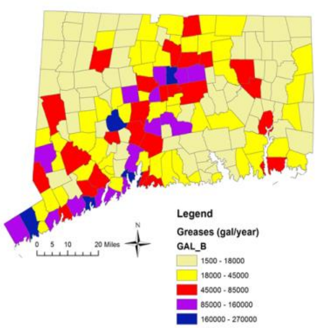
2013 DOE Bioenergy Technologies Office (BETO) Project Peer Review

Bio Energy Initiative for Connecticut

Date: May 23, 2013
Technology Area Review: Bioenergy Technologies

Principal Investigator: Steven L. Suib
Organization: The University of Connecticut



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Goals of the Research

1. DOE recommends **Poplar** as one of the best Bioenergy Crops for the NE US and we have made **Field Evaluations and Genetic Improvement** of Poplar Trees.
2. **Heterogeneous Catalysts** have been developed for Biomass Conversion and Screened in Several Biomass Catalytic **Small Scale Reactions**.
3. **Biofuels Processing Systems** Built for Economic Evaluation Of UCONN Tech.
4. **Outreach Activities for Commercial Agricultural Producers** for Production of Biomass Feedstocks with Emphasis on Direct-Burn Technologies.
5. A **Comprehensive Inventory of Feedstocks** (Total and Available Biomass of Forest and Agricultural Residues, Idle and Marginal Farmlands.
6. Connecticut Center for Economic Analysis Developed **Analyses to Measure Current and Potential Net Economic Impact** for the CT Biofuels Industry.

Relation to USDOE Bioenergy Technology Office

"The Bioenergy Technologies Office is helping transform the nation's renewable and abundant biomass resources into cost-competitive, high-performance biofuels, bioproducts, and biopower."

http://www1.eere.energy.gov/biomass/integrated_biorefineries.html

Quad Chart Overview

Timeline

- Project start date – 6/5/10
- Project end date – 3/1/13
- Percent complete – 100%

Budget

- Funding for FY11(DOE $831,056 / Cost share $11,028)
- Funding for FY12(DOE $595,514/ Cost share$74,031)
- Funding for FY13 (DOE $70,539 / Cost share, $0)
- Years the project has been funded 3.5 Years / average annual funding $500,000.

Barriers

- Barriers addressed:

1. Development of Active Stable Catalysts with High Conversion.
2. Scale-Up of Reactors.
3. Economic Analyses.

Partners

- CCAT, UCONN, RPM Sustainable Technologies, Catelectric.
- Project Management – S. L. Suib, PI; Marilyn Moir, Administrative Assistant; UCONN Office of Sponsored Programs, UCONN Technology Transfer Office.

Project Overview

History - Dr. Yi Li, Plant Science Dept., Rapid Growth of Trees. Genetically Improved Biomaterials. Dr. Steve Suib, Chemistry Dept., Catalyst Development, Mechanistic Studies. Dr. Rich Parnas, Chemical Engineering Department, Scale-up of Reactors + Processes. Dr. Harrison Yang, Natural Sciences Department, Database Platform Development for Feedstocks from Forest and Agricultural Residues and Idle and Marginal Land for Energy Crops. Dr. Fred Carstensen, Economics Dept., Economic Potential of Local CT Feed Stocks.

Context – This Collaborative Research has been co-developed with CT Agency Support like CCAT, CT Innovations, and UCONN.

High Level Objectives – The major High Level Objective is to move the Results of this Project via Technology Transfer to Local Biomass industries.

1 - Approach

The **Overall Technical Approach** was to First Develop Genetically Engineered Rapidly Growing Trees. These were used as Feedstocks in Lab Scale Catalytic Experiments. These Reactions were then Scaled Up. In addition, CT Agricultural Feedstocks were Analyzed. Economic Analyses were also done.

The **Management Approach** involved Joint Individual and Collective Meetings. Group Meeting presentations were given A Southern New England Consortium was initiated. Joint publications were developed. Milestones were used to Monitor and Assess Progress. Unique aspects of our approach involved hand in hand joint development of all parts of the study with the whole team.

2 - Technical Accomplishments/ Progress/Results

- **Excellent Progress** was made in Making Genetically Engineered Plants, in Development of Catalysts, In Biomass Conversion Studies, In Scale-Up, In Tech Transfer, In Resource Assessment, and Economic Analyses.

- The Most Important Technical Accomplishment Achieved Was the Scale Up and Tech transfer of Our Research to RPM Sustainable Technologies which has created 6 jobs in CT and 2 jobs in France. A Contract is in place for the **first commercial project in** Torrington, CT.

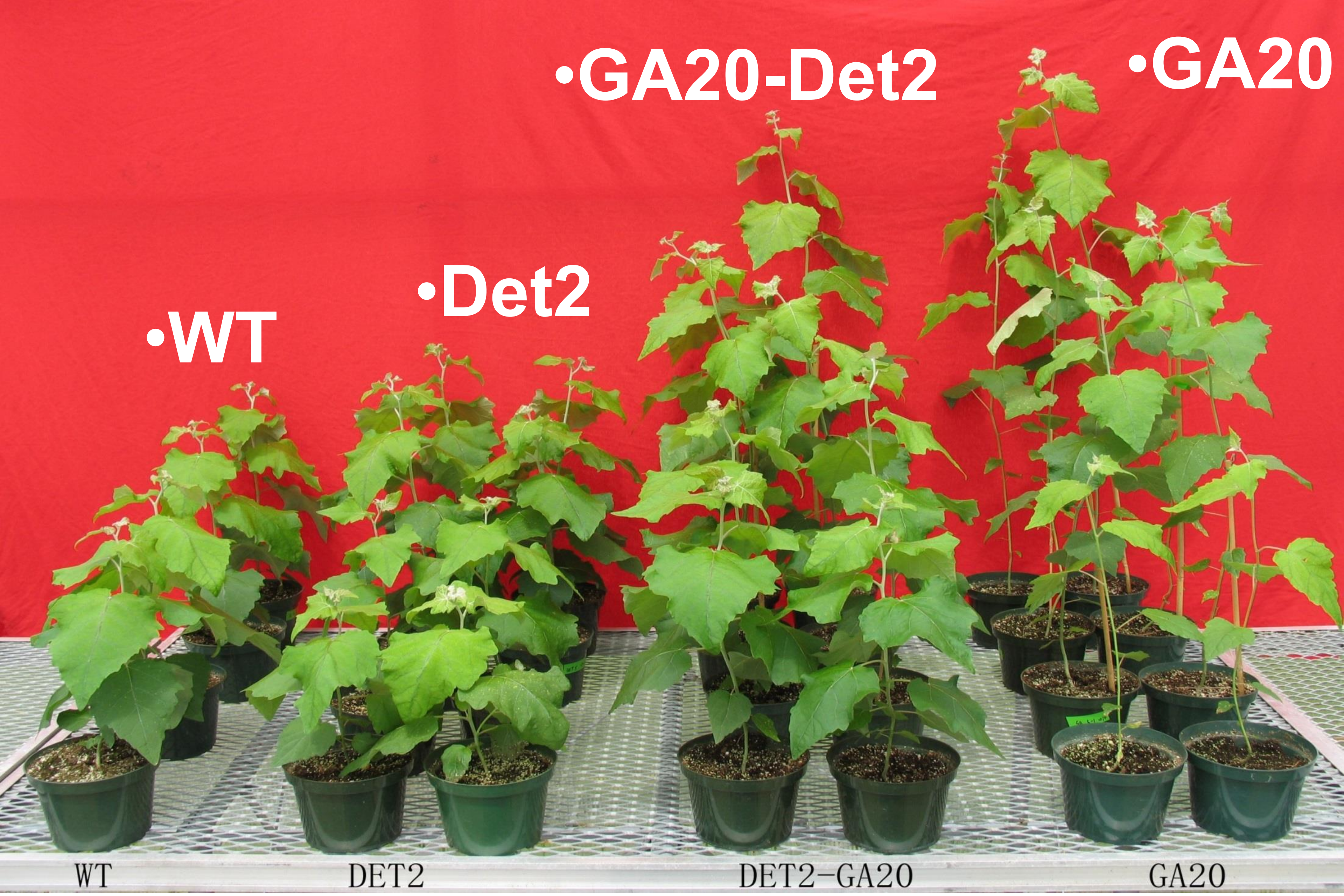
- Key Milestones Included Development of Poplar Trees, Development and Scale Up of Excellent Catalysts, Scale-Up of the Reactor, and Tech Transfer.

- Slides reading this Information Follow.

•Growth Promoting Effects of GA20 and DET2 Genes on Poplar

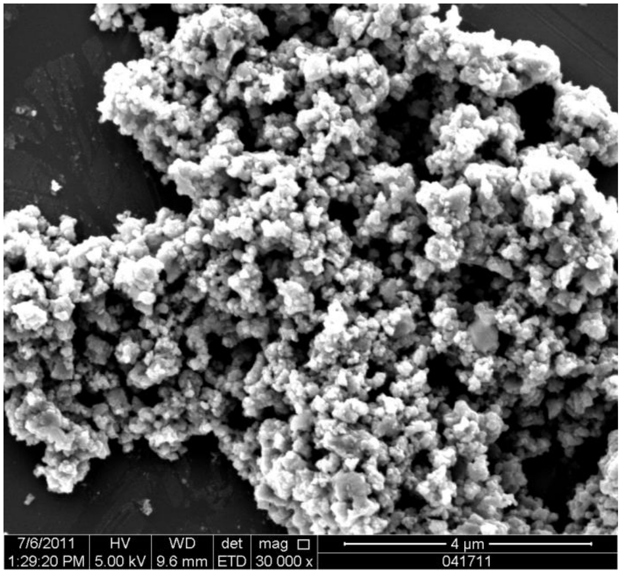
Organ	Wild Type	GA- #10	GA - #5	GA20- + Det2 - #5	GA 20 + Det2 #12	DET2 - #15
Leaf	3.2±0.2	3.3±0.4	1.5±0.1	5.3±0.9	5.2±0.4	4.2±0.4
Shoot	1.3±0.1	4.2±0.5	2.0±0.2	6.0±0.6	5.7±0.5	2.3±0.1
Root	3.5±0.4	1.1±0.2	0.7±0.1	4.1±0.3	4.7±0.1	6.3±0.6
Total	8.0	8.6	4.2	15.4	15.6	12.8

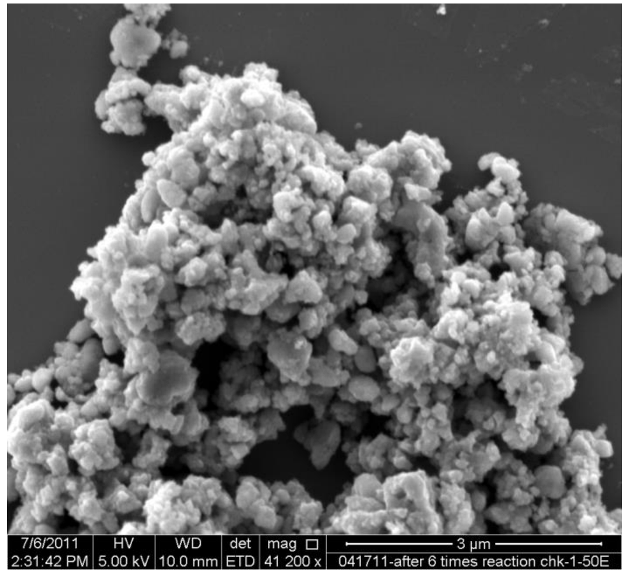
•Overexpression of GA20 oxidase gene alone can reduce biomass production in poplar, but over-expressing both GA20 oxidase and Det2 genes drastically increased their biomass production.

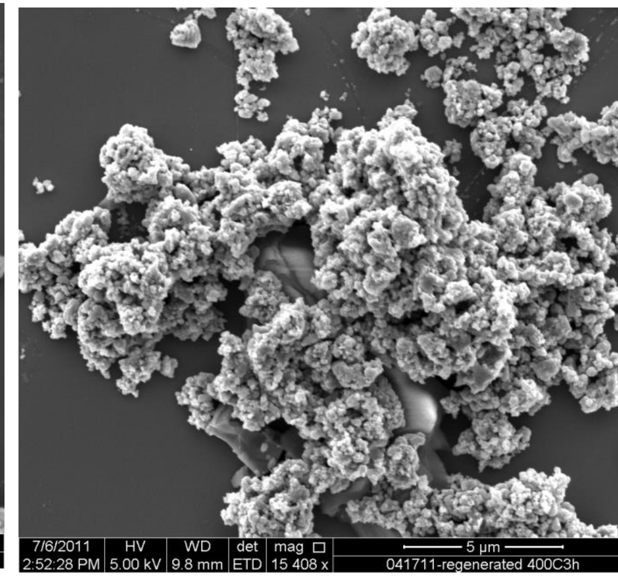


•Transgenic poplar grow faster than wild type controls

SEM Images of Catalyst



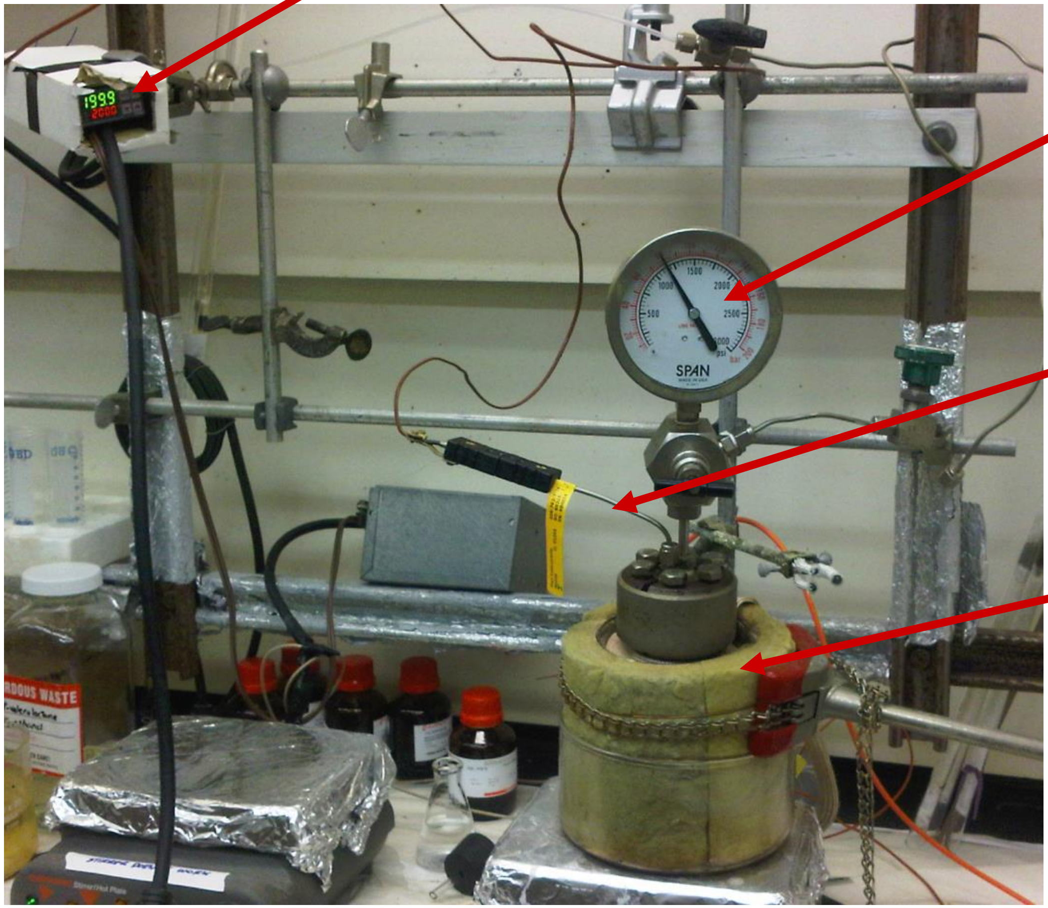




- **Before reaction**
- **After 6 times rxn**
- **Calcination**
- **Found no big difference under STM images**

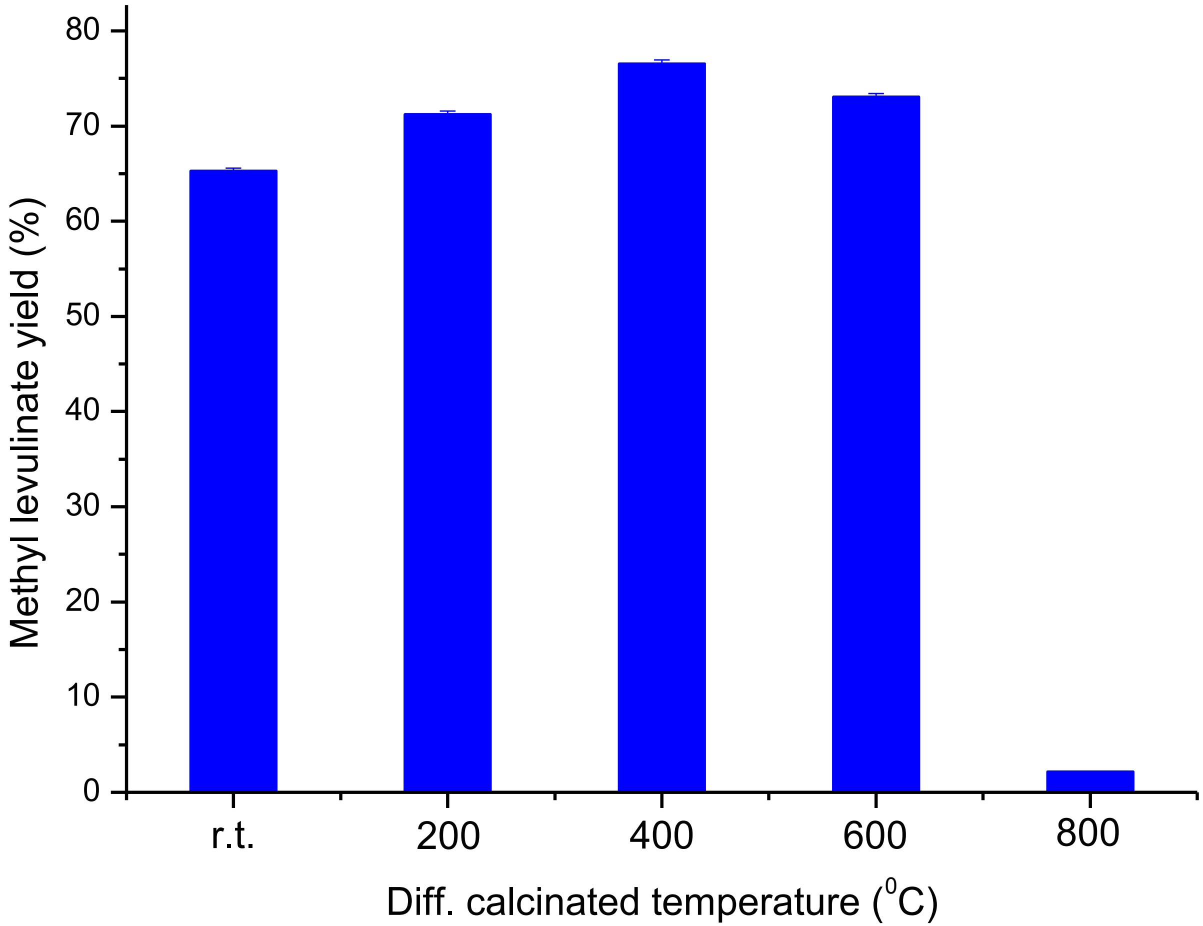
Sugar Conversion- Batch Reactor Setup

- Thermo Controller



- Pressure Gauge
- Thermocouple
- Sand Bath

Different calcination temperature



•**Reaction conditions:** Total reaction time: 1h; initial pressure: 20 bar H_2; 0.18g fructose, 0.1g nano-TiO_2 cat.; 20 mL methanol; reaction temperature 200 ^{o}C.

Verification of System Performance

- **ASTM Bound Glycerin:**
- **Gas Chromatography**

- **Feed – Yellow Grease**
- **Hourly samples all passed**

- **Free glycerin also passed due to effective wash**

- **Many more experiments, all with same results**

Hours	Conversion, %	Bound Glycerin	ASTM Result
3	99.31420368	0.098	Pass
4	98.30066719	0.202	Pass
5	99.15531765	0.107	Pass
6	99.28216343	0.102	Pass
7	99.55567416	0.054	Pass
8	99.46085984	0.078	Pass
9	98.46921055	0.196	Pass
10	98.22683796	0.215	Pass
11	99.49926247	0.071	Pass
12	99.52921909	0.078	Pass
13	99.01678495	0.124	Pass
14	99.1615341	0.111	Pass
15	99.49016029	0.069	Pass

- **These results verify the system performed the chemistry correctly – many other parameters depend on factors outside the project scope, e.g. wash water purity. Final product passed all D6751.**

Selected Results
Forest Volume and Biomass in the State of Connecticut

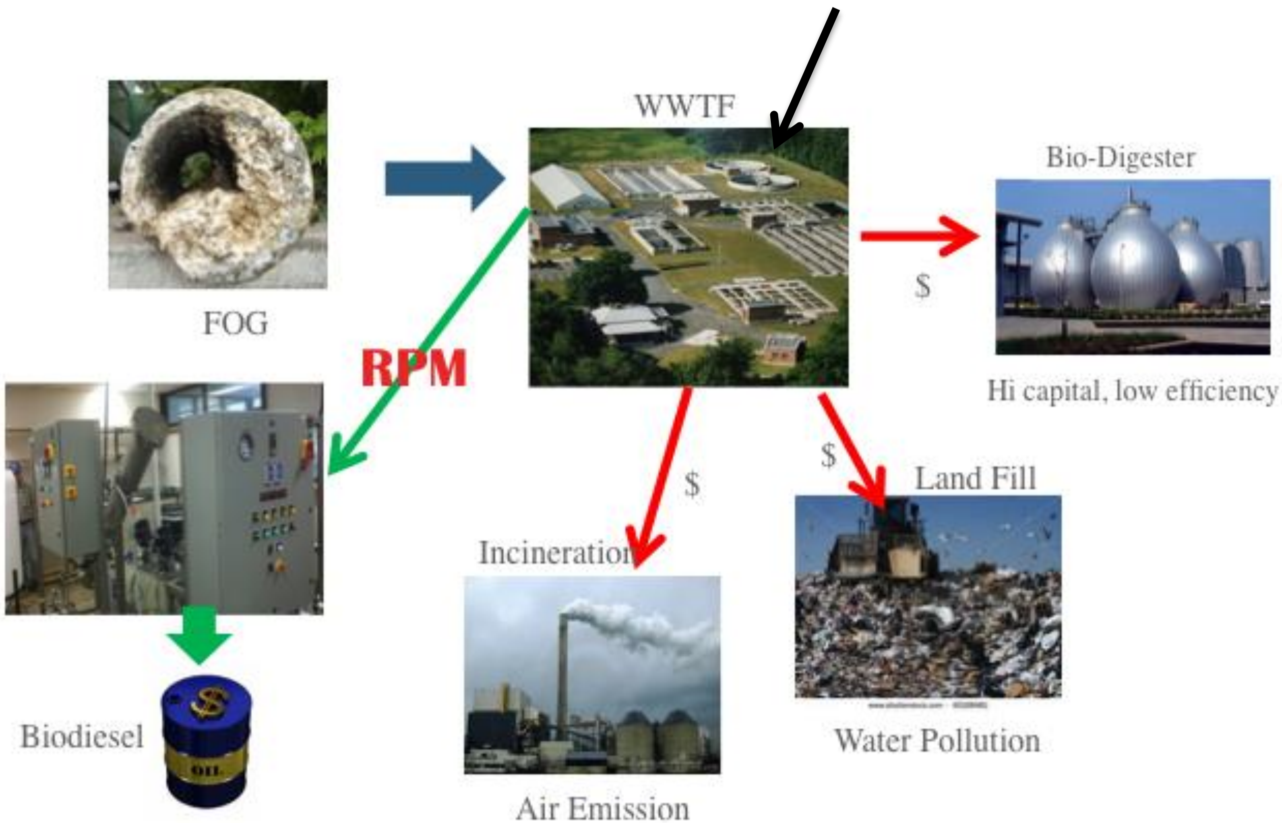
Forest Type	Parameter	Min.	Max.	Mean	Std. Dev.
Deciduous	Volume(m^3)/ha	6.94	350.65	156.16	89.32
	Biomass(Mg)/ha	11.11	269.01	117.31	62.53
	Basal area(m^2)/ha	2.3	34.44	15.97	8.21
Coniferous	Volume(m^3)/ha	8.32	278.99	100.45	66.42
	Biomass(Mg)/ha	4.67	81.65	33.66	19.95
	Basal area(m^2)/ha	2.3	36.73	13.61	8.11
Mixed	Volume(m^3)/ha	31.68	350.93	156.85	72.6
	Biomass(Mg)/ha	20.06	175.75	81.49	38.93
	Basal area(m^2)/ha	4.59	36.73	16.84	6.68

•2. Economic impact of waste-based biodiesel

	Low Case Scenario		High Case Scenario	
Variable	Average Annual Change	Net Present Value	Average Annual Change	Net Present Value
Employment generated	61	-	81	-
Increase in Gross State Product ($2010)	$11,904,762	$178,635,563	$16,476,190	$247,986,697
Increase in Real Disposable Income ($2010)	$3,523,810	$53,929,334	$4,857,143	$74,134,221
Increase in Net State Tax Revenues ($2010)	$1,000,000	$14,444,150	$1,000,000	$14,444,150

RPM ST – First project
Brown Grease to Biodiesel

•**Torrington, CT. Wastewater Treatment Facility (WWTF)**



- **All current brown grease disposal methods cost lots of money.**

•**RPM proposes a money-making solution for 28,000 WWTF in the USA**

2 - Technical Accomplishments/ Progress/Results (cont'd)

- Benchmark the progress versus previously reported results - Not Applicable.

- Benchmark the Accomplishments against the technical targets – All Goals were Met (rapid plant growth, excellent catalysts, economic scale-up of catalysts, scale –up of reactor, tech transfer.

- For projects presented at the 2011 Platform Review, please provide a status of your current progress in reaching specific technical targets versus the status shown in 2011. Not Applicable.

3 - Relevance

- **How Project Accomplishments Meet the Goals and Objectives of the Biomass Program** – "Develop and transform our renewable biomass resources into cost competitive, high performance biofuels, bioproducts, and biopower through targeted research, development, demonstration, and deployment supported through public and private partnerships." This is Exactly What was Done.

- **How the Project Considered Applications of the Expected Outputs**.

Several Chemical Transformations Including Transesterification, esterification, Fischer Tropsch, and Sugar Conversions were Tried. Applications Involved Several feeds Cellulose, Poplar, Wood Chips, Sugars, vegetable oil, etc.

- **This Project was Directly Relevant to the Bioenergy Technologies Office**, alignment with MYPP goals, and relevance for the overall Bioenergy Industry in CT and Elsewhere.

4 - Critical Success Factors

- **Technical and Commercial Viability depend on** the following criteria: cost of Catalyst, Implementation of Heterogeneous Catalysts, Type of Biomass Source, Desired Product, Cost of genetically engineered Plant Source, Scale-Up Costs, Potential Subsidies, Other factors.

- **The Top 2-3 Potential Challenges** (technical and non-technical) to be overcome for achieving successful project results are:

1. Economic Aspects of New technology.
2. Operation Costs of Commercial Plant.
3. Market Need.

- **The State of Technology has been Advanced** in terms of High Yield High Value Products. The **Commercial Viability of Biomass and Biofuel Production is being Implemented** Commercially Via Tech Transfer.

5. Future Work

- This Project Was Completed March 1, 2013. We still plan Improvements of Catalyst Synthesis and Manufacturing.
- Provide a Gantt Chart to show estimated timeline. Not Applicable.
- Highlight Upcoming Key Milestones – go/no go decision points. The Project is Completed.
- Address how you will deal with any decision points during that time and any remaining issues. Not Applicable.

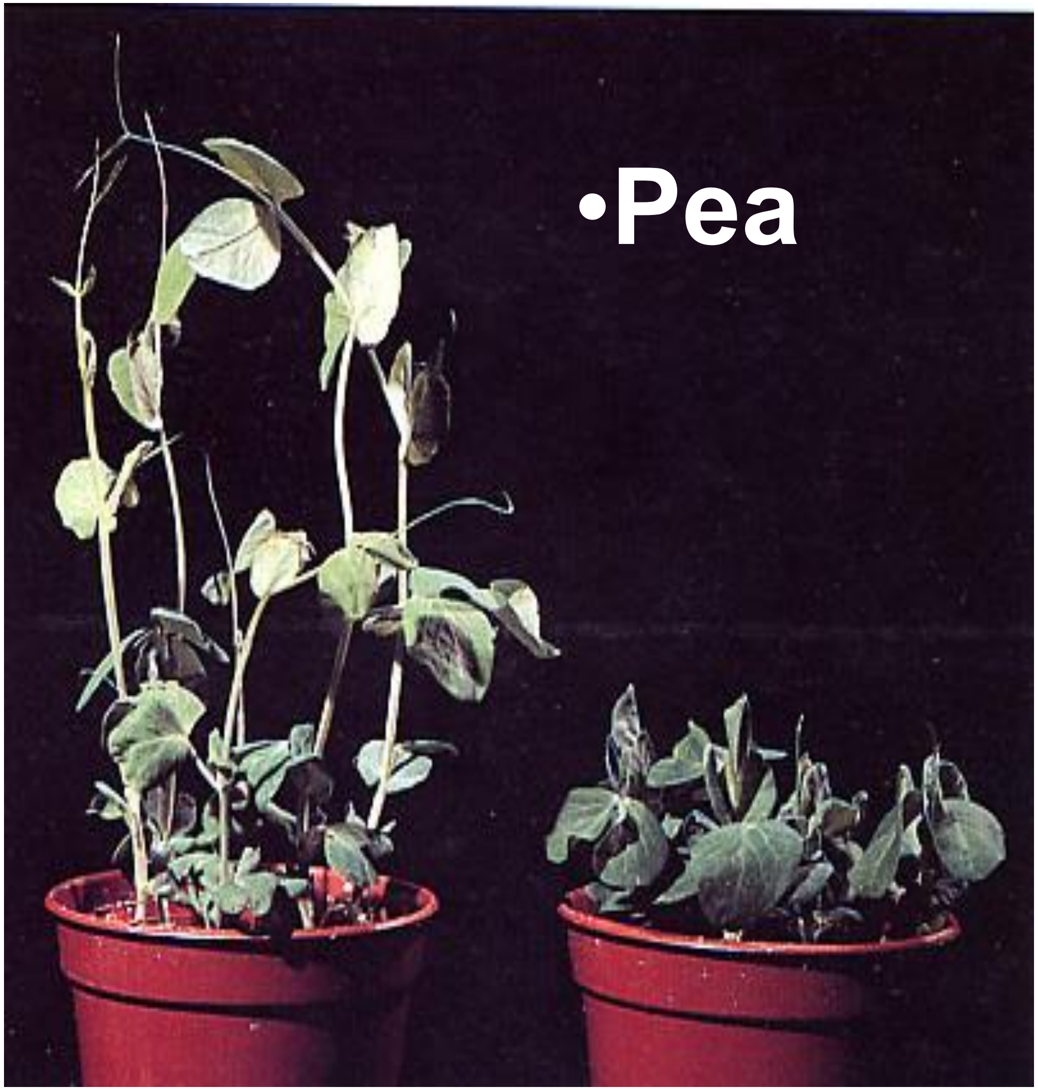
Summary

- Summarize the **Key Points** you wish the audience and reviewers to take away from your presentation in the categories of:

1) **Approach** – We Used a **MultiProng Integrated Approach** Involving Biology, Chemistry, Chemical Engineering, Natural Resources and Economics.
2) **Technical Accomplishments** – New Catalysts, Plant Sources, Scaled Up Reactors, Economic Analyses, and Resource Analyses were Done.
3) **Relevance** – This Preoject is Relevant to the Biomass Conversion and Biofuel, Strategy of the State of CT.
4) **Critical Success Factors and Challenges** – Success in Catalyst Synthesis, Catalytic Reactivity, Scale-Up and Analyses Have been Made.
5) **Future Work** – Continued Licensing and Tech Transfer.
6) **Technology Transfer** – this is well underway. We hope to expand to more Companies.

- **Our strategy to improve the yield of cellulosic bioenergy crops is through manipulation of plant hormone levels *in planta***
-

The plant hormone gibberellin (GA) plays a key role in plant growth



•Wild-type • GA deficient

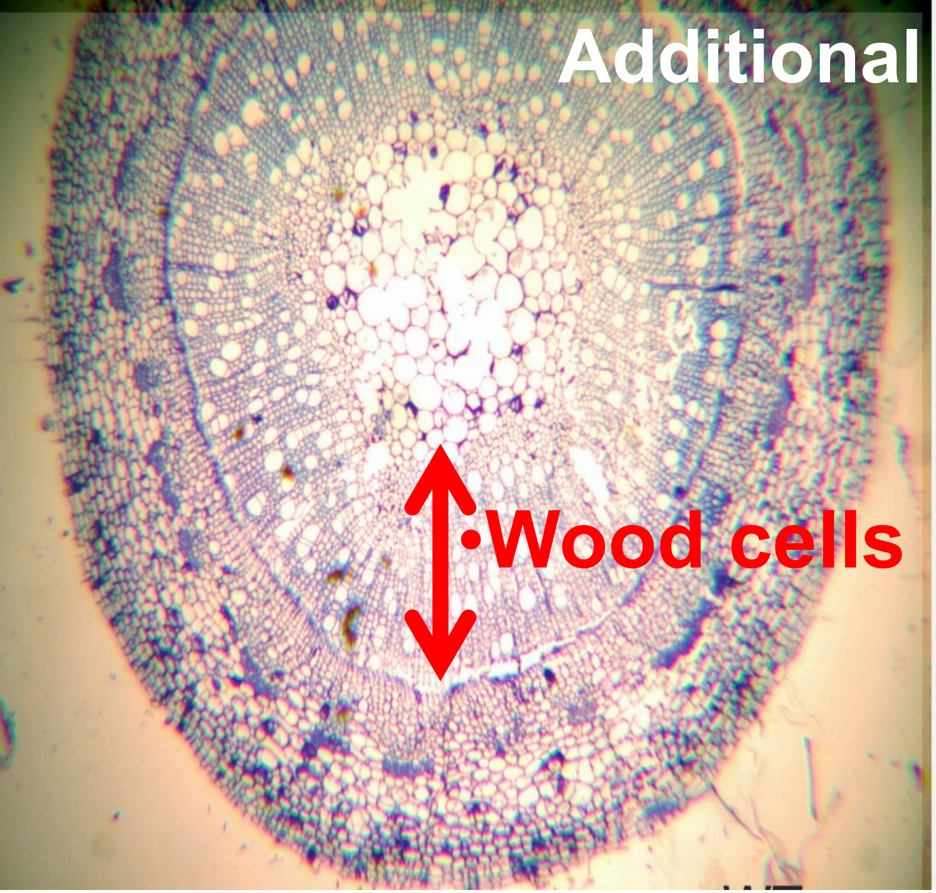
• Wild-type Sprayed w/ GA

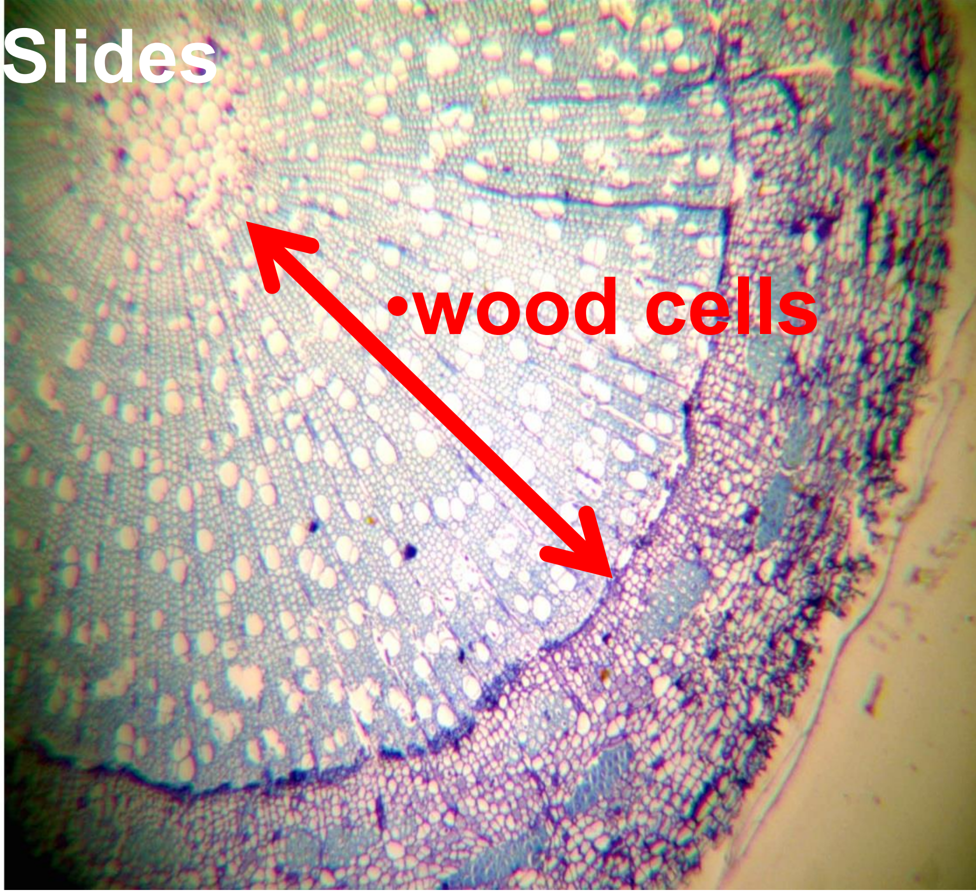
•We have constructed GA20, Det2 and both hgenes & BR over-production:

•GA20: Gibberellin biosynthetic gene

•Det2: Brassinosteroid biosynthetic gene

Additional Slides

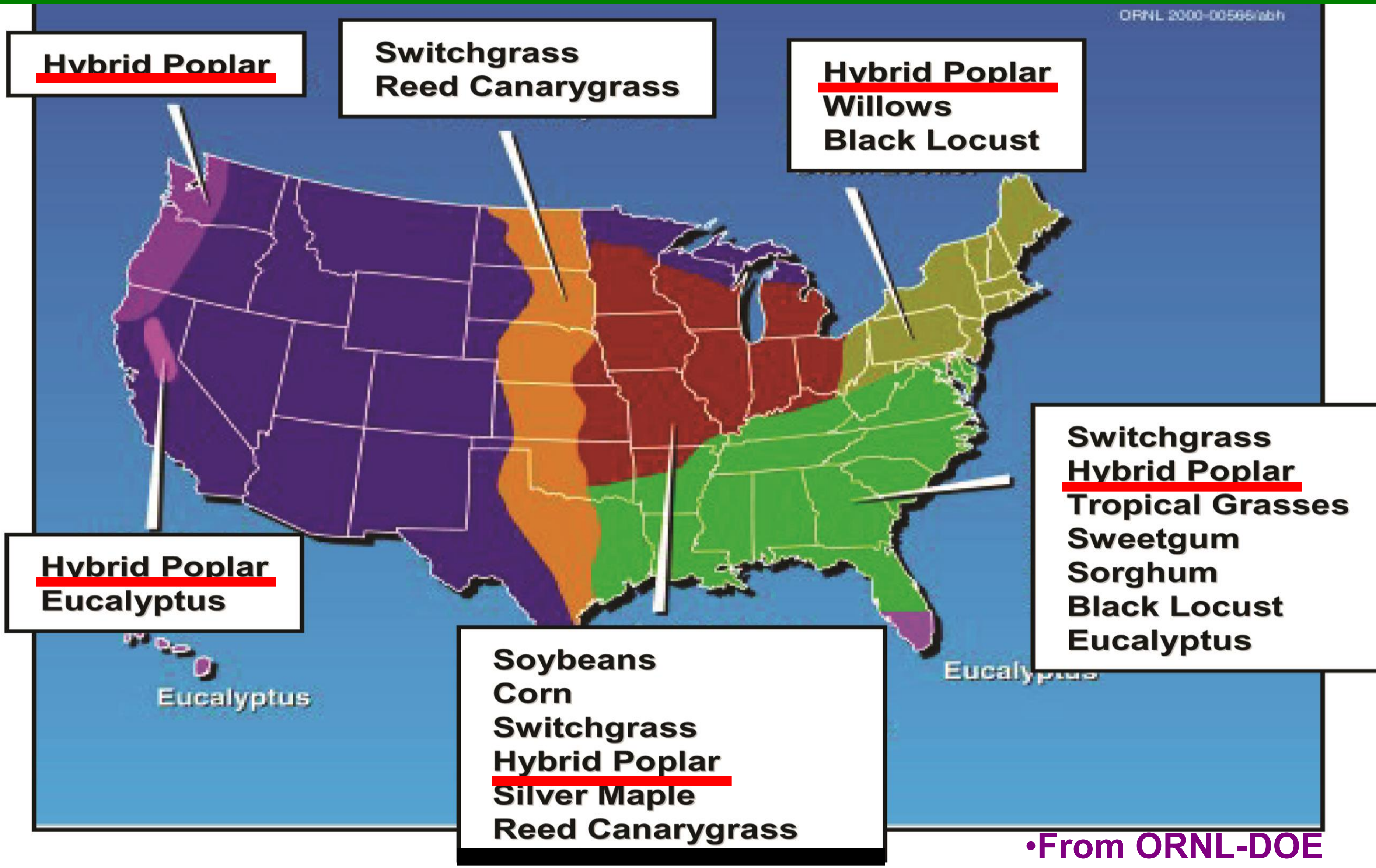




•Wild type stem **GA20+Det2 stem**

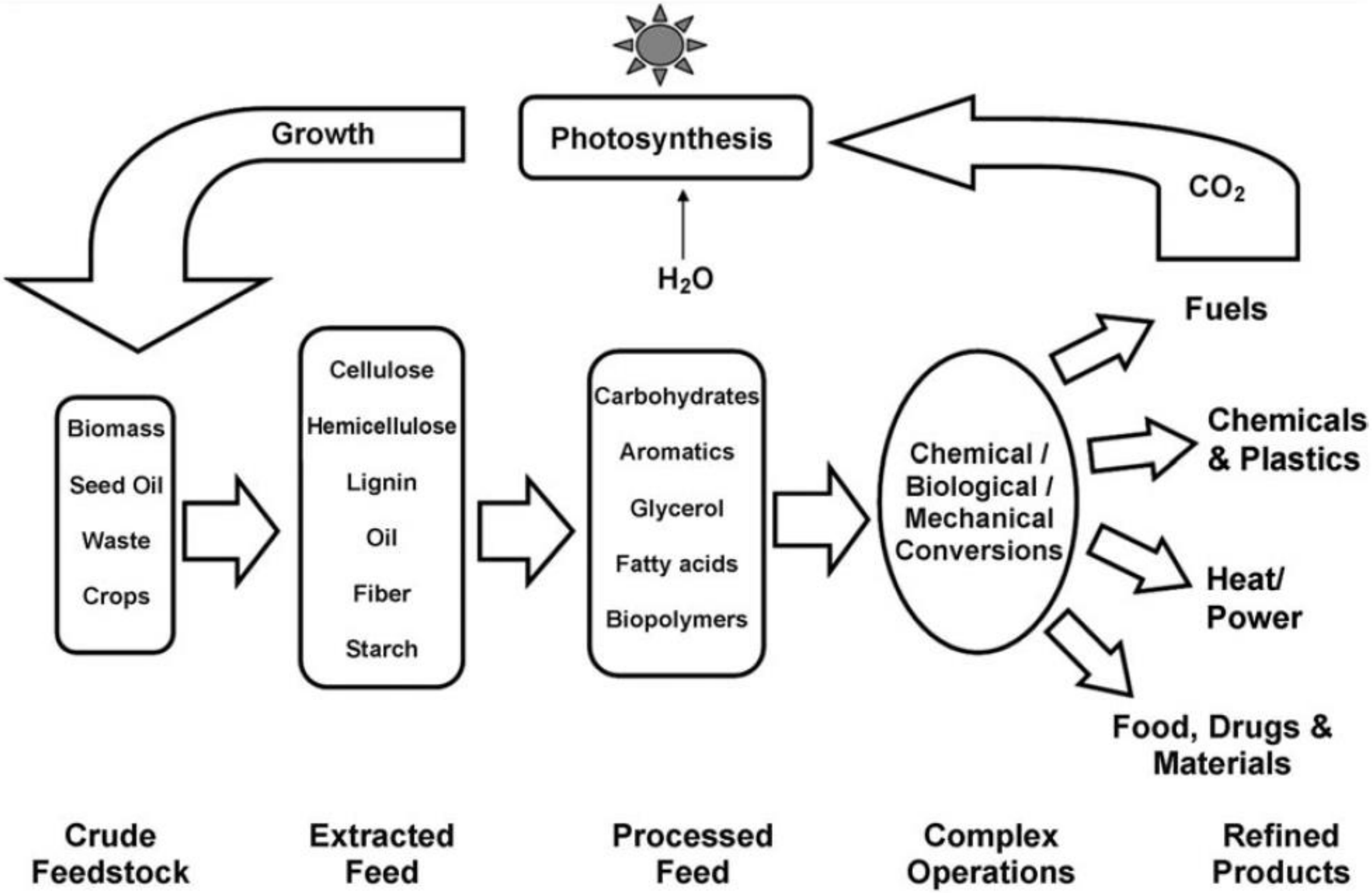
•Stem cross sections of two month old poplar plants. GA20+Det2 produced much more wood cells than the non-transgenic ones.

•Since poplar is an energy crop in U.S, we have produced transgenic poplar plants with GA20 and Det2 genes

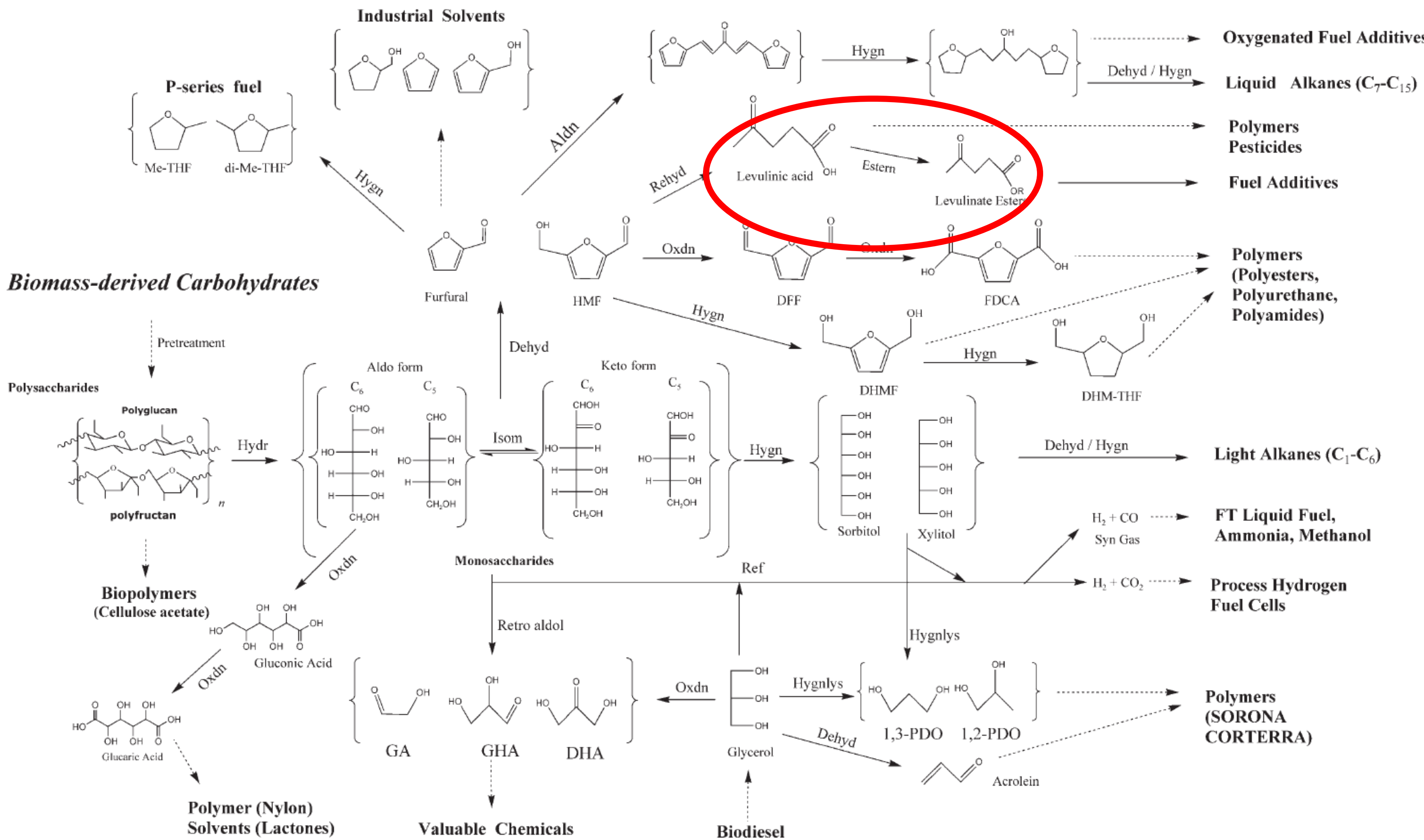


•From ORNL-DOE

Overview of the processing of crude feedstocks to refined products in a sustainable biorefinery



•*Ref: Angew. Chem. Int. Ed.* **2007**, *46*, 7164-7183



•Ref: *Angew. Chem. Int. Ed.* **2007**, *46*, 7164-7183

Methyl Levulinate (ML)

- **A very useful precursor to various chemicals.**

  --fuel additives, polyacrylates, polycarbonates, bio-degradable herbicides, and photo-synthesis promoters etc.

- **A promising "green" liquid fuel*.**

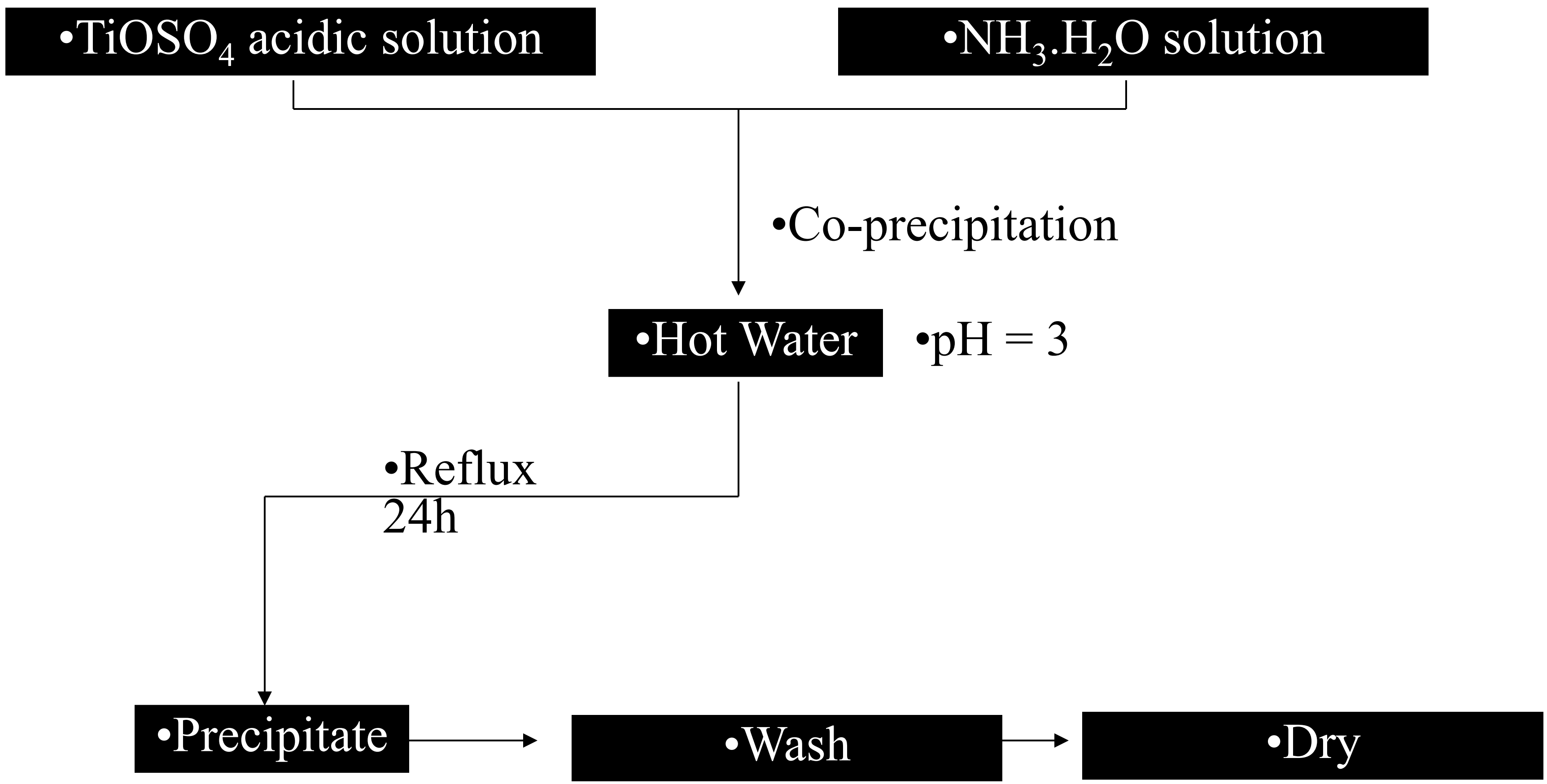
  -- promising diesel additive to replace methanol and ethanol.

- **Important intermediate formation in biomass to fuel conversion.**

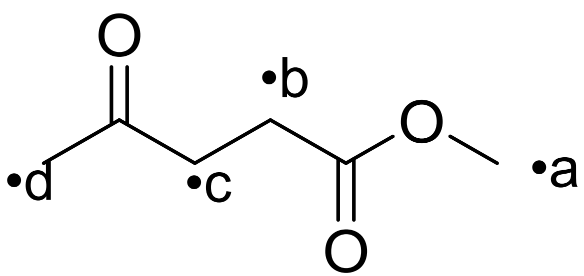
•*** Lake et al. "Diesel fuel compositions containing levulinate ester" US Patent: US20100313467 A1.**

•**Tominaga et al. *Green Chem*. 2011, 13, 810**

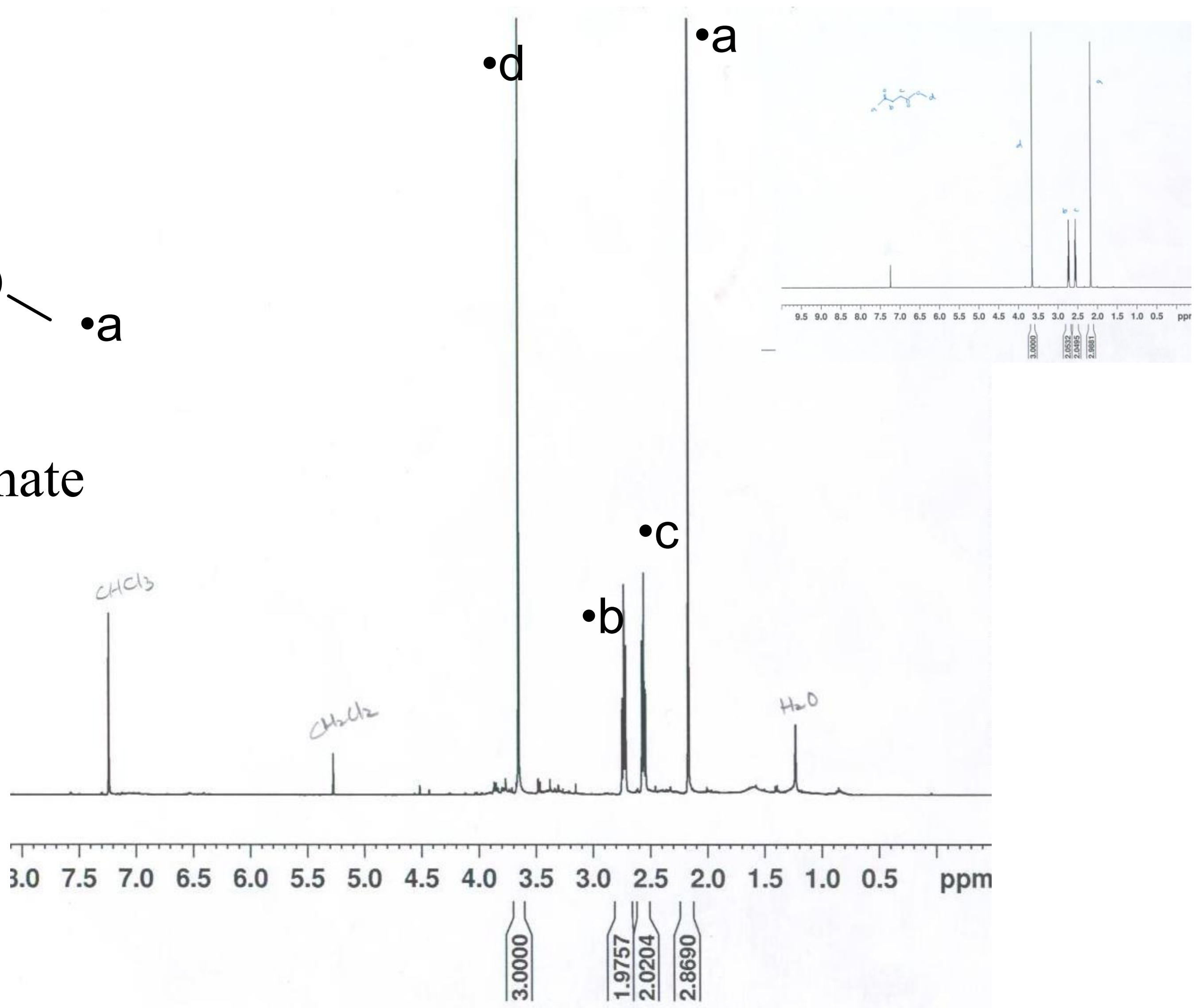
Nano TiO_2 Heterogeneous Catalyst - Preparation



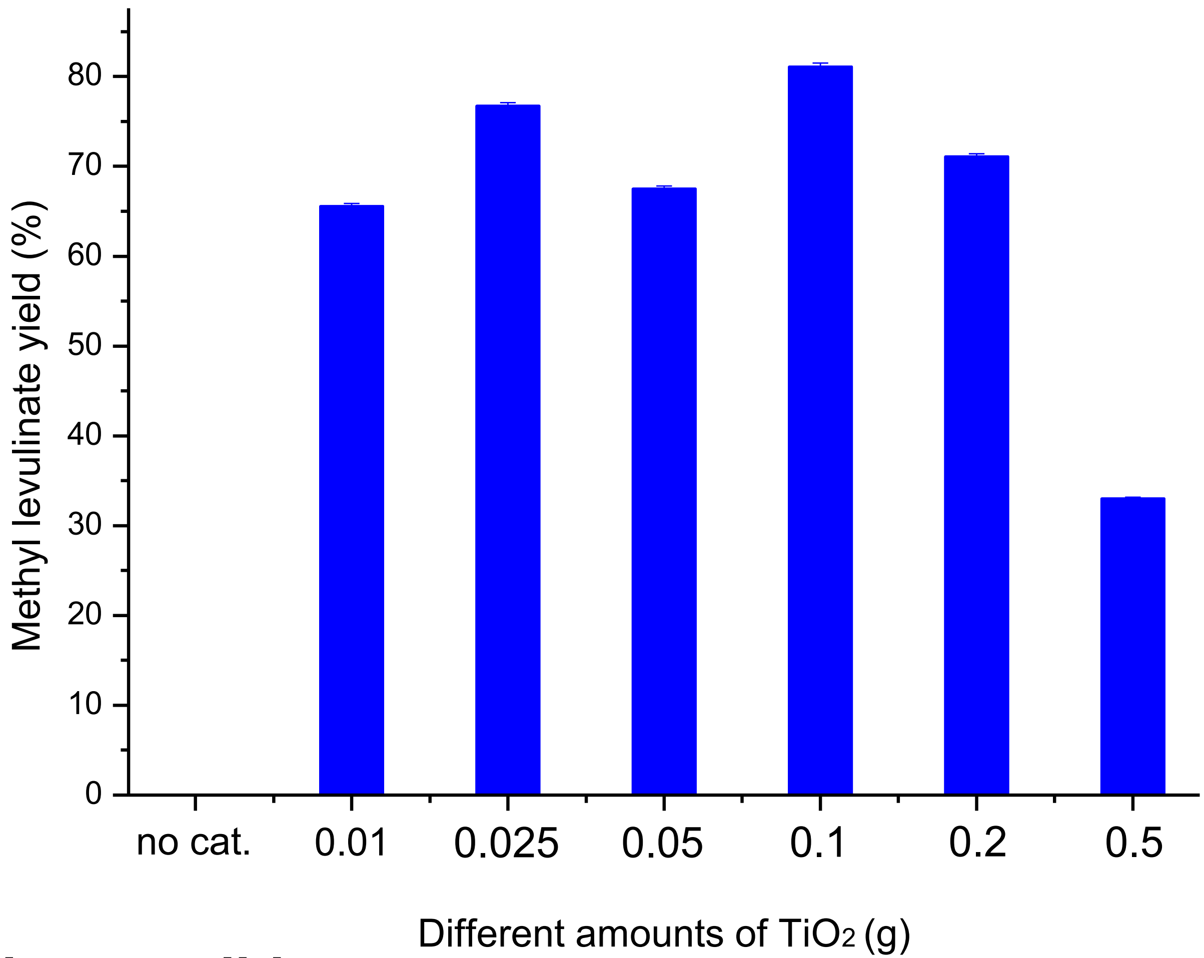
Products – H-NMR



•Methyl Levulinate

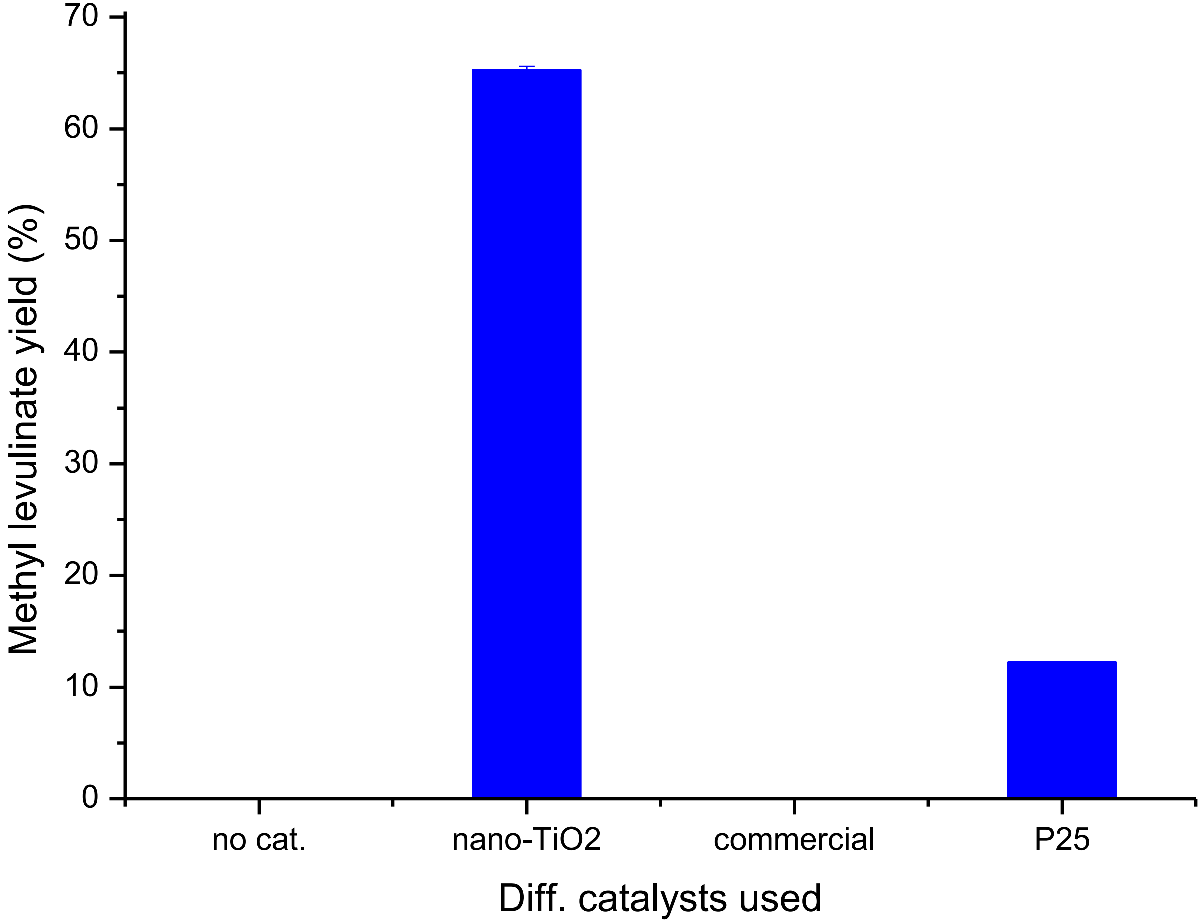


ML Yields VS Amounts of Catalyst Loading



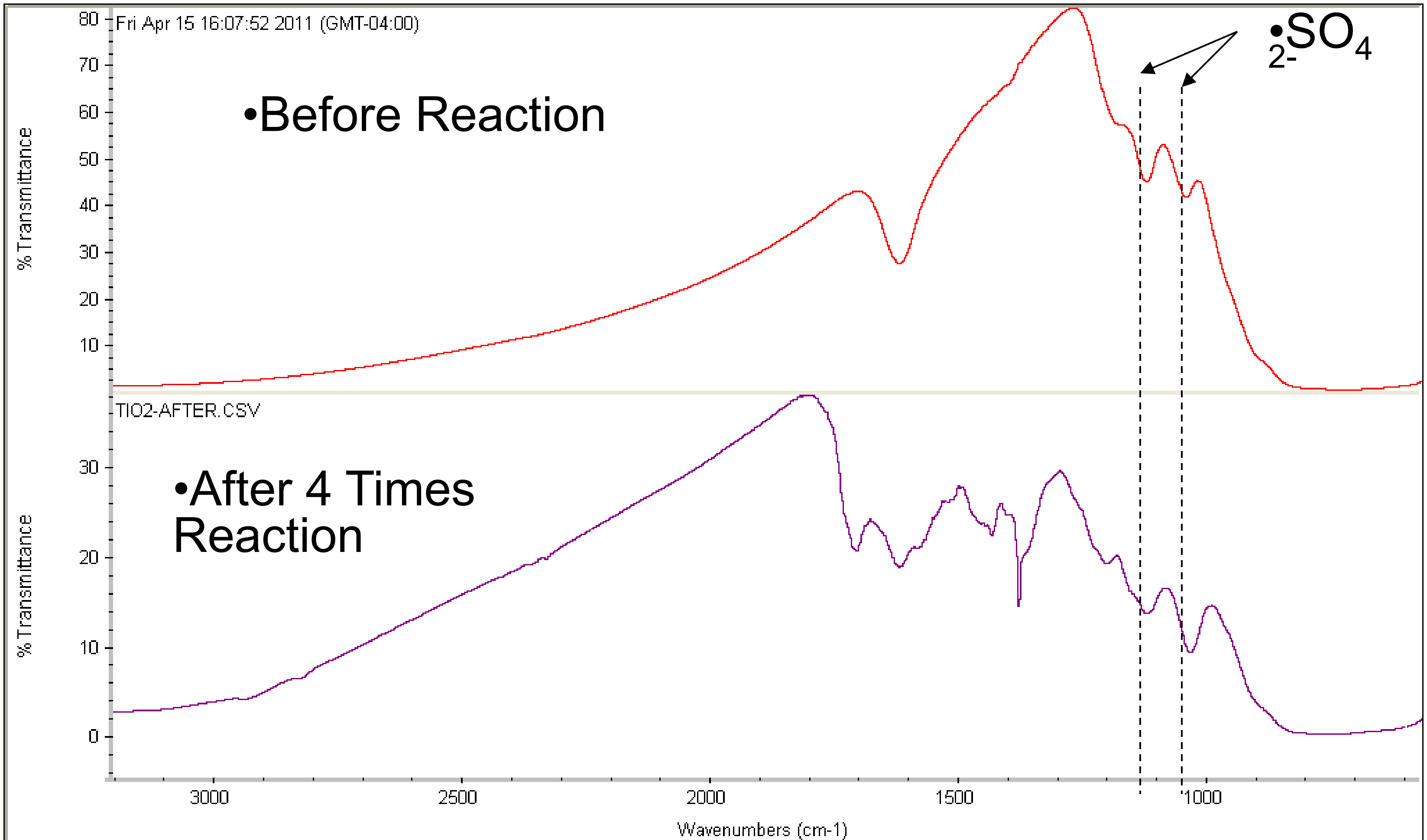
•**Reaction conditions:** Total reaction time: 20 h; initial pressure: 20 bar N_2; 1 mmole fructose; 20 mL methanol; reaction temperature 200 ^oC

Comparison of different TiO_2 catalysts



- **Reaction conditions:** Total reaction time: 1h; initial pressure: 20 bar N_2; 0.18g fructose, 0.2g cat.; 20 mL methanol; reaction temperature 200 ^oC.

SO_4^{2-} Residue – FTIR



•Dong et al. *J. Phys. Chem. C*, 2009, 113, 16717-16723

Conclusion

•High surface area sulfated nano-TiO_2 was successfully prepared.

•The prepared TiO_2 has novel catalytic activity for biomass conversion.

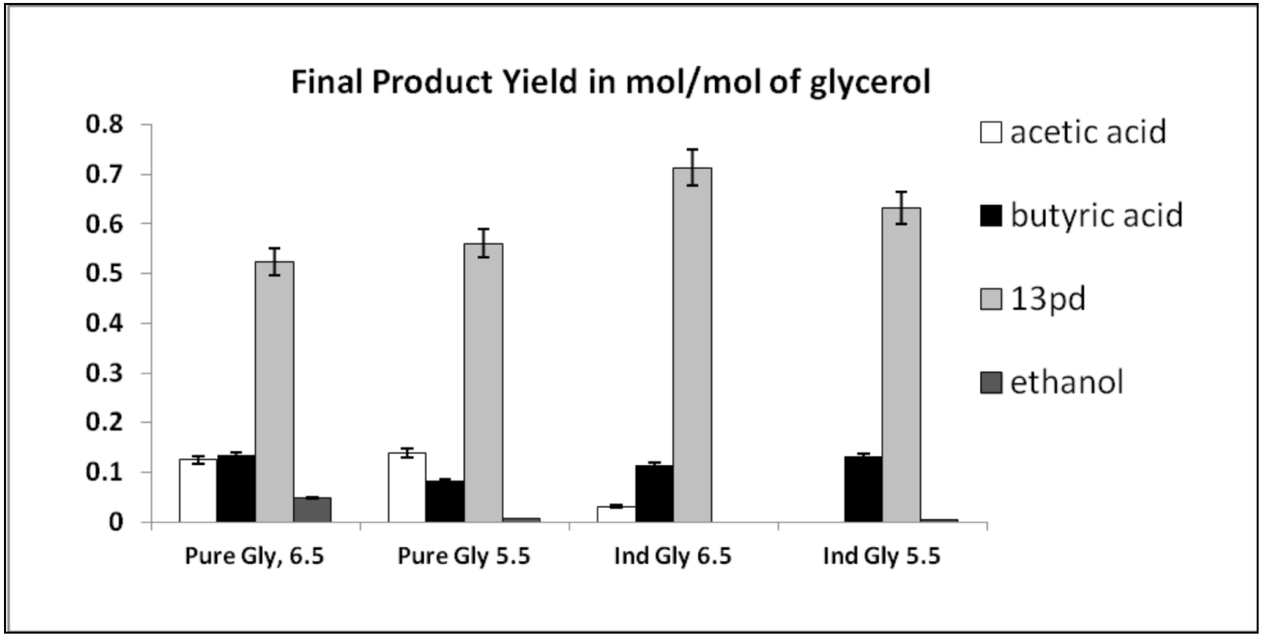
•High selectively of methyl levulinate product

•Only 5 wt.% nano-TiO_2 is needed for the reaction.

•H_2 condition can maintain the activity of catalyst.

•Regeneration of catalyst activity by simple calcination.

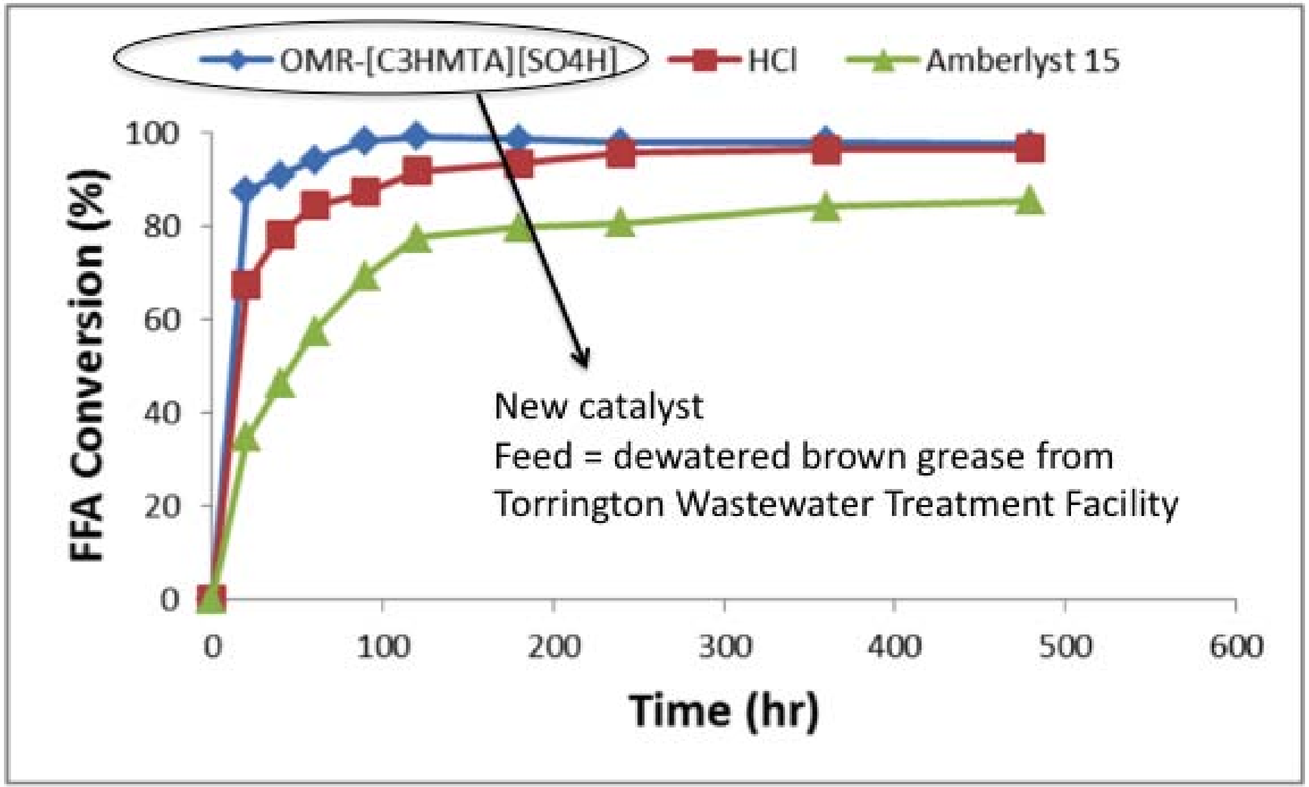
New work started in this project – specialty chemicals



- **Illustration of 1,3-PD work.**
- **New process to produce HMF and Levulinic Acid also yielding positive results.**

- **70% molar yield, best in the world for 1,3-propanediol without GMO.**
- **Feedstock = waste glycerol from biodiesel production.**
- **Designed and controlled fermentation to manipulate metabolic pathway of multi-species bacterial consortium.**

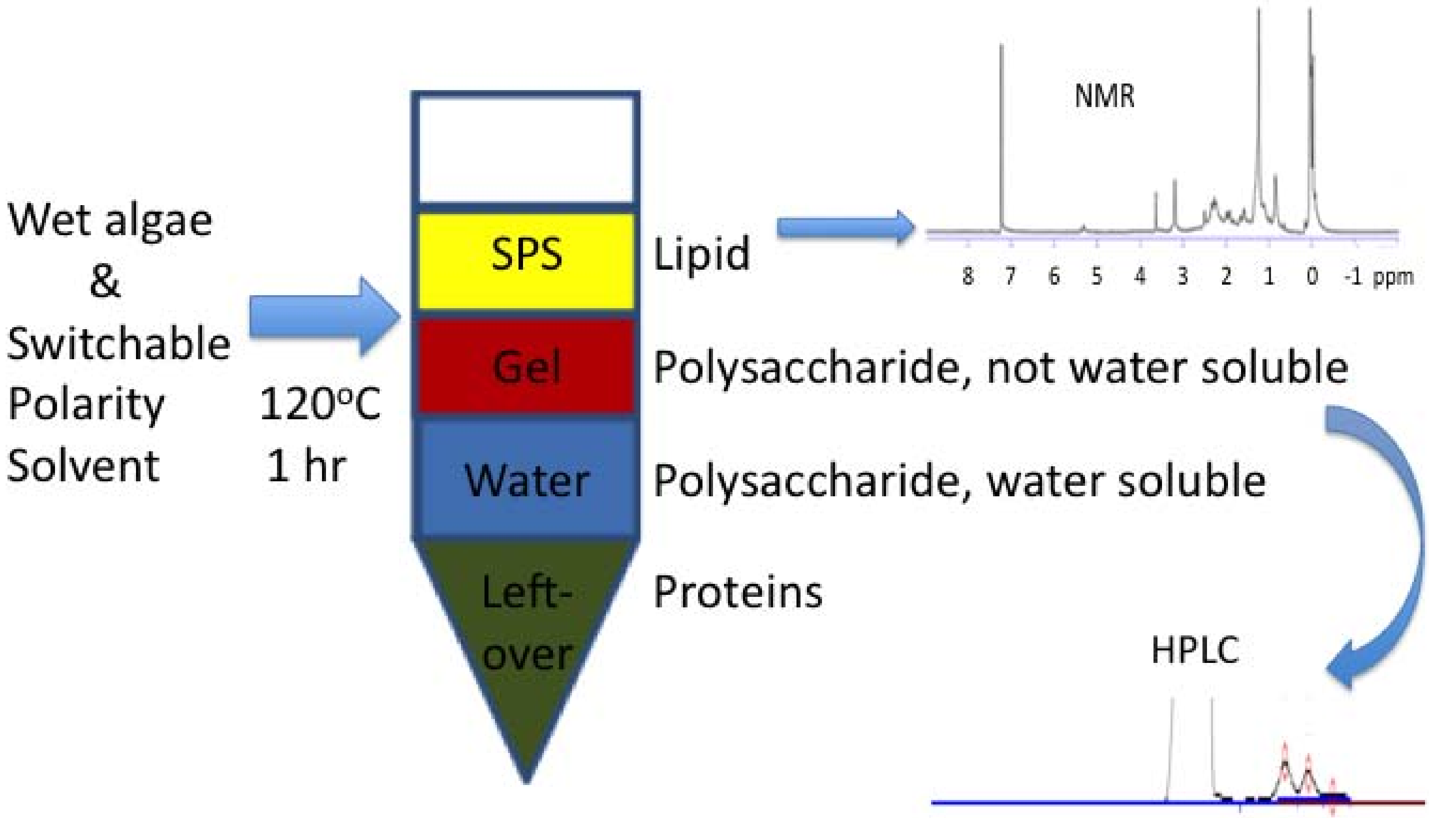
New work started in this project – solid catalysts



- **Illustration of super acid work.**
- **New super base catalyst also yielding positive results.**

- **New super acid outperforms homogeneous acids like HCl and H_2SO_4 as well as commercial super acids such as Amberlyst.**

New work started in this project – Soft Biomass Extraction

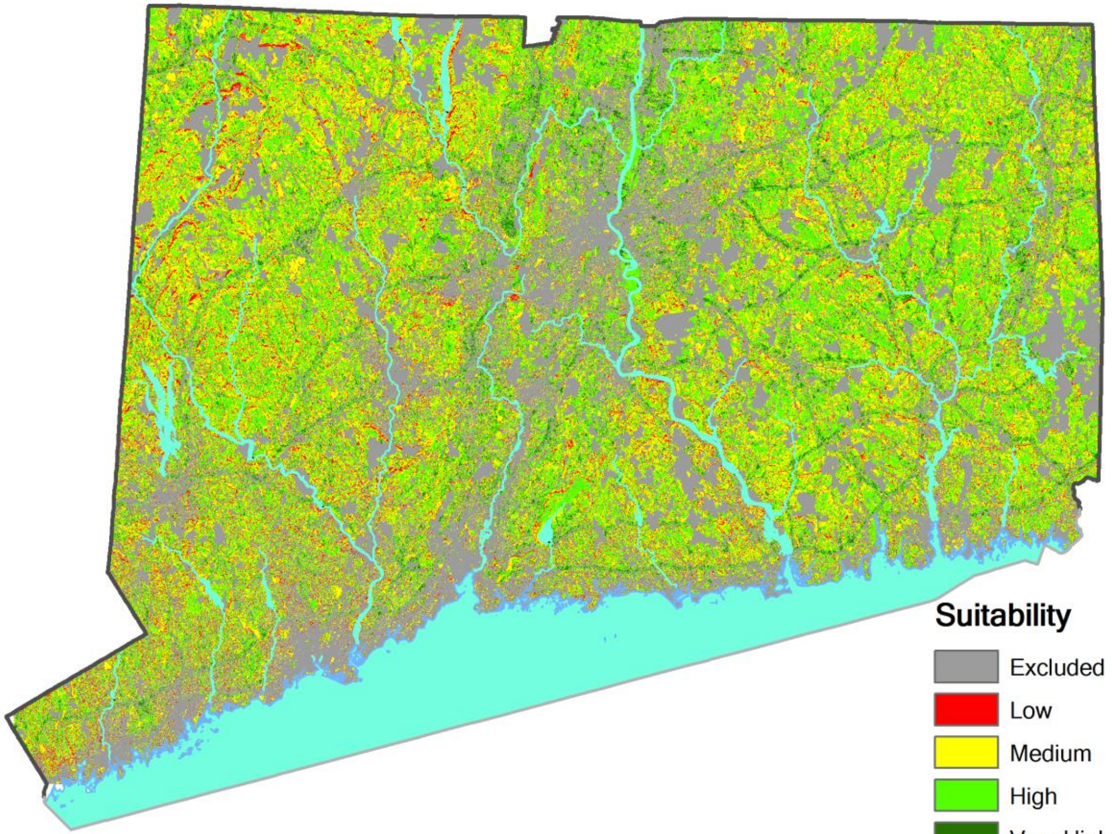


- **Quantitative and simultaneous extraction of oils and sugars from both micro-algae and macro-algae. Preliminary design of engineered system to recycle solvent and run continuously.**

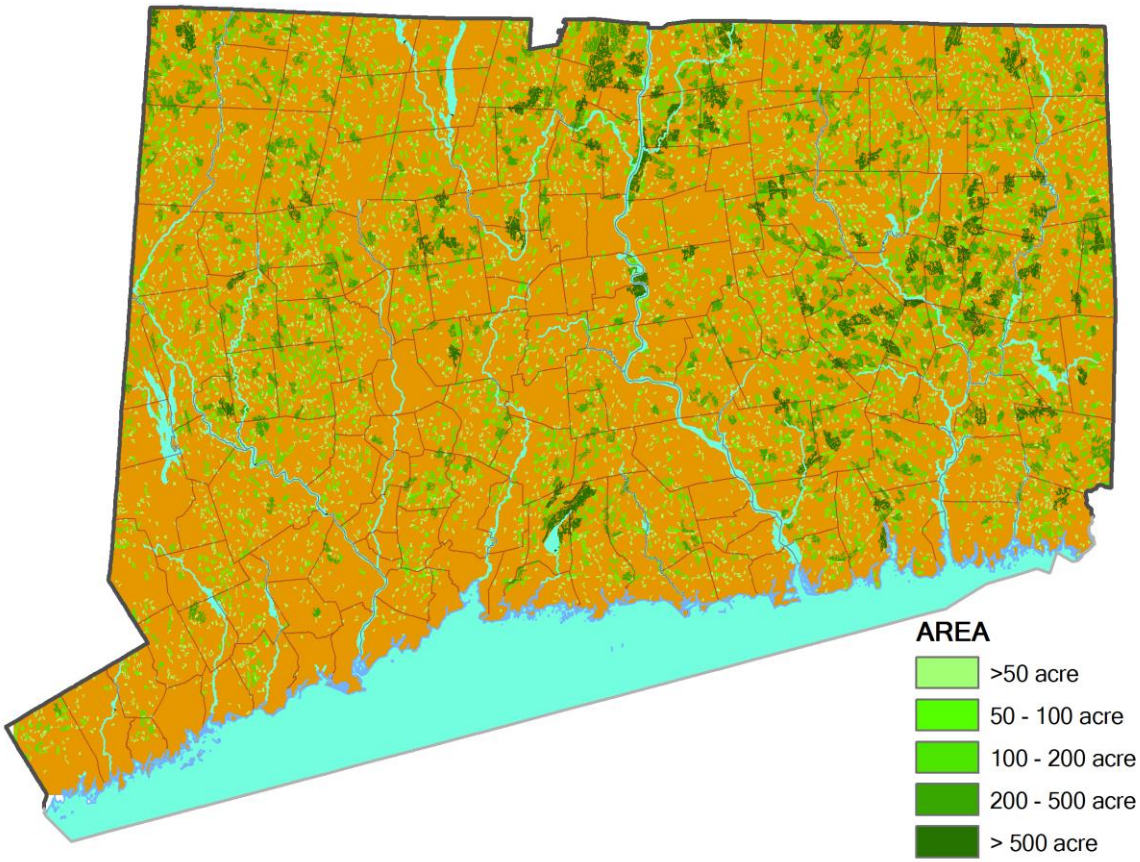
•Major Research Findings

- **Connecticut does not have a significant source of virgin feedstocks;**
- **Connecticut is rich in waste-based and advanced feedstocks;**
- **Reducing diesel-related emissions through increased use of biofuels would deliver health benefits to Connecticut residents;**
- **High costs of waste management makes waste-based feedstocks use in biofuels attractive;**
- **Development of high-value byproducts in the refining process provides critical supplemental cash-flow to biofuels production;**
- **Development of biofuels and bioenergy should be done in conjunction with reforms in Connecticut's waste management sector.**

Selected Results
Hybrid poplar suitability map of Connecticut



Selected Results
Economically Viable Lands for Hybrid Poplar in Connecticut

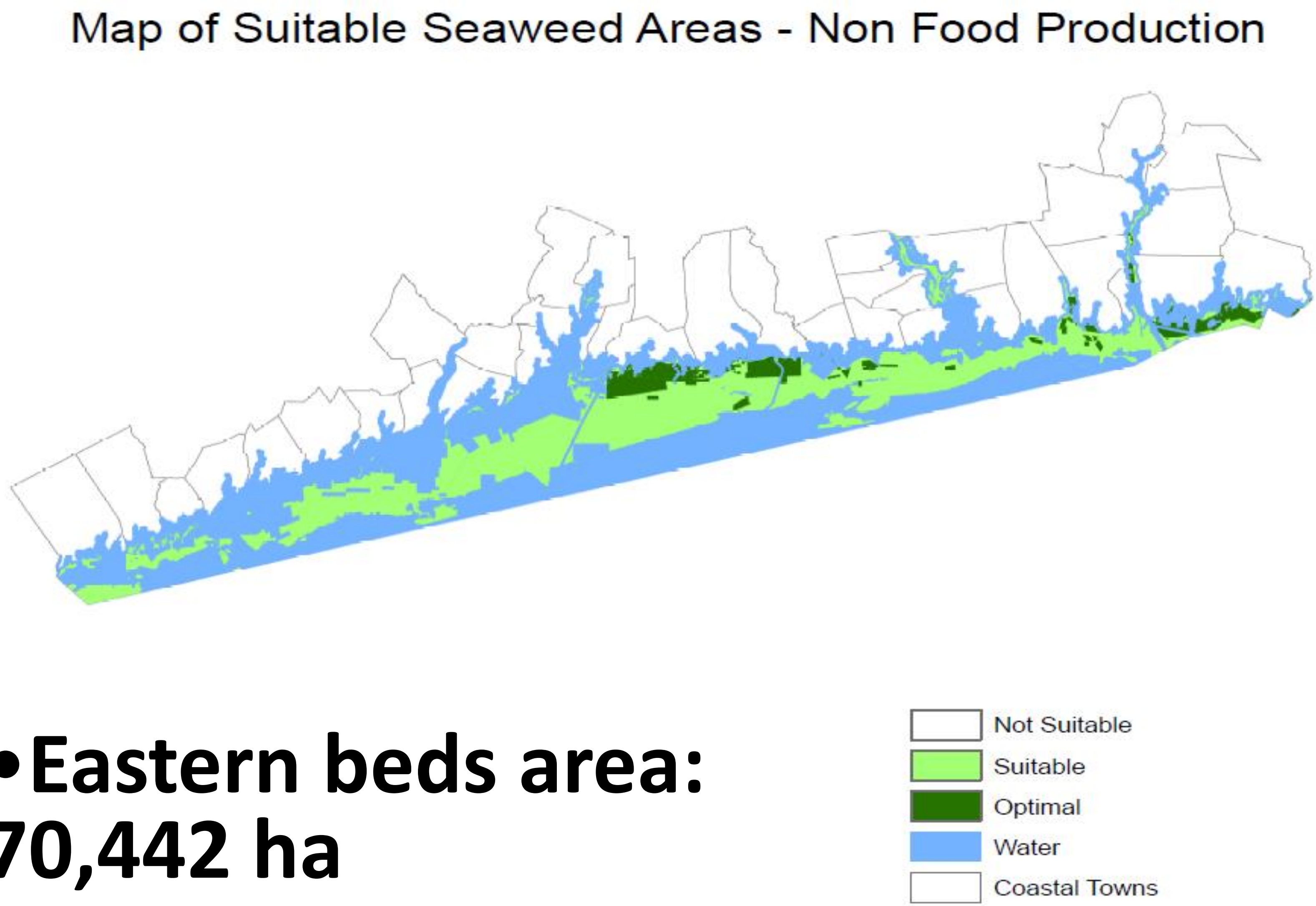


•3. Potential of Seaweed Production in LIS – State-wide Economic Impact

- Model based on inputs from refinery currently under development in Fairfield County, CT;
- Assumes use of all dry Gracilaria (60,000 ton/year);
- NPV calculation based on 12.5% discount rate, 20 year time-frame, and assuming 10% annual growth (of plants).

Variable	Unit	Average	NPV
Total Employment	*Jobs*	1078	N/A
Farm, fishing, forestry occupations	*Jobs*	18	N/A
All Races	*Jobs*	867	N/A
Real Gross Domestic Product f.d.	*Millions of 2000$*	$212.4	$924.8
State Expenditures at State Average Rates	*Millions of 2008$*	$3.6	$9.9
State Revenues at State Average Rates	*Millions of 2008$*	$14.8	$65.5
Net State Revenues	*Millions of 2008$*	$11.2	$55.6

•3. Potential of Seaweed Production in LIS – State-wide Economic Impact



- **Eastern beds area: 70,442 ha**
- **Total Potential**

•4. Anaerobic Digestion Strategies in CT

- Project Overview:
  - – CCEA conducted this study as part of the overall biofuels intiative; its results are included in a forthcoming publication.
  - – Results were presented to the XXXI U.S. Energy Association for Energy Economics Conference in Austin, TX.

- Background:
  - – CT is encouraging the opening anaerobic digestion facilities to deal with organic waste, mainly food residues;
  - – CT residents and businesses generate 150,000 tons of food scraps annually;
  - – The study considered residues generated by large generators only, about 9,500 tons per year.
  - – CCEA used a multiple-step approach to select the location(s), size, and the economic viability of anaerobic digestion systems for generating electricity and producing fertilizer production.

- Findings:
  - – Anaerobic Digesters will require State support to finance capital expenditures;
  - – A single, large facility is more efficient than multiple, small facilities, even considering transportation costs;
  - – Annual electricity generation would be about 1 million kWh per year;
  - – Annual sequestrated CO2 will be 1.1 million tons per year;
  - – The systems would generate 65 jobs, contributing to the state’s economy by $85 MM/y;
  -

•5. 2005 Biodiesel and Health Study Update

- Project Overview:
  - – The study updated the findings from the 2005 CCEA study: *Biodiesel: Fuel for Thought, Fuel for Connecticut's Future*.

- Background:
  - – New biodiesel price data were used to estimate the cost of substituting 20% biofuel;
  - – No specific feedstock was identified;
  - – The study used new values for emissions reduction benefits from the U.S. EPA.

- Findings:
  - – The evaluation is sensitive to the initial assumptions about emission quantities;
  - – Using historic price data and current price data, mandating 20% biodiesel using 2005 consumption data generate a net loss of $92 million per year;
  - – Using the new EPA values on health benefits from emissions reductions, benefits in 2015 would be positive for CT, with gains of $72 million per year;
  - – Further benefits such as amenity values and jobs created through the use of local feedstocks have not been included, but constitute additional sources of cost mitigation.

Responses to Previous Reviewers' Comments

- If yours is an on-going project that was reviewed previously, address 1-3 significant questions/criticisms from the previous reviewers' comments. Not Applicable.

Publications, Presentations, and Commercialization

- US Patent 8,119,832 B2, R.S. Parnas, Systems for Alkyl Ester Production, February 21, 2012.
- S.Y. Li, R. Srivastava and **R.S. Parnas**, Study of *in situ* 1-butanol Pervaporation from A-B-E Fermentation Using a PDMS Composite Membrane: Validity of Solution-Diffusion Model for Pervaporative A-B-E Fermentation, *Biotechnology Progress*, **27**(1), 111-20, 2011.
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- Several other patents and papers are in preparation.

Publications, Presentations, and Commercialization

- Sustainable Energy in the 21st Century, 18th Ann.Conf. on Environmental Issues, Medgar-Evers College, March 9, 2013.
- FOG to Fuel: A Remarkable Project in Northwest Connecticut, 85th Annual Meeting of NYWEA, Feb.6, 2013.
- The role of separations in biofuel production, Tunghai University, July 18, 2012, Taiwan.
- The Importance of Separations in Biomass Conversion Processes, International Top-level Forum on Engineering Science and Technology Development Strategy, July 7, 2012, Beijing, China.
- Separation Processes in Biofuels Production, Sichuan University Chemical Eng. College, June 25, 2012.
- Industrial Chemistry for Biofuels Production, Chemistry Dept., University of Connecticut, Nov.30, 2011.
- Renewable Fuels and Renewable Polymers at UConn, Hebei University, November 10, 2011.
- Systems Integration for Biofuels Production, The 6th Sino-US Chemical Engineering Conference, November 7, 2011, Beijing China.
- How We can Produce and use Biofuels in Connecticut, CT Farm Energy Fair, Eastern CT State University, Keynote Speech, July 21, 2011.
- Systems Integration for Efficient Biofuels Production, Sichuan University, June 20, 2011.
- Renewable Polymers and Polymers for Renewable Energy, Fudan University, June 16, 2011.
- Industrial Chemistry in the Biofuels World: It’s not just the reactor, Brown University Chemistry Dept., February 22, 2011.
- Kickstarting a Biofuels Industry in New England, Chemical Engineering Dept., Worcester Polytechnic Institute Chemical Engineering Dept., November 17, 2010.

Business Development – New Company Description & New Funding

- RPM Sustainable Technologies formed March 2011.
- **RPM** stands for **R**obson (CEO), **P**arnas (CTO), **M**adrak (COO), the original 3 founders.
- RPM Sustainable Technologies licensed all Parnas IP from Uconn.
- RPM Sustainable Technologies has created 6 jobs in CT and 2 jobs in France.
- RPM has attracted 750 k$ in CT State Funding and 250 k$ in private investment, with an additional 2.4 M$ of private investment verbally committed.
- RPM has been publicized in American, French and Italian News articles.
- Contract for **first project in place**: Torrington, CT WWTF