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LIFE CYCLE ASSESSMENT OF DEWATERING ROUTES FOR ALGAE-DERIVED BIODIESEL PROCESSES

by
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A thesis

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Abstract

Daniel John O'Connell
LIFE CYCLE ASSESSMENT OF DEWATERING ROUTES FOR ALGAE-DERIVED BIODIESEL PROCESSES
2011/12
Mariano Savelski, Ph.D.
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Master of Science in Chemical Engineering

Biodiesel derived from algae is considered a sustainable fuel, but proper downstream processing is necessary to minimize the environmental footprint of this process. Algae is grown in dilute liquid cultures, and achieving the low water contents required for extraction represents one of the greatest challenges for the production of algae derived biodiesel. An analysis of the life cycle emissions associated with harvesting, dewatering, extraction, reaction, and product purification stages for algae biodiesel was performed. This "base case" found 10,500 kg of total emissions per t BD with 96% of those attributed to the spray dryer used for dewatering. Alternative cases were evaluated for various sequences of mechanical and thermal dewatering techniques. The best case, consisted of a disc stack centrifuge, followed by the chamber filter press, and a heat integrated dryer. This resulted in 875 kg emissions /t BD, a 91% reduction from the base case. A model indicated the optimal case of the disc stack centrifuge, spiral plate centrifuge, heat assisted rotary filter press, and then drying, resulting in equivalent reductions. Significant reductions in life cycle emissions were achieved compared to the base case, but further improvements using these existing technologies were limited. Additional improvements will require the development of new techniques for water removal or wet extractions.

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Chapter 1

Introduction

The manufacture of biodiesel from algae feedstock has become an important issue due to the increased demand for alternative fuels. Algae have several advantages over other renewable feedstocks. They can naturally mitigate CO_2 and unlike sourcing biofuels from crops, algae do not compete for the use of arable land.[1] Algae can be used as a feedstock to produce methane and biodiesel.[2, 3, 4] They are adaptable, have the ability to multiply rapidly, and contain a high oil content making it a feasible feedstock in the production of biodiesel.[1] Species, such as *Schizochytrium* sp. and *Botryococcus braunii*, can have high lipid contents of up to 70 wt% oil.[1, 5] This oil is composed mostly of triacylglycerides (TAGs), which can be processed into biodiesel and further blended into conventional diesel fuel, lessening the burden on petroleum derived liquid fuels.[6]

The algae biodiesel process begins with algae cultivation, followed by harvesting to separate the algae from the water. The TAGs are then extracted from the biomass and reacted to break down into fatty acid methyl esters (FAMEs), which are high energy content carbon chains with properties similar to those of diesel fuel. Converting an algae feedstock into biodiesel is energy intensive, which results in the emission of greenhouse gasses, and in turn contributes to the carbon footprint of algae-derived biodiesel. Algae-derived biodiesel plants are not in existence and as a result, it is unknown whether it is a sustainable technology. Life cycle assessments (LCAs) can serve as a decision making tool when determining the most environmentally effective production route for algae-derived biodiesel.

1.1 Process Literature Review

As no industrially proven algae biodiesel process exists, most researchers have proposed a system similar to existing systems for obtaining and converting oil from oleaginous sources such as soybeans. The typical sequence (Figure 1) consists of five steps: growth, harvest, extraction, reaction and purification. Each step may consist of one or more unit operations.

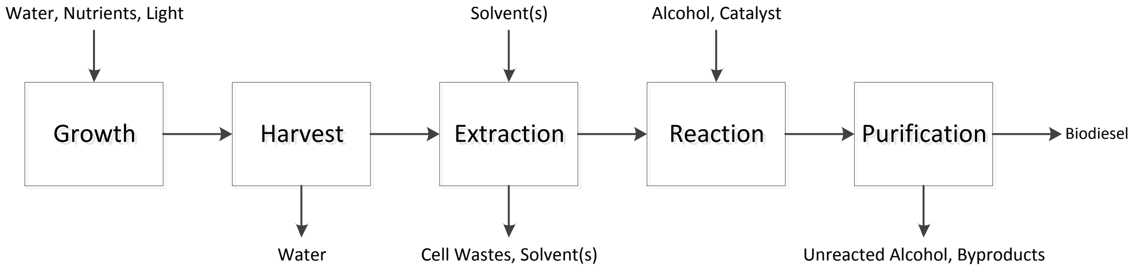


Figure 1. Block diagram of algae biodiesel production.

1.1.1 Growth

The first step in producing algae-derived biodiesel is the cultivation of the algae. Open raceway ponds and photobioreactors (PBRs) are the two main methods of cultivating microalgae. Raceway ponds are outdoor pond systems which utilize solar energy, from which microalgae can convert carbon dioxide and water into sugars. PBRs are controlled systems which can utilize solar energy, both solar energy and artificial lighting, or purely artificial lighting. PBRs are capable of achieving higher microalgae densities, higher productivities, as well as greatly reducing the risk of contamination.[7] Although raceway ponds are capable of producing large volumes of dilute algae cultures, they lack the control required to maintain a homogenous species of microalgae.

The growth phase of the production presents options of algae strain, growth system, and source of nutrients. After growth, the algae biomass is harvested and dried in preparation for extraction of the lipids. TAGs are then extracted from the cell debris; converted into FAMEs during the reaction phase, which are then purified to remove reaction byproducts and impurities from the biodiesel.

1.1.2 Harvesting

The algae growth solution is highly dilute: values of 1 kg algae per m^3 of solution or less are common; however these values vary from 0.5 to 25 kg algae per m^3 depending on the source. [8, 9, 10] It is necessary to reduce the water content by harvesting, thereby increasing the concentration of the biomass for extraction. [8] Water removed is recovered and recycled back to the growth system. This also prevents the need to introduce new, potentially contaminated water and reduces the water consumption.

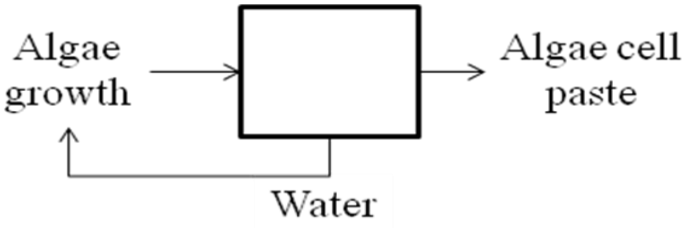


Figure 2. Block flow diagram of algae harvesting.

The harvesting step consumes the largest percentage of energy in the algae biofuel production process and is responsible for 20 to 30 percent of the final cost of the algae biomass.[5, 11] Several methods for harvesting are available: flocculation, filtration, centrifugation, flotation and settling.

A recent analysis compared two methods of harvesting algae: by centrifuge and by filter press.[11] Centrifugation is significantly more energy demanding than filtration. Notably, hexane extraction was chosen, requiring an extra step to dry the algae biomass, creating significant demand on energy and emitting carbon dioxide. Waste heat should be used when the process requires a drying step.[12] Multiple methods for harvesting may be combined to increase the algae concentration.

Flocculation is the agglomeration of multiple molecules into a larger body (a “flocc”) by the attraction of individuals to each other or a flocculating agent. Flocculation is used because the microscopic size of the algae and similar density to water make centrifugation and filtration ineffective on the raw harvest. This process effectively increases the volume and mass of the discrete particles, allowing filters and centrifuges to be sized appropriately, lowering their costs.[8] This decreases the water processed by the dewatering equipment, requiring less process energy.

The floccs are suspended in water and must be collected. Settling, floating, filtration and centrifugation are all possible collection methods.[4, 13, 14] Centrifugation and filtration are unlikely choices because of the high volume of liquid being processed. If the floccs are formed within the algae growth system, they must be harvested without disrupting the continuing growth of the other algae in the system. The major input for flocculation is the flocculant itself. Common flocculants for algae are iron (III) chloride, aluminum sulfate and chitosan and are inexpensive, making flocculation an attractive method for harvesting.[15] In addition, chitosan is obtained from crustaceans and is a renewable source.

Particle flotation is a common process in wastewater treatment plants and one method of isolating the algae floccs. The solution containing suspended solids is sparged with fine air bubbles. The bubbles entrain the algae in a froth that floats to the surface where it forms a scum on the surface. A mechanical harvester, such as a rotating arm collects the froth and delivers it to the next processing step.[14, 16] Currently proposed processes for algae production suggest the use of flotation following flocculation.[13]

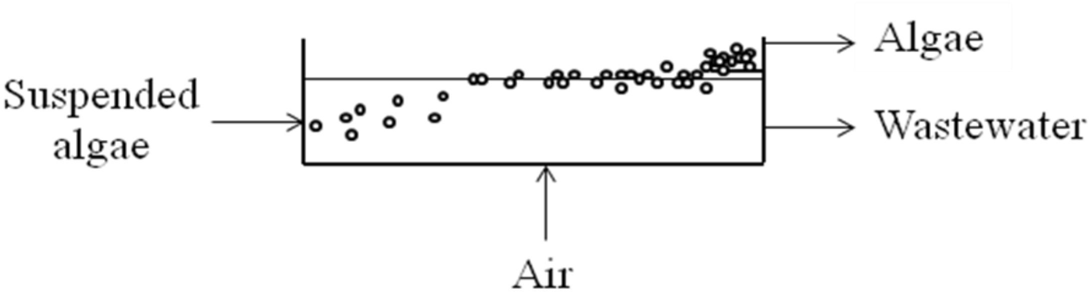


Figure 3. Schematic of the flotation process.

Particles denser than the surrounding solvent may be separated by settling. As with flotation, this is a common method for wastewater treatment.[16] A wide and shallow tank with low fluid velocity is provided and the solution passes through it. The particles settle out on the bottom and are collected by a scraping mechanism. Settling is commonly seen in wastewater treatment but not generally proposed in algae harvesting. As with flotation the tank dimensions require a significant outlay in area for a large production system.

An obvious disadvantage to both flotation and settling is that its throughput is a function of surface area. Since surface area for flotation must be horizontal, increasing capacity directly increases the area required. Building and land costs make this technology difficult to scale.

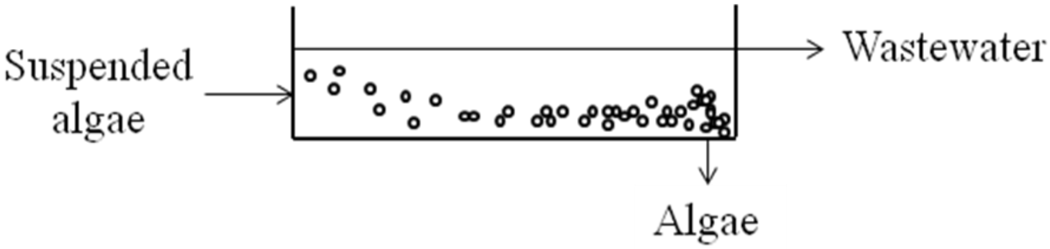


Figure 4. Settling tank schematic.

Centrifugation is a well established method of separating solutions by density and can be operated on a continuous basis.[7] A summary of studies of algae centrifugation show that all reviewers obtained high recoveries, but only at high accelerations, [17] which carry correspondingly high energy demands. Some researchers specifically note that it “is feasible for high value products”, while others suggest flocculation followed by a centrifugation process. [10, 18] While centrifugation is sometimes suggested as a process for harvesting algae, it is energy intensive and hence emissions intensive. Even preceded by a different harvesting method, it is uncertain centrifugation can become economically feasible for the production of algae-derived biofuels.

Filtration is a chemical engineering separation process which discriminates by particle size. The solution is forced against a fine screen or membrane which selectively permits passage. Specific methods such as tangential flow filtration [8] allow continuous operation. Filters are prone to blinding and tearing, unlike centrifuges. They do, however, have much lower energy demands than centrifuges.[11] When a continuous filtration system was evaluated for energy consumption and found it more energetically efficient than flocculation at a pilot scale (~100 L).[8] However, filtration is not suitable for very small algae.[5] Filtration shows promise as a secondary harvesting step after flocculation, and can be used to further decrease the percent water in the algae biomass.

No single process appears ideal for the task of harvesting dilute algae in large quantities economically and environmentally. The best method is likely to be a combination of two processes with an appropriate design to reduce the size of both processes to a minimum.

1.1.3 Extraction

After harvesting, the algae cells are concentrated as a slurry or paste. Before the TAGs can be converted to FAMEs, the TAG-bearing lipid bodies must be extracted from the algae cells. The most common method operates by using a solvent to remove the lipids from the algae and then physically separating the solid cellular remnants from the liquid solvent and lipid phase. The disadvantage of solvents is that they present environmental concerns. Typical solvents are hexane, with or without a cosolvent, and chloroform with methanol. Supercritical fluids (SCF) have been investigated for use, but SCF use is associated with significant costs and hazards, and might not suited for this application.

After extraction, it has been suggested that the cell debris be digested to produce methane or fermented to ethanol.[4, 11, 19] This approach produces additional fuels, improving overall process sustainability as the methane or ethanol is considered an avoided product. An analysis should be performed specifically to determine if either option is economically or environmentally desirable. The additional processing of the cell debris may become a standard side process of algae biodiesel production if it generates an additional salable substance, such as ethanol. Because the cellular nitrogen or phosphorous are not consumed, these waste products of the digestion or fermentation process are reusable as fertilizer and may be used as nutrient in algae growth. (Figure 5)

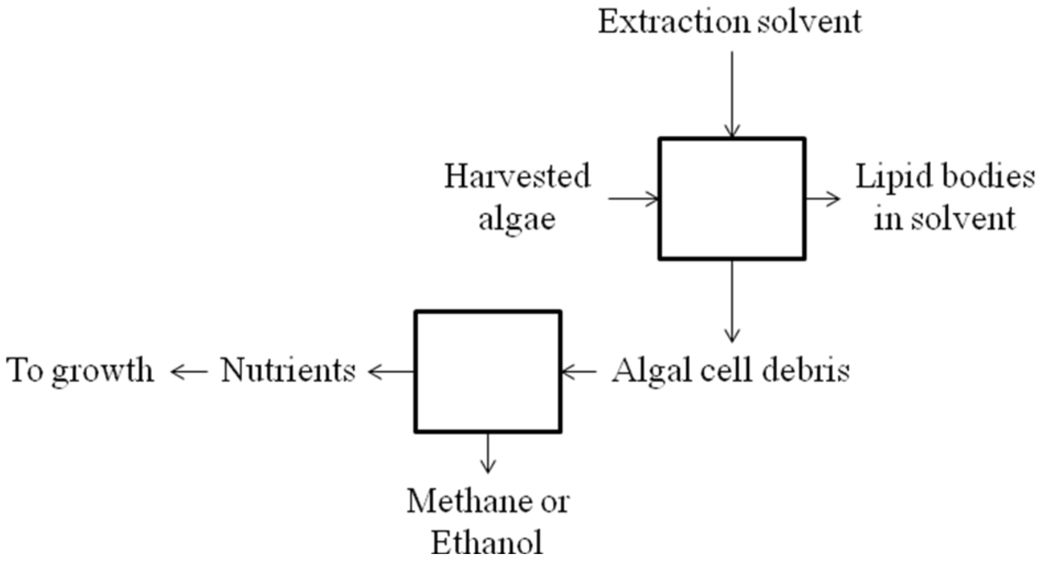


Figure 5. Block flow diagram of generic extraction with recycle loop.

Hexane, alone or with a cosolvent, is widely used to extract oil from soybeans and has also been used in experimental algae extraction.[11, 20, 21, 22] Hexane is added to the algae biomass after drying to no more than 9% wt water.[11] As a nonpolar solvent, hexane dissolves the hydrophobic TAGs from the biomass in a uniphasic solution.

Hexane is commonly sourced from hydrocarbons, and while the extraction process can be designed to recycle solvents, a continual makeup of hexane will be required. This presents concerns that dependence on petroleum is not being offset but shifted upstream from the consumer.

Use of hexane requires an additional heating step that impacts process sustainability because harvesting methods alone do not efficiently dry the algae biomass to the required level. The thermal energy used to dry the algae biomass prior to hexane extraction is commonly obtained from natural gas or waste heat from nearby plants.[12] Use of natural gas to dry the algae biomass resulted in significant carbon emissions and strongly altered the energy balance in an LCA comparing wet and dry extraction.[12, 19]

Use of waste heat is recommended for sustainability, and is an elegant reuse of a normally discarded resource. Solar drying has been suggested, but not yet analyzed for feasibility.[11] There are concerns that solar drying could only be feasible if continuous and dependable, and it has been suggested that sunlight may have a destructive effect on the TAGs.[19]

The use of a 2:1 by volume mixture of chloroform and methanol to extract lipids from cells was described by Bligh and Dyer in 1959 and is frequently referred to as the "Bligh and Dyer" method. [23] It is commonly used as a standard method of determining the lipid content of cells because of its extractive efficiency. The chloroform and methanol mixture contacts the harvested algae solution. After the lipids have transferred to the solution, water is added to cause separation into two phases. The lipids partition to the organic (chloroform) phase completely that is separated from the water phase. The TAG containing organic phase is reacted to produce FAMEs, while the methanol containing water phase must be treated as process waste.

One study includes the laboratory-scale three step chloroform/methanol system scaled directly up to an industrial scale.[24] The three steps, while useful on a small scale to be able to extract nearly all lipids from the cells, are not practical on an industrial scale and certainly impact the analysis. The circumstances of the study, a natural lagoon suffering algae blooms, are ideal to test potential production methods; however the one presented in that study is unworkable. The use of chloroform and methanol to extract lipids presents environmental concerns. Methanol is commonly derived from petroleum stocks, causing similar concerns to hexane. Additionally methanol is toxic to humans and chloroform is a human carcinogen. [25, 26] Use of either will add a significant regulatory burden to any operation using them in quantity.

SCF are substances elevated above critical temperature and pressure, possessing properties similar to both gases and liquids, and are currently used in industrial extraction.[27] To extract the TAGs, harvested algae biomass is contacted by the fluid, which then dissolves the lipids. The SCF is then separated and the pressure is bled off. As the pressure falls below critical, the fluid reverts to a gas and the solute precipitates.

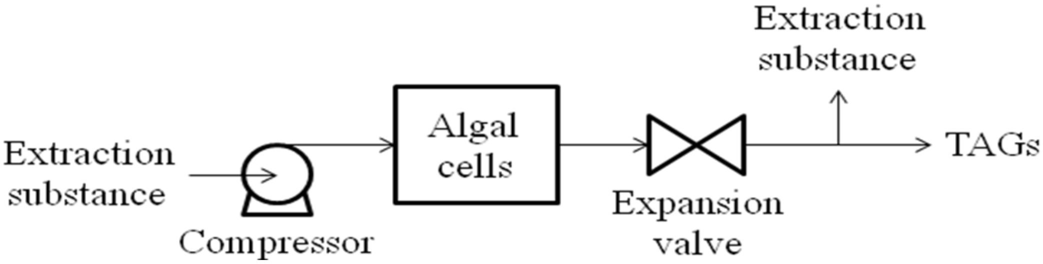


Figure 6. Block diagram of supercritical fluid operation

Carbon dioxide and methanol have been proposed as supercritical solvents for extraction of algae oil. [28, 33] Use of carbon dioxide simply extracts the TAGs. Extraction with methanol offers the advantage of combining extraction and reaction steps. Because methanol is the reagent of choice in the conversion of TAGs to FAMEs, use of methanol in supercritical extraction will also perform the conversion reaction. If feasible, this is a fundamental improvement over processes which require separate extraction and reaction stages.

However, SCF processes suffer from drawbacks: high energy demands to heat and pressurize the SCF substance used, risky operating pressures, necessity of materials capable of withstanding the fluid, and difficulty in design of continuous processes. The high energy demands in particular make the process energetically unsustainable and likely unprofitable.

Other solvents and solvent combinations have been investigated. Butanol and ethanol were tested with extractive efficiencies of 90% and 74% respectively.[29] These are in the early stages of process development, and have only been shown effective at a lab scale. Not having been investigated thoroughly, they cannot yet be considered for use in a large scale industrial process.

Ultrasonication has been shown to significantly improve the efficiency of extractions by mechanically disrupting cells. It has been used in the extraction of DHA containing lipids from algae and improved extraction efficiency by over 5 times.[30] This is an energy intensive process and was evaluated for its ability to disrupt the cells without also disrupting some high value molecules. It is unlikely to be cost effective for a low priced commodity, such as biodiesel.

1.1.4 Reaction

Numerous methods are physically capable. However, all processes currently proposed have environmental or cost draw-backs, and it is possible that the ideal method has not yet been found. The reaction step chemically converts the extracted algae TAGs to fatty acid methyl esters (FAMEs) which, when purified, become biodiesel. Stoichiometrically, three molecules of methanol react with one triacylglyceride to yield three FAMEs and one glycerine molecule. FAMEs are nonpolar and glycerine is polar, resulting in the formation of a biphasic reaction product.

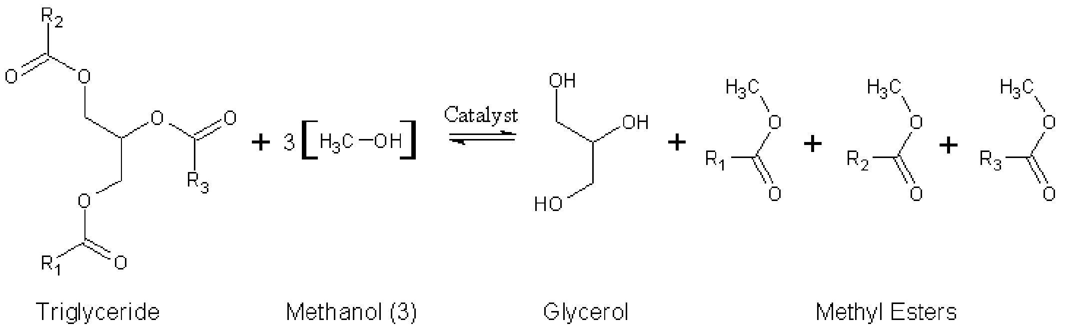


Figure 7. Transesterification of TAG to produce FAMEs.

If stoichiometric amounts of methanol are used, 0.10 g are required per kg of biodiesel produced. Biodiesel has an average density of 0.87 kg/m^3, therefore, approximately 13 metric tons (tonnes or t) of methanol are required to produce 40 billion gallons, or 30% of United States 2010 use.[7, 31] In practice, methanol is usually fed in excess to ensure complete conversion.[32] At a molar excess of 1.6, 21 metric tons are required to meet the same demand. Both of these are well below the common production of over 454,000 metric tons of methanol per year in the United States.[33]

While it is possible to use other alcohols in the transesterification reaction, methanol is nearly universally used as it is the most inexpensive alcohol and easily dissolves basic catalysts.[34] Methanol is commonly produced from petroleum refining, raising concerns about dependency on a non-renewable resource. Other sources of methanol include distillation of wood, a renewable resource. Use of waste wood from sawmills, papermills and construction may partially offset petroleum-based production of methanol. However, this may not satisfy demand if biodiesel production is carried out on an industrial scale. Harvesting wood solely for biodiesel processes presents risks, as wood is often harvested unsustainably for current uses, and additional demands could accelerate deforestation. If algae-derived biodiesel is to be a sustainable fuel independent of oil, a renewable source of methanol capable of competitive production at industrial levels must be found.

Alcohol does not react spontaneously with the fatty acids, and the reaction is commonly promoted by catalysis. Three methods of catalysis exist; basic, acidic and enzymatic. Basic catalysis is used industrially as it is the least expensive method. Acid catalysis is not favored because its reaction time is the longest of any method. Enzymatic catalysts currently are not durable enough for commercial use and have comparatively low yields.

Research is currently being conducted on non catalytic reaction processes.[35] The two non catalytic transesterification methods are supercritical fluid synthesis and cosolvent synthesis. SCF was discussed in the extraction section, and is notable for the possibility of combining the extraction and reaction steps. SCF is also notable for high energy requirements. Cosolvent synthesis is beneficial for having a short reaction time and mild reaction conditions.

Table 1. Characteristics of transesterification methods [31, 34, 36, 37, 38]

	Basic	**Acidic**	**Enzymatic**	**Supercritical**	**Cosolvent**
Temp. (°C)	22 – 70	~ 100	22 – 45	239 - 450	22 – 30
Reaction time (h)	1 – 8	3 – 48	4 – 8	< 1	< 10 minutes
Yield (%)	> 95	> 90	80 – 90	~99	~99
FFA sensitivity	High	None	Low	None	Low
Water sensitivity	High	Moderate	Low		
Examples	NaOH, KOH	H_2SO_4, HCl	*Rhizomucor mieher,* *Candida antarctica,* *Chlorella vulgaris*	CO_2, CH_3OH	Tetrahydrofuran, MTBE, dimethyl ether

Basic catalysis uses an alkaline substance such as sodium or potassium hydroxide to promote the transesterification reaction.[34] The alcohol and base are initially mixed to form an alkoxide before being added to the extracted oil. The reaction mixture is stirred between one and eight hours, at a temperature between 22°C and 70°C. Yields of greater than 95% are achieved.[38] A major concern when using basic catalysis is the formation of soap, called saponification, by the unwanted side reaction of the base with free fatty acids. Soap will form an emulsion of water and FAMEs, hindering separation.[31] When using basic catalysis in this reaction, FFAs must not be present in concentrations above 0.5 wt% and water 0.1 - 0.3 wt% or saponification will result.[39] Despite the potential for unwanted side products, basic catalysts are most widely used industrially because they are inexpensive.[7, 38]

Common industrial acids such as sulfuric and hydrochloric have been used successfully in acid catalysis. This synthesis occurs more slowly than basic catalysis; at 100°C the reaction can take between three and 48 hours. Yields are generally above 90%.[38] Acidic catalysis is not sensitive to the presence of FFA; there is no hydroxide and FFAs are esterified therefore soap cannot form.[35] Acidic catalysis is not practiced industrially due to its comparatively long reaction time, and the corrosiveness of acids used.

Specific enzymes called lipases, when immobilized on a surface, may be used to perform the transesterification reaction.[35] Reaction time ranges from four to eight hours at temperatures between 22°C and 45°C. Yields are generally in the range of 80 to 90%.[31, 40] These enzymes are highly selective and are not impacted by the presence of water and FFAs, however excess alcohol, heat, and glycerine will denature them.[31, 41] Efficient separation of the glycerine is necessary to maintain the lipase. Alternately, a different reaction path using methyl acetate in place of methanol may be usable, but information on this mechanism is insufficient and is untested commercially.[41] Currently, enzymatic catalysis is not used commercially because of the short life of the lipases, at most 50 uses.[31] Future use depends on improvement in enzyme life and resistance to denaturing.

Cosolvent synthesis uses a solvent which is capable of dissolving both the alcohol and TAGs. When the TAGs and alcohol are both dissolved in a common phase, they react without additional processing. This method has been shown to produce a 99% yield in 5 to 10 minutes at 30°C, significantly improving on other methods of reaction promotion.[31, 38] Currently tetrahydrofuran, dimethyl ether, and methyl t-butyl ether (MTBE) have been proposed, but currently has not reached commercialization. [31, 38, 40]

Fermentation of the waste cell mass from the extraction step to produce ethanol has been proposed, which could then be used to transesterify TAGs. [11] This is an elegant process as it draws a needed raw material from a waste product generated elsewhere in the process.

Several different methods of performing the conversion reaction from algae oil to biodiesel are available. Unlike harvesting and extraction, the reaction step is industrially mature. A single method, basic catalysis, is widely accepted by biofuels producers. New methods, including cosolvents, are being researched and may improve on current standards. The results of reaction step are an organic phase containing FAMEs and a water phase containing glycerine. The FAMEs must be separated and further refined in a purification step.

1.1.5 Purification

During the reaction process the TAGs are converted into FAMEs and glycerine. In the purification process glycerine, water, unreacted alcohol and any impurities introduced in the reaction step, such as catalysts and soap, must be removed.[34] All reaction methods produce organic and water phases. The organic phase is composed of approximately 94% FAMEs with trace impurities, while the water layer is 50% glycerine.[34, 42]

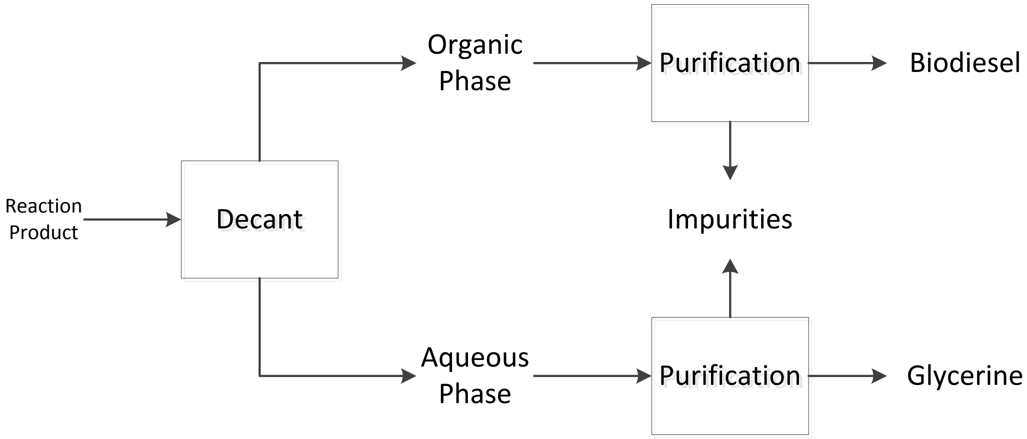


Figure 8. Separation and purification of biodiesel and coproduct glycerine

The common purification train (Figure 8) separates the two phases before individually purifying each. The FAMEs are decanted for further purification. In parallel, the organic phase is purified to produce a solution of FAMEs that satisfy standards for biodiesel.

The first step of the purification process is the removal of the glycerine. The water phase of the reaction contains glycerine, which is significantly denser than FAMEs (1.26 g/mL compared to an average 0.85 g/mL).[38] The phase mixture is separated by settling for several hours before the water phase is decanted off.[34] The water phase is about 50% glycerine, and when purified to above 80% the glycerine can be sold.[34] It is expected that new uses will be found for glycerine if biodiesel is industrially produced as the algae biodiesel process has the potential to completely flood the already saturated glycerine market. [7, 41]

The remaining organic phase is a solution of FAMEs with trace impurities, and must be refined to produce biodiesel. Fewer impurities are present in this phase as they are hydrophilic and most were removed when the water phase was decanted off in the previous step. The FAMEs are commonly purified by water washing, dry washing, or membrane filtration; and then heated to produce biodiesel.[34]

Water washing entails adding water to the FAMEs, mixing and settling. Because the impurities are hydrophilic they are dissolved in the water, which is then decanted off. While chemically and physically simple, the use of water potentially usable to humans presents ethical concerns similar to the food-versus-fuel debate concerning current biodiesel crops, such as corn and soy. An analysis of this process is needed to determine its sustainability, especially for locations which do not have plentiful amounts of fresh water.

Dry washing removes the impurities by passing the crude biodiesel through an adsorbent material, such as silica, alumina, or magnesium silicate. Filtration uses a pressure to force the stream against a selectively permeable barrier. Leung reported an experiment using a hollow fiber polysulfone membrane to obtain 90% pure biodiesel in preliminary testing.[34] Membranes have not been evaluated to determine how well they scale for industrial purification of biodiesel.

This refining process, either washing or filtration, is repeated until the biodiesel is pH neutral, indicating removal of all pH-affecting impurities. To drive off any remaining water the biodiesel is then heated to approximately 55°C for 15 to 20 minutes or until translucent. Regional standards for biodiesel may dictate further purification, which is carried out by distillation at about 200°C for 30 minutes. [31, 43]

1.2 Current State of Life Cycle Assessments

LCAs can be used to determine the most environmentally friendly method of producing algae-derived biodiesel. A review of the currently existing LCAs was conducted and allowed for the identification of the locations where the greatest improvement could be made. These locations were then used as the focus for this LCA.

Extensive research is being conducted to determine the most efficient techniques of processing algae into biodiesel. An assessment comparing petroleum-derived diesel to algae- and canola-derived biodiesel found that algae biodiesel had significantly lower greenhouse gas emissions. [13] Similar research was conducted comparing petroleum and soybean based fuel production to algae-derived biodiesel grown in a photobioreactor.[7] This research found that the net energy ratios, the ratio of energy consumed to energy produced, were 0.19 for petroleum fuels and 0.93 for algae, respectively. Algae biodiesel had the lowest greenhouse gas emissions by sequestering 75.29 g $CO_{2\ eq}$ /MJ energy.[7] Another study compared algae grown using photobioreactors to soybean biodiesel production, finding that the process energy for the production of algae was only less than soybeans when recovering waste heat.[12] A LCA comparing biodiesel produced through raceway ponds to photobioreactors showed that raceway ponds are significantly more energy efficient for cultivating algae.[44] Although raceway ponds are currently the industry standard, photobioreactors are still in development and offer a higher degree of process control, resulting in less contamination risk and higher yields.[45]

The LCAs performed on the growth phase demonstrate that improvements in algae cultivation are necessary. Raceway ponds are currently capable of efficiently achieving the required production values; however the higher risk of contamination and lower control over the process can result in lower algae oil content and yields.[45] The algae culture obtained from the algae growth stage is dilute and requires water removal. This dewatering stage is also energy intensive due to extensive thermal drying needed to eliminate the intercellular water.[46] Algae cells can contain anywhere from 40 to 80% intercellular water.[18, 46, 47] Water removal is required to effectively extract the TAGs from the algae and is most efficient at moisture contents between 5 and 15%.[12, 46] Achieving these moisture contents represents one of the major bottlenecks of using microalgae as a feedstock for biodiesel. [19,44, 48] The dilute nature of the algae culture is the most challenging aspect of producing biodiesel from algae.[9] The dewatering stage can be improved by sequencing various methods. Flocculation is the most efficient way of initially concentrating the algae in solution; however, the resulting dry solids concentration will not exceed 5% and additional dewatering is necessary to achieve lower moisture contents.[17] A life cycle assessment found that the dewatering stage contributed to 84.9% of the total process energy.[19] This study was based on extrapolations of lab scale studies, and served to identify the major obstacles in algae biodiesel manufacture. An additional study explored the reduction of the process energy demand through using a series of dewatering and drying technologies.[46] Their study obtained a fossil fuel energy rating of 1.5, meaning 50% more energy was recovered as biodiesel when compared to the energy consumed to create it. They have shown that using thermal drying methods to dewater algae contributes to over 90% of the process energy demand in the downstream production of algae biodiesel. The process energy was estimated from laboratory observations as well as published data of others, and a comprehensive LCA was not performed. This work demonstrated that more energy is generated than consumed using a dry route, but a comprehensive LCA was not performed on this work.

The LCAs on dewatering demonstrate that this stage is a major bottleneck in the commercialization of algae-derived biodiesel. As previously stated, this is due to the low moisture contents (5- 15%) required to effectively extract the TAGs from the biodiesel. Analyzing different extraction techniques can reveal better methods of extracting these oils.

There are a few different methods of extracting the TAGs from algae. The most common is using an oil press which is capable of extracting up to 70% of the oils contained within the algae cells.[49] A more efficient method is to use a solvent, usually hexane, to break down the cellular mass and recover over 95% of the total oils in the algae cells.[44] However, these two extraction methods require dried algae. Studies are being performed involving alternative extraction techniques which are capable of extracting TAGs from higher-water content algae, called wet extractions. One method of accomplishing this is through the use of supercritical fluids. Supercritical CO_2 is capable of performing extraction with up to 30% water content and is shown to aid extraction by functioning as a co-solvent with water.[22] This method requires conditions of 30 MPa and 80°C which are not likely to be commercially scalable.[22] Another possibility is the use of supercritical methanol, which can simultaneously perform the TAG extraction and transesterification reaction. Although the conditions required are less extreme and could transform algae with moisture content up to 90%, this is still only performed at the lab scale.[28] A LCA compared multiple methods of producing algae-derived biodiesel by extrapolating experimental data from algae growth, extraction, and reaction including supercritical CO_2 and methanol as possible production routes.[50] This work found that using supercritical methanol to simultaneously perform the extraction and reaction resulted in the lowest cumulative energy demand (CED). The CED is defined as the total primary energy required in the production, use, and disposal of the good in question. It is unknown whether these techniques are potentially scalable, but this work can be used to determine which areas warrant further research. Another approach to extraction is called single step extraction developed by Origin Oil which simultaneously performs dewatering and extraction. They perform cell lysis through a patented process called quantum fracturing which uses pulsed electromagnetic fields, followed by a gravity separation, resulting in an effective lipid, cell mass, and water separation.[48, 51] Unfortunately, wet extraction techniques are only in the development stage, therefore, accurate assumptions cannot be made regarding the commercial application of these techniques.

Once these TAGs have been extracted from the algae, they can be reacted to form fatty acid methyl esters (FAMEs). The four major methods of reacting the TAGs to FAMEs are acid catalyzed, base catalyzed, enzymatic catalyzed, and supercritical conditions.[6] Generally, the base catalyzed reaction is widely preferred in industry due to its short residence time of 20 minutes.[52] The acid catalyzed reaction is time consuming, taking 5 hours, and supercritical conditions require energy to achieve conditions of 1,200 psi and between 240 and 260°C.[28, 52] The enzymatic catalyzed has not been demonstrated at the large scale due to the high price of the enzyme and its short operational life.[6] This stage has a low impact compared to other stages, as shown by previous LCAs and will therefore not be the focus of the study described in this paper.[19, 44]

1.3 Purpose Statement

An extensive life cycle assessment for the dewatering stage is required to provide an analysis of more environmentally efficient processing steps. The approaches presented in this paper use viable methods of producing algae-derived biodiesel on the commercial scale by adapting and coupling dewatering technologies rather than extrapolating from lab scale experiments. This study expanded on previous findings from Xu *et al.* by using a wider range of dewatering equipment. Their research focused on the energy demand required for algae processing, but the work does not address the emissions associated with production of biofuels. For this reason, our work consisted of a rigorous LCA to compare these dewatering technologies when fully integrated into biodiesel production.

Material and energy balances for an industrial scale algae production facility were estimated, and served as the basis to conduct a LCA by evaluating total emissions. This “base case facility” was compared with alternative processing cases, created by implementing potentially scalable dewatering technologies. Total emissions from each stage were quantified, the optimal sequence of dewatering equipment was determined, and the life cycle emissions were compared.

Chapter 2

Base Case Process Development

The overall inputs and outputs for the algae to biodiesel process need to first be specified in order to perform a LCA. The literature review was used to develop a process for the production of algae-derived biodiesel. This process was not the optimal method of producing biodiesel, but was used as a starting point from which alternatives could be developed and compared. The algae growth, harvesting, extraction, reaction, and product purification stages were investigated. The following sections describe the base case algae biodiesel process.

2.1 Algae and Oil Properties

Before the process can be modeled, the primary chemical constituents were identified for modeling purposes. The molecular weights and densities were also required to obtain the required quantity of oils (lipids) and the necessary mass of algae. An algae cell, much like a plant or animal cell, is made up of four main classes of molecules: lipids, carbohydrates, proteins, and nucleic acids.[53] The lipids serve as the storage of energy for the algae cells. The lipid content of these cells comes in the form of a triacylglycerol (TAG) which is essentially a glycerol molecule with three fatty acid chains. The fatty acid is a methyl ester of varying degree of saturation, but within the algae cell, four main structures are the major constituents.[54] An analysis of the biodiesel produced from algae, shows the chemical contribution of each of these specific FAMEs.[22] Properties of these typical acids and TAGs as well as typical compositions within algae cells are shown in Table 2. The main constituents are: palmitic acid, stearic acid, oleic acid, and linoleic acid. Oleic acid is the largest of these FAME constituents. Oleic acid is produced from the transesterification of triolein. From this information, it was concluded that triolein is the major component of the TAGs in the algae cell.

Table 2. Main methyl ester compounds with their associated triacylglyceride.[22, 54]

Class	***Chemical***	***Formula***	***MW***	***Density***	***Melting Point***	***Boiling Point***	***Lipid Content***
			(kg/kmol)	***(kg/m³)***	***(°C)***	***(°C)***	***(%)***
Fatty Acids (Methyl Esters)	**Palmitic acid**	$C_{16}H_{32}O_2$	256.42	853	62.9	351	17-26
	Stearic acid	$C_{18}H_{36}O_2$	284.48	847	69.6	383	2-6
	Oleic acid	$C_{18}H_{34}O_2$	282.46	895	14	360	52-66
	Linoleic acid	$C_{18}H_{32}O_2$	280.45	900	-5	365	0-20
Lipids (Triglyceride)	**Tristearin**	$C_{57}H_{110}O_6$	891.48	862	75	N/A	N/A
	Triolein	$C_{57}H_{104}O_6$	885.432	950	5	554	N/A

Aspen Plus® was used to simulate the solvent recovery following the TAG extraction. The process simulator contains properties for the TAG triolein, the major constituent in algae lipids. Since many of these lipids behave in the same manner, it was assumed that triolein will properly model the behavior of these TAGs.

The species of algae used for the base case process was in the *Scenedesmus* family. The distribution of the composition of the lipids found the *Obliquus* variety of algae can contain up to 75% weight mono unsaturated fatty acids. This quality makes the oil derived from this species of algae highly resistant to oxidation and a good candidate for a fuel source.[55] A comparison of compositions in common vegetable oils to algae is seen in Table 3. Oleic acid is an example of a monounsaturated fatty acid present in algae. Since 75% of the lipid composition is monounsaturated acid, its properties should represent the system adequately in Aspen Plus® (Figure 9). The Aspen Plus® simulation and additional assumptions made regarding physical and chemical properties are discussed in the *Extraction* and *Evaporation* section.

Table 3. Common compositions of vegetable oils.[54]

Common name	***Chemical***	***Palm***	***Soybean***	***Corn***	***Algae***
Fatty acid	***Methyl ester***				
Palmitic acid	Methyl palmitate	32 - 45 %	7-11%	8-12%	17-26%
Stearic acid	Methyl Stearate	2 - 7 %	2-6%	2-5%	2-6%
Oleic acid	Methyl oleate	38-52%	15-33%	19-49%	52-66%
Linoleic acid	Methyl linoleate	5-11%	43-56%	34-62%	0-20%
Linolenic acid	Methyl linolenate		5-11%		

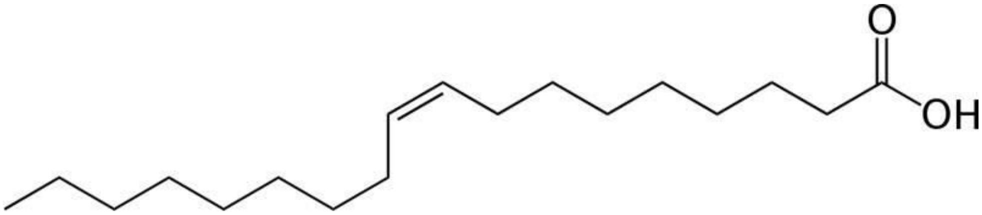


Figure 9. Structure of monounsaturated Oleic acid (Fatty acid methyl ester).

2.2 Process Design

A basis of one tonne of biodiesel (t of BD) was used for the calculations and all numbers were reported on this basis. Some of the unit operations required a flow rate to determine energy consumption. Therefore, an average per year basis of biodiesel production of 15.7 MM gal per year (52,300 t BD/year) was assumed. This value is based on the geometric average of the typical biodiesel plant production rates provided by the National Biodiesel Board.[56] The plant capacity was designed to reach these production values. To create a comparable basis of one t of BD, this capacity was divided by 52,300. The microalgae species considered in this process was *Scenedesmus Obliquus* due to its high lipid yields and wide availability. This species was estimated to be capable of producing 61.3% lipids from dry algae biomass (0.613kg TAG/kg dry algae) at optimized growth conditions.[55] This value was reasonable because it was assumed the PBR was capable of producing a highly controllable, and optimized algae product, the primary advantage of a PBR. The process will be detailed in following sections and the complete proposed process flow diagram is found in Appendix A for reference.

2.2.1 Photobioreactor

The PBR is a system capable of growing algae in a closed environment while maintaining optimal growth conditions determined for a specific algae species. The growth medium used for the base case was a common Bold’s Basal medium, and was fed into the system along with the water and algae seed stock. The contents of this medium are shown in Table 4. This medium is a common nutrient mixture for the growth of microalgae. The total mass present in the system is shown in Appendix A. For a commercial scale system it may be optimal to utilize simpler growth mediums fewer chemical components. The Bold’s Basal medium is a more complicated medium and was a conservative choice in terms of a LCA. Throughout the mass balances, these medium chemicals were assumed to be absorbed by the algae at the same rate and were present at the same mass fraction at all points in the system. These chemicals were referred to as the medium and not by individual chemical due to the large number of individual chemicals present in the mixture. The total mass of each chemical component in the medium are located in Table 4.

Table 4. Concentrations of components in Bold's-Basal medium.

Chemical	**Quantity (kg/t BD)**
KH_2PO_4	14.5
$CaCl_2*2H_2O$	2.07
$MgSO_4*7H_2O$	6.21
$NaNO_3$	20.7
K_2HPO_4	6.21
NaCl	2.07
Na2EDTA	0.828
KOH	0.513
$FeSO_4*7H_2O$	0.412
H_2SO_4	0.152
H_3BO_3	0.666
H_3BO_3	0.237
$MnCl_2*4H_2O$	0.150
$ZnSO_4*7H_2O$	0.0184
$NaMoO_4*5H_2O$	0.0323
$CuSO_4*5H_2O$	0.00654
$Co(NO_3)_2*6H_2O$	0.00409

Carbon dioxide is bubbled into the system and is assumed to be the primary carbon source for the algae. Algae utilize the energy from sunlight, photons of light, to convert water and carbon dioxide to simple sugars. These simple sugars are the food source for algae which is converted into the biomass. Biomass primarily consists of proteins, carbohydrates, and lipids.[57] In particular, algae have high lipid contents when compared to other phototrophic plant species.

There were many studies on small scale cultivation systems, however very little was done in terms of pilot scale or industrial scale PBRs. One such system was constructed in Wolfsburg, Germany and began operating in the year 2000. This system was the largest PBR system and led to the successful production of algae and proved an economically feasible cultivation system. It contained a PBR with a total volume of 700 m^3, and required an area of 10,000 m^2. Annual productivities of this facility were between 130 and 150 metric tonnes of dry biomass. This system was constructed in a glasshouse, and solely relied on solar lighting.[58]

The details for the seed PBRs to start the system were not considered in this model. Once the system is started, a portion of the algae culture was drained for harvesting and the remaining algae were re-grown to the harvest concentration with fresh makeup medium. Energy was used to heat, mix and provide photons required for photosynthesis. The algae were allowed to grow four to ten days and consume CO_2, absorb light, and utilize nutrients. The PBR was the final step in a series of seed reactor systems. These systems were necessary to reach the appropriate culture density to maximize the algae growth and rapidly reach the harvest density. A patent application from Bright Source Energy Inc. suggested a harvest concentration of 25 g dry algae per liter of solution.[59] This translated to an outlet algae mass fraction of 0.024 kg dry algae per kg solution. This value was used to specify the best case scenario for a harvest density. The outlet concentration of the medium was reported as a total mass per tonne of biodiesel since the individual concentrations were essentially negligible compared to the algae and water. In addition, the algae were assumed to absorb 70% of the nutrients.[60] This assumption was based on measured values of nitrogen consumption by microalgae. The nutrients were present in the algae and assist with metabolic function, but were not consumed. The presence of these nutrients eventually became too dilute to support the growth of additional algae biomass.[57] All absorbed nutrients remained present in the microalgae and were sent with the expended biomass through the extraction as they are all polar compounds.

The quantity of required biomass was calculated based on the required TAG's, extraction efficiency, and flocculation efficiencies. From transesterification and purification, the quantity of TAGs required to create a tonne of BD was found to be 1,090 kg. When applying the extraction efficiency, along with the lipid content in algae, the mass of biomass required to achieve 1,090 kg of TAGs/t BD was 1,920 kg of dry algae biomass/t BD. With the knowledge of the quantity of algae lost in the flocculation step, the quantity of algae which is grown to produce a tonne of BD is found to be approximately 2,020 kg/t BD. As was previously specified, the concentration of algae at the time of harvest was used to find the volume of medium solution required. This was calculated to be 82,800 kg/t BD or 82.8 m^3/t BD after using the density of water as an approximate density.

Carbon dioxide was also a raw material and was bubbled through the PBR and absorbed by the algae. CO2 sequestration studies stated the algae were capable of absorbing at least 90% of the CO2 fed to the system.61 Estimations showed that approximately 1.83kg of CO2 was consumed to create 1 kg of biomass.62 With the mass of dry algae required, the necessary feed rate of CO2 was calculated as 3,520 kg/t BD.

However using this method, the mass of water consumed and oxygen produced cannot be accurately calculated. For this reason, the equation of photosynthesis was used and is shown in Equation 1.[57] Every mole of biomass produced, consumed a mole of CO2 as well as a mole of water and created a mole of O2. This mass balance is summarized in Table 5.

Compared to the estimated 1.83 kg CO_2, the calculated CO_2 consumption was comparable at 1.5 kg CO_2 consumed to create 1 kg of algae biomass or 2,820 kg of CO_2 absorbed/t BD produced. This method was not used to calculate the growth of algae or energy consumption, but provided an estimation of the CO_2 and water consumption and O_2 production. This value was used as a conservative number of CO_2 consumption.

$$2nCO_2(g) + 2nH_2O(aq) + Photons \rightarrow 2(CH_2O)_n + 2nO_2(g) \tag{1}$$

Table 5. Carbon dioxide, oxygen, biomass, and water flows for algae (1 t BD basis)

Chemical	***Formula***	***MW (kg/kmol)***	***IN (kg/t BD)***	***OUT (kg/t BD)***
Carbon Dioxide	CO_2	44	3,130	313
Water	H_2O	18	1,150	0
Oxygen	O_2	32	0	2,050
Algae (Biomass)	CH_2O	30	0	1,920

The PBR system utilized a recycle system that integrated the water extracted from the following processing steps. Two recycled streams, one from the flocculation tank and the other from the spray dryer system, returned water to the PBR system and thereby minimized the necessary water make-up required to achieve the original operating volume. The flocculation system also contained a percentage of the growth medium that was not absorbed or contained within the algae cell. This reduced the quantity of added make-up growth medium (salts).

Since no energy details on the actual industrial scale PBRs were available, these values were estimated. Utilizing several resources, estimations were performed of the different energy consumption rates detailed for each reference's method of calculation. In an LCA conducted by Stephenson, the energy consumption obtained per tonne of BD produced was specified at 231 GJ or 64,000 kWhr/t BD.[44] Posten specified power estimates for larger scale PBRs as being above 2,000 W/m³ of algae culture. This was converted based on the quantity of energy consumed over a time of 10 days, the upper limit of the growth period, and for the volume required to produce 2,020 kg of dry algae/t BD. This volume was calculated using the density of water as an estimation and is approximately 82.8 m^3/t BD. This resulted in and energy consumption of 40,000 kWhr/t BD. The Wantanabe estimation was based on a bench scale PBR. The bench scale PBRs were 6.23 L in size, and each consumed 1,249 kJ of energy per day. [63] Each 6.23 L vessel was found to consume 1,249 kJ of energy per day. This energy consumption for the bench scale PBR is 200.5 kJ/L day. The base case system has a 10 day growth period and volume of 82.8 m^3/t BD. This energy calculation resulted in a value of 46,000 kWhr/t BD. All methods were based on a volume of algae solution processed basis. Stephenson did not specify their methods to determine energy consumption, but reported results in terms of GJ/t of BD. Posten's estimation of energy requirements was less than that of the bench scale system of Wantanabe. Since the scaled up PBR was likely to have lower energy consumption than the bench scale system, Posten's evaluation was the best energy consumption choice. This resulted in an energy estimate for the modeled PBR of 40.0

MWh/t BD.[45] The material flows and compositions are summarized for each stream entering and leaving the PBR in Table 6.

Table 6. Mass flow summary of streams entering and leaving the PBR (kg/t BD).[44, 45, 63]

Stream	**[2] PBR Make Up**		**[8] Recycle (Dryer)**		**[6] Recycle (Flocc)**	
Chemical	***m (kg/t BD)***	***x (kg/kg)***	***m (kg/t BD)***	***x (kg/kg)***	***m (kg/t BD)***	***x (kg/kg)***
Algae	SEED	SEED	0	0	96	0
Water	1,240	0.97	36,400	1	44,200	1
Medium	38	0.03	0	0	16	0
Carbon Dioxide	0	0	0	0	0	0
Oxygen	0	0	0	0	0	0
Calcium Sulfate	0	0	0	0	0	0
Total	1,280	1	36,400	1	44,300	1
Stream	**[1] CO2 Feed**		**[3] PBR Product Flow**		**[22] Vented Gases**	
Chemical	***m (kg/t BD)***	***x (kg/kg)***	***m (kg/t BD)***	***x (kg/kg)***	***m (kg/t BD)***	***x (kg/kg)***
Algae	0	0	2,020	0.02	0	0
Water	0	0	80,800	0.98	0	0
Medium	0	0	55	0	0	0
Carbon Dioxide	3,130	1	0	0	313	0.13
Oxygen	0	0	0	0	2,050	0.87
Calcium Sulfate	0	0	0	0	0	0
Total	3,130	1	82,800	1	2,360	1

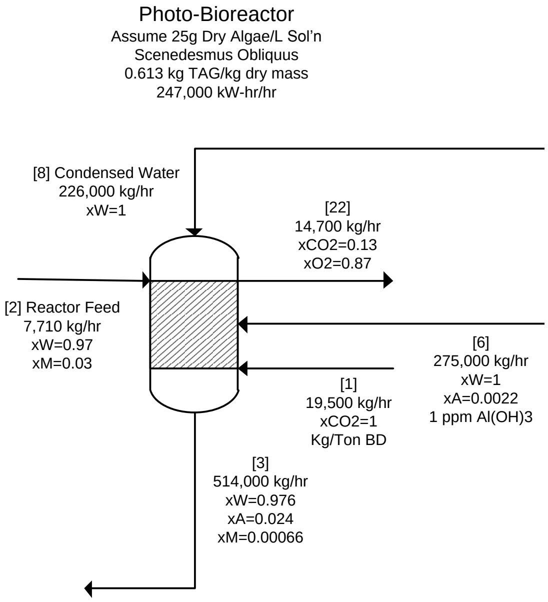


Figure 10. Detail of PBR section of the biodiesel manufacturing process.

(Notation clarification can be found in Appendix A)

2.2.2 Harvesting

The harvesting section of the process was where the water content of algae was reduced to 5% wt. water.[44] Here, the output of the PBR was fed to a flocculation vessel where chemical flocculants were added and allowed to agglomerate to remove excess water. This resulted in algae slurry consisting of 95% wt. water which was then sent to a spray dryer. The spray dryer was used to reduce the moisture content to 5% for the TAG extraction.

2.2.2.1 Flocculation

The flocculation system introduced the flocculant and gently mixed the chemicals and algae to ensure particle coagulation and settling rate.[64] A common method of introducing flocculant to a system with minimal power input was through an inline or static mixer.[65] This was a modified section of pipe containing obstructions that produced turbulence and high energy-per-mass input to achieve a homogenized state. The flocculant chemicals were combined by sending a partitioned stream from the PBR vessel output to an addition tank where the chemicals were added to the solution.

This concentrated mixture was then reintroduced into the main process stream and mixed using the in-line mixer. The resulting, homogenized stream was then fed into a settling tank which was gently mixed using a jet mixer. The jet mixer recirculates the tank and was designed for a set mixing time. Once mixed, the particles were given enough time to settle and the algae-flocc phase was isolated from the water phase. The design of the static mixer system, its power consumption, and the design of the settling tank system are specified in detail below.

Aluminum sulfate, ferric sulfate, and lime were considered as possible flocculants for this operation. Aluminum sulfate required the smallest concentration at 80-250 mg/L compared with 50-90 g/L and 500-700 g/L for ferric sulfate and lime, respectively. Aluminum sulfate is commonly used in waste water operations to flocculate systems and was chosen as a suitable chemical. It was found effective at flocculating *Chlorella* as well as *Scenedesmus*, and made it an ideal choice for our species.[44] The concentration required to flocculate with aluminum sulfate is small in comparison to other chemicals and minimized the chemical presence and waste in later operations. This flocculant is capable of achieving a concentration factor of 25 for lower density algae cultures.[15] The culture being harvested from the PBR is higher and would result in 0.385 mass fraction algae and 0.651 mass fraction water. Upon professional consultations with an expert in the flocculation field, it was found that flocculation- settling would only be capable of achieving 0.05 mass fraction algae. This value will be used as the concentration of algae being removed from the flocculation tank.

Aluminum sulfate reacts with calcium carbonate to form aluminum hydroxide. Aluminum hydroxide is the active coagulant chemical. To introduce the two chemicals into the system, the product stream from the PBR was split such that a small portion flows to an intermediate mixing vessel where the flocculant chemical precursors were prepared. The flow was fed back into the system upstream of the static mixer. The static mixer homogenized the two concentrations, and was sent to the settling tank system.

The active flocculant chemical, aluminum hydroxide, was prepared by reacting calcium bicarbonate and aluminum sulfate. Calcium carbonate reacted with water to form calcium bicarbonate (Equation 2). The reaction between aluminum hydroxide and calcium bicarbonate, in addition to aluminum hydroxide, produced calcium sulfate and carbon dioxide (Equation 3). The aluminum hydroxide formed a net-like material which slowly settled through the tank, and collected the algae. The resulting mixture was a gelatinous slurry substance on the bottom of the settling tank, and a purified water phase above the tank.

$$CaCO_3 + CO_2 + H_2O \rightarrow 3Ca(HCO_3)_2 \tag{2}$$

$$Al_2(SO_4)_3 \cdot 18H_2O + 3Ca(HCO_3) \rightarrow 3CaSO_4 + 2Al(OH)_3 + 6CO_2 + 18H_2O \tag{3}$$

The calcium sulfate remained in solution in a small concentration. It was unknown whether the calcium sulfate could harm the algae system if the stream were returned as recycle. Should this be the case, the calcium sulfate could be precipitated by cooling the recycle stream or flocculated via a polymer flocculant. Since the concentration were very small (on the order of 150 to 2,100 PPM), the effects of presence of this chemical (a simple mineral found in municipal water) were assumed negligible in the PBR and flocculation system. The maximum concentration it can reach before the solution is saturated is 2,100 ppm or 2.1 g/L. The compound was precipitated out of solution and removed with the algae slurry. The aluminum hydroxide concentration resulting from this reaction was 58.5 ppm. CO_2 was also formed, but not released to the atmosphere. The quantities formed were completely soluble in water, and returned to the PBR where the CO_2 was consumed by algae growth. Equations 2 and 3 were used to calculate the concentrations of the flocculation components present in the mixture. These concentrations and chemical properties and are presented in Table 7.

Table 7. Chemical information on the flocculant reactants and products.

Chemical	***MW (kg/kmol)***	***Density (kg/m³)***	***Solubility @ 20°C (PPM)***	***Concentration (PPM)***	***Concentration Ratio To $Al_2(SO_4)_3$***
$Al_2(SO_4)_3$	666.7	1,620	364,000	250	1
$Ca(HCO_3)_2$	162	Aqueous Only	166,000	182	0.73
$CaCO_3$	100	2,710	15	112	0.45
$CaSO_4$	136	2,960	2,100	153	0.61
$Al(OH)_3$	78	2,420	1	58.5	0.23
CO_2	44	1.98	1,450	99.0	0.40

To harvest and collect the algae from the PBR product stream, a chemical coagulant or flocculant was used to cause the algae cells to form an aggregate mixture. A small portion of the product stream was used to introduce the flocculants. This fraction was sent to a mixing vessel where the chemicals were mixed and dissolved before being reintroduced to the PBR product stream.

A static or in-line mixing system was an effective and energy efficient method to accomplish the reintroduction of the split stream which was highly concentrated in chemical flocculant. Static mixers are augmented sections of pipe containing baffles. The presence of these baffles causes increased turbulence and shear forces, resulting in a well mixed solution. This system is also ideal for low-viscosity applications.[65] Shown below in Figure 11 is a Sulzer SMX in-line mixer, which is highly effective in turbulent flow regimes for low viscous mixtures.

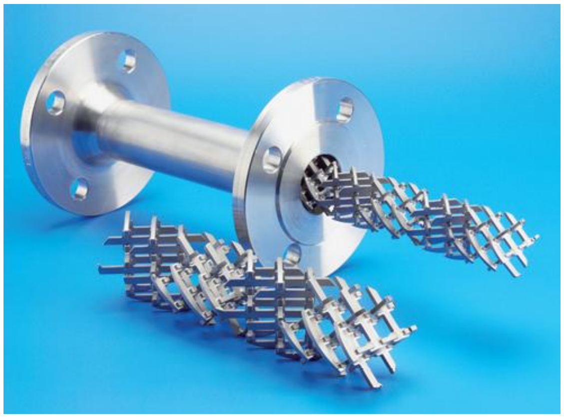


Figure 11. Sulzer SMX in-line static mixer.

The addition of a static mixer to the pipeline from the PBR required pumping energy. To calculate this energy, the methods described in the Handbook of Industrial Mixing were utilized and summarized below. A design flow rate was calculated by multiplying the 52,300 t BD/yr basis and the 82,800 kg/t BD exiting the PBR and dividing by 351 day operating period (assuming two weeks down time) and 24 hours per day. This resulted in a flow rate of 501 m^3/hr or 0.139 m^3/s. The pumping energy was calculated by determining the pressure drop across the static mixer.

The static mixer pressure drop was calculated by first finding the pressure drop across a regular pipe of equal length (with no mixing elements present) using the modified Bernoulli's equation. Next, an experimental/ measured constant was multiplied to this pressure drop and represented the additional pressure drop caused by the static mixer elements. This constant was well known for the Sulzer SMX, and was provided in the Handbook of Industrial Mixing as 200. The modified Bernoulli's equation with the static mixer coefficient included is shown in Equation 4. The length of a static mixer was measured by the ratio between the length and diameter of the pipe. For a turbulent flow regime, the degree of mixing is independent of mixer length after an L:D of five, therefore for this application an L:D of five was assumed.[65]

$$\Delta P_{MIXER} = C_{\substack{MIXER\\TYPE}} \cdot 4 f \frac{L}{D} \rho \frac{v^2}{2} \tag{4}$$

Where:

ΔP is the pressure drop across the mixer (Pa)

C is the characteristic coefficient associated with a given static mixer

f is the Fanning friction factor

L is the length of the static mixer section (m)

D is the diameter of the static mixer section (m)

v is the velocity of the process fluid (m/s)

ρ is the density of the process fluid (kg/m^3)

The velocity was assumed and checked using the Reynolds number so that the system operates in the turbulent flow regime. The diameter of the pipe was necessary for this calculation and was found by assuming a velocity and iterating using excel to find an acceptable pipe size to handle the design flow rate. For this application, a process fluid velocity of 4 m/s resulted in a pipe diameter of 0.22 m and a Reynolds number of 842,000. This Reynolds number was in the turbulent flow regime.[66]

The modified Bernoulli equation employed the Fanning friction factor to represent friction losses to the pipe walls. A steel pipe was assumed with an associated roughness of 0.00015 m.[66] The Fanning friction factor was calculated by Equation 5.

$$f = 0.001375 \cdot \left[1 + \left(20000 \frac{\varepsilon}{D} + \frac{10^6}{\mathrm{Re}} \right)^{1/3} \right] \tag{5}$$

Where:

ε is the roughness of the pipe (m)

D is the diameter of the pipe (m)

The pressure drop through a pipe was calculated using the modified Bernoulli equation which includes friction losses, simplified for a horizontal, steady state system (Equation 4). A length to diameter ratio (L:D) of five was also assumed to achieve complete homogenization in the turbulent regime.[65] The energy required to pump 52,300 t BD/yr resulted in an energy consumption of 6.16 kW-hr/t BD or 322,000 kW-hr/yr using this methodology.

Several settling tanks were needed to maintain a continuous process operation. The volume of one tank was specified to determine the number of tanks. The system flow rate was calculated by converting the specified production flow rate of biodiesel, 52,300 t BD/yr, and multiplying it by the amount of liquid exiting the PBR, ~82,800 kg H_2O/t BD. This was then converted to m^3/hr assuming 351 days of operation per year (assuming two weeks of downtime). The density and viscosity of the algae-water mixture was assumed to be nearly that of water at standard temperature and pressure due to the dilute nature of the algae mixture at this stage. This resulted in a design flow rate of 501 m^3/hr. An efficient method to mix and flocculate a colloidal mixture is by using a free jet mixed tank. This type of system used a recirculation pump loop, and drew liquid from within the tank and pushed the liquid through a jet nozzle back into the tank (Figure 12). The necessary jet velocity, nozzle size, and the required energy to operate the pump were determined.

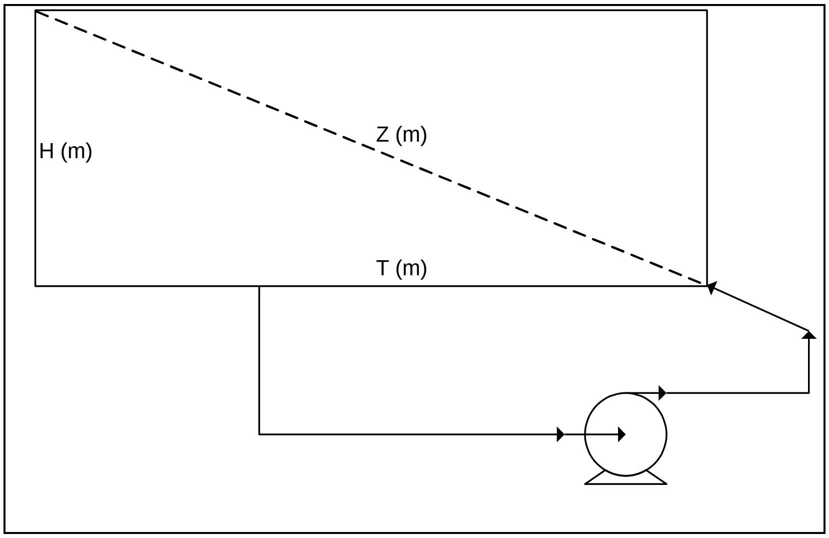


Figure 12. Side View Diagram of a Circular Free-Jet Mixed tank.

A cycle time for a given settling tank were calculated to determine the total number of tanks necessary to maintain continuous operation. A 501 m^3 tank was used and would take one hour to fill and one hour to drain. The dimensions of this tank were specified knowing that Jet-Mixed tanks function properly when the ratio of the tank height, H, to tank diameter, T, is between 0.2 and 2.0. A shallow tank reduced the time required for particles from the surface to reach the bottom of the tank; therefore a H/T ratio of 0.2 was be used. Assuming a cylindrical tank, the diameter was calculated by substituting 0.2T for H and solving for T (equation 6).[65]

$$T = \left[\frac{4}{\pi} \frac{V}{0.2} \right]^{1/3} \tag{6}$$

Where:

T is the tank diameter (m)

V is the volume of the tank (m^3)

0.2 represents the specified H/T ratio

The result was a tank that is three meters in height and 15 meters in diameter. These dimensions were reasonable tank sizes based on waste water treatment facilities and were considered valid for this model.[67] The settling time for a particle or flocc were assumed as two m/hr based off Lardon's assumption where a three meter deep tank resulted in a 1.5 hour settling period.[19]

To determine the required energy to operate this system, the mixing time for the tank was calculated. The time required to gently mix the system to ensure proper particle coagulation was calculated using the techniques described in the Handbook of Industrial Mixing and summarized below.[65] Considering the dimensions of the settling vessel, the hypotenuse of the triangle formed between the height and diameter of the tank, Z, was first calculated (Figure 12). Z also represented the trajectory of the jet used to mix the tank. The velocity through the jet and the desired mix time were required to obtain a turbulent jet velocity. The turbulence and required jet nozzle diameter were calculated using Equation 7 and solving for the nozzle diameter. The diameter and velocity were then substituted in combination with the fluid properties into Equation 8 to calculate

Reynolds number. A Reynolds number greater than 4,000 is considered to be in a turbulent flow regime and will ensure that the jet will thoroughly mix the tank.[65]

$$D_{Jet} = 3.00\left(\frac{Z^2}{v_{Jet}\theta_{99}}\right) \tag{7}$$

Where:

θ_{99} is the mix time for 99% homogeneity (s)

D_{Jet} is the diameter of the Jet nozzle (m)

V_{Jet} is the velocity of the fluid through the Jet in (m/s)

Z is the trajectory of the Jet (m)

$$\mathrm{Re} = \frac{\rho v_{Jet} D_{Jet}}{\mu} \tag{8}$$

For this case, the mix time was varied using Goal Seek® in Excel® to ensure an integer number of total tanks. This was first done by specifying the velocity of the jet at 10 m/s. Z was calculated using Pythagorean Theorem (Figure 12). A spreadsheet was used to calculate the number of tanks by multiplying the design flow rate by the total cycle time (assumed a place holder) and divided by the volume of a tank. Using Goal Seek®, the mixing time was varied until the number of tanks reaches four. Four tanks set the mix time at 30 minutes and when used in Equation 7, resulted in a nozzle diameter and Reynolds number of 0.037 m and 373,000, respectively. A 30 minute mixing time is a typical flocculation system mixing time.[64] This corresponded to a cycle time which includes the fill/drain time, mixing time, and settling time of four hours per tank.

The pumping power was calculated by determining the flow rate through the jet in m^3/s using the calculated nozzle diameter and fluid velocity (Equation 9).

$$\dot{V} = v_{Jet} \frac{\pi}{4} D_{Jet}^2 \tag{9}$$

Where:

$\dot{V}$ is the volumetric flow rate through the jet (m³/s).

Next the pressure drop required to push the fluid through the nozzle was calculated using jet velocity and the density of the fluid. An assume water density 1,000 kg/m³ was used in Equation 10. The constant, *C*, was assumed to be 2.5 which represents the head loss associated with a jet nozzle and is found in the Handbook of Industrial Mixing.[65]

$$\Delta P = C\rho \frac{v_{Jet}^2}{2} \tag{10}$$

Where:

ΔP is the pressure drop (Pa)

C is the velocity head loss through the nozzle

The power required for a pump to generate the required head was calculated by multiplying the flow rate through the jet by the pressure drop (Equation 11).

$$P = \Delta P \cdot \dot{V} \tag{11}$$

Where:

P is the power required by a pump (Watts)

The power used over an operational year for a four-tank system was calculated by considering the operation time of a pump in a given tank compared to the settling and fill/drain time. Considering the fill/drain time and flocc settling time, the pump operated 13% of the total cycle time. The jet flow rate and pressure drop are then calculated across the pump and are 0.0109 m³/s and 125,000 Pa, respectively. This corresponded to a 1.36 kW pump. This pump operated for 13% of a 24 hour day and 351 days of an operational year. For a system which included four pumps, the annual energy requirement was 5,700 kWhr/yr or 0.110 kWhr/t BD. Combined with the static mixer, the total energy for the flocculation system was 6.27 kW-hr/t BD.

The material balance on the flocculation system was calculated as follows. It was assumed that 95% of the algae were recovered in a gelatinous phase at the bottom of the tank.[17] The remaining water phase was then removed at an algae mass fraction of 0.05. Two streams exited the settling vessel, the essentially pure water stream and the flocculated water-algae slurry. The water-algae slurry had compositions of 95% wt. water and 5% wt. algae. The growth medium and flocculant amounts were still negligible and are shown in Table 8. It was assumed the flocculant would stay with the algae mass in stream 5 as it flowed through the system. The amount of aluminum hydroxide exiting in the pure water stream was less than one PPM and is negligible (Figure 13). These numbers were based on the calculated dry algae requirement going into the spray dryer of 1,920 kg dry algae/t BD.

Table 8. Mass flow of streams entering and leaving flocculation system (kg/t BD).

Stream	**[3] PBR Output**		**[4] Flocculant**		**[6] Water Phase**		**[5] Slurry Phase**	
Chemical	***m*** ***(kg/t BD)***	***X*** ***(kg/kg)***	***M*** ***(kg/t BD)***	***X*** ***(kg/kg)***	***M*** ***(kg/t BD)***	***X*** ***(kg/kg)***	***M*** ***(kg/t BD)***	***X*** ***(kg/kg)***
Algae	2,020	0.024	0	0	96	0.0022	1,920	0.05
Water	80,800	0.98	0	0	44,200	1.0	36,500	0.95
Medium	55	0.00066	0	0	16	0.00037	38	0.0010
Al2(SO4)3	0	0	21	0.69	0	0	0	0
CaCO3	0	0	9	0.31	0	0	0	0
Al(OH)3	0	0	0	0	0	0	5	0.00013
CaSO4	0	0	0	0	0	0	13	0.0003
Total	82800	1	30	1	44,300	1	38,500	1

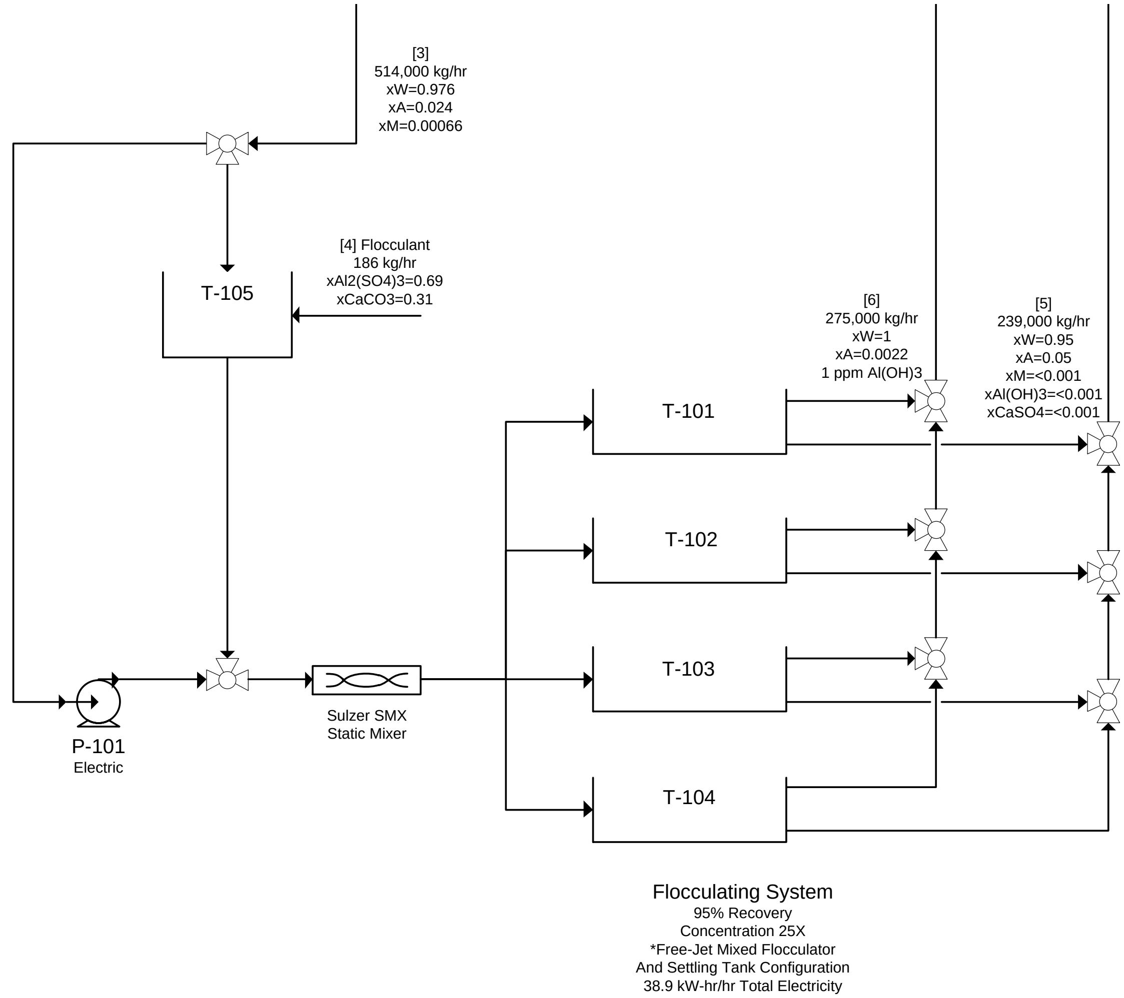


Figure 13. Detail of Flocculation system for the biodiesel manufacturing process.

(Notation clarification can be found in Appendix A)

Stream 6 from the flocculant step contained minimal amounts of calcium sulfate and was returned to the PBR. Any additional calcium sulfate from the flocculation tank reached its maximum concentration, precipitated out of solution and exited in stream 5 (Table 7).

2.2.2.2 Drying

The exiting algae rich slurry stream was then fed to a spray dryer to reduce the moisture content from 95% to 5%.[12] A spray dryer was chosen due to its common use in drying fine slurries, its fast processing time, and because it created porous, dried particles easily digestible by solvents during the extraction step.[68] This process had the benefit of a short residence time (seconds), and limited the slurry's exposure to high temperatures. Hot air at 180°C, 1 atm, and 0.02 kg H_2O/kg DA absolute humidity was fed into the spray dryer. This temperature of hot air lies within an appropriate temperature range for spray dryers.[69] The average heat capacity of air over the temperature range of 25 – 180°C is 1.007 kJ/kgK and the average heat capacity of water over this temperature range was 4.195 kJ/kgK. The mass of dry air (DA) required to reduce the moisture content was calculated by using these average heat capacities of air and water. The assumptions of this calculation include: the enthalpy change of liquid water was negligible compared to the enthalpy changes undergone by the water vapor, and the energy required to increase the liquid water to the air temperature was negligible compared to the latent heat of evaporation of water.[70] These assumptions resulted in the simplified energy balance for a spray dryer (Equation 12).

$$\dot{m}_{air} = \frac{\dot{m}_{Evap}}{\frac{1}{\Delta H_{H2O}^{Vap}}\left(C_{P\,air} + \frac{\dot{m}_{W1}}{\dot{m}_{air}} C_{P\,H2O}\right)(T_{air,in} - T_{air,out})} \tag{12}$$

Where:

$\dot{m}_{Evap}$ is the water being evaporated/removed (kg/kg t BD)

$\dot{m}_{air}$ is the hot air being fed to the spray dryer (kg/t BD)

$\dot{m}_{W1}$ is the water contained in the incoming hot dry air (kg/kg DA)

$C_{P\,air}$ is the heat capacity of dry air at standard temperature and pressure (1.009 kJ/kg K)

$C_{P\,H2O}$ is the heat capacity of water at standard temperature and pressure (4.186 kJ/kg K)

$T_{air,in}$ is the temperature of the air entering the dryer (°C)

$T_{air,out}$ is the temperature of the air exiting the dryer (°C)

ΔH_{H2O}^{Vap} is the heat of vaporization of water (kJ/kg)

The enthalpy of humid air at any given temperature and absolute humidity was calculated using Equation 13. The dried algae biomass exiting the spray dryer needed to contain 5.0 % wt. water. The reduction in water content was necessary for the extraction step since the presence of water reduces the hexane extraction efficiency.[19] The flow rate of dry air required to reduce the water content to specifications was calculated using Equation 12. For this case, 1,019 t DA/t BD was needed to remove 36,400 kg H_2O/t BD.

$$H_w = C_{P\,air} \cdot T + \frac{\dot{m}_{W1}}{\dot{m}_{air}} (C_{P\,wv} \cdot T + \Delta H_{H2O}^{Vap}) \tag{13}$$

Where:

H_w is the enthalpy of humid air at standard pressure and temperature T (kJ/kg DA)

$C_{P\,wv}$ is the heat capacity of water vapor at standard pressure (1.84 kJ/kg K)

The humidified air leaving the spray dryer, now containing 0.06 kg H_2O/kg DA, was sent to a heat exchanger where it was used to preheat the recycled, dried air. A mass balance on water was used to determine the absolute humidity of the air leaving the spray dryer. Equation 12 was used to determine the enthalpy of the humid air, and an energy balance was done to determine the resulting stream temperatures. The exiting humid air from the spray dryer and the recycle of air and water are discussed in spray dryer heat integration section. After 36,400 kg of H_2O/t BD were removed to achieve 5% water content, the mass fractions of the remaining components in the stream were calculated given the stream 5 mass flow rates. The water was transferred to the dry air stream 19 and the addition of water is seen in stream 9. The resulting algae slurry in stream 10 contained 92% algae, 5% water, less than 2% medium, and 1% flocculant, by mass (Table 9, Figure 14).

Table 9. Mass flow summary for streams entering and leaving spray dryer (kg/t BD).

Stream	**[5] Slurry Phase**		**[19] Dry Air In**		**[9] Humid Air Out**		**[10] Dried Slurry**	
Chemical	***m (kg/t BD)***	***x (kg/kg)***	***m (kg/t BD)***	***x (kg/kg)***	***m (kg/t BD)***	***x (kg/kg)***	***m (kg/t BD)***	***x (kg/kg)***
Algae	1,920	0.05	0	0	0	0	1,920	0.95
Water	36,500	0.95	20,400	0.020	56,800	0.052	101	0.050
Medium	38.3	0.0010	0	0	0	0	38.3	0.019
Al(OH)3	4.84	0.00013	0	0	0	0	4.84	0.0024
Dry Air	0	0	1,040,000	1	1,000,000	1	0	0
Total	38,500	1	1,040,000	1	1,100,000	1	2,020	1

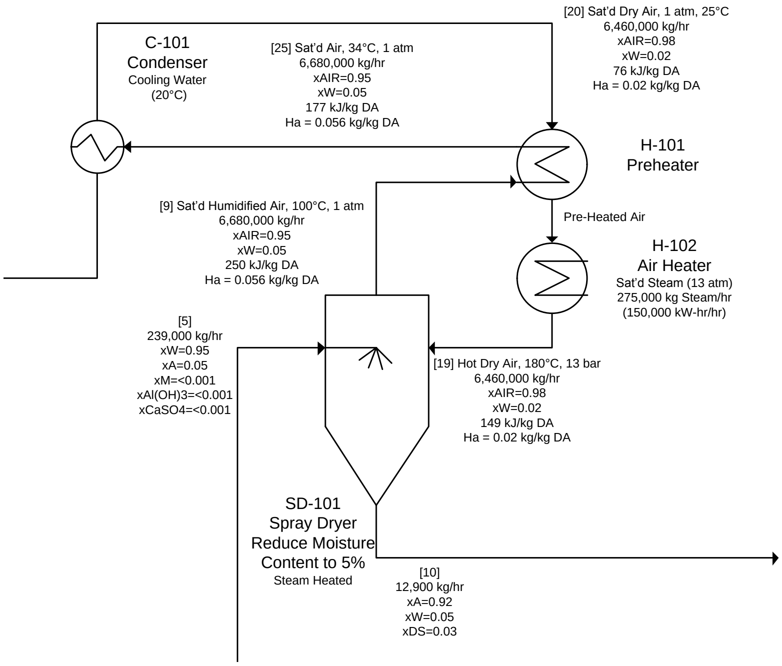


Figure 14. Detail of spray dryer, heater, and preheater, with recycle system for the spray dryer. (Notation clarification can be found in Appendix A)

The material flows to produce a tonne of biodiesel (Table 9) were converted to kg/hr using the plant capacity of 52,300 t BD/yr. The stream flows in kg/hr are presented in Appendix A. Commercial spray dryers are offered by SPX Corporation and are capable of capacities up to 80 t/hr.[71] Since these values are on the same order of magnitude, spray drying was feasible on the scale of this size production facility.

In order to determine energy requirements for the spray dryer system, heat integration was performed to minimize the energy consumption. This was done by establishing recycle loops for recovering energy from the air leaving the spray dryer at 100°C and absolute humidity of 0.06 kg H_2O/kg DA. The water removed by the dryer was condensed from the air stream and returned to the PBR. The humid air stream contained energy which was used to preheat the incoming dry air stream to minimize the energy (steam) necessary to achieve the specified process conditions. Mass and energy balances, as well as Equation 12 were used to determine the conditions of the heat integration system (Table 10). The humid air stream at 100°C leaving the spray dryer was fed into a heat exchanger where it heated the incoming 25°C dry air. The exiting temperature was assumed to be 95°C to maintain a driving force for the energy and a temperature of 35.1°C was calculated through energy balances for the humid air stream exit temperature.

Table 10. Summary stream conditions for dry air recycle system for the spray dryer.

Stream	**Temp. (°C)**	**Ha (kg H_2O/kg DA)**	**Enthalpy (kJ/kg DA)**
[9]	100	0.060	262
[25]	35.1	0.060	190
[20]	25.0	0.020	76
[19]	95.0	0.020	149

The system was defined as the boundary around the preheater (H-101) and the heater (H-102). This allowed the energy balance to be closed around this system and determined the necessary flow of steam to achieve the specified spray dryer air feed conditions. The air was recovered and assumed to be completely recycled, resulting in a constant dry air mass in all four streams (9, 25, 20, 19).

The heat input of steam was determined by the steady state energy balance in combination with the calculated enthalpy in kJ/kg dry air (Equation 14). This resulted in an energy requirement of 159.0 GJ/t BD.

$$\dot{Q}_{Steam} = -\dot{m}_{DA}(\hat{H}_{[9]} + \hat{H}_{[20]} - \hat{H}_{[25]} - \hat{H}_{[19]}) \tag{14}$$

Where:

$\dot{Q}_{Steam}$ is the energy required by the H-102 exchanger (kJ/t BD)

$\dot{m}_{DA}$ is the flow rate of dry air used by the spray dryer (kg/t BD)

$\hat{H}_{[9]}$ is the enthalpy of the humid air entering H-101 (kJ/kg DA)

$\hat{H}_{[20]}$ is the enthalpy of the dry air entering H-101 (kJ/kg DA)

$\hat{H}_{[25]}$ is the enthalpy of the humid air leaving H-101 (kJ/kg DA)

$\hat{H}_{[19]}$ is the enthalpy of the humid air leaving H-101 (kJ/kg DA)

Next, using this calculated value as well as the latent heat of steam at 1,300 kPa and 191.6°C, the flow rate of steam is determined (Equation 15). This pressure of saturated steam was chosen to provide a driving force to heat the dry air up to 180°C.

$$\dot{m}_{Steam} = \frac{\dot{Q}_{Steam}}{\lambda} \tag{15}$$

Where:

$\dot{m}_{Steam}$ is the required flow of steam to bring the dry air to the spray dryer operation conditions (kg/t BD)

λ is the latent heat of steam at 1,300 kPa (kJ/kg)

The utilization of the heat integration technique reduced the energy requirement by 55%. Prior to heat integration, approximately 4.4 MJ/kg of water removed was needed. Typical dryers use between 3.3 and 3.9 MJ/kg water removed.[46] Depending on the application for spray drying, up to 6 MJ/kg of water removed can be consumed.[69] The designed spray dryer lies between reported values and is considered an appropriate approximation. Following heat integration, approximately 2.5 MJ/kg of water removed. The flow rate of saturated steam required for H-102 was 44,300 kg/t BD or equivalent to 24,200 kW-hr/t BD at 1,300kPa and 191.6°C. The cooling water in C-101 was assumed to cool the air to 25°C and bring its absolute humidity to 0.02 kg H_2O/kg DA. The air was then heated to 180°C and the initial conditions of the dry hot air were restored.

2.2.3 Extraction

The next stage in the refinement of algae into biodiesel is the recovery of the primary oil from the dried algae cake. This involves the use of an organic solvent to dissolve and extract the lipid (TAG) from the algae cell followed by purification of the lipid before it can be reacted with methanol to form biodiesel.

The triacylglycerols (TAGs) are contained within the algae cells. N-hexane was determined as a suitable solvent capable of extracting lipid molecules from algae at a volumetric ratio of one cubic meter of solvent for a cubic meter of dried algae cake.[44] At this stage in the process, the feed stream was made up of the dried algae biomass, water, growth medium, and aluminum hydroxide flocculant (Table 11). The volume of the dry slurry was calculated by dividing the component mass flow by the component density. At a 1:1 ratio, the volume of dried algae biomass was also the volume of hexane required. The mass flow rate of hexane was then calculated using the density of hexane.

Table 11. Summary of mass and volume flows entering the extraction phase.

Chemical	**Flow (kg/t BD)**	**Flow (m^3/t BD)**
Algae	1,920	1.748
Water	101.20	0.101
Aluminum Hydroxide	4.84	0.002
Medium sodium nitrate	38.33	0.017
Total	2,070	1.868

Stephenson's work demonstrated that a five stage mixer-settler system can achieve a 90% TAG recovery.[44] This separation was achieved using a counter current mixer-settler operation with an agitated tank and gravity settling basin.[65, 72] This configuration allowed for maximum concentration driving forces and a minimal fresh solvent requirement. The exiting organic phase was assumed to contain only hexane and TAGs while the residual sludge contained the remainder of cell debris and chemicals. Figure 15 shows a representation of the equipment. The dried algae slurry that exits the spray dryer fed the fifth stage mixing unit where it was contacted with the hexane solvent. Fresh hexane solvent entered the first stage where it contacted the algae sludge which is mostly depleted of TAGs. The fresh hexane solvent contacting the depleted algae sludge maximized the mass transfer driving force.

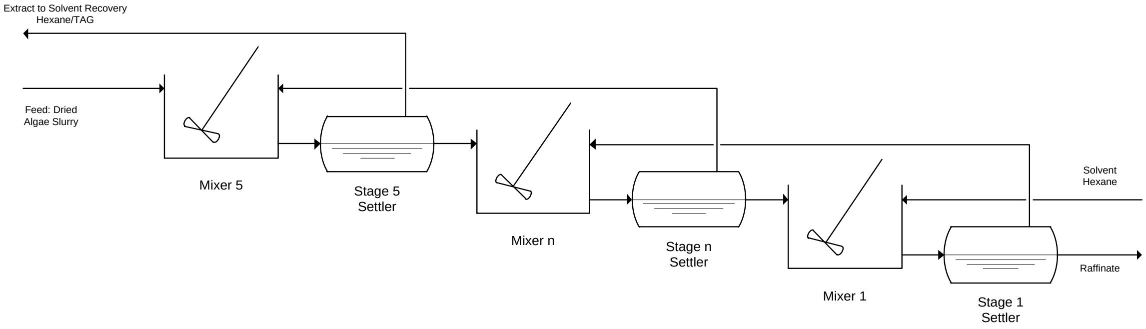


Figure 15. Multi-stage counter-current mixer-settler design.

The slurry or mixture properties are necessary to estimate the energy input in a mixer-settler system. The energy requirement is obtained from the motor powering the impeller-mixed vessel and depends on the properties of the fluid being agitated. The density of algae was assumed to be 1,100 kg/m^3.[73] The viscosity of a 30 g dry algae cells and 300 ml hexane mixture at the conditions of 50°C was 0.056 Pa-s.[74] This was assumed to be valid for the process operating conditions of ambient temperature, 25-30°C. The density of aluminum hydroxide was 2,420 kg/m^3. The growth medium was a mixture of similar minerals, and its density was assumed to be represented by the component of highest concentration. This component was sodium nitrate and has a density of 2,257 kg/m^3. To determine the mixing energy, the slurry density and viscosity was calculated. Mass fractions and component densities and viscosities are shown in Table 12.

Table 12. Summary of chemical and mixture properties of the feed solution to a mixing vessel.

Chemical	Density (kg/m³)	Viscosity (Pa-s)	Slurry Concentration Including Solvent
Algae	1,100	0.056	0.582
Water	1,000	0.001	0.031
Aluminum Hydroxide	2,420	N/A	0.001
Medium (sodium nitrate)	2,257	N/A	0.012
Hexane	654	0.0029	0.370

The slurry density was calculated using Equation 16.[65]

$$\rho_{Slurry} = \frac{1}{\sum_i \frac{x_i}{\rho_i}} \tag{16}$$

Where:

x_i is the mass fraction of component *i*

ρ_{Slurry} is the slurry density (kg/m³)

ρ_i is the density of component *i* (kg/m³)

The trace minerals in the slurry were omitted from the calculations since they are present in negligible quantities. This viscosity was calculated using Equation 17.

$$\mu_{MIX} = \sum_i^n x_i \cdot \mu_i \tag{17}$$

Where:

μ_{MIX} is the mixture viscosity based on weighted contributions (Pa-s)

μ_i is the viscosity of component *i* (Pa-s)

The resulting values for the density and viscosity of the mixture are shown in Table 13.

Table 13. Density and viscosity of the extraction slurry

Density (kg/m^3)	**Viscosity (Pa-s)**
882.55	0.034

The energy consumption for the mixing unit in the mixer-settler system was determined using methodologies described in the Handbook of Industrial Mixing. The mixing vessel was the sole contributor to the energy requirements. This vessel used an electric motor to turn an impeller and agitates the hexane and dry algae mixture. The residence time of the tank needed to be greater than the mixing time to make this operation continuous. The energy consumed by the gravity settling basin was assumed to be negligible.

In a design scenario for a mixing tank design, several parameters needed to be specified, but were varied to alter the process conditions. For example, the tank dimensions or the mix time was manipulated to achieve the desired flow regime. The turbulent flow regime was appropriate for this application as it minimized the mix time while maximizing mass transfer.

The first step in the mixing tank design was to specify the ratio of tank height, H, to tank diameter, T, the ratio of tank diameter to impeller diameter, D as well as the volume as the tank, V. The H:T ratio was set no less than 0.6 as stated in the Industrial Handbook of Mixing.[75] Figure 16 shows a diagram of a mixing vessel. The residence time in the tank could be altered by varying the volume of the tank. A mix time for 95%

homogeneity, θ_{95}, was initially specified. If the resulting system was not turbulent, θ_{95} was altered to achieve a turbulent flow regime.[65] A standard high-flow mixing impeller such as a Pitched Blade Turbine was an appropriate impeller for this application.[75]

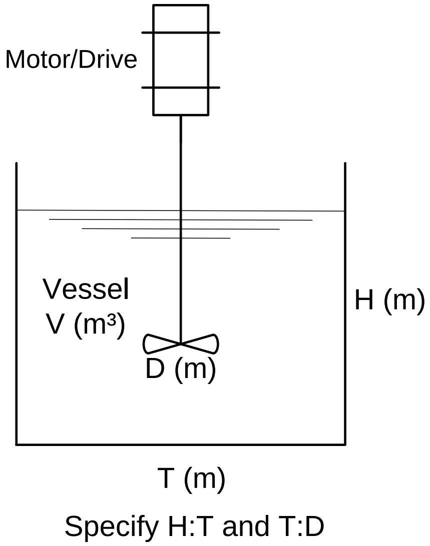


Figure 16. Diagram with characteristic dimensions for mixing vessel design.

A vessel volume of 5.0 m^3 was selected and the ratio of H:T was set at one. These values are not necessarily the optimal dimensions, but serve to approximate the energy demand of the system. The H:T ratio was above 0.6, making it an adequate value. Using the volume of 5.0 m^3, Equation 6 was used to determine the tank diameter. The tank diameter was calculated as 1.85 m.

$$T = \left[\frac{4}{\pi}\frac{V}{0.2}\right]^{1/3} \tag{6}$$

Where:

T is the tank diameter (m)

V is the volume of the tank (m^3)

0.2 represents the specified H/T ratio

The tank height was calculated using the H:T ratio of 1 and resulted in a height of 1.85. The T:D ratio was set at a value of 4, a common and recommended value for a T:D ratio in the Industrial Handbook of Mixing.[65] The impeller diameter was calculated as 0.46 m using this T:D ratio. The resulting vessel specifications are summarized in Table 14.

Table 14. Summary of mixing vessel specifications and dimensions.

Parameter	**Dimension**
Volume (m³)	5
T/D	4
H/T	1
T (m)	1.85
H (m)	1.85
D (m)	0.46

The next step was to specify a mixing time and use the vessel dimensions and fluid properties to calculate the Fourier number for a turbulent flow regime (Equation 18).[65] A value of 30 seconds for the blend time was used, but subject to change if the system was not turbulent. The value of the Fourier number was 0.0018.

$$Fo = 5.40\left(\frac{\mu_{MIX}}{\rho_{SL}}\right)\left(\frac{\theta_{95}}{T^2}\right) \tag{18}$$

Where:

Fo is the Fourier number (Dimensionless)

θ_{95} is the blend time for 95% homogeneity (s)

T is the tank diameter (m)

To determine the Reynolds number of the system, the impeller Power number was specified. In the turbulent regime, the Power number approached a constant value. For a pitched blade turbine (PBT) with 4 blades at 45°, the power number was 1.74.[65] The Reynolds number was calculated using the relationship between the Fourier, Power, and Reynolds numbers for a turbulent regime in an agitated vessel (Equation 19).[65]

$$Po^{1/3}\,\mathrm{Re} = \frac{5.40}{Fo} \tag{19}$$

Where:

Po is the power number for a given impeller/turbine type/model (dimensionless)

The calculated Reynolds number was 1,725. The mixing vessel and impeller should result in a turbulent Reynolds number to ensure sufficient mixing and mass transfer. For the system to be turbulent, the Reynolds number needed to be greater than 4,000.[66] The mix time was decreased to 10 seconds, and the resulting flow was turbulent with Fourier and Reynolds numbers of 0.0006 and 5,180, respectively. The Reynolds number for a mixed tank was used to determine the rotational speed of the impeller and then determine the power required to operate the impeller (Equation 20).[65]

$$\mathrm{Re} = \frac{\rho N D^2}{\mu} \tag{20}$$

Where:

N is the angular speed of impeller rotation (RPS)

D is the diameter of the impeller (m)

The angular speed of the impeller was 0.92 RPS. The power was then calculated using Equation 21.[65]

$$P = Po \cdot \rho N^3 D^5 \tag{21}$$

Where:

P is the power required to turn the impeller in a given fluid (W)

The power to operate five mixing tanks was calculated by multiplying the output of Equation 21 by the number of blending tanks, each with its own mixer. The energy requirements for the system were 1,075 kW-hr/yr or 0.02 kW-hr/t BD assuming a 24 hr/day and 351 day operating year.

The residence time was calculated using Equation 22 and compared to the mixing time. To ensure mass transfer is maximized, the residence time in the mixing tank needs to be greater than the required mixing time. This ensured that there was sufficient phase contact.[75]

$$\tau = \frac{V}{\dot{V}} \tag{22}$$

Where:

τ is the residence time (s)

$\dot{V}$ is the volumetric flow rate (m^3/s)

V is the mixing tank volume (m^3)

Using the tank volume of 5 m^3 and the volumetric flow rate of the system of 6.4E-03 m^3/s, the residence time was 776 seconds (~13 minutes). This was 78 times larger than the mix time which means the tank contents were thoroughly mixed. The results of the calculations described above are shown in Table 15.

Table 15. Summary of mixing tank specifications and results of calculations.

Parameter	***Value***	***Parameter***	***Value***
Flow (m^3/s)	0.0064	**Power (Watts)**	25.5
Vessel Volume (m^3)	5	**Power (1 Stage) (kW-hr/yr)**	215.
Mix time (s)	10	**Power (1 Stage) (kW-hr/t BD)**	0.0041
Flow Residence Time (s)	776	**5 Stage (kW-hr/yr)**	1,075
Fourier Number	0.0006	**5 Stage (kW-hr/t BD)**	0.02
Reynolds Number	5,176	**N (RPS)**	0.92
Power Number (PBT 4 Blades)	1.74	**N (RPM)**	55

The material balance around the mixer-settler was used to determine how much TAGs were recovered by extraction. The 1,920 kg algae/t BD contained 61.3% lipids or TAGs and 95% of these TAGs were recovered.[46, 55] The quantity of TAGs extracted was calculated, as well as the TAGs lost. The extracted TAGs from the dry algae cake was 1,120 kg TAGs/t BD. The water, growth medium, aluminum hydroxide, algae waste, calcium sulfate, and 5% of the TAGs exited the extraction process as waste. The solvent make-up accounted for the lost hexane in the solvent recovery process which is described in the evaporator section. The extract contained the TAG-Hexane phase which was sent to the solvent recovery process. The solvent recovery system recycled the reclaimed hexane solvent back to the extraction process with trace amounts of TAGs and entered as fresh solvent once mixed with the required solvent make-up stream (Table 16, Figure 17).

Table 16. Mass flow summary of the mixer/settler system.

Stream	**[10] Dried Slurry**		**[11] Solvent**		**[13] Extract**	
Chemical	***m (kg/t BD)***	***x (kg/kg)***	***m (kg/t BD)***	***x (kg/kg)***	***m (kg/t BD)***	***x (kg/kg)***
Algae	1,920	0.92	0	0	0	0
Water	101	0.049	0	0	0	0
Al(OH)3	4.84	0.0023	0	0	0	0
Medium	38.3	0.018	0	0	0	0
Hexane	0	0	1,420	0.99	1,220	0.48
TAG	0	0	14.5	0.010	1,120	0.44
Total	2,080	1	1,430	1	2,540	1

Stream	**[12] Raffinate**		**[24] Solvent Make-Up**	
Chemical	***m (kg/t BD)***	***x (kg/kg)***	***m (kg/t BD)***	***x (kg/kg)***
Algae	759	0.78	0	0
Water	101	0.104	0	0
Al(OH)3	4.84	0.0050	0	0
Medium	38.3	0.040	0	0
Hexane	0	0	5	1.0
TAG	59	0.06	0	0
Total	970	1	5	1

The extract was transferred to an evaporator to recover the hexane and prepare the TAGs for the transesterification process. A likely choice for an industrial scale unit is a rising or falling film system.[72] These industrial scale systems can be applied in multiple effect systems. Aspen Plus® was used to model the separation of the hexane from the TAGs.

Aspen Plus® was used to simulate the evaporation and purification of the extracted triglycerides. Triolein was used to model this separation since it is the only triglyceride available in the Aspen Plus® databases. The methyl ester of triolein is oleic acid which is a monounsaturated fatty acid. The oil content of *Scenedesmus Obliquus* is 61.3%. This oil is composed of 75% monounsaturated fatty acid.[55] Since many of these oils behave similarly, using triolein and oleic acid with their associated chemical and physical properties in this simulation was a proper assumption to model this process. The boiling points of hexane, oleic acid, and triolein are shown in Table 17.

Table 17. Comparison of boiling points for chemicals used in the Aspen Plus®.

Chemical	**Boiling Temp (°C)**
Hexane	69
Oleic Acid	360
Triolein	540

Several thermodynamic packages were considered for this simulation. When considering possible packages, it was observed that hexane is a non-polar compound while oleic acid and triolein have several polar sites. UNIQUAC and NRTL both account for compound polarity and were considered valid models for this process. The main consideration in choosing a thermodynamic package was maintaining consistency throughout the course of research. The thermodynamic model used in the reaction and product purification step by Pokoo-Atkins, which uses the same chemical constituents, is NRTL.[52] Therefore, the NRTL model was chosen.

A series of flash drums was used to model the evaporator. The operating conditions for the system were chosen to minimize the undesirable triglyceride oxidation which occurs at sustained time intervals at elevated temperatures of 180°C.[76] Operating under vacuum allowed the operating temperature to be reduced. Maintaining the system at less than 100°C minimized the degradation of the TAGs and maximized the separation. A total of three flash drums were necessary to obtain a 99.6% pure triolein product. Triolein losses were negligible since the vapor stream of hexane and trace triolein were directly recycled and the triolein is fed back into the system.

For the first drum, the evaporator would operate at 101.3 kPa and 90°C. The next flash drum was then installed in the simulation and a new pressure is selected. In order to achieve an effective separation while reducing the temperature, a significant decrease in pressure was required. The second drum would operate at 30.4 kPa and 80°C. In the third flash drum, the hexane in the mixture was present in such small quantities that the pressure was reduced to 5.1 kPa to achieve an effective separation at a temperature of 70°C. The corresponding vapor fraction was 0.22. Table 18 summarizes the solvent recovery simulation operating conditions.

Table 18. Summary of flash drum simulation operating conditions.

Stage	**T (°C)**	**P (kPa)**	**Vapor Fraction (V/F)**
1	90	101.3	0.85
2	80	30.4	0.38
3	70	5.1	0.21

The material balance for the evaporator system was obtained from the Aspen Plus® simulation. The compositions of each stream in the evaporator system were programmed into the overall process simulation in Excel to update the compositions for changes in individual process flows. These compositions are shown in Table 19.

Table 19. Results of component separation between hexane and triolein.

Stream	**Liquid Phase**			**Vapor Phase**		
Stage	x_{TAG}	x_H	**Flow (kg/t BD)**	y_{TAG}	y_H	**Flow (kg/t BD)**
1	0.901	0.0994	1,230	0.011	0.989	1,320
2	0.969	0.0309	1,140	0.0404	0.960	91.0
3	0.995	0.005	1,100	0.218	0.782	36.7

The methodology for the steam requirement calculations was found in *Introduction to Food Engineering* and is used to estimate the steam generation or to evaluate the performance of multiple effect evaporators.[77] The heat capacities, enthalpies, and heats of vaporization were obtained for hexane and triolein and are shown in Table 20. Properties for hexane were found in the DIPPR® database. An experimental heat capacity was found for triolein for 60°C. This was used for the heat capacity and assumed to be constant for this range of temperatures.

Table 20. Properties for hexane and triolein.

Property	**Hexane**	**Triolein**
C_p (kJ/kg K)		
70°C	2.48[78]	2.026[79]
80°C	2.53[78]	2.026[79]
90°C	2.58[78]	2.026[79]
H_{vap} (kJ/kg)		
70°C	333.0278	N/A
80°C	324.97[78]	N/A
90°C	316.60[78]	N/A

The mass balance for the three effect system was defined and defined in Equation 23.

$$\dot{m}_f = \dot{m}_{v1} + \dot{m}_{v2} + \dot{m}_{v3} + \dot{m}_p \tag{23}$$

Where:

$\dot{m}_f$ is the mass flow rate of the liquid feed to the first effect

$\dot{m}_{v1}$ is the mass flow rate of the vapor from the first effect

$\dot{m}_{v2}$ is the mass flow rate of the vapor from the second effect

$\dot{m}_{v3}$ is the mass flow rate of the vapor from the third effect

$\dot{m}_p$ is the mass flow rate of the concentrated product

The quantity of product, 1,094 kg/t BD, was known. The mass fraction of TAGs present in the incoming mixture was 0.44 and the desired TAG purity was 99.5%. Equation 24 was then used to find the total flow into the first effect.

$$x_f \dot{m}_f = \dot{m}_p x_p \tag{24}$$

The total flow rate into the first effect was 2,540 kg/t BD. The total amount of hexane evaporated was 1,304 kg/t BD. Enthalpy balances were then written around each effect separately. These are shown in Equations 25, 26, and 27.

$$\dot{m}_f H_f + \dot{m}_s H_{vs} = \dot{m}_{v1} H_{v1} + \dot{m}_{f1} H_{f1} + \dot{m}_s H_{cs} \tag{25}$$

$$\dot{m}_{f1} H_{f1} + \dot{m}_{v1} H_{v1} = \dot{m}_{v2} H_{v2} + \dot{m}_{f2} H_{f2} + \dot{m}_{v1} H_{c1} \tag{26}$$

$$\dot{m}_{f2} H_{f2} + \dot{m}_{v2} H_{v2} = \dot{m}_{v3} H_{v3} + \dot{m}_p H_p + \dot{m}_{v2} H_{c2} \tag{27}$$

Where:

$\dot{m}_{f1}$ is the mass flow rate into effect 2

$\dot{m}_{f2}$ is the mass flow rate into effect 3

$\dot{m}_s$ is the steam flow rate

H_{vs} is the enthalpy of saturated steam

H_{cs} is the enthalpy of the condensed water leaving the first effect

H_f is the enthalpy of the mixture flowing into the first effect

H_{f1} is the enthalpy of the mixture flowing into the second effect

H_{f2} is the enthalpy of the mixture flowing into the third effect

H_{c1} is the enthalpy of the condensed hexane leaving the second effect

H_{c2} is the enthalpy of the condensed hexane leaving the third effect

H_{v1} is the enthalpy of the hexane vapor leaving the first effect

H_{v2} is the enthalpy of the hexane vapor leaving the second effect

H_{v3} is the enthalpy of the hexane vapor leaving the third effect

H_p is the enthalpy of the purified TAGs leaving the third effect

The heat transfer across heat exchangers can be expressed by Equations 28, 29, and 30. It was assumed that the overall heat transfer coefficient for each of the three effects is 1,000 W/m^2 K.

$$q_1 = U_1 A_1 (T_s - T_1) = \dot{m}_s H_{vs} - \dot{m}_s H_{cs} \tag{28}$$

$$q_2 = U_2 A_2 (T_1 - T_2) = \dot{m}_{v1} H_{v1} - \dot{m}_{v1} H_{c1} \tag{29}$$

$$q_3 = U_3 A_3 (T_3 - T_3) = \dot{m}_{v2} H_{v2} - \dot{m}_{v2} H_{c2} \tag{30}$$

Where:

q_i is the rate of heat transfer across effect i

U_i is the overall heat transfer coefficient of effect i

A_i is the area of the heat exchanger

T_s is the temperature of the steam

T_i is the boiling temperature maintained in effect i

Assuming that the area of heat transfer for all three effects are the same, Equation 31 was derived.

$$\frac{\dot{m}_s H_{vs} - \dot{m}_s H_{cs}}{U_1(T_s - T_1)} = \frac{\dot{m}_{v1} H_{v1} - \dot{m}_{v1} H_{c1}}{U_2(T_1 - T_2)} = \frac{\dot{m}_{v2} H_{v2} - \dot{m}_{v2} H_{c2}}{U_3(T_2 - T_3)} \tag{31}$$

The enthalpies of the TAG/hexane mixtures and hexane vapors were calculated. The heat capacities for the TAG/hexane mixtures were calculated using Equation 32. The enthalpies were then calculated using Equation 33.

$$C_{pmix} = \sum_i x_i C_{pi} \tag{32}$$

Where:

C_{pi} is the heat capacity of component i

x_i is the mass fraction of component i

$$H_i = C_{pi}(T_i - 0) \tag{33}$$

The enthalpy of steam at 120°C and 2 bar is 2,706.6 kJ/kg. The enthalpy of the condensed water is 504.8 kJ/kg. The heat of vaporization for hexane is 368.18 kJ/kg. The heat of vaporization of hexane can be added to the enthalpy of liquid hexane at that specific pressure and temperature to acquire enthalpy values for the vapor. The resulting enthalpies and heat capacities are shown in Table 21.

Table 21. Calculated heat capacities and enthalpies.

C_{pf} = 2.18 kJ/kg K
C_{pf1} = 2.15 kJ/kg K
C_{pf2} = 2.11 kJ/kg K
H_f = 43.6 kJ/kg
H_{f1} = 193.3 kJ/kg
H_{f2} = 168.7 kJ/kg
H_{f3} = 145.78 kJ/kg
H_{c1} = 232.2 kJ/kg
H_{c2} = 202.4 kJ/kg
H_{c3} = 173.6 kJ/kg
H_{v1} = 548.8 kJ/kg
H_{v2} = 527.37 kJ/kg
H_{v3} = 506.62 kJ/kg

The heat capacities and known flow rates were inserted into Equations 25, 26, 27, and 31. This resulted in Equations 34, 35, 36, 37, and 38. The material balance in Equation 23 is then used to find the sixth equation and is shown in Equation 39. This produces a system of equations with six equations and six unknowns. The unknown variables are $\dot{m}_s$, $\dot{m}_{v1}$, $\dot{m}_{v2}$, $\dot{m}_{v3}$, $\dot{m}_{f1}$, and $\dot{m}_{f2}$.

$$72.83\dot{m}_s - 31.66\dot{m}_{v1} = 0 \tag{34}$$

$$31.66\dot{m}_{v1} - 32.50\dot{m}_{v2} = 0 \tag{35}$$

$$2201.74\dot{m}_s - 548.8\dot{m}_{v2} - 193.32\dot{m}_{f1} = -30 \tag{36}$$

$$193.32\dot{m}_{f1} + 316.6\dot{m}_{v1} - 527.37\dot{m}_{v2} - 168.72\dot{m}_{f2} = 0 \tag{37}$$

$$168.72\dot{m}_{f2} + 324.9\dot{m}_{v2} - 506.63\dot{m}_{v3} = 56.69 \tag{38}$$

$$\dot{m}_{v1} + \dot{m}_{v2} + \dot{m}_{v3} = 0.384 \tag{39}$$

The system of equations was solved using Microsoft Excel®. The quantity of steam required for the multiple effect evaporators is 226.4 kg/t BD. To convert this to an hourly basis, the mass of steam on the basis of one tonne of biodiesel is multiplied by the plant capacity (52,300 t BD/yr). Therefore, the amount of steam required on an hourly basis is 1,406 kg/hr.

Using these compositions the materials flows were calculated via material balance using the output flow from the extraction system (Table 22, Figure 17).

Table 22. Mass flow summary for the multiple effect system (kg/t BD).

Operating Conditions	**Stream**	**[13] (Feed)**		**[14] (Vap)**		**[15] (Liq)**	
	Chemical	***m (kg/t BD)***	***x (kg/kg)***	***m (kg/t BD)***	***x (kg/kg)***	***m (kg/t BD)***	***x (kg/kg)***
Stage 1 (F-101) ***{0.85=V/F, 1 atm}***	**Triolein (TAG)**	1,120	0.44	14.5	0.011	1,110	0.901
	Hexane	1,430	0.56	1,300	0.989	121	0.099
	Total	2,540	1	1,320	1	1,230	1
Stage 2 (F-102) ***{0.38=V/F, 0.2 atm}***	**Stream**	**[15] (Feed)**		**[26] (Vap)**		**[27] (Liq)**	
	Triolein (TAG)	1,110	0.90	3.60	0.04	1,100	0.97
	Hexane	121	0.10	87.4	0.96	33.7	0.03
	Total	1,230	1	91.0	1	1,140	1
Stage 3 (F-103) ***{0.22=V/F, 0.05 atm}***	**Stream**	**[27] (Feed)**		**[28] (Vap)**		**[29] (Liq)**	
	Triolein (TAG)	1,100	0.97	7.98	0.22	1,090	1.00
	Hexane	33.7	0.03	28.7	0.78	5.00	0.00
	Total	1,140	1	36.7	1	1,100	1

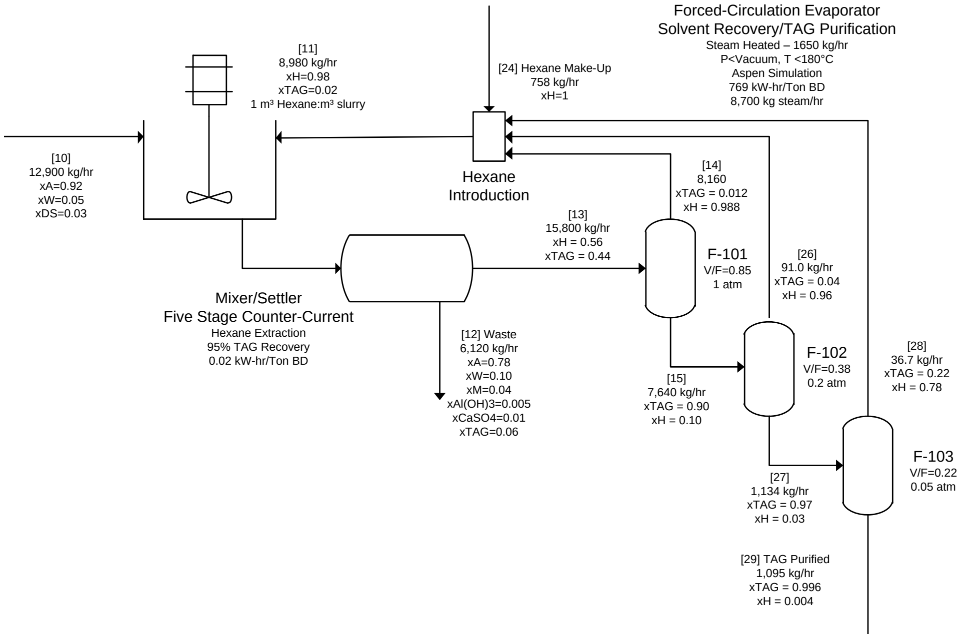
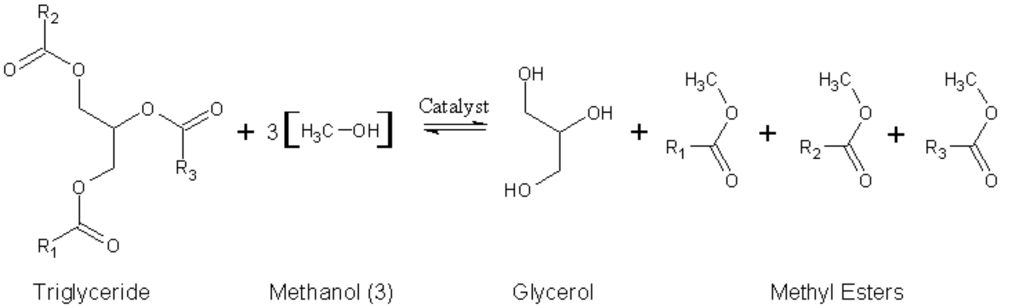


Figure 17. Detail of PFD showing extraction and purification steps. (Notation clarification can be found in Appendix A)

2.2.4 Reaction and Product Purification

The transesterification reaction is where the biodiesel is produced. In this reaction (Equation 40), a triglyceride molecule reacts with three alcohol molecules to form a glycerol molecule and three fatty acid methyl esters. This reaction is not spontaneous and must be carried out under special conditions, such as in the presence of a catalyst or at high temperatures.[35] The alcohols used in transesterification are usually methanol or ethanol due to their cost and commercial availability compared to other alcohols.[34, 39] The various methods of transesterification are differentiated by the conditions under which they are carried out and can be separated into the following: basic catalysis, acidic catalysis, enzymatic catalysis, non-catalytic supercritical synthesis, and non-catalytic co-solvent synthesis.



(40)

The transesterification and purification steps in the manufacture of biodiesel from microalgae are well understood stages in this process. Pokoo-Aikins and Nadim provide a well defined Aspen Plus® simulation that documents the reaction of the TAGs and purification of the crude biodiesel as well as the reclamation of the glycerol byproduct and the complete purification system.[52] Two reactor designs were investigated; Reactor Design One assuming a 70% conversion in each reactor and Reactor Design Two assuming a 90% conversion. In order to take a conservative approach, the 70% reactor conversion case was chosen which resulted in a total TAG conversion to methyl esters (biodiesel) of 91% of the input TAGs. The designed system has the capacity of producing 130,000 t BD/yr which is different than the proposed system of 52,300 t BD/yr. The process was proportionally scaled down to achieve the desired production values for this system. These production values were then applied to the proposed inputs and values for the required inputs and shown in terms of kg/t BD.

The overall process parameters of Pokoo-Aikins transesterification and purification were as follows. The simulation assumed 99.5% pure triglycerides in the extracted algae oil with impurities of this feed stream consisting of individual fatty acids. Alkali-catalyzed transesterification was used as it was found throughout several studies as an effective method of converting triglycerides and methanol to glycerol and fatty acid alkyl esters (FAMEs or biodiesel). Although our system also contained hexane, this component is present in such small quantities, 0.3% wt., that hexane was unlikely to have any significant effect on the transesterification.[52]

This reaction was accomplished through a two stage transesterification where a 70% conversion was assumed in each reactor vessel. First methanol and NaOH were mixed together to form a 1% wt. solution with a methanol feed rate of a 6:1 molar ratio of methanol to TAG's.[52] The excess TAGs from the first reactor were then fed into the second reactor with makeup NaOH and methanol to bring the methanol concentration back to a 6:1 molar ratio.[52]

The products coming out of each reactor, FAMEs and Glycerol were first cooled to 33.3°C and 1 atm. The knowledge of these two component's immiscibility and difference in specific gravity was exploited for separation via a decanter.[52] The excess unreacted methanol was recovered using a distillation column and collected as vapor. The excess sodium hydroxide was neutralized with hydrogen chloride. Hydrogen chloride was also used to split any soap that may form. The FAMEs were purified by water washing to remove residual catalyst, salts, methanol, free glycerol and soaps resulting with a biodiesel purity of 99.65% by weight. Glycerol was purified where residual FAMEs exit the column as vapor and glycerol exits from the bottom and was then considered a purified by-product. This Aspen flow diagram is shown in Appendix A.

Only total system input mass flows were given. From these values as well as using the conversions through each reactor, the resulting mass generated of each component were calculated. The system described by Pokoo-Atkins was listed in such a way as to make a balance on each individual unit operation impossible without further details; therefore, calculations were done on the system as a whole using the author's initial assumptions and process parameters. Using the specified reactor conversions, the quantity biodiesel produced, methanol consumed, and glycerol produced was calculated. Pokoo-Atkins performed energy integration on this process as well, resulting in optimized energy consumption. The mass requirements of each chemical and total system energy balance for this process were specified, and reported on a t BD basis.

The compositions for individual streams were not provided and several assumptions were necessary to separate the system into individual output streams. The molecular weight of oleic acid was used as the molecular weight of the FAMEs and the TAGs consisted of three molecules of oleic acid, and one molecule of glycerol.

Streams 17 and 18, the exiting biodiesel and glycerol streams, were assumed to be pure streams of usable product under the assumption that all life cycle emissions, due to these very small quantities of impurities, will be insignificant when compared to the overall transesterification and purification process. There were two waste streams in this process, one from the water washing, and one from decanting. In the waste from the water washing, it was assumed that purely salts will be taken out in the water. In the decanter waste, it was assumed that this was unreacted TAGs, excess sodium hydroxide catalyst, and the residual hexane. A PFD with mass and energy flows is shown in Figure 18.

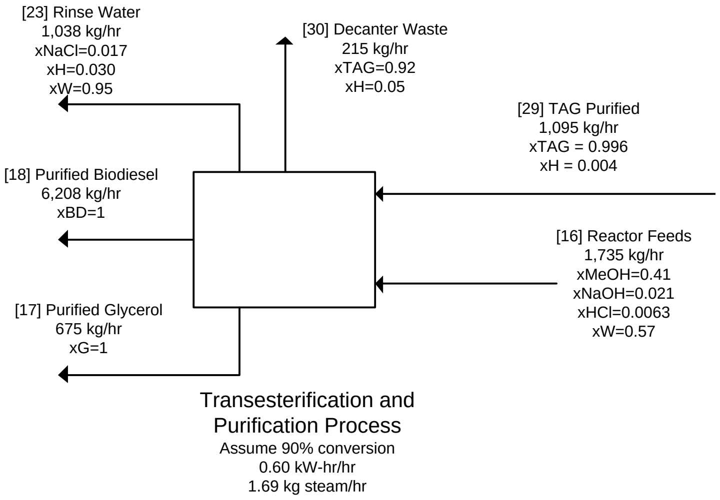


Figure 18. Detail of transesterification and biodiesel purification process PFD. (Notation clarification can be found in Appendix A)

The mass flow rate of each stream was then calculated using the assumptions and system inputs. Each stream was separated in a way which would allow for an effective life cycle assessment (LCA) of the entire transesterification and purification process. Energy requirements were found by proportionally scaling down Pokoo-Aikins energy requirements to the design basis.

The unreacted methanol produced is purified by distillation and recycled back into the reactor. This greatly reduces then quantity of methanol required. The resulting streams are shown in Table 23. The cooling energy required is 0.10 kWhr/t BD and the heating requirement is 0.15 kWhr/t BD. This heating requirement was then converted to mass of steam by utilizing the latent heat of saturated steam at 13 bar and results in 0.27 kg/t BD.

Table 23. Optimized reaction and purification stream table.

Stream	**[16] Reaction Inputs**		**[29] Pure TAGs**		**[18] Pure FAME's (Biodiesel)**	
Chemical	***m (kg/t BD)***	***x (kg/kg)***	***m (kg/t BD)***	***x (kg/kg)***	***m (kg/t BD)***	***x (kg/kg)***
TAG	0	0	1,094	1	0	0
MeOH	113.5	0.40	0	0	0	0
NaOH	5.806	0.02	0	0	0	0
HCl	1.759	0.0062	0	0	0	0
H2O	158.5	0.56	0	0	0	0
FAME	0	0	0	0	1,000	1
Glycerol	0	0	0	0	0	0
NaCl	0	0	0	0	0	0
Hexane	5.0	0.018	5	0	0	0
Total	285	1	1,099	1	1,000	1
Stream	**[17] Glycerine**		**[23] Rinse Waste**		**[30] Decanter Waste**	
Chemical	***m (kg/t BD)***	***x (kg/kg)***	***m (kg/t BD)***	***x (kg/kg)***	***m (kg/t BD)***	***x (kg/kg)***
TAG	0	0	0	0	98	0.92
MeOH	0	0	0	0	0	0
NaOH	0	0	0	0	4	0.036
HCl	0	0	0	0	0	0
H2O	0	0	159	0.98	0	0
FAME	0	0	0	0	0	0
Glycerol	109	1	0	0	0	0
NaCl	0	0	3	0.017	0	0
Hexane	0	0	0	0	5	0.047
Total	109	1	162	1	107	1

2.3 Summary of Base Case

A summary of the energy requirements for each unit operation is shown in Table 24. The PBR contributed to nearly all of the electricity consumption. The other process' contributions were negligible in comparison. The energy estimations for the PBR have many uncertainties such as lack of data on a commercial system design. This resulted in large variations in energy consumption depending on the method of estimation. In Stephenson's LCA, it was also found that the PBR was also the major contributor to energy consumption.[44] The lack of commercial scale PBRs suggest that this is a major obstacle to overcome in making algae-derived biodiesel a feasible process.

Table 24. Summary of the relative energy requirements of the process stages.

Process Energy Breakdown						
Unit	**Electricity (kWh/t BD)**	**Electricity (%)**	**Steam (kg/t BD)**	**Steam (%)**	**Total Energy (kWh/t BD)**	**Total Energy (%)**
PBR	39,800	>99.9%	0	0%	39,800	62%
Flocculation	6.3	<0.1%	0	0%	6.3	<0.1%
Spray Drying	0	0%	44,300	99.5%	24,200	38%
Extraction and Solvent Recovery	0.0206	<0.1%	226	0.5%	124	0.2%
Reactor/Purification	0.1	<0.1%	0.27	<0.1%	0.25	<0.1%
Total	39,800		44,500	100.0%	64,100	

If the PBR electricity consumption is removed from consideration, the resulting energy contributions are shown in Table 25. The major contributor becomes the spray drying step, contributing to nearly 99.5% of the total energy requirements. This was an expected result due to the large quantity of water removed from the algae during this operation. All other processes are insignificant when compared to this stage.

Table 25. Summary of the relative energy requirements without PBR.

Process Energy Breakdown						
Unit	**Electricity (kWh/t BD)**	**Electricity (%)**	**Steam (kg/t BD)**	**Steam (%)**	**Total Energy (kWh/t BD)**	**Total Energy (%)**
Flocculation	6.3	98%	0	0%	6.3	<0.1%
Spray Drying	0	0%	44,300	99.5%	24,200	99.5%
Extraction and Solvent Recovery	0.0206	0.3%	226	0.5%	124	0.5%
Reactor/Purification	0.1	1.6%	0.27	<0.1%	0.25	<0.1%
Total	6		44,500		24,400	

Chapter 3

Development of Life Cycle Inventories

In order to make an accurate assessment of the environmental impact, a comprehensive life cycle inventory of each process must be developed. This inventory includes the production of all raw materials, all energy requirements, and management of waste streams, as well as direct emissions from the manufacturing process. The life cycle inventories were obtained using SimaPro® software. SimaPro® contains a large database of life cycle inventories for materials and energy. These established databases were used for the majority of the compounds in this process. When the material was not found in the database, a new LCI for that material was developed, and the methodology used to develop a life cycle inventory properly documented. Figure 19 shows the information included in a comprehensive LCI for any given manufacturing process.

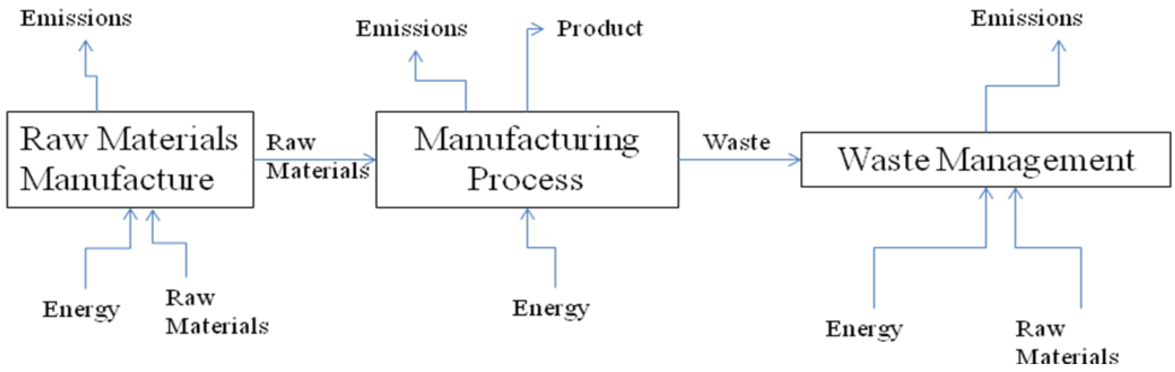


Figure 19. Flow diagram for life cycle inventories of a manufacturing process

3.1 Raw Materials LCIs

Life cycle inventories were obtained for each individual processing stage within the production of algae-derived biodiesel. The process was divided into the algae growth stage, flocculation stage, spray drying stage, extraction stage, solvent recovery stage, and reaction/final purification stage. All of the raw material and energy inputs were compiled (Table 26) and then defined in SimaPro®. Each raw material and energy input has associated emissions, energy consumption, and raw material consumption values. Every material input below 0.1 kg/t BD was considered to be insignificant towards the life cycle analysis and was not considered as part of the LCI. Components considered to be insignificant include: zinc sulfate, copper sulfate, sodium molybdate, and cobalt(II) nitrate.

Table 26: Raw material inputs into the algae biodiesel process.

Inputs	Growth (kg/t BD)	Flocculation (kg/t BD)	Extraction and Solvent Recovery (kg/t BD)	Reaction and Purification (kg/t BD)
Water	1,150	0	0	158
KH_2PO_4	14.5	0	0	0
$CaCl_2$	2.07	0	0	0
$MgSO_4$	6.21	0	0	0
$NaNO_3$	20.7	0	0	0
K_2HPO_4	6.21	0	0	0
NaCl	2.07	0	0	0
Na_2EDTA	0.828	0	0	0
KOH	0.513	0	0	0
$FeSO_4$	0.412	0	0	0
H_2SO_4	0.152	0	0	0
H_3BO_3	.903	0	0	0
$MnCl_2$	0.237	0	0	0
$ZnSO_4$	0.0184	0	0	0
$NaMoO_4$	0.0323	0	0	0
$CuSO_4$	0.00654	0	0	0
$Co(NO_3)_2$	0.00409	0	0	0
$CaCO_3$	0	9.32	0	0
$Al_2(SO_4)_3$	0	20.7	0	0
CO_2	3,130	0	0	0
Hexane	0	0	5.03	0
MeOH	0	0	0	113
NaOH	0	0	0	5.81
HCl	0	0	0	1.76

Some of the LCIs for components which are significant contributors to the process were not available in SimaPro®. Table 27 shows a list of available and unavailable chemicals in the database. Inventories unavailable in the SimaPro® database were generated by other means. These methodologies are described within the LCI generation section of the report.

Table 27. Inventories available and unavailable in SimaPro®

Available Inventories	**Unavailable Inventories**
Tap water, H_2O, at user/RER U	Na_2 EDTA
Calcium chloride, $CaCl_2$, at plant/RER U	Dipostassium phosphate (K_2HPO_4)
Magnesium sulfate ($MgSO_4$), at plant/RER U	Manganese Chloride ($MnCl_2$)
Sodium chloride (NaCl), powder, at plant/RER U	Monopotassium phosphate (KH_2PO_4)
Potassium Hydroxide (KOH), at regional storage/RER U	Sodium Nitrate ($NaNO_3$)
Iron sulfate ($FeSO_4$), at plant/RER U	
Sulphuric acid (H_2SO_4), liquid, at plant/RER U	
Boric acid (H_3BO_3), anhydrous, powder, at plant/RER U	
Aluminum sulfate ($Al_2(SO_4)_3$), powder, at plant/RER U	
Limestone ($CaCO_3$), milled, loose, at plant/CH U	
Hexane (C_6H_{14}), at plant/RER U	
Methanol (CH_3OH), at plant/GLO U	
Sodium hydroxide (NaOH), 50% in H2O, production mix, at plant/RER U	

The LCI for each raw material can be found in Table 28 and Table 29. Each impact category is measured on a one kg basis. The relative impact of each given component can then be compared to find the major contributors to each impact category. Figure 20 shows the comparison of the overall life cycle emissions of the chemicals and indicates that the two components with the largest emissions are monopotassium phosphate and dipotassium phosphate. Figure 21 shows a comparison of the Cumulative Energy Demand (CED) of each component. The CED is the entire demand of primary energy associated with the raw material production, manufacturing process, and waste disposal of the component. The two components with the largest energy demand are Na_2EDTA and hexane respectively.

Each raw material inventory in SimaPro® has its own set of assumptions and includes all energy, material, emissions, and waste management impacts. This data can be derived from stoichiometric relationships, reported literature values, or measured data from existing production facilities. The selected database entry for each component available in SimaPro® is shown in Table 27.

Table 28. LCIs for all materials used in the algae biodiesel process on a per kilogram basis.

Impact Category	**Tap water**	**$CaCl_2$**	**$MgSO_4$**	**NaCl**	**KOH**	**$FeSO_4$**	**H_2SO_4**	**H_3BO_3**	**$Al_2(SO_4)_3$**
Raw Materials Used (kg)	0.000686	2.42	1.32	1.24	2.78	0.200	0.137	3.082	0.496
Emissions to Air (kg)	0.000328	0.873	0.294	0.201	1.88	0.188	0.153	0.761	0.501
CO_2 (kg)	0.000324	0.860	0.289	0.199	1.86	0.185	0.135	0.725	0.486
CO (kg)	1.21E-06	0.00167	0.000132	0.000643	0.00196	0.000559	0.00041	0.00163	0.000458
CH_4 (kg)	6.77E-07	0.00210	0.000481	0.000343	0.00392	0.00035	0.000203	0.00122	0.000736
NMVOC (kg)	1.28E-07	0.000229	8.15E-05	7.72E-05	0.000660	6.52E-05	7.44E-05	0.000491	0.000194
NO_x (kg)	6.2E-07	0.00208	0.00061	0.000377	0.00339	0.000363	0.000804	0.00321	0.00141
SO_2 (kg)	8.93E-07	0.00394	0.000932	0.000621	0.00484	0.000638	0.0129	0.0156	0.00782
Particulates (kg)	4.12E-07	0.00148	0.00317	0.000335	0.00167	0.000336	0.000216	0.00664	0.00156
Emissions to Water (kg)	4.55E-05	0.305	0.00778	0.0136	2.38	0.00844	0.00912	0.0269	0.0438
VOCs (kg)	3.14E-10	6.14E-07	2.98E-07	3.16E-07	2.46E-06	1.82E-07	5.67E-07	1.86E-06	1.21E-06
Emissions to Soil (kg)	7.33E-08	0.000277	6.66E-05	0.000189	0.000662	4.54E-05	0.000154	0.000526	0.000282
Total Emissions (kg)	**0.000374**	**1.18**	**0.302**	**0.215**	**4.26**	**0.196**	**0.163**	**0.788**	**0.545**
CED (MJ)	0.00618	11.5	6.29	3.69	37.1	3.80	2.36	13.6	9.51
Water Used (kg)	3.04	2,500	2,080	1,200	8,870	1,320	466	2,770	2,480

Table 29. LCIs for all materials used in the algae biodiesel process on a per kilogram basis.

Impact Category	**$CaCO_3$**	**C_6H_{14}**	**CH_3OH**	**NaOH**	**K_2HPO_4**	**$MnCl_2$**	**KH_2PO_4**	**Na_2 EDTA**	**$NaNO_3$**
Raw Materials Used (kg)	1.01	1.593	0.834	1.79	3.54	2.27	4.674	4.15	1.01
Emissions to Air (kg)	0.0128	0.884	0.647	1.11	3.22	0.636	4.23	4.02	0.0128
CO_2 (kg)	0.0125	0.855	0.640	1.10	3.16	0.626	4.15	3.96	0.0125
CO (kg)	2.2E-05	0.00144	0.000433	0.00112	0.00439	0.00124	0.00574	0.00441	2.2E-05
CH_4 (kg)	1.44E-05	0.00271	0.00423	0.00190	0.00676	0.00157	0.00904	0.0342	1.44E-05
NMVOC (kg)	1.37E-05	0.0161	0.00108	0.000277	0.00381	0.00016	0.00513	0.00376	1.37E-05
NO_x (kg)	5.97E-05	0.00234	0.000917	0.002	0.00557	0.00152	0.00733	0.00681	5.97E-05
SO_2 (kg)	1.95E-05	0.00531	0.000636	0.00358	0.0251	0.00296	0.0324	0.00929	1.95E-05
Particulates (kg)	0.000186	0.000767	0.00012	0.00121	0.00459	0.00101	0.00598	0.00308	0.000186
Emissions to Water (kg)	0.000486	0.175	0.00639	0.0533	2.22	0.223	2.94	0.467	0.000486
VOCs (kg)	6.59E-08	2.55E-05	1.72E-07	1.07E-06	4.07E-06	4.18E-07	5.35E-06	2.81E-06	6.59E-08
Emissions to Soil (kg)	1.26E-05	0.00593	0.000127	0.000357	0.00321	0.000199	0.00415	0.000978	1.26E-05
Total Emissions (kg)	**0.0133**	**1.06**	**0.654**	**1.16**	**5.43**	**0.859**	**7.17**	**4.492279**	**0.013331**
CED (MJ)	0.380	61.6	37.6	23.3	44.7	8.30	59.4	95.8	0.380
Water Used (kg)	875	1,680	544	7,810	9,830	1,310	13,100	13,500	875

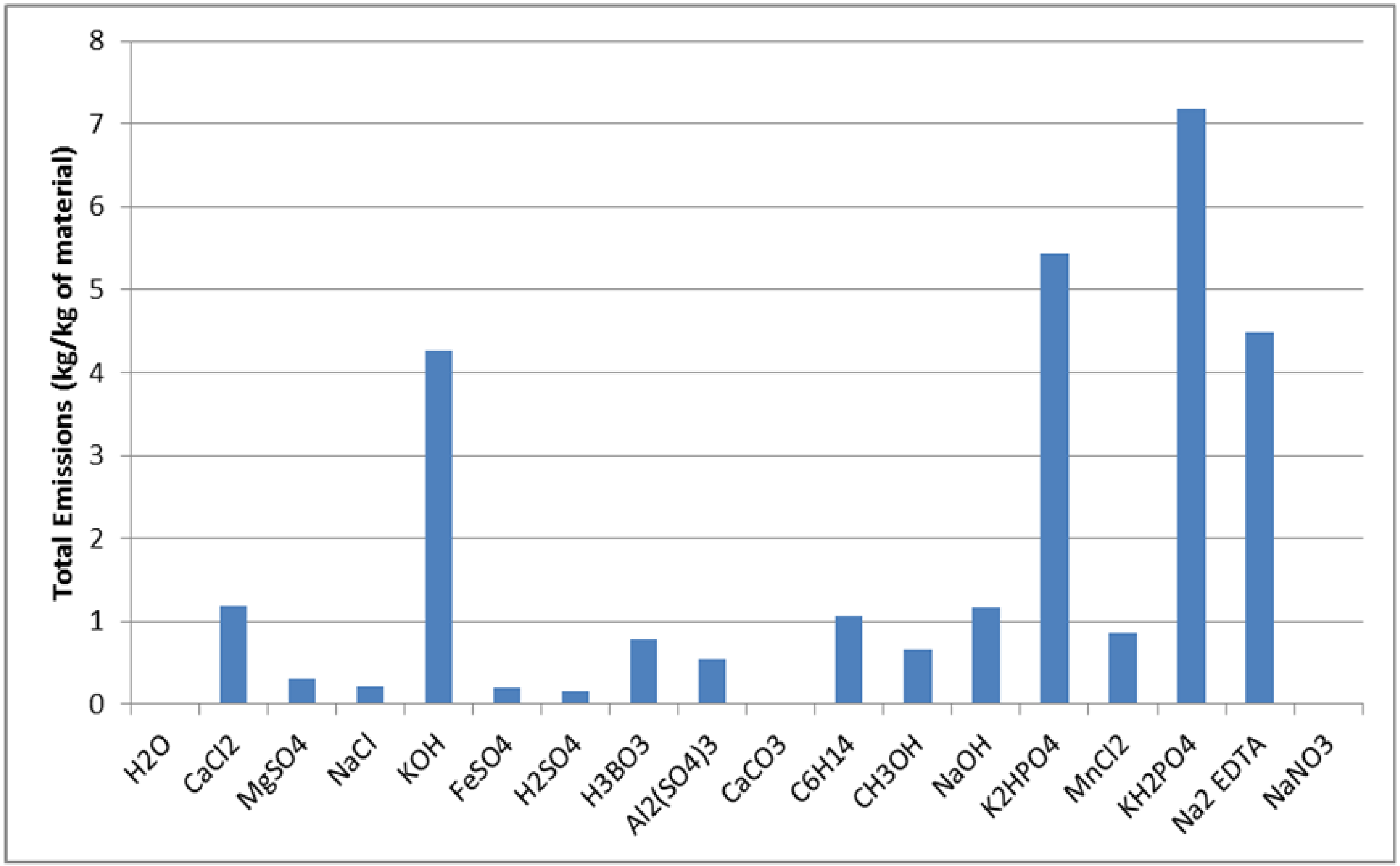


Figure 20. Comparison of total emissions from each raw material

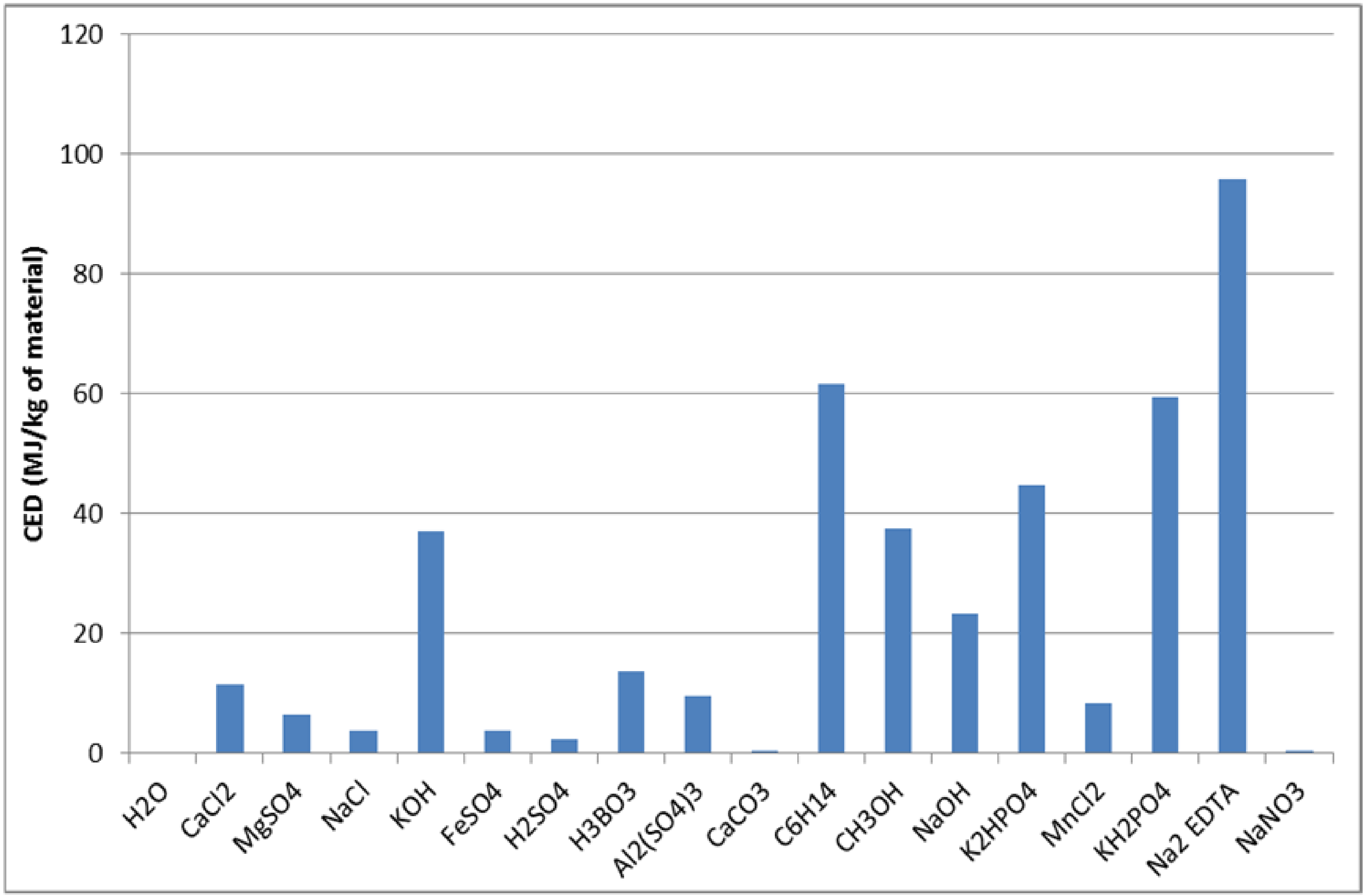


Figure 21. Comparison of CED from each raw material

Water was defined in SimaPro® as tap water. The resulting total emissions from the generation of tap water are insignificant compared to other processes at 3.7 x 10^{-4} kg. The majority of these emissions are to air (88%). The CED was 0.006 MJ for every kg of tap water generated. Tap water includes the impact of infrastructure as well the energy used for water treatment and the transportation to the end user. There are no emissions from the water treatment process. Tap water is based on data from Switzerland and energy estimations from Denmark.

Calcium chloride is present in the growth medium for the algae. The total emissions generated from each kg of calcium chloride are 1.18 kg. The emissions to soil are essentially negligible, while 74% and 25% of the total emissions are to air and water, respectively. The CED for the generation of calcium chloride is 11.5 MJ/kg. This was modeled by the manufacturing process using the Solvay technique. It includes: the consumption of raw materials, auxiliaries, energy, infrastructure and land use, and the transport of raw materials, auxiliaries, and wastes. It also includes the generation of wastes and emissions into the air and water. Byproducts and coproducts are not considered. The data is based on measurements from two plants in Germany.

Magnesium sulfate is also a component of the growth medium. The total emissions are low at 0.3 kg with 97% being emitted to air. The CED for this process is 6.29 MJ. The model within the SimaPro® database includes the raw materials, machinery, and energy consumption for the production and infrastructure of the site. It is based on average European data from existing production plants.

Sodium chloride is present as part of the growth medium. Total emissions from the production of sodium chloride are 0.21 kg with air emissions contributing to 93% of these emissions. The CED of this process is 3.69 MJ. This process includes the solution mining process of sodium chloride, the removal of impurities, as well as the drying step. Mining is modeled by thermo compressing technology. It is based on data acquired from one European mining site.

Potassium hydroxide is another component of the growth medium and is a cradle to gate LCI including precursors, ancillary materials as well as transportation requirements. It is produced by the electrolysis of potassium chloride brine in electrolytic cells. This is based on industry data from the United States. The resulting total emissions are relatively high at 4.26 kg. The majority of these emissions are to water (56%) while 44% are to air. Soil emissions are negligible. The CED for potassium hydroxide production is 37.1 MJ.

Iron sulfate is present in the growth medium. This is a by-product of the steel and iron manufacturing. This database entry is specified as a rough estimation of electricity use for the purification of this byproduct in Switzerland. This result is emissions of 0.20 kg with 96% emitted to air. The CED for this process is 3.8 MJ.

Sulfuric acid is also present in small quantities within the growth medium. The total emissions are 0.16 kg with 94% being to air. The CED is 2.4 MJ. This is modeled as the collection of SO_2 containing gas by means of oxidation of the sulfur containing raw materials. It includes the conversion of SO_2 to SO_3 and the absorption of SO_3 into aqueous solution to yield sulfuric acid. It includes all auxiliaries, raw materials, energy, infrastructure and land use, as well as the transportation of raw materials, auxiliaries and wastes. These values are based on literature and European data from 1990 to 2000.

Boric acid is a component of the growth medium and is based on the average European plant data for the raw materials, transportation requirements, and electricity usage. Emissions were estimated and the infrastructure of the plant was approximated. The resulting emissions are 0.79 kg with 97% contributing to emissions to air. The CED for this process is 14 MJ.

Aluminum sulfate is a flocculating agent which is added during the flocculation stage of the algae process. The total emissions are 0.54 kg with 92% emitted to air. The CED for this process is 9.5 MJ. This database entry includes the raw materials and energy consumption for the production and infrastructure of the plant. They are based on average European plant data.

Calcium carbonate is also a flocculating agent which reacts with aluminum sulfate. This was defined as limestone which is included in the SimaPro® database. This includes all the raw materials, emissions, waste treatment, and utilities required to mine, crush, and mill the limestone. The data comes from one company in Switzerland. The resulting emissions are low at 0.01 kg. The CED for this process is also low at 0.4 MJ.

Hexane is used for the extraction of the TAGs from the dried algae biomass. The emissions for the production of hexane are 1.06 kg with 83% emitted to air and 17% emitted to water as VOCs. The CED is high at 62 MJ. It was modeled through the molecular sieve separation of naphtha. This includes the materials, energy consumption, infrastructure, as well as plant emissions. This data is modeled with data from plants located in the United States.

Methanol is a reactant for the transesterification of the TAGs. Total emissions are 0.65 kg with 99% of them being emitted to air. The CED for this process is 37.6 MJ. The

SimaPro® database entry is obtained from modeling the process of producing methanol from natural gas. It includes the raw materials, processing energy, estimations on catalyst use, emissions to air and water, as well as the plant infrastructure. These values come from various plants at different locations as well as literature related to the design of methanol plants.

Sodium hydroxide is the catalyst for the reaction stage of the biodiesel process. The database value is based on the average European production of sodium hydroxide from mercury, diaphragm, and membrane electrolysis cell technologies. The total emissions from this process are 1.16 kg with 59% contributing to air emissions and 41% contributing to water emissions. The resulting CED is 23 MJ.

3.2 LCI generation

For species not available in the SimaPro® database, a new process had to be created to appropriately model the environmental impact. Only five components were not available in the existing SimaPro® database and were defined as follows.

Monopotassium phosphate is found in small quantities as a component of the growth medium. In order to model monopotassium phosphate, a compound which would have a similar production pathway was found. Sodium phosphate is defined in the SimaPro® database and is very likely to have a comparable production pathway since is a similar salt. This entry is based on the production of sodium phosphate from phosphoric acid and soda. The raw material input of sodium phosphate uses soda, or sodium carbonate. The values are based on a United Kingdom production plant. In order to create the potassium salt, potassium carbonate was used as the replacement raw material. It was assumed that the same molar quantities of potassium carbonate as sodium carbonate will be required since the two molecules have the same ratio of cation to anion. The quantity of sodium carbonate required is given within SimaPro® entry for sodium phosphate. This mass was converted to the moles of sodium hydroxide. The mass of potassium carbonate required to replace sodium carbonate was then calculated using this same number of moles. The result of this gives total emissions of 7.17 kg with 59% emitted to air and 41% emitted to water. The CED for this process is 59 MJ.

Dipotassium phosphate is another component of the growth medium. Dipotassium phosphate is an intermediate in the production of monopotassium phosphate. Additional phosphoric acid is added to dipotassium phosphate to produce monopotassium phosphate. For this reason, the same chemical process and methodology as used with monopotassium phosphate was applied to assess the emissions associated with this raw material. The only difference was in the required moles of potassium carbonate compared to phosphoric acid. This change was calculated through the difference in molecular weight of dipotassium phosphate and monopotassium phosphate. This process results in total emissions of 5.43 kg with 59% to air and 41% to water. The CED is 45 MJ.

Manganese chloride is a component of the growth medium and is not present in the SimaPro® database. Using the methodology that was done to generate the monopotassium phosphate inventory; a similar production route was found. Magnesium chloride is found in the database and will be assumed to have a similar production route as manganese chloride. The raw material input for magnesium chloride is defined as magnesium, in ground. This refers to mined raw magnesium compounds. Manganese, in ground is also available in SimaPro®. In order to create the life cycle inventory for manganese chloride, we used the process for magnesium chloride and substitute manganese, in ground for magnesium in ground. The same molar quantity of manganese will be added. This was calculated using the same procedure as for monopotassium phosphate. Total emissions are 0.86 kg with 74% to air and 26% to water. The CED of this process is 8 MJ.

Na_2EDTA is required for the growth medium. Since this compound is not available in SimaPro®, the most similar available compound is used. EDTA is available which is based on the production using ethylenediamene by alkaline cyanomethylation. This entry is based solely on stoichiometric calculations. There is one additional step required to create Na_2EDTA. This is created by adding sodium hydroxide to EDTA in solution. Since EDTA's database entry was based on stoichiometric calculations, the stoichiometric relationship between the quantity of EDTA and sodium will be used. For every mole of EDTA, two moles of sodium hydroxide are required. This can simply be added to the existing EDTA entry by adding the required mass of sodium hydroxide to the input section, since the addition of sodium hydroxide is likely to have minimal energy impact on the existing process. The resulting emissions are 4.49 kg with 90% of emissions from air. The CED of the process is high at 96 MJ.

Sodium nitrate is an ingredient in the growth medium. SimaPro® contains sodium nitrate in the database, but only as a raw material. This only contributes to the raw material used impact category and does not contribute to the remainder of the impact categories. Assuming there are no emissions associated with the mining and processing would be inaccurate. For this reason, a more appropriate sodium nitrate inventory was generated. In order to make an estimate of the energy required to mine sodium nitrate, an existing mining operation in SimaPro® was used. The limestone mining process was utilized to approximate the mining. Instead of using calcite as a raw material, sodium nitrate was specified as the raw material consumed. All of the fuel, energy, emissions, and infrastructure requirements for this process were assumed to be similar. Since this process is based on the milled limestone process, the resulting emissions are the same at 0.01 kg with 96% emitted to air. The CED for this process is 0.4 MJ.

3.3 Generating LCIs: Methanol Example

A LCA requires that all of the impacts associated with the inputs are defined. These are commonly obtained through databases. SimaPro® contains extensive databases and users can easily compile inputs, outputs, energy requirements, and the waste products. The databases contain LCAs for the production of a wide range of specific inputs. These databases do not always contain every required component for a comprehensive LCA of a process. If the database does not contain information for an input, the analysis requires research, assumptions, and estimations to develop a LCA for the process. This walks through the generation of a LCI for methanol.

Methanol is a good example for the generation of a LCA because it has very few inputs, and is commonly used in industrial processes. The production of methanol is a commercially established technology with extensive data regarding the feedstocks, energy input, products, and emissions. Steam reforming is the primary method of producing methanol and accounts for 60% of the world production.[80] The synthesis gas preparation reactions are found in equations 41 and 42 and the methanol synthesis reactions are shown in equations 43 and 44.

$$CH_4 + H_2O \rightarrow CO + 3H_2 \tag{41}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{42}$$

$$CO + 2H_2 \rightarrow CH_3OH \tag{43}$$

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \tag{44}$$

The overall process flow diagram for the steam reforming system is shown in Figure 22. This system is highly integrated with a complicated steam system and heat recovery system. Steam is used both as a raw material and an energy source, causing complications when calculating the required inputs for such a system. Known data is the most accurate method of compiling an LCI and as a result, the efficiency, energy consumption, and raw materials were obtained from measured data. All of the inputs and emissions are specified on the basis of producing 1 kg of methanol. The following sections describe the required inputs and emissions from methanol production to generate the methanol inventory.

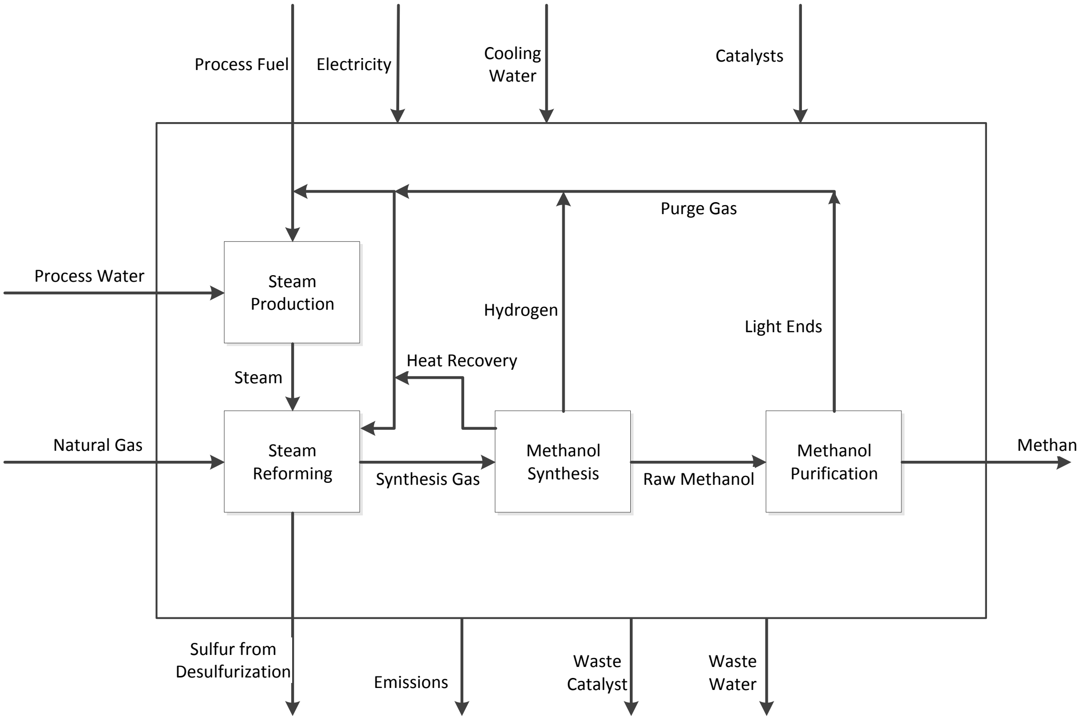


Figure 22. Simplified PFD for methanol production using steam reforming.[81]

The major resource in the production of methanol is natural gas, which serves as a raw material and an energy source. The natural gas consumption was determined for a typical size methanol plant to be 750,000 t/yr.[81] This equates to a total natural gas requirement was 32.7 MJ/kg of methanol. This gas requirement includes that needed for both the raw material production and heating requirements. To quantify the emissions from burning natural gas, the fuel and feedstock must be separated. It was determined that 76.5% of the natural gas is used as a raw material and the remainder is used for the generation of steam. This yields 25 MJ of natural gas as raw material, and 7.7 MJ of natural gas burned in a furnace for every kilogram of methanol produced. Hydrogen is a byproduct of this process where 0.06 kg is generated for every kilogram of methanol produced, and is assumed to be burned in the furnace for the generation of steam. The emissions calculations are discussed in the emissions section.

Water is used as both a raw material and for cooling. Data from plants of similar size were used. Between 0.3 kg and 0.85 kg of deionized water for steam is required as a feedstock for the generation of methanol. Cooling water is also required for this process, and varies from plant to plant. An average value of cooling water makeup was used which was 8.16 kg/kg of methanol.[81] The water requirements are known, but the impact of water is unlikely to influence the LCA of methanol production (Figure 20, Figure 21) and was not considered in this model.

Electricity is used to operate rotary machines such as compressors, fans, and pumps within the methanol process. The average electricity consumption was found to be 0.27 MJ/kg of methanol, based on the use of external electricity from an average of methanol plants. [81]

The production of methanol requires 3 different catalysts: Desulfurization, steam reforming, and synthesis catalyst. The first of which is for the desulfurization process and consists of 4% NiO, 14% MoO_3, with the remainder being Al_2O_3. The steam reforming process requires 16% NiO with the remainder of Al_2O_3 and the methanol synthesis uses 64% CuO, 24% ZnO, with the balance made up of Al_2O_3. Using an isothermal converter, the catalyst yield factor is approximately 1,000 kg of methanol/h·m^3 of catalyst bed.[82] For these estimations, the catalyst density was assumed to be 1,300 kg/m^3, and 8,000 h/yr production time was used. The expected lifetime of all of these catalysts is 5 years. This yields approximately 40 mg of catalyst for 1 kg of methanol with 25 mg of Al_2O_3, 9 mg of CuO, 2 mg of NiO, 3 mg of ZnO, and 1 mg of MoO_3. Since these quantities are orders of magnitude smaller compared to other inputs, they will not have a significant impact on the LCA, therefore their impact was considered negligible for the purpose of this example.

The majority of the emissions to air is generated by the combustion of natural gas in the furnace and is described in the natural gas combustion section. Hydrogen combustion, desulfurization, and fugitive emissions generate additional emissions to air. NO_X is generated by the combustion of the hydrogen produced in the methanol synthesis and was specified in Faist Emmenegger & Heck (2007) as 23.3 mg/MJ of H_2 burned.[83] The lower heating value (LHV) of H_2 is 108 MJ/kg of H_2. Using this information 0.06 kg of H_2 was generated for every kilogram of methanol produced, resulting in 0.15×10^{-3} kg of NO_X emissions. Natural gas requires desulfurization before it can be used in the methanol production process. Faist Emmenegger & Heck (2007) specified that 0.55 mg of SO_2 is released for every megajoule of natural gas combusted.[83] This was assumed to be the quantity of SO_2 that required removal from the feedstock of the gas and resulted in 13.8×10^{-6} kg of SO_2 emissions. Non-methane volatile organic compounds (NMVOC) and methane emissions were reported in Delucchi et al. 1996.[84] All NMVOC were specified as methanol and were 0.53×10^{-3} kg/ kg methanol and 0.98×10^{-3} kg of methane.

The liquid exiting the bottoms after the distillation for methanol purification (Figure 22) contains water, methanol, ethanol, higher alcohols, oxygen-containing organic compounds, and variable quantities of paraffin.[82] Every kilogram of methanol results in 0.2 kg of waste.[81] This waste is sent to a biological treatment unit and the emissions following treatment are shown in Table 30.[85] The biological oxygen demand (BOD) was assumed to be the quantity of methanol, formaldehyde, and phenol assuming a degradation of 96% in the biological treatment unit. The emissions from the cooling water discharge were assumed to be the minimum requirements for cooling water discharge as described in IPPC 2000.[86]

Table 30. Emissions to the water for methanol production (g/kg methanol produced)

Emission	**Emissions from waste water**	**Emissions from cooling water**	**Total Emissions to water**
COD	0.3	0.19	0.49
BOD	0.18	-	0.18
DOC, TOC	0.18	0.06	0.24
AOX	-	0.001	0.001
Phosphor (P_{tot})	-	0.01	0.01
Formaldehyde, CH_2O	0.1	-	0.1
Methanol, CH_3OH	0.03	-	0.03
Phenol, C_6H_6	0.01	-	0.01
Suspended solids	0.02	-	0.02
Chloride, Cl^-	-	0.002	0.002

Emissions to soil were not considered in this analysis. All catalysts were assumed to be recovered and no emissions were accounted for the spent catalyst.

3.3.1 Raw materials generation

The inputs into the methanol production which significantly impact the LCA were natural gas as a raw material, natural gas burned in a furnace as a heat source, and the required electricity. Electricity generated from natural gas will be modeled for simplicity purposes. The general process flow diagram for natural gas is shown in Figure 23.

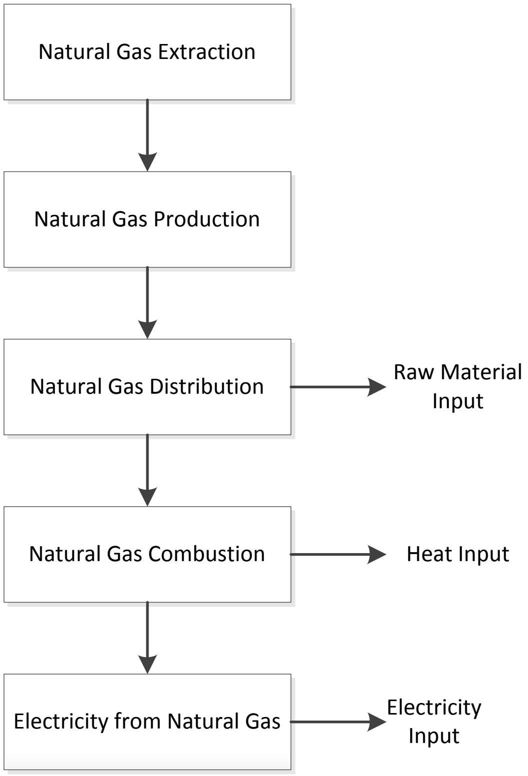


Figure 23. Natural gas process flow diagram. The natural gas distribution, combustion, and electricity from natural gas are all inputs into the methanol process.

To accurately model the generation of electricity from natural gas, the inputs, outputs, and emissions for the 5 processes in Figure 23 need to be specified. The 3 direct inputs into methanol are natural gas distribution, natural gas combustion, and electricity from natural gas. The electricity for the methanol plant is assumed to be sourced from natural gas which simplifies the electricity LCI. It is not likely this will have a large influence on the LCA because of the relatively small amount of electricity required. This will serve as an appropriate estimation for this process.

3.3.1.1 Natural Gas Extraction

The emissions associated with the extraction of the natural gas are described in this section. To determine the emissions associated with natural gas extraction, the National Renewable Energy Laboratory (NREL) database was used.[87] NREL contains information regarding the material inputs, energy requirements, and emissions from extracting the natural gas as of 2007. These data were considered to be a good representation of emissions for the US natural gas extraction process. The inputs and emissions were on a basis of 1 m^3 of unprocessed natural gas. The natural gas extracted from the ground is assumed to have a LHV of 38.3 MJ/m^3. The electricity requirement for the extraction of natural gas is 104 kJ/m^3 natural gas. This is ignored since we are defining electricity and it will likely not have a large impact on the total LCA. The only emission to air considered by NREL was methane, which was 0.00882 kg methane. The emissions to water are shown in Table 31.

Table 31. Emissions to water from natural gas extraction (kg/m^3 unprocessed gas)

Emission	**Quantity**	**Emission**	**Quantity**
4-methyl-2-pentanone	1.33E-8	Lithium, ion	3.41E-3
Acetone	3.17E-8	Magnesium	1.99E-3
Acidity, unspecified	6.67E-7	Manganese	3.22E-6
Aluminum	5.84E-5	Mercury	6.23E-10
Ammonium, ion	3.91E-5	Molybdenum	7.29E-8
Antimony	3.57E-8	*m*-Xylene	9.61E-8
Arsenic, ion	7.01E-7	Nickel, ion	5.55E-7
Barium	09.03E-4	Oils	6.09E-5
Benzene	5.32E-6	*o*-Xylene	7E-8
Benzene, ethyl-	2.99E-7	Phenol	1.42E-6
Beryllium	3.18E-8	Selenium	7.05E-9
BOD, Biological Oxygen Demand	5.52E-4	Silver, ion	6.65E-6
Boron	9.96E-6	Sodium, ion	3.23E-2
Bromine	6.8E-4	Solved solids	1.41E-1
Cadmium, ion	1.02E-7	Strontium	1.73E-4
Calcium, ion	1.02E-2	Sulfate	2.34E-4
Chloride	1.15E-1	Sulfur	8.41E-6
Chromium, ion	1.61E-6	Thallium	7.54E-9
Cobalt	7.03E-8	Tin, ion	3.49E-7
COD, Chemical Oxygen Demand	9.13E-4	Titanium, ion	5.48E-7
Copper, ion	4.48E-7	Toluene	5.03E-6
Cyanide	2.29E-10	Vanadium, ion	8.62E-8
Fluoride	1.11E-9	*p*-Xylene	2.54E-6
Iron, ion	1.84E-4	Zinc, ion	1.57E-6
Lead	1.01E-6		

3.3.1.2 Natural Gas Production

This section quantifies the emissions associated with processing natural gas into a useable product. This is also based off NREL 2007 measured data.[87] The electricity required by this process is 57 kJ, but this was not considered as it is unlikely to have a significant influence on the LCA. The resulting emissions are shown in Table 32. This is reported on the basis of 1 m^3 of processed natural gas, which requires 1.05 m^3 of unprocessed gas as an input.

Table 32. Emissions to air from natural gas processing (kg/m^3 natural gas)

Emission	**Quantity**
Methane, fossil	0.00142
Sulfur dioxide	0.0184
NMVOC	0.000581
Hydrocarbons, aromatic	0.00026

3.3.1.3 Natural Gas Distribution

The emissions from natural gas distribution were also quantified in the NREL 2007 study.[87] This section includes the distribution and transportation of the natural gas from the production facility to the consumer on the basis of 1 MJ of natural gas. Using an LHV of 38.3 MJ/m^3 and assuming a transportation loss of 2.6%, a volume of 0.0268 scm processed natural gas is required to deliver 1 MJ of natural gas to the consumer.[88] The production of the pipeline was not considered. The resulting emissions can be seen in Table 33.

Table 33. Emissions to air from the distribution of natural gas (kg/MJ natural gas)

Emission	**Quantity**	**Emission**	**Quantity**	**Emission**	**Quantity**
Methane, fossil	2.82E-05	Bromine	3.61E-15	Hexane	6.20E-15
Particulates, > 10 um	2.52E-07	Cadmium	3.86E-11	Hydrogen fluoride	2.59E-08
Particulates, > 2.5 um, and < 10um	1.14E-07	Carbon disulfide	1.20E-14	Isoprene	1.05E-14
Particulates, < 2.5 um	2.28E-07	Methane, tetrachloro-, CFC-10	4.40E-12	Lead	1.01E-10
Nitrogen oxides	6.84E-06	CFC-12	9.84E-15	Magnesium	1.90E-09
NMVOC	1.33E-06	Benzene, hexachloro-	2.03E-15	Manganese	2.65E-10
Sulfur dioxide	3.98E-05	Chloroform	5.46E-15	Mercury	2.30E-11
Carbon monoxide, fossil	5.7E-06	Chlorine	7.73E-11	Methane, bromo-	1.48E-14
Carbon dioxide, fossil	4.83E-03	Chromium	8.53E-11	Nickel	4.33E-10
Carbon dioxide, biogenic	1.91E-05	Chromium VI	1.36E-11	Ethene, tetrachloro-	8.00E-12
Acenaphthene	8.8E-14	Cobalt	4.34E-11	Phenol	3.48E-11
Acetaldehyde	5.58E-10	Copper	3.19E-12	PAH	6.00E-11
Acrolein	5.10E-10	Cumene	4.90E-16	Propanal	3.51E-14
Aldehydes	3.75E-09	Cyanide	2.31E-13	Propene	8.31E-10
Ammonia	1.83E-09	Dinitrogen monoxide	9.84E-08	Selenium	2.36E-10
Antimony	3.88E-12	Dioxins	1.64E-13	Styrene	2.31E-15
Arsenic	8.50E-11	Ethene, chloro-	3.70E-15	Toluene	3.08E-06
Benzene	1.99E-06	Fluorine	1.57E-13	HCFC-140	1.01E-14
Benzo(*a*)pyrene	6.56E-15	Formaldehyde	7.87E-09	Xylene	1.80E-06
Benzal chloride	6.47E-14	Furan	7.86E-16	Zinc	2.12E-12
Beryllium	5.72E-12	Hydrogen chloride	2.14E-07		

3.3.1.4 Natural Gas Combustion

The emissions from the combustion of the natural gas was determined using data from two different sources. The EPA AP42 document contained a compilation of air pollutant emission factors for the combustion of fuels.[89] This document was used to obtain estimates for trace contaminants in combustion in terms of lbs/mmscf of natural gas. These were converted to kg/m^3 and can be found in Table 34.

Table 34. EPA specified emissions to air from natural gas combustion (kg/MJ natural gas)

Emission	**Quantity**
CO	3.54E-05
Lead	2.11E-10
PM (Total)	3.2E-06
PM (Condensable)	2.4E-06
PM (Filterable)	8.01E-07
TOC	4.64E-06
VOC	2.32E-06

The Emissions and Generation Resource Integrated Database (eGRID) is an EPA database and contains measured data for all the power plants within the US during 2010.[90] Only power plants using 100% natural gas as an electricity source were considered in this assessment. The emissions of NO_X, SO_2, CO_2, CH_4, and N_2O were all listed on an annual basis. This database also contains the quantity of fuel burned on an annual basis. The emissions were divided by the quantity of fuel burned by the power plant, resulting in emissions per 1 MJ of natural gas burned (Table 35).

Table 35. eGRID 2010 emissions to air from natural gas combustion (kg/MJ natural gas)

Emission	**Quantity**
NO_X	8.8E-05
SO_2	1.2E-06
CO_2	0.050479
CH_4	1E-06
N_2O	1E-07

3.3.1.5 Natural Gas Electricity

The conversion efficiency of natural gas to electricity was determined using eGRID 2010.[90] The total electricity output of natural gas power plants was divided by the total energy content of natural gas burned in the US. This conversion assumes a uniform efficiency and resulted in 6.94 MJ of natural gas to obtain 1 MJ of electricity.

3.3.2 Methanol LCI Comparison

The LCI for each of the stages in the natural gas production was categorized and can be found in Table 36.

Table 36. Natural gas production LCI

	Natural gas unprocessed	Natural gas at production	Natural gas at consumer	Natural gas combustion	Electricity from natural gas
Basis	1 m^3	1 m^3	1 MJ	1 MJ	1 MJ
Emissions to Air (kg)	0.00882	0.0299	0.00574	0.0564	0.391
Carbon Dioxide (kg)	0	0	0.00485	0.0553	0.384
Carbon Monoxide (kg)	0	0	5.70E-06	4.11E-05	0.000285
Methane (kg)	0.00882	0.0107	0.000314	0.000344	0.00239
NMVOC	0	0.000581	1.69E-05	1.69E-05	0.000117
NO_X (kg)	0	0	6.84E-06	9.49E-05	0.000659
SO_2 (kg)	0	0.0184	0.000533	0.000534	0.00371
Particulates (kg)	0	0	5.94E-07	7.00E-06	4.86E-05
Emissions to Water (kg)	0.308	0.323	0.00866	0.00866	0.0601
VOCs (kg)	0	0	0	2.32E-06	1.61E-05
Emissions to Soil (kg)	0	0	0	0	0
Total Emissions (kg)	0.317	0.353	0.0144	0.0650	0.451
CED (MJ)	38.4	40.4	1.08	1.08	7.51

There is a similar entry in SimaPro® for the natural gas distribution in the US. The results of this LCA are shown in Table 37. These values are very similar, with the exception of the electricity from natural gas. This is due to an assumed efficiency of 34%. This is compared to the measured data from eGRID which results in a 14% efficiency. This shows the need for accurate assumptions. Poor assumptions can yield inaccurate LCAs.

Using these values, the inventory for methanol can be completed. The methanol LCI is shown in Table 37. The LCA of methanol was performed using the information in Table 37 and the quantity of each resource required. Emissions to soil were neglected for all cases because of the small overall contribution to the total emissions.

Table 37. Methanol LCI

	Natural Gas Distribution	**Natural Gas Combustion**	**Natural Gas Electricity**	**Methanol Process Emissions**	**Methanol Total**
Emissions to Air (kg)	0.144	0.434	0.104	1.70E-03	0.683
Carbon Dioxide (kg)	0.121	0.426	0.102	0	0.650
Carbon Monoxide (kg)	0.000143	0.000317	7.6E-05	0	0.000535
Methane (kg)	0.00786	0.00265	0.000635	9.80E-04	0.0121
NMVOC (kg)	0.000423	0.00013	3.12E-05	5.30E-04	0.00111
NO_X (kg)	0.000171	0.000731	0.000175	1.80E-04	0.00126
SO_2 (kg)	0.0133	0.00411	0.000988	1.38E-05	0.0184
Particulates (kg)	1.49E-05	5.39E-05	1.29E-05	0	8.17E-05
Emissions to Water (kg)	0.217	0.0667	0.0160	0.00108	0.300
VOCs (kg)	0	1.79E-05	4.29E-06	0	2.21E-05
Emissions to Soil (kg)	0	0	0	0	0
Total Emissions (kg)	0.360	0.501	0.120	2.79E-03	0.984
CED (MJ)	27.1	8.33	2.00	0.00E+00	37.4

These results were compared with the SimaPro® inventory as shown in Table 38. The major differences are in the emissions to water because of data used in the extraction step of the natural gas. Since this data was acquired from NREL 2007, we assumed the data is accurate and up to date.[87] Depending on the assumptions made and the method of calculation, these values can vary. Our case was based off data valid for the US and will be considered accurate for US applications. The entry for methanol in SimaPro® is based on European natural gas extraction/processing/distribution chain, which differs from that of the US.

Table 38. SimaPro® entry compared to the generated entry

Impact category	**SimaPro® Entry**	**Generated Entry**
Emissions to Air (kg)	0.647	0.731
Carbon Dioxide (kg)	0.640	0.698
Carbon Monoxide (kg)	0.000433	0.000569
Methane (kg)	0.00423	0.0122
NMVOC (kg)	0.00108	0.00111
NO_X (kg)	0.000917	0.00134
SO_2 (kg)	0.000636	0.0184
Particulates (kg)	0.00012	8.78E-05
Emissions to Water (kg)	0.00639	0.300
VOCs (kg)	1.72E-07	2.43E-05
Emissions to Soil (kg)	0.000127	0
Total Emissions (kg)	0.654	1.03
CED (MJ)	37.6	37.4

3.4 Energy LCIs

A life cycle inventory was developed for the energy used by each process. Two different forms of energy were defined: electricity and heat. Steam will be used as the source of heat on a kg basis. The quantity of each required for the production of algae-derived biodiesel is shown in Table 39. Both the electricity and steam were available in the SimaPro® database.

Table 39. Energy requirements for each step in the algae biodiesel process

Inputs	Growth	Flocculation	Spray Drying	Extraction and Solvent Recovery	Reaction and Purification
Electricity (kWh/t BD)	39,800	6.3	0	0.02	0.10
Steam (kg/t BD)	0	0	44,300	226	0.27

The electricity requirement for each operation in the process was defined as high voltage electricity in the United States. The United States electricity at grid includes all emissions, raw materials, and wastes from the production, transmission, and infrastructure of energy production. This electricity inventory is based on distribution data from the United States. Swiss data was used for the electricity grid infrastructure requirements. The resulting effect on the impact categories is shown in Table 40. The values are reported on a per MJ energy basis.

The heating requirement was met through the use of steam. Steam for chemical processes was chosen and includes the water and energy input for the production of steam. The inventory steam for chemical processes is based on the average steam production data from 11 European chemical sites. The LCI for steam is shown in Table 40. This is reported on a basis of one kg of steam.

Table 40. LCIs for electricity and steam

Impact category	**Electricity (MJ basis)**	**Steam (kg basis)**
Raw Materials Used (kg)	0.124	0.0902
Emissions to Air (kg)	0.205	0.224
CO_2 (kg)	0.203	0.223
CO (kg)	8.23E-05	5.84E-05
CH_4 (kg)	0.000377	0.000451
NMVOC (kg)	4.19E-05	9.43E-05
NO_x (kg)	0.0004	0.0002
SO_2 (kg)	0.00110	0.000382
Particulates (kg)	0.000186	4.61E-05
Emissions to Water (kg)	0.00735	0.00231
VOCs (kg)	1.01E-07	3.91E-07
Emissions to Soil (kg)	2.54E-05	9.63E-05
Total Emissions (kg)	**0.213**	**0.226**
CED (MJ)	3.52	3.97
Water Used (kg)	808	37.2

3.5 Waste/Byproduct LCIs

The production of biodiesel also yields glycerine (a.k.a. glycerol). This is generated during the reaction and purification section. Typically allocation should be avoided, which will require the expansion of the system boundaries to include the emissions associated with a separate glycerine production route. The impact of producing glycerine will be subtracted from the algae biodiesel process in our life cycle analysis. The SimaPro® database has an entry for the production of glycerine through the esterification of soybean oil. This was chosen as an appropriate model and includes: the production of the soybean, extraction of the soybean oil, the esterification process, as well as the waste treatment. The total glycerine process emissions are 1.33 kg with 86% being emitted to air and 14% being emitted to water. The CED for producing glycerine through this process is 39 MJ. These results can be seen in Table 41.

Carbon dioxide produced as emissions from energy generation will be used during the algae growth stage. The quantity of CO_2 absorbed by the algae was estimated when completing the mass balance on the PBR. In order to account for consuming CO_2 rather than producing it, a SimaPro® entry was created. This allows for a credit to be taken by assigning a negative emission value. For every kg of CO_2 consumed, a kg of CO_2 produced by this process is offset. This entry is added into the algae growth stage of the process and will alleviate some of the CO_2 emissions associated with the process. The LCI can be seen in Table 41.

Table 41. LCIs for byproducts and carbon sequestration

Impact category	Glycerine (kg basis)	CO_2 Absorbed (kg basis)
Raw Materials Used (kg)	2.53	0
Emissions to Air (kg)	1.14	-1
CO_2 (kg)	1.13	-1
CO (kg)	0.000678	0
CH_4 (kg)	0.00107	0
NMVOC (kg)	0.00337	0
NO_x (kg)	0.00211	0
SO_2 (kg)	0.00141	0
Particulates (kg)	0.000427	0
Emissions to Water (kg)	0.187	0
VOCs (kg)	1.01E-06	0
Emissions to Soil (kg)	0.00106	0
Total Emissions (kg)	**1.33**	**-1**
CED (MJ)	39	0
Water Used (kg)	824	0

There were three waste streams for the algae biodiesel process: stream 10, 23, and 30. Stream 10 is waste from the extraction step which consists of expended biomass, some water, medium salts, and waste flocculant. The other two waste streams come from the reaction and purification section. Stream 30 is an organic stream, and stream 23 is a salt water mixture. The stream compositions can be seen in Table 42.

Table 42. Composition of waste streams

Chemical	**Stream 12**	**Stream 23**	**Stream 30**
Algae (kg)	770	0	0
Water (kg)	101	159	0
$Al(OH)_3$ (kg)	4.84	0	0
$CaSO_4$ (kg)	12.7	0	0
Hexane (kg)	0	0	5.03
TAG (kg)	58.9	0	98.4
NaOH (kg)	0	0	3.88
NaCl (kg)	0	2.82	0

The solid wastes will be sent to a landfill. The liquid organic waste stream containing hexane (stream 30), is incinerated. The aqueous waste stream containing salt (stream 23) can be sent to a wastewater treatment plant. Ecosolvent® software will be used to address life cycle emissions associated with the bulk waste disposal of these two liquid streams. The disposal of the solid waste stream can be modeled by SimaPro®. This is defined in SimaPro® as long term waste and high active chemical landfill. This database entry is based on European landfill studies. This assumes that all emissions from a landfill are to water. Based on this approach, for every kg of material sent to a landfill, there is 0.19 kg of life cycle emissions to water.

Chapter 4

Base Case Life Cycle Assessment

The SimaPro® generated LCIs and the previously calculated quantities of the component were used to perform a life cycle assessment (LCA). LCAs couple the inventory of relevant energy inputs, material inputs, and environmental releases, evaluate the impacts associated with the inputs and releases, and interpret these results. This interpretation can then be used to make an accurate assessment of the impact for each stage in the algae biodiesel production. The LCA consists of the summation of all LCIs multiplied by the quantity of each inventory and shown in Equation 45. The biodiesel production stages were analyzed and the impact for each was obtained. These were inserted into a new process defined as biodiesel, so the various production stages and their resulting impact could be compared. The LCA was defined within SimaPro® to categorize emissions, raw material usage, and energy consumptions.

$$\sum_{i}^{r}(LCI_i \cdot R_i)+\sum_{i}^{e}(LCI_i \cdot E_i)+\sum_{i}^{w}(LCI_i \cdot W_i)=LCA \tag{45}$$

Where:

LCI_i is the life cycle inventory of component i (per kg component i)

R_i is the quantity of raw material i (kg)

E_i is the quantity of energy i (MJ)

W_i is the quantity of waste i (kg)

The total emissions and the cumulative energy demand were the impact categories compared. This LCA is shown in Table 43. This table contains a comprehensive report of all emissions and the cumulative energy demand associated with each section of the process (Figure 31). This preliminary assessment illustrates the portions of the production where alternatives should be considered.

Table 43. Life cycle assessment of the base case algae biodiesel process (t of BD basis)

Impact category	**Growth**	**Flocculation**	**Drying**	**Extraction and Solvent Recovery**	**Reaction and Product Purification**	**Total**
Raw Materials Used (kg)	17,900	22.5	4,000	28.4	-125	21,900
Emissions to Air (kg)	28,400	15.1	9,920	55.1	179	38,600
Carbon Dioxide (kg)	26,000	14.8	9,870	54.6	179	36,200
Carbon Monoxide (kg)	11.9	0.0115	2.59	0.0204	-0.0177	14.5
Methane (kg)	54.2	0.0238	20.0	0.115	0.174	74.4
NMVOC (kg)	6.11	0.00510	4.18	0.102	-0.226	10.2
Nox (kg)	57.5	0.0387	8.87	0.0570	-0.163	66.3
SO2 (kg)	158	0.187	16.9	0.113	-0.109	176
Particulates (kg)	26.8	0.0381	2.04	0.0143	-0.0404	28.8
Emissions to Water (kg)	1,110	1.08	102	189	-14.6	1,390
VOCs (kg)	0.0146	2.80E-05	0.0173	0.000216	0.000961	0.0331
Emissions to Soil (kg)	3.72	0.00652	4.27	0.0514	0.137	8.18
Total Emissions (kg)	29,500	16.2	10,000	245	164	40,000
CED (MJ)	506,000	280	176,000	1,200	408	683,000
Water Used (kg)	1.16E+08	77,800	1,650,000	16,900	20,200	1.18E+08

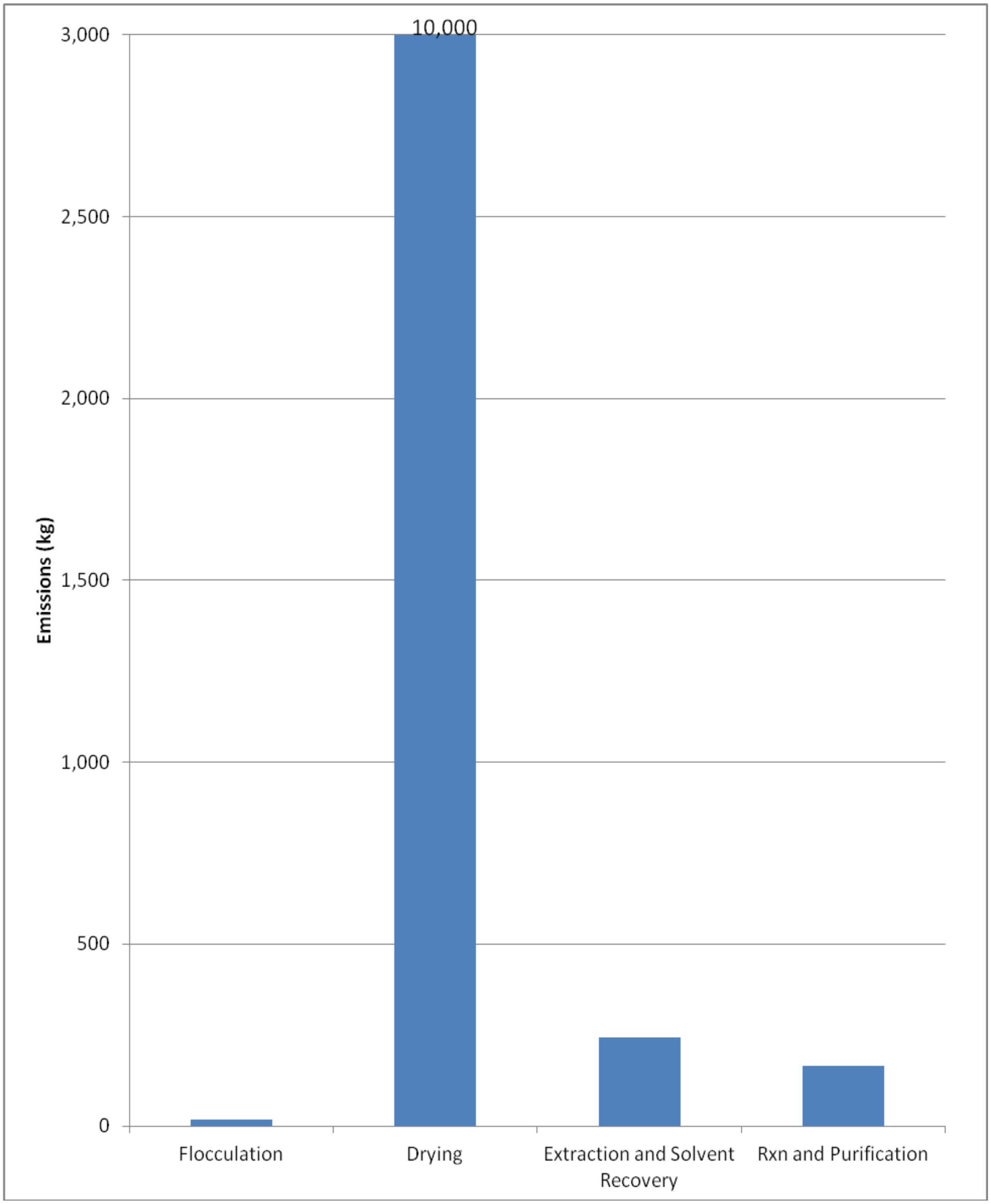


Figure 24. The total emissions for each step of the base case biodiesel process

The total emissions from Table 43 were analyzed according to their respective production stages shown in Figure 24. The total emissions category is the summation of all emissions to the air, water, and soil. Due to the large emissions from the growth stage,

Figure 24 excludes the emissions from this step. The emissions to air, water, and soil are shown in Table 44. Figure 24 exemplifies the high emissions during the drying step. This is due to the high energy expenditures associated with thermally separating the water from the algae. A large amount of energy is needed to generate the steam required to dry the algae through thermal methods.

Table 44. Process emissions

Processing stage	**Emissions to air (kg/t BD)**	**Emissions to water (kg/t BD)**	**Emissions to soil (kg/t BD)**	**CO_2 emissions (kg/t BD)**	**Total Emissions (kg/t BD)**
Growth	28,400	1,110	3.72	26,000	29,500
Flocculation	15.1	1.08	0.007	14.8	16.2
Drying	9,920	102	4.27	9,870	10,000
Extraction and Solvent Recovery	55.1	189	0.051	54.6	245
Reaction and Purification	179	-14.6	0.137	179	164

Table 45 shows the percent contribution of each emission category towards the total emissions. The analysis indicates that the vast majority of all emissions are to the air. The emissions to water are high within the extraction and solvent removal step (contributing to 77% of the total emissions), due to the landfilling of solid biomass waste. The reaction and purification step is where a credit is taken for producing glycerine. This results in negative emissions to water, denoting that these emissions are offset as a result of the transesterification process. The component air emissions (179 kg) are larger than the total emissions (164 kg) due to the credit taken as a result of emissions to water (-14.6 kg). In all cases emissions to soil can be considered insignificant, contributing to under

0.1% in all stages. The contribution of CO_2 to the total emissions is also shown in Table 45. With the exception of the extraction stage, CO_2 contributes to the majority of emissions. In most processing stages, the CO_2 emissions are similar to the emissions to air. Figure 25 shows the contribution of emission categories in the algae biodiesel process.

Table 45. Categorization of total emissions

Processing stage	**Emissions to air**	**Emissions to water**	**Emissions to soil**	**CO_2 emissions**
Growth	96%	4%	<0.1%	88%
Flocculation	93%	7%	<0.1%	91%
Drying	99%	1%	<0.1%	98%
Extraction and Solvent Recovery	23%	77%	<0.1%	22%
Reaction and Purification	109%*	-9%**	<0.1%	109%*

* The value is greater than 100% since the air emissions exceeds the total emissions when the emission credit to water is incorporated

** The negative value represents the credit from the emissions to water as a percent of the total emissions

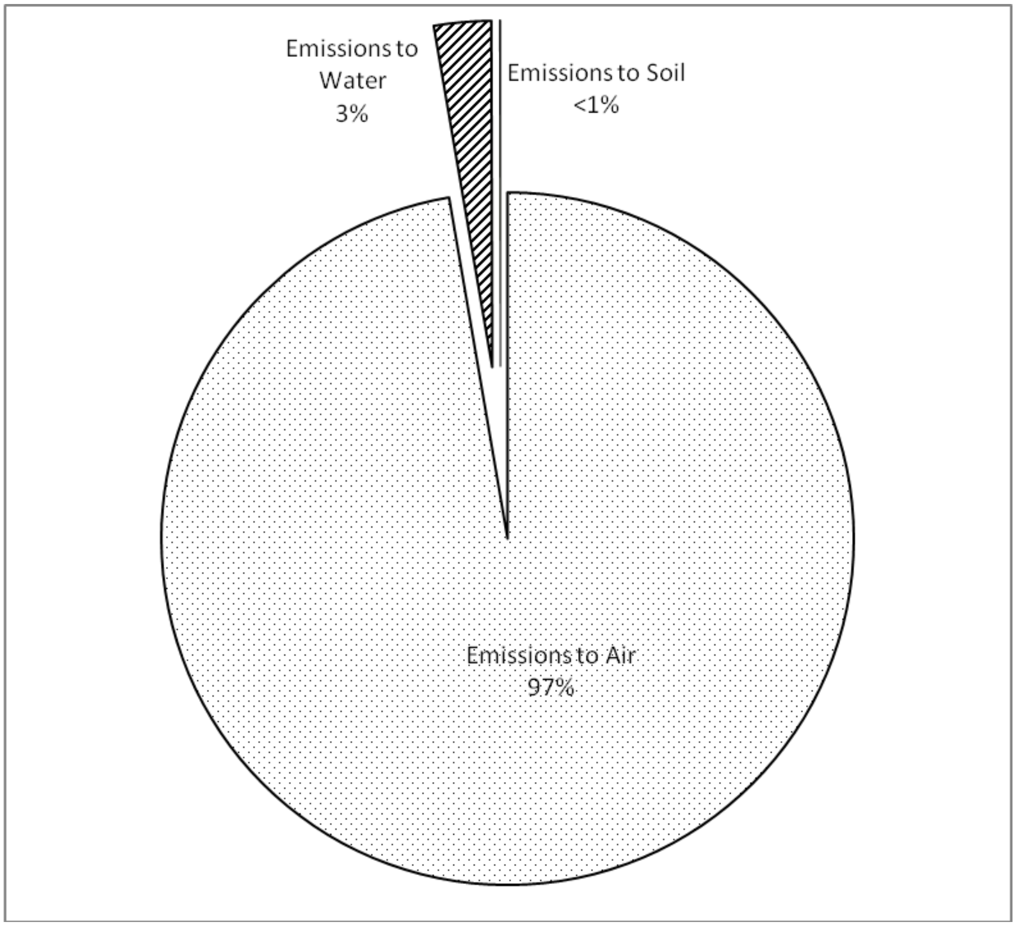


Figure 25. Pie chart comparing emission categories for the algae biodiesel process

In Figure 26, the various processing stages were compared. The PBR has the highest contribution to emissions; this is due to the high energy costs associated with the algae growth in a tubular PBR. The algae growth step produced 73.9% of the total emissions, while 25.1% of the total emissions were a result of the drying step. Due to the high emissions in the PBR, this stage was removed from our analysis to more carefully review the downstream processing stages. When comparing the remaining processes (Figure 27), the drying step contributes the majority of the emissions due to the large quantity of steam required. The remaining stages have relatively low contributions to the total process emissions. When the PBR is removed, the spray drying produces 95.9% of the total emissions.

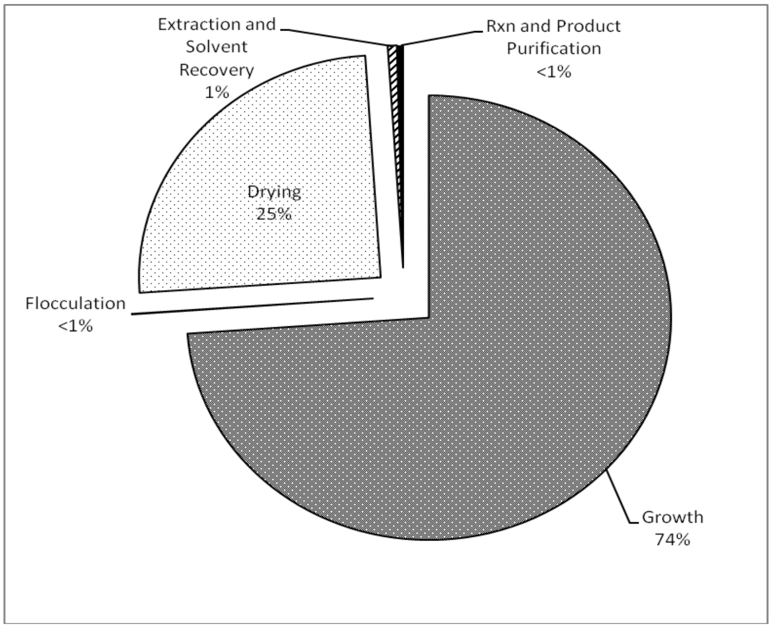


Figure 26. Pie chart of total emissions for all algae biodiesel processes

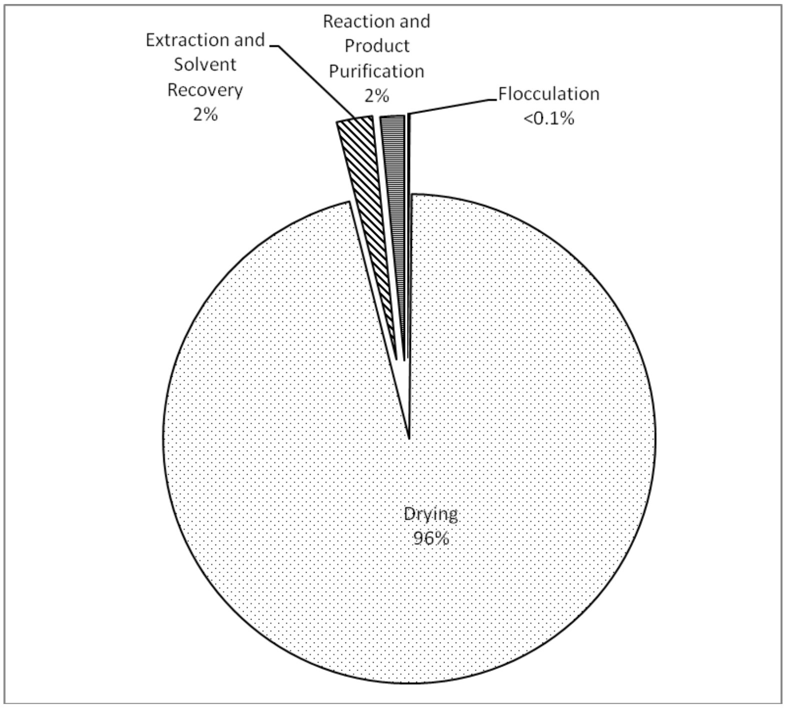


Figure 27. Pie chart of total emissions excluding PBR

The next impact category compares the cumulative energy demand (CED) of each processing stage. The CED is the entire demand of primary energy associated with the raw material production, manufacturing process, and waste disposal. Table 46 shows how much energy was used by each unit operation in MJ. The CED of the PBR is much larger than the other processes. The dryer is the second highest contributor due to the large quantity of energy required in the steam generation.

Table 46. CED of the algae biodiesel processing stages

Processing stage	**CED (MJ)**
Growth	506,000
Flocculation	280
Drying	176,000
Extraction	1,200
Reaction and Purification	407

Figure 28 compares the CED of the various stages. This illustrates that the PBR has a larger CED than any other operation. Figure 29 shows the comparison excluding the PBR. The spray dryer also has a large CED when evaluated against the other operations. When considering all cases, the PBR contributes to 74.0% of the total CED and the spray dryer contributes to about 25.7%. The remaining four operations make up less than 1% of the CED. When the PBR is excluded from consideration, the drying step contributes to 98.9% of the total CED. This is analogous to other studies which show drying directly after flocculation consumes 99% of the downstream processing energy.[46]

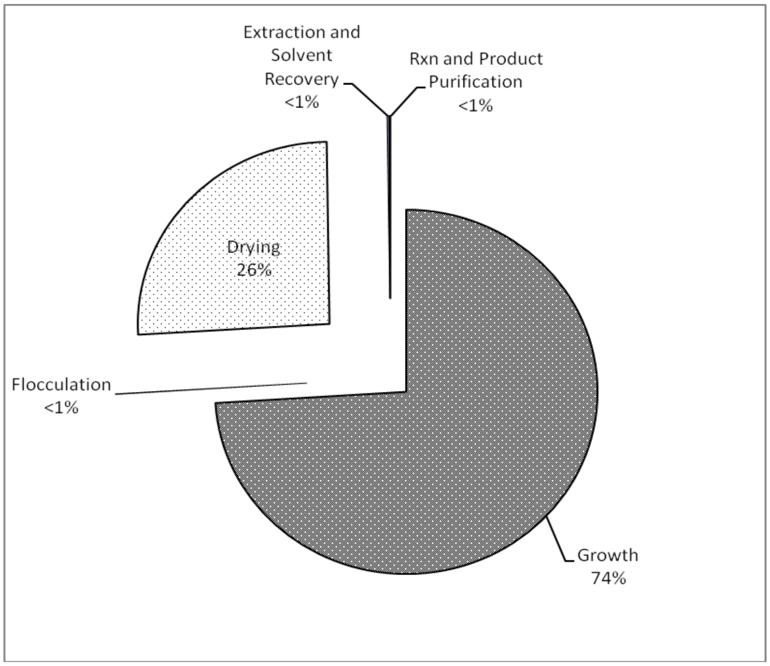


Figure 28. Pie chart showing the CED for all steps in the algae biodiesel process

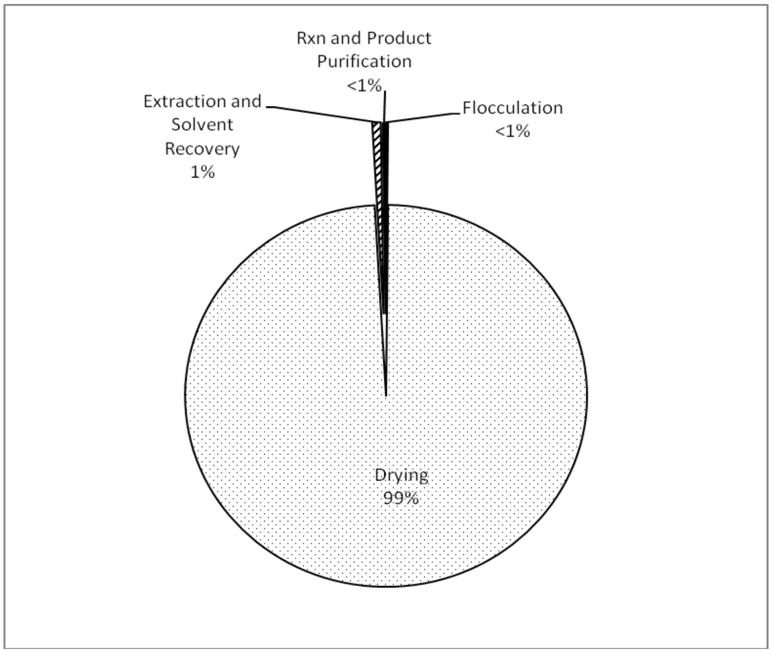


Figure 29. Pie chart showing the CED excluding PBR

Figure 30 shows the CO_2 emissions resulting from each process excluding the growth stage. In this case, the CO_2 mitigated by the algae growth was separated from the algae consumed during this stage. This was done by taking the known quantity of CO_2 consumed, adding it to the growth phase, and displaying it as a negative emission under the CO_2 mitigation column. Initially, SimaPro® had combined the CO_2 emissions and mitigation to acquire a net quantity of CO_2 emitted. Figure 21 also shows that out of the downstream processing steps, spray drying is responsible for the highest carbon footprint.

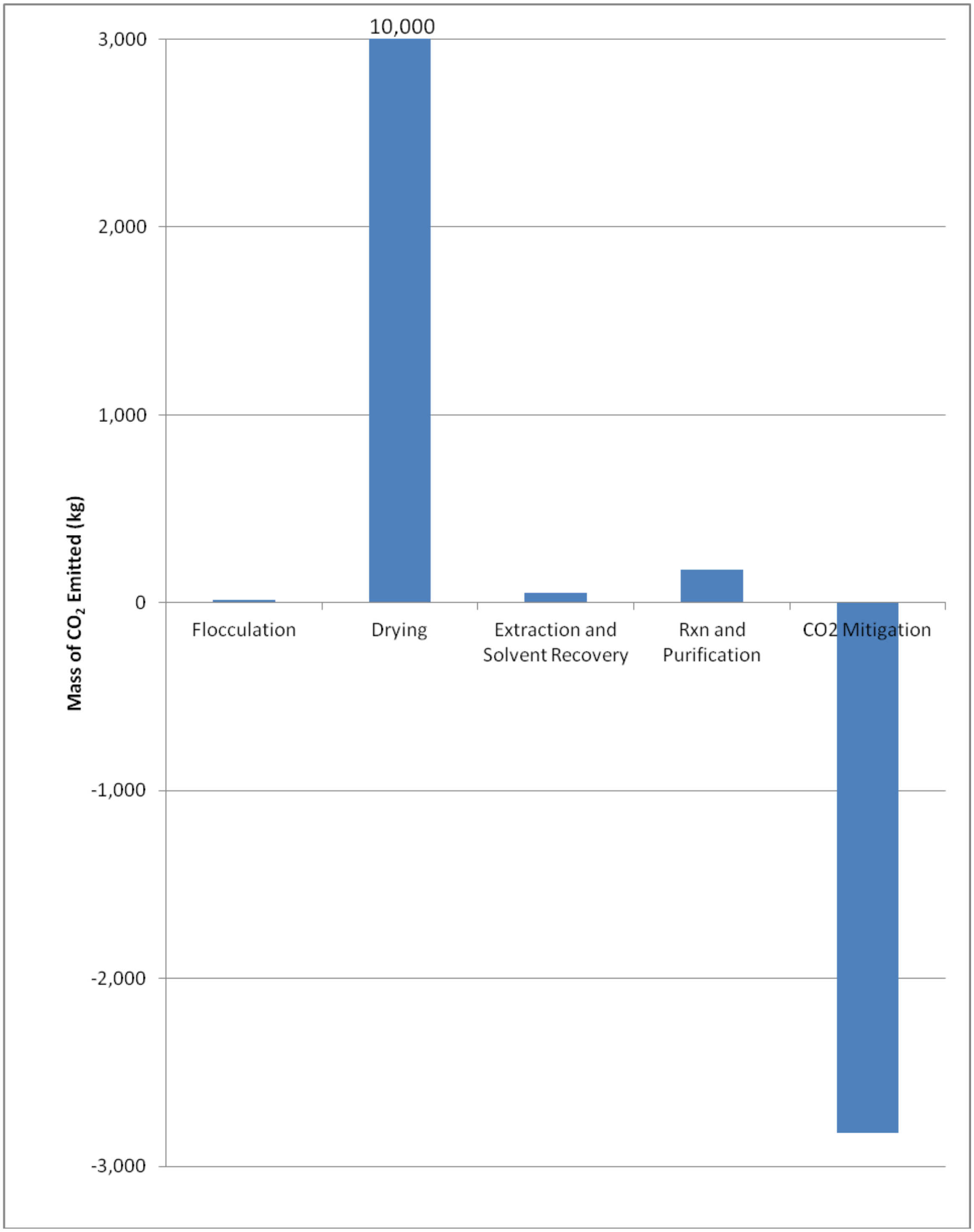


Figure 30. The amount of CO_2 emissions for each step in the algae biodiesel process

The LCA for the base case shows the parts of the biodiesel production which have the greatest opportunity for improvement. These processes can then be compared to alternative methods and a comprehensive LCA can be performed for each alternative. A comparative analysis will then be executed. This analysis will be used as a decision making tool for determining the algae biodiesel production pathway.

The results of the base case LCA were reported and analyzed in terms of total emissions and CED. The algae growth stage made up 73.9% of the total emissions. This method of growth was based on using a tubular PBR, and contributed to 74.0% of CED. This is due to the energy required to constantly pump the algae mixture through tubes at turbulent velocity. Although this was established as a commercially feasible technology, other technologies will likely be more suitable for the algae growth stage. This will not be the focus of this LCA. This assessment will be towards the downstream processing.

The drying step is another operation which can be improved greatly. Instead of sending the flocculated algae directly to a spray dryer, mechanical separation methods were investigated. Minimizing the amount of water which requires thermal separation can decrease the energy requirement for the drying step and its respective impact.

Chapter 5

Development and Analysis of Alternatives

5.1 Dewatering Alternatives Background

Despite its many advantages, the process of producing biodiesel from algae is energy intensive and leaves a significant carbon footprint. A majority of this energy can be attributed to dewatering, or the removal of water from the algae.[11] Xu *et al.* state that approximately 85% of the energy of the overall production of biodiesel is taken up by the dewatering step. The cultivation of algae results in a dilute solution of algae and water. The removal of this water is energy intensive, but necessary to achieve the high dry solid weight content required to effectively extract the lipids. Currently, there are several dewatering methods that have been proven on the industrial scale to be effective. However, certain technologies require a higher energy investment, while other technologies are incapable of sufficiently reducing the water content. Therefore, either new methods need to be developed, or existing technologies have to be optimized to find an energy efficient process.

The goal of this project is to analyze alternative harvesting and dewatering methods, and conduct a life cycle assessment (LCA) of these processes to serve as a decision making tool in commercial algae biofuel production. Figure 31 shows the boundaries of this study.

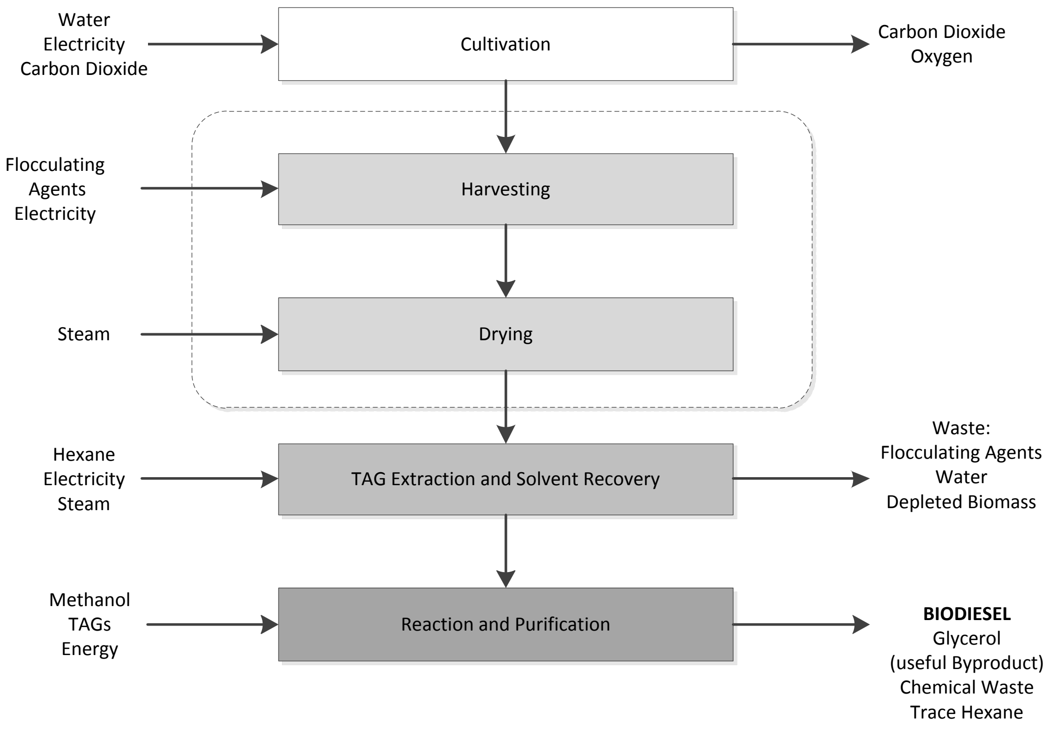


Figure 31: Process flow diagram for the production of biodiesel- boundaries for this study are shown with a dashed line

Various dewatering technologies were evaluated to find an efficient alternative processes to serve as comparisons to the current base case scenario. The base case concentrates the algae slurry using flocculation and is further dried using a spray dryer. This is very energy intensive because of thermal drying. An alternative dewatering process would include various mechanical and thermal means of dewatering that would yield lower water content without as high an energy investment. In order to determine the extent to which each type of process is used, a comparison was done between mechanical and thermal drying to evaluate energy demands for each. From this, preliminary scenarios were developed based of an existing model that maps out energy demands for thermal versus mechanical drying, which was developed by Xu et al.[46] From these scenarios, comparisons were performed using the life cycle emissions of each in order to develop an alternative dewatering process that improves upon the base case.

5.2 Dewatering Theory

Following cultivation of the algae, the water needs to be separated before the extraction of the lipids can take place. The algae slurry needs to have a dry algae content of 95%, to maximize extraction efficiency.[12] This is based on commercially available solvent extraction systems such as those using hexane. Several dewatering technologies were explored in order to find the most effective means to remove the water from the algae. These technologies, primarily utilized in wastewater treatment, have been proven to be effective at removing water from biomass. The technologies being considered for the purposes of dewatering algae are the following: flocculation, centrifugation, filtration, and thermal drying. Table 47 shows the general operating conditions for each of these types of equipment. Flocculation is determined to be the ideal method of initial concentration, while thermal dryers should be used as little and as efficiently as possible. The base case demonstrated that flocculation removed approximately 50% of the total water, while consuming the least energy of all the processing steps. In the following sections, in depth analyses of each of these technologies were performed in order to determine the advantages and disadvantages of each. This analysis will provide the basis for an industrially scaled dewatering scheme, which can then be compared to the base case.

Table 47: Dewatering equipment and their relative operating conditions

Dewatering Equipment	**Initial Water Content**	**Final Water Content**	**Energy Consumption**	**Equipment Capacity**
Flocculation	Very High	High	Very Low	Very High
Centrifugation	High	Medium	Medium	High
Filtration	High	Medium	Medium	Medium- High
Thermal Dryers	Medium	Very Low	Very High	High

5.2.1 Centrifugation

Centrifugation uses centrifugal forces to separate mixture components based on the size of the particles and the densities of the different mixture components.[91] Operational guidelines for centrifugation vary with different types of centrifuges. Usually, the choice of centrifuge is case specific.

Centrifugation has been considered extensively for the purposes of dewatering algae and is the preferred method of recovering algae cells as high rotational speeds make it very effective both at lab and industrial scale.[10, 92] Centrifugation is reliable in separating highly dilute solutions using appropriate rotational speeds. The main downside is the high energy demand necessary to operate the centrifuge to attain high centripetal acceleration (Table 48). This acceleration can yield a high degree of separation but results in further emissions.[17] Operating the centrifuge at lower rotational speeds can also be energy intensive as the separation requires more time and the degree of separation is significantly less. This was demonstrated in a study using centrifugal speeds of 13,000*g*, 6,000*g*, and 1,300*g*. "*g"* is a denotation of g-force which is a measure of the force from centripetal acceleration.[17] This study demonstrated that at 13,000*g*, greater than 95% of the cells were recovered from the feed stream, about 60 % were recovered at 6,000*g*, and only 40% at 1,300*g*.[17] The centrifuge becomes less effective as the rotational speed is decreased. The algae recovery varies depending on the type of centrifuge and the incoming dry algae concentration. Molina Grima et al. summarized various types of centrifuges and documented their energy consumption for algae feedstocks (Table 48).[10] The final algae concentrations are based on experimental data and actual final algae concentrations can vary depending on the species.

Table 48: Various continually operating centrifuges and their operating demands[10]

Centrifuge Type	**Initial Algae Concent-ration**	**Final Algae Concent-ration**	**Energy Consumed**[1] **(kWh/m^3 feed processed)**	**Energy consumed**[2] **(Wh/kg water removed)**
Disc Stack	0.1%	12%	1	1.0
Nozzle Discharge	0.1%	2-15%	0.9	0.9
Decanter Bowl	2.0%	22%	8	8.8
Hydrocyclone	0.1%	0.4%	0.4	0.53

[1] Energy consumed for each m^3 of feed volume processed

[2] Energy consumed for each kg of water removed. This assumes a feed density of water, and uses the initial and final algae concentrations to calculate the water removed.

Xu et al. use an Alfa Laval® PX-115 disc-stack centrifuge for algae dewatering.[93] The centrifuge operates at 4,800 rpm and consumes 45 kW of power to process 85 m^3/h of an algae solution at an initial concentration of 2% to a final concentration of 16%.[46] This corresponds to an energy consumption of 0.53 kWh/m^3 of algae slurry processed and 0.00078 kWh/kg water removed. Comparing this centrifuge to the values in Table 48, the disc stack centrifuge is able to remove the most water while consuming the least energy. Figure 32 shows a schematic of the disc stack centrifuge.

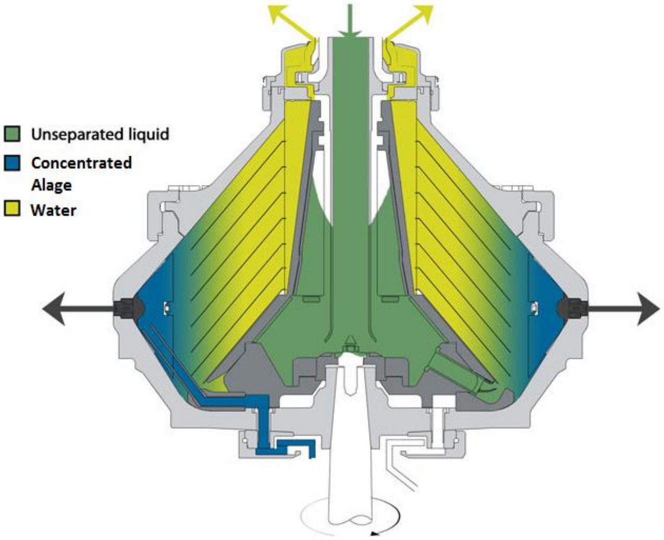


Figure 32: Disc stack centrifuge [93]

5.2.2 Filtration

There are different filter designs, including pressure filters and vacuum filters that can be considered in algae separation. Pressure and vacuum filters have several different designs, including plate and frame presses, pressure and vacuum belts, and rotary presses. Experimental comparisons of pressure filters showed that they are more energy efficient, reliable, and reach higher algae concentrations than vacuum filters (Table 49).[94] Another filter technology proposed for algae separation is tangential flow filtration (TFF). The process works with the pressurized feed mixture flowing parallel to the membrane filter as shown in Figure 33.

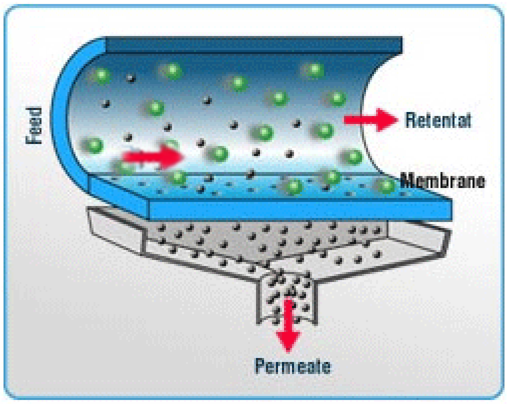


Figure 33: Tangential flow filtration [95]

The membrane pores are between 1 and 2 nm in size, small enough to prevent algae from transferring across the membrane. The tangential flow of the mixture avoids the formation of a cake on the filter, resulting in improved performance.[96] A study conducted by Danquah et al, investigated the energy consumption of other filtration and flocculation technologies compared to a lab scale tangential flow filter. The initial and final algae concentrations as well as their power consumption per cubic meter of algae solution can be found in Table 49.

Table 49: Demands of various filtrations methods

Filtration Process	Algae Initial Concentration	Final Algae Concentration	Energy Consumption (kWh/m^3)	Energy consumption (Wh/kg water removed)
TFF	0.06%	8.88%	2.06	2.1
Pressure Filter	0.5%	22-27%	0.88	0.90
Vacuum Filter	0.5%	18%	5.9	6.1

Overall, it was found that the TFF energy consumption is higher than in a pressure filter and lower than in vacuum filters for every kg of water removed.[9] The rotary pressure filter is energy efficient, can continuously operate, and is commercially available. For these reasons, a rotary pressure filter is the most promising filtration technology for algae dewatering. Figure 34 shows a schematic of the rotary pressure filter.

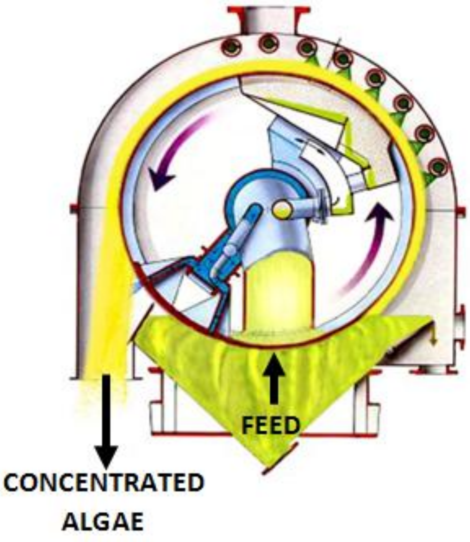


Figure 34: Schematic of rotary pressure filter[97]

5.2.3 Thermal Drying

Depending on the quantity of water removed mechanically, thermal drying can represent up to 99% of the energy consumed in the dewatering process. This is a result of the high heat of vaporization of water which is 2,257 kJ/kg at atmospheric pressure.[91] Since energy consumption is directly related to life cycle emissions, it is essential to find the most efficient method for separating water and algae. Driers are generally used as the last step in the dewatering process to reduce overall energy consumption and reduce water content to levels that cannot be achieved by mechanical drying methods. Six drying technologies were compared to see which was the least energy intensive. They are band dryers, rotary dyers, steam rotary dryers, pressurized fluid-bed dryers, pneumatic steam dryers, and a heat integrated dryer developed by Delft University.

Fagernäs et al. compared commercially available band, rotary, steam rotary, pressurized fluid-bed, and pneumatic steam dryers used in woody biomass drying.[98] Band dryers blow hot air perpendicular to the belt direction, carrying water vapor with it. The air is usually between 90-120°C and the belt is typically permeable. A band dryer is illustrated in Figure 35.

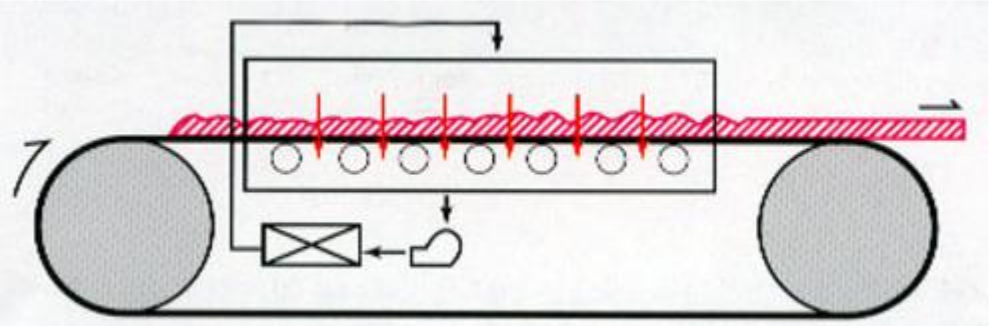


Figure 35: Illustration of band dryer operation[99]

Rotary and steam rotary dryers are continuous processes that utilize a spinning drum. Biomass is passed through the inside of the drum, while hot gas or steam is passed through a shell on the exterior of the drum. An illustration is shown in Figure 36.

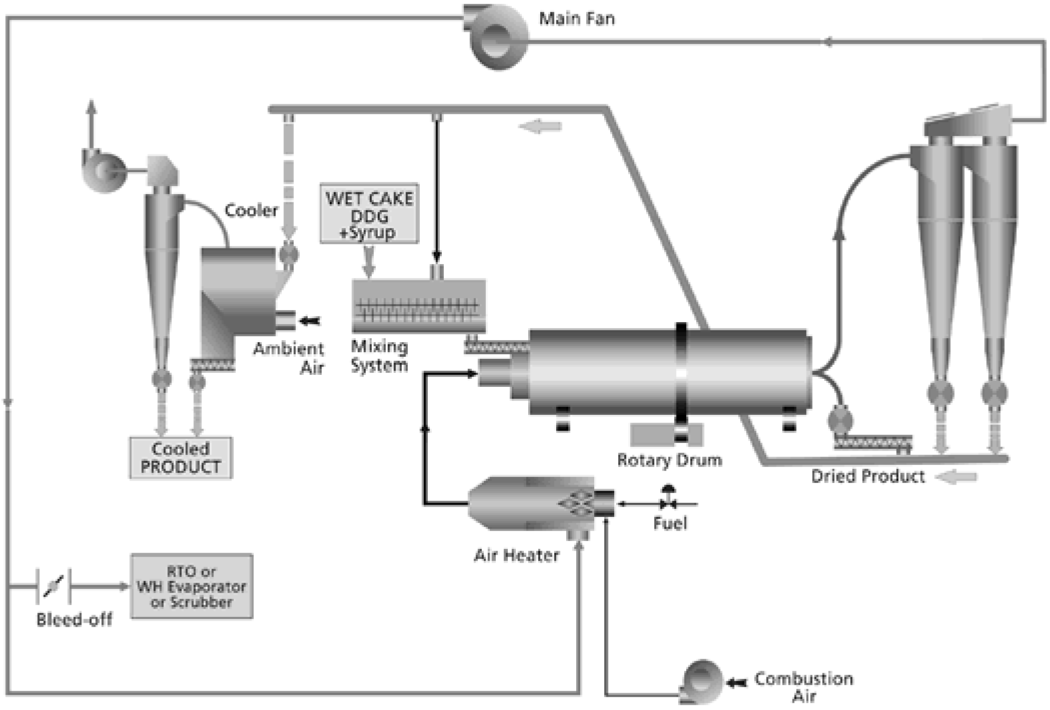


Figure 36: Illustration of rotary and steam rotary dryer[100]

Pressurized fluid-bed dryers utilize the principles of fluidization of solid particles to dry biomass. Superheated steam is sent through a bed of biomass, where water is evaporated. Finally, a pneumatic steam dryer uses superheated steam to transport wet particles through a series of heat exchangers, where the biomass is dried. The biomass is then separated from the steam via a cyclone.[98] A pneumatic steam dryer diagram can be found in Figure 37.

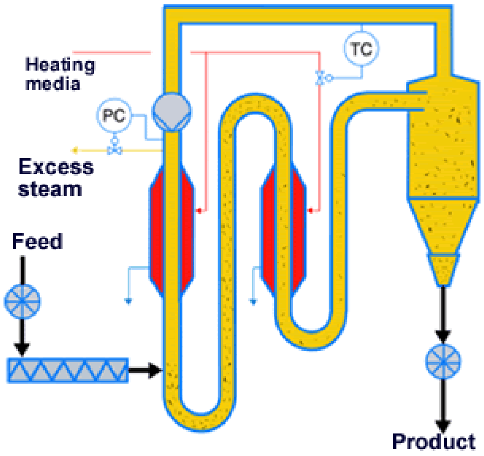


Figure 37: Diagram of pneumatic steam dryer[101]

A novel drying technology was developed at the Delft University of Technology.[102] This heat integrated dryer mixes steel balls heated by steam with wet medium in an auger under vacuum. Once the medium reaches the desired moisture content, the dried material is mechanically removed from the steel balls and leaves the system. The clean steel balls are sent to a second, counter currently flowing auger. The water vapor produced by the first auger is sent to this second auger via multiple channels, where the balls recover the heat from the vapor. Once the balls have been reheated, condensed water vapor is mechanically removed. The steel balls are then passed through a steam heater, where they reach the desired temperature to be recycled back into the first auger. This dryer was also considered as a potential dryer for algae drying in a study by Xu et al.[46, 102, 103]

Differences in design and heat carriers results in varying efficiencies for each system. Table 50 summarizes the energy consumption required for each drying technology as well as the system's energy carrier.

Table 50: Summary of energy consumption and energy carriers for dryer technologies. Adapted from Fagernas et al.[98]

Dryer Type	**Energy Carrier**	**Energy Consumption (kWh/kg H_2O removed)**
Band	Air (90-120°C)	1.1-1.4
Rotary	Air (250-400°C)	1.1-1.4
Steam Rotary	Steam (0.6-1 MPa)	0.83-1.1
Fluidized Bed	Steam (2.6 MPa)	0.61
Pneumatic Steam	Steam (0.7-2.6 MPa)	0.56-0.83
Heat Integrated Dryer [46]	Steam (0.2 MPa and 120°C) [46]	0.56[46]

Although it is not currently a commercial technology, the heat integrated dryer has the potential to be the most energy efficient drying system. For the alternative dewatering scenarios, a heat integrated dryer and steam rotary dryer were chosen as the drying technologies. These were compared to illustrate differences between using driers with different efficiencies.

5.3 Development of Alternative Dewatering Cases

The base case analysis revealed that thermal drying required much more energy input than any other downstream operation in biodiesel production, and therefore should be optimized. From this, it was determined that if the dry solids concentration were increased prior to the thermal drying step using mechanical separations, then the energy input of the overall dewatering process would decrease. Thermal drying, unlike mechanical drying, is capable of removing water from within the cells and is required to achieve the 5% target dry weight. First, preliminary alternative cases were developed by adapting equipment from Xu et al.'s study. This preliminary study was used to make initial comparisons towards the base case. Different types of mechanical drying were sequenced prior to thermal drying to develop four alternative cases. These cases were later refined and expanded upon as a result of the reductions achieved by these cases.[46] These preliminary cases are not described, since the resulting final alternatives are more comprehensive.

The preliminary alternative cases revealed that thermal drying required much more energy input than the mechanical operations. Therefore, the dewatering operations were refined utilizing a wider range of dewatering equipment. The Xu et al. (2011) study provides comparison of the heat integrated dryer, heat assisted rotary filter, and disc stack centrifuge energy requirements.[46] Our study incorporates these as well as other types of dewatering techniques and performs a LCA when they are integrated into the biodiesel production process.

Thermal drying was inevitably required as a result of bound intercellular water. Typical algae cells can contain between 40 and 80% water. [18, 46, 47] This water cannot be removed by mechanical techniques such as centrifugation or filtration. A thermal dryer can achieve the low moisture contents needed, but the base case shows that this is not energy efficient for high moisture content slurries. This work used various types of dewatering equipment and sequenced them to effectively lower the environmental impact of dewatering. The energy consumption is determined by the extent and sequence these dewatering technologies are used. Without heat integration, spray drying is typically considered inefficient. This is because air is used as the medium to transfer heat which has a relatively low heat transfer coefficient. This coupled with the fast processing time means that less heat is transferred to the medium, allowing a large portion of the energy to go unutilized.

Since thermal drying will be required, two methods of drying were compared. A steam rotary dryer and a novel heat integrated dryer were considered as alternative methods of thermal drying. The steam rotary dryer consumes approximately 3 MJ/kg of water removed.[98] The heat integrated dryer was developed by Delft University for drying a biomass-type sludge and consumes 2 MJ/kg of water removed.[103] This dryer uses hot balls to contact the algae slurry under a vacuum, and condenses the water vapor over the metal balls to recover the heat. Although this is a new method of drying, the production capacity is 1,000 kg of dried sludge/hr.[102]

Three different types of centrifuges were considered. The first was a disc-stack centrifuge capable of removing water to approximately 12% dry algae content.[10] This centrifuge has a processing capacity of 85 m^3/hr and a power consumption of 45 kW. The second centrifuge used was a decanter bowl centrifuge. The decanter bowl centrifuge produces a 22% dry algae, is available at commercial capacities, and consumes 8 kWh/m^3

of feed processed.[10] The third centrifuge was a novel spiral plate centrifuge developed by Evodos® (Breda, The Netherlands), specifically for dewatering algae.[104] It is capable of achieving 31.5% dry algae weight, consumes 0.95 kWh/m^3 of algae slurry processed, and can process up to 40 m^3 of slurry/hr. [105]

The three filtration methods investigated were a tangential flow filtration, chamber filter press, and a heat assisted rotary pressure filter. The tangential flow filtration was based on a study by Danquah et al. (2009) which found an energy consumption of 0.00206 kWh/kg of water removed and achieved a final dry algae content of 8.8%.[9] The chamber filter press consumes 0.88 kWh/m^3 of water removed and can achieve a 27% dry algae content. The heat assisted rotary filter was used in a study conducted by Mahmood et al. (1998) on biomass-type sludge drying.[106] This study used a filter that increased the solids concentration from 33% to 56% while using 60 kWh/dry t sludge. This filter was capable of operating at a capacity of 200 tons of sludge/hr. It was assumed that this equipment can handle algae contents as low as 22% for the purpose of sequencing technologies. These filtration units require electricity as the energy input. Even though the pressure filter uses heat, this is still supplied through electricity rather than steam.

Centrifugation, filtration, and thermal drying equipment were sequenced to establish alternative cases. The energy consumption and the resulting dry algae content were calculated based on the dry algae content of the incoming slurry, the attainable dry weight content, and the energy consumption for each dewatering operation. The alternatives were generated on the basis of 1 t of biodiesel (BD). Since only energy was an input for these processes, the electricity and steam consumption for each case was known. The dryers required steam, while the remaining dewatering equipment consumed electricity. The LCA could then be performed using the energy consumption and the LCIs for electricity and steam.

5.3.1 Case 1 and Case 2

Case 1 and case 2 were developed to investigate alternative thermal drying methods instead of using a spray dryer. Case 1 used a steam rotary dryer and case 2 used the heat integrated dyer developed by Delft University. The input into these dryers is assumed to be the same as those from the base case. A process flow diagram of case 1 and case 2 can be found in Figure 38. Both cases consist of the same process configuration, but differ by the type of dryer and resulting energy expenditures. The mass and energy balance for case 1 can be found in Table 51.

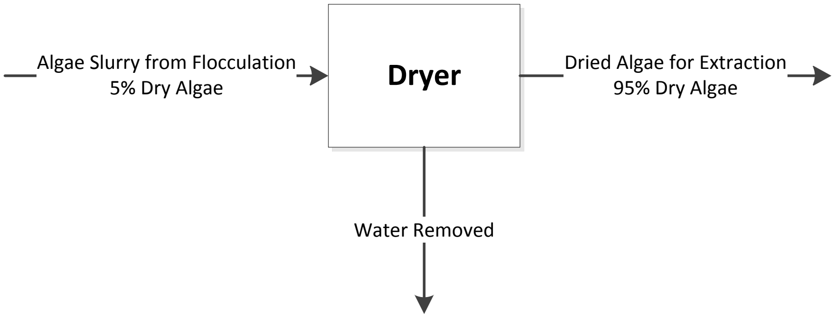


Figure 38: Process flow diagram for case 1 and case 2.

The steam rotary dryer consumes 3 MJ/ kg of water.[98] The heat integrated dryer uses 2 MJ/ kg of water removed, which is significantly less than other dryer technologies.[46] The output conditions of the flocculation unit were 5% algae by weight and 95% water and are shown in Table 51 and Table 52. This assumed that the mass of flocculants are negligible compared to the algae and water in solution. The desired output concentrations are 95% algae and the remainder water. The material and energy balances for case 1 and case 2 are shown in Table 51 and Table 52 respectively.

Table 51: Material and energy balance for streams in case 1

Steam Rotary Dryer						
	Mass fraction		Mass (kg/t BD)			
	Algae	Water	Algae	Water	Water removed	Water removed (t/t BD)
In	0.05	0.95	1,920	36,500	N/A	N/A
Out	0.95	0.05	1,920	101	36,400	36.4
Energy Input (GJ/t BD)	109					

It was found that the steam rotary dryer consumed 109 GJ/t BD, while removing 36.4 t of water per t BD. This is compared to 87.3 GJ that were consumed by the spray dryer in the base case. The steam rotary dryer consumes 25% more energy than the spray dryer. The dryers use steam as an energy source, therefore this needs to be converted to quantity of steam. Using steam under the same conditions as the base case (191.6°C, 13 bar), 55,500 kg of steam/t BD is required.

Table 52: Material and energy balance for streams in case 2

Heat Integrated Dryer						
	Mass fraction		Mass (kg/t BD)			
	Algae	Water	Algae	Water	Water removed	Water removed (t/t BD)
In	0.05	0.95	1,920	36,500	N/A	N/A
Out	0.95	0.05	1,920	101	36,400	36.4
Energy Input (GJ/t BD)	72.9					

The heat integrated dryer consumed 72 GJ/t BD and also removed 36.4 t of water per t of BD. This consumes 21% less energy than the spray dryer and corresponds to

37,000 kg of steam/ t BD. The heat integrated dryer was used for cases 3 through 6 because it was found as the more efficient dryer.

5.3.2 Case 3

Case 3 consists of the disc stack centrifuge, the chamber filter press, and the heat integrated dryer. Figure 39 contains the process flow for Case 3. The input concentrations to the centrifuge were 5% dry algae. The outlet conditions of the disc stack centrifuge were 12% dry weight algae.[10] Using the conditions from the flocculation stage, the disc stack centrifuge consumed approximately 3.27 kJ/kg of water removed. The chamber filter press followed this, and dewatered to 27% dry algae and then to 95% dry algae by the heat integrated dryer.[10] The chamber filter press removed approximately 3.17 kJ/kg of water removed in this case.

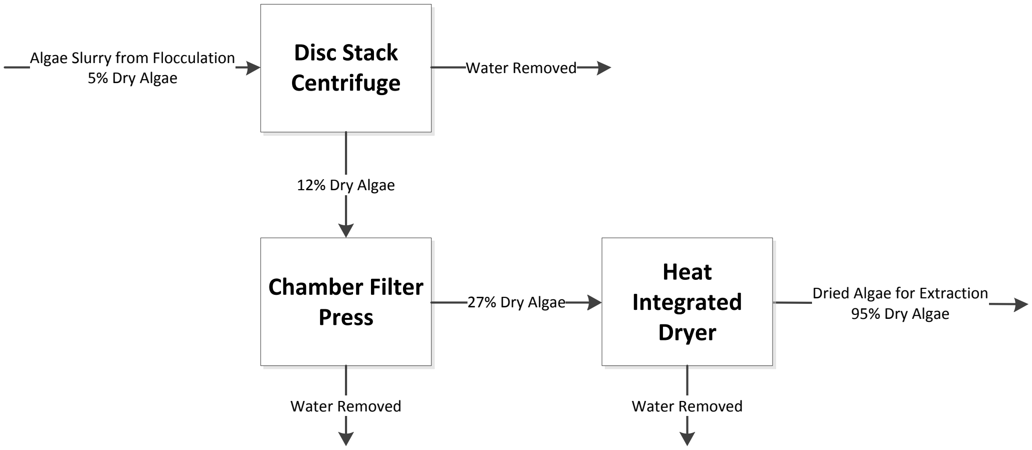


Figure 39: Process flow diagram for case 3.

The material and energy balances for the process can be found in Table 53. The total energy consumed is 10.3 GJ/t BD, with 99% of the energy being consumed in the thermal drying step. By adding the centrifugation step, the energy input for the drying process was reduced by 61.7 GJ/t BD as compared to case 2. The water removed by the centrifuge was 22.4 t, the chamber filter press removed 8.9 t of water, and 5.1 t were removed by the dryer. The disc stack centrifuge and chamber filter press consumed electricity, but the heat integrated dryer consumes steam. When this energy is converted to steam, the heat integrated dryer consumes 5,180 kg of steam/t BD.

Table 53: Material and energy values for streams in case 3

Disc Stack Centrifuge						
	Mass fraction		Mass (kg/t BD)			
	Algae	Water	Algae	Water	Water removed	Water removed (t/t BD)
In	0.0500	0.95	1,920	36,500	N/A	N/A
Out	0.12	0.88	1,920	14,100	22,400	22.4
Energy Input (GJ/t BD)	0.073					
Chamber Filter Press						
	Mass fraction		Mass (kg/t BD)			
	Algae	Water	Algae	Water	Water removed	Water removed (t/t BD)
In	0.12	0.880	1,920	14,100	N/A	N/A
Out	0.27	0.0500	1,920	5,200	8,900	8.9
Energy Input (GJ/t BD)	0.028					
Heat Integrated Dryer						
	Mass fraction		Mass (kg/t BD)			
	Algae	Water	Algae	Water	Water removed	Water removed (t/t BD)
In	0.27	0.730	1,920	5,200	N/A	N/A
Out	0.950	0.0500	1,920	101	5,100	5.1
Energy Input (GJ/t BD)	10.19					

5.3.3 Case 4

In case 4, the spiral plate centrifuge, heat assisted rotary pressure filter, and heat integrated dryer were used. The spiral plate centrifuge dewatered the algae to 31.5% dry algae content and the heat assisted rotary pressure filter brought the slurry to 56% dry algae content. The spiral plate centrifuge was found to consume approximately 4.07 kJ/kg water removed. Mahmood et al. used a filter that increased the dry solids concentration from 33% to 56% while consuming 60 kWh/t of dried solids.[106] The filter used 173 kJ per kg of water removed. The heat integrated dryer was used to increase the algae concentration to 95% following the pressure filter. Figure 40 contains the process flow diagram for case 4. Mass and energy balances can be found in Table 54.

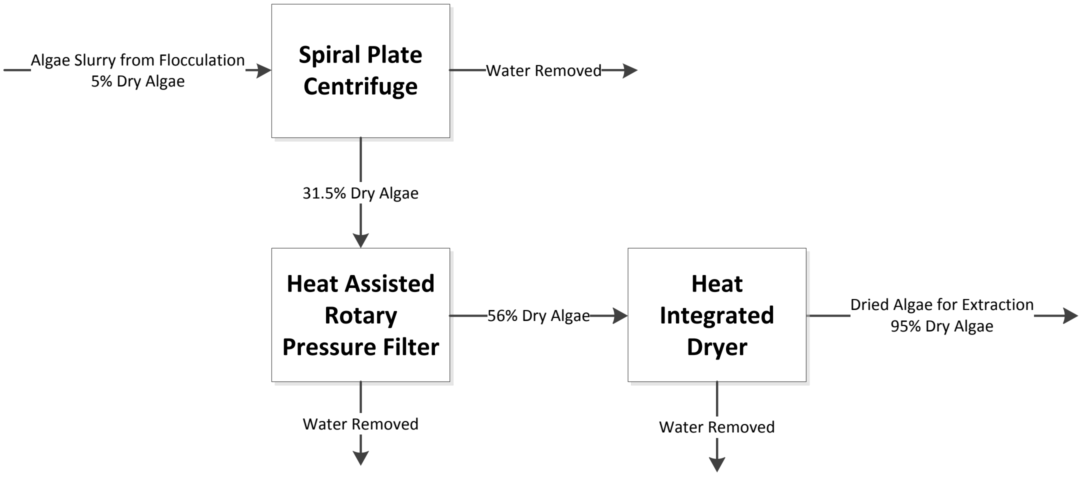


Figure 40: Process flow diagram for case 4.

The energy demand for this process is 3.41 GJ/t BD. This is 6.9 GJ/t BD less than case 3. Once again, the majority of the energy consumed in Case 4 is during the drying step, constituting 83% of the total. The centrifugation step removed 89% of the total water during the process. The centrifugation and pressure filter used electricity as an energy source, while the heat integrated dryer consumed 1,430 kg of steam/t BD.

Table 54: Material and energy balance for Case 4

Spiral Plate Centrifuge						
	Mass fraction		Mass (kg/t BD)			
	Algae	Water	Algae	Water	Water removed	Water removed (t/t BD)
In	0.0500	0.950	1,920	36,500	N/A	N/A
Out	0.315	0.685	1,920	4,180	32,400	32.4
Energy Input (GJ/t BD)	0.132					
Rotary Pressure Filter						
	Mass fraction		Mass (kg/t BD)			
	Algae	Water	Algae	Water	Water removed	Water removed (t/t BD)
In	0.315	0.685	1,920	4,180	N/A	N/A
Out	0.56	0.44	1,920	1,510	2,670	2.67
Energy Input (GJ/t BD)	0.463					
Delta Dryer						
	Mass fraction		Mass (kg/t BD)			
	Algae	Water	Algae	Water	Water removed	Water removed (t/t BD)
In	0.56	0.44	1,920	1,510	N/A	N/A
Out	0.95	0.05	1,920	101	1,410	1.41
Energy Input (GJ/t BD)	2.82					

5.3.4 Case 5

Case 5 consisted of the chamber filter press, followed by the heat assisted rotary pressure filter, and dried using the heat integrated dryer. The chamber filter press dewaters the algae slurry to 27% dry algae, the heat assisted rotary pressure filter dewaters the algae to 56% dry algae, and the heat integrated dryer is used to reach 95% dry algae. Figure 41 contains the process flow diagram for case 5.

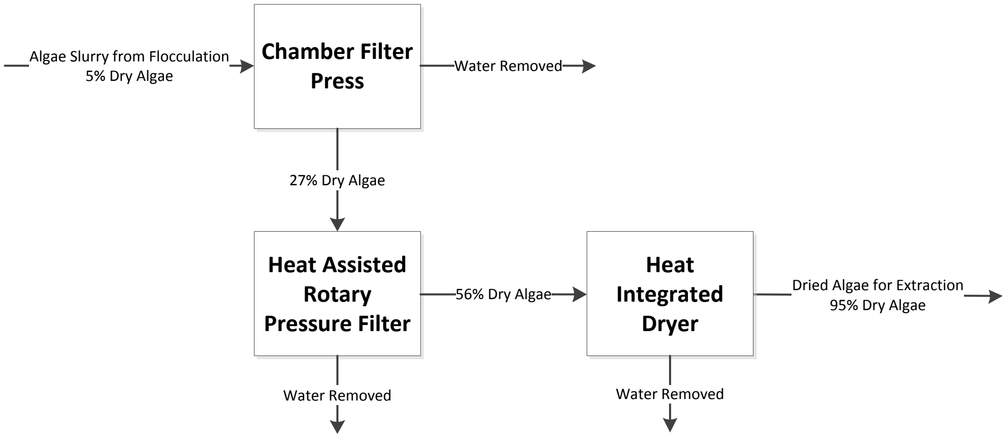


Figure 41: process flow diagram for case 5.

The total energy consumption for the process is 3.58 GJ/t BD, slightly higher than that of case 4. The majority of energy is consumed by the heat integrated dryer, representing 79% of the total dewatering energy in Case 5. The heat integrated dryer consumed 1,430 kg of steam/ t BD. The results of the material and energy balances can be found in Table 55.

Table 55: Material and energy balance for case 5

Chamber Filter Press:						
	Mass fraction		Mass (kg/t BD)			
	Algae	Water	Algae	Water	Water removed	Water removed (t/t BD)
In	0.05	0.95	1,920	36,500	N/A	N/A
Out	0.27	0.73	1,920	5,200	31,300	31.3
Energy Input (GJ/t BD)	0.122					
Rotary Pressure Filter						
	Mass fraction		Mass (kg/t BD)			
	Algae	Water	Algae	Water	Water removed	Water removed (t/t BD)
In	0.27	0.73	1,920	5,200	N/A	N/A
Out	0.56	0.44	1,920	1,510	3,690	3.69
Energy Input (GJ/t BD)	0.640					
Heat Integrated Dryer						
	Mass fraction		Mass (kg/t BD)			
	Algae	Water	Algae	Water	Water removed	Water removed (t/t BD)
In	0.56	0.44	1,920	1,510	N/A	N/A
Out	0.95	0.05	1,920	101	1,410	1.41
Energy Input (GJ/t BD)	2.82					

5.3.5 Case 6

Case 6 consisted of tangential flow filtration, followed by the decanter bowl centrifuge, the heat assisted rotary pressure filter, and the heat integrated dryer. Tangential flow filtration dewaters the algae slurry to 8.8% dry algae, the decanter bowl centrifuge dewaters the algae to 22% dry algae, the rotary pressure filter attains a 56% dry weight content, and the heat integrated dryer is used to reach 95% dry algae. The tangential flow filter consumed 7.42 kJ/kg of water removed using the conditions specified. The decanter bowl centrifuge was found to consume 28.8 kJ/kg of water removed. Figure 42 contains the process flow diagram for Case 6.

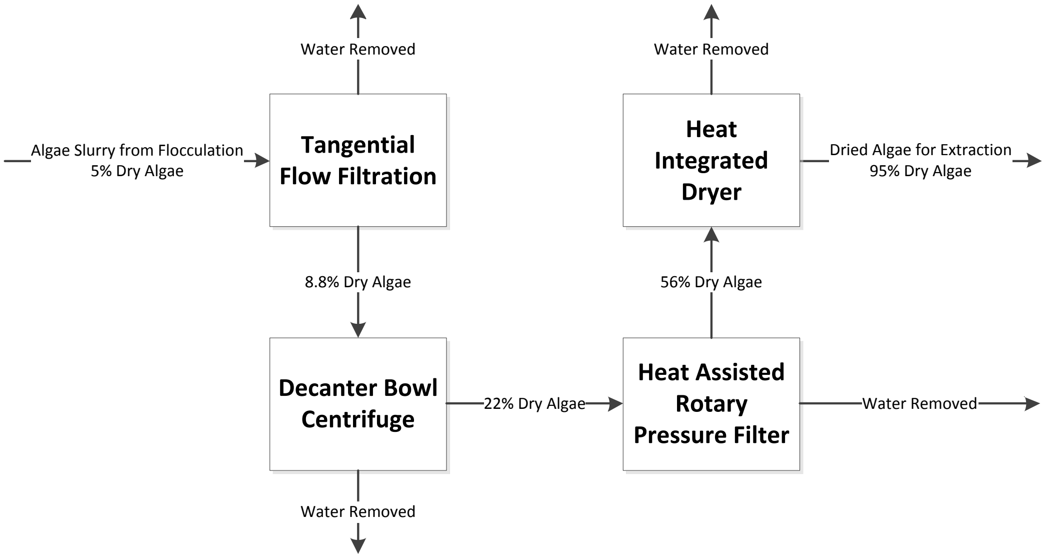


Figure 42: Process flow diagram for case 6.

The total energy consumption for the process is 4.49 GJ/t BD, higher than case 4 and case 5. The majority of energy is consumed by the heat integrated dryer, representing 63% of the dewatering process energy. The heat integrated dryer consumed 1,430 kg of steam/t BD. The results of the material and energy balances can be found in Table 56.

Table 56: Material and energy balance for case 6

Tangential Flow Filtration						
	Mass fraction		Mass (kg/t BD)			
	Algae	Water	Algae	Water	Water removed	Water removed (t/t BD)
In	0.05	0.95	1,920	36,500	N/A	N/A
Out	0.088	0.91	1,920	19,700	16,800	16.8
Energy Input (GJ/t BD)	0.125					
Decanter Bowl Centrifuge						
	Mass fraction		Mass (kg/t BD)			
	Algae	Water	Algae	Water	Water removed	Water removed (t/t BD)
In	0.088	0.91	1,920	19,700	N/A	N/A
Out	0.22	0.78	1,920	6,820	12,900	12.9
Energy Input (GJ/t BD)	0.624					
Heat Assisted Rotary Pressure Filter						
	Mass fraction		Mass (kg/t BD)			
	Algae	Water	Algae	Water	Water removed	Water removed (t/t BD)
In	0.22	0.78	1,920	6,820	N/A	N/A
Out	0.56	0.44	1,920	1,510	5,310	5.31
Energy Input (GJ/t BD)	0.921					
Heat Integrated Dryer						
	Mass fraction		Mass (kg/t BD)			
	Algae	Water	Algae	Water	Water removed	Water removed (t/t BD)
In	0.56	0.44	1,920	1,510	N/A	N/A
Out	0.95	0.05	1,920	101	1,410	1.41
Energy Input (GJ/t BD)	2.82					

5.3.6 Summary of Cases

Table 57 contains a summary of all the energy inputs for the various dewatering technologies used in Cases 1-6. The energy values follow a basis of energy per tonne of BD. It also states the energy source for each dewatering method. This will be used to perform life cycle assessments (LCA) on each dewatering case to determine their environmental impact.

Table 57: Summary of the dewatering equipment and energy consumption (the total dewatering energy in case 4 is bold because it has the lowest process energy demand)

	Overall Comparison of Dewatering Processes							
			Energy Values (GJ/t of BD)					
	Energy source for dewatering	Dry algae content (%)	**Case 1**	**Case 2**	**Case 3**	**Case 4**	**Case 5**	**Case 6**
Disc Stack Centrifuge	Electricity	12	N/A	0.116	0.0733	N/A	N/A	N/A
Spiral Plate Centrifuge	Electricity	31.5	N/A	N/A	N/A	0.132	N/A	N/A
Decanter Bowl Centrifuge	Electricity	22	N/A	N/A	N/A	N/A	N/A	0.624
Tangential Flow Filter	Electricity	8.8	N/A	N/A	N/A	N/A	N/A	0.125
Chamber Filter Press	Electricity	27	N/A	N/A	0.0282	N/A	0.122	N/A
Rotary Pressure Filter	Electricity	56	N/A	N/A	N/A	0.463	0.640	0.921
Steam Rotary Dryer	Steam	95	109	N/A	N/A	N/A	N/A	N/A
Delta Dryer	Steam	95	N/A	72.9	10.2	2.82	2.82	2.82
Total Dewatering Energy Demand			109	72.9	10.30	**3.41**	3.58	4.49

5.4 Alternatives Life Cycle Inventory

The life cycle inventory (LCI) was compiled for the alternative cases. No additional inventories were developed for the alternative cases. The only alterations to the base case were in the energy required to operate the additional/alternate drying operations. Electricity and steam were used as the primary forms of energy and their LCI's remained consistent with the base case. The electricity used was high voltage electricity in the United States. Heating was performed through the use of steam and defined as steam for chemical processes in SimaPro®. This maintained consistency with the steam used throughout the base case analysis to provide for an accurate comparison. The chemical processes that use steam for heating requirements included both water and energy inputs to generate the steam. Table 40 shows the LCI's generated for electricity and steam using SimaPro®. The steam inventories are reported on a per kg of steam basis and electricity inventory is reported on a per MJ energy basis.

5.5 Alternative Cases Life Cycle Assessment

The LCIs generated by SimaPro® and the previously calculated energy requirements were used to perform a life cycle assessment (LCA). The biodiesel production stages were analyzed and the impact for each was obtained. These were inserted into a new process defined as biodiesel, so the various production stages and their resulting impact could be compared. The LCA was defined within SimaPro® to categorize emissions, raw material usage, and energy consumptions.

The total life cycle emissions was the impact category used for comparisons. Each process was categorized and then compared to the base case. Each of the LCA's contains an assessment of each stage represented in Figure 31. The only modifications to the process were performed on the dewatering and drying stages. Additional mechanical and alternative thermal drying technologies were compared. The goal was to minimize the energy demand and environmental impact of the drying step by studying a wider range of dewatering methods. As was found in the base case, the impact of algae growth is significantly larger than the other cases. For the purposes of this analysis, emissions and the energy demand of algae growth was omitted to focus on downstream processing. No analysis was included on the algae growth stage.

The CED was not analyzed for each process stage. The CED is the total energy expenditure that goes into raw material processing, manufacturing processes, and the waste disposal. The analysis of the CED for the preliminary alternatives showed similar trends in both the total life cycle emissions and the CED. Analyzing both impact categories proved repetitive and was therefore not performed on the CED. The values for the CED are included in the LCA tables for reference, but are not discussed.

5.5.1 Case 1 and Case 2

Cases 1 and 2 were comparisons on using different dryers. Table 58 shows the life cycle assessment of case 1.The difference between the base case and case 1 is the spray dryer was replaced with a steam rotary dryer.

Table 58: LCA of case 1 (basis of 1 t BD)

Impact category	**Flocculation**	**Steam Rotary Dryer**	**Extraction and Solvent Recovery**	**Reaction and Product Purification**	**Total**
Raw Materials Used (kg)	22.5	5,010	28.4	-125	4,930
Emissions to Air (kg)	15.1	12,400	55.1	179	12,700
Carbon Dioxide (kg)	14.8	12,400	54.6	179	12,600
Carbon Monoxide (kg)	0.0115	3.24	0.0204	-0.0177	3.26
Methane (kg)	0.0238	25.0	0.115	0.174	25.3
NMVOC (kg)	0.00510	5.23	0.102	-0.226	5.11
Nox (kg)	0.0387	11.1	0.0570	-0.163	11.0
SO2 (kg)	0.187	21.2	0.113	-0.109	21.4
Particulates (kg)	0.0381	2.56	0.0143	-0.0405	2.57
Emissions to Water (kg)	1.08	128	189	-14.6	304
VOCs (kg)	2.8E-05	0.0217	0.000216	0.000961	0.0229
Emissions to Soil (kg)	0.00652	5.34	0.0514	0.137	5.54
Total Emissions	16.2	12,500	245	164	13,000
CED (MJ)	280	220,000	1,205	408	222,000
Water Used (kg)	77,800	2,060,000	16,900	20,200	2,180,000

The total emissions resulting from the steam rotary dryer are 12,500 kg/t BD which is approximately 25% higher than the total life cycle emissions of the base case (Figure 43). This is because of the decreased efficiency of the dryer compared to the designed spray dryer. The high emissions are because of the energy required to thermally reduce the water content of the algae to 5%. As with the base case, this case requires a large quantity of steam to evaporate the water present in the algae slurry to achieve the low water content.

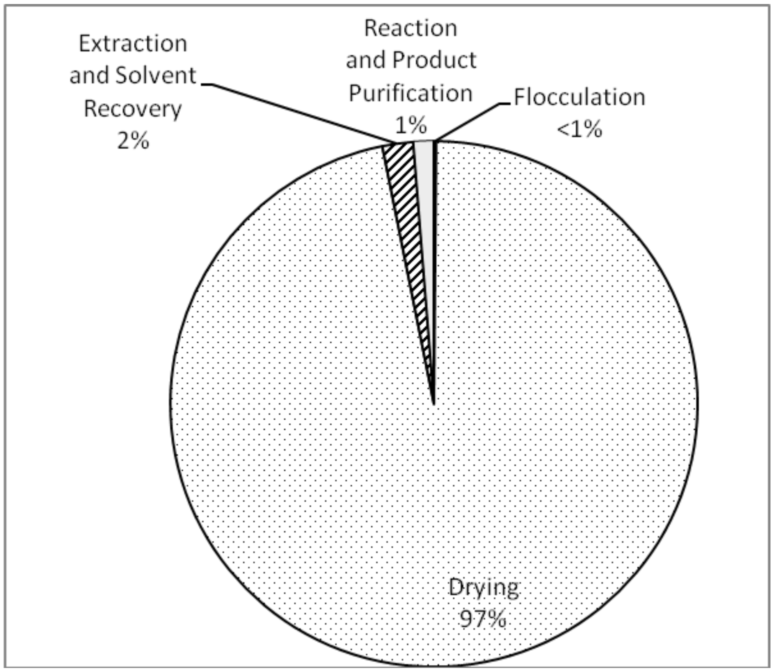


Figure 43: Percent contribution of emissions associated for case 1

Table 59 shows the life cycle assessment of case 2. Case 2 used a heat integrated dryer instead of a spray dryer. The replacement of spray dryer with the heat integrated dryer in case 2 reduced emissions of drying by 2,700 kg/t BD. This is a result of the lower energy demanded by the heat integrated dryer to achieve the same water content as the spray dryer.

Table 59: LCA of case 2 (basis of 1 t BD)

Impact category	**Flocculation**	**Heat Integrated Dryer**	**Extraction and Solvent Recovery**	**Reaction and Product Purification**	**Total**
Raw Materials Used (kg)	22.5	3,340	28.4	-125	3,260
Emissions to Air (kg)	15.1	8,290	55.1	179	8,540
Carbon Dioxide (kg)	14.8	8,240	54.6	179	8,490
Carbon Monoxide (kg)	0.0115	2.160	0.0204	-0.0177	2.18
Methane (kg)	0.0238	16.7	0.115	0.174	17.0
NMVOC (kg)	0.00510	3.49	0.102	-0.226	3.37
Nox (kg)	0.0387	7.41	0.0570	-0.163	7.34
SO2 (kg)	0.187	14.1	0.113	-0.109	14.3
Particulates (kg)	0.0381	1.70	0.0143	-0.0405	1.72
Emissions to Water (kg)	1.08	85.5	189	-14.6	261
VOCs (kg)	2.8E-05	0.0144	0.000216	0.000961	0.0157
Emissions to Soil (kg)	0.00652	3.56	0.0514	0.137	3.76
Total Emissions	16.2	8,380	245	164	8,800
CED (MJ)	280	147,000	1,205	408	149,000
Water Used (kg)	77,800	1,380,000	16,900	20,200	1,490,000

The heat integrated dryer had 8,380 kg/t BD of total emissions. This is 16% less total life cycle emissions than was generated with the base case. Drying is once again the major contributor to the total emissions. The distribution of the total life cycle emissions is shown in Figure 44.

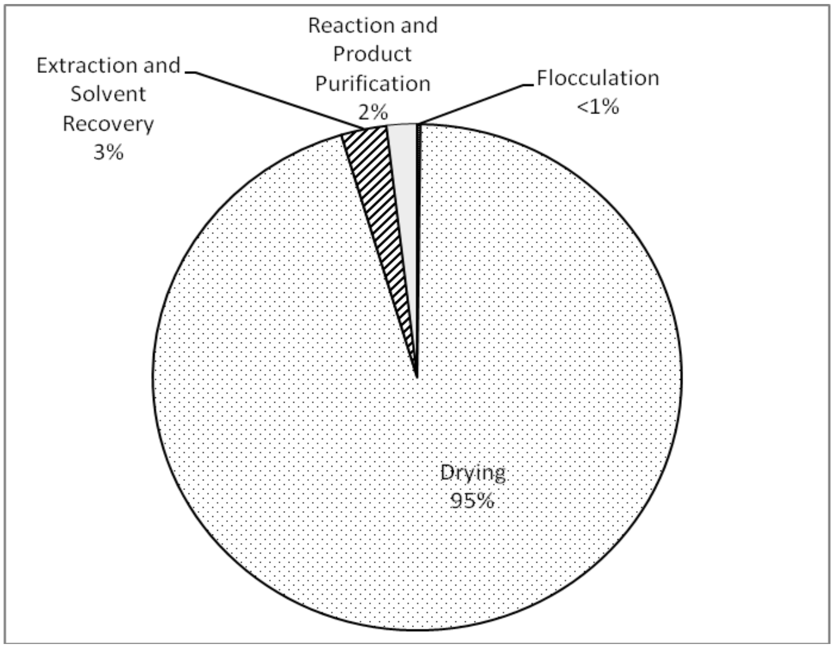


Figure 44: Percent contribution of emissions for case 2

There were 12,500 kg/t BD of total emissions by using the steam rotary dryer and 8,380 kg/t BD from the heat integrated dryer. Comparing both of these cases and the base case shows the heat integrated dryer to be the most efficient of the selected processes (Figure 45).

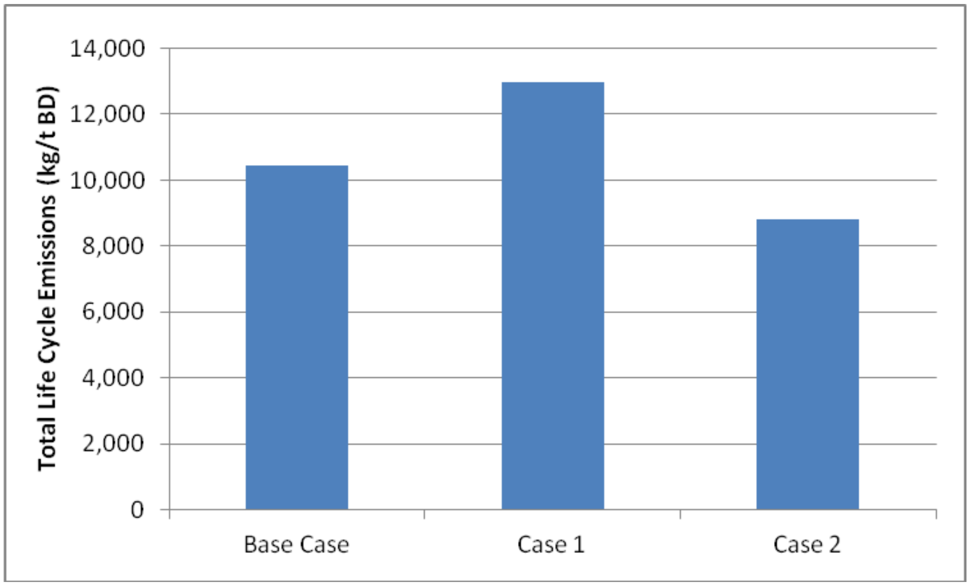


Figure 45: Total emissions of base case versus case 1 and case 2

The large variation between using dryers results from the different efficiencies of the dryers. The heat integrated dryer consumes 2 MJ/kg of water removed, while the steam rotary dryer consumes 3 MJ/kg of water removed. This is higher than the spray dryer which uses 2.5 MJ/kg of water removed. Case 2 has high emissions associated with the production of algae-derived biodiesel, but is still an improvement over the base case and case 1. This heat integrated dryer was chosen for the thermal drying in the remaining cases as a result of these findings.

5.5.2 Case 3

Table 60 contains the results of the case 3 life cycle assessment. This case consisted of a disc stack centrifuge and chamber filter press following flocculation and prior to drying. The total life cycle emissions were analyzed and compared to the base case.

Table 60: LCA of case 3 (basis of 1 t BD)

Impact category	Flocculation	Disc Stack Centrifugation	Chamber Filter Press	Drying	Extraction and Solvent Recovery	Reaction and Product Purification	Total
Raw Materials Used (kg)	22.5	9.10	3.46	467	28.4	-125	405
Emissions to Air (kg)	15.1	15.0	5.73	1,160	55.1	179	1,430
Carbon Dioxide (kg)	14.8	14.9	5.66	1,150	54.6	179	1,420
Carbon Monoxide (kg)	0.0115	0.00603	0.00225	0.302	0.0204	-0.0177	0.325
Methane (kg)	0.0238	0.0276	0.0105	2.33	0.115	0.174	2.68
NMVOC (kg)	0.00510	0.00308	0.00117	0.488	0.102	-0.226	0.373
Nox (kg)	0.0387	0.0293	0.0112	1.04	0.0570	-0.163	1.01
SO2 (kg)	0.187	0.0807	0.0307	1.98	0.113	-0.109	2.28
Particulates (kg)	0.0381	0.0136	0.00517	0.238	0.0143	-0.0405	0.269
Emissions to Water (kg)	1.08	0.539	0.205	12.0	189	-14.6	189
VOCs (kg)	2.8E-05	7.39E-06	2.81E-06	0.00202	0.000216	0.000961	0.00324
Emissions to Soil (kg)	0.00652	0.00186	0.000708	0.498	0.0514	0.137	0.696
Total Emissions	16.2	15.6	5.93	1,170	245	164	1,620
CED (MJ)	280	258	98.2	20,500	1,205	408	22,800
Water Used (kg)	77,800	59,200	22,500	192,000	16,900	20,200	389,000

The total life cycle emissions resulting from case 3 is 1,620 kg/t BD. Figure 46 shows that the most of the total life cycle emissions are associated with the heat integrated dryer. This is because of the energy required to vaporize the water in the algae slurry. In case 3, the total emissions released during the delta dryer stage are 1,170 kg/t BD, which is 73% of the total emissions from case 2. This can be compared to the case 2 value of 95%. The addition of centrifugation resulted in less thermal drying, thus reducing the contribution of drying to the total process emissions.

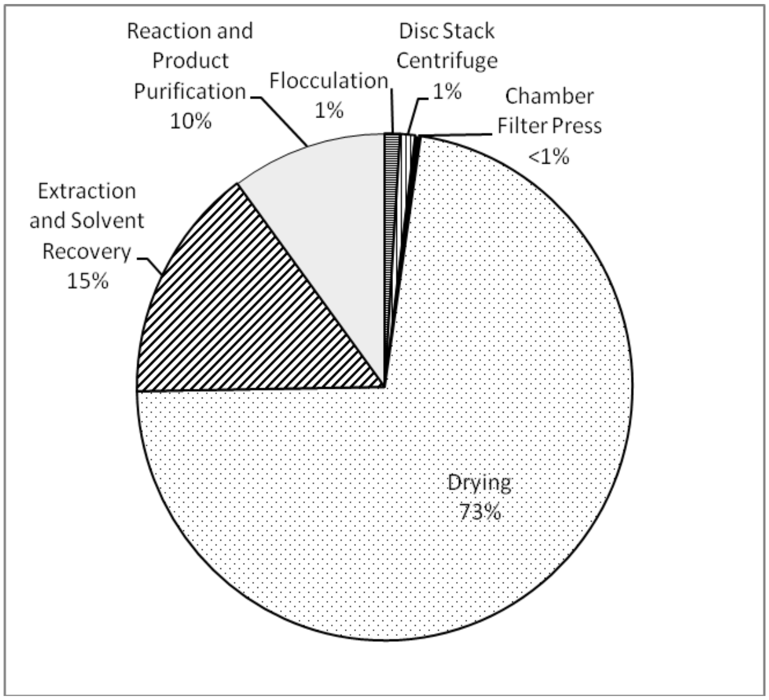


Figure 46: Percent contribution of the emissions for case 3

The addition of mechanical dewatering reduces the total life cycle emissions by approximately 82% when compared to case 2. The addition of the disc stack centrifuge increases the dry algae content to 12%, consuming 3.27 kJ/kg of water removed. The chamber filter press results in algae slurry of 27% dry algae, using 3.88 kJ/kg of water removed. This is compared to thermal drying at 2 MJ/kg of water removed which emphasizes the importance of minimizing the thermal drying. The disc stack centrifuge removed 22,400 kg of water and the chamber filter press removed 8,900 kg of water. This left only 5,100 kg of water for the heat integrated dryer to remove rather than the full 36,400 kg of water.

5.5.3 Case 4

Case 4 used the spiral plate centrifuge, followed by the heat integrated rotary pressure filter. The algae slurry was then fed into the heat integrated dryer at 56% dry weight and was dried to 95% dry algae. The resulting total life cycle emissions for case 4 were then analyzed and compared to the base case. Table 61 contains the results of the life cycle assessment.

Table 61: LCA of case 4 (basis of 1 t BD)

Impact category	**Flocculation**	**Spiral Plate Centrifuge**	**Rotary Pressure Filter**	**Drying**	**Extraction and Solvent Recovery**	**Reaction and Product Purification**	**Total**
Raw Materials Used (kg)	22.5	16.1	57.5	129	28.4	-125	128
Emissions to Air (kg)	15.1	26.7	95.1	321	55.1	179	691
Carbon Dioxide (kg)	14.8	26.4	94.0	319	54.6	179	687
Carbon Monoxide (kg)	0.0115	0.0105	0.0381	0.0836	0.0204	-0.0177	0.146
Methane (kg)	0.0238	0.0490	0.174	0.645	0.115	0.174	1.18
NMVOC (kg)	0.00510	0.00546	0.0194	0.135	0.102	-0.226	0.0410
Nox (kg)	0.0387	0.0521	0.185	0.287	0.0570	-0.163	0.457
SO2 (kg)	0.187	0.143	0.510	0.547	0.113	-0.109	1.39
Particulates (kg)	0.0381	0.0241	0.0860	0.0659	0.0143	-0.0405	0.188
Emissions to Water (kg)	1.08	0.956	3.40	3.31	189	-14.6	184
VOCs (kg)	2.8E-05	1.31E-05	4.67E-05	0.000559	0.000216	0.000961	0.00182
Emissions to Soil (kg)	0.00652	0.00330	0.0118	0.138	0.0514	0.137	0.348
Total Emissions	16.2	27.7	98.5	324	245	164	875
CED (MJ)	280	458	1,630	5,670	1,205	408	9,660
Water Used (kg)	77,800	105,000	374,000	53,200	16,900	20,200	647,000

The total life cycle emissions for case 4 was 875 kg/t BD. Figure 47 shows the total life cycle emissions distribution for case 4. The dryer released 324 kg emissions/t BD in this case which corresponds to 37% of the total emissions. The heat assisted rotary pressure filter contributed to 11% of the total life cycle emissions, but further reduced the total demand of thermal drying.

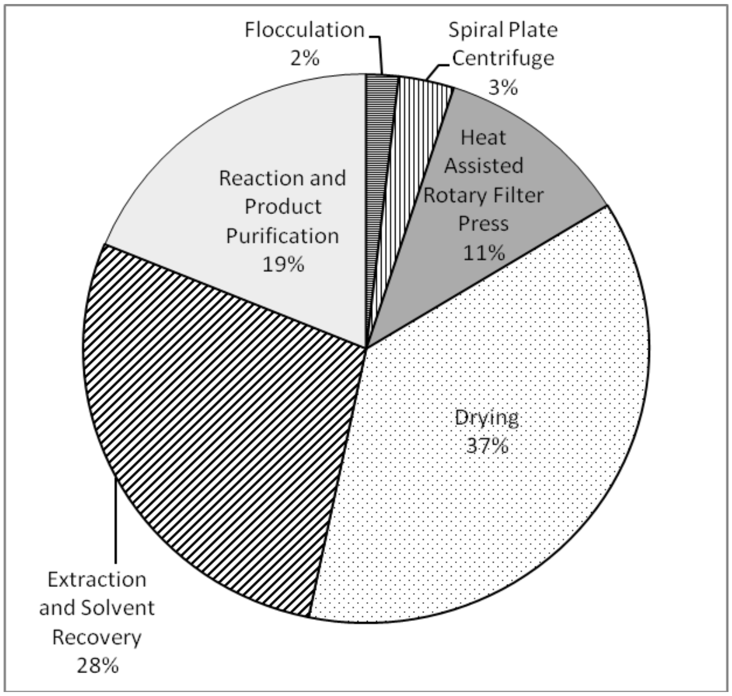


Figure 47: Percent contribution of the emissions for case 4

Case 4 is a 46% reduction compared to case 3. Adding the heat assisted rotary pressure filter lessened the extent of thermal drying, and resulted in a decrease of total emissions produced by the biodiesel production process. The spiral plate centrifuge dewatered to 31.5% dry algae slurry, which removed 32,400 kg of water and only consumed 4.07 kJ/kg water removed. The addition of the pressure filter increased the dry algae content to 56%. This removed 2,670 kg of water while using 173 kJ/kg water removed. The rotary pressure filter consumes significantly higher amounts of energy compared to the spiral plate centrifuge, but can achieve higher dry algae contents. Compared to the heat integrated dryer which consumes 2 MJ/kg water removed, the pressure filter is significantly less energy demanding. In this case only 1,410 kg of water was removed by the dryer.

5.5.4 Case 5

Case 5 consists of the chamber filter press, followed by the heat assisted rotary pressure filter, and dried using the heat integrated dryer. The LCA was performed, and the total life cycle emissions were analyzed and compared to the previous cases. Table 62 contains the results of the LCA.

Table 62: LCA of case 5 (basis of 1 t BD)

Impact category	Flocculation	Chamber Filter Press	Rotary Pressure Filter	Drying	Extraction and Solvent Recovery	Reaction and Product Purification	Total
Raw Materials Used (kg)	22.5	15.1	79.5	129	28.4	-125	149
Emissions to Air (kg)	15.1	25.0	131	321	55.1	179	726
Carbon Dioxide (kg)	14.8	24.7	130	319	54.6	179	722
Carbon Monoxide (kg)	0.0115	0.0100	0.0527	0.0836	0.0204	-0.0177	0.161
Methane (kg)	0.0238	0.0459	0.241	0.645	0.115	0.174	1.24
NMVOC (kg)	0.00510	0.00511	0.0268	0.135	0.102	-0.226	0.0480
Nox (kg)	0.0387	0.0488	0.256	0.287	0.0570	-0.163	0.524
SO2 (kg)	0.187	0.134	0.705	0.547	0.113	-0.109	1.58
Particulates (kg)	0.0381	0.0226	0.119	0.0659	0.0143	-0.0405	0.219
Emissions to Water (kg)	1.08	0.895	4.70	3.31	189	-14.6	185
VOCs (kg)	2.8E-05	1.23E-05	6.45E-05	0.000559	0.000216	0.000961	0.00184
Emissions to Soil (kg)	0.00652	0.00309	0.0163	0.138	0.0514	0.137	0.353
Total Emissions	16.2	25.9	136	324	245	164	911
CED (MJ)	280	429	2,250	5,670	1,205	408	10,200
Water Used (kg)	77,800	98,500	517,000	53,200	16,900	20,200	784,000

Case 5 had 911 kg of total life cycle emissions/t BD. The emissions for the dryer contribute to 34% of the total life cycle emissions (Figure 48). The total emissions from the drying stage was constant between case 4 and case 5. This was because the algae slurry leaving the heat assisted rotary pressure filter was 56% in both cases and only 1,410 kg of water was removed. Therefore, the only difference between these two cases is the spiral plate centrifuge was replaced by the chamber filter press and resulted in only a 36 kg/t BD difference compared to case 4.

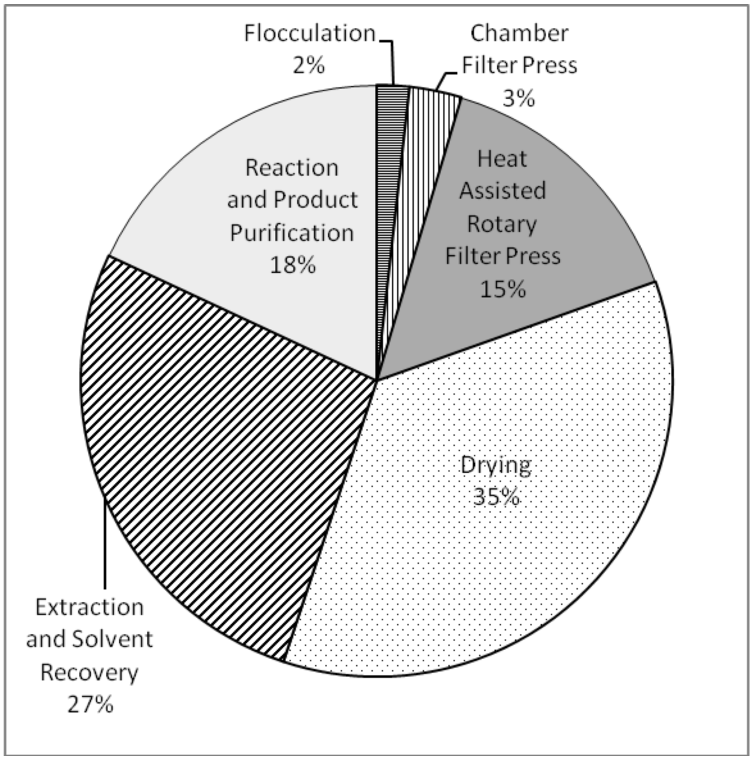


Figure 48: Percent contribution of the emissions for case 5

Case 5 did not further decrease the total emissions associated with the algae biodiesel process. Although this was a 36 kg/t BD increase in total life cycle emissions, case 4 and case 5 are not significantly different. The major similarity between these two cases is the heat assisted rotary pressure filter. This does not further decrease the extent of drying, and the resulting life cycle emissions did not vary significantly even though the configuration of the dewatering operations was altered.

5.5.5 Case 6

Case 6 consisted of tangential flow filtration, followed by the decanter bowl centrifuge, and the heat assisted rotary pressure filter which was dried using the heat integrated dryer. The LCA was performed, and the total life cycle emissions were analyzed and compared to the previous cases. Table 63 contains the results of the case 6 life cycle assessment.

Table 63: LCA of case 6 (basis of 1 t BD)

Impact category	**Flocculation**	**Tangential Flow Filtration**	**Decanter Bowl Centrifuge**	**Rotary Pressure Filter**	**Drying**	**Extraction and Solvent Recovery**	**Reaction and Product Purification**	**Total**
Raw Materials Used (kg)	22.5	15.5	77.5	114	129	28.4	-125	262
Emissions to Air (kg)	15.1	25.6	128	189	321	55.1	179	912
Carbon Dioxide (kg)	14.8	25.3	127	187	319	54.6	179	906
Carbon Monoxide (kg)	0.0115	0.0103	0.0513	0.0758	0.0836	0.0204	-0.0177	0.235
Methane (kg)	0.0238	0.0469	0.235	0.347	0.645	0.115	0.174	1.59
NMVOC (kg)	0.00510	0.00523	0.0262	0.0386	0.135	0.102	-0.226	0.0861
Nox (kg)	0.0387	0.0499	0.250	0.368	0.287	0.0570	-0.163	0.887
SO2 (kg)	0.187	0.137	0.687	1.01	0.547	0.113	-0.109	2.58
Particulates (kg)	0.0381	0.0232	0.116	0.171	0.0659	0.0143	-0.0405	0.388
Emissions to Water (kg)	1.08	0.916	4.58	6.77	3.31	189	-14.6	192
VOCs (kg)	2.8E-05	1.26E-05	6.28E-05	9.28E-05	0.000559	0.000216	0.000961	0.00193
Emissions to Soil (kg)	0.00652	0.00317	0.0158	0.0234	0.138	0.0514	0.137	0.376
Total Emissions	16.2	26.5	133	196	324	245	164	1,100
CED (MJ)	280	439	2,200	3,240	5,670	1,205	408	13,400
Water Used (kg)	77,800	101,000	504,000	744,000	53,200	16,900	20,200	1,520,000

The total life cycle emissions for case 6 were 1,100 kg/t BD. Figure 49 shows the distribution for the total life cycle emissions of each process stage in case 6. As with case 4 and 5, the total life cycle emissions were the same at 324 kg/t BD for the dryer since the dry algae content from the heat assisted rotary pressure filter is 56%. The life cycle emissions from case 6 were 225 kg/t BD greater than case 4, which suggests that either one or more of the dewatering methods were inappropriate for algae drying.

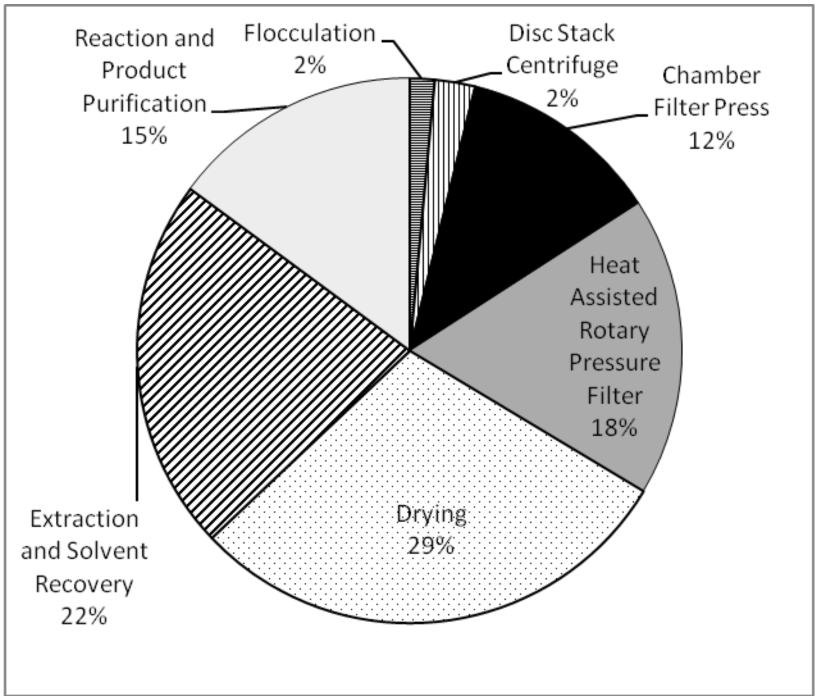


Figure 49: Percent contribution of the emissions for case 6

The tangential flow filtration was able to dewater the algae slurry to 8.8% dry weight algae while consuming 7.42 kJ/kg water removed. This technique is not capable of achieving high dry algae contents, and consumes more energy than the disc stack centrifuge, spiral plate centrifuge, and chamber filter press. These technologies should be utilized instead of the tangential flow filtration as this is not an appropriate application for this technology.

The decanter bowl centrifuge also proves to have a higher energy demand than the aforementioned technologies at 28.8 kJ/kg of water removed. Using a mixture which does not consist of biomass, decanter bowl centrifuges are capable of reaching higher dry weight contents. The attainable dry weight contents are lower for algae than other applications because of bound intercellular water. This lower achievable algae content and higher energy consumption makes the decanter centrifuge an inappropriate technology for algae dewatering.

5.6 Discussion of the Dewatering Alternatives

Table 64 contains a summary of the life cycle assessment performed on each alternative and the base case. The decrease in total life cycle emissions was largest between case 2 and case 3 at 7,180 kg/t BD. The least improvement was seen between cases 4 and 5. These two only differed by 36 kg/t BD, which is not a significant difference. This is because the extent of drying was not altered between these two cases. Each of these cases had 56% dry content algae being sent to the heat integrated dryer. Mechanical methods are unable to further dry the algae because of bound intercellular water.[46] Typical algae cells can contain between 40 and 80% water.[11, 46, 47]

Table 64: Summary of all the LCA's for all the cases including the base case

Impact Category	Base Case	Total	Case 2	Case 3	Case 4	Case 5	Case 6
Raw Materials Used (kg)	3,920	4,930	3,260	405	128	149	262
Emissions to Air (kg)	10,200	12,700	8,540	1,430	691	726	912
Carbon Dioxide (kg)	10,100	12,600	8,490	1,420	687	722	906
Carbon Monoxide (kg)	2.60	3.26	2.18	0.325	0.146	0.161	0.235
Methane (kg)	20.3	25.3	17.0	2.68	1.18	1.24	1.59
NMVOC (kg)	4.06	5.11	3.37	0.373	0.0410	0.0480	0.0861
Nox (kg)	8.80	11.0	7.34	1.01	0.457	0.524	0.887
SO2 (kg)	17.1	21.4	14.3	2.28	1.39	1.58	2.58
Particulates (kg)	2.05	2.57	1.72	0.269	0.188	0.219	0.388
Emissions to Water (kg)	278	304	261	189	184	185	192
VOCs (kg)	0.0185	0.0229	0.0157	0.00324	0.00182	0.00184	0.00193
Emissions to Soil (kg)	4.46	5.54	3.76	0.696	0.348	0.353	0.376
Total Emissions (kg)	10,500	13,000	8,800	1,620	875	911	1,100
CED (MJ)	178,000	222,000	149,000	22,800	9,660	10,200	13,400
Water Used (kg)	1,760,000	2,180,000	1,490,000	389,000	647,000	784,000	1,520,000

The total emissions category is a summation of all the emissions to the air, water, and soil. Table 65 shows the percent of the total emissions that is released into the air, water, and soil for each alternative dewatering operation considered. The dewatering options were broken down into mechanical and thermal methods. This is because the mechanical methods consumed electricity and had the same emissions distribution between air, water and soil. All thermal methods used steam as the source and had the same emissions distribution. The majority of the total emissions are released into the air. This excludes the extraction stage which emits 23% of the total emissions to the air while

77% is released into water. This is attributed to the landfilling of solid biomass that is expended during this stage. The negative emission percentage within the reaction and purification stage is a result of the credit taken from the production of glycerine. Therefore, the total emissions are actually smaller than that of the emissions going into air. The emissions to soil contribute less than 0.1% to the total emissions of all stages within case 1. Emissions to soil could be considered negligible compared to air and water emissions.

Table 65: Percent contribution of each emission category to the total emissions

Process Stage	**Emissions to Air**	**Emissions to Water**	**Emissions to Soil**	**CO_2 Emissions**
Flocculation	93%	7%	<0.1%	91%
Mechanical Dewatering	97%	3%	<0.1%	95%
Thermal Drying	99%	1%	<0.1%	98%
Extraction and Solvent Recovery	23%	77%	<0.1%	22%
Reaction and Product Purification	109%	-9%	<0.1%	109%

Each case shows a significant improvement compared to the base case when looking at the total emissions released and the cumulative energy demand. Figure 50 shows the decrease in total emissions of each case with respect to the base case.

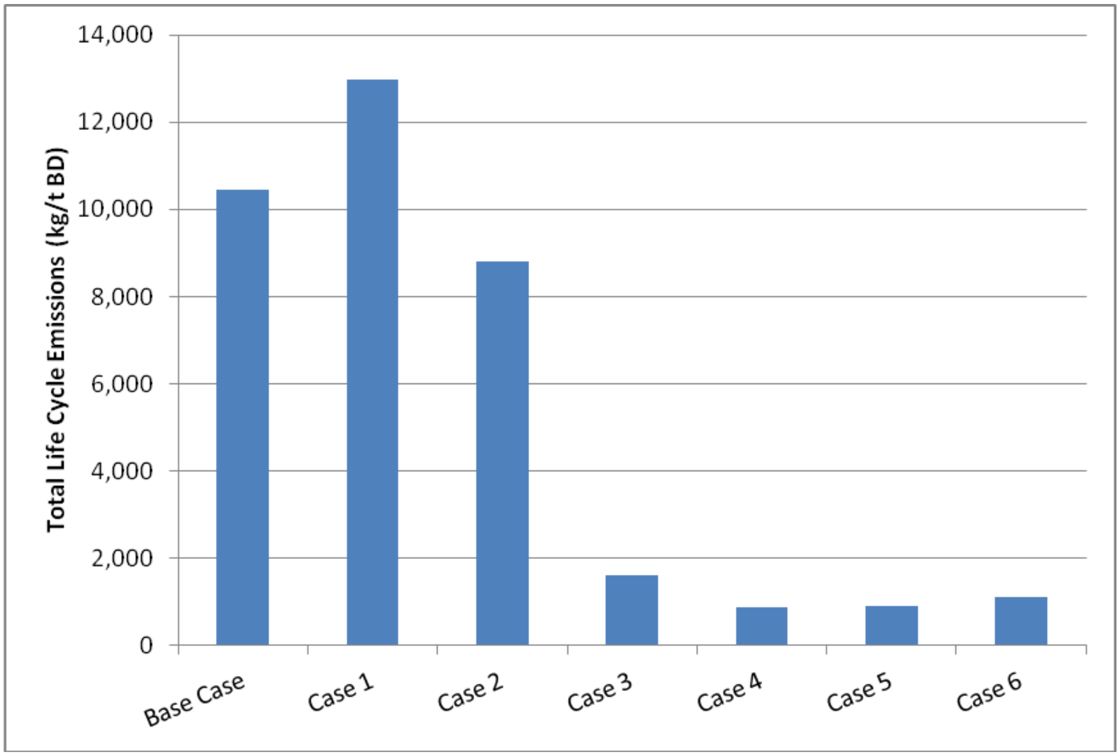


Figure 50: Total emissions of alternative dewatering cases including the base case

As shown in Figure 50, the further utilizing mechanical drying significantly reduced the total emissions released by each case. This was because of the reduction in the extent of thermal drying. Since the mechanical drying units require much less energy input compared to the thermal drying stage, the energy input for each process was significantly reduced. Thus, the total emissions were also decreased. The addition of more mechanical separations prior to thermal drying decreases the energy of the overall process. However, there is a point where additional mechanical drying will no longer result in a decrease in moisture content. In Figure 50, the reduction between case 4, case 5, and case 6 is small compared to the initial reduction achieved by utilizing thermal drying. It suggests that although the configuration of the mechanical dewatering units has an effect on the total life cycle emissions, it is not as significant as decreasing the extent of using a thermal dryer. Mechanical dewatering is not likely to be utilized beyond the

56% dry algae content because of bound intracellular water content within the algae. Therefore thermal drying is still required to reach this water content within the algae slurry.

5.6.1 Modeling the Life Cycle Emissions

Additional analysis was performed to determine the optimal configuration for the equipment and if it is a significant improvement over the six developed cases. Each unit was individually analyzed, and the total emissions per t of water removed were calculated. These values were based on the operating conditions for the dewatering ranges studied. The total life cycle emissions of each dewatering process for every t of water removed was found since the energy consumption is directly related to the life cycle emissions (Table 66). As was shown before, drying is the least efficient processing method. The disc stack centrifuge, spiral plate centrifuge, tangential flow filtration, and chamber filter press all have low emissions/ t of water removed. The decanter centrifuge has higher emissions than the other filtration and centrifugation methods. The attainable dry weight contents are lower for algae than other applications because of bound intercellular water. This lower achievable algae content and higher energy consumption makes the decanter centrifuge an inappropriate technology for algae dewatering. The heat assisted rotary pressure filter incorporates heating into the mechanical separation resulting in a higher dewatering capability. This results in higher energy expenditures, and therefore higher emissions.

Table 66: Dewatering Equipment Emissions

Operation	**Category**	**Emissions (kg/t water removed)**
Spray Dryer	Drying	287.35
Delta Dryer	Drying	229.9
Steam Rotary Dryer	Drying	344.86
Disc Stack Centrifuge	Centrifugation	0.69
Spiral Plate Centrifuge	Centrifugation	1.14
Decanter Centrifuge	Centrifugation	10.67
Tangential Flow Filtration	Filtration	1.58
Chamber Filter Press	Filtration	0.83
Heat Assisted Rotary Filter Dryer	Filtration	36.88

The dewatering stages were analyzed using linear programming. The objective function sums the emissions based on the quantity of water removed by each piece of equipment (Equation 46). Minimizing the objective function provides the configuration with the minimum total emissions. This can be performed with any impact assessment parameter, including CO_2 emissions and CED by swapping the desired parameter with the total emissions parameter.

$$0.69 * M_S + 10.67 * M_D + 1.14 * M_E + 1.58 * M_T + 0.83 * M_C + 36.88 * M_R + 287.35 * M_{SD} + 229.9 * M_{HID} + 344.86 * M_{SRD} \tag{46}$$

Where:

M_S is the mass of water removed by the disc stack centrifuge (t)

M_D is the mass of water removed by the decanter centrifuge (t)

M_E is the mass of water removed by the spiral plate centrifuge (t)

M_C is the mass of water removed by the chamber filter press (t)

M_T is the mass of water removed by tangential flow filtration (t)

M_R is the mass of water removed by the heat assisted rotary filter press (t)

M_{SD} is the mass of water removed by the spray dryer (t)

M_{HID} is the mass of water removed by the heat integrated dryer (t)

M_{SRD} is the mass of water removed by the steam rotary dryer (t)

The constraint functions were then defined. Equation 47 specifies the quantity of water that must be removed in order to achieve a dry weight percentage of 95%. Equations 48, 49, 50, 51, 52, and 53 represent the quantity of water that can be removed by each respective component. These are resulting from the known limitations on attainable dry weight percentages for each piece of equipment. To achieve a dry weight content of 95%, 36.431 t of water needs to be removed. Tangential flow filtration is only able to achieve 8.8% dry weight algae, which is reached when 16.605 t of water is removed. The disc stack centrifuge is only capable of attaining 12% dry algae content, corresponding to 22.432 t of water removed. Decanter centrifugation can only concentrate the algae to 22% dry weight, which occurs when 29.716 t of water is removed. The chamber filter press can only remove 31.334 t of water which is 27% dry weight algae. The disc stack centrifuge can only achieve 31.5% dry algae content which corresponds to removing 32.351 t of water, and the heat assisted rotary filter press can remove 35.022 t of water, or 56% water content.

$$M_T + M_S + M_D + M_C * B_C + M_E * B_E + M_R + M_{SD} + M_{HID} + M_{SRD} \geq 36.431 \qquad (47)$$

$$M_T \leq 16.605 \tag{48}$$

$$M_T + M_S \leq 22.432 \tag{49}$$

$$M_T + M_S + M_D \leq 29.716 \tag{50}$$

$$M_T + M_S + M_D + M_C * B_C \leq 31.334 \tag{51}$$

$$M_T + M_S + M_D + M_C * B_C + M_E * B_E \leq 32.351 \tag{52}$$

$$M_T + M_S + M_D + M_C * B_C + M_E * B_E + M_R \leq 35.022 \tag{53}$$

Where:

B_C is a binary number for the chamber filter press

B_E is a binary number for the spiral plate centrifuge

The spiral plate centrifuge and the chamber filter press both process the algae to low quantities of extracellular water. Since the algae solution is not likely to flow under these water contents, the spiral plate centrifuge and chamber filter press cannot be operated in series. This requires the generation of the constraint in Equation 54. This is a binary constraint which specifies that one, the other, or neither may be operated, but not both. These binary constraints are multiplied to their respective variable in the previous constraints.

$$B_C + B_E \leq 1 \tag{54}$$

This system was solved to find the configuration which generates the lowest total emissions. This was found at 22.432 t of water removed by the disc stack centrifuge, 9.919 t of water removed by the spiral plate centrifuge, 2.671 t of water removed by the heat assisted rotary pressure filter, and 1.409 t of water removed by the heat integrated dryer. The sequence of this configuration was then logically deduced from knowing the equipment's capabilities for dewatering and the acceptable ranges they can operate. The disc stack centrifuge can only dewater to 12% which removes 22.432 t of water, the spiral plate centrifuge can then be used to remove 9.919 t of water to bring the slurry to 32% dry algae. The additional 2.671 t of water removed by the heat assisted rotary filter press dewaters to 56% dry algae and the remaining 1.409 t of water is results in 95% dry algae. This sequence is shown in Table 67.

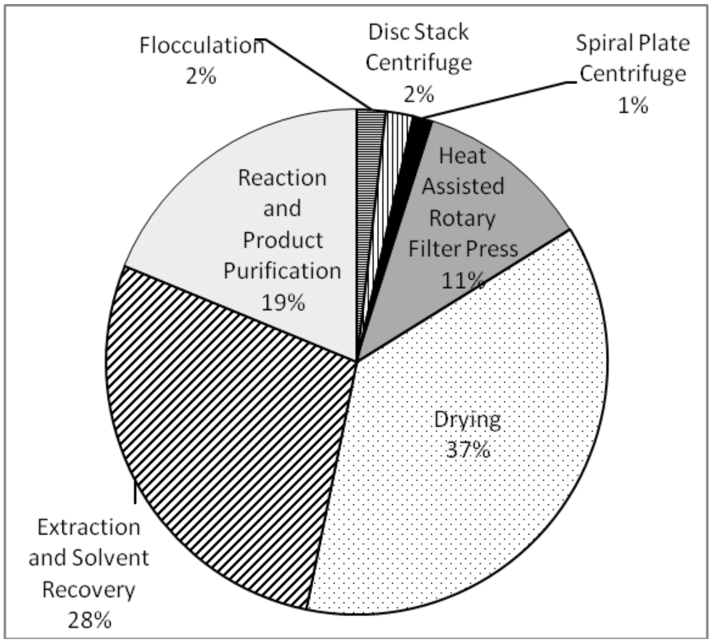


Figure 51. Total emissions distribution for the optimal case

Figure 51 shows the distribution of the total life cycle emissions for the optimal case. Total life cycle emissions of 450 kg/t BD resulted from the dewatering and drying section of this configuration. This was added to the remainder of the algae biodiesel process, producing 874 kg of total emissions are produced for one t of biodiesel. This optimal case is essentially the same as case 4, which had 875 kg of total emissions per t of biodiesel produced. This suggests that the correct sequencing is only beneficial to a certain point. Estimation was performed using the objective function to quickly analyze the emissions from replacing the spiral plate centrifuge in the optimal case, with the chamber filter press. This case was used to investigate the significance of altering the sequence of the dewatering equipment. These two cases are shown in Table 67.

Table 67: The optimal case and the variation from the linear programming model

Optimal Case		**Optimal Case Variation**	
Equipment	**Dry algae content**	**Equipment**	**Dry algae content**
Disc Stack Centrifuge	12%	Disc Stack Centrifuge	12%
Spiral Plate Centrifuge	31.5%	Chamber Filter Press	27%
Heat Assisted Rotary Pressure Filter	56%	Heat Assisted Rotary Pressure Filter	56%
Heat Integrated Dryer	95%	Heat Integrated Dryer	95%
Total Life Cycle Emissions	874 kg	Total Life Cycle Emissions	908 kg

The total life cycle emissions from these two cases only differed by 4%. The optimal case, the variation, case 4, and case 5 vary by only 36 kg of life cycle emissions/t BD. This suggests the sequencing does not significantly affect the total life cycle emissions. Instead, maximizing the mechanical dewatering is more crucial than the proper sequencing. Therefore, future work should focus on removing the required thermal drying which is responsible for 37% of the total downstream emissions. However, this aspect is limited because of bound intercellular water which can represent 40 to 80% of the cellular mass and cannot be removed by mechanical means. [18, 46, 47] Since removing this intercellular water may not be possible without thermal drying, additional research should focus on extraction methods capable of handling mixtures with significant water content, 40 - 80%. This would eliminate the need for thermal drying, and remove the largest contributor to the downstream total life cycle emissions. Unfortunately these techniques are not currently commercially available. Future research should investigate these technologies and determine the scalability as well as the environmental sustainability of wet extraction techniques.

In addition to comparing the different algae biodiesel processing methods, algae can be evaluated against other sources of biodiesel. Case 4, the best case, was compared against the GWP of biodiesels from various sources (Table 68). Cultivation was not considered in our cases; therefore, these were also not included for these sources. To determine the GWP for case 4, emission factors of 1, 25, and 298 were applied to the CO_2, CH_4, and N_2O emissions respectively.[107] This resulted in a GWP of 663 kg CO_2eq/t BD. The allocation of glycerine avoids potential N_2O emissions, resulting in a lower GWP than the CO_2 emissions. This is shown in Table 68.

Table 68. LCAs for biodiesel originating from a variety of sources

Source	**GWP (kg CO_2/t BD)**	**Oil Content (%)**
Soybean	1,290[108]	17 [109]
Rapeseed	578 [108]	40 [110]
Jatropha	391 [108]	30 [109]
Algae (Case 4)	663	61.3

The varying GWP seen between these sources is because of the differences in oil contents between these sources. More raw material must be processed to attain the same quantity of oil, resulting in a greater GWP in downstream processing. Algae have a higher GWP than rapeseed and jatropha because of their high water contents compared to terrestrial plants. Algae have significantly higher water contents than terrestrial plants. A large portion of the GWP is associated with the extensive dewatering and drying. Algae are capable of being produced space efficiently, and rapidly which might give algae the long term advantage over terrestrial plants.

Chapter 6

Conclusions

A base case was developed for the downstream processing of algae into biodiesel and resulting life cycle emissions were obtained. Alternative cases were investigated to reduce the total life cycle emissions. The equipment compared for these alternatives were a disc stack centrifuge, spiral plate centrifuge, decanter centrifuge, tangential flow filter, chamber filter press, heat assisted rotary pressure filter, steam rotary dryer, and heat integrated dryer. Comparing the base case to the dewatering alternatives led to a significant decrease in emissions. The optimal sequence was found using linear programming and was a disc stack centrifuge, followed by a spiral plate centrifuge, heat assisted rotary pressure filter, and a heat integrated dryer. This had 874 kg emissions/t BD, with 53% attributed to dewatering and was a 91% improvement compared to the base case. Increasing the extent of mechanical dewatering resulted in significant life cycle emissions reduction. This is because the driving force for thermal drying had a high energy demand at 2 MJ/kg water removed.

This optimal case was a significant improvement over the base case, but was essentially the same as the next best case which had 875 kg emissions/t BD. Additional investigation found that four of the developed cases varied by 36 kg emissions/t BD. This demonstrates that increasing the extent of dewatering is more important than the proper arrangement. The drying component was responsible for 37% of the total downstream emissions in case 4 and the optimal case. Additional improvements can be made by lessening or removing the thermal drying, but current mechanical technologies are incapable of removing bound intercellular water.

Even in the optimal configuration, 51% of the total emissions were from operating the disc stack centrifuge, spiral plate centrifuge, heat assisted rotary filter press, and heat integrated dryer. Although this is a 91% improvement compared to the base case, the dewatering and drying still accounts for the majority of total emissions. An alternative method of achieving lower total emissions would be to remove the drying step entirely. Performing the TAG extraction under considerable water content would avoid thermal drying, which may decrease the total emissions. Wet extraction methods would remove the stage with the largest impact towards total emissions, potentially resulting in a lower environmental footprint.[46, 51]

Appendix

Table 69. Stream tables detailing material flows and compositions.

Stream Tables {kg/hr} - Main Process Streams														
	1		2		3		4		5		6		8	
Chemical	**m (kg/hr)**	**x (kg/kg)**	**m (kg/hr)**	**x (kg/kg)**	**m (kg/hr)**	**x (kg/kg)**	**m (kg/hr)**	**x (kg/kg)**	**m (kg/hr)**	**x (kg/kg)**	**m (kg/hr)**	**x (kg/kg)**	**m (kg/hr)**	**x (kg/kg)**
Algae	0	0	SEED	SEED	1.25E+04	0.024	0	0	1.19E+04	0.05	597	0.0022	0	0
Water	0	0	7.71E+03	0.97	5.01E+05	0.97	0	0	2.27E+05	0.95	2.75E+05	1	2.26E+05	1
Medium	0	0	238	0.03	340	0.00066	0	0	238	0.0010	102	0.0004	0	0
Al(OH)3	0	0	0	0	0	0	0	0	30.1	0.0001	0	0	0	0
CaSO4	0	0	0	0	0	0	0	0	78.7	0.0003	0	0	0	0
Al2(SO4)3	0	0	0	0	0	0	128	0.69	0	0	0	0	0	0
CaCO3	0	0	0	0	0	0	57.9	0.31	0	0`	0	0	0	0
CO2	1.95E+04	1	0	0	0	0	0	0	0	0	0	0	0	0
Total	1.95E+04	1	7.95E+03	1	5.14E+05	1	186	1	2.39E+05	1	2.75E+05	1	2.26E+05	1

Main Process Streams - Continued												
	9		10		11		12		13		14	
Chemical	**m (kg/hr)**	**x (kg/kg)**	**m (kg/hr)**	**x (kg/kg)**	**m (kg/hr)**	**x (kg/kg)**	**m (kg/hr)**	**x (kg/kg)**	**m (kg/hr)**	**x (kg/kg)**	**m (kg/hr)**	**x (kg/kg)**
Algae	0	0	1.19E+04	0.92	0	0	4.78E+03	0.78	0	0	0	0
Water	3.53E+05	0.05	628	0.05	0	0	628	0.10	0	0	0	0
Medium	0	0	238	0.02	0	0	238	0.04	0	0	0	0
Al(OH)3	0	0	30.1	0.0023	0	0	30.1	0.0049	0	0	0	0
CaSO4	0	0	78.7	0.0061	0	0	78.7	0.01	0	0	0	0
Hexane	0	0	0	0	8.82E+03	0.98	0	0	8.88E+03	0.56	8.07E+03	0.99
TAG	0	0	0	0	162	0.02	366	0.06	6.95E+03	0.44	90	0.01
Dry Air	6.33E+06	0.95	0	0	0	0	0	0	0	0	0	0
Total	6.68E+06	1	1.29E+04	1	8.98E+03	1	6.12E+03	1	1.58E+04	1	8.16E+03	1

Main Process Streams - Continued

	15		26		27		28		29	
Chemical	**m (kg/hr)**	**x (kg/kg)**	**m (kg/hr)**	**x (kg/kg)**	**m (kg/hr)**	**x (kg/kg)**	**m (kg/hr)**	**x (kg/kg)**	**m (kg/hr)**	**x (kg/kg)**
Algae	0	0	0	0	0	0	0	0	0	0
Water	0	0	0	0	0	0	0	0	0	0
Medium	0	0	0	0	0	0	0	0	0	0
Al(OH)3	0	0	0	0	0	0	0	0	0	0
CaSO4	0	0	0	0	0	0	0	0	0	0
Hexane	751	0.10	87.4	0.96	33.7	0.030	28.7	0.78	5.00	0.0046
TAG	6.89E+03	0.90	3.60	0.04	1100	0.97	7.98	0.22	1090	0.995
Total	7.64E+03	1	91.0	1	1134	1	36.7	1	1095	1

Main Process Streams - Continued

	19		20		22		24		25	
Chemical	**m (kg/hr)**	**x (kg/kg)**	**m (kg/hr)**	**x (kg/kg)**	**m (kg/hr)**	**x (kg/kg)**	**m (kg/hr)**	**x (kg/kg)**	**m (kg/hr)**	**x (kg/kg)**
Algae	0	0	0	0	0	0	0	0	0	0
Water	1.27E+05	0.02	1.27E+05	0.02	0	0	0	0	3.53E+05	0.05
CO2	0	0	0	0	1.95E+03	0.13	0	0	0	0
O2	0	0	0	0	1.27E+04	0.87	0	0	0	0
Hexane	0	0	0	0	0	0	31	1	0	0
TAG	0	0	0	0	0	0	0	0	0	0
Dry Air	6.33E+06	0.98	6.33E+06	0.98	0	0	0	0	6.33E+06	0.95
Total	6.46E+06	1	6.46E+06	1	1.47E+04	1	31	1	6.68E+06	1

Table 70. Transesterification and Purification process material flows and compositions.

Reactor Purification Section {kg/hr}										
	16		17		18		23		30	
Chemical	**m (kg/hr)**	**x (kg/kg)**	**m (kg/hr)**	**x (kg/kg)**	**m (kg/hr)**	**x (kg/kg)**	**m (kg/hr)**	**x (kg/kg)**	**m (kg/hr)**	**x (kg/kg)**
TAG	0	0	0	0	0	0	0	0	98.4	0.92
MeOH	705	0.41	0	0	0	0	0	0	0	0
NaOH	36.0	0.021	0	0	0	0	0	0	3.88	0.04
HCl	10.9	0.0063	0	0	0	0	0	0	0	0
H2O	984	0.57	0	0	0	0	0	0	0	0
FAME (Oleic Acid)	0	0	0	0	6208	1	0	0	0	0
Glycerol	0	0	675	1	0	0	0	0	0	0
NaCl	0	0	0	0	0	0	17.5	0.017	0	0
Hexane	0	0	0	0	0	0	31.1	0.030	5.00228	0.046614
Waste Water	0	0	0	0	0	0	989	0.95	107	0
Total	1735	1	675	1	6208	1	1038	1	215	1

Table 71. Chemical breakdown of medium constituents and mass quantities.

Medium Breakdown {kg/hr}	
KH2PO4	8.99E+01
CaCl2*2H2O	1.28E+01
MgSO4*7H2O	3.85E+01
NaNO3	1.28E+02
K2HPO4	3.85E+01
NaCl	1.28E+01
Na2EDTA	5.14E+00
KOH	3.19E+00
FeSO4*7H2O	2.56E+00
H2SO4	9.46E-01
H3BO3	4.14E+00
H3BO3	1.47E+00
MnCl2*4H2O	9.30E-01
ZnSO4*7H2O	1.14E-01
NaMoO4*5H2O	2.00E-01
CuSO4*5H2O	4.06E-02
Co(NO3)2*6H2O	2.54E-02
Total	3.40E+02

Table 72. Material flows for SimaPro® on per tonne of biodiesel basis.

***Stream Tables* {kg/t BD} - Main Process Streams**							
Chemical	**1**	**2**	**3**	**4**	**5**	**6**	**8**
Algae		SEED	2019		1923	96	
Water		1242	8.08E+04		36533	4.42E+04	36431
Medium		38.3	54.8		38.3	16.4	
Al(OH)3					4.84	0	
CaSO4					12.7		
Al2(SO4)3				20.7			
CaCO3				9.32			
CO2	3133						
Total	3133	1281	8.28E+04	30.0	38511	4.43E+04	36431

Main Process Streams - Continued							
Chemical	**9**	**10**	**11**	**12**	**13**	**14**	**15**
Algae	0	1923		770			
Water	56822	101		101			
Medium	0	38.3		38.3			
Al(OH)3		4.84		4.84			
CaSO4		12.7		12.7			
Hexane			1420		1430	1300	121
TAG			26.0	59	1120	14.5	1110
Dry Air	1.02E+06						
Total	1.08E+06	2080	1446	986	2550	1315	1231

Main Process Streams - Continued									
Chemical	**19**	**20**	**22**	**24**	**25**	**26**	**27**	**28**	**29**
Algae									
Water	20391	20391			56822				
CO2			313						
O2			2051						
Hexane				5		87.4	33.7	28.7	5.00
TAG						3.60	1100	7.98	1090
Dry Air	1.02E+06	1.02E+06			1.02E+06				
Total	1.04E+06	1.04E+06	2364	5	1.08E+06	91.0	1134	36.7	1095

Reactor Purification Section {kg/t BD}					
Chemical	**16**	**17**	**18**	**23**	**30**
TAG					98.4
MeOH	113				
NaOH	5.81				3.88
HCl	1.76				
H2O	158				
FAME (Oleic Acid)			1000		
Glycerol		109			
NaCl				2.82	
Hexane					5.00
Waste Water				159	
Total	280	109	1000	162	107

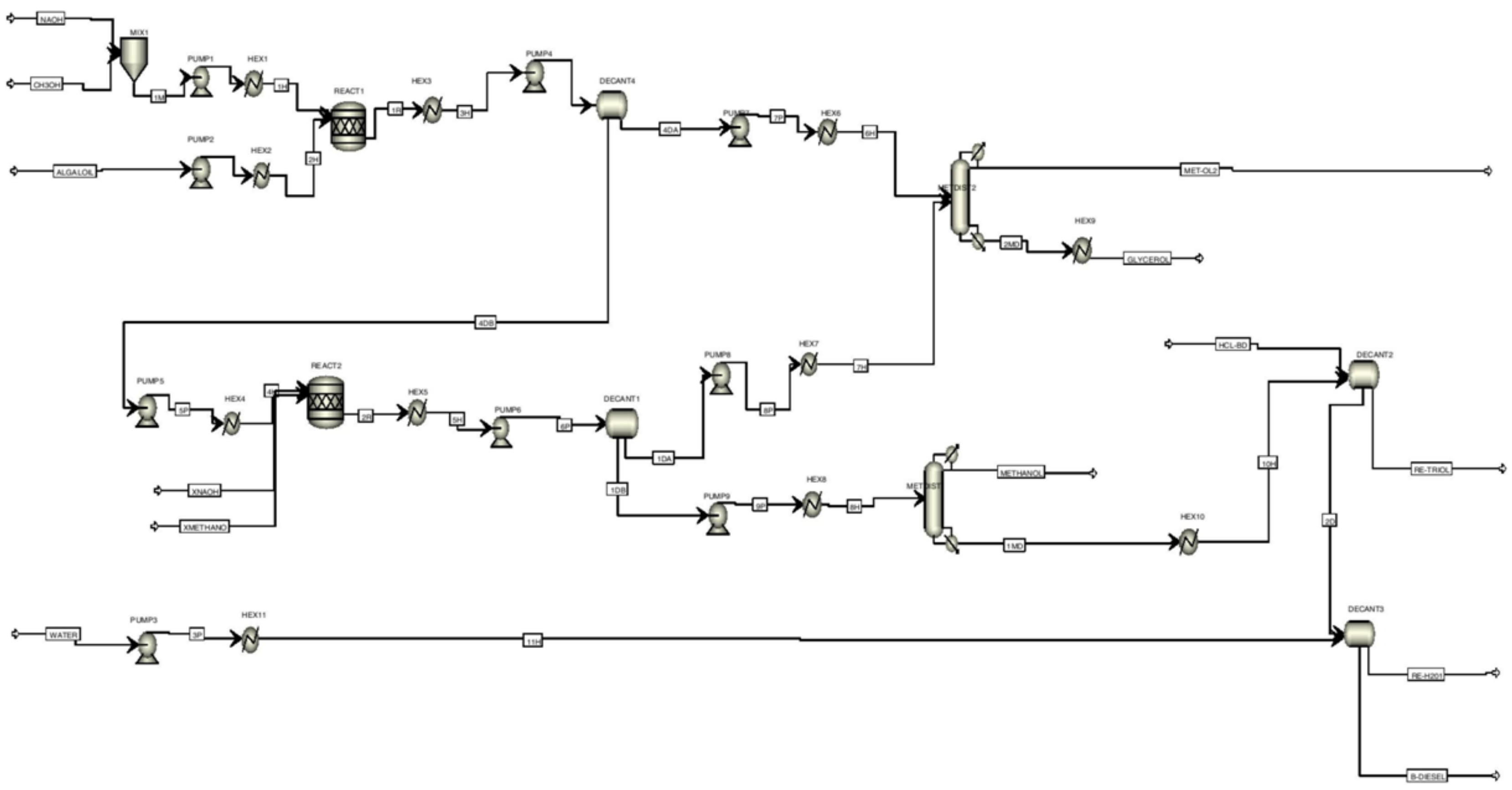
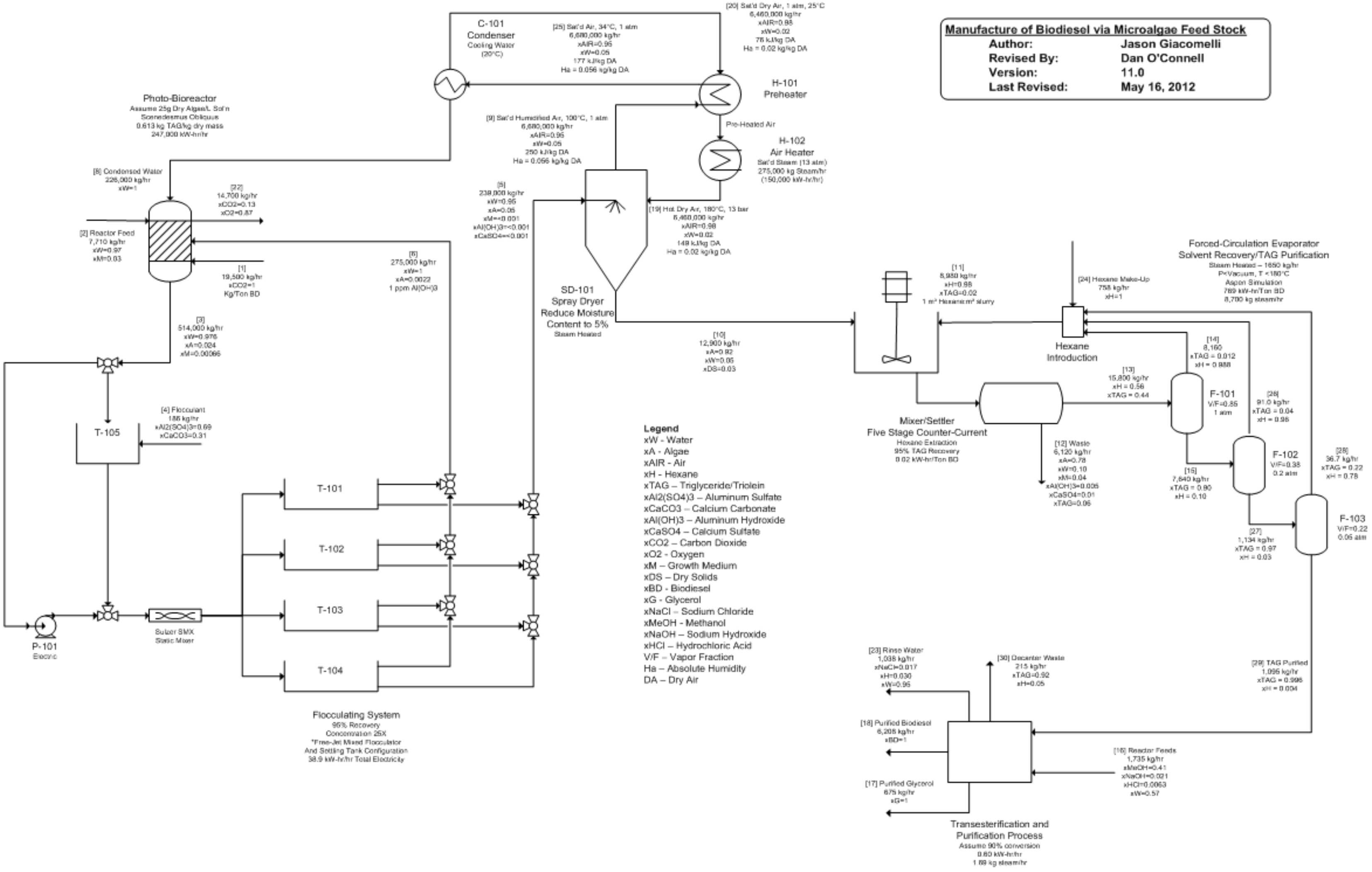


Figure 52. Process flow diagram for the purification and reaction process.[52]

Manufacture of Biodiesel via Microalgae Feed Stock
Author: Jason Giacomelli
Revised By: Dan O'Connell
Version: 11.0
Last Revised: May 16, 2012
C-101
Condenser
Cooling Water
(20°C)
[25] Sat'd Air, 34°C, 1 atm
6,680,000 kg/hr
xAIR=0.95
xW=0.05
177 kJ/kg DA
Ha = 0.056 kg/kg DA
[20] Sat'd Dry Air, 1 atm, 25°C
6,460,000 kg/hr
xAIR=0.98
xW=0.02
76 kJ/kg DA
Ha = 0.02 kg/kg DA
H-101
Preheater
Pre-Heated Air
H-102
Air Heater
Sat'd Steam (13 atm)
275,000 kg Steam/hr
(150,000 kW-hr/hr)
Photo-Bioreactor
Assume 25g Dry Algae/L Sol'n
Scenedesmus Obliquus
0.613 kg TAG/kg dry mass
247,000 kW-hr/hr
[8] Condensed Water
226,000 kg/hr
xW=1
[22]
14,700 kg/hr
xCO2=0.13
xO2=0.87
[2] Reactor Feed
7,710 kg/hr
xW=0.97
xM=0.03
[1]
19,500 kg/hr
xCO2=1
Kg/Ton BD
[6]
275,000 kg/hr
xW=1
xA=0.0022
1 ppm Al(OH)3
[9] Sat'd Humidified Air, 100°C, 1 atm
6,680,000 kg/hr
xAIR=0.95
xW=0.05
250 kJ/kg DA
Ha = 0.056 kg/kg DA
[5]
238,000 kg/hr
xW=0.95
xA=0.05
xM=<0.001
xAl(OH)3=<0.001
xCaSO4=<0.001
[19] Hot Dry Air, 180°C, 13 bar
6,460,000 kg/hr
xAIR=0.98
xW=0.02
149 kJ/kg DA
Ha = 0.02 kg/kg DA
SD-101
Spray Dryer
Reduce Moisture
Content to 5%
Steam Heated
[10]
12,900 kg/hr
xA=0.92
xW=0.05
xDS=0.03
[3]
514,000 kg/hr
xW=0.976
xA=0.024
xM=0.00066
[4] Flocculant
186 kg/hr
xAl2(SO4)3=0.69
xCaCO3=0.31
T-105
T-101
T-102
T-103
T-104
P-101
Electric
Sulzer SMX
Static Mixer
Flocculating System
95% Recovery
Concentration 25X
*Free-Jet Mixed Flocculator
And Settling Tank Configuration
38.9 kW-hr/hr Total Electricity
Legend
xW - Water
xA - Algae
xAIR - Air
xH - Hexane
xTAG – Triglyceride/Triolein
xAl2(SO4)3 – Aluminum Sulfate
xCaCO3 – Calcium Carbonate
xAl(OH)3 – Aluminum Hydroxide
xCaSO4 – Calcium Sulfate
xCO2 – Carbon Dioxide
xO2 - Oxygen
xM – Growth Medium
xDS – Dry Solids
xBD - Biodiesel
xG - Glycerol
xNaCl – Sodium Chloride
xMeOH - Methanol
xNaOH – Sodium Hydroxide
xHCl – Hydrochloric Acid
V/F – Vapor Fraction
Ha – Absolute Humidity
DA – Dry Air
[11]
8,980 kg/hr
xH=0.98
xTAG=0.02
1 m³ Hexane/m³ slurry
[24] Hexane Make-Up
758 kg/hr
xH=1
Hexane
Introduction
Forced-Circulation Evaporator
Solvent Recovery/TAG Purification
Steam Heated – 1650 kg/hr
P<Vacuum, T <180°C
Aspen Simulation
789 kW-hr/Ton BD
8,700 kg steam/hr
Mixer/Settler
Five Stage Counter-Current
Hexane Extraction
95% TAG Recovery
0.02 kW-hr/Ton BD
[12] Waste
6,120 kg/hr
xA=0.78
xW=0.10
xM=0.04
xAl(OH)3=0.005
xCaSO4=0.01
xTAG=0.06
[13]
15,800 kg/hr
xH = 0.56
xTAG = 0.44
[14]
8,160
xTAG = 0.012
xH = 0.988
F-101
V/F=0.85
1 atm
[26]
91.0 kg/hr
xTAG = 0.04
xH = 0.96
F-102
V/F=0.38
0.2 atm
[15]
7,840 kg/hr
xTAG = 0.90
xH = 0.10
[28]
36.7 kg/hr
xTAG = 0.22
xH = 0.78
F-103
V/F=0.22
0.05 atm
[27]
1,134 kg/hr
xTAG = 0.97
xH = 0.03
[23] Rinse Water
1,038 kg/hr
xNaCl=0.017
xH=0.030
xW=0.95
[30] Decanter Waste
215 kg/hr
xTAG=0.92
xH=0.05
[29] TAG Purified
1,095 kg/hr
xTAG = 0.996
xH = 0.004
[18] Purified Biodiesel
6,208 kg/hr
xBD=1
[16] Reactor Feeds
1,735 kg/hr
xMeOH=0.41
xNaOH=0.021
xHCl=0.0063
xW=0.57
[17] Purified Glycerol
675 kg/hr
xG=1
Transesterification and
Purification Process
Assume 90% conversion
0.80 kW-hr/hr
1.69 kg steam/hr

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