Aug 20th, 10:10 AM - 10:35 AM

Biofuels-biomass group NV-REC

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Outline

- Task 1.1 Hydrothermal pretreatment of woody biomass
- Task 1.2 Thermal treatment of biomass
- Task 1.3 Algal-based biofuels
- Task 1.4 Chemically promoted mechanical dewatering of wastewater sludge

Tasks 1.1/1.2- Hydrothermal/thermal Pretreatment of Woody Biomass

- **Participants**
  - Faculty: Chuck Coronella, S. Kent Hoekman, Victor Vasquez, and Barbara Zielinska
  - Postdocs: Wei Yan, Amber Broch, Curt Robbins
  - Graduate students: Toufiq Reza, Tapas Acharjee, Joan Lynam,
- **Builds off prior collaborative project with GTI and DRI**
- **Treat lignocellulosic biomass with hot compressed water or heat to produce carbonized solid with increased fuel value, reduced oxygen content**

Background and Introduction

- **Lignocellulosic biomass is a promising feedstock for production of heat, chemicals, fuels, and electrical power**
- **Large diversity biomass sources**
  - Wood – forest waste, deliberate crops
  - Agricultural waste – corn stover, rice straw, others
  - Grasses – switchgrass, miscanthus, others
  - **Other – green waste, municipal solid waste, etc.**




Thermal Conversion of Biomass

- **Three main approaches:**
  - Combustion → heat and electrical power
  - Gasification → syngas → fuels
  - Pyrolysis → pyrolysis oil → upgraded oils
- **Large diversity of biomass sizes, shapes, compositions, and other parameters**
  - **Difficult to use different feedstocks in a single thermal conversion unit**




Purpose of Pre-Treatment

- **Three main objectives:**

1. **Homogenize feedstocks**
   - Reduce handling difficulties
   - Convert multiple materials into a single feedstock
2. **Increase energy density**
   - Raw biomass contains about 40% oxygen
   - Higher energy density reduces transportation costs
3. **Improve storage stability and logistics**
   - Address seasonality of some feedstocks

- **Overall Goal: Convert biomass into biochar that resembles low grade coal**

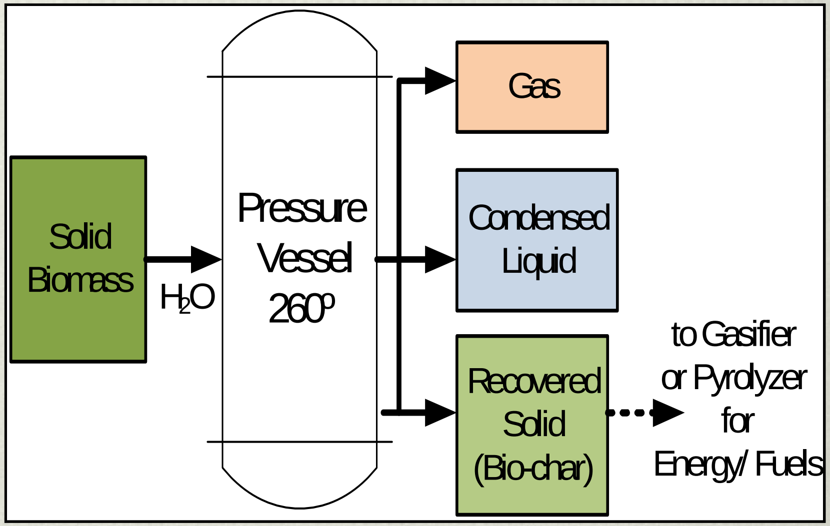
Biomass Pre-Treatment Processes

- Many different pre-treatment processes have been developed. Two are of interest here:

1. **Torrefaction**
   - Mild form of pyrolysis
   - Dry conditions, low O_2 levels

2. **Hydrothermal Carbonization (HTC)**
   - Also known as wet torrefaction
   - Treatment in hot, pressurized water
   - Produces gases, liquids, and solids

HTC Process



HTC Laboratory Process and Products

- **Process conditions:**
  - 2-L Parr pressure reactor
  - Water/Biomass ratio > 4/1
  - Temperatures: 220-280^{o}C
- **Reaction Products**
  - Gas phase:
    - mostly CO_2
    - Traces of CO, CH_4, others
  - Aqueous-phase:
    - Degradation of hemi-cellulose
    - Sugars, furans, organic acids
  - Solid-phase:
    - Cellulose and lignin
    - Adsorbed organic compounds
    - Friable, brittle materials (suitable for pelletization)

Loblolly Pine before and after HTC Process

Task 1.2- Thermal Treatment of Woody Biomass

- Carbonization (torrefaction) produces a soft friable solid
- Odor of "charcoal"

Raw loblolly pine

Treated at 260 ° C

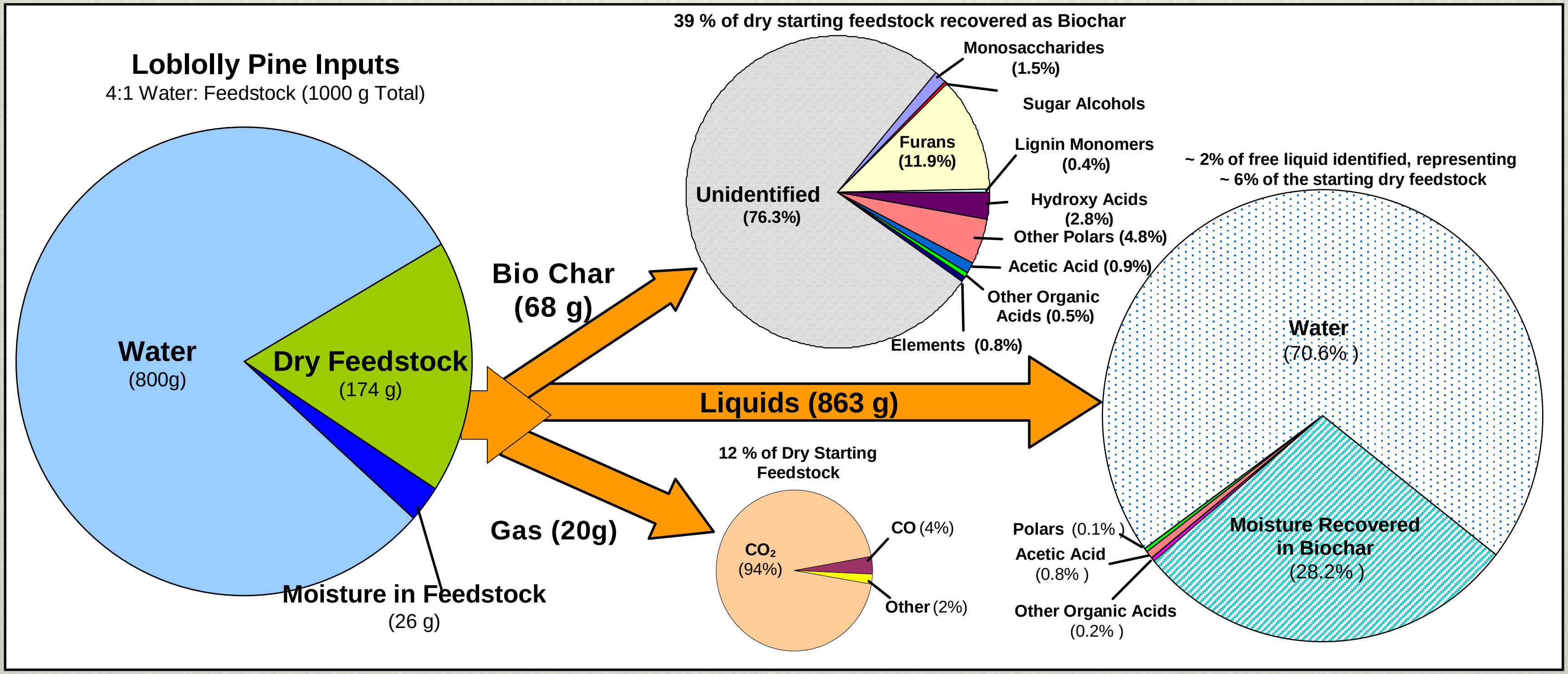
Task 1.2- Thermal Treatment of Woody Biomass

- Biomax 15 research unit
- Biomass undergoes gasification to produce synthetic gas (syngas) that is burned in the internal combustion engine to product electricity
- Characterize a variety of raw and torrified wood feedstocks from Nevada
- Characterize biochar

Figure 1. Biomax 15 gasification unit at UNR.

Mass Balance of HTC Process

- Product fractions vary with process severity
  - Higher temperature → more gas; less solid
  - Higher temperature → more water
- Accurate mass balance is difficult to obtain
  - "Typically" 60% solid, 15% gas, 15% water, 10% water solubles



Composition and Properties of Biochar

- Biochar is the main desirable product of HTC process
- Impacts of HTC process on biomass properties
  - Decrease oxygen content
  - Increase carbon content
  - Increase energy density

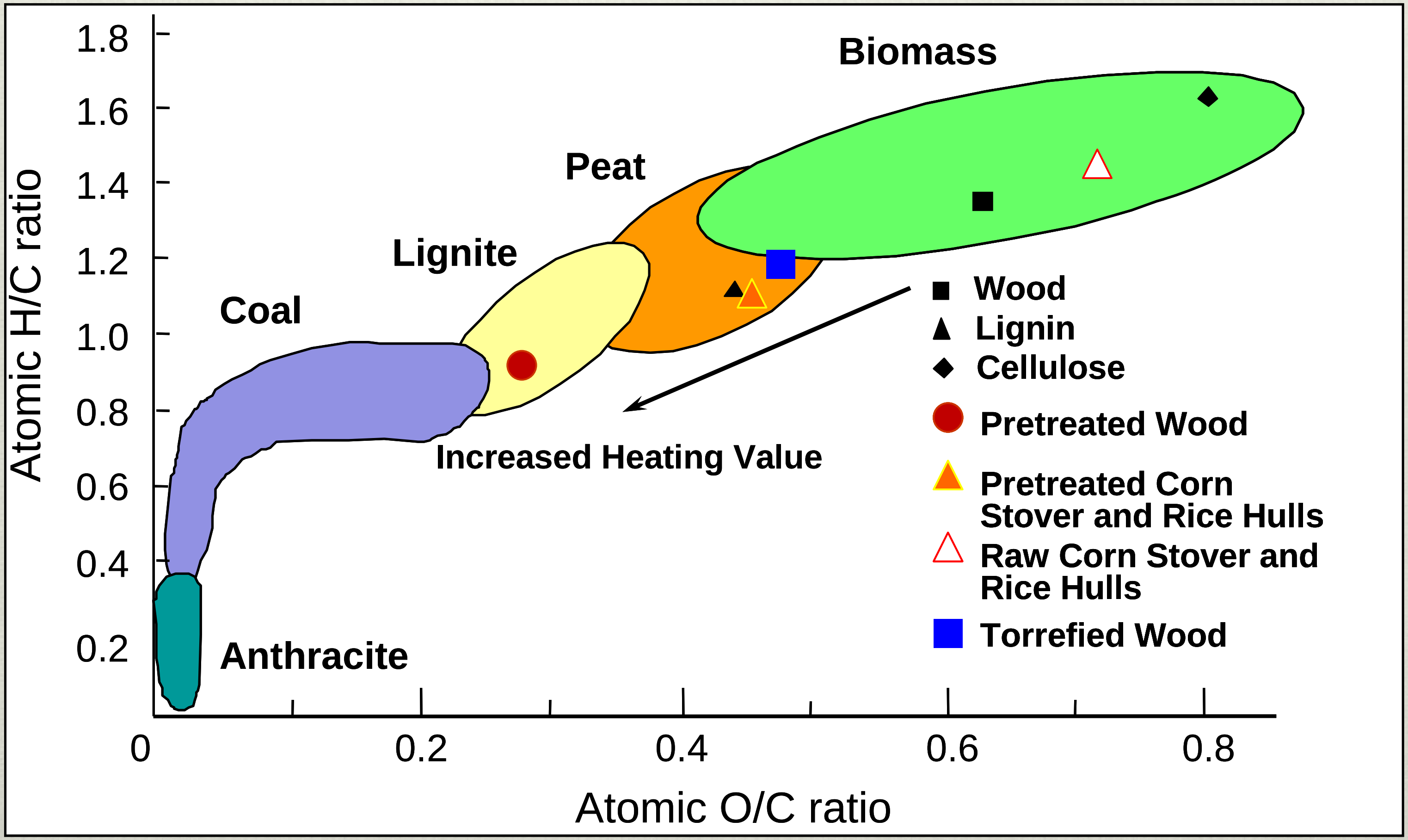
Results from HTC Process at 270°C

Ultimate Analysis %	Loblolly Pine		Corn Stover		Rice Hulls	
	Feedstock	Biochar	Feedstock	Biochar	Feedstock	Biochar
C	51.4	**68.3**	43.1	**48.7**	39	**43.2**
H	5.9	**5.1**	5.3	**4.7**	4.8	**4**
N	0.23	**0.37**	0.75	**0.94**	0.26	**0.4**
S	0.04	**0.03**	0.09	**0.1**	0.06	**0.05**
O	42.1	**25.9**	40.1	**30.7**	35.6	**24**
Ash	0.39	**0.27**	10.9	**14.7**	20.4	**27.9**
Dry HV (Btu/lb)	8511	**11793**	7207	**8239**	6650	**7328**

Coal-like properties of Biochar

Greater HTC severity increases heating value of biochar

Van Krevelen Diagram



Conclusions

- **HTC process is an effective way to increase the value of biomass feedstocks**
  - Improve storage and handling properties
  - Increase energy density (by 10-40%)
  - Can be applied to wide variety of biomass types

- **"Leapfrogging" opportunities:**
  - Co-firing biochar with coal to reduce carbon footprint of power plants
  - Use of biochar for soils improvement and carbon sequestration
  - Beneficial uses of water-soluble products

Acknowledgements:

- This work was performed under a subcontract to the Gas Technology Institute to support the technical goals of US DOE Cooperative Agreement DE-FG36-01GO11082
- Acknowledge Craig Einfeldt (formerly of Changing World Technologies) for assistance in conducting Parr pressure reactor experiments.

References:

- Yan, W., et al., “Mass and energy balances of wet torrefaction of lignocellulosic biomass,” Energy and Fuels (in press) 2010.
- Yan, W., et al., “Thermal pretreatment of lignocellulosic biomass,” Environ. Progress and Sustainable Energy 28 (3) 435-440 (2009).

Task 1.3- Algal-based Biofuels

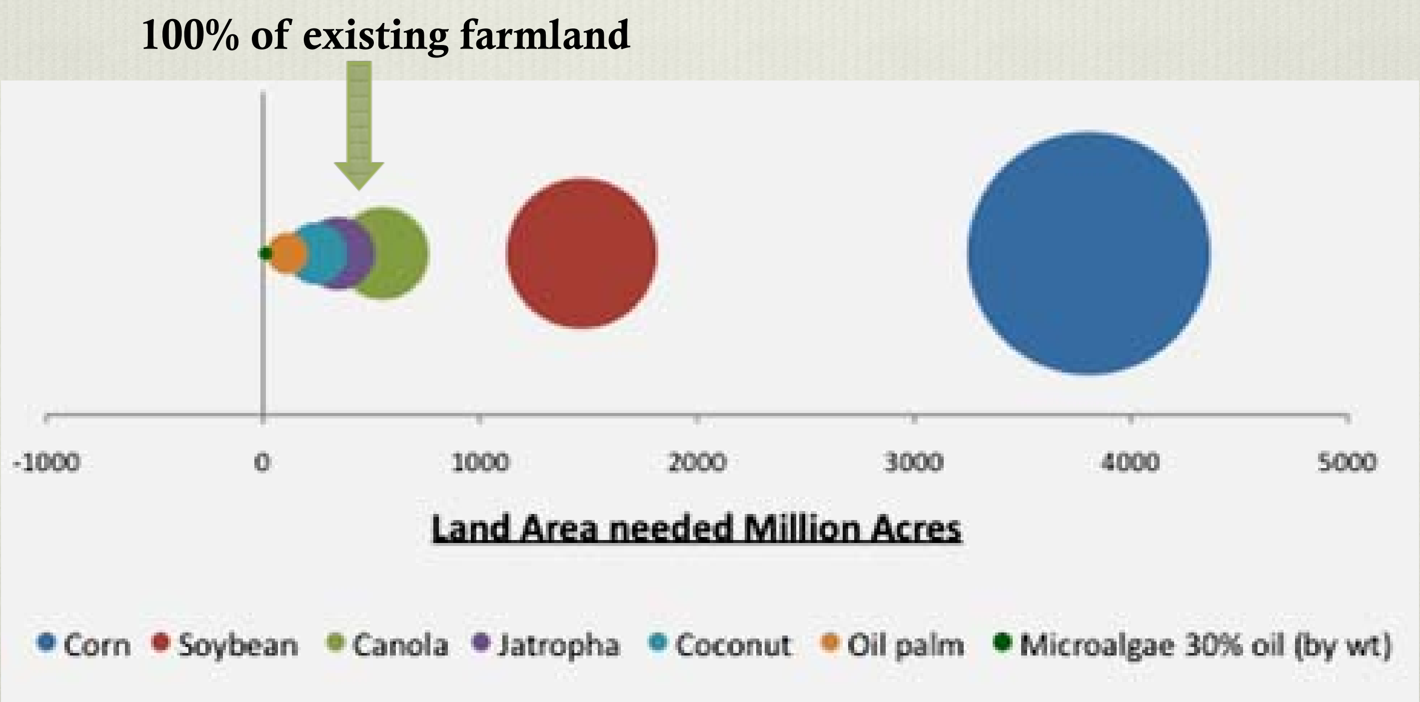
- **Participants**
  - Faculty: John Cushman, Vera Samburova, Barbara Zielinska, Jian Ma, Oliver Hemmers, Chulsung Bae, and Chuck Coronella.
  - Postdoc: Sage Hiibel, Amber Broch
- **Develop analytical methods for characterization of algal lipids**
- **Create culture collection of indigenous Nevada microalgae**
- **Investigate parameters affecting algal growth rates and compositions**
- **Production and characterization of algal biomass and biodiesel**

Background and Introduction

- Algae are 10-30-fold more productive than land crops

- Can be grown on non-arable land; do not compete with food; able to use a variety of water sources.

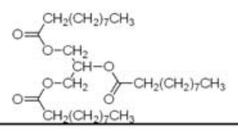
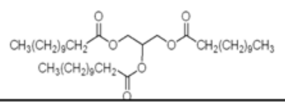
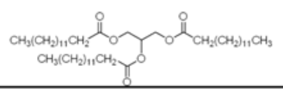
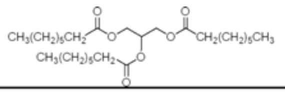
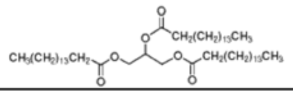
- Land area required to meet 50% of liquid transportation needs in U.S.

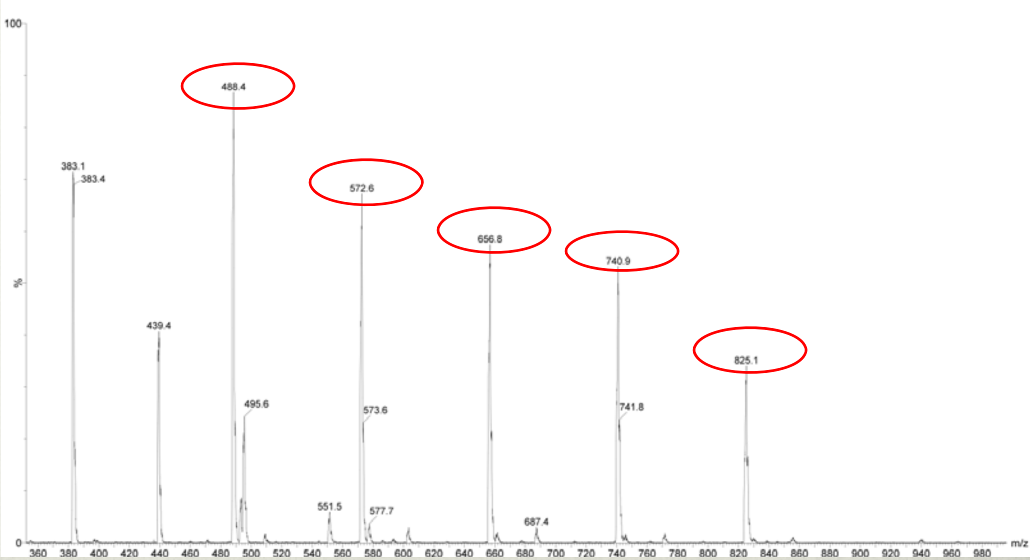


Task 1.3- Algal-based Biofuels

- Develop analytical methods for characterization of algal lipids

- TAG standards analyzed by UPLC/MS and ESI-MS/MS

Name	Structure	MW	
		TAG	TAG + NH_4^+
Glyceryl tridecanoate		554.8	572.9
Glyceryl tridodecanoate		639.0	657.0
Glyceryl trimyristate		723.26	741.2
Glyceryl trioctanoate		470.78	488.7
Tripalmitin		807.3	825.4



Vera Samburova, Barbara Zielinska

Create culture collection of indigenous Nevada microalgae

Sampling Locations at TMWRF

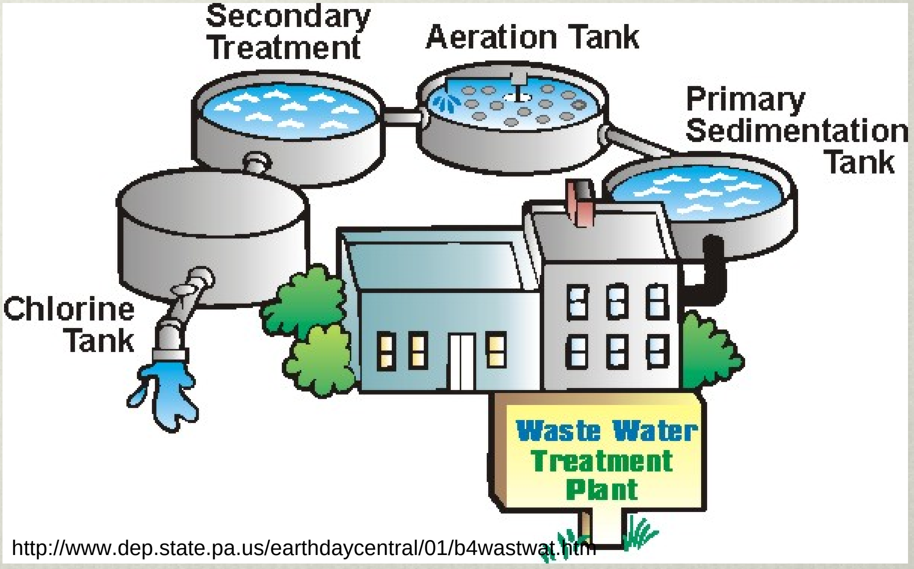
Las Vegas Wash

N and P Removal from Waste Water

- Algae grown on municipal or farm waste water can remove 80-99% of NH_x and PO_4

- Centrate is the liquid fraction of dewatered anaerobically digested sludge

- Municipal waste is 25-30% solids (sludge) which is currently sent to landfills (contains 7-35% lipids)



Centrate-to-Biofuels Project

- **Centrate is nutrient rich:**
  - Nitrogen (~1,000 mg/L NH_4^+-N)
  - Phosphorus (~225 mg/L PO_4^{3} -P)
  - Inorganic carbon (~650 mg/L -C)

- **946,000 L/day of centrate**

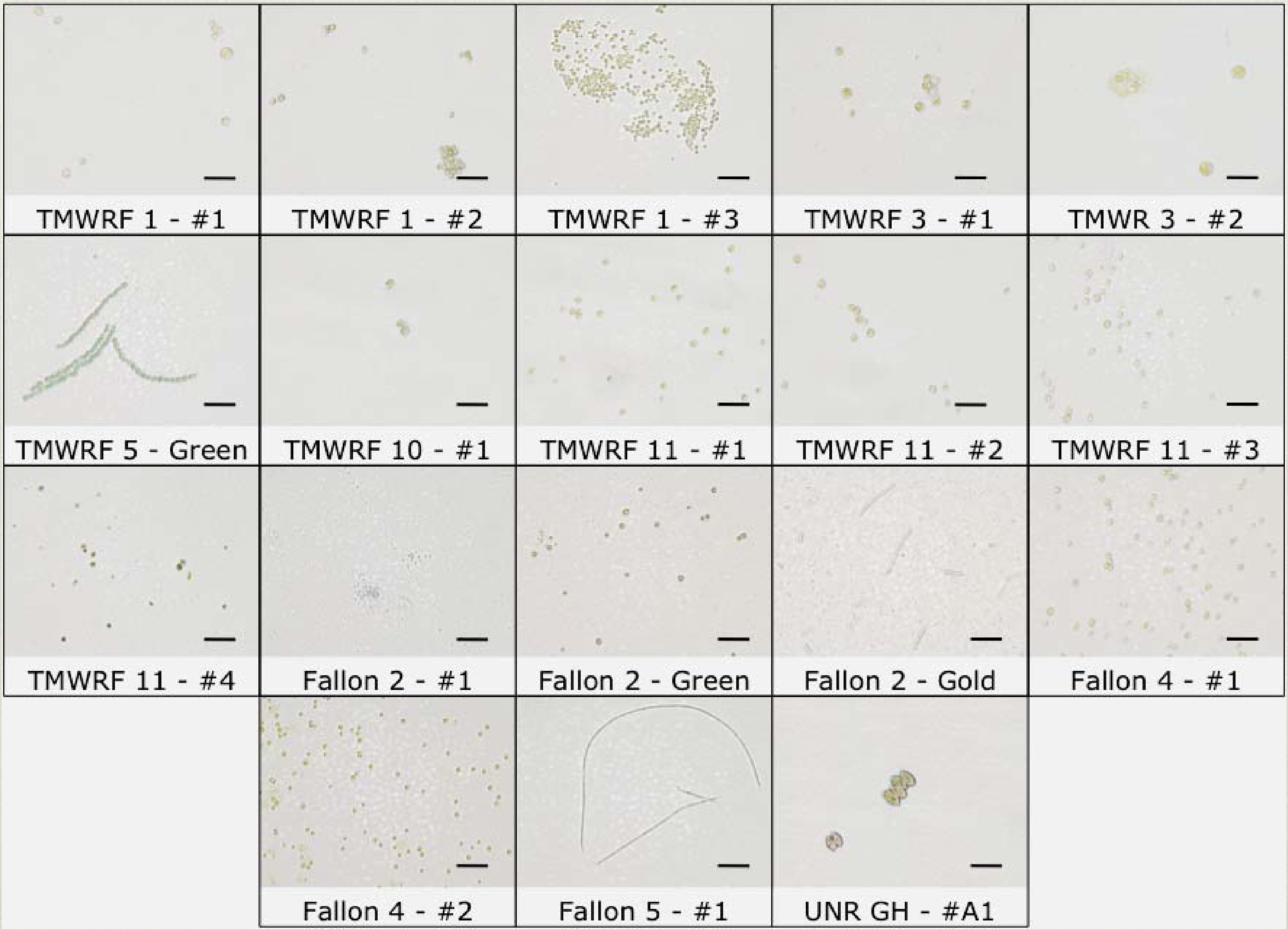
- **18,143 Kg/day algal dry biomass**

- **6,000 L/day of biodiesel (30% lipid content)**

Truckee Meadows Water Authority, May 15, 2009

http://www.TMWRF.org

Survey of Algal Isolates



60X – scale bar = 25 μm

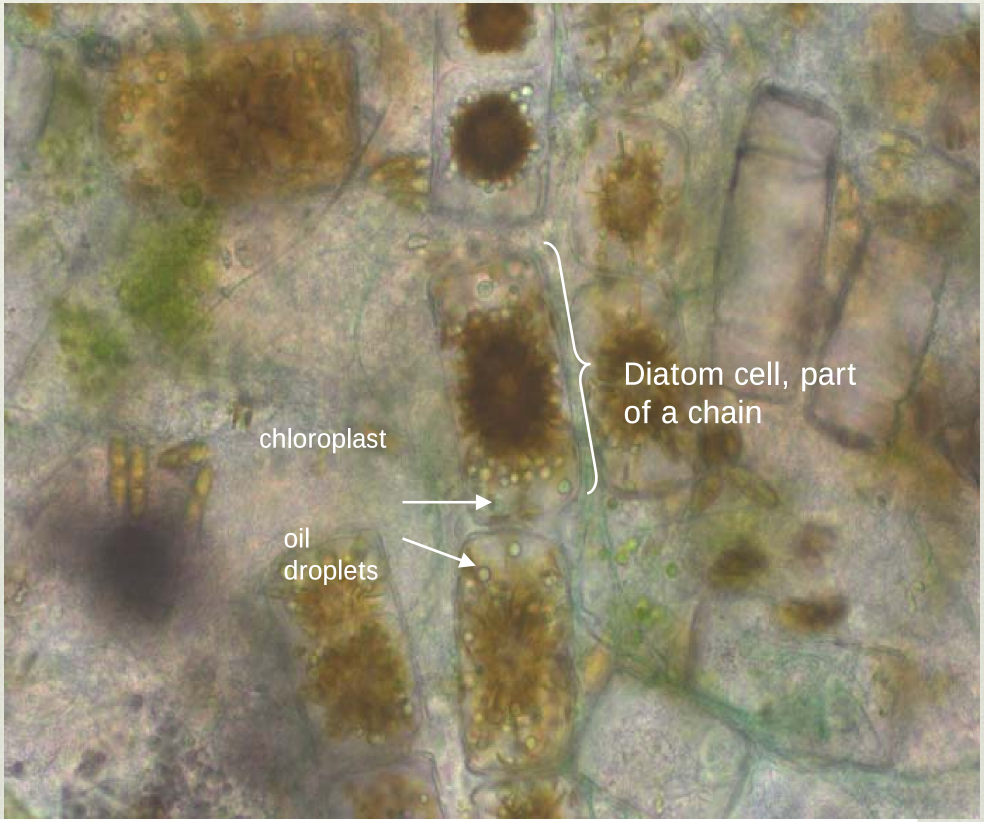
Sage Hiibel - UNR

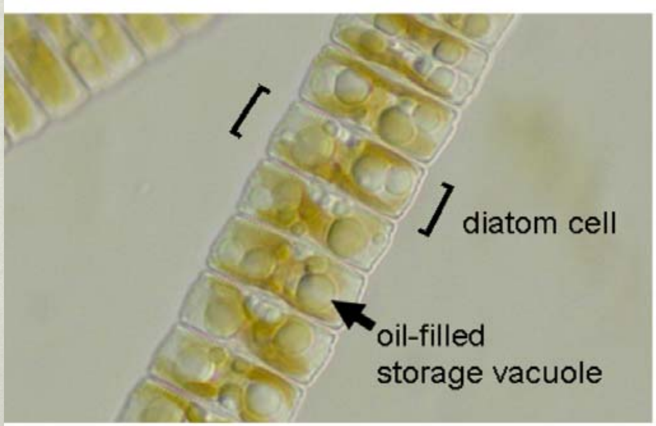
Survey of Algal Isolates - Identification

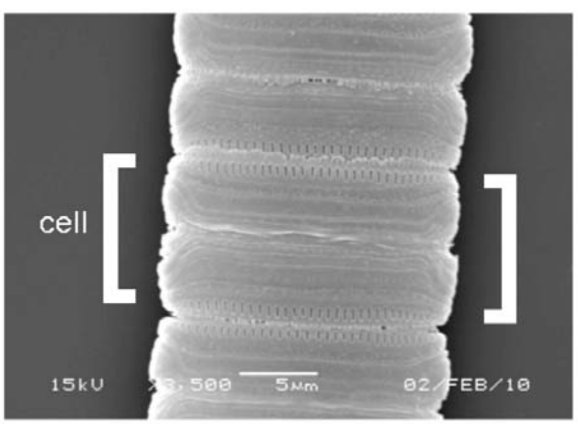
Sampling Location	Description	Potential Isolates	Putative Isolate ID
TMWRF 1	Primary sedimentation tank	3	Class: Chlorophyceae
TMWRF 2	Water activated sludge secondary sedimentation tank	-	
TMWRF 3	Aeration tank 2C	2	Class: Chlorophyceae
TMWRF 4	Phosphorus stripping tank	-	
TMWRF 5	Phosphorus stripping tank	1	Division: Cyanobacteria; Order: Oscillatoriales; Genus: *Geitlerinema*, *Leptolyngbya*, *Microchaete*, *Stichococcus*, or *Pseudanabaena*
TMWRF 6	Phosphorus stripping tank	-	
TMWRF 7	Secondary sedimentation tank	-	
TMWRF 8	Secondary sedimentation tank	-	
TMWRF 9	Post-aeration tank	-	
TMWRF 10	Backwash settling tank	1	Class: Chlorophyceae
TMWRF 11	Steamboat Creek - outfall	4	Class: Chlorophyceae
TMWRF 12	Steamboat Creek - upstream	-	
Fallon 1	Agricultural pond	-	
Fallon 2	Moody Lane Waste Water Treatment Plant - fallow aeration tank	3	Division: Cyanobacteria; Order: Oscillatoriale;s Genus: *Geitlerinema*, *Leptolyngbya*, *Microchaete*, *Stichococcus*, or *Pseudanabaena*
Fallon 3	Moody Lane Waste Water Treatment Plant - evaporative holding pond	-	
Fallon 4	Dairy milking parlor washout pond	2	Class: Chlorophyceae
Fallon 5	Irrigation drainage ditch	1	Division: Cyanobacteria; Order: Oscillatoriales; Genus: *Geitlerinema*, *Leptolyngbya*, *Microchaete*, *Stichococcus*, or *Pseudanabaena*
UNR GH	Recurring open pond contaminant	1	*Scenedesmus dimorphus* (Turpin) Kützing

Sage Hiibel - UNR

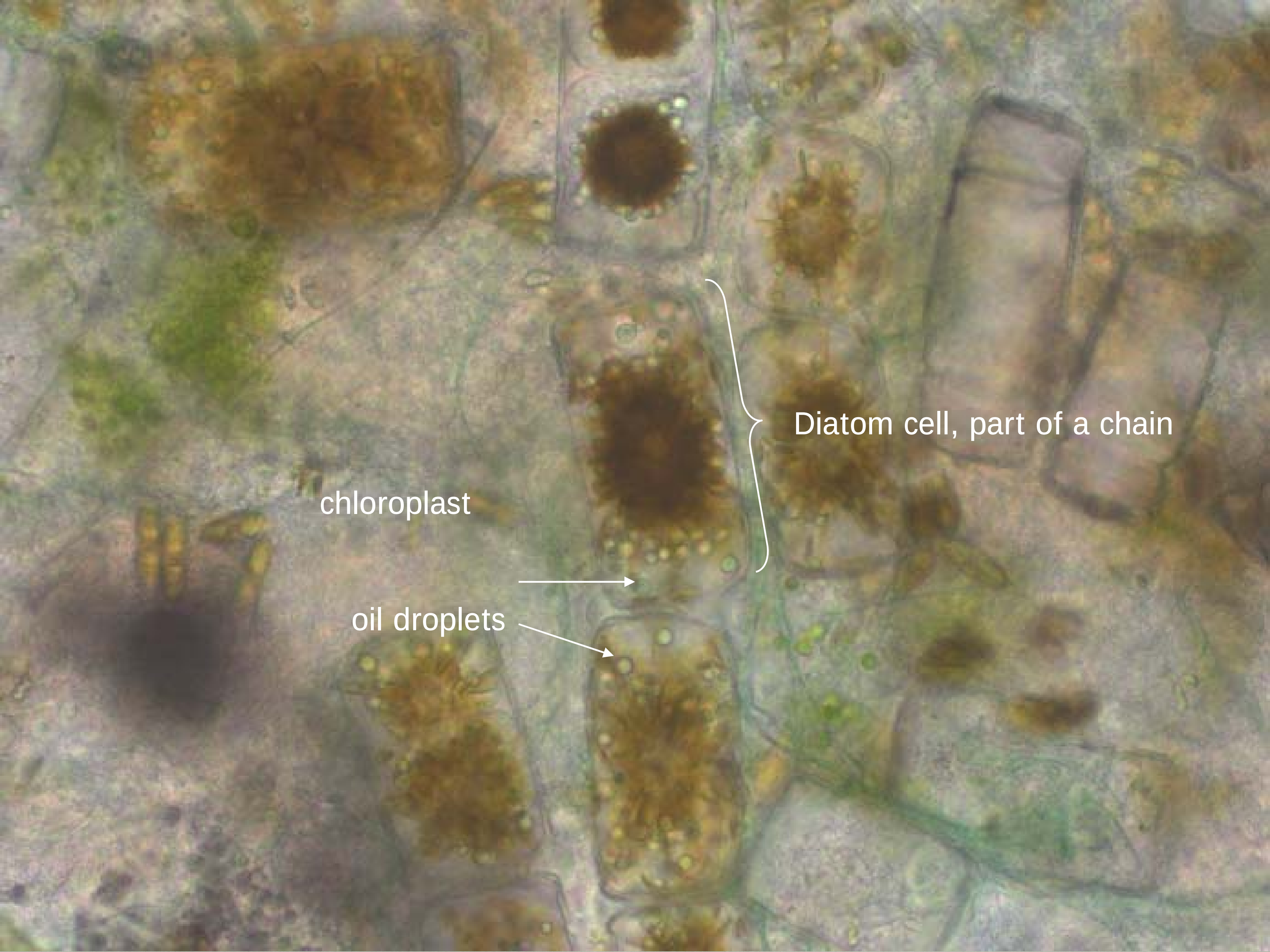
Lipid-rich Filamentous Diatom from the Las Vegas Wash



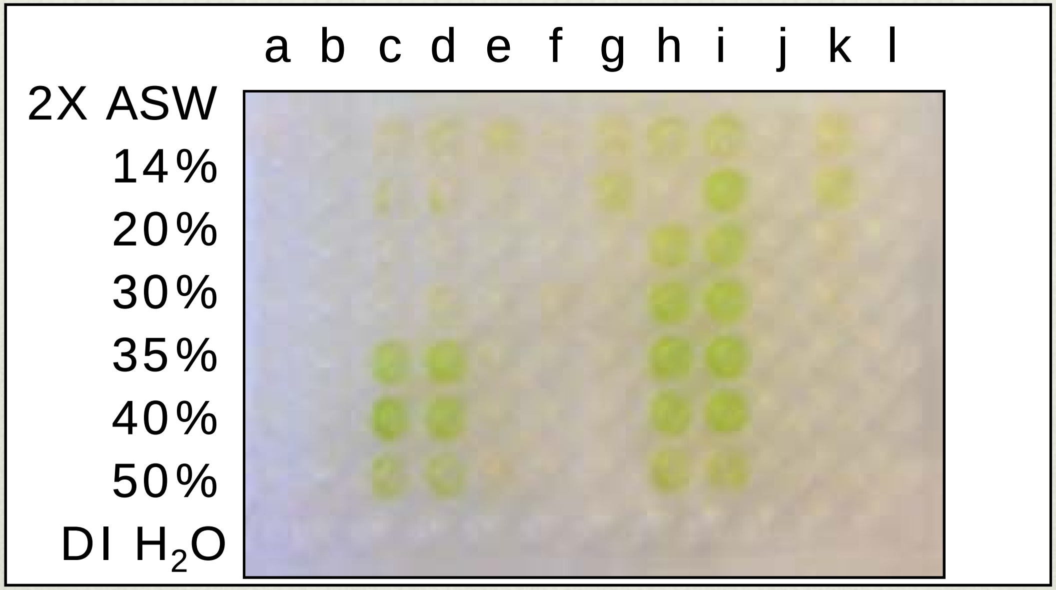




Henry Sun - DRI


Diatom cell, part of a chain
chloroplast
oil droplets

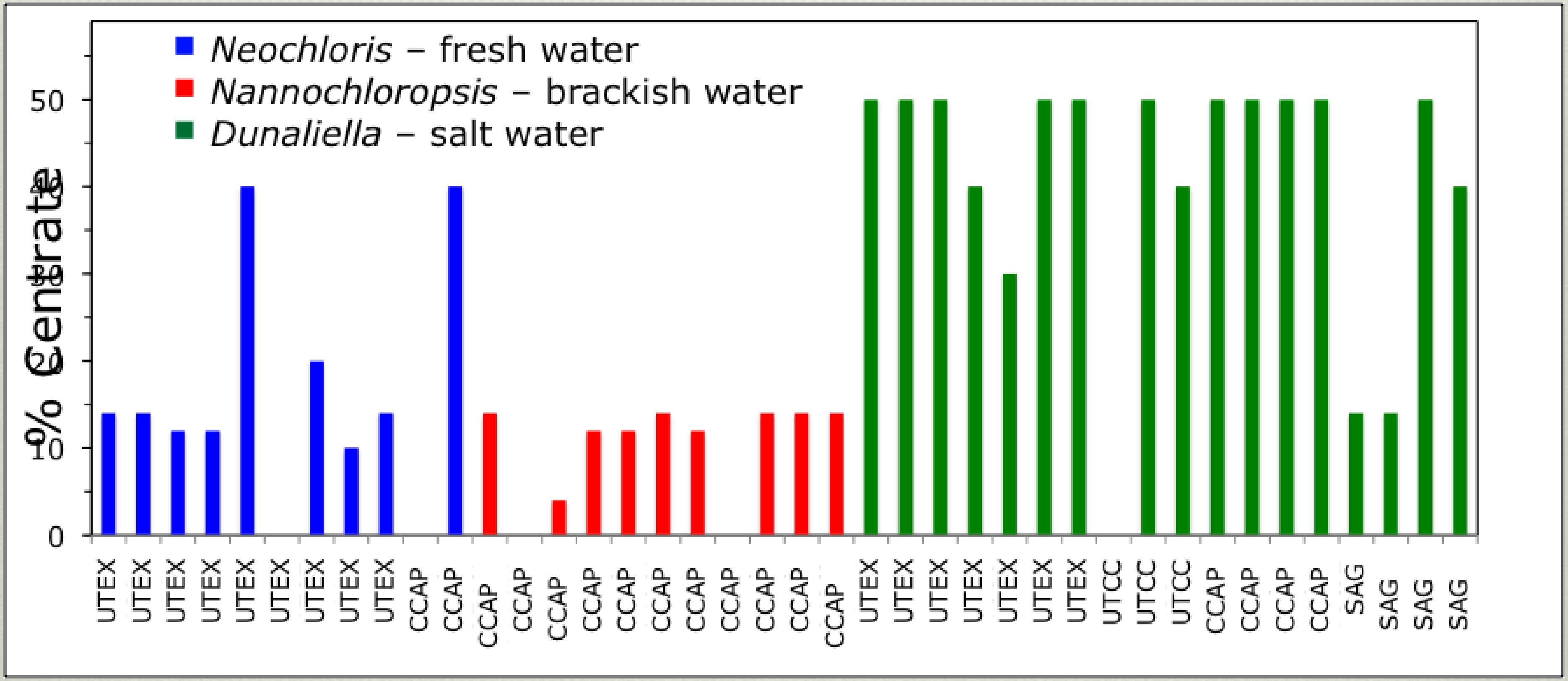
Centrate Tolerance: 96-Well Plate Screening



Dunaliella species after 8 days of growth. Percentages in rows indicate the centrate concentrations (% v/v). Columns were inoculated with: a,l - sterile water; b – 2X ASW; c - UTEX 199; d - UTEX 200; e - UTEX 999; f - UTEX 1000; g - UTEX 1644; h - UTEX 2192; i - UTEX 2358; j - UTCC 197; k - UTCC 420.

Sage Hiibel - UNR

Centrate Tolerance across fresh, brackish, and salt water species



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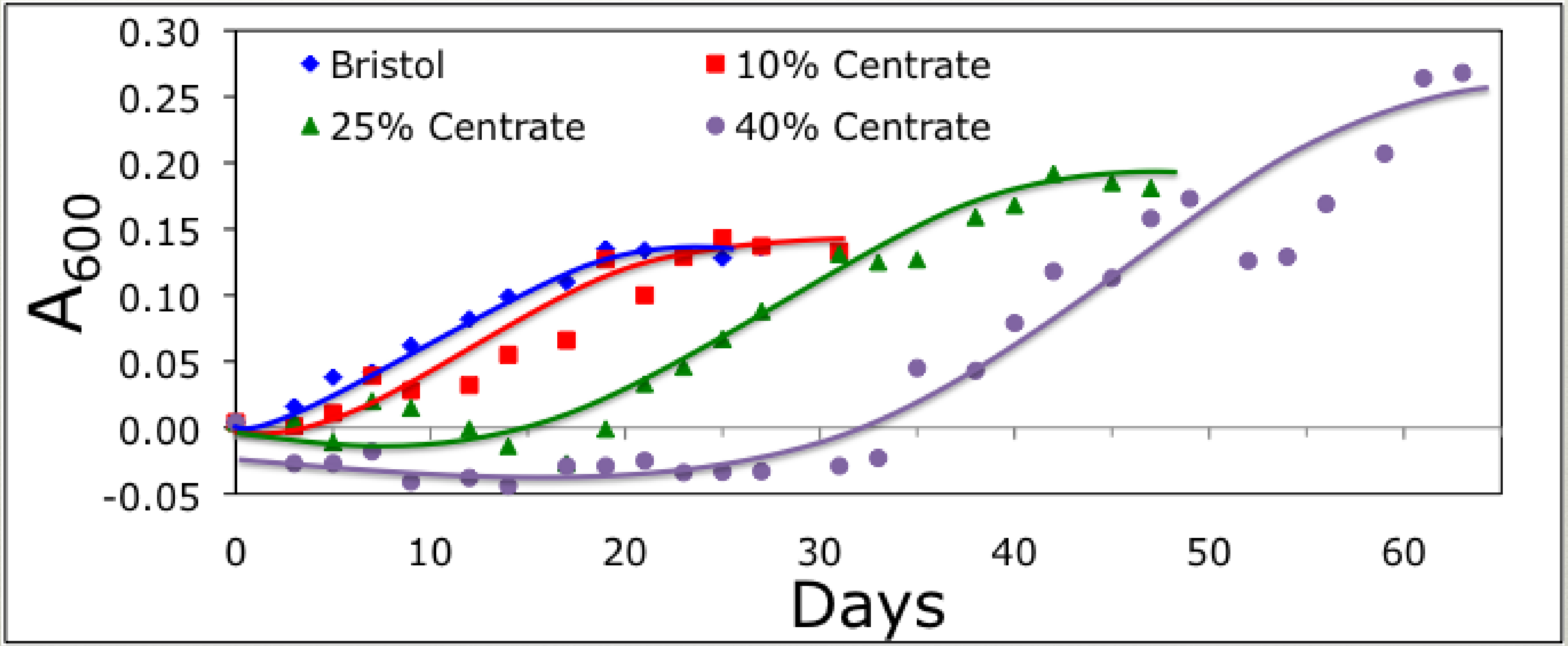
Dose-Dependent Growth Inhibition of Centrate



- ❖ **Characterization of inhibitory compounds necessary**

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Investigate parameters affecting algal growth rates and compositions

- Maximum productivity of algal biomass: The ideal maximum productivity of algal biomass is 0.104 kg/m2/day (or 379.6 ton/ha/yr).
- Minimum ideal requirement of water for growing algal biomass is: 0.41 kilogram water is needed if one kilogram CO_2 is captured during cultivation process.
- Minimum reflection loss using photobioreactor is about 4% of total incident light if incident angle is kept smaller than 46° .
- **Other estimates:**

  - Pond system: 109.5 ton/ha/yr (Hawaii ARP, 1986-1987)

  - Closed photo-bioreactor: 365 ton/ha/yr (AlgaeLink)

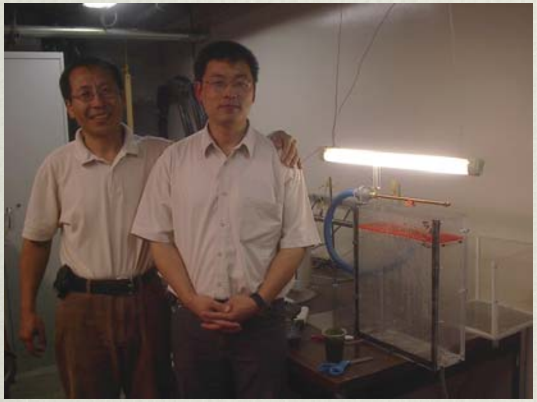
Solar Conversion Efficiency of Microalgae

- The total maximum solar conversion efficiency of microalgae (from solar energy into stored chemical energy) can be obtained by production of photosynthesis efficiency and 42% visible light intensity of solar radiation at sea level, which is 42%×26%, **10.9%**.

CAP for maximum biomass productivity, biodiesel productivity, space requirement

Photobioreactors at UNLV

- **Closed Photobioreactor System with less water evaporation and more controllable parameters, makes cultivation of microalgae in Southern Nevada practical.**



1. Photobioreactor for macro-algae, collected in Flamingo Wash, Las Vegas

2. Photobioreactor with new design for various control parameters, such as temperature, pH value, flow rate, light intensity for laboratory scale studies.

3. Prototype of hanging bag Photobioreactor for large scale production of microalgae etc.

On-going Algal Research:

- The effect of CO_2 concentration to the growth rate of microalgae
- Temperature management for outdoor photobioreactor (PBR)
- The outdoor reliability test of PBR material—polyethylene
- Microalgae screening in outdoor PBR by natural selection using municipal wastewater and flue gas

Publication

- Ma, J., O. Hemmers, *Thermo-economic Analysis of Microalgae Co-firing Process for Fossil Fuel-fired Power Plants*, ASME 4th International Conference on Energy Sustainability, May 19-22, Phoenix, Arizona 2010.

Development of New Solid (recyclable) Acid Catalyst and Its Application for Biodiesel Production

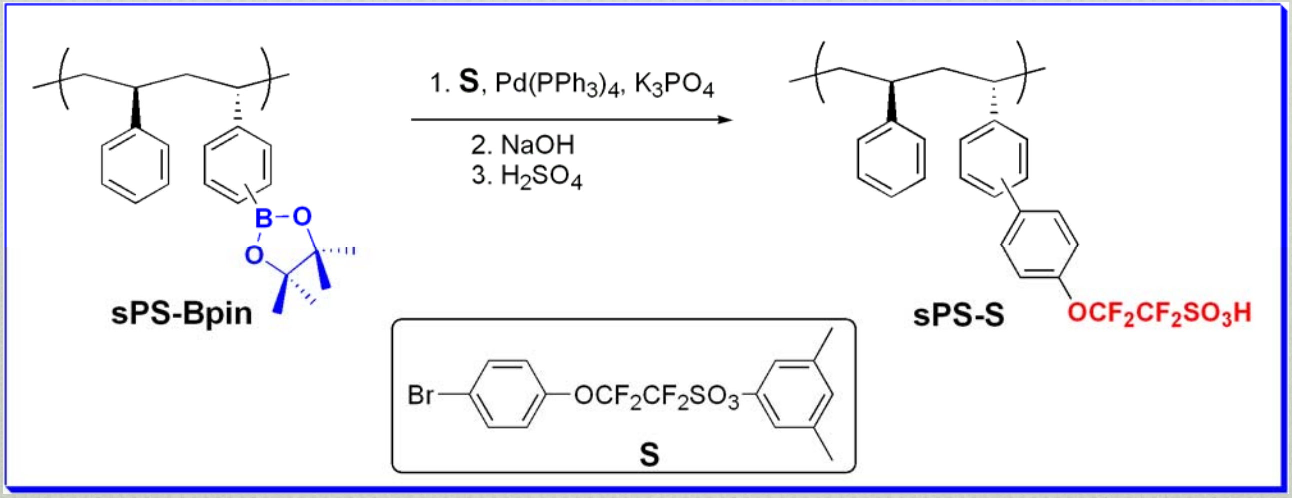


Table 1. Properties of Syndiotactic polystyrene sPS-S

Catalyst	BET Surface area (m^2 g^{-1})	Average pore volume (cm^3 g^{-1})	Average pore diameter (nm)	SO_3H[a] (mmol g^{-1})
40-sPS-S	0.1033	2.08×10^{-3}	8.0647	1.67
A15[a]	45	4.8	24	4.8
NR50[b]	0.02	--	--	0.9

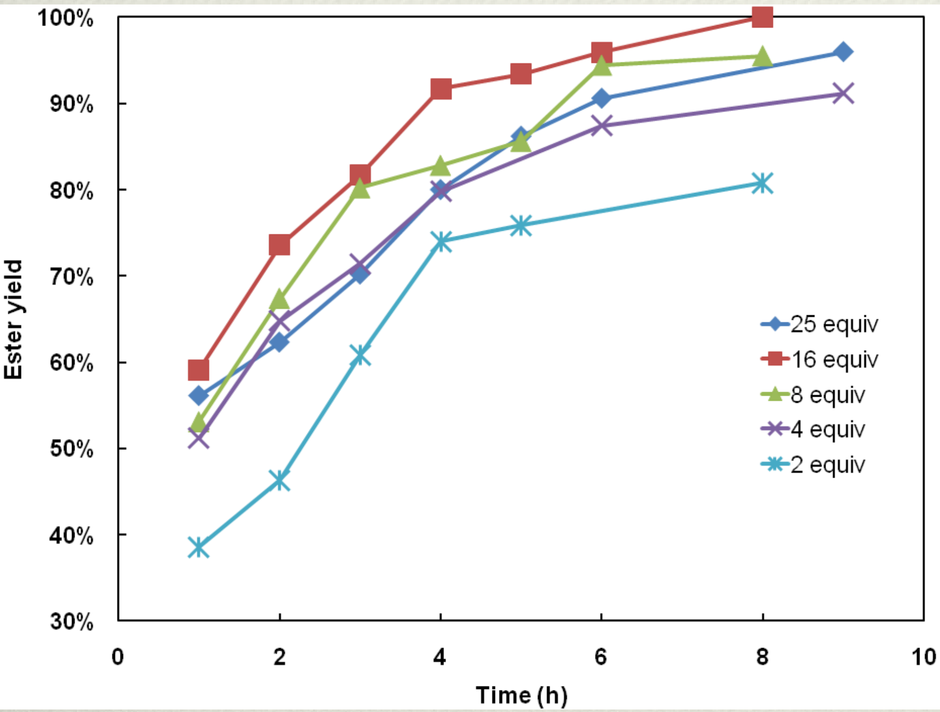
[a] M. Marchionna, M. D. Girolamo and R. Patrini, *Catal. Today*, 2001, **65**, 397-403.
[b] M. A. Harmer and Q. Sun, *Appl. Catal. A: Gen.*, 2001, **221**, 45-62.

Esterification Conditions

$$C_{11}H_{23}CO_2H + CH_3OH \xrightarrow{cat.} C_{11}H_{23}CO_2CH_3$$

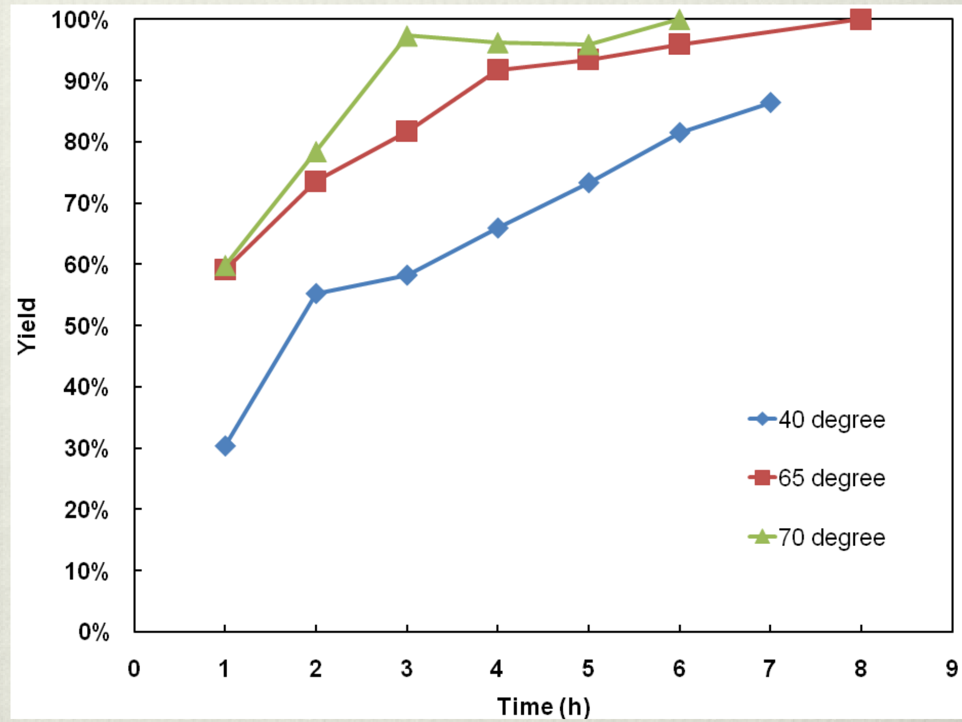
Biodiesel

Fig 1. Effect of Dodecanoic Acid to Methanol



temperature 65 ^{o}C,
catalyst loading 0.5 w%,
stirring speed 700 rpm.

Fig 2. Effect of Temperature



$C_{11}H_{23}CO_2H$: MeOH = 1 : 16,
catalyst loading 0.5w%.

Esterification Conditions

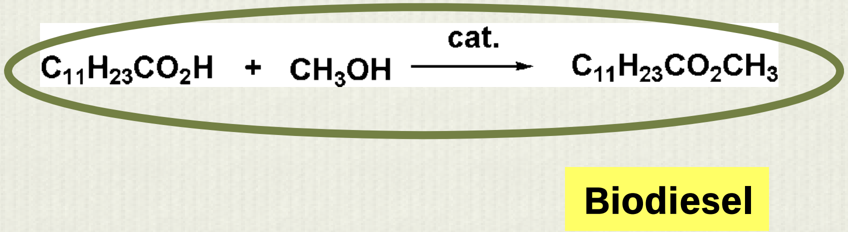
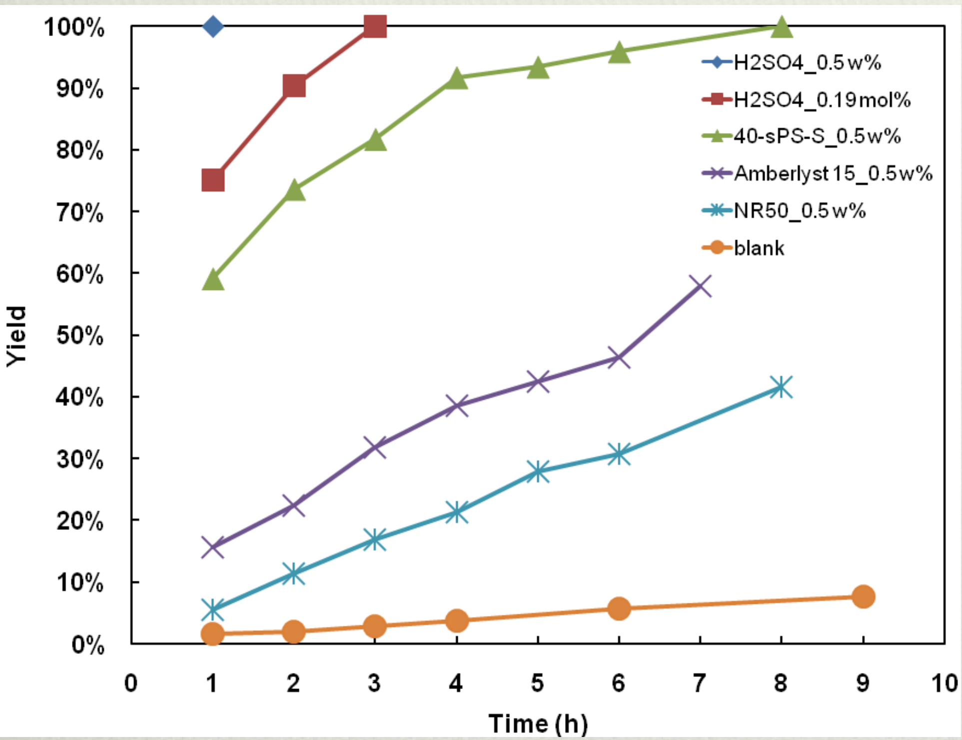
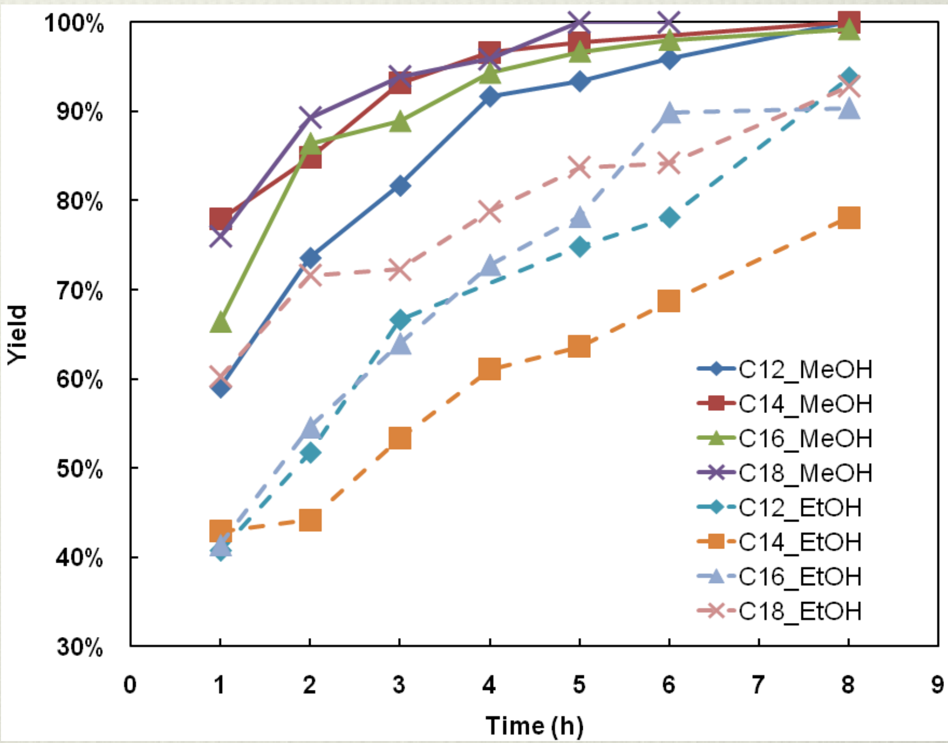


Fig 3. Comparison of Catalyst



$C_{11}H_{23}CO_2H$: MeOH = 1 : 16,
65 ^oC, catalyst loading 0.5w%.

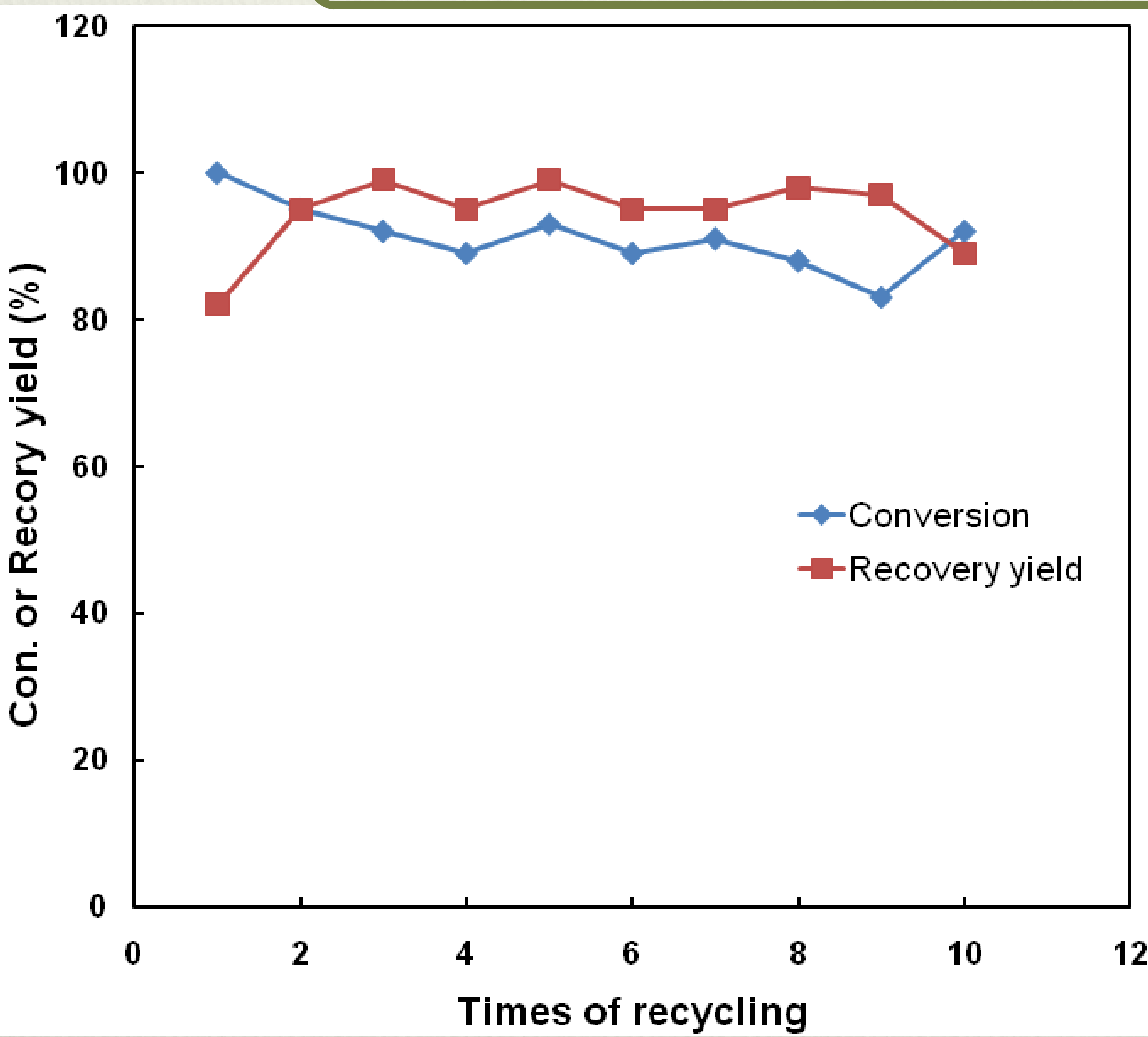
Fig 4. Reaction Scope



65 ^oC for MeOH and 80 ^oC for EtOH,
catalyst loading 0.5w%.

Catalyst Recycling

$$C_{11}H_{23}CO_2H + CH_3OH \xrightarrow[65\ ^{o}C,\ 8\ h]{0.5\ w\%\ 40\text{-sPS-S}} C_{11}H_{23}CO_2CH_3$$



[a] $C_{11}H_{23}CO_2H$ (20.0 g), methanol (16 equiv), 40-sPS-S (0.5w%), 65 °C.

[b] From the second run, reaction scale was based on the recovered catalyst (0.5 w%) without additional fresh catalyst.

[c] GC-MS conversion.

[d] Recovered yield (weight%) of 40-sPS-S after filtered, washed with hot methanol and dried.

Task 1.3- Production and characterization of algal biomass and biodiesel

- **Carbonization of algae residue.**
- **Participants**
  - Faculty: Chuck Coronella, John Cushman
  - Postdoc: Sage Hiibel
  - Undergraduate student: Samantha Kertsen
- **After extracting oils from algae, evaluate properties of algae residue as feedstock for carbonization.**
- **Residue is treated in hot compressed water.**
- **Results are pending.**

Task 1.4- Chemically promoted mechanical dewatering of wastewater sludge

- **Participants-**
  - Faculty: Chuck Coronella, Victor Vasquez
  - Graduate students: Kevin Schmidt, Mike Matheus
  - Undergraduate students: Chris Moore, Nathan Roysden, Diane Mar
- **Extending the effort of a project funded by CEC and UNR TTO for sludge drying**

Task 1.4- Chemically promoted mechanical dewatering of wastewater sludge

- **Objectives:**
  - Design, build, test, and operate a continuous low-temperature fluidized bed sludge dryer
  - Currently being tested on site at TMWRF
  - Identify additives that enable increased dewatering by centrifugation
  - Testing
    - NaCl, NaOH, protease enzyme, organic solvent
  - Inconclusive results (so far)

Biofuels-Biomass Group
NV-REC

- Questions?

University of Nevada, Las Vegas

Desert Research Institute