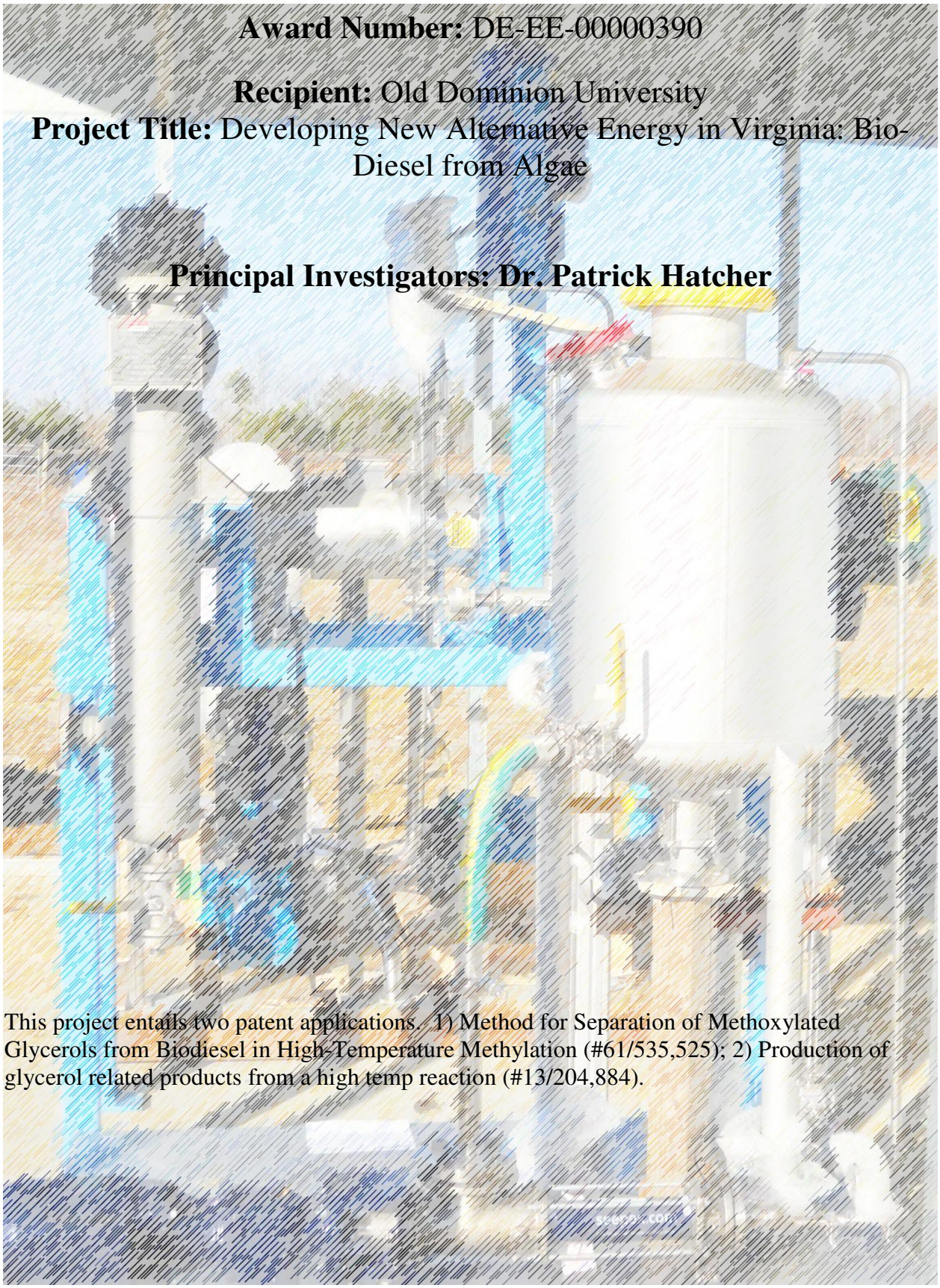
Award Number: DE-EE-00000390

Recipient: Old Dominion University

Project Title: Developing New Alternative Energy in Virginia: Bio-Diesel from Algae

Principal Investigators: Dr. Patrick Hatcher



This project entails two patent applications. 1) Method for Separation of Methoxylated Glycerols from Biodiesel in High-Temperature Methylation (#61/535,525); 2) Production of glycerol related products from a high temp reaction (#13/204,884).

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3.0 Executive Summary

The overall objective of this study was to select chemical processing equipment, install and operate that equipment to directly convert algae to biodiesel via a reaction patented by Old Dominion University (Pat. No. US 8,080,679B2). This reaction is a high temperature (250-330^{o}C) methylation reaction utilizing tetramethylammonium hydroxide (TMAH) to produce biodiesel. As originally envisioned, algal biomass could be treated with TMAH in methanol without the need to separately extract triacylglycerides (TAG). The reactor temperature allows volatilization and condensation of the methyl esters whereas the spent algae solids can be utilized as a high-value fertilizer because they are minimally charred. During the course of this work and immediately prior to commencing, we discovered that glycerol, a major by-product of the conventional transesterification reaction for biofuels, is not formed but rather three methoxylated glycerol derivatives are produced. These derivatives are high-value specialty green chemicals that strongly upgrade the economics of the process, rendering this approach as one that now values the biofuel only as a by-product, the main value products being the methoxylated glycerols. A horizontal agitated thin-film evaporator (one square foot heat transfer area) proved effective as the primary reactor facilitating the reaction and vaporization of the products, and subsequent discharge of the spent algae solids that are suitable for supplementing petrochemical-based fertilizers for agriculture. Because of the size chosen for the reactor, we encountered problems with delivery of the algal feed to the reaction zone, but envision that this problem could easily disappear upon scale-up or can be replaced economically by incorporating an extraction process. The objective for production of biodiesel from algae in quantities that could be tested could not be met, but we implemented use of soybean oil as a surrogate TAG feed to overcome this limitation.

The positive economics of this process are influenced by the following: 1. the weight percent of dry algae in suspension that can be fed into the evaporator, 2. the alga species' ability to produce a higher yield of biodiesel, 3. the isolation of valuable methoxylated by-products, 4. recycling and regeneration of methanol and TMAH, and 5. the market value of biodiesel, commercial agricultural fertilizer, and the three methoxylated by-products. The negative economics of the process are the following: 1. the cost of producing dried, ground algae, 2. the capital cost of the equipment required for feedstock mixing, reaction, separation and recovery of products, and reactant recycling, and 3. the electrical cost and other utilities.

In this report, the economic factors and results are assembled to predict the commercialization cost and its viability. This direct conversion process and equipment discussed herein can be adapted for various feedstocks including: other algal species, vegetable oil, jatropha oil, peanut oil, sunflower oil, and other TAG containing raw materials as a renewable energy resource.

4. Actual accomplishments in comparison with goals of the project.

A set of 8 objectives were defined for this project whose overarching goal was to demonstrate the commercial feasibility of using the ODU-patented approach for converting algae to biodiesel and co-products such as fertilizer. The following discussion presents each of those objectives and provides an evaluation of the accomplishments made with what was anticipated.

4.1. Objective 1: Determine and select an optimum technology.

We were to conduct trials of identified reactor technologies (fluidbed and wiped/thin film) with identified engineering firms (LCI Corporation, Charlotte, NC and Artisan Industries,

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Waltham, MA) to select the best approach and reactor design. This objective was met in its entirety as the reactor chosen (horizontal thin film reactor) was much better suited than fluidized bed technology, especially for the high solids content of the feedstock algae. Use of a fluidized bed reactor in our laboratory indicated that the spent residue from algae became sticky and quickly clogged the reactor bed.

4.2 Objective 2: Determine optimal design and scale of the selected reactor technology and distillation/condensation system for product separation.

In this objective, we would work with potential manufacturers to select the optimum reactor design, feed system, and product recovery (condenser) system. This objective was accomplished as foreseen at the time. We could not predict that we would encounter delivery problems with the algal feed.

4.3. Objective 3: Purchase and install optimal reactor technology with distillation/condensation system.

We selected Artisan Industries, Inc. as the vendor whose equipment would be best suited for our reactor system. Moreover, they could deliver the equipment within the timeframe mandated by the Commonwealth of Virginia for equipment purchased with funds made available as cost-sharing on this project. The equipment was delivered and installed at the ODU algal farm near Hopewell, Virginia. We sought other locations on campus but these were not acceptable for a variety of reasons, the cost of setting them up being a major one. The downside of having the reactor, now called the Algaenator, at a remote location was that travel to the site for project personnel was an important scheduling and cost consideration. These activities and the inability of subcontractors to Artisan to deliver components in a timely manner led to delays in the timeframe allocated for installation and a request was made and granted to extend the project at no cost to DOE.

4.4. Objective 4: Determine the optimal character of algal biomass (e.g., algal species, water content, mix of algal paste + methanol + catalyst) for injection and conversion in the reactor.

The major goal of this objective was to determine how algal biomass could be most effectively fed to the Algaenator for efficient conversion to biodiesel and other co-products, we encountered two problems. First, we determined that the algae must be dried prior to mixing with the TMAH/methanol reactants. Second, the feed mixture was not compatible with the original Algaenator feed system. Some modifications were made to overcome this difficulty with partial success which limited successful completion of other objectives. The main issue was the dried algae mixed with methanol/TMAH reagent induced plugged feed lines due to low feed rates required. This was due mainly to the heat-transfer area size (1 square foot) that was chosen based on cost and available resources. To overcome the solids feed limitation, we experimented with soybean oil as a surrogate for algae oil to demonstrate that the Algaenator could efficiently convert the oil to biodiesel and other products. In doing this, we discovered some very important by-products of our process. Instead of glycerol, the common transesterification reaction by-product of soybean oil conversion, the TMAH methylation reaction yields methoxylated glycerols that are much more valuable chemical products than glycerol. We filed for patents, realizing that the high value of methoxylated glycerols (more than $100/gallon) improves the economics of this conversion process.

4.5. Objective 5: Optimize operating conditions in the reactor.

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The goal of this objective was to determine optimum operating conditions in the Algaenator. We utilized soybean oil as a surrogate for algal oil because of the problems we encountered in the delivery system for the algal solids. Once we established optimum conditions of temperature, feed rate, condenser temperatures, and pressure, we established conditions upon which we could test delivery and production of biodiesel products from algae. We consider this objective being met as the soybean oil performed well and gave excellent recoveries upon which to base system economics, energy balances, and material balances. Only minor adjustments were required to obtain optimum operating conditions for algal feed.

4.6. Objective 6: Characterize gaseous, liquid, and solid products produced from the various tests conducted in Objective 5.

The goal of this objective was to isolate and characterize by advanced analytical methods (GC/MS, HPLC, NMR, etc.) the products from the Algaenator. Detailed chemical composition of products that include biodiesel, recovered water and methanol, and other gaseous and condensed liquid products was to be obtained from all test runs produced in the work of Objective 5. From section 5.3 below, one can show that this objective was met for the most part. Several of the early test runs were not examined in as much detail because we were mainly optimizing the reactor temperature conditions to obtain optimum product yields and characterization of the various products was not as important. Once the main operating temperatures were established and there appeared to be a more predictable yield from the various product streams of the Algaenator, we systematically characterized the products. In some cases, the batch runs were replicates and designed to accumulate products. In these instances, we pooled the products for analysis.

4.7. Objective 7: ASTM testing of biodiesel from the various test runs of the chemoreactor.

The goal was to isolate and characterize the biodiesel fuel by standard methods either in house or by commercial labs, provided that yields were sufficient. The yields for biodiesel from algae were not sufficient to obtain the required 2 L sample for testing. Thus, we were unable to meet this objective for the algal biodiesel. For the soybean oil, we were able to collect sufficient biodiesel by pooling of several runs but only one analysis was provided.

4.8. Objective 8: Determine financial and energy budget for the reactor at the proposed scale.

The pilot scale reactor provided essential data for determining financials and energy to demonstrate the commercial feasibility of using the ODU-patented approach for converting algae to biodiesel and co-products.

4.9. Objective 9: Determine the best estimate of the financial and energy budget for the developed technology at industrial scales (ranging from one hundred to one million metric ton algae per day).

From observations of energy usage for the pilot scale facility, economic projections were estimated for the developed technology at industrial scale. A ten metric ton of algae per day (dry weight) and a one hundred metric ton of algae per day production operations were considered. Contiguous installations larger than 100 metric tons of algae per day would likely be unwieldy. Units as large as one million metric tons of algae per day would likely require multiples of 100 metric ton, non-contiguous units.

5. Summary of project activities within each of the project objectives

All protected data is indicated throughout the report highlighted in yellow.

5.1. Objective 1 (Task 1). Determine optimum reactor technology

This objective is to seek out the optimum design for a pilot-scale reactor that allows us to demonstrate the feasibility of our patented technology in which algae is converted in a one-step process to biodiesel and other valuable by-products. We evaluated design options for a reactor capable of taking wet algal concentrate (paste) into the reaction zone with added reagent (TMAH), heating the mixture to an operating temperature of 250^{o}C, and then separating volatile products from liquid products and from solid residues. We determined that the most suitable design that allows wet paste to be heated in an oxygen-free atmosphere (required for our process) is the horizontal, agitated, thin film reactor described below. Several manufacturers and design options were available and this portion of the research sought out the best design for our needs. Algae paste and appropriate reagents were sent to each of three potential vendors and tested for the efficacy of handling and conversion to liquid products. The reactor design with best performance and handling of our algae paste/catalyst mixture was to be selected for the construction task. In our original proposed study, we had subdivided this objective into two tasks, one to select the optimum reactor technology and another to select an optimum distillation/condensation system. We determined that our project funds were not sufficient to implement a very sophisticated distillation/condenser system and that the reactor manufacturer was able to supply a low-cost two-stage condenser system that would adequately serve our needs.

5.1.1. Selection of an optimum reactor technology including condenser (Objective 2)

Early laboratory work was conducted on feeding algae slurry to batch reactor equipment and continuous feed system. The batch reactor equipment, consisting of an electric heater and a condenser, was inefficient for large quantities because algal solids, called "residue," necessitated cleaning and translated to significant downtime. A continuous feed system was the preferred reactor type. A fluidized bed reactor was constructed in the laboratory and evaluated using sand as the fluidized medium. However, algae residue remained in the sand after the volatiles were vaporized and the sand became sticky and no longer fluidized and blocked the algae slurry feed. Our experiments clearly indicated that fluidized bed technology could not be employed for our patented one-step process of converting algae to biodiesel.

Design options were evaluated for a reactor capable of transporting algae slurry into the reaction zone with added TMAH, heating the mixture to an operating temperature of 250-330^{o}C in an oxygen-free environment, and then separating volatile products from solid residue. Also, the demonstration plant should be able to process biomass produced by a one acre algae growing facility (100 kg of algae per day). The most suitable design to meet these criteria was determined to be the horizontal agitated, thin-film reactor. The equipment also was specifically designed to discharge solids without physically inhibiting the heat transfer area or accumulate in the equipment.

The design utilizes rotating blades within a cylindrical reactor to deliver centrifugal force flinging the feed material against the heated cylinder wall (heated by a flow of heat transfer oil to 250-332°C) and producing a thin film of feed between the rotor blades and process wall. The algae, methanol, and TMAH mixture are fed into one end of the reactor, flung on the hot wall of the cylinder, and moved along the heated reactor wall while evaporation of the products occurs. The solids move along the cylinder wall and become progressively more concentrated until the spent algae (or algae residue) is discharged (Figure 5.1). The solids' short residence time (on the order of seconds) is vital for preserving the integrity of the fertilizer potential. Methanol,

trimethoxypropane, glycerol derivatives, and fatty acid methyl esters (FAME) are vaporized and carried from the reactor by an inert carrier gas and vacuum to a condenser.

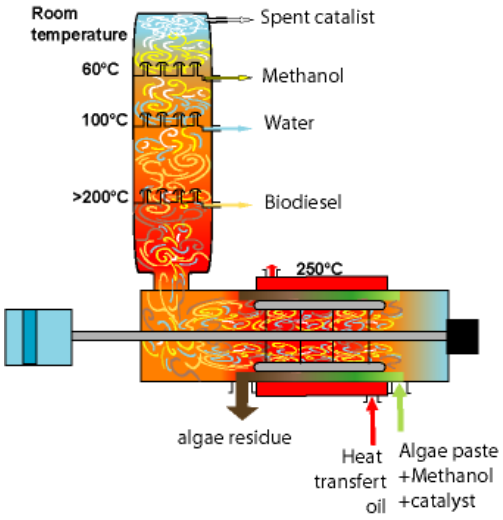

Figure 5.1: Depiction of agitated, horizontal, thin film evaporator

5.1.2. Purchase and installation of reactor and condenser (Objective 3)

Several manufacturers and design options of vertical and horizontal thin-film evaporators were considered and contacted (LCI Corporation, Charlotte, NC; Artisan Industries Inc., Waltham, MA; Pfaudler, Inc., Rochester, N.Y; VTA GmbH, Niederwinkling, Germany; Chem Tech Services, Rockdale, IL).

Some preliminary testing of algae slurry was done by LCI Corporation and Artisan Industries, Inc. However, a purchasing and delivery deadline attached to the project funding from the Commonwealth of Virginia (cost sharing on this grant) necessitated the selection of Artisan Industries, Inc. They provided a one square foot Rototherm E horizontal thin-film evaporator with condenser and associated equipment that met the aforementioned criteria and the purchasing deadline (see detailed drawings in Appendix Figure A5.1.2). Other equipment in the system included: a hot oil heating and circulating unit, a 7.5 $ft.^2$ U-tube condenser, a condenser fluid temperature control and circulating unit, and a liquid nitrogen cold trap for collecting gaseous products followed by a vacuum pump for the entire system (see Appendix Table A5.1).

The equipment was installed 62 miles northwest of the ODU campus on rural land near Spring Grove, VA. An appropriate site closer to the campus was sought but various issues related to safety prevented a cost-effective solution. A steel building was built on a concrete pad 18 ft. x 31 ft. The building provided safety compliance for the hazardous chemical processing equipment, heating, cooling, and electrical power distribution (see Figures 5.2-5.5). The local utility company could not provide 460-480 V, 3 phase service, so a 150 kW portable electric generator provided the power supply required. A freshwater well was also installed to supply adequate cooling for the system.

A mechanical and electrical contracting company (Quality Plus Services) installed mechanical components, insulated heated materials, and safely engineered the wiring of the entire system.

The equipment trials were commenced in early April 2011. By mid-April, conversion experiments were performed using soybean-based vegetable oil as a feedstock for biodiesel.

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These reactions provided indispensable operational experience of the entire system and its capabilities concerning the reaction, condensation settings, and vacuum control. The hot oil supply was limited to 340˚C, so a vacuum was necessary to lower the boiling points of longer carbon chain components and achieve full evaporation of biodiesel components.

Artisan Industries furnished a standard slurry feeding system (see Figure 5.6 where the detailed drawing is provided for the entire system). The initial attempt to feed 35% slurry by weight of ground algae and methanol based liquids obstructed the system immediately and prompted a redesign of the entire feed system. At this point, a time extension was requested for completion of the project, and revision of the slurry feed system was undertaken. The extension was granted and slurry characteristics and system requirements were studied and redesigned for successful operation. Further discussion will be detailed elsewhere in the report.

In the meantime, the equipment was used to react triglycerides from vegetable oil (soybean based) in order to refine operational experience and generate enough FAME and by-products to facilitate the separation of these materials which formed complex mixtures. Separation methods will be discussed in detail later.

Figure 5.2: Photograph of pilot scale demonstration facility.

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Figure 5.3: Photograph of agitated, thin-film evaporator.

Figure 5.4: Motor control center.

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Figure 5.5: Hot oil unit and Delta T condenser control unit.

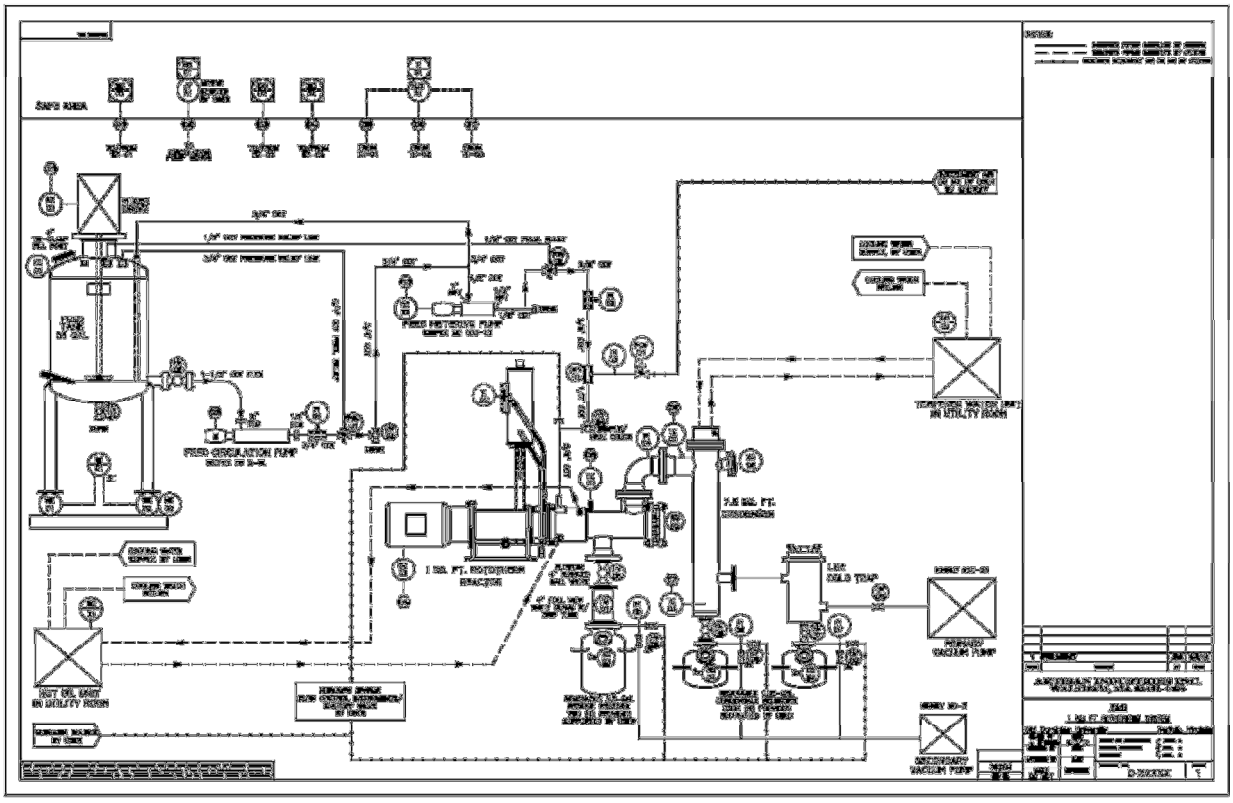

Figure 5.6: Process and instrumentation diagram for the system

5.2 Optimizing operation of the reactor system (Task 2, Objectives 4 and 5)

All protected data is indicated throughout the report highlighted in yellow.

Once constructed, the reactor (called the Algaenator) operating with full supply of feedstock needed to be tested and its characteristics and efficiency evaluated. Small design modifications were undoubtedly needed to optimize operation. Isolated fractionally-distilled products from various Algaenator runs were collected and chemically tested in our laboratories using a full range of analytical tools specifically designed to evaluate the organic compounds recovered (see section 5.3). The biodiesel fraction was analyzed by gas chromatography/mass spectrometry to evaluate chemical composition. We have already shown that the process yields biodiesel with fatty acid methyl esters as the main products which compare well with biodiesel that is commercially available from soybean oil. The biodiesel was to be tested for ASTM fuel specifications if sufficient material was available.

The Algaenator testing evaluated operating temperatures, rate of feedstock introduction, relative proportion of TMAH used, and conversion efficiency based on algal feedstock composition. We obtained records of energy use and product recovery to evaluate mass and energy balances under each of the planned test conditions. In addition to algal feedstock, we deemed it necessary to examine the Algaenator performance with pure vegetable oil. We chose vegetable oil from soybeans. This material provided the model feedstock upon which we could base Algaenator performance, with the assumption that the triglyceride composition of the soy vegetable oil was somewhat similar to that expected from algae oil.

A large number of experimental tests of the performance of the Algaenator system in converting both soybean oil and algae were made over the course of this study. Each experiment is denoted by a batch # whose conditions, product yields, and other information are listed in Table 5.1.

5.2.1 Optimal feedstock character (e.g., algal species, water content, mixture of algae, methanol, and catalyst) for injection and conversion in the reactor (Objective 4)

A survey of native wild-type natural algal species was taken to determine the ideal species for biodiesel conversion according to carbon, nitrogen, and lipid content. The algae samples collected were analyzed for their ability to produce biomass and lipids that can be converted to fatty acid methyl esters (FAME). Analysis of a concentrated dried algae by an independent laboratory (Solution Recovery Services) indicated that the lipid contents of 21.2% can be expected. The direct conversion of biomass to FAME was accomplished using an ODU patented reaction (Pat. No. US 8,080,679B2). The FAME produced from different algae samples were compared using gas chromatography mass spectrometry (GC-MS, Johnson et al., in press). The ODU reaction generated similar FAME for various algal species. The amount of FAME produced from each native algal candidate was compared for selection. In addition, each native species was analyzed by Dr. Elizabeth Canuel (Virginia Institute of Marine Sciences) by conventional Soxhlet extraction coupled to FAME analysis by GC-MS.

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Table 5.1: Experiment table with specified reaction conditions.

Batch								Start Feed Wt.			Start	Rototherm	Condenser		Leftover	Amount injected				
#	Reactant	Date & Time	Hot Oil T	Pressure	T1 °C	T2 °C	T3 °C	Sample	TMAH/MeOH	MeOH	Total	R bot	Cond.	Cold Trap	Feed Jar	kg inj.	Notes:			
			°C	Torr	vapor	Reactor	Cond.	kg	kg	kg	kg	kg	kg	kg	kg	kg				
1	VegOil	4/13/11 18:07	270	750	177.8	218.3	29.4	0	0	0	23.09	3.49	0.88	3.90	0	N.D	Feed tank load cells not working			
	Feed rate=2.0 gal/hr																			
2	FlocAlgae	4/20/11 14:00	298.9		Recirculation Pump broke while pumping 2mm ground, dried, flocculated algae											N.D	Feed system needs redesigned			
3	VegOil	5/4/11 17:00	297.2	715-735	93.3	247.5	20.0	1.02	1.61	0.00	2.77	1.72	1.11	0	0.05	2.72	Peristaltic pump used			
	Feed rate=2.0gph					256.7										2.88	# recovered			
4	VegOil	5/10/11 13:55	301.7	500	105.2	253.9	21.7	1.16	1.63	0.00	2.79	0.36	0.25	0.16	0.00	2.79				
	Feed rate=2.0 gal/hr		300.0		130.6	263.8	23.3									0.77	kg recovered			
5	VegOil	5/11/11 12:23	293.3	700	62.8	214.4	19.4	1.16	1.61	0.00	2.77	1.56	0.66	0	0.00	2.77				
		hold T constant and vary Press			83.3	86.1	16.1									2.22	kg recovered			
6	VegOil	5/11/11 14:29	310.0	700-640	73.6	263.3	23.3	1.16	1.61	0.00	2.77	1.11	1.25	0.05	0.00	2.77				
	Feed rate=2.0 gal/hr				123.9	276.1	21.7									2.40	kg recovered			
7	AlgPaste	5/12/11 14:45	340.6	600-640	101.7	136.7	23.9	0.40	0.30	0.32	2.62	0.45	1.75	0	0.06	2.56				
	Feed rate=2.0 gal/hr							2.00	kg wet weight of Centrifuged algae paste							2.20	kg recovered			
8	FlocAlg	6/14/11 17:06	341.7	300	82.8	300.6	23.9	0.11	0.05	0.11	0.27	0.02	1.13	0.00		0.81				
	Feed rate=2.0 gal/hr							1.78	kg total wet weight at start							1.16	kg recovered			
9	FlocAlg	6/16/11 0:00	293.3	300	62.2	282.2	17.2	3.76	1.66	7.08	12.49	0.20	3.79	0.00	1.1229	31.13	solid residue collected			
	Feed rate=2.0 gal/hr				108.3	298.9	21.7	23.52	kg total wet weight at start							3.99	kg recovered			
10	FlocAlg	6/24/11 15:46	341.7	360-405	47.8	235.6	19.4	2.81	0.98	10.52	14.31	1.54	12.00	0	N.D.	N.D.				
	Feed rate=2.0 gph		338.9		115.0	293.3	14.4		Hot Oil fuse blew at around 5:30pm							13.54	kg recovered			
11	VegOil	7/20/11 17:22	332.2	700	142.8	303.3	57.8	0.86	2.31		3.18	0.18	0.09	0.73	1.77	1.41				
	Feed rate=2.0 gal/hr		26 min run		154.4	315.6	60.6									1.00	kg recov'd	71.0%	recov'd	
12	VegOil	7/20/11 18:21	332.2	700	159.4	317.8	26.9	0.48	1.29	0.00	1.41	0.27	1.34	0.00	0.00	1.40				
	Feed rate=2.0 gal/hr				188.9	328.3	25.0									1.61	kg recov'd	114.9%	recov'd	
13	VegOil	7/26/11 14:06	304.4	700-760	87.2	253.3	37.8	0.83	2.17	0.00	3.00	0.17	0.05	0.66	1.33	1.66	Condenser set to 82°C			
	Feed rate=2.0 gal/hr				127.8	267.2	52.2		1.17					0.26	0.00	0.00	0.89 kg recov'd	53.3%	recov'd	
14	VegOil	7/26/11 14:44	304.4	600-500	118.3	262.2	55.0	0.37	0.96	0.00	1.33	0.31	0.05	0.73	0.00	1.33	Condenser set to 82°C			
	Feed rate=2.0 gal/hr				132.2	265.6	58.3									1.08	kg recov'd	81.3%	recov'd	
15	VegOil	7/28/11 14:23	304.4	100	98.3	258.9	30.0	0.62	1.62	0.00	2.24	0.11	0.74	0.85	0.03	2.21				
	Feed rate=3.0gal/hr				99.4	267.8	21.7									1.70	kg recov'd	76.7%	recov'd	
16	VegOil	7/28/11 15:34	304.4	100	133.9	260.6	21.1	0.72	1.93	0.00	2.65	0.15	0.91	0.87	0.06	2.59				
	Feed rate=3.5gal/hr						30.0									1.92	kg recov'd	74.4%	recov'd	
17	VegOil	8/9/11 12:15	332.2	100	151.1	281.7	26.1	0.816	2.177	0.00	2.994	0.166	1.276	0.857	0.002	2.991				
	Feed rate=3.0gal/hr						21.7									2.30	kg recov'd	76.8%	recov'd	
18	VegOil	8/16/11 16:10	332.2	100	166.7	292.2	27.8	1.633	4.058	0.00	5.691	0.346	1.385	2.776	0.011	5.680				
	Feed rate=3.0gal/hr						28.9									4.51	kg recov'd	79.3%	recov'd	
19	VegOil	8/19/11 13:44	332.2	100	165.0	282.2	25.0	1.546	4.324	0.00	5.870	0.414	2.099	1.912	0.007	5.863				
	Feed rate=3.0gal/hr						27.2									4.42	kg recov'd	75.5%	recov'd	
20	VegOil	8/24/11 11:32	332.2	100	142.2	281.7	26.7	4.099	21.917	0.00	26.016	1.932	8.268	13.528	0.003	26.013				
	Feed rate=3.5gal/hr						27.2									23.73	kg recov'd	91.2%	recov'd	
21	VegOil	8/25/11 14:40	332.2	100	165.0	276.7	27.2	10.750	28.401	0.00	39.151	2.213	9.867	19.389	0.007	39.144				
	Feed rate=3.5gal/hr						29.4									31.47	kg recov'd	80.4%	recov'd	
22	VegOil	8/31/11 14:40	332.2	100	175.6	285.0	28.3	4.921	13.217	0.00	18.138	1.166	5.427	8.108	0.008	18.129				
	Feed rate=3.5gal/hr						27.8									14.70	kg recov'd	81.1%	recov'd	
23	VegOil	9/9/11 14:40	332.2	100	183.3	282.2	28.3	8.214	21.889	0.00	30.103	1.620	9.005	13.351	0.029	30.073				
	Feed rate=3.5gal/hr						30.6									23.98	kg recov'd	79.7%	recov'd	
24	VegOil	9/19/11 13:00	332.2	100	183.3	282.2	28.3	1.636	4.371	0.00	6.007	0.303	2.914	1.625	0.003	6.004				
	Feed rate=3.5gal/hr						30.6									4.84	kg recov'd	80.6%	recov'd	
25	CrudeSoy	10/6/11 13:04	332.2	100	183.3	282.2	28.3	1.652	4.336	0.00	5.988	0.303	2.461	1.813	0.000	5.988				
	Feed rate=3.5gal/hr						30.6									4.58	kg recov'd	76.4%	recov'd	
25b	Algae mixture with TMAH/MeOH did not feed into the Rototherm at 5.5 gph. It could not travel 2.5' vertically and 3' horizontally into a 1/4" I.D. tubing.																			
	The input to Rototherm also plugged badly due to MeOH boil off.																			
26	Algae	10/12/11 15:20	315.6	200	52.8	277.8	21.1	1.996	0.689	3.95	6.632	0.386	1.420	0.558	0.000	2.631				
	Feed rate=5.5gal/h excess polymer															2.36	kg recov'd	89.8%	recov'd	
27	Algae	10/14/11 14:42	315.6	200	118.3	283.3	22.8	2.000	0.671	4.21	6.886	1.061	3.359	0.000	1.422	5.463				
	Feed rate=5.5gal/hr									0.612						4.42	kg recov'd	80.9%	recov'd	
28	Algae	10/18/11 13:38	315.6	200	118.3	283.3	22.8	4.007	1.143	8.10	13.246	1.758	4.229	1.706	6.967	6.279				
	Feed rate=5.5gal/hr		injected for ~25 mins, meoh was added to unplug the line							0.6759						7.69	kg recov'd	122.5%	recov'd	
29	Alg. <1mm	10/21/11 14:41	315.6	150	91.7	273.3	27.2	2.041	0.680	3.83	6.550	1.513	2.321	0.762	1.172	5.378				
	Feed rate=8.5gal/hr															4.60	kg recov'd	85.5%	recov'd	
30	Alg. <1mm	10/25/11 14:42	315.6	150	94.4	292.2	22.8	4.001	1.325	8.17	13.498	2.130	6.146	1.814	5.135	8.363				
	Feed rate=5.5 (5.8)gal/hr															10.09	kg recov'd	120.6%	recov'd	
31	SoyOil	11/3/11 11:20	332.2	100	126.7	273.9	27.8	1.476	4.082	0.00	5.558	0.249	1.573	2.148	0.122	5.437				
	Feed rate=3.5gal/hr															3.97	kg recov'd	73.0%	recov'd	
32	Alg. <1mm	11/11/11 15:21	315.6	150	43.3	265.6	12.8	4.011	1.315	7.93	13.255	0.635	1.860	0.028	10.433	2.822				
	Feed rate=5.5gal/hr															2.52	kg recov'd	89.4%	recov'd	
33	Alg. <0.6mm	11/29/11 16:00	315.6	190	83.3	251.1	28.3	3.937	1.129	7.92	12.987	2.930	4.545	1.287	2.930	10.057				
	Feed rate=5.5gal/hr							3.048	estimated lbs algae injected							8.762	kg recov'd	87.1%	recov'd	
34	Alg. <1mm	12/9/11 14:45	332.2	190	93.9	272.8	17.2	5.162	1.499	10.24	16.903	3.821	8.447	0.000	3.303	13.600				
	Feed rate=5.5gal/hr					237.8		4.080	estimated kg algae injected							12.268	kg recov'd	90.2%	recov'd	
35	Alg. <1mm	12/14/11 14:39	332.2	170	66.7	278.3	17.2	5.459	1.588	11.19	18.233	3.219	7.092	0.000	7.194	11.039				
	Feed rate=5.5gal/hr			190		236.7		3.305	estimated kg algae injected							10.311	kg recov'd	93.4%	recov'd	
36	VegOil	1/12/12 14:50	331.7	210	81.7	273.9	18.9	6.913	13.542	0.00	20.455	0.886	7.201	1.444	2.486	17.969	Feed rate 3.5 gal/hr			
	Feed rate=3.5gal/hr			220		281.7		4.713	estimated kg algae injected							9.531	kg recov'd	53.0%	recov'd	
	dual feed system: 0.907 gph VegOil + 2.593 gph TMAH/MeOH																			
37	VegOil	2/1/12 14:30	332.2	150	81.7	273.9	18.9	5.680	12.605	0.00	18.285	1.223	12.912	1.961	0.809	17.476				
	Feed rate=3.5gal/hr			200		281.7										35.485	kg recov'd	92.1%	recov'd	
	dual feed system: 0.943 gph VegOil + 2.561 gph TMAH/MeOH															0.021	absolute uncertainty			
38	VegOil	2/9/12 13:51	332.2	150	81.7	273.9	18.9	11.100	23.140	0.00	34.239	2.511	24.765	2.888	2.263	31.977				
	Feed rate=3.20gal/hr	3.0 hr run		175		281.7										66.632	kg recov'd	94.5%	recov'd	
	dual feed system: 0.860 gph VegOil + 2.341 gph TMAH/MeOH							amnt injected								0.000				
39	VegOil	2/29/12 11:20	332.2	150	129.4	269.4	16.1	5.593	8.514	0.00	14.107	1.239	7.972	0.877	3.450	10.657				
	Feed rate=3.20gal/hr			160		271.7										22.374	kg recov'd	95.2%	recov'd	
	Dual feed system: 0.860 gph VegOil + 2.341 gph TMAH/MeOH																			

All protected data is indicated throughout the report highlighted in yellow.

Scenedesmus/Desmodesmus sp. contained 6% FAME, but its rapid reproduction rate (doubling every 1-2 days) demonstrated favorable characteristics for overall biomass production and large scale biodiesel production. The solid-state ^{13}C NMR spectrum shown in Figure 5.7 indicates that this algal mixture contains mostly proteinaceous material as well as lipids and carbohydrates in lower abundance. The lipids are mainly fatty acids associated with triacylglycerides (TAG). We have developed an NMR method to determine the TAG content of dried algae samples (Johnson et al., in preparation). The procedures for measuring the fat contents in algae are tedious, time consuming, and usually involve large quantities of toxic organic solvents. In this study, we evaluated noninvasive methods involving different NMR techniques including direct polarization magic angle spinning (DPMAS) and high resolution magic angle spinning (HR-MAS) NMR for quantification of fat contents in algae samples collected from different aquatic environments, as well as cultured algae. DPMAS provides an accurate estimation of polymethylene units, the major structural component of algal fats, but it requires about one hundred milligrams of algal matter and about 20 h of instrumentation time. In contrast, HR-MAS only requires several milligrams of dried algal matter that is swelled in a mixture of deuterated methanol and dichloromethane. Within less than half a minute, a HR-MAS ^{1}H NMR spectrum of an algae sample can be obtained for quantification of fat content based on the CH_2 peak (Figure 5.8), whose peak area is in excellent linear relationship with the amount of fats (FAMEs) in algae (Figure 5.9). Now, not all fatty acids are bound as glyceryl esters; however, the TMAH approach methylates both ester bound and free fatty acids, so the calibration below gives a good estimate for expected yields of FAME in our reactor.

Growth studies showed that high nutrient concentrations can selectively favor growth of Chlorophycean (green) algae such as *Scenedesmus/Desmodesmus sp*. (Hyenstrand et al., 2000). *Scenedesmus/Desmodesmus sp*. was able to overcome competition from other invasive species by means of high nitrogen and phosphorous concentrations in the growth media. This key advantage was essential to maintaining favorable species for feedstock conversion. However, the water content of *Scenedesmus/Desmodesmus sp*. was not favorable for efficient conversion. The heat of vaporization of water was an inefficient process (2257 kJ/kg); contrastingly, hydrocarbons required approximately one-half the amount of heat (methanol-1104 kJ/kg) to vaporize in the reaction. Therefore, the water was removed before the reaction to reduce energy consumption.

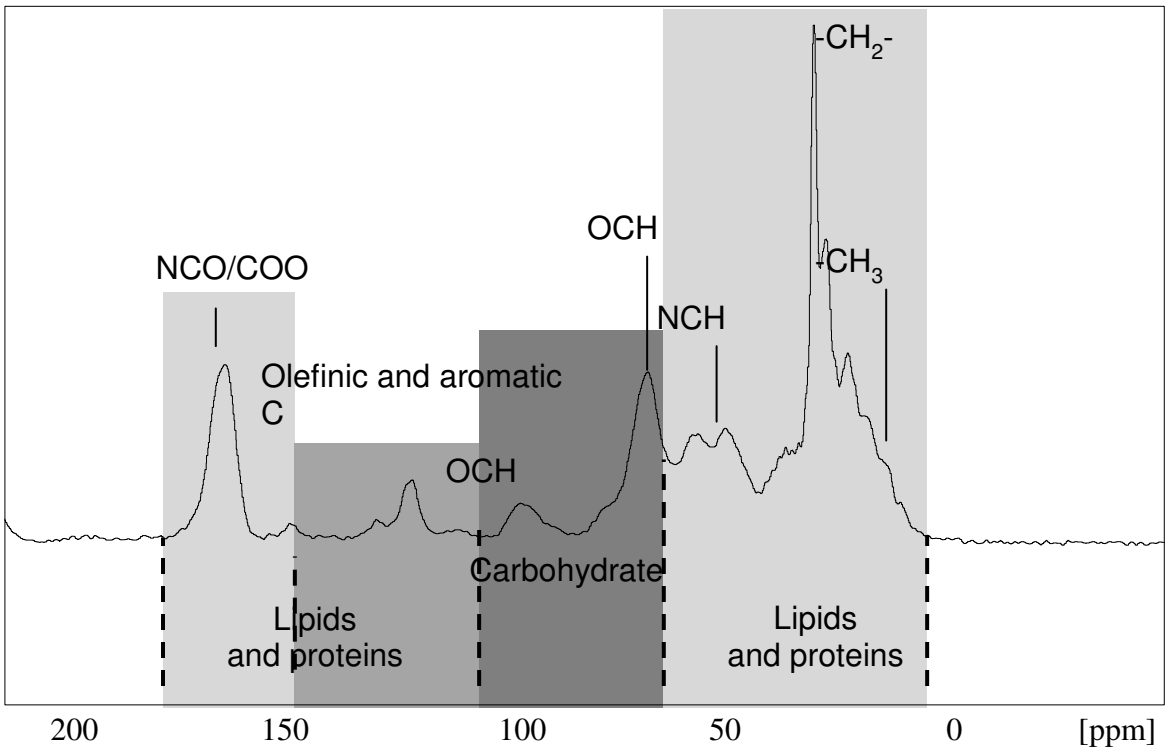


Figure 5.7: Solid-state ^{13}C NMR spectrum for the dried algae showing the various components.

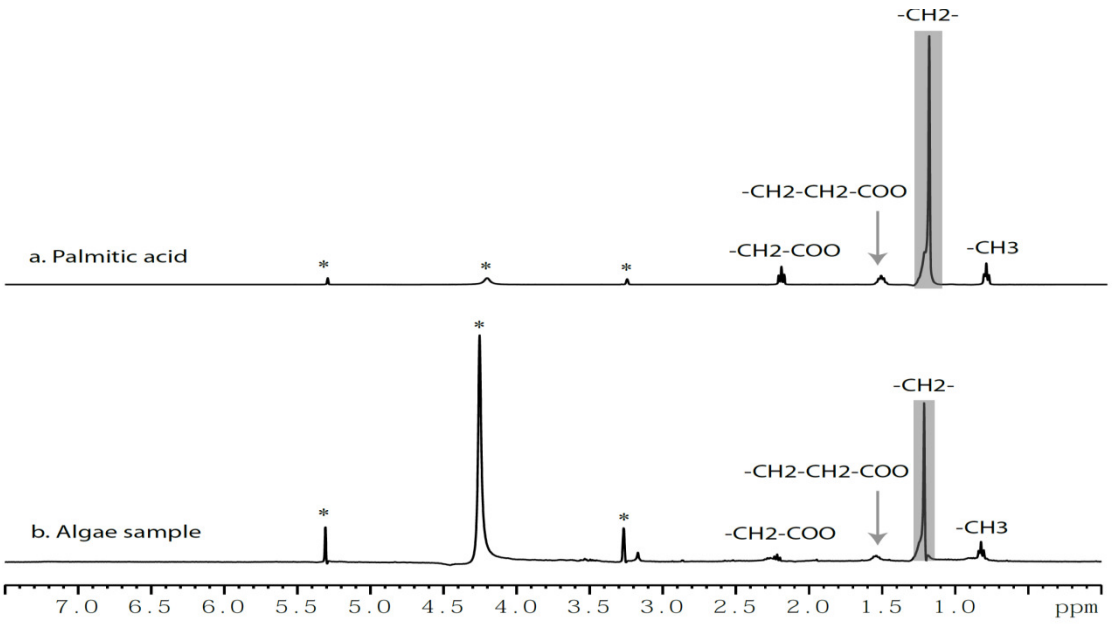


Figure 5.8. HR-MAS ^{1}H spectra of algae and palmitic acid which is used as a calibrant to measure the intensity of CH_2 groups. Peaks labeled with * are solvent.

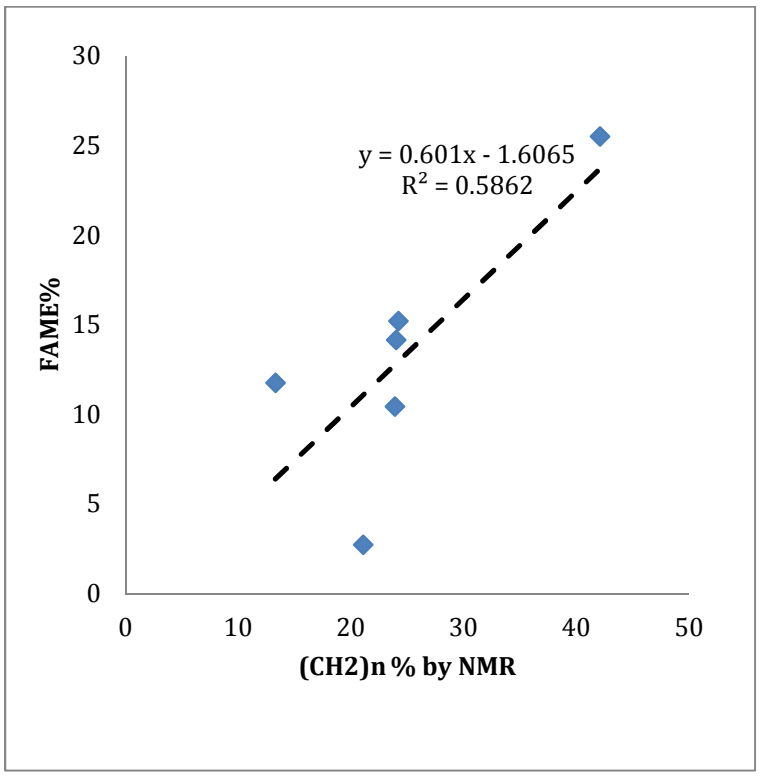


Figure 5.9. Calibration curve relating the amounts of fatty acid methyl esters produced from various algae and the peak areas of the CH_2 peak in the HR-MAS ^1H NMR spectra.

Separating algal biomass from its aqueous medium presents some difficulty because of the small physical size (typically 3-8 µm) of *Scenedesmus/Desmodesmus sp*. Two common methods of water treatment for suspended solids removal are sedimentation and centrifugation. Sedimentation utilizes gravity to settle out suspended solids, and centrifugation, similarly, utilizes a density difference to separate water effectively. Initial studies indicated the removal of only 43% of solids from continuous feed centrifuges operating at the one-acre algal farm. Therefore, some aggregation or pretreatment was necessary for water removal. A survey of common inorganic and organic coagulants was performed, and a high charge, high molecular weight polyacrylamide flocculant was efficient at a low dose so as not to interfere with the conversion process. The flocculated algae were then separated more easily from the supernatant water using rapid throughput filtration. Flocculated algae was dried and ground to a particle size that passed through a 2.0 mm screen.

Ground algae were mixed with other reactants based on triglycerides available for conversion. Initially, we calculated the stoichiometric amounts according to the average molecular weight of triglycerides detected in *Scenedesmus/Desmodesmus*, and we used a 3:1 molar ratio of TMAH reactant to triglycerides to methylate all three fatty acids into fatty acid methyl esters (FAME). However, from the studies conducted with soybean oils (see section 5.3), we determined that three methoxylated glycerol by-products were detected. These other by-products also required methylation and are methylated glycerol derivatives of high value. Therefore, an excess molar ratio of 6:1 (catalyst: triacylglycerides) was used to insure complete reaction of FAME and methylated glycerol derivatives.

5.2.2. Feedstock throughput determinations

The feed rate of slurry to the reactor was dependent on the ability of the one square foot heat transfer surface area to drive the reaction, vaporize the products, and effectively expel the spent algae residue. The reaction required temperatures above 250^{o}C to convert triglycerides to FAME but low enough temperature to not degrade the proteins (<400^{o}C) and other organic hydrocarbons. The reaction must occur in oxygen (O_2) free environment to prevent pyrolysis or charring; therefore, nitrogen (N_2) gas was used to purge the reactor before injection and aid in driving the feed. Injection rate or feed rate of the reactants was initially calculated according to the heat capacity range of the one square foot heat transfer area of the Rototherm recommended by the manufacturer. For algae slurry at 30% solids, the Rototherm could handle a heat flux calculated at a feed rate of 20.8 L/hr (5.5 gph).

The mixture of reactants, in addition to soybean oil and algae, also included methanol as the solvent for the TMAH. Sample introduction into the reactor was designed for pumped slurry. The horizontal thin film evaporator was designed for solids and liquids. A consistent, metered feed rate was necessary to establish equilibrium and determine the capacity and efficiency of the reactor and reaction at the pilot scale. In our initial test (batch #1), we utilized soybean oil and the system performed well. We immediately discovered with the initial design of the feed system (Figure 5.6) with algae as the feed (batch #2), that suspended algae particles would settle and obstruct the flow of slurry of methanol/algae because mechanical velocity is essential for keeping the solid dispersed. The problem was so severe that we destroyed a positive displacement pump in this first experiment with algae. This led to the realization that our feed system on the pilot reactor was not going to work properly. We recognize, however, scale-up of this reactor to a larger heating area (as one would scale to a 100 or more acre algae farm) would allow higher throughputs and concomitantly large bore sizes for the tubes delivering feed to the reactor. This would completely mitigate the problems we encountered as we could attain higher throughput velocities. Thus, the problems we encountered could not be readily solved at the scale of the designed reactor. We immediately abandoned the initial feed system and implemented a redesigned system (Figure 5.10) that used a peristaltic pump to deliver feed to the reactor. It functioned better than the designed system but also displayed settling and plugging. This limited the length of time we could operate with algae feed. The delivery of soybean oil and TMAH/methanol to the reactor was not impacted significantly.

One solution to increase throughput of algae slurry to the reactor was to use wet algae (20% solids, batches #7-9), but the miscibility of methanol, water, and FAME caused significant problems detecting and separating biodiesel from the other products of much greater abundance (91% H_2O, 6%CH_3OH, 2% TMAH, 1% FAME). By thoroughly drying the algae, a higher feed rate could be employed because H_2O vaporization was not necessary.

Batch #2 was mixed with 65% liquid to 35% solids ratio (w/w). However, dried algae required more liquid to maintain uniform suspension as observed by pumping slurry studies in the lab. Additional methanol was added to the 25%TMAH in 75% methanol to reach a 30% solids and 70% liquids ratio (w/w). The feed to the Rototherm was still intermittent because of the rapid sedimentation rate of algal particles in methanol. Agitation in the feed tank was crucial for mixing the slurry (500 rpm) as well as reducing the particle size of dried algae to pass through a 1.0mm sieve (18 US mesh). Some progress was observed in this respect (Batches #26-30); however, blockage still occurred sporadically because methanol's low viscosity compared to water caused particles to settle out faster in methanol than in water. As a reference point, we used a 5-7 ft./sec velocity rate for suspending sand (particle size 20-200 US mesh) in liquid to design a pump system to deliver the feed to the reactor effectively. A circulation loop at high

velocity (7.3 ft./sec) kept the mixture in suspension, whereby an aliquot could be pumped a short distance from the circulation loop to the reactor (Figure 5.10).

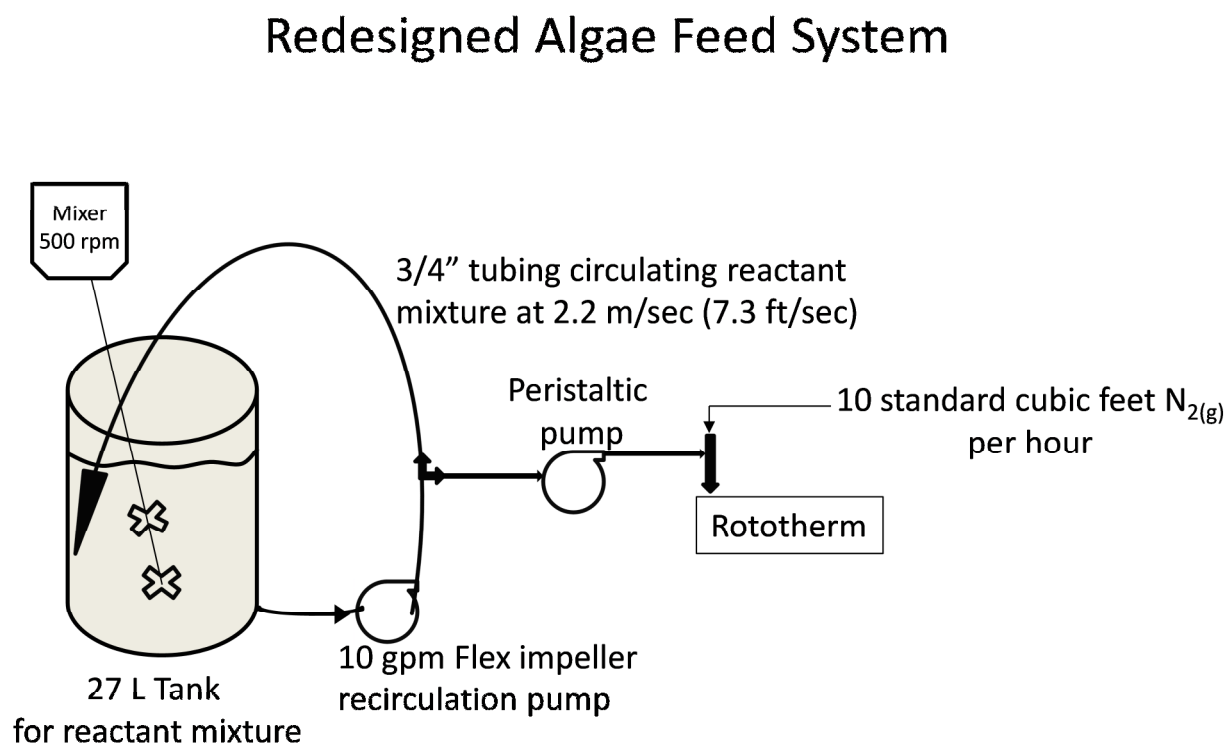


Figure 5.10: Redesigned algae slurry feed system schematic (not drawn to scale).

5.2.3 Optimizing reactor operating conditions (Objective 5)

Optimizing the operating conditions in the Algaenator reactor is essential for economic evaluation. Varying the thermochemical conditions needed for efficient and economic operation of the reactor/distillation system is an essential component of this objective. While our initial strategy was to utilize algal feedstock for this purpose, we decided to instead concentrate on vegetable oil due to its ready availability and the fact that it represents a concentrated model for triglycerides that might be expected in the algal biomass. Our belief was that the conditions under which vegetable oil were converted to biodiesel and other products would be very similar to what could be expected for algae.

There are numerous operating parameters requiring optimization. These included temperature of the reactor, the operating pressure (vacuum), condenser temperatures, and feed rate of vegetable oil or algal slurry. All experiments were conducted in runs that are labeled as batch # given in Table 5.1.

5.2.3.1 Optimizing reactor temperature

In the patented ODU reaction, a temperature of 250^{o}C was required to facilitate the reaction and vaporize the products. To begin, the reactor was set at a temperature of 270^{o}C. We labeled this experiment Batch #1. Observation of the process film temperature (TE01 in Figure 5.6) which read 218^{o}C clearly indicated that the operating temperature of the Algaenator was much lower than the temperature required for the reaction. For Batch #3, the temperature was increased to 297^{o}C, but the process film temperature was still lower (247.5^{o}C) than the target temperature. The temperature was increased to 310^{o}C for Batch #6, and we observed a process

film temperature of 263°C. This temperature was sufficient for accomplishing the reaction, but it did not provide enough driving force to vaporize all of the products to the condenser (45%). The hot oil system temperature was increased to its upper limit at 332°C for Batches #11 and 12, but it was apparent that the vaporization of products to the condenser needed more vacuum based on the weight percent recovery of products collected from the bottom of the Algaenator. At 332°C, only 80% of the products were being vaporized to the condenser. Therefore, vacuum was utilized to drive the product vaporization (further described in section 5.2.3.2). These same temperature and pressure conditions were used on multiple experiments (Batches #20-25, 31, 34-39) for reproducibility and product recovery studies. Additionally for Batches #26-30 and 32-33, the temperature setting was lowered to 315.5°C in order to confirm whether or not proteins and carbohydrates were degraded by the higher temperature. Batches #8 and 10 were run at 341°C and some evidence of temperature degradation was detected (further described in section 5.3).

5.2.3.2 Optimizing reactor pressure (vacuum)

The vacuum was employed to aid in the vaporization of the products and recovery. During the initial temperature study, the vacuum was maintained close to atmospheric pressure at 700-750 Torr. For Batch #14, the vacuum was brought to 550 Torr with the temperature held at 304°C; however, the Algaenator only effectively vaporized 80% of the products to the condenser and cold trap. The pressure was reduced to 100 Torr for Batch #15 to drive 95% of the vapor to the condenser and cold trap. However, algae feed required different vacuum conditions because methanol was the predominant condensate. The slurry mixture required 67.5% methanol by weight to maintain suspension which translated to smaller percent composition of FAME, glycerol by-products, and trimethylamine. The condenser was more effective at maintaining its film temperature for Batches #26-30 and 32-35 which in turn required less vacuum 150-200 Torr. Batches #36-39 also required less vacuum for maximum product recovery.

5.2.3.3 Optimizing feed rate

Initially, for the optimization of the reactor, the feed rate was lower than the recommended rule-of-thumb by the manufacturer. For Batches #1-14 the feed was 6.8 kg/hr (2.0 gph or 7.57 L/hr) which was below 11.3 kg/hr recommended. The feed rate was held constant until temperature and pressure settings of the system were understood more fully as discussed previously. As we began to try to explore the limits of the system by increasing the feed rate, we looked more closely at the thermodynamic capacity of the Algaenator in terms of heat flux or heat transfer capacity. Heat flux was calculated from a summation of the heat of vaporization, the sensible heat, and the superheating capacity of all the products. The feed rate of 7.57 L/hr (6.8 kg/hr) required a heat flux of 10,644 kJ/hr (10,089 BTU/hr). The manufacturer of the Algaenator gave a heat flux range of 8,440-18,991 kJ/hr*ft^2 (8,000-18,000 BTU/hr*ft^2). The feed rate was increased to 11.36 L/hr (3.0 gph) for Batch #15 and 13.25 L/hr (3.5 gph) for Batch #16. The heat flux for a feed rate of 13.25 L/hr (3.5 gph) was calculated to approach the upper limit of the heat load capacity of the Algaenator. Thus for Batches #38-39, the feed rate was reduced to 12.1 L/hr (3.2 gph) which required a total heat flux of 16,705 kJ/hr (15,833 BTU/hr) to maximize product recovery.

5.2.3.4 Condenser temperature

The temperature of the condenser was set according to the boiling points of the products formed during the reaction and the desired distribution of those products. The Delta-Therm Unit provided the temperature control for the condenser. It was designed to maintain condenser temperatures by means of 50% ethylene glycol/water solution through a heat exchanger that

utilized well water (17-18°C year round) to regulate temperatures between 18-121°C. The Delta-Therm pump provided 45.4 L/min (12 gpm) to the reactor condenser for heat exchange to maintain set point temperature.

The condenser proved effective for 18°C (actual operating temperatures were 20-25°C) for Batches #3-10, 12, 15-39, but a slight difference between vegetable oil and algae feedstock was noticed with the amount of methanol that was carried to the cold trap due to film temperature of the condenser. For higher temperatures, the condenser proved ineffective for separating product components from their mixtures. The relative proportions of the products remained very similar as the condenser temperature was varied for Batches #11-14. Therefore, the condenser was held constant and the vacuum setting was used for varying the amount of products condensed in the condenser and the cold trap. A more refined product separation was designed based upon lab separations detailed in the appendix (Figure A5.4.3).

5.3 Characterization of products (Task 3, Objective 6)

The isolation and characterization of products formed by the TMAH methylation reaction was imperative for understanding benefits and challenges of the process. The Algaenator has numerous product streams collected in different zones of the reactor (Figure 5.11) depending upon the feed. Be it algae or soybean oil, the feedstock is mainly triacyl glycerides (TAG). When these react with TMAH at high temperature (250°C or more) the fatty acids in TAG produce the corresponding methyl esters which constitute the biodiesel. The glyceryl backbone, however, is also methylated and yields at least 3 products: 1,2,3-trimethoxy propane (TMP), 1,3-dimethoxy-2-propanol (DMP) and its structural isomer 1,2-dimethoxy-3-propanol, and the various isomers of monomethoxy propanediol (MDP). TMAH is consumed to produce trimethylamine (TMA) and the methanol solvent permeates reactants and products. When using soybean oil near complete conversion to products is observed and these are distributed in each of the zones. Because the Algaenator was mainly designed for conversion of algae, the reactor tube, called 'Rototherm', collected a solid product that appeared to be a condensate of fatty acids in the case of soybean oil runs (see section 5.3.2). When algae feedstock was used , the spent algal residue was collected in this zone of the reactor. The condenser and liquid nitrogen trap collected most of the gaseous and liquid products and the relative amounts of liquids in each of these traps were dependent upon the operating conditions of the Algaenator. For soybean oil runs, the condenser collected the major liquid products composed of methanol, TMA, the methoxylated glycerols, and biodiesel (Table 5.2). When algal biomass, harvested from the Old Dominion University Algae Farm, was used as feedstock in the Algaenator, the same liquid and gaseous products were identified as were present with soybean oil but the Algaenator collected a solid spent algae analyzed in this report as a possible fertilizer. Soybean oil and algae produced a different distribution of FAMEs as shown in Figures 5.12, 5.13, 5.15 and 5.16 and Table 5.2. The algae also contained additional products derived from volatilization during heating in the Algaenator.

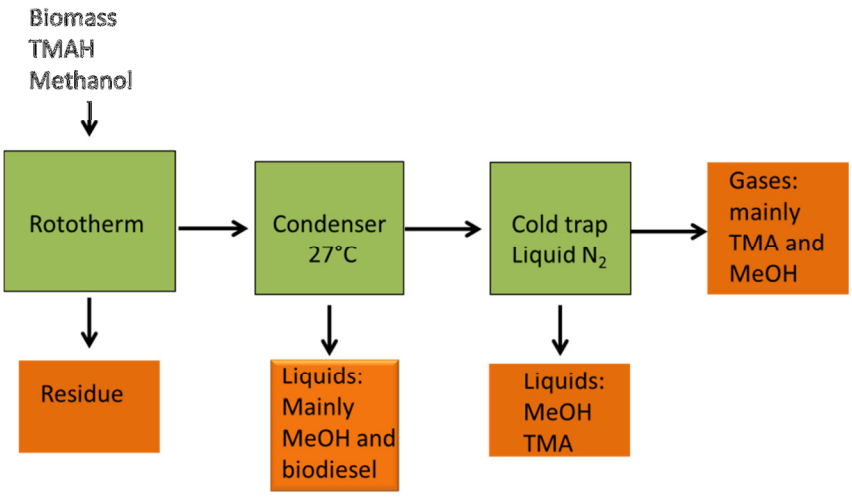


Figure 5.11: Diagram of the products generated during the conversion.

The liquid and solid products from the various tests were characterized by gas chromatography mass spectrometry (GC-MS), gas chromatography flame ionization detector (GC-FID), elemental analysis (EA), and nuclear magnetic resonance (NMR). All chromatograms and spectra are reported in an Appendix (A5.3.1 and A5.3.2). This was carried out to provide a detailed chemical composition of the liquid products including the FAME, methanol, and specialty chemicals such as the methoxylated glycerols. The solid residue's chemical composition was also characterized to explore the fertilizer potential of the algae residue. Major products identified are listed in Table 5.2.

In our system most of the products are vaporized then ideally condensed in the condenser and the nitrogen trap. The gas products are the products that are not condensable in either of the traps and that will escape to the atmosphere. We would expect these gases to be trimethylamine (TMA) and methanol. At the outlet of the liquid nitrogen trap, we intended to measure and collect gas effluents. However we could not measure flow in the range between $2.4x10^{-5}$ and $2.5x10^{-2}$ m^3/min, so no flow measurements were measured and no gas could be sampled for characterization. TMA is the main gaseous product expected but its high solubility in methanol insured that it would be collected by one of the two condensers. We expect that some may have escaped into the vacuum pump oil.

We have established that the highest value products from the conversion of soybean oil are the methoxylated glycerols. Thus, we conducted tests to determine the quantitative recovery of these products from soybean oil. Table 5.3 shows the quantitative yields for the individual methoxylated glycerols and biodiesel from one of the batch runs. We can determine that the yields are approximately stoichiometric if we assume that three methyls of TMAH are required for each fatty acid ester and each glyceryl unit. Thus, a total of six moles of TMAH are required for each mole of triglyceride to give optimum FAMEs and optimum yield of TMP. The yield of TMP is only 5% compared to a value of 15% that would be expected if the reaction quantitatively yielded only TMP and FAMEs. The observation that DMP and MDP are produced in the same approximate yields as TMP suggests that the reaction is less that stoichiometric for TMP and FAME production.

Initial feedstock	Gases	Liquids	Solids
Vegetable oil			Residue
Tetramethyl ammonium hydroxide	Trimethylamine	Trimethylamine	
Methanol	Methanol	Methanol	Methanol
		Methoxylated glycerols	
		1,2,3-trimethoxypropane	
		1,3-dimethoxy-2-propanol and structural isomers	
		3-methoxy-1,2-propanediol and structural isomers	
		others derived methoxylated glycerols	
		Fatty acid methyl esters	Fatty acid methyl esters
		Hexadecanoic acid, methyl ester (FA 16:0)	Hexadecanoic acid, methyl ester (FA 16:0)
		9-Octadecenoic acid (Z)-, methyl ester (FA 18:0)	9-Octadecenoic acid (Z)-, methyl ester (FA 18:0)
		9,12-Octadecadienoic acid, methyl ester (FA 18:1)	9,12-Octadecadienoic acid, methyl ester (FA 18:1)
Algae			Spent algae
Tetramethyl ammonium hydroxide	Trimethylamine	Trimethylamine	
Methanol	Methanol	Methanol	Methanol
		Methoxylated glycerols	
		1,2,3-trimethoxypropane	
		1,3-dimethoxy-2-propanol and structural isomers	
		3-methoxy-1,2-propanediol and structural isomers	
		others derived methoxylated glycerols	
		Fatty acid methyl esters	Fatty acid methyl esters
		Methyl tetradecanoate (FA 14:0)	Methyl tetradecanoate (FA 14:0)
		7,10-Hexadecadienoic acid, methyl ester (FA 16:1)	7,10-Hexadecadienoic acid, methyl ester (FA 16:1)
		Hexadecanoic acid, methyl ester (FA 16:0)	Hexadecanoic acid, methyl ester (FA 16:0)
		9-Octadecenoic acid (Z)-, methyl ester (FA 18:0)	9-Octadecenoic acid (Z)-, methyl ester (FA 18:0)
		Phytol	Phytol

Table 5.2: List of the major products identified.

Summary Table: Actual Yields

Product	Condenser Top Layer		Condenser Bottom Layer		Liquid N2 Trap		Bottom of the Rototherm	
	Weight % in layer	Weight % of veg oil input	Weight % in layer	Weight % of veg oil input	Weight % in layer	Weight % of veg oil input	Weight % of veg oil input	
Methanol	66.53	NA	7.20	NA	69.50	NA		
TMA*	7.20	NA	0.21	NA	47.77	NA		
1,2,3 TMP	3.70	3.54	1.55	0.41	0.43	0.71		
DMP	5.19	4.96	0.71	0.19	1.05	1.74		
Biodiesel	13.80	13.20	89.80	23.80	6.67	11.05		
Sum of % within layers	96.42		99.48		125.42			
								Total sums of % from veg oil
Sum of % from veg oil		21.70		24.40		13.50	27.91	87.51

Table 5.3: Yields of various products from soybean oil.

5.3.2 Conversion of soybean oil to biodiesel in the Algaenator

The first few experiments performed on the pilot reactor, i.e., Batch #1, 3 and 6, were not run at high enough temperature to allow a proper analysis of the reaction. Therefore products from these experiments were not further analyzed. Overall the numerous different runs using soybean oil as a feedstock produced a consistent pattern of products that included a condensate in the main condenser that separated to a two phase liquid upon standing. The top phase is composed mainly of methyoxylated glycerols (MG), biodiesel products, TMA and methanol (Figure 5.12) whereas the bottom phase contains essentially fatty acid methyl esters (FAMEs),

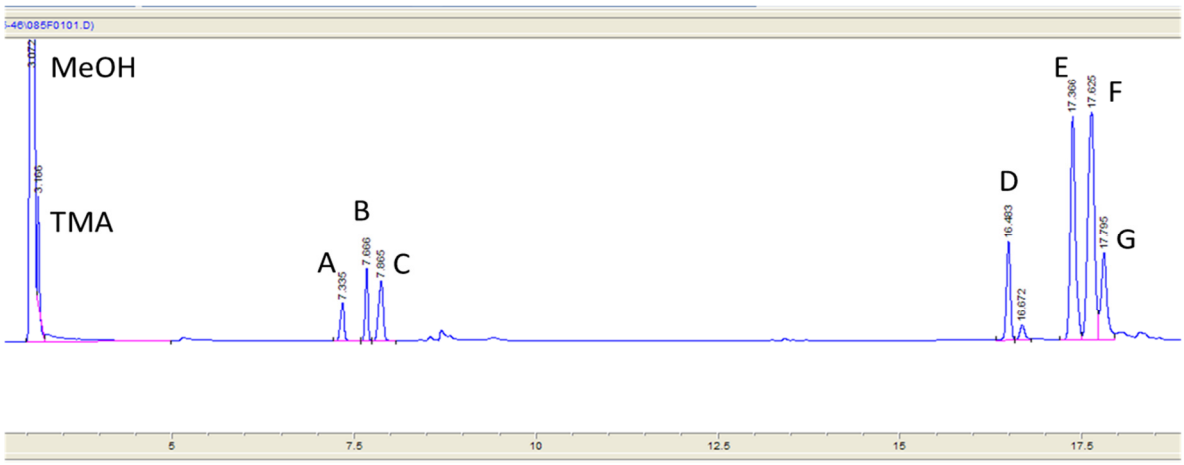


Figure 5.12: Gas chromatogram of the liquid top phase. A-C are the methoxylated glycerols and D-G are FAMEs constituting biodiesel.

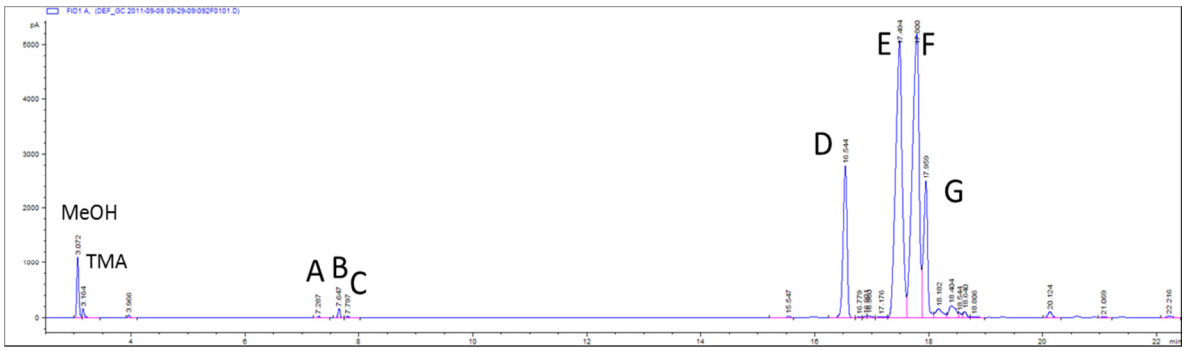


Figure 5.13: Gas chromatogram of the liquid bottom phase. Lettered peaks are as noted in Figure 5.12.

(see Figure 5.13) with a trace of methoxylated glycerols. Products collected in the nitrogen trap mostly are methanol and TMA with traces of MG and FAMEs (Figure A5.3.1.5.2.3). No evidence for triglycerides was detected in the liquid samples analyzed either by GC nor by NMR (Appendix A5.3.1.1.3.1, A5.3.1.4.3.1, A5.3.1.4.3.2, A5.3.1.4.3.3). This suggests that all triglycerides were converted to a product. The bottom phase is readily separated on standing and is treated to remove a trace amount of methanol prior to testing for fuel combustion characteristics.

Attempts to recover and purify the methoxylated glycerols were made and some problems were encountered. This part of the project is not specifically a part of the work plan but is important to the strategy for economic calculations made later. The problem encountered was

one in which a gel is formed as one attempts to distill and purify the methoxylated glycerols. This gel prevented efficient purification of the methoxylated glycerols. We determined that the biodiesel mixed in with the methoxylated glycerols activated gel formation. A process involving cation exchange treatment was discovered to effectively separate the methoxylated glycerols from the biodiesel and we filed for a patent (U.S. Provisional Application Ser. No. 61/535,525). Once biodiesel components were isolated from the methoxylated glycerols, distillation proved an adequate process for the purification of trimethoxy propane. However, we were unable to separate the dimethoxy and monomethoxy glycerols from each other using the less than ideal distillation system. Having a higher resolution distillation apparatus would allow us to separate these two components. In principle, the individual methoxylated glycerols could be separated and purified. It is important to mention that the discovery of these products significantly impacts the economics of the process. In the normal transesterification, the glycerol formed is of low commercial value. The economics of the process rests on profit margins related to the biodiesel produced at about $5/gallon. In our process, the methoxylated glycerols are much more valuable, with conservative estimates of values being more than $100 per gallon and even as high as $100,000 per gallon. This renders the methoxylated glycerols as valuable products and the biodiesel is simply a co-product.

The solid residue collected at the bottom of the reactor was analyzed by solid state NMR which is displayed in Figure 5.14. The spectrum is only composed of a broad peak between 14 and 40 ppm corresponding to aliphatic structures, a smaller peak around 130 ppm corresponding to double bonds and a small peak at 180 ppm corresponding to carboxylic groups. The absence of signals between 50 and 100 ppm suggests that the carboxylic groups at 180 ppm are more likely carboxylic acids rather than ester. This residual material probably is not composed of triglycerides or FAMEs but rather of fatty acid. It represents probably free fatty acids that have polymerized to a solid.

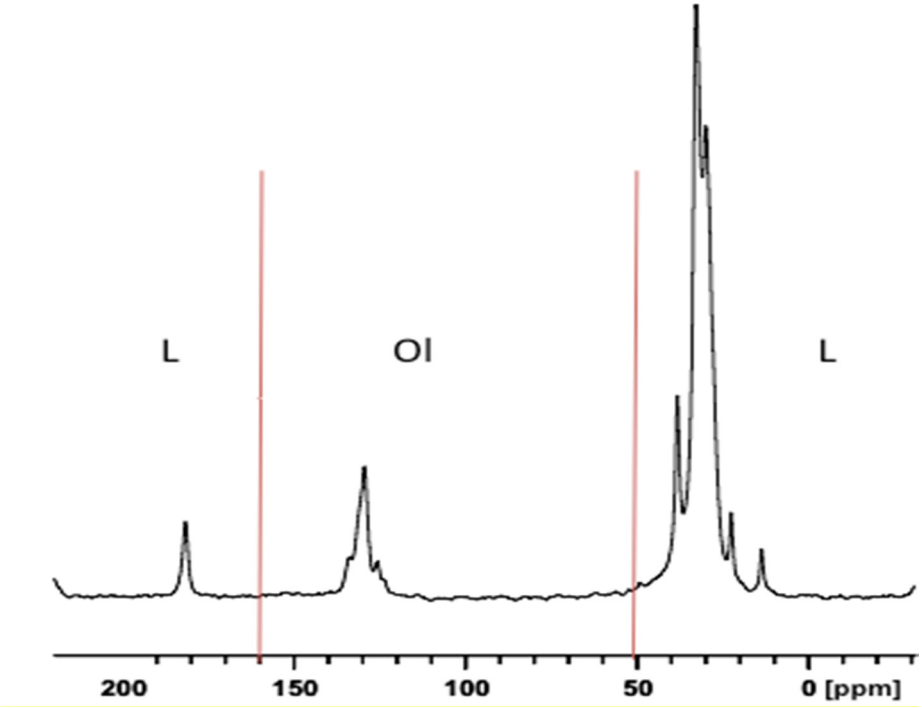


Figure 5.14 CPMAS spectrum of the solid residue collected at the bottom of the reactor for batch #36. The spectrum display only aliphatic structures with L regions corresponding to the lipids structures and Ol region being for olefins.

In the sections below, we present the data describing the products from the test runs made on soybean oil to optimize the reactor. These test runs yielded the various product streams mentioned above and analyses of these product streams allowed us to evaluate the impact the optimizing conditions had on the distribution of products. Except in just a few instances, the relative distribution of the various products was invariant. We surmise that this was because the reaction occurred quite rapidly and in high yields. Any variations in absolute amounts of products in each of the product receptacles was probably dictated by volatilization/condensation conditions downstream of the reaction. Thus, the differences in the product stream discussed below is most likely a product of reactor heat and material transfer efficiency rather than changes in progress of the reaction.

5.3.2.1 Optimizing reactor temperature

The less severe conditions, i.e., 304°C/ 700-760Torr, was performed for batch #13 compared to most other batches. The GC-MS chromatogram of batch #13 (in Appendix A5.3.1.3.1.1) displays only the distribution of methoxylated glycerols and FAMEs collected in the condenser. Under these conditions mostly C_{17}, C_{19} FAMEs were collected. Small amounts of lower molecular weight FAMEs (C_9, C_{11} and C_{15} FAMEs) and methoxylated glycerols are also detected. The same experiment performed at atmospheric pressure and slightly higher temperature, 332°C (batches #11 and 12) produce the same peak distributions on the GC-MS chromatogram (Appendix A5.3.1.1.1 and A5.3.1.2.1).

At a vacuum of 100 Torr, the increase of temperature from 304°C (batches #15 and 16) to 332°C (batches #18 and 19) did not change product distributions observed by GC-MS and GC-FID for any of the fractions collected in the condenser, the liquid nitrogen trap or the solid residue at the bottom of the reactor (Appendix A5.3.1.5, A5.3.1.6, A5.3.1.8 and A5.3.1.9).

These results suggest that the range of temperatures applied have no significant effect on the conversion of triglycerides to FAMEs and methoxylated glycerols.

5.3.2.2 Optimizing reactor pressure (vacuum)

Liquid fractions collected in the condenser for Batch #11 and 12 and analyzed by GC-MS (Appendix A5.3.1.1.1 and 5.3.1.2.1) show that, in addition to the C_{17} and C_{19} FAMEs and the methoxylated glycerols, lower molecular weight C_6, C_8, C_{15} FAMEs are detected in significant amounts. However at a temperature of 332°C and decreasing the vacuum from 700Torr (Batches #11 and 12) to 150 or 100 Torr (Batches #22, 23, 24 and 37, 38, Appendix A5.3.1.10, A5.3.1.12 and A5.3.1.13) produces lower molecular weight FAMEs in only trace amounts. Therefore, we believe that the decrease of the pressure creates a better vaporization of the higher molecular weight FAMEs and a more efficient transfer to the condenser. Thus, this apparent decrease in lower molecular weight FAMEs is not due to the decomposition of FAMEs but rather is due to an increase in C_{17} and C_{19} FAMEs in the condenser trap.

The other fractions collected in the nitrogen trap and at the bottom of the reactor with the solid residue seem to be unchanged when optimizing reactor pressures.

5.3.2.3 Optimizing feed rate

Multiple experiments run at the same temperature and pressure but different feed rate can be compared such as batches #15 and 16; 18, 19 and 22, 23, 24; and 37 and 38. Chromatograms of the samples collected in the condenser and the nitrogen trap for these experiments are

displayed in Appendix A5.3.1.1.5 to A5.3.1.1.10 and A5.3.1.1.12 and A5.3.1.1.13. Product distributions are very similar, no significant changes are observed with the variation of feed rate.

5.3.3 Conversion of Algae to Biodiesel in the Algaenator

From the experiments using vegetable oil as feedstock we saw that the conversion of TAG to FAMEs is not affected by the different parameters employed (Algaenator temperature, vacuum, feed rate and condenser temperature). It is only the redistribution among the different traps of the different products that changes.

Therefore for the experiment for which algae were fed into the reactor, temperature, vacuum, feed rate and the condenser temperature were not significantly changed. The main parameter that has been modified is the nature of the feedstock. Wet (Batch #8) and dry algae (Batches #26, 28, 29, 33, 34, 35) were tested as well as the particulate size distribution for the dry algae. Chromatograms of the products collected in the condenser are displayed in Appendix and in Figure 5.15 and 5.16. Because the presence of water led to emulsification of the product collected, the emulsion was extracted using dichloromethane (DCM) before injection into the GC-MS. The most dominant FAMEs present were the ones derived from the fatty acids C_{16}:0 and C_{18}:0 but other FAMEs were detected including the ones derived from the fatty acids C_8:0, C_{10}:0, C_{12}:0, C_{14}:0 and C_{24}:0 and C_{26}:0. Phytol and phytenol (C_{20}) were also detected corresponding to products of decomposition of chlorophyll.

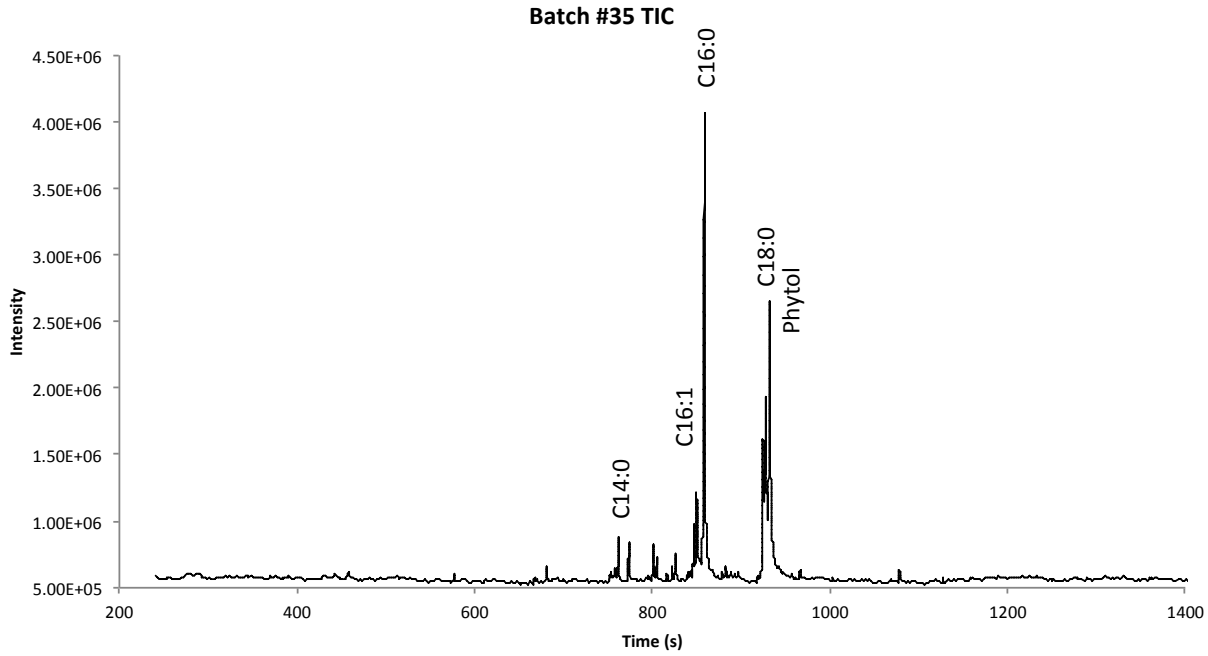


Figure 5.15: Total ion current chromatogram for products from batch 35 (algae)

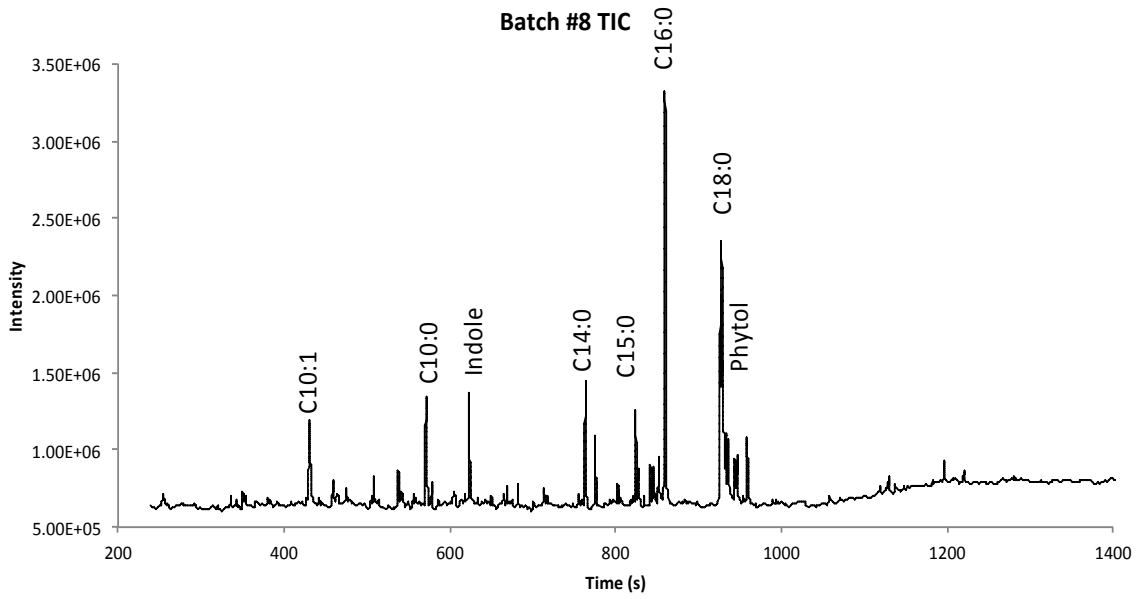


Figure 5.16: Total ion current chromatogram for products from batch 8 (algae)

Products from Batch #8 (Figure 5.16) in which wet algae was processed the lowest molecular weight FAMEs C_9, C_{11}, and C_{13} were in larger abundance compared with other batches #26, 28, 29, 33, 34, 35 in which dry algae was processed. This distribution may also be explained by the fact that for batch #8 less vacuum, i.e., 300 Torr, was applied compared with other runs, i.e., around 150-200 Torr. We observe for the conversion of vegetable oil to FAMEs in the Algaenator that, when more vacuum was applied, a larger proportion of higher molecular weight FAMEs were collected. This implies that the relative abundance of peaks assigned to lower molecular weight FAMEs decreases in the chromatograms.

The residue or spent algae collected at the bottom of the Algaenator was analyzed by elemental analysis (Appendix A5.3.2.8) and solid state ^{13}C NMR (Figure 5.17). The elemental composition shows that a significant proportion of nitrogen, i.e., 10%, is preserved in the residue. The solid state ^{13}C NMR spectrum confirms this result. The peak at 175 ppm corresponds mostly to amide groups from proteins. Peaks in the region between 45 and 110 ppm correspond to carbohydrates and suggest that the principal component of the algae are not altered by our process. Only the triglycerides are converted to FAMEs and methoxylated glycerols.

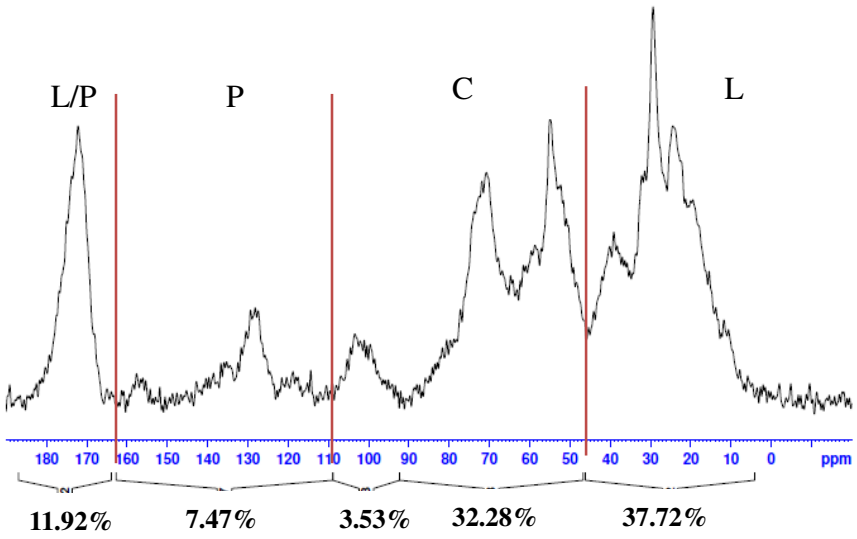


Figure 5.17: Solid-state ^{13}C NMR spectrum for spent algae from batch #34. L=lipids; C= carbohydrates; P=proteins

5.3.4 Testing of the biodiesel (Objective 7).

Our original objective was to produce sufficient amounts of biodiesel from each run of the reactor to all for ASTM testing of the biodiesel. It became clear that the yields from each test were insufficient to supply the requisite 2 L sample for ASTM testing. We were unable to collect sufficient biodiesel from any of the runs in which algae was utilized as feedstock (due to plugging of feed lines). However, we did manage to collect sufficient biodiesel from a composite of several batch runs of the soybean oil. The biodiesel sample was from the condenser region of the Algaenator. A sample was submitted to Midwest Laboratories, Inc. and the following Table 5.3 shows the results of analysis using ASTM D6751methods.

Table 5. 3: ASTM tests of the biodiesel sample from soybean oil.

Midwest Laboratories, Inc.

13611 B Street • Omaha, Nebraska 68144-3693 • (402) 334-7770 • FAX (402) 334-9121 • www.midwestlabs.com

Certificate of Analysis Report #: 12-044-2152

Reported to:	OLD DOMINION UNIV CHEM DEPT 4402 ELKHORN AVE NORFOLK VA 23529	Acct #: 29036

Lab #: 1951999
Sample ID: ODU BIODIESEL

Analysis	Level Found	Status	ASTM 6751 Limits	Method	Date of Analysis
Cetane Number*	44	Fail	47 min.	ASTM D613	02/10/12
Oxidation Stability (hrs)	3	Pass	3 hour min	EN 15751	02/08/12
Flash Point (deg C) **	87	Fail	93 or 130 min	ASTM D93	02/08/12
Methanol (% volume)	0.1	Pass	0.2 max	EN 14110	02/08/12
Water and Sediment (% volume)	<0.01	Pass	0.05 max	ASTM D2709	02/08/12
Viscosity Kinematic (mm²/s)	5.63	Pass	1.9-6.0	ASTM D445	02/13/12
Sulfated Ash (% mass)	<0.01	Pass	0.02 max	ASTM D874	02/09/12
Sulfur (total) (ppm)	1.4	Pass	15 ppm	ASTM D5453	02/08/12
Copper corrosion (3hr 50°C)	1a	Pass	No. 3 max	ASTM D130	02/09/12
Cloud Point (deg C)	4	NA	Report	ASTM D2500	02/08/12
Carbon Residue (% mass)	<0.02	Pass	0.05 max	ASTM D4530	02/09/12
Acid Number (mg KOH/g)	0.59	Fail	0.50 max	ASTM D664	02/09/12
Free Glycerine (% mass)	<0.001	Pass	0.020 max	ASTM D6584	02/10/12
Total Glycerine (% mass)	0.006	Pass	0.240 max	ASTM D6584	02/10/12
Monoglycedride (% mass)	0.002			ASTM D6584	02/10/12
Diglyceride (% mass)	0.004			ASTM D6584	02/10/12
Triglycerides (% mass)	n.d.			ASTM D6584	02/10/12
Boiling Temp-Dist Temp (deg C)	336	Pass	360 max	ASTM D1160	02/13/12
Phosphorus (% mass)	<0.0001	Pass	0.001 max	ASTM D4951	02/08/12
Magnesium/Calcium (ppm)	<1.00	Pass	5 max	EN 14538	02/08/12
Potassium/Sodium (ppm)	15.36	Fail	5 max	EN 14538	02/08/12
Biodiesel Visual Inspection	#1		N/A	D4176	02/08/12
Cold Soak Filtration (seconds)	94	Pass	360 sec. max	ASTM D7501	02/08/12

Heather Ramig
Client Services - Midwest Laboratories, Inc.

* Cetane Number analysis is performed by a subcontracted Laboratory.
Methods revision are effective as of October 8, 2009

** If Flash Point is < 130 Celcius, then the Methanol test is done.
If Methanol passes and Flash Point is above 93 Celcius,
then the Flash Point passes.

The results of testing provided us with a clear indication that the biodiesel produced passed many of the required certification tests but some values were not within acceptable specifications. The cetane number was a bit low testing at 44 compared to the specification of 47. We surmise that this was due to molecularly heavier and, thus, higher cetane FAME components were condensed in the reactor horizontal tube and not transferred to the condenser trap. This was most likely related to the design of the reactor tube in which no heating was provided downstream of the heat transfer region to maintain the higher boiling fractions in the gas phase. Attempts to mitigate this problem involved addition of insulation but the best solution would have been to add a post-heat transfer heater or to extend the heat transfer region further down the horizontal axis of the reactor. This modification was too expensive and time consuming to make. In retrospect, we should have added the biodiesel from the reactor bottoms to the biodiesel collected from the condenser region prior to analysis. This correction will also mitigate the slight difference of flash point.

The magnesium/calcium content, and acid number was three times the passing rate at 15.36 ppm. This level was high because technical grade TMAH contained a significant level of magnesium present. Exchange resin will reduce the amount of magnesium/calcium in our biodiesel sample. After removing magnesium/calcium by exchange resin the acid number will improve to the point of passing these ASTM tests.

5.4. Evaluating the economics (Task 4, Objectives 8 and 9)

Our objective was to utilize the pilot scale reactor to measure energy usage and project the financial and energy commercial feasibility of the ODU-patented reaction for converting algae to biodiesel and co-products. For the reactor at the pilot scale, energy balance was estimated based on 21.26 kg/hr feed rate, but the financial budget at this scale was not completed because by definition pilot scale facilities have small size equipment designed to gather data for the design of larger more efficient facilities.

Energy measured from the pilot scale facility demonstrated the inefficiency of the small size equipment. For the entire system, 42% of the total energy supplied to was lost heat of the system. Heat loss can be reduced by better insulation and lower surface-to-volume ration at commercial equipment size.

We used data gathered from the pilot scale facility to estimate economics for this chemical process at commercial scale. Projections for commercial facilities were based upon conceptual flow-sheet process diagrams detailed in the appendix Figures A5.4.1-4. Additionally, Table A5.4.1 detailed the theoretical production based on algae feedstock and Table A5.4.2 estimated associated cost estimates of additional equipment.

5.4.1 Summary of energy of the pilot scale reactor.

For the Algaenator, we calculated a heat balance for the system comparing the energy input and the energy output by the reaction process for a typical algae batch. The pilot scale system lost a considerable amount of heat (19%) compared to the total heat input (Table 5.3). These losses would be mitigated to 1% or less for commercial units. The reaction required 11% of the heat input for the total heat input for the system (Table 5.3).

Table 5.3: Energy (heat) balance of a typical reaction for pilot scale reactor and condenser.

	Dry Algae Feed and Products		Energy Balance	
Heat Input:	**Units**	**Quantity**	**Units**	**Heat Value**
Dry Algae	kg/hr	5.84	kJ/hr	145895
Methanol	kg/hr	12.85	kJ/hr	305
25%TMAH/75%MeOH	kg/hr	1.80	kJ/hr	43
Tryglycerides	kg/hr	0.38	kJ/hr	14633
Water	kg/hr	0.06	kJ/hr	3
Nitrogen, gas	kg/hr	0.34	kJ/hr	0
Heat required for reaction			kJ/hr	24304
Heat Input for system			kJ/hr	44260
			kJ/hr	229441
Heat Output:				
Fertilizer (spent solids)	kg/hr	5.84	kJ/hr	148744.5
Condenser demand (FAME, methanol, etc.)	kg/hr	45.60	kJ/hr	19025.7
Heat retained by Condensate mixture	kg/hr	15.09	kJ/hr	14480.4
Nitrogen, gas	kg/hr	0.34	kJ/hr	48
Heat Output loss from system			kJ/hr	44260
			kJ/hr	226558
			Accuracy	99%

The reactants fed into the system consisted mainly of methanol and algae solids. The heat input requirement was a summation of heat required for heating, vaporizing, and superheating all the reactants (methanol, TMAH/methanol, algae, TAG, H_2O, and N_2 gas). The heat output was a combination of the heat demand for products entering the condenser typically at 94^oC and collecting in the condenser typically at 27.7^oC (methanol, TMA, FAME, N_2 gas, and a small amount of H_2O).

5.4.2 Summary of Financial and Energy estimates for industrial scale operation: Case I (10 metric ton dry algae per day) and Case II (100 metric ton dry algae per day).

The three methyl glycerol derivatives (MDP, DMP and TMP) produced by TMAH methylation chemistry at high temperature are very valuable and result in attractive process economics (Table 5.4). The projected prices are for typical current product volumes. As production of methoxylated glycerols from algae increases, the product prices will decrease and additional markets, such as renewable solvents, will expand to consume additional product.

The input costs of energy and dry algae exceeded the value of biodiesel and spent algae (fertilizer) products alone. As previously discussed, the relatively low 30% (w/w) algae in slurry feed limited the ability to produce FAME per unit time and negatively impacted the economics. We conclude: 1) algae species with higher triglyceride content need to be used, 2) extractable triglycerides need to be increased and 3) and both triglyceride extract and algae can be fed to the reactor.

Methanol constituted about 70 % (w/w) of the feed and had to be vaporized, condensed and separated from the liquid products. Increasing the feed slurry concentration would decrease the amount of methanol in the feed and reduce the energy consumption for recovering methanol. Replacing methanol with water does not help because the water heat of vaporization is significantly higher than methanol.

For Case I, the industrial scale financial projection for a 10 metric ton per day dry algae feed is based upon the production from an open pond raceway system (see Appendix Table A5.4.1). The amount of extractable TAG in the algae feed is approximated to 6% by weight. The process assumes recycling and regeneration of TMAH and most of the methanol (see appendix conceptual flow-sheet A5.4.4). Methanol consumed in the regeneration of TMAH catalyst is replenished. Natural gas provides heat for the hot oil unit and other needs (reboilers, etc.), and electrical costs are based on commercial rates (estimated at 40% of energy load for the process).

Increasing the process plant size from 10 to 100 metric tons per day improves the economics due to economy-of-scale. The investment per unit feed rate decreases as the plant capacity increases. Production of algae is based on 1,000+ acres of open raceway (Table A5.41). Other assumptions such as TAG amount, reactant recycling, and energy costs are the same percentages for Case II. The costs and products for Case II are a factor of ten times Case I. Contiguous installations larger than 100 metric tons per day dry algae could prove unwieldy. It is more likely 100 metric ton size units would consist of non-contiguous, multiple 100 metric ton units.

From an energy perspective, a large percentage of heat required for the Algaenator process is used to vaporize methanol. The products contain 58% of the input energy(Table 5.5). By reducing methanol in the algae slurry feed, the process efficiency would significantly improve to 80%. Also, increased TAG content in the algae would offer substantial improvement. Energy lost as waste heat due to small size equipment can be reduced by better insulation and lower surface-to-volume ration at commercial equipment size.

Table 5.4: Financial projections for Case I (10 metric ton algae dry weight per day production) and Case II (100 metric ton algae dry weight per day production) industrial scale operations.

Financials for Algaenator Cases

				Case I	Case II
Dry Algae Feed, MT/Day				**10**	**100**
Investment, MM$				**10**	**60**
	10 MT/Day Dry Algae Feed			**Economics**	
Product Revenue:	**Units**	**Quantity**	**$/unit**	**MM$/yr**	**MM$/yr**
Fertilizer (spent solids)	kg/hr	391.67	0.33	1.13	11.35
Biodiesel (FAME)	kg/hr	23.13	0.31	0.06	0.63
Trimethoxypropane (TMP)	kg/hr	1.47	2809	36.17	361.72
Dimethoxypropanol (DMP)	kg/hr	1.32	619	7.16	71.58
Methoxypropanediol (MDP)	kg/hr	1.17	1181	12.10	121.04
NaCl (TMAH regeneration)	kg/hr	11.58	0.17	0.02	0.17
				56.65	566.49
Variable Costs:					
Dry Algae	kg/hr	420.56	0.51	1.88	18.75
Methanol Make-up	kg/hr	5.28	0.09	0.00	0.04
Power, MW	MW	0.55	103	0.49	4.94
Natural Gas, MMBTU/hr	MMBTU/hr	5.33	8.99	0.42	4.20
NaOH Flake (TMAH regeneration)	kg/hr	8.31	0.58	0.04	0.43
Anhydrous HCl (TMAH regen.)	kg/hr	7.22	1.65	0.10	1.05
				2.94	29.41
Fixed Costs, $1.4 million + 3% investment/year				1.70	3.20
Depreciation, 10% investment/year				1.00	6.00
Total Costs:				5.64	38.61
Gross Profit:				51.01	527.88
Income Tax, 35% gross profit				17.85	184.76
Net Profit:				33.15	343.12
Simple Return: (Net Profit + Depreciation) / Investment, %				342	582

Table 5.5: Energy balance for Case I (10 metric tons dry weight algae production per day).

Energy Balance for 10 MT/Day Algaenator Case					
	Dry Algae Feed and Products		Energy Balance		
Energy Input:	**Units**	**Quantity**	**Units**	**Quantity**	**MJ/hr**
Dry Algae	kg/hr	420.56	MJ/kg	25.0	10514
Methanol Make-up	kg/hr	5.28	MJ/kg	22.7	120
Power, MW	MW	0.55	MW	0.55	1972
Natural Gas, MMBTU/hr	MMBTU/hr	5.33	MMBTU/hr	5.33	5627
					18233
Energy Output:					
Fertilizer (spent solids)	kg/hr	391.67	MJ/kg	25.0	9792
Biodiesel (FAME)	kg/hr	23.13	MJ/kg	32.3	746
Trimethoxypropane (TMP)	kg/hr	1.47	MJ/kg	27.7	41
Dimethoxypropanol (DMP)	kg/hr	1.32	MJ/kg	25.3	33
Methoxypropanediol (MPD)	kg/hr	1.17	MJ/kg	22.2	26
					10638
				Efficiency	58%

Variable costs and product value basis for Financials and Energy balance for Case I and Case II

Algae, dry- $0.509/kg, based on break-even price for 1000 acre open pond.

Methanol (MeOH)- 3/12/2012 Methanex bulk price for tank truck and RR tank quantities, $1.34 per gallon.

Energy- Table 2 U.S. Energy Prices, Energy Information Administration / short-term Energy Outlook- March 2012.

Electricity- End use prices, commercial sector, year 2013, 10.39 cents per kilowatt.

Natural gas- End use prices, commercial sector, year 2013, $8.99 dollars per 1000 cubic feet.

Sodium Hydroxide (NaOH)- March 2012, bulk price, F.O.B., US, $530 per ton.

Anhydrous Hydrochloric (HCl)- March 2012, bulk price, F.O.B., US $1,500 per ton.

Rototherm Solids discharge- based on the value of slow release fertilizer ($300 per ton).
(fertilizer)

Biodiesel (FAME)-	based on $5.00 per gallon selling price from Virginia BioDiesel, West Point, VA 23180, January 2012.
TMP (1,2,3 Trimethoxypropane)-	$10,000 per gallon, based on estimates of market value for large quantities.
DMP (1,3 Dimethoxypropanol)-	$2,000 per gallon, based on estimates of market value for large quantities.
MDP (1-Methoxy- 2,3 Dihydroxypropane)-	$5,000 per gallon, based on estimates of market value for large quantities
Sodium Chloride (NaCl)	snow melting quality, $170 per metric ton

References:

Hyenstrand, P., Bukert, U., Pettersson, A., and P. Blomqvist. 2000. Competition between the green alga *Scenedesmus* and the cyanobacterium *Synechoococcus* under different modes of inorganic nitrogen supply. *Hydrobiologia*. 435: 91-98.

Mulbry, Walter, Kondrad, Shannon, and Pizaro, Carolina. 2006. Biofertilizers from algal treatment of dairy and swine manure effluents: characterization of algal biomass as slow release fertilizer. *Journal of Vegetable Science*. 12(4): 107-125.

Reeves, D.W. 1997. The role of soil organic matter in maintaining soil quality in continuous cropping systems. *Soil & Tillage Research*. 43: 131-167.

5.6 Identify products developed under the award and technology transfer activities

5.6.1. Publications, conference papers, or other public releases of results.

The following references correspond to papers that are in process of been published to scientific journals.

Liu, Z., Johnson E. A., Salmon E., Mesfioui R., Zhong J., Egerton T., Gordon A., Marshall H., Stubbins A., and Hatcher P. Estimation of fatty acid contents in microalgae using advanced NMR. In Preparation

Johnson, E.Adair, Zhanfei Liu, Salmon, Elodie, Hatcher, P. The one-step transesterification of algae to biodiesel using reagent tetramethylammonium hydroxide (TMAH). Advanced Biofuels & Bioproducts (In Press).

Results from this study were also presented to the NRC Panel's Sustainable Development of Algal Biofuels Committee:

Patrick G. Hatcher, 2011. The ODU algae to biodiesel project. Webinar presentation to the NRC Panel's Sustainable Development of Algal Biofuels Committee, August 11, 2011.

5.6.2. Web site or other Internet sites that reflect the results of this project

Pictures of the installation of the Algaenator have been displayed in the following website:
http://sci.odu.edu/hatchergroup/algae_fuel/News.html
http://sci.odu.edu/hatchergroup/algae_fuel/farm/farm.html

Some corn was grown using dry algae as fertilizer to demonstrate its potential. Pictures of this demonstration are displayed in the following website:
http://sci.odu.edu/hatchergroup/algae_fuel/farm/algae_fertilizer.html

5.6.1. Inventions/Patent Applications

Based on the founding that methoxylated glycerols are generated from the conversion of TGA to biodiesel using ODU patented process; two applications patents were submitted. The first one is a continuation of the initial patent (US Patent No. 8,080,679 B2), the second one is a method to separate the methoxylated glycerols from the biodiesel.

Hatcher, P.G., Liu, Z., and **Salmon, E.**, 2011. Production of glycerol-related products from a high temperature reaction. Old Dominion University, US patent application 20110289830, U.S. Provisional Application Ser. No. 13/204,884.

Hatcher, P.G., **Salmon, E.**, 2011. A method to separate methoxylated glycerols from the biodiesel in high-temperature methylation with tetramethylammonium hydroxide Old Dominion University, U.S. Provisional Application Ser. No. 61/535,525.

5.6.4 Networks or collaborations.

Multiple collaborations have been developed during the project.

The strongest one is the collaboration the Artisan Industries who provide the reactor for this project and assist us with technical supports and equipments for optimizing the Algaenator. Other companies approach us that are interested in the products.

Afton Chemical is interested in using the methoxylated glycerol as fuel additives.

Nutrients plus show an interest in utilizing the spent algae that is collected after the conversion to biodiesel as fertilizer. In order to demonstrate the potential of the spent algae as fertilizer corn crops have been performed. However because we run into some problems for feeding the reactor with algae, we were not able to produce enough spent algae on time for the

corn growing season. Therefore dry algae have been use and we successfully demonstrate that our algae bring as much nutrients to the corn that commercial fertilizer.

Phytonix Corporation is also interested in using the developed technologies to develop businesses for the biofuels industry.

5.6.5 Technologies/Techniques.

During this project we installed, developed and optimized a reactor capable of converting algae or vegetable oil to biodiesel, we named the reactor Algaenator. In the laboratory scale, we also developed other techniques for the quantification of lipids in the algae using NMR techniques, tested the recovery of TMAH from TMA, developed a technique for the separation of methoxylated glycerols from biodiesel and also separated the different methylated glycerols produced. Scientific publications are currently in preparation to report the development of all these techniques.

5.7 Appendix (Outline of contents)

A5.1. Objective 1 (Task 1). Determine optimum reactor technology

A5.3- Characterization of products:

- **A5.3.1- Conversion of vegetable oil to Biodiesel in the Rototherm Reactor**
  - **A-5.3.1.1 Batch #11, vegetable oil, 332°C/700Torr**
    - **A-5.3.1.1.1 GC-MS data**
    - **A-5.3.1.1.2 GC-FID data**
    - **A-5.3.1.1.3 NMR spectroscopy data**
  - **A5.3.1.2 Batch #12, vegetable oil, 332°C/700Torr**
    - **A-5.3.1.2.1 GC-MS data**
    - **A-5.3.1.2.2 GC-FID data**
  - A-**5.3.1.3 Batch #13, vegetable oil, 304°C/700-760Torr**
    - **A-5.3.1.3.1 GC-MS data**
    - **A-5.3.1.3.2 GC-FID data**
  - **A-5.3.1.4 Batch #14, vegetable oil, 2 gal/hr, 304°C/500-600 Torr**
    - **A-5.3.1.4.1 GC-MS data**
    - **A-5.3.1.4.2 GC-FID data**
    - **A-5.3.1.4.3 NMR spectroscopy data**
  - **A5.3.1.5 Batch #15, vegetable oil, 3 gal/hr, 304°C/100 Torr**
    - **A-5.3.1.5.1 GC-MS data**
    - **A-5.3.1.5.2 GC-FID data**
  - **A-5.3.1.6 Batch #16, vegetable oil, 3.5 gal/hr, 304°C/100 Torr**
    - **A-5.3.1.6.1 GC-MS data**
    - **A-5.3.1.6.2 GC-FID data**
  - **A-5.3.1.7 Batch #17, vegetable oil, 2 gal/hr, 304°C/500-600 Torr**
    - **A-5.3.1.7.1 GC-FID data**

A5.1. Objective 1 (Task 1). Determine optimum reactor technology

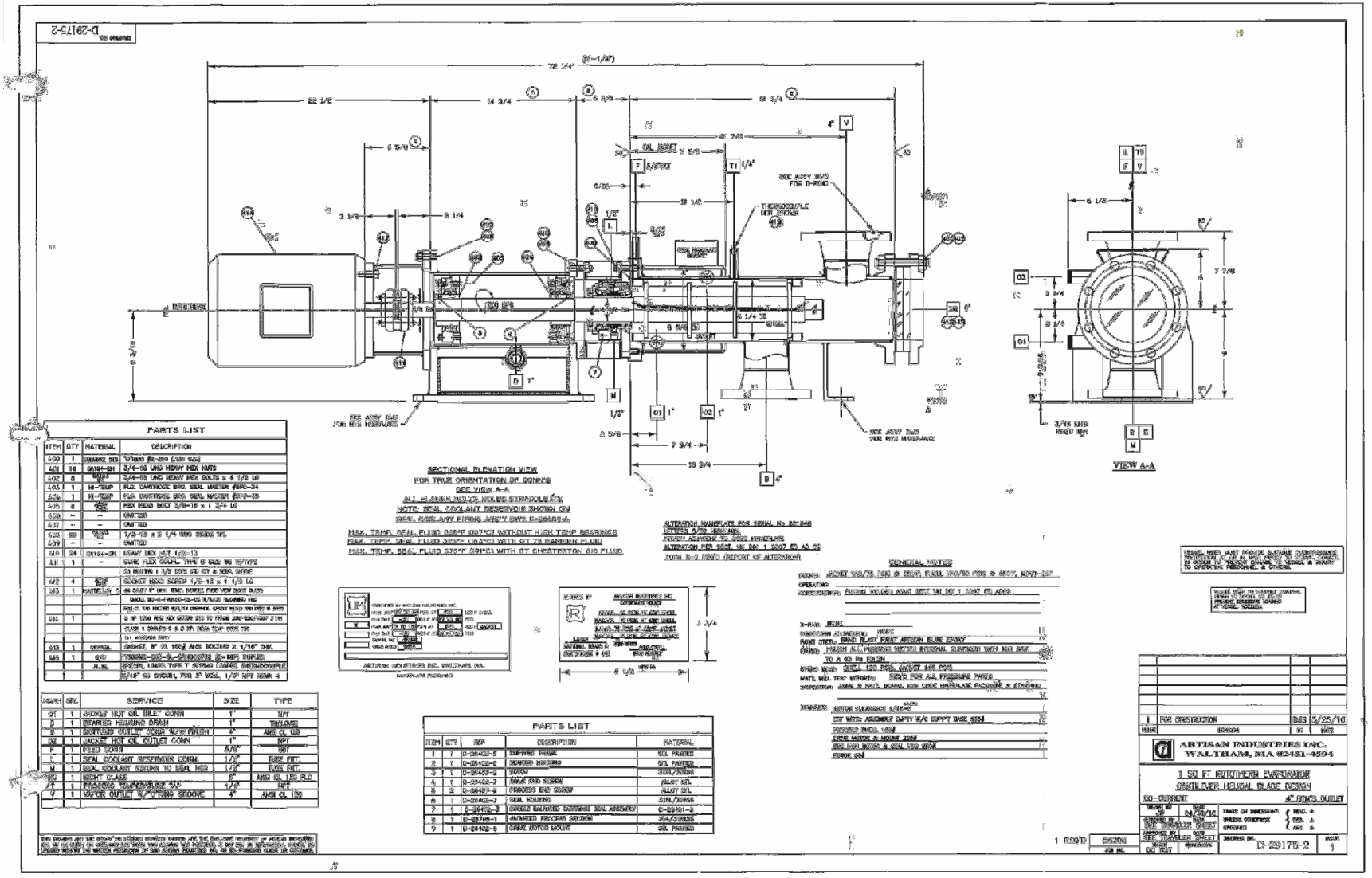


Figure A5.1.2: Artisan drawing of Rototherm E.

A5.3- Characterization of products:

All the analytical data collected by are presented below. In section A5.3.1 are reported all the runs that utilized vegetable oil as feedstock and section A5.3.1 contains all the data of the batches for which algae is fed into the reactor.

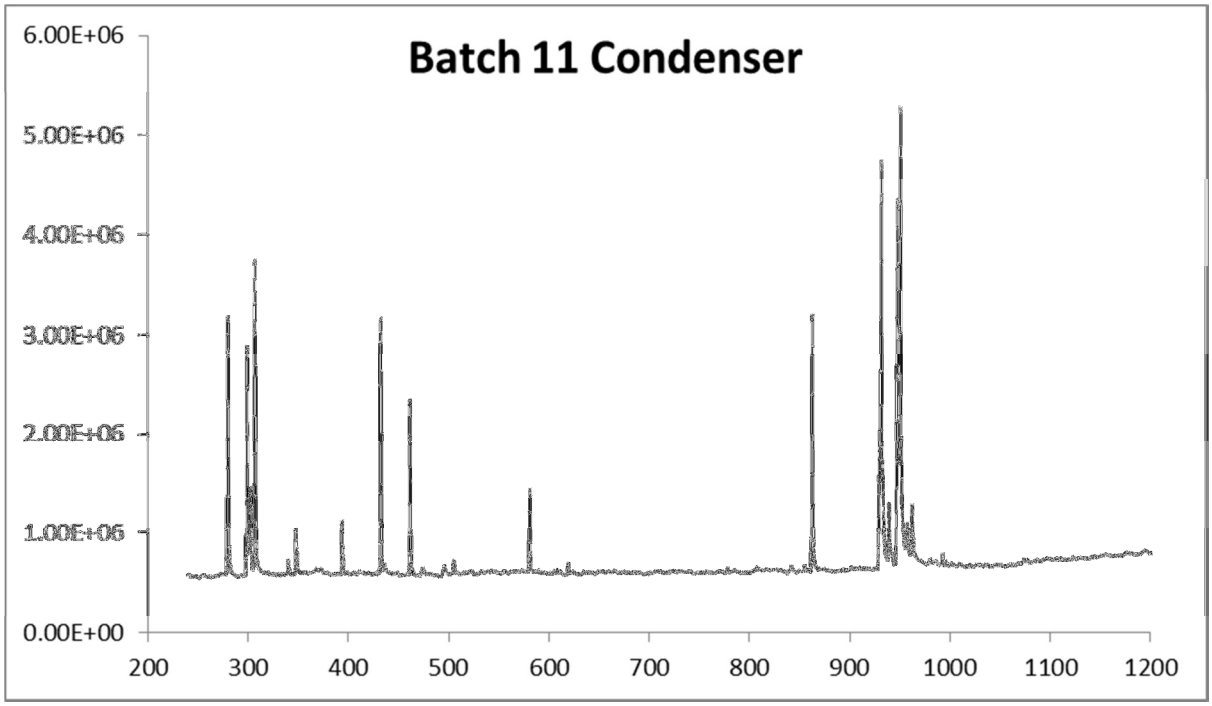
A5.3.1- Conversion of vegetable oil to Biodiesel in the Rototherm Reactor

The table below summarizes all the experiments that were performed. Appendix numbers are reported for experiments for which products were characterized. In each appendix first GC-MS second GC-FID and third NMR data are displayed. For each type of analysis data are successively presented for the products collected in the condenser, then for those collected in the nitrogen trap, then for the liquid products collected at the bottom of the reactor with the solid residue.

Appendix Number	Batch Number	Feedstock Description	Flow rate (gal/hr)	Temperature (°C)	Pressure (Torr)
A5.3.1.1	11	Vegetable Oil		332.2	700
A5.3.1.2	12	Vegetable Oil		332.2	700
A5.3.1.3	13	Vegetable Oil		304.4	700-760
A5.3.1.4	14	Vegetable Oil	2.0	304.4	500-600
A5.3.1.5	15	Vegetable Oil	3.0	304.4	100
A5.3.1.6	16	Vegetable Oil	3.5	304.4	100
A5.3.1.7	17	Vegetable Oil	3.0	332.2	100
A5.3.1.8	18	Vegetable Oil	3.0	332.2	100
A5.3.1.9	19	Vegetable Oil	3.0	332.2	100
	20	Vegetable Oil	3.5	332.2	100
	21	Vegetable Oil	3.5	332.2	100
A5.3.1.10	22	Vegetable Oil	3.5	332.2	100
A5.3.1.10	23	Vegetable Oil	3.5	332.2	100
A5.3.1.10	24	Vegetable Oil	3.5	332.2	100
	25	Crude Soy Oil	3.5	332.2	100
	31	Crude Soy Oil	3.5	332.2	100
A5.3.1.11	36	Vegetable Oil	3.5	322.8	200
A5.3.1.12	37	Vegetable Oil	3.5	332.2	150
A5.3.1.13	38	Vegetable Oil	3.2	332.2	150
	39	Vegetable Oil	3.2	332.2	150

A-5.3.1.1 Batch #11, vegetable oil, 332°C/700Torr

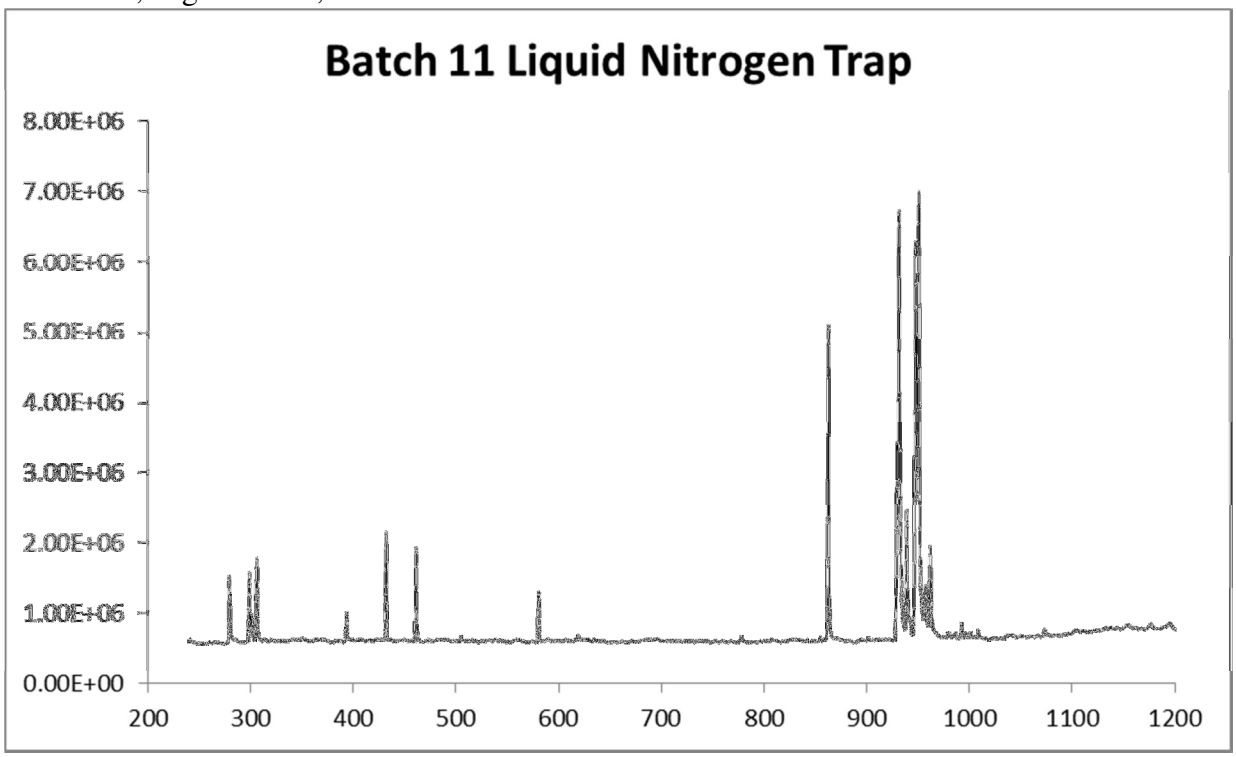
A-5.3.1.1.1 GC-MS data



Batch #11	Condenser	
R.T. (s)	Compound Name	
279	2-Propanol,1,3-dimethoxy-	
298	Propane,1,2,3-trimethoxy-	
300	1,2-Propanediol, 3-methoxy-	
339	Methyl glycerol derivative	
347	Methyl glycerol derivative	
393	Hexanoic acid, methyl ester	C6:0
431	Octenoic acid, methyl ester	C8:1
461	Octanoic acid, methyl ester	C8:0
580	Decanoic acid, methyl ester	C10:0
862	Hexadecanoic acid, methyl ester	C16:0
929-939	9-Octadecenoic acid (Z)-, methyl ester and isomers	C18:1
947-962	9,12-Octadecadienoic acid, methyl ester and isomers	C18:0

Figure A5.3.1.1.1.1: GC-MS chromatogram of products collected in the condenser for batch #11. Retention time and peaks assignments are reported in the table.

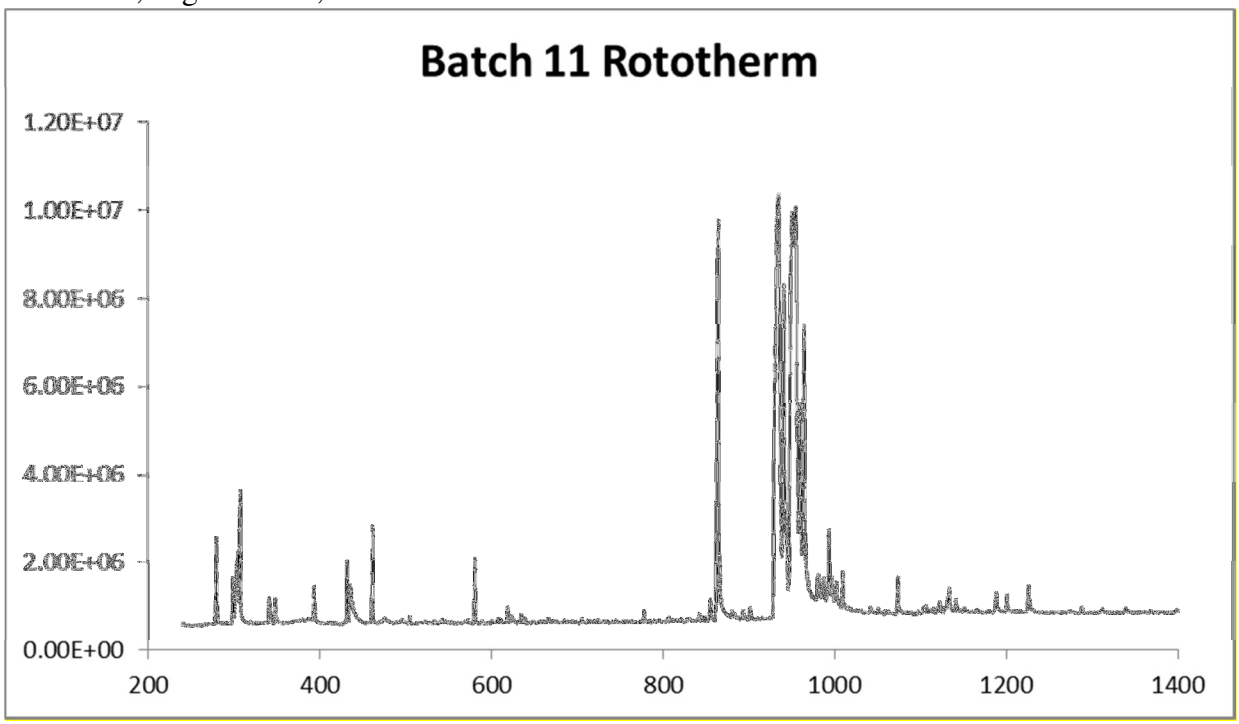
Batch #11, vegetable oil, 332°C/700Torr



Batch #11	Liquid Nitrogen trap	
R.T. (s)	Compound Name	
279	2-Propanol,1,3-dimthoxy-	
298	Propane,1,2,3-trimethoxy-	
300	1,2-Propanediol, 3-methoxy-	
393	Hexanoic acid, methyl ester	C6:0
431	Octenoic acid, methyl ester	C8:1
461	Octanoic acid, methyl ester	C8:0
580	Decanoic acid, methyl ester	C10:0
777	Methyl tetradecanoate	C14:0
862	Hexadecanoic acid, methyl ester	C16:0
929-939	9-Octadecenoic acid (Z)-, methyl ester and isomers	C18:1
942-992	9,12-Octadecadienoic acid, methyl ester and isomers	C18:0

Figure A5.3.1.1.1.2: GC-MS chromatogram of products collected in the liquid nitrogen trap for batch #11. Retention time and peaks assignments are reported in the table.

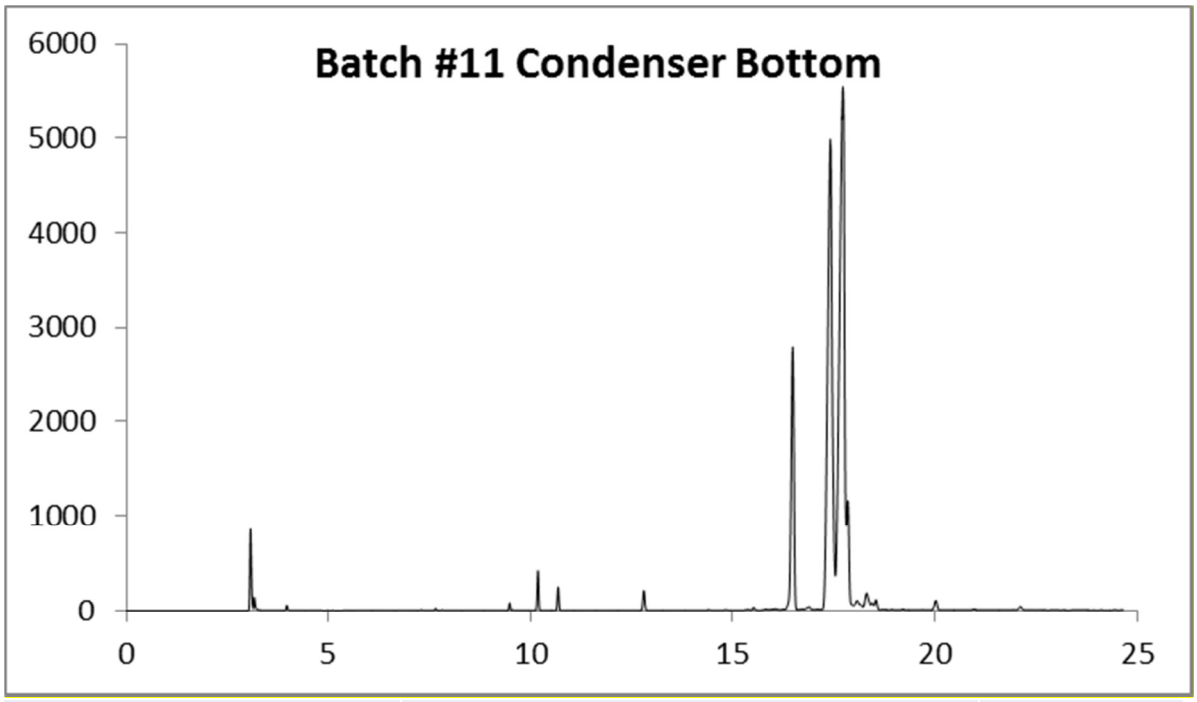
Batch #11, vegetable oil, 332°C/700Torr



Batch #11	Rototherm	
R.T. (s)	Compound Name	
279	2-Propanol,1,3-dimthoxy-	
298	Propane,1,2,3-trimethoxy-	
304	1,2-Propanediol, 3-methoxy-	
341	Methyl glycerol derivative	
347	Methyl glycerol derivative	
393	Hexanoic acid, methyl ester	C6:0
431	Octenoic acid, methyl ester	C8:1
461	Octanoic acid, methyl ester	C8:0
580	Decanoic acid, methyl ester	C10:0
778	Methyl tetradecanoate	C14:0
864	Hexadecanoic acid, methyl ester	C16:0
931-940	9-Octadecenoic acid (Z)-, methyl ester and isomers	C18:1
955-996	9,12-Octadecadienoic acid, methyl ester and isomers	C18:0

Figure A5.3.1.1.1.3: GC-MS chromatogram of the products collected at the bottom of the reactor where residue is collected for batch #11. Retention time and peaks assignments are reported in the table.

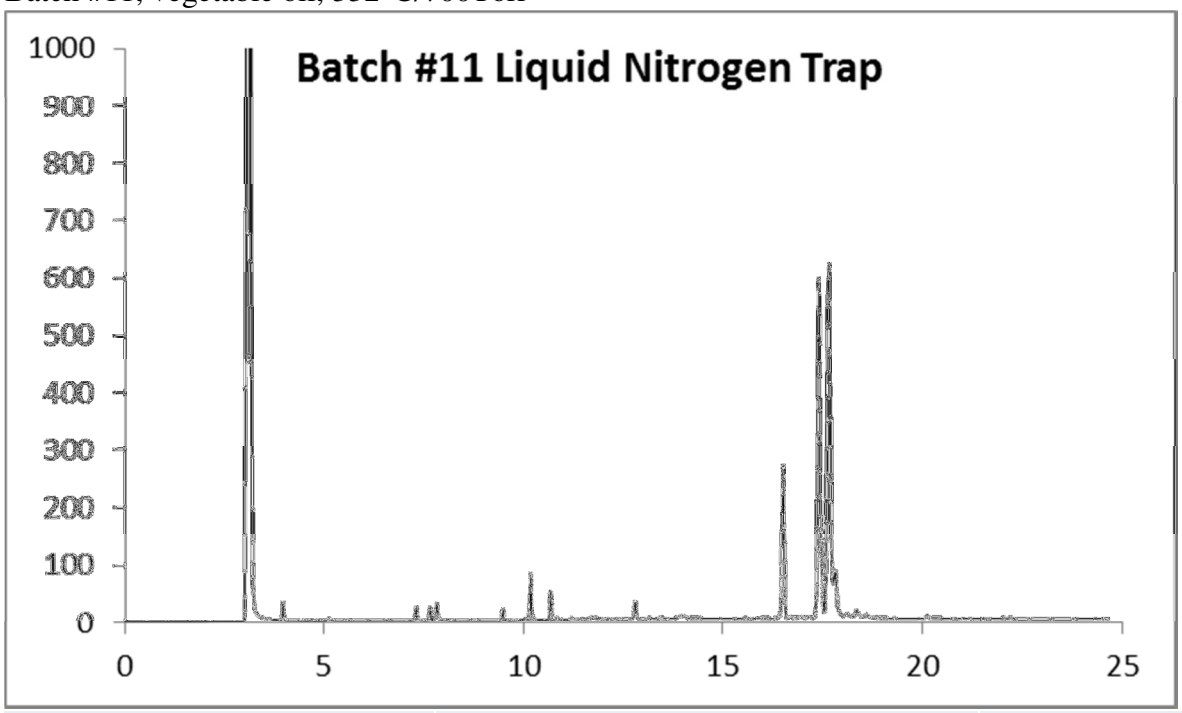
A-5.3.1.1.2 GC-FID data



Batch 11 Condenser Bottom		
Retention time (minutes)	Compound name	Peak Area %
3.075	methanol	1.93
3.167	Trimethylamine (TMA)	0.36
7.326	1,3-dimethoxy-2-propanol (DMP)	0.02
7.661	1,2,3-trimethoxypropane (TMP)	0.05
7.841	3-methoxy-1,2-propanediol (MMP)	0.02
16.462	Hexadecanoic acid methyl ester	11.54
17.329	9-octadecenoic acid methyl ester	33.71
17.575	9,12-octadecadienoic acid methyl ester	41.04
17.747	9,11-octadecadienoic acid methyl ester	4.32

Figure A5.3.1.1.2.1: GC-FID chromatogram of the products collected in the condenser for batch #11. Retention time, peaks assignments and relative peak area are reported in the table.

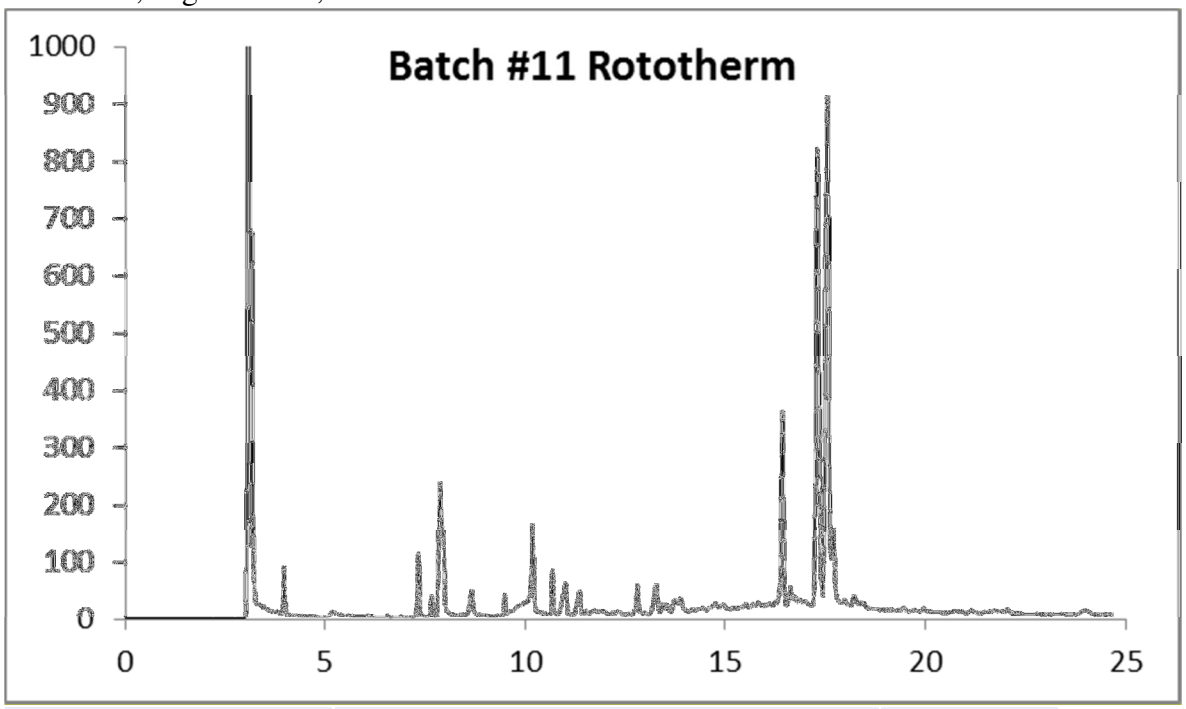
Batch #11, vegetable oil, 332°C/700Torr



Batch 11 Liquid Nitrogen Trap		
Retention time (minutes)	Compound name	Peak Area %
3.075	methanol	61.58
3.167	Trimethylamine (TMA)	14.44
7.326	1,3-dimethoxy-2-propanol (DMP)	0.17
7.661	1,2,3-trimethoxypropane (TMP)	0.13
7.841	3-methoxy-1,2-propanediol (MMP)	0.30
16.462	Hexadecanoic acid methyl ester	2.24
17.329	9-octadecenoic acid methyl ester	6.24
17.575	9,12-octadecadienoic acid methyl ester	8.23
17.747	9,11-octadecadienoic acid methyl ester	1.09

Figure A5.3.1.1.2.2: GC-FID chromatogram of the products collected in the liquid nitrogen trap for batch #11. Retention time, peaks assignments and relative peak area are reported in the table.

Batch #11, vegetable oil, 332°C/700Torr



Batch 11 Rototherm		
Retention time (minutes)	Compound name	Peak Area %
3.075	methanol	42.47
3.167	Trimethylamine (TMA)	2.23
7.326	1,3-dimethoxy-2-propanol (DMP)	0.70
7.661	1,2,3-trimethoxypropane (TMP)	0.18
7.841	3-methoxy-1,2-propanediol (MMP)	2.15
16.462	Hexadecanoic acid methyl ester	3.22
17.329	9-octadecenoic acid methyl ester	8.34
17.575	9,12-octadecadienoic acid methyl ester	10.93
17.747	9,11-octadecadienoic acid methyl ester	2.00

Figure A5.3.1.1.2.3: GC-FID chromatogram of the products collected at the bottom of the reactor where residue is collected for batch #11. Retention time, peaks assignments and relative peak area are reported in the table.

Batch #11, vegetable oil, 332°C/700Torr

A-5.3.1.1.3 NMR spectroscopy data

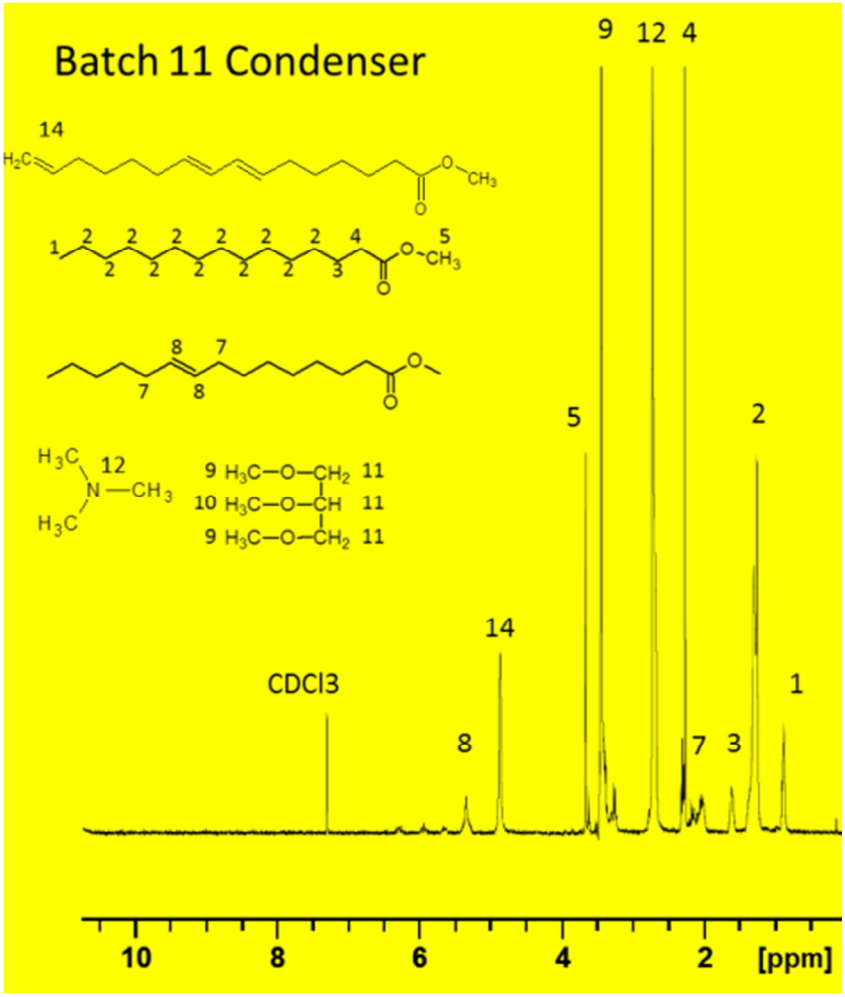
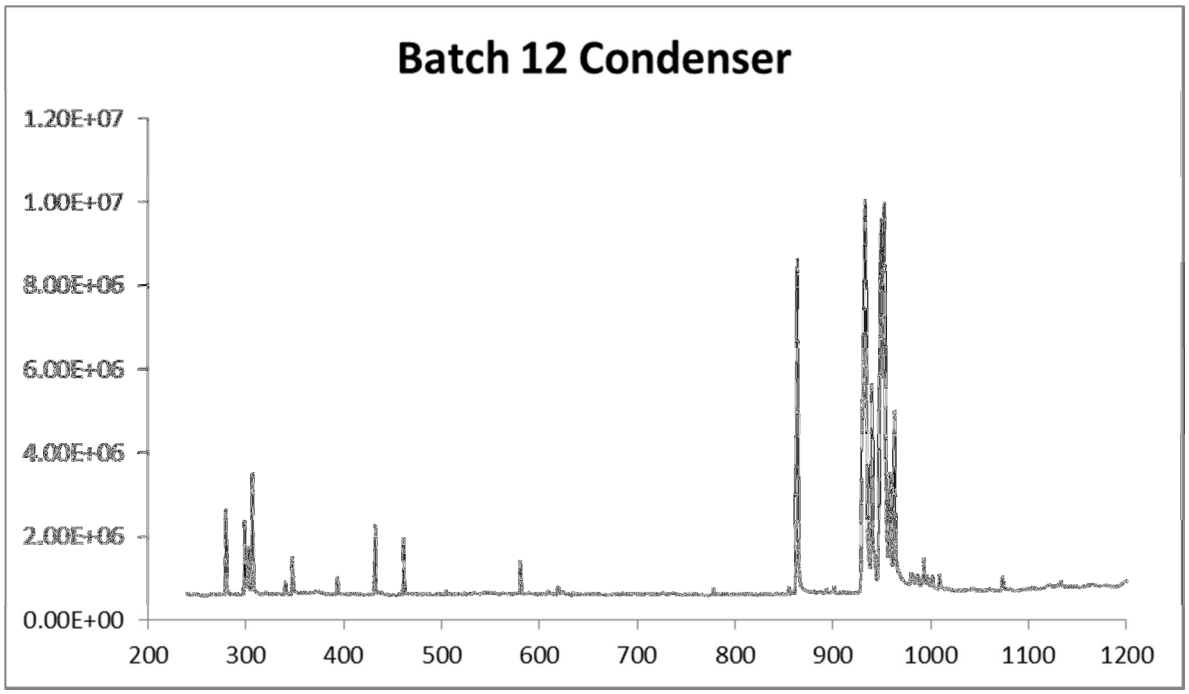


Figure A5.3.1.1.3.1: NMR spectrum of products collected in the condenser for batch #11. The sample has been diluted in deuterated chloroform ($CDCl_3$) for the analysis.

A5.3.1.2 Batch #12, vegetable oil, 332°C/700Torr

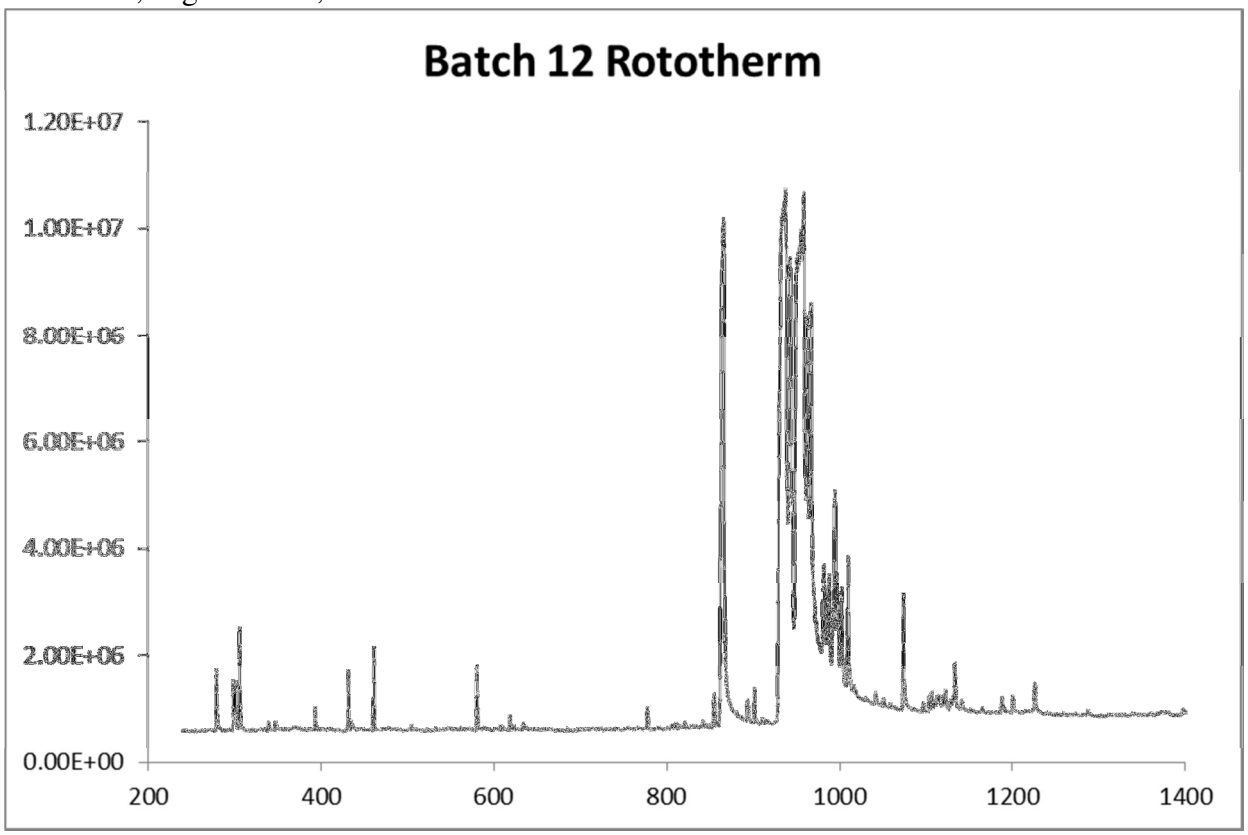
A-5.3.1.2.1 GC-MS data



Batch #12	Condenser	
R.T. (s)	Compound Name	
279	2-Propanol,1,3-dimthoxy-	
298	Propane,1,2,3-trimethoxy-	
300	1,2-Propanediol, 3-methoxy-	
340	Methyl glycerol derivative	
347	Methyl glycerol derivative	
393	Hexanoic acid, methyl ester	C6:0
431	Octenoic acid, methyl ester	C8:1
461	Octanoic acid, methyl ester	C8:0
580	Decanoic acid, methyl ester	C10:0
778	Methyl tetradecanoate	C14:0
862	Hexadecanoic acid, methyl ester	C16:0
929-939	9-Octadecenoic acid (Z)-, methyl ester and isomers	C18:1
947-993	9,12-Octadecadienoic acid, methyl ester and isomers	C18:0

Figure A5.3.1.2.1.1: GC-MS chromatogram of products collected in the condenser for batch #12. Retention time and peaks assignments are reported in the table.

Batch #12, vegetable oil, 332°C/700Torr

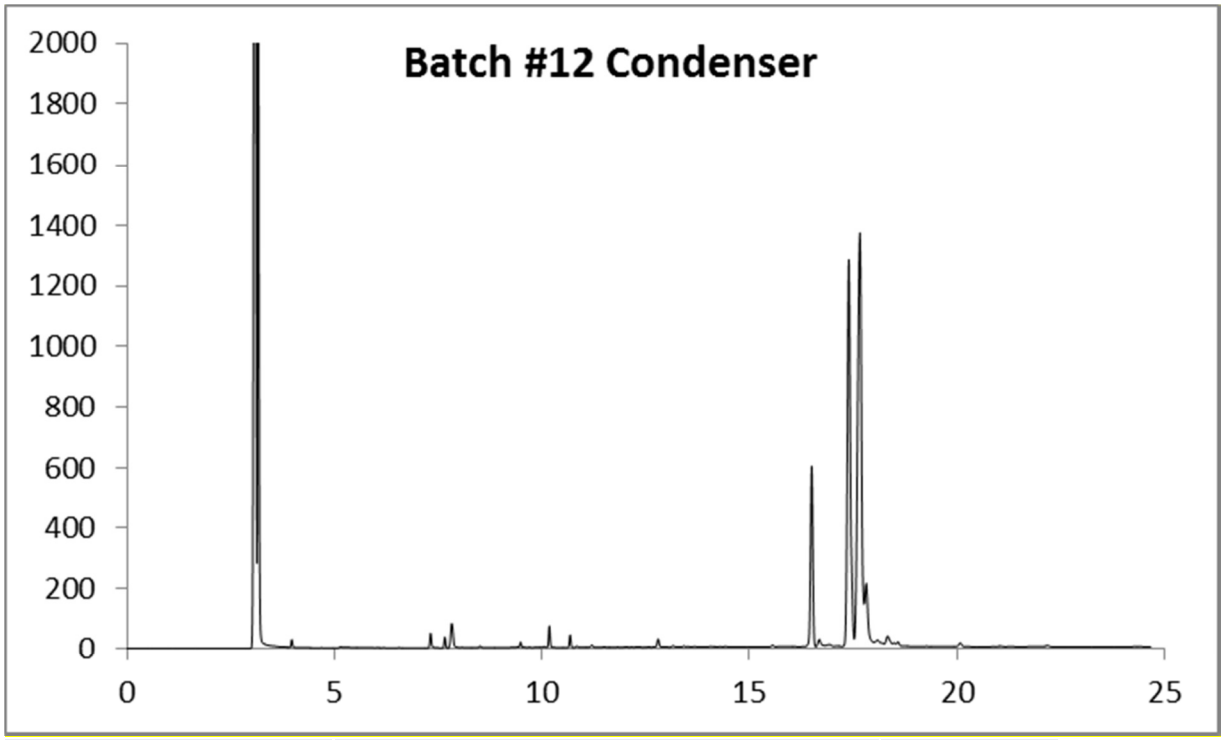


Batch #12	Rototherm	
R.T. (s)	Compound Name	
279	2-Propanol,1,3-dimthoxy-	
298	Propane,1,2,3-trimethoxy-	
300	1,2-Propanediol, 3-methoxy-	
340	Methyl glycerol derivative	
347	Methyl glycerol derivative	
393	Hexanoic acid, methyl ester	C6:0
431	Octenoic acid, methyl ester	C8:1
461	Octanoic acid, methyl ester	C8:0
580	Decanoic acid, methyl ester	C10:0
777	Methyl tetradecanoate	C14:0
862	Hexadecanoic acid, methyl ester	C16:0
929-939	9-Octadecenoic acid (Z)-, methyl ester and isomers	C18:1
947-997	9,12-Octadecadienoic acid, methyl ester and isomers	C18:0

Figure A5.3.1.2.1.2: GC-MS chromatogram of the products collected at the bottom of the reactor where residue is collected for batch #12. Retention time and peaks assignments are reported in the table.

Batch #12, vegetable oil, 332°C/700Torr

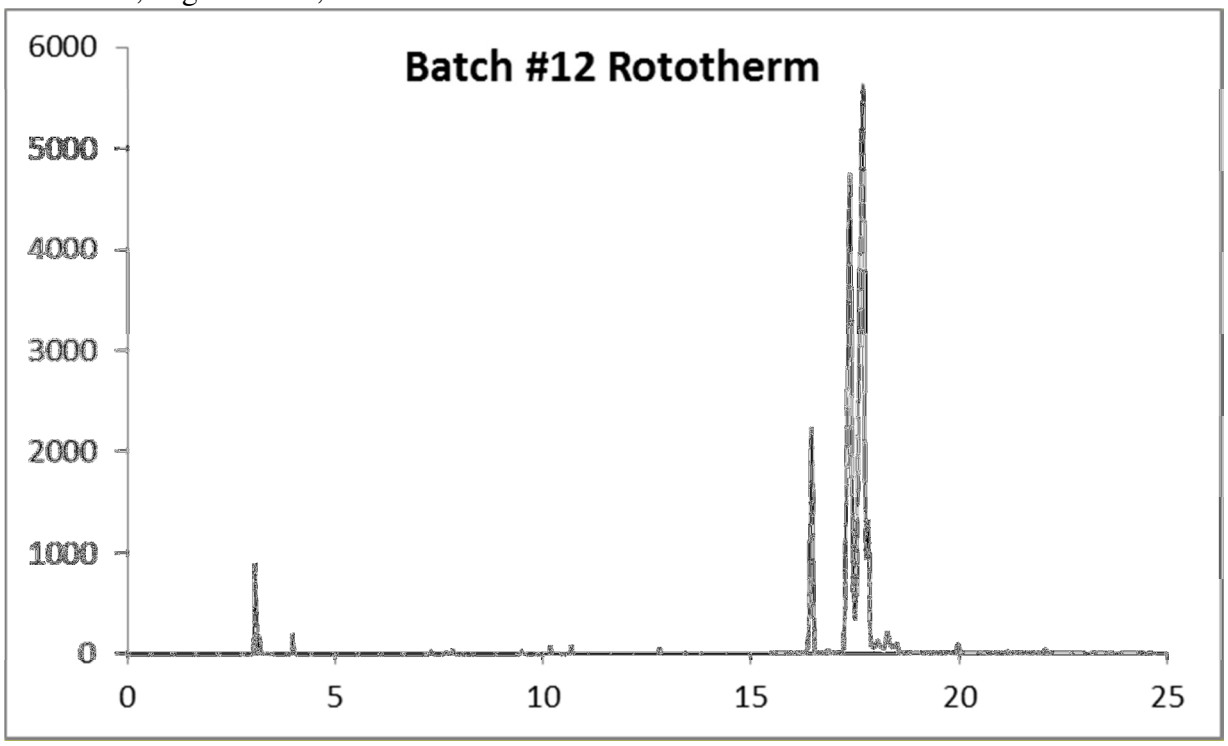
A-5.3.1.2.2 GC-FID data



Batch 12 Condenser		
Retention time (minutes)	**Compound name**	**Peak Area %**
3.075	**methanol**	**44.82**
3.167	**Trimethylamine (TMA)**	**14.23**
7.326	**1,3-dimethoxy-2-propanol (DMP)**	**0.27**
7.661	**1,2,3-trimethoxypropane (TMP)**	**0.16**
7.841	**3-methoxy-1,2-propanediol (MMP)**	**0.66**
16.462	**Hexadecanoic acid methyl ester**	**4.31**
17.329	**9-octadecenoic acid methyl ester**	**12.25**
17.575	**9,12-octadecadienoic acid methyl ester**	**16.51**
17.747	**9,11-octadecadienoic acid methyl ester**	**2.27**

Figure A5.3.1.2.2.1: GC-FID chromatogram of the products collected in the condenser for batch #12. Retention time, peaks assignments and relative peak area are reported in the table.

Batch #12, vegetable oil, 332°C/700Torr

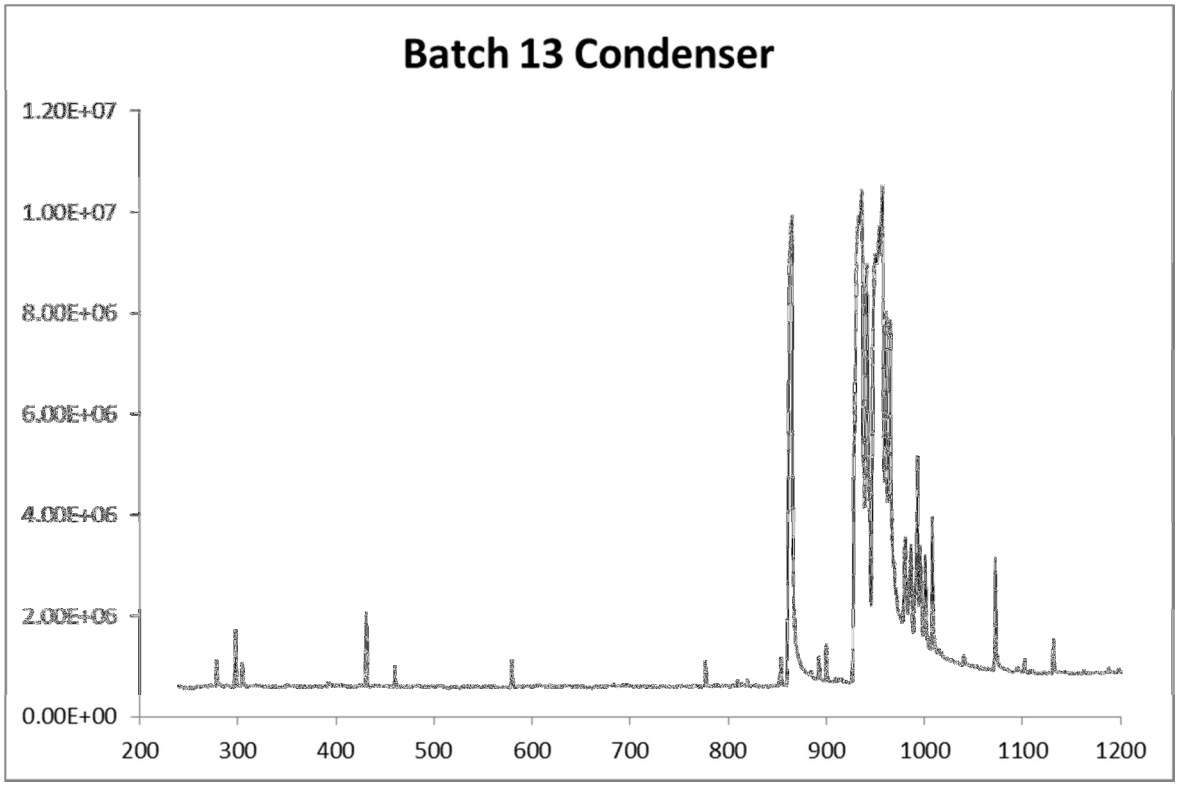


Batch 12 Rototherm		
Retention time (minutes)	Compound name	Peak Area %
3.075	methanol	1.97
3.167	Trimethylamine (TMA)	0.43
7.326	1,3-dimethoxy-2-propanol (DMP)	0.07
7.661	1,2,3-trimethoxypropane (TMP)	0.05
7.841	3-methoxy-1,2-propanediol (MMP)	0.10
16.462	Hexadecanoic acid methyl ester	8.82
17.329	9-octadecenoic acid methyl ester	30.97
17.575	9,12-octadecadienoic acid methyl ester	42.66
17.747	9,11-octadecadienoic acid methyl ester	5.17

Figure A5.3.1.2.2.2: GC-FID chromatogram of the products collected at the bottom of the reactor where residue is collected for batch #12. Retention time, peaks assignments and relative peak area are reported in the table.

A-5.3.1.3 Batch #13, vegetable oil, 304°C/700-760Torr

A-5.3.1.3.1 GC-MS data

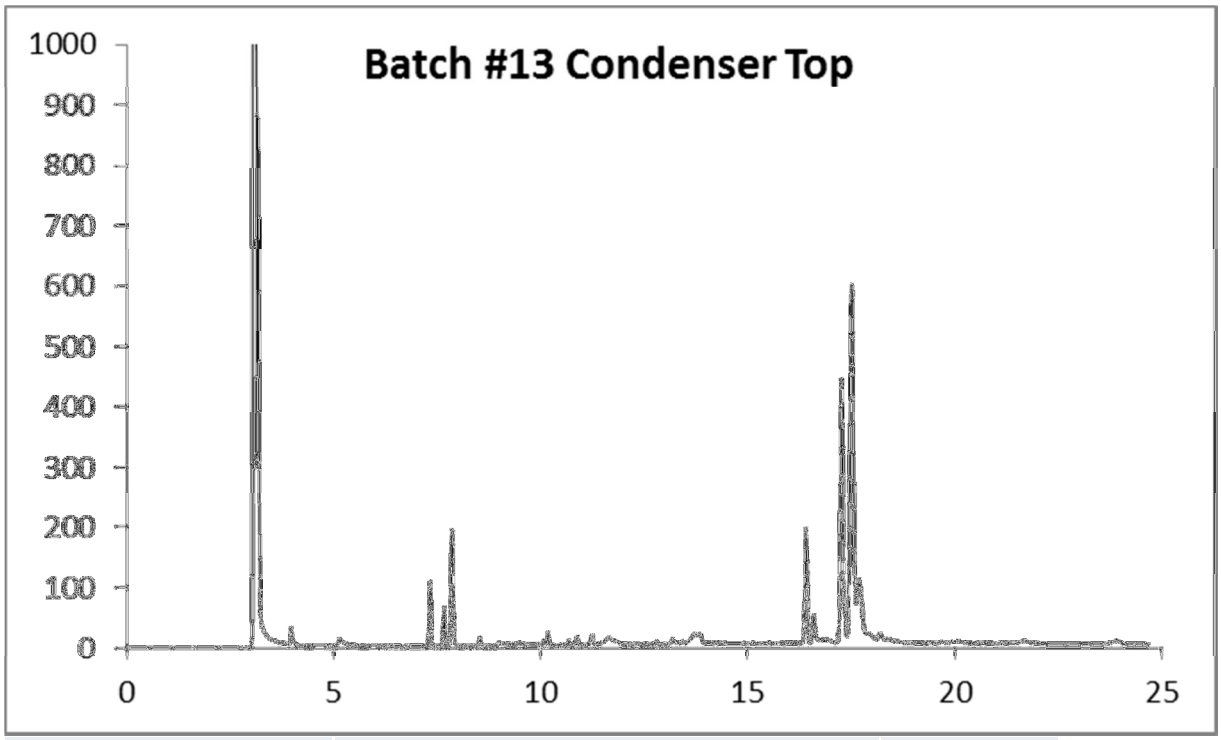


Batch #13	Condenser	
R.T. (s)	Compound Name	
279	2-Propanol,1,3-dimthoxy-	
298	Propane,1,2,3-trimethoxy-	
300	1,2-Propanediol, 3-methoxy-	
431	Octenoic acid, methyl ester	C8:1
461	Octanoic acid, methyl ester	C8:0
580	Decanoic acid, methyl ester	C10:0
777	Methyl tetradecanoate	C14:0
862	Hexadecanoic acid, methyl ester	C16:0
929-939	9-Octadecenoic acid (Z)-, methyl ester and isomers	C18:1
947-997	9,12-Octadecadienoic acid, methyl ester and isomers	C18:0

Figure A5.3.1.3.1.1: GC-MS chromatogram of products collected in the condenser for batch #13. Retention time and peaks assignments are reported in the table.

Batch #13, vegetable oil, 304°C/700-760 Torr

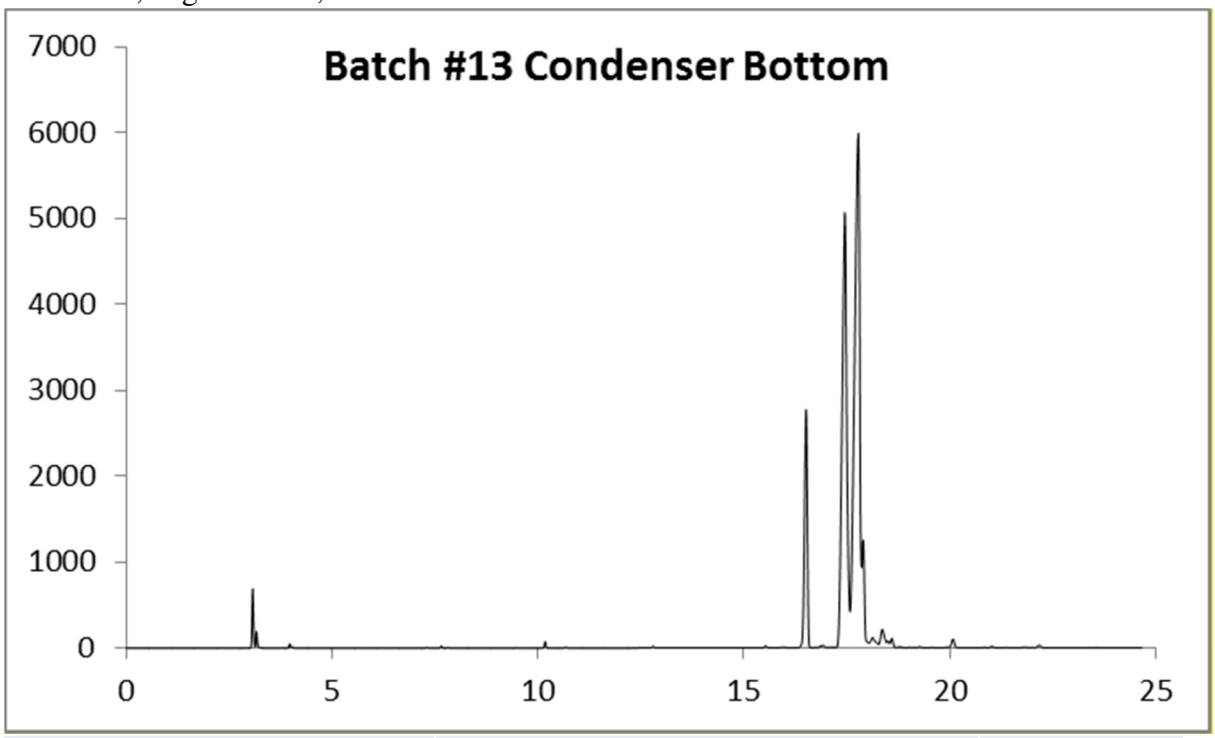
A-5.3.1.3.2 GC-FID data



Batch 13 Condenser Top		
Retention time (minutes)	Compound name	Peak Area %
3.075	methanol	63.19
3.167	Trimethylamine (TMA)	6.96
7.326	1,3-dimethoxy-2-propanol (DMP)	0.81
7.661	1,2,3-trimethoxypropane (TMP)	0.40
7.841	3-methoxy-1,2-propanediol (MMP)	1.91
16.462	Hexadecanoic acid methyl ester	1.80
17.329	9-octadecenoic acid methyl ester	5.10
17.575	9,12-octadecadienoic acid methyl ester	8.90
17.747	9,11-octadecadienoic acid methyl ester	2.74

Figure A5.3.1.3.2.1: GC-FID chromatogram of the top layer of liquids collected in the condenser for batch #13. Retention time, peaks assignments and relative peak area are reported in the table.

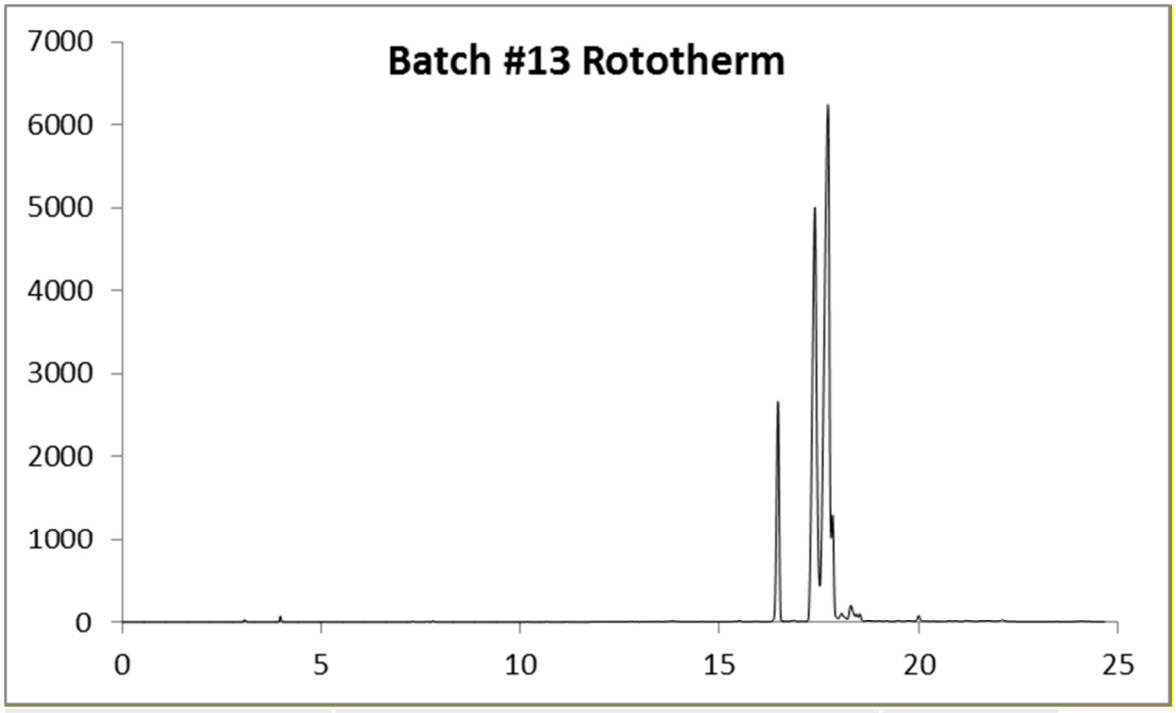
Batch #13, vegetable oil, 304°C/700-760 Torr



Batch 13 Condenser Bottom		
Retention time (minutes)	Compound name	Peak Area %
3.075	methanol	1.44
3.167	Trimethylamine (TMA)	0.40
7.326	1,3-dimethoxy-2-propanol (DMP)	0.02
7.661	1,2,3-trimethoxypropane (TMP)	0.05
7.841	3-methoxy-1,2-propanediol (MMP)	0.02
16.462	Hexadecanoic acid methyl ester	10.91
17.329	9-octadecenoic acid methyl ester	33.38
17.575	9,12-octadecadienoic acid methyl ester	44.20
17.747	9,11-octadecadienoic acid methyl ester	4.50

Figure A5.3.1.3.2.2: GC-FID chromatogram of the bottom layer of liquids collected in the condenser for batch #13. Retention time, peaks assignments and relative peak area are reported in the table.

Batch #13, vegetable oil, 304°C/700-760 Torr

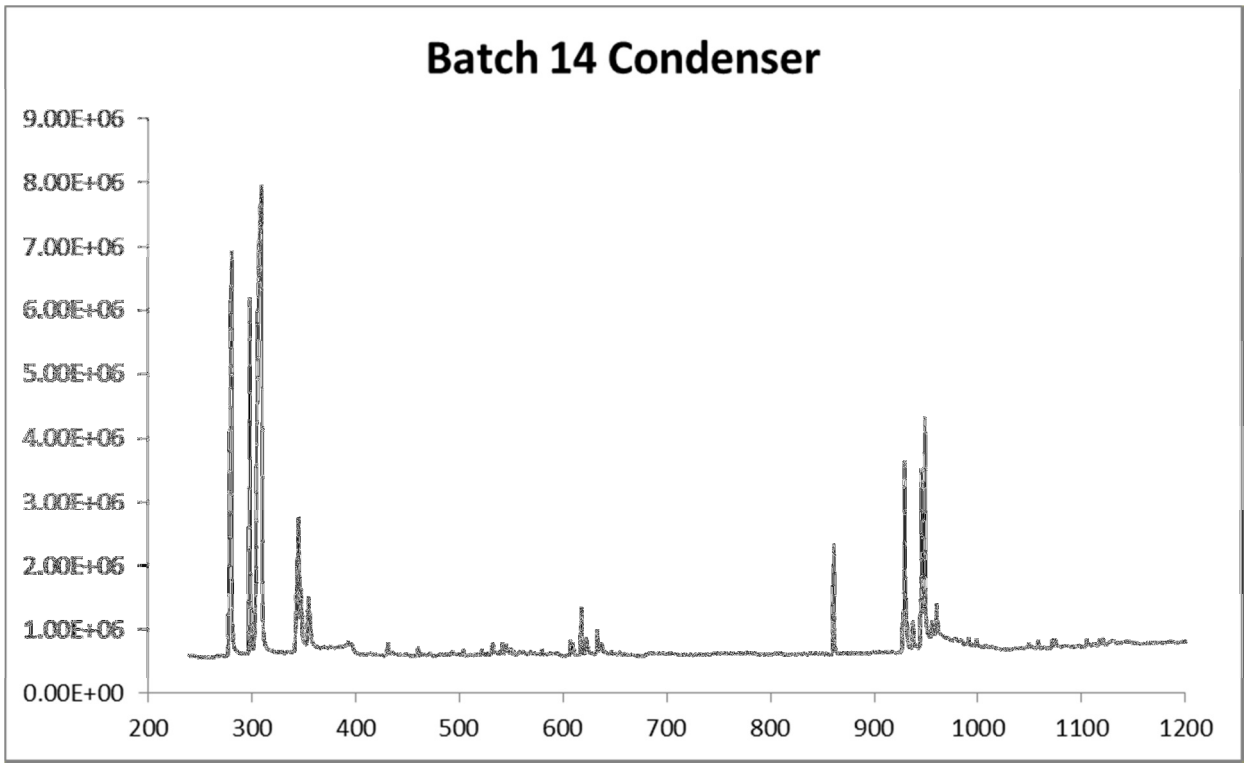


Batch 13 Rototherm		
Retention time (minutes)	Compound name	Peak Area %
3.075	methanol	0.10
3.167	Trimethylamine (TMA)	0.00
7.326	1,3-dimethoxy-2-propanol (DMP)	0.03
7.661	1,2,3-trimethoxypropane (TMP)	0.02
7.841	3-methoxy-1,2-propanediol (MMP)	0.05
16.462	Hexadecanoic acid methyl ester	10.06
17.329	9-octadecenoic acid methyl ester	31.07
17.575	9,12-octadecadienoic acid methyl ester	45.00
17.747	9,11-octadecadienoic acid methyl ester	4.50

Figure A5.3.1.3.2.3: GC-FID chromatogram of the products collected at the bottom of the reactor where residue is collected for batch #13. Retention time, peaks assignments and relative peak area are reported in the table.

A-5.3.1.4 Batch #14, vegetable oil, 2 gal/hr, 304°C/500-600 Torr

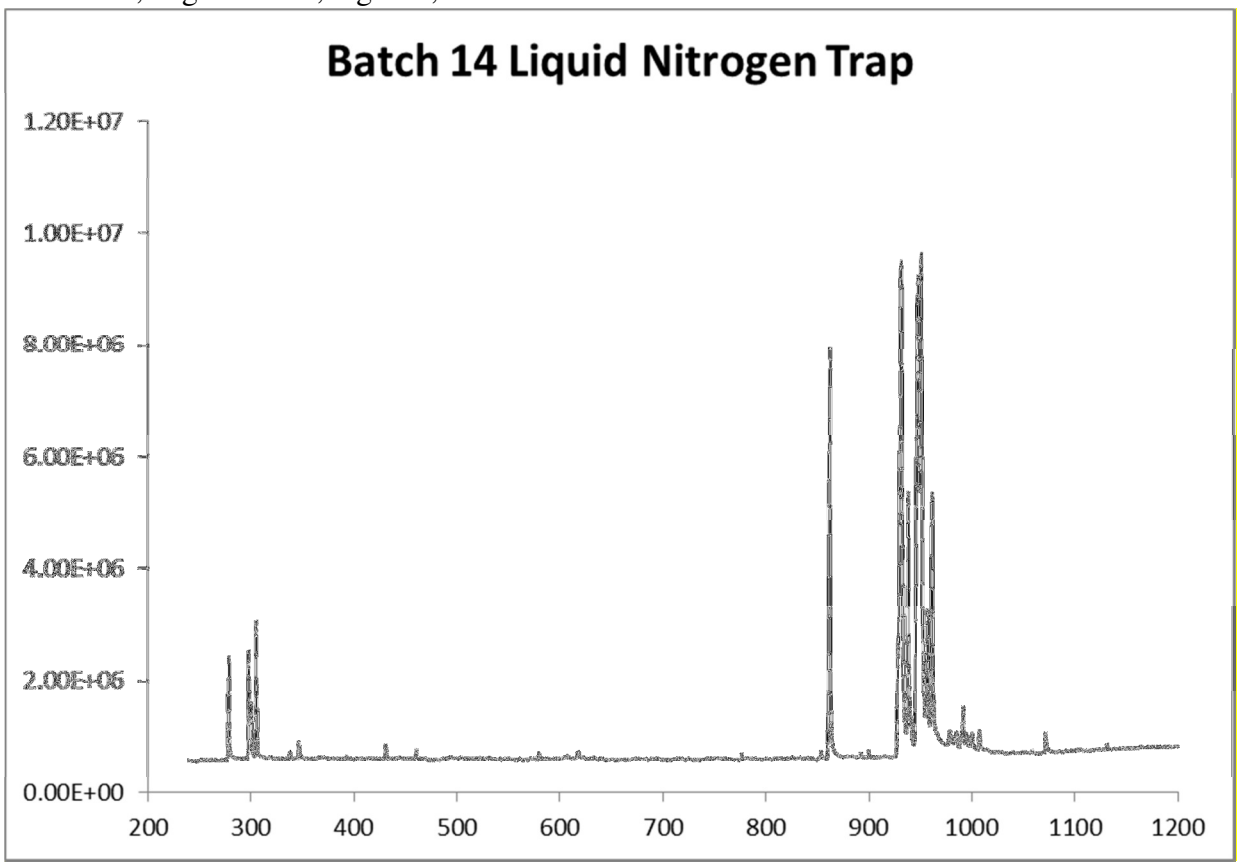
A-5.3.1.4.1 GC-MS data



Batch #14	Condenser	
R.T. (s)	Compound Name	
279	2-Propanol,1,3-dimthoxy-	
298	Propane,1,2,3-trimethoxy-	
300	1,2-Propanediol, 3-methoxy-	
339	Methyl glycerol derivative	
345	Methyl glycerol derivative	
860	Hexadecanoic acid, methyl ester	C16:0
926-928	9-Octadecenoic acid (Z)-, methyl ester and isomers	C18:1
939-960	9,12-Octadecadienoic acid, methyl ester and isomers	C18:0

Figure A5.3.1.4.1.1: GC-MS chromatogram of products collected in the condenser for batch #14. Retention time and peaks assignments are reported in the table.

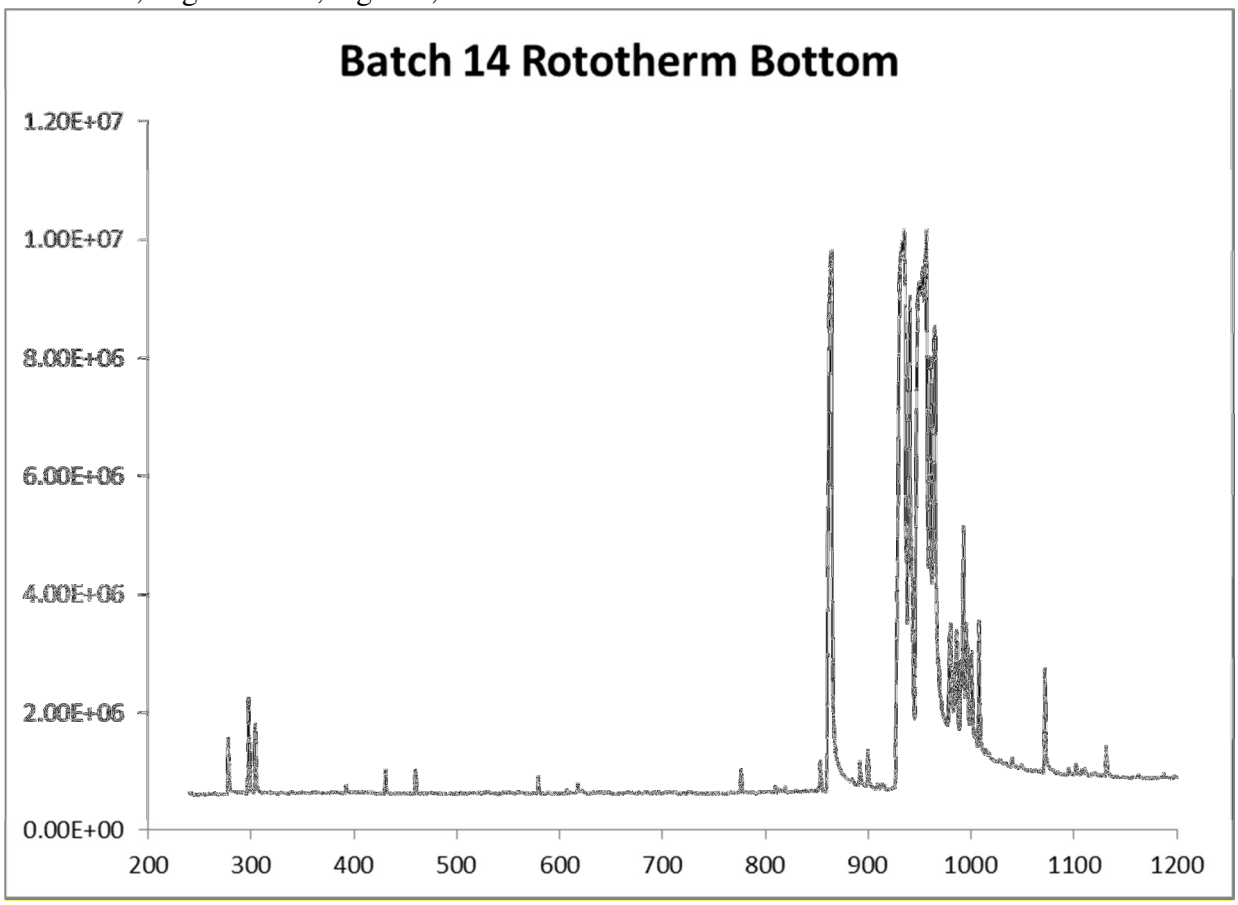
Batch #14, vegetable oil, 2 gal/hr, 304°C/500-600 Torr



Batch #14	Liquid Nitrogen trap	
R.T. (s)	Compound Name	
279	2-Propanol,1,3-dimthoxy-	
298	Propane,1,2,3-trimethoxy-	
300	1,2-Propanediol, 3-methoxy-	
431	Octenoic acid, methyl ester	C8:1
461	Octanoic acid, methyl ester	C8:0
580	Decanoic acid, methyl ester	C10:0
777	Methyl tetradecanoate	C14:0
862	Hexadecanoic acid, methyl ester	C16:0
929-939	9-Octadecenoic acid (Z)-, methyl ester and isomers	C18:1
947-991	9,12-Octadecadienoic acid, methyl ester and isomers	C18:0

Figure A5.3.1.4.1.2: GC-MS chromatogram of products collected in the nitrogen trap for batch #14. Retention time and peaks assignments are reported in the table.

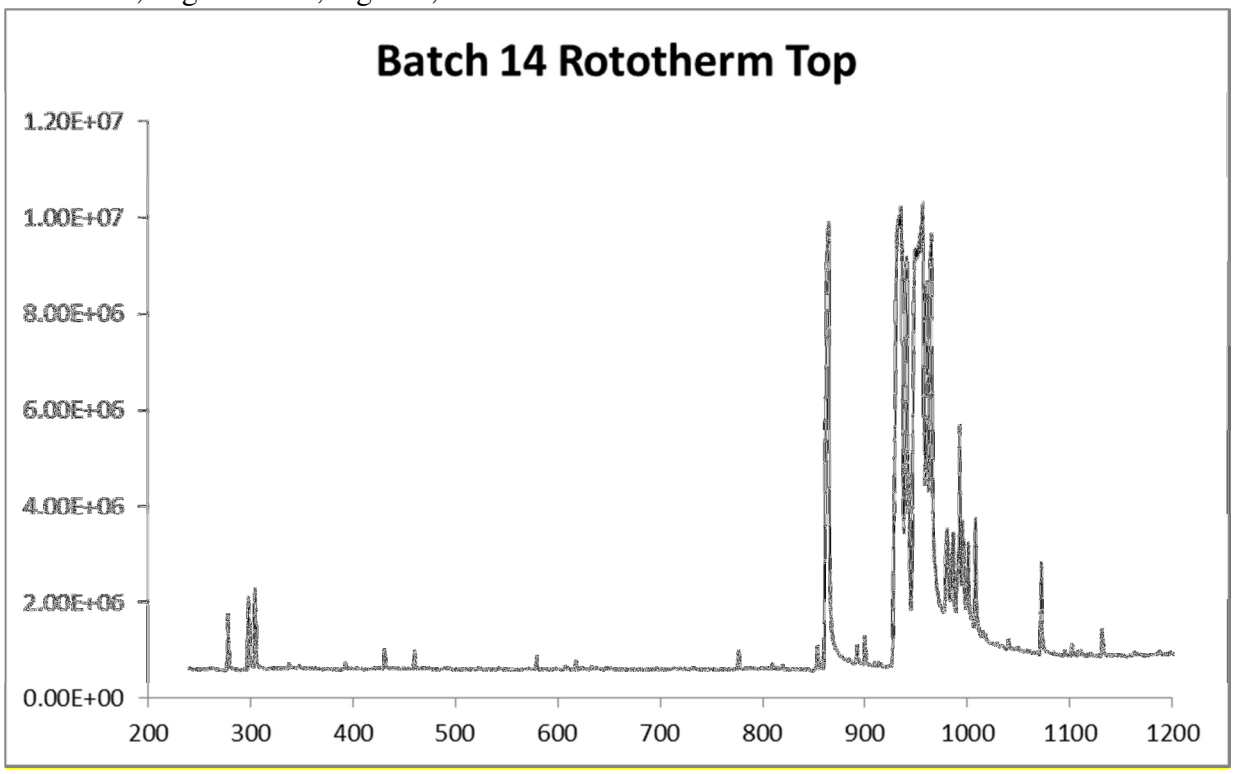
Batch #14, vegetable oil, 2 gal/hr, 304°C/500-600 Torr



Batch #14	Rototherm Bottom	
R.T. (s)	Compound Name	
279	2-Propanol,1,3-dimthoxy-	
298	Propane,1,2,3-trimethoxy-	
300	1,2-Propanediol, 3-methoxy-	
393	Hexanoic acid, methyl ester	C6:0
431	Octenoic acid, methyl ester	C8:1
461	Octanoic acid, methyl ester	C8:0
580	Decanoic Acid, methyl ester	C10:0
778	Methyl tetradecanoate	C14:0
862	Hexadecanoic acid, methyl ester	C16:0
929-939	9-Octadecenoic acid (Z)-, methyl ester and isomers	C18:1
947-991	9,12-Octadecadienoic acid, methyl ester and isomers	C18:0

Figure A5.3.1.4.1.3: GC-MS chromatogram of the top layer of liquids collected at the bottom of the reactor where residue is usually collected for batch #14. Retention time and peaks assignments are reported in the table.

Batch #14, vegetable oil, 2 gal/hr, 304°C/500-600 Torr

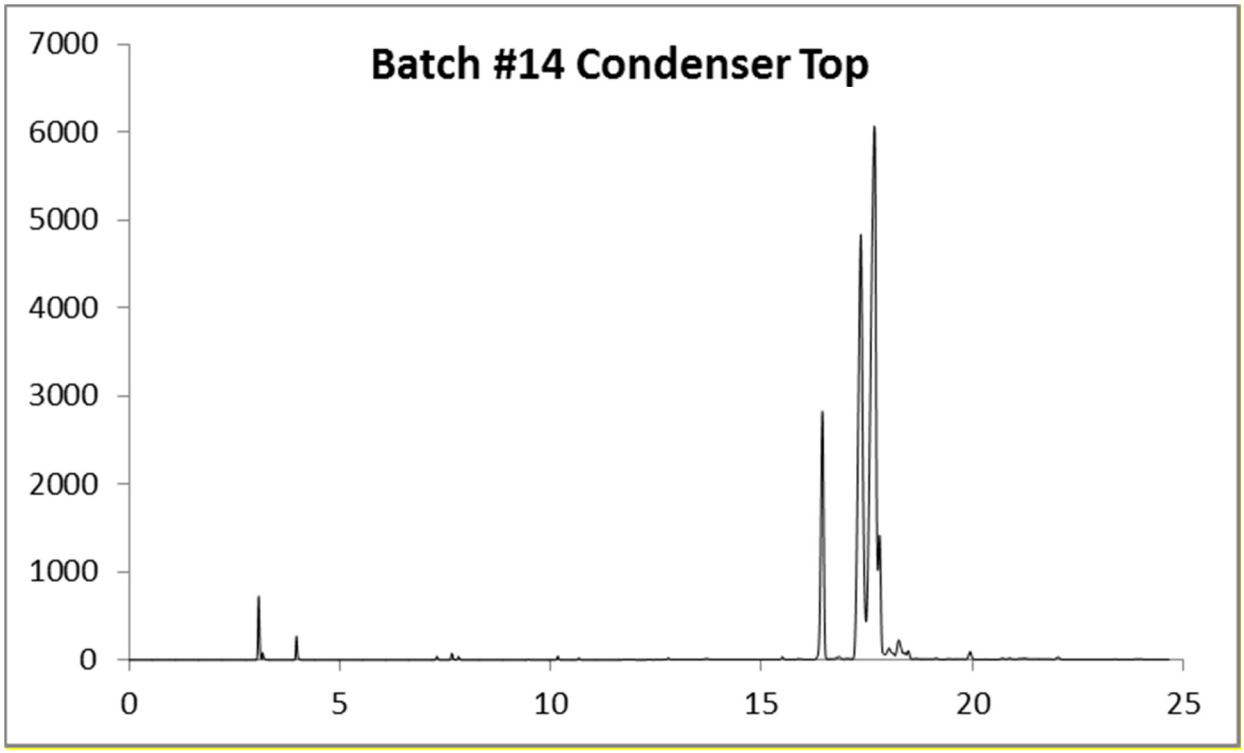


Batch #14	Rototherm Top	
R.T. (s)	Compound Name	
279	2-Propanol,1,3-dimthoxy-	
298	Propane,1,2,3-trimethoxy-	
300	1,2-Propanediol, 3-methoxy-	
393	Hexanoic acid, methyl ester	C6:0
431	Octenoic acid, methyl ester	C8:1
461	Octanoic acid, methyl ester	C8:0
580	Decanoic acid, methyl ester	C10:0
777	Methyl tetradecanoate	C14:0
862	Hexadecanoic acid, methyl ester	C16:0
929-939	9-Octadecenoic acid (Z)-, methyl ester and isomers	C18:1
947-991	9,12-Octadecadienoic acid, methyl ester and isomers	C18:0

Figure A5.3.1.4.1.4: GC-MS chromatogram of the bottom layer of liquids collected at the bottom of the reactor where residue is usually collected for batch #14. Retention time and peaks assignments are reported in the table.

Batch #14, vegetable oil, 2 gal/hr, 304°C/500-600 Torr

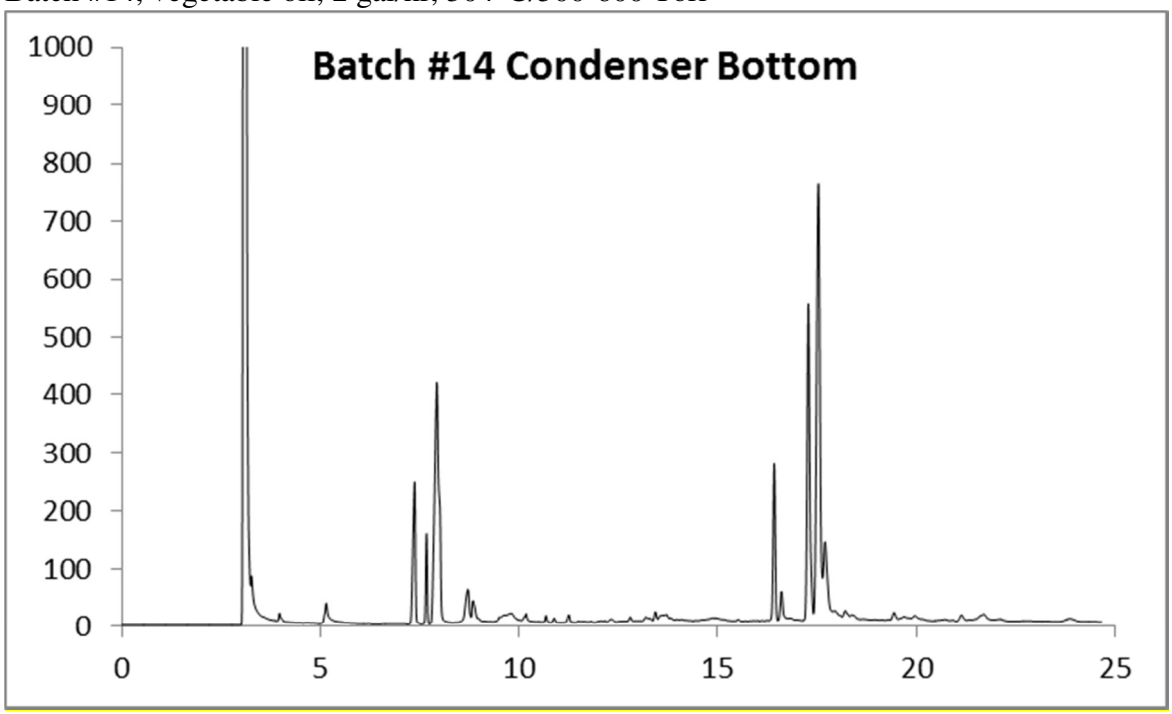
A-5.3.1.4.2 GC-FID data



Batch 14 Condenser Top		
Retention time (minutes)	**Compound name**	**Peak Area %**
3.075	**methanol**	**1.48**
3.167	**Trimethylamine (TMA)**	**0.18**
7.326	**1,3-dimethoxy-2-propanol (DMP)**	**0.09**
7.661	**1,2,3-trimethoxypropane (TMP)**	**0.17**
7.841	**3-methoxy-1,2-propanediol (MMP)**	**0.09**
16.462	**Hexadecanoic acid methyl ester**	**10.97**
17.329	**9-octadecenoic acid methyl ester**	**29.96**
17.575	**9,12-octadecadienoic acid methyl ester**	**43.80**
17.747	**9,11-octadecadienoic acid methyl ester**	**5.04**

Figure A5.3.1.4.2.1: GC-FID chromatogram of the top layer of liquids collected in the condenser for batch #14. Retention time, peaks assignments and relative peak area are reported in the table.

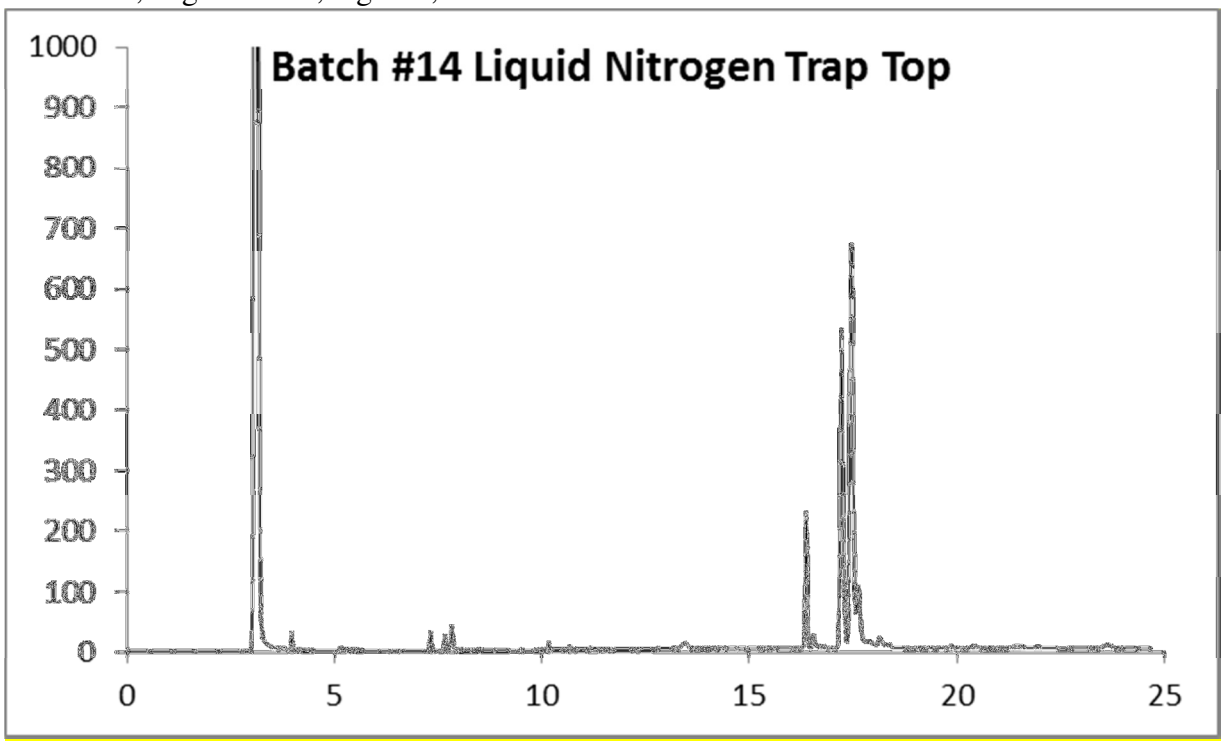
Batch #14, vegetable oil, 2 gal/hr, 304°C/500-600 Torr



Batch 14 Condenser Bottom		
Retention time (minutes)	Compound name	Peak Area %
3.075	methanol	55.67
3.167	Trimethylamine (TMA)	0.02
7.326	1,3-dimethoxy-2-propanol (DMP)	2.44
7.661	1,2,3-trimethoxypropane (TMP)	0.97
7.841	3-methoxy-1,2-propanediol (MMP)	7.47
16.462	Hexadecanoic acid methyl ester	2.39
17.329	9-octadecenoic acid methyl ester	5.90
17.575	9,12-octadecadienoic acid methyl ester	10.40
17.747	9,11-octadecadienoic acid methyl ester	2.40

Figure A5.3.1.4.2.2: GC-FID chromatogram of the bottom layer of liquids collected in the condenser for batch #14. Retention time, peaks assignments and relative peak area are reported in the table.

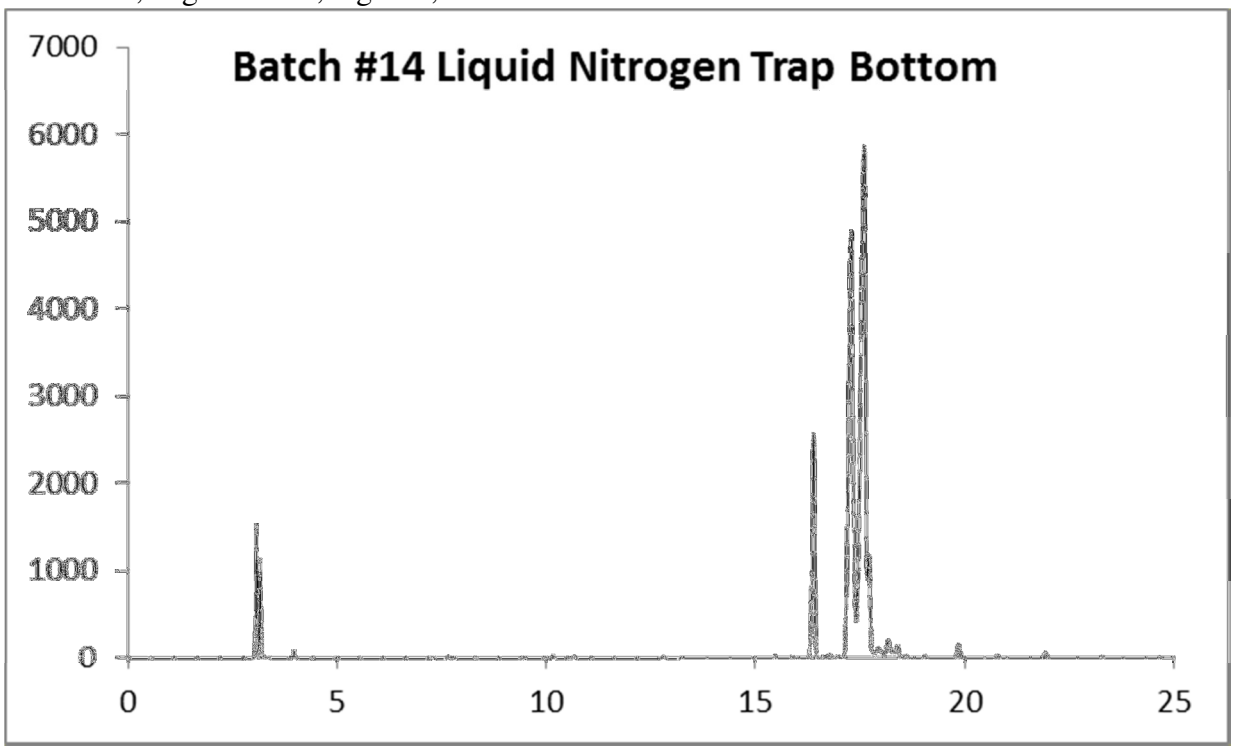
Batch #14, vegetable oil, 2 gal/hr, 304°C/500-600 Torr



Batch 14 Liquid Nitrogen Trap Top		
Retention time (minutes)	**Compound name**	**Peak Area %**
3.075	**methanol**	**59.39**
3.167	**Trimethylamine (TMA)**	**18.84**
7.326	**1,3-dimethoxy-2-propanol (DMP)**	**0.21**
7.661	**1,2,3-trimethoxypropane (TMP)**	**0.14**
7.841	**3-methoxy-1,2-propanediol (MMP)**	**0.34**
16.462	**Hexadecanoic acid methyl ester**	**1.88**
17.329	**9-octadecenoic acid methyl ester**	**5.49**
17.575	**9,12-octadecadienoic acid methyl ester**	**8.75**
17.747	**9,11-octadecadienoic acid methyl ester**	**1.48**

Figure A5.3.1.4.2.3: GC-FID chromatogram of the top layer of liquids collected in the liquid nitrogen trap for batch #14. Retention time, peaks assignments and relative peak area are reported in the table.

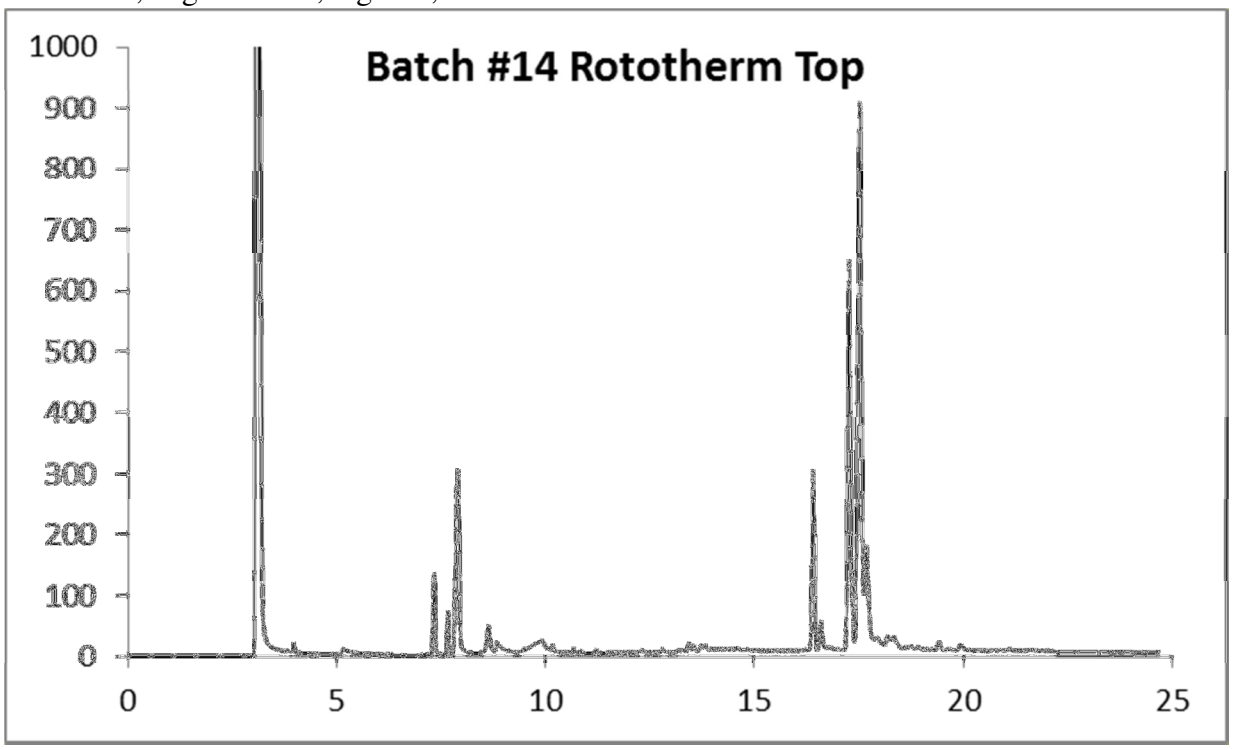
Batch #14, vegetable oil, 2 gal/hr, 304°C/500-600 Torr



Batch 14 Liquid Nitrogen Trap Bottom		
Retention time (minutes)	**Compound name**	**Peak Area %**
3.075	**methanol**	**3.33**
3.167	**Trimethylamine (TMA)**	**2.14**
7.326	**1,3-dimethoxy-2-propanol (DMP)**	**0.01**
7.661	**1,2,3-trimethoxypropane (TMP)**	**0.03**
7.841	**3-methoxy-1,2-propanediol (MMP)**	**0.01**
16.462	**Hexadecanoic acid methyl ester**	**10.04**
17.329	**9-octadecenoic acid methyl ester**	**32.27**
17.575	**9,12-octadecadienoic acid methyl ester**	**42.79**
17.747	**9,11-octadecadienoic acid methyl ester**	**4.33**

Figure A5.3.1.4.2.4: GC-FID chromatogram of the bottom layer of liquids collected in the liquid nitrogen trap for batch #14. Retention time, peaks assignments and relative peak area are reported in the table.

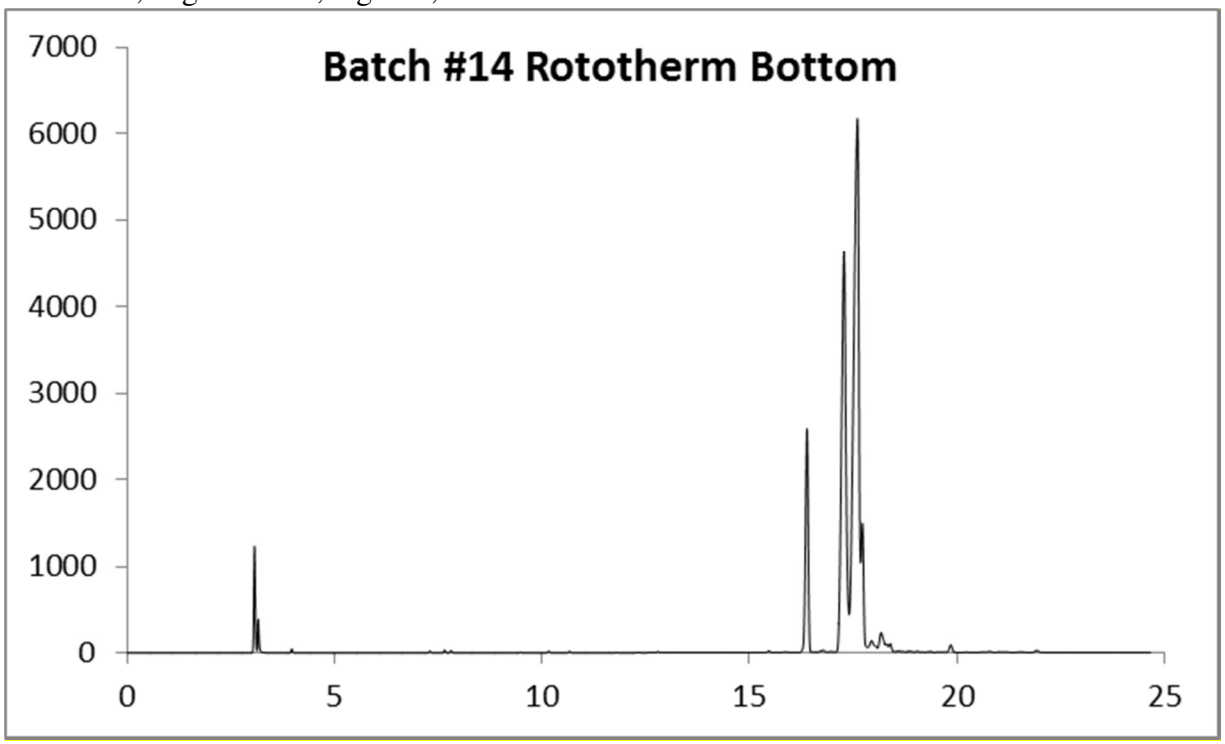
Batch #14, vegetable oil, 2 gal/hr, 304°C/500-600 Torr



Batch 14 Rototherm Top		
Retention time (minutes)	**Compound name**	**Peak Area %**
3.075	**methanol**	**53.53**
3.167	**Trimethylamine (TMA)**	**7.75**
7.326	**1,3-dimethoxy-2-propanol (DMP)**	**0.91**
7.661	**1,2,3-trimethoxypropane (TMP)**	**0.37**
7.841	**3-methoxy-1,2-propanediol (MMP)**	**3.78**
16.462	**Hexadecanoic acid methyl ester**	**2.39**
17.329	**9-octadecenoic acid methyl ester**	**6.35**
17.575	**9,12-octadecadienoic acid methyl ester**	**11.31**
17.747	**9,11-octadecadienoic acid methyl ester**	**2.44**

Figure A5.3.1.4.2.5: GC-FID chromatogram of the top layer of liquids collected at the bottom of the reactor where residue is collected for batch #14. Retention time, peaks assignments and relative peak area are reported in the table.

Batch #14, vegetable oil, 2 gal/hr, 304°C/500-600 Torr



Batch 14 Rototherm Bottom		
Retention time (minutes)	**Compound name**	**Peak Area %**
3.075	**methanol**	**2.63**
3.167	**Trimethylamine (TMA)**	**0.79**
7.326	**1,3-dimethoxy-2-propanol (DMP)**	**0.06**
7.661	**1,2,3-trimethoxypropane (TMP)**	**0.08**
7.841	**3-methoxy-1,2-propanediol (MMP)**	**0.07**
16.462	**Hexadecanoic acid methyl ester**	**9.96**
17.329	**9-octadecenoic acid methyl ester**	**29.21**
17.575	**9,12-octadecadienoic acid methyl ester**	**45.74**
17.747	**9,11-octadecadienoic acid methyl ester**	**5.49**

Figure A5.3.1.4.2.6: GC-FID chromatogram of the bottom layer of liquids collected at the bottom of the reactor where residue is collected for batch #14. Retention time, peaks assignments and relative peak area are reported in the table.

Batch #14, vegetable oil, 2 gal/hr, 304°C/500-600 Torr

A-5.3.1.4.3 NMR spectroscopy data

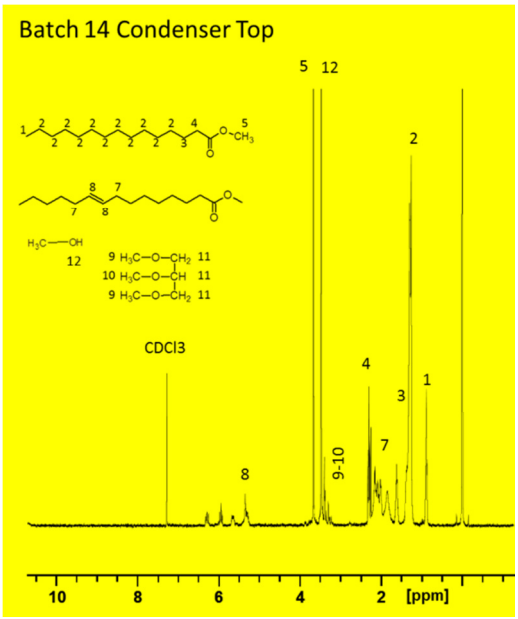


Figure A5.3.1.4.3.1: NMR spectrum of products collected in the condenser for batch #14. The sample has been diluted in deuterated chloroform ($CDCl_3$) for the analysis.

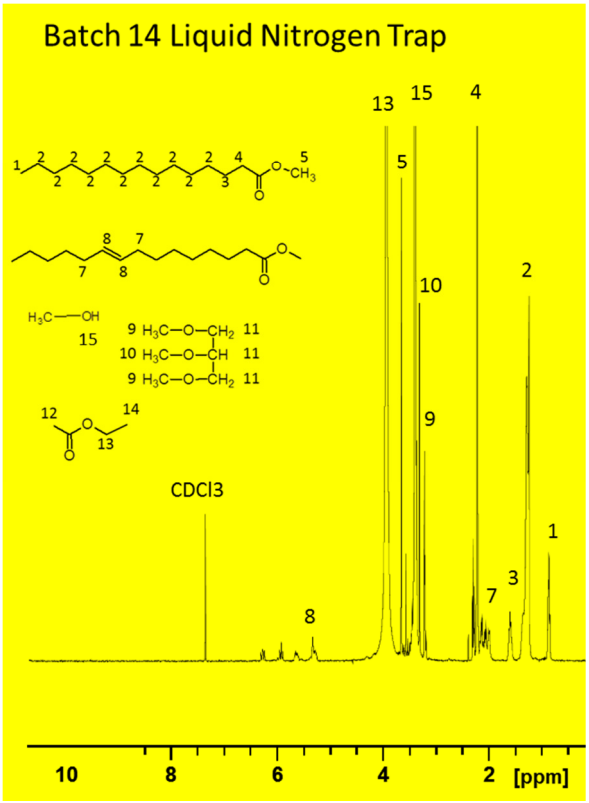


Figure A5.3.1.4.3.2: NMR spectrum of products collected in the nitrogen trap for batch #14. The sample has been diluted in deuterated chloroform ($CDCl_3$) for the analysis.

Batch #14, vegetable oil, 2 gal/hr, 304°C/500-600 Torr

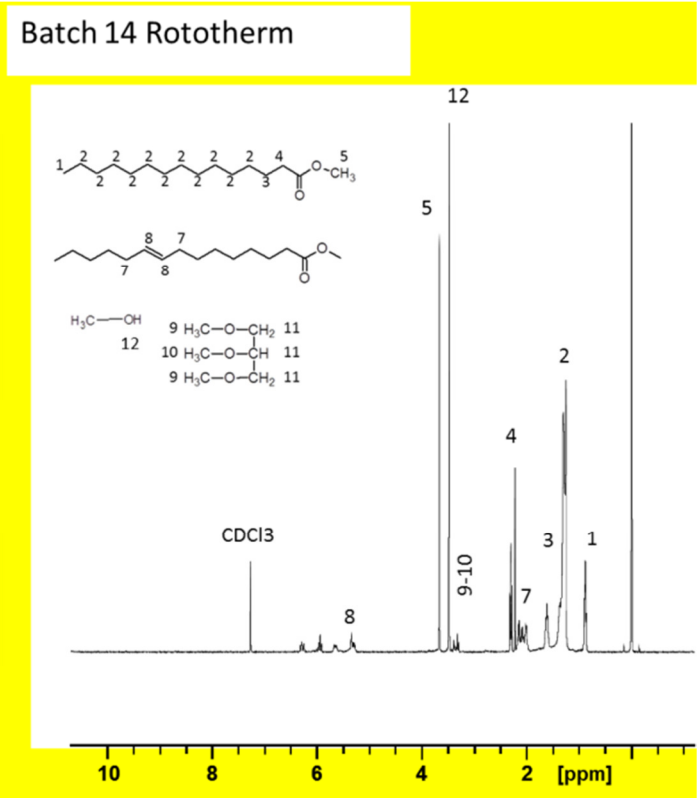
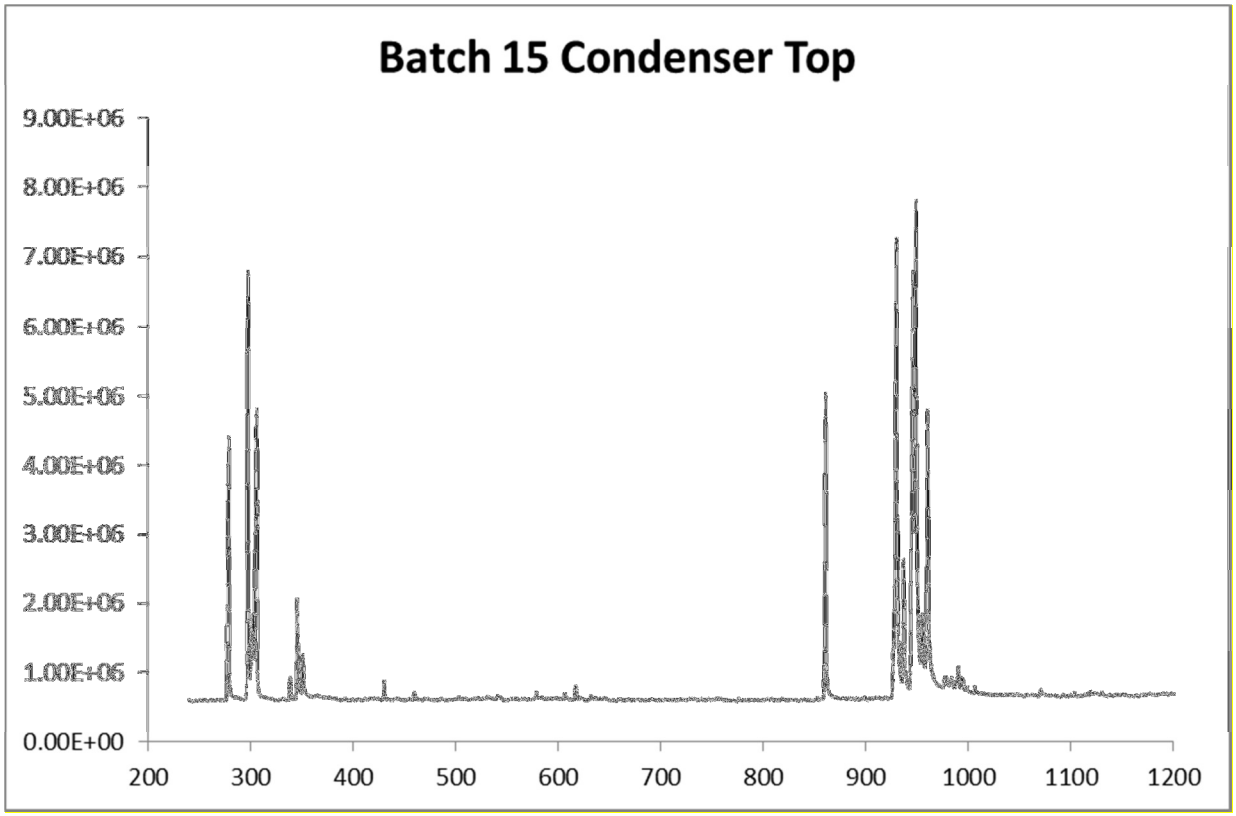


Figure A5.3.1.4.3.3: NMR spectrum of products collected at the bottom of the reactor where residue is collected for batch #14. The sample has been diluted in deuterated chloroform ($CDCl_3$) for the analysis.

A5.3.1.5 Batch #15, vegetable oil, 3 gal/hr, 304°C/100 Torr

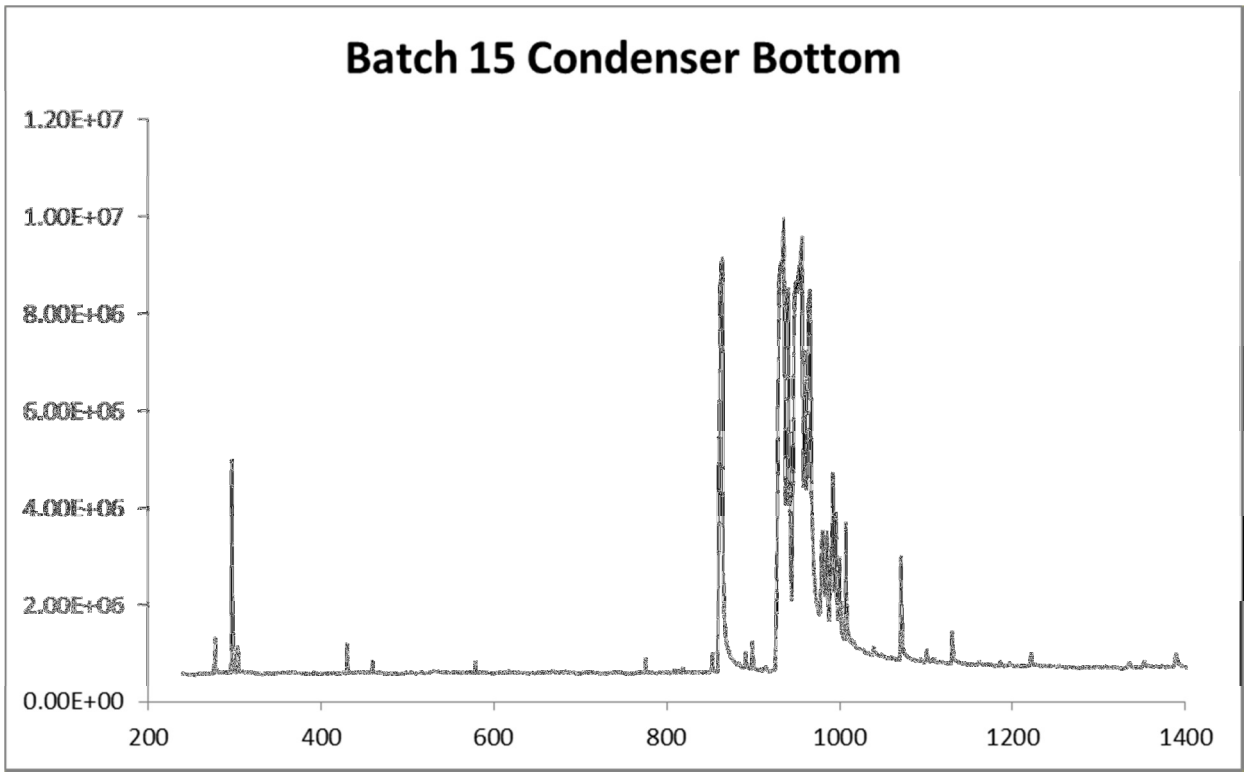
A-5.3.1.5.1 GC-MS data



Batch #15	Condenser Top	
R.T. (s)	Compound Name	
279	2-Propanol,1,3-dimthoxy-	
298	Propane,1,2,3-trimethoxy-	
300	1,2-Propanediol, 3-methoxy-	
340	Methyl glycerol derivatives	
347	Methyl glycerol derivatives	
431	Octenoic acid, methyl ester	C8:1
461	Octanoic acid, methyl ester	C8:0
862	Hexadecanoic acid, methyl ester	C16:0
929-939	9-Octadecenoic acid (Z)-, methyl ester and isomers	C18:1
947-991	9,12-Octadecadienoic acid, methyl ester and isomers	C18:0

Figure A5.3.1.5.1.1: GC-MS chromatogram of the top layer of liquids collected in the condenser for batch #15. Retention time and peaks assignments are reported in the table.

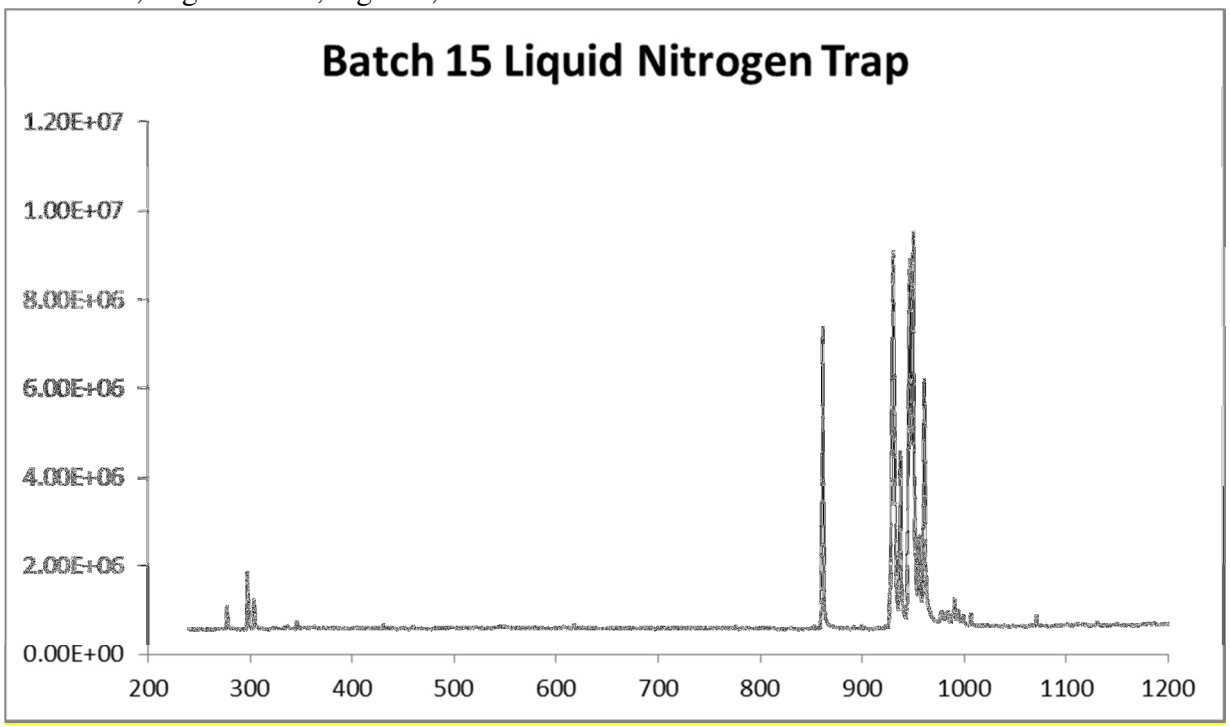
Batch #15, vegetable oil, 3 gal/hr, 304°C/100 Torr



Batch #15	Condenser Bottom	
R.T. (s)	Compound Name	
279	2-Propanol,1,3-dimthoxy-	
298	Propane,1,2,3-trimethoxy-	
300	1,2-Propanediol, 3-methoxy-	
431	Octenoic acid, methyl ester	C8:1
461	Octanoic acid, methyl ester	C8:0
580	Decanoic acid, methyl ester	C10:0
777	Methyl tetradecanoate	C14:0
862	Hexadecanoic acid, methyl ester	C16:0
929-939	9-Octadecenoic acid (Z)-, methyl ester and isomers	C18:1
947-991	9,12-Octadecadienoic acid, methyl ester and isomers	C18:0

Figure A5.3.1.5.1.2: GC-MS chromatogram of the bottom layer of liquids collected in the condenser for batch #15. Retention time and peaks assignments are reported in the table.

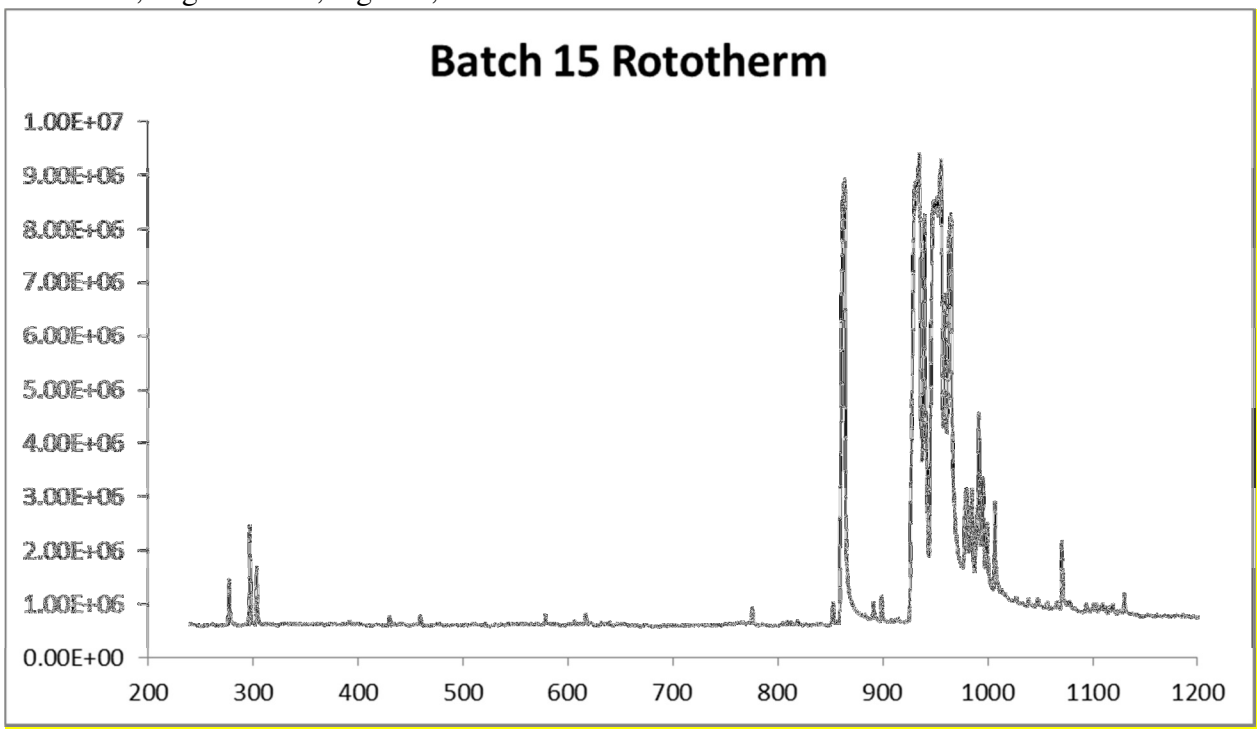
Batch #15, vegetable oil, 3 gal/hr, 304°C/100 Torr



Batch #15	**Liquid Nitrogen trap**	
R.T. (s)	**Compound Name**	
279	**2-Propanol,1,3-dimthoxy-**	
298	**Propane,1,2,3-trimethoxy-**	
300	**1,2-Propanediol, 3-methoxy-**	
862	**Hexadecanoic acid, methyl ester**	**C16:0**
929-939	**9-Octadecenoic acid (Z)-, methyl ester and isomers**	**C18:1**
947-991	**9,12-Octadecadienoic acid, methyl ester and isomers**	**C18:0**

Figure A5.3.1.5.1.3: GC-MS chromatogram of products collected in the nitrogen trap for batch #15. Retention time and peaks assignments are reported in the table.

Batch #15, vegetable oil, 3 gal/hr, 304°C/100 Torr

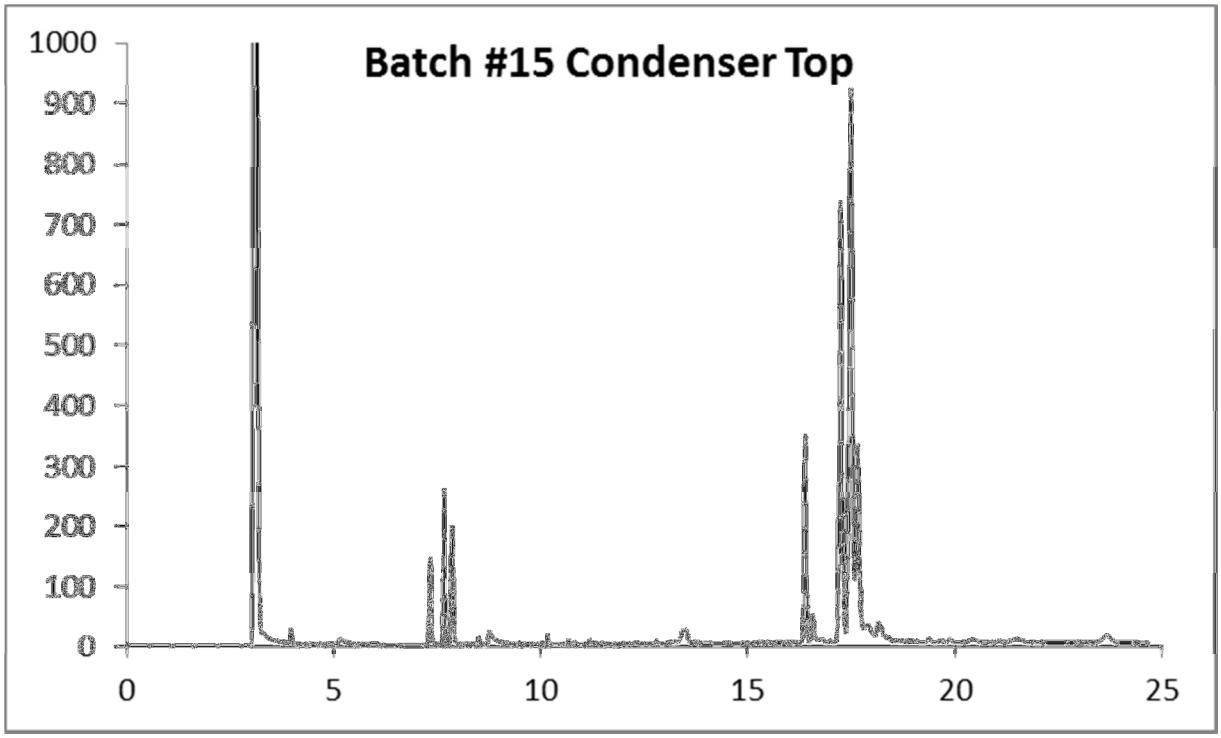


Batch #15	Rototherm	
R.T. (s)	Compound Name	
279	2-Propanol,1,3-dimthoxy-	
298	Propane,1,2,3-trimethoxy-	
300	1,2-Propanediol, 3-methoxy-	
862	Hexadecanoic acid, methyl ester	C16:0
929-939	9-Octadecenoic acid (Z)-, methyl ester and isomers	C18:1
947-991	9,12-Octadecadienoic acid, methyl ester and isomers	C18:0

Figure A5.3.1.5.1.4: GC-MS chromatogram of the products collected at the bottom of the reactor where residue is collected for batch #15. Retention time and peaks assignments are reported in the table.

Batch #15, vegetable oil, 3 gal/hr, 304°C/100 Torr

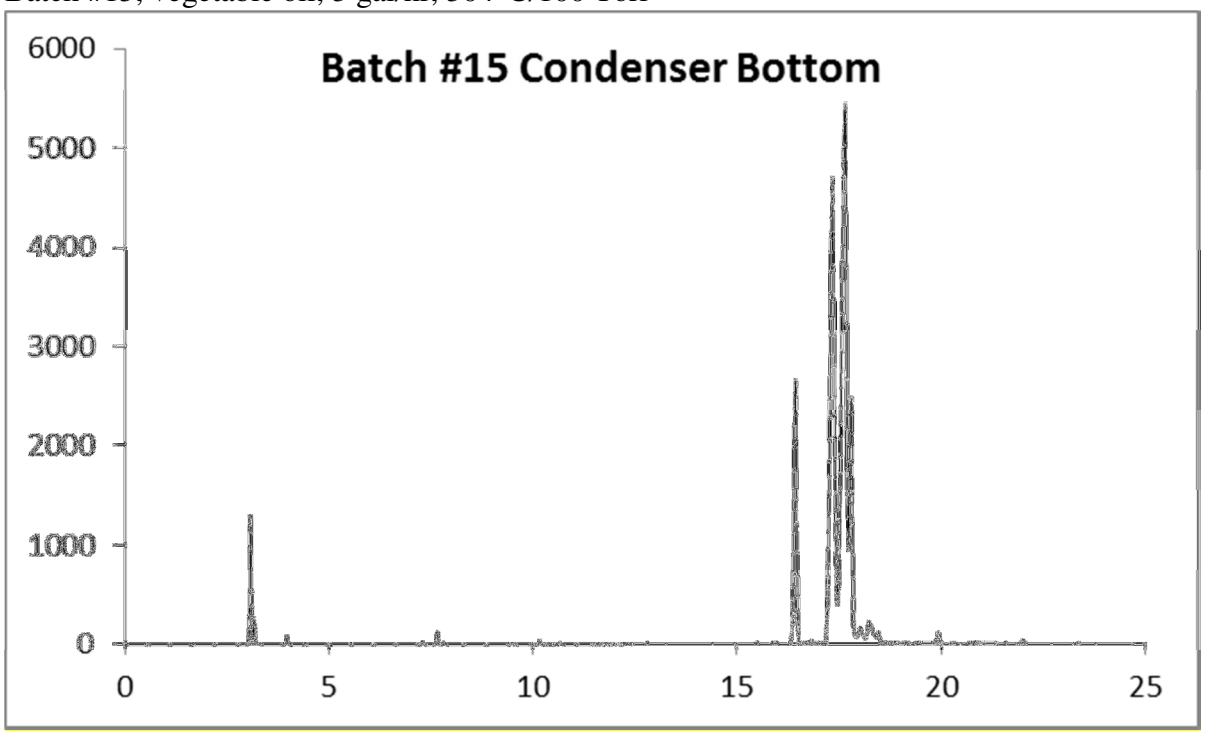
A-5.3.1.5.2 GC-FID data



Batch 15 Condenser Top		
Retention time (minutes)	**Compound name**	**Peak Area %**
3.075	**methanol**	**56.87**
3.167	**Trimethylamine (TMA)**	**5.13**
7.326	**1,3-dimethoxy-2-propanol (DMP)**	**1.08**
7.661	**1,2,3-trimethoxypropane (TMP)**	**1.40**
7.841	**3-methoxy-1,2-propanediol (MMP)**	**1.82**
16.462	**Hexadecanoic acid methyl ester**	**2.68**
17.329	**9-octadecenoic acid methyl ester**	**7.21**
17.575	**9,12-octadecadienoic acid methyl ester**	**11.33**
17.747	**9,11-octadecadienoic acid methyl ester**	**3.79**

Figure A5.3.1.5.2.1: GC-FID chromatogram of the top layer of liquids collected in the condenser for batch #15. Retention time, peaks assignments and relative peak area are reported in the table.

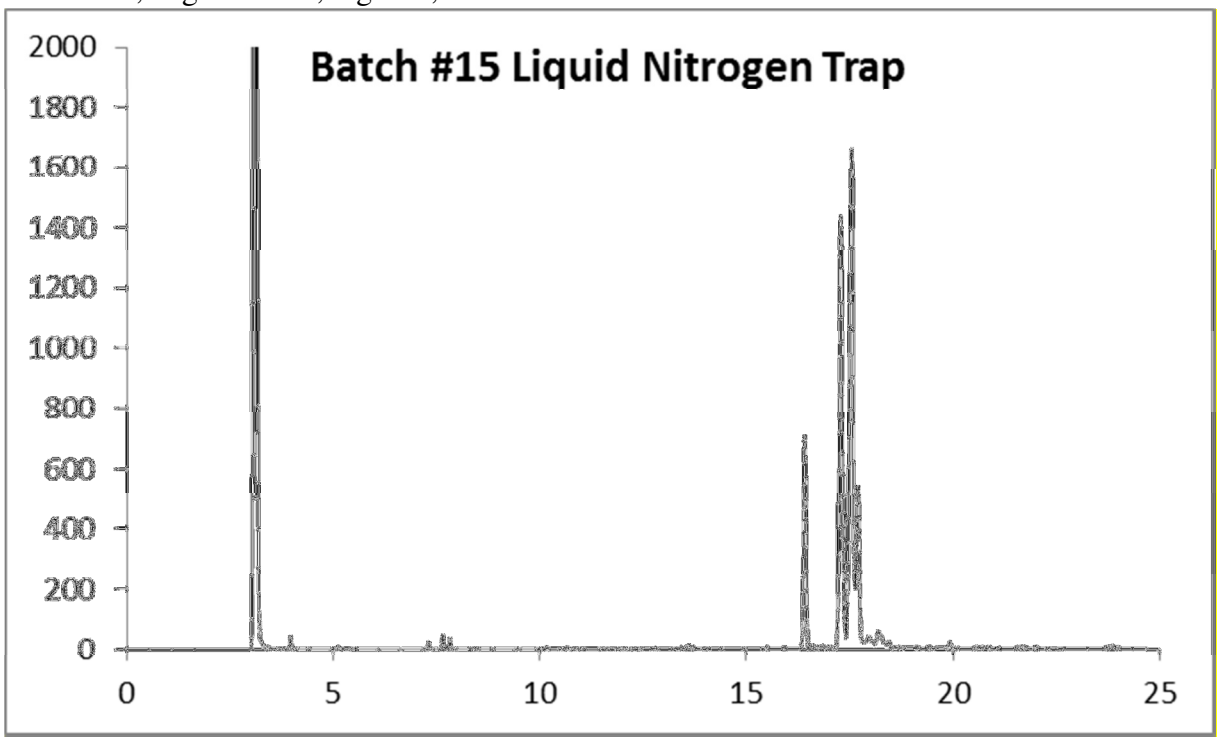
Batch #15, vegetable oil, 3 gal/hr, 304°C/100 Torr



Batch 15 Condenser Bottom		
Retention time (minutes)	Compound name	Peak Area %
3.075	methanol	2.75
3.167	Trimethylamine (TMA)	0.53
7.326	1,3-dimethoxy-2-propanol (DMP)	0.06
7.661	1,2,3-trimethoxypropane (TMP)	0.26
7.841	3-methoxy-1,2-propanediol (MMP)	0.05
16.462	Hexadecanoic acid methyl ester	10.38
17.329	9-octadecenoic acid methyl ester	30.31
17.575	9,12-octadecadienoic acid methyl ester	39.12
17.747	9,11-octadecadienoic acid methyl ester	10.46

Figure A5.3.1.5.2.2: GC-FID chromatogram of the bottom layer of liquids collected in the condenser for batch #15. Retention time, peaks assignments and relative peak area are reported in the table.

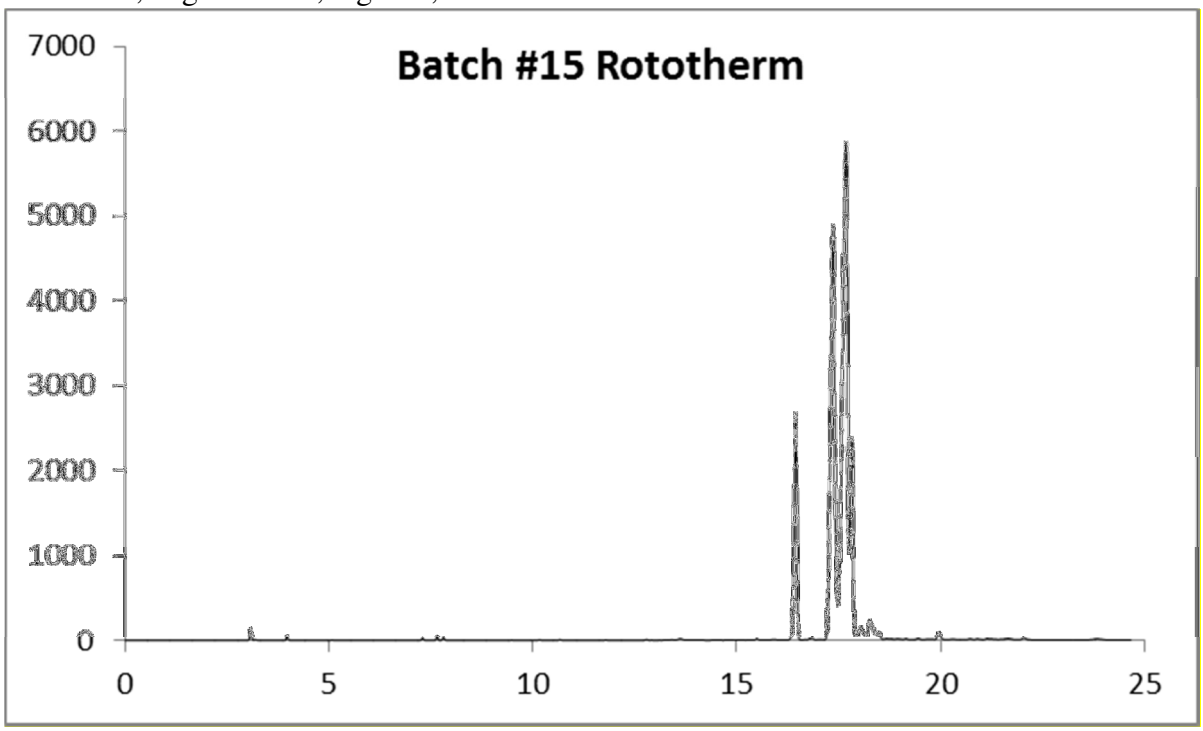
Batch #15, vegetable oil, 3 gal/hr, 304°C/100 Torr



Batch 15 Liquid Nitrogen Trap		
Retention time (minutes)	**Compound name**	**Peak Area %**
3.075	**methanol**	**41.61**
3.167	**Trimethylamine (TMA)**	**13.55**
7.326	**1,3-dimethoxy-2-propanol (DMP)**	**0.12**
7.661	**1,2,3-trimethoxypropane (TMP)**	**0.20**
7.841	**3-methoxy-1,2-propanediol (MMP)**	**0.20**
16.462	**Hexadecanoic acid methyl ester**	**4.59**
17.329	**9-octadecenoic acid methyl ester**	**12.72**
17.575	**9,12-octadecadienoic acid methyl ester**	**18.31**
17.747	**9,11-octadecadienoic acid methyl ester**	**4.44**

Figure A5.3.1.5.2.3: GC-FID chromatogram liquids collected in the liquid nitrogen trap for batch #15. Retention time, peaks assignments and relative peak area are reported in the table.

Batch #15, vegetable oil, 3 gal/hr, 304°C/100 Torr

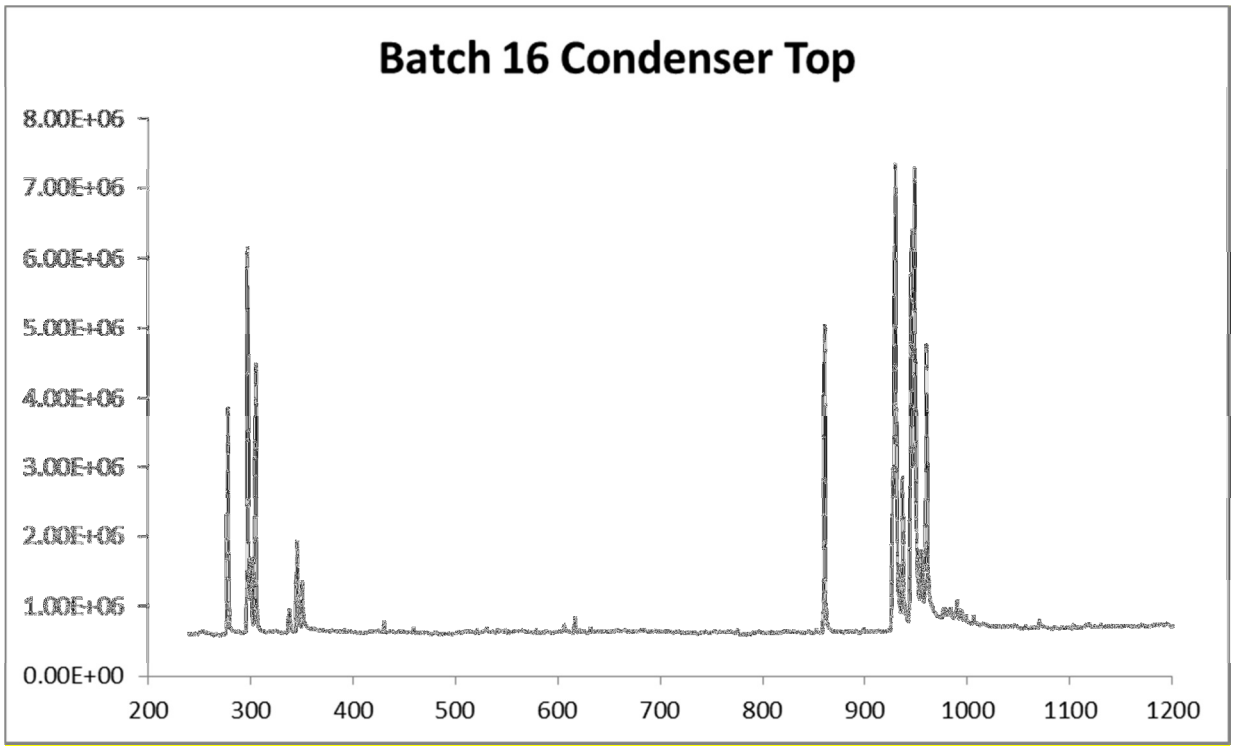


Batch 15 Liquid Nitrogen Trap		
Retention time (minutes)	Compound name	Peak Area %
3.075	methanol	41.61
3.167	Trimethylamine (TMA)	13.55
7.326	1,3-dimethoxy-2-propanol (DMP)	0.12
7.661	1,2,3-trimethoxypropane (TMP)	0.20
7.841	3-methoxy-1,2-propanediol (MMP)	0.20
16.462	Hexadecanoic acid methyl ester	4.59
17.329	9-octadecenoic acid methyl ester	12.72
17.575	9,12-octadecadienoic acid methyl ester	18.31
17.747	9,11-octadecadienoic acid methyl ester	4.44

Figure A5.3.1.5.2.4: GC-FID chromatogram liquids collected at the bottom of the reactor where residue is collected for batch #15. Retention time, peaks assignments and relative peak area are reported in the table.

A-5.3.1.6 Batch #16, vegetable oil, 3.5 gal/hr, 304°C/100 Torr

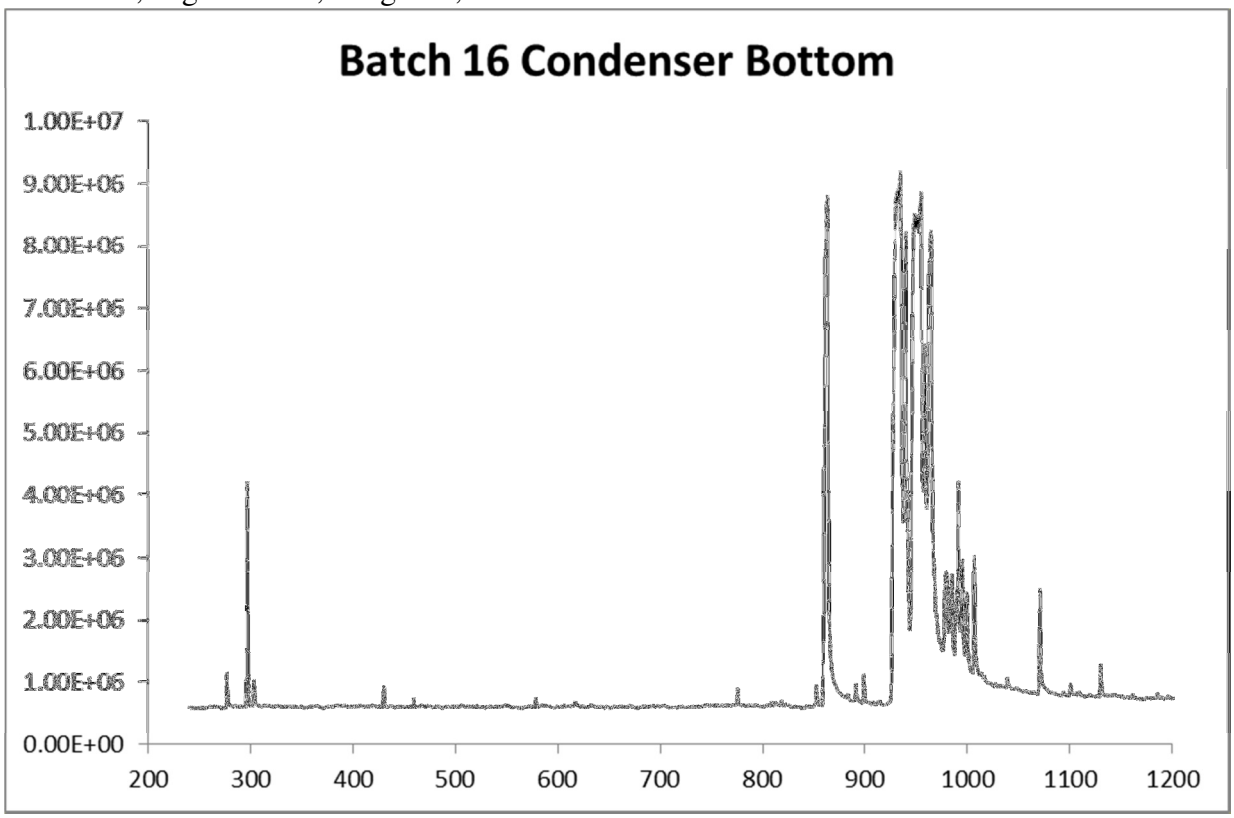
A-5.3.1.6.1 GC-MS data



Batch #16	Condenser Top	
R.T. (s)	Compound Name	
279	2-Propanol,1,3-dimthoxy-	
298	Propane,1,2,3-trimethoxy-	
300	1,2-Propanediol, 3-methoxy-	
862	Hexadecanoic acid, methyl ester	C16:0
929-939	9-Octadecenoic acid (Z)-, methyl ester and isomers	C18:1
947-991	9,12-Octadecadienoic acid, methyl ester and isomers	C18:0

Figure A5.3.1.6.1.1: GC-MS chromatogram of the top layer of liquids collected in the condenser for batch #16. Retention time and peaks assignments are reported in the table.

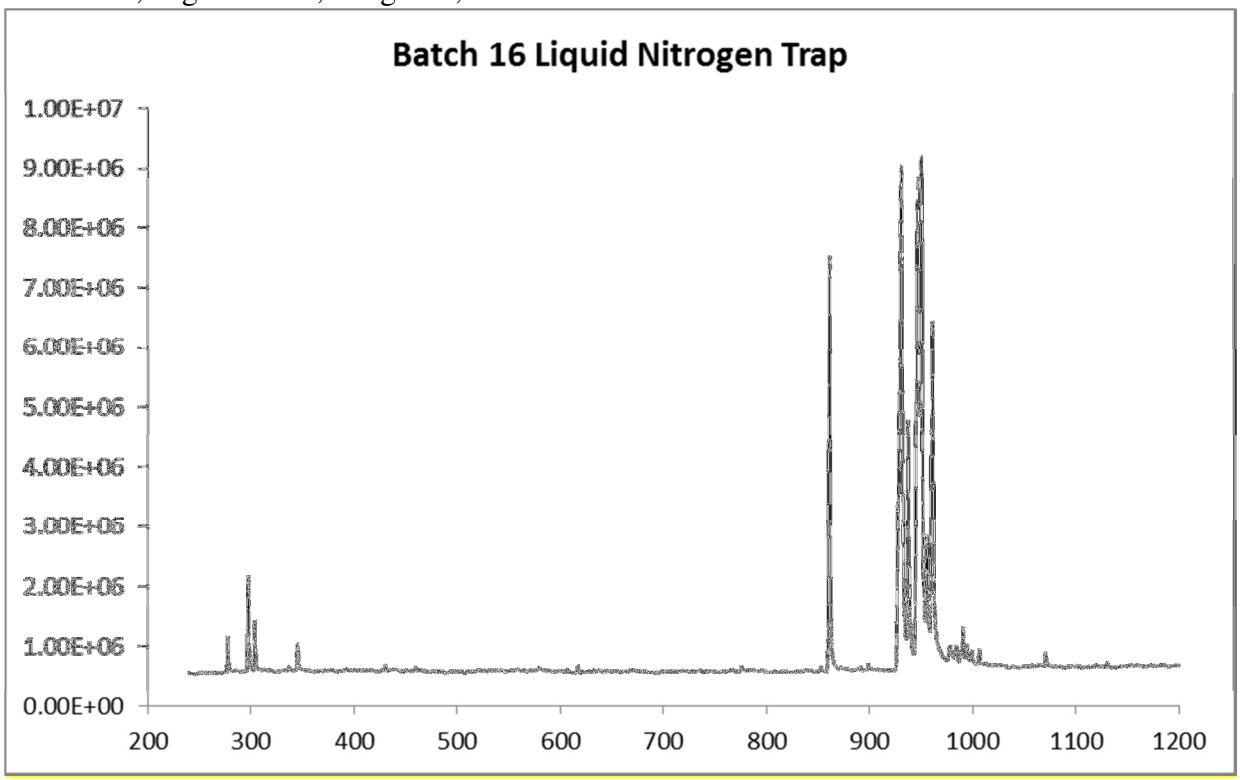
Batch #16, vegetable oil, 3.5 gal/hr, 304°C/100 Torr



Batch #16	**Condenser Bottom**	
R.T. (s)	**Compound Name**	
279	**2-Propanol,1,3-dimthoxy-**	
298	**Propane,1,2,3-trimethoxy-**	
300	**1,2-Propanediol, 3-methoxy-**	
862	**Hexadecanoic acid, methyl ester**	**C16:0**
929-939	**9-Octadecenoic acid (Z)-, methyl ester and isomers**	**C18:1**
947-991	**9,12-Octadecadienoic acid, methyl ester and isomers**	**C18:0**

Figure A5.3.1.6.1.2: GC-MS chromatogram of the bottom layer of liquids collected in the condenser for batch #16. Retention time and peaks assignments are reported in the table.

Batch #16, vegetable oil, 3.5 gal/hr, 304°C/100 Torr

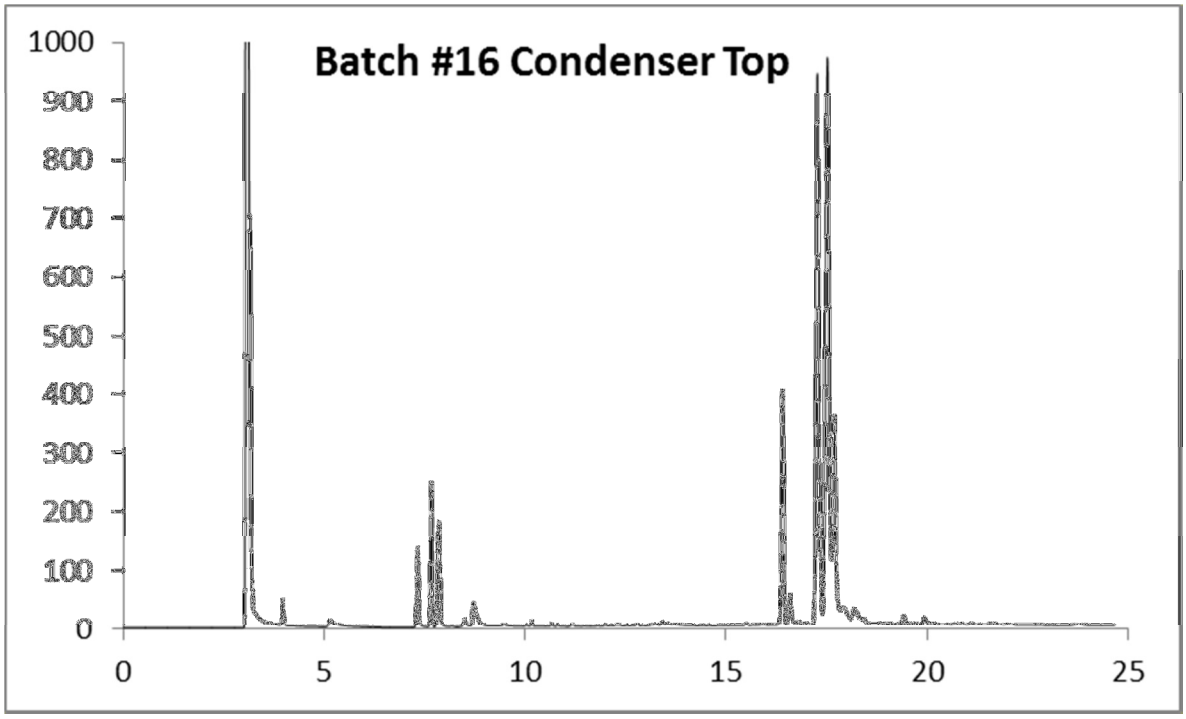


Batch #16	**Liquid Nitrogen trap**	
R.T. (s)	**Compound Name**	
279	**2-Propanol,1,3-dimthoxy-**	
298	**Propane,1,2,3-trimethoxy-**	
300	**1,2-Propanediol, 3-methoxy-**	
862	**Hexadecanoic acid, methyl ester**	**C16:0**
929-939	**9-Octadecenoic acid (Z)-, methyl ester and isomers**	**C18:1**
947-991	**9,12-Octadecadienoic acid, methyl ester and isomers**	**C18:0**

Figure A5.3.1.6.1.3: GC-MS chromatogram of products collected in the liquid nitrogen trap for batch #16. Retention time and peaks assignments are reported in the table.

Batch #16, vegetable oil, 3.5 gal/hr, 304°C/100 Torr

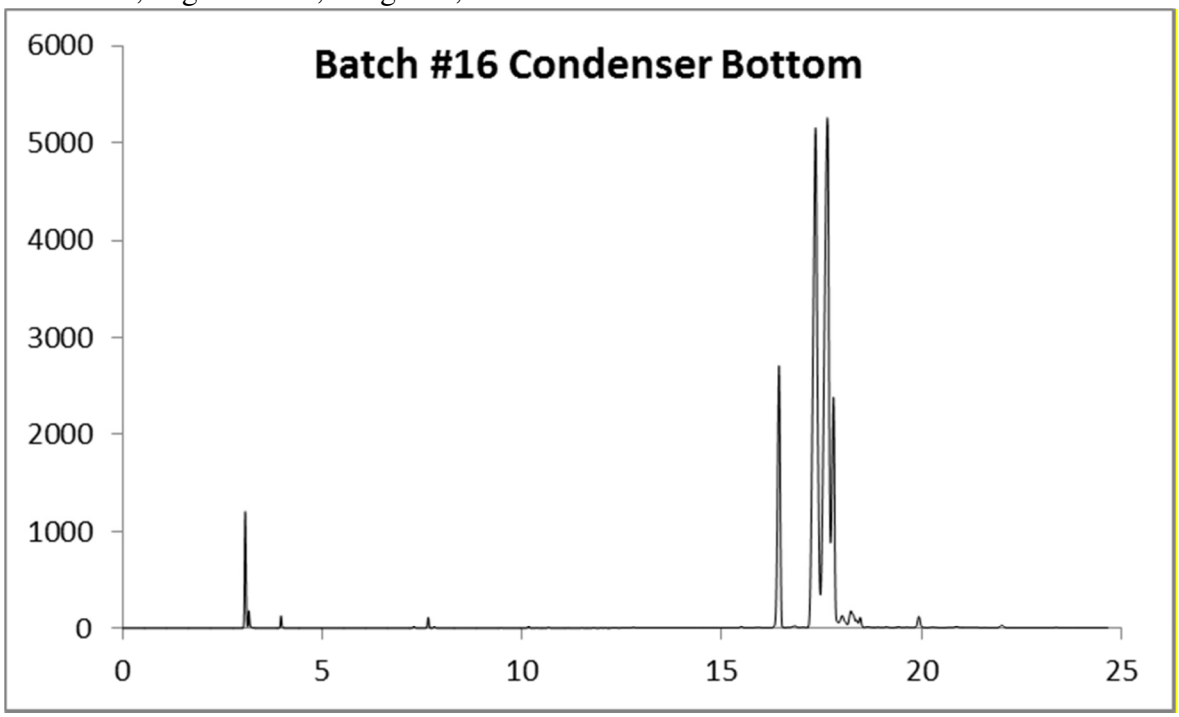
A-5.3.1.6.2 GC-FID data



Batch 16 Condenser Top		
Retention time (minutes)	**Compound name**	**Peak Area %**
3.075	**methanol**	**55.96**
3.167	**Trimethylamine (TMA)**	**4.33**
7.326	**1,3-dimethoxy-2-propanol (DMP)**	**1.01**
7.661	**1,2,3-trimethoxypropane (TMP)**	**1.35**
7.841	**3-methoxy-1,2-propanediol (MMP)**	**1.74**
16.462	**Hexadecanoic acid methyl ester**	**3.16**
17.329	**9-octadecenoic acid methyl ester**	**9.58**
17.575	**9,12-octadecadienoic acid methyl ester**	**12.46**
17.747	**9,11-octadecadienoic acid methyl ester**	**4.19**

Figure A5.3.1.6.2.1: GC-FID chromatogram of the top layer of liquids collected in the condenser for batch #16. Retention time, peaks assignments and relative peak area are reported in the table.

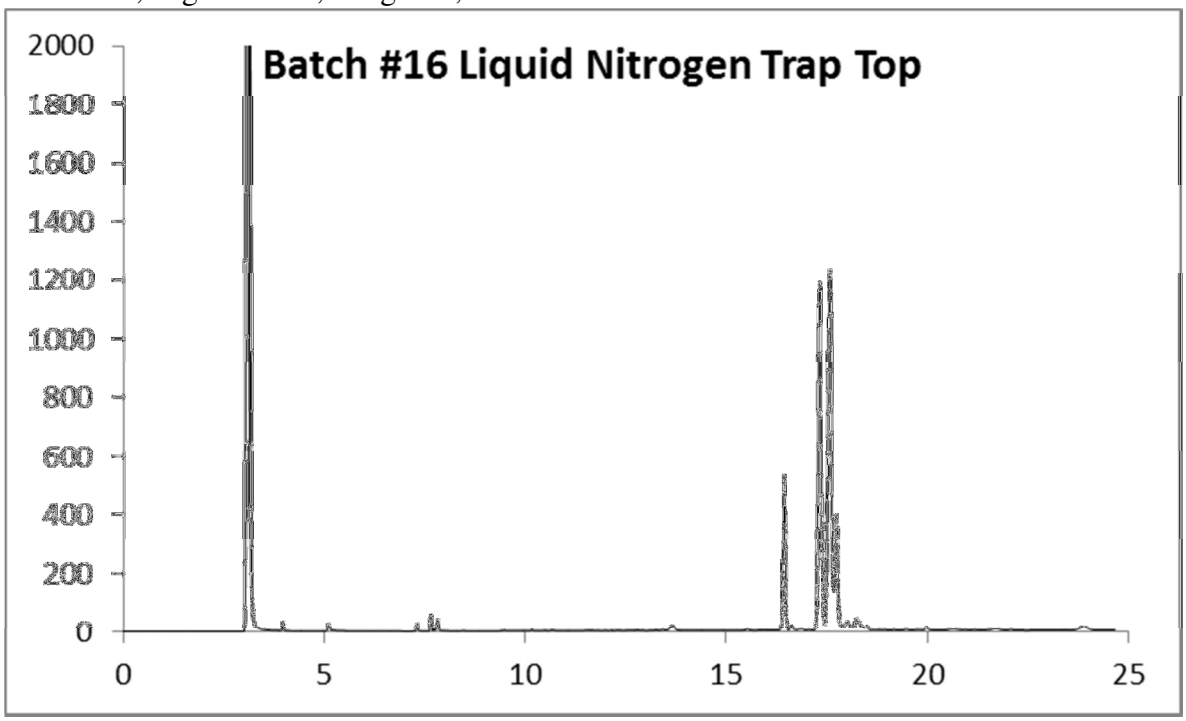
Batch #16, vegetable oil, 3.5 gal/hr, 304°C/100 Torr



Batch 16 Condenser Bottom		
Retention time (minutes)	Compound name	Peak Area %
3.075	methanol	2.55
3.167	Trimethylamine (TMA)	0.37
7.326	1,3-dimethoxy-2-propanol (DMP)	0.05
7.661	1,2,3-trimethoxypropane (TMP)	0.25
7.841	3-methoxy-1,2-propanediol (MMP)	0.05
16.462	Hexadecanoic acid methyl ester	10.60
17.329	9-octadecenoic acid methyl ester	34.09
17.575	9,12-octadecadienoic acid methyl ester	36.38
17.747	9,11-octadecadienoic acid methyl ester	9.85

Figure A5.3.1.6.2.2: GC-FID chromatogram of the bottom layer of liquids collected in the condenser for batch #16. Retention time, peaks assignments and relative peak area are reported in the table.

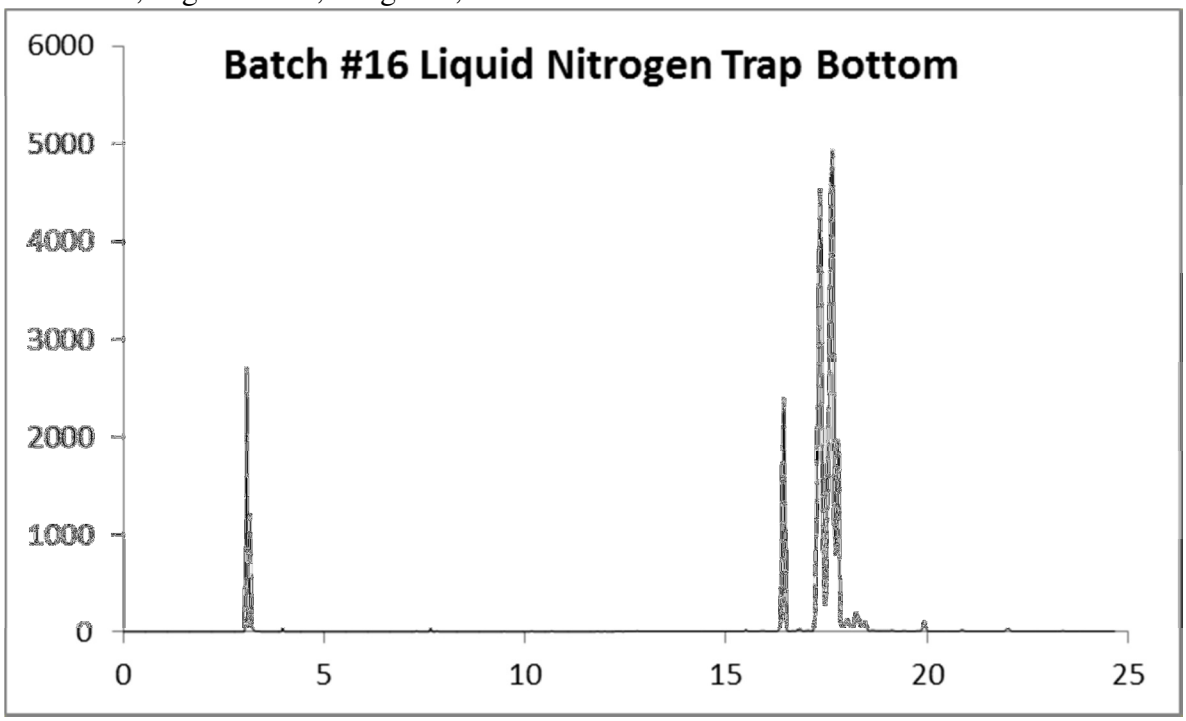
Batch #16, vegetable oil, 3.5 gal/hr, 304°C/100 Torr



Batch 16 Liquid Nitrogen Trap Top		
Retention time (minutes)	**Compound name**	**Peak Area %**
3.075	**methanol**	**50.71**
3.167	**Trimethylamine (TMA)**	**11.44**
7.326	**1,3-dimethoxy-2-propanol (DMP)**	**0.15**
7.661	**1,2,3-trimethoxypropane (TMP)**	**0.27**
7.841	**3-methoxy-1,2-propanediol (MMP)**	**0.24**
16.462	**Hexadecanoic acid methyl ester**	**3.78**
17.329	**9-octadecenoic acid methyl ester**	**11.16**
17.575	**9,12-octadecadienoic acid methyl ester**	**14.58**
17.747	**9,11-octadecadienoic acid methyl ester**	**3.70**

Figure A5.3.1.6.2.3: GC-FID chromatogram of the top layer of liquids collected in the liquid nitrogen trap for batch #16. Retention time, peaks assignments and relative peak area are reported in the table.

Batch #16, vegetable oil, 3.5 gal/hr, 304°C/100 Torr



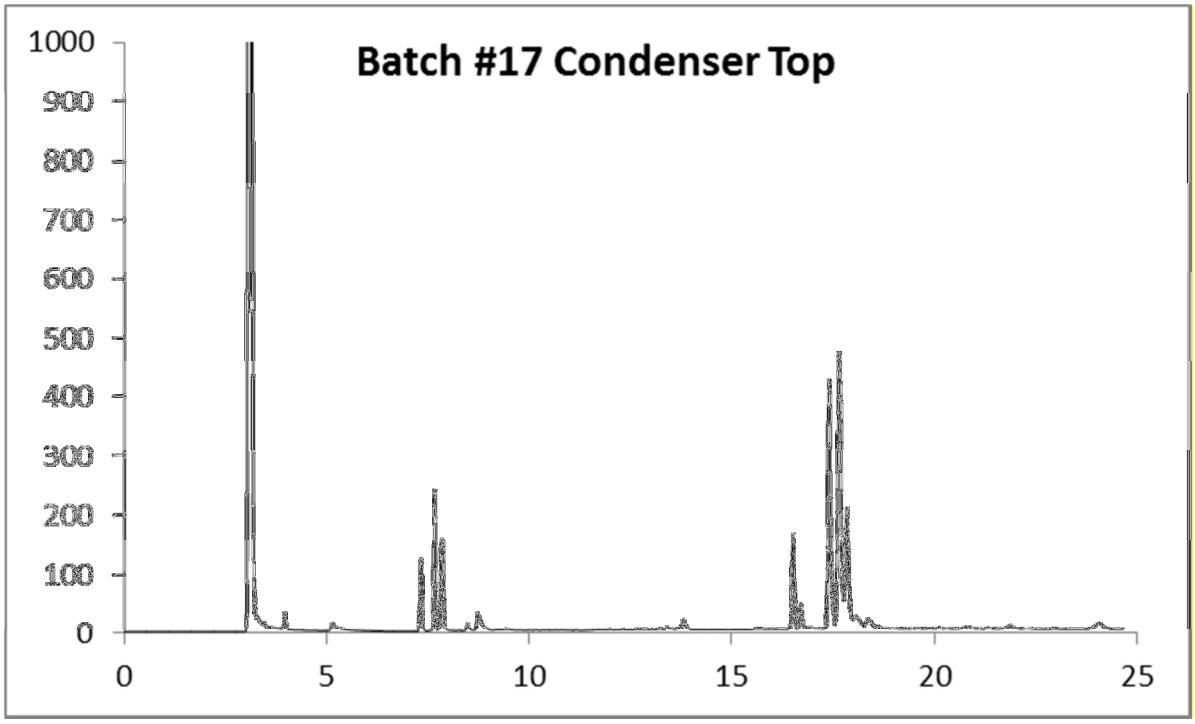
Batch 16 Liquid Nitrogen Trap Bottom		
Retention time (minutes)	**Compound name**	**Peak Area %**
3.075	**methanol**	**6.14**
3.167	**Trimethylamine (TMA)**	**2.38**
7.326	**1,3-dimethoxy-2-propanol (DMP)**	**0.02**
7.661	**1,2,3-trimethoxypropane (TMP)**	**0.08**
7.841	**3-methoxy-1,2-propanediol (MMP)**	**0.03**
16.462	**Hexadecanoic acid methyl ester**	**9.90**
17.329	**9-octadecenoic acid methyl ester**	**30.87**
17.575	**9,12-octadecadienoic acid methyl ester**	**36.68**
17.747	**9,11-octadecadienoic acid methyl ester**	**8.78**

Figure A5.3.1.6.2.4: GC-FID chromatogram of the bottom layer of liquids collected in the liquid nitrogen trap for batch #16. Retention time, peaks assignments and relative peak area are reported in the table.

Batch #17, vegetable oil, 3 gal/hr, 332°C/100 Torr

A-5.3.1.7 Batch #17, vegetable oil, 2 gal/hr, 304°C/500-600 Torr

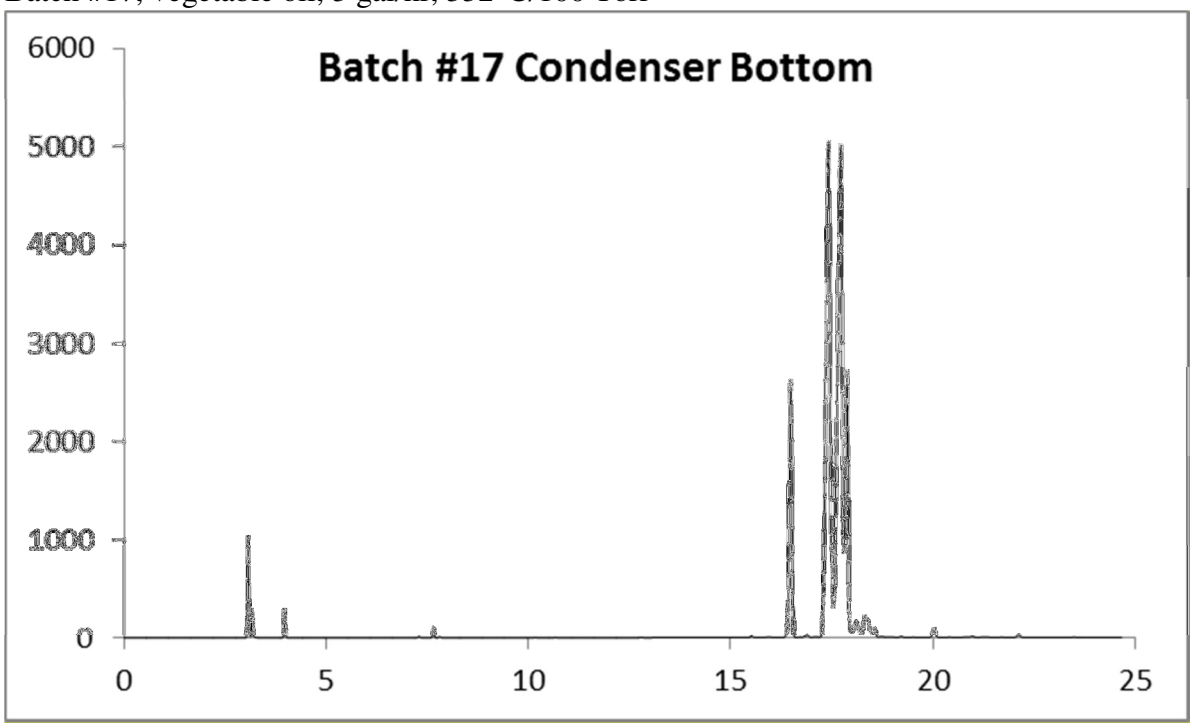
A-5.3.1.7.1 GC-FID data



Batch 17 Condenser Top		
Retention time (minutes)	**Compound name**	**Peak Area %**
3.075	**methanol**	**62.57**
3.167	**Trimethylamine (TMA)**	**6.44**
7.326	**1,3-dimethoxy-2-propanol (DMP)**	**0.93**
7.661	**1,2,3-trimethoxypropane (TMP)**	**1.42**
7.841	**3-methoxy-1,2-propanediol (MMP)**	**1.74**
16.462	**Hexadecanoic acid methyl ester**	**1.49**
17.329	**9-octadecenoic acid methyl ester**	**4.47**
17.575	**9,12-octadecadienoic acid methyl ester**	**6.27**
17.747	**9,11-octadecadienoic acid methyl ester**	**2.79**

Figure A5.3.1.7.1.1: GC-FID chromatogram of the top layer of liquids collected in the condenser for batch #17. Retention time, peaks assignments and relative peak area are reported in the table.

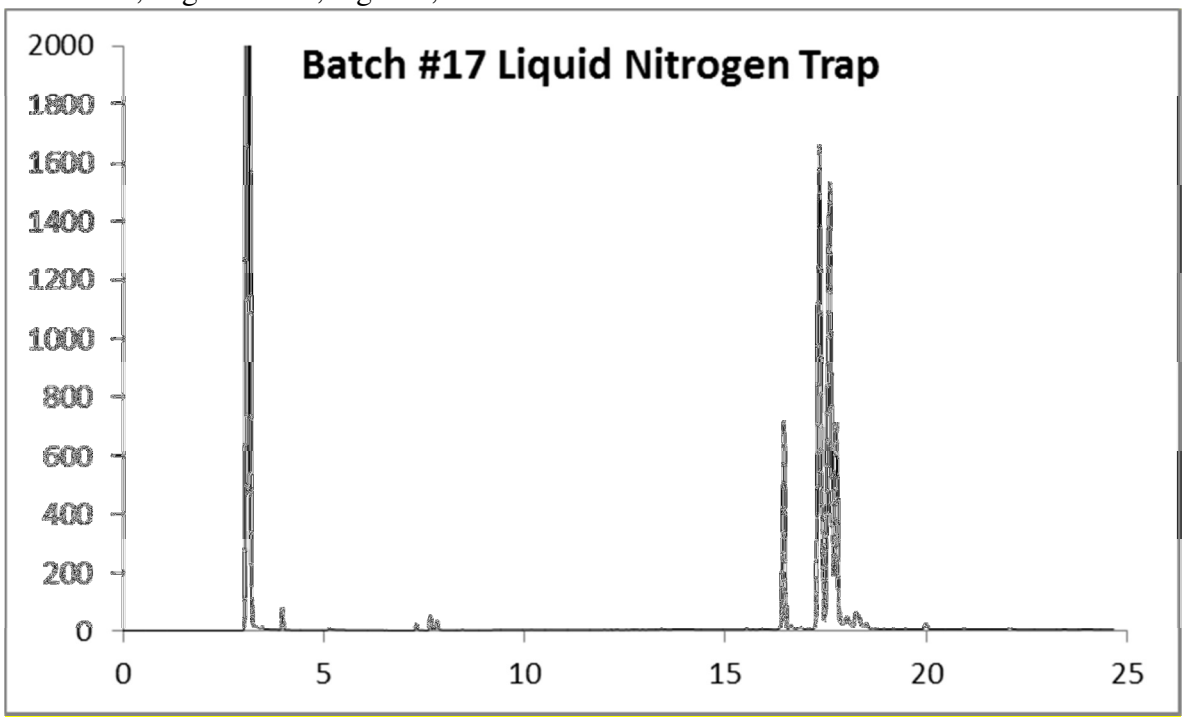
Batch #17, vegetable oil, 3 gal/hr, 332°C/100 Torr



Batch 17 Condenser Bottom		
Retention time (minutes)	**Compound name**	**Peak Area %**
3.075	**methanol**	**2.16**
3.167	**Trimethylamine (TMA)**	**0.56**
7.326	**1,3-dimethoxy-2-propanol (DMP)**	**0.04**
7.661	**1,2,3-trimethoxypropane (TMP)**	**0.23**
7.841	**3-methoxy-1,2-propanediol (MMP)**	**0.04**
16.462	**Hexadecanoic acid methyl ester**	**10.42**
17.329	**9-octadecenoic acid methyl ester**	**33.67**
17.575	**9,12-octadecadienoic acid methyl ester**	**35.22**
17.747	**9,11-octadecadienoic acid methyl ester**	**11.80**

Figure A5.3.1.7.1.2: GC-FID chromatogram of the bottom layer of liquids collected in the condenser for batch #17. Retention time, peaks assignments and relative peak area are reported in the table.

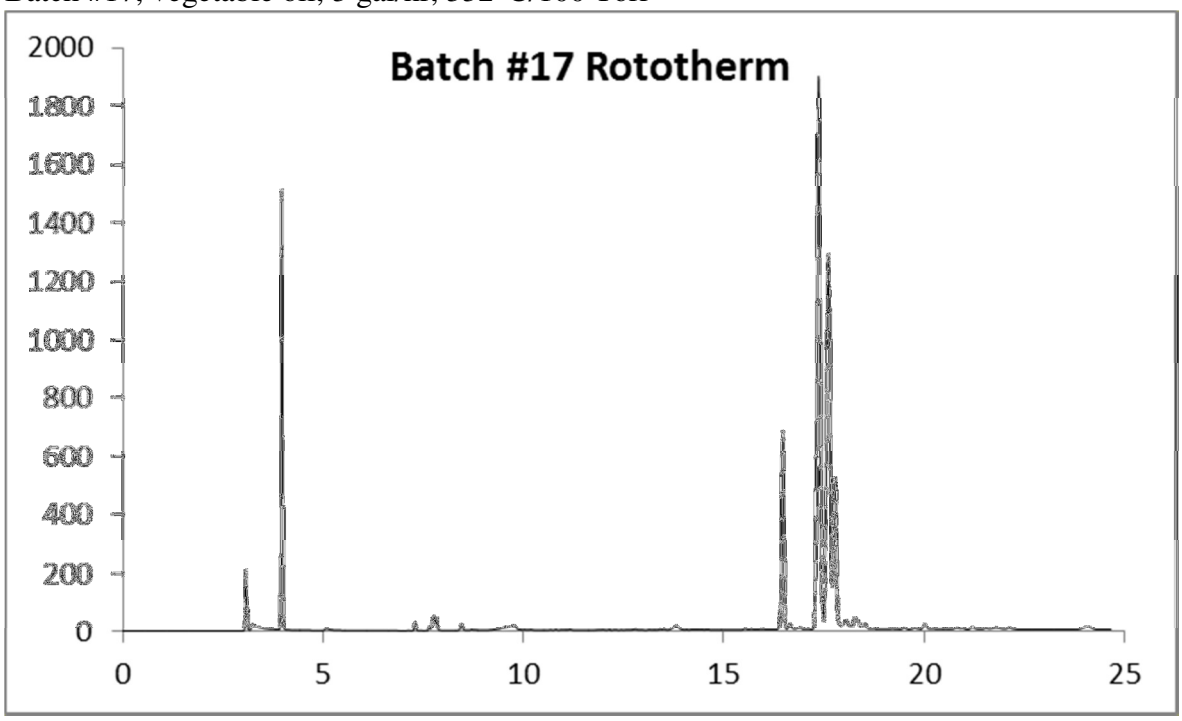
Batch #17, vegetable oil, 3 gal/hr, 332°C/100 Torr



Batch 17 Liquid Nitrogen Trap		
Retention time (minutes)	Compound name	Peak Area %
3.075	methanol	39.27
3.167	Trimethylamine (TMA)	15.32
7.326	1,3-dimethoxy-2-propanol (DMP)	0.11
7.661	1,2,3-trimethoxypropane (TMP)	0.21
7.841	3-methoxy-1,2-propanediol (MMP)	0.18
16.462	Hexadecanoic acid methyl ester	4.57
17.329	9-octadecenoic acid methyl ester	14.75
17.575	9,12-octadecadienoic acid methyl ester	16.31
17.747	9,11-octadecadienoic acid methyl ester	5.68

Figure A5.3.1.7.1.3: GC-FID chromatogram of liquids collected in the liquid nitrogen trap for batch #17. Retention time, peaks assignments and relative peak area are reported in the table.

Batch #17, vegetable oil, 3 gal/hr, 332°C/100 Torr

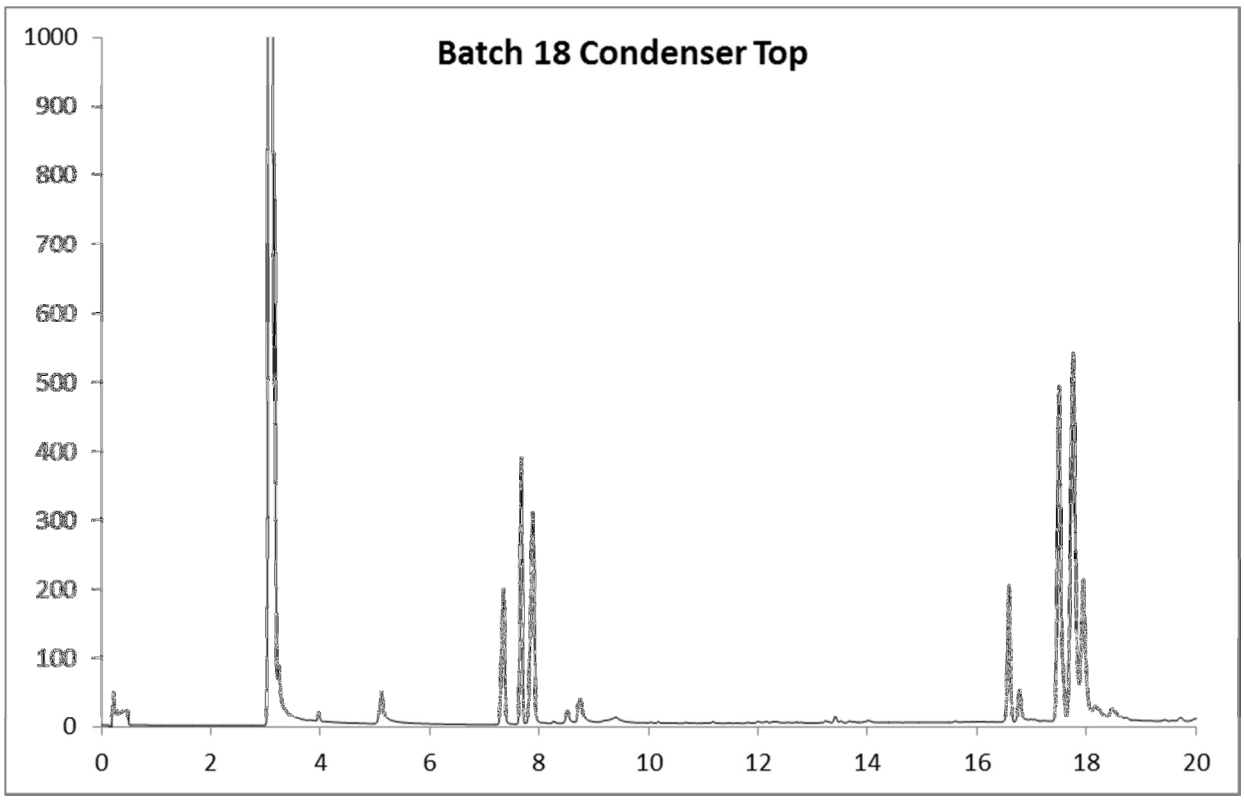


Batch 17 Rototherm		
Retention time (minutes)	**Compound name**	**Peak Area %**
3.075	**methanol**	**1.59**
3.167	**Trimethylamine (TMA)**	**1.35**
7.326	**1,3-dimethoxy-2-propanol (DMP)**	**0.24**
7.661	**1,2,3-trimethoxypropane (TMP)**	**0.13**
7.841	**3-methoxy-1,2-propanediol (MMP)**	**0.46**
16.462	**Hexadecanoic acid methyl ester**	**8.28**
17.329	**9-octadecenoic acid methyl ester**	**32.24**
17.575	**9,12-octadecadienoic acid methyl ester**	**25.47**
17.747	**9,11-octadecadienoic acid methyl ester**	**8.05**

Figure A5.3.1.7.1.4: GC-FID chromatogram of liquids collected at the bottom of the reactor where residue is collected for batch #17. Retention time, peaks assignments and relative peak area are reported in the table.

A5.3.1.8- Batch #18, vegetable oil, 3gal/hr, 332°C/100 Torr

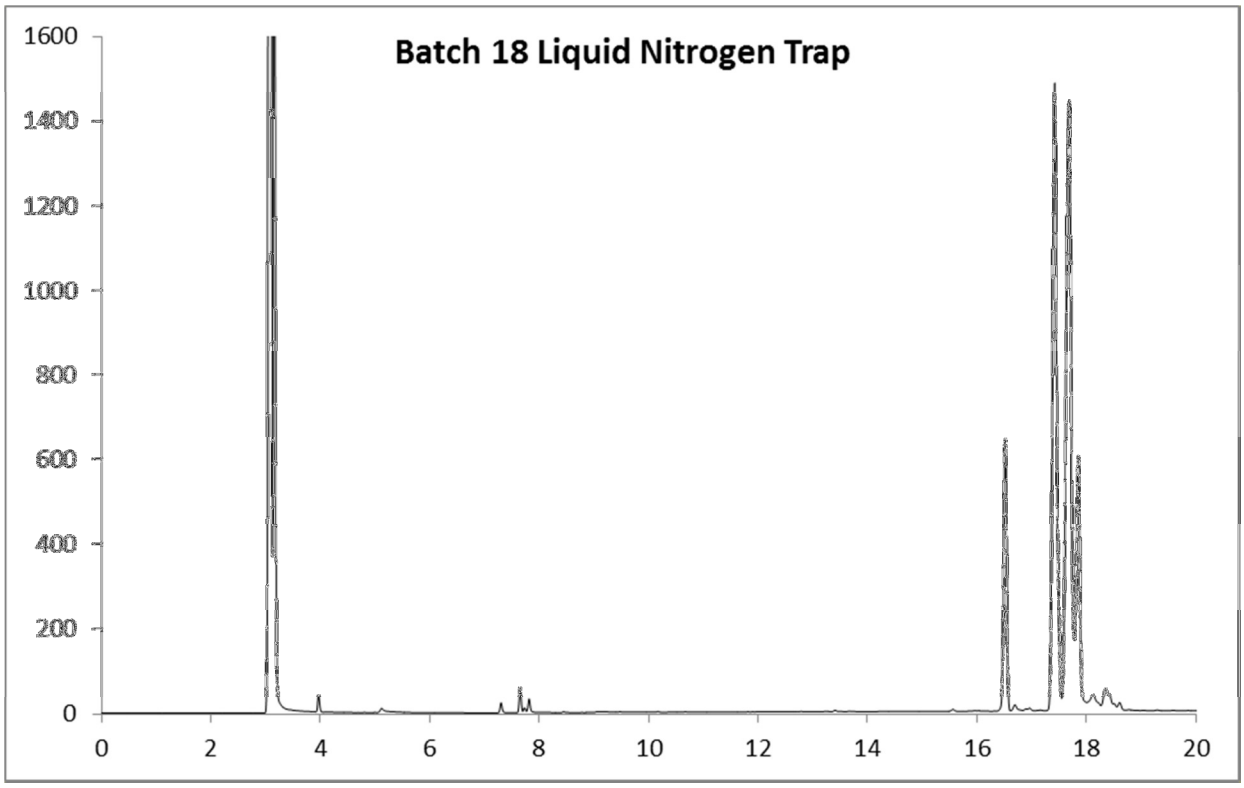
A-5.3.1.8.1 GC-FID data



Batch 18 Condenser Top		
Retention time (minutes)	**Compound name**	**Peak Area %**
3.072	**methanol**	**68.9**
3.166	**Trimethylamine (TMA)**	**0.1**
7.335	**1,3-dimethoxy-2-propanol (DMP)**	**1.9**
7.666	**1,2,3-trimethoxypropane (TMP)**	**2.5**
7.865	**3-methoxy-1,2-propanediol (MMP)**	**3.3**
16.483	**Hexadecanoic acid methyl ester**	**1.7**
17.366	**9-octadecenoic acid methyl ester**	**5.2**
17.625	**9,12-octadecadienoic acid methyl ester**	**7.5**
17.795	**9,11-octadecadienoic acid methyl ester**	**2.9**

Figure A5.3.1.8.1.1: GC-FID chromatogram of the top layer of liquids collected in the condenser for batch #18. Retention time, peaks assignments and relative peak area are reported in the table.

Batch #18, vegetable oil, 3gal/hr, 332°C/100 Torr

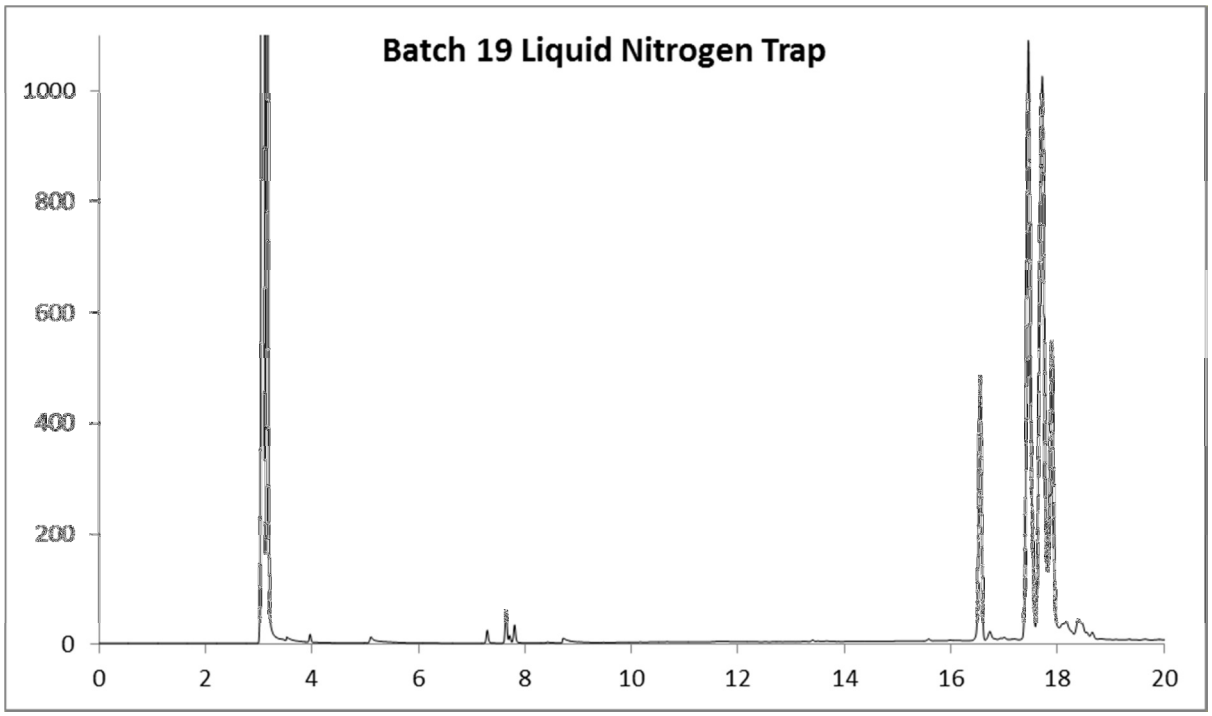


Batch 18 Liquid Nitrogen Trap		
Retention time (minutes)	**Compound name**	**Peak Area %**
3.072	**methanol**	**43.2**
3.166	**Trimethylamine (TMA)**	**13.9**
7.335	**1,3-dimethoxy-2-propanol (DMP)**	**0.1**
7.666	**1,2,3-trimethoxypropane (TMP)**	**0.3**
7.865	**3-methoxy-1,2-propanediol (MMP)**	**0.0**
16.483	**Hexadecanoic acid methyl ester**	**4.4**
17.366	**9-octadecenoic acid methyl ester**	**13.7**
17.625	**9,12-octadecadienoic acid methyl ester**	**16.4**
17.795	**9,11-octadecadienoic acid methyl ester**	**5.2**

Figure A5.3.1.8.1.2: GC-FID chromatogram of products collected in the liquid nitrogen trap for batch #18. Retention time, peaks assignments and relative peak area are reported in the table.

A5.3.1.9- Batch #19, vegetable oil, 3gal/hr, 332°C/100 Torr

A-5.3.1.9.1 GC-FID data

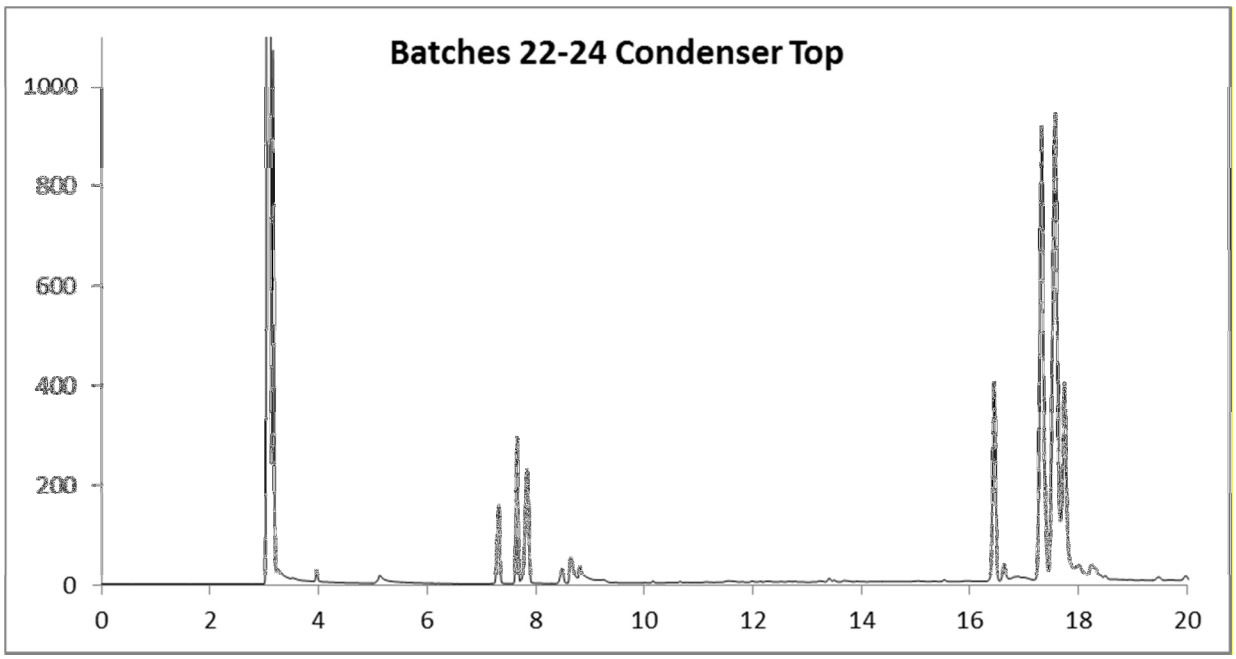


Batch 19 Liquid Nitrogen Trap		
Retention time (minutes)	**Compound name**	**Peak Area %**
3.072	**methanol**	**47.5**
3.166	**Trimethylamine (TMA)**	**17.7**
7.335	**1,3-dimethoxy-2-propanol (DMP)**	**0.1**
7.666	**1,2,3-trimethoxypropane (TMP)**	**0.3**
7.865	**3-methoxy-1,2-propanediol (MMP)**	**0.1**
16.483	**Hexadecanoic acid methyl ester**	**3.4**
17.366	**9-octadecenoic acid methyl ester**	**10.6**
17.625	**9,12-octadecadienoic acid methyl ester**	**12.4**
17.795	**9,11-octadecadienoic acid methyl ester**	**5.2**

Figure A5.3.1.9.1.1: GC-FID chromatogram of products collected in the liquid nitrogen trap for batch #19. Retention time, peaks assignments and relative peak area are reported in the table.

A5.3.1.10- Batches #22, 23, 24, vegetable oil, 3.5 gal/hr, 332°C/100 Torr

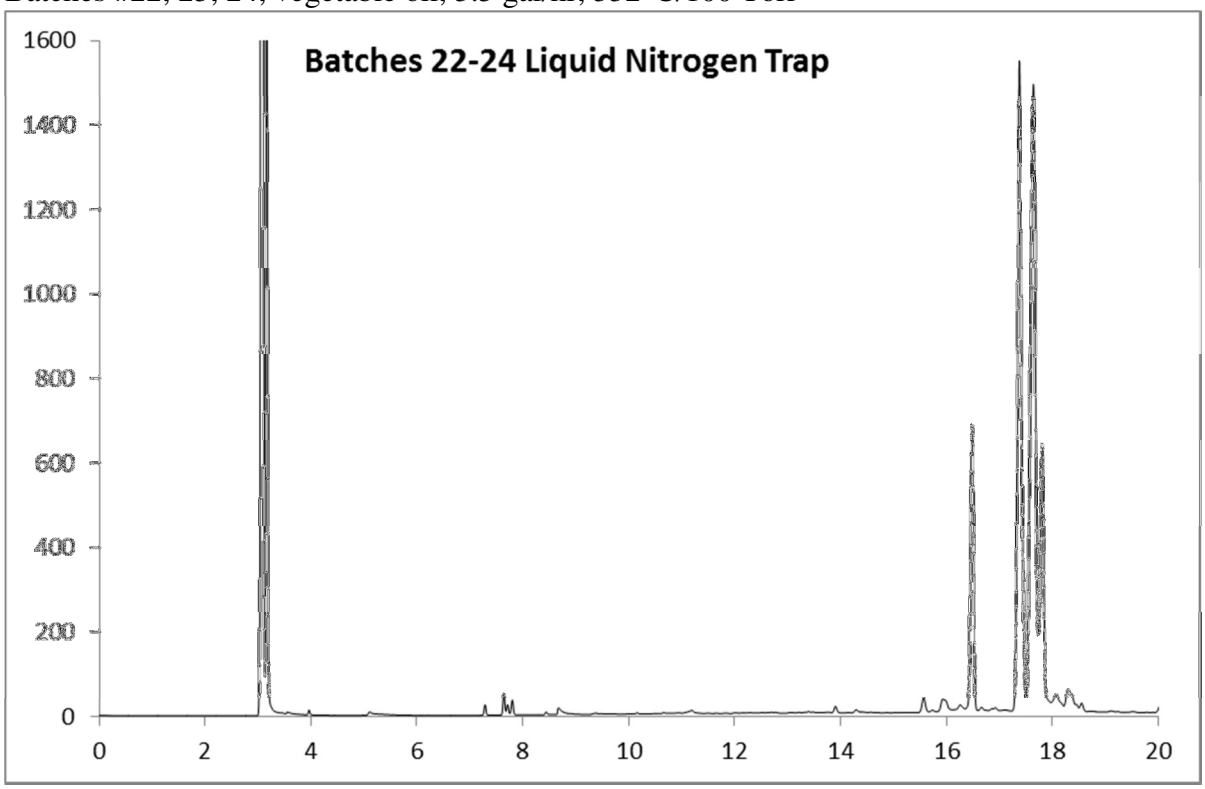
A-5.3.1.10.1 GC-FID data



Batch 22-24 Condenser Top		
Retention time (minutes)	Compound name	Peak Area %
3.072	methanol	58.7
3.166	Trimethylamine (TMA)	3.0
7.335	1,3-dimethoxy-2-propanol (DMP)	1.1
7.666	1,2,3-trimethoxypropane (TMP)	1.6
7.865	3-methoxy-1,2-propanediol (MMP)	2.3
16.483	Hexadecanoic acid methyl ester	3.2
17.366	9-octadecenoic acid methyl ester	9.5
17.625	9,12-octadecadienoic acid methyl ester	12.4
17.795	9,11-octadecadienoic acid methyl ester	4.7

Figure A5.3.1.10.1.1: GC-FID chromatogram of the top layer of liquids collected in the condenser for combined batches #22, 23, 24. Retention time, peaks assignments and relative peak area are reported in the table.

Batches #22, 23, 24, vegetable oil, 3.5 gal/hr, 332°C/100 Torr

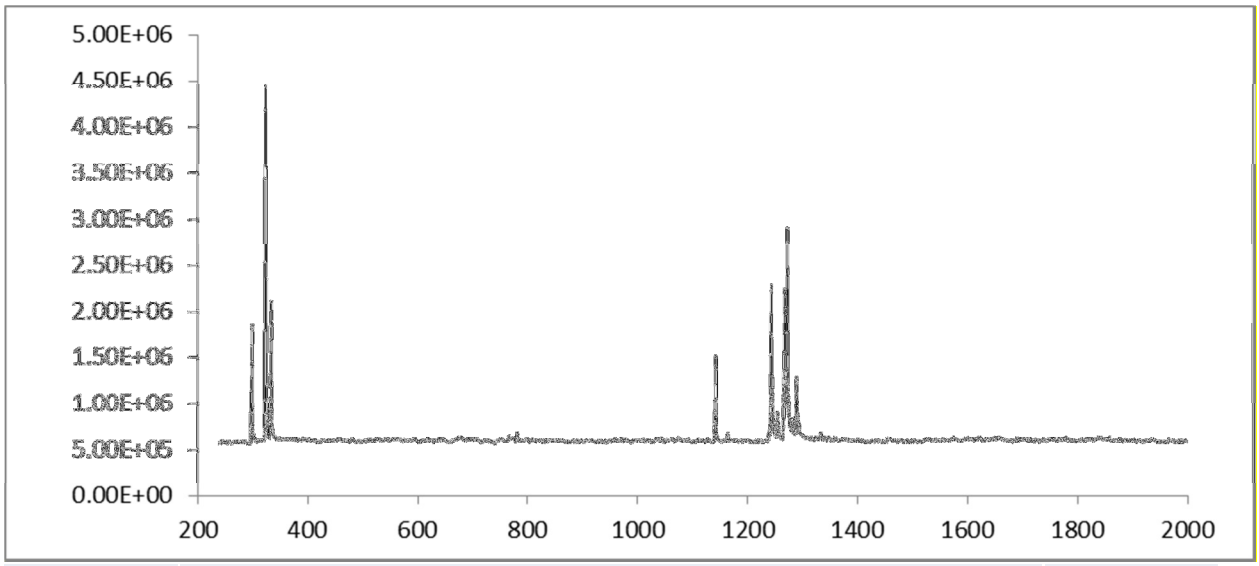


Batch 22-24 Liquid Nitrogen Trap		
Retention time (minutes)	**Compound name**	**Peak Area %**
3.072	**methanol**	**40.3**
3.166	**Trimethylamine (TMA)**	**13.7**
7.335	**1,3-dimethoxy-2-propanol (DMP)**	**0.2**
7.666	**1,2,3-trimethoxypropane (TMP)**	**0.1**
7.865	**3-methoxy-1,2-propanediol (MMP)**	**0.2**
16.483	**Hexadecanoic acid methyl ester**	**4.6**
17.366	**9-octadecenoic acid methyl ester**	**14.1**
17.625	**9,12-octadecadienoic acid methyl ester**	**16.6**
17.795	**9,11-octadecadienoic acid methyl ester**	**5.4**

Figure A5.3.1.10.1.2: GC-FID chromatogram of products collected in the liquid nitrogen trap for combined batches #22, 23, 24. Retention time, peaks assignments and relative peak area are reported in the table.

A-5.3.1.11 Batch #36, vegetable oil, 323°C /200Torr

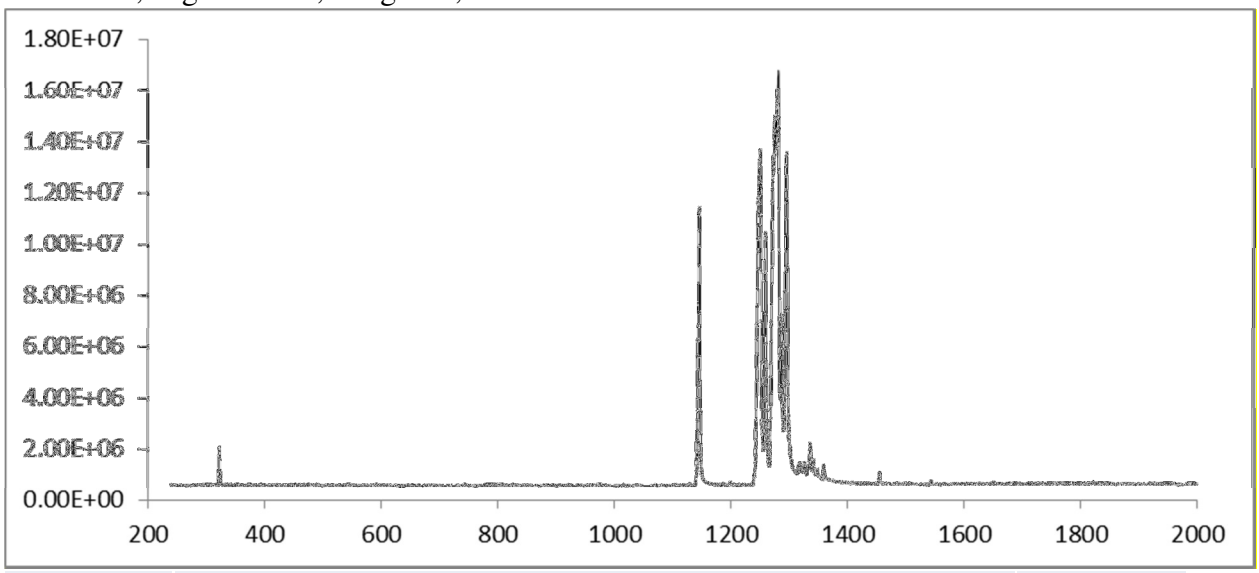
A-5.3.1.11.1 GC-MS data



Batch #36	Condenser Top	
R.T. (s)	Compound Name	
298	2-Propanol,1,3-dimthoxy-	
323	Propane,1,2,3-trimethoxy-	
333	1,2-Propanediol, 3-methoxy-	
1141	Hexadecanoic acid, methyl ester	C16:0
1243	9-Octadecenoic acid (Z)-, methyl ester	C18:1
1272	9,12-Octadecadienoic acid, methyl ester	C18:0

Figure A5.3.1.11.1.1: GC-MS chromatogram of the top layer of the liquid products collected in the condenser for batch #36. Retention time and peaks assignments are reported in the table.

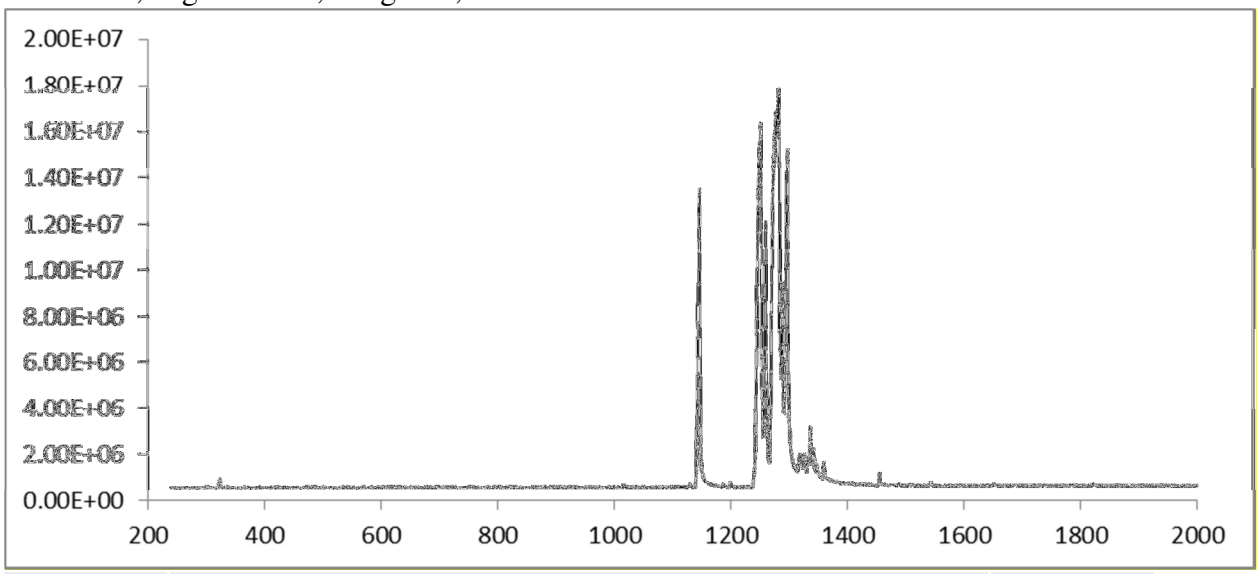
Batch #36, vegetable oil, 3.5 gal/hr, 323°C/200 Torr



Batch #36	Condenser Bottom	
R.T. (s)	Compound Name	
322	Propane,1,2,3-trimethoxy-	
1146	Hexadecanoic acid, methyl ester	C16:0
1250	9-Octadecenoic acid (Z)-, methyl ester	C18:1
1273	9,12-Octadecadienoic acid, methyl ester	C18:0

Figure A5.3.1.11.1.2: GC-MS chromatogram of the bottom layer of the liquid products collected in the condenser for batch #36. Retention time and peaks assignments are reported in the table.

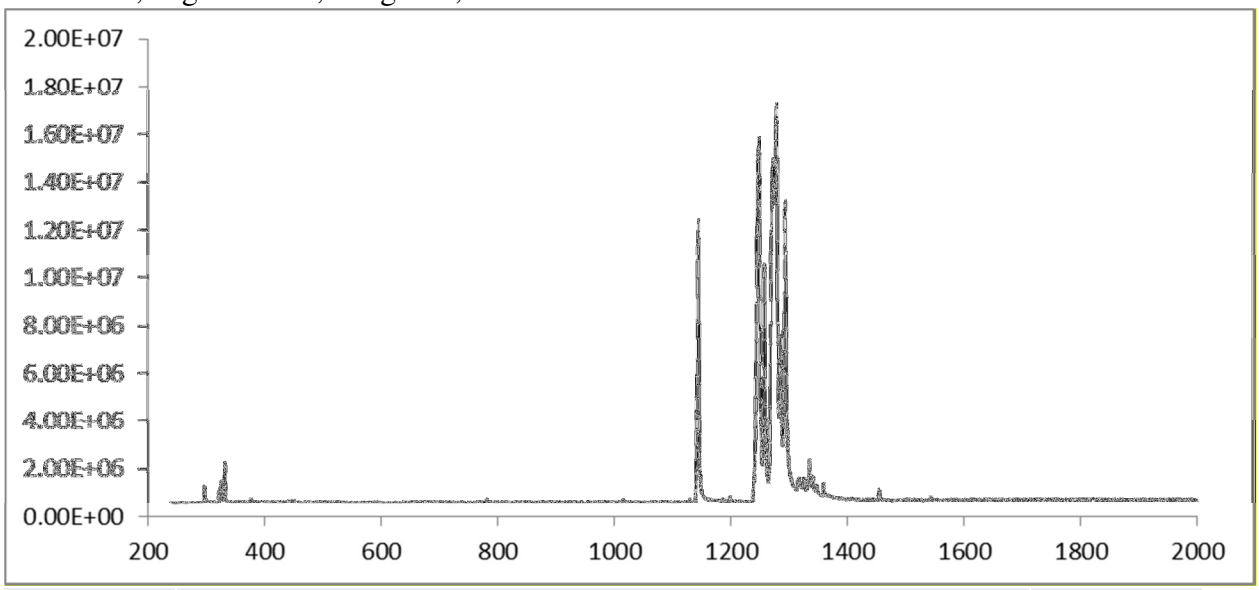
Batch #36, vegetable oil, 3.5 gal/hr, 323°C/200 Torr



Batch #36	Rototherm Top	
R.T. (s)	Compound Name	
322	Propane,1,2,3-trimethoxy-	
1146	Hexadecanoic acid, methyl ester	C16:0
1250	9-Octadecenoic acid (Z)-, methyl ester	C18:1
1273	9,12-Octadecadienoic acid, methyl ester	C18:0

Figure A5.3.1.11.1.3: GC-MS chromatogram of the top layer of liquids collected at the bottom of the reactor where residue is usually collected for batch #36. Retention time and peaks assignments are reported in the table.

Batch #36, vegetable oil, 3.5 gal/hr, 323°C/200 Torr



Batch #36	Rototherm Bottom	
R.T. (s)	Compound Name	
297	2-Propanol,1,3-dimthoxy-	
322	Propane,1,2,3-trimethoxy-	
331	1,2-Propanediol, 3-methoxy-	
1144	Hexadecanoic acid, methyl ester	C16:0
1247	9-Octadecenoic acid (Z)-, methyl ester	C18:1
1278	9,12-Octadecadienoic acid, methyl ester	C18:0

Figure A5.3.1.11.1.4: GC-MS chromatogram of the bottom layer of liquids collected at the bottom of the reactor where residue is usually collected for batch #36. Retention time and peaks assignments are reported in the table.

A-5.3.1.11.2 NMR spectroscopy data

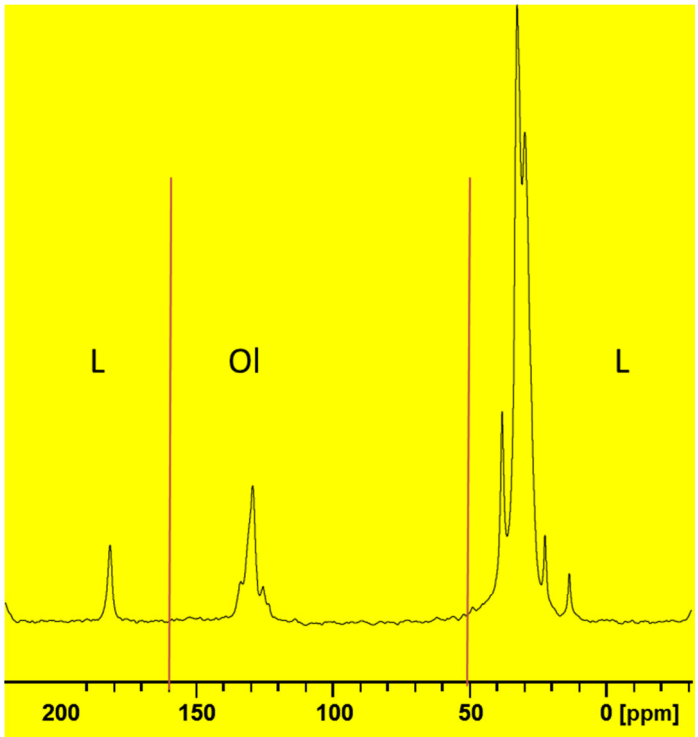
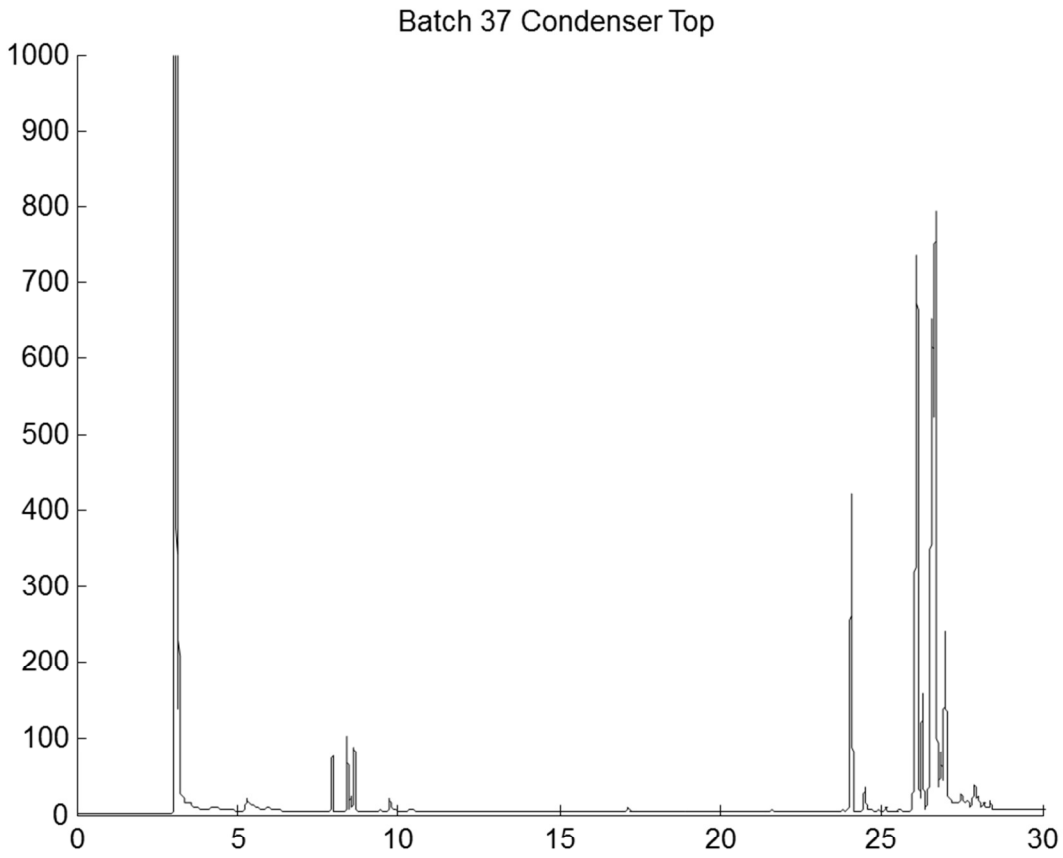


Figure A5.3.1.11.5: CPMAS spectrum of the solid residue collected at the bottom of the reactor for batch #36. The spectrum display only aliphatic structures with L regions corresponding to the lipids structures and Ol region being for olefins.

A5.3.1.12- Batch #37, vegetable oil, 3.5 gal/hr, 332°C/150 Torr

A-5.3.1.12.1 GC-MS data

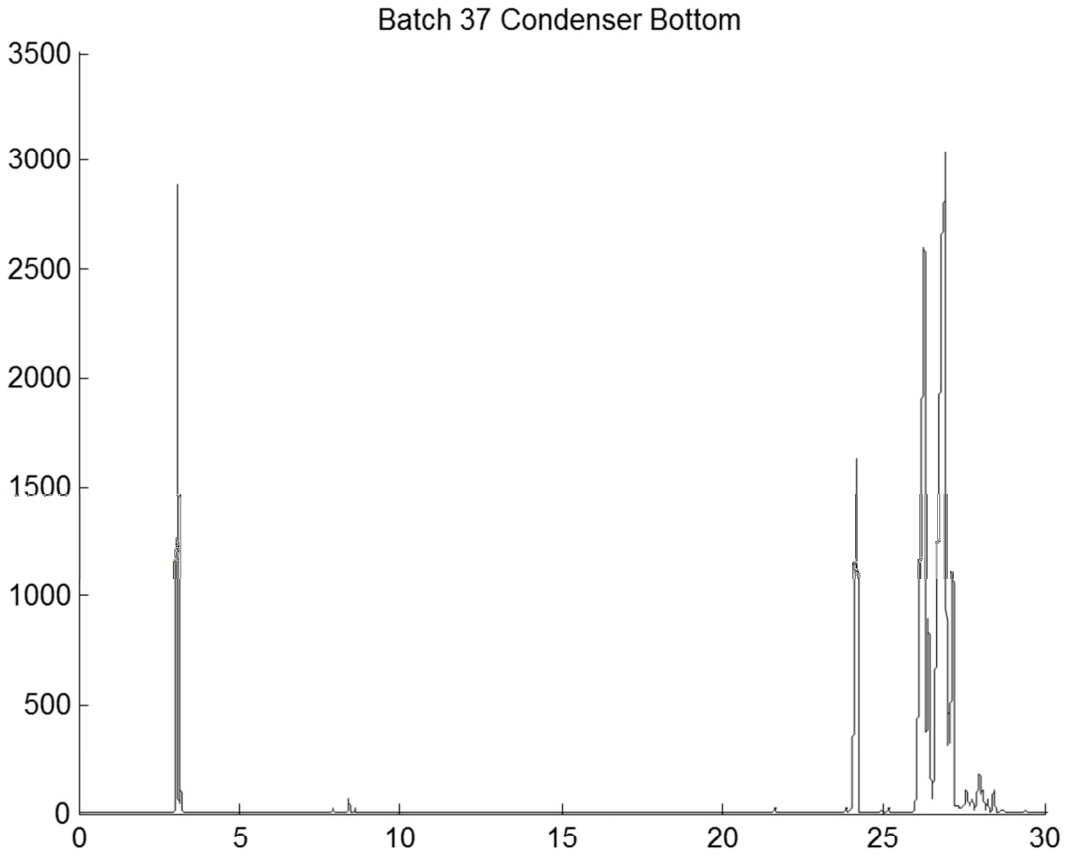


Batch 37 Condenser Top		
Retention time (minutes)	Compound name	Peak Area %
3.062	methanol	52.2
3.148	Trimethylamine (TMA)	10.2
8.416	1,3-dimethoxy-2-propanol (DMP)	0.5
8.524	1,2,3-trimethoxypropane (TMP)	0.2
8.636	3-methoxy-1,2-propanediol (MMP)	0.6
24.083	Hexadecanoic acid methyl ester	3.4
26.115	9-octadecenoic acid methyl ester	8.3
26.597	9,12-octadecadienoic acid methyl ester	7.8
26.693	9,11-octadecadienoic acid methyl ester	7.7

Figure A5.3.1.12.1.1: GC-FID chromatogram of the top layer of the liquid products collected in the condenser for batch #37. Retention time, peaks assignments and relative peak area are reported in the table.

Batch #37, vegetable oil, 3.5 gal/hr, 332°C/150 Torr

A-5.3.1.12.2 GC-FID data

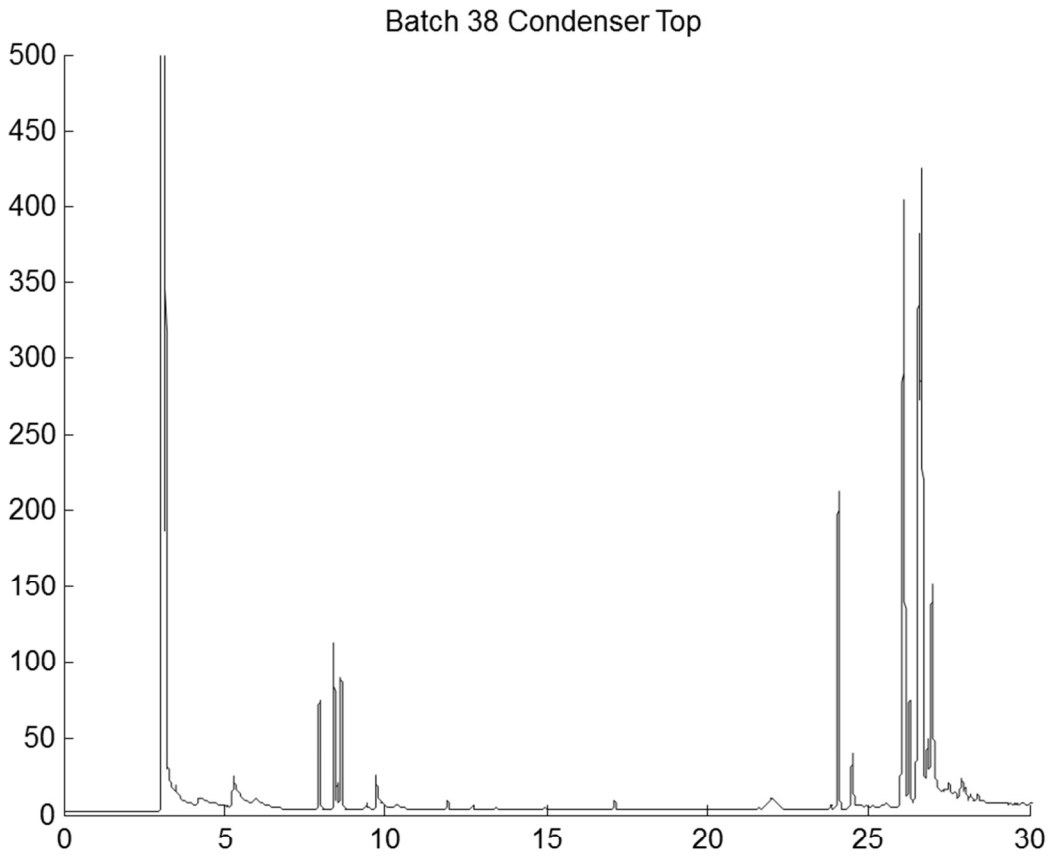


Batch 37 Condenser Bottom		
Retention time (minutes)	Compound name	Peak Area %
3.062	methanol	6.0
3.148	Trimethylamine (TMA)	2.5
8.416	1,3-dimethoxy-2-propanol (DMP)	0.2
8.524	1,2,3-trimethoxypropane (TMP)	0.0
8.636	3-methoxy-1,2-propanediol (MMP)	0.1
24.169	Hexadecanoic acid methyl ester	9.6
26.265	9-octadecenoic acid methyl ester	24.2
26.915	9,12-octadecadienoic acid methyl ester	40.7
27.156	9,11-octadecadienoic acid methyl ester	5.6

Figure A5.3.1.12.2.1: GC-FID chromatogram of the bottom layer of the liquid products collected in the condenser for batch #37. Retention time, peaks assignments and relative peak area are reported in the table.

A5.3.1.13- Batch #38, vegetable oil, 3.2 gal/hr, 332°C/150 Torr

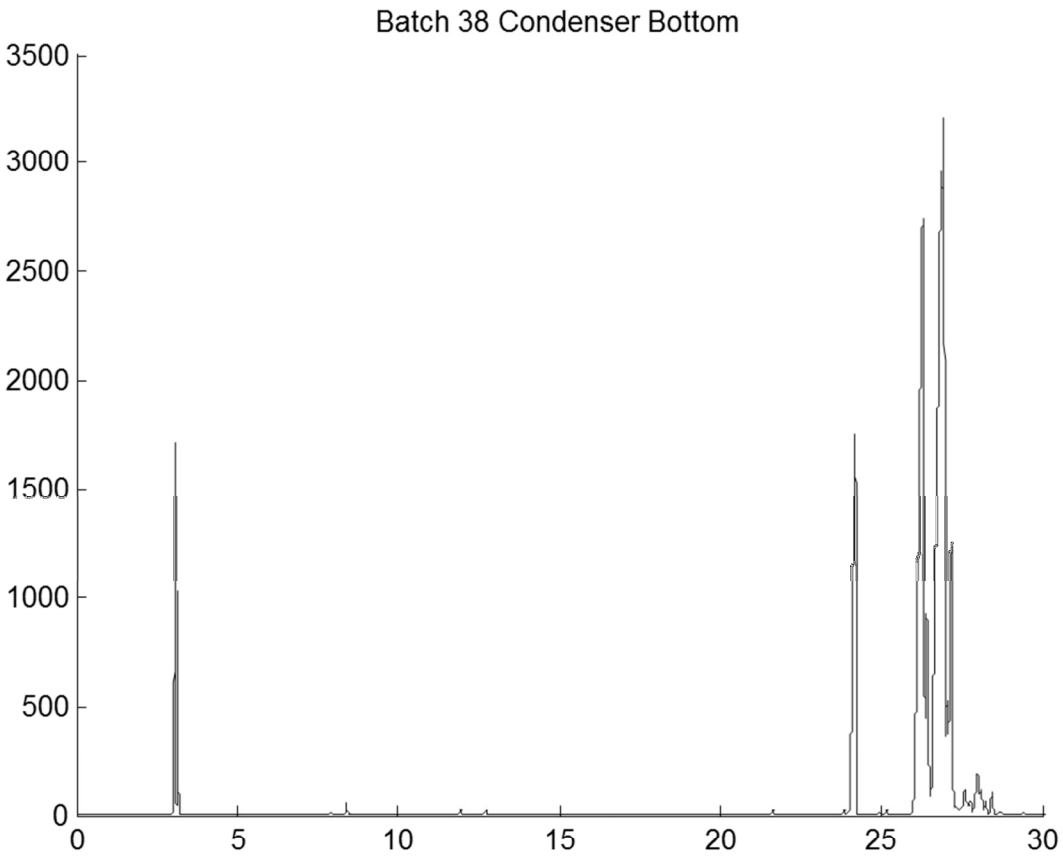
A-5.3.1.13.1 GC-FID data



Batch 38 Condenser Top		
Retention time (minutes)	Compound name	Peak Area %
3.063	methanol	60.22
3.149	Trimethylamine (TMA)	14.12
8.419	1,3-dimethoxy-2-propanol (DMP)	0.68
8.515	1,2,3-trimethoxypropane (TMP)	0.14
8.636	3-methoxy-1,2-propanediol (MMP)	0.68
24.063	Hexadecanoic acid methyl ester	1.75
26.087	9-octadecenoic acid methyl ester	4.50
26.563	9,12-octadecadienoic acid methyl ester	4.37
26.650	9,11-octadecadienoic acid methyl ester	4.35

Figure A5.3.1.13.1.1: GC-FID chromatogram of the top layer of the liquid products collected in the condenser for batch #38. Retention time, peaks assignments and relative peak area are reported in the table.

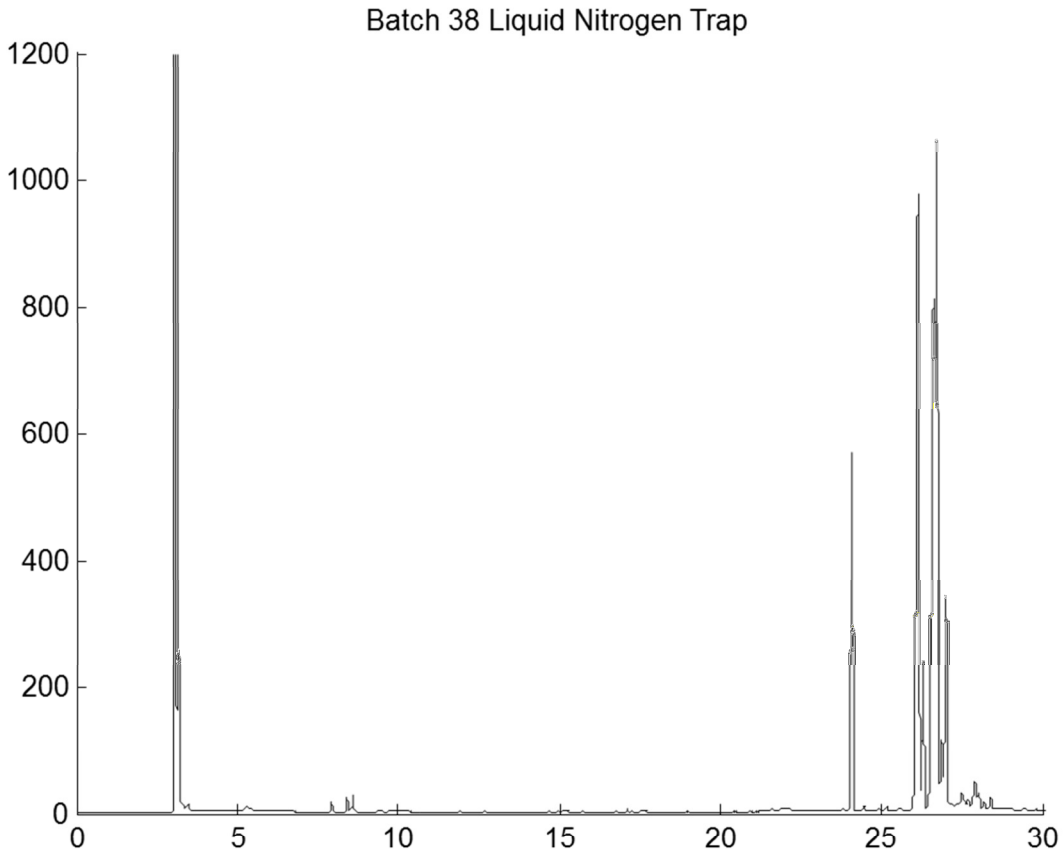
Batch #38, vegetable oil, 3.2 gal/hr, 332°C/150 Torr



Batch 38 Condenser Bottom		
Retention time (minutes)	Compound name	Peak Area %
3.063	methanol	3.4
3.149	Trimethylamine (TMA)	1.7
8.419	1,3-dimethoxy-2-propanol (DMP)	0.1
8.515	1,2,3-trimethoxypropane (TMP)	0.0
8.636	3-methoxy-1,2-propanediol (MMP)	0.04
24.179	Hexadecanoic acid methyl ester	10.1
26.278	9-octadecenoic acid methyl ester	25.4
26.859	9,12-octadecadienoic acid methyl ester	28.3
26.931	9,11-octadecadienoic acid methyl ester	13.3

Figure A5.3.1.13.1.2: GC-FID chromatogram of the bottom layer of the liquid products collected in the condenser for batch #38. Retention time, peaks assignments and relative peak area are reported in the table.

Batch #38, vegetable oil, 3.2 gal/hr, 332°C/150 Torr



Batch 38 Liquid Nitrogen Trap		
Retention time (minutes)	Compound name	Peak Area %
3.063	methanol	32.0
3.149	Trimethylamine (TMA)	25.5
8.419	1,3-dimethoxy-2-propanol (DMP)	0.2
8.515	1,2,3-trimethoxypropane (TMP)	0.0
8.636	3-methoxy-1,2-propanediol (MMP)	0.1
24.179	Hexadecanoic acid methyl ester	4.2
26.278	9-octadecenoic acid methyl ester	10.5
26.859	9,12-octadecadienoic acid methyl ester	9.4
26.931	9,11-octadecadienoic acid methyl ester	9.1

Figure A5.3.1.13.1.3: GC-FID chromatogram of products collected in the liquid nitrogen trap for batch #38. Retention time, peaks assignments and relative peak area are reported in the table.

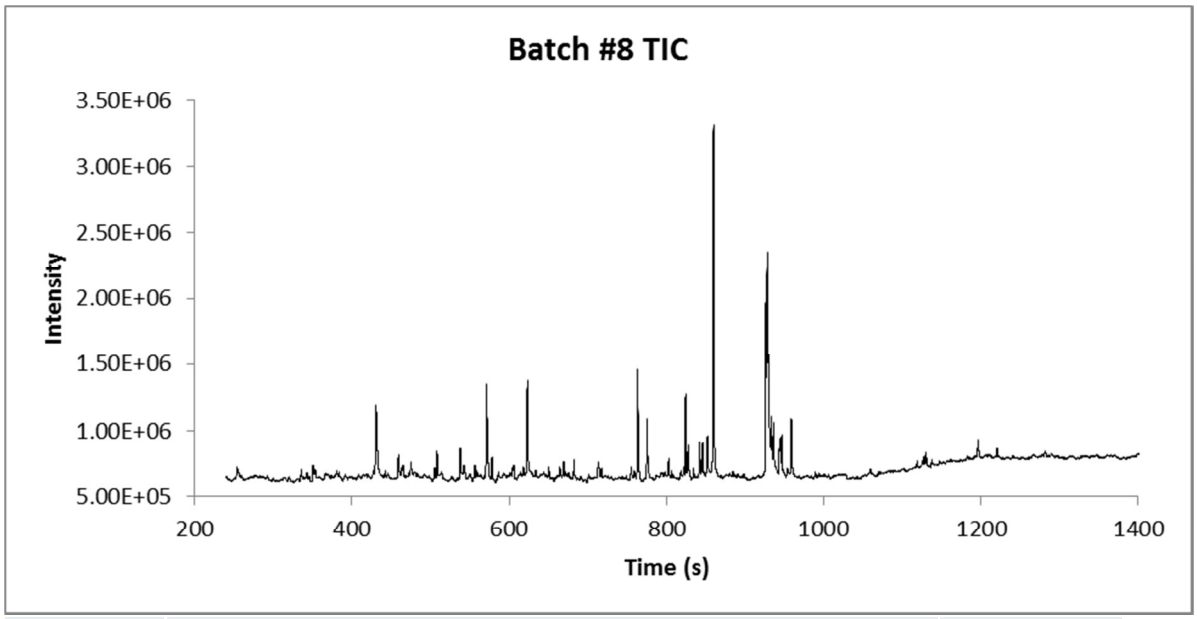
A-5.3.2- Conversion of Algae to Biodiesel in the Rototherm Reactor

The table below summarizes all the experiments that were performed. In each appendix GC-MS, then NMR data are displayed. For each type of analysis data are successively presented for the products collected in the condenser, then for those collected in the nitrogen trap, then for the liquid products collected at the bottom of the reactor with the solid residue.

Appendix Number	Batch Number	Feedstock Description	Temperature (°C)	Pressure (Torr)
A-5.3.2.1	8	wet flocculated algae	341.7	300
A-5.3.2.2	26	algae/polymer slurry	315.6	150
A-5.3.2.3	28	algae/polymer slurry	315.6	150-200
A-5.3.2.4	29	algae/polymer slurry	315.6	150
A-5.3.2.5	33	algae/polymer slurry, dried flocculated algae 0.6mm	315.6	150-190
A-5.3.2.6	34	algae/polymer slurry, dried flocculated algae 1mm	332	190-200
A-5.3.2.7	35	algae/polymer slurry, dried flocculated algae 1mm	332	170-190

A-5.3.2.1 Batch #8, wet flocculated algae, 342°C /300Torr

A-5.3.2.1.1 GC-MS data

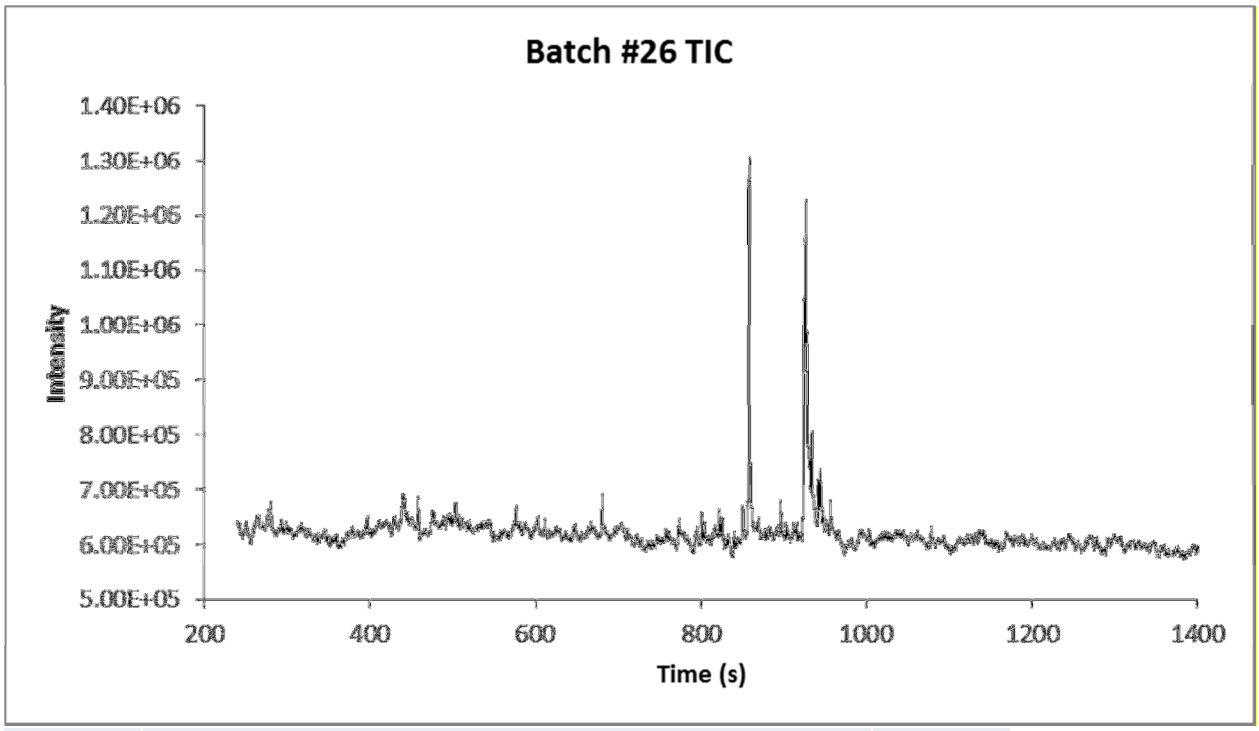


R.T. (s)	Compound Name	
430	Heptanoic acid, 3,5-dimethyl-,methyl ester	C10:1
458	Octanoic acid, methyl ester	C8:0
576	Decanoic acid, methyl ester	C10:0
623	1H-Indole, 4-methyl-	
680	Dodecanoic acid, methyl ester	C12:0
775	Methyl tetradecanoate	C14:0
802	Pentadecanoic acid, methyl ester	C15:0
824	3,7,11,15tetramethyl-2-hexadecen-1-ol (phytenol)	
852	Hexadecanoic acid, methyl ester	C16:0
928	9-Octadecenoic acid (Z)-, methyl ester	C18:1
934	Phytol	
936	Octadecanoic acid, methyl ester	C18:0
1130	Tetracosanoic acid, methyl ester	C24:0
1196	Hexacosanoic acid, methyl ester	C26:0

Figure A5.3.2.1.1.1: GC-MS chromatogram of DCM extracted liquids collected in the condenser for batch #8. Retention time and peaks assignments are reported in the table.

A-5.3.2.2 Batch #26, air dried flocculated algae, 315°C /150Torr

A-5.3.2.2.1 GC-MS data

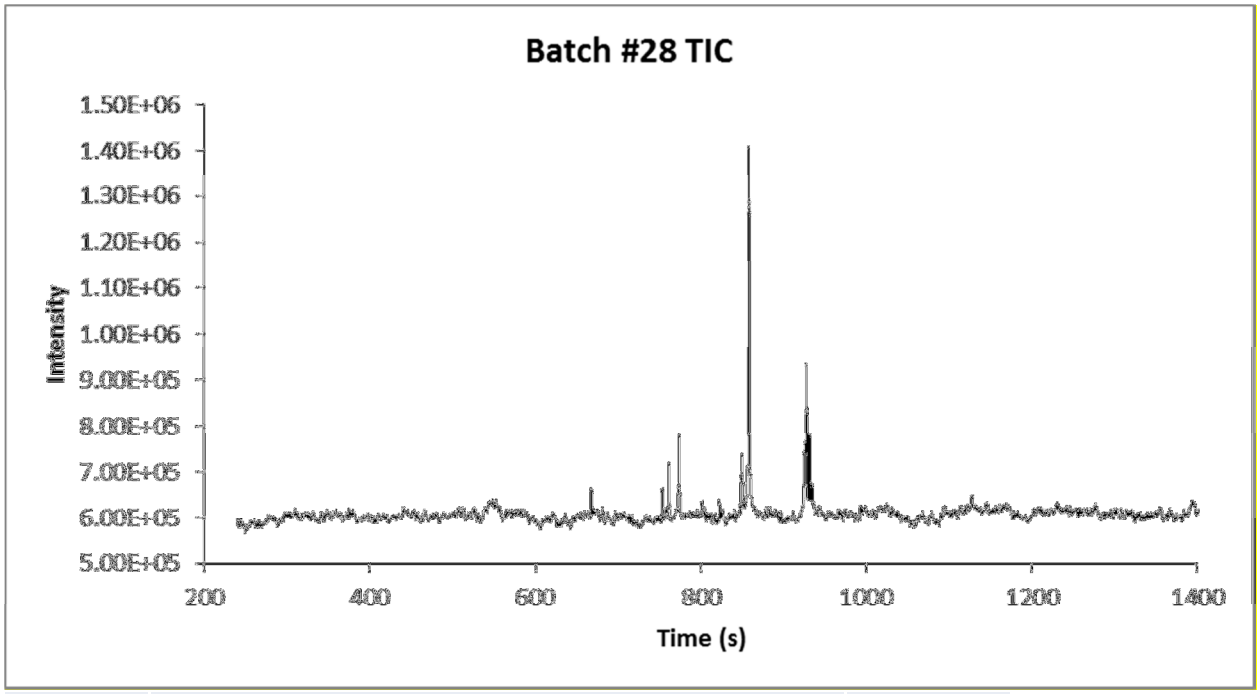


R.T. (s)	Compound Name	
458	Octanoic acid, methyl ester	C8:0
576	Decanoic acid, methyl ester	C10:0
680	Dodecanoic acid, methyl ester	C12:0
775	Methyl tetradecanoate	C14:0
858	Hexadecanoic acid, methyl ester	C16:0
926	9-Octadecenoic acid (Z)-, methyl ester	C18:1
936	Octadecanoic acid, methyl ester	C18:0
931	Phytol	C20:0

Figure A5.3.2.2.1.1: GC-MS chromatogram of DCM extracted liquids collected in the condenser for batch #26. Retention time and peaks assignments are reported in the table.

A-5.3.2.3 Batch #28, air dried flocculated algae, grounded to < 2 mm, 316°C /150-200Torr

A-5.3.2.3.1 GC-MS data

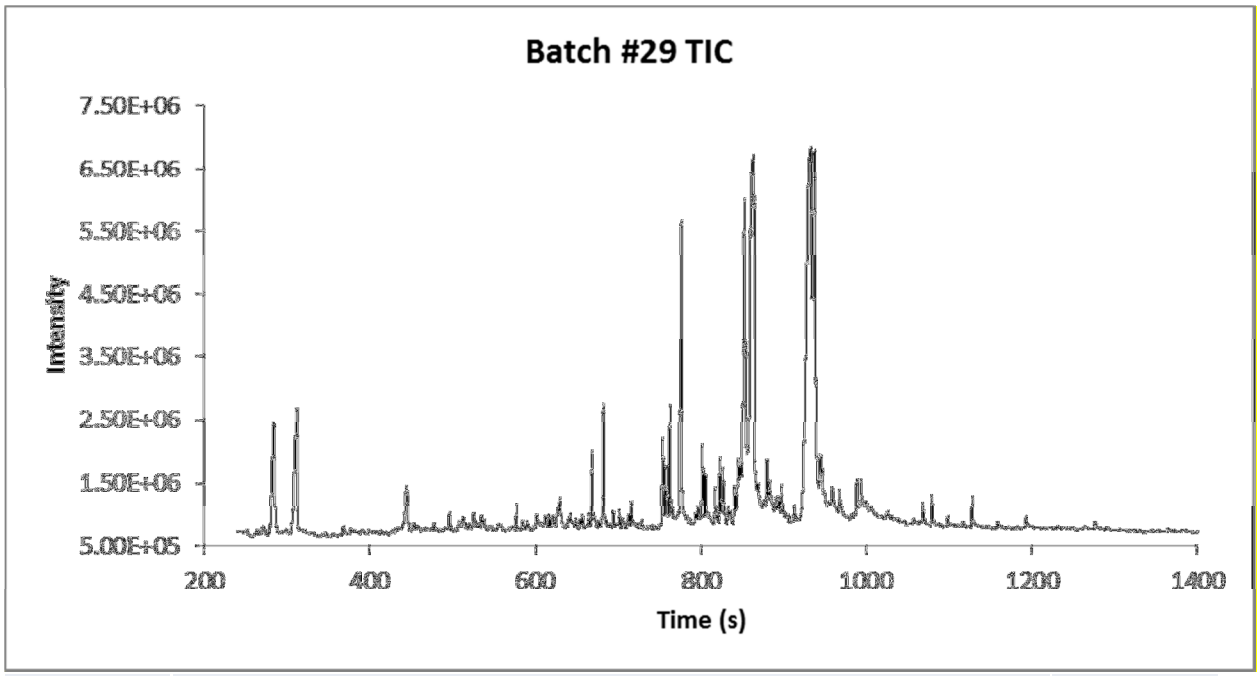


R.T. (s)	Compound Name	
680	Dodecanoic acid, methyl ester	C12:0
773	Methyl tetradecanoate	C14:0
858	Hexadecanoic acid, methyl ester	C16:0
924	9-Octadecenoic acid (Z)-, methyl ester	C18:1
931	Phytol	C20:0
936	Octadecanoic acid, methyl ester	C18:0

Figure A5.3.2.3.1.1: GC-MS chromatogram of DCM extracted liquids collected in the condenser for batch #28. Retention time and peaks assignments are reported in the table.

A-5.3.2.4 Batch #29, air dried flocculated algae, grounded to < 1 mm, 316°C /150Torr

A-5.3.2.4.1 GC-MS data



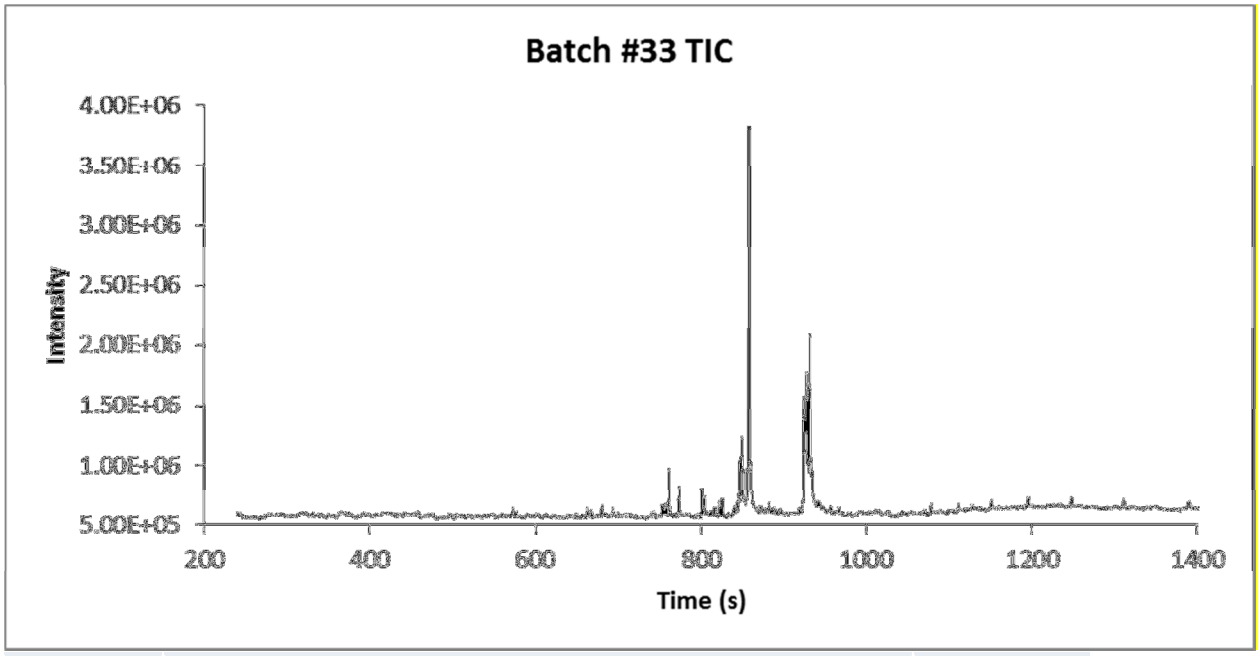
R.T. (s)	Compound Name	
283	2-Propanol, 1,3-dimethoxy-	
298	Propane, 1,2,3-timethoxy-	
444	Phenol, 3-methyl-	
682	Dodecanoic acid, methyl ester	C12:0
776	Methyl tetradecanoate	C14:0
852	7,10-Hexadecadienoic acid, methyl ester	C16:1
887	Hexadecanoic acid, methyl ester	C16:0
928	9-Octadecenoic acid (Z)-, methyl ester	C18:1
934	Phytol	C20:0
936	Octadecanoic acid, methyl ester	C18:0

Figure A5.3.2.4.1.1: GC-MS chromatogram of DCM extracted liquids collected in the condenser for batch #29. Retention time and peaks assignments are reported in the table.

Batch #34, air dried flocculated algae, grounded to less than 1mm, 332°C/200 Torr

A-5.3.2.5 Batch #33, air dried flocculated algae, grounded to < 0.6 mm, 316°C /150Torr

A-5.3.2.5.1 GC-MS data

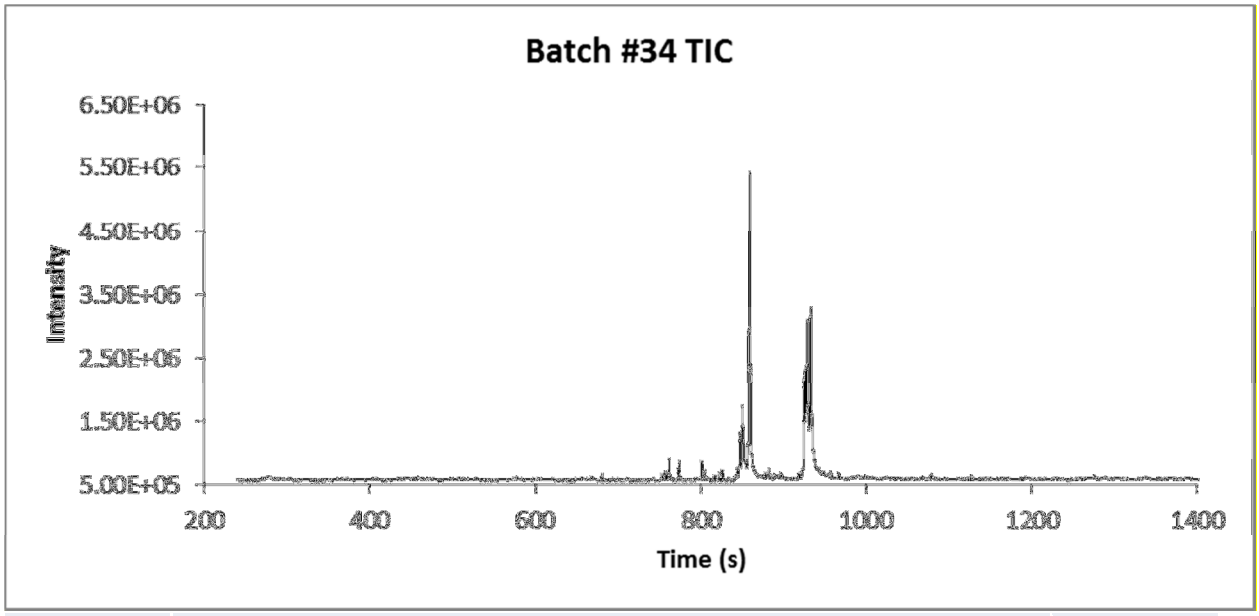


R.T. (s)	Compound Name	
458	Octanoic acid, methyl ester	C8:0
576	Decanoic acid, methyl ester	C10:0
680	Dodecanoic acid, methyl ester	C12:0
773	Methyl tetradecanoate	C14:0
846	7,10-Hexadecadienoic acid, methyl ester	C16:1
858	Hexadecanoic acid, methyl ester	C16:0
926	9-Octadecenoic acid (Z)-, methyl ester	C18:1
931	Phytol	C20:0
936	Octadecanoic acid, methyl ester	C18:0

Figure A5.3.2.5.1.1: GC-MS chromatogram of DCM extracted liquids collected in the condenser for batch #33. Retention time and peaks assignments are reported in the table.

A-5.3.2.6 Batch #34, air dried flocculated algae, grounded to < 1 mm, 332°C /200Torr

A-5.3.2.6.1 GC-MS data



R.T. (s)	Compound Name	
680	Dodecanoic acid, methyl ester	C12:0
773	Methyl tetradecanoate	C14:0
846	7,10-Hexadecadienoic acid, methyl ester	C16:1
859	Hexadecanoic acid, methyl ester	C16:0
926	9-Octadecenoic acid (Z)-, methyl ester	C18:1
932	Phytol	C20:0
936	Octadecanoic acid, methyl ester	C18:0

Figure A5.3.2.6.1.1: GC-MS chromatogram DCM extracted liquids collected in the condenser for batch #34. Retention time and peaks assignments are reported in the table. Retention time and peaks assignments are reported in the table.

Batch #34, air dried flocculated algae, grounded to less than 1mm, 332°C/200 Torr

A-5.3.2.6.2 NMR spectroscopy data

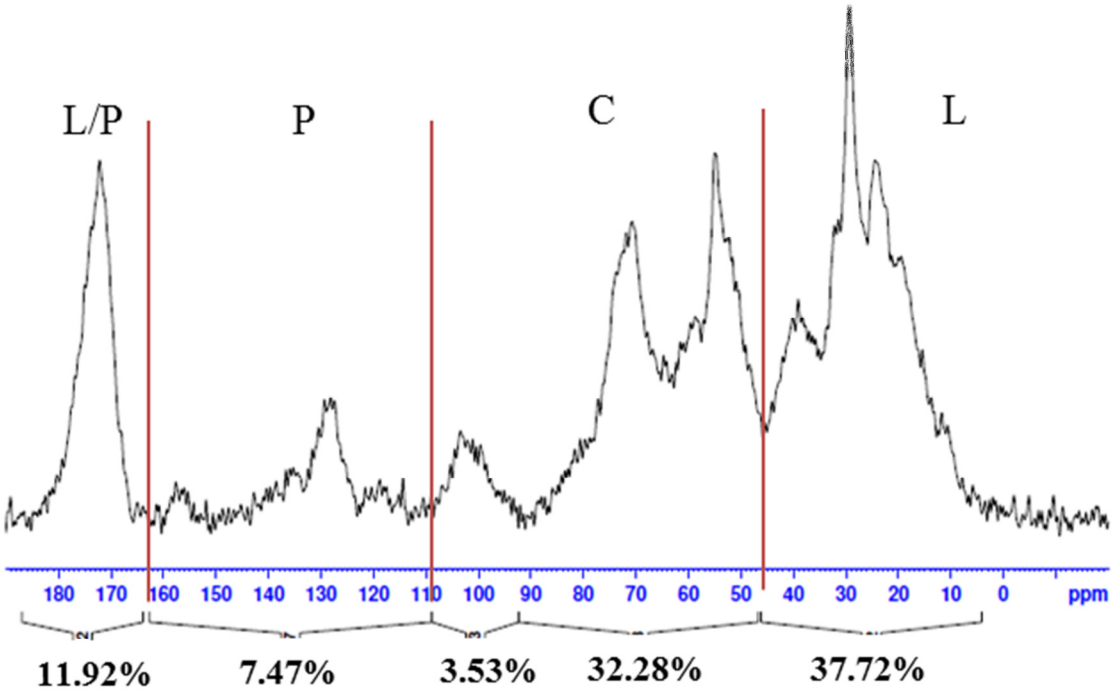
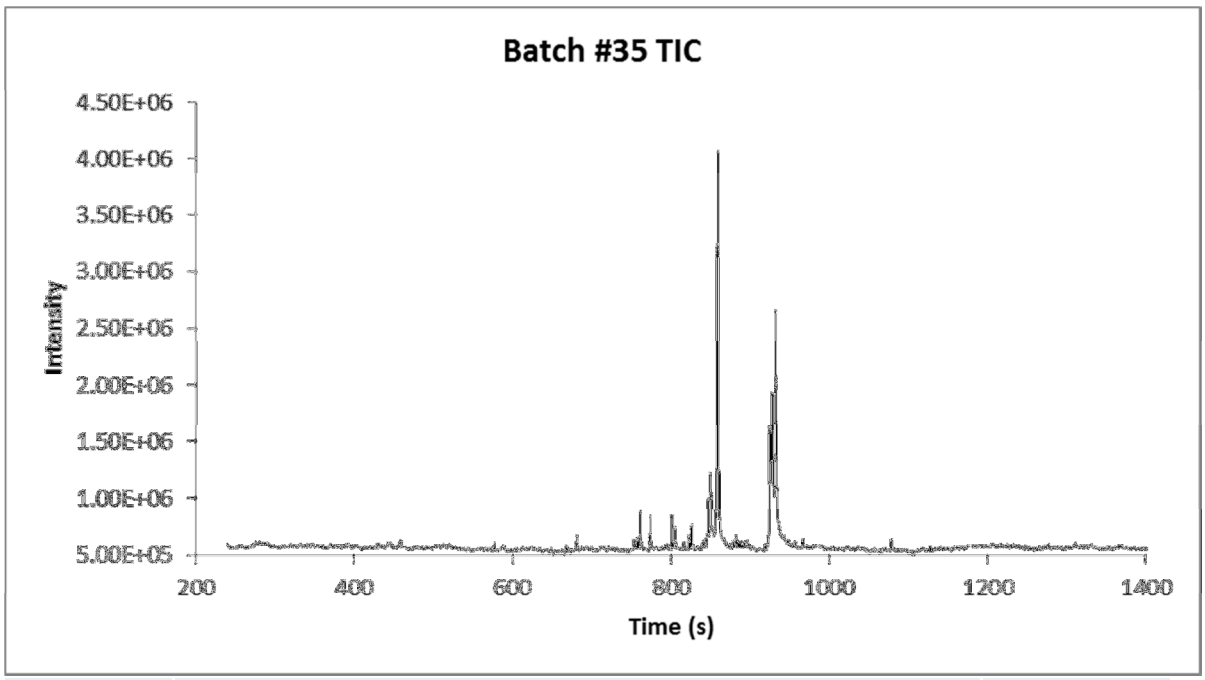


Figure A5.3.2.6.2.1: Solid-state ^{13}C CPMAS NMR spectrum of the spent algae collected at the bottom of the Algaenator for Batch #34.

A-5.3.2.7 Batch #35, air dried flocculated algae, grounded to < 1 mm, 332°C /170-190Torr

A-5.3.2.7.1 GC-MS data



R.T. (s)	Compound Name	
458	Octanoic acid, methyl ester	C8:0
576	Decanoic acid, methyl ester	C10:0
680	Dodecanoic acid, methyl ester	C12:0
773	Methyl tetradecanoate	C14:0
846	7,10-Hexadecadienoic acid, methyl ester	C16:1
858	Hexadecanoic acid, methyl ester	C16:0
926	9-Octadecenoic acid (Z)-, methyl ester	C18:1
932	Phytol	C20:0
936	Octadecanoic acid, methyl ester	C18:0

Figure A5.3.2.7.1.1: GC-MS chromatogram of DCM extracted liquids collected in the condenser for batch #35. Retention time and peaks assignments are reported in the table.

A-5.3.2.8 Elemental composition of algae residues

Summary	%N		%C		%H	
	AVG	SD	AVG	SD	AVG	SD
Algae Residue Batch 26	3.22	0.30	29.57	1.58	4.15	0.41
Algae Residue Batch 33 <0.6mm	10.99	0.73	49.07	0.91	7.57	0.06
Algae Residue Batch 34 after run	11.05	0.77	50.34	0.99	7.19	0.14

A-5.3.3- Methods for analysis

Sample Collection and Preparation. Both flocculation and centrifugation were used to obtain highly concentrated samples of algae. Algae were collected from the ODU Algae Farm located in Spring Grove, VA. This farm is an open pond design in which mainly *Scenedesmus/Desmodesmus spp*. algae are being grown and harvested. Samples of algae were concentrated by use of a continuous flow centrifuge (Lavin Centrifuge Model 12-413V) and also by the use of a chemical flocculent. Algae was then introduced into the Algaenator reactor as either wet or dry biomass and processed under various conditions.

Identification by GC-MS and GC-FID. Samples were analyzed by an Agilent 6890 gas chromatograph interfaced to a Leco III mass spectrometer. The temperature was programmed from 50ºC to 300°C at a rate of 15°C/min. The mass spectrometer was repeatedly scanned in the low-resolution mode from 45 to 500 mass (u) at a rate of 20 spectra/second. Compounds were identified by their mass spectra. Most peaks were identified by comparison with the Wiley/NBS library and some were confirmed by comparison with standards. Quantitative measurements of the concentrations of individual peaks were made using an internal standard n-tetracosane as well as with external fatty acid methyl ester (FAME) standards. FAME standards were GLC-40, 50, and 90 standard mixtures (Supelco Analytical) containing fatty acid mixtures of $C_{16:0}$, $C_{18:0}$, $C_{20:0}$, and $C_{22:0}$; $C_{16:1}$, $C_{18:1}$, $C_{20:1}$, and $C_{22:1}$; $C_{13:0}$, $C_{15:0}$, $C_{17:0}$, $C_{19:0}$, and $C_{21:0}$; respectively.

Samples were also analyzed by an Agilent Technologies 7890 Gas Chromatography System with a flame ionization detector (FID). The GC-FID with a capillary column (10 m × 530 µm i.d. × 2.65 µm) was operated in the direct injection mode with an injector temperature of 350°C and a detector temperature of 370°C. Helium was used as carrier gas at a constant flow rate of 20 ml/min. The oven temperature was programmed from 40°C and 350°C at a rate of 20°C/min.

Elemental Carbon (C) and Nitrogen (N) Analysis of Algae Residue. The Carbon (C) and nitrogen (N) contents of algae residues were determined by standard combustion analysis. Elemental analysis was carried out in triplicate using a Thermo Finnigan Flash 1112 Elemental Analyzer using a nicotinamide standard for calibration. Approximately 1-2mg of each solid sample was placed in a 3.3 x 5mm tin capsule for combustion. The method used for analysis was a furnace at 900°C, oven at 75°C, and carrier gas at 91 ml/min.

Solid-state ^{13}C NMR. The NMR experiments were performed using a Bruker Avance II 400 spectrometer operating at 100 MHz for ^{13}C and 400 MHz for ^{1}H. All the experiments were

conducted using a 4-mm triple resonance probe. Dry algae and spent algae residue after conversion were packed into a 5-mm Zirconia NMR rotor fitted with a Kel-F cap for analysis. We applied cross polarization magic angle spinning (CPMAS) ^{13}C NMR to quantify the mobile fraction of CH_2 groups, which are contributed mainly by fatty acids in an algal sample. To highlight the mobile components such as aliphatic groups, we applied a CPMAS ^{13}C NMR with a short recycle delay time of 1.0 s and 2000 scans. Experiments were conducted at the ODU College of Sciences Instrument Cluster (COSMIC) facility.

A5.4. Evaluating the economics (Task 4, Objectives 8 and 9)

A5.4.1 Tables

Table 3: Artisan Industries, Inc. Equipment list for Rototherm System

INSTRUMENTS & ACCESSORIES LIST — ODURF JOB 86209 — AS OF

TAG	ITEM	DESCRIPTION
XG-01	FEED TK XG	4" TRI CLMP J.M. CANTY S4A6C100A0 SANITARY FULL VIEW FUSEVIEW SIGHT GLASS, HC
TI-0	FEED TANK THERMOMETER	3" DIAL WIKA TYPE TI.30 BIMETAL THERMOMETER, 0-250°F, 6" STEM LENGTH, BACK CONNECTED
HV-01	FEED TK BTM VALVE	2" FLOWTEK 316 SS TANK BTM BALL VALVE W/ CAVITY FILLERS TK7408-3-JCF-R-L
HV-02	FEED TK FEED VALVE	1 1/2" TRICLAMP FLOWTEK 316SS TUBE BORE BALL VALVE W/ CAVITY FILLERS S7507-3-TCF-T-L
WE-01/02/03	FEED TK WEIGH SCALE	FAIRBANKS 9101 SERIES LOAD CELL STANDS (3) W/ REMOTE 5200A ELECTRONICS & ISB PKG
PSV-01	CIRC PUMP PSV	1/2" GRIFFCO 3-PORTED RELIEF VALVE PRM050S 316 SS/ TFE ON EPDM SET AT 50 #
PSV-02	FEED PUMP PSV	1/4" GRIFFCO 3-PORTED RELIEF VALVE PRM025S 316 SS/ TFE ON EPDM SET AT 50 #
PI-01	CIRC PUMP PI	3/4" TRI CLMP 316 SS WIKA I981.22 FLO THRU PRESS SENSOR W/ AMERSHAM (WIKA) 60# SS GAUGE
PI-02	FEED PUMP PI	1/2" TRI CLAMP LARAD FLO THRU PRESS SENSOR P/N 1/2"-34-01S-05-04 W 316 SS ENDS & NEOPRENE LINER, 2 1/2" SS CASE 1009SW -02L GAUGE 30" VAC -0-30 #
HV-03	CIRC PUMP OUTLET DRAIN	3/4" TRICLAMP TRIAD 316 SS 3-WAY BALL VALVE W/ CAVITY FILLERS 30T-92061 90 DEGREE T PORT
HV-04	FEED PUMP OUTLET DRAIN	1/2" ODT 316 SS SWAGELOK 3-WAY L-PORTED BALL VALVE SS-45XS6
BPV-01	FEED BPV	1/4" FPT RED VALVE MINIFLEX 2600 AIR LOADED PINCH VALVE, SS ENDS WITH NEOPRENE LINING
PCV-01/PI-03	PCV/PI FOR FEED BPV	CONTROL AIRE 400-BB-K PRESSURE REGULATOR, W/TRERICE 800B-20-02B-A100, 2" 60# BACK-CONNECTED PRESSURE GAUGE
TE-01	ROTO TE	PYROMATION TT38GMZ-003-SL-8RNBC2331 (Z=187) DUPLEX TYPE T SPRNG LDD TC ASSBLY W/ AL SCRW CVR HEAD
XG-02	ROTO XG	6" J. M. CANTY S7ARC101HA HI-TEMP FUSEVIEW, HC276 (INNER), STL (OUTER), STL RETAINER FLG DUAL LENS
HV-05	ROTO BTMS VALVE	4" 150# FLGD FLOWTEK 316SS F153-R-11-3-KCF-G-L FULL PORTED BALL VALVE W/ TEKFIL SEATS AND CAVITY FILLERS, GRAPHITE SEALS RATED FOR FV – 15 PSIG AT 600F
FG-01	ROTO BTMS FG	LJ STAR VFI-1145 4" RFF 316 SIGHT FLOW INDICATOR, DRIP TUBE, QUARTZ, GRAFOIL, 800F RATING
PI-04	VAPOR LINE PI	US VACUUM USCG-760 0-760 TORR ABS PRESSURE GAUGE,
TE-02	VAPOR LINE TE	PYROMATION TT38GMZ-007-00-9HP31 (Z=187) DUPLEX TYPE T TC ASSBLY W/ AL SCRW CVR HEAD, 3/16" OD SHEATH 7" LG
TE-03	DISTILLATE TE	PYROMATION TT38GMZ-007-00-9HP31 (Z=187) DUPLEX TYPE T TC ASSBLY W/ AL SCRW CVR HEAD, 3/16" OD SHEATH 7" LG
OMIT	WAS CONDENSER XG BUT NO CONNECTION	2" J. M. CANTY S7AED101HA HI-TEMP FUSEVIEW, HC276 (INNER), STL (OUTER), STL RETAINER FLG DUAL LENS
HV-06	DISTILLATE VALVE	1" 150# FLANGED 316 SS APOLLO 87 SERIES STD PORT BALL VALVE
HV-07	COLD TRAP DRAIN VALVE	1" SW FLOWTEK 316 SS 7205-3-R-R-L BALL VALVE
PI-05/06/07	COLLECTOR PLATE PI (3)	2-1/2" PRESSURE GAUGE, 0-30" HG VAC, 1/4" MPT BRASS LOWER CONNECTION, ASHCROFT 25W1005PH-02L OR =
HV-09	COLLECTOR PLATE VALVES (6)	1/4" MPT BRASS SWAGELOK PLUG VALVE B-4P4T2
XG-03/04	12 XG FOR ALL COLLECTING POTS (6)	LJ STAR DN50 (2") 316L SS TYPE MV SIGHT GLASS SW-1137-1 W/ STD GLASS AND SPCL GRAFOIL SEALS, RATED 90 PSIG @ 500° F PER QUOTE 18859
TI-01/HJS-01	MULTI POINT TE READOUT	DORIC 610-1-1-20 6-POINT DIGITAL THERMOCOUPLE READOUT
HV-08	VACUUM CONTROL/PUMP ISOLATING VALVE	1 1/2" SW STEEL FLOWTEK 8207-3-R-K-R-V60 BALL VALVE W/ 60 DEGREE 316 SS V BALL
SIC-01	MIXER VFD	1 HP ALLEN-BRADLEY POWERFLEX 40 480 VAC NEMA 1 ENCLOSED VFD 22B-D2P3N104 W/ 22-JBAB
SIC-02	FEED METERING PUMP VFD	1 HP ALLEN-BRADLEY POWERFLEX 40 480 VAC NEMA 1 ENCLOSED VFD 22B-D2P3N104 W/ 22-JBAB
SIC-03	ROTOTHERM VFD	5 HP ALLEN-BRADLEY POWERFLEX 40 480 VAC NEMA 1 ENCLOSED VFD 22B-D010N104 W/ 22-JBAB

EQUIPMENT LIST — ODURF JOB 86209 — AS OF 9-Sep-10

ITEM	QTY	DESCRIPTION	SUPPLIER
FEED TANK	1	35 GALLON (GROSS) 20" OD VERTICAL 304 SS TANK, 23" SW, UM STAMPED	APACHE STAINLESS EQUIPMENT CORP
FEED TANK MIXER	1	CHEMINEER 50DTA-0.50 316 SS WITH 1/2 HP XP BLACK MAX INV DTY MOTOR	CHEMINEER C/O MARTELL ASSOC
FEED SKID	1	46.5 X 60" 304 SS SKID W/ COVER PLATE AND PUMP MOUNT STAND 46" ABOVE FLOOR, MOUNT LOAD CELLS AND TANK	APACHE STAINLESS EQUIPMENT CORP
1 SF ROTOTHERM	1	650°F JKT, 4" BTMS, COCURRENT, 5/8" ODT FEED, 316 SS	ARTISAN 86154
ROTOTHERM MOTOR	1	5 HP 1200 RPM BALDOR 215TC XP INVTR DTY FOOTLESS	
SEAL RESERV	1	2-GALLON STEEL	CRANE/LEMCO
INITIAL SUPPLY OF SEAL FLUID	1	5 GALLON CAN OF CHESTERTON 610 FLUID	CHESTERTON
CONDENSER	1	7.5 SF ARTISAN VERTICAL U-TUBE DESIGN, 316 SS, CODE STAMPED	ALLEGHENY BRADFORD CORP
COLD TRAP	1	A & N VSCI-5000-QF50 LIQUID NITROGEN COLD TRAP W/ QF50 CONNECTIONS, SS	A & N
MAIN VACUUM PUMP	1	KINNEY KTC-21 W/ 1 1/2 HP XP MOTOR	TUTHILL VACUUM & BLOWER SYSTEMS
SECONDARY VACUUM PUMP	1	KINNEY KC 5 W/ 1/2 HP XP MOTOR	TUTHILL VACUUM & BLOWER SYSTEMS
FEED CIRCULATING PUMP	1	SEEPEX 5 GPM BN 2-6L/ SERIES W/ 1 HP WEG XP MOTOR, 316 SS/EPDM	DIVERSIFIED PUMP
FEED METERING PUMP	1	SEEPEX .05 GPM MD 003-12/ SERIES W/ 1/2 HP BLACK MAX XP INVTR DTY MOTOR, 316 SS/EPDM	DIVERSIFIED PUMP
BOTTOMS POT	2	2.5 GAL 9" ID W/ 6" TRICLAMP TOP INLET, ROUND BOTTOM W/ SHORT SKIRT, UM STAMPED 500° F	APACHE STAINLESS EQUIPMENT CORP
DISTILLATE POT	2	1.25 GAL 9" ID W/ 1 1/2" TRICLAMP TOP INLET, ROUND BOTTOM W/ SHORT SKIRT, UM STAMPED 400° F	APACHE STAINLESS EQUIPMENT CORP
COLD TRAP POT	2	1.25 GAL 9" ID W/ 1 1/2" TRICLAMP TOP INLET, ROUND BOTTOM W/ SHORT SKIRT, UM STAMPED 400° F	APACHE STAINLESS EQUIPMENT CORP
BTTMS COLLECTOR PLATE	1	ARTISAN STANDARD FOR 4" ANSI RFF MOUNTING	ARTISAN
DISTILLATE COLLECTOR PLATE	1	ARTISAN STANDARD FOR 1" ANSI RFF MOUNTING	ARTISAN
COLD TRAP COLLECTOR PLATE	1	ARTISAN STANDARD FOR 1" ANSI RFF MOUNTING, EXCEPT WELDED TO 1" PIPE	ARTISAN

EQUIPMENT LIST — ODURF JOB 86209 — AS OF 9-Sep-10

ITEM	QTY	DESCRIPTION	SUPPLIER
HOS	1	18 KW HOT OIL SYSTEM SL650-18-R3-MWC-463	HEAT EXCHANGE AND TRANSFER, INC.
HWS	1	9 KW/ HOT WATER CIRCULATING SYSTEM KB-341S WITH 7.4 SF COOLER	DELTA T SYSTEMS INC.

Table A5.4.1: Theoretical yields form algae feedstock for Case I (10 metric tons of dry algae by weight per day) and Case II (100 metric tons of alge dry weight per day).

Theoretical Algaenator Yields from Algae Feedstock

137.2 Acre Algae Farm						**1372 Acre Algae Farm**				
Triglycerides, wt%			6			Triglycerides, wt%			6	
H_2O, wt%			1						1	
Slurry solids, wt%			30						30	
	BP, °C	MW	kg/hr	gm-mols/hr			BP, °C	MW	kg/hr	gm-mols/hr
H_2O	100	18	4.21	233.67		H_2O	100	18	42.06	2336.67
Triglycerides	290	765.1	25.24	32.98		Triglycerides	290	765.1	252.36	329.84
Dry Solids			391.16			Dry Solids			3911.58	
Total Solids			420.60			Total Feed			4206.00	
	mol/mol TAG						mol/mol TAG			
TMAH reacted	5					TMAH reacted	5			
Excess TMAH	1					Excess TMAH	1			
TMAH make-up	6	91.2	18.05	197.90		TMAH make-up	6	91.2	180.49	1979.04
MeOH Produced+ or Consumed-		32.04	1.06	32.98		MeOH Produced+ or Consumed-		32.04	10.57	329.84
MeOH w/TMAH			54.15			MeOH w/TMAH			541.46	
MeOH Recycle			927.25			MeOH Recycle			9272.54	
Total MeOH		32.04	981.40	30630.49		Total MeOH		32.04	9814.01	306304.85
Rototherm Feed			**1420.05**			**Rototherm Feed**			**14200.50**	
TMA	2.9	59.11	11.70	197.90		TMA	2.9	59.11	116.98	1979.04
MeOH	64.7	32.04	982.46	30663.47		MeOH	64.7	32.04	9824.58	306634.69
H_2O	100	18	7.17	398.59		H_2O	100	18	59.87	3326.19
TMP	150	134	1.47	10.99		TMP	150	134	14.73	109.95
DMP	170	120	1.32	10.99		DMP	170	120	13.19	109.95
MPD	222	106	1.17	10.99		MPD	222	106	11.65	109.95
FAME	218.5+	256	23.13	0.09		FAME	218.5+	256	243.19	0.95
Triglycerides	290	765.1		0.00		Triglycerides	290	765.1		0.00
Other Compounds			0.47			Other Compounds			4.72	
Dry Solids			391.16						3911.58	
Rototherm Products			**1420.05**			**Rototherm Products**			**14200.50**	
Product Recovery Ratios:										
Specialty Chemicals/MeOH			0.00						0.00	
FAME/MeOH			0.02						0.02	
					scfm					
TMA	2.9	59.11	11.70	197.90	2.61	TMA	2.9	59.11	116.98	531.62
MeOH	64.7	32.04	491.23	15331.73	202.06	MeOH	64.7	32.04	4912.29	1000.61
Condenser Vapor			502.93	15529.64	204.67	**Condenser Vapor**			5029.27	1532.24
MeOH	64.7	32.04	491.23	15331.73		MeOH	64.7	32.04	4912.29	153317.35
H_2O	100	18	7.17	398.59		H_2O	100	18	59.87	3326.19
TMP	150	134	1.47	10.99		TMP	150	134	14.73	109.95
DMP	170	120	1.32	10.99		DMP	170	120	13.19	109.95
MPD	222	106	1.17	10.99		MPD	222	106	11.65	109.95
FAME	218.5+	256	23.13	90.36		FAME	218.5+	256	243.19	949.95
Condenser Liquid			525.49	15853.66		**Condenser Liquid**			5254.93	157923.33
TMA	2.9	59.11	11.70	197.90		TMA	2.9	59.11	116.98	1979.04
MeOH	64.7	32.04	982.46	30663.47		MeOH	64.7	32.04	9824.58	306634.69
H_2O	100	18	7.17	398.59		H_2O	100	18	59.87	3326.19
Methoxypropane Stripping Distillate			1001.33	31062.06		**Methoxypropane Stripping Distillate**			10001.43	309960.88
TMP	150	134	1.47	10.99		TMP	150	134	14.73	109.95
DMP	170	120	1.32	10.99		DMP	170	120	13.19	109.95
MPD	222	106	1.17	10.99		MPD	222	106	11.65	109.95
FAME	218.5+	256	23.13	90.36		FAME	218.5+	256	243.19	949.95
Methoxypropane Stripping Bottoms			27.09	123.34		**Methoxypropane Stripping Bottoms**			282.77	1279.79
TMA	2.9	59.11	11.70	197.90		TMA	2.9	59.11	116.98	1979.04
MeOH	38.8	74.12	982.46	13254.96		MeOH	38.8	74.12	9824.58	132549.59
Methanol Topping Distillate			994.16	13452.86		**Methanol Topping Distillate**			9941.56	134528.63
Water	64.7	32.04	7.17	223.93		**Water**	64.7	32.04	59.87	1868.64
Recycle MeOH	38.8	74.12	927.25	12510.18		**Recycle MeOH**	38.8	74.12	9272.54	125101.77
TMA	2.9	59.11	11.70	197.90		TMA	2.9	59.11	116.98	1979.04
MeOH	38.8	74.12	55.20	744.78		MeOH	38.8	74.12	552.03	7447.82
TMA to TMAH Regeneration			66.90	942.69		**TMA to TMAH Regeneration**			669.01	9426.86
TMP	150	134	1.47	10.99		**TMP**	150	134	14.73	109.95
DMP	170	120	1.32	10.99		DMP	170	120	13.19	109.95
MPD	222	106	1.17	10.99		MPD	222	106	11.65	109.95
FAME	218.5+	256	23.13	90.36		FAME	218.5+	256	243.19	949.95
DMP Topping Feed			25.62	112.35		**DMP Topping Feed**			268.04	1169.85
DMP	170	120	1.32	10.99		DMP	170	120	13.19	109.95
MPD	222	106	1.17	10.99		MPD	222	106	11.65	109.95
FAME	218.5+	256	23.13	90.36		FAME	218.5+	256	243.19	949.95
MPD Topping Feed			24.30	101.35		**MPD Topping Feed**			254.84	1059.90
MPD	222	106	1.17	10.99		MPD	222	106	11.65	109.95
FAME	218.5+	256	23.13	90.36		FAME	218.5+	256	243.19	949.95

Table A5.4.2: Capital costs for 100 acre algae-to-biodiesel production facility.

Conceptual Algaenator Plant Order-of-Magnitude Factored Cost Estimate (100 acre Algae farm basis):

					Purchased Equipment Cost, $ 2007 USGC	
Equip. No.	Description	Capacity	Material	Pressure	Cost	Equipment estimating basis
B-1	Belt Conveyor for Dry Algae	1.5 x 150 ft.	C.S.	Atmos.	$ 65,200	Belt closed w/walkway long
G-1	Algae Grinder	2 ft. diam.	C.S.	Atmos.	$ 19,900	Cage Mill
D-1	Algae Dryer	95 ft^2	C.S.	Atmos.	$ 40,900	Rotary, indirect gas fired
H-1	Algae Feed Hopper	1200 cu.ft.	C.S.	Atmos.	$ 17,000	Hopper with bottom, bolted
I-1	Inline Feed Mixer	25 cu.ft.	316 S.S.	Atmos.	$ 17,300	Ribbon
V-1	Vegetable Oil Feed		C.S. & API	Atmos.	$ 10,400	Tank vert. shop fab. Small
V-2	Methanol Feed	6000 gal	Stainless steel	Atmos.	$ 69,800	Tank vert. shop fab. Small
V-3	TMAH Feed	650 gal	Stainless steel	Atmos.	$ 31,600	Tank vert. shop fab. Small
V-4	Feed Mixer, stirred	330 gal	Stainless steel	Atmos.	$ 27,500	Inoculum tank & propeller agitato
V-5	Feed Tank, stirred	330 gal	Stainless steel	Atmos.	$ 27,500	Inoculum tank & propeller agitato
P-1	Vegetable Oil Feed		Steel		$ 9,300	Chemical injection, variable spee
P-2	Methanol Feed	4 gpm	SS & packing		$ 3,000	Gear chemical
P-3	TMAH Feed	0.5 gpm	Stainless steel		$ 21,100	Chemical injection, variable spee
P-4	Feed Transfer Pump	6 gpm	Stainless steel		$ 3,500	Gear chemical
P-5	Vegetable Oil Transfer					Included in offsites factor
P-6	Methanol Transfer					Included in offsites factor
P-7	TMAH Transfer					Included in offsites factor
T-1	Vegetable Oil Tank					Included in offsites factor
T-2	Recycle Methanol Tank					Included in offsites factor
T-3	TMAH Tank					Included in offsites factor
	Subtotal Feed Preparation Purchased Equipment Cost				$ 364,000	
	Subtotal Feed Preparation Fixed Capital Investment				$1,557,920	
R-1	Rototherm Reactor				$ 400,000	Includes hot oil system
R-2	Wiped Film Solids Cooler				$ 132,906	Prorated based on heat transfer
B-2	Dry biomass belt conveyor	1.5 x 150 ft.	C.S.	Atmos.	$ 65,200	Belt closed w/walkway long
E-2	Overhead Condenser		Stainless Steel 316	vacuum	$ 1,100	Shell & tube fixed/U. medium
K-1	Product Vapor Compressor	67 HP			$ 52,900	Screw
V-6	Liquid Product Accumulator	421	Stainless Steel 316	Sched. 10	$ 15,700	Horizontal, no internals medium
V-7A	Cation Exchange Operating	421	Stainless Steel 316	Sched. 10	$ 10,800	Vertical, no internals medium
V-7B	Cation Exchange Regeneration	421	Stainless Steel 316	Sched. 10	$ 10,800	Vertical, no internals medium
F-1	Hot Oil Heater	0.76 Mbtu/hr	C.S.	150 psig	$ 52,000	Dowtherm
P-8	Hot Oil Pump	4 gpm	Steel		$ 2,500	Gear, chemical
P-9	Liquid Product Pump	1 gpm	Stainless Steel		$ 2,000	Gear, chemical
	Subtotal Reaction Section Purchased Equipment Cost				$ 745,906	
	Subtotal Reaction Section Fixed Capital Investment				$3,192,478	
		Algae				
C-1	Methoxypropane Stripping	4711	Stainless Steel 316	Sched. 10	$ 67,375	Vertical, no internals medium x 1.
C-2	Methanol Topping	4711	Stainless Steel 316	Sched. 10	$ 67,375	Vertical, no internals medium x 1.
C-3	Methanol Stripping	4711	Stainless Steel 316	Sched. 10	$ 67,375	Vertical, no internals medium x 1.
C-4	TMP Topping	22	Stainless Steel 316	Sched. 10	$ 5,500	Vertical, no internals medium x 1.
C-5	DMP Topping	22	Stainless Steel 316	Sched. 10	$ 5,500	Vertical, no internals medium x 1.
C-6	FAME/MPD Spitter	22	Stainless Steel 316	Sched. 10	$ 5,500	Vertical, no internals medium x 1.
C-7	TMA Absorber	24	Stainless Steel 316	Sched. 10	$ 5,500	Vertical, no internals medium x 1.
C-8	FAME Stripping	33	Stainless Steel 316	Sched. 10	$ 34,746	Vertical, no internals medium x 1.
V-8	Cation Separator	421	Stainless Steel 316	Sched. 10	$ 8,336	Horizontal, no internals medium
V-9	Methoxypropane Stripping Accumulator	83	Stainless Steel 316	Sched. 10	$ 12,300	Horizontal, no internals medium
V-10	Methanol Topping Accumulator	82	Stainless Steel 316	Sched. 10	$ 12,300	Horizontal, no internals medium
V-11	Methanol Stripping Accumulator	7	Stainless Steel 316	Sched. 10	$ 2,800	Horizontal, no internals medium
V-12	TMP Topping Accumulator	7	Stainless Steel 316	Sched. 10	$ 2,800	Horizontal, no internals medium
V-13	DMP Topping Accumulator	7	Stainless Steel 316	Sched. 10	$ 2,800	Horizontal, no internals medium
V-14	MDP/FAME Topping Accumulator	7	Stainless Steel 316	Sched. 10	$ 2,800	Horizontal, no internals medium
E-2	Methoxypropane Stripping Condenser	154	Stainless Steel 316	150 psig	$ 15,500	Vertical, no internals small
E-3	Methoxypropane Stripping Reboiler		Stainless Steel 316	150 psig	$ 8,800	Shell & tube fixed/U. medium
E-4	Methanol Topping Condenser		Stainless Steel 316	150 psig	$ 15,500	Shell & tube fixed/U. medium
E-5	Methanol Topping Reboiler		Stainless Steel 316	150 psig	$ 15,500	Shell & tube fixed/U. medium
E-6	Water Cooler	1	Stainless Steel 316	150 psig	$ 700	Double Pipe Small
E-7	Methanol Stripping Condenser	9	Stainless Steel 316	150 psig	$ 1,700	Shell & tube fixed/U. medium
E-8	Methanol Stripping Reboiler		Stainless Steel 316	150 psig	$ 1,700	Shell & tube fixed/U. medium
E-9	Methanol Cooler		Stainless Steel 316	150 psig	$ 1,400	Double Pipe Small
E-10	TMP Topping Condenser		Stainless Steel 316	150 psig	$ 1,700	Shell & tube fixed/U. medium
E-11	TMP Topping Reboiler		Stainless Steel 316	150 psig	$ 1,700	Shell & tube fixed/U. medium
E-12	TMP Product Cooler		Stainless Steel 316	150 psig	$ 700	Double Pipe Small
E-13	DMP Topping Condenser		Stainless Steel 316	150 psig	$ 1,700	Shell & tube fixed/U. medium
E-14	DMP Topping Reboiler		Stainless Steel 316	150 psig	$ 1,700	Shell & tube fixed/U. medium
E-15	DMP Product Cooler		Stainless Steel 316	150 psig	$ 700	Double Pipe Small
E-16	MDP/FAME Spitter Condenser		Stainless Steel 316	150 psig	$ 1,700	Shell & tube fixed/U. medium
E-17	MDP/FAME Spitter Reboiler		Stainless Steel 316	150 psig	$ 1,700	Shell & tube fixed/U. medium
E-18	MDP Product Cooler		Stainless Steel 316	150 psig	$ 700	Double Pipe Small
E-19	FAME Product Cooler	3	Stainless Steel 316	150 psig	$ 1,000	Shell & tube fixed/U. medium
E-20	FAME Stripping Condenser		Stainless Steel 316	150 psig	$ 2,577	Shell & tube fixed/U. medium
E-21	FAME Stripping Reboiler		Stainless Steel 316	150 psig	$ 2,577	Shell & tube fixed/U. medium
E-22	FAME StrippingProduct Cooler	3	Stainless Steel 316	150 psig	$ 1,000	Shell & tube fixed/U. medium
P-10	Methoxypropane Stripping Reflux Pump	15	Stainless Steel		$ 5,200	Gear, chemical
P-11	Methoxypropane Stripping Bottoms Pur	10	Stainless Steel		$ 4,300	Gear, chemical
P-12	Methanol Topping Reflux Pump	15	Stainless Steel		$ 5,200	Gear, chemical
P-13	Methanol Topping Bottoms Pump	15	Stainless Steel		$ 5,200	Gear, chemical
P-15	Methanol Stripping Reflux Pump	1	Stainless Steel		$ 2,000	Gear, chemical
P-14	Methanol Stripping Bottoms Pump	1	Stainless Steel		$ 2,000	Gear, chemical
P-16	TMP Topping Reflux Pump	0.1	Stainless Steel		$ 1,500	Gear, chemical
P-17	TMP Topping Bottoms Pump	0.25	Stainless Steel		$ 1,600	Gear, chemical
P-19	DMP Topping Reflux Pump	0.1	Stainless Steel		$ 1,500	Gear, chemical
P-20	DMP Topping Bottoms Pump	0.25	Stainless Steel		$ 1,600	Gear, chemical
P-21	FAME/MPD Spitter Reflux Pump	0.1	Stainless Steel		$ 1,500	Gear, chemical
P-22	FAME/MPD Spitter Bottoms Pump	0.25	Stainless Steel		$ 1,600	Gear, chemical
P-23	FAME Stripping Reflux Pump	0.25	Stainless Steel		$ 1,600	Gear, chemical
P-24	FAME Stripping Bottoms Pump	0.25	Stainless Steel		$ 1,600	Gear, chemical
T-4	Water Tank					Included in offsites factor
T-5	TMP Product Tank					Included in offsites factor
T-6	DMP Product Tank					Included in offsites factor
T-7	MDP Product Tank					Included in offsites factor
T-8	FAME Product Tank					Included in offsites factor
	Water Treating Facilities					Included in offsites factor
	TMA Shipping Facilities					Included in offsites factor
	Subtotal Product Recovery Purchased Equipment Cost				$ 419,661	
	Subtotal Product Recovery Fixed Capital Investment				$2,115,093	
Total Purchased Equipment Cost					$1,529,567	
Total Fixed Capital Investment					$6,865,491	
	Escalate to 2012 @ 2%/year				$7,580,057	
Contingency @ 30% for Screening Estimate					$2,274,017	
Total Project Capital investment, 2012					$9,854,074	

A5.4.2 Process flow diagrams

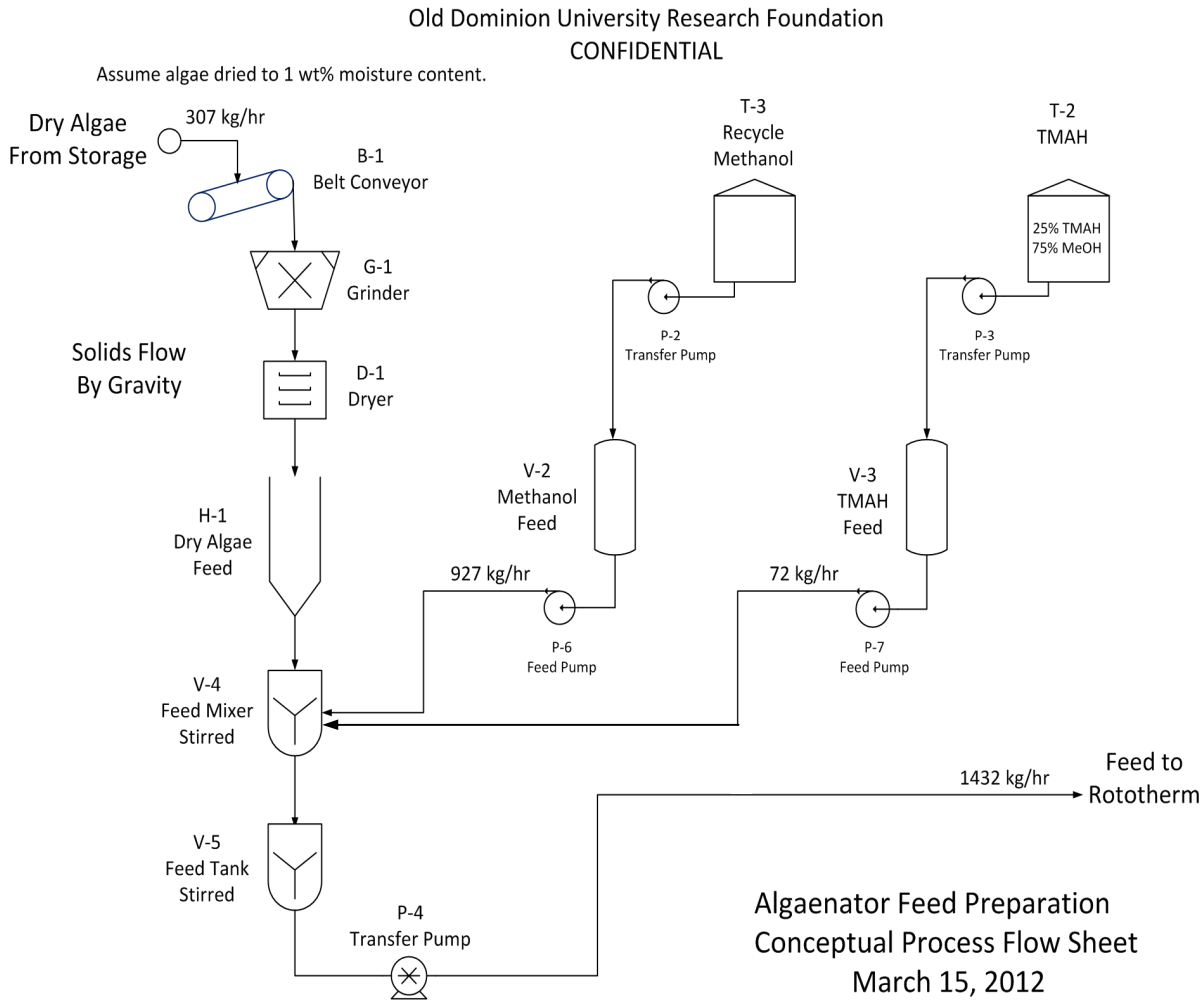


Figure A5.4.1: Feed preparation process flow diagram for a 10 metric ton facility.

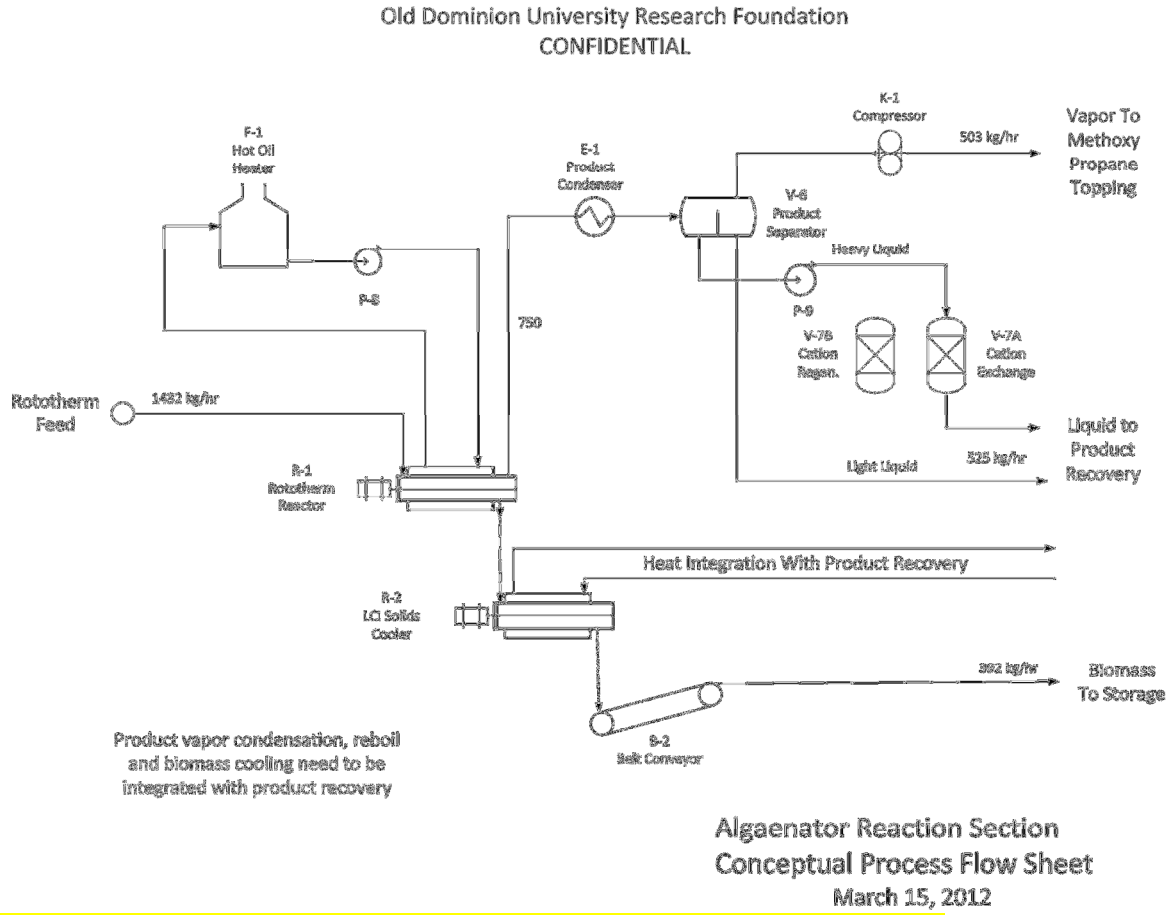


Figure A5.4.2: Reaction process flow diagram for a 10 metric ton facility.

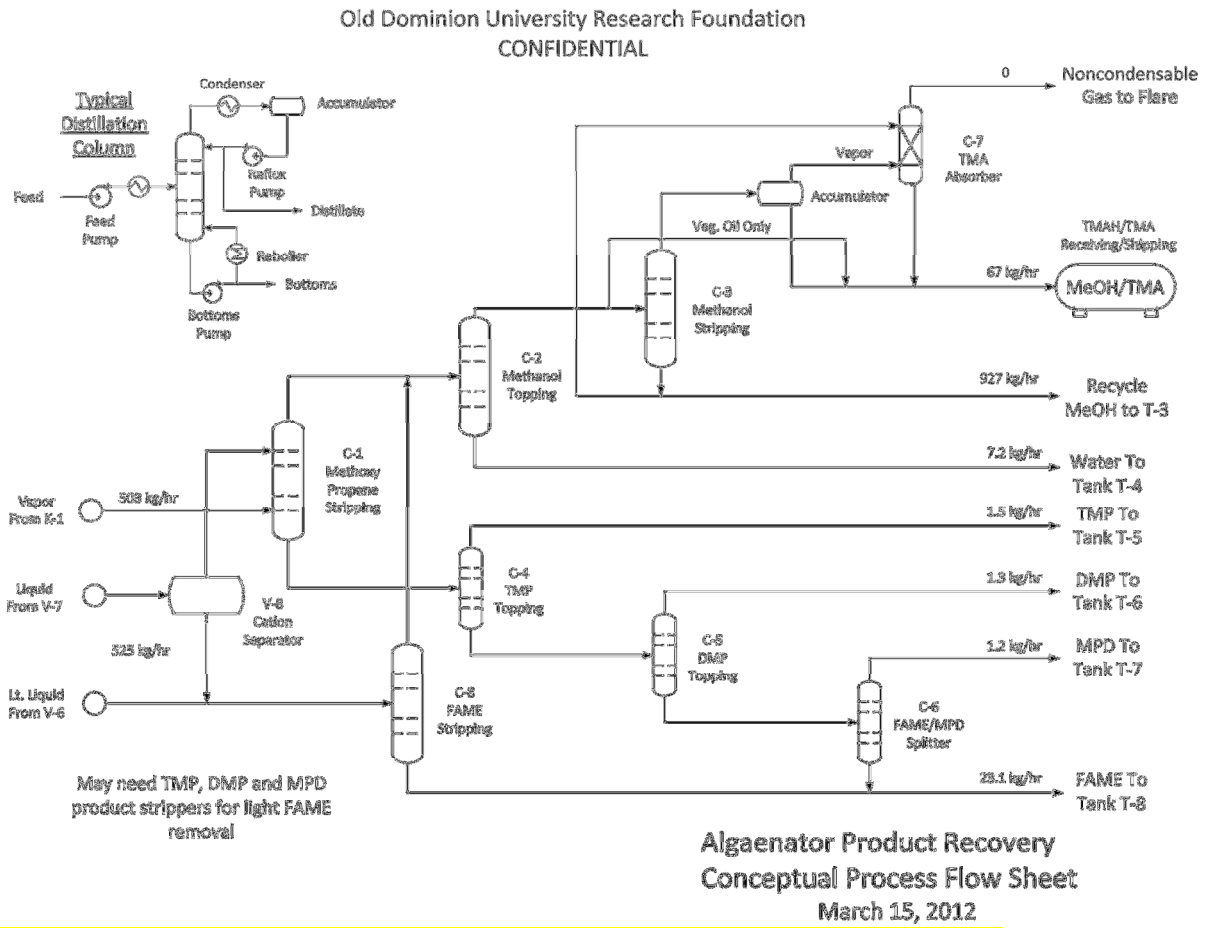


Figure 5.4.3: Product recovery flow sheet diagram for a 10 metric ton facility.

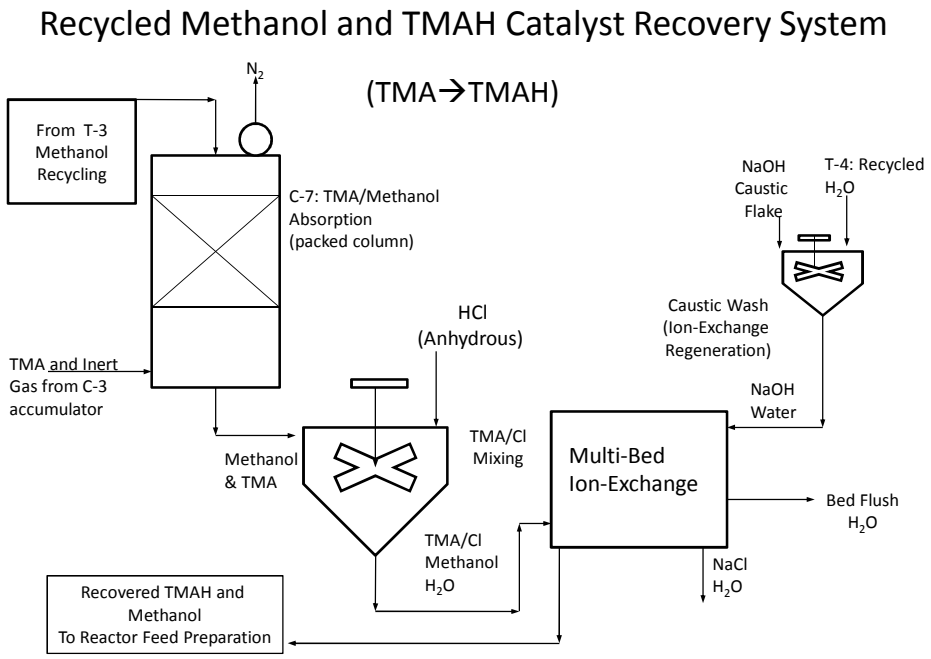


Figure A5.4.4: Regeneration of Tetramethylammonium hydroxide (TMAH).