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Biodiesel production from microalgae: co-location with sugar mills

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BIODIESEL PRODUCTION FROM MICROALGAE: CO-LOCATION WITH SUGAR MILLS

A Thesis

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
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in

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by
Christian Lohrey
B.S., University of Idaho, 2008
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Abstract

Co-location of algae production facilities with sugarcane mills in Louisiana was investigated as a way to address the bottlenecks for algal biodiesel production. Using the process modeling software Sugars™, an algal biodiesel production process was integrated with the operation of a typical-sized 10,000 metric tons/day (11,000 short tons/day) sugarcane mill to evaluate material and energy balances. A process is proposed wherein alga production is supplemented with energy, water, and CO_2 available from a sugarcane mill. The Energy Return on Invested, EROI (a ratio of the energy produced/energy required) of the proposed algal biodiesel production process was 1.25; meaning 25% more energy can be produced than is required by the process. A sensitivity analysis showed that this number ranged from 0.8 to 1.4 when the range of values for oil content, CO_2 utilization, oil conversion and harvest density reported in the literature were evaluated.

A locally sourced alga, *Louisiana strain*, was evaluated for its suitability as a biodiesel feedstock and to justify some of the assumptions used in the model. Hexane and ethanol were compared as neutral and polar solvents for extracting oil from the alga in order to establish a range for oil yield; it was found that 5% and 37% by wt. of the alga could be extracted as ’crude oil’ by the two solvents, respectively. The crude oil was subjected to an acid catalyzed esterification to produce fatty acid methyl esters (FAME, i.e. biodiesel). Using gas chromatography mass spectrometry (GC-MS) it was determined that 17-19% of the crude oil was converted FAME for both solvents; therefore ethanol is a more effective solvent. By incorporating the lab-generated results into the assumptions of the computer model, biodiesel yield was projected to be 920,000 liters biodiesel/yr (240,000 gallons biodiesel/year) on 440 hectares (1,100 acres) with an EROI of 0.91.

Chapter 1: Introduction

In order to supply the world's energy requirements sustainably it is apparent that our use of renewable resources must be expanded. As petroleum resources are depleted at an increasing rate, the necessity of developing alternative fuel supplies that can integrate with existing infrastructure is becoming more urgent.

1.1 Demand for Renewable Energy Resources

In order to promote production of renewable fuels, the Environmental Protection Agency published the second revision of the Renewable Fuel Standard (RFS2) in 2007. This program outlines a plan to increase production of biofuels in the US from 34 billion liters per year (9 billion gallons/yr) in 2008 to 136 billion liters per year (36 billion gallons/yr) by 2022 [1]. The biofuel production quotas for 2012 are shown in Table 1.

Table 1. RFS2 Standards for 2012 adapted from [2].

Fuel Category	**Percentage of Fuel Required to be Renewable**	**Volume of Renewable Fuel In billions of liters (gallons)**
Cellulosic biofuel	0.006%	0.03 (0.0086)
Biomass-based diesel	0.91%	3.78 (1.0)
Total Advanced biofuel	1.21%	7.57 (2.0)
Renewable fuel	9.23%	57.54 (15.2)

In 2009, 129 billion liters (34.1 billion gallons) of petroleum diesel were consumed; only 1.1 billion liters (0.3 billion gallons) of that was from renewable sources [3]. By comparing the amount of renewable diesel fuel produced in 2009 to the 2012 production goal of 3.78 billion liters (1 billion gallons), one can see that the demand for biofuels has increased dramatically in recent years. The biodiesel production capacity in the US for 2012 is expected to be 11 billion liters (2.9 billion gallons) [4]; producing enough feedstock to support that capacity will be a challenge.

1.1.1 Biodiesel as a Renewable Fuel

According to the U.S. Energy Information Administration, diesel accounted for 22% of transportation fuel consumed in 2009 [3]. If this petroleum diesel were replaced with biodiesel - a carbon neutral fuel - net emissions of CO_2 could be reduced by about 551 million tons (500 million metric tons), or 8% of total CO_2 emissions in the US [5]. Biodiesel is attractive as an alternative to petroleum diesel because it is considered a drop-in replacement to petrol diesel: both are chemically analogous, perform comparably [6], and biodiesel can be integrated into the existing distribution infrastructure. The American Society for Testing and Materials has developed ASTM D6751-10, which is the specification regulating the quality and testing of pure biodiesel (B100) for commercial sale in the US. As biofuel production increases, this specification ensures that biodiesel is able to integrate into existing infrastructure.

Biodiesel is currently distributed at over 700 refueling stations around the US [7]. It can be produced from a variety of feedstock such as vegetable oil, used cooking oil, and animal fats. A chemical transesterification reaction converts triglycerides (oils and fats) into biodiesel using an alcohol and a base as catalyst. Soybean oil is the most commonly used feedstock for production of biodiesel in the US, whereas Camelina oil is the predominate feedstock in European countries [8]. For the RFS mandates set forth, with the current feedstocks, more arable land would be required than is available - therefore a new solution is required. Crops such as jatropha and oil palm yield more oil per acre than traditional crops as shown in Table 2, however monoculture plantation operations dedicated to biofuels could divert resources and arable land from food production - a more imperative need than fuel. Additionally, environmentalist agree that monoculture cropping is unsustainable and can result in negative environmental impacts such a deforestation and eutrophication [10].

Table 2. Crop Oil Yield Comparison
adapted from Chisti [9]

CROP	**OIL YIELD (gallons/acre/year)**	**OIL YIELD (liters/ha/year)**
Soybean	48	449
Camelina	62	580
Sunflower	102	954
Jatropha	202	1,890
Oil Palm	635	5,940
Algae	1,000-6,500	9,355-60,807

The cost to produce biodiesel depends heavily on the price of the oil feedstock used, which can account for 60-75% of the total biodiesel production cost or more [11] [12]. Used cooking oil and waste animal fats from industrial food processing facilities are produced as a by-product, and therefore, at relatively low cost which has enabled biodiesel to be sold economically competitive to petroleum diesel. This method, however, is not scalable to the capacity called for in the RFS2 because the feedstock availability is inherently dependent on food resources.

In order to achieve the biodiesel production goals set by the RFS2 more feedstock is required, therefore oil yield must be increased and competition for resources with food crops must be minimized. Microalgae are estimated to yield between 9,000-61,000 L oil/ha/yr (1,000 to 6,500 gallons oil/acre/year), and they can be grown on non-arable land using waste resources.

1.1.2 Microalgae as a Feedstock for Biodiesel Production

Microalgae have been shown to produce oils that can be converted to biodiesel more efficiently than any other biological organism, converting 3-8% of the energy from sunlight to biomass as compared to 0.5% with terrestrial crops [13]. Like conventional crops, algae use the process of photosynthesis to convert carbon dioxide and sunlight into biomass and oxygen.

What sets algae apart from terrestrial crops as a potential feedstock for biodiesel production are their fast growth rate, high oil content, and ability to be grown on non-arable land and with water not suitable for crops. The idea of algae as a renewable fuel resource has been investigated since the 1950's [14]. Besides oil, the bulk of algal biomass includes carbohydrates, minerals and proteins, which can be valuable co-products of a biodiesel production process.

Table 3. Oil Content and Growth Rate for Various Microalgae adapted from Mata [11].

MICROALGAE SPECIES	**OIL CONTENT (% dry weight)**	**GROWTH RATE (g/L/day)**
Botryococcus *braunii*	25-75	0.02
Chlorella *sp.*	28-32	0.02-2.5
Nannochloris *sp.*	20-35	0.17–0.51
Nannochloropsis *sp.*	31-68	0.17–1.43
Scenedesmus *obliquus*	11-55	0.004–0.74

Due to the energy intensive processing techniques currently employed, commercial algae production facilities today focus on high-value products such as nutraceuticals [15]. For example, production costs on the order of $30/kg dry wt. have been projected to be achievable for the marine microalga P. *tricornutum* producing eicosapentaenoic acid (EPA), an omega-3 fatty acid [16]. Economics dictates that the cost to produce alga as a feedstock for biofuel be about two orders of magnitude less in order to be competitive with current petroleum prices. A recent collaborative effort between some of the top algal biofuel research institutes worldwide compared 12 different cost analysis studies, and concluded that a reasonable estimate to produce algal oil is between \$2.87/L - \$3.52/L (\$10.87/gal - \$13.32/gal) [17]. The variability was considerably improved from a previous study published in 1996 that had a range of two orders of magnitude by establishing a consistent set of assumptions for algal growth and economics.

1.2 Biodiesel Production from Microalgae: Current Technologies and Challenges

The Aquatic Species Program, which was funded by the US Department of Energy, carried out groundwork for algae-to-biodiesel technology from 1978 to 1996. This program studied alga production in outdoor growth ponds to investigate its potential as a renewable energy resource. Growth rate, oil content, CO_2 sequestration ability, and general algae biology of nearly 3,000 algae species were evaluated and refined to 300 algae species that showed potential for production of biofuels. A close-out report of the program was published in 1998 concluded that although not economically feasible at the time due to the low price of petroleum (approximately \$20/barrel in 1998), “Land, water and CO_2 resources can support substantial biodiesel production and CO_2 savings.” [18]

1.2.1 Resource Availability

In addition to the basic requirements for photosynthesis, production of algal biodiesel requires nutrients to grow algae, and energy to process it into biodiesel. The amount of energy required to process algae into biodiesel is poorly understood, and is debated in the literature [19, 20]. The reason for the uncertainty is each proposed algae biofuel production pathway is unique depending on the location and available resources. An integrated system approach, where algae production is coupled with an existing CO_2 generating process has been considered a more economically feasible approach for developing production of biofuels because the low value of a fuel product is offset by the added value of waste remediation or emissions reduction [21].

- <u>CO_2</u>

The concentration of CO_2 in air is 0.04%, which is too low to support high growth rates of algae required for biodiesel production [22]. For each ton of alga produced, 1.83 tons of CO_2 are sequestered [9]. In order to produce volumes consistent with transportation fuels, a concentrated source is required that can provide hundreds of metric tons of CO_2/day. Therefore, algae production naturally gravitates toward energy producing facilities. Combustion flue gasses such as those from natural gas or coal fired boilers generally contain between 12-15% CO_2 by volume [23]. Biomass fired boilers have been shown to produce lower concentrations of compounds toxic to algae such as SOx and NOx [24] [25].

- <u>ENERGY</u>

The energy required to grow, harvest, and convert alga into fuel is not well established, and often overlooked, because no facility currently does this on commercial scale. The energy required depends on the species of microalgae cultivated, geographic location, the techniques used to harvest and convert the algae into fuel, etc. It is generally understood that alga production is an energy intensive process due to large volumes of water that must be handled. To harvest 1kg of algae essentially entails purifying 2,000-5,000 kg of water.

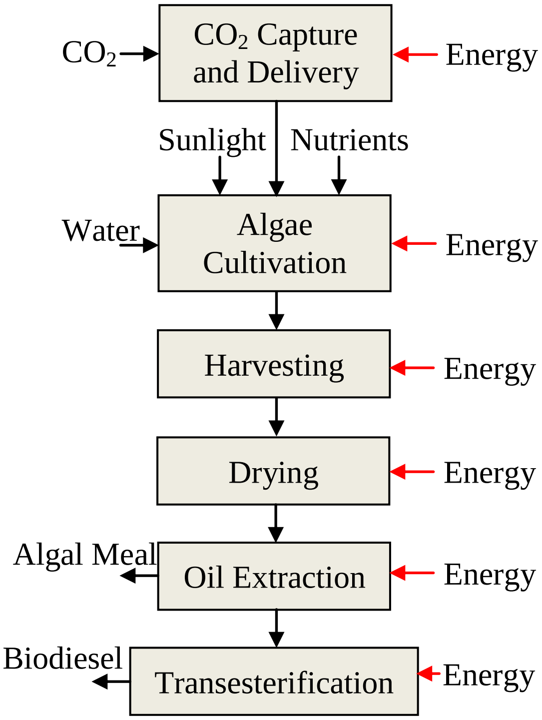

Figure 1. Generalized PFD for Algal Biodiesel Production

The most important design criterion for sustainable production of renewable fuel is that more energy must be produced than is required by the process. This concept is commonly expressed as Energy Returned on Invested or EROI, which is simply a ratio of the energy output to the energy input of the process.

In the case of producing biodiesel from alga, the ‘Energy Output’ consists of energy contained in the biodiesel as well as the energy contained in the co-produced algal meal. The ‘Energy Input’ is the sum of the energy requirements of each of the six steps in the process.

$$\mathrm{EROI} = \frac{(\text{Energy Output})}{(\text{Energy Input})} = \frac{\mathrm{BD}{*}u_{\mathrm{BD}} + \mathrm{AM}{*}u_{\mathrm{AM}}}{\mathrm{AB}{*}\sum_{i=1}^{i=6} E_{c,i}} \qquad \text{(Eq. 1)}$$

Where:
EROI = Energy Returned on Invested (unit less)
$\dot{m}$ = mass rate produced (kg/yr); biodiesel (BD), algal meal (AM), algae biomass (AB)
u = specific energy (kWh/kg)
$E_{C,i}$ = Energy consumption of each step (kWh/kg algae dry wt.), steps 1-6.

When describing a system or process that generates fuel, an EROI of 1 means there is no net gain in energy, the system produces exactly as much energy as it needs to continue operating; the product (fuel) is completely used by the process. A system with an EROI>1 produces more energy than it requires to operate thus leads to a net gain in energy, and we say that process is ‘thermodynamically feasible.’ Thermodynamic feasibility simply means the process generates usable energy, whereas sustainability implies the process produces enough energy such that it requires no outside resources. A previous report has suggested that 3 is a minimum EROI that a process or system must have to be sustainable, the argument being: a sustainable process must produce energy for operation (taking into consideration process inefficiencies), maintenance, and investment in itself for continued growth [26]. Sustainability implies thermodynamic feasibility. For this study, we are only interested to know if algal biodiesel production is thermodynamically feasible.

Recently, researchers have calculated the EROI for an algal "biocrude" pilot production research facility in operation at the University of Texas at Austin [27]. The reported EROI was 9.2×10^{-5} – significantly less than 1 – using the following method:

> Using centrifugation for harvesting, electromechanical cell lysing, and a microporous hollow fiber membrane contactor for lipid separation. The separated algal lipids represent a biocrude product that could be refined into fuel and the post-extraction biomass could be converted to methane.

The achieved EROI indicates that far more energy is required by the system than can be produced; therefore, this process is not thermodynamically feasible for production of fuel. The unit operations employed were not suitable for production of biofuel because they consumed more energy than is contained in the algae.

- WATER

Algae cultures are very dilute, typically containing 0.02-0.06% ds [28]. Harvesting 1 kg of algal biomass requires separating 2,000-5,000 kg of water [29]. The amount of water consumed during algae production process depends on the type of production system employed. For example, open ponds are subject to evaporation, and, therefore, require more water than closed systems. The amount of water lost due to evaporation can be estimated by the class A pan evaporation rate which, in Louisiana, is about 165 cm/yr [30]. At this rate, a 600 ha (1,500 acre) open pond algae farm would require 23 million L/day (6 million gallons/day) of make-up water. Conversely, rainfall into open ponds can be unpredictable and can cause culture instability resulting in lost productivity. Closed, or covered, systems can avoid such significant water fluxes by reducing environmental influences, but may be prohibitive in terms of costs and energy consumption. Therefore, finding a reliable supply of water remains a challenge for a potential alga production facility.

- <u>NUTRIENTS</u>

The minimum nutritional requirements for algae can be estimated based on the approximate molecular formula for microalgal biomass, $CO_{0.48}H_{1.83}N_{0.11}P_{0.01}$ [9]. Similar to land based crops, main nutrients required by algae to grow and are N-P-K (Nitrogen, Phosphorus, and Potassium). These elements come in the form of typical fertilizers such as urea, phosphate, potash, that once solubilized in water, are easily accessed by algae; which contributes to their fast growth rates compared to land based crops. Fertilizer nutrients represent a major cost for alga production facilities, estimated to be 30% of operating costs [31]. Therefore, in order to compete economically as a fuel an algal biodiesel production facility must be located near a consistent supply of nutrients.

Municipal wastewater facilities have been suggested as a source for nutrients such as P, K, and N [32] [33]. One study showed that over 80% of nitrogen and 89% of phosphorus was removed from municipal wastewater by algae in only 14 days [34]. Most MW locations, however, typically don’t produce power [35], and thus may not have the required CO_2 or energy availability for a potential algal biofuel production facility.

The Mississippi River transports millions of tons of nitrogen and phosphate fertilizer annually as runoff from agricultural operations in the Midwest to the Gulf of Mexico [36]. This nutrient loading causes seasonal harmful algae blooms in the Gulf and subsequent hypoxic affects, which degrade natural marine estuaries and is a serious concern of environmentalists.

- LAND

Further assessment of locations where algal biodiesel production may be viable limits this technology to climates with average annual temperatures greater than 15^{o}C due to the low productivity of algae in cold environments [37]. Ample rainfall and minimal evaporation are also key climate factors that suggest the lower half of the continental US as the most practical for algal biodiesel production [38]. Louisiana was recognized as a promising location for outdoor algae production in ponds due to the relatively steady climate, cheap land near carbon emitting sources, and ample rainfall, as identified by a study in 2009 [39].

Currently, commercial alga production facilities do not produce fuels, and instead focus on high-value products like food supplements or nutraceuticals, where they can be economically competitive. The largest algae production facility in operation in the US is Earthrise Nutraceuticals (earthrise.com) with 108 acres of open ponds that can produce about 500 tons/yr of dried Spirulina biomass for human consumption. Comparatively, a commercial scale biodiesel production plant (defined as at least 3.785 million L/yr or 1 million gallons/yr in this study), would require a facility roughly 1,500 acres - 14 times larger.

1.2.2 Current Processing Technologies and Limitations

There are many different process options available to carry out the six main steps in the algal biodiesel production process. Figure 2 shows the technologies that were considered for algal biodiesel production in this study. Technologies were evaluated based on their dewatering performance, productivity (scalability), and energy intensity. Two different process scenarios were are compared and are further discussed in section 3.1.1.

CO_2 Capture and Delivery	Algae Cultivation	Harvesting	Drying	Oil Extraction	Transesterification
MEA Absorption	Open Ponds	Gravity Settling	Spray Drying	Expeller Press	Acid Catalyzed Esterifiaction
Direct Flue Gas Injection	Covered Ponds	Dissolved Air Flotation (DAF)	Drum Drying	Solvent Extraction	Base Catalyzed Transesterifiaction
	Photobioreactors	Centrifugation	Solar Drying	Supercritical CO_2	Acid Catalyzed Transesterifiaction
		Belt Filter Press	No Drying		
		Flocculation			

Figure 2. Processing Technologies for Algal Biodiesel Production.

The number of different options available for processing algae is vast and continues to grow almost daily. It follows that different processing scenarios will have different resource requirements. Many authors have published a wide range of estimates for the energy required and overall performance of numerous technologies. In a recent study (Lohrey et. al., 2011) compared published values of the energy demand for each step in the biodiesel production process. As is immediately apparent, drying consumes 2-3 times more energy than any other step. Depending on the technique used, drying alone can consume more energy than is contained in the algal oil. Estimates range from 45-90% of the energy required to produce algal oil is due to the drying requirement [13] [40] [41].

As shown in Figure 3 below, estimates can vary by more than 100%, there is a general agreement that drying is a main bottleneck in the process, requiring many times the energy requirement of the other stages. The span between the studies is due to different assumptions used, and emphasizes the importance of geographical location (for access to resources), selection of the most efficient processing technologies depending on the available resources, particular species of algae being cultivated and desired end product.

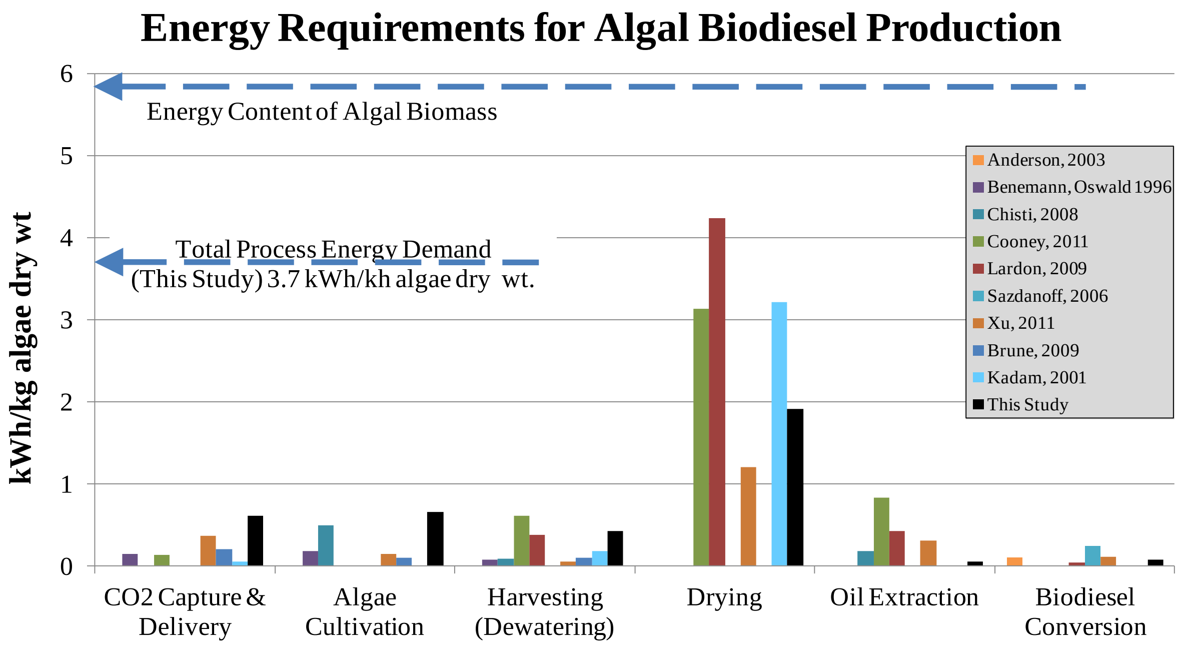

Figure 3. Comparison of Energy Requirements Published in Literature for Processing Algae modified from Lohrey 2012 [42].

1.2.3 Modeling of an Algal Biodiesel Production Process

Despite decades of research and development, efforts to scale up production of algal biofuels from lab-scale to industrial-scale have not yet been successful. The National Algal Biofuels Technology Roadmap was published by the US Department of Energy in 2010 to outline challenges and streamline R&D efforts in order to accelerate commercialization of this technology. The roadmap summarizes a strategy to overcome the technological and economic barriers of algal biofuels this way:

> Given the multiple technology and system options and their interdependency, an integrated techno-economic modeling and analysis spanning the entire algae to biofuels supply chain is crucial in guiding research efforts along select pathways that offer the most opportunity to practically enable a viable and sustainable algae-based biofuels and co-products industry. [43]

Early modeling studies on algal biodiesel have been life-cycle assessments (LCA) - not techno-economic analysis - focused on analyzing the environmental impacts of algal biofuel production-and-use [44] [45]. Typical modeling software for LCA studies include Gabi, TEAM, and GREET. These software reference databases such as Ecoinvent or USLCI (US Life-Cycle Inventory) to compile relevant information regarding resource consumption and emissions of a proposed process. As pointed out in Starbuck's response [46] to Clarens et. al. 2010 LCA study [47], the influence of assumptions used in a model can skew the results to be either in favor or not in favor of algal biofuels. The wide range of reports either for or against algal biofuels from various LCA studies suggests a need to standardize assumptions used in the models based on actual field data.

Currently, there is little data made available from actual algae production facilities. Techno-economic modeling is therefore used to estimate production and costs based on available data from similar processes; it allows a virtual analysis of various process configurations to determine the most efficient and cost effective combination of technologies. Computer modeling software such as Aspen, HySys, and Pro/II have been used to model material and energy balance for proposed algal biodiesel production processes [48] [49] [50]. Most models calculate the material and energy balance flows, show the unit operations employed, and, some include economics. This study focused on material and energy balances, therefore the criteria used to evaluate the potential of algal biodiesel projects are the EROI and biodiesel production (L/yr).

To summarize the challenges that must be addressed for a successful algal biodiesel production process: resources such as CO_2, water, and energy must be available, climate must be conducive to photosynthesis, and processing concepts must be proven. Sugarcane mills in Louisiana have been identified as potential sites where these resources come together [51].

1.3 Objectives

The general goal of this project was to determine if algal biodiesel could feasibly be produced by co-locating algae production facilities with sugarcane mills. To evaluate the potential synergies between sugarcane mills and algal biodiesel production, process simulation modeling was utilized to integrate alga production into the operation of a typical 10,000 metric ton/day (11,000 short ton/day) sugarcane mill in Louisiana. Because many assumptions in the model are specific to the algae species, an effort was made to validate certain assumptions used in determining the EROI and biodiesel yield based on data derived from locally sourced alga. The lab data results were used as inputs to the model to estimate realistically how much biodiesel could be produced. The specific tasks involved are stated below:

- ☐ Compare the resources required for algal biodiesel production and resources available at a typical sugarcane mill.
- ☐ Synthesize an algal biodiesel production process incorporating state of the art processing technologies.
- ☐ Identify bottlenecks of the algal biodiesel production process.
- ☐ Develop a material and energy balance simulation model to analyze algal biodiesel processing scenarios and integrate with sugarcane mill model.
- ☐ Evaluate the proposed process based on criteria of EROI and biodiesel production (gal/yr), and describe how these criteria are affected by changes in the values of inputs and assumptions used.
- ☐ Evaluate ethanol and hexane as potential solvents for algal oil; determine overall biodiesel yield ($Y_{Biodiesel}$ = (mass biodiesel)/(mass algae dry wt.)), and compare results with the computer model developed.

Chapter 2: Materials and Methods

To satisfy the objectives of the project, integration of an algal biodiesel production process with a sugarcane mill was undertaken using computer modeling. Laboratory experiments were conducted in order to generate data that was used to validate certain assumptions about the oil yield and composition. The process modeling portion was initiated by defining the amount of resources required for algal biodiesel production; selection of appropriate processing technologies was then carried out which enabled material and energy balances to be developed.

2.1 Evaluating the CO_2 and Energy Resources Available at a Sugarcane Mill

An Excel calculation spreadsheet was developed to estimate CO_2, water, and energy resources available at a typical 10,000 metric TPD (11,000 TPD) sugarcane mill. Energy and resource requirements of algal biodiesel production were included in the model, and are based on published values found in the literature. An algal biodiesel production process flow diagram was developed based on the selected process technologies (see Figure 7 below). The spreadsheet developed as the first step allows the user to input certain assumptions about algae production and quickly see how much biodiesel can be produced and what the overall energy balance is. The spreadsheet calculations are included in Appendix A, pages 60-68.

2.1.1 Material and Energy Balance Simulations

A material and energy balance computer simulation for an algal biodiesel production process integrated with a cane sugar mill was developed in Sugars™

(http://www.sugarsonline.com/). Sugars™ is a modeling program specifically designed for the sugar industry; it is widely used to design sugar factories, evaluate R&D projects, increase yield, and train engineers. The program is able to simulate different operating/production scenarios of a mill and allows the user to evaluate potential improvements in efficiency and/or production. By adding an algal biodiesel production process into the sugar mill material and energy balance simulation model, the benefits of co-location can be quantified (emissions reduction, biodiesel production) using realistic assumptions, and the user is able to evaluate different processing options. The Sugars™ model is included in Appendix B, pages 69-76.

2.1.2 Design Parameter Definition

The computer model developed was based on the operation of a typical 10,000 metric TPD (11,000 TPD) sugarcane mill in Louisiana. Design parameters were not specific to a particular mill; instead, generalized parameters were used to present a hypothetical "base case." Because there is no algae production facility in operation similar to what is described, production parameters such as growth rate, oil content, etc. were derived from literature. Commonly, the values published in literature were derived from laboratory experiments making it difficult to find reasonable estimates of what could be expected in the field on a commercial scale. In addition, reported values often spanned a wide range from one author to the next, therefore conservative estimates were used when appropriate. Values for assumptions used as a base case in this study are shown in Table 4, with the typical range found in literature in parenthesis.

Table 4. Design Parameter Assumptions

DESCRIPTION	VALUE	REFERENCE
Sugarcane crop area (ha)	13,000	Based on typical sugar mill operation in Louisiana. [52]
Sugar Cane Processed (tons)	1.1x10^6	
Mill Capacity (tons/day)	11,000	
Bagasse dry wt. (% on cane)	13% (12-16%)	
Excess Bagasse (% total bagasse)	15% (0-20%)	
Surplus water produced at mill (% on cane)	18.8%	
Diesel Required for Sugarcane Harvest and Transportation, ave. 30mi farm to mill (gal/acre)	36	[53]
Boiler Efficiency	55% (36-66%)	[54]
Heat content of Bagasse (BTU/lb dry wt.)	7893	[55]
CO_2 Produced, (ton CO_2/ton bagasse dry)	3.12	[25]
CO_2 captured from flue gas, (% total CO_2)	90%	[56], [57]
CO_2 utilization (% converted to algae)	60% (40-90%)	[58], [59]
CO_2 required for algae, (lb CO_2/lb algae dry)	1.83	[9]
Solar Insolation (kWh/m^2/day)	4.2	[60]
Algae growth rate (g/m^2/day)	20 (10-30)	[11] [61] [62]
Algae Oil Content	30% (5-40%)	[63] [11]
Whole algae biomass energy content (BTU/lb dry at 30% oil content)	8977	[13] [64]
Algae oil energy content (BTU/lb oil)	16406	[13] [64]
Culture density (g/L)	.5 (0.1-2)	[64] [65]
Algal oil extraction efficiency	75% (21-95%)	[66] [67]
% oil converted to FAME (% by wt)	98% (80-100%)	[68] [69] [63]
Percent of algae farm land needed for infrastructure	15%	

The model was developed to estimate the material flows of the processes; associated energy requirements for processing the algae were then estimated based on values reported in published literature. The main criteria with which the scenarios were compared were EROI, and biodiesel production (L/yr). Due to the inherent uncertainty when using estimates to model production scenarios, it was desired to understand what effect the variations in assumed values would have on the evaluation criteria. Thus, a sensitivity analysis was performed to demonstrate how the EROI and amount of biodiesel produced were affected when the range of values reported in literature was evaluated.

2.2 Extraction of Algal Oil Using Solvents

The assumptions of 'Algae Oil Content,' 'Extraction Efficiency' and '% Oil Converted to FAME' were measured in the laboratory for a locally sourced green algae in order to establish a basis for the model and to compare with literature. Commonly referenced techniques for extracting oils from alga using solvents include Bligh and Dyer [70], Folch [71] and Soxhlet. Both the Bligh and Dyer and Folch methods involve two steps, and use a binary solvent mixture containing polar and neutral solvents that is separated into two phases with the neutral lipids predominantly in the neutral phase and relatively pure. Soxhlet extraction, on the other hand, involves a single step and typically one solvent, although solvent combinations can also be used. Generally, methods incorporating combinations of polar and neutral solvents have been shown to obtain higher yields of lipids compared to a single solvent [72]; however results have been disparate [73], and depend heavily on the species of algae, culturing conditions and the physical state of the biomass (i.e. powder, flakes, dry, wet) [66].

Oil was extracted from algal biomass using two methods: Soxhlet extraction was used to define the maximum crude oil yield from the algae; secondly, a 3-stage cross-current extraction was performed to estimate the extraction performance compared to the Soxhlet method. The extracted lipid product was termed 'crude oil,' converted to FAME and analyzed by GC-MS to quantify the overall FAME conversion and identify components in the algal oil.

2.2.1 Production of Algal Biomass

Algal biomass was produced in the Hydraulically Integrated Serial Turbidostat Algal Reactor (HISTAR) in 1406 Patrick F. Taylor Hall, LSU, and was concentrated by centrifugation to approximately 17% dry solids/wt. The algae paste was dried in an oven at 55^{o}C to constant weight and desiccated overnight. The dried algal biomass was ground using a mortar-and-pestle and sieved through a 500-micron mesh screen. Approximately 5 grams of algae powder was used per sample, all experiments were conducted in triplicate.

2.2.2 Soxhlet Extraction Procedure

Hexane (99.9% HPLC grade) and ethanol (200 proof, denatured) were purchased from Fischer Scientific (Pittsburg, PA, USA) and used as solvents for all extraction experiments. A SoxTec 2050 (FOSS, Eden Prairie, MN) automated Soxhlet extractor was used to extract lipid components from algal biomass with the solvents in order to determine the maximum crude oil yield.

The extraction procedure has three stages: boiling, refluxing, and recovery. Boiling lasts 5 minutes, during which a thimble containing sample is submerged in boiling solvent. During refluxing, the solvent is continuously boiled and condensed over the sample; this period lasted 12 hours. The final stage, recovery, lasted 15 minutes during which the solvent is boiled off leaving extracted components in a collection cup and spent biomass in the thimble. The bottom plate temperature was set to 180^{o}C for ethanol and 150^{o}C for hexane as per the manufacturer's recommendations.

$$\mathrm{Y}_{\mathrm{CrudeOil}} = \frac{\text{oil extracted by soxhlet (g)}}{\text{mass of sample (g)}} \qquad \text{(Eq. 2)}$$

2.2.3 3-Stage Cross-Current Extraction Procedure

The following procedure was used to determine the oil extraction efficiency of a 3-stage cross-current extraction process:

1. Weigh 5g dry solids wt. sample algae biomass
2. Add solvent in a 5:1 mass ratio to the algae in a 50ml Erlenmeyer flask. Stir with magnetic stir bar allowing time for equilibrium to be reached (~1 hour).
3. Centrifuge algae and solvent solution at 5000 rpm for 10 minutes and decant solvent + extractable components into a pre-weighed evaporation dish. Allow solvent to evaporate in hood. Record mass of residue.
4. Repeat steps 2 through 3 twice to simulate a 3-stage cross current solvent extraction system. Calculate percentage oil extracted in each stage.
5. Analyze percentage methyl esters (biodiesel) by GC-MS.

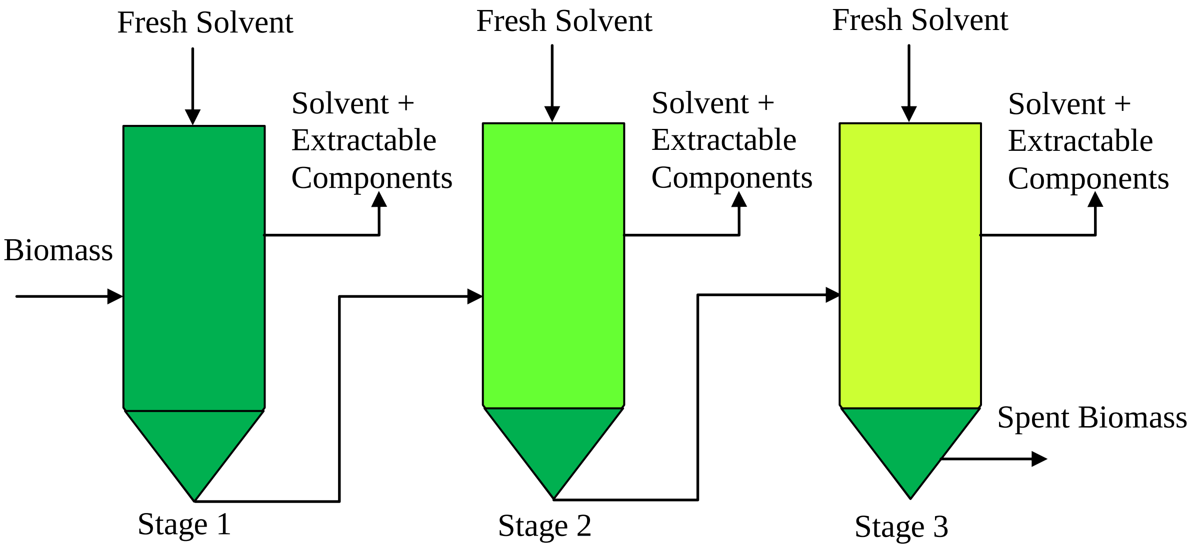

Figure 4. Diagram of 3-Stage Cross-Current Algal Oil Extraction

Figure 4, shows an overview of the 3-stage cross current extraction process. The solvent and extractable components from each stage were combined, and the solvent was evaporated leaving a crude oil. The yield of crude oil from the 3-stage cross current method was compared to the yield of crude oil obtained using the Soxhlet method, and this was defined as the extraction efficiency:

$$\mathrm{E}_{\mathrm{extraction}} = \frac{\text{crude oil extracted (g)}}{(\text{mass of sample} * \mathrm{Y}_{\mathrm{CrudeOil}})} \qquad \text{(Eq. 3)}$$

Where:

$\mathrm{E}_{\mathrm{extraction}}$ is efficiency of the extraction process, in percentage.

$\mathrm{Y}_{\mathrm{CrudeOil}}$ is the maximum crude oil yield, in percentage by wt. determined by Soxhlet.

2.2.4 Quantification and Characterization of Algal Oil by GC-MS

Gas chromatography mass-spectrometry was performed on the extracted algal crude oil to determine its composition and to quantify the production of FAME. The following materials used in the experiments were purchased from Sigma-Aldrich (St. Louis, MO, USA): tricosanoic acid 99.9%, as an external standard; nervonic acid methyl ester 99.9%, as an internal standard; and a 37 component FAME mixture used to as a standard to identify the components in the algal oil samples. Methanol, benzene, and acetyl chloride (≥99.9%) available in the lab were used. FAME samples were analyzed using an Agilent 7980A gas chromatography system (Agilent, Santa Clara, CA) fitted with a Zebron ZB-WAX plus (30 m, 2.5 mm ID, 0.25-µm film thickness) capillary column (Phenomenex, Torrance, CA), auto-sampler, and mass spectrometer. Nitrogen was used as the carrier gas with a total flow rate of 54 mL/min. Sample injection volume was 1 µL, with a split ratio of 1:50. Injection port and detector temperatures were 250°C and 280°C respectively.

The following method was used to convert the oil samples into FAME, and is based on method B in [74]:

1. Pipette 5-50µL (2mg minimum) of lipid into sample vial.
2. Add 40µL of tricosanoic acid, 1000µg/mL as an external standard (to check response factor of the GC column).
3. Add 2mL MeOH:Benzene (4:1, $\rho=0.8045\pm0.012$ g/mL)
4. Vortex
5. Chill solution in a deep freezer for 10 minutes to -74°C.
6. To the chilled solution add 200µL of acetyl chloride - Take care! Very exothermic reaction!
7. Flush with N_2.
8. Keep tubes in dark at room temperature for 24 hours.
9. Add 5mL of saturated $NaHCO_3$.
10. Vortex
11. Add 40µL Nervonic acid, methyl ester, 1000µg/mL as an internal standard (to calculate quantitative yield).
12. Collect top layer and place into sample vial for GC-MS analysis.

To calculate the total amount of FAME that was produced, the internal standard was used as a reference that all other peaks were compared. The concentration of IS was known, and therefore, relative concentrations of each fatty acid component in the sample could be related to mass percentage using the equation:

$$C_{FA} = \frac{A_{FA}}{A_{IS}} * C_{IS} \qquad \text{(Eq. 4)}$$

Where:

$C_{(FA)}$ is the concentration of fatty acid to be determined

$A_{(FA)}$ is the peak area of the fatty acid to be determined

$A_{(IS)}$ is the area of the internal standard, and

$C_{(IS)}$ is the concentration of internal standard.

Once the concentration of FAME was determined, the percent of crude oil sample that was converted could be calculated. The overall biodiesel-from-algae yield was defined as:

$$Y_{\text{Biodiesel}} = \frac{\text{mass of FAME (biodiesel) (g)}}{\text{mass of algae dry wt. (g)}} \qquad \text{(Eq. 5)}$$

At the beginning of the project, it was assumed that a solvent extraction system would be used on industrial scale, and it was desired to obtain lab data that could be used as a starting point for scale up. Mid-way through the project it was realized that an oil press would actually be a more suitable method to extract the algal oil because this: would by-pass any need for solvents, could achieve fairly high extraction efficiencies (70-75%), consumes little energy compared to a solvent extraction system, and is a relatively established process, although not yet with algae. Therefore, although not directly translatable to industrial production of fuels, the extraction experiments performed allowed for quantification and characterization of the oil components - a necessary step in evaluating the feasibility of biodiesel production. The extracted oil was converted to biodiesel, also known as fatty acid methyl ester, or FAME, thus, an overall yield of biodiesel from algae could be calculated.

Chapter 3: Integration of Algal Biodiesel Production and Sugarcane Mills with Process Simulation Modeling

The challenges of resource availability and limited algae processing experience/knowledge are addressed by integrating algal biodiesel production technology with existing agricultural infrastructure at sugarcane mills. Process simulation modeling of sugarcane mills was adapted to incorporate an algal biodiesel production process. The model compares the resource requirements of algal biodiesel production to what is available at a typical sugarcane mill; it also calculates material and energy balances. The model allows users to input a range of certain assumptions about algae production and quickly calculate the amount of biodiesel able to be produce and the energy return on investment, EROI.

Utilizing available CO_2, energy, and water resources from a sugarcane mill reduces the amount of outside resources required by the alga production process while producing two value-added products: biodiesel for harvesting and transportation of the sugarcane, and algal meal, which can be used as a feed, fertilizer, or further processed into bio-energy.

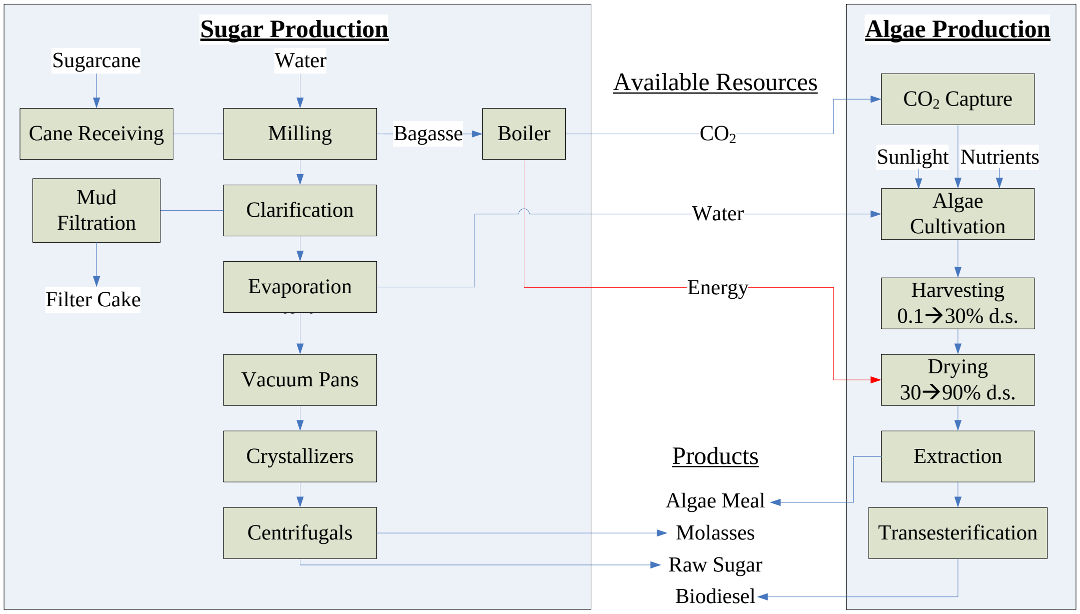

Figure 5. Block Diagram of Sugar Production (left) Coupled with Algae Production (right)

Figure 5 describes how the general algal biodiesel production process integrates with sugar production. In the proposed concept, energy and CO_2 from bagasse are generated in the sugar mill boilers. CO_2 can be captured and delivered to algae ponds, and energy used in the algae drying process. Clean water from the evaporation step in sugar production can supplement algae cultivation.

3.1 Resources Available at a Sugarcane Mill for Algal Biodiesel Production

In Louisiana, sugarcane mills typically operate about 100 days between October and January. Figure 6 describes how much energy, CO_2, and water resources are required for algal biodiesel production, how much a typical size mill in Louisiana mill can provide, and when. Year-round production of algae for biodiesel will take maximum advantage of the seasonal operation of cane mills and the resource availability.

- $\underline{CO_2}$

During grinding, as sugar is produced, 85% of bagasse is sufficient fuel to supply energy for sugar production for the base case. The 15% excess bagasse provides energy and CO_2 for alga production during the remainder of the year, while the mill is not processing sugar. As a result, CO_2 is available year round for alga production, however at a rate lower than is typically produce during grinding. As shown in Figure 6, CO_2 is available year-round at a minimum rate of 230 metric tons/day; considering the algae growth parameters listed in Table 4 (pg. 17), this rate is enough to support production of approximately 27,200 metric tons of algal biomass annually, and would require 440 ha, (1,100 acres).

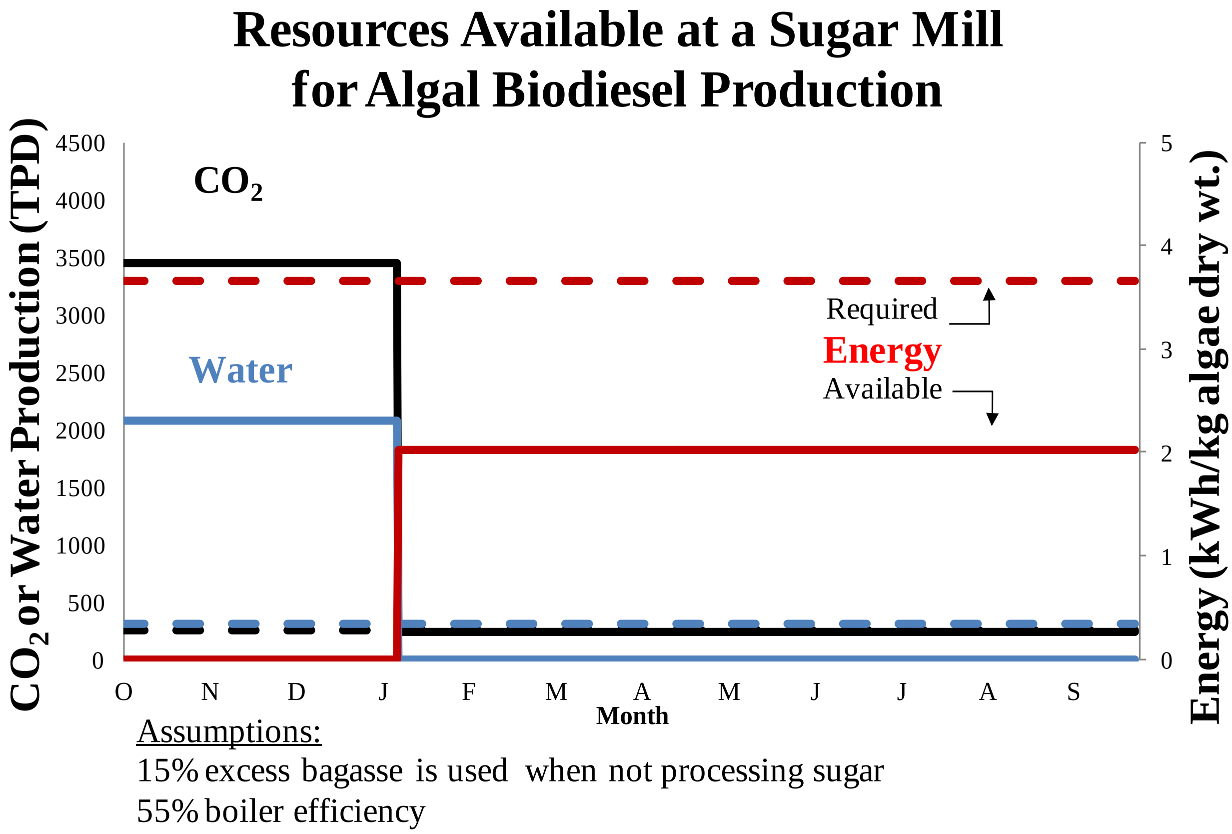

Figure 6. Resources Available at a Sugar Mill (solid) and Required for Algal Biodiesel (dashed)

In the figure above, dashed lines represent the amount of CO_2, energy, and water that are required for the base case: a process scenario that theoretically can produce 4.8 million L/yr (1.3 million gal/yr) of algal biodiesel based on generalized assumptions. Solid lines represent the amount of resources available from a typical sugarcane mill throughout the year.

- ENERGY

The assumed 15% excess bagasse is available after all the sugarcane is processed; therefore, energy from this resource is only available 9 months out of the year. Figure 6 shows that the excess bagasse can provide approximately 2.0 kWh/kg algae dry wt. during this time; averaged over the year, the excess bagasse contributes 50% of the total energy required to produce algal biodiesel. To supply the remainder of the energy required, it is suggested to use the algal meal as an energy resource possibly via co-combustion with bagasse or through anaerobic digestion.

The energy content of the algal meal depends on how much oil is extracted from the original biomass. Since algal oil has a higher energy density compared to the rest of the algal biomass, higher extraction efficiencies would leave less oil in the meal and, thus, would result in the meal having lower energy content. Conversely, if less oil is extracted from the algal biomass, more oil remains in the meal resulting in higher energy content in the meal. At an oil extraction efficiency of 61% it was found that the energy content of the resulting algal meal would be sufficient to supply the remaining 50% of energy required to produce algal biodiesel assuming that energy could be utilized at 55% efficiency.

- WATER

Sugarcane contains approximately 60-70% moisture as delivered to the mill [52]. The majority of this water leaves in the combustion flue gas, but approximately 2,000 metric tons/day of water must be treated and disposed of. Regulations established by the EPA have set limits on the acceptable BOD and COD before this water can be safely discharged. As such, mills typically have nearby holding ponds that can provide a resonance time of several days. Although not available consistently throughout the year due to the seasonal operation of the mill, the water as well as the existing infrastructure for processing relatively large quantities of water is one example that makes this co-location scenario attractive.

3.1.1 Process Option Selection

The model first calculates the material flows of the processes; associated energy requirements for processing the algae are then estimated based on values reported in published literature for each specific process option selected making sure to stay within the physical limits of the process equipment.

Two hypothetical production scenarios were investigated: Scenario 1 used energy intensive algae harvesting techniques - dissolved air flotation (DAF) followed by centrifugation to achieve 30% d.s. (dry substance) algae in the dewatering stage. In Scenario 2 less energy intensive harvesting techniques flocculation/clarification followed by belt pressing were estimated to achieve 20% d.s. algae paste.

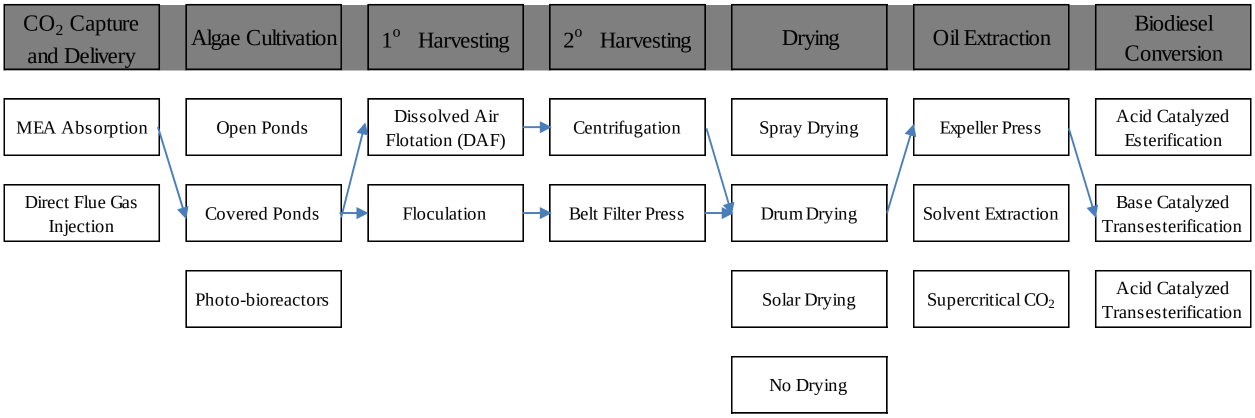

Figure 7. Block Diagram Showing Two Operating Scenarios

- <u>CO_2 CAPTURE AND DELIVERY</u>

In the conceptual process, only a portion of the CO_2 generated at the mill during sugar production is used to grow alga November through January (see Figure 10). The excess bagasse is burned during the remainder of the year to generate CO_2 and energy for algal biodiesel production. Algae production was assumed to be light limited; therefore the amount of CO_2

available from the mill determined the size of the algae farm and therefore the amount of biodiesel that can be produced from this source. Capture and compression of the CO_2 from flue gas using monoethanolamine (MEA) was selected. The energy consumption for this process was assumed to be 0.2 kWh/kg CO_2 based on estimates for a similar process with 13% CO_2 in flue gas [57]. Energy consumption for the transportation of the compressed CO_2 to the ponds was not accounted for, but is expected to contribute as little as \$0.02/ton CO_2/km [56].

- ALGAE CULTIVATION

The relatively low energy requirements of ponds compared to PBR makes ponds the method of choice for a cultivation system for fuel. In the proposed system, covered raceway ponds are used in order to reduce water loss via evaporation, and lower susceptibility to environmental conditions and contaminants. The majority of harvested pond water (97%) is recycled to the system. Paddlewheel mixing energy was accounted for at a rate of 0.1 kWh/kg algae dry wt. [75]. Absorption of CO_2 into the pond water has been demonstrated at over 90% mass transfer efficiency using a 1.5 meter deep carbonation sump [59] and as low as 10% with simple sparing into a shallow pond [22]. A baseline CO_2 utilization efficiency of 60% was used in this model as a conservative approach, to account for mass transfer inefficiencies of CO_2 into pond water and respiratory loses of the microalgae. The energy requirement for pumping of culture water was estimated using the total flow rate, 20 ft head, and a pump efficiency of 60%.

- HARVESTING

Dewatering was conducted in three stages for both scenarios. Gravity settling was the first stage of biomass concentration to bring the culture density from 0.1% d.s. to 0.5% d.s. In Scenario 1, DAF is used after gravity settling to achieve 6% d.s., followed by centrifugation to achieve 30% d.s. [76]. For Scenario 2, flocculation/clarification is used after gravity settling to raise the concentration to 2% d.s., followed by belt pressing to achieve 20% d.s. Energy required to operate the belt press was assumed to be 0.5 kWh/m^3 of algal slurry processed [77] and 0.05 kWh/m^3 for clarification. DAF and centrifugation energy consumption was accounted for at 1.5 and 5 kWh/m^3 processed respectively [78].

- <u>DRYING</u>

Drying the algal biomass from 20% to 90% d.s. can account for 60% or more of process energy consumption [40]. It is pointed out that conventional thermal dryers may require 160% the heat of vaporization [58], but performance data published specifically for algae driers is scarce. The model estimates the energy required for the drying step based on the latent heat of vaporization, rate of water removal, and a heat transfer efficiency of 60% (i.e., single effect evaporation with process inefficiencies) as would be typical for drum drying [79].

- <u>OIL EXTRACTION</u>

An oil press was selected as the method to extract oil from the dried algae. This method is assumed to be able to remove up to 70% of the oil [67]. Based on equipment specifications, the Pacific Oil Type 90 oil press requires only 0.05 kWh/kg of dry biomass [80]. The press produces a crude oil product and a de-oiled algal meal containing approximately 10-12% residual oil. A scarcity of data is available on algal oil extraction using an expeller press, and it was assumed that pressing of the dried algal biomass produces sufficient quality for transesterification without need for refining. It has been found that some algal oils can contain relatively high amounts of free fatty acids (>10%) [81]; this suggests a preprocess step may be necessary to purify the oil prior to transesterification in order to achieve high conversion and prevent excessive catalyst use or fouling of equipment; however this was not accounted for in this study.

- BIODIESEL CONVERSION

Energy required to convert oil to biodiesel is based on data from conventional industrial scale transesterification of vegetable oil using methanol and potassium hydroxide [82], and equated to 0.08 kWh/kg dry algae. This assumes that the oil is of sufficiently high quality (i.e. low FFA and moisture content); however, it has been shown that algal oils may contain as much as 10% FFA which may necessitate additional equipment and costs [83]. For the transesterification of algal oils containing relatively high amount of FFA, a preprocessing step may be required to reduce the amount of soap by-product formed, however this additional energy was not accounted for in the model. A by-product of the process is a crude glycerin ~70-85% pure at a rate of 10% by wt. of the biodiesel produced.

3.2 Material and Energy Balance Modeling Using Sugars™

A material and energy balance simulation model of an algal biodiesel production process integrated with a cane sugar mill was developed in Sugars™ (http://www.sugarsonline.com/). This modeling program is specifically designed for the sugar industry; it is widely used to design sugar factories, evaluate R&D projects, increase yield, and train engineers. The program is able to simulate different operating/production scenarios of a mill and allows the user to evaluate potential improvements in efficiency and/or production. By adding an algal biodiesel production process into the sugar mill material and energy balance simulation model, the benefits of co-location can be quantified (emissions reduction, biodiesel production) using realistic assumptions, and the user is able to evaluate different processing options. The Sugars™ model is included in Appendix B.

3.2.1 Proposed Algal Biodiesel Production Process

Figure 8 is a screenshots from the Sugars™ model that show the algal biodiesel production process integrated with the sugarcane mill facilities, and the two algae dewatering scenarios that were compared. Other operating scenarios are presented in Appendix B for comparison.

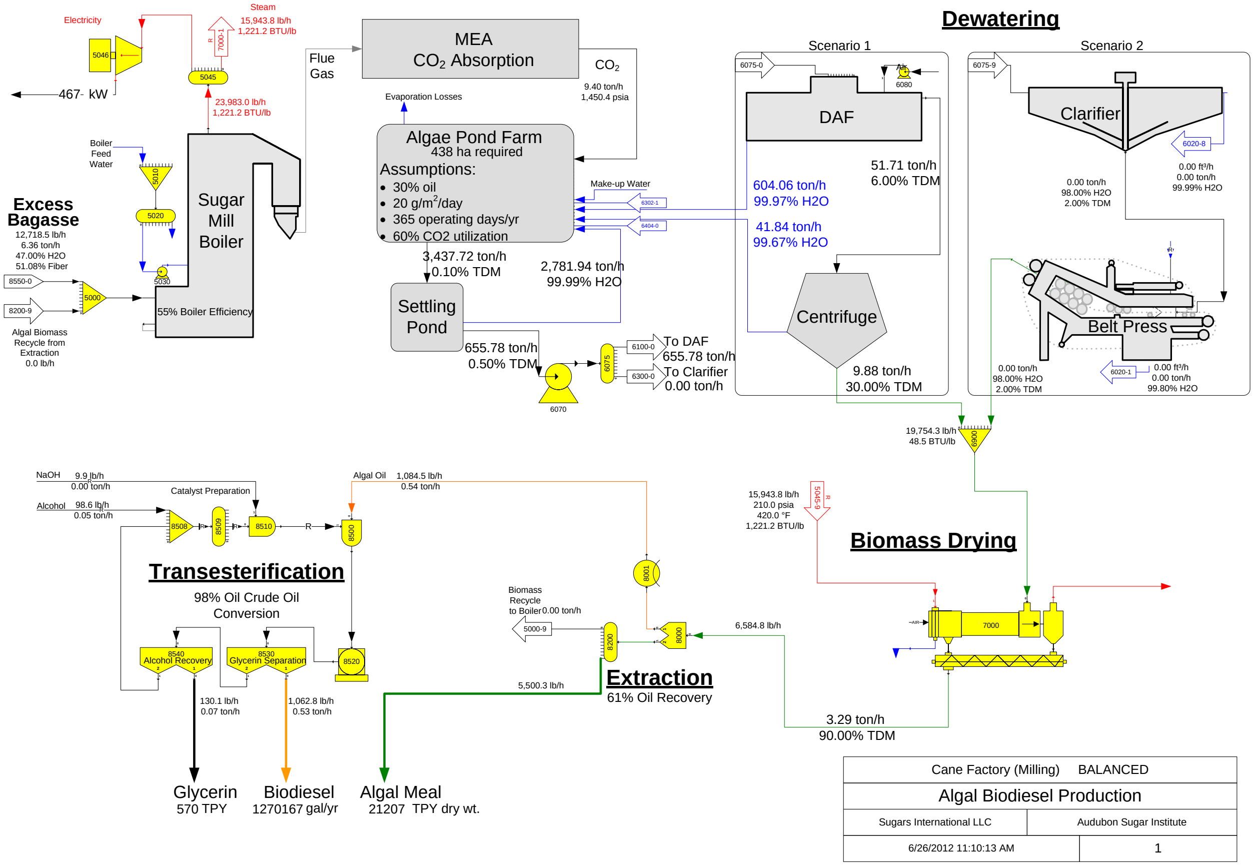

Figure 8. Illustration of Scenario 1: Algal Biodiesel Production Integrated with Sugar Mill

In Scenario 1, a 10% drier algal paste could be produced because of the more energy intensive harvesting methods used. This reduced the mass of dewatered alga to be dried by 32% and reduced the amount of energy required in the drying step by 43%; and resulted in Scenario 1 having the higher overall EROI of 1.3, compared to 1.0 for Scenario 2. For this reason, Scenario

1 is the proposed algal biodiesel production process. Other process scenario screenshots for Scenarios 1, 2, and the results from this study can be found in Appendix B pgs. 74, 75, and 76. Page 76 shows that energy balance for Scenario 2 canor be complee by the "unbalanced" in the bottom right title box. More energy was required to dry the alga than was avaiable from the excess bagasse. The simulation screenshots depicting scenario 2, as well at the lab derived data can found in Appendix B.

Figure 9 further illustrates the EROI for the two scenarios, which is simply the ratio of energy produced/energy consumed. Although both scenarios produce the same amount of algae and biodiesel, scenario 1 requires less energy to achieve this and therefore is the more feasible option.

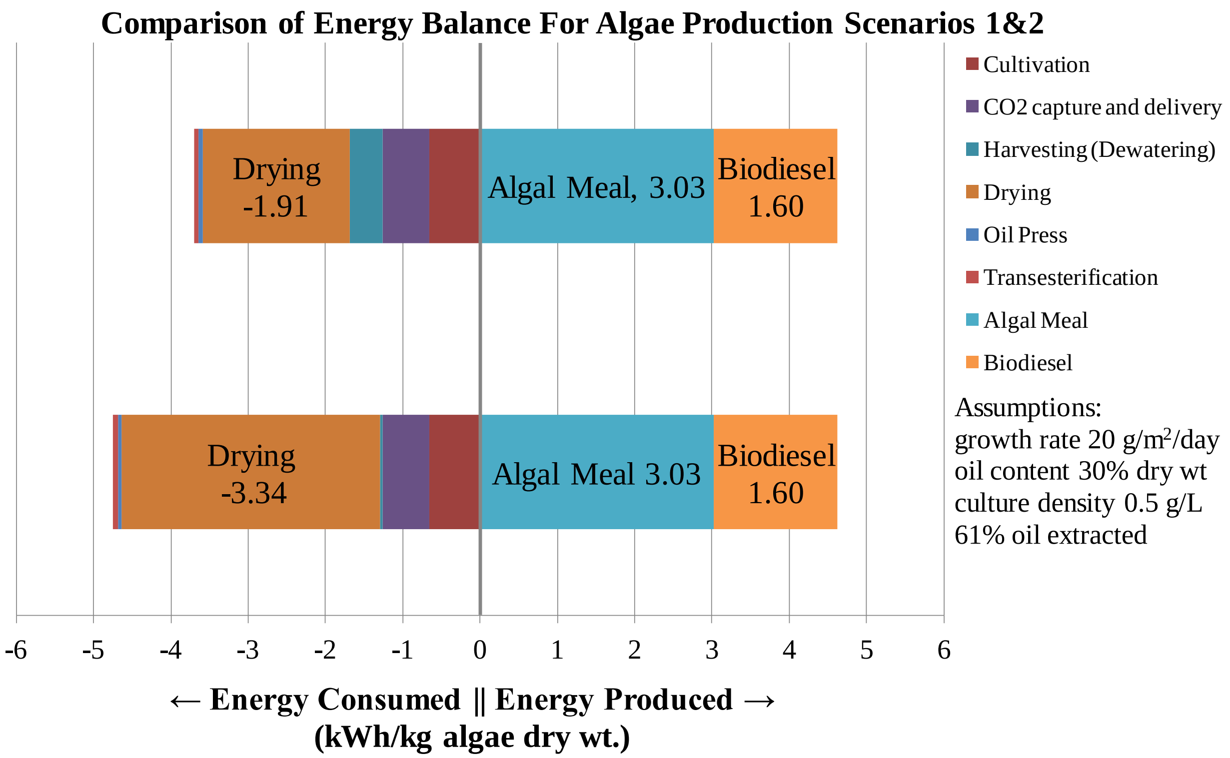

Figure 9. A Comparison of the Energy Input and Output of Two Scenarios

Algal meal is an important co-product of the algae-to-biodiesel process that contains residual oil, proteins, and carbohydrates. It can provide essential nutrients in the form of feed or fertilizer, or can be further processed into bio-energy. Approximately 3-4 times more meal is produced than biodiesel by weight. The meal has a lower energy density than biodiesel, but due to the amount that is produced this component actually contains more energy (i.e. biofuel potential) as shown in Figure 9, above. Ideally, the algal meal would contain sufficient energy to power the algal biodiesel production system. Figure 9 shows that nearly as much energy is produced in the algal meal than is consumed for Scenario 1, however, utilizing the meal as a source of energy (e.g. by co-firing in the sugar mill boilers at 55% efficiency) will result in a deficiency in the amount of energy available. Because the algal meal alone is not sufficient, an additional source of energy is needed, and is available from a sugar mill in the form of excess bagasse.

Reducing the energy requirements for the process, or, more efficient use of the algal meal, will result in less meal needed for energy generation, and the remainder could be sold. The conversion of algal meal into energy is an active area of research. The meal can be directly co-fired in the boiler [44]; further processed into fuel as by pyrolysis; anaerobically digested in order to generate biogas and recycle nutrients [41] [75]; or used for aquaculture feed or organic fertilizer. As the meal may be a valuable co-product, economics will dictate how much can be used for energy generation and how much meal can be sold.

3.2.2 Sensitivity Analysis

Algal biodiesel production is modeled as a downstream process from the sugar mill, therefore any changes to mill inputs affecting sugar production will have subsequent effects on biodiesel production. To evaluate which parameters are most influential in the model, a sensitivity analysis is used to show which parameters have the largest influence on the model. As previously mentioned, the amount of biodiesel produced and the EROI were the two criteria with which the scenarios were evaluated. Figures 10 and 11 show various parameters of the model that were evaluated spanning the typical range that has been reported in literature, and the corresponding influence on the amount of biodiesel and the EROI can be estimated. Each parameter was varied from the base case independently of the other parameters.

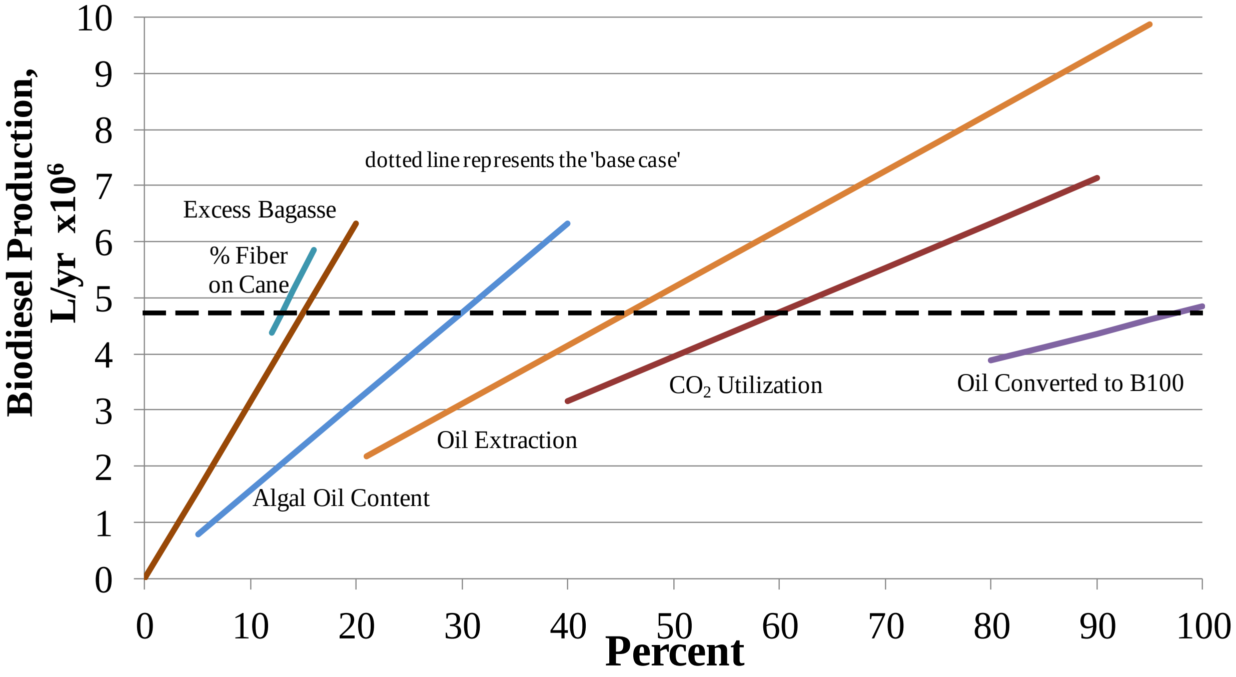

Figure 10. A Comparison of the Influence of Various Parameters on the Model Output: Biodiesel Production

The most critical parameters of the process in terms of biodiesel production were related to the carbon source. Every additional percent excess bagasse that the mill is able to generate could be converted into about 300,000 L (84,000 gal) of biodiesel. This important result confirms that a reliable and robust source of CO_2 is the most important factor for a feasible algal production process. Algal oil content was more significant in determining how much biodiesel could be produced than the oil extraction, CO_2 utilization, or the amount of oil that was converted to biodiesel, as indicated by the steeper slope.

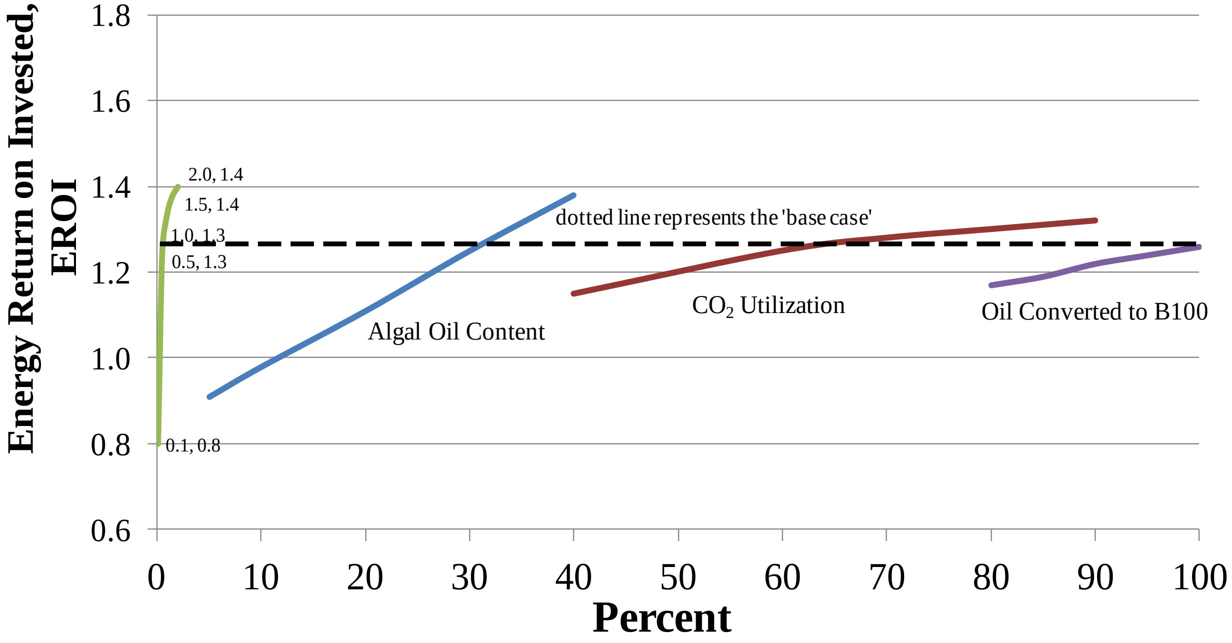

Figure 11. A Comparison of the Influence of Various Parameters on the Model Output: Energy Return on Invested, EROI

The EROI of the process was most significantly affected by culture density. At a density of 0.1 g algae dry wt./L, the model suggests that the energy ratio will be less than 1, indicating that the process would not be thermodynamically feasible due to large energy demand for pumping. As the culture density was increased, the energy ratio quickly rose above 1, and at a density of 0.5 g algae dry wt./L culture, the energy ratio is 1.3. There are two options available to improve the EROI, they are: the energy required by the process can be reduced (e.g. by reducing drying energy consumption), or the amount of energy produced by the algae can be increased (e.g. by increasing lipid productivity).

For the base case, modeling and simulations carried out in this study indicate that 4.8 million L (1.3 million gallons) of algal biodiesel can be produced annually using available resources from a 10,000 metric TPD sugarcane mill generating 15% excess bagasse. Table 5 shows the results of the base case scenario.

Table 5. Algal Biodiesel Modeling Calculations Base Case.

Selected Main Input Variable	Value	Range
Excess Bagasse Available	15%	0-20
Algae Oil Content	30%	5-40
CO_2 Utilization	60%	40-100
Culture Density (g/L)	0.5	0.1-2
% Oil Converted to Biodiesel	98%	22-100
Boiler Efficiency	55%	40-60
Cane Fiber Content	13%	12-16
Oil Extraction	61%	21-95
Algae Produced	27,200	metric tons dry wt/yr
Farm Area Required	438	ha (3.3% of sugarcane area)
Biodiesel Produced	4,752,359	L Biodiesel/yr
CO_2 Emissions Reduction of Mill	11%	EROI = 1.25
10,841 L Biodiesel/ha/yr	62	metric tons algae/ha/yr

In the base case scenario, the required size of the algae production facility is 438 hectares (1083 acres), which is approximately 10 times larger than the current largest algae producer in the US. This amount of area would need to be located near a sugar mill to take advantage of the available resources, and thus would displace about 3.3% of sugarcane crop area – potentially less if there is non-arable land that can be utilized for algae cultivation. Producing 27,200 metric tons of algal biomass sequesters 11% of the sugarcane mill's CO_2 emissions.

Chapter 4: Algal Oil Characterization as a Biodiesel Feedstock

The extraction and characterization of algal oil allows us to determine what portion of the produced algal biomass can be converted into a useable biodiesel fuel. Concerning the computer modeling performed in Chapter 3, the parameters of 'algal oil content,' 'extraction efficiency' and 'oil converted to biodiesel' were measured in the lab using the techniques discussed in Chapter 2. Recall, that ethanol and hexane were compared as potential solvents, and two extraction techniques were employed. The hypothesis was that hexane, being a neutral solvent, would preferentially extract the neutral algal oils, which are desirable for biodiesel production, and thus lead to higher biodiesel yields, however, this was disproved.

Hexane is an established solvent used to extract oil from soybeans, but because this is a potentially hazardous chemical, it was desired to evaluate another less toxic solvent that could be made readily available at sugarcane processing facilities. Ethanol is a more polar solvent compared to hexane, and therefore is expected to be less selective of the neutral bio-molecules that are desirable for biodiesel feedstock. Ethanol can be readily produced at a sugarcane mill by fermentation of molasses or lignocellulosic conversion of bagasse. By comparing the relative extraction performance of each solvent, a basis for estimates for the model input parameters could be established. After extraction, the crude algal oil was esterified using an acid catalyzed reaction to produce fatty acid methyl esters (FAME). The resulting organic layer was analyzed using gas chromatography to determine its FAME composition as well as how much of the crude oil was converted to FAME (i.e. biodiesel) by weight. Results from these tests were incorporated into the simulation model and extrapolated estimate an approximate overall algae-to-biodiesel conversion.

4.1 Evaluation of Ethanol and Hexane as Solvents of Algal Oil

Soxhlet extraction mimics what extraction would be like with an unlimited supply of solvent and an infinite number of extraction stages. It allows for an estimation of the maximum crude oil yield of a sample, and the extracted product contains different amounts of soluble bio-molecules depending on the solvent. The graph below shows how much crude oil was obtained using the Soxhlet and 3-stage cross current oil extraction methods with ethanol and hexane as solvents.

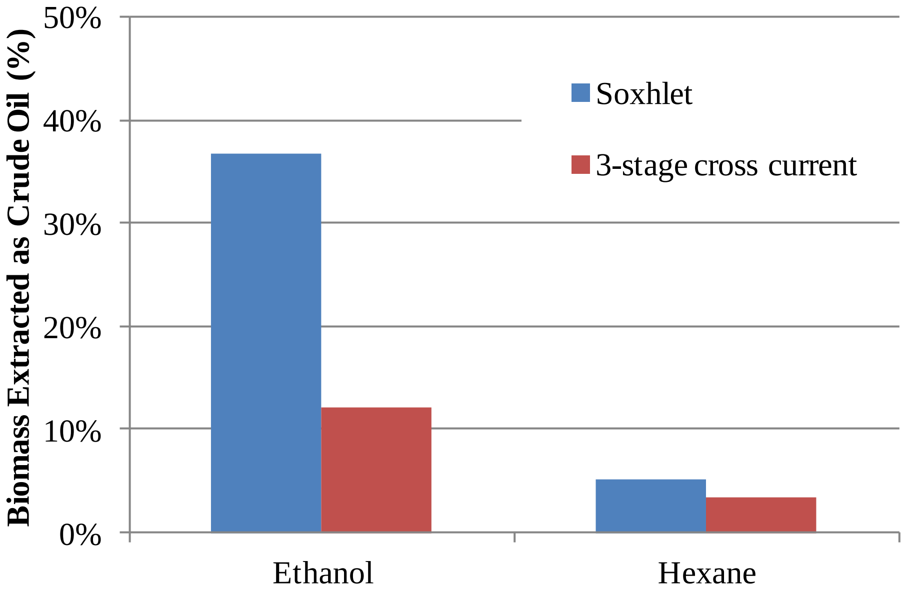

Figure 12. Yield of Crude Oil Using Ethanol and Hexane as Solvents

Ethanol extracted more mass from the alga than hexane for both extraction procedures. The polar nature of ethanol enhanced the ability of this solvent to penetrate the polar cell membrane lipids, and thus was able to free more cellular material. Hexane, being less polar, was not able to penetrate the tough cell walls of the algae and thus extracted less mass. The crude oil yield is not enough to estimate how much biodiesel can be produced, we also need to qualify how much of the oil can be converted to FAME, or biodiesel. The extracted crude oil included impurities such as chlorophyll, cell membrane lipids, proteins, etc which were more pronounced in the ethanol-extracted product. The crude oils produced were esterified without any additional processing step to remove the impurities. Some of the co-extracted bio-molecules besides triglycerides and free fatty acids, such as phospholipids, may be able to be converted to FAME [84]. To calculate how much biodiesel could be produced from the crude oil, the samples were esterified as described in section 2.1.4, and the amount of FAME produced from the chemical reaction was analyzed using gas chromatography mass-spectrometry. The mass of FAME was compared to the initial mass of crude oil to determine the percentage oil converted.

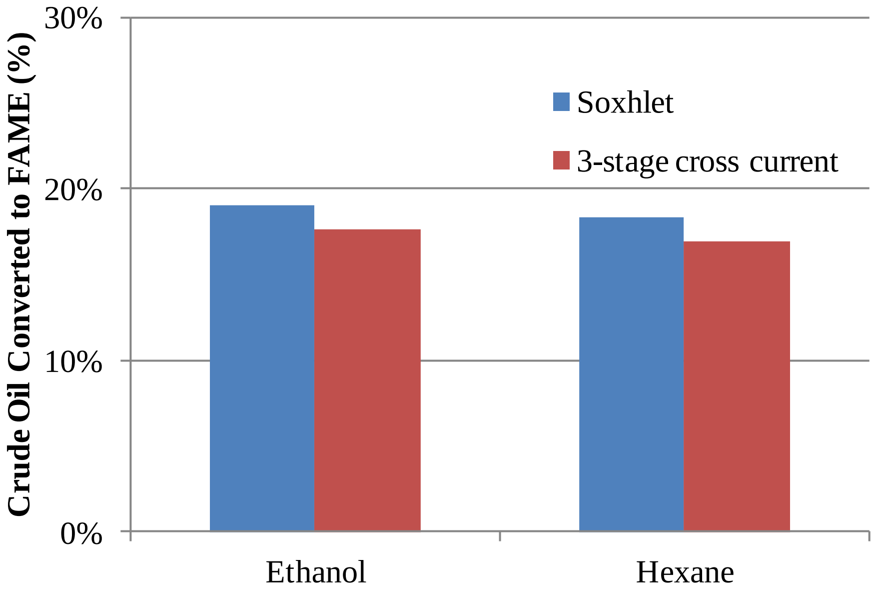

Figure 13. Crude Oil Converted to FAME (Biodiesel) by wt. with Ethanol and Hexane as Solvents

The mass of FAME produced from the crude oil was about 20% by wt in all samples. The Soxhlet extraction technique resulted in 1% better conversions than the 3-stage cross current technique, with ethanol outperforming hexane by the same amount. Plainly stated, the crude algal oil extracted contained more than 80% impurities that could not be converted into biodiesel. This finding is similar to previous algal biodiesel production studies, which have acknowledged that only a small fraction (0.23-0.44) of the crude oil sample was converted using the acid catalyzed esterification technique [85] [86]. If a co-solvent of opposing polarity were added to the extraction mixture, it is expected that biodiesel yield could be increased. Solvent extraction of wet algal biomass has been shown to improve lipid yield compared to dry alga because the water acts as a polar co-solvent [85].

The finding that the hexane and ethanol-extracted crude oils' produced similar amounts of FAME contradicts the original hypothesis that hexane would be more selective of the neutral lipids. As such, it can be concluded that ethanol would be a more applicable solvent due to its availability near sugar mills, lower toxicity, and higher overall oil yield than hexane. It should be reiterated, however, that a solvent extraction system is not recommended as a method of oil extraction if the goal is to produce biofuels, because more energy is consumed in regenerating the solvent than can be produced as energy, unless very high oil contents of over 40% can be achieved [41].

4.2 Determination of Lipid Profile and Potential Biodiesel Yield of *Louisiana strain*

The crude oil that was extracted from the algal biomass and converted to biodiesel was analyzed by gas chromatography to identify the fatty acids and compare them to the conventional biodiesel feedstock soybean oil. The four most prevalent fatty acids in the algal oil were identified by comparing the gas chromatographs to that of known standards, and are shown in Table 6. The remaining 38% of the oil consisted of components each less than 5% by wt.

Table 6. Algal Oil Composition

Component	% of FAME by mass
Linoleic acid	20%
Palmitic acid	15%
Oleic acid	12%
Stearic acid	10%
Eicosanoic acid	5%

The algal oil produce was found to be of similar composition to soybean oil containing mainly linoleic, palmitic and oleic acids [87]. As such, it is predicted that the alga produced could be a suitable biodiesel feedstock, however, oil conversion to FAME would need to be increased above the 17-19% achieved in order to be feasible.

Figure 14 below shows that similar lipid components were extracted and converted from the algal biomass using both solvents.

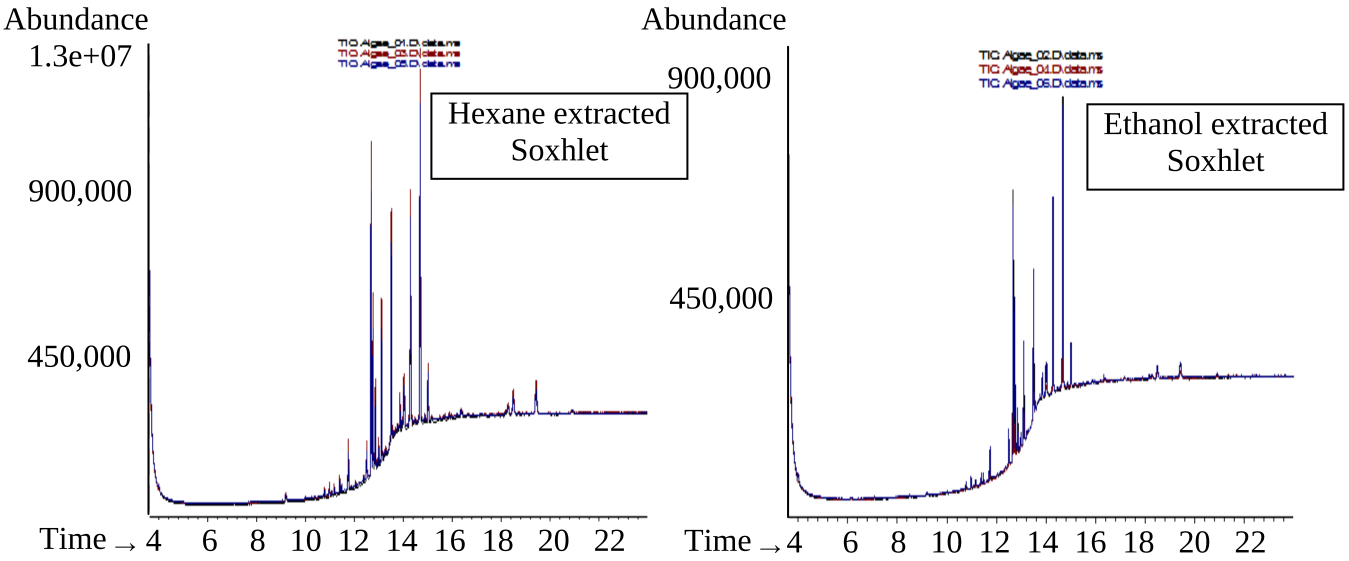

Figure 14. Comparison of FAME chromatograms obtained using ethanol and hexane as solvents

The elution times and ratio of peak heights in the two chromatograms shown in Figure 14 suggest that both solvents extracted the same oil components from the algae.

Table 7 shows a comparison of the values achieved in lab to the values projected in literature that were initially used to build the material and energy balance simulations. For reference, the definitions of the modeling parameters that were evaluated in the lab are:

$$Y_{\text{CrudeOil}} = \frac{\text{oil extracted by soxhlet (g)}}{\text{mass of alga dry wt. (g)}} \qquad \text{(Eq. 2)}$$

$$E_{\text{extraction}} = \frac{\text{crude oil extracted in 3−stages(g)}}{(\text{mass of sample (g)} * Y_{\text{CrudeOil}})} \qquad \text{(Eq. 3)}$$

$$Y_{\text{Biodiesel}} = \frac{\text{mass of FAME (biodiesel) (g)}}{\text{mass of algae dry wt. (g)}} \qquad \text{(Eq. 5)}$$

Table 7. Model Parameters Derived from the Literature Compared to what was Achieved in the Laboratory.

	Achieved in Lab Hexane	Achieved in Lab Ethanol	Projected in Literature
$Y_{CrudeOil}$	5%	37%	30%
Oil Extraction Efficiency	66%	33%	61%
Oil Converted to FAME	18%	19%	80%
$Y_{Biodiesel}$ (maximum)	0.6% (0.9%)	2.1% (7%)	15%+
Calculated Maximum Biodiesel Production, L/yr (gal/yr)	42,000 (157,000)	615,000 (162,000)	4,750,000 (1,250,000)

The overall yield of biodiesel from algae achieved in lab was significantly lower than originally projected in the model based on literature. The discrepancy between the biodiesel yield originally projected in the model and what was achieved in lab can be attributed to the low conversion of oil obtained (17-19%), whereas in the model, it was projected that 98% of the oil would be converted to biodiesel. The assumptions of 'crude oil yield' and 'oil extraction efficiency' fell within the range achieved in the lab, therefore, they were verified as reasonable assumptions and these values were not changed. The 'oil converted to FAME' was drastically different from what had been predicted; therefore this assumption was revised to more accurately reflect the laboratory results, and the estimated biodiesel production decreased accordingly. The calculated maximum biodiesel production based on laboratory experiments underscores the need for further R&D in the area of oil extraction and conversion before algal biodiesel can become a viable option.

4.3 Co-Product Value Analysis

Algal meal contains carbohydrates, proteins, residual oil, and ash. This co-product of algal biodiesel production can contribute added value to the process as a source of fuel, or an alternative revenue stream as feed or fertilizer. The energy content of the algal meal was found to be 6 kWh/kg (9,300 BTU/lb) algae dry wt., which is comparable to other boiler fuels (bagasse 5.2 kWh/kg (8,000 BTU/lb); charcoal 7.9 kWh/kg (12,300 BTU/lb). If the algal meal were sold as a high protein livestock feed supplement, rather than used for energy generation, it would be comparable to distillers dried grains from corn production or soybean meal, which currently sell for around $200-300/ton [88]. Economics dictates how much of the meal can be used for energy and how much should be sold.

If the meal were used for energy generation rather than sold on the market at $250/ton, the cost of that energy would equate to approximately $19/MMBTU. In comparison, natural gas, currently one of the cheapest industrial fuels sells for around $3/MMBTU, which suggests that from an economic perspective it is more realistic to consider selling the meal and buying natural gas to provide energy for the facility. Contrarily, this study suggests using the meal as an energy source to reduce or eliminate the dependency on petroleum fuels in the sugar industry.

Chapter 5: Results and Discussion

This study presented a concept of how available resources at a sugarcane mill can be utilized to address the current main bottleneck of algal biodiesel production - the energy requirement for drying the biomass. For the base case, it is shown that the energy contained in 15% excess bagasse is sufficient to supply all of the energy required for drying the algae, which is about 50% of total process energy requirements. Using current algae production and harvesting technologies, co-location of an algal biodiesel production facility with a sugarcane mill can improve the overall economic feasibility of algae bio-energy projects by having available resources, infrastructure, and established markets for the produced biodiesel and algal meal. Advantages of co-locating algae production with sugarcane mills are:

- CO_2, water, and energy resources available from mill.
- Nutrients available from agricultural runoff.
- Climate suitable for algae production.
- Established agricultural infrastructure and markets.

Where laboratory results verified an assumption used in the model, these assumptions were not changed. The 'oil converted to FAME' was the only assumption revised, and this went from 98% to 19%. Table 5 (pg. 38) is re-displayed below taking into account this change.

Table 8. Algal Biodiesel Modeling Calculations with Experimental Results.

Selected Main Input Variable	Value	Range
Excess Bagasse Available	15%	0-20
Algae Oil Content	30%	5-40
CO_2 Utilization	60%	40-100
Culture Density (g/L)	0.5	0.1-2
% Oil Converted to Biodiesel	**19%**	22-100
Boiler Efficiency	55%	40-60
Cane Fiber Content	13%	12-16
Oil Extraction	61%	21-95
Algae Produced	27,200	metric tons dry wt/yr
Farm Area Required	438	ha (3.3% of sugarcane area)
Biodiesel Produced	**921,376**	L Biodiesel/yr
CO_2 Emissions Reduction of Mill	11%	**EROI = 0.91**
2,102 L Biodiesel/ha/yr	43	metric tons algal meal/ha/yr

The EROI of less than one indicates that the algal biodiesel production process proposed in Figure 8 (pg. 33) would not be thermodynamically feasible. The amount of biodiesel able to be produced was calculated to be 920,000 L/yr (240,000 gal/yr) or about 2,100 L/ha/yr (251 gal/acre/yr), which is competitive with the two highest oil yielding terrestrial crops: jatropha and oil palm, and outpaces the common biodiesel feedstock - soybeans - by 5-fold. There is the potential to increase the yield of biodiesel from algae through concerted R&D efforts as well as practical field studies; therefore, while this co-location scenario may not be viable at present, it does provide an opportunity to minimize the amount of outside resources required, and thus improve the overall sustainability of an algae biofuel production facility.

Chapter 6: Conclusions

Co-location of algae production facilities with sugarcane mills in Louisiana has potential to improve resource utilization and add value by diversifying the products of the mills. A synergy between sugar and algae production is created in which algae utilize waste resources from the mill, and, in turn, can be converted to biodiesel that can be used in sugarcane harvesting and transportation. Specific accomplishments and insights derived during this research are listed below.

- Available resources at a 10,000 metric TPD (11,000 TPD) sugarcane mill generating 15% excess bagasse can realistically support production of 920,000 L/yr (240,000 gal/yr) of algal biodiesel and 21,000 metric tons/yr of algal meal.
- An algal biodiesel production process was synthesized incorporating state of the art technologies. An EROI of 0.91 was projected by the model based on laboratory experiments, which suggests that the process would require more energy than can be produced.
- The bottleneck of the algal biodiesel production process was identified as the drying stage, requiring 54% of total process energy requirements.
- The above bottleneck is addressed by utilizing excess bagasse as a supplemental energy resource available from a sugarcane mill. The 15% excess bagasse projected in the base case can supply 50% of the total algal biodiesel processing energy requirements.
- Algal meal must be used for energy co-generation to supply the remaining 50% of process energy requirements in order to eliminate the need to use fossil fuels.
- A sensitivity analysis showed that the amount of excess bagasse that could be produced at a mill was the most significant parameter affecting the amount of biodiesel that could be

produced; culture density (g algae dry wt/L culture media) was the most important parameter affecting the energy return on invested, EROI.

- As an algal oil solvent, ethanol yielded overall higher conversions of algae to biodiesel than hexane. An oil purification step should be included before transesterification for commercial production of biodiesel.
- Actual conversion of algae to biodiesel ranged from 0.5-7% by wt. based on laboratory experiments; and was significantly lower than what was initially estimated to be 15% based on values derived from literature.

Looking ahead, microalgal biofuel technologies are expected to improve in feasibility with the development of more efficient processing techniques, specifically in the drying stage and oil extraction and conversion. Capital costs of building such facilities should be considered in order to determine at what point biofuels created using this method could become economically competitive with petroleum fuels.

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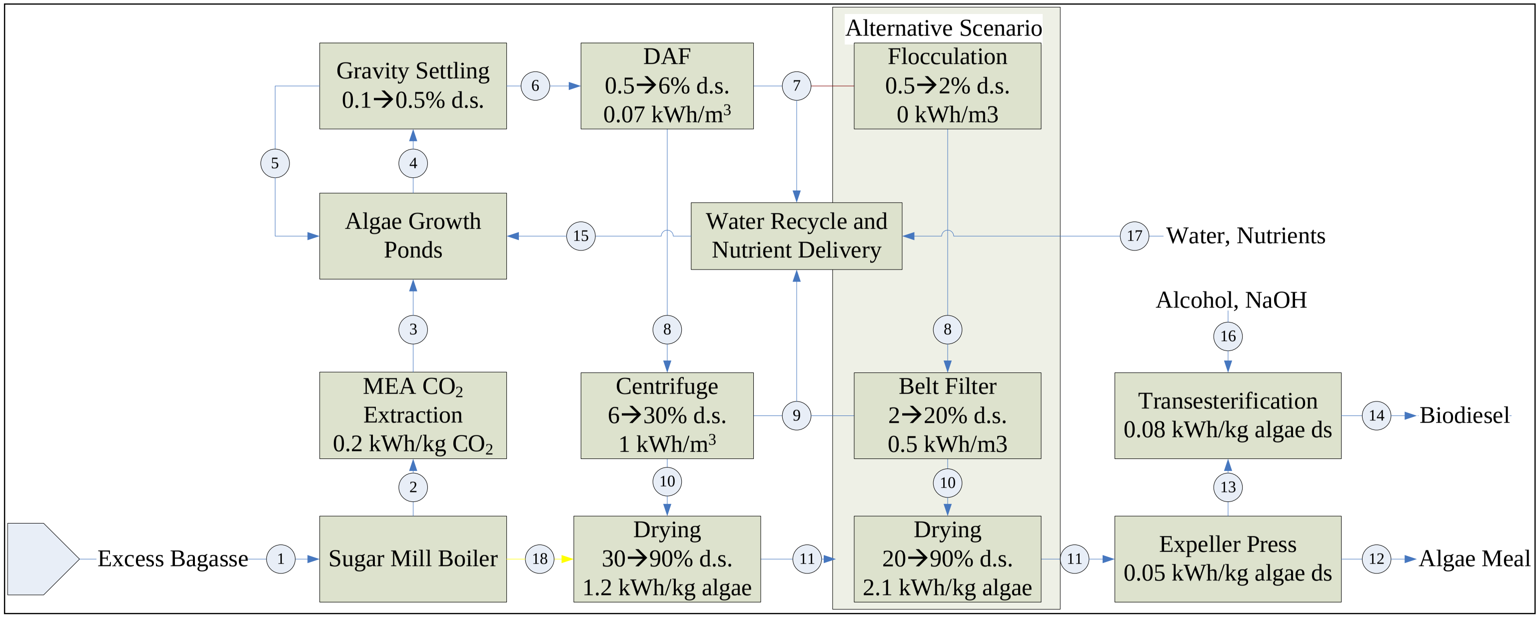
Appendix A: Material and Energy Balance Excel Model



English Units (Il Stream No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Component																	
Excess Bagasse (TPD)	81	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
CO2 (TPD)	-	253	227	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Algae (TPD)	-	-	-	82	4	78	4	74	4	70	70	-	-	-	-	-	-
Water (TPD)	-	-	-	163,946	148,367	15,575	14,338	1,159	995	234	8	-	-	-	15,567	-	234
Algal Oil (TPD)	-	-	-	-	-	-	-	-	-	-	-	8	13	-	-	-	-
Algal Meal (TPD)	-	-	-	-	-	-	-	-	-	-	-	49	-	-	-	-	-
Alcohol (TPD)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1	-
Catalyst (TPD)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1	-
Biodiesel (TPD)	-	-	-	-	-	-	-	-	-	-	-	-	-	13	-	-	-
Glycerin (TPD)	-	-	-	-	-	-	-	-	-	-	-	-	-	1	-	-	-
Nutrients (TPD)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.5
Total Mass	81	253	227	164,028	148,371	15,653	14,342	1,233	999	305	78	57	13	14	15,567	1.4	235
algae concentration				0.1%		0.5%		6%		30%	90%						

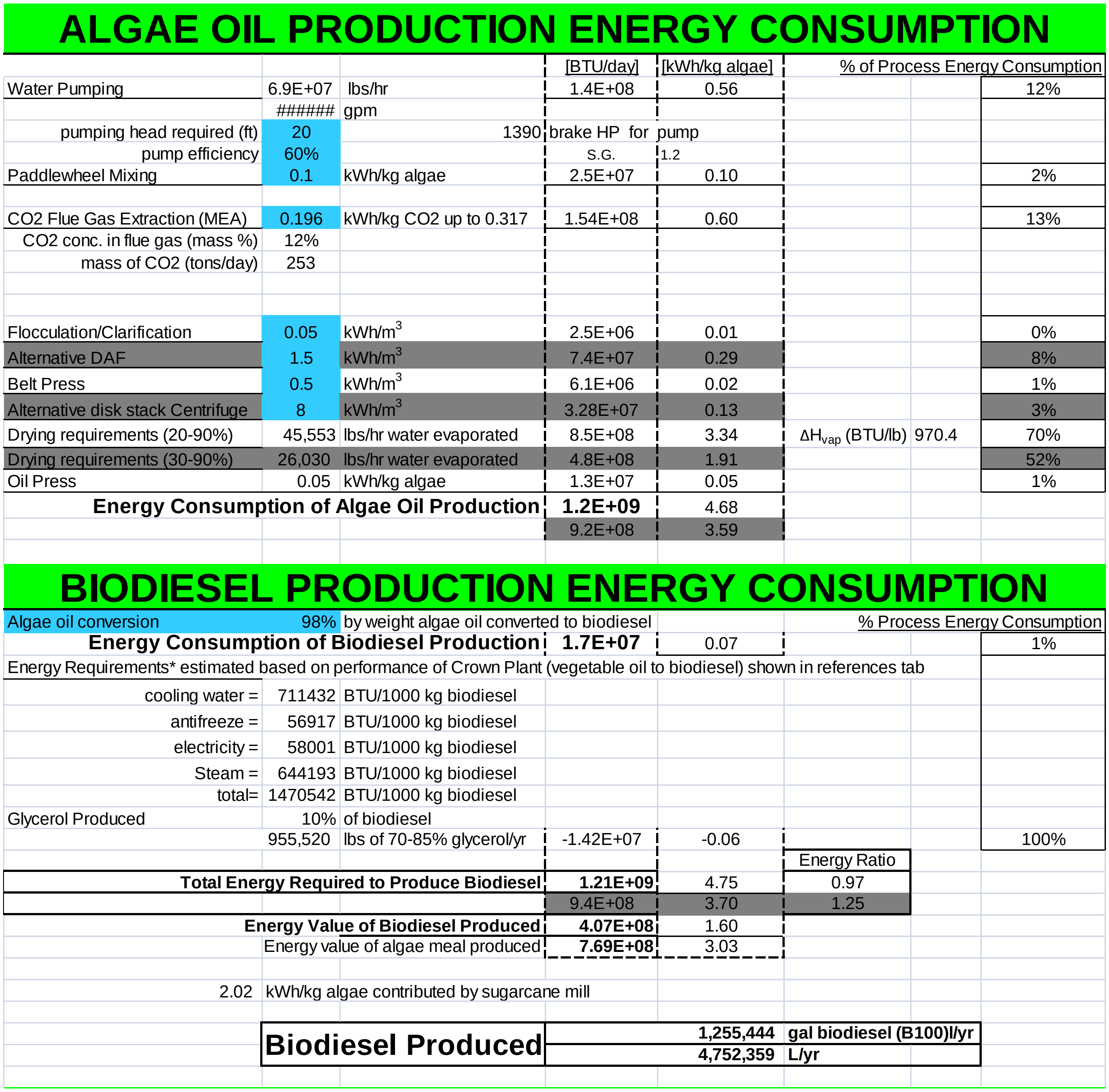
ALGAE PRODUCTION AT A SUGARCANE MILL

DESCRIPTION	Value	Units	Value	Units		
Sugar Cane Acres, Harvested	32,353	acres	34	tons/acre	13092.7708	
Sugar Cane Yield	1,100,000	tons sugarcane/yr				
Cane Processed	11,000	tons/day			diesel requirec	23
Operating Season, Sugar Cane	24	hr/day	100	days/yr	744,118	gal/yr
Operating Season, Algae	12	hr/day	365	days/yr		
--Cane Composition--						
Sugar introduced with the Cane	13%	% on cane	143,000	tons/year		
Fiber introduced with the Cane	13%	% on cane	143,000	tons/year	bagasse dry weight	
Water introduced with the Cane	66%	% on cane	7,260	tons/year		
Raw Sugar Produced	0.12	tons/ton cane	136,180	tons/year	95%	Sugar Recovery
Molasses Output	0.03	tons/ton cane	33,000	tons/year		
diesel consumption for harvesting	23	gal/ac	cane transportation	0.075 L/ton cane/km		17.85
Excess Bagasse Produced	15%	Moisture content	50%	Ash content	2.5%	
Heating value of bagasse	9229.25	kJ/kg with moisture	3976.2	BTU/lb wet	7952.4	BTU/lb dry wt
					5.1	kWh/kg dry
		Bagasse Combustion	Energy Generated	CO2 Available	Water Produced	
boiler efficiency	55%	(tons dry wt/seaon)	(BTU/season)	(tons)	ton	
3 month season Sugarcane processing		121,550	1.06E+12	379,236	206,800	
Excess Bagasse		**21,450**	**1.88E+11**	**66924**	**0**	
	Total (/yr)	143,000	1.251E+12	446,160		
				1.56	ton CO2/ton wet as fired bagass	
CO2 available for algae (tons/day)	253		CO2 capture efficiency	90%		
CO2 required (tons CO2/ton algae d.s.)	1.83	CO2 converted to algae (tons CO2/day)		136	29920.1824	
CO2 utilization (% converted to algae)	60%					
Mill CO2 Emissions Reduced	**11.2%**	**Algae Produced**			**lbs dry wt/yr**	**5.98E+07**
					kg dry wt/yr	**2.720E+07**
average solar radiation (kWh/m^2/day)=	4.2	1.58E+08	kWh/yr produced in biomass			
Algae Production Rate (g/m^2/day)	20	10-30 range			photosynthetic efficiency=	2.77%
Pond Area Required (m^2)	3.726E+06	pond area =	85%	of total farm area required		
			Farm Area Required		**acres**	**1083**
			3.3%	**of sugarcane**	**ha**	**438**
Individual Pond Area (m^2/pond)	10000	1	ha/pond		# ponds required	373
pond height (m)	0.5		pond volume (L)	5,000,000	1,863,025	
Culture density (SS concentration)	0.5	g/L				
Harvest Rate (kg algae d.s./day/pond)	200	400000	l/day/pond			
		Biomass	Energy content (kWl	Energy Content	BTU/yr	kWh/yr
Oil content	30%	8,160,050	10.6	16469	1.34E+11	8.68E+07
Protein content	40%	10,880,066	4.3	6665	7.25E+10	4.69E+07
Carbohydrate content	25%	6,800,041	3.6	5590	3.80E+10	2.46E+07
Ash content	5%	1,360,008	0.0	0	0	0

ALGAE PRODUCTION MASS BALANCE

DESCRIPTION

Settling Pond Mass Balance				IN	OUT	RECYCLE	
			Stream (lb/hr)	4	6	5	
	95%	recovery	algae	13662	12979	683	
Concentration	IN	OUT	water	27310705	2582836	2.5E+07	
	0.1%	0.5%	total	27324367	2595815	24728552.6	
			x =	0.05%	0.5%	0%	
Clarifier Mass Balance							
Alternative: Dissolved Air Flotation, DAF			Stream (lb/hr)	6	8	7	
	95%	recovery	algae	12979	12330	649	
Concentration	IN	OUT	algae	12979	12330	649	
	0.5%	2%	water	2.6E+06	604176	1978660	
	0.5%	6%	water	2582836	193172	2389664	
			total	2.6E+06	616506	2.0E+06	
			total	2.6E+06	205502	2.4E+06	
						0.033%	
Belt Press Mass Balance							
Alternative: Centrifuge			Stream (lb/hr)	8	10	9	
	95%	recovery	algae	12330	11714	617	
Concentration	IN	OUT	algae	12330	11714	617	
	2%	20%	water	604176	46854	557321	
	6%	30%	water	193172	27332	165840	
			total	616506	58568	557938	
			total	205502	39045	166457	
Drying Mass Balance							
			Stream (lb/hr)	10	11		
	100%	recovery	algae	11714	11714		
Concentration	IN	OUT	algae	11714	11714		
	20%	90%	water	46854	1302	386,820,289	L water/yr
	30%	90%	water	27332	1302	110,520,083	L water/yr
			total	58568	13015	79,990	gal/day
			total	39045	13015		
Oil Extraction Mass Balance				IN (lbs/hr)	OIL OUT	MEAL OUT	
oill press produces oil and algae meal			Stream (lb/hr)	11	13	12	
the meal can be fed to anaerobic digester			biomass	8200	0	8200	
	Oil recovery	61%	water	1302	0	1302	
			Algae Oil	3514	2144	1370	
			total	13015	2144	10872	
Transesterification Process							
	acid number		Stream (lb/hr)	13	16	14	
	KOH		Algae Oil	2144	0	0	
	NaOH		Alcohol	0	214	0	
	H2SO4		Catalyst	0	21	0	
	Water		Glycerin	0	0	236	
	glycerol		Biodiesel	0	0	407	
	Methanol or Ethanol	10%					
	Catalyst	1%					



ALGAE OIL PRODUCTION ENERGY CONSUMPTION

			[BTU/day]	[kWh/kg algae]			% of Process Energy Consumption
Water Pumping	6.9E+07	lbs/hr	1.4E+08	0.56			12%
	######	gpm					
pumping head required (ft)	20	1390	brake HP for	pump			
pump efficiency	60%		S.G.	1.2			
Paddlewheel Mixing	0.1	kWh/kg algae	2.5E+07	0.10			2%
CO2 Flue Gas Extraction (MEA)	0.196	kWh/kg CO2 up to 0.317	1.54E+08	0.60			13%
CO2 conc. in flue gas (mass %)	12%						
mass of CO2 (tons/day)	253						
Flocculation/Clarification	0.05	kWh/m^3	2.5E+06	0.01			0%
Alternative DAF	1.5	kWh/m^3	7.4E+07	0.29			8%
Belt Press	0.5	kWh/m^3	6.1E+06	0.02			1%
Alternative disk stack Centrifuge	8	kWh/m^3	3.28E+07	0.13			3%
Drying requirements (20-90%)	45,553	lbs/hr water evaporated	8.5E+08	3.34	ΔH_{vap} (BTU/lb)	970.4	70%
Drying requirements (30-90%)	26,030	lbs/hr water evaporated	4.8E+08	1.91			52%
Oil Press	0.05	kWh/kg algae	1.3E+07	0.05			1%
Energy Consumption of Algae Oil Production			**1.2E+09**	4.68			
			9.2E+08	3.59			

BIODIESEL PRODUCTION ENERGY CONSUMPTION

							% Process Energy Consumption
Algae oil conversion	98%	by weight algae oil converted to biodiesel					
Energy Consumption of Biodiesel Production			**1.7E+07**	0.07			1%
Energy Requirements* estimated based on performance of Crown Plant (vegetable oil to biodiesel) shown in references tab							
cooling water =	711432	BTU/1000 kg biodiesel					
antifreeze =	56917	BTU/1000 kg biodiesel					
electricity =	58001	BTU/1000 kg biodiesel					
Steam =	644193	BTU/1000 kg biodiesel					
total=	1470542	BTU/1000 kg biodiesel					
Glycerol Produced	10%	of biodiesel					
	955,520	lbs of 70-85% glycerol/yr	-1.42E+07	-0.06			100%
					Energy Ratio		
Total Energy Required to Produce Biodiesel			**1.21E+09**	4.75	0.97		
			9.4E+08	3.70	1.25		
Energy Value of Biodiesel Produced			**4.07E+08**	1.60			
Energy value of algae meal produced			**7.69E+08**	3.03			
2.02	kWh/kg algae contributed by sugarcane mill						
	Biodiesel Produced			**1,255,444**	**gal biodiesel (B100)l/yr**		
				4,752,359	**L/yr**		

COSTS

Flocculant Requirement	$2,154	/ha-yr for 30g/m2/day			$ 802,591	/yr	
Fertilizer Requirement	$ 1,731	/ha-yr			$ 644,979	/yr	
Phosphate (PO_4^{3-})	0.6%	dry wt of algae	163,201	lbs (PO_4^{3-})/yr			
Nitrogen as Nitrate (NO_3^-)	0.8%	dry wt of algae	217,601	lbs (NO_3^-)/yr			
Chemicals Required for Transesterification					$ 202,602	/yr	
KOH	14	g/L oil	28,378	lb KOH/yr	$ 4.00	/kg	$ 113,513
Methanol	10%	by wt. of algal oil	26,996	gal methanol/yr	$ 3.30	/gal	$ 89,088
Ethanol	0.3	L ethanol/L of algal oil	276,413	L ethanol/yr			
				COSTS	**$**	**1,650,172**	/yr
Makeup Water Requirement	0.45	cm/day evaporation rate	1.68E+07	L/day	225.00	L/kg algae	
	mill supplies	0.00E+00	L	4.43E+06			
		Cost of energy if bought at $3/MMBTU @ 60% efficiency			$ 1,693,566	/yr	

REVENUE

Value of Algae Meal ($/ton)	$ 250				$ 5,952,166	/yr potential revenue	
Value of Glycerol ($/ton)	$ 100				$ 8,421	/yr potential revenue	
Value of Biodiesel ($/gal)	$ 2.00				$ 486,805	/yr potential revenue	
				REVENUE	**$**	**6,447,392**	
Algal Meal Produced	20,958	short tons/yr					
Energy content of algal meal	6,698	BTU/lb dry wt	2580.3	BTU/lb			
Cost of energy using algal meal	$ 18.66	/MMBTU	0.92	kWh/kg			

By linking the input values from the "Algae Production" tab to the highlighted inputs below, a quick evaluation of these assumptions on the results can be observed. For example, set 'Algae Production'B15 equal to 'Results'D5, then vary the input to see the effect on biodiesel production and Energy ratio.

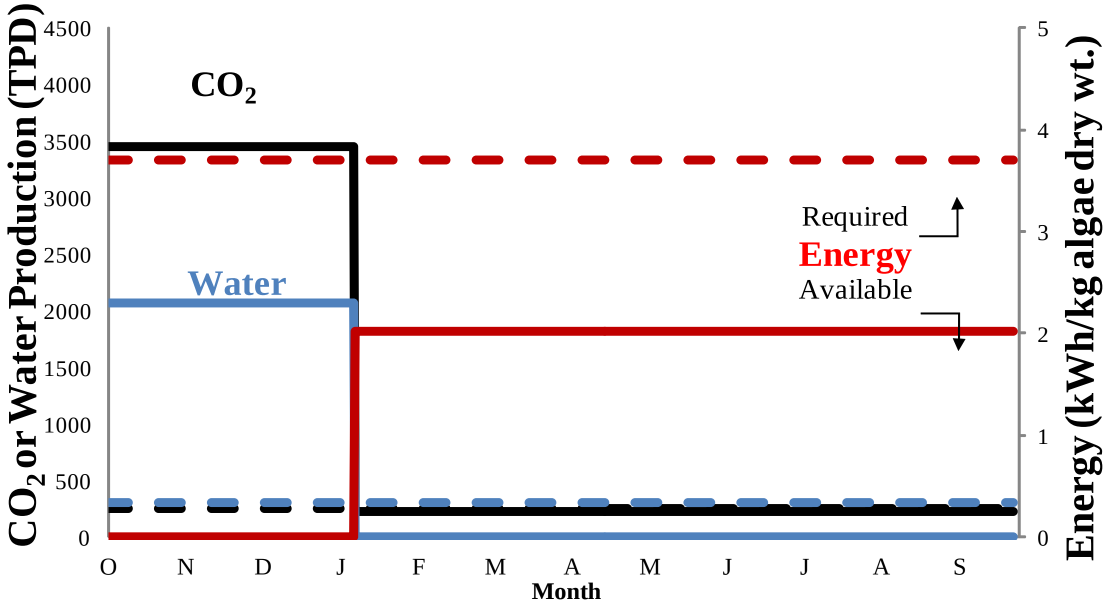
Selected Main Input Variables	base case	range
Excess Bagasse Available	15%	0-20
Algae oil content	30%	10-40
CO2 utilization	60%	40-100
culture density (g/L)	0.5	0.1-2
% oil converted to B100	98%	80-100
Boiler efficiency	55%	40-60
cane fiber content	13%	12-16
oil extraction	61%	21-95

Original Estimates

Algae Produced	**29920**	tons dry wt/yr
	27200	metric tons dry wt/yr
Farm Area Required	**1083**	acres
3.3% of sugarcane	**438**	ha
2,278 gal oil/acre/yr	**39**	tons meal/acre/yr
21,305 L/ha/yr	**87**	metric tons/ha/yr
Biodiesel Produced	**1,255,444**	gal B100/yr
	4,752,359	L B100/yr
Overall Photosynthetic Efficiency	**2.8%**	EROI
CO2 Emissions Reduction of Mill	**11%**	1.25

1159 gal/acre
10841 L/ha

Resources Available at a Sugar Mill for Algal Biodiesel Production



Assumptions:
15% excess bagasse is used when not processing sugar
55% boiler efficiency

By linking the input values from the "Algae Production" tab to the highlighted inputs below, a quick evaluation of these assumptions on the results can be observed. For example, set 'Algae Production'B15 equal to 'Results'D5, then vary the input to see the effect on biodiesel production and Energy ratio.

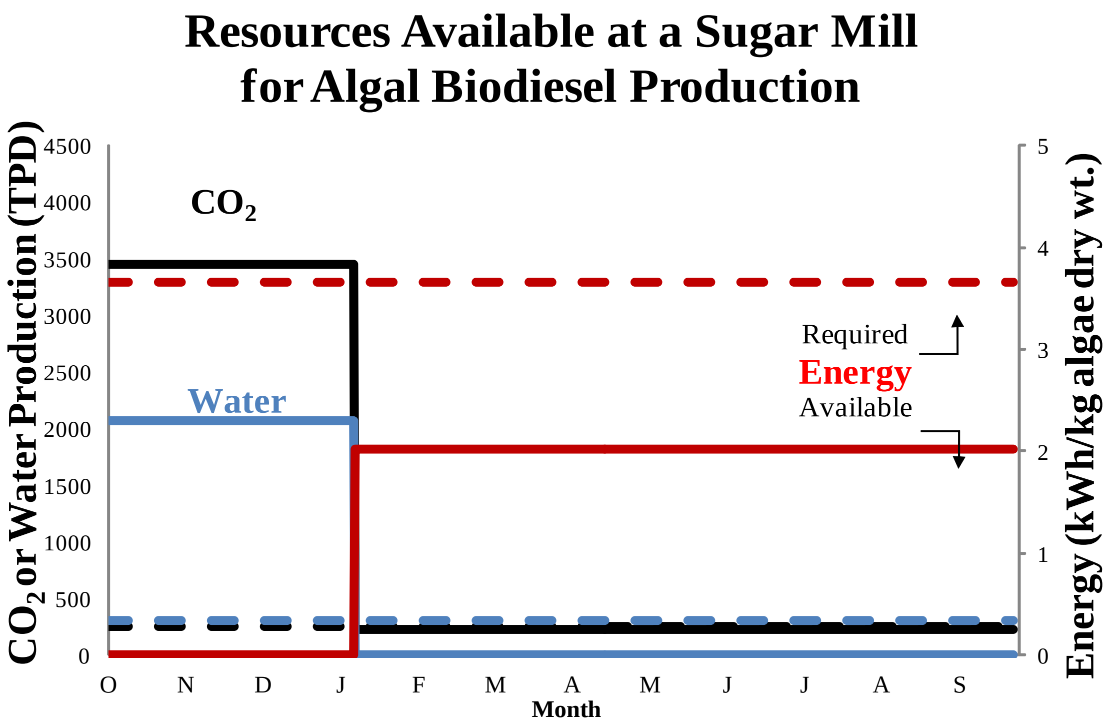
Selected Main Input Variables	base case	range	
Excess Bagasse Available	15%	0-20	
Algae oil content	30%	10-40	
CO2 utilization	60%	40-100	
culture density (g/L)	0.5	0.1-2	
% oil converted to B100	19%	80-100	
Boiler efficiency	55%	40-60	
cane fiber content	13%	12-16	
oil extraction	61%	21-95	
Algae Produced	**29920**	tons dry wt/yr	
	27200	metric tons dry wt/yr	
Farm Area Required	**1083**	acres	
3.3% of sugarcane	**438**	ha	
2,278 gal oil/acre/yr	**39**	tons meal/acre/yr	
21,305 L/ha/yr	**87**	metric tons/ha/yr	
Biodiesel Produced	**243,402**	gal B100/yr	
	921,376	L B100/yr	
Overall Photosynthetic Efficiency		**2.8%**	EROI
CO2 Emissions Reduction of Mill		**11%**	0.91

Revised Estimates

incorporating laboratory results

225 gal/acre

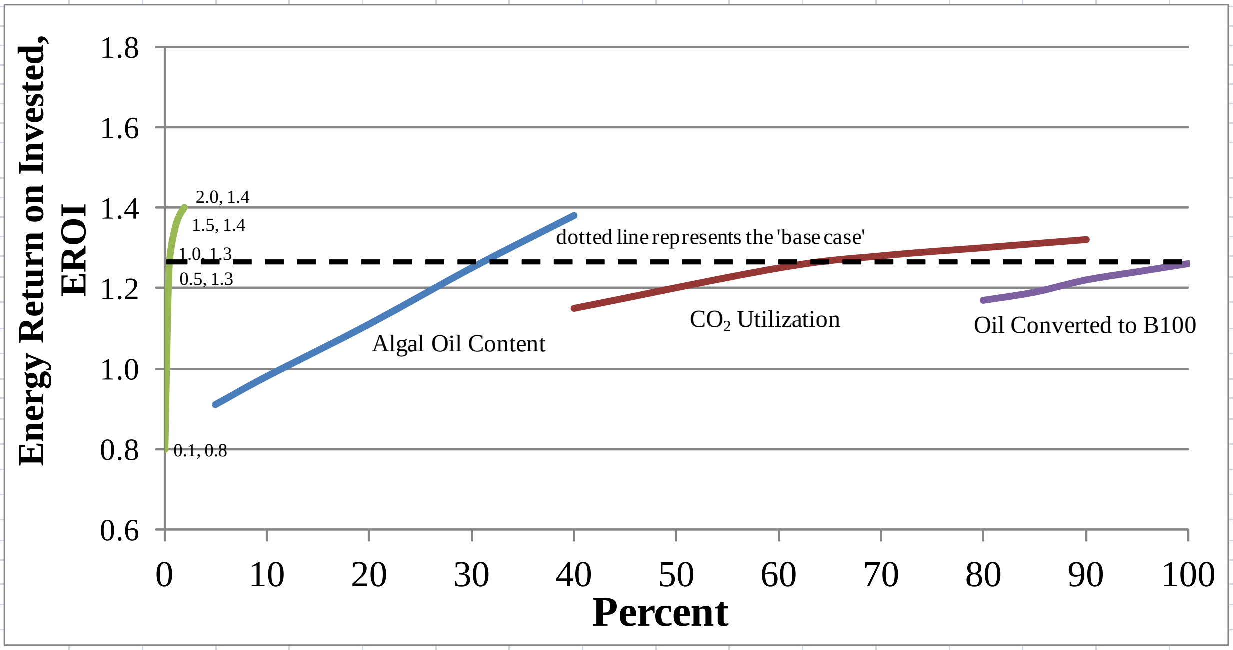
2102 L/ha


Resources Available at a Sugar Mill for Algal Biodiesel Production

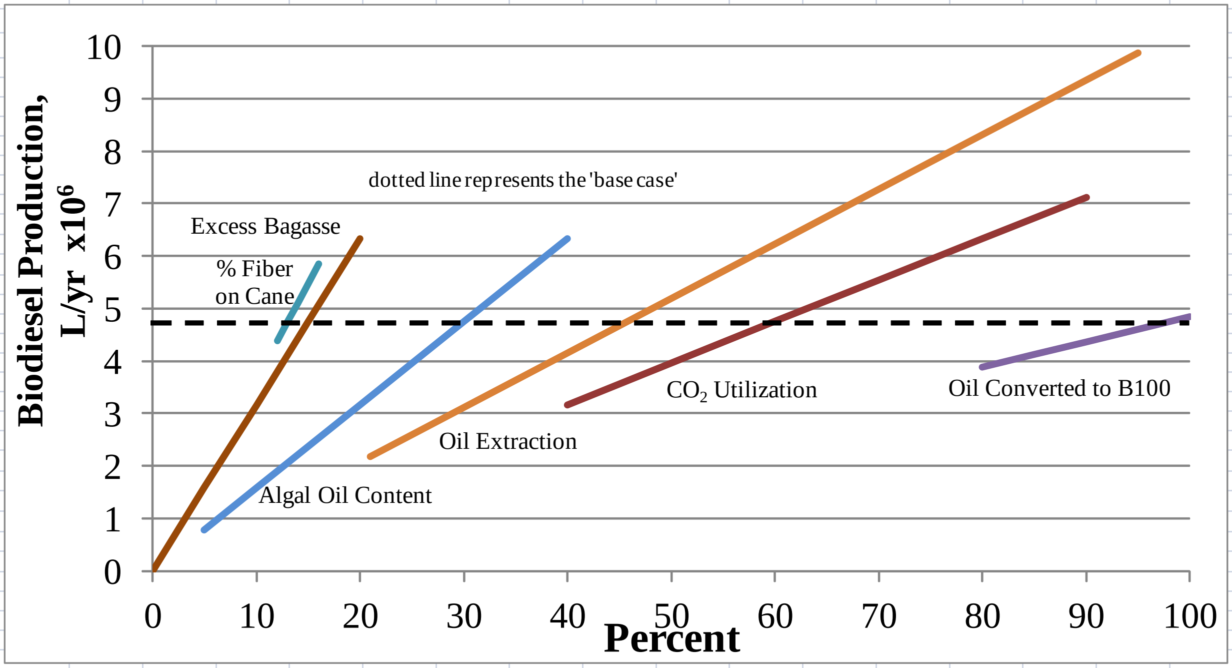
Assumptions:

15% excess bagasse is used when not processing sugar

55% boiler efficiency

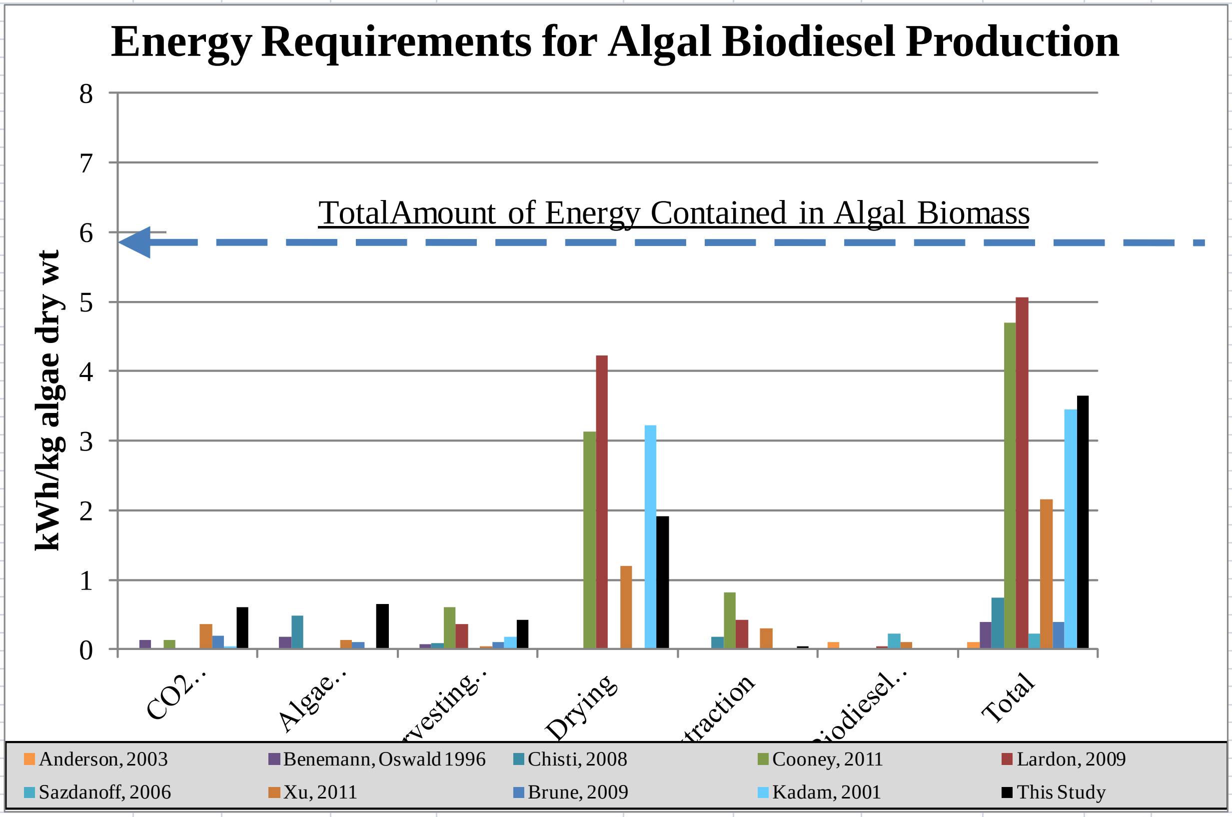


Energy Return on Invested, EROI
1.8
1.6
1.4
1.2
1.0
0.8
0.6
2.0, 1.4
1.5, 1.4
1.0, 1.3
0.5, 1.3
0.1, 0.8
dotted line represents the 'base case'
Algal Oil Content
CO$_2$ Utilization
Oil Converted to B100
0
10
20
30
40
50
60
70
80
90
100
Percent

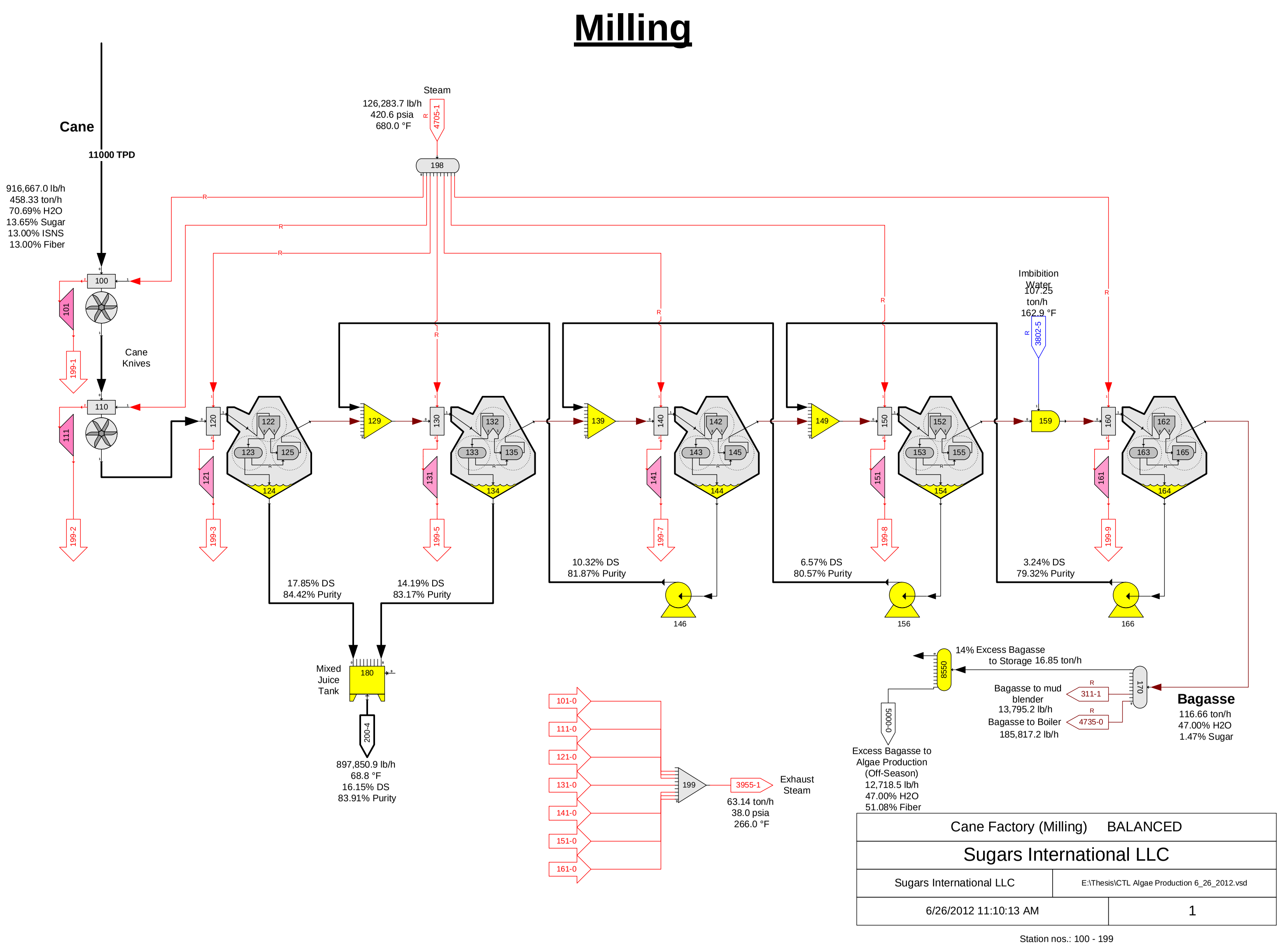


Biodiesel Production, L/yr x10^6
10
9
8
7
6
5
4
3
2
1
0
dotted line represents the 'base case'
Excess Bagasse
% Fiber on Cane
CO$_2$ Utilization
Oil Converted to B100
Oil Extraction
Algal Oil Content
0
10
20
30
40
50
60
70
80
90
100
Percent

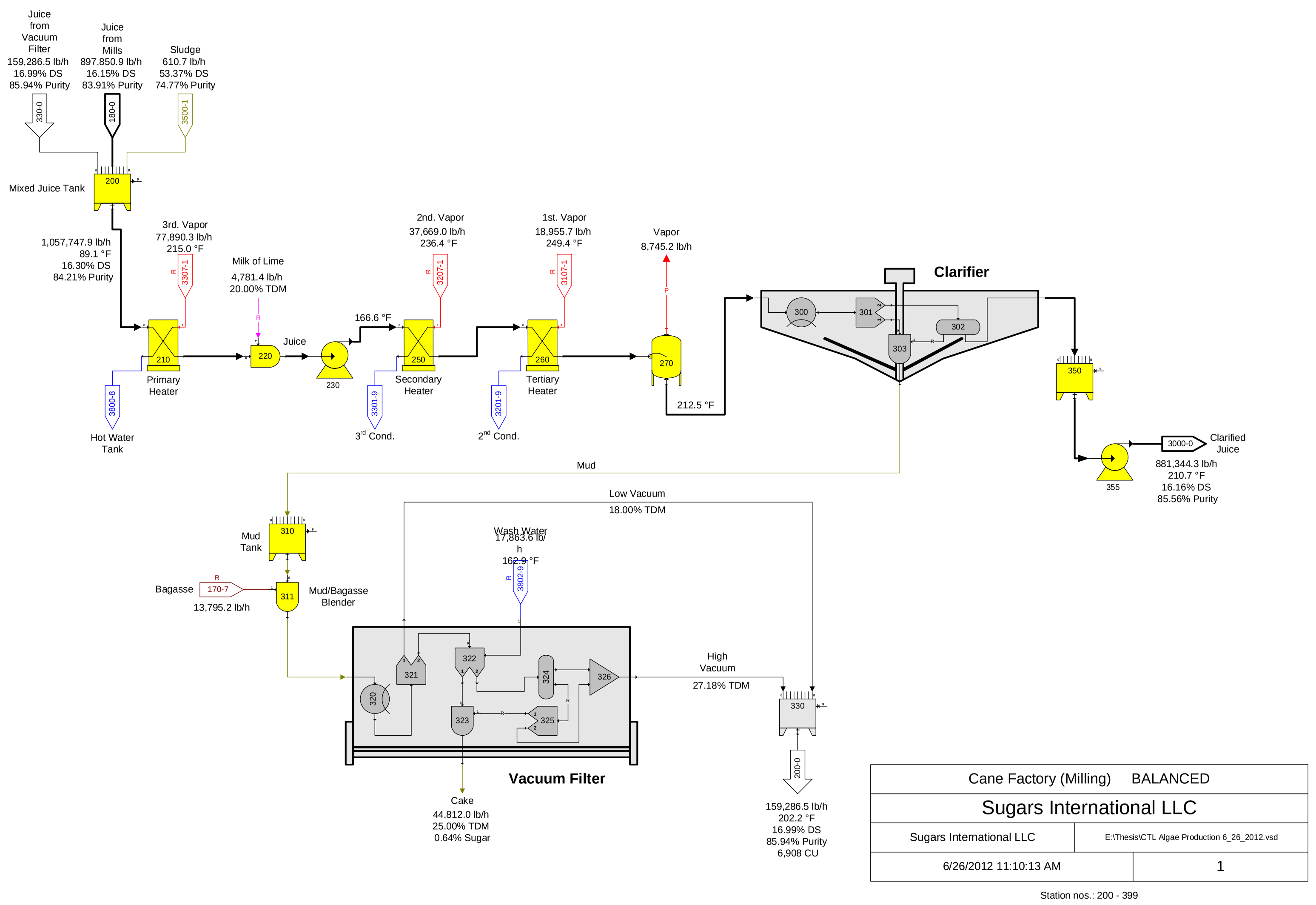
Comparison of Reported Value (kWh/kg algae)										
Comparison kWh/kg algae dw		Table 5 pg.17	pg.176	. Table 8.3 pg.146	Table 1 pg.351	* assuming 30% by wt oil 80% recovery				
	This Study	Kadam, 2001	Cooney, 2011	Benemann, Oswald 1996	Chisti, 2008	Sazdanoff, 2006	Anderson, 2003	Lardon, 2009	Xu, 2011	Brune, 2009
CO_2 Capture & Deli	0.60	0.05	0.13	0.14					0.36	0.20
Algae Cultivation	0.66			0.18	0.49				0.14	0.10
Harvesting (Dewate	0.42	0.18	0.60	0.07	0.08			0.37	0.05	0.10
Drying	1.91	3.22	3.13					4.23	1.20	
Oil Extraction	0.05		0.83		0.18			0.42	0.30	
Biodiesel Conversio	0.01					0.23	0.10	0.04	0.11	
Total	3.65	3.44	4.69	0.39	0.75	0.23	0.10	5.06	2.15	0.40



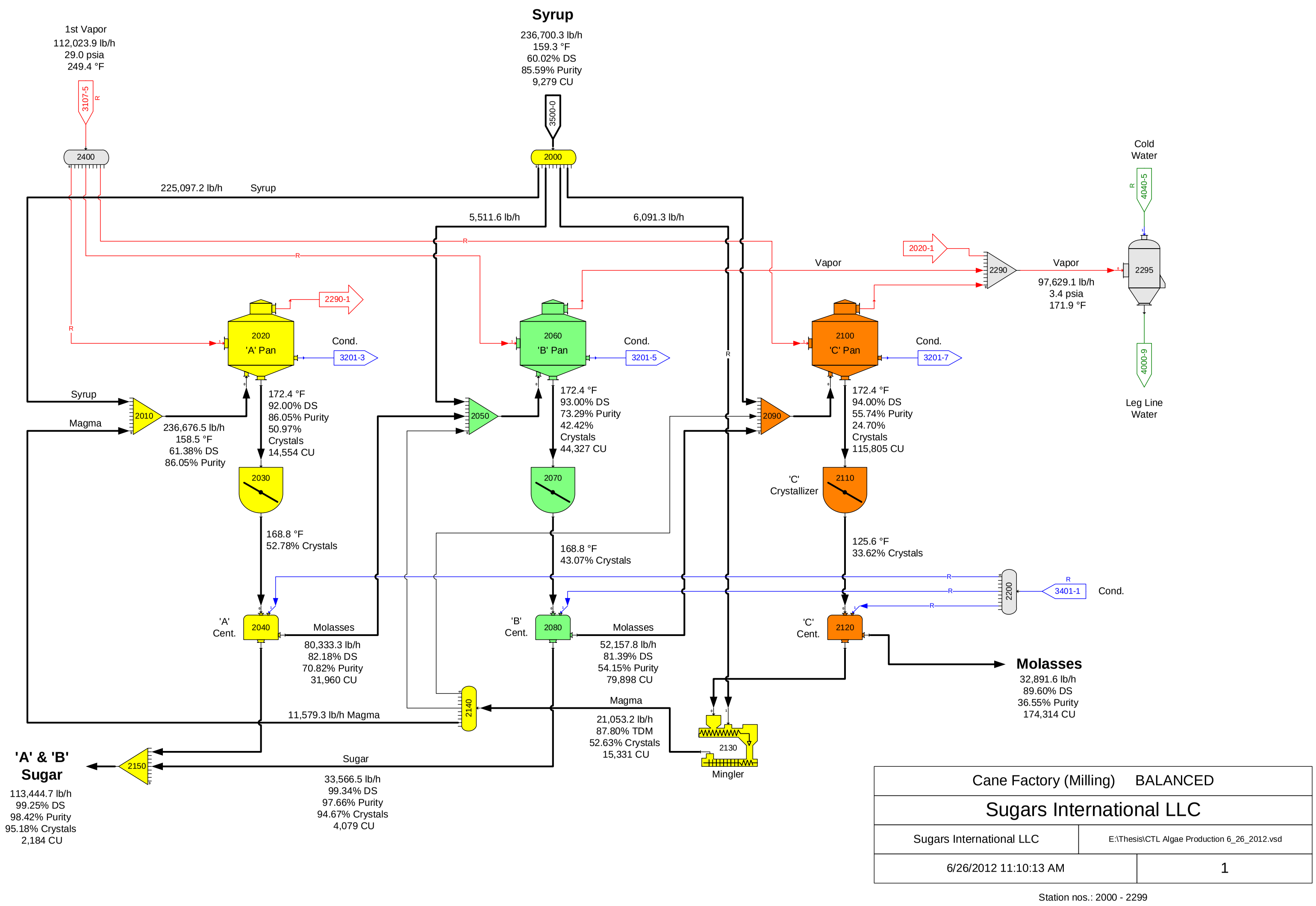
Appendix B: Material and Energy Balance Sugars Model



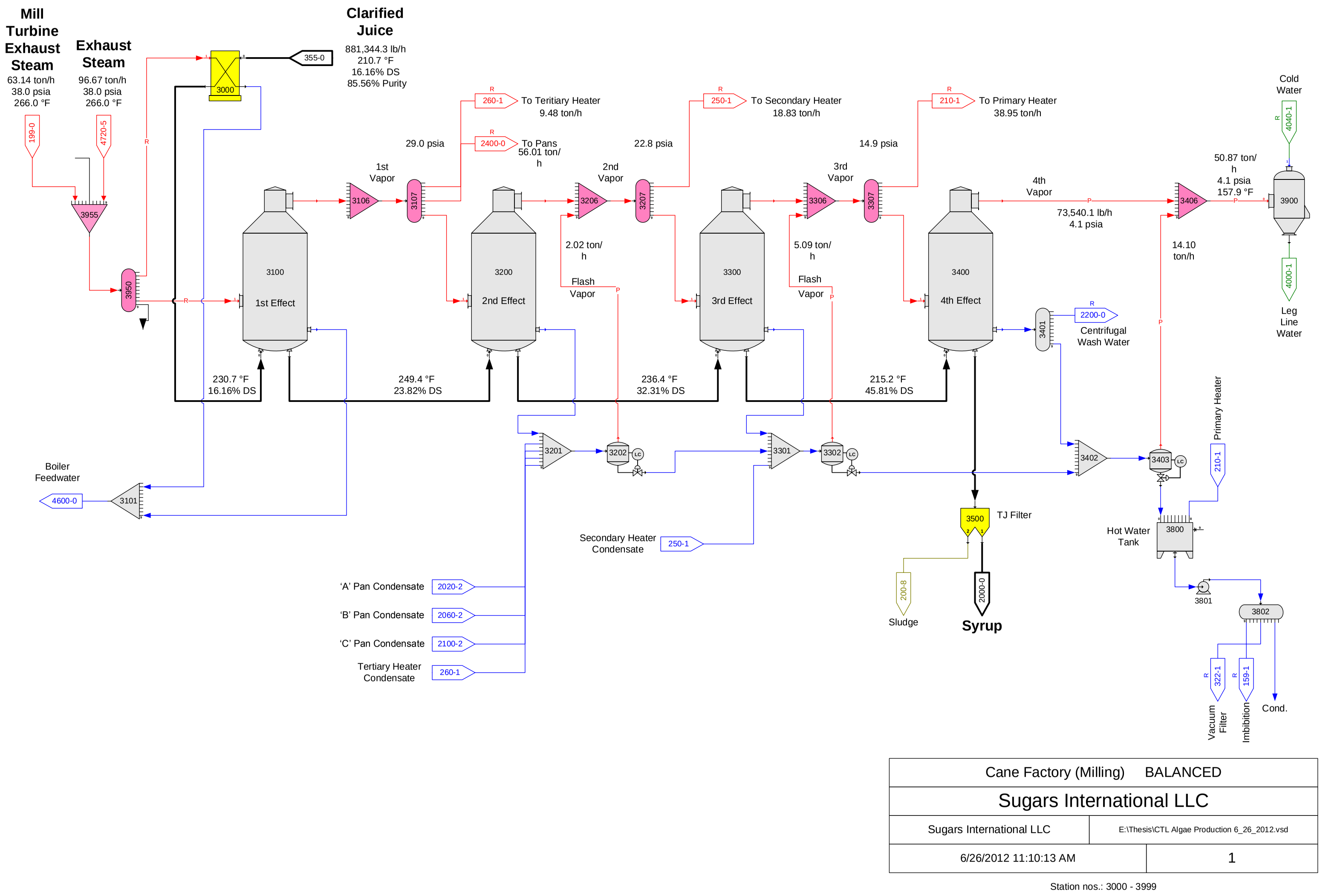
Clarification



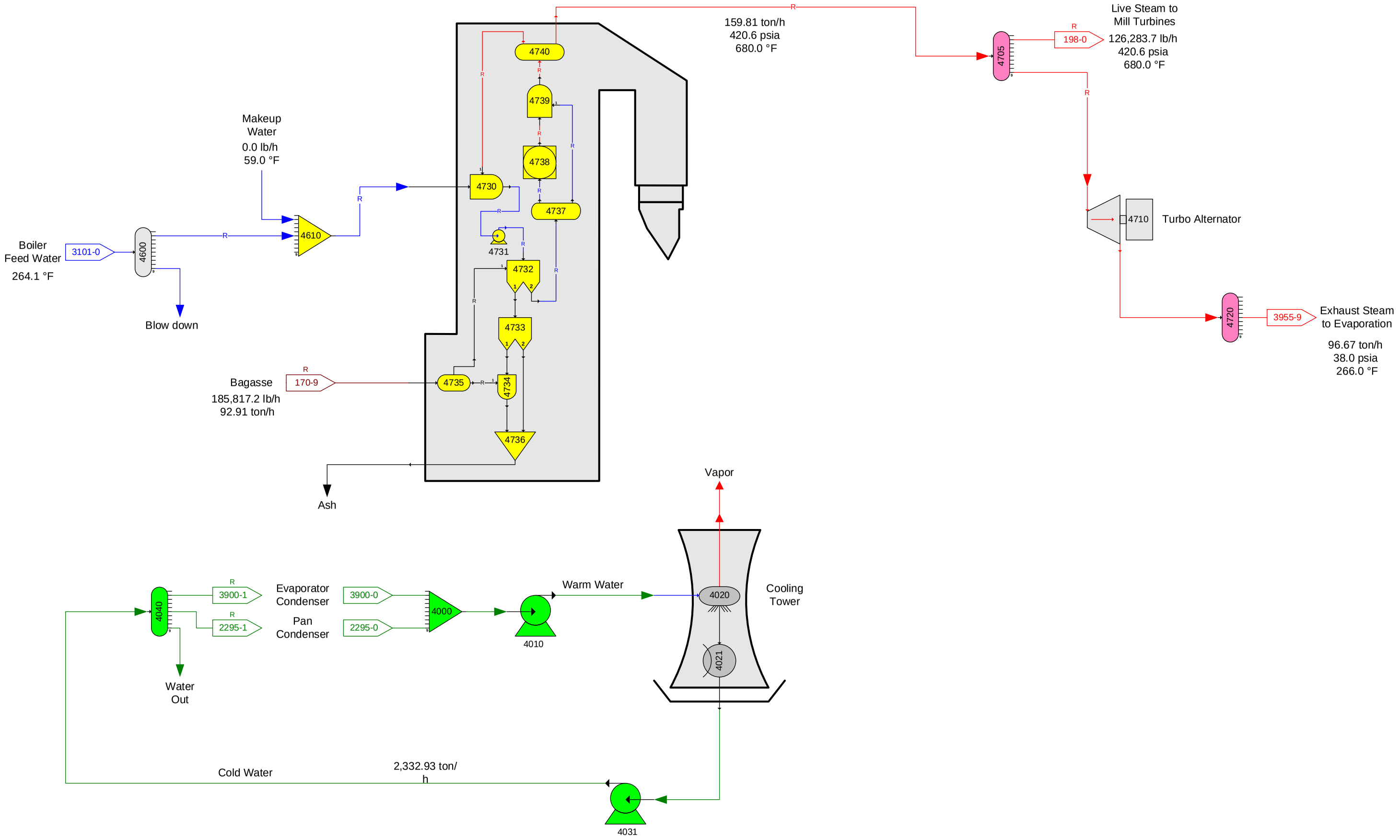
Crystallization



Evaporation

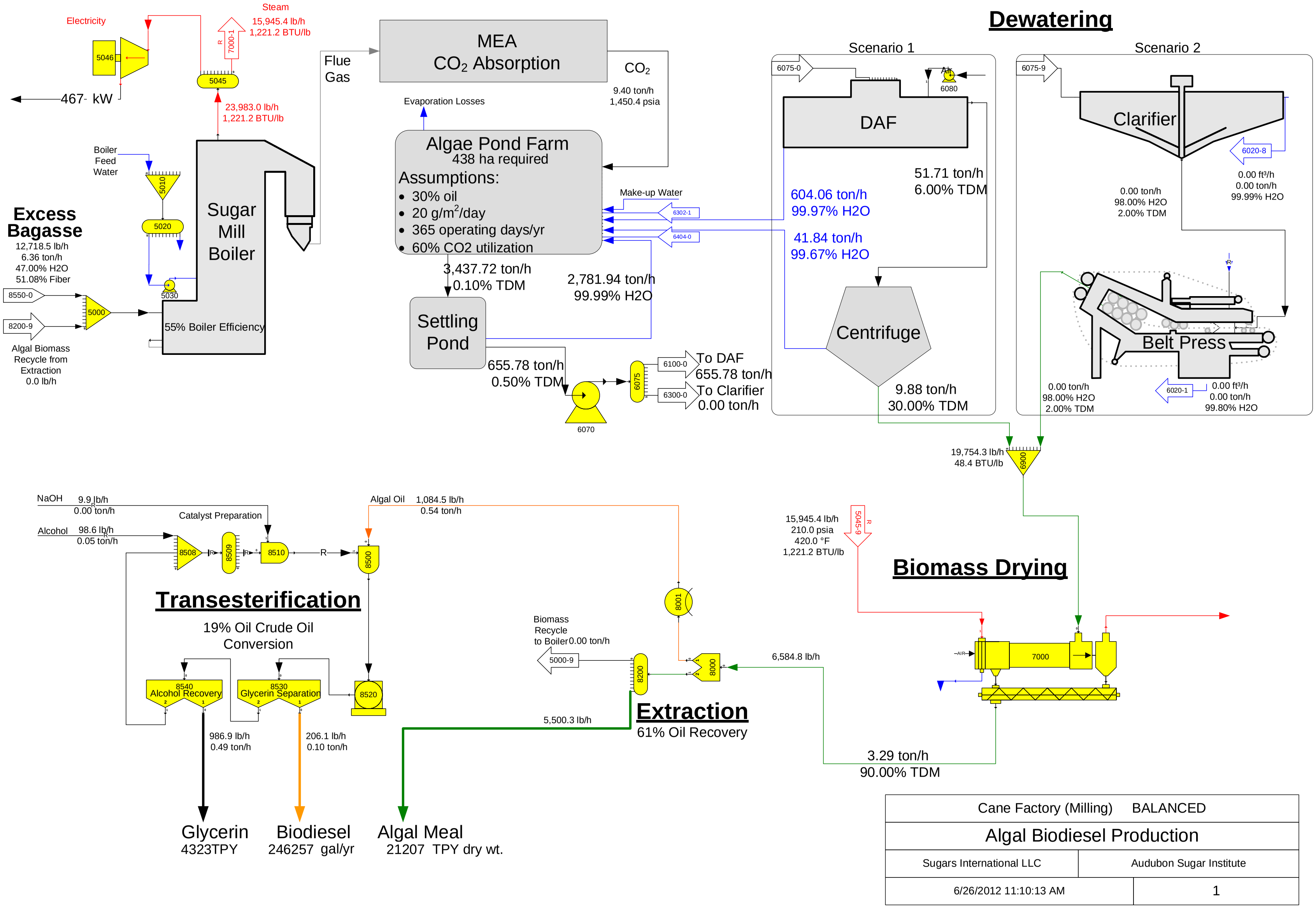


Steam And Water



Cane Factory (Milling) BALANCED	
Sugars International LLC	
Sugars International LLC	E:\Thesis\CTL Algae Production 6_26_2012.vsd
7/13/2012 10:07:20 AM	1

Station nos.: 4000 - 4799


Dewatering
Scenario 1
Scenario 2
6075-0
6080
Air
DAF
51.71 ton/h
6.00% TDM
604.06 ton/h
99.97% H2O
41.84 ton/h
99.67% H2O
Centrifuge
9.88 ton/h
30.00% TDM
6075-9
Clarifier
6020-8
0.00 ft³/h
0.00 ton/h
99.99% H2O
0.00 ton/h
98.00% H2O
2.00% TDM
Belt Press
6020-1
0.00 ton/h
98.00% H2O
2.00% TDM
0.00 ft³/h
0.00 ton/h
99.80% H2O
Electricity
5046
467- kW
Steam
15,945.4 lb/h
1,221.2 BTU/lb
7000-1
R
5045
23,983.0 lb/h
1,221.2 BTU/lb
Boiler Feed Water
5010
5020
5030
Excess Bagasse
12,718.5 lb/h
6.36 ton/h
47.00% H2O
51.08% Fiber
8550-0
8200-9
5000
Algal Biomass Recycle from Extraction
0.0 lb/h
Sugar Mill Boiler
55% Boiler Efficiency
Flue Gas
MEA
CO2 Absorption
CO2
9.40 ton/h
1,450.4 psia
Evaporation Losses
Algae Pond Farm
438 ha required
Assumptions:
30% oil
20 g/m²/day
365 operating days/yr
60% CO2 utilization
Make-up Water
6302-1
6404-0
3,437.72 ton/h
0.10% TDM
2,781.94 ton/h
99.99% H2O
Settling Pond
655.78 ton/h
0.50% TDM
6070
6075
6100-0
6300-0
To DAF
655.78 ton/h
To Clarifier
0.00 ton/h
6069
19,754.3 lb/h
48.4 BTU/lb
Biomass Drying
5045-9
R
15,945.4 lb/h
210.0 psia
420.0 °F
1,221.2 BTU/lb
7000
AIR
3.29 ton/h
90.00% TDM
6,584.8 lb/h
8000
8001
8200
Biomass Recycle to Boiler 0.00 ton/h
5000-9
Extraction
61% Oil Recovery
5,500.3 lb/h
NaOH 9.9 lb/h
0.00 ton/h
Alcohol 98.6 lb/h
0.05 ton/h
Catalyst Preparation
8508
8509
8510
R
Algal Oil 1,084.5 lb/h
0.54 ton/h
8500
Transesterification
19% Oil Crude Oil Conversion
8540
Alcohol Recovery
8530
Glycerin Separation
8520
986.9 lb/h
0.49 ton/h
206.1 lb/h
0.10 ton/h
Glycerin
4323TPY
Biodiesel
246257 gal/yr
Algal Meal
21207 TPY dry wt.
Cane Factory (Milling) BALANCED
Algal Biodiesel Production
Sugars International LLC
Audubon Sugar Institute
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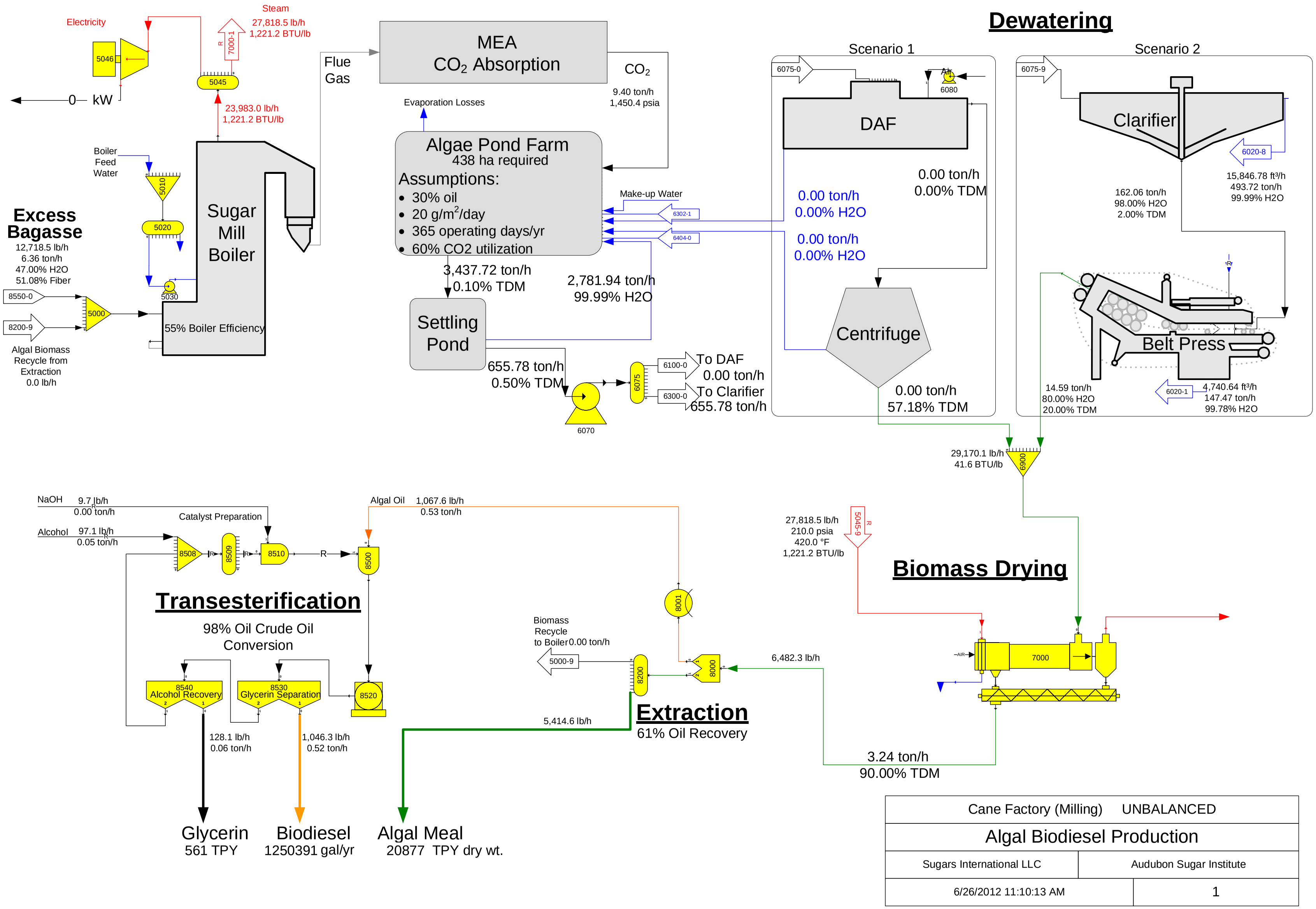
Dewatering
Scenario 1
Scenario 2
6075-0
6075-9
Air
6080
DAF
Clarifier
6020-8
15,846.78 ft³/h
493.72 ton/h
99.99% H2O
162.06 ton/h
98.00% H2O
2.00% TDM
0.00 ton/h
0.00% TDM
0.00 ton/h
0.00% H2O
0.00 ton/h
0.00% H2O
Centrifuge
0.00 ton/h
57.18% TDM
Belt Press
14.59 ton/h
80.00% H2O
20.00% TDM
6020-1
4,740.64 ft³/h
147.47 ton/h
99.78% H2O
Electricity
5046
0 kW
Steam
27,818.5 lb/h
1,221.2 BTU/lb
7000-1
5045
23,983.0 lb/h
1,221.2 BTU/lb
Boiler Feed Water
5010
5020
5030
Sugar Mill Boiler
55% Boiler Efficiency
Excess Bagasse
12,718.5 lb/h
6.36 ton/h
47.00% H2O
51.08% Fiber
8550-0
8200-9
5000
Algal Biomass Recycle from Extraction
0.0 lb/h
Flue Gas
MEA
CO$_2$ Absorption
CO$_2$
9.40 ton/h
1,450.4 psia
Evaporation Losses
Algae Pond Farm
438 ha required
Assumptions:
30% oil
20 g/m^2/day
365 operating days/yr
60% CO2 utilization
Make-up Water
6302-1
6404-0
3,437.72 ton/h
0.10% TDM
2,781.94 ton/h
99.99% H2O
Settling Pond
655.78 ton/h
0.50% TDM
6070
6075
6100-0
To DAF
0.00 ton/h
6300-0
To Clarifier
655.78 ton/h
29,170.1 lb/h
41.6 BTU/lb
6900
27,818.5 lb/h
210.0 psia
420.0 °F
1,221.2 BTU/lb
5045-9
Biomass Drying
AIR
7000
6,482.3 lb/h
3.24 ton/h
90.00% TDM
NaOH
9.7 lb/h
0.00 ton/h
Alcohol
97.1 lb/h
0.05 ton/h
Catalyst Preparation
8508
8509
8510
R
8500
Algal Oil
1,067.6 lb/h
0.53 ton/h
8001
8000
Biomass Recycle to Boiler
0.00 ton/h
5000-9
8200
5,414.6 lb/h
Extraction
61% Oil Recovery
Transesterification
98% Oil Crude Oil Conversion
8540
Alcohol Recovery
8530
Glycerin Separation
8520
128.1 lb/h
0.06 ton/h
1,046.3 lb/h
0.52 ton/h
Glycerin
561 TPY
Biodiesel
1250391 gal/yr
Algal Meal
20877 TPY dry wt.
Cane Factory (Milling) UNBALANCED
Algal Biodiesel Production
Sugars International LLC
Audubon Sugar Institute
6/26/2012 11:10:13 AM
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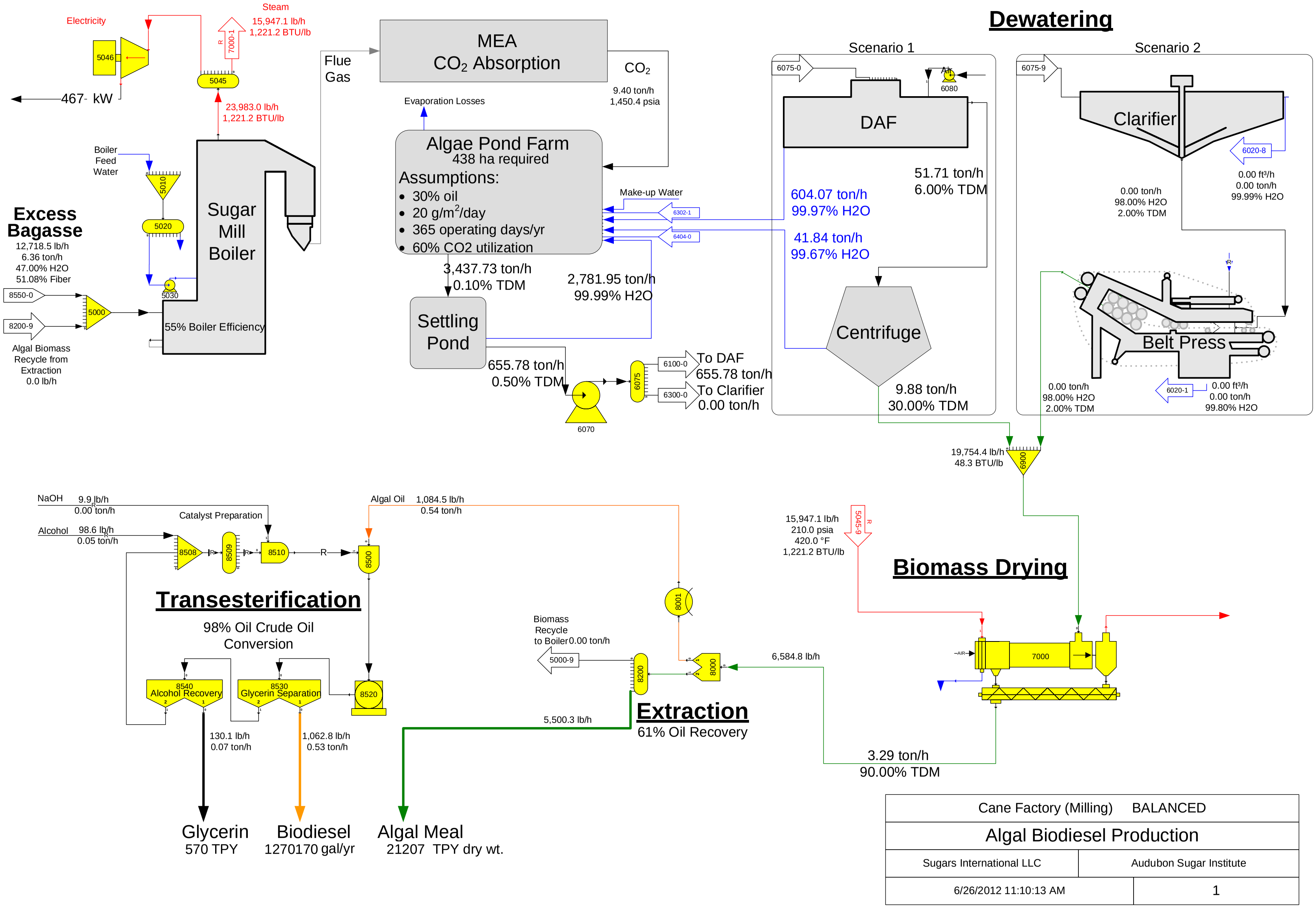
Dewatering
Scenario 1
Scenario 2
6075-0
6080
Air
DAF
51.71 ton/h
6.00% TDM
604.07 ton/h
99.97% H2O
41.84 ton/h
99.67% H2O
Centrifuge
9.88 ton/h
30.00% TDM
6075-9
Clarifier
6020-8
0.00 ft³/h
0.00 ton/h
99.99% H2O
0.00 ton/h
98.00% H2O
2.00% TDM
Belt Press
0.00 ton/h
98.00% H2O
2.00% TDM
6020-1
0.00 ft³/h
0.00 ton/h
99.80% H2O
19,754.4 lb/h
48.3 BTU/lb
6900
MEA
CO2 Absorption
Flue
Gas
CO2
9.40 ton/h
1,450.4 psia
Evaporation Losses
Algae Pond Farm
438 ha required
Assumptions:
• 30% oil
• 20 g/m2/day
• 365 operating days/yr
• 60% CO2 utilization
Make-up Water
6302-1
6404-0
3,437.73 ton/h
0.10% TDM
2,781.95 ton/h
99.99% H2O
Settling
Pond
655.78 ton/h
0.50% TDM
6070
6075
6100-0
To DAF
655.78 ton/h
6300-0
To Clarifier
0.00 ton/h
Electricity
5046
467- kW
Steam
15,947.1 lb/h
1,221.2 BTU/lb
7000-1
R
5045
23,983.0 lb/h
1,221.2 BTU/lb
Boiler
Feed
Water
5010
5020
5030
Sugar
Mill
Boiler
55% Boiler Efficiency
Excess
Bagasse
12,718.5 lb/h
6.36 ton/h
47.00% H2O
51.08% Fiber
8550-0
8200-9
5000
Algal Biomass
Recycle from
Extraction
0.0 lb/h
NaOH
9.9 lb/h
0.00 ton/h
Alcohol
98.6 lb/h
0.05 ton/h
Catalyst Preparation
8508
8509
8510
R
8500
Algal Oil
1,084.5 lb/h
0.54 ton/h
Transesterification
98% Oil Crude Oil
Conversion
8540
Alcohol Recovery
8530
Glycerin Separation
8520
130.1 lb/h
0.07 ton/h
1,062.8 lb/h
0.53 ton/h
Glycerin
570 TPY
Biodiesel
1270170 gal/yr
Algal Meal
21207 TPY dry wt.
8001
8000
8200
Biomass
Recycle
to Boiler0.00 ton/h
5000-9
5,500.3 lb/h
Extraction
61% Oil Recovery
6,584.8 lb/h
3.29 ton/h
90.00% TDM
15,947.1 lb/h
210.0 psia
420.0 °F
1,221.2 BTU/lb
5045-9
R
Biomass Drying
AIR
7000
Cane Factory (Milling) BALANCED
Algal Biodiesel Production
Sugars International LLC
Audubon Sugar Institute
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Appendix C: Algal Oil Extraction Calculations

Moisture Content

Sample	pan weight (g)	paste weight (g)	dry weight (g)		mass of dry algae	
1	2.1928	20.4095	5.4672	16%	3.2744	
2	2.1870	20.2936	5.4190	16%	3.2320	
3	2.1930	20.2913	5.6100	17%	3.4170	
4	2.1913	20.5445	5.5828	17%	3.3915	
5	2.1955	20.4761	5.6576	17%	3.4621	
6	2.1988	20.4772	5.7861	18%	3.5873	
7	2.2069	20.5633	5.8233	18%	3.6164	
8	2.1737	20.0462	5.4661	16%	3.2924	
9	2.1977	20.2444	5.5161	16%	3.3184	
10	2.2075	20.4325	5.5789	17%	3.3714	
11	2.2078	20.4207	5.7103	17%	3.5025	
12	2.2066	20.2160	5.6374	17%	3.4308	
13	2.2165	20.1107	5.7552	18%	3.5387	
14	2.2153	20.4384	6.0883	19%	3.8730	
15	2.2142	20.4153	5.5604	16%	3.3462	
16	2.2104	20.0389	6.0613	19%	3.8509	
17	2.2025	20.1539	5.7341	18%	3.5316	
18	2.1914	20.2823	6.6642	22%	4.4728	* note: was not dried thoroughly
19	2.1987	20.2014	5.4660	16%	3.2673	
20	2.1871	20.1617	5.5246	17%	3.3375	
21	2.2091	20.3392	5.4149	16%	3.2058	
22	2.2052	20.4513	5.5764	16%	3.3712	
23	2.1720	20.1500	5.4008	16%	3.2288	
24	2.1843	20.2006	5.4160	16%	3.2317	
25	2.1799	21.5272	5.6646	16%	3.4847	
			AVERAGE =	17%	86.6364	g algae dry weight total
			AVERAGE DEVIATION=	0.7%		

Soxhlet Hexane Extraction

Cup #	biomass (g)	cup weight (g)	thimble weight (g)	
7	4.9270	46.7341	30.0394	
15	4.9929	45.9335	29.5455	
16	5.0634	46.1325	29.9651	
Average	4.9944			
	Oil Content	cup w/ oil weight (g)	de-oiled biomass & thimble weight (g)	
	5.2%	46.9904	34.3358	
	5.1%	46.1899	33.9428	
	5.1%	46.3895	34.4325	
average	5.1%			
		Difference		% recovery
		0.2563	4.2964	92.4%
		0.2564	4.3973	93.2%
		0.2570	4.4674	93.3%

Oil collected in 50mL centrifuge tubes, a nitrogen stream was used to evaporate any residual solvent and provide an inert blanket.

The tubes were stored at room temperature until analyzed.

Sample #	Vial Tare Weight	Vial + Extract	Extract "Oil" (g)
Soxhlet-Hexane 1	13.4338	13.9038	0.4700
Soxhlet-Hexane 2	13.4026	13.9081	0.5055
Soxhlet-Hexane 3	13.4169	13.8998	0.4829
		Oil Extraction	9.7%

Soxhlet Ethanol Extraction

Cup #	biomass (g)	cup weight (g)		thimble weight (g)		
11	4.9330	45.8552		30.1274		
13	5.1353	46.3290		29.7516		
14	4.9787	45.6555		29.7618		
	Oil Content	cup w/ oil weight (g)		de-oiled biomass & thimble weight (g)		
	36.2%	47.6411		34.5391		
	43.5%	48.5604		33.9414		
	30.6%	47.1776		34.3784		
average	36.7%					
		Difference			% recovery	
		1.7859	-1.2646	4.4117	125.6%	<-- >100%
	0.3585078	2.2314	-1.2859	4.1898	125.0%	due to
		1.5221	-1.1600	4.6166	123.3%	residua
						solvent
	Sample #	Vial Tare Weight		Vial + Extract	Extract "Oil" (g)	
	Soxhlet-Ethanol 1	13.4661		15.512	2.0459	0.41473748
	Soxhlet-Ethanol 2	13.322		15.9009	2.5789	0.50219072
	Soxhlet-Ethanol 3	13.5104		13.7124	0.2020	* note:
					45.8%	

3-Stage Cross Current Extraction - Hexane

Sample #	dried alga	vial tare we	aluminum evap dish tare weight (g)						
1	4.9670	13.4912	2.7362						
2	5.0180	13.4118	2.7299						
3	5.0032	13.3603	2.7644						
Average	4.9961							% of max	
Stage 1	25.23667	g, hexane per sample.						crude oil	
sample	oil + evap	tube with		Oil Extracted in Stage 1 (g)					
1	2.8547	20.2257			0.1185			46%	
2	2.8517	20.1718			0.1218			47%	
3	2.8866	20.3415			0.1222			48%	
				Average	0.1208	StDev	0.0020	47%	AVG
				bottoms biomass	Residual s	solvent/biomass		0.6%	STDEV
				6.7345	1.7675	0.355849			
				6.7600	1.7420	0.34715			
				6.9812	1.9780	0.395347			
			average	6.8252	1.8292	0.3661			
Stage 2	25.23667	g, hexane per sample.							
sample	oil + evap	tube with		Oil Extracted in Stage 2 (g)					
1	2.8867	20.2617			0.0320			0.1254	
2	2.8827	20.2072			0.0310			0.1202	
3	2.9175	20.0490			0.0309			0.1202	
				Average	0.0313	StDev	0.0006	12%	AVG
				bottoms biomass	Residual s	solvent/biomass		0.3%	STDEV
				6.7705	1.8035	0.363096			
				6.7954	1.7774	0.354205			
				6.6887	1.6855	0.336884			
			average	6.7515	1.7555	0.3514			
Stage 3	25.23667	g, hexane per sample.							
sample	oil + evap	tube with		Oil Extracted in Stage 3 (g)					
1	2.9008	20.3029			0.0141			6%	
2	2.9011	20.2437			0.0184			7%	
3	2.9376	20.2821			0.0201			8%	
				Average	0.0175	StDev	0.0031	7%	AVG
				bottoms biomass	Residual s	solvent/biomass		1%	STDEV
				6.8117	1.8447	0.371391			
				6.8319	1.8139	0.361479			
				6.9218	1.9186	0.383475			
			average	6.8551	1.8591	0.3721			
sample	Total Oil C	Biomass % c	% oil extrac	% oil extracted compared to Soxhlet			66.1%		
1	0.1646	3.3%	65%						
2	0.1712	3.4%	66%						
3	0.1732	3.5%	67%	residual solvent in biomass (g)			0.36321		
Total oil colleted		0.5090	g						

3-Stage Cross Current Extraction - Ethanol

Sample #	dried alga	vial tare we	aluminum evap dish tare weight (g)						
1	5.0028	13.5785	2.7643						
2	5.0226	13.4442	2.6960						
3	5.0152	13.7480	2.7299						
Average:	5.0135							% of max	
Stage 1	25.0243	g, ethanol (200 proof) per sample						crude oil	
sample	oil + evap	tube with		Oil Extracted in Stage 1 (g)					
1	3.1093	20.4830			0.3450			19%	
2	3.0208	20.3647			0.3248			18%	
3	3.0399	20.6739			0.3100			17%	
				Average	0.3266	StDev	0.0176	18%	AVG
				bottoms biomass	Residual s	solvent/biomass		1.0%	STDEV
				6.9045	1.9017	0.380			
				6.9205	1.8979	0.3794			
				6.9259	1.9107	0.3819			
			average	6.9170	1.9034	0.3805			
Stage 2	25.0243	g, ethanol (200 proof) per sample							
sample	oil + evap	tube with		Oil Extracted in Stage 2 (g)					
1	3.2739	20.3454			0.1646			9%	
2	3.1964	20.2951			0.1756			10%	
3	3.1967	20.4242			0.1568			9%	
				Average	0.1657	StDev	0.0094	9%	AVG
				bottoms biomass	Residual s	solvent/biomass		0.5%	STDEV
				6.7669	1.7641	0.3526			
				6.8509	1.8283	0.3655			
				6.6762	1.6610	0.3320			
			average	6.7647	1.7511	0.3500			
Stage 3	25.0243	g, ethanol (200 proof) per sample							
sample	oil + evap	tube with		Oil Extracted in Stage 3 (g)					
1	3.4129	20.3800			0.1390			8%	
2	3.3036	20.4258			0.1072			6%	
3	3.3026	21.0294			0.1059			6%	
				Average	0.1174	StDev	0.0187	6%	AVG
				bottoms biomass	Residual s	solvent/biomass		1.0%	STDEV
				6.8015	1.7987	0.3595387			
				6.9816	1.9590	0.3915807			
				7.2814	2.2662	0.4529863			
			average	7.0215	2.0080	0.4014			
				% oil extracted compared to Soxhlet			33.1%		
sample	Total Oil C	Biomass %	% oil extracted						
1	0.6486	13.0%	35%						
2	0.6076	12.1%	33%	residual solvent in biomass (g)			0.37729		
3	0.5727	11.4%	31%						
Total oil colleted		1.8289	g						

Soxhlet Hexane GC-MS Analysis

Cup #	e vial weig	tare weigl	mass of oi	mass of oil used for analysis (μg	% IS GCMS	mass of FAME (μg)	yeild (g FAME/g oi	overall yeild (g FAME/g algae)	
7	13.9178	13.4338	0.4840	10800	2.109	1896.633476	18%	0.9%	
15	13.8936	13.4026	0.4910	8900	2.228	1795.332136	20%	1.0%	
16	13.8839	13.4169	0.4670	10700	2.18	1834.862385	17%	0.9%	stdev
						average	18%	0.9%	0.000842424

Soxhlet Ethanol GC-MS Analysis

Cup #	e vial weig	tare weigl	mass of oi	mass of oil used for analysis (μg	% IS GCMS	mass of FAME (μg)	yeild (g FAME/g oi	overall yeild (g FAME/g algae)	
11	15.5113	13.4661	2.0452	13700	1.88	2127.659574	16%	5.7%	
13	15.9134	13.3220	2.5914	7700	3.25	1230.769231	16%	5.9%	
14	13.7139	13.5104	0.2035	9400	1.667	2399.520096	26%	9.4%	stdev
						average	19%	7.0%	0.020741341

3 Stage Cross Current Hexane GC-MS Analysis

Vial #	ın weight (	re weight (	f oil collec	nass of oil used for analysis (μg	% IS GCMS	mass of FAME (μg)	corrected yeild (g	overall yeild (g FAME/g algae)	
181	2.9011	2.7362	0.1649	11500	1.512	2645.502646	17%	0.6%	
171	2.9017	2.7299	0.1718	12100	1.62	2469.135802	15%	0.5%	
161	2.9387	2.7644	0.1743	10500	1.559	2565.747274	18%	0.6%	stdev
						average	17%	0.6%	0.000520262

3 Stage Cross Current Ethanol GC-MS Analysis

Vial #	ın weight (	re weight (	f oil collec	nass of oil used for analysis (μg	% IS GCMS	mass of FAME (μg)	yeild (g FAME/g oi	overall yeild (g FAME/g algae)	
blank	3.3935	2.7643	0.6292	13700	1.876	2132.196162	12%	1.4%	
131	3.2963	2.6960	0.6003	7700	1.881	2126.528442	21%	2.5%	
121	3.3039	2.7299	0.5740	9400	1.559	2565.747274	20%	2.5%	
						average	18%	2.1%	0.006263999

Appendix D: HISTAR Operating Conditions

TRIAL RUN, February 02, 2011

Media used : F/2 nutrients + tap water

Volume of 1 CFSTR **(V_n)** = 120 gal = **454 L** CFSTR Total = 8

Total volume **(V_T)** = 980 gal = **3634 L**

System Dilution Rate (D_S) : optimized to give highest productivity / optimal composition

In this trial **(D_S)** will be set to : **$0.4\ day^{-1}$**

>>compare to microalgal specific growth rate = 0.31 day^{-1} in batch experiment using Basal media<<

Flushing rate **(Q_T)** = $D_S * V_T = 0.4\ day^{-1} * 3634\ L = 1454\ L\ day^{-1}$ = **$1.01\ L\ min^{-1}$**

Local Dilution Rate (D_n) = $Q_T/V_n = 1454\ L\ day^{-1} / 454\ L = 3.20\ day^{-1}$

F/2 media dosage = 1 mL per 2.5 L

>>in nutrient tank, F/2 is diluted 2x, thus dosage will be 2 mL per 2.5 L

Nutrient addition = $1454\ L\ day^{-1} / (2.5L/2mL) = 1163\ mL\ day^{-1} = 0.81\ mL\ min^{-1}$

This will be added by using FlexFlo peristaltic pump, set to add nutrients for 4 seconds every 3 minutes. *Approximate flowrate of pump : 0.75 mL sec^{-1}

Incoulum will be added by opening turbidostat valve (T1/T2) for 20 seconds every 20 minutes

Data logging : **4** times a day

Data to be logged : pH, T, irradiance (surface,middle,bottom), optical density (664nm,750nm)

Vita

Christian Lohrey was born in San Jose, CA in 1985. He received his Bachelor of Science degrees in Chemical Engineering and Chemistry from the University of Idaho in 2008. Christian started his Master of Science in Biological & Agricultural Engineering at LSU in 2010. While pursuing his MS degree, Christian became familiar with Louisiana's sugar industry through his work at Audubon Sugar Institute where he led research and development projects in cooperation with local sugarcane mills. Mr. Lohrey plans to continue to develop Louisiana's unique agrarian economy with sustainable, renewable production of fuels and chemicals through entrepreneurism.