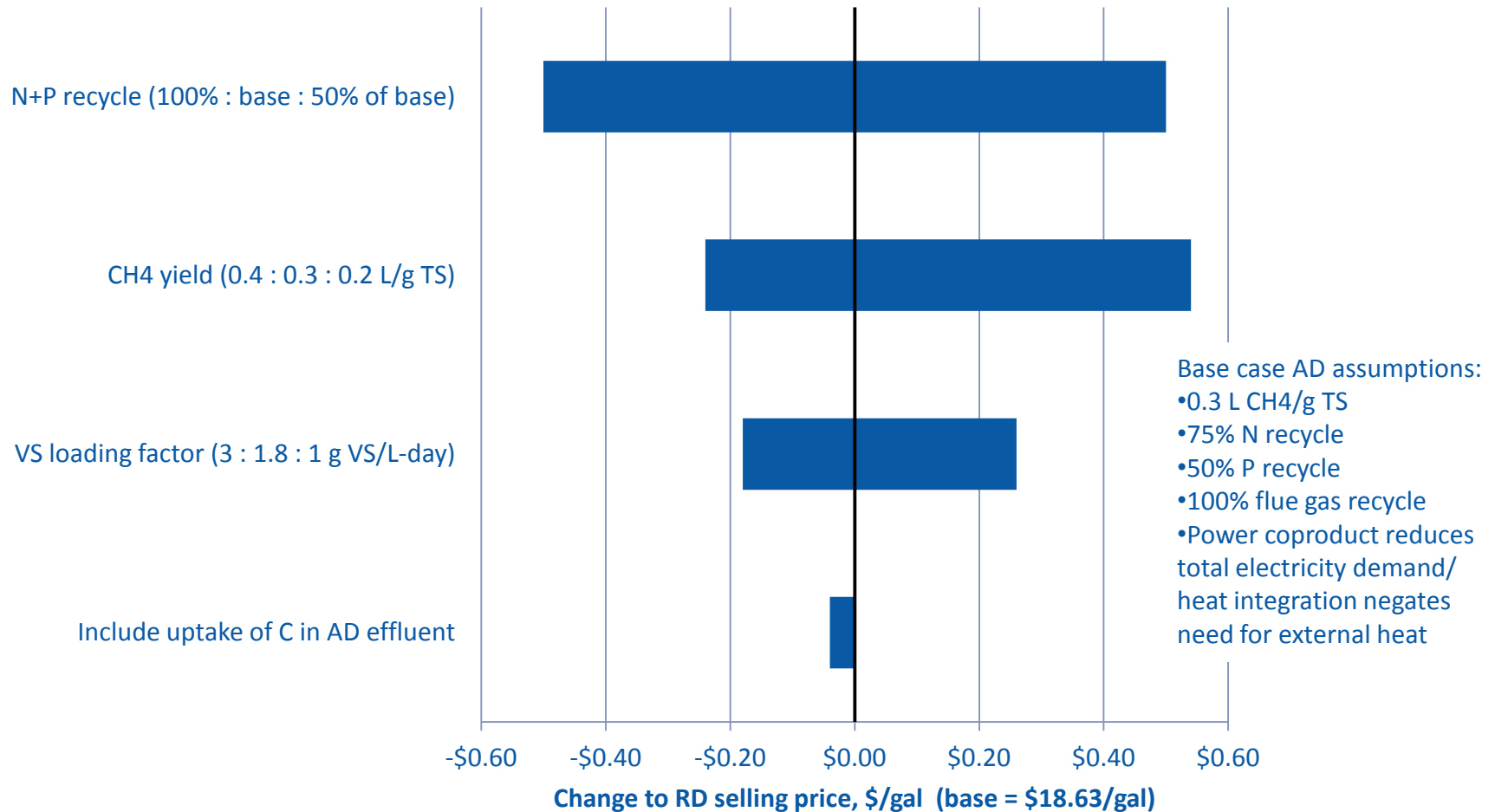
3 - Relevance

- Economic viability of fuels from algae requires gaining value from the remaining 50+% of the biomass stream after lipid extraction

- AD for biogas/biopower is a generic process, and we have helped to demonstrate applicability across disparate, industrially-relevant algal species

- Optimization of AD lowers overall cost of producing algal biofuels

- We have demonstrated yields and retention times to help justify current assumptions in cost modeling

3 - Relevance, cont…

- Nitrogen recycle has been shown to be feasible

- Helps to address fertilizer, energy, and CO_2 inputs for algal cultivation

- Publication of results will provide important data to the algal biofuels industry and will help provide confidence to industry around this process component

- This work provides a basis for comparison to competing residue utilization pathways

4 - Critical Success Factors

Success Factors:

- For biopower to become a commercially viable co-product of algal biofuels production, three factors are important:
    1) Sufficient yield of biogas (overcome cell wall recalcitrance and inhibitors such as ammonia) – *demonstrated for five species (no issues of recalcitrance, ammonia inhibition)*
    2) Moderate capital costs (primarily a factor of retention time) – *moderate retention times demonstrated*
    3) Efficient recycle of nitrogen and phosphorous (bioavailability) – *effluent can replace chemical nitrogen input*

Challenges:

- Co-product (biogas/biopower) value is low (but infinitely scalable)
- Other co-product pathways may be more attractive (but potential synergies between AD and SABC, HTL, etc.)
- Every algal feedstock will be different (but this work provides optimism for AD of any feedstock)

5 - Future Work

Work planned through end of project:

1) Wrap up nutrient recycle experimentation

2) Further Techno-Economic Analysis, sensitivity studies (Milestone)

3) Interact with Argonne regarding Life Cycle Analysis

4) Prepare Final Report

Possible follow-on work:

1) Interface with alternative pathways

   a) Leverage SABC project (feedstocks, fermentation residues)

   b) HTL process residues

2) Investigate other industrial algal feedstocks, possible additional challenges (solvent carryover, salt levels, etc.)

3) Explore mobilization of non-ammonia nitrogen in effluent

Summary

Relevance

- Commercial success of algal biofuels will require co-products of sufficient value and market size -- AD for biopower holds promise

Approach

- Biogas production was optimized for five species, one feedstock was scaled up, nutrient recycle was demonstrated, and results are being used to inform TE and LCA models

Technical accomplishments

- Many of the anticipated challenges were not encountered; AD of algal residues was quite successful on the five species tested
- Scale-up demonstrated long-term, stable performance and good biogas yields, supporting moderate cost assumptions

Success factors and challenges

- Need to integrate with potentially more lucrative co-product pathways

Summary

Technology transfer and future work

- Data are being freely shared to benefit the entire algal biofuels community
  - Algae Summit presentation, at least two more planned
  - Three journal articles in development, at least one more planned

Thank you to….

- The BETO Algae Team (Dan Fishman, Joyce Yang, Christine English, Christy Sterner, Kristen Johnson)
- NREL: Ryan Davis, Lieve Laurens, Nick Sweeney, Will Long, Stefanie Van Wychen, Phil Pienkos, and Adam Bratis
- WSU: Craig Frear, Baisuo Zhao, Jingwei Ma, Quanbao Zhao, and Shulin Chen
- ANL: Ed Frank

Additional Slides

Responses to Previous Reviewers' Comments

Reviewers' Comments	Response
The reviewers suggested that we not spend time and resources at NREL generating algal biomass, but rather obtain it from industrial sources.	The NREL production of *C. vulgaris* and *P. tricornutum* added diversity to the feedstocks tested. However, this was good advice, and we reached out to Cellana and Solix for additional feedstocks, which proved very valuable to the project.
One reviewer was concerned that we had not sufficiently accounted for previous work in the literature on AD of microalgae.	There are a fair number of studies in the literature on AD of microalgae. However, in general those studies are lacking in process relevancy (for example, looking at intact rather than lipid-extracted algae). The broad scope of species, the time scale of our continuous digestions, our nutrient recycle studies, and our focus on application to techno-economic modeling set this project apart from previous work.
One reviewer asserted that "AD of defatted microalgae biomass won't produce much methane (relative to CO_2) unless you add in added carbon."	This actually highlights one of the valuable contributions of this project, in that we were able to demonstrate quite good methane yields from all five defatted algae types tested. The lowest fraction of methane in biogas observed was 59%, which is still quite acceptable. This is only one of the anticipated problems that either was not encountered or was overcome through careful optimization.

Publications and Presentations

<u>Manuscripts in preparation</u>:

1) Zhao, B., Ma, J., Zhao, Q., Laurens, L., Jarvis, E., Frear, C. Anaerobic digestion of whole and lipid-extracted microalgae from five industrial strains—Determination of important methane and nutrient information. Applied Energy.

2) Ma, J., Zhao, Q., Laurens, L., Jarvis, E., Frear, C. Continuous anaerobic digestion of whole cell and lipid-extracted microalgae biomass in sequencing batch reactors—Methane and nutrient production with microbial population shifts. Bioresource Technology.

3) Zhao, Q., Yu, L., Ma, J., Laurens, L., Jarvis, E., Frear, C. Kinetic model for long-chain fatty acid (LCFA) degradation in microalgae, both whole cell and lipid extracted. Bioresource Technology.

<u>Conference Presentations</u>:

1) Frear, C., Zhao, B., Zhao, Q., Ma, J., Pienkos, P., Laurens, L., Sweeney, N., Davis, R., Nagle, N., Jarvis, E. 2012. Anaerobic digestion of algal biomass residues with nutrient recycle. Algae Biomass Summit, September 24th-27th, 2012, Denver, Colorado, USA.

2) Frear, C., Zhao, B., Zhao, Q., Ma, J., Pienkos, P., Laurens, L., Sweeney, N., Davis, R., Nagle, N., Jarvis, E. 2013. Anaerobic Digestion of Whole and Lipid-Extracted Algal Biomass from Four Industrial Strains--Determination of Important Methane and Nutrient Information. ASABE National Conference, July 22th-24th, 2013, Kansas City, MO, USA.

3) Ma, J., Zhao, Q., Laurens, L., Jarvis E., Nagle, N., Frear, C. Anaerobic digestion of whole and lipid-extracted algal biomass—Continuous digestion in sequencing batch reactors. Algae Biomass Summit, September 30th-October 3rd, 2013, Orlando FL, USA (submitted).

Supporting Data