[M.L. 2014] Project Abstract
For the Period Ending June 30, 2017

PROJECT TITLE: Demonstrating innovative technologies to fully utilize wastewater resources
PROJECT MANAGER: Roger Ruan
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FUNDING SOURCE: Environment and Natural Resources Trust Fund
LEGAL CITATION: M.L. 2014, Chp. 226, Sec. 2, Subd. 08c

APPROPRIATION AMOUNT: $1,000,000.00
AMOUNT SPENT: $1,000,000.00
AMOUNT REMAINING: $0

Overall Project Outcomes and Results

Minnesota municipal wastewater treatment plants (MWTP) generate large amounts of oily scum, concentrated liquid (also called "centrate"), and sludge each year. These waste streams are either used as landfill (scum) and direct burning (sludge), or subjected to additional treatment (centrate). The goal of the project was to demonstrate the feasibility and effectiveness of implementing innovative technologies in municipal wastewater treatment plants. Three main activities were carried out during the project: (1) Processes have been developed to convert wastewater scum to biodiesel meeting the relevant ASTM standards, (2) Processes have been developed for sustainable growth of microalgae on centrate and full utilization of nutrients in the centrate stream, and (3) new processes have been developed thermochemically convert sludge to high value energy and materials.

During the research, the processes were evaluated for effectiveness and efficiency. Pilot scale systems for designed and fabricated for scum to biodiesel conversion, mass cultivation of microalgae on centrate supplemented by glycerol, and microwave assisted conversion of sludge to bioenergy and biomaterials. Four graduate students and four research scientists were involved and trained during the project. One patent for scum to biodiesel production was filed and one propitiatory technology for fast microwave assisted pyrolysis has been licensed to a company. More than 30 papers have been published on peer-reviewed journals. More than 10 presentations have been presented in state, national, and international meetings. Demonstration of the pilot systems has been given to Superior Process Technology, Resynergi Inc., Minnesga Inc., LZL Engineering, eVende, Metro Council Environmental Service. Media interviews have been given to Minnesota Daily, Channel 5, and Channel 11. The outcome of the project has significant impacts on Minnesota's renewable energy production, environment conservation and protection, and economy and jobs. The new technologies can be implemented in mid to large size municipal wastewater treatment plants in Minnesota and elsewhere, producing significant amounts of renewable energy for internal use or to be distributed to the market, resulting in significant savings for waste management and disposal, generating considerable revenues.

Project Results Use and Dissemination

1. The research activities were used to train students and junior researchers. Research findings were used to enhance classroom teaching materials
2. Research findings were published in peer-reviewed papers (>30), presented in state, national, and international meetings (>10)

3. One patent was filed and one propitiatory technology has been approved and licensed to a US company
4. The technologies developed from the project have been demonstrated to various stakeholders
5. The project was reported by local newspapers and TV stations

Environment and Natural Resources Trust Fund (ENRTF)
M.L. 2014 Work Plan - Final Report

Date of Report: June 30, 2017
Date of Next Status Update Report: June 30, 2017
Date of Work Plan Approval: June 4, 2014
Project Completion Date: June 30, 2017
Does this submission include an amendment request? _Yes_

PROJECT TITLE: Demonstrating innovative technologies to fully utilize wastewater resources

Project Manager: Roger Ruan
Organization: University of Minnesota
Mailing Address: 1390 Eckles Ave
City/State/Zip Code: St. Paul, MN 55108
Telephone Number: (612) 625-1710
Email Address: ruanx001@umn.edu
Web Address:

Location: St. Paul, MN

Total ENRTF Project Budget:	**ENRTF Appropriation:**	**$1,000,000.00**
	Amount Spent:	**$1,000,000.00**
	Balance:	**$0.00**

Legal Citation: M.L. 2014, Chp. 226, Sec. 2, Subd. 08c

Appropriation Language:
(c) Demonstrating Innovative Technologies to Fully Utilize Wastewater Resources
$1,000,000 the second year is from the trust fund to the Board of Regents of the University of Minnesota to demonstrate innovative technologies to utilize and treat wastewater streams for conversion of treatment by-products to biofuels. This appropriation is subject to the provisions of M.S. 116P.10 Royalties, Copyrights, patents, and Sale of Products and Assets. This appropriation is available until June 30, 2017, by which time the project must be completed and final products delivered.

I. PROJECT TITLE: Demonstrating innovative technologies to fully utilize wastewater resources

II. PROJECT STATEMENT:

Minnesota municipal wastewater treatment plants (MWTP) generate large amounts of oily scum, concentrated liquid (also called "centrate"), and sludge each year. For example, each year, the 7 Metropolitan Council Environment Services (MCES) MWTPs treat more than 100,000 million gallons of wastewater and at the same time generate 1,000 tons of scum, 500 million gallons of centrate, and 85 million kg of dry sludge. These waste streams are either used as landfill (scum) and direct burning (sludge), or subjected to additional treatment (centrate). New technologies, developed by UMN researchers led by Dr. Ruan through several projects funded by federal and state grants, especially two ENRTF grants, can help capture the values from and lower the treatment costs for these waste streams (Figure 1). The **goal** of the project is to demonstrate the feasibility and effectiveness of implementing innovative technologies in municipal wastewater treatment plants. This project is expected to generate significant impacts including: (1) producing significant amounts of renewable energy for internal use or distributed to the market. About 5 million gallons of biofuels and similar quantity of other biochemicals could be produced from the waste streams in MCES' facilities alone; (2) generating considerable revenues. Estimated potential annual revenue of $20 million could be generated from the fuels and other chemicals derived from scum, centrate, and sludge in these facilities; (3) improving wastewater treatment efficiency and cost effectiveness. The waste streams are effectively treated while they are converted to renewable energy; utilization of scum results in hundreds of thousands of dollars savings in landfill cost; algae are more effective than current processes in removing low level phosphorus; and (4) reducing environment pollutants. Landfill and fossil fuel and coal use will be significantly reduced; algae will sequester a large amount of carbons; CO_2 emission from sludge burning will be reduced.

Currently, there are approximately 20,000 municipal wastewater treatment facilities operating in the US serving 226.4 million people. Many wastewater facilities are in the midst of a financial struggle, and face lower revenues combined with the potential of increasing costs. This scum-to-biodiesel conversion could not only bring them economic benefit but greatly reduce environmental impact. Take the wastewater treatment plant at St. Paul, MN (Metro Plant) as an example, the plant generates 3.5 wet ton scum per day; if all converted to biodiesel, it could bring $350,000/year revenue and save $100,000 landfill fee/year to the Metro Plant. This is an attractive financially sound and environmentally friendly approach to solving the scum problem.
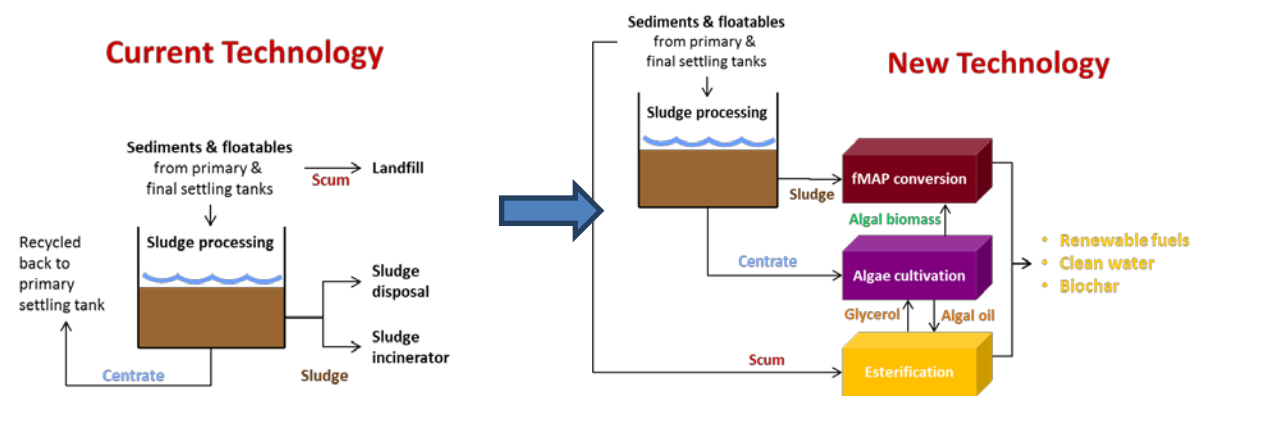

Figure 1. A comparison of waste stream pathways between the current and proposed new technologies.

III. PROJECT STATUS UPDATES:

Project Status as of December 31, 2014: (1) We developed protocols for extracting and cleaning oil from semi-solid scum collected from wastewater treatment plan. Two new processes for converting the oil to biodiesel are

being developed. Good quality biodiesel was produced. Our next step is to optimize the processes to improve the product quality so that it meets the ASTM standards. (2) We conducted research on processes for cultivating algae using centrate and other waste streams from wastewater treatment plan. Algae strains are being screened and growth of algae on crude glycerol was tested. The preliminary results show that the selected algae strain was able to assimilate crude glycerol. Our next step is to investigate the effects of several key process variables on the growth algae. (3) Sewage sludge was collected and its physiochemical properties were characterized. Preliminary tests on microwave assisted pyrolysis of the sludge were conducted. The effect of temperature on the pyrolysis was evaluated. The preliminary results show the sludge is a good candidate for microwave assisted pyrolysis.

Project Status as of June 30, 2015:
(1) Significant progress has been made in converting scum to biodiesel. New processes have been added to the basic process flow to improve oil extraction and cleaning and reduce sulfur content. Biodiesel samples meeting the ASTM standards have been produced. A patent application has been filed. A tour to our lab and experiment setup was given to attendees from LCCMR, MDA, Metro plant, and OTC. A plan for demonstrating the technology in pilot scale has been created.
(2) The effect of waste crude glycerol on algae growth and nutrient removal in municipal wastewater was investigated to optimize glycerol addition. In optimal condition, glycerol was found to significantly improve algal biomass yield and nutrient removal. It was also found the initial pH of the culture media is critical.
(3) In pyrolysis of sludge, the effect of catalysts was examined and biochar was characterized. Catalyst loading was found to affect both bio-oil and gas yield and chemical profile of bio-oil. High loading tended to promote cracking of bio-oil to form gas and thus reduce bio-oil yield. However, catalysts improved the bio-oil quality. The essential elements were concentrated in the bio-char after the pyrolysis process, suggesting bio-char can be used as a soil amendment to achieve mineral recovery and increase soil fertility in addition to activated carbon.

Project Status as of December 31, 2015:

(1) For scum to biodiesel activity, the extraction and cleaning of oil from scum was further studied. Catalysts were tested and found not cost effective. A new batch process was designed based on the findings. Comprehensive economic analysis of scum to biodiesel was carried out and comparison between our process and other pathways for scum handling indicates many of advantages of our process.
(2) For the algae cultivation component, we focused on the analysis of lipid properties of algae grown on glycerol at different concentrations and pH values. Our studies show that variations in glycerol concentration and pH did not affect the lipid profile significantly.
(3) For the pyrolysis component, we studied the synergetic effect of adding hydrogen rich biomass such as scum to lower hydrogen biomass to improve the hydrocarbon especially aromatics yield and quality. Positive effects were demonstrated. We also found that use of catalyst increased the aromatics yield when the CaO to HZSM-5 ratio was at optimal. A continuous microwave assisted conversion system has been designed and is being fabricated for demonstration and further study purpose.

Amendment
Although this is not a change in work scope and is due to how the University of Minnesota codes design activities of fabricated equipment, we request permission to move $40,000 from capital equipment in Activity 2 "Develop and demonstrate centrate to algae fuel system" to the supply category. We are still developing the algae cultivation and harvesting demo system including multi-layer photo-bioreactors, greenhouse, circulation system as planned. The University does not capitalize design research until after the project is completed since the components may change as the unit is developed. Since we are now modifying a unit we need to move those funds to how they will be reflected in the university system. (Individual items at the University capitalization threshold will still be capitalized.)

Amendment Approved (07/29/2016)

Project Status as of June 30, 2016:
  (1) Scum to biodiesel research and development:
      o   Continued development meetings with Metropolitan water treatment facility representatives and U. of M project members regarding the building of a pilot-scale scum-to-biodiesel process on-sight in St. Paul.
      o   Completed the design and specification stages of the scum-to-biodiesel pilot-scale process and have started the purchasing of custom equipment.
  (2) Algae cultivation on centrate with waste glycerol:
      o   Our study found that addition of glycerol to culture media significantly improved nutrient removal (from around 60% to around 90%)
      o   We have started pilot study in metro plant
      o   Demonstrate unit is being developed
  (3) Pyrolysis of sludge:
      o   A two-step process was developed for fast microwave assisted pyrolysis and catalytic product upgrading. The effect of pyrolysis and catalysis temperature on pyrolysis and product properties were investigated.
      o   The demonstration unit is being fabricated.
  (4) Dissemination:
      o   Numerous peer-reviewed papers and conference presentations
      o   Development of demonstration units has begun.

Project Status as of December 31, 2016:

1) Scum to biodiesel research and development:
   a) Completed the purchasing and fabrication of custom scum-to-biodiesel demo system mounted on a trailer.
   b) Held meetings between the Metropolitan waste water treatment facility and U. of M project members regarding the operation of the newly completed pilot-scale scum-to-biodiesel process, on-sight in St. Paul, MN.
   c) Developed and distributed the final component list as well as the utility and waste disposal requirements for the mobile system to the St. Paul facility managers.
2) Algae cultivation on centrate with waste glycerol:
   a) Constructed two photo bioreactor for comparison test for glycerol addition effect on algae biomass production and nutrient removal
   b) Completed the pilot scale experiments at the Metro Wastewater Treatment Plant at St. Paul, MN
   c) Conducted a lab comparison experiment using real centrate wastewater to study the glycerol effect
3) Pyrolysis of sludge:
   a) Investigated the effect of catalyst loading on two-step catalytic fMAP
   b) Quantitative analysis of major components in the bio-oil
   c) Characterized the catalyst and determine its stability during the catalytic upgrading process
4) Dissemination and demonstration:
   a) Numerous peer-reviewed papers and conference presentations
   b) Development of demonstration units has begun.

Project Status as of June 30, 2017:
1) Scum to biodiesel research and development:
   a) Completed the fabrication and installation of custom equipment for the scum to biodiesel trailer.

b) Completed the site preparation at the Rosemount Outreach and Research Center for the scum to biodiesel trailer i.e. clean-up, electricity modifications, chemical delivery and storage, gas mounting and piping.
c) Completed testing for the mobile scum to biodiesel trailer, confirming the yields and product quality of previous laboratory testing.
2) Algae cultivation on centrate with waste glycerol:
a) Completed experiments on effect of centrate-borne bacteria on nutrient removal with glycerol addition
3) Pyrolysis of sludge:
a) Conducted experiments on fast microwave-assisted gasification (fMAG) of scum and sewage sludge for biofuels production
b) Fabricated the lab-scale continuous microwave based system
c) completed the fabrication of the pilot scale continuous fast microwave assisted conversion system
4) Dissemination and demonstration:
a) Numerous peer-reviewed papers and conference presentations
b) Tested and showed demonstration units

Overall Project Outcomes and Results:

Minnesota municipal wastewater treatment plants (MWTP) generate large amounts of oily scum, concentrated liquid (also called "centrate"), and sludge each year. These waste streams are either used as landfill (scum) and direct burning (sludge), or subjected to additional treatment (centrate). The goal of the project was to demonstrate the feasibility and effectiveness of implementing innovative technologies in municipal wastewater treatment plants. Three main activities were carried out during the project: (1) Processes have been developed to convert wastewater scum to biodiesel meeting the relevant ASTM standards, (2) Processes have been developed for sustainable growth of microalgae on centrate and full utilization of nutrients in the centrate stream, and (3) new processes have been developed thermochemically convert sludge to high value energy and materials. During the research, the processes were evaluated for effectiveness and efficiency. Pilot scale systems for designed and fabricated for scum to biodiesel conversion, mass cultivation of microalgae on centrate supplemented by glycerol, and microwave assisted conversion of sludge to bioenergy and biomaterials. Four graduate students and four research scientists were involved and trained during the project. One patent for scum to biodiesel production was filed and one propitiatory technology for fast microwave assisted pyrolysis has been licensed to a company. More than 30 papers have been published on peer-reviewed journals. More than presentations have been presented in state, national, and international meetings. Demonstration of the pilot systems has been given to Superior Process Technology, Resynergi Inc., Minnesga Inc., LZL Engineering, eVende, Metro Council Environmental Service. Media interviews have been given to Minnesota Daily, Channel 5, and Channel 11. The outcome of the project has significant impacts on Minnesota's renewable energy production, environment conservation and protection, and economy and jobs. The new technologies can be implemented in mid to large size municipal wastewater treatment plants in Minnesota and elsewhere, producing significant amounts of renewable energy for internal use or to be distributed to the market, resulting in significant savings for waste management and disposal, generating considerable revenues.

Project Results Use and Dissemination

1. The research activities were used to train students and junior researchers. Research findings were used to enhance classroom teaching materials
2. Research findings were published in peer-reviewed papers (>30), presented in state, national, and international meetings (>10)
3. Two patents were filed and one has been approved and licensed to a US company
4. The technologies developed from the project have been demonstrated to various stakeholders
5. The project was reported by local newspapers and TV stations

IV. PROJECT ACTIVITIES AND OUTCOMES:

ACTIVITY 1: Develop and demonstrate scum to biodiesel process and system

Description: Scum is the floatable materials skimmed from the surface of primary and secondary settling tanks of the wastewater treatment plant. It contains grease, vegetable and mineral oil, animal fats, waxes, soaps, food wastes, plastic materials and other impurities. High energy content was found in scum that could be recycled and reused. In our lab study, it was found at least 60% of the dry matter of the scum can be converted to high quality biodiesel. In our lab study, it was found at least 60% of the dry matter of the scum can be converted to high quality biodiesel (Figure 2). The conventional technology to recover energy from scum is to co-process scum with sludge in anaerobic digestion (AD) where the biogas produced is used to generate electricity for plant use (Outwater 1994). However, this technology causes many problems in operation. For example, the scum floats on the top of the digester and forms a thick layer that impedes digester performance. As a result, many wastewater treatment plants choose to directly dispose scum in landfills. The scum disposal increases the cost of treatment facilities. For instance, the Metropolitan Wastewater Treatment Plant at St. Paul. MN (Metro plant) spends $100,000 a year just for landfilling the scum. Therefore, there is an urgent need to develop other technology to recover energy stored in scum effectively. In addition, the biodiesel produced from scum oil will be more desirable than biogas produced from traditional AD process. It is also expected that the economic benefits for scum-to-biodiesel production will be superior over the traditional AD process. With this in mind, we propose to develop and demonstrate a scum-to-biodiesel technology with following objectives: (1) to develop a cost effective conversion process capable of converting scum oil to biodiesel that meets ASTM standard, and (2) compare the optimized biodiesel production process with traditional anaerobic digestion system for LCA and economic analysis.
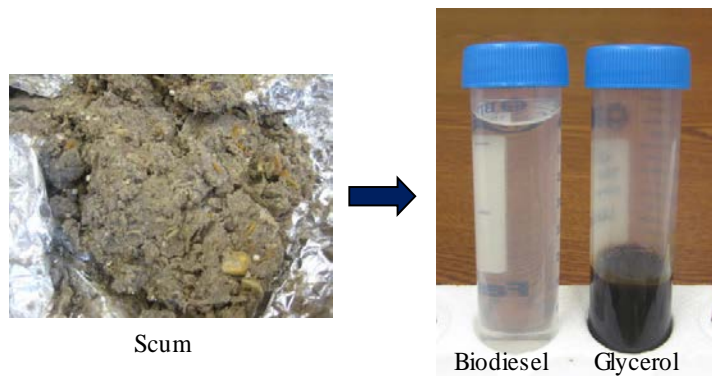

Scum

Biodiesel   Glycerol

Figure 2. In our lab, oil was extracted from scum (left) and converted to biodiesel and glycerol.

The concept of converting scum to biodiesel is easy to prove; however, there are several process steps which must be taken to deal with the physical and chemical properties of the scum unique to a wastewater source. For example, we need to develop and optimize (1) a cost effective dewatering process that can be incorporated with the existing wastewater treatment operations, (2) an oil extraction and recovery process which is efficient and allows recycling of extraction solvent, and (3) a robust conversion process capable of dealing with lipid profiles which are quite different from that of traditional biodiesel oil feedstock.

Since the trans/esterification process has been developed in our lab, we will focus on the supercritical methanol method and compare these two processes with AD process in terms of technical, economic, and environment performance. The specific objectives of the scum to biodiesel component are (1) to optimize trans/esterification process, (2) to develop and optimize supercritical methanol method, (3) to compare these two processes with the conventional AD process, and (4) develop a scum to biodiesel demonstration system based on the optimum process. The process flow chart is illustrated in Figure 3.

Specific task will be:
1. Optimize trans/esterification process. This task is intended to optimize the processes in conversion pathways and determine conversion efficiency, chemical use, and operation parameters.

    a. Minimize acid usage during the acidification process; investigate the possibility of using recycled acid from acid-esterification process to reduce the material cost.
    b. Investigate effect of catalyst and methanol to oil ratio for oil conversion efficiency
    c. Determine optimized parameter incorporated with task 3. Design parameters of unit processes will be determined for process design and modeling. The quality of final products and byproducts will be also examined.
2. Develop and optimize supercritical methanol method
    a. Lab scale system development
    b. Investigate catalysts, temperature and pressure effects on oil conversion efficiency
    c. Determine optimized the process incorporated with task 3.
3. Compare these two processes with the conventional AD process
    a. Process modeling for three different pathway for material balance and energy balance using ASPEN Plus, discuss the relationship and trade-offs among the energy yields and energy/material inputs
    b. Optimize the process with the goal of maximum oil conversion rate and minimum energy consumption.
    c. Economic analysis. Based on the model established, an economic analysis will be conducted to show the initial investment and estimated operational costs, and to prove the economic validity of scum-to-biodiesel technology. ASPEN Plus has a function for economic analysis, which will be used as a tool in our analysis. Costs of equipment and chemicals will be based on literature review and supplier's information.
4. Development of scum to biodiesel demonstration system. Based on the information provide in task 3, a scum to biodiesel demonstration system will be developed according to the optimized parameters. An estimated capacity of 150 ton biodiesel/year facility or smaller system will be developed depends on the budget. A complete scum to biodiesel production system will be designed and then bided for contract-fabrication. More accurate data will be obtained through the demonstration system that can be used for further comparison.
5. Environmental impacts analysis (Optional). Our analysis will follow the LCA standards created by International Organization for Standardization (ISO): ISO 14040 and ISO 14044. The LCA analysis will include all direct impacts and upstream impacts of chemicals and energy inputs. The process simulation models combined with existing modeling software will be applied in developing life cycle inventory. Software for modeling efforts, including Excel, GREET, GaBi, and Ecoinvent database, are currently owned by the research group. The LCA will include of environmental impact of fossil fuel use (MJ) and GHG emissions (kg CO_2 eq.) and final results of scum-to-biodiesel technology are supposed to compare with conventional biodiesel production.
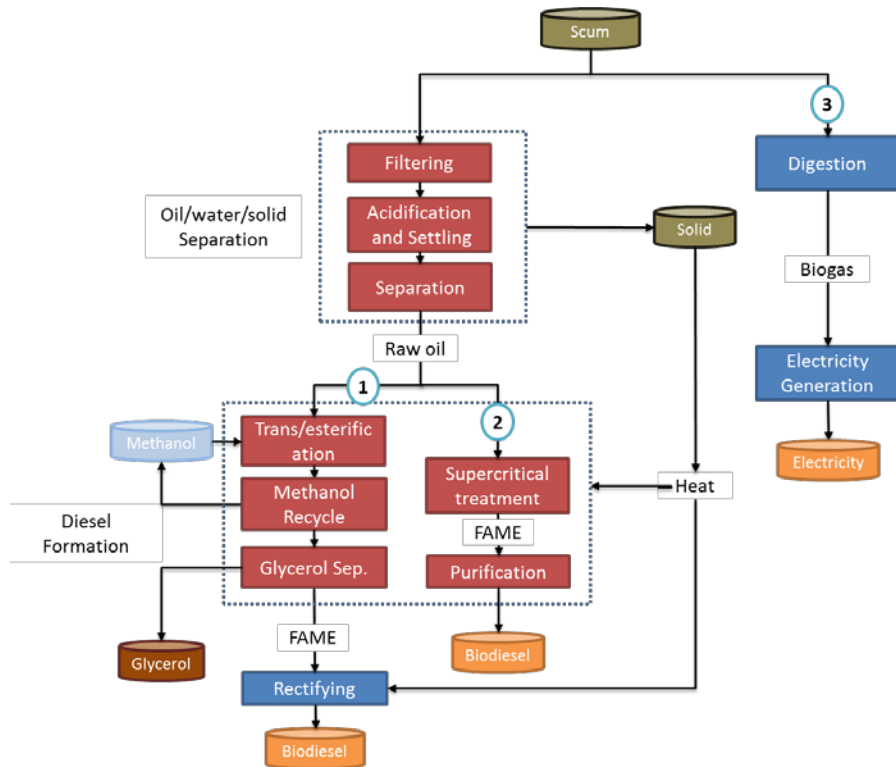
Figure 3. Scum conversion pathways for analysis: 1) trans/esterification for biodiesel production; 2) supercritical methanol method for biodiesel production; 3) AD with electricity generation.

Summary Budget Information for Activity 1:

ENRTF Budget:	$394,060.00
Amount Spent:	$394,060.00
Balance:	$0.00

Activity Completion Date:

Outcome	Completion Date	Budget
1. *Develop and optimize oil recovery, conversion, and upgrading processes; Streamline processes and design the complete system.* Specific outcomes include: 1.1. The trans/esterification process will be developed and optimized for conversion of low grade oil to biodiesel. 1.2. A supercritical methanol based conversion method will be developed and optimized for conversion of low grade oil to biodiesel. 1.3. The new conversion methods will be compared with the conventional AD process 1.4. Scale-up process parameters will be developed.	6/30/2015	$110,000
2. *Fabricate and install the system at demonstration site.* Specific outcome include: Based on the information provide in task 1, a scum to biodiesel demonstration system will be developed according to the optimized parameters. An estimated capacity of 300 ton biodiesel/year facility or smaller system will be developed. A complete scum to biodiesel production system will be designed and then bided for contract-fabrication.	12/31/2016	$180,000
3. *Test the system and collect mass and energy balance data; conduct technoeconomic analysis (TEA) and life cycle assessment (LCA).*	03/31/2017	$80,000

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Specific outcome includes: The environmental and economic impacts of the technologies developed will be quantified and reported.		
4. *Demonstrate the systems to stakeholders*. Specific outcome includes: Demonstration of the technologies developed to the stakeholders will be carried out by the end of the project.All demonstration schedules will be discussed with LCCMR office and announced to the stakeholders through UMN and LCCMR's channels.	06/30/2017	$24,060

Project Status as of December 31, 2014:
The tasks are on target. The scum samples were collected from Metropolitan Wastewater Treatment Plant at St. Paul, MN. A step-wise process was developed for oil extraction and cleaning and biodiesel production (*Details of the process cannot be disclosed at this point due to patentability issue*). In this period, we focused on preparation of oil from scum for biodiesel production. Different process variables were tested. We are working to determine an optimal processing condition for best yield and energy efficiency. Preliminary tests on making biodiesel from the oil samples obtained were conducted. The quality of the biodiesel was quite good. However, additional efforts are needed to improve both the oil preparation and biodiesel making processes so that the products will meet ASTM standards.

Project Status as of June 30, 2015:
The major accomplishments during this time period were:
  ➢ Published one journal paper, "Process development for scum to biodiesel conversion" on Bioresource technology, 185, 185-193.
  ➢ Submitted one patent application, "Production of biodiesel from scum", Serial No. 62/113,853
  ➢ Organized a lab scale demonstration with the attendees from LCCMR, MDA, Metro plant, and OTC.

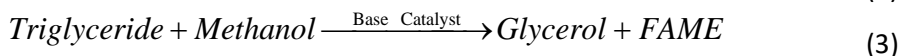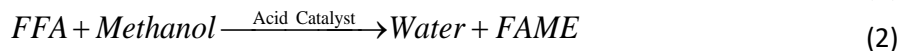The specific objectives in this time period were:
Objective 1: to develop and optimize scum-to-biodiesel conversion process
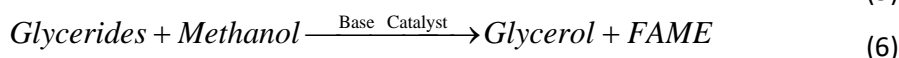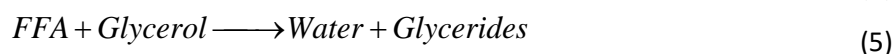Objective 2: to design a full scale system
Objective 3: to evaluate techno-economic feasibility of the project

Results of Objective 1: to develop and optimize scum-to-biodiesel conversion process

Two different conversion processes were designed and evaluated (please see the Figure 2a and Figure 2b). The first process was based on the reaction described in following equations:

$$Soap + Acid \rightarrow Salt + FFA \qquad (1)$$

$$FFA + Methanol \xrightarrow{\text{Acid Catalyst}} Water + FAME \qquad (2)$$

$$Triglyceride + Methanol \xrightarrow{\text{Base Catalyst}} Glycerol + FAME \qquad (3)$$

The second process followed Equations 4-6:

$$Soap + Acid \rightarrow Salt + FFA \qquad (4)$$

$$FFA + Glycerol \longrightarrow Water + Glycerides \qquad (5)$$

$$Glycerides + Methanol \xrightarrow{\text{Base Catalyst}} Glycerol + FAME \qquad (6)$$

Both methods are effective in converting scum to ASTM standard biodiesel. The steps, temperature, material usage and energy cost are different for each process. The first process of using acid catalyzed esterification operates at moderate temperature but involve methanol and water separation which can be energy intensive.

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The second process of using glycerolysis needs use higher temperature, but the steps are less and process is easier to operate. Therefore the second option was chosen for the further system design.
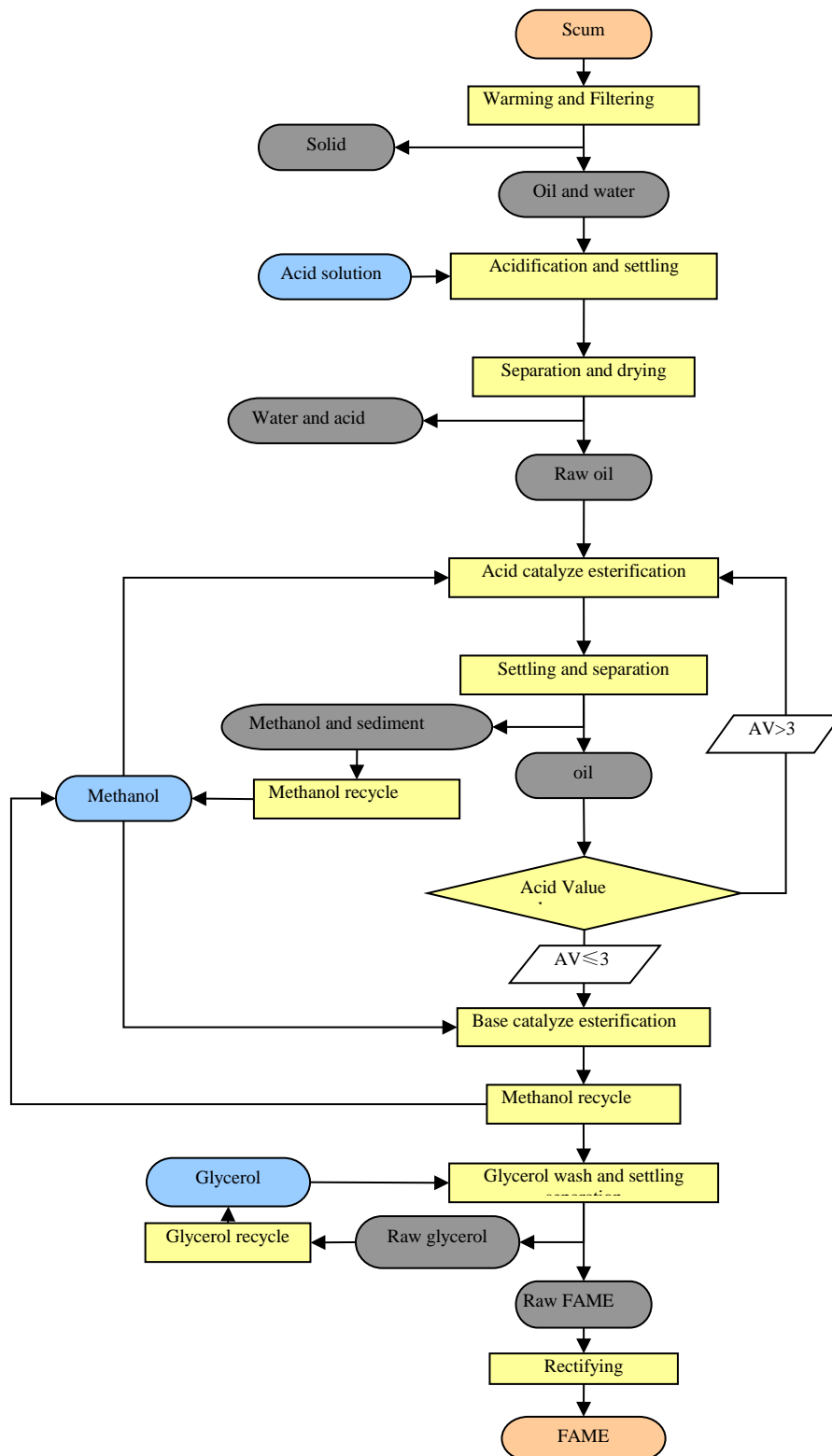

Figure 2a. The scum to biodiesel conversion process flow chart which is using acid catalyzed esterification for FFA reduction.

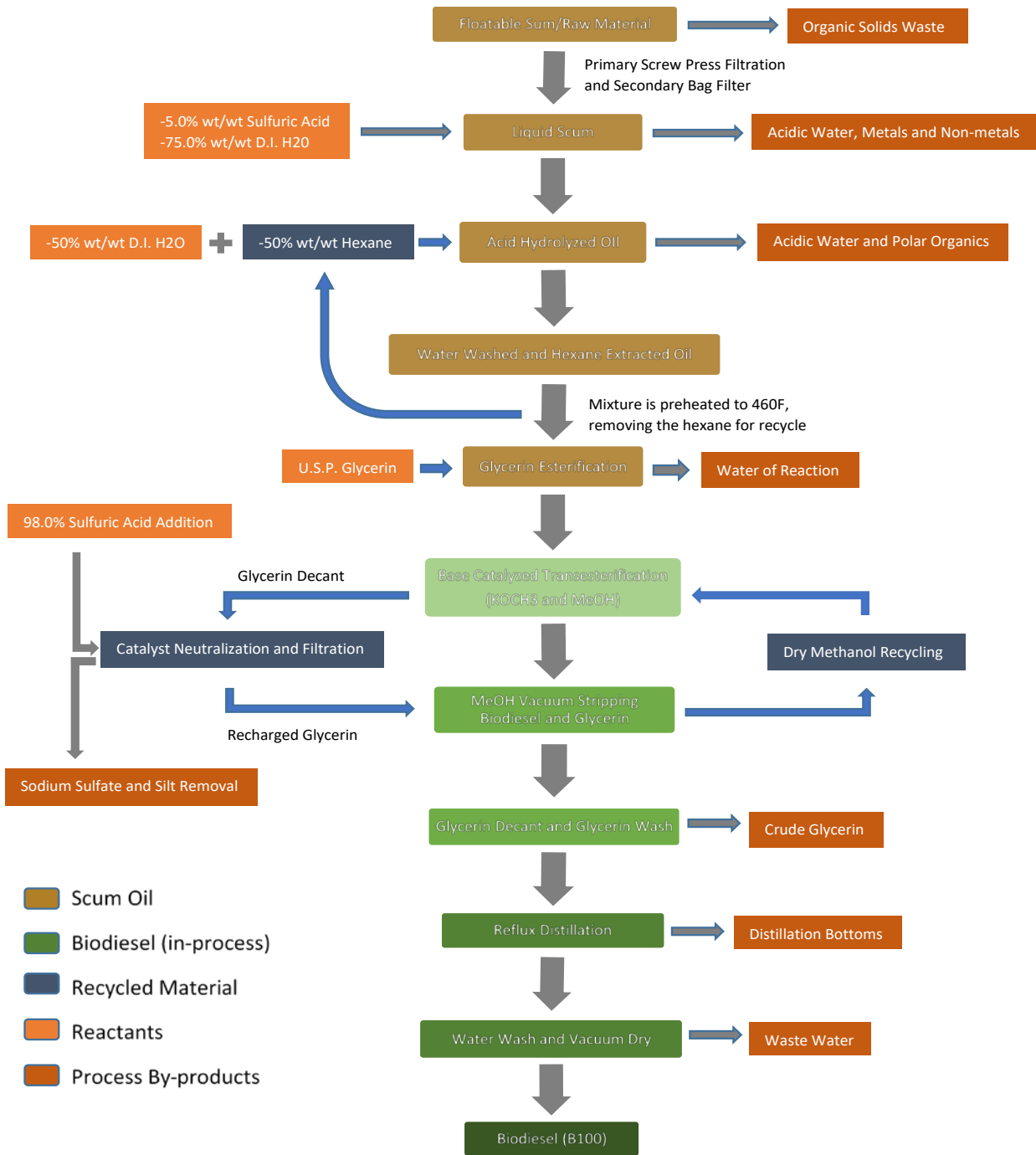**St. Paul Waste Water – Scum to Biodiesel**
Process Flow Diagram

Figure 2b. The scum to biodiesel conversion process flow chart which is using glycerolysis for FFA reduction.

As the results, the total biodiesel yield from the dried and filtered scum oil was about 70% which was equivalent to about 1.24 ton per day biodiesel production or about 134,000 gallon biodiesel per year for the Metro Plant. Based on the biodiesel B100 selling price at the Twin city that ranged from $3.8-$4.9 in 2014, the potential biodiesel production could bring about $518,000-$668,000 revenue to the Metro Plant at Saint Paul, MN.

A potential problem we encountered is the higher sulfur content in the final biodiesel product (table 1). Several processes are under optimization to solve this issue. The approach we are investigating is fractional distillation, catalyzed glycerolysis, solvent extraction, etc. More results will be reported later on.

Table 1. Biodiesel product analysis, ASTM D6751-12.

Test	Method	Result	Unit	ASTM limit	Pass/Fail
Calcium &Magnesium	EN14538	0.0	ppm	5, max	P
Flash point, Closed cup	D93	176.0	°C	93, min	P
Alcohol Control:					
Option1: Methanol	EN14110		mass%	0.2, max	
Option2: Flash point	D93	1760.	°C	130, min	P
Water and Sediment	D2709	<0.005	%volume	0.050, max	P
Kinematic Viscosity cSt@40°C	D445	4.941	mm2/sec	1.9-6.0	P
Sulfated Ash	D874	0.001	%mass	0.020, max	P
Sulfur	D5453	33.6	ppm	15, max	Fail
Copper Corrosion at 50°C	D130	1A	n/a	No. 3, Max	P
Cloud Point	D2500	13	°C	Report	Report
Carbon Residue	D4530	0.000	%mass	0.050, max	P
Total Acid Number	D664	1.43	mgKOH/g	0.50, max	Fail
Cold Soak Filterability	D7501	114	seconds	360, max*	Report
Free Glycerin	D6584	0.000	%mass	0.020, max	P
Total Glycerin:	D6584	0.002	%mass	0.240, max	P
Monoglyceridess	D6584	0.000	%mass	n/a	
Diglycerides	D6584	0.014	%mass	n/a	
Triglycerides	D6584	0.000	%mass	n/a	
Phosphorus	D4951	0.000000	%mass	0.001, max	P
Distillation at 90%rec., ATE	D1160	351.7	°C	360, max	P
Sodium&Potassium	EN14538	0.1	ppm	5, max	P
Oxidation Stability	EN15751	0.1	hours	3, min	Fail
Visual Inspection	D4176	1	haze	2	P

*360 max for Grade 2B, 200 max for Grade 1B, with max 0.400 for monoglycerides.

Results of Objective 2: to design a full scale system

Based on the finding from the Objective 1 and the availability of the scum, a batch system with three reactors will be adopted for low capital cost, high throughput, and flexible operation. Figure 3 illustrates a system design that could treat all scum produced by the Metro Plant. The system design is based on 30 hr/batch with a process capacity of 2,577 gallon/batch. After screw presser, scum will be transferred to the first tank and subjected to acid wash and solvent extraction. In the second reactor, solvent recycle, glycerolysis and transesterification will be carried out. Then the separated raw biodiesel will go through distillation tower and be refined. In the 3rd reactor, water wash with vacuum drying will clean up the final biodiesel product to meet ASTM B100 standard.
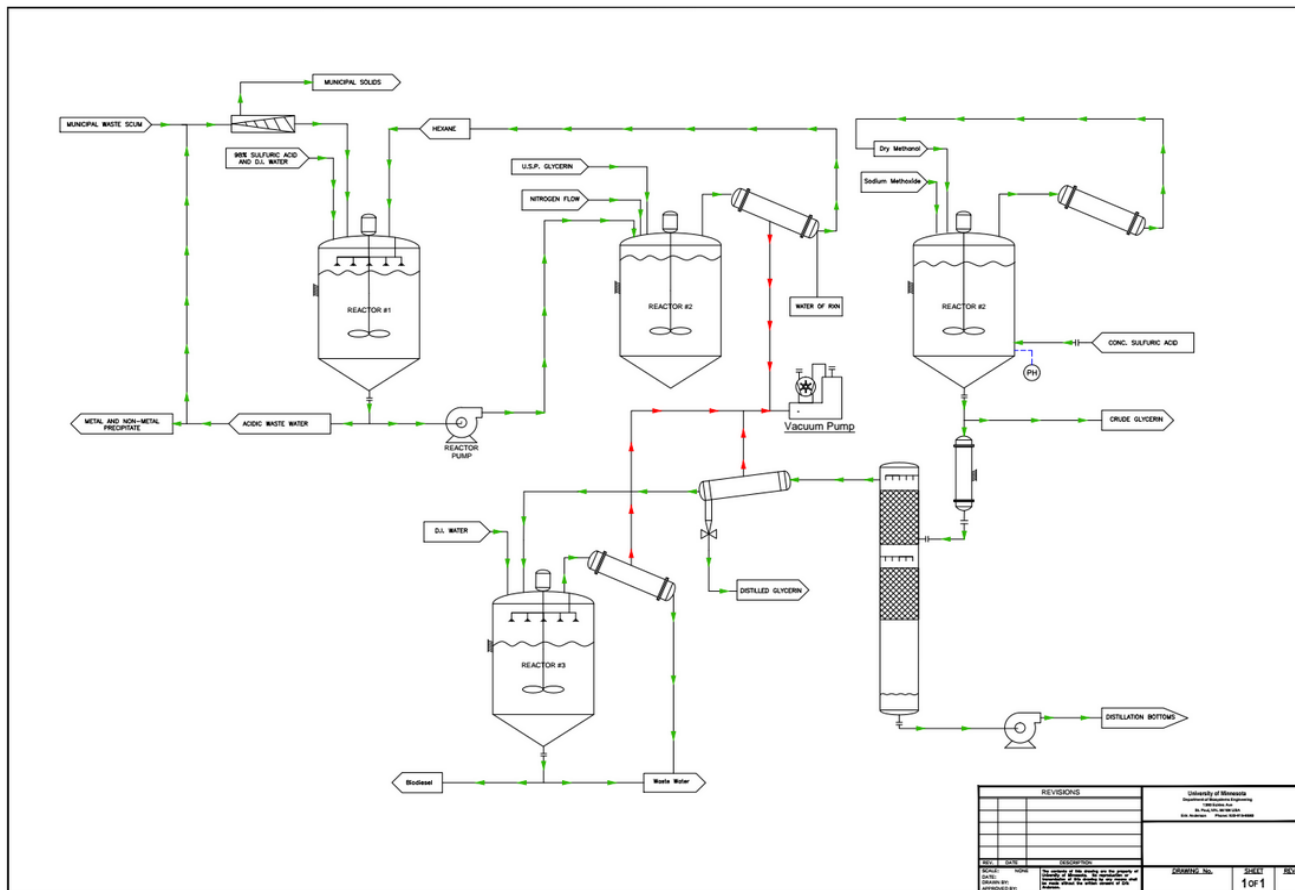
Figure 3. A batch wise 3-tank system design diagram.

Results of Objective 3: to evaluate techno-economic feasibility of the project

Table 1 summarizes the basic material balance and analysis of the economic feasibility of the proposed process and system. The total biodiesel production is estimated at about 134, 000 gallon per year, with the tax credit and RIN value, the total revenue will add up to $595,389/year. The estimated capital cost is about $1.2M; the operation cost is about $198,613/year. Based on the calculation the payback year of such a system is about 2.75 year, which indicates a very promising technology for commercialization. For the detailed economic analysis, please check Table 2.

Table 1. Economic analysis of the proposed process and system.

Item	value	Unit
Plant Capacity	134000	Gallons/year
Plant Operations	1,560	Hours/year
Biodiesel Produced	2,577	gallons/week
Biodiesel Yield from Scum Oil	70	%
Cost		
Estimated capital Cost	1,200,000	$
Operation Cost	198,613	$/year
Revenue		
Biodiesel production	472,109	$/year
RINs and Tax credited	123,280	$/year

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Total revenue	**595,389**	$/year
Payback Period, Years	**2.75**	year
Cost of biodiesel	1.482	$/gallon

Table 2. Detailed economic analysis for the process.

Scum to Biodiesel – Economic Summary

(Detailed rotated spreadsheet table — key values shown below)

Item	Value
Plant Capacity	134000 Gallons/year
Plant Capacity	0.134 MGPY
Plant Operations	1,560 Hours/year
Biodiesel Produced	2,577 gallons/week @ 3.75 days/week, 2.0 people
Biodiesel Produced	18,915 pounds/week

Compound	Molecular Weight
Fatty Acids	278
MGs	352
DGs	612
TGs	872
Glycerin	92
Methanol	32
Na-Methoxide	54
Sulfuric Acid	98
Water	18
Soap	300
Methyl Esters	292

Sub-Total = $198,613 ($1,482 /gallon)

Total Revenue = $595,389

Total Savings = $40,000.00

Estimated Plant Cost = $1,200,000

Payback Period, Years = 2.75

Gross Profit = $406,776

Project Status as of December 31, 2015:
The major accomplishments during this time period were:
➢ Published two journal papers, "Glycerin Esterification of Scum Derived Free Fatty Acids for Biodiesel Production" in Bioresource technology, 200, 153-160 and "A Life Cycle Assessment and Economic

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Analysis of the Scum-to-Biodiesel Technology in Wastewater Treatment Plants"
Bioresource Technology, in-press.

➢ Planning and development meetings began between Metropolitan water treatment facility representatives and U. of M project members regarding the building of a pilot-scale scum-to-biodiesel process on-sight in St. Paul.

➢ The formation of the S corporation AEMR, Scientific, Inc, which will be an advantage when applying for SBIR grants and seeking investors.

The specific objectives in this time period were:
Objective 1: to optimize the scum oil extraction stage and research the FFA remediation process glycerolysis.
Objective 2: to design a full scale system located on-sight at the St. Paul facility.
Objective 3: to evaluate the economic feasibility of the project relative to two other alternative energy pathways being considered, anaerobic digestion and direct incineration.

Results of Objective 1: to optimize the scum oil extraction stage and research glycerolysis, the catalyzed remediation of FFA.

Combining acid hydrolysis and solvent extraction, a free fatty acid and acyl-glycerol rich product was produced. Free fatty acids (FFA) present were converted to acyl-glycols via several reaction pathways involving glycerin and FFA (equations 1-4). The inorganic catalysts zinc aluminum oxide and sodium sulfate were tested during glycerolysis to compare the reaction kinetics of converting FFA to acyl-glycerols. It was concluded that the zinc-based catalyst increased the reaction rate significantly, from a "k" value of 2.57 (uncatalyzed) to 5.63, completing the reaction in 60 minutes, half the time it took the uncatalyzed reaction (120 min). Sodium sulfate's presence however slowed the reaction, resulting in a "k" value of 1.45, completing the reaction in 180 minutes. Use of the external catalyst $Zn-Al_2O_3$ showed the greatest catalytic potential, but also assumes additional costs.

Free Fatty Acid + Glycerol → Mono-acyl-glycerol + Water	Eq. 1
Free Fatty Acid + Mono-acyl-glycerol → Di-acyl-glycerol + Water	Eq. 2
Free Fatty Acid + Di-acyl-glycerol → Tri-acyl-glycerol + Water	Eq. 3
Tri-acyl-glycerol + Glycerol → Mono-acyl-glycerol + Di-acyl-glycerol	Eq. 4

It was concluded that it may be infeasible to using an inorganic catalyst in a commercial setting because of the additional costs associated with the material handling and processing. Therefore, because of its performance relative to the uncatalyzed reaction, an uncatalyzed glycerolysis would be suggested for any actual scale-up of the technology. Shown below is the % composition by mass of the glycerin and FFA during glycerolysis, along with the formation of the acyl-glycerols (Table 1).
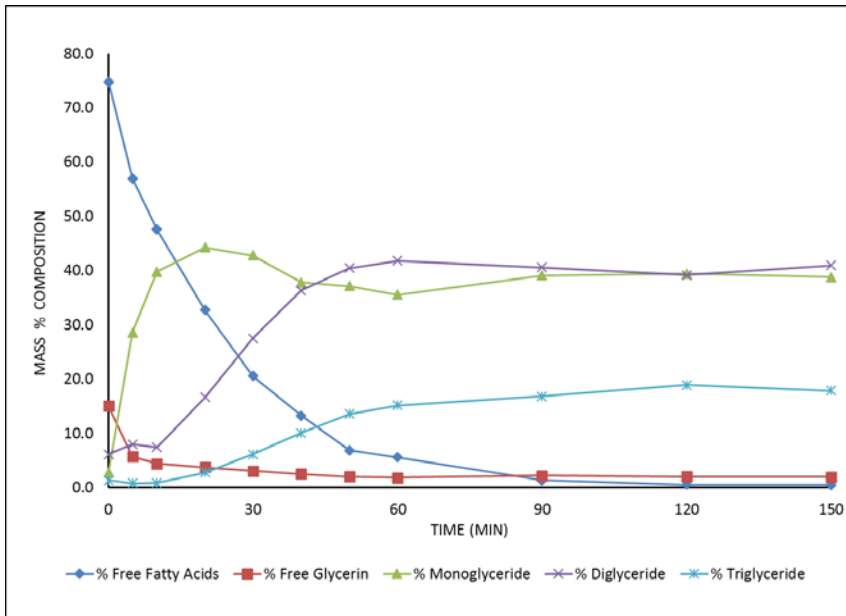
Figure 1. Uncatalyzed free fatty acid reduction and acyl-glycerol formation during glycerolysis.

Results of Objective 2: to design a full scale system located on-sight at the St. Paul facility.

Based on the finding from the Objective 1 and the availability of the scum, a batch system with three reactors will be adopted for low capital cost, high throughput, and flexible operation. Figure 2 illustrates a system design that could treat all scum produced by the Metro Plant. The system design is based on 30 hr/batch with a process capacity of 2,577 gallon/batch. After screw presser, scum will be transferred to the first tank and subjected to acid wash and solvent extraction. In the second reactor, solvent recycle, glycerolysis and transesterification will be carried out. Then the separated raw biodiesel will go through distillation tower and be refined. In the 3rd reactor, water wash with vacuum drying will clean up the final biodiesel product to meet ASTM B100 standard. The distillation of biodiesel is currently being studied for its potential as a "reactive" distillation unit. By controlling the residence time of the biodiesel during the application of latent heat, a forced reverse reaction may help reduce the amount of free glycerin in the product stream.
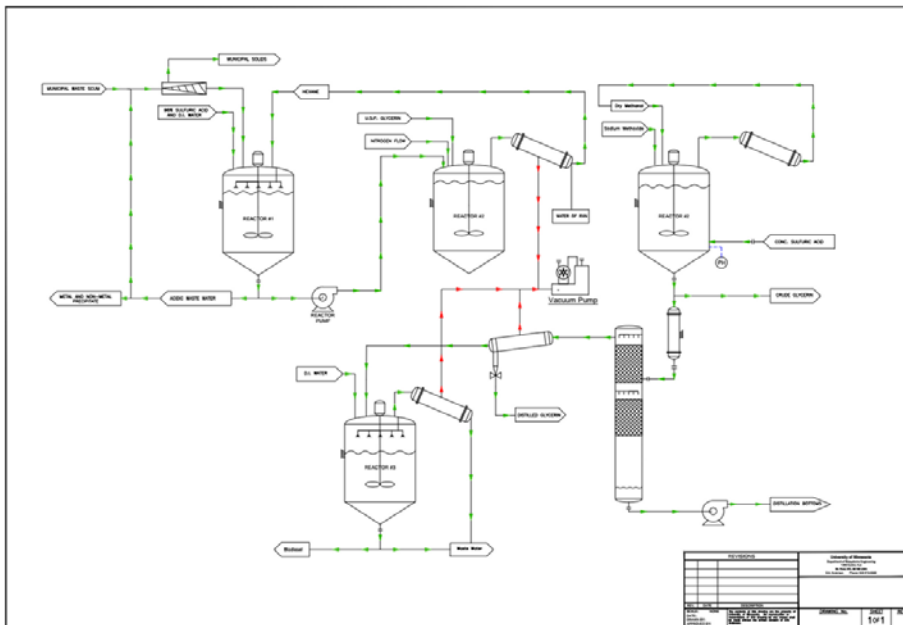

Figure 2: Process flow diagram for a scum to biodiesel process.

Results of Objective 3: to evaluate the economic feasibility of the project relative to two other alternative energy pathways being considered, anaerobic digestion and direct incineration.

Scum incineration-The first scum to energy route modeled was the direct incineration of the scum to generate electricity via steam turbines. Incineration represents the simplest and most common approach used in the U.S. It is the direct combustion or incineration of the scum, without any filtration or extraction of any kind. At the St. Paul facility there is a dewatering stage where the scum is concentrated in large holding tankers fit with a mesh screen. The screen allows for water carried over from the holding tanks is passively drained from the bottom of the tankers, leaving behind the raw "wet" scum. Based on the proximate analysis, the scum contains on average 24.5% water, but since this value is dependent on drain time, moisture content can fluctuate more so than any other scum component. Assuming all of the water is removed from scum and biosolids, the combined amount of organic material available for incineration represent 76.2% of the original "wet" scum. The heating value of the biosolids or sludge's on a dry basis is generally thought to be 10,000 BTUs/lb, according to a waste sewage management reference guide. In contrast, oil derived from scum oil has an assumed heat value of 16,000 BTUs/lb as it contains mostly mono-, di-, tri-glycerides. This value was used during the extrapolation of energy for the oil rendered from scum, but not for raw scum containing trace moisture and elemental impurities like sulfur, phosphorous, and metals. In order to test the cited heating values of oil and sludge, the scum was broken down into its respective components (Figure 1). The scum was acid washed using 5% (wt/wt) sulfuric acid in 40% (wt/wt) D.I. water. Next the mixture was allowed to settle and the top oil layer was extracted using 40% (wt/wt) heptane. After a final vacuum stripping stage to recover the heptane, a yield of 62.5% dry oil was extracted from the "wet" scum, leaving behind 13.7% dried sludge. Factoring in water's heating capacity of 1 BTU/lb/°F, the amount of thermal energy required to dry the oil and sludge mixture can be calculated and subtracted from the overall thermal output of combusting the oil and sludge. Applying the newly generated BTU value for the incineration of raw scum to the facility parameters at the St. Paul treatment plant, electrical generation potentials were calculated and compared to anaerobic digestion and biodiesel.

Scum Incineration - Mass Balance and Economic Summary
St.Paul Waste Water Treatment Plant

PROXIMATE ANALYSIS OF SCUM AND BIOSOLIDS

Water, 24.5%; Volatile Organic Solids, 13.7%; Other, 19.8%; Oil, 62.5%; Ash, 0.7%; Water, 5.4%

Components - In and Out	Lbs/Week	Gallons/Week	Gallons/Year	MGPY
Feed Oil feed rate =	34,419.21	4,689.27	243,842	0.243842
Biosolids feed rate =	9702			

	In-coming Scum			
	lbs/day	Wt %	COD/Lb	COD/day
Protein	893	12.75%	1.8	1,607
Fats & Oils	3,920	56.00%	2.9	11,368
Water	1,610	23.00%	0.0	0
Ash/Inerts	578	8.25%	0.0	0
Total =	**7,000**	100.00%		12,975

Energy Summary

Energy Usage

									Cost/year
Electricity :	260	KWHRS/Day at	$0.13	per KWH for					$6,583

Removing Moisture

Sensible Heat :	9,526	BTU's/hour (assuming a room temp of 70F)							
Heat of Vaporization (latent heat) :	67,083	BTUs/hour (heat capacity of water= 1BTU/lb/F)							
Total Thermal Energy :	76,609	BTU's/hour at	80.00%	Boiler Efficiency	$5.00	per Million BTU's	8,760	Hours/year =	$3,355
								Total =	$9,939

Energy Production

Energy Content of Scum =	550,707,291	BTU's/Week (assuming 16000 BTU/lb)	
	78,672,470	BTU's/day	
	28,636,779,156	BTU's per year	

Energy Content of biosolids=	155,232,000	BTU's/Week (assuming 16000 BTU/lb)	
	22,176,000	BTU's/day	
	8,072,064,000	BTU's per year	

Converting to Electricity

Assume :	10,000	BTU's/kwhour for steam generated electricty		
	0.42	MegaWatts of possible Electrical Power Generation		
Potential Electrical Power =	3,680,969	KiloWatt-Hours per year (at 3413 BTU's/KWHR)=	12,563,147,752	BTU's
Annual Electricity Value =	$478,526	with Electricity valued at	$0.13	per kwhr

Compared to Natural Gas

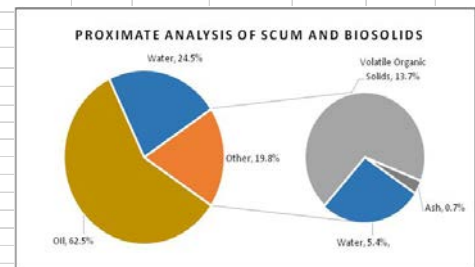|		
Compressed Natural Gas (CNG) =	$5.00	per million BTU
Potential Natural Gas Off-set =	**183,544**	

Table 1: Mass and energy balance for the potential electrical generation of a scum incineration process.

Anaerobic digestion of scum- The biogas produced in a digester (also known as "digester gas") is actually a mixture of gases, with methane and carbon dioxide making up more than 90 percent of the total. Biogas

typically contains smaller amounts of hydrogen sulfide, nitrogen, hydrogen, methylmercaptans and oxygen. Methane is a combustible gas. The energy content of digester gas depends on the amount of methane it contains. Methane content varies from about 55 percent to 80 percent. Typical digester gas, with a methane concentration of 65 percent, contains about 600 Btu of energy per cubic foot. In order t model a scum to methane process, the scum was broken down into its respective components; fats/oils, proteins, inerts, and water. Once the amount of digestible material was determined, average molecular weights of proteins and lipids were assumed and methane potentials per lb of COD was established and applied to the available volumes. Using industrial established energy conversion factors, the amount of electricity per BTU was determined for the overall conversion of a year's worth of scum.

Scum to Anaerobic Digestion - Mass Balance and Economic Summary
St.Paul Waste Water Treatment Plant

FATS ---> (Hydrolysis) ---> Fatty Acids ---> (Acidogenesis) ---> Carbonic acids & Alcohols ---> (Acetogenesis) ---> Acetic Acid & CO2 ---> (Methanogenesis) ---> Methane and CO2

Proteins ---> (Hydrolysis) ---> Amino Acids ---> (Acidogenesis) ---> Carbonic acids & Ammonia ---> (Acetogenesis) ---> Acetic Acid & CO2 ---> (Methanogenesis) ---> Methane and CO2

Based on literature, assume for any generic biomass, that the yield of methane is ~ 25% by weight from the dry biomass.

Assume	COD = 10% of total Feed Slurry				**Methane from Proteins**			
Assume	**80%**	of the "VS" are converted to BioGas			Assumed Protein, as Amino Acids = C-107 : H-198 : O-49 : N-29 : S-2			
					COD of Protein : C-107 : H-160 : O-30 : N-29 : S-2 + **134** O2 ------> 107 CO2 + 80 H2O + 14.5 N2 + 2 SO2			
In-coming Scum		(based on experimental daa)			1.7911 gms COD/ gm of Protein			
	lbs/day	Wt %	COD/Lb	COD/day	COD/min	MW = Protein Weight =	2,394.0	lbs
Protein (biosolids)	959	13.70%	1.8	1,726	1.199			
Fats & Oils	4,375	62.50%	2.9	12,688	8.811	BioGas	Total Moles	MW	Gas Wt (lbs)
Water	1,715	24.50%	0.0	0	0	CH4	54.625	16	874
Ash/Inerts	49	0.70%	0.0	0	0	CO2	52.375	44	2304.5
Total =	**7,000**	101.40%	4.7	14,414	10.01	NH3	29	17	493
Incoming Water						H2S	2	34	68
	lbs/min	gal/min					Total Wt. "OUT" =	3,739.5	Lbs
Added Water =	90.085625	10.8016337							
Total Feed Slurry =	100.10	12.0018152							
Water Added =	129,723	lbs/day =	15,554	Gallons/day					
Micro-Nutrients =	250	lbs/day =	Micro-Nutrient Solution added			**Methane from Lipids and Oils**			
						Assumed Lipids, as Oleic Acid = C-18 : H-34 : O-2			
						COD of Lipids and Oils : C-18 : H-34 : O-2 + **25.5** O2 ------> 18 CO2 + 17 H2O			
Product Streams	Lbs/day	Lbs/day	Lbs/day	Lbs/day		2.8936 gms COD / gm of Oil			
	CH4	CO2	NH3	H2S		MW = lbs of Oil or Fat =	282	Lbs	
Protein	280.1	738.5	158.0	21.8					
Fats & Oils	2531.9	2867.0	0	0		BioGas	Total Moles	MW	Gas Wt
Water	0	0	0	0		CH4	12.75	16	204
Ash/Inerts	0	0	0	0	Total Gas	CO2	5.25	44	231
Total =	2812.00	3605.54	157.99	21.79	6597.33		Total Wt. "OUT" =	435.0	Lbs

Energy Summary			
Energy Production			
Total Methane Gas Produced =	2,812	lbs/day	
CH4 LHV =	21,000	BTU's/lb of methane	
Energy Produced	2,460,503	BTU's/hour	
	21,554,008,993	BTU's/year	
Converting to Electricity			
Assume :	9,000	to	8,000	BTU's/kwhour for gas turbine generated electricity
	0.27	to	0.31	MegaWatts of possible Electrical Power Generation
Annual Electrical Power =	2,394,890	to	2,694,251	KiloWatt-Hours per year (at 3413 BTU's/KWHR)=	8,173,759,188	BTU's
Annual Sales Value =	**311,336**	to	**$350,253**	with Electricity valued at	$0.13	per kwhr
Compared to Natural Gas			
Compressed Natural Gas (CNG) =	$5.00	per million BTU	
Potential Natural Gas Off-set =	**107,770**		

Table 2: Mass and energy balance and potential electrical generation for the anaerobic digestion of scum.

Scum to biodiesel- The economic modeling of a scum to energy process must make several assumptions in order to predict potential outcomes. The first major assumption was estimating the potential volume of available material. The MCES Metro Wastewater Treatment facility produces roughly 3.5 tons or 7,000 lbs of wet scum each day. The solids portion of the scum accounts for roughly 14.4% or less of the scum material, while the moisture content can vary anywhere from 22 to 32%. Assuming a constant supply of scum material over 365-day period, a yield of between 189,000-216,500 gallons of dry "oil" could be produced annually. At the conservatively estimated process efficiency of 69%, the oil could yield between 130,000 and 149,500 gallons of biodiesel each year.

Scum to Biodiesel - Mass Balance and Economic Summary
St.Paul Waste Water Treatment Plant
Erik Anderson - 10/1/14

Plant Capacity :	140000	Gallons/year		Biodiesel Yield from Scum Oil =	**65.00%**		
Plant Capacity :	0.134	MGPY		Biodiesel Distillate Bottoms Yield =	**20.00%**		
Plant Operations :	1,560	Hours/year	@ 3.75 days/week, 2.0 people	Feed Oil % FFA =	**86.00%**		
Biodiesel Produced :	2,692	gallons/week					
FFA's in Feed Oil =	27,784.62	pounds/batch					
Biodiesel Sales Price =	$0.41	per pound					

1 Batch	=	3.75	days/week =	30	hrs/batch =	2,692	gallons/batch

Components - In and Out	Lbs/Batch	Gallons/Batch	Gallons/Year		Component	Density	
Feed Oil feed rate =	32,307.69	4,307.69	224,000		Feed Oil Density =	7.5	pounds/gallon
Biodiesel Production =	19,761.54	2,692.31	140,000		Biodiesel Density =	7.34	pounds/gallon
Savings from Landfill	25,842.01				Crude Glycerin Density =	10.0	pounds/gallon
Value of "RINS" =	1.5	RINs per gallon	$0.800		Methanol Density =	6.59	pounds/gallon
Tax Credits $/Gal =			$1.00		25% Methoxide Solution Density =	8.25	pounds/gallon
Bottoms Production =	6,080.47	828.40	43,077		93% Sulfuric Acid Density =	15.0	pounds/gallon
Soap in Bottoms = ~	76.01				Water Density =	8.34	pounds/gallon
Crude Glycerin Production =	477.21	47.72	2,481				
Soap in Crude Glycerin = ~	6.20				Fatty Acids	278	
Anti-Oxidant =	13.17	1.59	83		MG's	352	
Methanol Charging =	6,043.28	917.04	47,686		DG's	612	
Na Methoxide Charging =	673.08	81.59	4,242		TG's	872	
Methanol with Methoxide =	471.15	71.50	3,718		Glycerin	92	
Methanol Consumed =	3198.23	485.32	25,236		Methanol	32	
Recycled Methanol =	3,316.21	503.22	26,167		Na-Methoxide	54	
Fresh Methanol needed =	2,727.08	413.82	21,519		Sulfuric Acid	98	
93% Sulfuric Acid =	1779.57	118.64	6,169		Water	18	
(5% acid pretreatment+neutralization acid)					Soap	300	
Na_2SO_4 production =	2398.06	124,699	lbs/year		Methyl Esters	292	
Filter Discharge =	4796.11	249,398	lbs/year				
Wash Water -Acid Pretreatment =	16153.85	1,936.91	100,719				
30% Waste Water from Glycerolysis =	1799.00						
Wash Water after Distillaiton =	3952.31	473.90	24,643				
Assume 1% water in Feed Oil =	323.08						
Total Waste Water =	6074.39	728.34	37,874				

Energy Summary

Energy Usage

								Cost/year
Electricity :	143	KWHRS/Day at	$0.13	per KWH for				$3,618
Thermal Energy :	65,660	BTU's/hour at	80.00%	Boiler Efficiency	$5.00	per Million BTU's	1,560 Hours/year =	$512
							Total =	$4,130

Energy Production

Energy Content Biodiesel =	316,184,615	BTU's/Batch (assuming 16000 BTU/lb)
	17,073,969,231	BTU's per year

Converting to Electricity

Assume :	10,000	BTU's/kwhour for steam generated electricity
	1.05	MegaWatts of possible Electrical Power Generation
Potential Electrical Power =	1,707,397	KiloWatt-Hours per year (at 3413 BTU's/KWHR)= 5,827,345,698 BTU's
Annual Sales Value =	$221,962	with Electricity valued at $0.13 per kwhr

Compared to Natural Gas

Compressed Natural Gas (CNG) =	$5.00	per million BTU
Potential Natural Gas Off-set =	85,370	

Economics as a Transportation Fuel

Biodiesel + RINs + $1.00 Tax Credit + Landfill Savings

	Biodiesel Revenue	1 dollar tax credit	RINs	Landfill Savings	Cost/year
Sub-Totals =	$420,000.00	$140,000.00	$168,000.00	$68,000.00	$185,100.00

Net Profit =	**$610,900.28**
Estimated Plant Cost =	**$1,200,000.00**
Payback Period, Years =	**$1.96**

Table 3: Mass and energy balance, potential electrical generation, and potential retail sales value of biodiesel derived from scum oil.

Project Status as of June 30, 2016

The major accomplishments during this time period were:

➢ Completed and sent the following paper in for publication in the journal of *Fuel Processing Technologies*, "A Techno-Economic Analysis of Renewable Energy Technologies Incineration, Anaerobic Digestion, and Biodiesel Production as Applied to Waste Oils".
➢ Continued development meetings with Metropolitan water treatment facility representatives and U. of M project members regarding the building of a pilot-scale scum-to-biodiesel process on-sight in St. Paul.
➢ Completed the design and specification stages of the scum-to-biodiesel pilot-scale process and have started the purchasing of custom equipment.

The specific objectives in this time period were:

Objective 1: to complete the techno-economic analysis comparing several waste to energy technologies relative to our own scum-to-biodiesel process.
Objective 2: to reevaluate the process design and establish new process flow diagrams.
Objective 3: to determine the exact equipment specifications and power requirements and start the purchasing process.

Results of Objective 1: to complete the techno-economic analysis comparing several waste to energy technologies relative to our own scum-to-biodiesel process.

Based on extensive economic modeling, a techno-economic comparison was written and sent in for publication in the journal of Fuel Processing Technologies. It is currently under review. The manuscript's abstract can be see below;

"In the U.S., millions of tons of wastes oils are produced annually from industrial and residential sources that require safe and environmentally sound disposal. Multiple technologies focused on energy reclamation have been developed. However, the way the energy is produced, distributed, and valued significantly affects the sustainability of the overall process. A techno-economic model was developed that compared the potential energy and economic value of three waste oil utilization technologies, namely incineration, anaerobic digestion, and biodiesel. Floatable wastewater scum was chosen as a model substrate due to its availability, abundance, and high oil content (62%). However, the model can be applied to any composition of waste organics suitable for energy reclamation. A St. Paul, MN wastewater treatment facility producing 3.5 "wet" tons of scum per day was used as a basis of comparison. Waste oil to biodiesel conversion was shown to have the greatest net economic profit potential, valued at $610,624/year, while the incineration of scum yielded the greatest reclaimed net energy potential at 27,126,179,775 BTU's/year".

Results of Objective 2: to reevaluate the process design and establish new process flow diagrams.

Drawing #1 - The biosolids removal stage was reinvented from a heated screw auger to a passive heat filtration system using a series of 55 gallon steel drums and mesh filter. From the heated filter vessels, the liquid scum component is pumped through a gear pump to the second reactor.
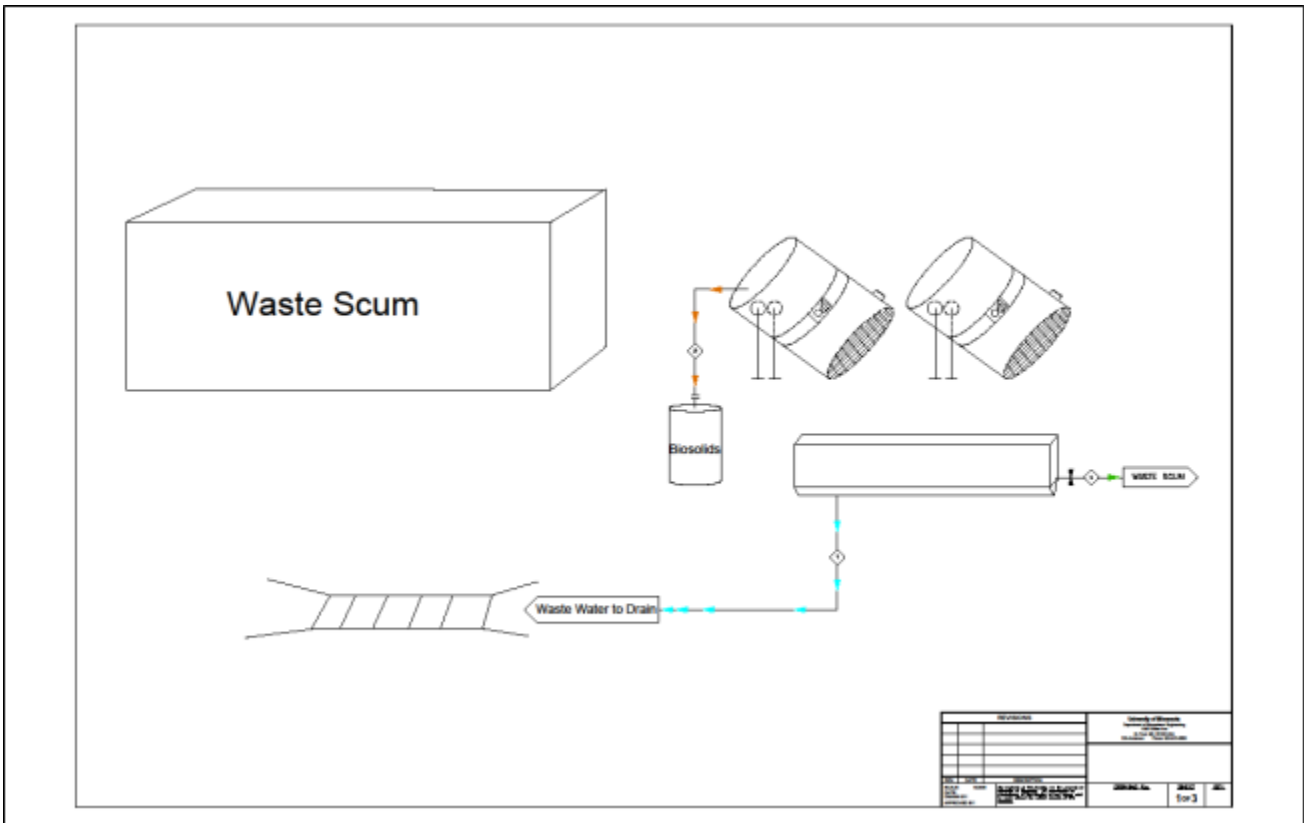
Drawing #2 – The second drawing was changed to reflect the petroleum distillation system designed and sold by B/r instrumentation. Our group is planning on using this system for all biodiesel conversion processes, following the oil extraction phases taken place in Tank #1.
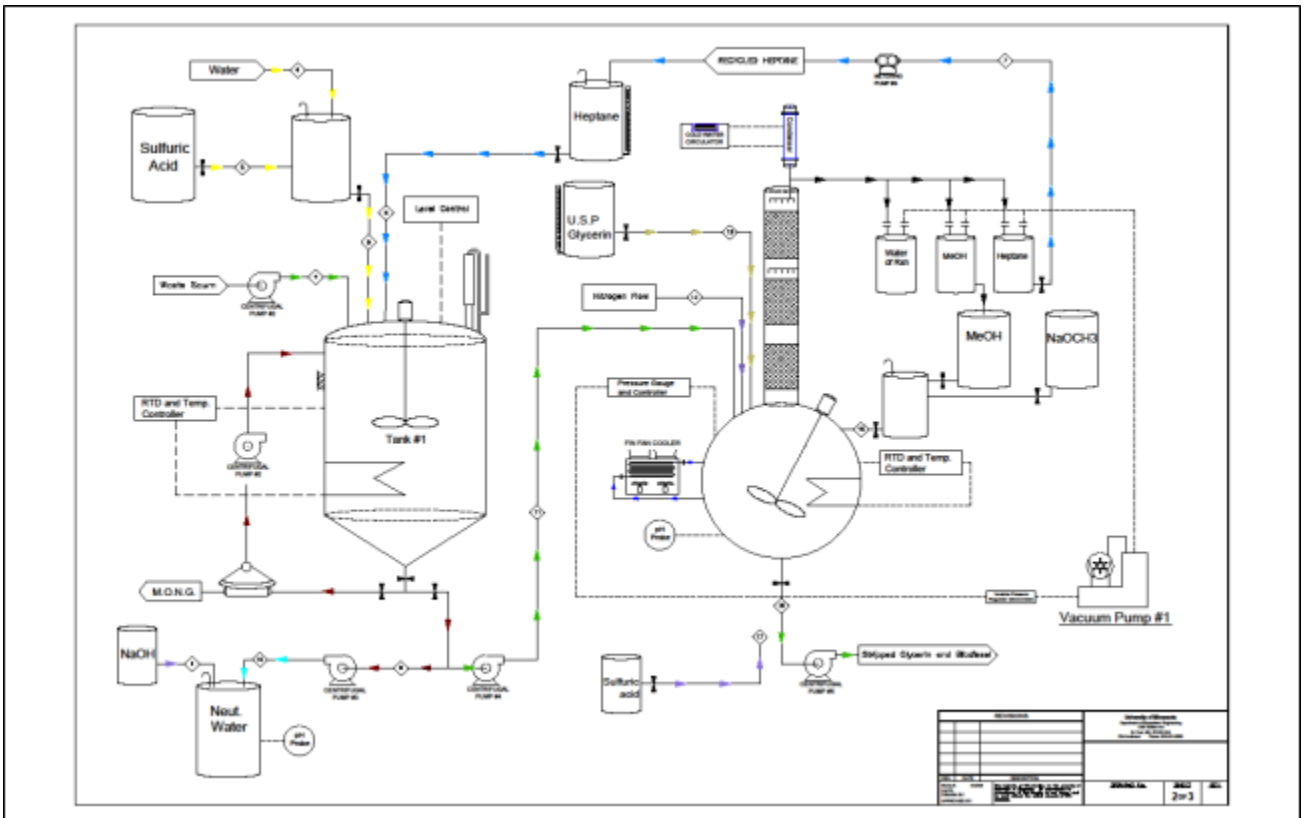
Drawing #3 – The third drawing was redrawn to show the same B/r instrument distillation system for the final methanol vacuum stripping and methyl ester distillation.
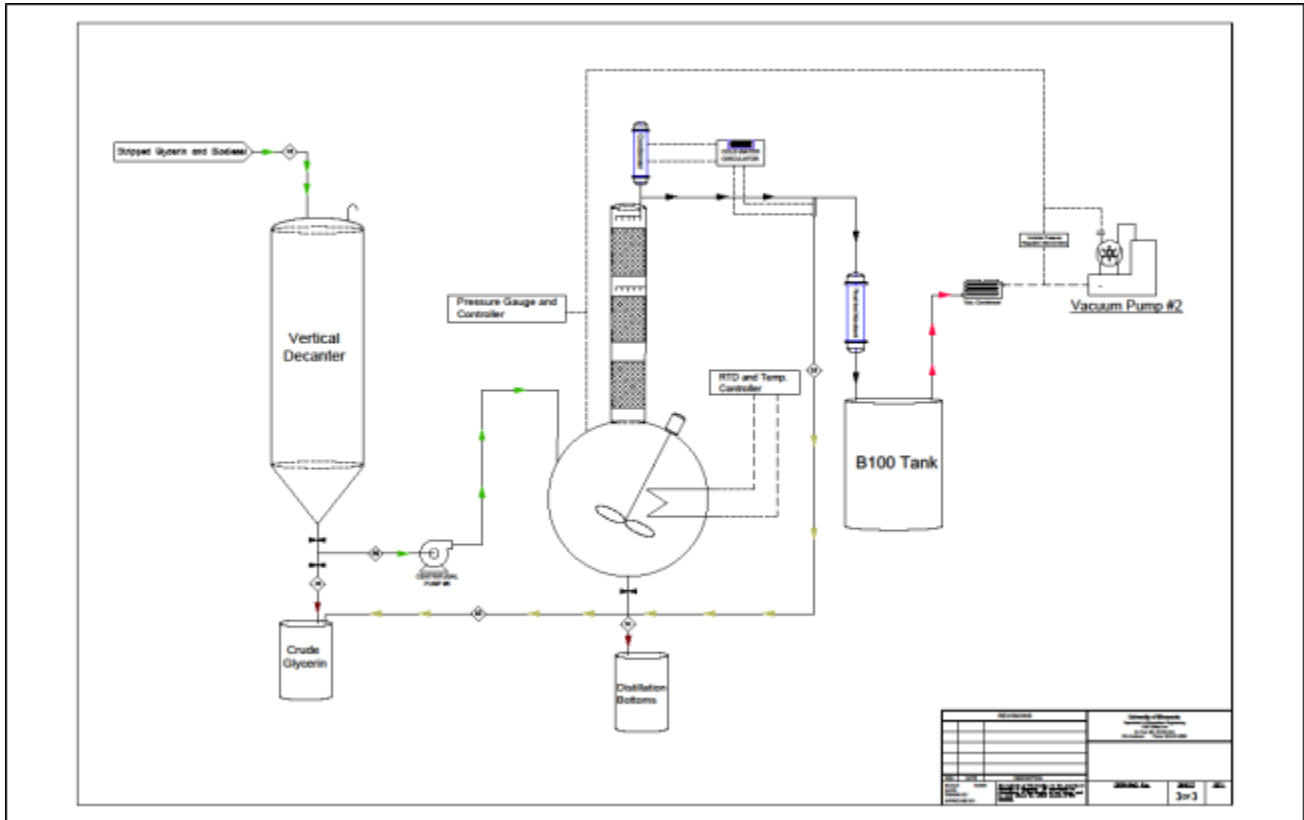
Objective 3: to determine the exact equipment specifications and power requirements and start the purchasing process.

Based on the scum to biodiesel mass and energy balance, materials and equipment were decided upon for the phase of building. The attached spreadsheet shows all of the pumps, tanks, heaters, etc, that will be needed for the complete fabrication of the demonstration facility. Each piece of equipment is color coded to reflect the items purchasing status.

	Equip. Specs. and Costs				
	Scum to Biodisel System -Trailer	Purchased =			
	3/17/2016	Received =			
Purchasing Type	Equipment Specs	Size (gallons)	Diameter (ft)	Dimensions (sq. ft.)	Estimated Costs ($)
Req. Request/Pcard - Trailer sales	Trailer 6.75x20	n/a	n/a	135	$2,000
Req. Request/Pcard -Uline	55 gallon drum	55	3	12.56	$98
	55 gallon drum	55	3	12.56	$98
Req. Request -Utah Biodiesel	Mesh screen	55	3	12.56	$108
	Mesh screen	55	3	12.56	$110
	Steel drum cone	n/a	n/a	n/a	$235
	Steel drum cone	n/a	n/a	n/a	$235
U Market - Dr. Min	Drum Heater 1600Watts 13.3Amps AC 55Gal				$1,600
U Market - Dr. Min	Drum Heater 1600Watts 13.3Amps AC 55Gal				$1,600
Req. Request/Pcard -Bubba's Barrels	Tank #1 w/ heating elements, insulation, tri-clamps, rheostat	85	2.3' dia X 3.25' tall	12.56	$2,695
Req. Request/Pcard -The Cary Company	XP mixer - T1	n/a	n/a	n/a	$1,250
Req. Request/Pcard -Still Dragon	Dephlagmater - T1	n/a	n/a	n/a	$269
Purchased and recieved (pcard) -Utah	liquid-liquid centrifuge	15-25gph	n/a	n/a	$1,664
Req. Request/Pcard -Plastic-Mart	1st Vertical decanter	55	n/a	n/a	$100
P.O.#-B/r instrument	200L tank w/ 6" column, condenser, heating mantle	55	n/a	n/a	$48,100
	Overhead agitator				$3,700
	Edwards HP-12 Pump				$4,950
	Edwards HP-12 Pump				$4,951
	MKS Pressure sensor				$1,900
	Vacuum control valve				$1,500
	Cold trap				$800
	Vacuum control circuitry				$1,500
	Misc (cabling, pipe, etc..)				$300
	Mounting Frame with Plexiglass doors				$5,900
	50 L stainless steel receiver				$2,600
	20 L stainless steel receiver				$2,350
	12 L stainless steel receiver				$1,950
	PC software and interface				$600
				5% Research discount =	-$4,055
				Crating cost =	$1,400
				Shipping cost =	$2,470
				Total =	$80,916
Buy in-store	Biosolids collection tank	55	n/a	n/a	$110
Req. Request -Utah Biodiesel	Sulfuric acid feed tank	5	2	3.14	$15
Buy in-store	Heptane feed tank	20	2.8	6.15	$15
Req. Request -Utah Biodiesel	Glycerin feed tank	5	2	3.14	$5.05
Req. Request -Utah Biodiesel	Methanol feed tank	(2) 5	2.8	6.15	$15
Buy in-store	NaOCH3 feed tank	1	1.66	2.16	$5.05
Buy in-store	Crude glycerin collection tank	5	n/a	n/a	$5.05
Buy in-store	Distilate bottoms collection tank	10	1.5	1.77	$5.05
Req. Request -Northern Tool	Fuel Transfer Pump - 115V AC, 13GPM, Model#SD602G	12			$662
	GPI Digital Turbine Flow Meter - Model #01A31GM	12			$88
	GPI Digital Turbine Flow Meter - Model #01A31GM	12			$88
	GPI Digital Turbine Flow Meter - Model #01A31GM	12			$88
	GPI Digital Turbine Flow Meter - Model #01A31GM	12			$88
Req. Request -Utah Biodiesel	12 GPM Goldstream gear pump, 120V	12			$662
	1" Processor Pump	12			$99
	1" Processor Pump	12			$99
	1" Processor Pump	12			$99
	1" Processor Pump	12			$99
	Chilled water circulator	25L	4	5	$2,000
	Chilled water circulator	25L	4	5	$2,000
Req. request -Utah Biodiesel	Biodiesel filling station w/ pump, filter, and flow meter				$1,850
	pH probe	n/a	n/a	n/a	$500
	pH probe	n/a	n/a	n/a	$500
		Total Cost ($)	% Project		
	Equipment =	$102,076	78%		
	Construction and labor =	$3,926	3%		
	Piping =	$3,926	3%		
	Structural steel =	$2,617	2%		
	Instrumentation =	$9,161	7%		
	Electrical =	$7,852	6%		
	Insulation =	$1,309	1%		
	Total Cost ($) =	$130,866	100%		
	w/ 10% contingency = 23	$145,407			

Project Status as of December 31, 2016:
The major accomplishments during this time period were:

- Publishing of the manuscript, "Economic screening of renewable energy technologies: Incineration, anaerobic digestion, and biodiesel as applied to waste water scum" in the Journal of Bioresource Technology.
- Completed the purchasing and fabrication of custom scum to biodiesel trailer.
- Held meetings between the Metropolitan waste water treatment facility and U. of M project members regarding the operation of the newly completed pilot-scale scum-to-biodiesel process, on-sight in St. Paul, MN.
- Developed and distributed the final component list as well as the utility and waste disposal requirements for the mobile system to the St. Paul facility managers.

The specific objectives in this time period were:

Objective 1: to complete the purchasing, fabrication, and utility installation of the mobile trailer system.
Objective 2: to update all process flow diagrams to reflect the actual fabricated demo-process.
Objective 3: to assess and document the utility, space, safety, and waste disposal requirements for the newly built scum to biodiesel trailer mounted system.

Results of Objective 1: to complete the fabrication of the mobile trailer system.

In late November of 2016, the trailer mounted scum to biodiesel pilot plant was completed. The trailer module requires a 240 V, 50 A outlet and access to a water source and drain. Biodiesel produced from the system is stored in, and distributed from a rear holding tank, while waste products require physical removal. The mobile trailer will be operated by the University of Minnesota biodiesel research group members. For better resource allocation, the trailer can be operated in parallel with the facilities current scum disposal technology. For simplicity, all pretreatment, conversion, polishing stages are contained within the mobile trailer mounted system, along with final product storage. External storage and waste holding tanks should be considered for improved ease of operations and overall economics. Shown below is a list of every system component purchased for the scum to biodiesel system.

MOBILE TRAILER COMPONENTS

1	Trailer and system - 6.75' W x 20' L x 19' H
2	(2) 55 gallon drum
3	(2) Mesh screens
4	(2) Steel drum cones
5	(2) Drum Heater 1600 Watts 13.3Amps AC 55Gal
6	Custom barrel stand with tri-clamp cone fittings
7	Custom reagent stand w/ table-top and pump stand
8	Tank #1 w/ heating elements, insulation, tri-clamps, rheostat
9	XP mixer - T1
10	Dephlagmater - T1
11	(2) liquid-liquid centrifuge
12	1st Vertical decanter
13	200L tank w/ 6" column, condenser, heating mantle
14	Overhead agitator

15	(2) Edwards HP-12 Pump
16	MKS Pressure sensor
17	Vacuum control valve
18	Cold trap
19	Vacuum control circuitry
20	Misc (cabling, pipe, etc.)
21	Mounting Frame with Plexiglass doors
22	50 L stainless steel receiver
23	20 L stainless steel receiver
24	12 L stainless steel receiver
25	PC software and interface
26	Biosolids collection tank
27	Sulfuric acid feed tank
28	Heptane feed tank
29	Glycerin feed tank
30	Methanol feed tank
31	NaOCH3 feed tank
32	Crude glycerin collection tank
33	Distillate bottoms collection tank
34	Fuel Transfer Pump - 115V AC, 13GPM, Model#SD602G
35	(4) GPI Digital Turbine Flow Meter - Model #01A31GM
36	12 GPM Goldstream gear pump, 120V
37	(4) 1" Processor Pump
38	Chilled water circulator
39	Biodiesel filling station w/ pump, filter, and flow meter
40	pH probe
41	Miscellaneous -tri-clamp fittings, gaskets, tubing

Results of Objective 2: to update all process flow diagrams to reflect the actual demo-process.

The entire process is depicted in the combine process flow diagram and instrumentation diagram shown. The first drawing (below) shows two fixed 55 gallon tanks fixed with two layers of filter mesh used to screen out the biosolids from the liquid oil/water. The scum is heated to temperatures above 180°F using waste heat from the water treatment facility. From the tank, a pump will force the liquid scum through a screen filter, further separating the liquid fraction from the biosolids. The liquid fraction is then pumped to the trailer mounted system (drawing 2 of 3), while the biosolids are stored or incinerated immediately.
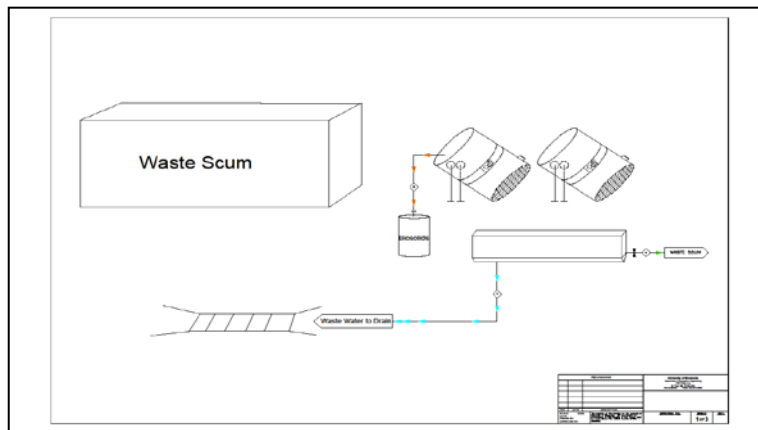
Drawing 2 shows the first tank (tank #1) of the conversion process, which represents the chemical extraction stage and the glycerolysis/transesterification stage. All reagent tanks are to be secured to the trailer system and fixed pressure relief valves and desiccators. Mass transfer between tanks is performed by centrifugal pumps, while reagents are fed using metering pumps. Temperature and pressure control systems are in place where they are needed along with all peripheral instrumentation i.e. pH meters, vacuum pumps, manometers. Chilled water circulators are assigned to condense and cool reaction liquids.
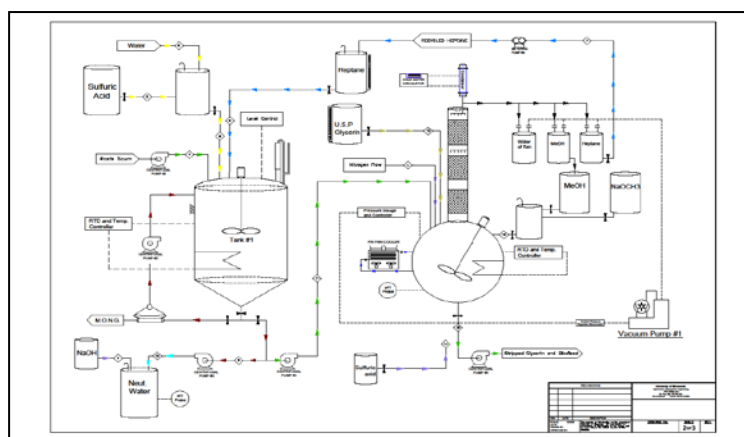
The third drawing depicts the vertical decanter and the reactive distillation units. The decanter is at atmospheric pressure, while the entire distillation system is designed to operate at pressures below 2.0 mmHg. Pressure and temperature controls are in place through both systems. Both vacuum systems on drawing 2 and 3 have secondary condenser traps prior to entering the vacuum pump.
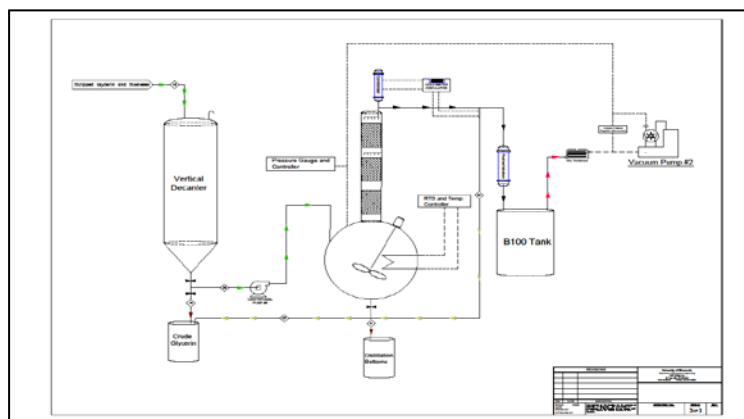
Results of Objective 3: to assess utility, space, safety, and waste disposal requirements for the newly built scum to biodiesel trailer mounted system.

Utility Requirements

Shown below are the total watts and amps required by the scum to biodiesel trailer. The power requirements were taken from the factory specification sheets of each purchased component that required electricity to operate.

Item #	Energy In-put	Watts (W)	Volts (V)	Amps (A)
1	55 gal drum heating mantles	1,600	120	13.3
2	55 gal drum heating mantles	1,600	120	13.3
3	Baldor gear pump	1,044	120	8.7
4	1/2 hp agitator -XP rated	372	230	1.6
5	6 kW heating mantle	6,000	240	25.0
6	6 kW heating mantle	6,000	240	25.0
7	Centrifuge	250	230	1.1
8	1' processor pump	372	110	3.4
9	xp rated transfer pump	172	115	1.5
10	heating mantle	8,000	240	33.0
11	vacuum pump	600	120	5.0
12	vacuum pump	600	120	5.0
13	circulating cooler	800	115	7.0
14	1' processor pump	372	110	3.4
15	Fuel pump station	372	120	3.4
	Total Watts =	28,154	Total Amps=	149.6

Circuit breaker and utility wiring

The wiring and powering of each piece of equipment was performed by a certified electrician (Mr. Sparky), on-site at the University of Minnesota, under the instruction of the project P.I. A 100 amp circuit breaker (right) was installed to act as a "relay switch" or on/off control for each individual electric motor. The circuit breaker itself is wired to a 240 V, 50 amp male outlet plug. According to the systems operating procedure, there is little to no overlap in process operation i.e. motors and heaters will be run one at a time. At no time should throughout the entire batch process will there be a load on the system greater than 70 amps. Individual components range from 115-240 volts, all wired appropriately. All components are wired for 1-phase power, with the exception of the 3-phase liquid-liquid centrifuge. A static frequency converter was purchased to convert the incoming single phase power to 3 phases for that single utility only.

Drainage and Waste Requirements

A single batch of biodiesel (205 lbs) will generate the following waste streams;

-89 lbs of filtered biosolids (moisture level < 30%)
-28 gallons of waste water (contains 28 lbs of neutralized Na_2SO_4)
-78 lbs of organic waste, water, and heptane (emulsified)
-1.3 gallons of water (reaction by-product)
-40 lbs of crude glycerin (to be used for research at the University of Minnesota)
-17.8 lbs of distillation "bottoms"

In theory, all of the organic waste streams (biosolids, organic emulsification, and distillation bottoms) can be combined with sludge wastes and fed to the incinerator. Each waste water stream will have some concentration of COD and BOD, but should be suitable to enter the water treatment process directly. All waste streams leaving the trailer will be stored adjacent to the trailer in HDPE containers sized appropriately.

Safety Requirements

Due to the unknown site of operation, the scum to biodiesel mobile trailer was designed to be operated outside, open to atmosphere. There are no positive pressures throughout the entire process that would require additional safety precautions. The following is a list of specific design implementations that were chosen to address all potentially harmful scenarios.

1) Water-proof electrical conduit was used throughout the entire trailer to protect against accidental leakage, chemical or reagent spills/leaks, or rainfall.
2) A water-proof circuit breaker box was purchased to house the systems relay switches.
3) A metal box was purchased to house the ABB drive (digital phase converter) in order to protect it from the elements.
4) An explosion-proof (xp-rated) agitator was purchased for the heptane and oil mixing stage.
5) An explosion-proof transfer pump was purchased to move the heptane/oil mixture from reactor #1 to the vacuum stripping vessel.
6) A dephlagmator (reflux-condenser) was purchased to condense ALL heptane vapors and return them to the reaction vessel.
7) Other pieces of equipment not rated explosion proof, but involved in the heptane/oil extraction do not come into direct contact with the liquid phase or exposed to the vapor.
8) The electrical components of the distillation reactor are not innately water-proof and should be covered when not in use, if stored outside.
9) Charging of the reagents sulfuric acid, heptane, methanol, and sodium methoxide will be performed using metering pumps, as to eliminate the potential for human contact. All chemicals will be stored in appropriately specified plastic holding tanks and mounted to structural storage racks.

Space and Storage Requirements

Due to the nature of scum its inherent odor, the optimal location for the scum to biodiesel trailer would be outside, next to the solids management building (SMB). Close enough to be able to power the system using a 240 V, 50 amp plug with extension cord and supply a fresh water source (hose).

Alternatively, the trailer could be operated inside the solids management building, next to the scum collection tanks. This would allow for easier transfer of initial scum to the system, as well as easier disposal of all waste streams, possibly eliminating certain waste holding tanks such as water storage.

All waste and product streams have their own designated plastic holding tanks, capable of retaining several batch productions worth of material. The finished product biodiesel tank has a fixed fuel pump attached for easy loading of the product into fleet vehicles.

Project Status as of June 30, 2017:

Amendment Request (06/30/2017)

We are requesting retroactively a shift from professional services and capital expenditures to additional supplies and personnel costs. The late request was due to a misunderstanding of the need to do so since this was relatively small amount in the final period of the project.

Rather than hiring a contractor, a staff member with the skills needed was hired on the research team. The balance from the pilot scale biodiesel was moved to a combination of additional staffing and supplies as we ended up fabricating the pilot scale systems ourselves instead of buying complete systems.

Activity 1: Moved $29,276.00 from professional/technical service contracts and $381.54 from capital expenditures to personnel. Because a decision was made to construct the system we designed in house, additional staffing was required.

Activity 2: Moved $1,805.89 from travel to personnel costs. Additional supplies and staffing were needed to construct the pilot scale system in house.

Activity 3: Moved $28,583.94 from capital expenditures and $675.25 from travel to supplies again to meet the need for construction of the pilot scale system in house.

The major accomplishments during this time period were:

- Completed the fabrication and installation of custom equipment for the scum to biodiesel trailer.
- Completed the site preparation at the Rosemount Outreach and Research Center for the scum to biodiesel trailer i.e. clean-up, electricity modifications, chemical delivery and storage, gas mounting and piping.
- Completed testing for the mobile scum to biodiesel trailer, confirming the yields and product quality of previous laboratory testing.

The specific objectives for this time period were:

Objective 1: to complete the utility installation (50-amp, 240 V) at the Rosemount Outreach and Research Center for start-up and testing.
Objective 2: to have the necessary chemical reagents, nitrogen, propane, delivered safely to the rural system and to modify the power supply to meet the 50-amp trailer requirements.
Objective 3: to perform the scum to biodiesel process using the pilot-scale system, collecting data and samples for testing and throughout the process.

Results of Objective 1: to complete the purchasing, fabrication, and utility installation of the mobile trailer system and transferred the unit to the Rosemount Outreach and Research Center for start-up and testing.

After the complete installation of all the individual pieces on the scum to biodiesel trailer, the system was tested to make sure the controls, heaters, and pumps work properly. Once it was confirmed that all of the components worked as intended, the trailer was prepped to be moved to Rosemount, MN. A 2500 F-150 was used to tow the mobile system approx. 40 miles to the research center, before it was unpacked and reassembles. Once the reassembly was complete (1 hr), the system was tested again to make sure no damage or shifting had occurred during transfer. A full vacuum was applied to the system while simultaneously heating water. Once it was confirmed the system was heating and the pressure measured at the preset unit, the pressure was relieved and the water was drained before the system inspected one last time before start-up.

Results of Objective 2: to have the necessary chemical reagents, nitrogen, propane, delivered safely to the rural system and to modify the power supply to meet the 50-amp trailer requirements. The chemical reagents for the process were purchased according to the scum trailers mass balance. Enough chemicals were acquired to perform two full batches of biodiesel at max system capacity. In addition to the chemical requirements, nitrogen and propane gases were shipped to the research facility and secured to the wall. In order to safely power the trailer, an electrician was hired to install an outlet equipped with 3 phase power at 50 amps and 240 volts. Copper grounding rods were also purchased and attached at several locations throughout the mobile system.

Results of Objective 3: to perform and record the scum to biodiesel process using the pilot-scale system, collecting data and samples for testing throughout the process.

Scum to Biodiesel – Experimental Process, Mass Balance, and Notes

Scum Collection
The scum was collected from the St. Paul Waste Water Treatment Facility in January of 2017. Scum had been collecting for approx. 14 days in a large semi-trailer sized filter bed. Dilute scum water was pumped into the large filter bed after being skimmed off the top of larger holding ponds. During a 1-2-week period that can vary based on collection rate, the filter bed was continuously fed from the top with the dilute scum water while filtered water leaves through a port in the bottom. Slowly over the 1-2-week period, solid scum accumulates until it reached the top of the filter bed. Using (3) 55-gallon plastic garbage bins lined with plastic, approximately 600 lbs. of scum was transferred into the bins before being closed and trucked to pilot-system.

Scum Filtration

Filtered Biosolids

Raw Scum

Scum Oil

Scum was loaded into the heated drum barrels using a spade shovel; the weight of scum (390 lbs) was measured using a 5-gallon pale and a scale before entering the drums. The lids were sealed using a bull-ring while the bung holes were left open to avoid any pressure build-up inside the drums. Once the barrels were sealed, the drums were heated to 120°C and maintained for 8 hrs to ensure complete liquefaction of the oil component. The fat/oil/grease and water mixture then drained through two stainless steel filters (1 and 5 mm^2 respectively) and collected below into heated conical bottoms. From here the scum oil was intermittently pumped into Reactor #1. 250.1 lbs of oil/water mixture in total was transferred to Reactor #1 using Pump #1. Due to human error

coupled to evaporation, approx. 37 lbs of scum material was unrecovered at this stage. Most of the unaccounted for material was in the form of evaporated water, while some of it was lost during transfer. Once all the oil/water mixture was removed, the drums were emptied of all residual material (filtered bio-solids) were weighed. Samples of the biosolids were taken for analysis of its heat of combustion using bomb calorimetry.

Acid Hydrolysis

After 250.1 lbs. of scum entered Reactor #1 from the filtration system, electric heating was applied. The mass and volume of the material transferred was determined independently using a scale (batch-wise measurements for mass) and an in-line digital flow-meter (volume). Two side-mounted 6 kW immersion heaters were used to heat the mixture to 68°C and a 0.5 horsepower agitator with explosion proof electric motor was used to homogenize the oil and water. Any independent water phase "fall-out" at higher temperatures were weighed and recorded, then removed through a valve on the bottom of the tank and released to Holding Tank #1. In a separate container, 98% concentrated sulfuric acid (12.5 lbs.) and water (75.0 lbs.) was premixed before being pumped to Reactor #1 using Reagent Pump #1. A reflux condenser or dephlegmator circulated an ethylene glycol and water mixture at 10°C and ran continuously on the top of the reactor throughout acid hydrolysis. The oil/water/acid mixture was agitated for 30 minutes while maintaining 68°C. After the complete reaction time, the agitation was removed and the mixture let settle for 45 minutes. The denser acidic water phase separated to the bottom of the reactor while the hydrolyzed oil phase remained on top. The lower acid water phase was drained into Holding Tank #1 and neutralized to a pH of 7 using incremental additions of 1N sodium hydroxide and a pH meter. The upper oil phase was left in the reactor, continuously mixed while maintaining a temperature of 68°C in preparation of solvent extraction.

In its present form, the primary component in the scum oil was free fatty acids, some innate to the oil while others a result of hydrolyzing soaps. The second largest fraction was acyl-glycerides (mono-, di-, and tri-glycerides), the precursors of commercial biodiesel production. The rest of the oil is comprised of complex mixture polar-organics, possibly a combination of protein breakdown, carbohydrate derivatives, or pharmaceutical by-products entering the waste water system. The waste stream collectively is known as MONG (matter organic, non glycerol) and can hinder the biodiesel conversion process if not removed.

Heptane Extraction

During chemical extraction, the high solubility of the free fatty acid and acyl-glyceride in hydrocarbon solvents was exploited to purify the oil stream before entering the biodiesel conversion process. Heptane (60.5 lbs.) and water (41.8 lbs.) was charged to Reactor #1 using Reagent Pump #1. The mixture was agitated at 76°C for 20 minutes with the reflux condenser set at 10°C to condense any solvent vapors back into the system. After the reaction was complete, the agitation was removed and the mixture was allowed to settle for 30 minutes. During this time, the lighter oil and solvent phase rose to the top of the reactor, leaving a mixture of water and polar-organics in the lower phase. The polar organic phase or MONG, made up of a large variety of organic molecules was decanted along with the aqueous phase into Holding Tank #1. In order to remove any residual MONG from the oil phase, the heptane/oil mixture was circulated through the liquid-solid centrifuge, and then back into Reactor #1 using Pump #2. The mixture was continuously circulated for 2-3 hrs, shutting down only to remove solids build-up. Once the residual MONG was physically removed, the oil and solvent mixture (222.1 lbs.) was transferred to the Distillation System using Pump #3. The Distillation System will be used throughout the rest of the procedure as the primary reactor, controlled using a PLC (programmable logic controller) with pre-set heating and vacuum profiles. Once the oil and heptane was completely charged, the system was sealed and all safety checks performed. The agitation and chilled circulator were started approx. 1 hour before the start of the reaction, in order to reach their desired set-points prior to charging any chemical reagents. Heptane receivers (20 gallon) were attached and the vacuum system integrity was checked. To start the solvent removal process, program #1 (HEPTANE EXTRACTION) was run on Distillation System software. The parameters for program #1

ramp the temperature from room temperature to 120°C, under a vacuum of 8 kPa. Once these parameters were reached, the reaction conditions were maintained for 20 minutes. The heptane solvent would vaporize and move upward through the distillation column before exiting through the distillate line. After the reaction was completed (all of the solvent was removed), the vacuum was broken with nitrogen and the pressure returned to atmospheric (101.3 kPa). However, the heat was not reduced because the next unit operation required temperatures higher than 120°C. Instead, program #1 was halted and the system prepared for the next operation.

Glycerin Esterification aka Glycerolysis
Any free fatty acids present in the oil must be remediated prior to a base catalyzed transesterification reaction. Glycerin esterification was used to combine the free, unbound glycerin reagent with the free fatty acids (86% wt/wt) to form mono- and di-glycerides and water. To ensure an inert atmosphere during glycerolysis, nitrogen was used to purge the reactor prior to the reaction. This was critical to glycerolysis as any oxygen present in the system can oxidize the scum oil to unwanted derivatives. A 19 liter distillation receiver was inserted into the collection stream and the vacuum pressure was tested. Program #2 (GLCEROLYSIS) was run on the PLC while the vacuum pressure was reduced to 80 kPa to help remove water of reaction from the reactor. With an initial temperature of 120°C, the oil was heated to 240°C under an inert nitrogen blanket. Once the reaction temperature was reached and maintained for 5 minutes, 32.6 lbs. of U.S.P. glycerin was charged to the reactor using Reagent Pump #2. Once the mixture reached a steady state, the temperature was maintained for 3.5 hrs. Water generated throughout the reaction by the dehydration synthesis was immediately vaporized at 240°C and removed from the system through the distillation column. The water of reaction, along with low-weight carboxylic acids, were condensed using a cold trap maintained at 10°C. The heat supply was removed after 3.5 hrs and the free fatty acid content tested to confirm it was below 1% FFA. An air-compressor was used through a quench coil to reduce the temperature below 100°C faster than by radiant cooling alone. The system was purged with nitrogen during cooling to avoid any unintentional oxidation.

Transesterification
The reaction product of glycerolysis was a mixture of mono- and di-glycerides. To convert these molecular precursors to biodiesel, methanol and the base catalyst sodium methoxide was needed to trans-esterify the acyl-glycerides into methyl esters and glycerin. Program #3 (TRANSESTERIFICATION) was run on the PLC while the agitator and reflux condenser were started simultaneously. According to the run parameters, the oil was heated to 76°C before charging 30% wt/wt $NaOCH_3$ in methanol (6.7 lbs.) and excess MeOH (55.2 lbs.) to the Distillation System using Reagent Pump #2. Once the reaction mixture reached a steady-state, the temperature was maintained for 60 minutes while agitating. After the reaction was complete, the heat was removed and the agitation stopped. In order to separate the product biodiesel from the product glycerin, gravity decanting was employed. The mixture (260.2 lbs) was allowed to settle for 1.5 hrs with no agitation or heat at atmospheric pressure. The two products phases separated based on their respective densities, biodiesel (0.88 g/ml) and glycerin (1.26 g/ml), both mixed in the co-solvent methanol (0.79 g/ml). During most commercial biodiesel processes, these two-product streams would be processed separately from here on out. One unique nuance to the process described in this manuscript is the combined processing of the byproducts biodiesel and glycerin. By adding 98% sulfuric acid (3.9 lbs.) directly to the lower glycerin phase, the polar $NaOCH_3$ present in the glycerin phase can be neutralized without affecting the upper biodiesel phase. It was important to agitate the separated mixture very gently during acid neutralization into order to mix the acid within the glycerin layer, without disturbing or emulsifying the two phases. A pH meter was used to determine the end-point of neutralization (ph=8.5) in conjunction with a theoretical limit (7.3 lbs) based on the stoichiometric equivalence of sulfuric acid to $NaOCH_3$. Once neutralized, the biodiesel/glycerin/methanol mixture (264.1 lbs.) was ready for the simultaneous removal of the co-solvent methanol.

Methanol Stripping and Glycerin Decant
To prepare the Distillation System for solvent stripping the methanol distillation receiver (10 gallon) was installed and the reactor purged with nitrogen. On the PLC, program #4 (METHANOL STRIPPING) was run while agitation and heat was applied. According to the run parameters, the pot and column temperatures were set at 120°C and maintained for 20 minutes. The methanol vapor was condensed at 15°C and removed from the system. The majority of methanol was removed under these conditions, prior to any vacuum being applied. After atmospheric stripping was complete, vacuum was applied to the system until a pressure of 8 kPa was maintained at steady-state conditions for 20 minutes. Once the vacuum removal of the co-solvent was complete, the pressure was returned to atmospheric and the temperature returned to 20°C (room temp). Agitation was halted at the end of the reaction and the biodiesel/glycerin mixture was allowed to settle for 2 hrs. Unlike the gravity decant following transesterification, the two components lacked the co-solvent that previously lowered the density differential between them. In theory, the higher density differential allowed the glycerin to settle to the bottom of the reactor faster than with the solvent present. No additional heat was introduced, but the insulation surrounding the reactor allowed for the separation to occur between 100-110°C. After the gravity decant, crude glycerin was removed from the bottom of the reactor until only biodiesel remained. Any impurities introduced into the transesterification process manifested themselves at this point as a "rag layer", emulsifying the plane of separation between the oil and glycerin layers. The rag layer was removed along with the glycerin phase to ensure a higher quality biodiesel move onto the next operation. An air compressor and quench coil was used to reduce the temperature faster than through radiant heating alone.

Biodiesel Distillation
To consistently produce biodiesel that meets ASTM certification, reflux distillation was employed to purify the biodiesel. A 20 gallon distillation receiver was installed for biodiesel collection and the system purged with nitrogen. Distillation was initiated by the running of program #5 (BD DISTILLATION) on the PLC. While the system was beginning to heat under vacuum, the agitation was started using a mechanically sealed, flange-mounted agitator. Program #5 heated the system to its maximum temperature of 260°C under the negative pressure of 0.25 kPa with continuous mixing. The initial distillate first appeared (condensed) at approx. 180°C, and the final distillate was collected at 270°C. As the biodiesel vapors traveled up the reflux column they were condensed using "bulb condensers", collected using an internal trough, then removed from the column via a condensate line that perforated the column wall and connected with the collection trough inside the column. The distillate collection was broken into 3 separate "cuts" or collections. The cuts can affectively be broken into 3 groups; the beginning, middle, and end. The primary difference between the cuts was the average temperature at which each one was distilled. Smaller chain methyl esters vaporize at lower temperatures because of their lower molecular weight relative to longer chain methyl esters, which inversely distill at higher temperatures.

When distillation was complete, as indicated by the lack of distillate stream at temperatures above 270°C, the heat source was turn-off and the system pressure was returned to atmospheric by slowly introducing nitrogen into the reactor. The product distillate from each cut was collected for the final polishing stage and the residual distillation bottoms were drained from the bottom of the reactor. The distillation bottoms were tested for several components including residual sulfur levels. Determining the before and after concentrations of sulfur during distillation is important to understanding the form sulfur takes in the hydrolyzed scum oil.

Water Washing and Vacuum Drying

The final stage of any biodiesel production process is the removal of residual free glycerin carried through during distillation. Heated water washing of the biodiesel will solubilize the polar glycerin molecule completely and allow it to be physically removed via gravity decanted phase separation. Water washing was crucial to ensuring no free glycerin remained in the fuel that could cause it to fail the ASTM D6751 specification of 0.02%. To water

wash the biodiesel, de-ionized water (19 lbs) was added to the distilled product (20% wt/wt) at 60°C and mixed rapidly to guarantee good mass transfer. After 15 minutes of mixing at the desired reaction temperature, the mixture was allowed to settle in a separator flask for 60 minutes. The heavier water phase fell to the bottom of the flask and could be removed after the full 60 minutes without loss of product due to emulsion (very clean split). The upper biodiesel layer was then placed into a vacuum dryer and the temperature was raised to 120°C, under a vacuum of 8 kPa. The vacuum drying conditions were maintained for 10 minutes until the mixture no longer generated steam bubbles. The biodiesel was cooled and collected for complete analytical analysis using the EPA certified ASTM D6751 test protocol.

Analytical Results

To test and certify the product biodiesel end use in transportation vehicles, the full range of the ASTM D6751 Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels was employed. In total, 6 liters of distillate and water washed biodiesel were sent to Gorge Analytical, located in Hood River, OR. Gorge Analytical is a certified biodiesel testing facility, able to supply certificates of analysis for biodiesel that meet EPA requirements for sale and tax credit valuation. The laboratory also participates in the BQ-9000 biodiesel quality assurance programming, ensuring their sample testing methods meet the highest standard available.

The list of analytical tests, their respective methods, and the results can be seen below in Table 1. The results and the reporting criteria (with units) are listed next to one another with a green "pass" or red "fail" indicating the analytical test was within the range of certification.

Table #1: The complete test profile results for the Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels, ASTM D6751.							
Analytical Test	**Method**	**Pass Criteria**	**Results Cut #1**	**Results Cut #2**	**Results Cut #3**	**Average Results**	**Pass/Fail**
Distillation Temp	ASTM D1160	360°C max	343	351	350	348	Pass
Copper Strip Corrosion	ASTM D130	No. 3 max	1a	1a	1a	1a	Pass
Cloud Point	ASTM D2500	n/a (°C)	16	11	8	12	n/a
Water and Sediment	ASTM D2709	0.05 % max	0	0	0	0	Pass
Visual Instepction-Part 1	ASTM D4176-P1	Haze rating	1	1	1	1	n/a
Visual Instepction-Part 2	ASTM D4176-P2	No particulate	Free of debris	Free of debris	Free of debris	Free of debris	Pass
Kinematic Viscosity @ 40°C	ASTM D445-40	1.9-6.0 mm^2/s	4.193	4.607	4.484	4.428	Pass
Micro-carbon Residue	ASTM D4530	0.05 % max	< 0.001	< 0.001	< 0.001	< 0.001	Pass
Phosphorus by ICP-OES	ASTM D4951	0.001 % max	< 0.0001	< 0.0001	< 0.0001	< 0.0001	Pass
Sulfur by UVF - S500, 1B criteria	ASTM D5453	500 ppm	17	77.2	12.4	35.5	Pass
Free & Total Glycerin	ASTM D6584-total	0.240 % max	0.007	0.008	0.008	0.008	Pass
Free Gycerin	ASTM D6584-free	0.020 % max	0.004	0.005	0.004	0.004	Pass
Total Mono-glycerides	ASTM D6584-1	n/a	0.008	0.006	0.002	0.005	n/a
Total Di-glycerides	ASTM D6584-2	n/a	< 0.013	< 0.013	< 0.013	< 0.013	n/a

Total Tri-glycerides	ASTM D6585-3	n/a	0.019	0.022	0.031	0.024	n/a
Total Acid Number	ASTM D664	0.50 mg KOH/g	0.26	0.78	0.37	0.47	Pass
Cold Soak Filtration Test	ASTM D7501	360 seconds	89	100	91	93	Pass
Sulfated Ash	ASTM D874	0.020 % max	< 0.005	< 0.005	< 0.005	< 0.005	Pass
Flash Point, Pensky Martens	ASTM D93	93°C	159.5	177.5	175.5	170.8	Pass
Ca, Mg, by ICP-OES	EN 14538:2006-Ca, Mg	5 ppm	< 2.0	< 2.0	< 2.0	< 2.0	Pass
Na, K by ICP-OES	EN 14538:2006-Na, K	5 ppm	< 2.0	< 2.0	< 2.0	< 2.0	Pass
Oxidative Stability at 110°C	EN15751:2009	3 hrs	7.3	6.7	5.1	6.4	Pass

As the tests indicate, the fuel passes the full range of ASTM D6751 tests required for biodiesel certification. Results for several different temperature collection ranges or "cuts" are shown to determine any early or late stage compounds that may come over as an azeotrope with methyl esters. Cut #1 was collected between the temperature ranges of 182-209°C, Cut #2 collected between 209-238°C, and Cut #3 collected between 238°C and the final temperature of 270°C. The reporting column, "averaged results" reports the overall distillate test result by averaging the 3 temperature range results, as if they had been collected into a single vessel.

Conclusion

According to third party analytical analysis, biodiesel generated from waste water treatment scum using our patented technology meets all the same federal and state testing guidelines imposed upon the commercial biodiesel industry. As the scum represents a current waste stream that is being landfilled with tax payer money, the economics of extracting and converting the waste oil to a transportation fuel are very attractive and would be a significant benefit to the water treatment facility, the tax payer, and any company that was started because of the new technology. Based on previous models, a full-scale system could produce approx. 140,000 gallons of biodiesel each year at the St. Paul water treatment plant. Indirectly, this would be removing approx. 87% of the scum material from the landfill each day. Eliminating waste and landfill volumes while producing as much recycled energy onsite should be the goal of every waste management facility.

Scum to Biodiesel – Process Photos

1) Scum to biodiesel system, in operation at the Rosemount Outreach and Research Center.

2) Acid

hydrolysis precipitate

3) Glycerin by-product

4) Filtered biosolids

5) Distilled B100 biodiesel

Final Report Summary:
In this activity, the researchers have successfully developed the processes to recover oil from scum, to pre-treat the recovered oil, and convert the pretreated oil to ASTM grade bio-diesel. They also successfully developed and demonstrated a pilot scale mobile system which implemented all the processes they developed. Specifically,

(1) The team developed protocols for extracting and cleaning oil from semi-solid scum collected from wastewater treatment plan. Methods were developed to reduce sulfur content.
(2) A new method based on glycerolysis was developed to convert high free fatty acids oil to a mixture of mono- and di-glycerides which were converted to biodiesel through transesterification process
(3) A new batch process was designed based on the findings. Comprehensive economic analysis of scum to biodiesel was carried out and comparison between our process and other pathways for scum handling indicates many of advantages of our process.
(4) Based on the findings, the team was able to scale up the process and determined the design and specification of the scum-to-biodiesel pilot-scale process.
(5) The team successfully fabricated and installed custom equipment for the scum to biodiesel on a trailer and completed testing of the pilot scale system
(6) It has been confirmed that biodiesel meeting the ASTM standards was produced from scum using the pilot system.

Techno-economic analysis and life cycle analysis show significant positive financial and environmental impacts of implementing this technology at the St. Paul Wastewater Treatment Plant. A patent application has been filed. A tour to the lab and experiment setup was given to attendees from LCCMR, MDA, Metro plant, and OTC. The technology and system are ready for demonstration.

ACTIVITY 2: Develop and demonstrate centrate to algae fuel system
Description:
The second wastewater stream of interest to this project is "centrate", which is generated from centrifuging of activated sludge. Centrate contains highest amount of ammonia nitrogen and active phosphorus among several wastewaters at different stages in a municipal wastewater treatment plant, which could be a suitable growth medium for microalgae for the dual purposes of removing nutrients and obtaining a feedstock for biofuel production.

Our previous research shows that algae consume organic carbon source in the centrate quickly while relatively large amount of N and P remain in the culture broth. In order to completely utilize and remove N and P from the wastewater to meet discharge standards, carbon source may be replenished through addition of glycerol from the scum to biodiesel conversion process, process water from hydrothermal treatment of algae, and CO_2 from fMAP and fMAG processes. The goal of this section is to use byproducts derived from scum to biodiesel process and waste gas from sludge to bio-fuels process to improve nutrients removal efficiency and obtain maximal algal biomass feedstock for biofuels application, and demonstrate a pilot-scale centerate to algae fuel system.
The specific objectives of centrate are (1) to evaluate and optimize the concentration of crude glycerol as sole carbon source for fast growth; (2) to develop and optimize best cultivation growth conditions for fast mixotophic growth; (3) to develop a mixotro-autotrophic two-stage cultivation strategy for improved nutrient removal and enhanced lipid production; (4) to develop a pilot-scale centrate to bio-fuels demonstration system based on the optimized process.
Specific tasks will be:
1. Evaluate and optimize the concentration of crude glycerol for maximal algal biomass production. Different facultative heterotrophic microalgae strains will be evaluated and different concentration of crude glycerol will be added to meet the requirements of enhanced algal biomass accumulation and improved nutrient removal efficiency.
    a. Evaluate and compare the capability of different facultative heterotrophic strains to utilize the purify and crude glycerol derived from scum-biodiesel process directly for fast growth;
    b. Optimize the concentration of crude glycerol in batch-scale experiment.
2. Optimize CO_2 concentration for fast mixotophic growth. This task is intended to select appropriate CO_2 concentration to obtain high cell density and fast nutrient removal efficiency.
    a. CO_2 concentration levels of 1%, 2%, 5%, 10%, 15% (v/v) will be tested and optimized in batch-scale experiment.
    b. CO_2 rich-waste gases collected from fMAP and fMAG processes will also be analyzed and evaluated for the feasibility of replacing above CO_2 to stimulate algae growth;
    c. Effect of temperature, light intensity, glycerol and CO_2 concentration on algae growth and nutrient removal under mixotrophic cultivation mode will be evaluated and optimized through Box-Wilson Central Composite design (CCD).
3. Develop a mixotro-autotrophic two-stage cultivation strategy for improved nutrient removal and enhanced lipid production. At the first mixotrophic dominated stage, both glycerol and CO_2 will be used to support the mixotrophic growth, the supernatant will be reused as culture media in the second autotrophic dominated stage and CO_2 will be injected to provide inorganic carbon source.
    a. A lab-scale two-stage cultivation system using 1-L PYREX Roux culture bottle as bioreactor will be used for process development and optimization;

b. Investigate the effects of temperature, light intensity, glycerol and CO_2 concentration on biomass accumulation and nutrient removal in the two-stage cultivation system.
c. The two-stage system will be further scaled up and the process will be optimized.
4. Develop a pilot-scale centrate to bio-fuels demonstration system based on the optimized process.
   a. A pilot-scale two-stage system based on multi-layer bioreactors will be developed and constructed.
   b. Light intensity, Temperature, pH, and glycerol and CO_2 concentration were further optimized in large-scale cultivation system.
   c. The 3M Building Illumination & Photo Voltiac (BIPV) power modules provided through a grant from the 3M Foundation will be incorporated into the system to provide power for pumping and mixing.
   d. Demonstrate the pilot-scale centrate to bio-fuels demonstration system.
5. Environmental impacts analysis (Optional). Our analysis will follow the LCA standards created by International Organization for Standardization (ISO): ISO 14040 and ISO 14044. The LCA analysis will include all direct impacts and upstream impacts of chemicals and energy inputs. The process simulation models combined with existing modeling software will be applied in developing life cycle inventory. Software for modeling efforts, including Excel, GREET, GaBi, and Ecoinvent database, are currently owned by the research group. The LCA will include of environmental impact of fossil fuel use (MJ) and GHG emissions (kg CO2 eq.) and final results of centrate to algae technology will be compared with previous cultivation models.

Summary Budget Information for Activity 2:   ENRTF Budget: $172,060.00
                                                 Amount Spent: $172,060.00
                                                 Balance: $0.00

Activity Completion Date:

Outcome	Completion Date	Budget
1. *Develop and optimize algae growth and nutrient removal involving crude glycerol; design the complete processes.* Specific outcomes include: 1.1. High performance facultative heterotrophic microalgae strains and optimal concentration of crude glycerol added to meet the requirements of enhanced algal biomass accumulation and improved nutrient removal efficiency will be determined. 1.2. Optimal CO_2 concentration for fast mixotophic growth, high cell density, and fast nutrient removal efficiency.will be determined 1.3. A mixotro-autotrophic two-stage cultivation strategy for improved nutrient removal and enhanced lipid production will be developed 1.4. Scale-up process parameters will be developed.	6/30/2015	$50,000
2. *Design and construct a greenhouse based algae based wastewater treatment facility.* Specific outcomes include: 2.1. A pilot-scale two-stage system based on multi-layer bioreactors will be developed and constructed. 2.2. Light intensity, Temperature, pH, and glycerol and CO_2 concentration will be further optimized in large-scale cultivation system.	12/31/2016	$70,000

2.3. The 3M Building Illumination & Photo Voltiac (BIPV) power modules provided through a grant from the 3M Foundation will be incorporated into the system to provide power for pumping and mixing.			
3. *Test the facility and collect mass and energy balance data; conduct TEA and LCA.* Specific outcome includes: The environmental and economic impacts of the technologies developed will be quantified and reported.	03/31/2017	$27,060	
4. *Demonstrate the systems to stakeholders.* Specific outcome includes: Demonstration of the technologies developed to the stakeholders will be carried out by the end of the project. All demonstration schedules will be discussed with LCCMR office and announced to the stakeholders through UMN and LCCMR's channels.	06/30/2017	$25,000	

Project Status as of December 31, 2014:

We tested algae strain's ability to assimilate crude glycerol from the scum to biodiesel process. We first characterized the glycerol sample (Table 1). The crude glycerol density is 0.95 g/mL. As shown in Table 1, crude glycerol sample mainly contained glycerol, soap, catalyst, methanol, metal and water. Glycerol and metal ion contents need for further analysis.

Table 1 Characterization of crude glycerol sample

Parameters	% (w/w)
Moisture	28.2±0.5
Ash	2.1±0.1
Catalyst	1.2±0.1
Soap	2.6±0.2
Total nitrogen	0.1±0.0
Total phosphorus	0.005±0.000
pH	10.3±0.2
Others	65.8±0.6

Autotraphic cultivation (Treatment 1) of *C. vulgaris* was carried out without crude glycerol with illumination of 50 µmol photons /m^2/s with a 12/12 h light/dark cycle. Mixotraphic cultivation (Treatment 2) of *C. vulgaris* was carried out with 5 g/L crude glycerol with illumination of 50 µmol photons /m^2/s with a 12/12 h light/dark cycle. Heterotrophic cultivation (Treatment 3) of *C. vulgaris* was carried out with 20 g/L crude glycerol in the flask covered with silver paper (in dark). Cultivation (Treatment 4) of *Chlorella vulgaris* with 10 g/L crude glycerol without TAP medium under light conditions was carried out. The initial biomass concentration of 0.10 g/L was used in all runs. The initial pHs of the media for all runs were adjusted to 6.5 with 0.5 M HCl or 0.5 M NaOH. The media were autoclaved at 121 °C for 30 min. The cells were centrifuged at 3, 200×g for 5 min at room temperature, washed with distilled water three times, and prepared for further analysis.

The variation of the medium color was shown in Table 2. The growth conditions of the 4th day were shown in Fig.1. As shown in Fig.1, all treatments grew. Treatment 1, 2, and 3 grew well. The details need further work.

Table 2 The variation of medium color

Parameters	Treatment 1	Treatment 2	Treatment 3	Treatment 4

Before autoclaving	Colorless	Light brown	Dark brown, droplets were appeared in the medium	Brown, droplets were appeared in the medium
After autoclaving	Colorless	Light brown, no droplets	Dark brown, small oil layer.	Crude glycerol was soluble.
After inoculation	Light green	Light brown with green	Brown	Brown
After 4-d cultivation	Dark green	Green, some cells stuck at sidewall	Cream, some cells stuck at sidewall	Light cream, few cells in the medium
Biomass concentration (g/L)	0.62	2.34	2.33	0.36
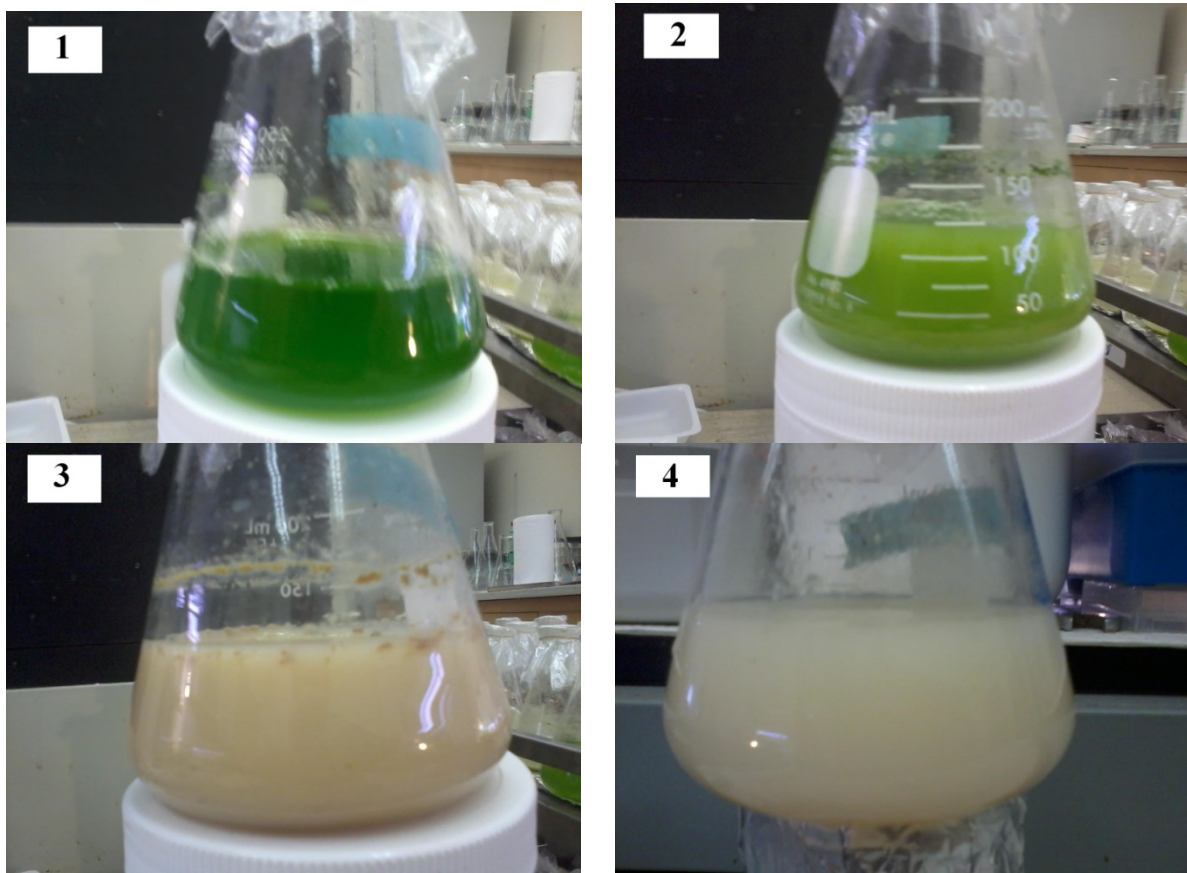
Fig.1 The growth conditions of 4 treatments after 4-d cultivation

Project Status as of June 30, 2015:

In order to accurately evaluate the effect of waste crude glycerol on nutrient removal in municipal wastewater-based algae cultivation system, well-controlled synthetic wastewater was used to replace real municipal wastewater in this study. The composition of artificial wastewater was shown in Table 1. HEPES was added as buffer, on the basis of 5 mM for microalgal culture.

Table 1 Composition of artificial wastewater

Chemical	Concentration (mg/L)
NH4Cl	230

NaCOOCH3	100
NaNO3	100
K2HPO4	200
KH2PO4	50
Na2HPO4	100
CaCl2.2H2O	100
MgSO4•7H2O	400

The effect of waste glycerol on nutrients removal from synthetic wastewater by *Chlorella vulgaris* was carried out. Different concentrations of crude glycerol (0, 1, 5 and 10 g/L) and pretreated glycerol (1, 5, 10 and 15 g/L) were tested using HPEPS as buffer. The initial pHs of the media for all runs were adjusted with 0.5 M HCl or 0.5 M NaOH. The media were autoclaved at 121 oC for 30 min. Microalga was cultured in 250 mL Erlenmeyer flasks containing 150 mL media. In all cases, C. vulgaris was inoculated at 1:10 (v/v) ratio into the flask. The cultivation of C. vulgaris was carried out with continual illumination of 50 μmol photons /m2/s. The initial biomass concentration was about 0.10 g/L in all runs. All treatments were cultivated for 7 days at 25 ± 2 °C.

Moisture content

The samples were dried to constant weight in an oven at 105 oC for 24 h to evaluate the moisture content.

Ash content

The samples were dried to constant weight in an oven at 550 oC for 4 h to evaluate the ash content.

Crude glycerol density

The crude glycerol was measured using an electronic scale and a graduated cylinder. The crude glycerol density is crude glycerol weight per unit volume.

Catalyst content

Prepare the solvent solution: 55mL of acetone mixed with 5mL of distilled H2O. Add 5 drops of phenolphthalein to the solvent solution. Zero the solution by adding a small amount of 0.1N KOH until the solution turns light pink in color. Add ~0.7g of analyte to the zeroed solution. The solution should turn pink if there is catalyst present. Titrate the solution with 0.1N HCl until the solution turns clear. Record the amount of 0.1N HCl required to neutralize the catalyst and calculate the catalyst number. Catalyst Number is calculated by multiplying the volume of HCl titrant required by the normality of the titrant and by the molecular weight of the HCl titrant. Then dividing this by 1000mg/g and by the mass of analyte sample used. Catalyst content=   mL HCl * 0.1N HCl * 54.0g/mol HCl / (1000mg/g *   grams sample).

Soap content

Soap Number Titration is used to determine the amount of alkiline soap present in the analyte. The analyte is titrated using 0.1N HCl in methyl blue indicator to determine the parts per million soap. The soap number can be performed in conjunction with the catalyst number. Once the catalyst has been completely titrated, 4 drops of methyl blue indicator can be added to the same sample and titrated to the methyl blue end point (yellow color). The difference between the catalyst end point and the methyl blue yellow end point is the amount of soap present. Soap Number is calculated by multiplying the volume of HCl titrant required by the normality of the titrant and by the molecular weight of the HCl titrant. Then dividing this by 1000mg/g and by the mass of analyte sample used. Soap Number =   mL HCl * 0.1N HCl * 304.4g/mol HCl / (1000mg/g *   grams sample).

Pretreatment of crude glycerol

Sample pH was adjusted to 2.0 using 2 M HCl. Then the whole content was centrifuged at 4000g for 20 min. The top layer which was dark was mainly free fatty acids. Glycerol was in the obtained bottom layer.

Measurement of glycerol concentration

To determine the glycerol concentration in the crude glycerol and the medium, the samples were analyzed by a spectrophotometric method as described in Sarma et al.`s (2014) study. The sample of the crude glycerol was diluted 500 times with distilled water. Ethanol (47.5%, v/v) of 5 mL was added into 5 mL of the above diluted sample. The resulting solution was mixed with 1.2mL of 0.2 M acetylacetone solution and 1.2 mL of 10 mM sodium periodate solution. Test tube with the above mixture was at 70 ± 2 oC in a water bath for 1 min; immediately cooled to 20 ± 2 oC by using water bath. Finally the absorbance of the solution was determined at 410 nm by using the spectrophotometer.

pH Measurement

Sample pH was measured using a pH meter.
Measurement of biomass concentration
Cell dry weight was measured with an electronic scale after drying the microalgal pellets in the dry oven at 105 °C over night.
Measurement of total phosphorus, ammonium, and total nitrogen
The samples were first centrifuged at 5000 rpm for 10 min and then the supernatants were properly diluted and analyzed for total phosphorus, ammonium (NH4-N), and total nitrogen following the Hach DR 5000 Spectrophotometer Manual (Hach, 2008).

Data Analysis

The experiments were carried out in triplicate and results were reported as mean ± standard deviation values. Analysis of variance (ANOVA) of data was carried out. When ANOVA gave at least one significantly different result, Duncan's multiple range test was performed (1955).

Results

Composition of waste glycerol

The waste glycerol density is 0.95 g/mL. As shown in Table 2, crude glycerol sample mainly contained glycerol, soap, catalyst, methanol, metal and water. The glycerol content was 38.5%.

Table 2 Characterization of crude glycerol sample

Composition	% (w/w)
Glycerol	38.5±0.8
Moisture	28.2±0.5
Ash	2.1±0.1
Catalyst	1.2±0.1
Soap	2.6±0.2
Total nitrogen	0.1±0.0
Total phosphorus	0.005±0.000
Others	27.3±0.6

Effect of waste glycerol concentration on Chlorella vulgaris growth and nutrients removal
Different concentrations of crude glycerol (0, 1, 5 and 10 g/L) and pretreated glycerol (1, 5, 10 and 15 g/L) were added in the synthetic wastewater for enhancing Chlorella vulgaris growth and nutrients removal with initial pH of 7.0. The pH, residual glycerol concentration, and biomass variation of different concentrations of waste glycerol without and with pretreatment was shown Figs.1-3. The residual glycerol in all treatments except the culture with 10 g/L crude glycerol and 15 g/L pretreated glycerol were 0 g/L at day 7. The results showed that all treatments except the cultures with 10 g/L crude glycerol and 15 g/L pretreated glycerol were used up at the late growth stage. The pHs of all other runs except the culture with 10 g/L crude glycerol and 15 g/L pretreated glycerol were increased slightly before they decreased with increasing culture time. The pHs of both the cultures with 10 g/L crude glycerol and 15 g/L pretreated glycerol were decreased. The highest biomass concentration was 2.92 g/L of the culture with 10 g/L pretreated glycerol. Compared with control, the cultures with optimal concentrations of crude glycerol or pretreated glycerol increased nutrients removal. The highest TN removal efficiency of 75%, TP removal efficiency of 81%, and NH4-N removal efficiency of 90% were obtained for the culture with 10 g/L pretreated glycerol.
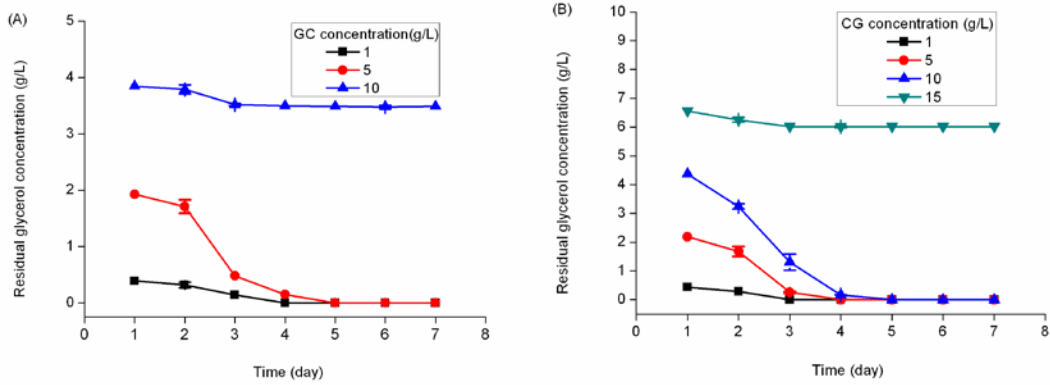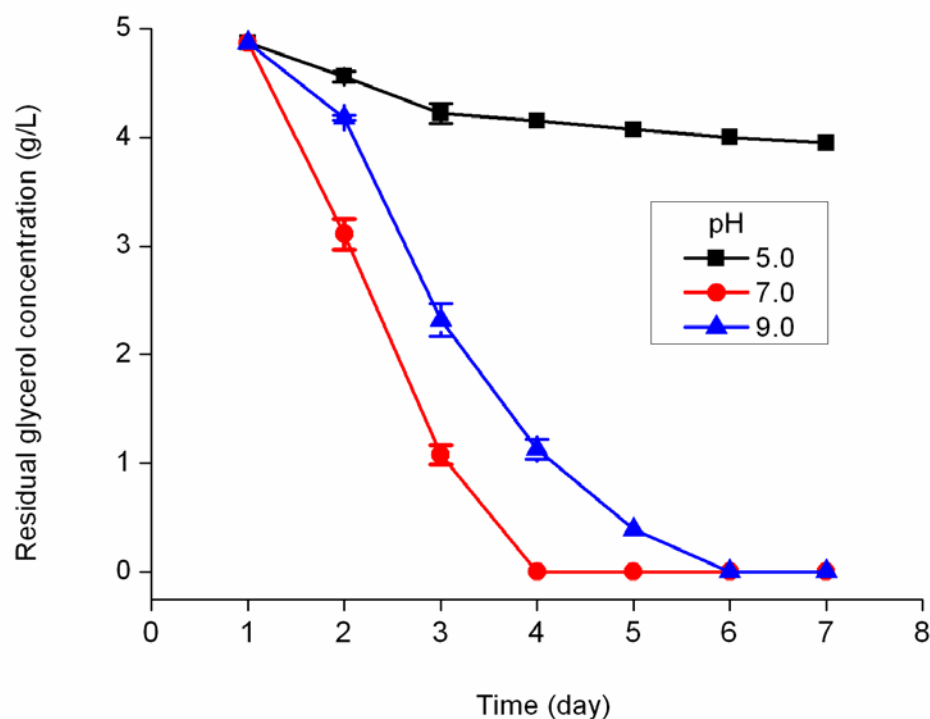
Fig.1 Glycerol uptake of Chlorella vulgaris with different concentrations of waste glycerol (A. Crude glycerol, B. Pretreated glycerol).
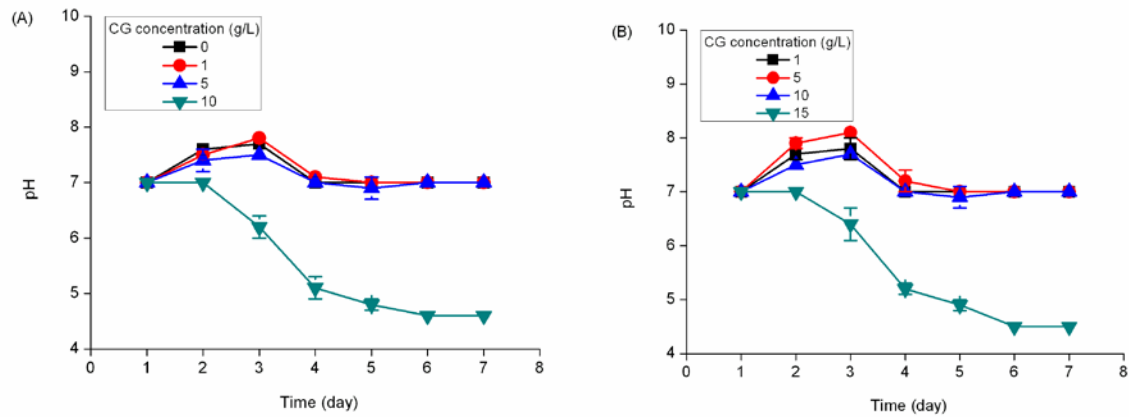
Fig.2 pH shift of Chlorella vulgaris using different concentrations of waste glycerol (A. Crude glycerol, B. Pretreated glycerol).
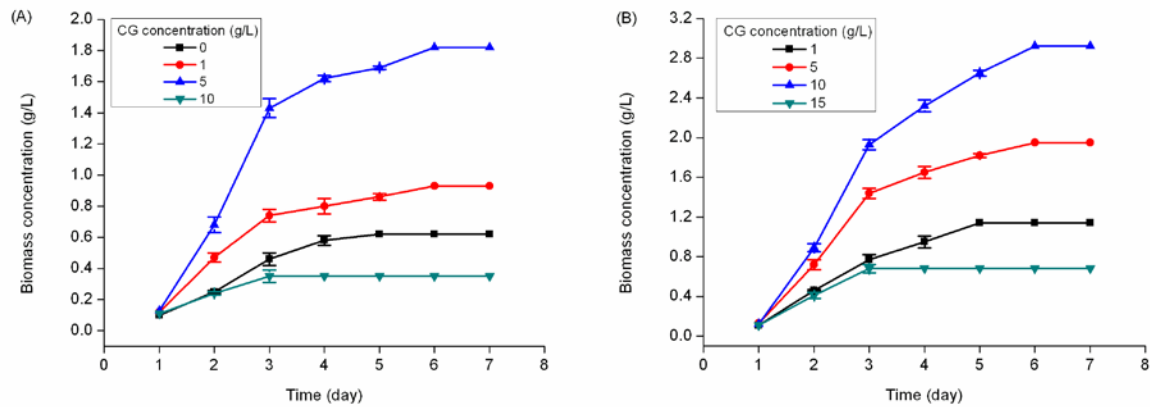
Fig.3 Biomass concentration of Chlorella vulgaris using different concentrations of waste glycerol (A. Crude glycerol, B. Pretreated glycerol).

Table 3 Nutrients removal of Chlorella vulgaris using different concentrations of waste glycerol.

Parameters	Crude glycerol concentration (g/L)				Pretreated glycerol concentration (g/L)			
	0	1	5	10	1	5	10	15
TN removal	25±1	44±2	61±1	17±3	49±2	72±2	75±1	18±3

efficiency (%)							
TP removal efficiency (%)	38±0	52±2	69±2	12±2	55±2	78±0	81±3	10±1
NH4-N removal efficiency (%)	53±3	61±0	77±1	37±2	65±1	87±2	90±1	34±3

Effect of initial pH on Chlorella vulgaris growth and nutrients removal

To investigate initial pH on Chlorella vulgaris growth and nutrients removal, three different initial pHs (5.0, 7.0 and 9.0) of the media with 10.0 g/L pretreated glycerol were carried out. As shown in Fig. 4, glycerol concentration in the media decreased with increasing culture time. Glycerol in the media of all the treatments except initial pH of 9.0 was used up at the late growth stage. The pHs of the cultures (initial pHs of 5.0 and 9.0) shifted significantly during cultivation (Fig. 5). The results showed that HEPES has little buffer effect when the initial pH was low or high. The cells of the culture with the initial pH of 5.0 were dead at the late growth stage. The culture with the initial pH of 7.0 had the best growth and nutrients removal performance (Fig. 6). The highest TN removal efficiency of 72%, TP removal efficiency of 80%, and NH4-N removal efficiency of 91% were obtained for the culture with the initial pH of 7.0.

Fig.4 Effect of initial pH on glycerol uptake of Chlorella vulgaris.
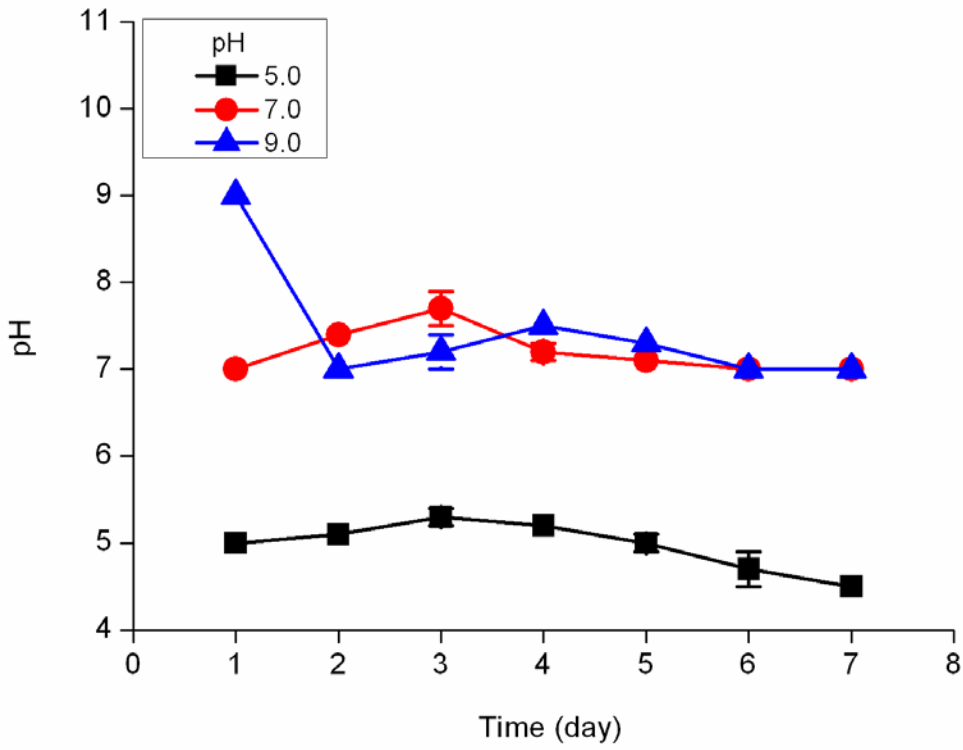
Fig.5 pH shift of Chlorella vulgaris with different initial pHs.
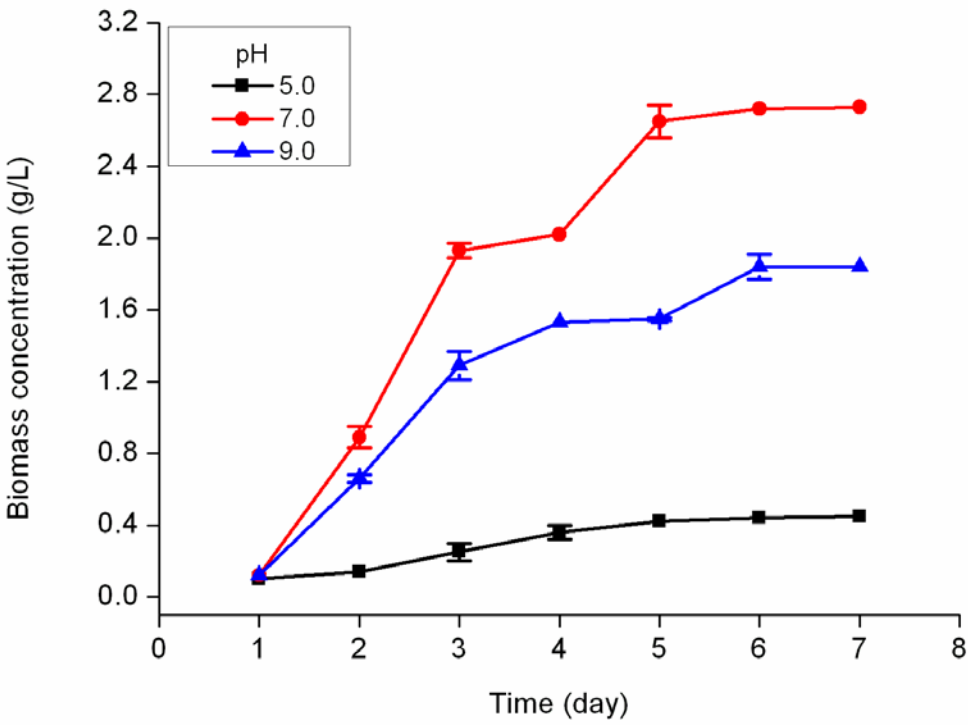
Fig.6 Growth performance of Chlorella vulgaris with different initial pHs.

References

Bi CH, Min M, Nie Y, Xie QL, Lu Q, Deng XY, Anderson E, Li D, Chen P, Ruan R. Process development for scum to biodiesel conversion. Bioresource Technology, 2015, 185:185-193.

Bondioli P, Bella LD. An alternative spectrophotometric method for the determination of free glycerol in biodiesel. European Journal of Lipid Science and Technology, 2005, 107:153-157.

Hach. Procedure Manual, 2008; Hach, Loveland, CO.

Duncan, D. B. Multiple range and multiple F tests. Biometrics, 1955, 11, 1–42.

Project Status as of December 31, 2015:
In this time period, lipid properties of algae grown on glycerol at different concentrations and glycerol with different pH values were analyzed.

Methods
After 7-day cultivation, total carbohydrates in *C. vulgaris* cells were analyzed according to the phenol-sulphuric acid method (Ben-Amotz et al., 1985). Protein contents in *C. vulgaris* cells (dry biomass) were determined from the nitrogen content data evaluated with a CE-440 elemental analyzer (Exeter Analytical Inc., North Chelmsford, the United States), using the nitrogen-to-protein conversion factor of 6.35 (Safi et al., 2013). And 0.2 g (dry weight) microalgal biomass was disrupted before lipid extraction. Microalgal suspension pH adjusted to 4.8 by acetic acid before disruption. The cellulase concentration was 500.00 mg L^{-1}. The cells were broken at 55 °C in a water bath for 10 h and the lipids were extracted from the cell slurries with chloroform-methanol method as described in our previous study (Zheng et al., 2011). The weights of the obtained lipids were determined with an electronic scale.

The extracted lipids of 0.1 mL were analyzed by gas chromatography–mass spectrometry (GC-MS) (Thermo Finnigan, the United States). Prior to GC-MS analysis, the methylation of fatty acids with boron trifluoride and methanol was carried out at 100 °C for 120 min (Doan & Obbard, 2012). Methylated fatty acids were dissolved in 2 mL hexane and dehydrated by 0.1 g anhydrous sodium sulfate for 30 min, followed by 1.0 μL injection for GC-MS analysis. The GC-MS method was according to Doan & Obbard 's study (2012).

Results
Effect of glycerol concentration on lipid production of C. vulgaris
C. vulgaris could accumulate lipids in synthetic wastewater with glycerol generating from biodiesel production using scum as oil feedstock in the cultures under different concentrations of crude glycerol when the initial pH was 7.0 (Table 1). There was a significant difference (P <0.05) in the lipid contents of the cultures. The lipid contents of the cultures increased with the presence of glycerol. However, high concentration of crude glycerol (10 g L^{-1}) did not provide a reasonable lipid accumulation. This could be explained by nitrogen limitation. Lipid accumulation was often triggered under nitrogen limiting conditions (Yeesang & Cheirsilp, 2011). The maximum lipid content and productivity of 32% and 78 mg $L^{-1} d^{-1}$, respectively were obtained for the culture with 5 g L^{-1} crude glycerol. Comparing with control (0 g L^{-1} crude glycerol), the culture with 1 and 5 g L^{-1} crude glycerol stimulated lipid accumulation. This is because tri-acyl-glycerols, the storage form of lipids of microalgae, are derived from glycerol and fatty acids. When lipid content of the cultures under different concentrations of crude glycerol was high, protein content was relative low. There was a significant difference (P < 0.05) in the lipid contents of the cultures with pretreated glycerol. The optimal glycerol concentration of pretreated glycerol was 10 g L^{-1} with the maximum lipid content and productivity of 39% and 163 mg $L^{-1} d^{-1}$, respectively. The lipid accumulation increased when the glycerol concentration was increased from 1 to 10 g L^{-1} (Table 1). However, a further increase in glycerol concentration discouraged the lipid accumulation of the strain. In terms of pretreated glycerol at 5 g L^{-1}, higher lipid content and productivity compared with those from crude glycerol at the same concentration have been observed (Table 1). Carbohydrate content showed similar tendency as lipid content.

Table 1. Chemical compositions and lipid productivity of *C. vulgaris*

Parameters	Crude glycerol (g L⁻¹)				Pretreated glycerol (g L⁻¹)				Pure glycerol (g L⁻¹)
	0	1	5	10	1	5	10	15	25
Protein content (%)	61±2	50±3	31±1	55±0	48±1	28±2	20±3	57±4	17±0
Lipid content (%)	10±0	18±1	32+3	18±3	20±1	34±0	39±2	17±1	42±1
Lipid productivity (mg L⁻¹ d⁻¹)	9±0	24±2	78±4	9±1	33±4	95±5	163±7	15±2	344±9
Carbohydrate content (%)	15±1	19±1	25±2	18±2	20±2	27±1	30±0	16±0	32±1

The composition of major fatty acids of the extracted lipids from the cultures with different glycerol concentrations was determined using a GC-MS system (Figure 1). The same eight varieties of fatty acids were identified, but the relative content of the fatty acids varied. C16:0, C18:1, and C18:2 were the three most abundant fatty acids and their total percentage was approximately 60%. The percentage of unsaturated fatty acids increased with increasing concentrations of crude glycerol. The results suggested that high concentration of crude glycerol could promote the degree of unsaturation in fatty acids of *C. vulgaris*. This might be that the increase in concentrations of crude glycerol could lead to high C/N ratio, thus increasing the content of polyunsaturated fatty acids (Morales-Sánchez et al., 2013). Similar tendency has been observed in the cultures of *C. vulgaris* with different concentrations of pretreated and pure glycerol. Comparing with soybean oil, the total percentage of C18 fatty acids in *C. vulgaris* was lower (Serio et al., 2006). The content of unsaturated fatty acids in the lipids of *C. vulgaris* was lower than that of soybean oil. C16:1, C16:2, and C16:3 were not present in soybean oil. It is worth pointing out that the fatty acids in soybean oil used in biodiesel production were also in those of *C. vulgaris*. There are primarily C16 and C18 fatty acids in both soybean oil and the lipids of *C. vulgaris*. Therefore, biodiesel from lipids of *C. vulgaris* and soybean oil, the main current biodiesel feedstock in the United States (Avinash et al., 2014), would have similar physical and chemical properties. Similar fatty acids profile has been obtained in the cultures of *C. vulgaris* with different concentrations of pretreated and pure glycerol. Therefore, fatty acids from *C. vulgaris* under different glycerol concentrations are likely suitable for the production of good-quality biodiesel.
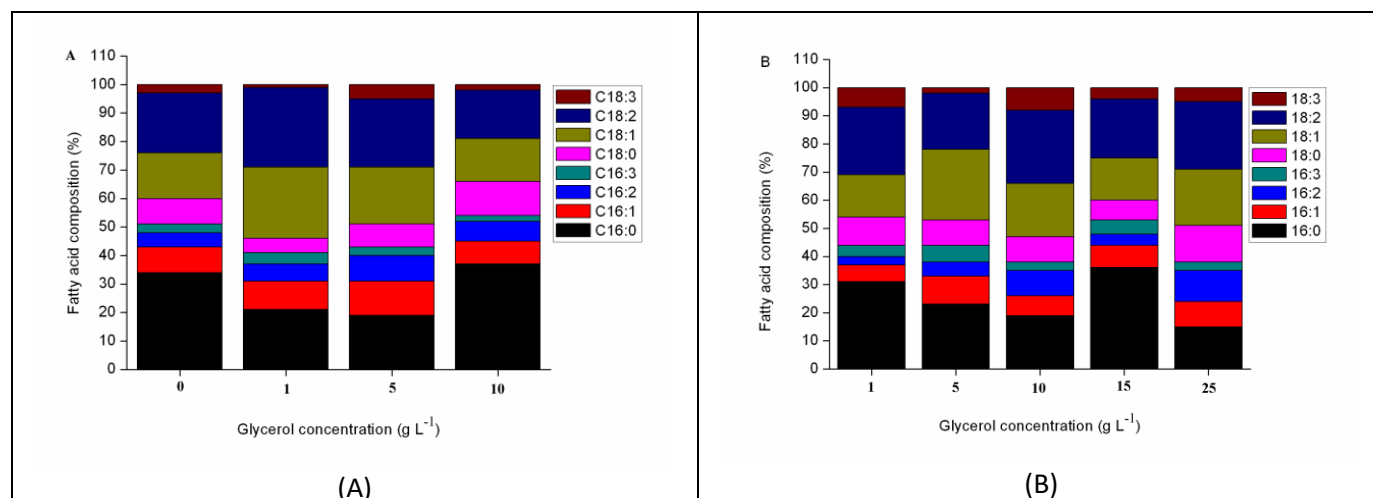
Figure 1. Fatty acid profiles of *C. vulgaris* with different glycerol concentrations (A Crude glycerol; B Pretreated glycerol).

Effect of initial pH on lipid production of *C. vulgaris*

There was significant difference ($P < 0.05$) in the lipid contents of the cultures at different initial pH values. The most suitable pH for *C. vulgaris* to accumulate lipids was 7.0 with the maximum lipid content and productivity of 39% and 163 mg L^{-1} d^{-1}, respectively. The lipid accumulation decreased from 39% to 33% and lipid productivity decreased from 164 to 95 mg L^{-1} d^{-1} when the initial pH was increased from 7.0 to 9.0 (Table 2). Microalgal cells of the culture at initial pH 5.0 were dead at the late growth stage and their lipid accumulation inhibited greatly. These results indicated that alkaline conditions prompted lipid accumulation of *C. vulgaris*. pH value affected lipid accumulation of *C. vulgaris* cultivated in the effluent of a low-cost waste fermentation system producing volatile fatty acids (Cho et al., 2015).

Table 2. Effect of initial pH on cell growth and lipid production of *C. vulgaris*

Parameters	Initial pH		
	5.0	7.0	9.0
Protein content (%)	54±3	19±0	26±1
Lipid content (%)	17±2	39±3	33±1
Lipid productivity (mg L^{-1} d^{-1})	5±0	164±7	95±4
Carbohydrate content (%)	18±2	30±1	28±0

Eight varieties of fatty acids were identified using the GC-MS system, and the relative content of the fatty acids from the cultures with different initial pH values was different (Figure 2). The contents of unsaturated fatty acids were higher than that of saturated fatty acids. There are mainly C16 and C18 fatty acids in the lipids of *C. vulgaris*. This observation is consistent with previous findings that C16 and C18 fatty acids are the main fatty acids of *C. vulgaris* cultivated in the effluent of a low-cost waste fermentation system producing volatile fatty acids (Cho et al., 2015). In particular, lipids of the cultures had similar fatty acid profile to those under different glycerol concentrations. Therefore, fatty acids from *C. vulgaris* under different initial pH values are also likely suitable for the production of good-quality biodiesel.
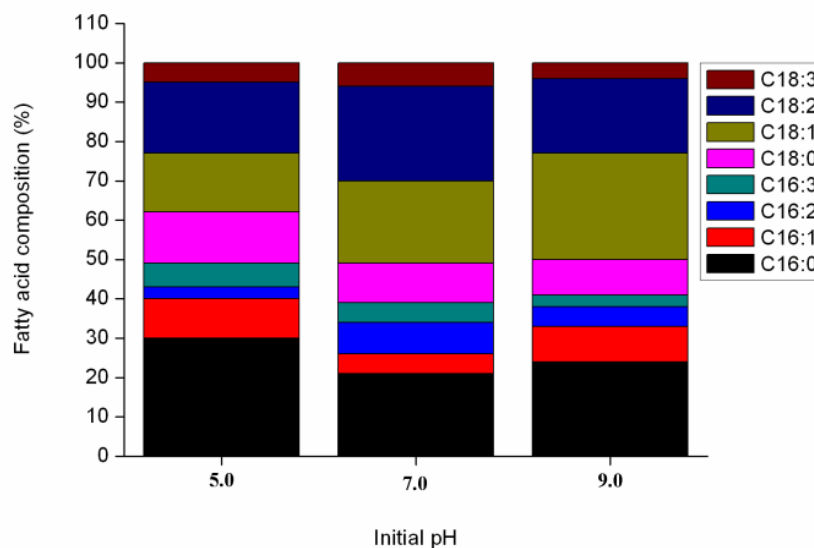
Figure 2. Fatty acid profile of *C. vulgaris* grown on glycerol with different initial pH values

References

Avinash, A., Subramaniam, D., Murugesan, A., 2014. Bio-diesel—A global scenario. Renew. Sust. Energ. Rev. 29, 517-527.

Ben-Amotz, A., Tornabene, T.G., Thomas, W.H., 1985. Chemical profiles of selected species of microalgae with emphasis on lipids. J. Phycol. 21, 72-81.

Cho, H.U., Kim, Y.M., Choi, Y.N., Xu, X., Shin, D.Y., Park, J.M., 2015. Effects of pH control and concentration on microbial oil production from *Chlorella vulgaris* cultivated in the effluent of a low-cost organic waste fermentation system producing volatile fatty acids. Bioresour. Technol. 184, 245-250.

Doan, T.T.Y., Obbard, J.P., 2012. Enhanced intracellular lipid in *Nannochloropsis* sp. via random mutagenesis and flow cytometric sorting. Algal Res. 1, 17-21.

Morales-Sánchez, D., Tinoco-Valencia, R., Kyndt, J., Martinez, A., 2013. Heterotrophic growth of *Neochloris oleoabundans* using glucose as a carbon source. Biotechnol. Biofuels 6, 100-111.

Safi, C., Charton, M., Pignolet, O., Silvestre, F., Vaca-Garcia, C., Pontalier, P., 2013. Influence of microalgae cell wall characteristics on protein extractability and determination of nitrogen-to-protein conversion factors. J. Appl. Phycol. 25, 523-529.

Serio, M. D., Ledda, M., Cozzolino, M., Minutillo, G., Tesser, R., Santacesaria, E., 2006. Transesterification of soybean oil to biodiesel by using heterogeneous basic catalysts. Ind. Eng. Chem. Res. 45, 3009-3014.

Yeesang, C., Cheirsilp, B., 2011. Effect of nitrogen, salt, and iron content in the growth medium and light intensity on lipid production by microalgae isolated from freshwater sources in Thailand. Bioresour. Technol. 102, 3034-3040.

Zheng, H. L., Yin, J. L., Gao, Z., Huang, H., Ji, X. J., Dou, C., 2011. Disruption of *Chlorella vulgaris* cells for the release of biodiesel-producing lipids: a comparison of grinding, ultrasonication, bead milling, enzymatic lysis, and microwaves. Appl. Biochem. Biotechnol. 164, 1215-1224.

Project Status as of June 30, 2016:
We continued to investigate the use of waste glycerol as an organic carbon source for algae growth. In the study, waste glycerol from the scum to biodiesel conversion process was added as the addition carbon source, and the results showed that nutrients removal can be improved and lipid production of C. vulgaris can be enhanced with the addition of waste glycerol (Ma et al., 2016). With 5g/L glycerol addition the total nitrogen removal rate can be increased from 65% to 93% and the total phosphorus removal rate can be increased from 58% to 90% (Table 1). Therefore in summer 2016, we are going to demonstrate the integrated system at the Metro Wastewater Treatment Plant at Saint Paul, MN.

Table 1
Cell growth, lipid production and nutrients removal of C. vulgaris with glycerol of different concentrations.

Parameters	Crude glycerol (g L^{-1})				Pretreated glycerol (g L^{-1})				Pure glycerol (g L^{-1})
	0	1	5	10	1	5	10	15	25
Biomass concentration (g L^{-1})	0.62 ± 0.01	0.93 ± 0.06	1.82 ± 0.11	0.35 ± 0.03	1.14 ± 0.08	1.95 ± 0.10	2.92 ± 0.00	0.64 ± 0.07	5.73 ± 0.09
Biomass productivity (mg L^{-1} d^{-1})	89 ± 2	133 ± 9	260 ± 11	50 ± 4	163 ± 8	279 ± 15	417 ± 13	91 ± 5	819 ± 11
Carbohydrate content (%)	15 ± 1	19 ± 1	25 ± 2	18 ± 2	20 ± 2	27 ± 1	30 ± 0	16 ± 0	32 ± 1
Protein content (%)	61 ± 2	50 ± 3	31 ± 1	55 ± 0	48 ± 1	28 ± 2	20 ± 3	57 ± 4	17 ± 0
Lipid content (%)	10 ± 0	18 ± 1	32 ± 3	18 ± 3	20 ± 1	34 ± 0	39 ± 2	17 ± 1	42 ± 1
Lipid productivity (mg L^{-1} d^{-1})	9 ± 0	24 ± 2	78 ± 4	9 ± 1	33 ± 4	95 ± 5	163 ± 7	15 ± 2	344 ± 9
TN removal efficiency (%)	65 ± 1	82 ± 2	92 ± 1	45 ± 2	88 ± 2	93 ± 2	95 ± 1	68 ± 3	98 ± 0
TP removal efficiency (%)	58 ± 0	75 ± 2	88 ± 2	32 ± 2	83 ± 2	90 ± 0	95 ± 3	51 ± 1	96 ± 0
NH$_4$-N removal efficiency (%)	74 ± 3	90 ± 0	100 ± 1	52 ± 2	94 ± 1	100 ± 0	100 ± 1	75 ± 3	100 ± 0
COD removal efficiency (%)	100 ± 0	97 ± 1	94 ± 0	42 ± 4	98 ± 2	98 ± 0	98 ± 0	55 ± 5	100 ± 0

The glycerol production from the scum which is about 54.56 gallon per day while the centrate flow rate is about 1 million gallon per day. By matching the amount of glycerol with the centrate waste, it is about 0.05 g of glycerol to one liter of centrate which is considered as very low density. Since 0.05 g/L of glycerol addition to centrate may not be able to cause any significant effect for improving algae productivity, we are considering using 0.5g/L glycerol addition for the test, therefore the experimental design is listed as following table.

	PBR 1	PBR 2	Data collection
June	centrate	Centrate with algae	Mass balance of water, nutrient, glycerol. pH, temperature, light, algae oil content will be collected.
July	Centrate with algae	Centrate with algae and 0.5 g/l glycerol addition	
August	With algae and 0.5 g/l glycerol addition	With algae and 0.5 g/l glycerol addition, but introduce the glycerol on second stage	

Based on previous experiment, four day HRT which is equal to harvest algae half of the volume per two day. Sample should be collected before and after harvesting. Nutrient data, oil data will be analyzed in the lab.

Currently we have finished the photo-bioreactor remodeling and start operating the system regularly. Previously, we had only one PBR outside in the greenhouse. Now we split the one PBR into two PBRs, so comparison experiments can be conducted. A central baffle was glued on the plastic tank, and a plastic filed was added in the tray to prevent leaking. Additional drainage holes, fittings, pipes, and pumps were added to the system, so both PBRs are nearly identical (see following figure).

Figure 1. Two PBRs system at the Metro Plant.

Project Status as of December 31, 2016:

The major accomplishments during this time period were:

- Constructed two photo bioreactor for comparison test for glycerol addition effect on algae biomass production and nutrient removal
- Completed the pilot scale experiments at the Metro Wastewater Treatment Plant at St. Paul, MN
- Conducted a lab comparison experiment using real centrate wastewater to study the glycerol effect

The specific objectives in this time period were:

Objective 1: Coordinate with the staff at the MWTP to prepare the photo-bioreactor for the pilot scale study.
Objective 2: Conduct the experiment at the MWTP, collect data and process data for a publication.
Objective 3: A parallel experiment was conducted at the lab using real wastewater.

Results of Objective 1: Coordinate with the staff at the MWTP to prepare the photo-bioreactor for the pilot scale study.

An innovative pilot-scale photobioreactors (PBRs) were developed and set up at the Metropolitan Wastewater Treatment Plant (Metro Plant) in Saint Paul, Minnesota. Previously, we had only one PBR outside in the greenhouse. Now we split the one PBR into two PBRs, so comparison experiments can be conducted. A central baffle was glued on the plastic tank, and a plastic filed was added in the tray to prevent leaking. Additional drainage holes, fittings, pipes, and pumps were added to the system, so both PBRs are identical (see Fig. 1). Each PBR had an overall dimension of 4 ft (W) × 4 ft (L) × 0.8ft (H) in which each tray can hold up to 8 in depth of water. The 4 inch depth of water, the volume of each tray is equivalent to 150 L. With the mixing tank and three trays, the total capacity of each PBR was 600L. In each tray, the water level was held up by using an overflow pipe. A 0.5-hp sump pump lifted the water from the mixing tank to the top layer of the PBR. The water then flowed down to the next layer through the overflow pipe by gravity and finally came back to the mixing tank. When algal density reached nearly the maximum density, about 200L of algae seeds was transferred to the multilayer PBRs at the Metro Plant. Centrate wastewater was subsequently introduced until the full scale of 600L was achieved. The suitable waste glycerol was introduced to the left PBR, and the right as the control. The harvesting rate was one half of the PBR water volume (600L) every other day (HRT of 4days). The centrate wastewater and the samples harvested from two systems were analyzed every other day. Temperature and pH were monitored every other day.

Fig.1 Two PBRs system at the Metro Wastewater Treatment Plant.

Results of Objective 2: Conduct the experiment at the MWTP, collect data and process data for a publication.

In the summer of 2016, *Chlorella vulgaris* was cultivated in a pilot-scale photobioreactor using centrate wastewater with one PBR adding 1 g L^{-1} waste glycerol. *Chlorella vulgaris* cultivation in another side with centrate no glycerol was the control. The pH value change in centrate and harvested algal broth was as shown in Fig.5. The pH value in harvested system of algae with centrate and glycerol (A+C+G) and algae with centrate only (A+C) were 7.2-8.5 and 7.1-8.6 respectively.
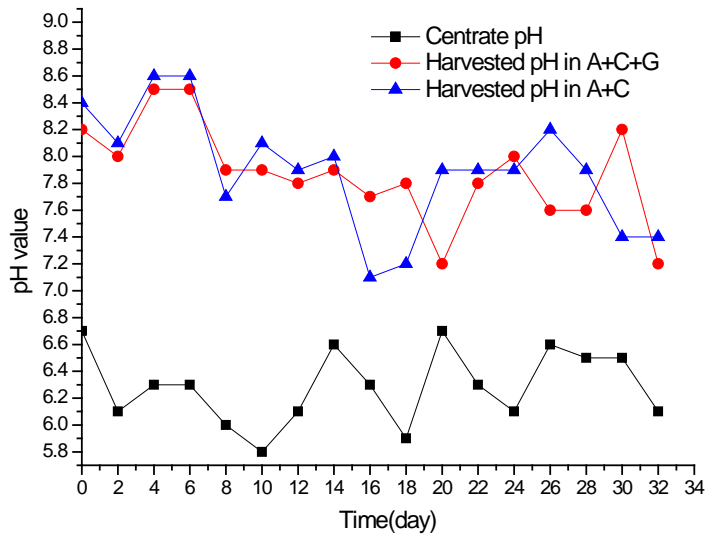
Fig.5 The pH value change in centrate and harvested algal broth.

Beside inoculated microalgae, other microflora presented naturally in the centrate. Therefore, activities of these microfloras must be considered in our data analysis. Biomass density and nutrient levels in harvested algal broth and the input centrate were as shown in Fig.6. After each two days cultivation, nutrients in centrate were removed to a lower level by the algae and bacterial. And the biomass productivity were both increased much higher than the centrate. Both PBR had the similar trend of change no matter with or without glycerol addition.
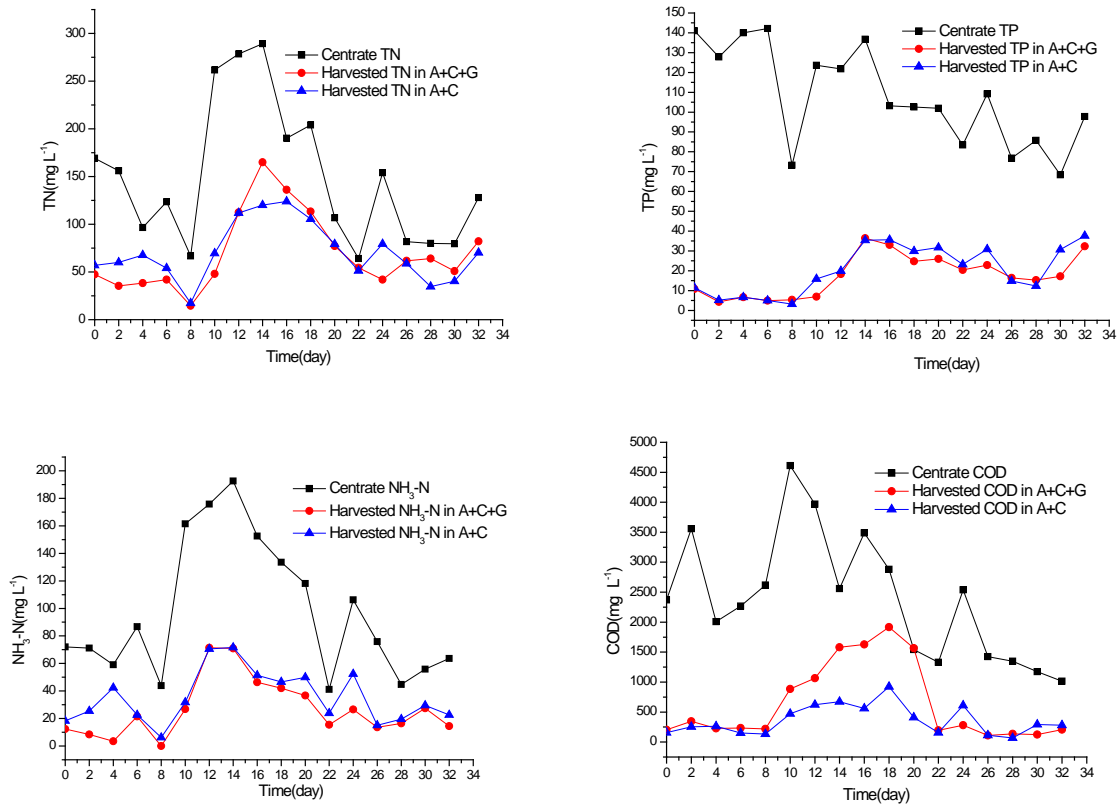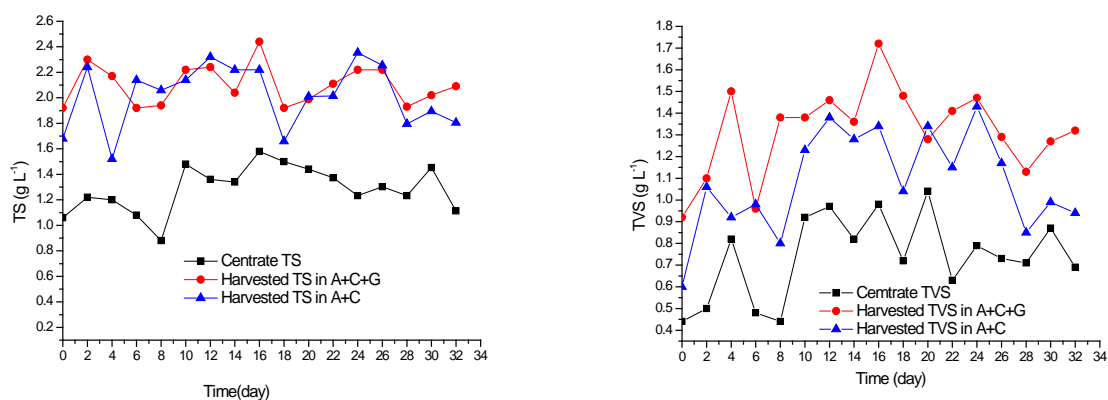
Fig.6 Biomass density and nutrient levels in harvested algal broth and input centrate. (a) Ammonia content. (b) COD content, (c) Total solid content, (d) Total volatile solid.

Table.3 Effect of glycerol on biomass productivity and nutrients removal.

	A+C+G	A+C
productivity, g/m^2 day		
TS	22.32±9.46	20.16±11.58
TVS	16.7±7.04	11.30±5.45
Nutrient removal,%		
NH$_3$-N	74.39±13.02	62.32±14.82
TN	49.55±22.66	49.18±16.59
TP	82.45±10.26	79.53±13.17
COD	83.59±6.57	84.29±9.27
Nutrient removal, g/m^2 day		
NH$_3$-N	2.37±1.10	2.09±1.20
TN	2.66±1.93	2.63±1.83
TP	3.03±0.96	2.94±1.01
COD	103.30±32.48	68.36±32.13
Lipid content,%	24.07±3	21.53±1
Protein content,%	52.03±3	43.68±1

A+C+G- algal cultivated in centrate with glycerol; A+C- algal cultivated in centrate

As shown in Table 3, during the 32-day cultivation with the crude glycerol, biomass productivity and the nutrient removal rates of NH$_3$-N, TP, and TN were all increased. With the glycerol addition, the initial COD in A+C+G increased, causing a slight reduction in COD removal rate compared with A+C; however the absolute removal quantity was greater than the control. The protein and lipid content increased from 43.69% to 52.03% and 21.53% to 24.07% respectively with the 1 g L^{-1} glycerol addition. The biomass productivity of TVS both lower than that of TS, suggesting that the increase in TS was not only due to the increase in TVS but also due to mineral precipitations from the centrate. Due to the high salinity in the centrate, high pH level could convert metal ions into insoluble salts. Interestingly, a thick layer of mineral deposits where later observed in the hoses and around the reactor fittings during the continuous experiment. These deposits needed to be periodically removed to prevent hose clogs and equipment failure.

The addition of crude glycerol increased the C/N ratio of the centrate wastewater in a way that favored microalgal growth. It may also enhance heterotrophic growth because of the fact C. vulgaris is capable of assimilating organic carbons such as glycerol.

Results of Objective 3: A parallel experiment was conducted at the lab using real wastewater.

To investigate the effect of the crude glycerol on *C. vulgaris* growth, the crude glycerol of six different concentrations (0.5, 1, 2, 5, 10.0 and 15.0 g L^{-1}) was applied in the centrate wasterwater. C.vulgaris cultured in the centrate wastewater without the addition of the crude glycerol (0 g L^{-1}) was used as control. The effect of the concentration of crude glycerol on the pH is shown in Fig.2. When the glycerol addition was less than 2.0 g L^{-1}, the pH value increased from 6.4 to 8.9. When 5.0 g L^{-1} glycerol was added, the pH value decreased in the first 24 hour, and then increased thereafter. While, the pH value still decreased to 4.4 with 10 and 15 g L^{-1} glycerol addition. Algae growth however, can raise the pH of centrate wastewater. From the color observation of microalgae liquid (As shown in Fig.3), we also could get the results that the algae did not grow when the glycerol concentration were 10 and 15 g L^{-1}. High concentration of the crude glycerol might result in growth inhibition.
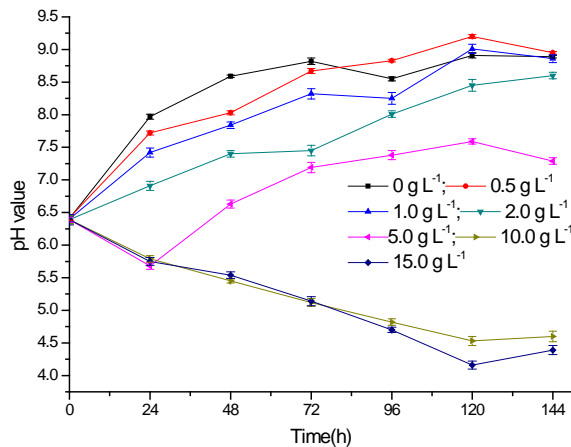
Fig.2 Effect of glycerol concentration on the pH value change.
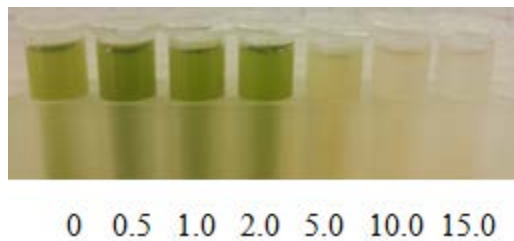
Fig.3 Algal broth after 144h cultivation with different glycerol concentration (g/L).

3.1.2 The nutrients concentration change with different glycerol concentration

During the 144-hour cultivation with the crude glycerol of different concentration, the nutrients concentration change were as shown in Fig.4a-d.
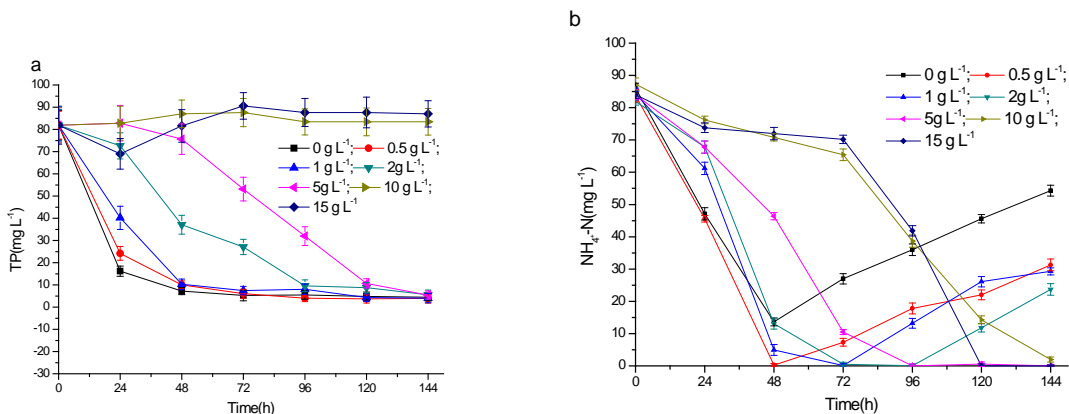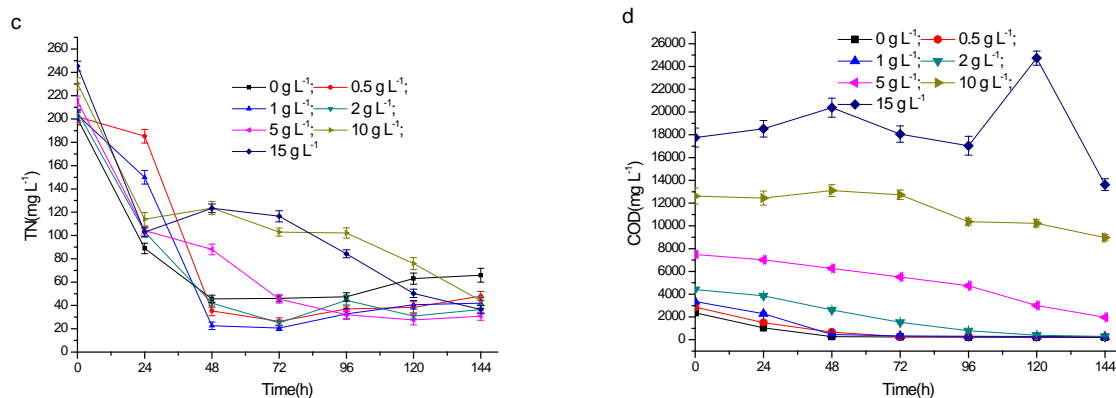
Fig.4 Nutrient removal during batch culture of *Chlorella vulgaris* in centrate wastewater with different glycerol concentration. (a) Total phosphorus removal; (b) NH$_4^+$-N removal; (c) total nitrogen removal; and (d) total COD removal. Each data indicates the mean ± SD (error) and were measured from three independent cultures.

With the additive glycerol concentration 0, 0.5 and 1.0 g L^{-1}, total phosphorus was drastically reduced from 81.9 to 10.0 mg/L after 48 hours cultivation and stayed at the similar level until the end of cultivation (Fig. 4a). Maximal removal efficiency respectively reached 94.5, 95.2 and 95.1%, and was thus much higher than those reported in other studies using municipal wastewater. When added glycerol concentration with 2.0 and 5.0 g L^{-1}, total phosphorus was slowly decreased to 5.5 g L^{-1} at 144 h. While, with the addition of glycerol 10 and 15 g L^{-1}, the total phosphorus did not be removed. One of reasons might be that algae could not grow with the high glycerol concentration. And phosphorus was difficult to precipitate under the acidity condition.

Almost 99% of NH$_4^+$-N was removed with the glycerol add, even the glycerol concentration was 10 and 15 g L^{-1}. Only the majority of the removal occurring during different days (Fig. 4b).The NH$_4^+$-N increased again after reduced to the lowest level with the long cultivation time, when the addition of crude glycerol was 0, 0.5,1 and 2g L^{-1}. That might due to NH$_4^+$-N uptake by new cells and nutrients decomposed and released from insoluble organic matter and dead cells. Removal of NH$_4$-N from concentrate wastewater by algae cultivation is caused by direct utilization of NH$_4$-N. While the loss of NH$_4$-N, could be attributed to both the absorption by algae and the wastewater-borne bacteria in the centrate.

Total nitrogen would be increased 3 mg L^{-1} when 1g L^{-1} glycerol was added to the centrate. The concentration of total nitrogen was all firstly decreased, and then slowly increased with the cultivation time prolong (Fig. 4c), the same change trend as the NH$_4^+$-N. TN was reduced firstly from 200 to 45.6, 26.34 and 20.58 mg/L respectively with 0, 0.5 and 1g L^{-1} glycerol addition after 72h cultivation. And most of the nitrogen in centrate was ammonium, which was readily available to algae[16]. The maximum 90% total nitrogen was removed with 1 g L^{-1} glycerol concentration. While, some organic compounds that could not be converted to ammonium nitrogen and assimilated by algae were still present.

The concentration of COD would be increased 1000 mg L^{-1} with per 1g L^{-1} glycerol addition. As shown in Fig 4d, the COD all decreased with the time. Like the total phosphorus, COD was drastically reduced with 0, 0.5 and 1g L^{-1} glycerol addition during 48 h cultivation.

The results showed the algae need longer time to adapt the condition when more than 2 g L^{-1} glycerol was added to the centrate. *Chlorella vulgaris* could not grow with 10 and 15 g L^{-1} glycerol addition. Furthermore, as the symbiotic relationship between algae and bacteria in the centrate, NH$_4^+$-N, TN and COD could be removed by both the algae and the wastewater-borne bacteria.

In order to compare the difference, the removal rate of nutrient and biomass productivity with different glycerol concentration after 48h cultivation was shown in Table.2. The optimal concentration of the crude glycerol was 1 g L^{-1} with the maximum biomass productivity of 460 mg L^{-1}d^{-1} TVS, the maximum lipid content of 27%, the maximum TN removal efficiency of 89%, the maximum protein content of 52%, and the COD removal efficiency of 86.3%, the TP removal efficiency of 88.5%, the NH$_4^+$-N removal efficiency of 94.31%. The removal rate of

nutrient and biomass productivity were obviously decreased when more than 5g L^{-1} glycerol was added. This result was different from other reports which claimed that the optimal concentrations of crude glycerol for a marine microalga, *S. limacinum* SR21, and a freshwater microalga, *Chlorella protothecoides* in artificial media were 25 and 30 g L^{-1}, respectively. The optimal concentration of crude glycerol varies for different microalgal species.

Table 2. The removal rate of nutrient and biomass productivity after 48h cultivation

	glycerol concentration, g/L						
	0	0.5	1	2	5	10	15
Removal rate,%							
COD	88.09	76.64	86.27	40.71	16.37	-3.83	-14.79
TN	77.24	82.48	88.89	79.65	59.11	46.35	49.73
TP	90.21	87.77	88.47	54.73	7.69	0	0.36
NH$_{4+}^-$N	84.18	96.72	94.14	84.0	44.79	18.9	14.29
Biomass productivity							
TS ,mg L^{-1}d^{-1}	415±7	480±5	570±9	430±4	80±5	35±3	15±5
TVS, mg L^{-1}d^{-1}	340±5	390±6	460±7	215±2	140±6	30±2	10±3
Lipid content,%	21.53±1	23.36±1	24.07±3	22.52±1	-	-	-
Protein content,%	43.68±0	50.67±1	52.033±2	49.49±1	-	-	-

Project Status as of June 30, 2017:

Amendment Request (06/30/2017)
See page 28-29.

Effect of centrate-borne bacteria on nutrient removal with glycerol addition
Centrate contains numerous species of bacteria. Bacterial infection is expected to influence the algal biomass accumulation, lipid content and nutrients removal. The centrate-borne bacteria influenced algal growth and nutrient removal efficiency in the wastewater-based algae cultivation system has been also studied by our team (Ma et al., 2014). However, the complex relationship between the algae and bacteria with glycerol addition deserves a further investigation.
Method:
The algal strain was inoculated at 1:10(v/v) ratio in 250 mL Erlenmeyer flasks containing 150mL centrate (sterilization and not) with and without 1 g L^{-1}crude glycerol. Another 250 mL Erlenmeyer flasks containing only 150mL centrate with and without 1 g L^{-1} crude glycerol as the controls (without algal inoculum). The flasks were all kept on a shaker at 150 rpm rotation speed. In all cases, the algae and bacteria were grown at 25 ± 2 ℃ with illumination at light intensity of 50μmol photons m^{-2}s^{-1}. All of the inoculations and cultivations were performed in triplicates. Samples were taken at the designated times for evaluation of growth rate, nutrients consumption, pH value, and bacterial counts.
Results:
As shown in Fig.1, it was clear that the growth profiles of the bacteria at different conditions followed the same trend. The initial number of bacteria was about 2.5×10^5 m L^{-1}. The bacteria grew rapidly at the beginning of cultivation and reached its maximum level at 24h. After that, the number of bacteria in the centrate decreased dramatically and maintained at a low level after 72h, about 1.8 ×10^5 m L^{-1}. The maximum bacterial numbers was 2.4×10^6 and 3.2 ×10^6 in centrate without and with 1 g L^{-1} glycerol, 1.95×10^6 and 2.4×10^6 in centrate with algal inoculums no and addition 1.0 g L^{-1} glycerol, respectively. These data indicate that (1) all cultures with glycerol showed higher bacterial counts, suggesting that glycerol facilitated bacterial growth as carbon source; and (2) microalgae cultivated in the centrate, decreased the number of bacteria at maximum,

suggesting that algae competed with bacteria for certain nutrients or produced certain substance that limited bacteria growth. These observations point to a complex relationship between algae and bacteria with or without glycerol. More detailed investigations are needed to further study.
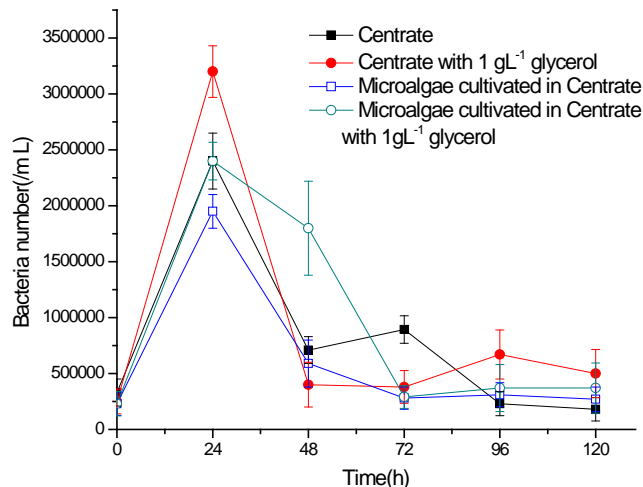

Fig.1 The number of bacteria in different initial inoculums.The experiments were performed in triplicate and the results in the figure show the average and standard deviation.

The biomass concentration and nutrients removal were as shown in Table.1. There were no significant difference for COD and TP removal rate under the six conditions, all could be achieved more than 88% and 80%, respectively. The results indicated that centrate-borne bacteria could remove certain COD and TP. Although glycerol supplied increase the initial COD, the similar removal rate of COD could also be attained. With microalgae inoculation to the centrate, the removal rate of TN and NH_4^+-N were both increased above 30% than the centrate only with or without glycerol. It indicated the microalgae mainly contributed to the N resource removal. It was also observed from the biomass data that the existence of glycerol increased the biomass and thus the nutrient removal could be improved. When the bacteria existing in the broth, lead to the algae biomass concentration TVSS decreased from 0.40 to 0.31 g $L^{-1}d^{-1}$ of no glycerol addition. Overall, the results showed the synergistic effect of centrate-borne bacteria and microalgae on nutrient removal performance.

Table.1 Cell growth and nutrients removal

All measurements were performed in triplicate, and results are expressed as mean value ± standard deviation (SD).

Parameters	Removal efficiency，%				Biomass Concentration，g $L^{-1}d^{-1}$	
	COD	TN	TP	NH_4^+-N	TSS	TVSS
C	91.6±1.2	35.2±1.3	80.3±1.2	32.8±1.8	0.04±0.01	0.01±0.01
C+G	92.1±2.0	47.1±2.3	82. 8±2.0	62.6±1.2	0.05±0.02	0.03±0.01
C+A	88.8±1.5	66. 6±2.1	92.1±1.8	71.1±1.3	0.46±0.01	0.31±0.02
C+A+G	92.4±1.2	82.2±1.4	93.4±1.6	88.9±1.0	0.61±0.03	0.44±0.03
A	90.1±1.4	62.1±1.7	90.3±1.5	68.9±1.4	0.50±0.11	0.40±0.06
A+G	91.2±1.3	70.3±1.4	91.4±1.9	78.6±1.5	0.57±0.09	0.48±0.05

C-centrate, C+G-centrate with 1 g L^{-1} glycerol, C+A-microalgae cultivated in centrate, C+A+G-microalgae cultivated in centrate with 1 g L^{-1} glycerol, A-microalgae cultivated in sterilized centrate, A+G- microalgae cultivated in sterilized centrate with 1 g L^{-1} glycerol

Final Report Summary:

In this activity, the team conducted experiments to study how algae grew on glycerol supplemented centrate wastewater and how nutrient removal was enhanced by such growth. They also successfully developed and tested a small pilot scale algae cultivation system on site of St. Paul Wastewater Treatment Plant. Specifically,

(1) The team screened and selected algae strains with high tolerance to glycerol
(2) The effect of waste crude glycerol on algae growth and nutrient removal in centrate wastewater was investigated to optimize glycerol addition. In optimal condition, glycerol was found to significantly improve algal biomass yield and nutrient removal (from around 60% to around 90%). It was also found the initial pH of the culture media is critical.
(3) Variations in glycerol concentration and pH did not affect the lipid profile significantly
(4) Completed experiments on effect of centrate-borne bacteria on nutrient removal with glycerol addition
(5) Constructed two photo bioreactor for comparison test for glycerol addition effect on algae biomass production and nutrient removal
(6) Completed the pilot scale experiments at the Metro Wastewater Treatment Plant at St. Paul, MN

The technoeconomic analysis and life cycle assessment showed benefits of using crude glycerol as additional carbon source, which enables algae to more fully use the nutrients in the wastewater. The studies also indicate that the centrate based algae cultivation is an important component in an integrated system to use all wastewater plant waste streams sustainably.

ACTIVITY 3: Develop and demonstrate sludge to bio-fuels system
Description:

The third waste steam of interest to the project is sludge, a solid biomass from primary and secondary settling processes. The sludge typically contains around 70% organic matter. Landfilling, land application and incineration are the common disposal processes for sludge. It is possible and beneficial to capture the energy contained in sludge biomass through thermochemical conversion because we not only capture the economic value, but also minimize pollutants associated with sludge. Thermochemical conversion (e.g., pyrolysis and gasification) of sludge to produce bio-oil, syngas and other products is an attractive solution to the sludge problems. However, the acceptance of this idea has been limited due to the low economic value of the products and the relative complexity of the processing equipment. Traditional gasification operated at temperature around 1,000C may not be able to destroy pollutants and toxic compounds such as dioxin. Therefore, we must improve the technology to enhance overall economic viability and environmental friendliness of the technology.

One of the major breakthroughs achieved in the endeavor to improve the microwave assisted pyrolysis process is the result of using properly designed microwave absorbents. Our research found that some microwave absorbents such as silicon carbide (SiC) are excellent in enabling rapid temperature rise, making fast pyrolysis and gasification feasible and efficient, and can achieve very efficient high temperature gasification, such as above 1,200C to avoid hazardous gas emission, therefore eliminating the need of expensive downstream gas treatment.

The goal of this activity is to use and compare fast microwave assisted pyrolysis and gasification processes for sludge conversion, and demonstrate a fast microwave assisted conversion system capable of providing processing conditions to meet fast pyrolysis and high temperature gasification requirements. While sludge will be the main feedstock, algal biomass harvested from Activity 4.2 can also be processed using this system.

The specific objectives of sludge to bio-fuels component are (1) to develop a cost effective sludge dewatering system, (2) to develop and optimize fast microwave assisted pyrolysis process, (3) to develop and optimize fast microwave gasification process, (4) to develop and optimize bio-fuel upgrading processes, and (5) develop a sludge to bio-fuels demonstration system based on the optimized process.

Specific tasks will be:

1. Develop a cost effective sludge dewatering system. As the sludge from primary and secondary settling processes still contains much water, this task is to develop a dewatering system to dry the sludge and meet the requirements of following processes.
   a. Compare different dewatering processes based on dewatering efficiency and the cost;
   b. Lab scale dewatering system development;
   c. Investigate the effect of feed rate on sludge dewatering efficiency.
2. Develop and optimize fast microwave assisted pyrolysis process. This task is intended to select appropriate microwave absorbents and develop a fast microwave assisted pyrolysis system to covert sludge or algal biomass to bio-oil, syngas, and bio-char.
   a. Develop a lab scale microwave assisted pyrolysis system and analyze the components of bio-oil, syngas, and bio-char;
   b. Investigate the effect of different microwave absorbents on heating rate and product distribution;
   c. Examine the effects of temperature, catalyst and catalyst to feed ratio on the yield of bio-fuels.
3. Develop and optimize fast microwave assisted gasification process. This task is to produce syngas from sludge or algal materials using a fast gasification system.
   a. Lab scale system development;
   b. Investigate the effects of temperature, catalyst, catalyst to feed ratio and steam addition on syngas yield and quality;
   c. Study the stability of catalyst during gasification process using X-ray Diffraction (XRD) technique.
4. Develop and optimize bio-fuel upgrading processes. This task is to upgrade the products of bio-oil, syngas, and bio-char for direct application.
   a. Develop a catalytic upgrading process to treat the bio-oil and make it mixable with gasoline for fuel;
   b. Introduce syngas into centrate system mentioned in 4.2 and CO_2 will be utilized and consumed by algae. Compare this novel system with traditional syngas conditioning processes based on CO_2 removal efficiency. Remove hydrocarbons from raw syngas by steam conditioning;
   c. Develop processes to separate bio-char from catalyst and further improve the quality of the bio-char to meet the requirements of soil amendment agent or activated carbon.
5. Development of a continuous sludge to bio-fuels demonstration system. Based on the data obtained from the above tasks, a pilot scale continuous fast microwave assisted conversion system with capacity estimated at about 25 kg/h will be designed and fabricated. The key features of the system is expected to include fast heating, high temperature, mechanisms for easy feeding of feedstock and discharge of solid residues, a motor-driven mixer/conveyer, air cooled condensers, integrated gas turbine power generator, multiple-point temperature detection, and automatic and accurate temperature control. The Pilot testing and demonstration facilities will be carried out in MCES St. Paul Wastewater Treatment Plant and/or FreightMasters/Minnesga Inc. Warehouse in Eagan. The space in FreightMasters/Minnesga Inc. warehouse is also appropriate for future potential commercial operations.
6. Environmental impacts analysis (Optional). Our analysis will follow the LCA standards created by International Organization for Standardization (ISO): ISO 14040 and ISO 14044. The LCA analysis will include all direct impacts and upstream impacts of chemicals and energy inputs. The process simulation models combined with existing modeling software will be applied in developing life cycle inventory. Software for modeling efforts, including Excel, GREET, GaBi, and Ecoinvent database, are currently owned by the research group. The LCA will include environmental impact of fossil fuel use (MJ) and GHG emissions (kg CO_2 eq.) and final results of fast microwave assisted sludge to bio-fuels technology are supposed to compare with conventional pyrolysis and gasification processes.

The Pilot testing and demonstration facilities will be carried out in MCES St. Paul Wastewater Treatment Plant and/or FreightMasters/Minnesga Inc. Warehouse in Eagan. The space in FreightMasters/Minnesga Inc. warehouse is also appropriate for future potential commercial operations.

Summary Budget Information for Activity 3:		**ENRTF Budget:**	**$433,880.00**
		Amount Spent:	**$433,880.00**
		Balance:	**$0.00**

Activity Completion Date:

Outcome	Completion Date	Budget
1. *Develop cost effective dewatering process; design microwave absorbent device; optimize catalytic bio-oil upgrading process.* Specific outcomes include: 1.1. A cost effective sludge dewatering processes will be developed. 1.2. Fast microwave assisted pyrolysis process will be developed and optimized for conversion of sludge and algal biomass to bio-oil, syngas, and bio-char. 1.3. Fast microwave assisted gasification process will be developed for conversion of sludge and algal biomass to syngas. 1.4. Refining processes will be developed and optimized for upgrading of bio-oil and syngas to high quality products. 1.5. Scale-up process parameters will be developed.	6/30/2015	$70,000
2. *Design and construct a complete facility for dewatering and conversion of sludge to bio-oil and syngas; the facility is expected to be fully or partially self-powered.* Specific outcome includes: Based on the data obtained from the above tasks, a pilot scale continuous fast microwave assisted conversion system with capacity estimated at 50 kg/h will be designed and fabricated. The key features of the system is expected to include fast heating, high temperature, mechanisms for easy feeding of feedstock and discharge of solid residues, a motor-driven mixer/conveyer, air cooled condensers, integrated gas turbine power generator, multiple-point temperature detection, and automatic and accurate temperature control.	12/31/2016	$320,000
3. *Test the facility and collect mass and energy balance data; conduct TEA and LCA.* Specific outcome includes: The environmental and economic impacts of the technologies developed will be quantified and reported.	03/31/2017	$23,880
4. *Demonstrate the systems to stakeholders.* Specific outcome includes: Demonstration of the technologies developed to the stakeholders will be carried out by the end of the project. All demonstration schedules will be discussed with LCCMR office and announced to the stakeholders through UMN and LCCMR's channels.	06/30/2017	$20,000

Project Status as of December 31, 2014:
   We conducted preliminary tests on pyrolysis of sewage sludge. The sewage sludge used as the raw material for this study was obtained from the Metropolitan Wastewater Treatment Plant, City of Saint Paul, Minnesota.

The sewage sludge was a mixture of primary and secondary sludge. The basic physico-chemical characteristics of the sewage sludge including proximate analysis, elemental analysis and mineral elements determination are shown in Table 1. According to the elemental analysis, the simplified chemical formula of the raw material that derives is $CH_{1.67}N_{0.10}O_{0.47}$. The higher heating value (HHV) observed for sewage sludge is similar to that of other conventional and non-conventional fuels such as paper, wood, black liquor or low rank coal. It is reported that the presence of inorganic matter can influence the thermal decomposition process. From Table 1 we can see there are considerable amounts of P, Ca and K in the sewage sludge, whereas other metals such as Co, Ni, Cu and Zn are in lower proportions. Prior to use, the sewage sludge samples were ground using a rotary cutting mill and then screened to limit the particle size smaller than 2 mm. These ground samples were then dried for more than 24 h at 80 ± 1 ºC.

Table 1. Characteristics of sewage sludge

Proximate analysis (wt.%)				Elemental analysis[a, b] (wt.%)				HHV[d] (MJ/kg)	NHV[e] (MJ/kg)
M	A[a]	V[a]	FC[a, c]	C	H	N	O[c]		
4.53	15.01	68.57	16.42	53.24	7.39	6.12	33.25	24.42	21.77

Mineral elements[a] (mg/L)										
Al	As	B	Be	Ca	Cd	Co	Cr	Cu	Fe	K
4188.5	6.2	22.4	0.36	20737.2	0.96	3.8	44.9	315.4	5108.5	6298.6
Li	P	Mg	Mn	Mo	Na	Ni	Pb	Ti	V	Zn
2.2	25641.3	5526.4	1153.0	5.0	1161.8	30.8	32.3	111.2	2.0	596.0

M: moisture content; A: ash content; V: volatile matter content; FC: fixed carbon.

[a] Dry basis;

[b] Ash free basis;

[c] Calculated by difference, FC (%) = 100 – A – V, O (%) = 100 – C – H – N;

[d] Higher heating value, calculated using the equation (Vallios et al., 2009) HHV (MJ/kg) = 34.1 C + 123.9 H – 9.85 O + 6.3 N + 19.1 S;

[e] Net heating value, calculated using the equation (Vallios et al., 2009) NHV (MJ/kg) = (HHV – 21.92 H) (1 – MCWB/100) – 0.02452 MCWB, where MCWB is the moisture content on a wet basis of biomass.

The tests of catalytic pyrolysis of sewage sludge were performed in a microwave oven (MAX, CEM Corporation), with the power of 750 W at a frequency of 2,450 MHz. The schematic diagram of experimental apparatus is shown in Fig. 1. The system is composed of: (1) biomass feeder; (2) inlet quartz connector; (3) microwave oven; (4) quartz reactor; (5) microwave absorbent bed; (6) thermocouple (K-type) to measure the temperature of cavity; (7) thermocouple (K-type) to measure the temperature of bed particles; (8) outlet quartz connectors; (9) liquid fraction collectors; (10) condensers; (11) connection for vacuum pump. For safety purpose, a microwave detector (MD-2000, Digital Readout) was used to monitor microwave leakage.
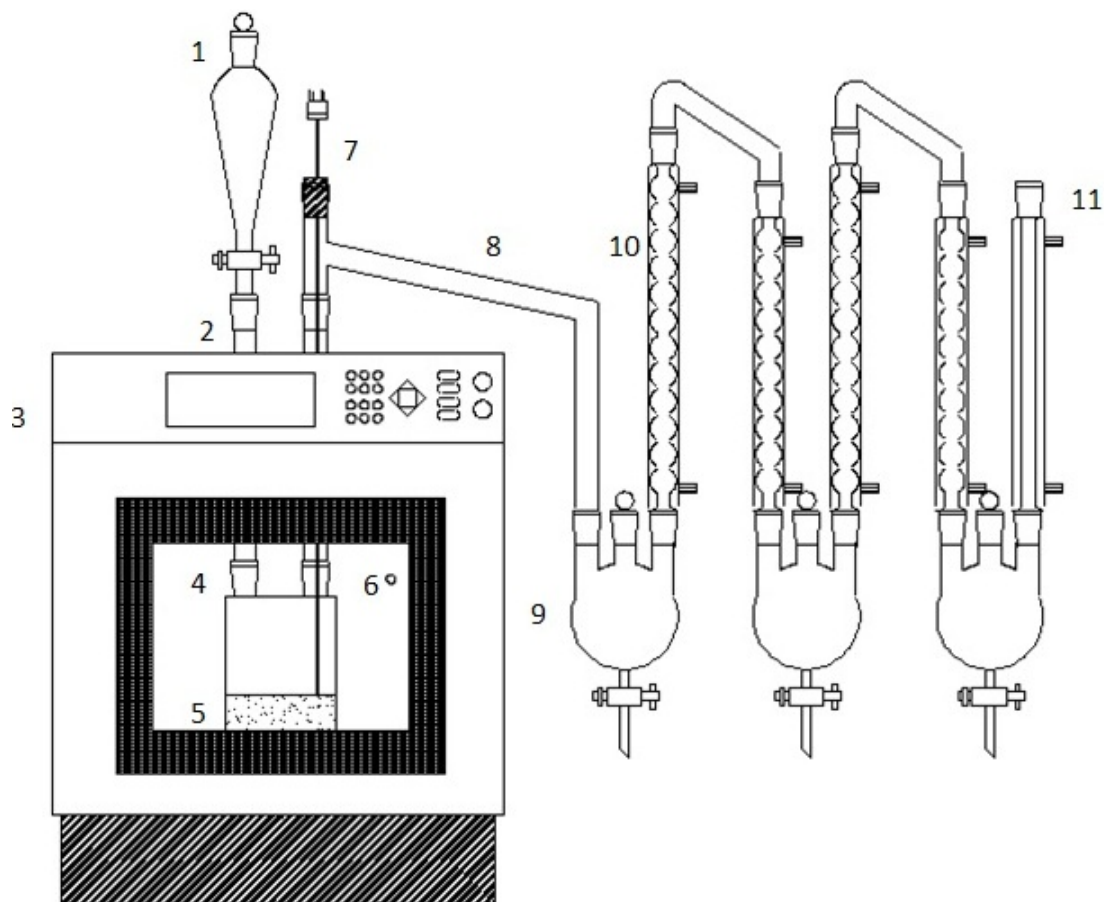
Fig. 1. Schematic diagram of microwave-assisted biomass catalytic gasification system.

The effect of pyrolysis temperature on the yield and composition of the bio-oil was investigated at temperatures ranging from 450 to 600 °C, with the catalyst to feed ratio being 2:1. As shown in Fig. 2, temperature has great influence on product distribution from sewage sludge pyrolysis. The oil yield increased with the pyrolysis temperature and reached a maximum yield of 20.9 wt% at the temperature of 550 °C. A decrease in oil yield was observed when the temperature increased above 550 °C. For the yield of bio-char, a continuous decrease was found when the temperature increased from 450 to 600 °C. The formation of bio-oil was mostly due to the devolatilization of organic matter in the sewage sludge, which was promoted by higher temperature as there was more energy available to break the strong organic bonds. This is the main reason for the initial increase in bio-oil yield with increasing temperature. The decrease in oil yield above the optimal temperature was probably because of the secondary reactions such as thermal cracking of the volatile compounds. Thermal cracking is an endothermic reaction and was reported to become significant at temperatures higher than approximately 500 or 550 °C. This can also explain the increase in gas yield when the temperature reached above 550 °C. In addition, the occurrence of carbonization of volatiles for charcoal is another possible reason for the decrease in oil yield. Since the ash content of sewage sludge is always high, the bio-oil yield is usually expressed on ash free basis, which is 24.4 wt% at 550 °C in this study. Similar results were obtained through sewage sludge pyrolysis in a fluidized bed reactor and in a fixed bed reactor under both CO_2 and N_2 atmospheres.

The chemical composition of bio-oil is also influenced by temperature. As shown in Fig. 3, the trends for the effect of temperature were different on the different chemical families present in the oil. The proportions of aliphatic hydrocarbons, aromatic hydrocarbons and polycylic aromatic hydrocarbons (PAHs) increased with temperature and reached the maximum at 550 °C. In contrary, the proportions of oxygen-containing aliphatic compounds, nitrogen-containing aliphatic compounds and nitrogen-containing aromatic compounds decreased with increasing temperature and reached the minimum at 550 °C. For oxygen-containing aromatic compounds,

the proportion decreased with temperature initially and reached the minimum at 500 °C, and then increased when the temperature continued to rise. From the perspective of bio-oil composition, the optimal temperature for microwave-assisted catalytic pyrolysis of sewage sludge was 550 °C since under this temperature, the highest proportions of aliphatic and aromatic hydrocarbons and the lowest proportions of oxygen- and nitrogen-containing compounds were obtained in the pyrolysis bio-oil, making it more suitable to be used as a fuel or feedstock for the production of valuable chemical products. The most dominant compounds in the bio-oil included naphthalene (9.5%), p-xylene (8.8%), 1,3,5-trimethyl-benzene (8.0%), 1-methyl-naphthalene (7.1%), 1-ethenyl-3-methylene-cyclopentene (6.6%) and indene (5.6%), which all belong to important chemical intermediates or precursors to other chemicals, or can be used as a solvent for chemical reactions.
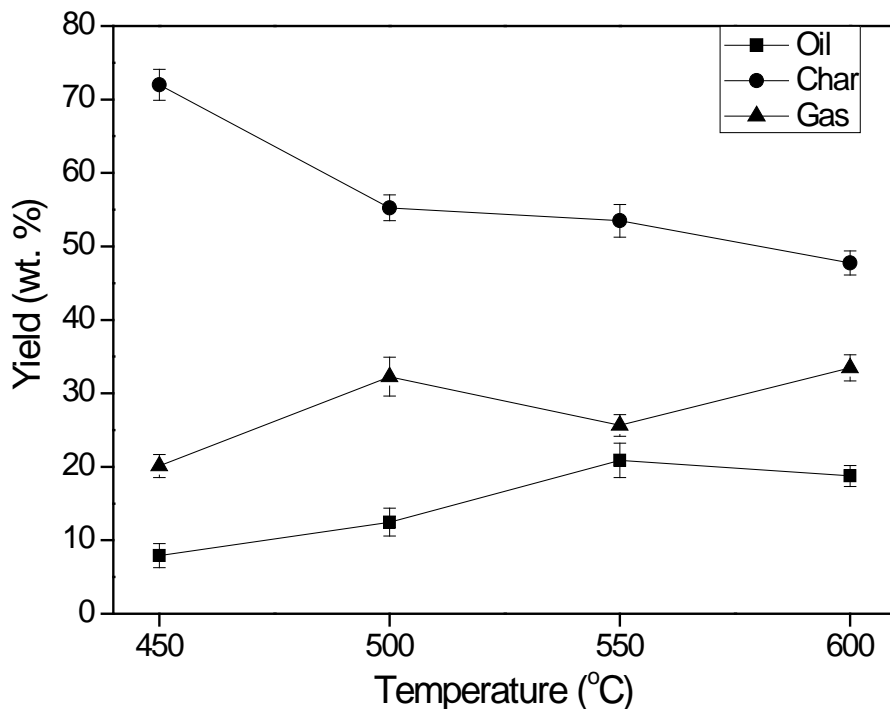
Fig. 2. Effect of temperature on product distribution from microwave-assisted pyrolysis of sewage sludge. Catalyst: HZSM-5, catalyst to feed ratio: 2:1.

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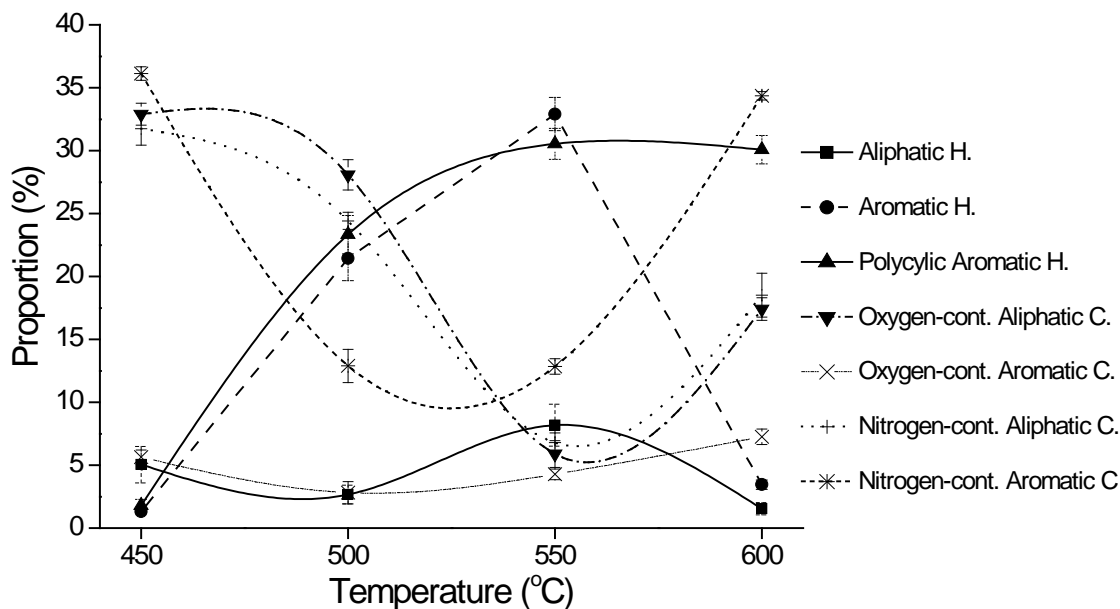
Fig. 3. Effect of temperature on bio-oil composition from microwave-assisted pyrolysis of sewage sludge. Catalyst: HZSM-5, catalyst to feed ratio: 2:1.

Project Status as of June 30, 2015:

The specific objectives in this time period were:
Objective 1: to investigate the effect of catalyst to feed ratio on bio-oil yield and composition from microwave-assisted pyrolysis of sewage sludge
Objective 2: to analyze the bio-char for its potential applications
Objective 3: to characterize the catalyst and determine its stability during the pyrolysis process

Results of Objective 1: to investigate the effect of catalyst to feed ratio on bio-oil yield and composition from microwave-assisted pyrolysis of sewage sludge

Previous research in catalytic pyrolysis of sewage sludge was very limited. In this study, we investigated the use of catalyst in sewage sludge pyrolysis and the effects of catalyst to feed ratio on bio-oil yield and composition. As shown in Fig. 1, the use of catalyst in the pyrolysis resulted in a slight decrease in oil yield. This is probably because the pyrolysis vapors had to pass through the catalyst particles, increasing the gas residence time. Consequently, the thermal cracking and carbonization reactions of volatiles occurred with higher probability, which would reduce the bio-oil yield. This explanation can be confirmed by the increase in the char yield when catalyst was used in the sewage sludge pyrolysis process. However, the oil yield increased and the gas yield decreased as the catalyst to feed ratio increased from 1:1 to 2:1. A possible reason was that the short-chain gas molecules from thermal cracking of volatiles recombined on the catalyst and underwent a series of aromatization, alkylation and isomerization reactions to produce aliphatic and aromatic compounds, increasing the bio-oil yield. From the perspective of product distribution, catalyst does not improve the bio-oil yield. The study of sewage sludge pyrolysis in a laboratory-scale horizontal batch reactor conducted by Kim and Parker (2008) demonstrated a decrease in liquid yield when the catalyst to feed ratio increased over 1.5. The authors attributed such a decrease to an increase in the catalytic cracking reactions, which resulted in increased conversion of volatiles to gas.
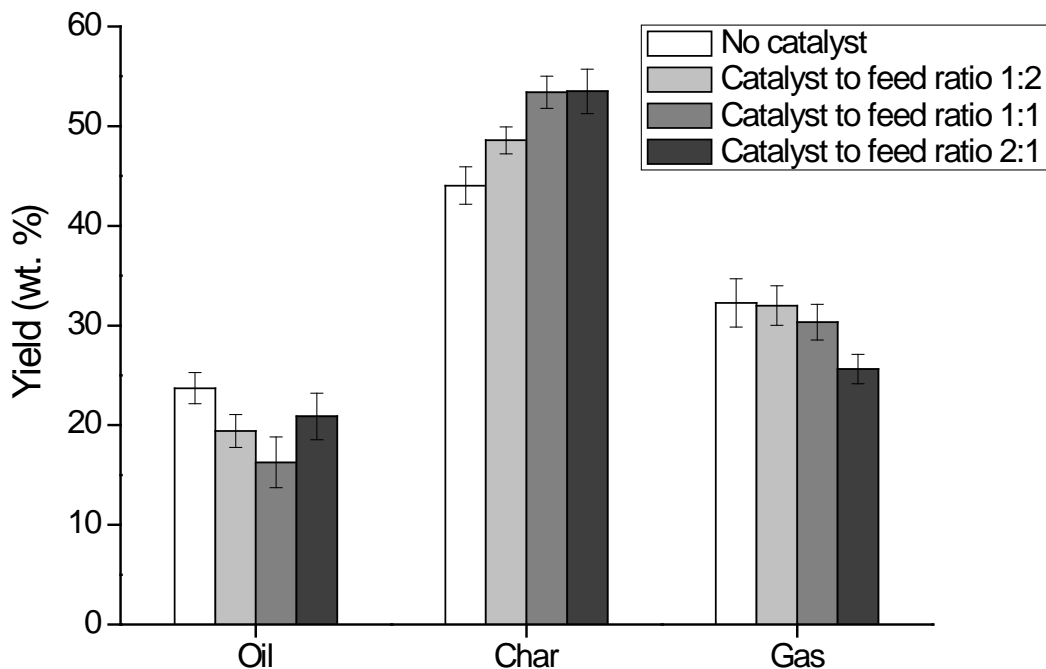
Fig. 1. Effect of catalyst to feed ratio on product distribution from microwave-assisted pyrolysis of sewage sludge. Catalyst: HZSM-5, pyrolysis temperature: 550 ºC.

Fig. 2 presents the effect of catalyst to feed ratio on bio-oil composition from microwave-assisted pyrolysis of sewage sludge at 550 ºC. It can be seen that although the proportion of aliphatic hydrocarbons in the bio-oil did not change too much with catalyst, significant increase in proportion of aromatic hydrocarbons was observed from catalytic pyrolysis compared with non-catalytic pyrolysis. This is consistent with previous studies on lignocellulosic biomass showing that the organics derived in the pyrolysis process could be deoxygenated and cracked to produce aromatics over the HZSM-5 catalyst (Mihalcik et al., 2011; Mullen and Boateng, 2010). The reaction mechanism and pathways can be illustrated using those postulated for the catalytic pyrolysis of carbohydrates and lignocellulosic biomass on HZSM-5 (Carlson et al., 2010; Williams and Horne, 1994). Carbohydrate derived organics, including alcohols, ketones, aldehydes and acids, were deoxygenated and cracked into C2-C6 olefins, which were transformed to benzene through a series of aromatization reactions. Benzene could be converted to other aromatics through alkylation and isomerization reactions. This was consistent with the decrease in the proportion of oxygen-containing aliphatic compounds in the bio-oil. In addition, the proportions of nitrogen-containing aliphatic and aromatic compounds were also decreased with catalyst, which was not mentioned in previous studies and needs further investigation. The proportions of oxygen- and nitrogen-containing compounds decreased significantly when the catalyst to feed ratio increased from 1:1 to 2:1. This was probably because the surface contact between the pyrolysis vapors and catalyst particles was not adequate when the catalyst to feed ratio was 1:1.
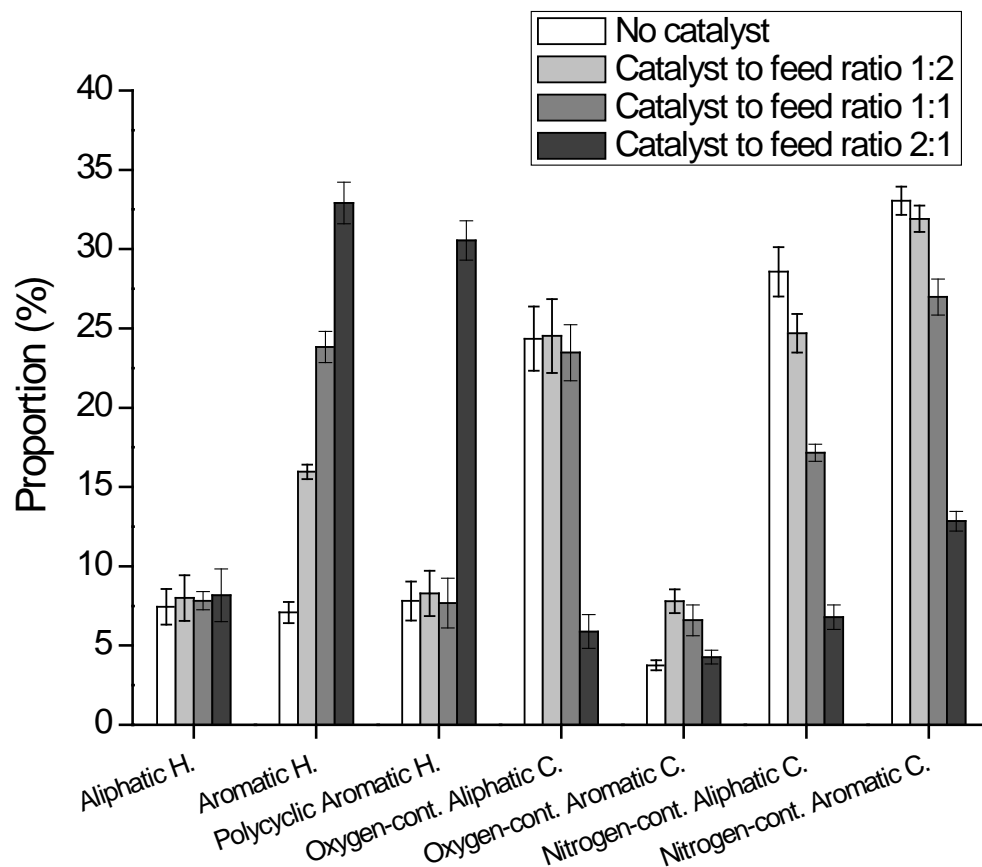
Fig. 2. Effect of catalyst to feed ratio on bio-oil composition from microwave-assisted pyrolysis of sewage sludge. Catalyst: HZSM-5, pyrolysis temperature: 550 ºC.

Results of Objective 2: to analyze the bio-char for its potential applications

The elemental analysis and ICP-OES multi-element determination were carried out for the bio-char from microwave-assisted pyrolysis of sewage sludge at 550 °C. The contents of C, H and N in the bio-char were 46.6%, 3.1% and 5.3%, respectively. The carbon content of bio-char from sewage sludge pyrolysis was lower than that from lignocellulosic biomass pyrolysis (Borges et al., 2014), which was probably due to the high ash content of sewage sludge.

Table 1 shows the contents of mineral elements in the bio-char. It can be seen that the contents of P, Ca, K and Mg which belong to essential elements to plants were very high, whereas the hazardous heavy metals including Cd, As, Ti and Pb were in very low proportions. Comparing the contents of mineral elements in the sewage sludge and bio-char, it can be concluded that the essential elements were concentrated in the bio-char after the pyrolysis process. Therefore, in addition to the use for adsorbent and fuel production, bio-char can be used as a soil amendment to achieve mineral recovery and increase soil fertility. Bio-char addition to soil can improve crop yield through reducing nutrient leaching and soil acidity, as well as enhancing the crop uptake of the essential nutrients. In addition, returning bio-char into soil reduces the need for fertilizers, thereby reducing the agricultural cost and environmental pollution caused by the fertilizer production and application.

Table 1 Contents of mineral elements in bio-char from microwave-assisted pyrolysis of sewage sludge at 550 °C

Mineral elements (mg/L)										
Al	As	B	Be	Ca	Cd	Co	Cr	Cu	Fe	K
9522.7	4.8	40.8	0.35	44401.5	2.6	8.2	114.4	623.5	7710.2	11364.0
Li	P	Mg	Mn	Mo	Na	Ni	Pb	Ti	V	Zn
3.7	53362.0	11842.0	2528.1	12.2	2542.0	79.0	72.0	49.7	5.2	1305.0

Results of Objective 3: to characterize the catalyst and determine its stability during the pyrolysis process

The HZSM-5 catalysts before and after pyrolysis reactions under different temperatures were characterized and compared using X-ray diffraction (XRD) technique to determine the effect of microwave-assisted pyrolysis process on the catalyst structure. As shown in Fig. 3, the primary diffraction peaks of the HZSM-5 catalyst occurred at the diffraction angles of 23.2°, 23.9° and 24.5°. The main crystalline phase existing in the catalyst was silicon-aluminum compound $Al_2O_3 \cdot 54SiO_2$ which was obtained through data analysis using the Jade 8.0. Comparing the XRD patterns of catalysts before and after pyrolysis reactions, little change of phase composition and crystalline structure on catalyst was observed for all the temperatures studied. It demonstrated that the HZSM-5 catalyst had good stability during the microwave-assisted pyrolysis process towards deactivation caused by coking or sintering.
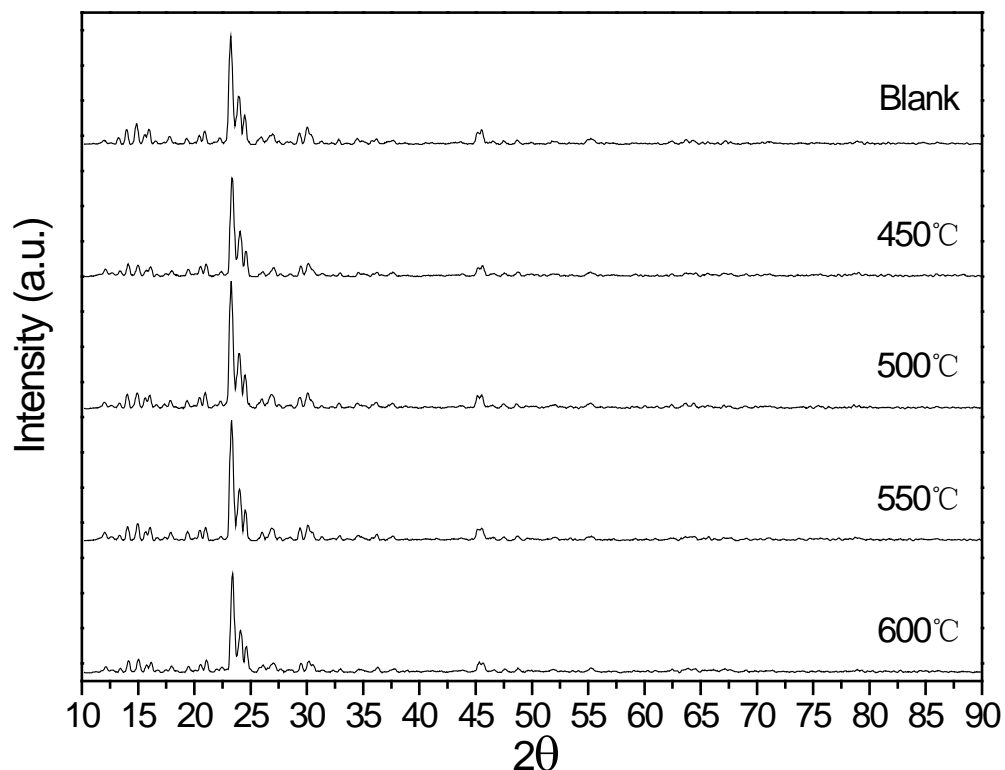
Fig. 3. XRD patterns for HZSM-5 catalysts before and after pyrolysis reactions under different temperatures.

The peak areas and crystalline sizes at the characteristic angels (23.2°, 23.9° and 24.5°) of HZSM-5 XRD patterns before and after pyrolysis reactions are shown and compared in Table 2. It can be seen that there is no obvious difference between peak areas of fresh catalyst and catalysts after reaction under different temperatures except at 500 °C. For the crystalline size estimated by the Scherrer equation, no significant increase was found for catalysts after reactions, even at 600 °C. It means that the HZSM-5 catalyst could stand high temperatures with negligible deactivation by coking and sintering, which was probably due to the short time on stream for the fast microwave-assisted pyrolysis process. Therefore, it can be concluded that HZSM-5 has good stability and is a suitable catalyst for the microwave-assisted catalytic pyrolysis of sewage sludge.

Table 2 Comparison of peak areas and crystallite sizes at characteristic diffraction angles of HZSM-5 XRD patterns before and after pyrolysis reactions under different temperatures

Catalyst	Area (a.u.)			Crystallite size (Å)		
	23.2°	23.9°	24.5°	23.2°	23.9°	24.5°
Fresh catalyst	6679	3563	1100	224	181	373
450 °C	6043	3365	958	224	185	374
500 °C	7183	4002	1678	244	184	279
550 °C	6825	3274	1240	247	216	351
600 °C	5651	3436	1232	239	164	293

References

[1] Borges, F.C., Du, Z., Xie, Q., Trierweiler, J.O., Cheng, Y., Wan, Y., Liu, Y., Zhu, R., Lin, X., Chen, P., Ruan, R., 2014. Fast microwave assisted pyrolysis of biomass using microwave absorbent. Bioresour. Technol. 156, 267–274.
[2] Carlson, T.R., Jae, J., Lin, Y.C., Tompsett, G.A., Huber, G.W., 2010. Catalytic fast pyrolysis of glucose with HZSM-5: the combined homogeneous and heterogeneous reactions. J. Catal. 270, 110–124.

[3] Kim, Y., Parker, W., 2008. A technical and economic evaluation of the pyrolysis of sewage sludge for the production of bio-oil. Bioresour. Technol. 99, 1409–1416.
[4] Mihalcik, D.J., Mullen, C.A., Boateng, A.A., 2011. Screening acidic zeolites for catalytic fast pyrolysis of biomass and its components. J. Anal. Appl. Pyrol. 92, 224–232.
[5] Mullen, C.A., Boateng, A.A., 2010. Catalytic pyrolysis–GC/MS of lignin from several sources. Fuel Process. Technol. 91, 1446–1458.
[6] Williams, P.T., Horne, P.A., 1994. Characterization of oils from the fluidized-bed pyrolysis of biomass with zeolite catalyst upgrading. Biomass Bioenergy 7, 223–236.

Project Status as of December 31, 2015:
The specific objectives in this time period were:
Objective 1: to investigate the effect of corn stover/scum ratio on co-pyrolysis product fractional yields and selectivity
Objective 2: to analyze the synergistic effect of CaO and HZSM-5 as the catalysts in microwave-assisted catalytic co-pyrolysis system
Objective 3: to design a continuous microwave based system

Results of Objective 1: to investigate the effect of corn stover/scum ratio on co-pyrolysis product fractional yields and selectivity

To improve the quality of the bio-oil, co-pyrolysis of biomass and materials containing higher hydrogen contents can be considered. In the present study, scum from municipal wastewater treatment plant was used as a hydrogen donor in the co-pyrolysis of corn stover and scum. In order to have a comprehensive understanding of the synergistic effect between corn stover and scum, a parameter called effective hydrogen index (H/Ceff) was used in this study to indicate the relative amount of hydrogen available in various feedstocks and assess the economic possibilities for biomass catalytic fast pyrolysis with zeolites. Synergistic effects obtained for the bio-oil and aromatic yields in the co-pyrolysis of cor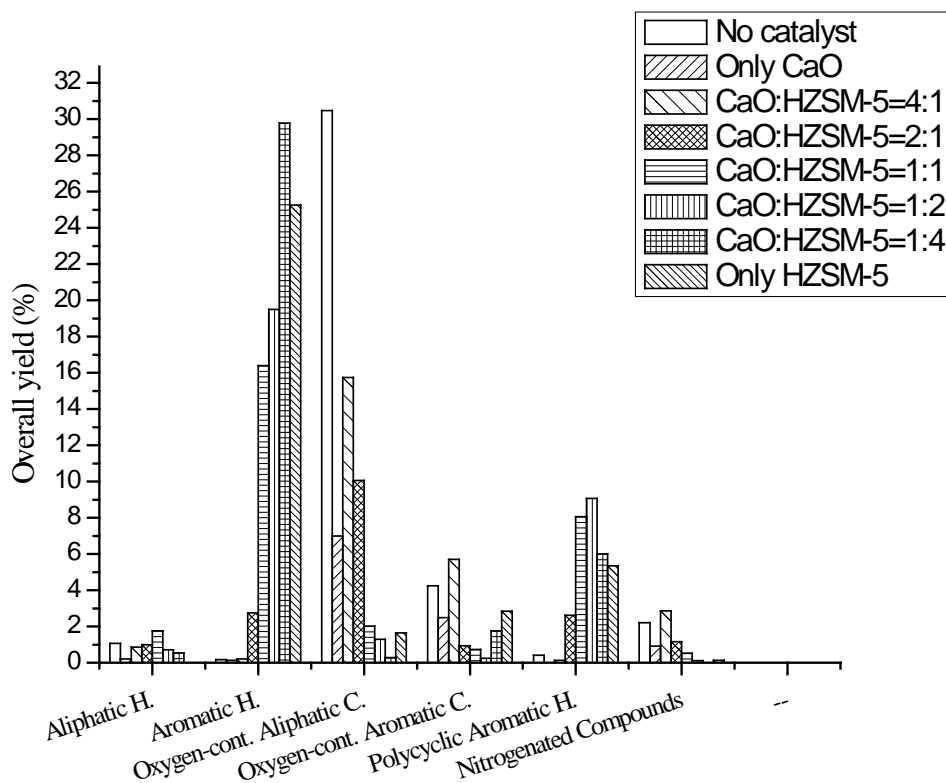n stover and scum under different corn stover to scum ratios are shown in Table 2. The H/C_{eff} value of scum was 1.65, whereas the corn stover had a H/C_{eff} of only 0.04. This result indicated that the corn stover was a hydrogen-deficient feedstock for catalytic fast pyrolysis (CFP) conversion, whereas scum was much more hydrogen-rich. A significant synergistic effect was observed when the corn stover to scum ratio was lower than 1:1, or the H/C_{eff} value exceeded 1. The extent of synergistic effect in the production of bio-oil increased with the addition of scum, and reached the maximum value of 27.3% when the corn stover to scum ratio was 1:2 and then decreased. Additionally, it is noticed that the synergistic effect dramatically enhanced the production of aromatics. When the corn stover to scum ratio was 1:1, the predicated value of aromatic yield was 11.5 wt.%, and the experimental value was 24.5 wt.% with an increase of 112.8%. The extent of synergistic effect in the production of aromatics reached the maximum value of 112.8% at the corn stover to scum ratio of 1:1. Considering both the bio-oil yield and the proportion of aromatics in the bio-oil, corn stover to scum ratio of 1:2 was selected as the optimal mixed ratio. In addition, synergistic effect became significant when the corn stove to scum ratio was lower than 1:1, whereas the H/C_{eff} ratio exceeded 1.

Table 2. Synergistic effects obtained for the bio-oil and aromatic yields in the co-pyrolysis of corn stover and scum under different corn stover to scum ratios.

Corn stover/scum ratio (w/w)	Bio-oil yield (wt%)		Aromatics yield (wt%)		Synergetic effect (%)[a]		H/C_{eff}[b]
	Y_p	Y_E	Y_p	Y_E	SE_b	SE_a	
Corn stover	26.4	26.4	0.0	0.0	–	–	0.04
4:1	25.9	23.5	4.6	0.0	–	–	0.47
2:1	25.5	17.1	7.7	0.2	–	–	0.73
1:1	25.1	29.2	11.5	24.5	16.3	112.8	1.00
1:2	24.7	31.4	15.3	29.3	27.3	91.5	1.25
1:4	24.4	27.5	18.4	25.4	12.7	38.2	1.42
Scum	23.9	23.9	23.0	23.0	–	–	1.65

[a] SE_b, SE_a : Synergetic effects of bio-oil and aromatic yields, respectively

[b] Calculated using the equation ((Chen et al., 1988)) $H/C_{eff} = (H-2O-3N-2S)/C$

Results of Objective 2: to analyze the synergistic effect of CaO and HZSM-5 as the catalysts in microwave-assisted catalytic co-pyrolysis system

The objective of this section was to study the synergistic effect of CaO and HZSM-5 as the catalysts in microwave-assisted catalytic co-pyrolysis system. To achieve this aim, the effect of CaO/HZSM-5 ratio on co-pyrolysis product fractional yields and selectivity at the temperature of 550 ℃ was investigated. As can be seen from Fig. 1, the use of catalyst in the pyrolysis resulted in a decrease in oil yield. This is because the pyrolysis vapors had to pass through the catalyst particles, which increasing the gas residence time. Besides, with an increasing amount of HZSM-5 catalyst, the bio-oil yield increased from 10.74 wt.% (CaO only) to the maximum value of 38.34 wt.% (CaO: HZSM-5=1:4), and then slightly decreased to 35.21 wt.% (HZSM-5 only). This indicates that CaO catalyst reduced the yield of the bio-oil. One possible reason is that with the addition of CaO catalyst, more time was needed for the volatiles to be released and hence the gas residence time was increased, which promoted the secondary thermal cracking and reduced the bio-oil yield.
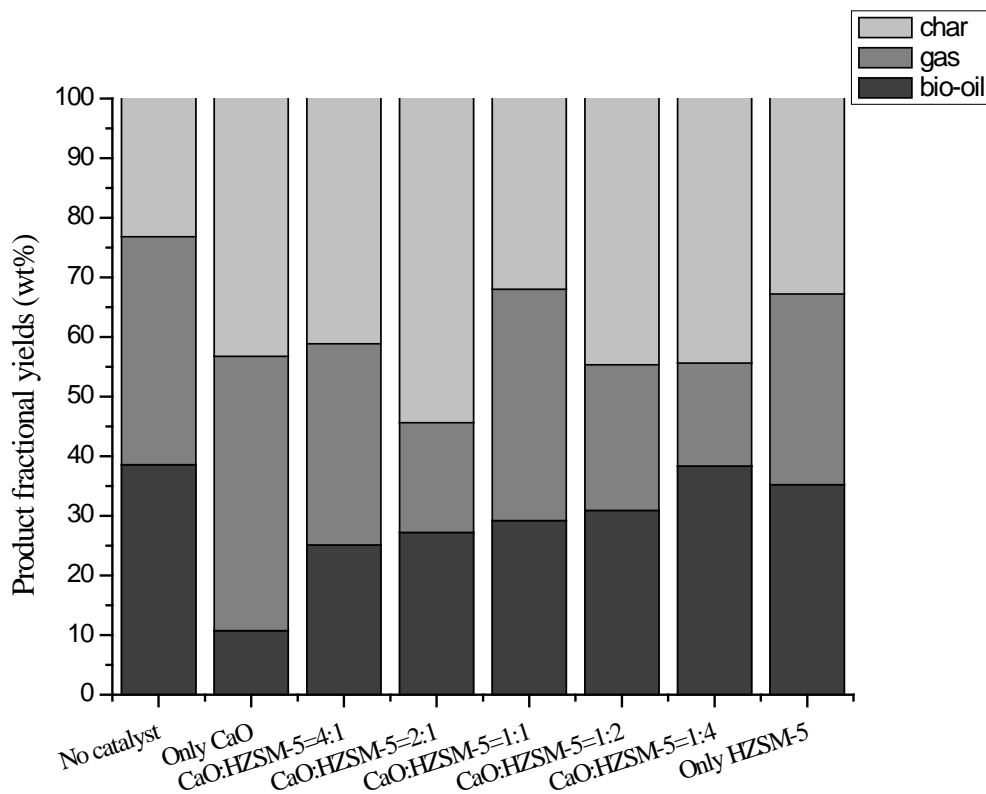
Fig. 1. The effect of CaO/HZSM-5 ratio on co-pyrolysis product fractional yields at the temperature of 550 ℃

Fig. 2 shows the overall yields of different chemical groups over different catalyst combinations. The proportion of aliphatic hydrocarbons did not change too much with catalyst. However, the proportion of aromatic hydrocarbons increased with the increasing addition of HZSM-5, and reached the maximum value of 35.77 wt.% when the ratio of CaO to HZSM-5 was 1:4, which was 17% higher than that with HZSM-5 alone. More aromatics were produced over the mixture of the two catalysts compared to either catalyst. The results indicated a synergistic effect between these two catalysts. With the addition of CaO catalyst, the yield of oxygen-containing products decreased to the minimum of 1.54 wt.% when the ratio of CaO to HZSM-5 was 1:2.

Fig. 2. The overall yields of different chemical groups over different catalyst combinations

Fig. 3 shows the proportions of different chemical groups in the bio-oil during catalytic co-pyrolysis of corn stover and scum with different CaO to HZSM-5 ratios. The aromatic proportion in the bio-oil significantly increased as the CaO to HZSM-5 ratio was lower than 2:1, and reached the maximum value of 93.30 wt.% when the CaO to HZSM-5 ratio was 1:4. In addition, the proportion of oxygen-containing compounds decreased with the addition of CaO catalyst and reached the minimum value of 4.98 wt.% when the CaO to HZSM-5 ratio was 1:2. Furthermore, there was almost no nitrogenated compounds in the bio-oil when the ratio of CaO to HZSM-5 was lower than 1:2. From the above results, the CaO catalyst also has a significant effect on deoxygenation of bio-oil (Li et al., 2012; Lin et al., 2010). The production of light phenols was improved at the expense of large oxygen-containing compounds on CaO catalyst, which was different from other catalysts reported to be selective to phenolic compounds (Lu et al., 2010a). On the other hand, HZSM-5 catalyst has been widely used in the catalytic fast pyrolysis of biomass (Dickerson & Soria, 2013) due to its attractive performance in removing the oxygenated organic compounds and favoring hydrocarbon production in bio-oil through the catalytic cracking reaction. Reduction of oxygen-containing compounds was positive to the quality of the bio-oil since oxygen-containing compounds in the bio-oil would cause the thermal instability and increase the viscosity and corrosiveness. The possible reaction mechanism can be surmised as follows: when pyrolysis vapor passed through the mesoporous CaO catalyst, the heavy compounds such as large phenols and anhydrosugars were cracked into light compounds, followed by conversion of the light compounds into hydrocarbons over the microporous HZSM-5 catalyst (Dickerson & Soria, 2013; Lu et al., 2010a).
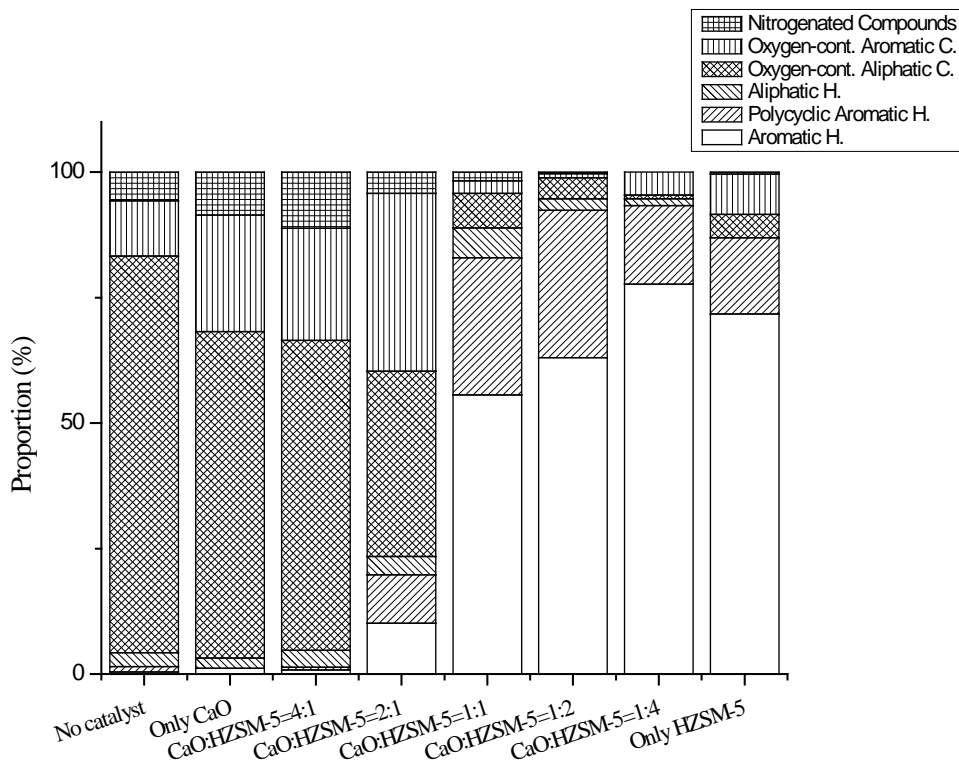
Fig. 3. The proportions of different chemical groups in the bio-oil during catalytic co-pyrolysis of corn stover and scum with different CaO to HZSM-5 ratios.

Results of Objective 3: to design a continuous microwave based system

The capacity of the whole continuous microwave based system is 15 kg/hr. It consists four parts, which are feeding system, reactor, cooling system and collecting system. The voltage, frequency and output of the microwave generator are 240 VAC/3-Phase, 2450 MHZ and 15 kW, respectively. The continuous microwave based system is shown in Figure 4. It works as follows: the 12 sticks are used to mix the microwave susceptors with the biomass when the main rod move up and down due to the rotation of the dark oval cam at the top. The auger system is for metering the airlock biomass feeding system. When the different kinds of biomass enter into the reactor from the hopper through the auger system, the reaction complete less then two seconds, the pyrolysis vapor come out, after going through the cooling system, the valuable bio-oil is collected. Besides, the bio-char is separated and collected at the bottom. Thermocouples (K-type) are inserted through the gas exit tube into the reactor. The thermocouples are connected to a 4-channel thermocouple probe thermometer (Sper Scientific 800023) for temperature read-out. A very mild vacuum is applied to draw the vapors and gas out of the reactor to a series of refrigerated water-cooled condensers. The vacuum may be varied to adjust the gas/vapor residence time. For safety purpose, a microwave leakage detector (MD-2000, Digital Readout) will be used to monitor if there is any leakage.

Fig. 4. The schematic diagram of continuous microwave based system

Reference
[1] Chen, N.Y., Walsh, D.E., Koenig, L.R. 1988. Fluidized-Bed Upgrading of Wood Pyrolysis Liquids and Related-Compounds. *Acs Symposium Series*, **376**, 277-289.
[2] Li, R., Zhong, Z.P., Jin, B.S., Zheng, A.J. 2012. Application of mineral bed materials during fast pyrolysis of rice husk to improve water-soluble organics production. *Bioresource Technology*, **119**, 324-330.
[3] Lin, Y.Y., Zhang, C., Zhang, M.C., Zhang, J.A. 2010. Deoxygenation of Bio-oil during Pyrolysis of Biomass in the Presence of CaO in a Fluidized-Bed Reactor. *Energy & Fuels*, **24**, 5686-5695.
[4] Lu, Q., Zhang, Z.-F., Dong, C.-Q., Zhu, X.-F. 2010a. Catalytic Upgrading of Biomass Fast Pyrolysis Vapors with Nano Metal Oxides: An Analytical Py-GC/MS Study. *Energies*, **3**(11), 1805-1820.
[5] Dickerson, T., Soria, J. 2013. Catalytic Fast Pyrolysis: A Review. *Energies*, **6**(1), 514-538.

Project Status as of June 30, 2016:
A novel technology of two-step fast microwave-assisted pyrolysis (fMAP) of corn stover for bio-oil production was investigated in the presence of microwave absorbent (SiC) and HZSM-5 catalyst. So far, most researches in literature focused on the one-step catalytic fast pyrolysis where the catalysts are mixed with the feedstock in the pyrolysis reactor. However, they had lots of disadvantages, such as fixed catalytic upgrading and cracking temperature, and high coke formation on the catalyst for the rapid catalyst deactivation. For our two-step fMAP, where the catalyst is separately placed, the catalytic upgrading and cracking operation can be flexibly controlled under different situation independent of pyrolysis, thus enable the optimum catalyst performances targeting at the desired products under optimized reaction temperature and residence time. This also allows the unreacted char and mineral components to be removed prior to exposing pyrolysis vapors to the upgrading catalyst. Which will extend the life of the catalyst and reduce the cost.

The specific objectives in this time period were:
Objective 1: to investigate the effect of pyrolysis temperature on two-step fMAP
Objective 2: to investigate the effect of catalyst temperature on two-step fMAP

Result of objective 1: to investigate the effect of pyrolysis temperature on two-step fMAP

To investigate the effect of pyrolysis temperature on two-step fMAP, catalyst temperature was fixed at 425 ℃ with constant ratio of catalyst to feed ratio being 1:5, and the fMAP temperatures were 450 ℃, 500 ℃, 550 ℃, 600 ℃ and 650 ℃, respectively. As shown in Fig. 1a, pyrolysis temperature has significant influence on product distribution. The bio-oil yield increased with the pyrolysis temperature and reached a maximum yield of 33.38 wt.% at 550 ℃. A decrease in bio-oil yield was observed after 550 ℃ to 23.97 wt.% at 650 ℃. The devolatilization reaction would be promoted by higher temperature, then the strong organic bonds were broken, which is the main reason for the increase in the bio-oil yield from 450 ℃ to 550 ℃. However, the decrease in bio-oil yield when the temperature was higher than 550 ℃ was due to the secondary thermal cracking reaction of the volatile compounds. This can also explain the increase in gas yield when the pyrolysis temperature increased above 550 ℃. Besides, the solid residue decreased with increasing pyrolysis temperature from 29.67%(450 ℃) to 19.6 wt.% (650 ℃). As shown in Fig. 1b, the amount of coke deposited on the catalyst bed was not significant influenced by the pyrolysis temperature. The coke yields were around 1.7 wt. % at the pyrolysis temperature over the range between 450℃ and 650℃.

In addition to the bio-oil yield, the composition of the bio-oil was also affected by pyrolysis temperature. The major components of bio-oil could be classified into several groups as aliphatic hydrocarbons, aromatic hydrocarbons, polycyclic aromatic compounds (PAHs), oxygen-cont. aliphatic compounds, oxygen-cont. aromatic compounds, and others (nitrogen-cont. compounds and unidentified compounds). It can be seen in Fig. 1c that increasing pyrolysis temperature from 450℃ to 650℃ increases aromatic hydrocarbons yield up to 26.20% at 550℃. When temperature higher than 550℃, there is little change in aromatic hydrocarbons yield. It is noted that there were almost no aliphatic hydrocarbons in this temperature range. Besides, the proportion of oxygen-cont. aromatic compounds fluctuated slightly, while the maximum yield was reached at 500℃ (50.86%). The polymerization reaction could lead to formation of aromatic compounds, many of which contained oxygen. This is the reason for pretty high yield of oxygenates. In addition, the proportion of PAHs slightly decreased from 31.87% (500℃) to 29.50% (650℃), including naphthalene. methyl-naphthalene, ethyl-naphthalene and anthracene. It seems changing pyrolysis temperature has little effect on the selectivity for C_{10+} aromatics. From the above results, higher selectivity to aromatics was observed at the temperature from 500℃ to 650 ℃. According to the yield and composition of bio-oil, the optimal temperature for two-step fMAP of corn stover with HZSM-5 as the catalyst was 550℃ at which the highest yield (33.38 wt.%) of bio-oil and maximum proportion of aromatic compounds (26.20%) were achieved. The potential industrial chemical compounds obtained from bio-oil at 550℃ including toluene (0.70%), xylene (3.73%), indene (5.14%), phenol (4.65%) and

naphthalene (15.62%), which are all important chemical intermediates to other useful chemicals. The optimal temperature of 550°C was used in the following experiments.
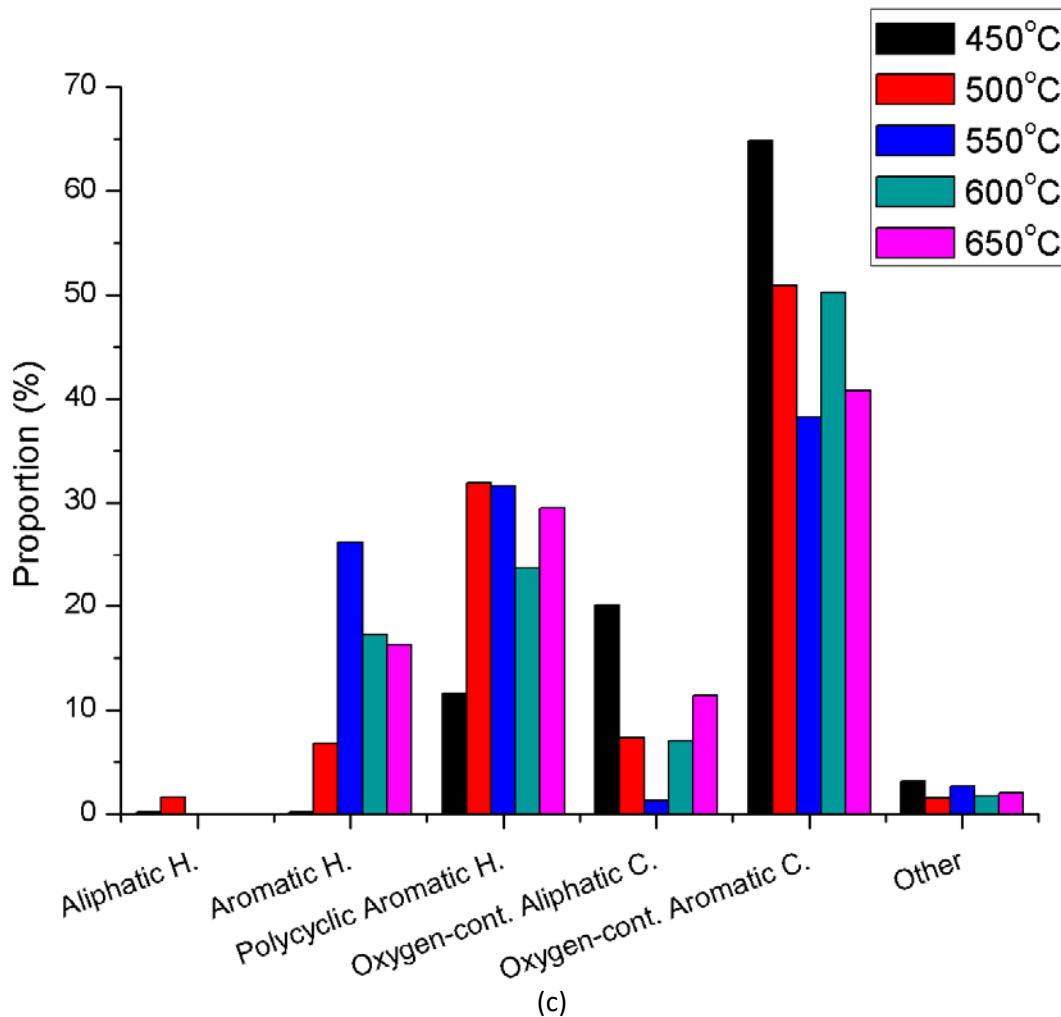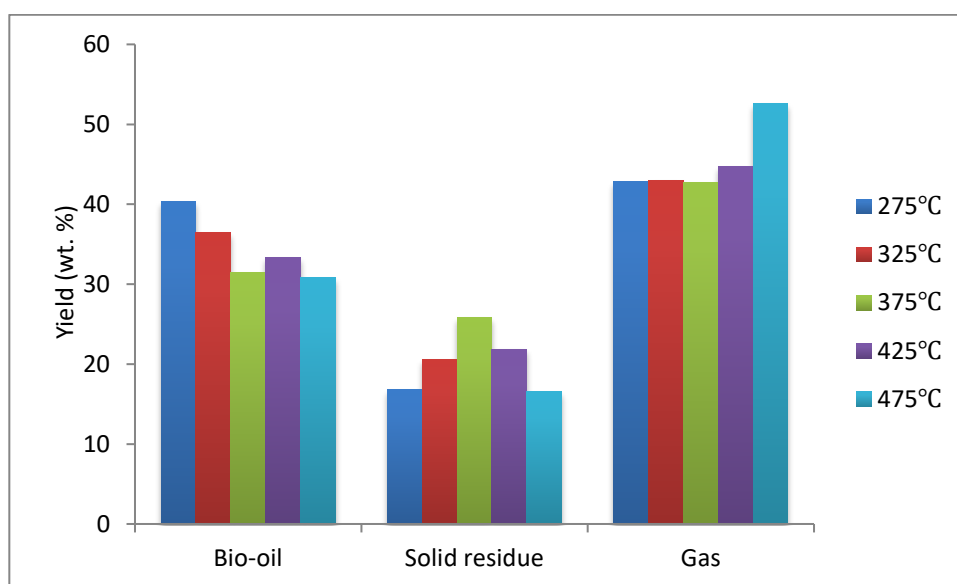

(a)

(b)

(c)
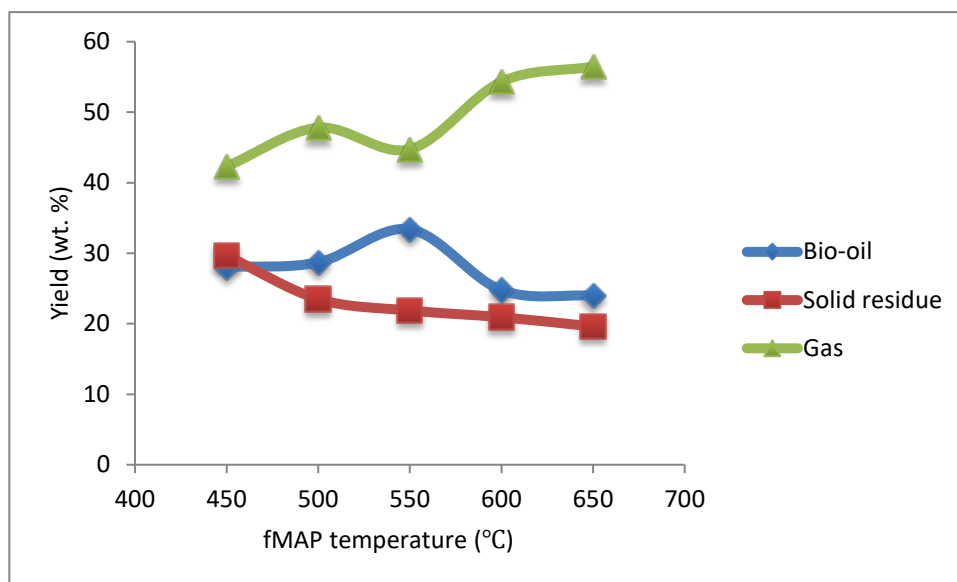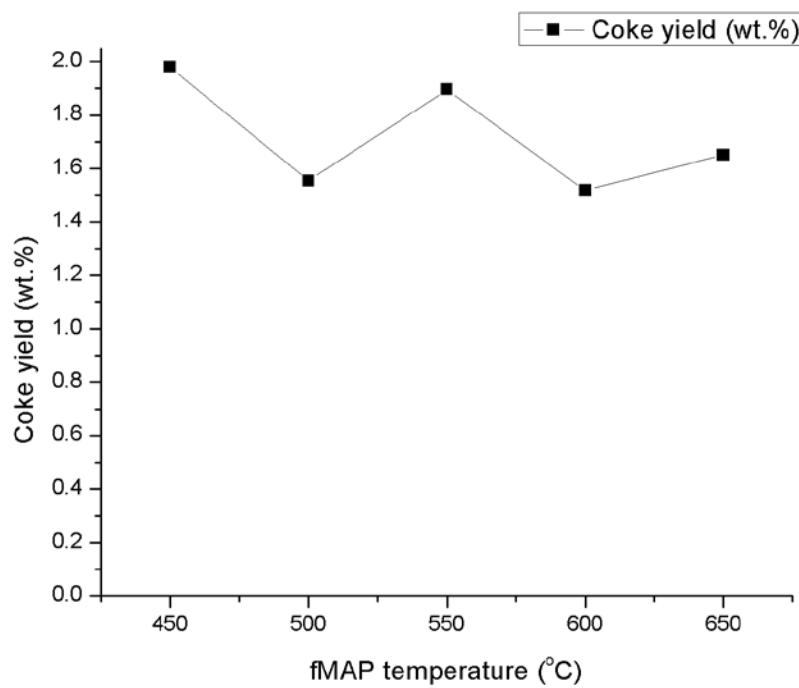
Fig. 1- Effect of pyrolysis temperature on two-step fMAP: (a) Product distribution. (b) Coking on catalyst (c) Bio-oil composition.

Results of objective 2: to investigate the effect of catalyst temperature on two-step fMAP

To investigate the effect of catalyst temperature on two-step fMAP, pyrolysis temperature was fixed at 550°C with constant ratio of catalyst to feed ratio being 1:5. Catalyst bed temperature of 275°C, 325°C, 375°C, 425°C and 475°C were tested. Fig. 2 shows the effect of catalyst temperature on two-step fMAP. As can be seen from Fig. 2a, the bio-oil yield decreased in the first stage from 40.38 wt. % (275°C) to 31.41 wt. % (375 °C), and then slightly increased to 33.38 wt. % (425 °C) in the second stage, and decreased to 30.83 wt. % (475°C) finally, while gas yield increased dramatically from 42.8 wt. % to 52.59 wt. % over the ranges of catalyst temperature studied. One possible reason is that the catalyst did not reach its active temperature in the first stage. In other words that it looks like the pyrolysis without the catalyst, especially at 275°C. Liu et al. (2016) mentioned that use of catalyst in the pyrolysis results in a decrease in bio-oil yield. This is because the pyrolysis vapors had to pass through the catalyst particles, which increases the gas residence time and promoted the secondary thermal cracking and reduced the bio-oil yield. Wang et al. (2014b) studied the influence of catalyst bed temperature on catalytic pyrolysis of Douglas fir pellets. They concluded that increasing catalyst packed-bed temperatures results in a decrease of the bio-oil yield. The similar results were indicated by Putun et al. (2009). Therefore, catalyst temperature at 425°C was considered as the optimum temperature for the catalyst. In addition, Fig. 2b shows the effect of catalyst temperature on the coke deposits on the catalyst. The coke formation was reduced from 3.03 wt. % to 1.90 wt. % as the catalyst temperature increased from 275°C to 475°C. Wang et al. (2014a) also showed that coke formation was reduced as the catalyst temperature was increased from 400°C to 700°C.
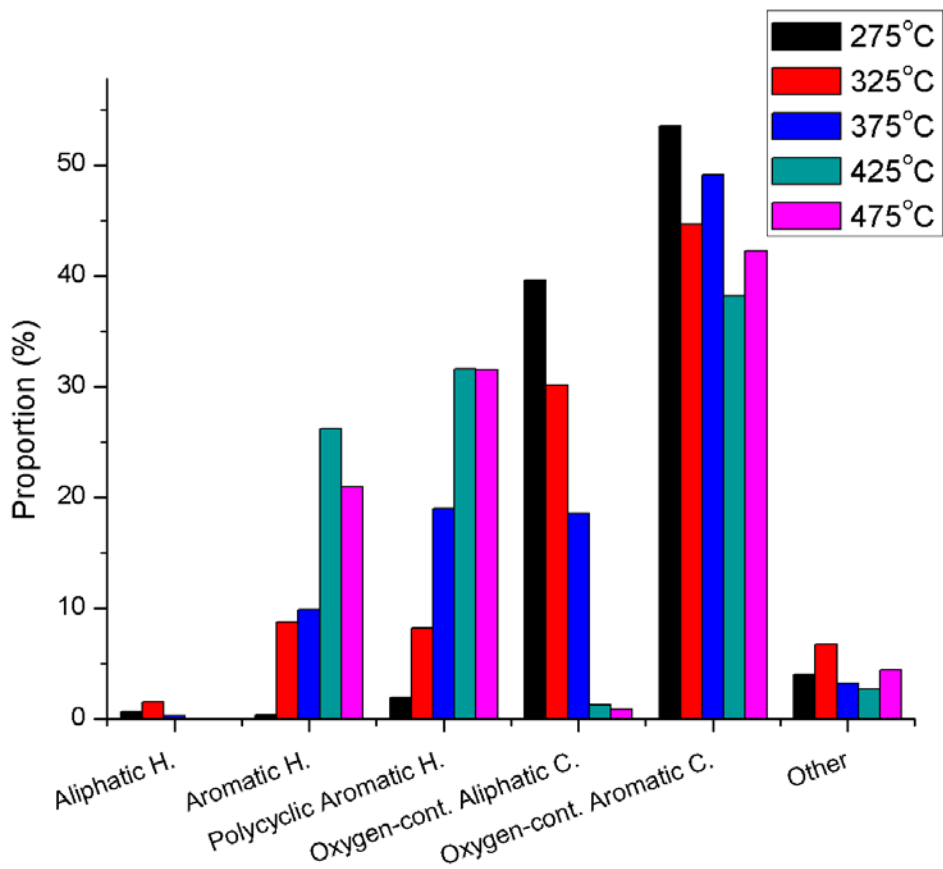
The effect of catalyst temperature on two-step fMAP on the chemical composition of bio-oil is shown in Fig. 2c. It was found that the proportion of aromatic hydrocarbons in the bio-oil increased with the catalyst temperature and reached the maximum yield of 26.20% at 425℃. A decrease in the proportion of aromatic hydrocarbons was observed after 425℃ to 20.93% at 475℃. It is noted that only 0.33% of aromatic hydrocarbons was obtained at 275℃ revealed that the catalyst did not reach active temperature at this point as previously conjecture. The proportions of aromatic hydrocarbons and PAHs in the bio-oil from two-step fMAP significantly increased compared with non-catalytic pyrolysis, at the expense of aliphatic hydrocarbons, oxygen-containing compounds. Selectivity for certain aromatic hydrocarbons varied significantly with temperature. Among of benzene, toluene and xylenes (BTX) were extremely low or were not detected among the monocyclic hydrocarbons at low catalyst temperature, which increased to around 5% (BTX) at 425℃. In addition, as another high amount of compound, phenols were first increased from 29.55% at 275 ℃ to 36.59% at 375℃ then decreased to 26.63% at 475℃. Overall, the optimal catalyst temperature for two-step fMAP was 425℃ considering both the bio-oil yield and composition.

(a)
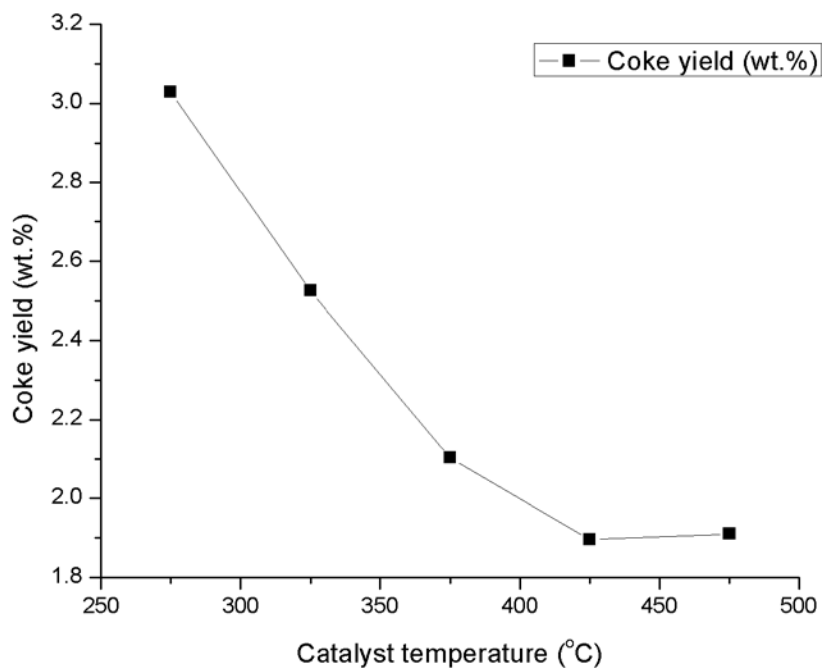
(b)

(c)

Fig. 2- Effect of catalyst temperature on two-step fMAP: (a) Product distribution. (b) Coking on catalyst (c) Bio-oil composition.

Reference:
[1] Liu, S.Y., Xie, Q.L., Zhang, B., Cheng, Y.L., Liu, Y.H., Chen, P., Ruan, R. 2016. Fast microwave-assisted catalytic co-pyrolysis of corn stover and scum for bio-oil production with CaO and HZSM-5 as the catalyst. *Bioresource Technology*, **204**, 164-170.
[2] Putun, E., Uzun, B.B., Putun, A.E. 2009. Rapid Pyrolysis of Olive Residue. 2. Effect of Catalytic Upgrading of Pyrolysis Vapors in a Two-Stage Fixed-Bed Reactor. *Energy & Fuels*, **23**, 2248-2258.
[3] Wang, K.G., Johnston, P.A., Brown, R.C. 2014a. Comparison of in-situ and ex-situ catalytic pyrolysis in a micro-reactor system. *Bioresource Technology*, **173**, 124-131.
[4] Wang, L., Lei, H.W., Bu, Q., Ren, S.J., Wei, Y., Zhu, L., Zhang, X.S., Liu, Y.P., Yadavalli, G., Lee, J., Chen, S.L., Tang, J. 2014b. Aromatic hydrocarbons production from ex situ catalysis of pyrolysis vapor over Zinc modified ZSM-5 in a packed-bed catalysis coupled with microwave pyrolysis reactor. *Fuel*, **129**, 78-85.

Project Status as of December 31, 2016:
The specific objectives in this time period were:
Objective 1: to investigate the effect of catalyst loading on two-step catalytic fMAP
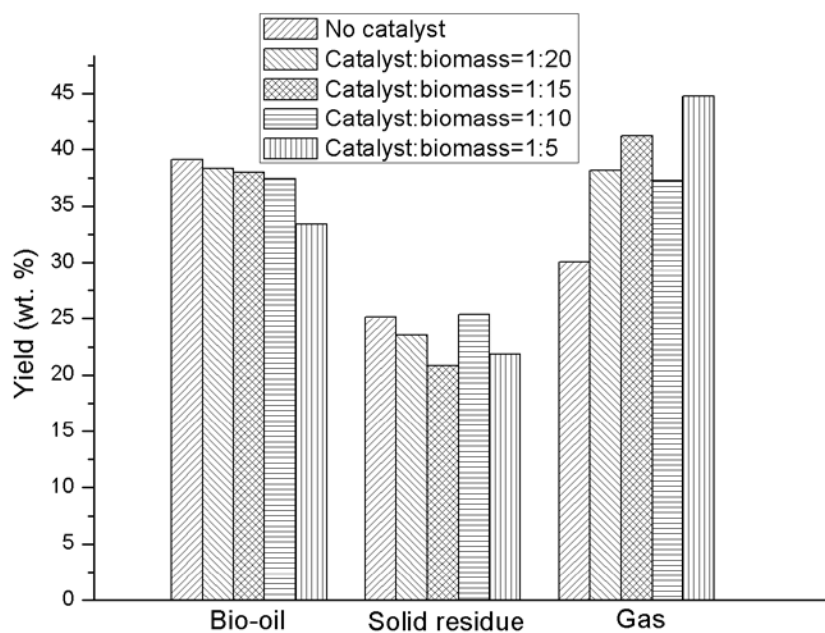Objective 2: to quantitative analysis of major components in the bio-oil
Objective 3: to characterize the catalyst and determine its stability during the catalytic upgrading process

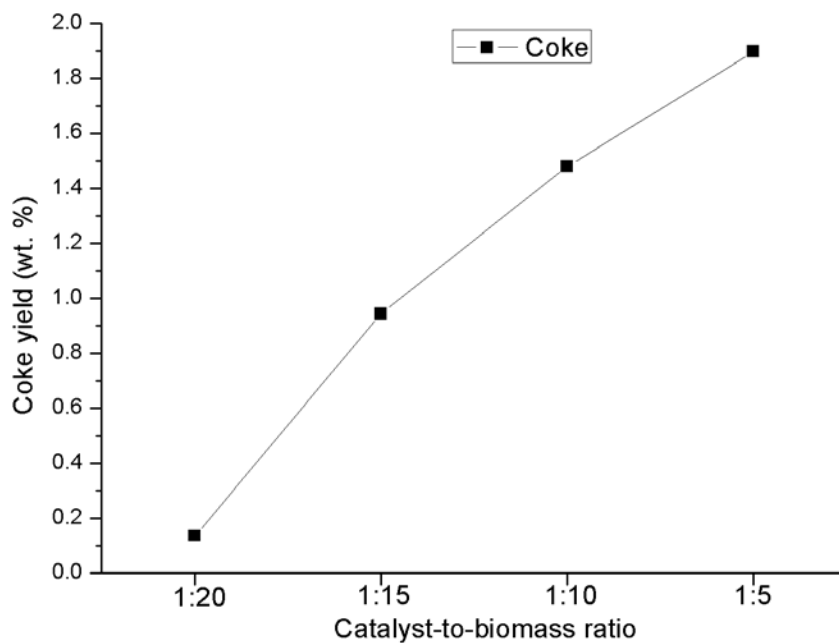Results of Objective 1: to investigate the effect of catalyst loading on two-step catalytic fMAP

The effect of catalyst loading on two-step catalytic fMAP was carried out in this section. To achieve this aim, the effect of catalyst to biomass ratio on product yields and chemical compositions were investigated. During experiments, the pyrolysis temperature was fixed at 550 ℃, and the catalyst to biomass ratios were no catalyst, 1:20, 1:15, 1:10, 1:5, respectively. Fig. 1 shows effect of catalyst loading on two-step catalytic fMAP of corn stover. As shown in Fig. 1(a), the use of catalyst in the second step resulted in a slight decrease in bio-oil yield. In addition, when catalyst to biomass ratio increased from 1:20 to 1:5, the bio-oil yield decreased linearly from 38.31 wt. % to 33.38 wt. % and gas yield increased significantly. This could be explained by the three-dimensional porous structure of the HZSM-5 [1]. When the pyrolysis vapor passed through the internal cavities of the catalyst, the large molecules of it were converted into smaller size of gaseous hydrocarbons, while oxygen was removed as H_2O, CO and CO_2, leading to in the increased yield of gas products. Similar results were reported by Seo et al. [2] and Zhang et al. [3]. Also Putun et al. [4] indicated that in two-stage catalytic upgrading of olive residue with three kind of catalyst (natural zeolite, HZSM-5, H-Y) in fixed-bed reactor, the increase in catalyst to biomass ratio resulted in an increase in gas products, especially for the HZSM-5. Fig. 1(b) shows the effect of catalyst to biomass ratio on the coke deposits on the catalyst. As it can be seen from Fig. 1(b), coke yield increased from 0.13 wt. % to 1.90 wt. % with increasing catalyst to biomass ratio. Meng et al. [5] studied the coking behavior for catalytic pyrolysis of heavy oil, and indicated that increasing catalyst-to-feedstock ratio resulted in higher average activation of catalysts while increasing the pyrolysis extent and promoting condensation reactions, leading to a coke yield increase.

The chemical composition was also influenced by catalyst to biomass ratio on the two-step catalytic fMAP. As shown in Fig. 1(c), the proportion of aliphatic hydrocarbons and oxygen-containing aliphatic compounds decreased with increasing catalyst to biomass ratio. Significant increases in proportion of aromatic hydrocarbons and PAHs were observed over the catalyst to biomass ratios tested. The aromatic hydrocarbons reached maximum value of 26.2 % at the catalyst to biomass ratio of 1:5. The possible reaction mechanism is that various oxygenated compounds produced in the catalytic pyrolysis of corn stover, including acid, alcohols, ketones and aldehydes, are intermediates in the production of aromatics [6, 7, 8]. When they passed through the internal pores of HZSM-5 catalyst, some of these intermediates were transformed to single-ring aromatic products

through a series of oligimerization, decarboxylation, decarbonylation and dehydration reactions. Other aromatics can be obtained through alkylation and isomerization reactions. In addition, single-ring aromatic products may further react with another oxygenate to form PAHs. This is the possible reason for the decreased proportion of oxygen-containing aliphatic compounds. Thus, HZSM-5 has been widely studied due to its shape selectivity for aromatic hydrocarbons [9].

(a)

(b)
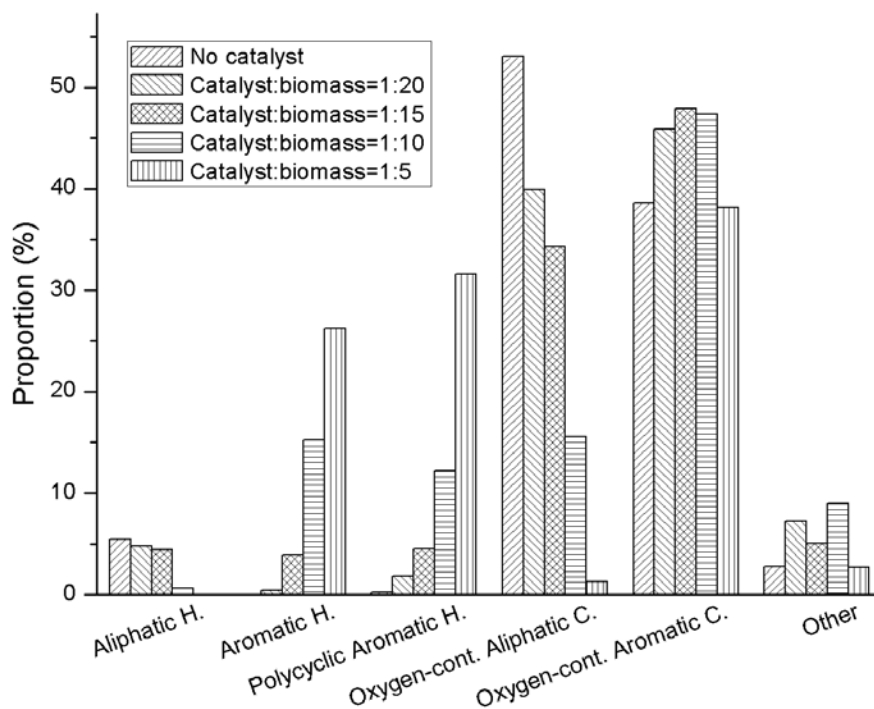
(c)

Fig. 1. Effect of catalyst loading on two-step catalytic fMAP of corn stover: (a) Product distribution; (b) Coke formation; (c) Bio-oil composition.

Results of Objective 2: to quantitative analysis of major components in the bio-oil

An external standard method was used for the quantification of 8 major components in the bio-oil. The five-point calibration curve with the R^2 above 0.99 was established using the standard solutions. The content of each compound in the bio-oil sample could be determined graphically. Table 1 shows mass contents of 8 major components of bio-oil analyzed by GC-MS quantitative method and physicochemical properties of the organic liquid phase. The identified compounds are as follows: toluene, p-xylene, indene, 1,2,3-Trimethylbenzene, 2,3-benzofuran, phenol, phenol, 3-methyl- and naphthalene. The aromatics are not detected in the non-catalytic pyrolysis, which indicates that HZSM-5 catalyst has a shape selectivity for aromatic hydrocarbons. Phenol, 3-methyl- and naphthalene were detected in large amounts in the organic liquid phase of catalytic pyrolysis at 2.37 wt. % and 2.60 wt. %, respectively. Most phenolic compounds were derived from thermal decomposition of lignin [10, 11]. And the high weight percentage of naphthalene indicates that lignocellulosic biomass is mainly selectively converted to PAHs with the HZSM-5 catalyst. The water content and HHV of the organic liquid phase from catalytic pyrolysis were within 9-14 wt. % and 29.85 MJ/kg, respectively while those of bio-oil from non-catalytic pyrolysis were 29.82 wt. % and 19.79 MJ/kg, respectively. The results showed that high quality bio-oil was obtained through sequential two-step catalytic fMAP.

Table 1 Mass contents of 8 major components of bio-oil analyzed by GC-MS quantitative method and physicochemical properties of the organic liquid phase.

|	Organic fraction[a]		No catalyst	
Major component	Relative content (%)	Content in bio-oil (wt.%)	Relative content (%)	Content in bio-oil (wt.%)
Toluene	0.70	0.21	_	_
p-Xylene	2.68	1.33	_	_
Indene	1.87	0.86	_	_
Benzene, 1,2,3-trimethyl-	3.04	1.02	_	_
2,3-Benzofuran	1.01	1.52	_	_
Phenol	1.96	1.38	4.84	0.15
Phenol, 3-methyl-	4.55	2.37	2.32	0.08
Naphthalene	5.83	2.60	_	_
Elemental composition (wt.%)				
C	68.43		48.13	
H	6.51		8.16	
N	1.62		1.66	
O[b]	23.44		42.05	
HHV (MJ/kg)[c]	29.85		19.79	
Water content (wt.%)	9.11		29.82	

[a] Pyrolysis temperature: 550 ℃ , catalyst bed temperature: 425 ℃, catalyst to biomass ratio: 1:5.
[b] Calculated by difference.
[c] Calculated using equation [12] $HHV(MJ/kg) = (3.55 \times C^2 - 232 \times C - 2230 \times H + 51.2 \times C \times H + 131 \times N + 20600) \times 10^{-3}$.

Results of Objective 3: to characterize the catalyst and determine its stability during the catalytic upgrading process

The fresh, spent and regenerated HZSM-5 catalysts were characterized and analyzed using XRD technique to investigate the effect of coke on the catalyst structure. Fig. 2 shows XRD patterns of catalyst. The diffractogram comparison of the fresh, spent and regenerated HZSM-5 catalyst showed obvious similarities. The crystal structure and crystallinity of the HZSM-5 catalyst were intact before and after the pyrolysis and regeneration process. Therefore, HZSM-5 has good stability in the catalytic upgrading process.
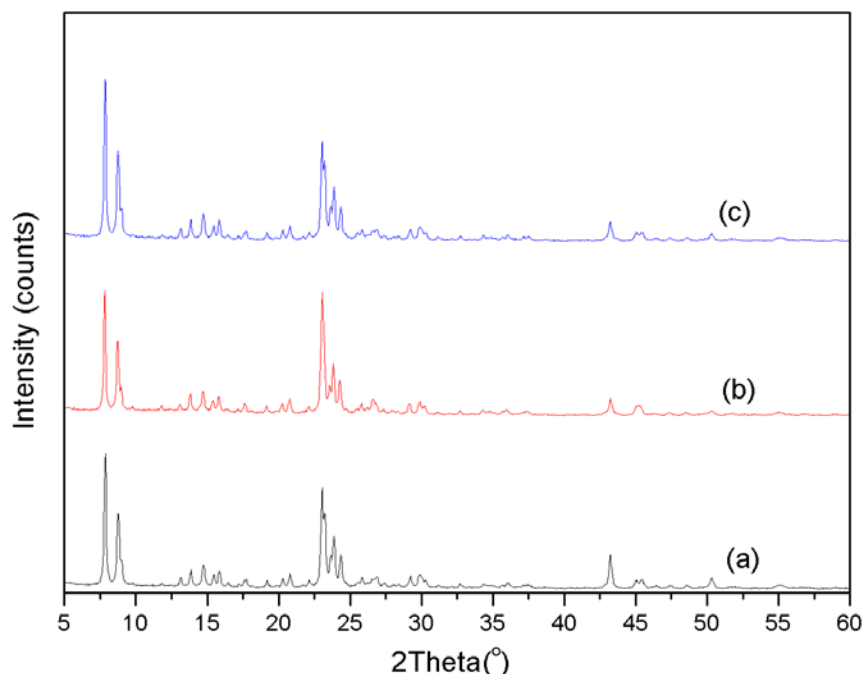
Fig. 2. XRD patterns of catalyst: (a) the fresh HZSM-5; (b) spent (coked) HZSM-5 from two-step catalytic fMAP; (c) the regenerated HZSM-5 from two-step catalytic fMAP.

Reference:
[1] Dickerson, T., Soria, J. 2013. Catalytic Fast Pyrolysis: A Review. *Energies*, **6**(1), 514-538.
[2] Seo, Y.H., Lee, K.H., Shin, D.H. 2003. Investigation of catalytic degradation of high-density   polyethylene by hydrocarbon group type analysis. *Journal of Analytical and Applied Pyrolysis*, **70**(2), 383-398.
[3] Zhang, B., Zhong, Z., Xie, Q., Liu, S., Ruan, R. 2016. Two-step fast microwave-assisted pyrolysis of biomass for bio-oil production using microwave absorbent and HZSM-5 catalyst. *Journal of Environmental Sciences,* (45), 240-247.
[4] Putun, E., Uzun, B.B., Putun, A.E. 2009. Rapid Pyrolysis of Olive Residue. 2. Effect of Catalytic Upgrading of Pyrolysis Vapors in a Two-Stage Fixed-Bed Reactor. *Energy & Fuels*, **23**, 2248-2258.
[5] Meng, X.H., Xu, C.M., Gao, J.S. 2007. Coking behavior and catalyst deactivation for catalytic pyrolysis of heavy oil. *Fuel*, **86**(12-13), 1720-1726.
[6] Carlson, T.R., Jae, J., Huber, G.W. 2009. Mechanistic Insights from Isotopic Studies of Glucose Conversion to Aromatics Over ZSM-5. *Chemcatchem*, **1**(1), 107-110.
[7] Dahl, I.M., Kolboe, S. 1994. On the Reaction-Mechanism for Hydrocarbon Formation from Methanol over Sapo-34 .1. Isotopic Labeling Studies of the Co-Reaction of Ethene and Methanol. *Journal of Catalysis*, **149**(2), 458-464.
[8] McCann, D.M., Lesthaeghe, D., Kletnieks, P.W., Guenther, D.R., Hayman, M.J., Van Speybroeck, V., Waroquier, M., Haw, J.F. 2008. A complete catalytic cycle for supramolecular methanol-to-olefins conversion by linking theory with experiment. *Angewandte Chemie-International Edition*, **47**(28), 5179-5182.
[9] Czernik, S., Bridgwater, A.V. 2004. Overview of applications of biomass fast pyrolysis oil. *Energy & Fuels*, **18**(2), 590-598.
[10] Dong, C.Q., Zhang, Z.F., Lu, Q., Yang, Y.P. 2012. Characteristics and mechanism study of analytical fast pyrolysis of poplar wood. *Energy Conversion and Management*, **57**, 49-59.
[11] Wang, K.G., Kim, K.H., Brown, R.C. 2014. Catalytic pyrolysis of individual components of lignocellulosic biomass. *Green Chemistry*, **16**(2), 727-735.

[12] Friedl, A., Padouvas, E., Rotter, H., Varmuza, K. 2005. Prediction of heating values of biomass fuel from elemental composition. *Analytica Chimica Acta*, **544**(1-2), 191-198.

Project Status as of June 30, 2017:

Amendment Request (06/30/2017)

The specific objectives in this time period were:

Objective 1: to conduct fast microwave-assisted gasification (fMAG) of scum and sewage sludge for biofuels production
Objective 2: to complete the fabrication of the lab-scale continuous microwave based system
Objective 3: to complete the fabrication of the pilot scale continuous fast microwave assisted conversion system

Results of objective 1: to conduct fast microwave-assisted gasification (fMAG) of scum and sewage sludge for biofuels production

    Scum and sewage sludge used as the raw material for this study were obtained from the Metropolitan Waster Treatment Plant, Saint Paul, Minnesota. Prior to use, the solid scum was dried at 105 ℃ for 24 h, and at the same time melted and filtered through a 100-micron polyester mesh filter bag to remove large solid particles. The elemental composition of the solid scum (on dry, ash free basis) was 73.2 wt.% carbon, 11.6 wt.% hydrogen, 0.06 wt.% nitrogen, and 15.1 wt.% oxygen (by difference). The sewage sludge was mixture of primary and secondary sludge.
    The fMAG of scum and sewage sludge was conducted at the temperature of 800 ℃, and 63.33 wt.% and 58.24 wt.% of gas could be obtained, respectively. It can be noticed that the hydrogen and C_1-C_3 hydrocarbons (methane, ethylene, ethane, propylene and propane) in the gas product from scum and sewage sludge could reach 50 % and 24 %, respectively. It can be also noticed that, the H_2 to CO ratio in the gas product could reach around 1, which is much higher than that from traditional biomass, and almost perfect mixture for the syngas reforming. A summary of the fMAG results is shown in Table 1.
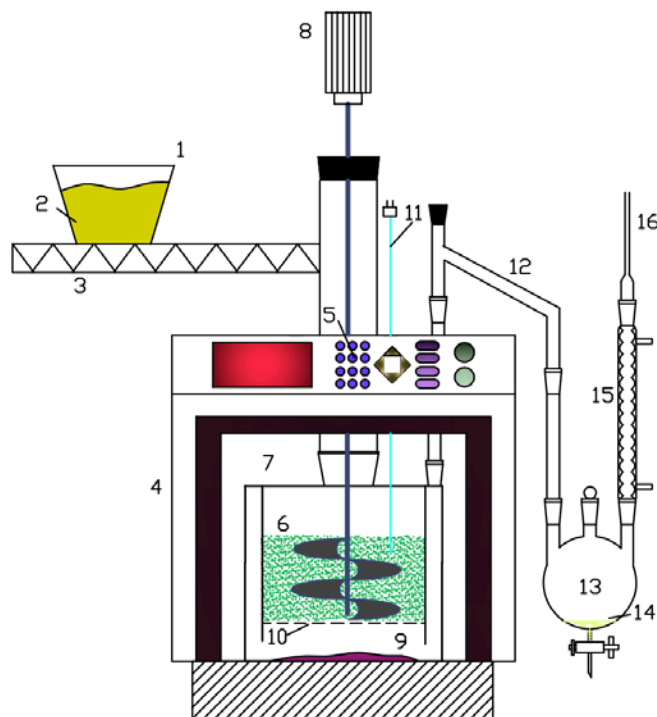
Table 1. Fast microwave-assisted gasification (fMAG) of scum and sewage sludge

	Gas composition (%)								Gas yield (wt.%)
	H_2	CO	CO_2	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	
Scum	12.77	16.43	19.92	20.94	11.88	5.31	7.28	5.48	63.33
Sewage sludge	20.13	21.95	33.89	14.15	2.75	1.51	1.62	4.00	58.24

Results of objective 2: to complete the fabrication of the lab-scale continuous microwave based system

    Microwave over (MAX, CEM Corporation) was operated with power of 750 W and a frequency of 2450 MHz. The schematic diagram of the lab-scale continuous microwave based system is shown in Fig.1. The experimental apparatus is composed of: (1) hopper; (2) biomass feedstock; (3) feeding auger system; (4) oven; (5) control panel; (6) SiC bed; (7) quartz reactor; (8) agitator; (9) char; (10) mesh; (11) thermocouple (K-type); (12) outlet quartz connectors; (13) liquid fraction collectors; (14) bio-oil; (15) condenser; (16) connection for vacuum pump.

It consists four parts, which are feeding system, reactor, cooling system and collecting system. The continuous microwave based system is shown in Figure 1. It works as follows: the agitator is used to mix the microwave absorbent with the biomass. The auger system is for metering the airlock biomass feeding system. When the different kinds of biomass enter into the reactor from the hopper through the auger system, the reaction complete less then two seconds, the pyrolysis vapor come out, after going through the cooling system, the valuable bio-oil is collected. Besides, the bio-char is separated and collected at the bottom. Thermocouples (K-type) are inserted through the gas exit tube into the reactor. The thermocouples are connected to a 4-channel thermocouple probe thermometer (Sper Scientific 800023) for temperature read-out. A very mild vacuum is applied to draw the vapors and gas out of the reactor to a series of refrigerated water-cooled condensers. The vacuum may be varied to adjust the gas/vapor residence time. For safety purpose, a microwave leakage detector (MD-2000, Digital Readout) will be used to monitor if there is any leakage.

Fig. 1. Schematic diagram of the lab-scale continuous microwave based system

Fig. 2 The lab-scale continuous microwave based system

Results of objective 3: to complete the fabrication of the pilot scale continuous fast microwave assisted conversion system

The system includes a feed storage and input section, a pyrolysis reactor section, and a product collection and separating section. The raw materials are initially fed into the feed storage section with pre-drying, which in turn feeds the pre-dried pieces into the pyrolysis reaction section. As the raw materials move through the pyrolysis section, volatile products are driven off by a vacuum pump and passed through a condensation column to separate and obtain the condensable bio-oil and non-condensable syngas products. Through the alkali liquid tower, washing tower (sulfur removal, etc.), and drying tower, the non-condensable syngas products are cleaned. The remaining portions of the solid residue after microwave pyrolysis are desirable materials such as char.

Biomass feeding is realized in the form of vacuum sucking, running or stopping movement is controlled by a feed level sensor, which leads to a fully-automatic control. It is made to ensure a continuous and steady feedstock conveying with a capacity around 15-20 kg/h. A rotary discharge valve, i.e. the air lock, is deployed in the line of feedstock hopper and pyrolysis reactor. This ensures the produced hot gas will not feed back to the feed bin when a continuous feeding under a vacuum state. The total power of the pyrolysis system is 18 KW, integrated with 15 sets of microwave generators. With the aid of a power adapter, the actual power can be adjusted. The material's temperatures are measured by means of temperature transducers (4 points) in a direct contact mode. Internal parts of the pyrolysis reactor, which are isolated, can be operated up to 850 °C, easy to clean up. Professional designed screw functionalizes an over-turning role as well as materials transport to ensure a uniform pyrolysis. The feed and mixing rates are controlled by a frequency converter; the actual feed rate can be displayed on the touch screen. The emitted fuel gas can also be combusted in a torch furnace, embodies a compact framework, comply with safety and industrial hygienic standards, ready for demonstration showing. Sampling ports of gaseous, liquid, and solid samples are all ready to use in the pyrolysis system.

In the trial run test, the wood pellets were used as the feedstocks shown in Fig. 5 (a). At temperature of approximately 550- 600°C with 20 Hz stirring speed, wood pellets underwent thermal decomposition to form volatile products. When the pyrolysis vapor traveled to the condensers, the condensable volatiles were converted to liquid form and collected as bio-oil fraction shown in Fig. 5 (b). The non-condensable gas was mainly composed of 4 compositions shown in Fig. 5 (c): H_2, CO, CO_2 and CH_4. The solid residue was cooled to the room temperature and collected after experiment as biochar fraction shown in Fig. 5 (d). The estimated products distribution was 50

% gas, 25 % bio-oil and 25 % biochar. Considering about the gas application and environmental impacts, the gas cleanup process was important. Fine particles and tar should be removed through spray cooling tower. CO2 should be removed through alkali-liquid tower. And sulfur should be removed though washing tower. All the cleanup process above ensured the quality of the gas for the next step application. If the gas is to be used for synthesis of high quality liquid fuels, the product not only be clean but also have specified molecular ratios of H2 and CO. We will consider the gas reforming in our future research.

Main components of pilot scale continuous fast microwave assisted conversion system

1 Hopper;
2 Elevator;
3 Feeder;
5 Microwave reactor;
6 Residue tank;
7 Catalyst bed;
8 Bio-oil tank 1;
9 Bio-oil tank 2;
10 Bio-oil tank 3;
11 Bio-oil tank 4;
12 Spray cooling tower;
13 Shell-and-tube condenser 1;
14 Shell-and-tube condenser 2;
15 Oil pump;
16 Gas-water separator;
17 Alkali-liquid tower;
18 Washing tower (sulfur removal, etc);
19 Drying tower;
20 Roots blower;
21 Cooling system.

Fig. 3 Demonstration of the pilot scale continuous fast microwave assisted conversion system.
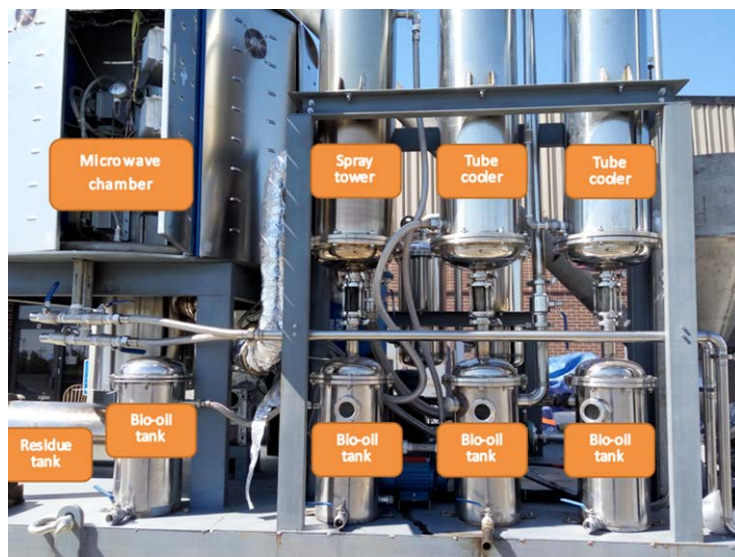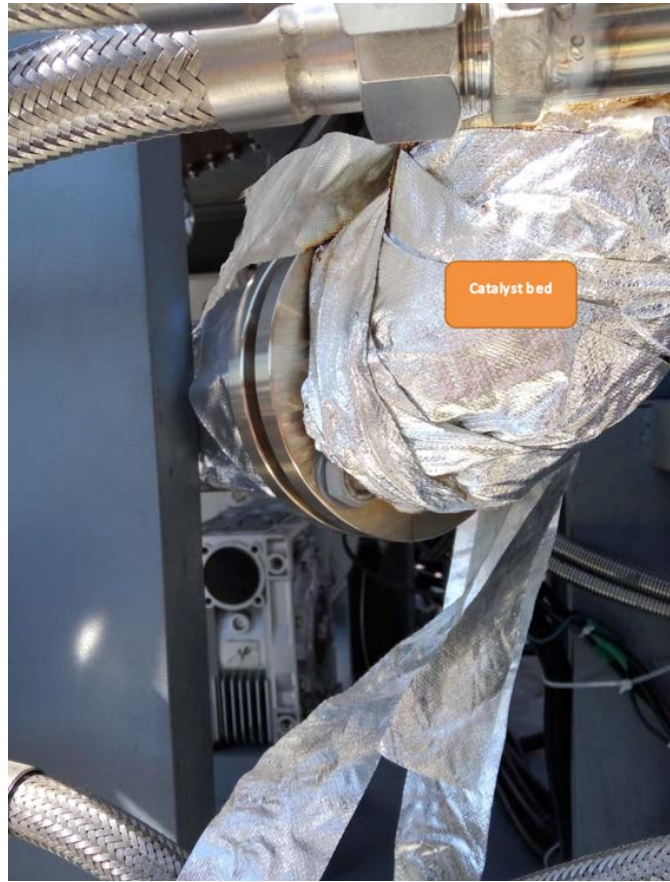

(a)

(b)

(c)

(d)

Fig. 4 Main components of pilot scale continuous fast microwave assisted conversion system

(a)

(b)

(c)

(d)

Fig. 5 (a) wood pellets; (b) bio-oil; (c) non-condensable gas; (d) biochar.

Final Report Summary:
Pyrolysis
The research team conducted studies aimed to develop processes and a system for cost effective conversion of sludge to energy. Specifically,

(1) The physiochemical properties of the sludge from St. Paul Wastewater Treatment Plant were characterized.
(2) The effect of temperature and use of catalysts on product yields was studied. Catalyst loading and ratio of Ca to HZSM-5 were found to be important processing parameters.

(3) Co-pyrolysis of sludge with hydrogen rich scum was found effective in improving the hydrocarbon especially aromatics yield and quality in the resultant bio-oil.
(4) A pilot scale continuous fast microwave assisted conversion system was successfully fabricated and tested.

Both TEA and LCA results indicate positive impacts of including sludge utilization in the integrated system.

V. DISSEMINATION:

Description:

The findings will be disseminated through:
(1) On site demonstration as described in the activities
(2) Public seminars
(3) Progress update on www.biorefining.cfans.umn
(4) Presentations at national and international technical conferences
(5) Communications with interested entrepreneurs
(6) Peer reviewed papers
(7) Collaboration with UMN extension

The technologies, if demonstrated successfully, may be implemented to many MWTPs in the State of Minnesota and beyond. Any intellectual properties and related revenues as a result of the program will be shared between UMN and LCCMR.

Project Status as of December 31, 2014:
Two manuscripts were prepared for publication. An invention disclosure was filed.

Project Status as of June 30, 2015:
Three manuscripts were published.
Project Status as of December 31, 2015:
Three manuscripts were published.
Project Status as of June 30, 2016:
(1) Five publications on peer reviewed journals
   1. Completed and sent the following paper in for publication in the journal of Fuel Processing Technologies, "A Techno-Economic Analysis of Renewable Energy Technologies Incineration, Anaerobic Digestion, and Biodiesel Production as Applied to Waste Oils".
   2. Ma, H., M. Addy, E. Anderson, W. Liu, Y. Liu, Y. Nie, P. Chen, Y. Cheng, H. Lei, R. Ruan. 2016. A novel process for low-sulfur biodiesel production from scum waste. Bioresource Technology. 214:826-35.
   3. Anderson, E., Addy, M., Xie, Q., Ma, H., Liu, Y., Cheng, Y., Onuma, N., Chen, P., Ruan, R. 2016. Glycerin esterification of scum derived free fatty acids for biodiesel production. Bioresource technology, 200, 153-160.
   4. Ma, H., Addy, M.M., Anderson, E., Liu, W., Liu, Y., Nie, Y., Chen, P., Cheng, B., Lei, H., Ruan, R. 2016a. A novel process for low-sulfur biodiesel production from scum waste. Bioresource technology, 214, 826-835.
   5. Ma, X., Zheng, H., Addy, M., Anderson, E., Liu, Y., Chen, P., Ruan, R. 2016b. Cultivation of Chlorella vulgaris in wastewater with waste glycerol: strategies for improving nutrients removal and enhancing lipid production. Bioresource technology, 207, 252-261.
(2) Numerous presentations were made in conferences
(3) Development of demonstration units has begun.

Project Status as of December 31, 2016:
   (1) Seven publications on peer reviewed journals
   1. Erik Anderson, Min Addy, Huan Ma, Paul Chen, Roger Ruan. 2016. Economic screening of renewable energy technologies: Incineration, anaerobic digestion, and biodiesel as applied to waste water scum. Bioresource Technology, http://dx.doi.org/10.1016/j.biortech.2016.09.076 0960-8524/© 2016 Published by Elsevier Ltd.
   2. Shiyu Liu, Qinglong Xie, Bo Zhang, Yanling Cheng, Yuhuan Liu, Paul Chen, Roger Ruan. 2016. Fast microwave-assisted catalytic co-pyrolysis of corn stover and scum for bio-oil production with CaO and HZSM-5 as the catalyst. Bioresource Technology 204 (2016): 164–170.
   3. Ma, X., H. Zheng, W. Zhou, Y. Liu, P. Chen, R. Ruan. 2016. Enhanced Harvesting of Chlorella vulgaris using Combined Flocculants. Applied Biochemistry and Biotechnology. DOI 10.1007/s12010-016-2133-5.
   4. Chunhua Xin, Min Addy, Jinyu Zhaoc, Yanling Cheng, Sibo Cheng, Dongyan Mu, Yuhuan Liu, Rijia Ding, Paul Chen, Roger Ruan. 2016. Comprehensive techno-economic analysis of wastewater-based algal biofuel production: A case study. Bioresource Technology. Volume 211, July 2016, Pages 584–593.
   5. Dongyan Mu; Min Addy; Erik Anderson; Paul Chen; Roger Ruan. 2016. A Life Cycle Assessment and Economic Analysis of the Scum-to-Biodiesel Technology in Wastewater Treatment Plants. Bioresource Technology. Volume 204, March 2016, Pages 89–97.
   6. Chen, P., Q. Xie, M. Addy, W. Zhou, Y. Cheng, Y. Liu, Y. Wang, Y. Wan, Q. Lee, H. Lei, R. Ruan. 2016. Utilization of municipal solid and liquid wastes for bioenergy and bioproducts production. Biorecource Technology. doi:10.1016/j.biortech.2016.02.094.
   7. Zhang B, Zhong Z, Chen P, Ruan R. 2016. Microwave-assisted catalytic fast pyrolysis of biomass for bio-oil production using chemical vapor deposition modified HZSM-5 catalyst. Bioresour Technol. 2015 Dec;197:79-84. doi: 10.1016/j.biortech.2015.08.063. Epub 2015 Aug 21.
   (2) Numerous presentations were made in conferences
   (3) Fabrication of scum to biodiesel and algae cultivation demonstration units has been completed. Fabrication of the MAP demonstration unit has begun.

Project Status as of June 30, 2017:
Peer-reviewed publications related to the research activities:
   1. Dongyan Mu, Sarah Mack, Roger Ruan, and Min Addy. 2017. Chapter 6. Life cycle assessment of beneficial reuse of waste streams for energy in municipal wastewater treatment plants. In *Life-cycle Assessment of Wastewater Treatment* (CRC Series "Part of the Life Cycle Assessment and Green Chemistry Series, edited by Vera Kolb"), edited by Dr. Mu Naushad. CRC Press (https://www.crcpress.com/), USA.
   2. Yaning Zhang, Paul Chen, Shiyu Liu, Liangliang Fan, Nan Zhou, Min Min, Yanling Cheng, Peng Peng, Erik Anderson, Yunpu Wang, Yiqin Wan, Yuhuan Liu, Bingxi Li and Roger Ruan. 2017. Chapter 6 Microwave‐Assisted Pyrolysis of Biomass for Bio‐Oil Production. In *Pyrolysis*. http://dx.doi.org/10.5772/65193. Edited by Mohamed Samer pages: 129-166. Published by InTech.
   3. Liangliang Fan, Yaning Zhang, Shiyu Liu, Nan Zhou, Paul Chen, Yuhuan Liu, Yunpu Wang, Peng Peng, Yanling Cheng, Min Addy, Hanwu Lei, Roger Ruan. 2017. Ex-situ catalytic upgrading of vapors from microwave-assisted pyrolysis of low-density polyethylene with MgO. *Energy Conversion and Management*. In Press.
   4. Liangliang Fan, Yaning Zhang, Shiyu Liu, Nan Zhou, Paul Chen, Yanling Cheng, Min Addy, Qian Lu, Muhammad Mubashar Omar, Yuhuan Liu, Yunpu Wang, Leilei Dai, Erik Anderson, Peng Peng, Hanwu Lei, Roger Ruan. 2017. Bio-oil from fast pyrolysis of lignin: Effects of process and upgrading parameters. *Bioresource Technology*. DOI: 10.1016/j.biortech.2017.05.129
   5. Xiang-Yuan Deng, Kun Gao, Ren-Chuan Zhang, Min Addy, Qian Lu, Hong-Yan Ren, Paul Chen, Yu-Huan Liu, Roger Ruan. 2017. Growing Chlorella vulgaris on thermophilic anaerobic digestion swine manure for

nutrient removal and biomass production. *Bioresource Technology*. Volume 243, November 2017, Pages 417-425.

6. Shanshan Luo, Richard Griffith, Wenkui Li, Peng Peng, Yanling Cheng, Paul Chen, Min M. Addy, Yuhuan Liu, Roger Ruan. 2017. A continuous flocculants-free electrolytic flotation system for microalgae harvesting. *Bioresource Technology* 238:439-449, https://doi.org/10.1016/j.biortech.2017.04.061

7. B.W. Hanson, Z.K. Zeng, G.C. Shurson, R. Ruan, C. Chen, and P. E. Urriola. 2017. In vitro dry matter digestibility of multiple sources of microalgae and microalgae products for growing pigs. J. Animal Science Vol. 95 No. supplement 2, p. 188.

8. Hui Liu, Qian Lu, Qin Wang, Wen Liu, Qian Wei, Hongyan Ren, Caibing Ming, Min Min, Paul Chen, Roger Ruan. 2017. Isolation of a bacterial strain, Acinetobacter sp. from centrate wastewater and study of its cooperation with algae in nutrients removal. *Bioresour Technol.* http://dx.doi.org/10.1016/j.biortech.2017.03.111 Volume 235, Pages 59-69.

9. H. M. Morgan, Q. Bu; J. Liang; Y.J. Liu, H. Mao, A.P. Shi; H. Lei, R. Ruan. 2017. A review of catalytic microwave pyrolysis of lignocellulosic biomass for value-added fuel and chemicals. *Bioresource Technology*, 230: 112–121.

10. Yaning Zhang, Paul Chen, Shiyu Liu, Peng Peng, Min Addy, Yanling Cheng, Erik Anderson, Nan Zhou, Liangliang Fan, Chenghui Liu, Guo Chen, Yuhuan Liu, Hanwu Lei, Bingxi Li, Roger Ruan. 2017. Effects of feedstock characteristics on microwave-assisted pyrolysis – A review. *Bioresource Technology*, 230: 143–151. http://dx.doi.org/10.1016/j.biortech.2017.01.046

11. Fan, L. ; Chen, P. ; Zhang, Y. ; Liu, S. ; Liu, Y. ; Wang, Y. ; Dai, L. ; Ruan, R.. 2017. Fast microwave-assisted catalytic co-pyrolysis of lignin and low-density polyethylene with HZSM-5 and MgO for improved bio-oil yield and quality. *Bioresource Technology*, 1 February 2017, Vol.225, pp.199-205.

12. Liu, S., Zhang, Y., Fan, L., Zhou, N., Tian, G., Zhu, X., Cheng, Y., Wang, Y., Liu, Y., Chen, P. 2017. Bio-oil production from sequential two-step catalytic fast microwave-assisted biomass pyrolysis. *Fuel*, 196, 261-268.

13. Mu, D., Ruan, R., Addy, M., Mack, S., Chen, P., Zhou, Y. 2017. Life cycle assessment and nutrient analysis of various processing pathways in algal biofuel production. *Bioresource Technology*, 230, 33-42.

14. Zhou, W., Wang, J., Chen, P., Ji, C., Kang, Q., Lu, B., Li, K., Liu, J., Ruan, R. 2017. Bio-mitigation of carbon dioxide using microalgal systems: Advances and perspectives. *Renewable and Sustainable Energy Reviews*, 76, 1163-1175.

Demonstration of pilot systems to stakeholders:
Demonstration of the pilot systems has been given to Superior Process Technology, Resynergi Inc., Minnesga, Inc., LZL Engineering, eVende, Metro Council Environmental Service, ….

Newspaper and TV publicity:
Media interviews have been given to Minnesota Daily, Channel 5, Channel 11

Patents and propitiatory technology:
Ruan, R., Addy, M.M., Nie, Y., Anderson, E.A., Bi, C., Li, D., Chen, L. Production of biodiesel from scum,   US patent, Application number: US 15/019,707, Publication date: Aug 11, 2016
Ruan, R., Chen, P., et al. 2017. Fast microwave assisted pyrolysis of biomass, propitiatory technology

Final Report Summary:
The project has generated significant amount of information that has been disseminated through different pathways for education, extension, and research benefits. Specifically,
1. The research activities were used to train students and junior researchers. Research findings were used to enhance classroom teaching materials
2. Research findings were published in peer-reviewed papers (>30), presented in state, national, and international meetings (>10)
3. One patent was filed and one propitiatory technology has been approved and licensed to a US company

4. The technologies developed from the project have been demonstrated to various stakeholders
5. *The project was reported by local newspapers and TV stations*

VI. PROJECT BUDGET SUMMARY:

A. ENRTF Budget Overview:

Budget Category	$ Amount	Explanation
Personnel:	$538,674.09 ~~$507,364~~	• Roger Ruan, PI/PD, 1%, 3 years, including 33.6% benefits, leading and managing project, overlooking R&D, leading demonstration, supervising postdocs and RA ($4,963) • Paul Chen, co-PI, 10%, 3yrs, including 33.6% benefits, project coordination, conducting R&D, project evaluation, progress report ($33,168) • 2 research associate 100%, 3yrs, including 33.6% benefits, conducting R&D, operations, demonstration, data analysis ($347,381) • 1 Graduate Research Assistants, 50%, 3yrs, including 15.7% benefits plus tuitions, conducting R&D, operation, demonstration ($121,852)
Professional/Technical/Service Contracts:	$724.00 ~~$30,000~~	Salary/fees for a consultant, helping with engineering design and development of demo system for scum to algae conversion
Supplies:	$125,866.43 ~~$96.454~~	Laboratory supplies including: • chemicals $2,454) • analytical supplies ($500) • microwave absorbents ($700) • catalysts ($500) • glassware ($1,000) • containers ($500) • Modification of algae cultivation and harvesting demo system including multi-layer photobioreactors, greenhouse, circulation equipment, harvest equipment, dewatering equipment ($40,000)
Capital Expenditures over $5,000:	$331,034.62 ~~$360,000~~	• Pilot scale biodiesel conversion demo system including oil extraction device, reaction tank, storage tanks, separation tanks, fractional rectifier, pumps, heaters, heat exchangers, control ($100,000) • Fast microwave assisted pyrolysis demo system including auto-feeder, magnitrons, reaction chamber, microwave absorbent

		bed, condenser, syngas scraper, gas turbine power generator ($260,000)
Travel Expenses in MN:	$3,700.86 ~~$6,182~~	Mileage for researchers to travel between campus and demonstration site over the 3yrs project period
TOTAL ENRTF BUDGET:	**$1,000,000**	

Explanation of Use of Classified Staff: None.

Explanation of Capital Expenditures Greater Than $5,000:
Capital expenditures are planned for development and demonstration of three technologies in the project. All these demo systems will be custom-designed. The fabrication may require sourcing the components from multiple suppliers. US Contractors will be selected through UMN bidding process.

- Pilot scale biodiesel conversion demo system: This system will be developed for converting scum to biodiesel. This system is essential for the completion of project objectives. It will be used for demonstration and collection of data for TEA and LCA. The system will consist of mainly oil extraction device, reaction tank, storage tanks, separation tanks, fractional rectifier, pumps, heaters, heat exchangers, and control panel. While the system is in a small demo scale, it will be capable of processing all the scum generated in MCES St. Paul Wastewater Treatment Plant.
- Fast microwave assisted pyrolysis demo system: This system will be developed for converting sludge to system gas and biofuels. This system is essential for the completion of project objectives. It will be used for demonstration and collection of data for TEA and LCA. The system will consist of an auto-feeder, magnitrons, reaction chamber, microwave absorbent bed, condenser, syngas scraper, gas turbine power generator

Number of Full-time Equivalents (FTE) Directly Funded with this ENRTF Appropriation: 7.83

Number of Full-time Equivalents (FTE) Estimated to Be Funded through Contracts with this ENRTF Appropriation: 1.5

B. Other Funds:

Source of Funds	$ Amount Proposed	$ Amount Spent	Use of Other Funds
Non-state			
MCES	$49,999	$10,442.01	Developing scum to biodiesel process
Gift fund	$80,000	$	Developing scum to biodiesel and sludge utilization processes
State			
Project Unrecovered (UMN unpaid F&A as in-kind support)	$286,638	$	Developing algae cultivation and microwave assisted conversion processes.
TOTAL OTHER FUNDS:	**$415,638**	**$**	

VII. PROJECT STRATEGY:
A. Project Partners:
Project Partners Not Receiving Funds:
- *MCES St. Paul Wastewater Treatment Plant*
- *FreightMasters/Minnesga Inc.*

B. Project Impact and Long-term Strategy:
The purpose of the project is to demonstrate innovative technologies to utilize and treat wastewater streams. Specifically, research will be conducted to optimize processes and develop demo systems for converting oily scum, sludge, and centrate to renewable bio-fuels. The essential qualities of the proposed research lie in the following features: (1) the project appropriately and timely addresses the needs of wastewater treatment industry to utilize various waste streams for renewable fuels and energy production, to reduce environment impact and treatment cost; (2) the project is largely built on the excellent outcomes from the previous research funded by LCCMR and others; (3) the project involves strong academic and industry partnership; and (4) the project is loaded with high impact and achievable objectives. The success of the project is expected to reduce landfill, improve water quality, reduce GHG emission, produce renewable energy, create revenue for wastewater treatment operators, and lower the overall wastewater treatment costs.

The proposed project, built on our existing technologies, does not need additional investment other than the requested ENRTF support to complete. However, further development and demonstration leading to eventual technology transfer and commercialization will be our long-term goal and will require additional funding. Next level commercial scale-up pilot facilities demonstrations may be necessary with federal, state, and private funding before the technologies can be commercialized.

C. Spending History:

Funding Source	M.L. 2008 or FY09	M.L. 2009 or FY10	M.L. 2010 or FY11	M.L. 2011 or FY12 &13	M.L. 2013 or FY14
USDA	1,025,676				
MCES Metro Council	484,999				
MECC/IREE	143,192				
LCCMR			899,999		
Corn Growers				7991	
SDSU/DOE	613,235				
IREE	601,552				

VIII. ACQUISITION/RESTORATION LIST:

IX. VISUAL ELEMENT or MAP(S):

X. ACQUISITION/RESTORATION REQUIREMENTS WORKSHEET:

XI. RESEARCH ADDENDUM:
Enclosed

XII. REPORTING REQUIREMENTS:
Periodic work plan status update reports will be submitted no later than September 2014, March 2015, September 2015, March 2016, September 2016, and March 2017. A final report and associated products will be submitted between June 30 and August 15, 2017.

Environment and Natural Resources Trust Fund

M.L. 2014 Project Budget

Project Title: *Demonstrating innovative technologies to fully utilize wastewater resources*

Legal Citation: *Fill in your project's legal citation from the appropriation language - this will occur after the 2014 legislative session.*

Project Manager: *Roger Ruan*

Organization: *University of Minnesota*

M.L. 2014 ENRTF Appropriation: $1,000,000

Project Length and Completion Date: *3 Years, June 30, 2017*

Date of Report: *December 31, 2016*

ENVIRONMENT AND NATURAL RESOURCES TRUST FUND BUDGET	Activity 1 Budget	Revised Activity 1 Budget 06/30/2017	Amount Spent	Activity 1 Balance	Activity 2 Budget	Revised Activity 2 Budget 06/30/2017	Amount Spent	Activity 2 Balance	Activity 3 Budget	Revised Activity 3 Budget 06/30/2017	Amount Spent	Activity 3 Balance	TOTAL BUDGET	TOTAL BALANCE
BUDGET ITEM	*Develop and demonstrate scum to biodiesel process and system*								*Develop and demonstrate sludge to bio-fuels system*					
Personnel (Wages and Benefits)	$240,000	$269,504.20	$269,504.20	$0.00	$120,000	$121,805.89	$121,805.89	$0.00	$147,364	$147,364.00	$147,364.00	$0.00	$538,674.09	$0.00
Roger Ruan, PI/PD, 1%, 3 years, including 33.6% benefits, leading and managing project, overlooking R&D, leading demonstration, supervising postdocs and RA			$1,600.74				$1,673.54							
Paul Chen, co-PI, 10%, 3yrs, including 33.6% benefits, project coordination, conducting R&D, project evaluation, progress report			$46,613.51				$26,431.46				$38,519.11			
2 research associate 100%, 3yrs, including 33.6% benefits, conducting R&D, operations, demonstration, data analysis			$51,468.43				$41,659.06				$59,590.99			
1 Graduate Research Assistants, 50%, 3yrs, including 15.7% benefits plus tuitions, conducting R&D, operationg, demonstration			$129,453.41				$39,339.78				$26,551.84			
Hourly and temporary employees, undergraduate students, temp and casual, civil service and bargaining unit			$40,368.11				$12,702.05				$22,702.06			
Professional/Technical/Service Contracts	$30,000	$724.00	$724.00	$0.00	$0	$0.00	$0.00	$0.00	$0		$0.00	$0.00	$724.00	$0.00
Consultants, helping with engineering design and development of demonstration facilities	$30,000	$724.00	$724.00	$0.00	$0		$0.00	$0.00	$0		$0.00	$0.00	$724.00	$0.00
Equipment/Tools/Supplies	$22,000	$22,153.34	$22,153.34	$0.00	$50,000	$50,000.00	$50,000	$0.00	$24,454	$53,713.09	$53,713.09	$0.00	$125,866.43	$0.00
Laboratory supplies including chemicals, analytical supplies, microwave absorbents, catalysts, glassware, containers, lab services, shipping of samples; laboratory services, repairs	$22,000	$22,153.34	$22,153.34	$0.00	$50,000	$50,000.00	$50,000.00	$0.00	$24,454	$53,713.09	$53,713.09	$0.00	$125,866.43	$0.00
Capital Expenditures Over $5,000	$100,000	$99,618.46	$99,618.46	$0.00	$0		$0.00	$0.00	$260,000	$231,416.16	$231,416.16	$0.00	$331,034.62	$0.00
Pilot scale biodiesel conversion demo system including oil extraction device, reaction tank, storage tanks, separation tanks, fractional rectifier, pumps, heaters, heat exchangers, control	$100,000	$99,618.46	$99,618.46	$0.00	$0		$0.00	$0.00	$0		$0.00	$0.00	#REF!	$0.00
Algae cultivation and harvesting demo system including multi-layer photobioreactors, greenhouse, circulation equipment,	$0		$0.00	$0.00	$0		$0.00	$0.00	$0		$0.00	$0.00	$0	$0.00
Fast microwave assisted gasification demo system including auto-feeder, magnitrons, reaction chamber, microwave	$0		$0.00	$0.00	$0		$0.00	$0.00	$260,000	$231,416.16	$231,416.16	$0.00	$231,416.16	$0.00
Travel expenses in Minnesota	$2,060	$2,060.00	$2,060.00	$0.00	$2,060	$254.11	$254.11	$0.00	$2,062	$1,386.75	$1,386.75	$0.00	$3,700.86	$0.00
Milleages for researchers to travel between campus and demonstration sites	$2,060	$2,060.00	$2,060.00	$0.00	$2,060	$254.11	$254.11	$0.00	$2,062	$1,386.75	$1,386.75	$0.00	$3,700.86	$0.00
COLUMN TOTAL	$394,060	$394,060.00	$394,060.00	$0.00	$172,060	$172,060.00	$172,060.00	$0.00	$433,880	$433,880.00	$433,880.00	$0.00	$1,000,000.00	$0.00