ECONOMIC AND LIFE CYCLE ASSESSMENT OF BIOMASS LIQUEFACTION TECHNOLOGY

by

YU QIU

(Under the Direction of Sudhagar Mani and Jim Kastner)

ABSTRACT

Microalgae are promising feedstock for biofuel production due to their high growth rate and lipid content, compared with other biomass. This study investigated the techno-economic and life cycle environmental impacts of a two-stage microalgae liquefaction plant with an annual design capacity of 0.5 million gallons of bio-crude oil. The total capital investment and annual operating cost were estimated as $113 million and $13 million respectively, with a minimum selling price of $49.80/gal ($44.30/gge) and the net greenhouse gas emission was evaluated as 15.55 $kgCO_2eq$/gal (114.63 gCO_2eq/MJ). The life cycle impacts of biochar/bio-oil production from pyrolysis technologies of woody biomass were also investigated to compare with algae liquefaction technology. The study suggests that bio crude oil production from algae is not economically competitive compared with fossil based crude oil. Further research is required to enhance algae productivity and bio crude oil yield.

INDEX WORDS: Algae, bio crude oil, hydrothermal liquefaction, plant cost analysis, life cycle analysis.

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CHAPTER 1

INTRODUCTION

Fossil fuel is an unsustainable resource with limiting reserve and long term environmental problems such as global warming to supply global energy demand (Hoel and Kverndokk, 1996). There is a need to search for alternative and sustainable source of fuels. In 2007, the combustion of fossil fuels in global contributed 76.3% of all CO_2 emissions, which is the main greenhouse gas (GHG) (Boden et al, 2009). To reduce the impact of global warming and develop under a sustainable way, finding a green and renewable substitute for fossil fuels is critical to meet global fuel demand and to reduce GHG emissions.

Biofuels is an umbrella name of all type of fuels produced from bio-renewable resources. It has the potential to minimize the CO_2 emissions and to improve national energy security due to its sustainability, and possibility to reduce consumptions of fossil fuels. There are various types of feedstock to produce biofuels but simply, all of them can be treated as biomass, such as crops, woods, grasses, algae and other potential plants or livestock byproducts. Biofuel from corn, soybean and other food based feedstock is called first generation biofuels, which is currently commercialized but raises the problem of food crisis. Lignocellulosic biomass as the feedstock of second generation biofuels has been researched to cool down the debate of food-vs-fuels, however, the economic feasibility of lignocellulosic biofuels is not very favorable under the current technology and efforts are still taken to overcome the technical barriers (Naik et al., 2010). Algal

biofuel is considered as the third generation of biofuels due to its potential to meet the global demand for fossil fuels (Chisti, 2007).

Microalgae are a very large group of simple and single cells photosynthetic organisms existing in the freshwater or marine system. They can absorb CO_2 in the atmosphere and then convert it into carbohydrates just as plants. The common microalgae species for biofuels production are *Nannochloropsis* sp., *Chlorella* sp., and *Spirulina platensis*. High growth rate and rich lipid content are two critical characteristics that make microalgae stand out among other biomass in the production of biofuels. The aerial growth rate of different algae species is ranging from 11.1 to 69.2 g/m^2/day for open raceway ponds and 10.2 to 47.7 g/m^2/day for closed photobioreactors (Brennan and Owende, 2010). Microalgae with production rate of 10 g/m^2/day and lipid content 30% (wt. dry algae) was estimated to produce biodiesel 12,000 L/ha/yr with 406 million hectares of cultivation land needed to satisfy global oil demand, while biodiesel production rate was estimated as 446 L/ha/yr for soybean and 5,950 L/ha/yr for oil palm (Schenk et al., 2008). Li et al. (2008) reported that algae could produce 15–300 times more oil than conventional crops on a per acre basis. The typical lipid content in microalgae is 20-50% (wt. dry) compared with 20% (wt.) for soybean or oil palm generally (Johnson, 2012; Becker, 1994). Higher lipid content exceeding 80% (wt.) of the dry algae was also reported (Metting, 1996; Spolaore et al., 2006). Besides lipid, microalgae also contains typical 14-29% carbohydrates, 37-57% proteins and 8-19% ashes on a dry wt. basis, but the composition has a very large variance among different species (Frank et al., 2013; Singh et al., 2011; Spolaore et al., 2006).

Algal biodiesel production is to extract rich lipids from dried microalgae and then use trans-esterification to convert lipids into biodiesel. This technology was demonstrated as technically viable but not economically feasible, and improvements for algal biology and cultivation economy are required in order to produce low cost microalgal biodiesel (Chisti, 2007). Besides, high energy (3,556 kJ/kg of water removed) is required during algae slurry drying from 0.05 to 91% w/w (Sander and Murthy, 2010). The need for enhanced algae harvesting technologies with high efficiency and low cost to produce sustainable and commercial algae biofuels was stated (Chen et al., 2011). Another problem with lipid extraction technology is the utilization of remained biomass, usually called lipid extracted algae (LEA). In the study of Lundquist et al. (2010), the residual algae was anaerobically digested in pond facility in order to recycle the remained nutrients to algae cultivation and to generate electricity using the produced biogas. Davis et al. (2011) investigated the economic feasibility of biodiesel production from autotrophic microalgae with electricity as byproduct from LEA anaerobic digestion but the results also showed that in current technology algal biodiesel would not be competitive with traditional fossil fuels.

Hydrothermal liquefaction (HTL), also called hydrous pyrolysis, is a high temperature and high pressure process for the decomposition of complex organic materials such as biomass into crude oil and other chemicals. In the HTL reaction, carbohydrates rapidly degrades into glucose and other saccharides that can be further decomposed to form furfurals, phenols and other intermediates (Toor et al., 2011). Lipids referred as triacylgycerides (TAGs) can by hydrolyzed into glycerol and fatty acids which then convert to long-chain hydrocarbons (Watanab et al., 2006). Proteins are disintegrated into

amino acids which produce hydrocarbons, amines, aldehydes and acids in further degradation process (Toor et al., 2011). The typical reaction condition of microalgae HTL is with temperature ranging from 200 to 375º C, pressure ranging from 10 to 20 MPa, and reaction time from 3 to 90 min depends on the mode of operation: batch or continuous (Elliott et al.,2013; Jazrawi et al.,2013; Zhu et al., 2013). HTL is a better conversion method of microalgae to fuel compared with algal lipids trans-esterification because no drying is required before processing, especially when harvested microalgae have high moisture content. In addition, the bio-crude can be generated not only from the algal lipid, but also from the carbohydrate and protein fractions of the algae. The oil yield for lipid, protein and carbohydrate were found to be in the range of 52 to 78% (wt.), 6 to 18% (wt.) and 4 to 21% (wt.), respectively (Biller & Ross, 2011). Clearly, lipid had the highest HTL oil yield among major algae compounds, thus, high lipid content algae strains are favorable in both lipid extraction and HTL processes.

The bio-crude oil yield from microalgae liquefaction technology varies from 20 to 64% (wt.) (Garcia et al., 2011). Most studies used small batch reactors (10 to 1000 ml) with slow heating rates and long residence times, typically 60 min, with bio-crude yield from 11.6 to 64% (wt.) and high heating value (HHV) from 33.2 to 40.1 MJ/kg (Biller & Ross, 2011; Dote et al., 1996; Duan and Savage, 2010; Jena and Das, 2011; Minowa et al., 1995; Ross et al., 2010; Valdez et al., 2012). A bench scale (1 liter) continuous HTL was performed using different sources of *Nannochloropsis sp.* under 350º C and 20 MPa with 1.5 L/h flow rate, which gave bio-crude oil yield from 38.0 to 63.6% (wt. dry ash free) and the feedstock slurry concentration was up to 35 wt.% dry solids (Elliott et al., 2013).

The composition of microalgae HTL bio-crude depends on algae species and reaction conditions with the range of 67.90-79.20% carbon, 8.70-11.10% hydrogen, 5.30-15.30% oxygen, 3.30-7.90% nitrogen and 0.30-0.96% sulfur (Valdez et al., 2012; Duan and Savage, 2010; Elliott et al., 2013; Jazrawi et al.,2013). The petroleum elements composition was reported with a narrow limits as 83.0-87.0% carbon, 10.0-14.0% hydrogen, 0.1-2.0% nitrogen, 0.05-1.50% oxygen, 0.05-6.0% sulfur and metals < 1000 ppm (Speight, 1999). Hydrodeoxygenation (HDO) and hydrodenitrogenation (HDN) are commonly used to remove high oxygen and nitrogen contents in crude oil. A study used egg albumin as model protein to investigate nitrogen distribution in direct liquefaction and found that about 80% nitrogen in albumin was distributed to the aqueous phase above 200º C (Dote et al., 1996).

A two stage continuous microalgae HTL system combining with HDO was proposed in this study in order to reduce the nitrogen and oxygen content of the oil. The first stage HTL of algae was conducted in a low temperature (225º C) in order to remove the aqueous phase with high nitrogen content, and the remained solid replenished with fresh water then went to second HTL (350º C) for completely degradation to form bio-crude, which then was treated with HDO process to reduce oxygen content. A system of bio-oil/bio-char production from pine wood (lignocellulosic biomass) via pyrolysis was investigated to compare with algae liquefaction technology. Techno-economic analysis and life cycle assessment were performed separately to evaluate and compare the two systems.

Techno-economic analysis (TEA) is a method to analyze an established system in concert with technology and market-driven prices. Algal biofuels have promising market

potential, however, thorough production cost analysis is needed to improve economic feasibility and process efficiency to make algal biofuels competitive with fossil fuels. Capital cost and operating cost are two essential value when conducting TEA. The former typically includes equipment purchased cost, installation cost, and other costs related to assets and plant construction. The latter refers to feedstock cost, utility cost, labor cost and other costs related to operation. The product price can be calculated using a discounted cash flow method with the capital cost, operating cost and plant life. The prices for large scale algae biofuels production from lipid extraction and hydrotreating processes were estimated as $9.84/gal for open pond and $20.53/gal for closed photobioreactors (PBR) with the cost reduction opportunities on enhancing lipid accumulation versus algae growth rate and the capital cost (establishing low-cost equipment, Davis et al., 2011). A bench-scale of LEA liquefaction technology following with hydrotreating and hydrocraking to produce liquid fuels was investigated and gave the annual production of 26.9 million gallon gasoline-equivalent (GGE) with $2.07 to $7.11/GGE of design parameters (Zhu et al., 2013).

Life cycle assessment (LCA) is a method which conducts cradle to grave analysis of processes or product systems with quantifying the material use and energy consumption, and estimating the environmental impacts. In order to produce green energy, it is very important to perform LCA to evaluate the environmental emissions of a certain system. The environmental impacts category typically includes global warming, ozone depletion, acidification, eutrophication, smog, ecotoxicity, natural resources depletion and so on. Each category is evaluated with caused emissions in life cycle inventory and their weighting number (optional). A study researched on utilizing marine macroalgae for CO_2

fixation and biofuels production found that energy benefits existed when using effluent water as algal cultivation nutrient source and 11,000 MJ/t dry algae of net energy gained using supercritical CO_2 conversion to produce biofuel (Aresta et al., 2005). A recent study stated that algae biodiesel required a large amount of fossil energy (3,556 kJ/kg of water removed) during thermal dewatering, which is a major obstacle of this new technology (Sander & Murthy, 2010). The effects of different culture conditions and extraction methods suggested that controlling fertilizer consumption and using wet extraction could reduce energy use for algae biodiesel production (Lardon et al., 2009). A comparison LCA study of algae biodiesl and HTL crude found that HTL used 1.8 fold less algae feedstock but required 5.2 times more ammonia compared with lipid extraction. The life cycle emissions of HTL crude and algal biodiesel were 31,000 gCO_2 eq and 21,500 gCO_2 eq per million BTU respectively (Frank et al., 2013). A reduction of 0.075 kg CO_2 per MJ of fuel combustion was estimated when substituting residual fuel oil with bio-oil from wood chips (Steele et al., 2012).

The main objective of this project is to investigate the economic and environmental impacts of microalgae bio-crude produced from a two-stage continuous liquefaction technology. The specific objectives are:

(1) Develop a process simulation model of two-stage continuous microalgae liquefaction technology at commercial scale to estimate mass balance, energy consumption and cost of the bio-crude production, and perform sensitivity analysis of key simulation parameters to evaluate the possibilities of cost reduction and directions of future process improvement.

(2) Conduct a life cycle assessment of the two-stage continuous microalgae liquefaction technology to evaluate the environmental and ecological impacts of producing microalgal bio-crude, and to compare with petroleum crude production system.

(3) Conduct a life cycle assessment of bio-oil/bio-char production from Southern pine wood to evaluate the environmental and ecological impacts of the system.

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CHAPTER 2

REVIEW OF LITERATURE

1. Algae

1.1. Introduction

Algae are a very large group of photosynthetic organisms which can categorize into two classes: microalgae and macro algae. Microalgae are usually simple and single cells existing individually or in groups in the freshwater or marine system. The typical size of microalgae is ranging from micrometers (μm) to hundreds of micrometers. Macro-algae, so called seaweed, are types of algae that are generally macroscopic and multi-cellular, which are used to produce food, medicine, fertilizer and so on. Based on trophic modes, algae can be separated into four major types: photoautotrophic, photoheterotrophic, mixotrophic and heterotrophic (Chojnacka and Marquez-Rocha, 2004).

The interests towards microalgae on biofuel production have increased in recent decades due to the strong abilities of algae to capture solar energy and to convert it to chemical energy. In the previous work, Dismukes et al. (2008) stated that 'Overall solar energy conversion to biofuel is about 0.05% for corn grain ethanol, 0.5% for switchgrass ethanol, and 0.5-1% for aquatic microbial oxygenic photoautotrophs (AMOPs) to ethanol or biodiesel.'

1.2. Productivity

The productivity of algae has many influence factors such as microalgae species, cultivation medium, cultivation system, illumination intensity, CO_2 supply, fluid

dynamics and so on (Borowitzka, 1999; Li et al., 2008; Chen et al., 2011). The productivity of different algae species are listed in the Table 2.1, which is modified from previous work (Chen et al., 2011; Mata et al., 2010). In the table, the volumetric algae productivities were mostly obtained from lab scale cultivation experiments so the unit was gram per liter per day. For the yields in gram per square meters per day, there was limited data because of high cost of large scale experiments in an industrial environment.

Algae productivity has been reported in the range from 0.002 to 7.4 g/L/d or 10.2 to 130 $g/m^2/d$ (Table 2.1) and is highly influenced by the class of algae species and type of cultivation system. Cultivation of microalgae has been widely practiced either in open raceway or enclosed tubular photobioreactors. The details of various cultivation systems are explained in the later section (2.4). Pulz (2009) stated that algae areal productivity differs widely across the various cultivation systems with 10-20 $g/m^2/d$ for open systems, 35-40 $g/m^2/d$ for closed systems and 80-100 $g/m^2/d$ for thin-film systems. Nevertheless, for the commercial algae production, an open system is usually selected due to its lower cost compared with to a closed system. The typical range of productivity for open systems range from 15 to 30 $g/m^2/d$ (Davis et al., 2012). Table 2.2 lists the productivity of different cultivation system.

Table 2.1 Lipid and biomass productivity of microalgae

Microalgae species	Lipid content dry wt.%	Lipid productivity (mg/L/d)	Algae Productivity (g/L/d)	Algae Productivity (g/m2/d)	Reference
Botryococcus braunii	20.8–75.0	5.5	0.03	–	Yoo et al. (2010); Chisti (2007)
Chaetoceros calcitrans	39.8	17.6	0.04	–	Rodolfi et al. (2009)
Chaetoceros muelleri	33.6	21.8	0.07	–	Rodolfi et al. (2009)
Chlorella emersonii	25.0–63.0	10.3–50.0	0.03–0.05	–	Scragg et al. (2002); Illman et al. (2000)
Chlorella minutissima	31.0-57.0	9.0-10.2	0.02-0.03	–	Illman et al. (2000)
Chlorella protothecoides	11.0–57.8	732.7–3701.1	0.002–7.4	–	Li et al. (2007); Xu et al. (2006); Xiong et al. (2008); Cheng et al. (2009)
Chlorella pyrenoidosa	–	–	2.90–3.64	72.5 - 130	Lee et al. (1995); Lee & Low (1991)
Chlorella sorokiniana	19.3–22.0	44.7	0.003-0.23	–	Rodolfi et al. (2009); Illman et al. (2000)
Chlorella sp.	28.0–34.0	121.3–178.8	0.37–2.5	25	Chiu et al. (2008); Doucha and Livansky (1995); Chisti (2007)
Chlorella vulgaris	5.1–58.0	4–54.0	0.01–0.25	–	Yoo et al. (2010); Scragg et al. (2002); Gouveia and Oliveira (2009); Illman et al. (2000); Rodolfi et al. (2009); Liang et al. (2009)
Chlorococcum sp.	19.3	53.7	0.28	–	Rodolfi et al. (2009)
Dunaliella tertiolecta	16.7–71.0	20–69.8	0.1-0.12	–	Gouveia and Oliveira (2009); Takagi et al. (2006)
Ellipsoidion sp.	27.4	47.3	0.17	–	Rodolfi et al. (2009)
Haematococcus pluvialis	25	–	0.05–0.06	10.2–36.4	Huntley and Redalje (2007)
Isochrysis galbana	21.9 - 38.5	–	0.32	–	Molina Grima et al.(1994); Fidalgo et al. (1998)
Isochrysis sp.	27.4–33	37.8	0.14	–	Rodolfi et al. (2009); Chisti (2007)
Monodus subterraneus	16	30.4	0.19	–	Rodolfi et al. (2009)
Nannochloris sp.	20–40.3	15.6–109.3	0.04–0.35	–	Takagi et al. (2000)
Nannochloropsis	29.2	49.7	0.17	–	Rodolfi et al. (2009)
Nannochloropsis oculata	22.7–29.7	84.0–142.0	0.37–0.48	–	Chiu et al. (2008)
Nannochloropsis sp.	31–68	25.8–60.9	0.09–0.21	–	Rodolfi et al. (2009); Gouveia and Oliveira (2009); Chisti (2007)
Neochloris oleoabundans	7.0 - 56.0	10.7–133.0	0.03–0.63	–	Gouveia et al. (2009); Li et al. (2008); Gouveia and Oliveira (2009)
Pavlova lutheri	35.5	50.2	0.14	–	Rodolfi et al. (2009)
Pavlova salina	30.9	49.4	0.16	–	Rodolfi et al. (2009)
Phaeodactylum tricornutum	18	44.8	0.24	–	Rodolfi et al. (2009)
Porphyridium cruentum	9–14	34.8	0.37	25	Rodolfi et al. (2009); Spolaore et al. (2006); Chaumont et al. (1988)
Scenedesmus obliquus	6.6–17.7	7.14–58.6	0.06–0.51	–	Gouveia and Oliveira (2009); Mandal and Mallick (2009)
Scenedesmus quadricauda	18.4	35.1	0.19	–	Rodolfi et al. (2009)
Scenedesmus sp.	9.5–21.1	20.7–53.9	0.21–0.26	–	Yoo et al. (2010); Rodolfi et al. (2009)
Skeletonema costatum	13.5–51.3	17.4	0.08	–	Rodolfi et al. (2009)
Skeletonema sp.	13.3–31.8	27.3	0.09	–	Rodolfi et al. (2009)
Spirulina maxima	4.0-9.0	8.6	0.21-0.25	25	Gouveia and Oliveira (2009); Torzillo et al. (1986)
Tetraselmis sp.	12.6-14.7	43.4	0.3	–	Rodolfi et al. (2009)
Tetraselmis suecica	8.5–30	27.0–36.4	0.32	19	Rodolfi et al. (2009); Otero and F´abregas (1997)
Thalassiosira pseudonana	20.6	17.4	0.08	–	Rodolfi et al. (2009)

Table 2.2. Algae productivity of different cultivation system

Cultivation system	Productivity assumption ($g/m^2/d$)	Reference
Open pond	25	Fisherman et al. (2012)
Open raceway	22	Lundquist et al. (2010)
Open pond	30	Dunahay et al. (1998)
Open system	10-20	Pulz (2009)
Closed system	35-40	Pulz (2009)
Thin-film system	80-100	Pulz (2009)

1.3. Compositions

The major biochemical compounds in algae biomass are carbohydrates, protein and lipids. The composition of algae varies over a wide range in different species (Table 2.3). The living environment of algae, such as temperature, light intensity, CO_2 concentration, nutrients supply and pH, have effects on the proportion of different constituents in algae composition (Becker, 1994). Spoehr and Milner (1948) investigated the effects of environmental conditions on the chemical composition of *Chlorella* and found that protein varied from 8.7 to 58.0%; carbohydrates ranged from 5.7 to 37.5 %; lipid content could vary from 4.5 to 85.6% wt. (dry and ash free) in different culture conditions of cell growth.

Table 2.3. Chemical composition of different algae species in dry % wt.*

Species	Protein	Carbohydrates	Lipids
Anabaena cylindrica	43-56	25-30	4-7
Chlamydomonas rheinhardii	48	17	21
Chlorella pyrenoidosa	51-58	12-17	14-22
Chlorella vulgaris	57	26	2
Dunaliella bioculata	49	4	8
Dunaliella salina	57	32	6
Euglena gracilis	39-61	14-18	14-20
Porphyridium cruentum	28-39	40-57	9-14
Prymnesium parvum	28-45	25-33	22-38
Scenedesmus dimorphus	8-18	21-52	16-40
Scenedesmus obliquus	50-56	10-17	12-14
Scenedesmus quadricauda	47	-	1.9
Spirogyra sp.	6-20	33-64	11-21
Spirulina maxima	60-71	13-16	6-7
Spirulina plantensis	46-63	8-14	4-9
Synechococcus sp.	63	15	11
Tetraselmis maculata	52	15	3

*. Data were collected from Becker (1994)

Algae also accumulate various valuable products, such as polyunsaturated fatty acids (PUFAs), polysaccharides, antioxidants and pigments, which can be used in the nutraceuticals, cosmetics, food and feed industries (Pulz and Gross, 2004). Microalgae is a primary source of PUFAs, which can help lower the risk of heart disease and stroke via

reducing blood bad cholesterol concentrations, according to American Heart Association. Docosahexaenoic acid (DHA) and eicosapentaenoic acid (EPA) are most common PUFAs; DHA can be produced from *Crypthecodinium* and *Schizochytrium* and EPA can be extracted from *Nannochloropsis*, *Phaeodactylum*, *Nitzschia* and *Pavlova* (Brennan and Owende, 2010). Agar, alginates and carrageenans are most important macroalgal polysaccharides applied in diverse fields of industries such as food, chemical and pharmaceutical. *Haematococcus pluvialis* is well known for its high content of astaxanthin which is a strong antioxidants used in cosmetics and pharmaceutical industries (Mata et al., 2010). Carotenoids and phycobiliproteins from algae are mainly used as colorants in food industries. β-Carotene content is up to 14% of dry weight of *Dunaliella salina* which is most suitable to produce natural β-Carotene (Metting, 1996). Phycobiliproteins mainly produced from cyanobacterium *Arthrospira* and the rhodophyte *Porphyridium*, are primarily applied as food pigments but have the potential in pharmaceutical applications due to their features in health benefits (Spolaore et al., 2006).

1.4. Lipid content

The major biochemical compositions of algae are carbohydrates, proteins and lipids. Ash content and moisture content are also commonly included in the measurement to evaluate an alga strain. Lipid content is a very critical factor in the algal oil production. Energy contained in lipid can be as twice as the energy stored per carbon atom of carbohydrates (Dismukes et al., 2008). Compared to other biomass, the typical lipid content in algae is 20-50% wt. while soybean and oil palm is around 20% wt. (Johnson, 2012). In a previous review of microalgae for biodiesel production, Mata et al. (2010) compared the lipid content and oil productivity of several energy plants with microalgae. The results are

simplified and shown in Table 2.4. From the comparison, it is obvious that the oil yield and biodiesel productivity of algae are remarkably higher than other plant sources while the oil content in algae is relatively higher than others. This may be caused by the high productivity of algae that mentioned in the previous section.

Table 2.4. Lipid content and oil productivity of different biomass*

Biomass	Oil content % wt.	Oil yield (L/ ha year)	Biodiesel productivity (kg/ha year)
Corn/Maize	44	172	152
Hemp	33	363	321
Soybean	18	636	562
Jatropha	28	741	656
Camelina	42	915	809
Canola/Rapeseed	41	974	862
Sunflower	40	1070	946
Castor	48	1307	1156
Palm oil	36	5366	4747
Microalgae	50	97,800	86,515

*. Date were collected from Mata et al. (2010)

The different algae species and strains can considerably vary the lipid content and productivity in algae. In the Aquatic Species Program (ASP) funded by the U.S. Department of Energy from 1978 to 1996, more than 3000 species of algae were collected to select for the biodiesel production. After screening and isolation, around 300 species of algae were chosen with the high lipid content, mostly green algae and diatoms (Sheehan et al., 1998). In an earlier work, Borowitzka summarized the commercial algae

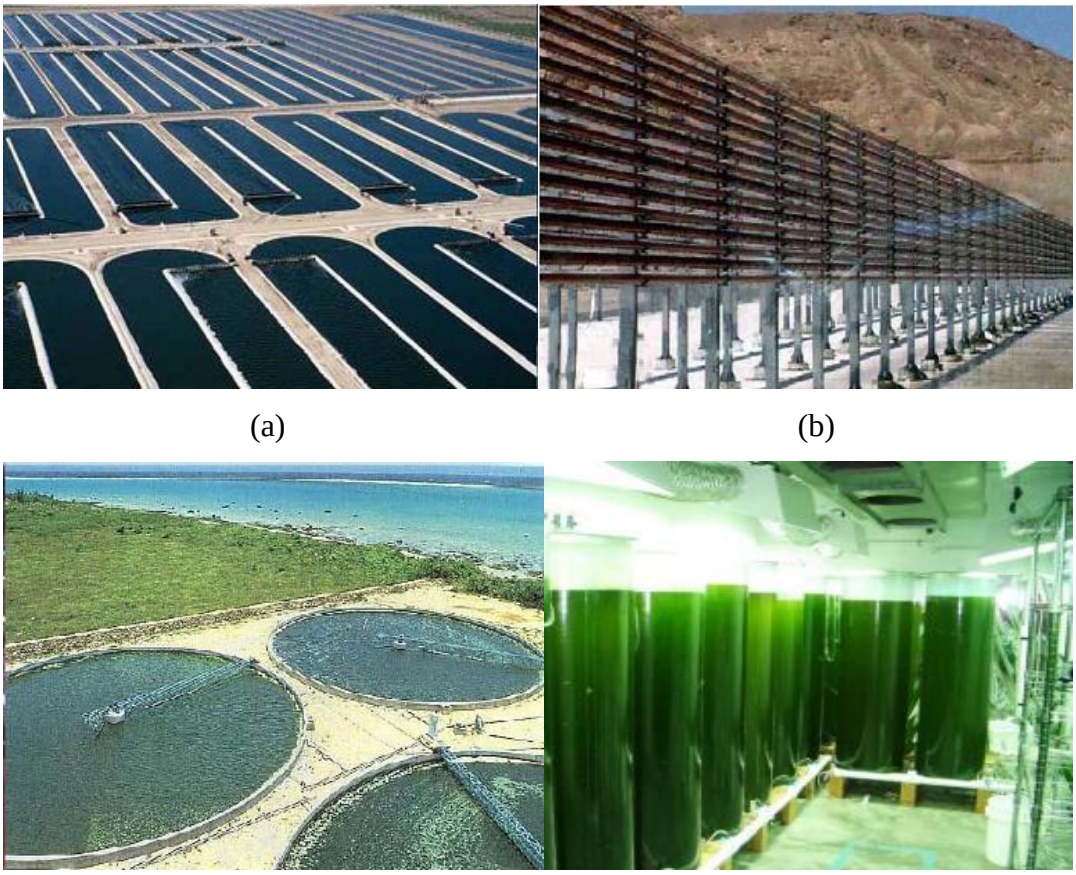
culture system in 90s. The most common microalgae species for industrial production are *Chlorella, Spirulina* and *Dunaliella* (Borowitzka, 1999). The lipid content and productivity of different microalgae species are summarized in Table 2.1 which is modified from previous work (Chen et al., 2011; Mata et al., 2010). Lipids in algae are mainly constituted of triacylglycerols (TAGs) which was found having an upper limit of 80% of total lipids (Hu et al., 2008). TAG is a type of ester that derived from glycerol and three fatty acids.

2. Algae Cultivation

2.1. Cultivation systems

Microalgae are suited to grow in an aquatic environment with sufficient light, nutrients and carbon dioxides (Harris, 2001). Algae cultivation system can be classified into two types: open culture system and closed culture system. Figure 2.1 illustrates two types of open system and closed system, respectively. Tanks, big ponds, circular ponds and race-way ponds are very commonly used open systems in the commercial production (Borowitzka, 1999). Photobioreactors, one of the closed culture systems, are studied a lot recently as a new technology for algae production because of its high yield and low contamination (Chen et al., 2011; Ma, 2011; Rodolfi et al., 2009; Ugwu et al., 2008; Chisti, 2007). A comparison of different algae cultivation systems are demonstrated in Table 2.5 (Borowitzka, 1999; Mata et al., 2010). Although closed system may have high yields and ability to prevent contamination, it is very expensive to scale up because of high requirements of the container and high energy costs such as light supply (Chen et al., 2011). Instead of providing artificial lights, the open system can use sunlight which is no

costs, however, the various illumination intensity caused by weather leads to unstable productivity (Ma, 2011; Lundquist et al., 2010).



(a) (b)

(c) (d)

Figure 2.1. Different algae cultivation systems. (a): Open raceway ponds in Earthrise Nutritionals, LLC, California. (b): Tubular photobioreactors in Algatech Co., Israel. (c): Circular ponds in Chlorella industries, Japan. (d): Vertical photobioreactors at the University of Georgia, Biorefining and carbon cycling program.

For the algae cultivation system design, several key factors are very important to take consideration with. They are algae features, reactor type, mixing condition, efficiency of light utilization, temperature control, gas transfer, hydrodynamic stress on algae, species control, sterility, difficulty of scale up, land use, nutrients, water consumption, climate,

energy usage, labor and operation costs, and the final product requirements (Borowitzka, 1992; Borowitzka, 1999). Different algal species have the different requirements towards the growth environment. For instance, *Spirulina* grows in the environment with high pH and bicarbonate concentration (Borowitzka, 1988) while *Chlorella* prefers high concentration of nutrients (Soong, 1980). When choosing the culture system for commercial production, one should balance aspects that influence the final yield and quality of the algae and also the economic cost. A previous study emphasized the importance of recycling water and nutrients during algae cultivation (Yang et al., 2011). By using freshwater without recycling to generate 1 kg of biodiesel, 3726 kg water, 0.33 kg nitrogen, and 0.71 kg phosphate were required. Recycling harvest water reduced 84% water and 55% nutrients consumption while using seawater save 90% water usage and only need to provide phosphate. Combination of algae cultivation and power plant flue gas treatment may significantly reduce the GHG emissions (Kadam, 2001).

Table 2.5. Comparison of cultivation systems*

Activities	Open system				Closed system	
	Tanks	Ordinary Ponds	Circular Ponds	Raceway Ponds	Tubular Reactors	Photobioreactors
Temperature control	None	None	None	None	Uniform	Uniform
Light utilization	Very Poor	Poor	Fair-Good	Fair- Good	High	High
Mixing	Poor	Very Poor	Fair	Fair- Good	Uniform	Uniform
Gas transfer	Poor	Poor	Poor	Poor	Low-High	High
Water evaporation	High	High	High	High	Low	Low
Contamination	Difficult	Difficult	Difficult	Difficult	Easy	Easy
Species control	Difficult	Difficult	Difficult	Difficult	Easy	Easy
Scale up	Difficult	Difficult	Difficult	Difficult	Fair	Difficult
Investment	Low	Low	Low	Low	High	High
Operation costs	Low	Low	Low	Low	High	High

*. Data were collected from borowitzka (1999) and Mata et al. (2010)

Algae cultivation system can be either batch or continuous. The comparison of batch system and continuous system was claimed by Williams in 2002. Compared to batch mode, there are several main advantages to use continuous system (Williams, 2002). Continuous system offers stability and accuracy of system investigation and analysis, providing a higher degree of control, and producing more reliable quality of the product. Nevertheless, disadvantages of continuous process may occur in controlling of non-growth-related products, and in regard of strain losses or contamination.

2.2. Algae growth

Algae growth is influenced by many factors such as nutrients concentration, CO_2 concentration, light intensity and temperature. The most common used equation to simulate the dynamic growth of algae is Monod equation described as following.

$$r_g = \frac{\mu_{max} C_s C_c}{K_s + C_s} \qquad \text{Eq (2.1)}$$

Where r_g is cell growth rate (g dm^{-3} s^{-1}), μ_{max} is a maximum specific growth reaction rate (s^{-1}), C_s is substrate (i.e., nutrient) concentration (g dm^{-3}), C_c is cell concentration (g dm^{-3}), and K_s is Monod constant (g dm^{-3}).

In 1974, Goldman and Carpenter built a model combined effects of temperature and nutrient limitation on the growth rate of algae (Goldman and Carpenter, 1974). They used Arrhenius equation and nutrient relationship with the Monod model and found the maximum specific growth rate $\hat{\mu}$ described by the equation.

$$\hat{\mu} = (1.80 \times 10^{10}) e^{-6842/T} \qquad \text{Eq (2.2)}$$

Where $\hat{\mu}$ is the maximum specific growth rate (day^{-1}) and T is temperature (^{o} C). Nicklisch and Kohl determined the dependence of the specific growth rate of *Microcystis*

aeruginosa towards temperature and light intensity under continuous illumination in batch system (Nicklisch and Kohl, 1983). The function was described as below.

$$\mu = \mu_{max}\{\exp\left[2{,}3\left(\frac{T_{opt}-T}{T_{opt}-T_{min}}\right)^2\right] + \frac{K_I}{I}\}^{-1} \qquad \text{Eq (2.3)}$$

Where μ_{max}=3.44 d^{-1}, T_{opt}=33.2 ℃, T_{min}=18.3º C and K_I=71.4 Wm^{-2}. This function was limited to use in the temperature from 10-28º C and light intensities from 5-25 Wm^{-2}. Three green and three blue-green algae were investigated on the inorganic carbon limited growth kinetics over a range of light and temperatures (Novak and Brune, 1985). Different algae species were found to have various optimal growth conditions. For instance, *Chlorella* was growing fastest in the range of 27-33º C under all light and inorganic carbon concentrations while *Selenastrum capricornutum* preferred to grow at low temperatures, and high light and carbon levels. In 1995, Osmond et al. demonstrated an empirical model of the carbon ratio of phytoplankton chlorophyll as a function of temperatures, daily irradiance and nutrient-limited growth rate (Osmond et al., 1995). De Morais and Costa presented the effects of different CO_2 concentrations on growth rates of eukaryotic microalgae, *Chlorella kessleri*, *C. vulgaris* and *Scenedesmus obliquus*, and the prokaryotic cyanobacterium, *Spirulina sp.*, culturing in flasks and in a photobioreactor (De Morais and Costa, 2007). Their study showed that *Spirulina sp.* had the highest growth rate and could live with up to 18% CO_2. Bhatti and Colman invested the mechanism of inorganic carbon uptake of three synurophyte algae, *Synura petersenii*, *Synura uvella* and *Tessellaria volvocina* and found that there was no external carbonic anhydrase and no capacity for direct bicarbonate uptake, and a low whole-cell affinity for inorganic carbon concentration for all these algae (Bhatti and Colman, 2008). James and Boriah constructed a model of algae growth in an open-channel raceway based on effects

of nutrients, light and temperatures (James and Boriah, 2010). In their model, the predation rate of algae and the fluid dynamics of raceway pond were included as well. Algae production rate was followed the equation below (Cerco and Cole, 1995).

$$P = P_M f(N) g(I) h(T) \qquad \text{Eq (2.4)}$$

Where P_M is the production under optimal conditions (day^{-1}), and $f(N)$ is the effect of non-optimal nutrient concentration ($0 \leq f(N) \leq 1$), and $g(I)$ is the effect of non-optimal illumination ($0 \leq g(I) \leq 1$), and $h(T)$ is the effect of non-optimal temperature ($0 \leq h(T) \leq 1$). Sasi et al. found the highest growth rate of *Chlorella vulgaris* could achieve 0.049 h^{-1} in a circulating loop photobioreactor under the optimum condition with 71.8 mW L^{-1} photosynthetic active radiation density, 10% CO_2 (v/v) in air and 8 h dark phase (Sasi et al., 2011). They concluded that *C. vulgaris* was able to grow exponentially and produce lipids up to 30% of cell dry weight in this bioreactor. A mathematical model of algae growth in the airlift-raceway reactor was presented by Ketheesan and Nirmalakhandan in 2013 based on CO_2, nitrogen, light and temperatures (Ketheesan and Nirmalakhandan, 2013). The specific growth rate μ was expressed in the function as follows.

$$\mu = \left[\frac{N_c}{N_c + K_n}\right]\left[\frac{C_1}{K_c + C_1 + C_1^2/K_s}\right]\left[\frac{I_{ave}}{K_e + I_{ave} + I_{ave}^2/K_i}\right][I(T)] \qquad \text{Eq (2.5)}$$

Where N_c is the concentration of nitrogen in the external medium (g m^{-3}), K_n is the half saturation constant for nitrogen (g m^{-3}), K_c is the half saturation constant for CO_2 (mol m^{-3}), K_s is the inhibit ion constant for CO_2 (mol m^{-3}), I_{ave} is the average light intensity (µE m^{-2} s^{-1}), K_e is the half saturation constant for light (µE m^{-2} s^{-1}), and K_i is the inhibit ion light intensity (µE m^{-2} s^{-1}).

3. Algae Harvesting

Microalgae harvesting is a series of processes that involves dewatering and drying the cultivated microalgae to a desired concentration. The typical algae slurry concentration in culture medium is from 0.02 to 0.06% wt. and after harvesting the algae slurry cake or paste is usually in the concentration of 5 to 25% wt. or more (Shelef et al., 1984). There are several major microalgae harvesting technologies including flocculation /sedimentation, flotation, filtration and centrifugation.

3.1. Flocculation

Flocculation is a method to let the dispersed particles to aggregate together to settle down in order to separate from the liquid phase. Chemicals, such as alum, lime, cellulose, salts, polyacrylamide polymers, surfactants, chitosan, and other man-made fibers have been studied as flocculents to add into slurry liquid to induce flocculation (Lee et al., 1998; Pan et al., 2001; Knuckey et al., 2006). Gravity settling tube combined with flocculation was used to promote algae sedimentation, achieving a slurry concentration of 1.5 % wt. (Mohn, 1980). Some key things are required to take into account regarding flocculation such as flocculent recovery, culture health and stability control, pollution of released flocculent and economic analysis for scale-up (DOE, 2010).

3.2 Filtration

Filtration is a process that can separate solids from liquids via passing liquids through a permeable medium which remains the solids cake on one side of the medium. Five pressure filtration devices were investigated for the algae harvesting of *Colastrum*. The harvested algae slurry concentration was 22-27% wt. for chamber filter press, 18% wt. for belt press, 16% wt. for pressure suction filter, 7.5% wt. for cylindrical sieve and 5%

wt. for filter basket, with the initial concentration of 0.1% wt. (Mohn, 1980). Harvesting of microalgae using filtration faces big challenges because most strains considered as energy feedstock are less than 10 μm in cell diameter (DOE, 2010). The relationship between pore-size of the harvester filter and the size of the algal species decided the effectiveness of filtration, which means that only the species of algae larger than the pore of the filter weave can be harvested (Sim et al., 1988). Filtration is conceptually simple but potentially very expensive in algae harvesting due to the requirement of the filter (DOE, 2010). Nevertheless, filtration is relatively economic than centrifugation because of less energy consumption (Sim et al., 1988; Sander & Murthy, 2010).

Figure 2.2. Flotation device from BIO-AQUA, Denmark

3.3. Flotation

Flotation is a method to use gas bubbles to bring the solid particle to the liquid surface in order to achieve separation. A device of flotation that is using in Denmark is displayed in Figure 2.2. Flotation was more efficiency and beneficial to recover algae compared with sedimentation (Chen et al., 1998). By collision and adhesion, gas bubbles can capture particles with a diameter less than 500 μm in flotation (Yoon and Luttrell, 1989). Dissolved air flotation (DAF) is a method to produce bubbles with a diameter of 10-100 μm by reducing the pressure of liquid water which is presaturated with air at excess

pressures (Uduman et al., 2010). A schematic diagram of dissolved air flotation is illustrated in Figure 2.3. Small bubbles created by electrolysis or pressure relief are introduced into the suspension, adhere to the surface of the alga cells and transport the algae to the surface of the water where they can be skimmed off. The combination of flocculation and DAF was likely promising with the improvement of the cost and effectiveness of flocculants (Sim et al., 1988). DAF after flocculation could remove 80 to 90% wt. algae biomass in the flotation tank with algal float concentrations averaging more than 6% solids (Koopman and Lincoln, 1983).

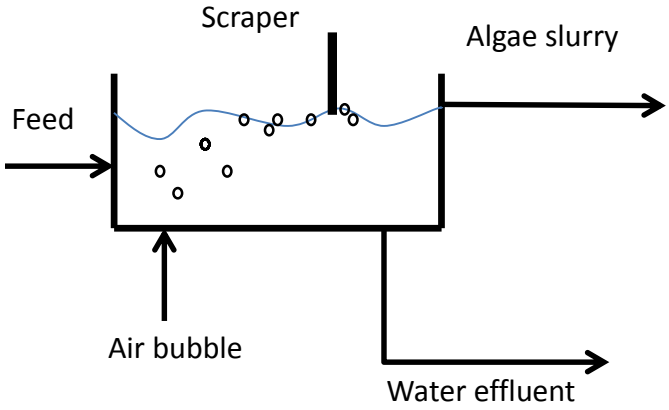


Figure 2.3. Schematic diagram of dissolved air flotation

3.4. Centrifugation

Centrifugation is utilized widely for separation process over the industrial field and it has been studied for the application of algae harvesting (Sim et al., 1988; Molina Grima et al., 2003). Figure 2.4 shows the fluid flow path of a disc stack centrifuge (Maybury et al., 1998). Centrifugation was preferred to harvest the algae, producing extended shelf-life concentrates for aquaculture (Molina Grima et al, 2003). The algae slurry concentration was achieved 12 to 22% wt. for self-cleaning plate centrifuge, 2 to 15% wt. for nozzle centrifuge, 0.4% wt. for hydro-cyclone and 22% wt. for decanter (Shelef et al., 1984);

however, centrifugation requires a lot of energy when using for commercial scale (Molina Grima et al, 2003; Molina Grima et al., 2003). The energy usage can be significantly reduced if centrifugation is used with initial pre-concentration (Sazdanoff 2006). Additional, centrifuge resulted in a relatively high residue of algae slurry in the outlet (Sim et al., 1988). Furthermore, algal cell structure can be destroyed by the high gravitational and shear forces created during centrifuging (Knuckey et al, 2006).

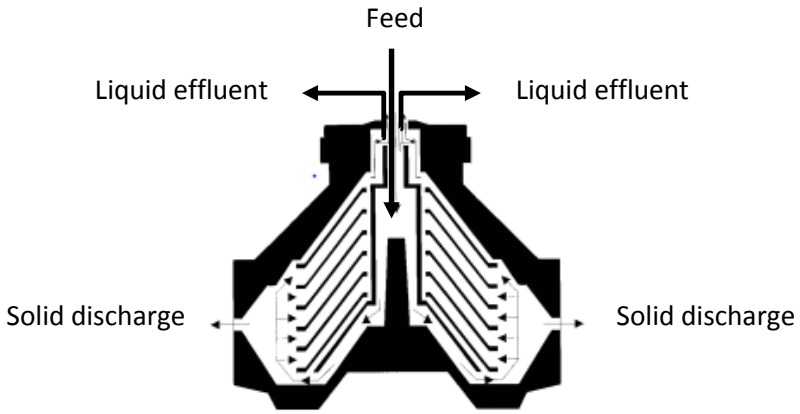


Figure 2.4. Schematic diagram of a disc stack centrifuge (Maybury et al., 1998)

3.5. Harvesting systems

Combinations of different technologies are usually used in the algae harvesting system to achieve the desired concentration of algae slurry. Microalgae was concentrated from 0.05 to 20% wt. using bio-flocculation, DAF and centrifugation in the harvesting process before lipid extraction in the production of biodiesel (Frank et al., 2012). Similar concentration change (0.01 to 20% wt.) achieved by flocculation with synthetic flocculant before lipid extraction was reported for producing algal biodiesel as well (Lardon et al., 2009). For algae HTL process, the slurry concentration was changing from 0.05 to 15% wt. during harvesting with bio-flocculation, DAF and centrifugation (Frank et al., 2013). In a harvesting system combined self-cleaning plate separator centrifuge or

chamber filter press with solar drying and natural gas dryer, a concentration as high as 91% wt. was obtained after dewatering and drying, however, the energy consumption was huge (Sander & Murthy, 2010).

A harvesting system combined of thickening, DAF and centrifugation, similar with Frank et al. (2013), was used in this study. Microalgae slurry was concentrated from 0.5 to 10 g/L (0.05 to 1.0% wt.) after thickening, 60 g/L (6.0% wt.) after DAF and 150 g/L (15.0% wt.) after centrifugation. The total harvesting efficiency was designed as 90%.

4. Conversion of Algae into Biofuels

4.1. Lipid extraction and trans-esterification

Algal lipid is a promising source to produce biodiesel instead of vegetable oils because it is non-food basis and has the possibility to satisfy the liquid fuels demand. Microalgal lipids can be extracted from concentrated and dewatered microalgae after cultivation, and then converted into biodiesel via trans-esterification process in which triglycerides react with a mono-alcohol in the presence of catalyst to produce long-chain alkyl esters (biodiesel) (Demirbas, 2009). The processes are similar to the biodiesel production from vegetable oils. However, the unsaturation level of microalgal oil is high compared to vegetable oils, which would result in the oxidation of the biodiesel during storage and the reduction of usage acceptability Thus, catalytic hydrogenation of the oil is needed (Chisti, 2007).

The major issue of algal biodiesel production is economic feasibility. To improve the economics, three cost reduction methods were claimed (Chisti, 2007). First is to use an integrated biorefinery to make the use of carbohydrates and proteins in algae besides lipids. Second is to enhance the biological features of microalgae, such as growth rate, oil

content, temperature tolerance, and so on, in order to improve the overall lipids yield. Last is to solve the engineering problems of photobioreactors, such as light utilization efficiency and culture mixing, to ensure high productivity of microalgae.

4.2. Anaerobic digestion (AD)

The first study of anaerobic digestion of algae was reported in 1957 to investigate the reaction under different conditions and it mentioned the possibility of algae anaerobic digestion to produce methane as fuel (Golueke et al., 1957). The reaction temperature ranges from 15 to 52º C with a typical of 35º C and the hydraulic retention time can vary from 3 to 64 days (Sialve et al., 2009).

One critical limitation of algae anaerobic digestion is the low C/N ratio of algae sludge which is about 6/1 (Yen and Brune, 2007). The typical range of C/N ratio of anaerobic digestion was claimed as 20/1 to 30/1 and the low C/N ratio feedstock would generate high total ammonia nitrogen and high volatile fatty acids which are potential inhibitors of the anaerobic digestion process (Parkin and Owen, 1986). One way to solve this problem is to co-digest algae with high carbon content feedstock. Yen and Brune (2007) studied the anaerobic co-digestion of algal sludge (mainly *Scenedesmus* spp. and *Chlorella* spp.) and waste paper to produce methane, and found out that the optimum C/N ratio range was from 20/1 to 25/1, which would improve the methane yield. The other two important bottlenecks of algae anaerobic digestion are the low biodegradability of microalgae and the presence of sodium in marine species (Sialve et al., 2009).

In the algal biofuels conversion strategy, anaerobic digestion process is usually utilized to further make use of the remained algae biomass after lipid extraction (Frank et al., 2012; Compbell et al., 2011; Singh and Olsen, 2011; Davis et al., 2011). Sialve et al. (2009)

discussed the good-and-bad of direct anaerobic digestion of whole algae biomass and indirect scenario after lipid recovery. They found that when the lipid content was lower than 40%, the direct anaerobic digestion of whole algae biomass appeared to be the optimal strategy regarding energy balance but they did not discuss the economic issue of the two scenarios.

4.3. Hydrothermal liquefaction technology (HTL)

Hydrothermal liquefaction is a thermochemical process to produce liquid fuels referred to bio-oil or bio-crude under a medium-temperature and high-pressure conditions (Toor et al., 2011; Peterson et al., 2008; Dote et al., 1996). The common reaction condition of HTL is with temperatures from 200 to 370º C, and pressures in the range of 4 to 20 MPa, sufficiently keeping the water in a liquid phase (Peterson et al., 2008). During HTL process, the macromolecules are first hydrolyzed or degraded into smaller molecules which then react and recombine into larger ones (Toor et al., 2011). Water is under these conditions is close to its critical point, acting as reactant and medium which has beneficial properties such as high solubility and low viscosity for fast and homogeneous reactions (Franck, 1983). The phase diagram of water related to pressure and temperatures in the region of hydrothermal processing is illustrated in Figure 2.5.

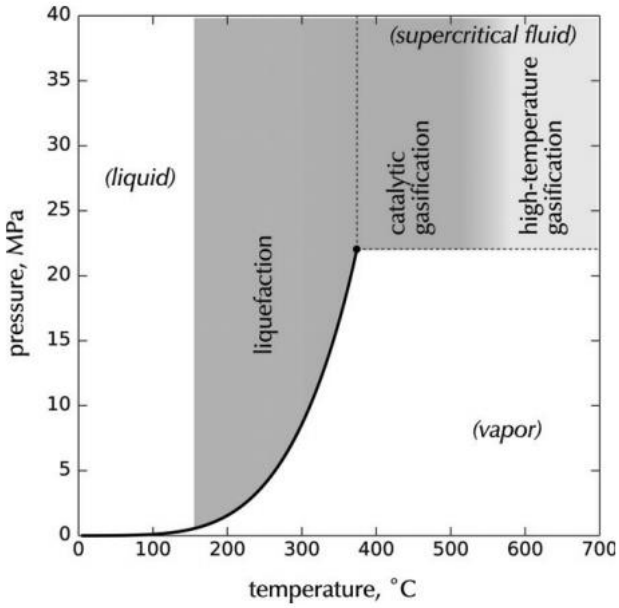


Figure 2.5. Pressure-temperature phase diagram of water (Peterson et al., 2008)

4.3.1. Algae HTL

A production system of biofuels from algae liquefaction is same with lipids extraction method until the hydrothermal liquefaction step (Elliott et al., 2013; Frank et al., 2013; Zhu et al., 2013). Instead of producing biodiesel, bio-crude oil is generated in this process and then goes to the hydrodeoxygenation and upgrading steps. In these steps, hydrogen is added into the reactor to consume the oxygen and nitrogen in the crude oil to increase the chemical stability.

The hydrothermal liquefaction of algae technology is typically performed with the condition of temperatures ranging from 200 to 375º C, pressure range from 10 to 20 MPa, reaction time from 5 to 90 minutes (Zhu et al., 2013). Some previous works of algae liquefaction are summarized in Table 2.6. With the test temperature of 300º C and 350º C, the general bio-crude yield from algae HTL is 30 to 40% wt. and the high heating value (HHV) of the oil produced are ranging from 33.2 to 40.1 MJ/kg.

In a typical HTL process, whole algae or lipid extracted algae (LEA) as feedstock are sent to the reactor treated with high temperature and high pressure, converting to gas, solid, liquid and crude oil. The solid phase usually contains char and ash (Valdez et al., 2012). CO_2 and CH_4 are the main compositions in the gas phase (Duan and Savage, 2011; Elliott et al., 2013). Aqueous phase basically is water containing 1.8 to 3.7% wt. carbon and 0.5 to 1.1% wt. nitrogen (Elliott et al., 2013). Crude oil is mainly made up of alkyl benzenes, phenols, C_{16} to C_{18} fatty acids and amides, naphthalene, cholesterol, other heavy compounds, and a small fraction of moisture (Duan and Savage, 2011; Ross et al. 2010; Zhu et al., 2013).

The elemental contents of bio-crude from algae HTL are shown in Table 2.7. The carbon content ranges from 67.9 to 79.2% wt.; hydrogen content ranges from 8.7 to 11.1% wt.; oxygen content ranges from 5.3 to 15.3% wt.; nitrogen content ranges from 3.3 to 7.9% wt.; sulfur content ranges from 0.30 to 0.96 % wt.. Compared to petroleum which is 83 to 87% wt. carbon, 10 to 14% wt. hydrogen, 0.1 to 2% wt. nitrogen, 0.05 to 1.5% wt. oxygen and 0.05 to 6.0% wt. sulfur (Speight, 1999), bio-crude has much higher nitrogen and oxygen contents, required upgrading to have a better performance.

Table 2.6. Comparison of HTL process

Reference	Algal species	Lipid	Protein	Carbohydrate	Reactor type	HTL temp. (° C)	HTL pressure (Mpa)	Holding time (min)	Oil yield (% wt.)	Oil HHV (MJ/kg)
Dote et al., 1994	*Botryococcus braunii*	—	—	—	Batch	300	—	—	57.0-64.0	—
Minowa et al., 1995	*Dunaliella tertiolecta*	20.50%	63.60%	15.90%	Batch	300	10	60	37.0	36.0
Ross et al. 2010	*Chlorella vulgaris*	—	—	—	Batch	300	—	60	19.6-23.0	34.2-37.2
	Chlorella vulgaris	—	—	—	Batch	350	—	60	19.1-27.3	33.2-39.9
	Spirulina	—	—	—	Batch	300	—	60	11.6-15.5	34.1-37.8
	Spirulina	—	—	—	Batch	350	—	60	14.2-20.2	33.4-35.6
Elliott et al., 2013	*Nannochloropsis sp.*	—	—	—	Continuous	350	20	15	38.0-63.6	—
Jazrawi et al., 2013	*Chlorella*	4%	60%	25%	Continuous	300	20	3	33.8	33.0
	Chlorella	4%	60%	25%	Continuous	350	20	3	41.7	33.8
Valdez et al., 2012	*Nannochloropsis sp.*	14%	59%	20%	Batch	300	—	60	39.9	—
	Nannochloropsis sp.	14%	59%	20%	Batch	300	—	90	39.4	—
	Nannochloropsis sp.	14%	59%	20%	Batch	350	—	60	40.2	—
	Nannochloropsis sp.	14%	59%	20%	Batch	350	—	90	41.1	—
Duan & Savage, 2011	*Nannochloropsis sp.*	28%	52%	12%	Batch	350	—	60	35.0-57.2	35.4-40.1
Brown et al., 2010	*Nannochloropsis sp.*	28%	52%	12%	Batch	350	—	60	43.0	39.0
Jena et al., 2011	*S. platensis*	13.30%	48.36%	30.21%	Batch	350	20.6	60	40.7	34.2
Biller & Ross, 2011	*Chlorella vulgaris*	25.00%	55.00%	9.00%	Batch	350	—	60	35.0	35.1
	Nannochloropsis oculata	32%	57%	8%	Batch	350	—	60	34.0	34.5
	Porphyridium cruentum	8%	43.00%	40%	Batch	350	—	60	21.0	35.7
	Spirulina	5%	65.00%	20%	Batch	350	—	60	28.0	36.8

Table 2.7. Elemental analysis of bio-crude

Reference	Carbon % wt.	Hydrogen % wt.	Oxygen % wt.	Nitrogen % wt.	Sulfur % wt.
Elliott et al., 2013	77.00-79.20	10.00-10.60	5.30-8.00	4.00-4.70	0.30-0.50
Jazrawi et al., 2013	67.90-70.70	8.70-8.90	12.00-15.30	7.20-7.90	0.80-0.90
Valdez et al., 2012	71.40-74.20	—	9.60-11.70	6.40-7.30	0.48-0.62
Duan and Savage, 2011	69.60-76.10	9.40-11.10	8.34-9.46	3.33-4.33	0.31-0.96

Bio-crude is required to upgrade for commercial application to reduce the high oxygen, nitrogen and sulfur content. Zhu et al. found that the oxygen and nitrogen elemental contents in bio-crude was reduced from 5.66 to 0.85, and 4.27 to <0.05 respectively (using what catalyst and conditions), calculated on % wt. dry basis (Zhu et al., 2013).

4.3.2. Carbohydrates HTL

Cellulose and starch are common carbohydrates which can be hydrolyzed to generate glucose and other saccharides as well as their further degraded derivatives under the condition of hydrothermal liquefaction process. Figure 2.6 illustrates the main steps of carbohydrates decomposition. Both cellulose and starch are made up of glucose monomers, however, chemical bonds in cellulose are β-(1→4)-glycosidic bonds while starches' are α-(1→4) and α-(1→6) bonds. Different carbohydrates are usually hydrolyzed in a various reaction rate. The degradation rate of starch is faster than cellulose.

Moreschi et al. (2004) hydrolyzed the ginger bagasse starch in subcritical water and carbon dioxide under the condition of 150 bar and temperatures of 176, 188 and 200º C. The results showed that in 200º C hydrolysis was performed with higher degree (97.1%

after 15 min) and higher reducing sugars yield (18.1% after 11 min). The reaction was assumed to be heterogeneous and in first-order. In kinetics study, activation energy was found to be 180.2 kJ/mol and preexponential factor was 5.79×10^{17} s^{-1}.

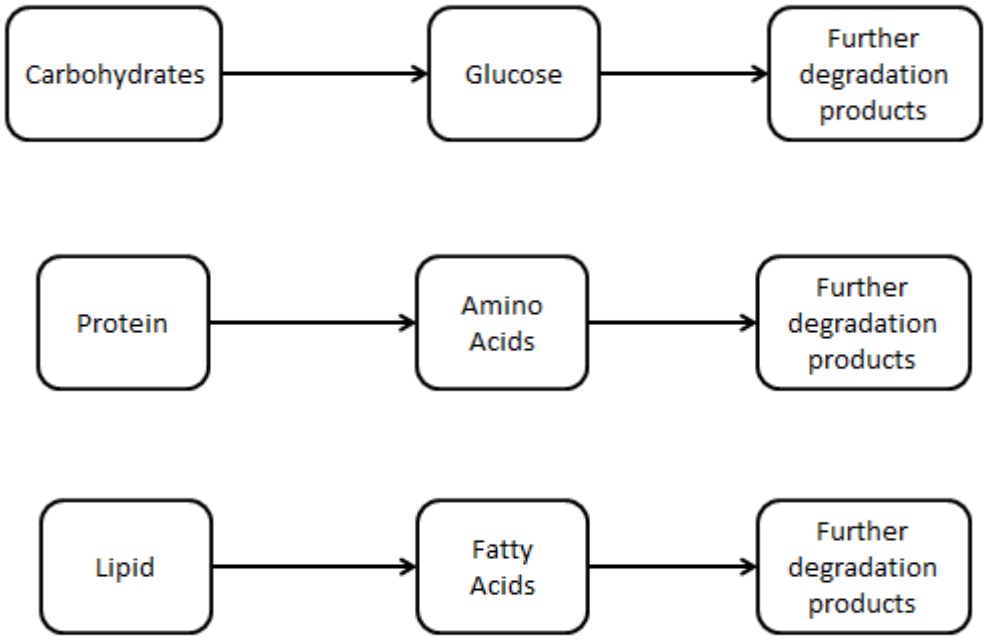


Figure 2.6. Sketch map of carbohydrates, protein and lipid decomposition

Sweet potato starch was converted into glucose in a batch reactor under the hydrothermal condition of 180-240º C by Nagamori and Funazukuri (Nagamori and Funazukuri, 2004). Glucose, maltose, fructose and aldehydes were found in the products, and they stated that at longer reaction times the produced sugars were easily decomposed, which increased aldehydes yield.

Saka and Ueno studied the chemical conversion of different cellulose to glucose and its derivatives via supercritical water (Saka and Ueno, 1999). They treated celluloses I and celluloses II for 3-105 s under the condition with temperature of 500º C and pressure of 35 MPa and found that glucose could achieve a high amount about 5-10 s supercritical

treatment after 15 s preheating up to 374º C. Comparing experimental results of celluloses and corn starch, they concluded that the hydrolysis proceeded in supercritical water was slight faster in starch than in cellulose.

Hydrolysis of microcrystalline cellulose in a continuous flow reactor was investigated (Kumar and Gupta, 2008). Under the temperature of 335º C, about 65% of cellulose decomposed to the oligomers and monomers in 4.8 s. Increasing the reaction time or temperatures, oligomers and monomers could further degrade to glycolaldehyde dimer, D-fructose, 1,3-dihydroxyacetone dimer, anhydroglucose, 5-HMF, and furfural.

Jing and LÜ (2008) researched on glucose decomposition in superheated water in the temperature range from 180 to 220º C with a pressure of 10 MPa. The main products were found to be 5-hydroxymethylfurfural (5-HMF) and levulinic acid (LA) and their degradation rate were investigated as well. The degradation activation energies of glucose, 5-HMF and LA were estimated respectively as 118.85, 95.40 and 31.29 kJ/mol, and preexponential factors were 1.40×10^{11} min^{-1}, 1.21×10^{8} min^{-1} and 0.31×10^{-1} min^{-1}, respectively.

4.3.3. Protein HTL

Proteins are major and important biomass components. A large amount of compounds in algae is protein. Peptide bonds connect amino acids together into peptide-chains which constitute protein. It is very important to understand the degradation of protein in the production of algal biofuels because a huge fraction of nitrogen in proteins will remain in the bio-oil, affecting smell, combustion, and other properties of the fuel. Figure 2.6 illustrates the main steps of protein decomposition. First, proteins are degraded into amino acids which then react to produce more complicated degradation products.

Rogalinski et al. used bovine serum albumin (BSA) as feedstock to study the production of amino acids in continuous subcritical water hydrolysis (Rogalinski et al., 2005). The highest yield of amino acids was achieved at a residence time of 65 s and temperature of 290º C. The activation energy and frequency factor of BSA degradation for the total amino acids were 114.8 kJ/mol and 2.326×10^{8} s^{-1}, respectively. For amino acids further decomposition, the activation energy and frequency factor were 122.2 kJ/mol and 2.485×10^{10} s^{-1}, respectively. The main products of amino acids degradation found in this study were acetic acid, propanoic acid, n-butyric acid, iso-butyric acid, iso-valeric acid, ethanolamine and omithine.

A previous study regarding biomass gasification found that protein could reduce the gas yield (Kruse et al., 2007). They used glucose as model compound of phyto mass and alanine as model compound of zoo mass. According to the results, they proposed that the carbohydrate and protein degradation pathway might interfere with each other via the Maillard reaction which promoted free radical scavengers and inhibited free radical chain reactions. Gases yield reduced because of the inhibition of the free radical reactions.

Bean dregs were used as protein material to study the kinetics of protein hydrolysis in subcritical water (Zhu et al., 2011). The optimum hydrolysis condition was at 200º C for a residence time of 20 min and the total amino acids yield achieved 52.9%. The activation energy and pre-exponential factor of total amino acids production found were 14.6 kJ/mol and 5.16×10^{-2} s^{-1}, respectively. For total amino acids degradation reactions, the activation energy and pre-exponential factor found were 79.1 kJ/mol and 2.696×10^{5} s^{-1}, respectively.

Klingler et al. (2007) investigated the decomposition of the amino acids alanine and glycine as model compounds for proteins. The decomposition rates of alanine and glycine was described by simple rate laws with the order of 0.47 and 0.78, respectively. The activation energies and pre-exponential factors were 160 kJ/mol and 3.6×10^{11} $mol^{0.53}$ $L^{-0.53}$ s^{-1} for alanine decomposition, and 156 kJ/mol and 1.4×10^{12} $mol^{0.22}$ $L^{-0.22}$ s^{-1} for glycine decomposition.

4.3.4. Lipid HTL

Lipid is a high energy containing compounds. The typical form of lipid in organism is triacylglycerides (TAGs) which consist of three fatty acids bounding to a glycerol as backbone. In hydrolysis process, a triglyceride (TG) reacts with water to produce fatty acid and a diglyceride (DG) which then degrades to a monoglyceride (MG) and fatty acid. Monoglyceride is continuously hydrolyzed to give a glycerol and fatty acid. At last, fatty acids can further react and produce more complicated long-chain hydrocarbons. The main steps of lipid decomposition are illustrates in Figure 2.6.

A previous kinetic model of thermal hydrolysis of sunflower oil was proposed, which showed the effects of different reaction temperatures and residence times on the reaction mechanism (Alenezi et al., 2009). The kinetics study was based on experiments conducted under the conditions of temperatures from 270 to 350º C and residence time up to 30 min at 20 MPa. They assumed three-step reaction was performed in the hydrolysis as mentioned in the previous paragraph. The kinetic parameters of their model were shown as the Table 2.8 below. From the results, they concluded that it required more energy to start the first reaction than the second and third reactions in the sunflower hydrolysis.

Table 2.8. Kinetic parameters of sunflower oil hydrolysis model*

Reaction	Activation energy E (kJ/mol)	Pre-exponential factor A (min^{-1})
TG to DG	98	5.2×10^{6}
DG to MG	38	1.1×10^{1}
MG to G	90	2.8×10^{6}

* Data were collected from Alenezi et al. (2009)

Soybean oil hydrolysis in subcritical water was also investigated (Milliren et al., 2013). Experiments were conducted in the temperature range of 250-300º C. The kinetic constants were assumed to be the same for TG, DG and MG. The activation energies and pre-exponential factors of specific reaction rate constants for the hydrolysis and its reversible reaction were 90.29 kJ/mol, 2.34×10^{5} min^{-1}, 158.75 kJ/mol, 7.76×10^{12} min^{-1}, respectively. Fatty acids from products were found to have the autocatalytic behavior of the reactions.

Hydrothermal processing of lipid in the whole algal cells were performed at temperatures of 250-350º C and residence time up to 3 h in order to study the kinetics (Jonson and Tester, 2013). The kinetics model included the degradation of unsaturated fatty acids as well. The authors found that short reaction times (< 30 min) with high temperatures (300-350º C) could obtain the maximum yield of free fatty acids before their degradations.

5. Assessments

5.1. Techno-economic analysis (TEA)

Techno-economic analysis (TEA) is a method to analyze an established system with the consideration of technology and costs. It can help make decisions in the management of

product and process developments. TEA is a very important and direction-steering tool when combining with process simulation and modelling in order to evaluate the feasibility economically. In the case of algae-biofuels, performing the techno-economic analysis of the algae liquefaction technology can greatly assist in avoiding misspent efforts and investment because algae biofuels technology is still under development and there is few commercial algae biorefinery plant been built today in USA. TEA can provide cost and performance boundaries of current potential algae biofuels conversion technologies to actually assist in creating new thoughts and solutions of process development and bottlenecks breaking.

To conduct TEA, the first step is to define the studied system processes and draw a simple flow diagram with each unit operations that used in the system. Second is to select the equipment for each processes and develop the basic theoretical configuration. Third, mass and energy balances for the system is performed. Fourth, cost analysis is conducted to estimate the total capital investment and annual operating cost of the system, meanwhile the price of the product is calculated. Last, the sensitivity analysis can be performed to determine the effects of key parameters to the costs. As the interest of algal biofuels increasing, many works have been done in the perspective of techno-economic on algal biofuels production in order to test the feasibility of commercialization (Lundquist et al., 2010; Davis et al., 2011; Ma, 2011; Rickman et al., 2013). These studies help understand how each unit operations in the production system relates to the cost of producing algal renewable alternatives.

Total capital investments and annual operating cost are two very critical values when performing TEA. Capital investments are referred to the cost usually spent before the real

operation of the industrial plant and the payment of expenses involved in the plant operation. Typically, it is including the cost of purchasing and installing the equipment, land and service facilities, piping, instruments, insulation, foundation, site preparations and working capital. Five types of capital cost estimation were summarized with the accuracy range and designations (Peters et al., 1991): 1) ratio estimation, with the accuracy over ±30%; 2) factored estimation, with the accuracy up to ±30%; 3) scope estimation, with the accuracy within ±20%; 4) project control estimate, with the accuracy within ±10%; 5) contractor's estimation, with the accuracy within ±5%. Among these five methods, factored estimation is based on the proportional factors of each category in the capital investment (Table 2.9), which is commonly used in the publications of techno-economic analysis. Purchased equipment cost is usually calculated based on the equipment sizing equation as below (Peters et al., 1991) and other components of capital investment are estimated based on the estimation factors.

$$Equip.\ cost = Ref.equip.cost \times (\frac{Vol.equip.}{Vol.ref.equip.})^{Exponent} \qquad \text{Eq (2.6)}$$

The exponent varies from 0.27 to 1.20 of different equipment but with a typical value of 0.6 (Peters et al., 1991). The installation cost of equipment is in the range of 20-90% of the equipment purchase cost based on the different type of equipment.

Annual operating cost typically includes the cost of raw materials, labor, utilities, facilities maintenance, and miscellaneous. The raw materials is usually involved in the chemical industries and their annual cost is based on the amount used in the mass balance and the unit cost. The labor cost can be referred to similar plant or previous published data and hourly wages or salary for different type of labors in different industries can be based on the data in the U.S. Bureau of Labor. For a 24/7 operating plant, three shifts is

commonly applied for the operating labors with one shift of 8 hrs. The utilities usually include electricity, fuels, natural gas, heat transfer agents such as steam and cooling water, and compressed air. Their annual cost can be obtained by multiplying their annual amount from the mass or energy balance by their unit cost. The maintenance cost can be various from 2% of the equipment cost to average 6% of the fixed-capital investment (Peters et al., 1991). Miscellaneous cost is usually estimated as 5% of the total operating cost.

Table 2.9. Estimation factors of each category of capital investment*

Category	Factors Range, %
Purchased equipment	15-40
Installation	6-14
Instrumentation	2-8
Piping	3-20
Electrical	2-10
Building	3-18
Yard Improvements	2-5
Service facilities	8-20
Land	1-2
Engineering and supervision	4-21
Construction	4-16
Contractor's fee	2-6
Contingency	5-15

*. Data were collected from Peters et al. (1991)

TEA has been used to evaluate the biomass and biofuels production systems to determine their economic sustainability compared with fossil fuels (Table 2.10). Wright et al. (2010) studied the cost of corn stover fast pyrolysis to produce bio-oil and found that bio-oil from biomass was potentially competitive by an n^{th} plant under current technology but for

a pioneer plant, the technology required further development to reduce uncertainties in costs. Ethanol from biomass thermochemical conversion process was also considered as potential cost-competitive substitute for gasoline (Dutta et al., 2011). Besides the technical issues, plant and facilities location could also highly influence the economic feasibility of fast pyrolysis biorefinery of biomass (Brown et al., 2013).

Table 2.10. Summary of TEA works of biofuel production

Reference	Feedstock	Technology	Yield (MM gal/yr)	Capital cost ($MM)	Operating cost ($MM/yr)	Product value ($/gal)
Wright et al., 2010	Corn stover	Fast pyrolysis (H_2 onsite)	35.4	287	109	3.09
	Corn stover	Fast pyrolysis	58.2	200	123	2.01
Dutta et al., 2011	Corn stover	Gasification	64.7	516	59	3.11
Brown et al., 2013	Biomass	Fast pyrolysis	-	363	84	-
Lundquist et al., 2010	Algae	Wastewater treatment-Lipid extraction	0.54	36	2.96	0.67
	Algae	Pond-Lipid extraction	0.52	31	2.18	7.90
	Algae	Pond-Lipid extraction	2.07	102	8.09	5.71
Davis et al., 2011	Algae	Pond-Lipid extraction	9.3	390	37	9.84
	Algae	PBR-Lipid extraction	9.3	990	55	20.53
Ma, 2011	Algae	Lipid extraction	0.48	-	2.95	0.49
Zhu et al., 2013	LEA	HTL	26.9	262	49	2.64
Jones et al., 2014	Algae	HTL	54.0	468	192	4.77

In case of economics of algae biofuels production, Lundquist et al. (2010) investigated five scenarios of algae biofuels production system with different emphasis on wastewater treatment, biogas production and biodiesel production and found that biofuels production of algae was not economically favorable unless it was as a byproduct of wastewater treatment and scaling up of the system could reduce the production cost of biodiesel. To

achieve a 10% rate of return, the algal biodiesel product selling prices were found to be $9.84/gal for open pond cultivation (Davis et al., 2011). Given the current petroleum diesel selling price of $3.5 to $4.0/gal, this results shows that microalgal biofuel will not be competitive with traditional fossil fuels if a large scale facility are to be built today. But, Zhu et al. (2013) demonstrated the promising potential of biofuels production from LEA HTL processes which might result in a competitive fuel selling price with conventional petroleum-based gasoline and diesel.

Sensitivity analysis is a study regarding how the uncertainty in the inputs of a mathematical model or system can influence the uncertainty in its output (Saltelli et al., 2008) and it is usually used in the cost analysis. Using sensitivity analysis for water usage during algal biodiesel production, Yang et al. (2011) found that the water consumption is mainly sensitive to recycling, evaporation rate, algal lipid content and growth rate. The key factor of sensitivity and uncertainty in the microalgae pond production system is the growth rate of the algae (Campbell et al., 2011). Oil yield in the HTL process has a large influence on the energy use during HTL (Frank et al., 2013).

5.2. Life cycle assessment (LCA)

Life cycle assessment (LCA) is a method which conducts cradle to grave analysis of processes or product systems. Generally, LCA is used to quantify material use, energy consumption and emissions of a certain system. Assessment of environmental, health and social impacts is usually included in LCA. The LCA process is a systematic, phased approach and consists of four components: goal definition and scoping, inventory analysis, impact assessment, and interpretation.

Goal definition and scoping stage defines and describes the system that is investigated, which the assessment is to be conducted and identify the boundaries and environmental effects to be reviewed for the assessment. Inventory analysis stage identifies and quantifies items usage such as energy, water, materials and environmental release. Assessment of the potential human and ecological effects of energy, water, and material usage and the environmental releases identified in the inventory analysis is performed in the impact assessment. Interpretation evaluates the results of the inventory analysis and impact assessment with a clear understanding of the uncertainty and the assumptions used to generate the results (SAIC, 2006).

Many works have been done on LCA of biofuels production from algae (Lardon et al., 2009; Sander and Murthy, 2010; Campbell et al., 2011; Singh & Olsen, 2011; Yang et al., 2011; Frank et al., 2013). A general system boundary of biofuel production is illustrated in Figure 2.7. LCA of algal biofuels starts with cultivation and ends with the final product. The application of biofuels sometimes is also included in the boundary (Frank et al., 2012).

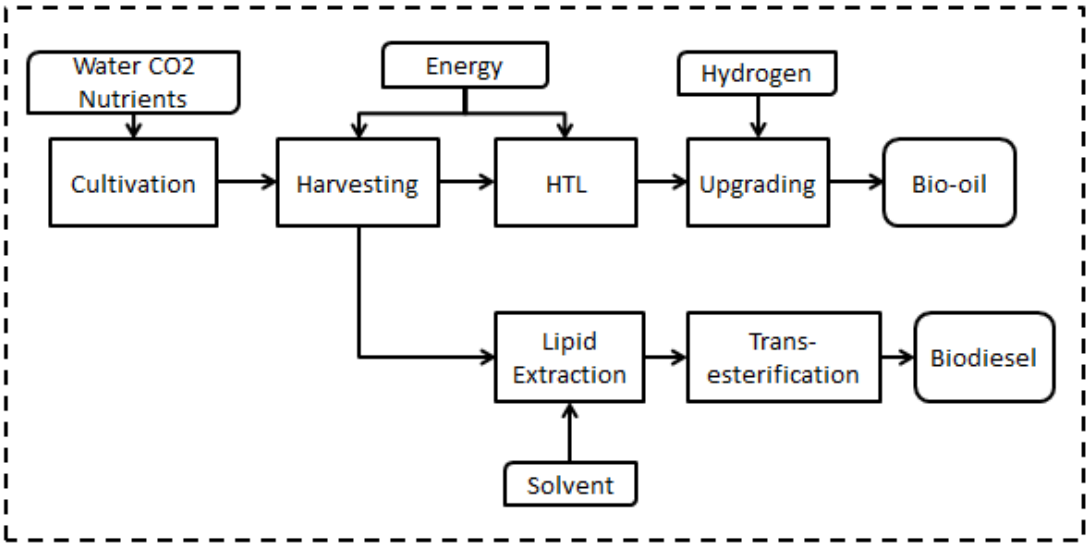


Figure 2.7. System boundary of biofuels production from algae

Most of these LCA papers have found that the huge energy consumption of microalgae cultivation and harvesting is a big drawback of the system. Thermal dewatering of algae cake was the largest energy consumption part which was 89% of total energy inputs (Sander & Murthy, 2010). Lardon suggested to control fertilizer consumption and to use wet extraction for lipids to reduce energy use (Lardon et al., 2009). Besides, recycling harvest water could reduce 84% water and 55% nutrients consumption while using seawater could save 90% water usage and only need to provide phosphate (Yang et al., 2011). A research investigating scenarios with different CO_2 supply source and different production rates of algae biodiesel found it had less GHG emissions than canola and ULS diesel while costs were similar (Campbell et al., 2011). Combination of algae cultivation and power plant flue gas treatment may significantly reduce the GHG emissions (Kadam, 2001). Several scenarios were built in a study with different nutrients recovery step. The baseline biofuel from algae produced 55,400 g CO_2 eq per million BTU which was about half of low-sulfur petroleum diesel (Frank et al., 2012).

6. Summary

Microalgae is a promising source for biofuels production due to its high growth rate and lipid content compared with other biomass. Open raceway ponds as algae cultivation system are more economically favorable than closed photobioreactors for the commercial scale production. Although photobioreactors have relatively high growth rate of microalgae, high cost for illumination is a big barrier for its scaling up. Combinations of several unit algae harvesting operations are commonly used for microalgae dewatering and drying in order to highly concentrate algae slurry before conversion process. HTL of microalgae can be performed in a liquid basis, thus the drying process of algae is no

longer needed. It can save considerable energy in the harvesting process compared with lipid extraction method for biodiesel production. An upgrading process is necessary for algal biofuels because of its high oxygen and nitrogen content which comes from the high protein and unsaturated fatty acids content in algae species. Microalgae biofuels have the potential of being both economically and environmentally sustainable, however, development is required to current technologies to reduce the cost and risk of investment.

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CHAPTER 3

TECHNO-ECONOMIC ANALYSIS OF ALGAE LIQUEFACTION TECHNOLOGY

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Abstract

Biofuel from algae liquefaction is a promising technology to produce renewable liquid fuels, primarily due to the high growth rate and high photosynthesis efficiency of algae organisms compared to woody biomass. Hydrothermal liquefaction (HTL) is a high temperature (200 to 375º C) and high pressure (10 to 20 MPa) conversion method to degrade complex organic compounds into bio-crude. The main objective of this study was to develop a process simulation model for algae liquefaction technology to estimate the mass flow rate, the total energy consumption and economic feasibility of producing algae bio-crude oil. The model included four major operation sections: algae cultivation, harvesting, two-stage hydrothermal liquefaction combining with hydrodeoxygenation and separation to produce bio-crude analogous to petroleum crude oil. The economics of simulated algae liquefaction refinery was conducted using discounted cash flow method. As the results showed, the refinery could produce 578,661 gallons of bio-crude per year with the total capital investment and annual operating cost estimated as $113,231,000 and $13,110,000 respectively. The minimum selling price of the bio-crude oil was estimated as $49.80/gal with the plant life of 30 years and 7% annual percentage rate (APR). When increasing the capacity to 10 million gallons bio-crude per year the price reduced to $42.95/gal. In the sensitivity analysis, the hydrothermal liquefaction yield was found to influence the oil price most and the fertilizer cost influenced least. The bio-crude price might be reduced significantly to compete with fossil crude due to the algae biofuel refinery technology improvement.

Keywords: biofuel, sustainability, hydrothermal conversion, algae production, biorefinery process design

1. Introduction

Renewable energy as a potential substitute for fossil energy has received increasing attentions nowadays. The energy independence and security act (EISA) approved by the US federal government in 2007 requires a continuous increase in the production of renewable fuels to achieve the goal of producing 36 billion gallons per year by 2022. Microalgae have been reported as a potential biomass resource to satisfy the production target of 2022 due to their high lipid content and growth rate. The typical lipid content in algae varies from 20 to 50% wt. while soybean and oil palm is around 20% wt. (Johnson, 2012). It was also claimed that the algae cell grown with a doubling time of 1 to 10 days (Schenk et al., 2008) and they had 15 to 300 times more oil production than conventional crops such as soybean on a per acre basis (Li et al., 2008).

Hydrothermal liquefaction (HTL) is a high temperature and high pressure process for the reduction of complex organic materials such as biomass into crude oil and other chemicals. The reaction is suitable for high moisture content slurry such as algae because it is liquid based and no drying is required for the feedstock. In addition, it was found that HTL could produce more biofuel than lipid extraction method because not only the algal lipid was used, but also the carbohydrate and protein fractions contributed to the oil (Frank et al., 2013). The typical reaction condition is of temperature range from 200 to 375º C, pressure range from 10 to 20 MPa, reaction time from 3 to 90 min depends on the mode of operation: batch or continuous (Elliott et al., 2013, Jazrawi et al., 2013 and Zhu et al., 2013). The bio oil yield from HTL process varies from 23.0 to 64.0 % wt. because of the large range of lipid content of algae (15 to 50 % wt.) (Zhu et al., 2013).

Water consumption and nutrients usage are critical factors of algae production, which must be taken into consideration when evaluating the algae liquefaction technology. Besides, the high oxygen and nitrogen content in the final product oil is another big issue for commercialization. Hydrodeoxygenation (HDO) is usually used for upgrading the bio oil. Jazrawi et al (2013) investigated the effect of reaction temperature (300 or 350º C) and slurry concentration (5 or 10% wt.) on the composition of the bio oil from *Chlorella* and found that the oxygen and nitrogen contents were ranging from 12.0 to 15.3% and 7.2 to 7.9%, respectively. Nevertheless, the oxygen and nitrogen content in the petroleum was stated in the range of 0.05 to 1.5% and 0.1 to 2.0%, respectively (Speight, 1999).

Techno-economic analysis (TEA) is a method to analyze of an established system in concert with technology and market-driven prices. In order to produce green energy, it is very important to perform TEA of algae liquefaction technology. Many researches have been done towards economic analysis of algae biodiesel production through lipid extraction (Davis et al., 2011, Lundquist et al., 2010, Ma, 2011 and Rickman et al., 2013), but few on algae liquefaction to produce biofuel. The cost of algae biodiesel was estimated in a very various range due to the different technologies, parameters and assumptions that were used in the evaluation such as cultivation method, algae productivity, and lipid content and so on. It was claimed that the cost of algae biofuel production varied from $1 to more than $40 per gallon in different studies (Sun, 2009). Apparently, algae biofuel technology is still under development and the optimum method is remained unidentified.

The main objective of this research is to evaluate the economic impacts of producing bio-crude oil from a continuous two-stage microalgae liquefaction technology which is

considered as a way to make the best use of the algae mass and to reduce the nitrogen content in final product oil, in order to give suggestions on possible opportunities to reduce the production cost in the future research. The simulation model was designed with a software, SuperPro Designer V8.5.

2. Simulation Design

2.1. Design Basis

The algae species and composition significantly influence the overall process design and cost estimation. Carbohydrate, lipid and protein are three key fractions in algae. In a previous work, it was claimed that *Spirulina* contains 65% protein, 20% carbohydrates and 5% lipid (dry and ash free basis % wt.) while *Chlorella* consists of 55% protein, 9% carbohydrates and 25% lipid (Biller and Ross, 2011). In this design model, the composition of algae was assumed as 28% carbohydrates, 25% lipid and 47% protein, which was modified from other studies (Frank et al., 2013 and Lardon et al., 2009).

The design capacity of the algae liquefaction plant of the base case is to produce 0.5 million gallons of bio-crude per year. It was assumed that the plant run 24 h/d and 330 d/yr with a plant life of 30 years. The plant was designed as a continuous system, which included nutrients storage and feeding, algae cultivation and harvesting, slurry storage, water, and nutrients recycling, two stages hydrothermal liquefaction, hydrodeoxygenation, liquid-liquid extraction and product storage. The whole plant was divided into four major sections: cultivation, harvesting, HTL and separation (Figure 3.1).

2.2. Process Design

In the cultivation section, sodium nitrate, dipotassium phosphate as nutrients mixed with water in the feeding tank, then sent to the open raceway pond as algae cultivation

medium. CO_2 was pumped directly to the pond to provide carbon source. A single unit pond was as large as 40,000 m^2 with depth of 30 cm and its design followed the previous work (Lundquist et al., 2010). The algae productivity was assumed as 25g/m^2/d and the algae growth was modeled with kinetics from other study (Goldman and Carpenter, 1974). More information about algae growth modeling can be found in the Appendix A.

Algae slurry from the open raceway pond was then sent to the harvesting section to dewater through thickening, dissolved air flotation and centrifugation from 0.5 to 150 g/L of the slurry concentration. The water collected from slurry dewatering was 100% recycled to reuse in the raceway pond.

Harvested algae slurry went to the HTL section to produce bio-crude oil. Two stages HTL process combined with HDO system were modeled to reduce nitrogen content in the crude oil. At the first stage, nitrogen dissolved in aqueous phase was removed by centrifugation after protein hydrolyzed in a plug flow reactor for 15 min at the low temperature of 225º C at which carbohydrate and lipid only slightly hydrolyzed. The solid phase was sent to the second stage PFR for further decomposition at 350º C for 60 min to generate crude oil which then was reacted with hydrogen with the presence of Ru/C as catalyst in a continuous stirred-tank reactor at the same temperature for 240 min to reduce nitrogen and oxygen content. Reactions were simulated based on the kinetics and the mass balance from experimental works. More details of HTL and HDO process are provided in the Appendix A.

After HDO process, remaining solid was filtered off by a rotary vacuum filter and upgraded crude oil was extracted from oil-water mixture by dichloromethane which

might be recycled by distillation. Final crude oil went to storage tanks for further transportation.

3. Cost Estimation

The techno-economic analysis (TEA) performed here used the concept of 'n^{th}-plant' economics which meant that the designed plant was not a pioneer plant and several plants using the same technology have already been built and used so that the risk financing, longer start-ups, equipment overdesign, and other costs associated with first-of-a-kind were not taken into consideration.

3.1. Total Capital Cost

The total capital cost refers to the fixed costs that are associated with a process, which includes direct fixed capital (DFC) and working capital (WC).

DFC is the cost of fixed assets such as equipment, which is calculated as the sum of the total plant cost (TPC), contractor's fee and contingency. In this model, the DFC was estimated from the purchase cost of major equipment and cost factors of other elements in DFC (Table 3.1).

The purchased costs (PC) refers to the vendor's selling price which is the free-on-board cost excluding the taxes, insurance, delivery and installation. The PC of the main equipment was calculated based on the follow equation. Where C_0 is the base cost, Q_0 is base capacity, Q is simulated capacity and a is scaling factor.

$$PC = C_0(\frac{Q}{Q_0})^a \qquad \text{Eq (3.1)}$$

The working capital refers to the costs that can cover the operation of the plant for a certain amount of time including labor, raw material, utilities and waste disposal. In the

model, it was assumed that the working capital cost was 18% of the direct fixed capital, which referenced from solid-liquid industry processes (Peters et al., 2003).

3.2. Annual Operating Cost

The annual operating cost (AOC) refers to the costs that are related to the annual demand of resources including feedstock, labor, heat transfer agent, power and additional operational costs.

The inputs to the plant include water, CO_2, sodium nitrate, dipotassium phosphate, hydrogen, dichloromethane and Ru/C, however, CO_2 and nutrient costs varied from different sources. The unit costs of feedstock are illustrated in the appendix. If the algae cultivation process combined with flue gas and wastewater treatment, CO_2 and nitrogen fertilizer will be much cheaper than the regular industrial prices. This was discussed and studied in the sensitivity analysis.

The employees' number and type of the plant were determined depended on previous work (Dutta et al., 201, Humbird et al., 2011, Knorr et al., 2013 and Lundquist et al., 2010). In the large capacity production plant, control technology for a fully automatic operation is installed and only needs several people to take care of the control system. The number of 15 operating labors were assigned to work in the algae production sections and 5 to work in the algae conversion sections. Each section had one supervisor and one quality control analysts. The details of labor cost and distribution can be found in the Appendix A.

The major energy cost in this system is the electricity and thermal energy. The overall electricity energy cost was assumed about $0.06/kWh which was depended on a previous

TEA work (Humbird et al., 2011). The electrical energy mainly consumed by heating and stirring the feedstock.

Solid wastes and wastewater were produced in the separation section from rotary vacuum filter and crude oil extractor respectively. The disposal cost of the unreacted algae biomass was estimated as $0.02886 per kg (Humbird et al., 2011) and the wastewater treatment cost was assumed as $0.01 per gallon.

The maintenance cost accounts for additional costs related to the use of a facility such as equipment maintenance. In the model, the maintenance cost of specific equipment was obtained by multiply the purchase cost with the maintenance cost factor which was 0.15 for thickener, flotation tank, bowl centrifuge and rotary vacuum filter, and 0.1 for other equipment. The miscellaneous operating cost was estimated as 5% of the annual operating cost.

4. Results and Discussion

4.1 Crude Oil Yield

The designed algae liquefaction plant runs 24 h/d and 330 d/yr which equals to 7920 h annually to produce 578,661 gallons crude oil per year. Table 3.2 gives the overall mass balance regarding to feedstock and products. The details of stream mass balance are shown in the Appendix A. The water consumption was remarkable for algae liquefaction technology compared with other feedstock usage due to low concentration of algae slurry (0.05% wt.) in the cultivation medium, thus, recycling of water is very important and necessary of microalgae production. The amount of 19.80 kg harvested algae (dry and ash free) was required to generate 1 gallon of final crude oil. With the assumption of oil density of 873.90 g/L, the overall conversion rate from harvested algae to final crude oil

was about 17% on the weight basis which matched with the experiments data. In the carbon balance, around 61% of the carbon in the initial input of CO_2 was end up remained in the crude oil produced. The rest about 39% of the initial carbon was lost during the production through emission, wastewater and solid disposal.

4.2 Water Balance

Water consumption of algae production is typically very high compared to other biomass cultivation in terms of gallons of water used per kg of biomass produced. Because of the huge amount of water required, algae production is usually combined with wastewater treatment or using seawater.

Based on the simulation model, about 88% of the water in the open raceway pond could be recycled from the harvesting and HTL processes and the add-on water from input was about 12%, which was estimated as 929 million gallons per year. The add-on water to the pond mainly compensated for the loss of evaporation. The detailed water balance is illustrated in the Figure 3.2. Taken together, the annual net water consumption of the algae liquefaction plant was 944 million gallons excepting the water used for heat transfer agents which was included in the energy balance section below. If recycling system was not utilized in the plant, then water usage would increase as 10 times larger of the amount with recycling on site. Taken the economic issue into account, water reuse in the algae industry was considered as a requirement to avoid remarkable feedstock cost.

4.3 Energy Balance

Two types of energy were provided in the simulation model to run the entire plant: electricity and heat transfer agents. Electricity was used for pumping, stirring and high temperature heating (350° C). Heat transfer agents included steam, steam with high

pressure, cooling water and chilled water. Details of the heat transfer agents are described in the supporting information in appendix.

The total of 37,988,573 kWh of electricity and 1,917,998 metric metric tons (MT) of heat transfer agents were used per year in the algal bio-crude plant which gave the total cost of $3,148,557 annually. For the electricity, the usage percentage of each operation section is illustrated in Figure 3.3. To reduce the high consumption of the electricity, it is better to improve the efficiency of the mixing in the open raceway pond or to improve the heat transfer rate in the HTL and HDO processes. In addition, off gases from the processes can be used to generate electricity in order to recover the heat and create electricity credits (Jones et al., 2014). For the heat transfer agents, chilled water and cooling water were consumed of a large amount of 759,977 and 1,124,003 MT per year, respectively, compared with the relatively low usages of the steam (21,414 MT) and steam with high pressure (12,604 MT). Together, the total cost of heat transfer was $869,242 and the total cost of the electricity was $2,279,315.

4.4 Cost Analysis

The cost summary of the whole plant is described in the Table 3.3 with details. The total capital investment was estimated as $113,231,000 and the annual operating cost was $13,110,000. The bio-crude was annually produced of 578,661 gallons with the annual unit production cost of $22.66 and the minimum selling price (MSP) of $49.80/gal. The minimum selling price was estimated as the selling price that made the net present value (NPV) equal to zero using the discounted cash flow method with an APR value of 7%, however, the annual unit production cost was calculated just by the annual operating cost divided by the bio-crude yield.

Jones et al. (2014) estimated the MSP of the algal biodiesel as $4.77/gal ($4.49/GGE) using the 2022 projection incorporating improvements to the current whole algae liquefaction technology. Nevertheless, the MSP of algae bio-crude was estimated as $49.80/gal ($44.30/GGE with energy density of the algal bio-crude as 40 MJ/kg) in this simulation, which is about 10 times higher than the estimation of Jones et al. (2014). The reasons why there was a very large difference between the MSPs were considered to be the high conversion yield, low feedstock price, and electricity and hydrogen generation onsite from the off gases that Jones et al. (2014) used in their simulation. They used the oil yield in the HTL process as 59% wt. of the feeding algae (dry and ash free) and 77% wt. upgrading yield in the hydro-treating process. Together, the yield from dry and ash free algae to the final upgraded oil was about 45% wt.; however, in this simulation, the conversion yield from algae to final crude oil was only around 17% wt. Besides, they did not model the costs for algae growth, harvest and dewatering, but instead, used a single feedstock cost of $430/ton ($474/MT) for wet algae at 20% wt. solids in 2022 target case. Furthermore, they accounted the credits of co-products such as naphtha and electricity so the utilities cost reduced and the profits increased, and their plant capacity was 54 million gallon of diesel per year which was 100 times of our plant capacity. Due to the engineering issue, increasing the plant capacity may reduce the cost of the production and it will be discussed in the next section.

Figure 3.4 illustrates the capital cost breaking down with the each section. From the figure, it is obvious that algae cultivation and HTL & HDO sections contribute most cost of the total capital investment with 38.80% and 39.06%, respectively. The cultivation section had a large amount of cost of the equipment due to 38 ponds used for the algae

growth and the high capital cost of HTL & HDO section was because the high cost of the installation of the high pressure equipment. Separation section had the lowest capital cost of 6.06% of the total and harvesting processes was about 16.08% of the total. Above all, to reduce the total capital cost, it is better to minimize the cost of algae cultivation and HTL & HDO sections.

The breakdown analysis of the operation cost was conducted and shown in Figure 3.5. From the results, the cost of the raw materials was the highest, which was 39.54% of the total operating cost. Nutrients, water and hydrogen possessed the majority cost of the feedstock. The second high operating cost was the utilities, which was about 23.19% of the total. Labor and facilities costs were more or less the same with each other, which were 14.09% and 14.94% respectively. The miscellaneous and waste treatment costs only contributed a little to the total operating cost. Reducing the cost of the feedstock would considerably decrease the total operating cost of the algae liquefaction technology. Instead of using fresh water, it might make a lot of advantage of growing the algae in wastewater and pumping flue gas instead of pure carbon dioxide. Also, using the emission gases from the HTL process to generate hydrogen on site could save the cost comparing to purchasing the hydrogen.

4.5 Sensitivity Analysis

The sensitivity analysis was conducted to find out the reflection of the minimum bio-crude selling price to the change of the key parameters such as algae growth rate and HTL yield percentage. The results of the sensitivity analysis are illustrated in the Figure 3.6. The base case was set as control group with the MSP of $49.80/gal. Five key parameters were investigated: HTL yield, HDO yield, algae growth rate, CO_2 cost and

fertilizer cost. To double the HTL yield of the base case, MSP of the bio-crude reduced about $24.11/gal from the baseline, but MSP increased by $43.13/gal when reducing the HTL yield to a half of the original value. Same trend was found when changing the HDO yield. Reducing the algae growth rate influenced the MSP more efficiently than increasing the rate. Feedstock cost did not influence the MSP much. If CO_2 is free, the price only goes down for $2.15/gal. Above all, the MSP of the crude were most sensitive to the HTL and HDO yield. To reduce the MSP, it was better to increase the HTL and HDO yield as well as the algae growth rate, and to decease the feedstock cost.

4.6 Scenario Analysis

The whole plant was designed with the capacity of 0.5 million gallons of bio-crude per year as base case, however, this capacity was very small compared to the target of 2022 with the biofuel production of 36 million annually. To see the relationship between the plant capacity and the cost of the bio-crude production, scenarios with 1 and 10 million gallons per year were analyzed and compared with the base case (Table 3.4). From the table, it was found that the production cost and the minimum selling price were reduced with the increasing of the plant capacity. The reduction was gradually decreased since the minimum selling price was decreased about 2 dollars from 0.5 million to 1 million capacity and 5 dollars from 1 million to 10 million. It was good to enlarge the plant capacity; however, it meant more investment in the beginning period.

5. Conclusion

Algae liquefaction technology is a promising alternative to produce bio-crude which can combine into the petroleum upgrading process to reduce the consumption of the non-renewable fuel. However, the high cost of the algae crude is a big issue to prevent

the commercialization of this technology. From the results of this simulation, the MSP of the crude from the baseline was about $49.80/gal which was about 20 times of the price of the petroleum crude oil if take it as 2013 average of $2.32/gal (FRED, 2013). To improve the technology with increasing the algae growth rate and the oil yield and decreasing the feedstock cost, the MSP of the algal crude might be reduced significantly to compete with petroleum.

Acknowledgements

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Table 3.1. Costs for determining the direct fixed capital[a]

Descriptions	Amount
Direct Cost (DC)	
Equipment Purchase Cost (PC)	100% of PC
Installation[b]	-
Process Piping	31% of PC
Instrumentation	26% of PC
Insulation	3% of PC
Electrical Facilities	10% of PC
Buildings	29% of PC
Yard Improvement	12% of PC
Auxiliary Facilities	55% of PC
Indirect Cost (IC)	
Engineering	15% of DC
Construction	20% of DC
Total Plant Cost (TPC)	TPC=DC+IC
Constructor's Fee	5% of TPC
Contingency	10% of TPC

a. Data were modified based on Peters et al. (1991)
b. Installation costs for equipment were specified for each facility based on the install factor

Table 3.2. Mass balance of algae liquefaction plant

Items	Annual Amount	Unit Amount (/kg of dry algae)	Unit Amount (/gal of algal crude)
CO_2	32,804,640 kg	2.59 kg	56.69 kg
$NaNO_3$	915,762 kg	0.07 kg	1.58 kg
K_2HPO_4	486,653 kg	0.04 kg	0.84 kg
Water	940,796,864 gal	74.15 gal	1625.82 gal
Hydrogen	712,886 kg	-	1.23 kg
DCM	370,460 kg	-	0.64 kg
Ru/C	886 kg	-	0.00 kg
Cultivated algae	12,687,998 kg	-	21.93 kg
Harvested algae	11,459,369 kg	-	19.80 kg
Final crude oil	578,661 gal	-	-

Table 3.3. Cost summary of the algal bio-crude plant

Description	Annual Cost($)	
Capital Cost		
Equipment Purchase Cost	$17,655,000	
Installation	$14,874,000	
Process Piping	$5,473,000	
Instrumentation	$4,590,000	
Insulation	$530,000	
Electrical	$1,766,000	
Buildings	$5,120,000	
Yard Improvement	$2,119,000	
Auxiliary Facilities	$9,710,000	
Total Plant Direct Cost	$61,836,000	
Engineering	$9,276,000	
Construction	$12,367,000	
Contractor's Fee	$4,174,000	
Contingency	$8,348,000	
Total Plant Indirect Cost	$34,165,000	
Direct Fixed Capital Cost	$96,001,000	
Working Capital	$17,230,000	
Investment Charged to This Project	$113,231,000	
Annual Operating Cost		
Raw Material	$5,226,000	
$NaNO_3$	$412,093	
K_2HPO_4	$728,479	
Carbon Dioxide	$1,312,186	
Water	$1,411,102	
Hydrogen	$1,069,329	
Dichloromethane	$185,230	
Ru/C	$107,000	
Waste Treatment/Disposal	$305,000	
Waste Solids	$124,844	
Wastewater	$180,066	
Utilities	$3,065,000	
Stand Power	$2,194,588	
Steam	$256,968	
Steam (High P)	$252,083	
Cooling Water	$56,200	
Chilled Water	$303,991	
Labor-Dependent	$1,862,000	
Facility-Dependent	$1,975,000	
Miscellaneous	$676,000	
Total Annual Operating Cost	$13,110,000	
Product Cost		
Bio-crude Yields	578,661	gal crude oil/yr
Unit Production Cost	22.66	$/gal crude oil
Minimum Selling Price	49.80	$/gal crude oil

Table 3.4. Comparison of the cost of scenarios with different plant capacity

Capacity (MM gallon)	Capital Cost ($)	Operating Cost ($/yr)	Production Cost ($/gal)	Minimum Selling Price ($/gal)
0.5*	113,231,000	13,110,000	22.66	49.80
1	188,182,000	21,793,000	21.57	47.81
10	1,681,725,000	194,292,000	19.23	42.95

*. The plant capacity with 0.5 MM gallon crude oil production per year is the baseline case.

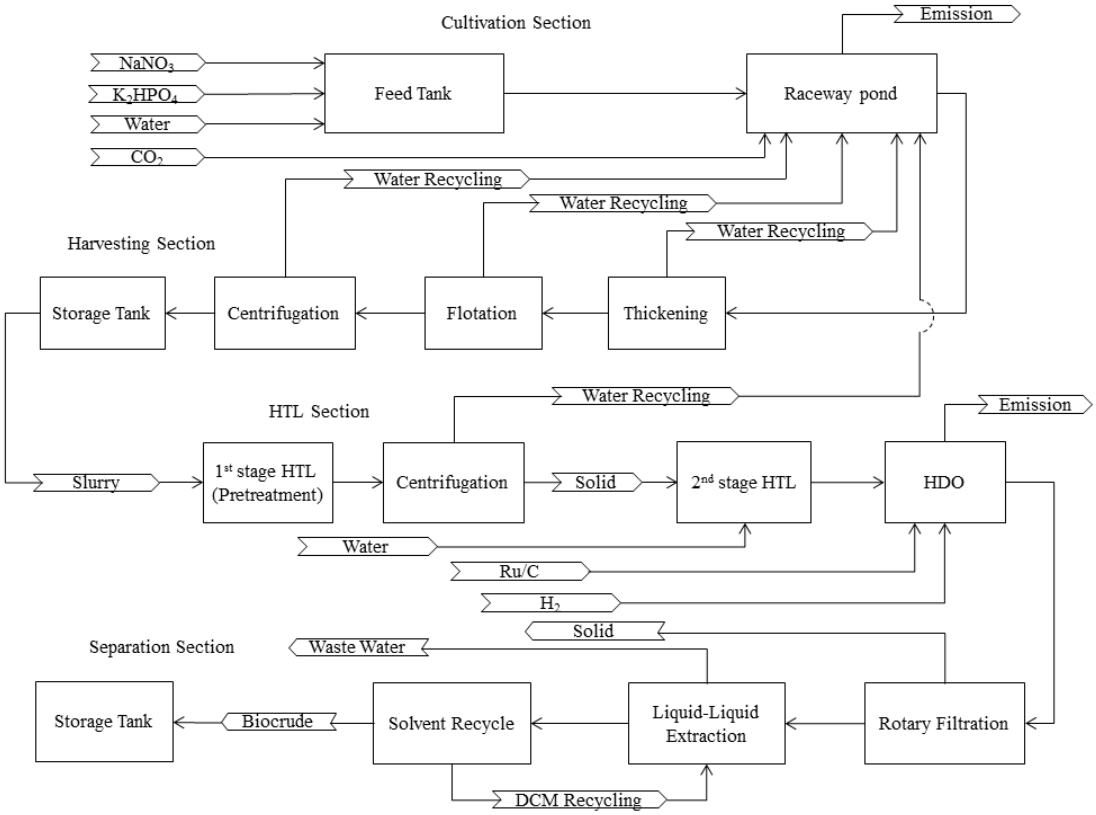

Figure 3.1. Simplified flow diagram of the overall process

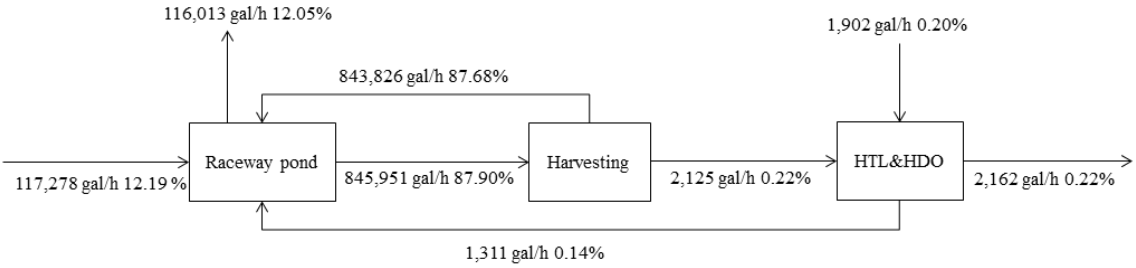

Figure 3.2. Water balance of the open raceway pond for algae cultivation

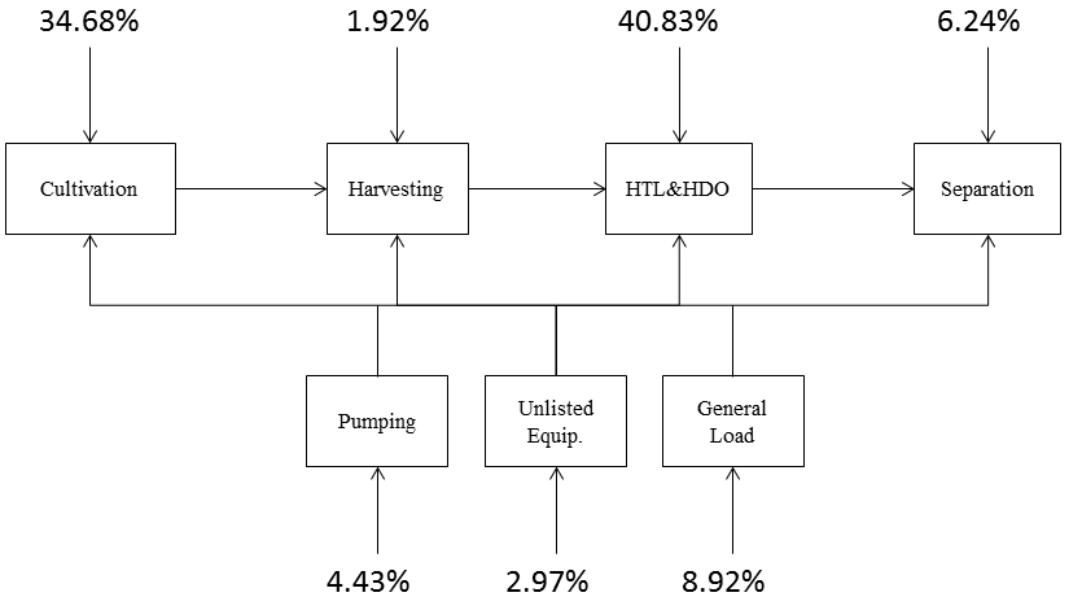

Figure 3.3. Section contribution of the total electricity consumption of the algae liquefaction plant

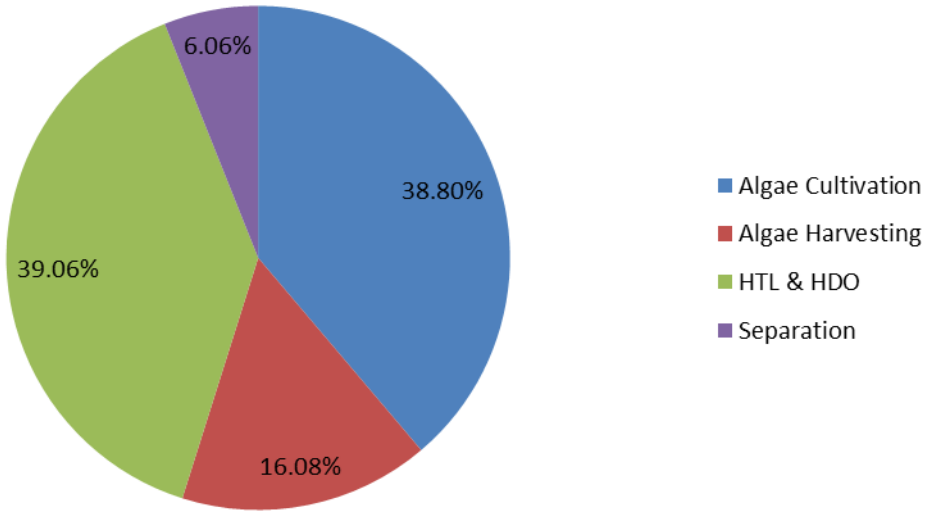

Figure 3.4. Breakdown of the capital cost of the algal bio-crude plant

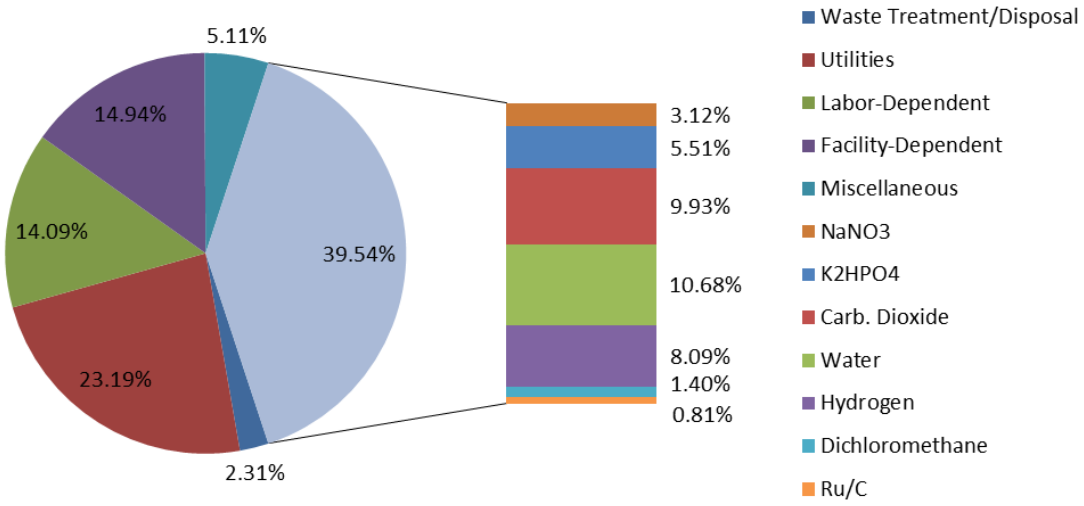

Figure 3.5. Breakdown of the operating cost of the algal bio-crude plant

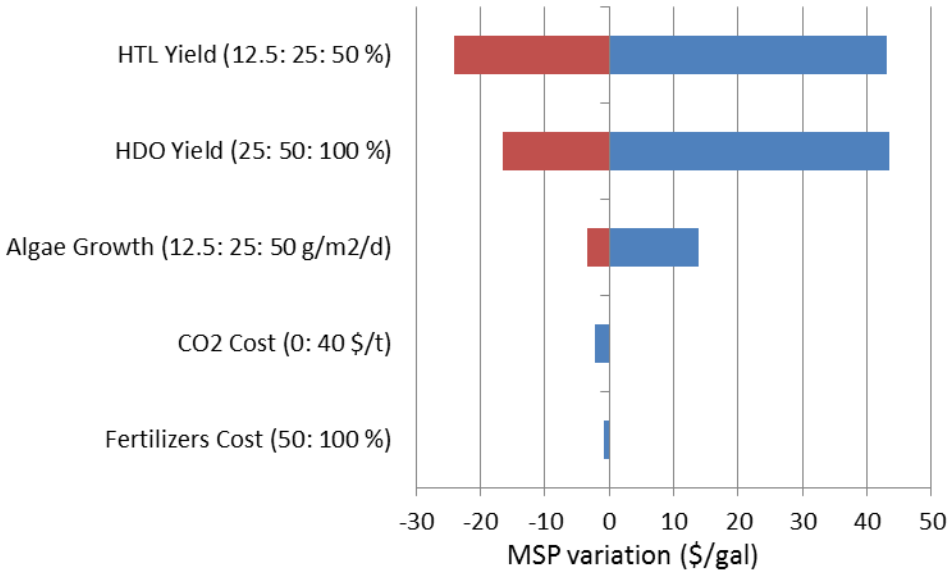

Figure 3.6. Sensitivity analysis of the minimum selling price of the algal bio-crude

CHAPTER 4

LIFE CYCLE ASSESSMENT OF ALGAE LIQUEFACTION TECHNOLOGY

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Abstract

Biofuels are drew attentions all over the world as promising substitutes of fossil fuels to reduce CO_2 emission and to perform sustainable development. Algae are standing out due to their high growth rates and lipid contents compared with other potential biomass to produce liquid fuels; however, biofuels from algae might consume a large amount of water and energy based on present technology. To this point, a life cycle assessment of bio-crude production from algae was conducted in this research in order to investigate the environmental impacts of a two-stage microalgae hydrothermal liquefaction system compared with fossil fuels production. The processes of the analysis included open raceway cultivation, three-step harvesting, two-stage hydrothermal liquefaction, hydrodeoxygenation, and oil extraction and separation. The total net CO_2 equivalent emission was estimated as 15.55 $kgCO_2eq/gal$ (114.63 gCO_2eq/MJ) for algal bio-crude oil compared with 90.27 gCO_2eq/MJ for low sulfur diesel and 94.38 gCO_2eq/MJ for gasoline from Argonne GREET Model. More than 60% of the CO_2 equivalent emission came from the of generation processes of electricity used in the algal bio-crude production. Sensitivity analysis was conducted regarding the algae growth rate, HTL yield, HDO yield and nutrients sources. The results showed that the total CO_2 equivalent emission was more sensitive to HTL and HDO yield.

Keywords: biofuel, renewable energy, hydrothermal liquefaction, environmental impacts, greenhouse gas emissions

1. Introduction

Biofuels have become very important for sustainable development and national security. The most popular technologies at present in U.S. to produce alternative fuels are ethanol from corn and biodiesel from soybean oil. According to the monthly biodiesel production report from the U.S. Energy Information Administration (EIA), about 101 million gallons of biodiesel were produced in May 2014, which consumed the total feedstock of 786 million pounds with 364 million pounds of soybean oil. Nevertheless, these feedstock are food based materials whose large consumption in renewable fuels could have food crisis problem arise. To avoid this issue, utilizing non-food feedstock such as woody biomass and algae to produce biofuels have been studied recently.

Microalgae have extremely high growth rate and so abundant lipid content that could potentially satisfy the huge amount of biodiesel requirement to completely substitute fossil diesel compared with other biomass. Microalgae could produce oil 58,700 l/ha with average 30 %wt. oil content in biomass and to satisfy 50% of all transport fuel annual demands of the United States, only 4.5 M ha of land area are needed compared to 594 M ha for soybean and 45 M ha for oil palm (Chisti, 2007). The theoretical maximum production of algal unrefined oil was claimed as high as 354,000 l/ha (38,000 gal/ac) per year while the best case in reality was estimated in the range from 40,700 to 53,200 l/ha (4,350 to 5,700 gal/ac) per year (Weyer et al., 2010). The lipid content of microalgae ranges from 20 to 50 % wt. while soybean and oil palm are around 20 % wt. on a dry basis (Johnson, 2012).

By using algae, it might significantly reduce the overall greenhouse gas (GHG) emission to the environment during the entire life cycle of the energy production because the

microalgae can absorb CO_2 and convert it into carbohydrates, protein and lipid during growth and cultivation, which creates carbon credits. Kadam (2001) found that using power plant flue gas to cultivate algae and co-fire it with coal to generate electricity could lower the GHG emission and air pollutant burdens but might increase the natural gas and oil consumption and the eutrophication potential (Kadam, 2001). Due to the rich lipid content, algae are also considered as a good feedstock for biodiesel to substitute the food-based soybean oil, however, it was claimed that the potential of algal biodiesel was affected by the fertilizer and energy consumptions for algae cultivation and drying before lipid extraction process (Lardon, 2009). The process efficiency in converting algae to lipid content and the dewatering energy consumption were considered as major obstacles in algae biodiesel technology and it showed the necessary to develop a new technology to produce algae biofuels with economic reality (Sander and Murthy, 2010).

To deal with these problems in the production of algae biofuels, a new technology called algae hydrothermal liquefaction (HTL) has come up to utilize whole algae components and avoid slurry drying process. HTL, also called hydrous pyrolysis, is a high temperature and high pressure process for the reduction of complex organic materials such as biomass into crude oil and other chemicals. It is typical with the condition of temperature range from 200 to 375° C, pressure range from 10 to 20 MPa, reaction time from 3 to 90 min depends on the mode of operation: batch or continuous (Elliott et al.,2013; Jazrawi et al.,2013; Zhu et al., 2013). HTL is considered as a good solution for high moisture content slurry such as algae because the reaction is liquid based and no drying is required for the feedstock. It was found that HTL process used 1.8 fold less algae than lipid extraction method to produced same amount of biofuels, however,

nitrogen fertilizer consumptions increased 5.2 times due to the nitrogen content in HTL oil was considered as lost and life cycle CO_2 equivalent emissions increased to 31,000g/MMBTU for HTL oil from 21,500g/MMBTU for lipid extraction oil (Frank et al., 2013).

To lower the nitrogen content in the algae HTL oil and reduce the fertilizer consumption, this study investigated the effect of a continuous two-stage microalgae liquefaction technology on the life cycle of the algae oil regarding the environmental impacts. Hydrodeoxygenation (HDO) process was combined with second HTL process to reduce the oxygen and nitrogen content in the final product oil. The evaluation of this system was provided in the study regarding to the life cycle environment impacts.

2. Methodology

2.1. Goal and scope

The goal of this study is to provide baseline information for the algae biofuels production using two-stage hydrothermal liquefaction technology. The idea of this technology is to improve the biofuels yield, and to reduce the nitrogen content in product oil and fertilizer consumption. This study estimated the mass balance, energy consumption and environmental impacts such as global warming of the algae HTL oil production system which comprised of four major stages: cultivation, harvesting, HTL and HDO processes, and separation. To evaluate the algae liquefaction technology, the model was compared with petroleum crude production system regarding the life cycle CO_2 equivalent emissions. The functional unit is per gallon of final product oil. Inputs data of production life cycle was collected from the USLCI database, European commercial database and published journal articles. The life cycle assessment is conducted following ISO

international standards: ISO 14040~14044 (ISO, 1997; ISO, 1998; ISO, 2000a; ISO, 2000b).

2.2. System boundary

This LCA study was conducted as “cradle to gate” but not “cradle to grave”. The whole idea is to combine the algae HTL crude oil into the petroleum refinery system to reduce the consumption of the fossil crude, thus, the system boundary ended with the production of the oil and consumption stage was not included in the system. The algal biofuel production system was made up of four major stages: cultivation, harvesting, HTL and HDO processes and separation with a plant life of 30 years. The system boundary of the processes is illustrated in Figure 4.1.

The system began with algae cultivation in open raceway ponds which were 690 m long, 60 m wide and 30 cm deep with no plastic liners. It was found that raceway ponds were more economic feasible than photobioreactors regarding algae commercial cultivation (Jorquera et al., 2010 and Lundquist et al., 2010). The algae production rate was estimated as 25 $g/m^2/d$ and all ponds were considered as continues system with flat growth rate. The inoculum and weather variations were not included in the system. Nitrogen, phosphorous fertilizers and water were mixed and pumped together into open raceway ponds while CO_2 pumped individually from the bottom of the ponds.

In the harvesting process, a combination of flocculation, dissolved air flotation (DAF) and centrifuge was used in the model to concentrate the slurry from 0.05% wt. to 15% wt. with 90% harvesting efficiency. No chemical flocculent applied in the flocculation process. Water and nutrients recycling rates from harvesting to the cultivation pond was assumed as 100%.

In the liquefaction processes, there are two stages HTL processes with the second stage combining with HDO process. HTL reaction was carried out in plug flow reactors while HDO reaction was conducted in CSTRs. After first stage HTL reacted at 225º C for 15 min, carbohydrates, protein and lipid were slightly hydrolyzed and decomposed into intermediates. Liquid and solid phases were separated in a centrifuge and then aqueous phase was recycled to the ponds in order to reuse the water and nutrients and reduce the nitrogen content in the solid phase (unreacted biomass) for further processing. The second stage HTL lasted 60 min at 350º C to further degrade algae biomass into oily complex compounds which then treated with hydrogen for 240 min to remove nitrogen and oxygen content. The catalyst in the HDO process was Ru/C which commonly used in the hydrotreating process. The outlet stream containing algae biofuels then pumped into separation process to extract and purify the oil. Gases were released from the reactor vent, taking account into the mass balance. Electricity and heat consumption were the major energy usages that took into account of the life cycle assessment.

In the separation process, remained solid were filtering off first through rotary drum filtration process and then went to the solid waste treatment. The oil-water mixture went to liquid-liquid extraction process to use dichloromethane (DCM) to extract oil from the aqueous phase which ended to the wastewater treatment. DCM was separated and recycled from the oil via low temperature distillation. The final product oil was stored in storage tanks. Transportation of the product was not included in the system, neither the utilization stage of the oil.

2.3. Life cycle inventory

The direct inputs and outputs of this algal biofuel production system were collected then summarized from the previous techno-economic model (Table 4.1). The indirect inputs and outputs were obtained from public life cycle database (Table 4.2). The model was specified to the location of USA, however, some data were adapted from the Europe due to data missing and limitation. The facilities' life cycle impacts to the algae liquefaction technology was estimated based on the U.S. economic inputs and outputs database.

2.4. Impacts assessment method

Life Cycle Impact Assessment (LCIA) is conducted as part of this LCA research to evaluate the potential environmental impacts of algal biofuels production. According to ISO standard (ISO, 2000a), Classification and Characterization steps are mandatory for a complete LCA study, while Normalization and Weighting are optional elements. Two American based Impact Assessment Methods is used in this research. The Tool for the Reduction and Assessment of Chemical and other environmental Impacts (TRACI) was developed by the U.S. Environmental Protection Agency (EPA), and Building for Environmental and Economic Sustainability (BEES) was developed by the National Institute of Standards and Technology (NIST).

The impact categories in TRACI include ozone depletion (kg CFC-11 eq), global warming (kg CO_2 eq), smog (kg O_3 eq), acidification (mol H^+ eq), eutrophication (kg N eq), carcinogenics (CTUh), non- carcinogenics (CTUh), respiratory effects (kg PM10 eq) and ecotoxicity (CTUe). The impact categories in BEES include global warming (g CO_2 eq), acidification (H^+ moles eq), HH cancer (g C_6H_6 eq), HH non-cancer (g C_7H_7 eq), HH criteria air pollutants (microDALYs), eutrophication (g N eq), ecotoxicity (g 2,4-D eq),

smog (g NO_x eq), natural resource depletion (MJ surplus), indoor air quality (kg TVOC eq), habitat alteration (T&E count), water intake (liters) and ozone depletion (g CFC-11 eq).

2.5. Sensitivity analysis

The sensitivity analysis was carried out in order to evaluate the effect of the main process parameters of the greenhouse gas emission. Key factors investigated in the sensitivity analysis of algal biofuels production were algae growth rate, HTL yield, HDO yield and nutrients sources (from fertilizer or wastewater). These factors were considered because of their potential influence towards the biofuel production rate and the direct or indirect operational emissions in the system.

3. Results and discussion

3.1 Environmental impacts

North American impact assessments, TRACI, was performed to investigate the environmental effect of the algae liquefaction system regarding each process section (Figure 4.2).

- Ozone depletion was computed by the equivalent emission of trichlorofluoromethane (CFC-11), so called Freon-11. It is the main chemical that causes the ozone depletion. To produce 1 gallon of algae HTL oil, about 0.0462 g CFC-11 equivalent emissions released to the environment in total with 0.0451 g CFC-11 eq came from the separation process. It was because of the DCM solution used to do the liquid-liquid extraction process in the separation section. The production of the DCM caused significant CFC-11 equivalent emission in the system.

- Global warming was represented by the mass of CO_2 equivalent emission. It was calculated based on the global warming potential of the greenhouse gas, mainly CO_2, CH_4 and N_2O (IPCC 2007). The total global warming emission of the system was 71.92 kg CO_2 eq with 23.61kg from cultivation, 1.52 kg from harvesting, 29.49 kg from HTL and HDO, and 17.30 kg from separation. The electricity consumption in each section was the main reason for the greenhouse gas emission. Nearly 61.4% of the total came from the electricity generation with 46.8% from coal burning and 9.91% from natural gas combustion. Steam used for heat exchange in the HTL and separation sections was account for about 17% of the global warming impact.
- Smog and acidification were reported as the emission of kg O_3 equivalent and mol H^+ equivalent, respectively. From the Figure 2, it was clear that they shared same trend with global warming impact. To figure out the inner relationship between the three impacts, the sources of the emission were investigated and it was found that the mainly contribution was the electricity generation from bituminous coal, about 56.6% for smog and 61.0% for acidification.
- Eutrophication was calculated in the kg N equivalent emission with the total of 0.92 kg N eq in the algae liquefaction system. About 83.2% of the total came from the direct emission in HTL & HDO processes, and 14.8% came from algae cultivation due to the production of the fertilizer. Improving the liquefaction technology to increase the oil yield and decrease the gas phase emission may significantly decrease the impact of eutrophication to the environment. Another way to solve the problem is to utilize the gas emission in this process to limit the

environmental impact. The offgas from algae HTL and hydrotreating processes was used to generate hydrogen which could be utilized in the oil upgrading process (Zhu et al., 2013; Jones et al., 2014).

- The carcinogenics and non carcinogenics were measured with CTUh. The carcinogenics impact mainly came from phosphorous fertilizer production, DCM production and steam generation with the percentage of 38.1%, 19.4%, and 18.1%, respectively.
- Respiratory effects was claimed based on the kg PM10 equivalent. The total was 0.08 kg PM10 eq with 0.03 kg for algae cultivation, 0.03 for HTL and HDO, and 0.02 for separation processes. The emission was mainly caused by the coal combustion of electricity generation, same major reason with the ozone depletion, global warming, smog and acidification. Obviously, reducing the electricity consumption will significantly limit the environment impact of the algae liquefaction system, however, it requires the improvement of production efficiency and equipment efficiency of the current technologies. Decreasing the coal utilization in the electricity generation or substituting thermal power generation with other green methods, such as wind power generation and solar power generation, will also be helpful regarding reducing environment impacts.
- Ecotoxicity was analyzed based on CTUe. It mainly caused by the natural gas consumption in the electricity generation and nitrogen fertilizer production.

From the analysis of all the environmental impact, it was found that the major reason to cause the environmental problems was the considerable electricity consumptions in the algae liquefaction technologies. During the algae cultivation, 13,153,156 kWh/yr of

electricity was used to power paddle wheels in open raceway ponds to mixture the algae slurry, which caused electricity usage of 1.15 kWh/kg dry algae. Another huge contribution was the electricity used to heat the reactors in the HTL and HDO processes, which was about 15,400,868 kWh/yr. To reduce the electricity consumption, it is better to improve the algae growth rate and conversion rate from harvested algae to final crude oil. It requires the development of current algae liquefaction technology.

3.2 Air emissions

Major air emissions of algae liquefaction technology were described in the Table 4.3. Fossil CO_2 emission was much higher than other major air emissions and it mainly came from the fossil fuels burned to generate electricity. If the electricity generates from renewable sources, total CO_2 equivalent emission may reduce more than 60% of the initial value. CO and NO_x emissions were mainly from HTL and HDO processes which generated gas emission from biomass decomposition. The ammonia emission data was missing from the experiment work but Jones et al. (2014) claimed that the nitrogen content in algae could result ammonia in the gas phase of liquefaction. Future work is required to investigate the influence of ammonia in HTL on the total GHG emissions.

Comparison of CO_2 equivalent emissions ($kgCO_2e$/gal) of algae HTL oil, low sulfur diesel and gasoline is illustrated in the Figure 4.3. Algae cultivation and HTL processes contributed most to the CO_2 equivalent emissions, however, harvesting process had few emissions. CO_2 absorbed in algae growth was treated as credits to balance the CO_2 equivalent emissions produced in the microalgae liquefaction processes. In the Argonne GREET model, the GHG emissions was 11,325 gCO_2e/gal for gasoline and 12,186 gCO_2e/gal for low sulfur diesel. In the LCFS' program, the GHG emissions was 11,325

gCO_2e/gal for petroleum derived gasoline and 12,987 gCO_2e/gal for petroleum derived low sulfur diesel (Liu et al., 2013). The average values of the two studies for low sulfur diesel and gasoline were used in the comparison. The results showed that development was required to improve the algae liquefaction technology if a commercial plant was built today.

3.3 Energy consumption

Energy used in the algae liquefaction technology can be categorized into two class: non-renewable energy and renewable energy. An impact method called cumulative energy demand in Simapro 7 was used to calculate energy consumption of the algae liquefaction system. The method was modified by PRe Consultants based on the method published by Ecoinvent version 2.0 (Frischknecht et al., 2007).

Fossil source non-renewable energy was the major provider of energy consumption in this study (Table 4.4). The total of 1044.70 MJ of fossil energy was consumed to produce 1 gallon of algal bio-crude oil. The heating value of algal HTL oil is approximately 35 MJ/kg (Frank et al., 2013). Nearly 76% of the total usage was coming from the electricity consumption of algae cultivation and HTL & HDO processes. Electricity was mainly utilized by paddling the open raceway ponds and heating the HTL and HDO reactors, thus, improvements of the mixing efficiency and heat transfer rate are very important. But, microalgae HTL technology could remarkably save energy in harvesting process. For algal biodiesel production, Sander and Murthy (2010) found the energy demand in harvesting process was 459.8 MJ/gal of biodiesel for filter press primary dewatering and 905.9 MJ/gal of biodiesel for centrifuge primary dewatering.

3.4 Water consumption

Algae cultivation is a very water-consumable process. This study evaluated the overall net fresh water consumption with 100% harvested water recycled. In this case, fresh water usage was considered as make-up water of evaporation from the open raceway pond with an evaporation rate about 12% of the total water in ponds. As the final results showed, the net water consumption to grow 1 kg of dry algae was estimated as 74 gallon or 279 kg. Campbell et al. (2011) claimed the water consumption of 704 kg/kg dry algae in a LCA study of algal biodiesel production in ponds, however, this rate was not considered recycling. They stated that if recycling was applied in the algae production, the water consumption would reduce to half of the total, approximately 352 kg/kg dry algae.

3.5 Sensitivity analysis

Sensitivity analysis was performed in this study to investigate how the key parameters, such as algae growth rate, HTL yield, HDO yield and nutrient sources, influence the global warming impact (Figure 4.4). To increase the HDO yield from 50% (wt.) to 100% (wt.), CO_2 equivalent emission deceased most significantly which was 32.1 kgCO_2eq. When HTL yield deceasing to 0.5 fold, greenhouse gas emission increased most, nearly 55 kgCO_2eq. CO_2 equivalent emission was more sensitive to decrease algae growth rate than increasing the growth rate. It was because the low growth rate strongly influenced the scaling up of the cultivation ponds and required more electricity to mix the medium. The source of nutrients had a little influence of CO_2 emission but combining wastewater treatment with algae cultivation could save considerable fresh water (Lundquist et al., 2010).

Sensitivity analysis of the key factors of algae liquefaction technology on other environmental impacts is showed in Figure 4.5. The scenario with 50% of HTL oil yield had best performance among all cases, therefore, increasing HTL oil yield is most important in the development of algae liquefaction technology in the perspective of environmental impacts.

4. Conclusion

Algae liquefaction technology is a promising method to produce renewable liquid fuels to substitute fossil petroleum, however, it still requires development under the current technology to improve the production rate of the algal oil and reduce the electricity consumption in the cultivation and HTL processes. The total of 1044.70 MJ of fossil energy was consumed and 15.55 kgCO_2eq net emission was released to produce 1 gallon of algal bio-crude oil.

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Table 4.1. Direct input/output data for algae liquefaction plant with 0.5 M gallon annual capacity

Input/Output	Items	Value	Unit	Comments
Feedstock	$NaNO_3$	916	t	N fertilizer
	K_2HPO_4	486	t	P&K fertilizer
	CO_2	32,805	t	Absorption in cultivation
	Water	3,574,896	t	Cultivation usage
	H_2	713	t	HDO usage
	Ru/C	1	t	HDO catalyst
	DCM	379	t	Oil extraction solution
Utilities	Electricity	36,500,071	kW-h	Direct usage
	Steam	21,680	t	Heat exchange agency
	Steam (High P)	12,604	t	Heat exchange agency
	Cooling Water	1,149,445	t	Heat exchange agency
	Chilled Water	893,961	t	Heat exchange agency
Air Emission	Oxygen	38,537	t	Release in cultivation
	Water evaporation	3,478,106	t	Loss in cultivation
	CO_2	3,603	t	Emission in HTL&HDO
	CO	15	t	Emission in HDO
	C_2H_6	978	t	Emission in HTL
	H_2	545	t	Emission in HDO
	CH_4	88	t	Emission in HTL&HDO
	N_2	2,938	t	Emission in HDO
Waste Solids	Unprocessed Biomass	4,402	t	Waste treatment
Wastewater	Aqueous Phase	78,131	t	Waste treatment
Product	Crude Oil	581,938	gal	Main product
	Harvested Algae	11,459	t	Intermediates

Table 4.2. Indirect data for algae liquefaction plant

Process	Description	Source
Fertilizer production	Average of the US production mix at plant, transportation included	USLCI
Electricity Production	US at grid, mixed fuels for electricity generation including coals, fuel oil, nuclear, hydroelectric, and unconventional energy sources. Data are weighted according to percent share of consumption.	USLCI
Water	Fresh water as natural resource	NA
CO_2	CO_2 fixation, treated as credit	NA
H_2 production	US average production mix at plant from chlor-alkali electrolysis, 85% diaphragm and membrane cell electrolysis and 15% mercury cell electrolysis.	USLCI
DCM production	Data from actual technology used in the companies in Europe, including raw materials, processing energy, emissions to air and water from process, energy services and transports. Infrastructure only partly included; no infrastructure of main process and land use data included.	Ecoinvent
Steam production	Average production data from11 European chemical sites. Input of water and energy for the production of steam. No further infrastructure is included.	Ecoinvent

Table 4.3. Section contributions of major emissions to air of 1 gallon algal crude

Substance	Algae Cultivation (g)	Algae Harvesting (g)	HTL & HDO (g)	Separation (g)
CO_2 (biogenic)	357.2	26.6	6605.6	76.3
CO_2 (fossil)	19800	14400	27900	13600
CO (biogenic)	-	-	26.5	0.04
CO (fossil)	10.9	0.74	13.4	10.3
CH_4	55.7	3	48.8	101
NOx	53.7	3.82	65	38.7
VOC	2.25	0.09	1.54	0.36
Particulates	12.3	0.88	13.8	2.29

Table 4.4. Section contributions of energy consumption of 1 gallon algal crude

Impact category	Algae Cultivation (MJ)	Algae Harvested (MJ)	HTL & HDO (MJ)	Separation (MJ)	Total (MJ)
Non-renewable, fossil	352.82	21.31	427.80	242.77	1044.70
Non-renewable, nuclear	-	-	0.75	9.38	10.13
Non-renewable, biomass	-	-	0.00	0.00	0.00
Renewable, biomass	-	-	0.04	0.07	0.11
Renewable, wind, solar, geothe	-	-	0.01	0.25	0.27
Renewable, water	-	-	0.16	0.65	0.81

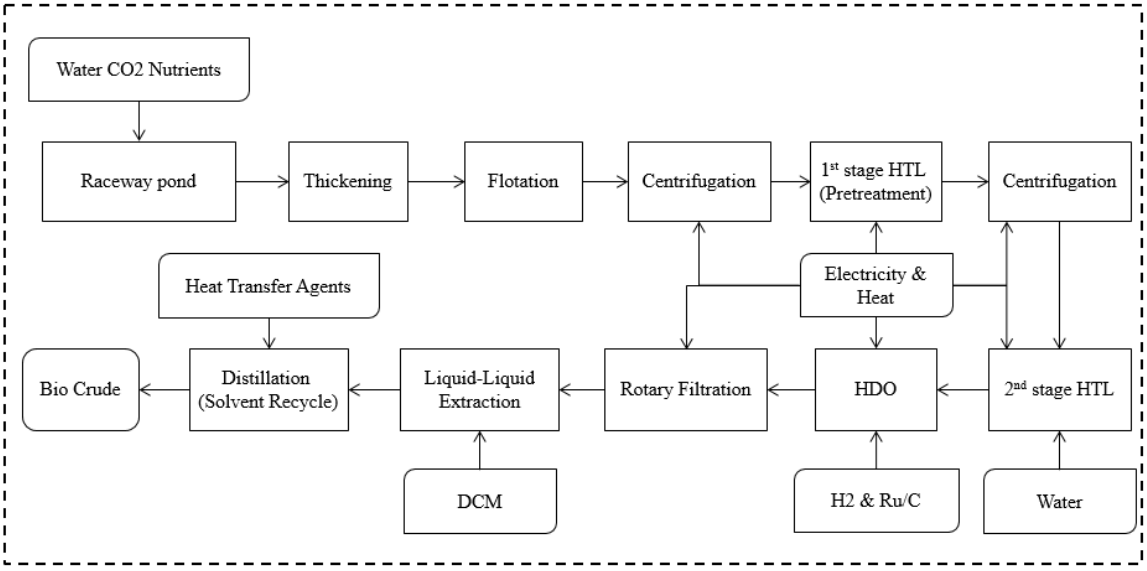

Figure 4.1. System boundary of life cycle assessment of algae liquefaction technology

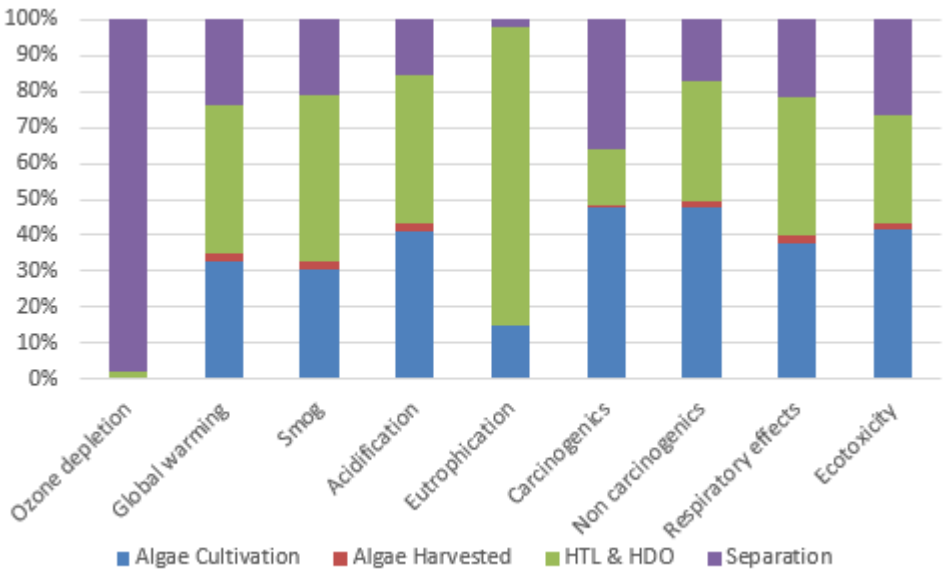

Figure 4.2. Environmental impacts of per gallon of algae liquefaction biofuels

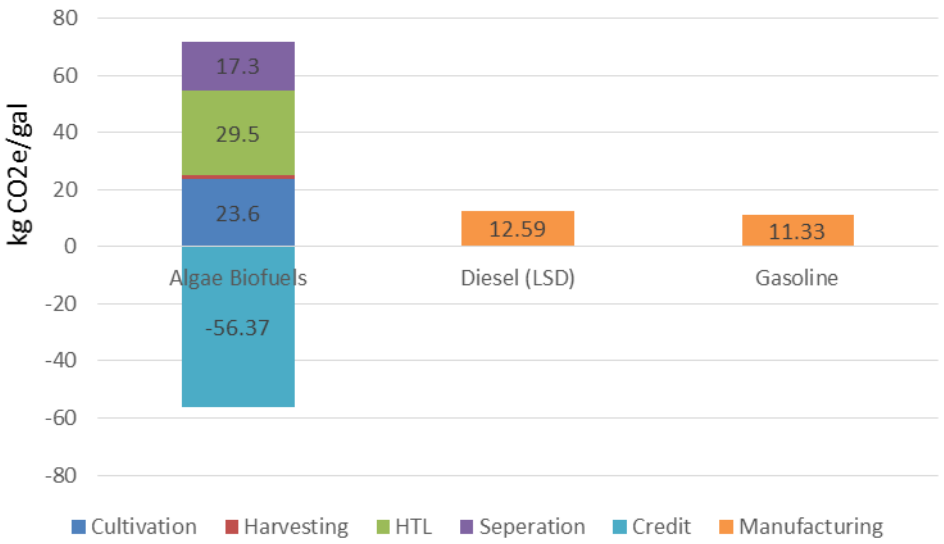

Figure 4.3. Comparison of CO_2 equivalent emission of algae bio-crude, diesel and gasoline

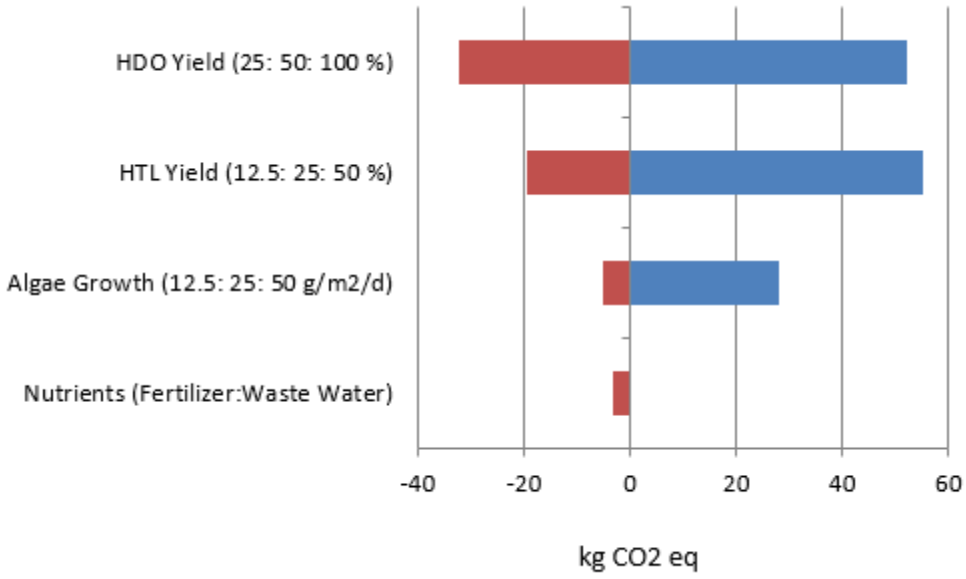

Figure 4.4. Sensitivity analysis of global warming impact of algae liquefaction technology

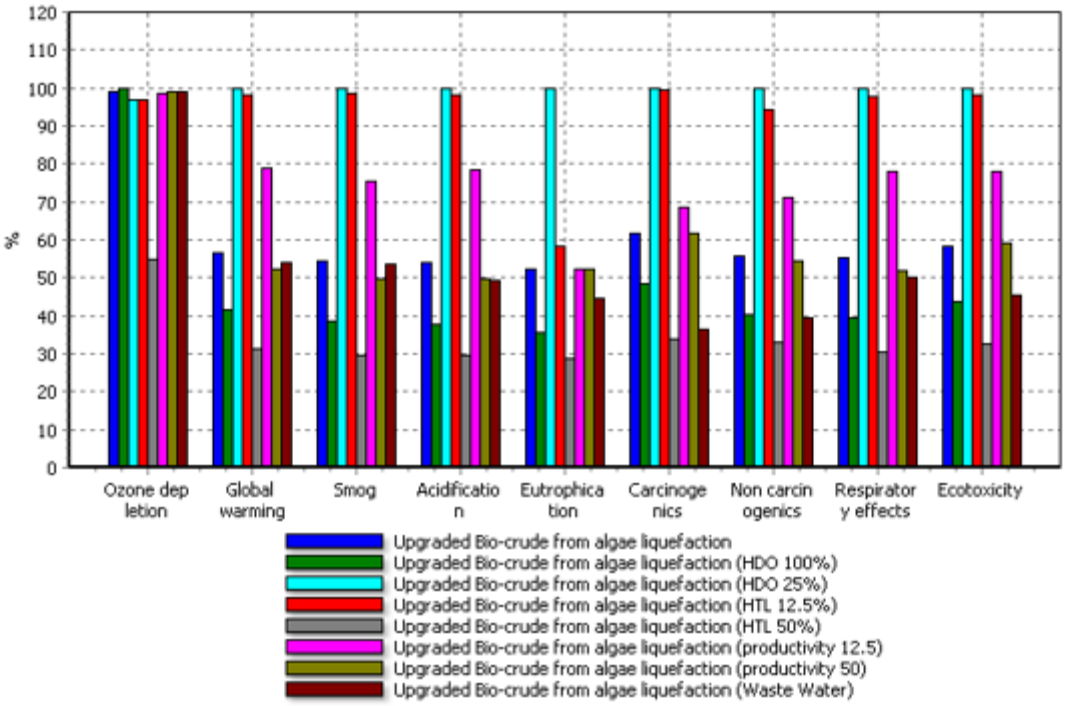

Figure 4.5. Sensitivity analysis of different environmental impact of algae liquefaction technology

CHAPTER 5

LIFE CYCLE ASSESSMENT OF BIOCHAR/BIO-OIL PRODUCTION FROM SOUTHERN PINE

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Abstract

Biochar is generally produced using a pyrolysis technology. The yield is different from various methods to conduct pyrolysis. Three methods were studied in this report: fast pyrolysis, slow pyrolysis and Missouri kiln. Life cycle assessment was used to estimate the energy consumption and mass balance of the production of biochar and its co-product from southern pine. The system boundary of biochar production was considered to set up from seedling to final products, including plantation, harvesting, pre-processing and pyrolysis. However, different scenarios were developed to compare different pathways. The functional unit of this life cycle assessment is per metric ton of biochar or bio-oil. Inputs data were collected from USLCI data base and published journal articles. Simapro 7 was used to obtain the emissions from the inputs of different scenarios. Sensitivity analysis was used to evaluate the distribution of each process and impact assessment was conducted by the method of TRACI 2 V4.00. Total energy consumptions, raw materials demand and environmental impacts of producing one metric ton of biochar or bio-oil were reported in the study. The contributions of each process were also analyzed.

Keywords: biomass, wood chips, fast pyrolysis, slow pyrolysis, Missouri kiln, mass and energy balance

1. Introduction

Pyrolysis is a conversion process which uses high temperature to convert biomass to a mixture of liquid, solid and gas. Usually, this process is carried out without the presence of air. There are two types of pyrolysis for the conversion of biomass distinguishing by the operation conditions that are processed. One is fast pyrolysis and the other is slow pyrolysis. However, these two types have no certain definition based on time or temperature for operation. Generally, pyrolysis processes are conducted at the temperatures which are not regarded as either fast or slow but in a range between the two extremes. (Mohan et al., 2006)

Fast pyrolysis is conducted with a high temperature in the absence of air. In this process, due to high heating and heat transfer rates, biomass first decomposes to generate mostly vapors, aerosols and some charcoal-like char. Second, the reactor is carefully maintained at the temperature around 500° C with the residence time of vapors less than 2 second. Third, vapors are rapidly cooled and then condensed to give a dark brown mobile liquid (Bridgwater et al., 1999). The temperature, heat transfer rate and vapor residence time highly influence the composition of the products (McKinley, 1989).

Slow pyrolysis is developed mainly for the production of charcoal (biochar). In the process, biomass is heated around 500° C as fast pyrolysis but the difference is that vapor residence time varies from 5 min to 30 min (Bridgwater et al., 2001). As a result, the different kinds of components in the vapor phase can react with each other to form solid char and any liquid. The heating rate of slow pyrolysis is much slower than fast pyrolysis. The feedstock is also slowly heated.

Three main products often mentioned in literatures are charcoal (biochar), bio-oil and fuel gas. The majority of literatures focused on the production of bio-oil due to not only its high production but also wide and effective applications. Fast pyrolysis (flash pyrolysis) is mainly used for bio-oil production and the yield can be up to 80%, however, the production of biochar is normally based on slow pyrolysis which enables the conversion efficiency up to 35% (McKendry, 2002).

Bio-oils are dark brown, free-flowing organic liquids that are comprised of highly oxygenated compounds. Bio-oil has a very complicated chemical composition that comes from the degradation of cellulose, hemicelluloses, lignin and other elements in biomass. (Piskorz et al., 1988) Due to its various chemical components and physical properties, bio-oil is observed undesirable changes with ageing. Viscosity is increasing and some phase separation may also occur.

Bio-oil can be generated from a variety of agricultural and forest biomass wastes but what kind of biomass to be utilized depends on operation region. Different regions have their own preferred biomass. For example, in North America, bio-oil is usually made from forest residues. The yields, in the range of 72-80% wt., depend on the relative amount of cellulose and lignin in the biomass (Mohan et al., 2006).

Biochar is the carbon-rich solid product obtained by the pyrolysis of biomass. Biochar can be applied as soil amendment, long-term carbon sequestration, renewable energy generation and biomass waste management (Roberts et al., 2009).

Different fast pyrolysis processes have been developed based on the used technologies. Fluid beds are the most common used configurations because of easy operation and ready scale-up. A typical bubbling fluid bed has five processes including drying, grinding,

reacting, separating and cooling (Bridgwater et al., 1999). Drying is used to reduce the water content in the product oil and the raw material is generally dried with the water content less than 10%. Grinding is required to reduce the feedstock's size to 2 mm to provide abundant small particles to ensure rapid heat transfer and reaction. After pyrolysis, the vapor and aerosol need to be separated from the biochar to be cooled to generate liquid bio-oil.

2. Methodology

2.1 Goal and scope

Life cycle assessment was used to estimate the energy consumption, mass balance and environmental impacts of the production of biochar and bio-oil from southern pine. Three pyrolysis methods were evaluated and compared with each other based on product yield, energy consumption and emissions of life cycle. Fast pyrolysis, slow pyrolysis and Missouri kiln pyrolysis were studied in this research. To compare the influence of different pyrolysis methods and different biomass pre-processing method, three scenarios were developed in the study: 1) Fast pyrolysis with clean chips, 2) Slow pyrolysis with clean chips, 3) Missouri kiln with small logs. Clean chips are referred to the chips obtained from debarking and chipping processes. The scope of life cycle in this research has four stages: plantation, harvesting, pre-processing and pyrolysis. The functional unit of all scenarios is per metric ton of product (biochar/bio-oil). Inputs data of production life cycle were collected from commercial database or published journal articles. SimaPro 7 was used to obtain the emissions from life cycle inventories of different scenarios and the impact assessment was conducted by the method of TRACI 2 V4.00.

2.2 System boundary

This life cycle assessment is a ‘cradle-to-gate’ assessment from pine wood seedlings to final products (biochar/bio-oil). System boundary of the different scenarios is illustrated in details in Figure 5.1. Heat required for pyrolysis was generated by the combustion of wood waste which is the co-product of pre-processing. Emissions were counted from the entire life cycle system. The input data of the model are provided in Table 5.1 with details.

2.3 Plantation

Plantation includes four sub-processes which are seedling, site preparation, planting and nursery, respectively. The study used the modified model of southern pine plantation described in previous study (Johnson et al., 2005). Three intensities were defined in the model based on the different types of forestry in southeast. The rate is 0.37: 0.58: 0.05 from low intensity to high intensity, respectively. Site preparation methods and fertilizer applications various with three intensities. In low intensity site preparation, only burning was performed to eliminate the stump on site. Medium intensity preparation was consist of shearing and burning. Dozers were used to remove debris in the forestry. Shearing and piling were utilized in high intensity site preparation. After cleaning the sites, seedlings could be planted both by hands and machines. In this study, it was assumed that all sites were used mechanical planting method. The planting density was 726 trees per acre and the rotation was 25 years. The data of seedling production was extracted from USLCI database, considering water, energy and fertilizer consumptions; however the transportation of fertilizers were not included. Diesel consumption and manufacturing of machinery were calculated in site preparation process. Types of machinery used in the

model are illustrated in appendix. Water use, fertilizer consumptions and carbon dioxide absorptions were considered in nursery part. The infrastructure of irrigation was included as well.

2.4 Harvesting

Full tree harvesting system is used to harvest pine trees in Southeastern forestry. It has five steps which are felling, skidding, delimbing, loading and transportation. Timbers were felled down by wheeled feller bunchers and transported to landing area by grapple skidders. Tops and limbs were cut off at the landing area by stroke delimbers. Then log loaders loaded processed logs onto trucks which transported biomass to pyrolysis plant for following processes. Transportation from landing to the plant was included in harvesting process and the distance for one way haul was assumed to be 57 miles. Diesel consumption and lubricant use of forestry harvest equipments were calculated from the data in published article (Johnson et al., 2005). The data of manufacturing of machineries were modified from previous study (Heller et al., 2003). Details of manufacturing consumption are shown in supplementary information in appendix. Truck manufacturing data was obtained from SimaPro 7.

2.5 Pre-processing

After logs arrived at pyrolysis plant, they would be processed with different methods. Three pre-processing systems were defined in the study to adapt to various pyrolysis scenarios. System A was including debarking and chipping; system B directly chipped the wood logs without debarking process; however, system C only reduced the log size to make it accommodate to Missouri kiln pyrolysis. The inputs data of energy consumption and manufacturing of equipments were collected separately for different systems.

Debarking raw data were extracted from USLCI database, which was mainly consist of diesel and electricity consumptions. The data of chipping and whole logs chipping were obtained and integrated from published literatures (Baker et al., 2010; Valente et al., 2011). Whole logs chipping is considered as a substitute method of debarking and chipping, the comparison of these two methods is in sensitivity analysis. Sawdust generation rate was assumed as 5% wt. for both chipping processes. Log size reduction was conducted by chainsaw and its energy consumption was calculated from the existing data in USLCI database. The manufacturing data of the chainsaw used existing data in SimaPro 7.

2.6 Pyrolysis

Fast pyrolysis, slow pyrolysis and Missouri kiln pyrolysis were studied and compared in this research. Fast pyrolysis has higher heating rate and bio-oil yield compared to slow pyrolysis which has more biochar production. To ensure high heat transfer rate in fast pyrolysis, wood chips are required to grind to powders after drying and then go to the pyrolysis reactor. The moisture content of green and dried wood chips were assumed as 50% and 10% (wet basis), respectively. Slow pyrolysis only has drying and pyrolysis processes. Energy consumptions and emissions of fast pyrolysis were gathered from published articles. Very limited data was related to slow pyrolysis. The heat requirement of slow pyrolysis was calculated based on reported equations of wood pyrolysis (Rath et al., 2003). Energy input of Missouri kiln was not the heat required of pyrolysis process because it consumed the energy inside the feedstock and only starting heat needed to be provided. Constructions of pyrolysis plant and Missouri kiln were included in the system. There is no built pyrolysis plant in practice so the material inputs were estimated from

liquefaction and gasification biomass plant (Roberts et al., 2009). Missouri kiln construction materials were calculated depending on the kiln parameters described in published book (Hollingdale et al., 1991).

3. Results and Discussion

3.1 Biochar and bio-oil yield

After harvesting, 3174 cubic feet of wood logs were generated per acre. During preprocessing, drying and grinding, there were some weight losses due to bark, sawdust and evaporated water. For fast pyrolysis, the yields for biochar, bio-oil and non-condensable gas (NCG) were 70.8%, 16.2% and 13%, respectively (Steele et al., 2012). For slow pyrolysis, the production rates were 50.4%, 31.2% and 18.4%, respectively (Das et al., 2008). Biochar yield of Missouri kiln is 33% (Hollingdale et al., 1991). The final products yields per acre were calculated based on mass allocation and the results are illustrated in Table B4. As it shows, Missouri kiln had the highest yield of biochar following by slow pyrolysis. Fast pyrolysis had the lowest biochar yield but higher bio-oil production. Scenarios using whole logs chipping generated more products than debarking and chipping method. This is possibly because whole log chipping has less biomass losses during processing.

3.2 Energy consumption

This research studied two products from pine wood pyrolysis, biochar and bio-oil. When there is more than one product being considered, the problem of life cycle assessment method is to allocate the inputs flows for the unit process appropriately among the product outputs. The most widely used allocation method is economic allocation (Torcellini et al., 2004). In this study, three allocation methods were used to compare with

each other and conducted the sensitivity analysis. The base case allocation method of this research depended on mass basis of biochar and bio-oil production while the economic and energy allocation were considered to be comparisons. The results of alternative allocation methods will be discussed in sensitivity analysis.

A method in SimaPro 7 database was used to calculate cumulative energy demand for biochar production. The method was based on ecoinvent version 2.0 and modified by PRé Consultants to adapt to SimaPro 7 databases' raw material. The results of energy consumption of biochar production from different scenarios are provided in Table 5.2. From the table, we can see that biochar produced from Missouri kiln had the lowest energy consumption per metric ton of biochar production which was 2.19 and 1.97 GJ/t for with and without machinery results, respectively. Slow pyrolysis energy use ranged from 5.11 to 5.89 GJ/t while fast pyrolysis consumes energy various from 8.33 to 9.08 GJ/t. By using slow pyrolysis, it could be saved around 3GJ of energy when producing 1 metric ton of biochar. A breakdown energy demand of each life cycle stage is illustrated in Figure 5.2 to display the difference between several scenarios. The figure shows that the most remarkable difference of energy consumption between fast and slow pyrolysis came from grinding. Fast pyrolysis needed to use powder feedstock to ensure its high heat transfer rate however slow pyrolysis can utilize wood chips. Missouri kiln had much lower energy demands for pyrolysis process than other two methods because it used the inner energy of small wood logs by combustion. No extra energy needed to be provided during the process except ignition material.

3.3 Impact assessment

TRACI is the main impact assessment method used in this research to compare the results. It is short for Tool for the Reduction and Assessment of Chemical and other environmental Impacts, which is developed by the U.S. Environmental Protection Agency. BEES was used to calculate the water intake of the three scenarios. The results of impact assessment from three calculation methods are shown in Table 5.3. The results comparisons of three pyrolysis methods based on percentage are displayed in Figure 5.3. In TRACI method results, fast pyrolysis had higher impacts on all impact categories except global warming. Missouri kiln attributed much more effects in global warming than other two pyrolysis methods however it had smaller influence on other impact factors. Considering BEES results, fast pyrolysis affected more on acidification, HH cancer, HH non cancer, eutrophication, ecotoxicity, natural resource depletion and ozone depletion while Missouri kiln made more influence on global warming, HH criteria air pollutants, smog, habitat alteration and water intake. From both impact assessments, the similar categories had the identical results even though the calculation methods might be various.

3.4 Emissions

In biochar production, carbon dioxides contributed most to the air emissions (Table 5.4). Except Missouri kiln scenario, carbon dioxides came from fossil were greater than those from biogenic sources. However, biogenic carbon dioxides emissions in kiln pyrolysis system were around 16 times of fossil carbon dioxides. Slow pyrolysis system released less emission to air than fast pyrolysis when producing the same amount of biochar.

Considering the carbon dioxides that absorbed in tree plantation, the biochar production system is a CO_2 negative system.

In order to control the emissions from the system, contribution of each stage in life cycle was analyzed in fast pyrolysis clean chips scenario (Figure 5.4). Pyrolysis process attributed the majority of emissions to air. In fossil carbon monoxide and volatile organic compounds (VOC) categories, the largest portion of emissions was from harvesting. Reducing emissions from pyrolysis and harvesting process might be an effective way to control the emissions for entire system.

3.5 Sensitivity analysis

Sensitivity analysis is very critical to life cycle assessment due to the uncertainty and the variety of the data. By doing sensitivity analysis, the most influenced input is revealed so that people can control and improve the system. The sensitivity analysis of allocation method, transportation distance, yield of biochar, pyrolysis energy use, preprocessing method and harvesting energy use were provided in Table 5.5. The variation of the input reflected on the total energy use, net energy use and the impacts on global warming, smog, acidification and eutrophication. Figure 5.5 shows the sensitivity chart of total energy use and global warming which are the key evaluations. Yield of biochar are the most sensitive input category for all scenarios however transportation distance affected the least of the results. Sensitivity analysis was a slight different between various pyrolysis methods.

4. Conclusion

Slow pyrolysis had better performance regarding to energy consumption than fast pyrolysis and Missouri kiln pyrolysis to produce biochar and bio-oil from the southern

pine wood. Biochar and bio-oil from biomass pyrolysis technology had lower CO_2 equivalent emission than the fossil energy regarding to this study, however, to commercialize the woody biomass pyrolysis technology, it requires to enhance the production rate of the technology.

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Table 5.1. Input data of mass balance and energy consumption per acre within the system boundary

Processes	Inputs	Units	Fast pyrolysis	Slow pyrolysis	Kiln	Data source
Plantation	Water	l	108382	108382	108382	USLCI database, (Johnson et al., 2005), (Frazier et al., 1981), American Pulpwood Association 1978 and John Deere Inc.
	Nitrogen	kg	76.51	76.51	76.51	
	Phosphate	kg	13.13	13.13	13.13	
	Potassium	kg	3.29E-05	3.29E-05	3.29E-05	
	Electricity	kWh	0.01	0.01	0.01	
	Gasoline	l	4.75E-03	4.75E-03	4.75E-03	
	Diesel	l	22.97	22.97	22.97	
	CO_2	t	103	103	103	
	Machinery	kg	2.83	2.83	2.83	
Harvesting	Diesel	l	271.54	271.54	271.54	USLCI database, (Johnson et al., 2005) and John Deere Inc.
	Lubricant	kg	4.09	4.09	4.09	
	Feller buncher	kg	3.05	3.05	3.05	
	Skidder	kg	14.04	14.04	14.04	
	Delimber	kg	5.69	5.69	5.69	
	Loader	kg	21.66	21.66	21.66	
	Tansportation	tkm	4536	4536	4536	
	Truck	kg	6.84	6.84	6.84	
Processing	Diesel	l	157	157	-	USLCI database, (Baker et al., 2010), (Valente et al., 2011), Nicholson company, and Caterpillar Inc.
	Electricity	kWh	686	686	-	
	Machinery	kg	5.17	5.17	-	
	Gasoline	l	-	-	5.25	
	Lubricant	kg	-	-	0.08	
	Power saw	p	-	-	3.70E-03	
Pyrolysis	Heat	MJ	133518	104706	-	(Steele et al., 2012) (Han et al., 2013) (Rath et al., 2003) (Das et al., 2008) (Bailis et al., 2012) (Hollingdale et al., 1991) (Thek& Obernberger, 2004) (Esteban & Carrasco, 2006) (Roberts et al., 2009) (Hollingdale et al., 1991)
	Electricity	kWh	11670	6573	-	
	Diesel	l	-	-	148.78	
	Construction	p	4.02E-06	8.04E-06	3.95E-03	

Table 5.2. Impact assessment of biochar production on per metric ton basis

Impact category	Units	Fast pyrolysis	Slow pyrolysis	Missouri kiln
TRACI				
Ozone depletion	kg CFC-11 eq	9.64E-05	4.94E-05	1.02E-06
Global warming	kg CO_2 eq	6.51E+02	4.17E+02	1.73E+03
Smog	kg O_3 eq	8.94E+01	6.53E+01	7.61E+01
Acidification	mol H^+ eq	3.42E+02	2.21E+02	7.21E+01
Eutrophication	kg N eq	5.87E-01	4.09E-01	2.40E-01
Carcinogenics	CTUh	1.51E-04	8.08E-05	8.56E-06
Non carcinogenics	CTUh	5.90E-05	4.24E-05	2.69E-05
Respiratory effects	kg PM10 eq	2.21E+00	1.22E+00	1.23E-01
Ecotoxicity	CTUe	5.26E+02	4.54E+02	4.16E+02
BEES				
Water intake	liters	3.61E+04	3.70E+04	6.32E+04

Table 5.3. Emissions to air of 1 metric ton biochar production from three scenarios

Substance	Unit	Fast pyrolysis	Slow pyrolysis	Missouri kiln
CO_2 (biogenic)	kg	580.71	299.23	1727.50
CO_2 (fossil)	kg	614.00	391.97	107.80
CO (biogenic)	kg	0.01	0.02	419.28
CO (fossil)	kg	2.80	1.85	0.86
CH_4	kg	1.30	0.82	64.53
VOC	g	65.49	56.78	11458.25
NO_x	kg	3.47	2.55	1.31
SO_x	g	290.55	203.59	111.84
SO_2	kg	3.51	2.04	0.21
Particulates	kg	1.87	1.01	13.36

Table 5.4. Sensitivity analysis of allocation methods of biochar production

Category	Units	Fast pyrolysis			Slow pyrolysis			Missouri kiln		
Allocation methods		mass(base)	economic	energy	mass(base)	economic	energy	mass(base)	-	-
total energy	GJ/t	9.08	13.9	30.5	5.89	4.41	9.62	2.19	-	-
net energy	GJ/t	18.92	14.1	-2.5	24.11	25.59	20.38	24.81	-	-
Global warming	kg CO_2 eq	651.05	998.96	2185.33	416.76	311.92	681.16	1726.00	-	-
Smog	kg O_3 eq	89.41	137.19	300.13	65.25	48.84	106.65	76.10	-	-
Acidification	mol H^+ eq	341.55	524.07	1146.45	221.46	165.75	361.96	72.08	-	-
Eutrophication	kg N eq	0.59	0.90	1.97	0.41	0.31	0.67	0.24	-	-

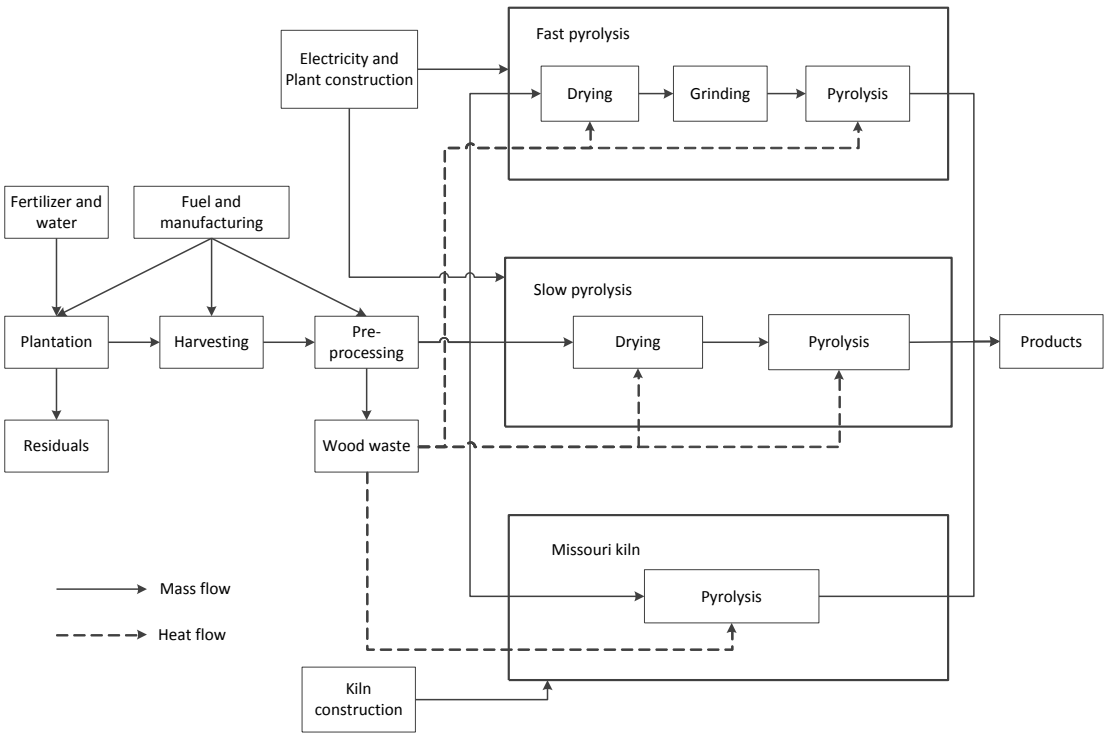


Figure 5.1. System boundary of different scenarios to produce biochar or bio-oil from southern pine

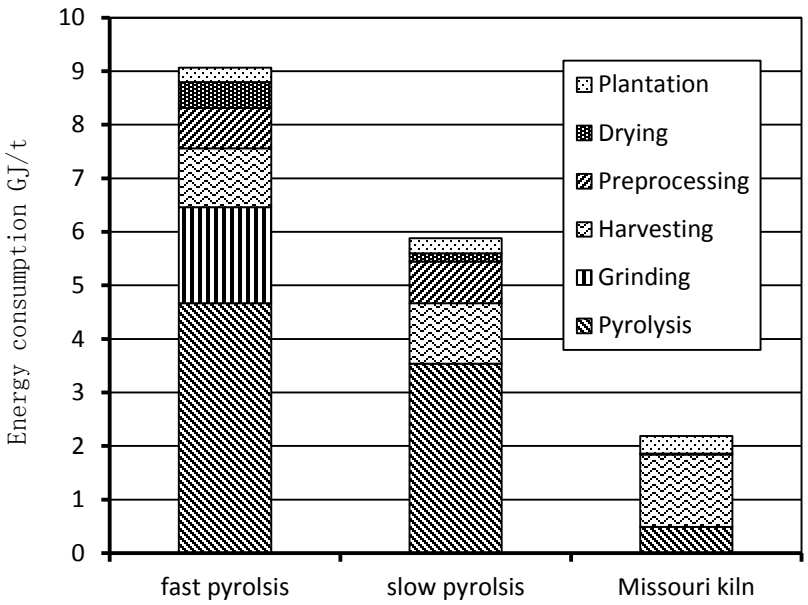


Figure 5.2. Breakdown energy consumption for each process of biochar production from three scenarios

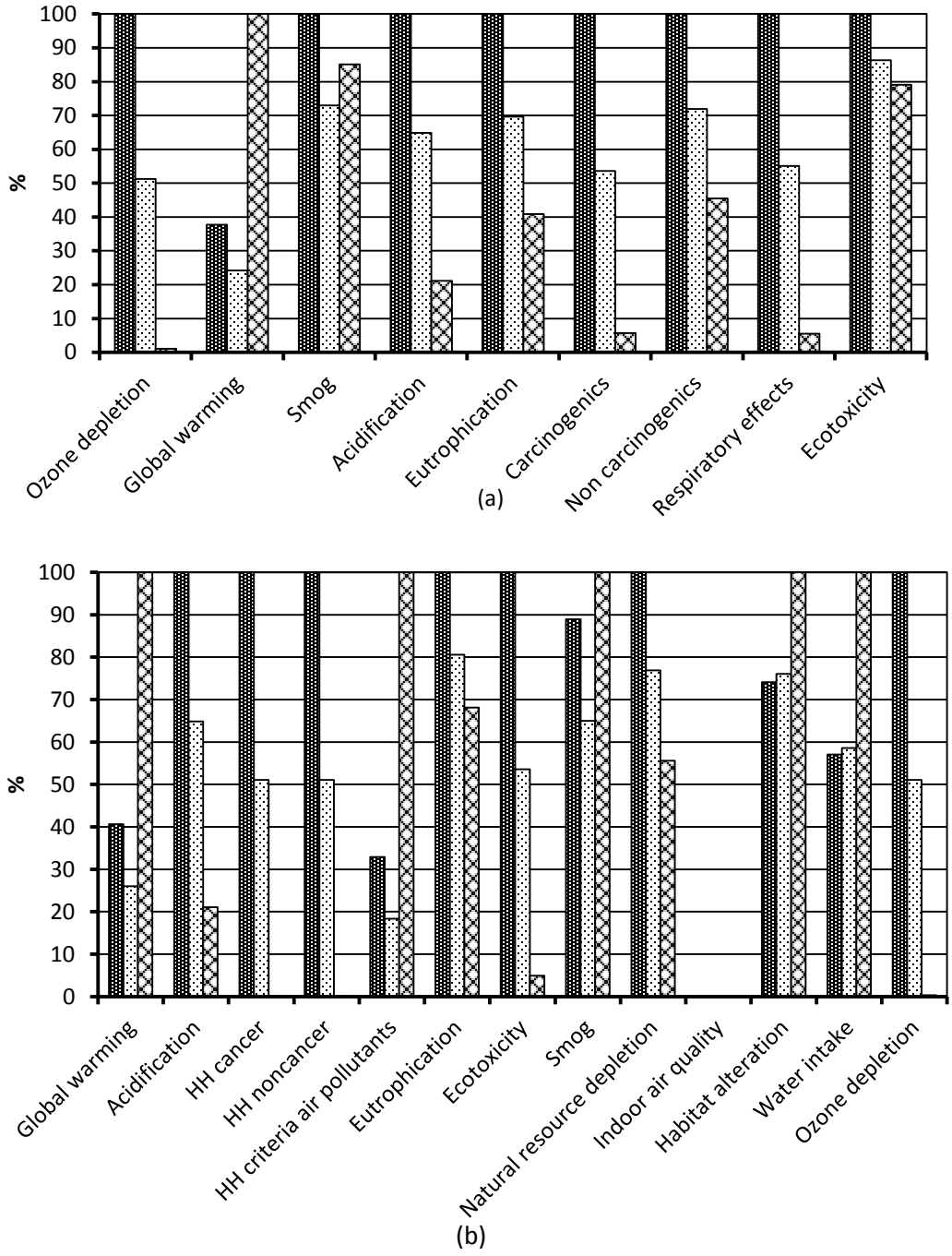


Figure 5.3. Comparison of impact assessment of biochar production from three scenarios (a) TRACI method (b) BEES method

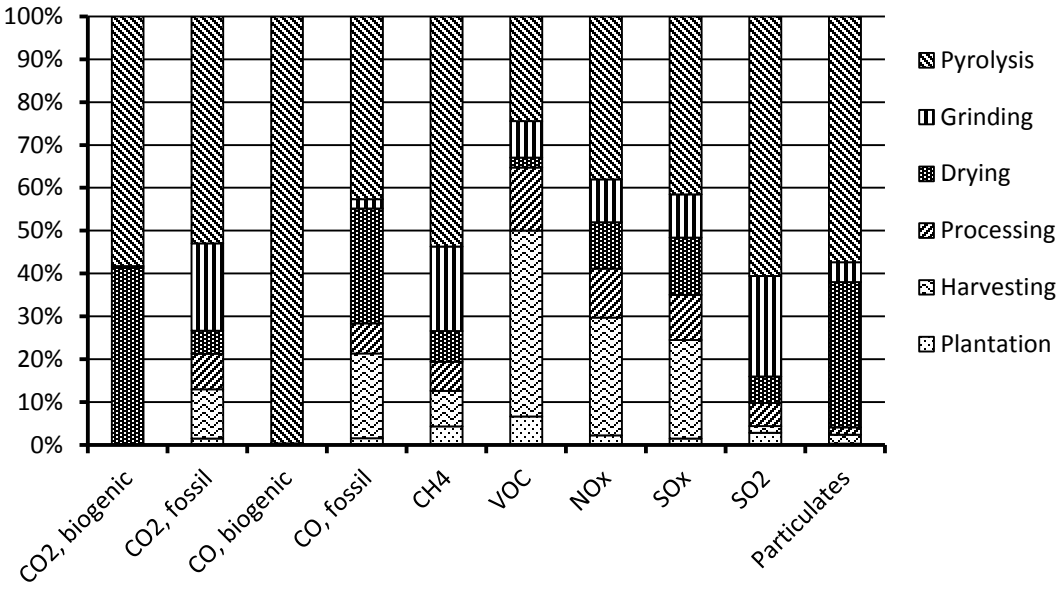


Figure 5.4. Process contribution of fast pyrolysis to airborne emissions

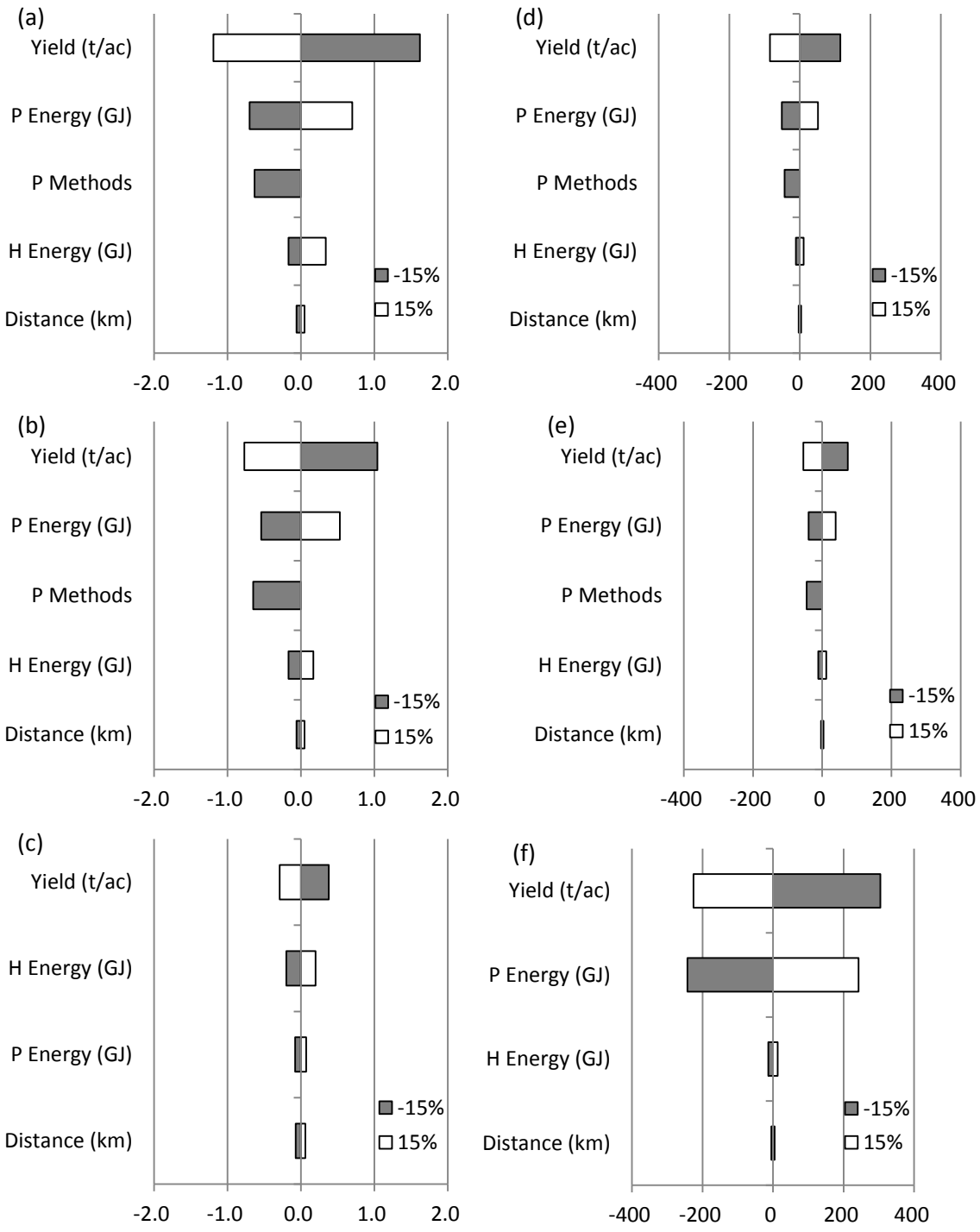


Figure 5.5. (a), (b) and (c) fast pyrolysis, slow pyrolysis and Missouri kiln sensitivity analysis of total energy use (GJ/t); (d), (e) and (f) fast pyrolysis, slow pyrolysis and Missouri kiln sensitivity analysis of CO_2 equivalent emission (kg CO_2 eq/t)

CHAPTER 6

CONCLUSION

In this study, the economic and environmental impacts of a new microalgae liquefaction technology were evaluated and compared with wood pyrolysis technologies. A continuous two-stage microalgae hydrothermal liquefaction technology combined with hydrodeoxygenation process was designed in a commercial scale in this research. The plant life was assumed as 30 years and the capacity was 0.5 million gallon bio-crude per year. Open raceway ponds with unit size of 10 acres (40468.6 m^2) was selected to grow microalgae in a commercial scale and three-step harvesting process was utilized to concentrate algae slurry from 0.05% to 15% before HTL reactions. The first stage HTL reacted in the temperature of 225º C for 15 min in order to decompose the protein compounds to remove the nitrogen content in the products. The second stage HTL was in the temperature of 350º C for 60 min to further degrade carbohydrates, proteins and lipids components to generate bio-crude oil which was then reacted with hydrogen in the presence of Ru/C as catalyst in the HDO process to reduce oxygen and nitrogen content.

The microalgae production rate of the designed plant was 11,459 MT/yr and the algae crude oil production rate was 578,661 gal/yr (2.19×10^6 L/yr). The total capital investment was estimated as $113.23 MM and the operating cost was $13.11 MM/yr, which resulted in a minimum selling price of $49.80 per gallon of bio-crude oil. Increasing in HTL and HDO yield were found to have the potential to significantly reduce the production cost of algae bio-crude. The minimum selling price might reduce to under $10/gal if the

microalgae growth rate, HTL yield and HDO yield increase 1 fold. Scaling up the algal bio-crude production system also had the potential to reduce the minimum selling price but it meant more investment in the pre-stage of the production.

In the life cycle assessment of microalgae liquefaction technology, the total of 1044.70 MJ of fossil energy was consumed and 15.55 kg CO_2 eq net emission was released to produce 1 gallon of algal bio-crude oil. The usage of electricity generated from fossil energy had around 60% proportion of the total GHG emissions. Therefore, electricity utilization efficiency of the system requires improvement in order to enhance the algal biofuels' overall environmental performance. Besides, reducing the indirect fossil energy used in the production system, such as electricity from coal, is another way to lower the life cycle GHG emissions from algal bio-crude, thus, it is a good way to improve the sustainability for all direct and indirect energy used in the algal biofuels production.

Life cycle assessment of various pyrolysis technologies to produce biochar/bio-oil from pine wood and energy crops was investigated to compare with the algae liquefaction technology. Biochar produced from Missouri kiln had the lowest energy consumption as 2.19 GJ/t of biochar and highest CO_2 equivalent emission as 1726 kgCO_2e/t of biochar. Slow pyrolysis had 5.89 GJ/t of total energy use and 416.76 kgCO_2e/t of emissions while fast pyrolysis resulted in 9.08 GJ/t of energy consumption and 651.05 kgCO_2e/t of GHG emissions. Slow pyrolysis technology had better overall performance in biochar production and fast pyrolysis technology was favorable for the bio-oil production. Whole chips (bark included) was found to have less environmental impact and energy consumption than clean chips.

Algae hydrothermal liquefaction is a promising means of converting algae to liquid transportation fuels. Using whole algae eliminates the need to promote lipid accumulation, and allows use of fast growing species. Nevertheless, there remains uncertainties on scale-up of the system in perspective of economics and sustainability. Further works are required to enhance the algae productivity and optimize the HTL and HDO operating conditions to increase yield and improve properties of bio-crude oil. Life cycle assessment of various pyrolysis technologies to produce biochar/bio-oil from pine wood and energy crops will be also investigated in the future to select both economic and environmentally benign technology and feedstock.

APPENDIX A

Supporting information of

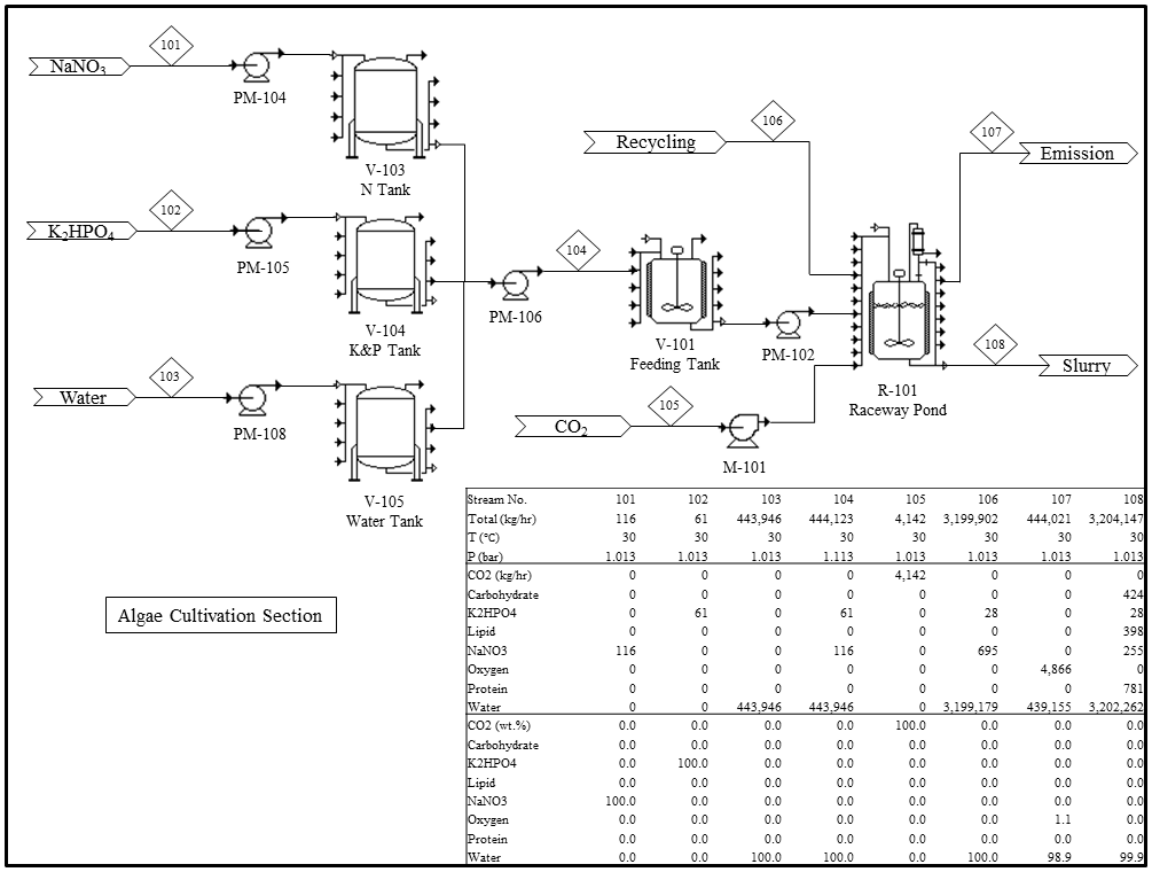
“Techno-economic analysis of algae liquefaction technology”

The Supporting Information contains 18 tables and 5 figures, for a total of 25 pages.

1. Process Design Details

1.1Algae Cultivation Section

In the beginning of this section, sodium nitrate, dipotassium phosphate and water were stored in tanks and pumped into the feeding tank to get mixed, and then sent to the open raceway pond where algae grown and lipid accumulated. CO_2 was pumped directly to the pond to provide carbon source (Figure A.1).



Stream No.	101	102	103	104	105	106	107	108
Total (kg/hr)	116	61	443,946	444,123	4,142	3,199,902	444,021	3,204,147
T (°C)	30	30	30	30	30	30	30	30
P (bar)	1.013	1.013	1.013	1.113	1.013	1.013	1.013	1.013
CO2 (kg/hr)	0	0	0	0	4,142	0	0	0
Carbohydrate	0	0	0	0	0	0	0	424
K2HPO4	0	61	0	61	0	28	0	28
Lipid	0	0	0	0	0	0	0	398
NaNO3	116	0	0	116	0	695	0	255
Oxygen	0	0	0	0	0	0	4,866	0
Protein	0	0	0	0	0	0	0	781
Water	0	0	443,946	443,946	0	3,199,179	439,155	3,202,262
CO2 (wt.%)	0.0	0.0	0.0	0.0	100.0	0.0	0.0	0.0
Carbohydrate	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
K2HPO4	0.0	100.0	0.0	0.0	0.0	0.0	0.0	0.0
Lipid	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
NaNO3	100.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Oxygen	0.0	0.0	0.0	0.0	0.0	0.0	1.1	0.0
Protein	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Water	0.0	0.0	100.0	100.0	0.0	100.0	98.9	99.9

Figure A.1. Process flow diagram and mass balance of algae cultivation

Open raceway ponds were selected for the algae cultivation. The pond design was followed of a previous work (Lundquist et al., 2010) which claimed to use the unit pond with the scale of 10 acres and the depth was 30 cm. Paddle wheels and CO_2 pumping station were built in the pond. $NaNO_3$ and K_2HPO_4 were designed as fertilizer to provide nitrogen and phosphorous for algae growth, which have been applied to the pilot scale raceway pond in the University of Georgia. The initial inputs for each unit pond were calculated based on the algae productivity of 25 $g/m^2/d$ (Frank et al., 2013). It was assumed that the slurry concentration was 0.5 g/L after algae cultivation. The water evaporation rate used in the simulation was 6.86 $kg/m^2/d$ which was an average rate of different evaporation equations in the condition of 25-30 ℃ with 45% relative humidity

for day time and 20-25 ℃ with 100% relative humidity for night time in free water surface (Sartori, 2000). The algae carbon content was 55.10 % wt. calculated from algae biochemical formula and CO_2 use efficiency was assumed as 78%, which gave the initial flow rate of CO_2 required. Same calculation was for $NaNO_3$ requirement with the nitrogen content of 7.5 % wt. and utilization efficiency of 90%. The consumption of K_2HPO_4 was dependent on the N: P rate of 8.4 (Wang et al., 2010). Table A.1 summarizes the initial feedstock and their flow rates for the algae cultivation. A considerable amount of water was required for algae growth which called for recycling when taken the economics into consideration. The details of recycling will be introduced in the harvesting section.

Table A.1. Initial inputs for algae cultivation

Feedstock	Flow Rates (kg/h/pond)
Water	95871.71
N ($NaNO_3$)	21.33
P/K (K_2HPO_4)	2.35
CO_2	109.19

Table A.2. Biochemistry compounds of algae

Compounds	Content (% wt.)	Chemistry Formula	Molecular Weight[a] (g/mol)
Carbohydrates	28	$C_6H_{12}O_6$	180
Protein	47	$C_{4.43}H_7O_{1.44}N_{1.16}$	100.1
Lipids	25	$C_{40}H_{74}O_5$	634
Algae	100	$C_{11.75}H_{20.65}O_{4.67}N_{1.39}$[b]	255.947

a. Molecular weight is calculated based on the components formula
b. The chemistry formula of algae is obtained based on the percentage composition of three fractions.

In this study, algae production was simulated within two stages: cell growth and lipid accumulation. The composition of algae is described with details in Table A.2. A continuous stirred tank reactor was utilized to model the algae cultivation in the open race way ponds. Algae can fix carbon from CO_2 in the presence of nutrient and sunlight. It was assumed that CO_2 was the rate limitation compound and Arrhenius equation was used to reflect the influence of temperature on algae growth rate as follow.

$$k = A\exp(-E/RT) \qquad \text{Eq (A.1)}$$

Where A = 6.19 × 104 s^{-1} and E = 53811.20 kJ/kmol (Goldman and Carpenter, 1974). The kinetics of algae growth was modeled as the first order reaction as follow.

$$r_g = \mu C_s \qquad \text{Eq (A.2)}$$

Where r_g is cell growth rate, μ is specific growth reaction rate related to temperature, C_s is substrate (i.e., nutrient) concentration. Same kinetics data were used for algae growth and lipid accumulation because of kinetics for lipid alone was missing. The reaction equations were shown in the Table A.3.

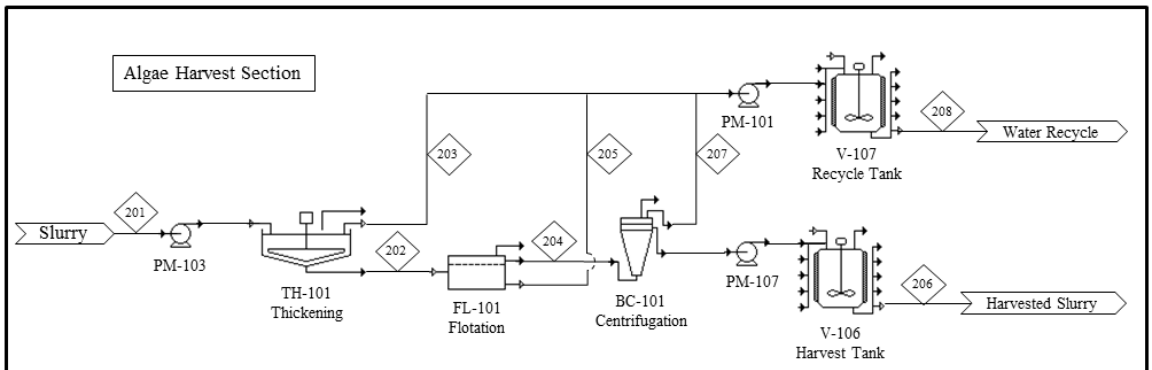
Table A.3. Algae cultivation reaction equations

Reaction	Stoichiometry Table
Algae growth	$10\ CO_2 + 0.07\ K_2HPO_4 + 1.39\ NaNO_3 + 10.29\ H_2O = 1Algae + 15.65O_2$
Algae to fraction	1 Algae = 0.5 Carbohydrates + 1.66 Protein
Lipid accumulation	$75\ CO_2 + 74\ H_2O = 1\ Lipid + 125\ O_2$

1.2 Algae harvesting Section

Algae harvesting was broken into three processes in the model: flocculation, dissolved air flotation (DAF) and centrifugation. The flow diagram and stream flow rates are described

in Figure A.2 with details. As stated in a previous model, the slurry concentration of algae in water before the first harvesting process was 0.5 g/L and the final solid concentration after harvesting was about 150 g/L (Frank et al., 2013).



Stream No.	201	202	203	204	205	206	207	208
Total (kg/hr)	3,204,147	155,791	3,048,355	24,849	130,942	9,491	15,359	3,194,655
T (°C)	30	30	30	30	30	30	30	30
P (bar)	1.013	1.013	1.013	1.013	1.013	1.013	1.013	1.013
Carbohydrate (kg/hr)	424	415	8	398	17	383	16	41
K2HPO4	28	1	27	0	1	0	0	28
Lipid	398	390	8	374	16	359	15	39
NaNO3	255	12	242	2	10	1	1	254
Protein	781	765	16	734	31	705	29	76
Water	3,202,262	154,207	3,048,054	23,340	130,867	8,043	15,297	3,194,218
Carbohydrate (wt.%)	0.0	0.3	0.0	1.6	0.0	4.0	0.1	0.0
K2HPO4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Lipid	0.0	0.3	0.0	1.5	0.0	3.8	0.1	0.0
NaNO3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Protein	0.0	0.5	0.0	3.0	0.0	7.4	0.2	0.0
Water	99.9	99.0	100.0	93.9	99.9	84.7	99.6	100.0

Figure A.2. Process flow diagram and mass balance of algae harvest

In flocculation, the material balances in the model were based on the removal percentage of particulate components and the solids concentration in sludge. The algae cells removal rate was assumed to be 98% in this step and the slurry concentration was increased to 10 g/L. The feed volumetric loading rate was specified as 0.5 $m^3/m^2 \cdot h$. The sedimentation area which was the cross sectional area of the basin was calculated by dividing the feed flow rate by the loading rate.

Dissolved air flotation was used to separate suspended algae cells from the continuous liquid phase using the buoyancy of air bubbles. Mass balance was based on the removal (flotation) percentage of algae cells and their concentration in slurry. A flotation tank was

used in the model to simulate this process. It was assumed that the removal percentage was 96% and the slurry concentration was 60g/L after the process. The cross sectional area of the flotation tank was calculated by dividing the combined flow rate to the unit by the surface loading rate. The usage of air was a very important consideration in this step, which was calculated by the following equation.

$$\frac{A}{S} = \frac{1.3 s_a (fP-1)}{S_a} \qquad \text{Eq (A.3)}$$

Where A/S is the air-to-solid ratio (in mL air/mg solids), s_a is air solubility (in mL/L), f is fraction of dissolved air at pressure P (usually 0.5), P is the pressure (in atm), and S_a is the solids concentration in the sludge (in mg/L). In the model, the air to solid ratio was specified as 0.03 mL/mg and solubility was assumed as 15.38 mL/L with a saturation level of 50%. The pressurized air recycle rate was set as 50% and the total surface loading rate was 2 $m^3/m^2 \cdot h$. The residence time was 20 min as a design parameter.

Separation by centrifugation is based on the sedimentation principle. According to the Sigma Theory, in order to separate particles of diameter greater than a limit particle diameter (d_{lim}), the throughput (Q) of a centrifugal separator can be calculated from the following equation:

$$Q = \eta \left(\frac{d_{lim}^2 \Delta\rho g}{18\mu}\right) \left[\frac{2\pi}{3g} \omega^2 N \cot\alpha (r_1^3 - r_2^3)\right] \qquad \text{Eq (A.4)}$$

Where η is the efficiency of the centrifuge, d_{lim} is the equivalent Stokes' diameter of the limit particle, $\Delta\rho$ is the density difference between the solid and the liquid, μ is the viscosity of the liquid, ω is the angular speed of the disks, N is the number of disks, α is the angle between the disks and the axis of the centrifuge, and r_1 and r_2 are the outer and inner diameter of the disks respectively. The term in the second pair of brackets of the equation is the Sigma Factor which indicates the size of a centrifuge with the

equivalent surface area of a sedimentation tank to perform the same separation process. A bowl centrifuge was selected to conduct the solid-liquid separation of algae cells and water medium. The efficiency of a typical disk-stack centrifuge is generally less than 50% and the average value is about 30% which was used in this step of harvesting. The removal percentage of the solid was the same with the DAF process (96%) and the slurry concentration desired was 150 g/L after the process. It was assumed that the minimum diameter of algae cell was 11 μm and the density was 1030 g/L. Water density was used for the liquid phase because of the very low concentration of the algae slurry which viscosity was 7 cP as an assumption. Water was collected from the three steps of the harvesting and then pumped to a blending tank to recycle the water and nutrients to the raceway pond.

1.3 Hydrothermal Liquefaction Section

Bio-crude is a mixture containing thousands of chemical compounds, mainly of hydrocarbons. The composition of the oil varies dependent upon the feedstock and process operation conditions. In this design research, the composition of bio-crude was modeled based on the elemental analysis of the algae HTL experimental work (Table A.4). Two compositions of the crude oil were simulated to represent the difference before and after the HDO process. Original crude oil (obtained directly from HTL process) usually contains more oxygen and nitrogen than the upgraded bio-crude (produced after HDO process).

Table A.4. Composition of bio-crude oil

Type	%C	%H	%O	%N	Formula	MW(g/mol)
Original	71.41	8.81	5.93	13.85	$C_{30}H_{44.41}O_{4.36}N_{2.14}$	504.13
Upgraded	78.98	11.99	6.06	2.97	$C_{30}H_{54.65}O_{1.73}N_{0.97}$	455.91

A two-stage HTL process was designed in this model in order to reduce the nitrogen and oxygen content in the bio-crude oil. Process flow diagram is illustrated in Figure A.3 and the stream details are listed in Table A.5.

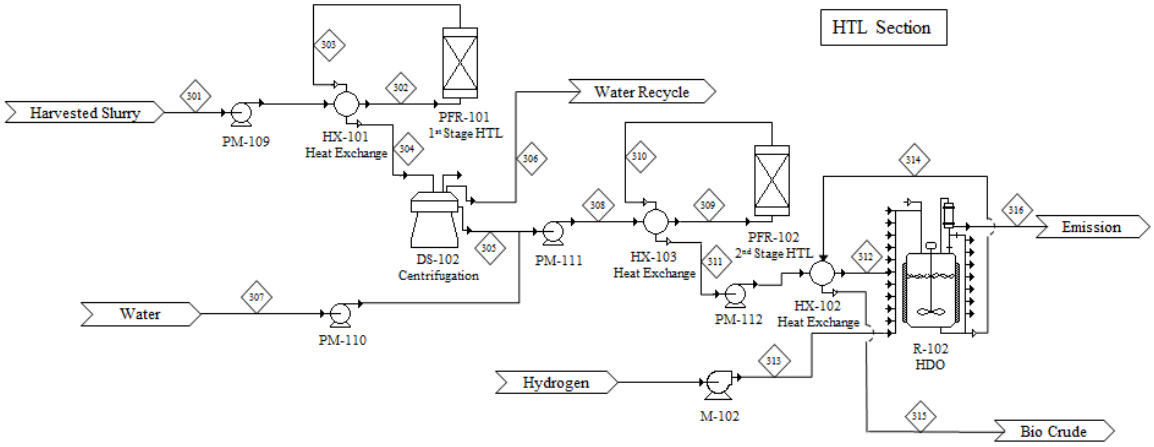


Figure A.3. Flow diagram of the HTL & HDO section

Two plug flow reactors with 100% working volume were used to simulate the HTL processes and HDO reaction was carried out in a CSTR of 90% working volume. Reactors sizing was the same with vessel sizing for storage tank. Reaction conditions are summarized in the Table A.6.

Table A.6. HTL reactions operating condition

Reaction	Temperature (℃)	Pressure (bar)	Residence Time (min)	Reactor Type
Stage 1 HTL	225	200	15	PFR
Stage 2 HTL	350	200	60	PFR
HDO	350	200	240	CSTR

Table A.5. Stream details of HTL and HDO section

Stream No.	301	302	303	304	305	306	307	308	309	310	311	312	313	314	315	316
Total (kg/hr)	9,491	9,491	9,491	9,491	4,144	5,347	7,200	11,344	11,344	11,344	11,344	11,344	90	9,043	9,043	2,391
T (℃)	30	145	225	111	111	111	90	98	275	350	180	275	80	350	225	350
P (bar)	1.01	201.01	201.01	100.12	1.01	1.01	1.01	201.01	201.01	201.01	103.31	201.013	200.01	200	128.57	200
2HTL tar (kg/hr)	0	0	0	0	0	0	0	0	0	188	188	188	0	188	188	0
2HTL water	0	0	0	0	0	0	0	0	0	7,999	7,999	7,999	0	1	1	0
Amino Acids	0	0	146	146	58	87	0	58	58	0	0	0	0	0	0	0
Bio-crude	0	0	0	0	0	0	0	0	0	220	220	220	0	5	5	0
CO2	0	0	0	0	0	0	0	0	0	997	997	997	0	0	0	1,074
Carbohydrate	383	383	308	308	305	3	0	305	305	0	0	0	0	0	0	0
CO	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	5
DG	0	0	1	1	1	0	0	1	1	161	161	161	0	161	161	0
Ethane	0	0	0	0	0	0	0	0	0	290	290	290	0	0	0	290
Fatty Acids	0	0	0	0	0	0	0	0	0	137	137	137	0	137	137	0
Glucose	0	0	74	74	74	1	0	74	74	0	0	0	0	0	0	0
Glycerol	0	0	0	0	0	0	0	0	0	6	6	6	0	6	6	0
HDO Solid	0	0	0	0	0	0	0	0	0	0	0	0	0	108	108	0
HDO water	0	0	0	0	0	0	0	0	0	0	0	0	0	6,916	6,916	0
Hydrogen	0	0	0	0	0	0	0	0	0	0	0	0	90	0	0	69
K2HPO4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Lipid	359	359	358	358	354	4	0	354	354	48	48	48	0	48	48	0
Methane	0	0	0	0	0	0	0	0	0	23	23	23	0	0	0	26
MG	0	0	0	0	0	0	0	0	0	8	8	8	0	8	8	0
NaNO3	1	1	1	1	0	0	0	0	0	0	0	0	0	0	0	0
Nitrogen	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	927
Protein	705	705	582	582	291	291	0	291	291	0	0	0	0	0	0	0
Upgraded Oil	0	0	0	0	0	0	0	0	0	0	0	0	0	198	198	0
Water	8,043	8,043	8,021	8,021	3,060	4,961	7,200	10,260	10,260	1,267	1,267	1,267	0	1,267	1,267	0
2HTL tar (% wt.)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.7	1.7	1.7	0.0	2.1	2.1	0.0
2HTL water	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	70.5	70.5	70.5	0.0	0.0	0.0	0.0
Algae	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Amino Acids	0.0	0.0	1.5	1.5	1.4	1.6	0.0	0.5	0.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Bio-crude	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.9	1.9	1.9	0.0	0.1	0.1	0.0
CO2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	8.8	8.8	8.8	0.0	0.0	0.0	44.9
Carbohydrate	4.0	4.0	3.2	3.2	7.4	0.1	0.0	2.7	2.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CO	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2
DG	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.4	1.4	1.4	0.0	1.8	1.8	0.0
Ethane	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.6	2.6	2.6	0.0	0.0	0.0	12.1
Fatty Acids	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.2	1.2	1.2	0.0	1.5	1.5	0.0
Glucose	0.0	0.0	0.8	0.8	1.8	0.0	0.0	0.6	0.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Glycerol	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.1	0.0
HDO Solid	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.2	1.2	0.0
HDO water	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	76.5	76.5	0.0
Hydrogen	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	100.0	0.0	0.0	2.9
K2HPO4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Lipid	3.8	3.8	3.8	3.8	8.5	0.1	0.0	3.1	3.1	0.4	0.4	0.4	0.0	0.5	0.5	0.0
Methane	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.2	0.2	0.0	0.0	0.0	1.1
MG	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.1	0.1	0.0	0.1	0.1	0.0
NaNO3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Nitrogen	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	38.8
Protein	7.4	7.4	6.1	6.1	7.0	5.4	0.0	2.6	2.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Upgraded Oil	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.2	2.2	0.0
Water	84.7	84.7	84.5	84.5	73.8	92.8	100.0	90.4	90.4	11.2	11.2	11.2	0.0	14.0	14.0	0.0

In the first HTL process, the algae slurry was pumped into a heat exchanger to preheat the inlet flow with the hot output from the first stage of HTL. The energy balance was calculated based on the equation below.

$$Q = \eta U A \Delta T_{lm} = \Delta H_{hot} = \Delta H_{cold} \qquad \text{Eq (A.5)}$$

Where Q is the heat transfer rate, η is a correction factor that accounts for deviation from counter-current or co-current flow, U is the overall heat transfer coefficient, A is the heat transfer area, ΔT_{lm} is the log mean of the temperature difference in the system, and ΔH_{hot} and ΔH_{cold} are the enthalpy changes of the hot and cold streams, respectively. The correction factor was 0.9 for the countercurrent flow as default and the heat transfer coefficient of 170 BTU/hr·ft2·°F was employed, which was used for a reactor feed/water product cross exchanger of HTL reactor design in a NREL report (Knorr et al., 2013). The outlet temperature of cold feedstock steam was set as 145℃ and the pressure drop of the hot product stream was calculated from the ideal gas law. The heat exchangers utilized in the second stage HTL and HDO followed the same design equation above; however, the heat transfer coefficients were set as 154 BTU/hr·ft2·°F for the reactor feed/hot oil exchanger,[6] and the cold stream outlet temperatures were designed as 275℃ to meet the reactions temperature of 350℃.

Carbohydrates (CH), proteins (P) and lipids (L) can be hydrolyzed in the HTL process to degrade to glucose (GC), amino acids (AA), and fatty acids (FA) and glycerol (G), respectively (Figure S4). The main compound in lipid is triglycerides (TG) which is firstly hydrolyzed to diglycerides (DG) and secondly to monoglycerides (MG) and finally to glycerol. Each steps of lipid decomposition of one molecular substrate gives one molecular of fatty acids which means that one mole triglycerides can generate three

moles of fatty acids and one mole of glycerol during hydrolysis. The hydrolysis products as intermediates can be further decompose to more complex compounds which constitute bio-crude oil (CO).

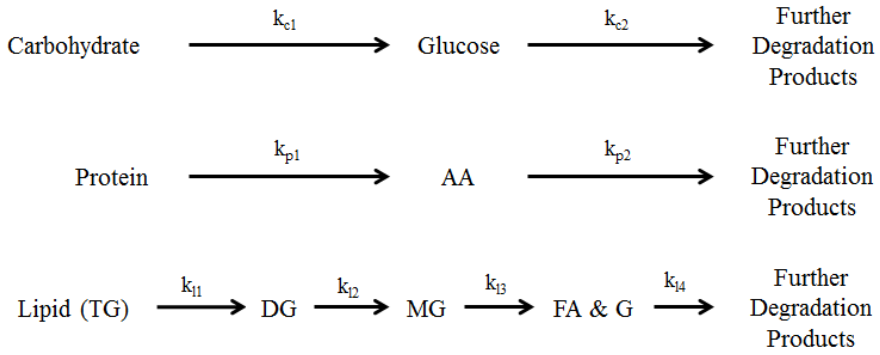


Figure A.4. Schematic diagram of algae decomposition

HTL reactions were modeled based on the kinetics of model compounds decomposition reported by previous publications (Table A.7), however, HDO reaction kinetics were missing so it was simulated only using stoichiometry table which were developed from the yield percentage of the algae liquefaction experiments of batch system (Table A.8). All reactions were assumed as first order reaction.

Table A.7. Kinetics of algae HTL reactions

Reactions	Activation Energies (kJ/kmol)	Pre-exponential factors (s^{-1})	
CH→ GC	134400	1.10×10^{11}	(Rogalinski et al., 2008)
GC → CO	72500	1.80×10^{5}	(Rogalinski et al., 2008)
P → AA	114800	2.33×10^{8}	(Rogalinski et al., 2008)
AA → CO	122200	2.49×10^{10}	(Rogalinski et al., 2008)
TG → DG	98000	8.67×10^{4}	(Alenezi et al., 2009)
DG → MG	38000	1.83×10^{-1}	(Alenezi et al., 2009)
MG → G	90000	4.67×10^{4}	(Alenezi et al., 2009)
FA & G→CO	7500	2.58×10^{-4}	(Jhnson and Tester, 2013)

Table A.8. Yield percentage from algae liquefaction experiments

Reaction	Solid (% wt.)	Aqueous (% wt.)	Oil (% wt.)	Gas (% wt.)				
				CO_2	CH_4	C_2H_6	CO	N_2
HTL	1.94	90.06	2.26	4.37	0.10	1.27	-	-
HDO	1.32	91.46	2.40	0.37	0.01	-	0.02	4.42

After first stage HTL, three model compounds in algae were partially hydrolyzed in different degrees to form intermediates which could be separated into two phase: one was aqueous phase containing soluble intermediates such as glucose and some amino acids; the other was solid phase containing unreacted biomass and insoluble compounds. A disk centrifuge was used for the separation process to recycle the water phase to the raceway pond and to send the solid phase to the second stage HTL. It was assumed that the solid removal rate for carbohydrates and lipid as well as their hydrolyzed intermediates were 99%, 40% for amino acids, and 50% for proteins. The design equation and parameters were the same with the blow centrifuge in algae harvest section. After phase separation, water was compensated to the stream to make the slurry concentration around 9 % wt. for the second HTL reaction. Heater exchanger was also used to increase the stream temperature before the reaction like it was in the first stage. At the second HTL process, rough bio-crude oil was produced and the entire products were pumped into HDO reactor for reducing the nitrogen and oxygen contents. Hydrogen was added with the ratio of 0.41 g H_2/g crude and Ru/C was used as catalyst. The features of catalyst are described in Table A.9. Products could be separated into four phases which were gas,

liquid, solid and oil phase. Gases were venting from the reactor and other three phases were sent to the separation section for oil extraction.

Table A.9. Features of catalyst for HDO process

Type	Load	price ($/kg)	Amount (g/g oil)	Life time (yr)	Recycle
Ru/C	5%	121.25	2.02	2	95%

1.4 Separation Section

Process flow diagram was illustrated in the Figure A.5 and stream details are shown in Table A.10. Upgraded bio-crude was extracted from water-oil mixture using dichloromethane (DCM) after filtering off the solid wastes. DCM was recycled using a distillation process and the extracted final bio-crude was stored in oil tanks for transportation.

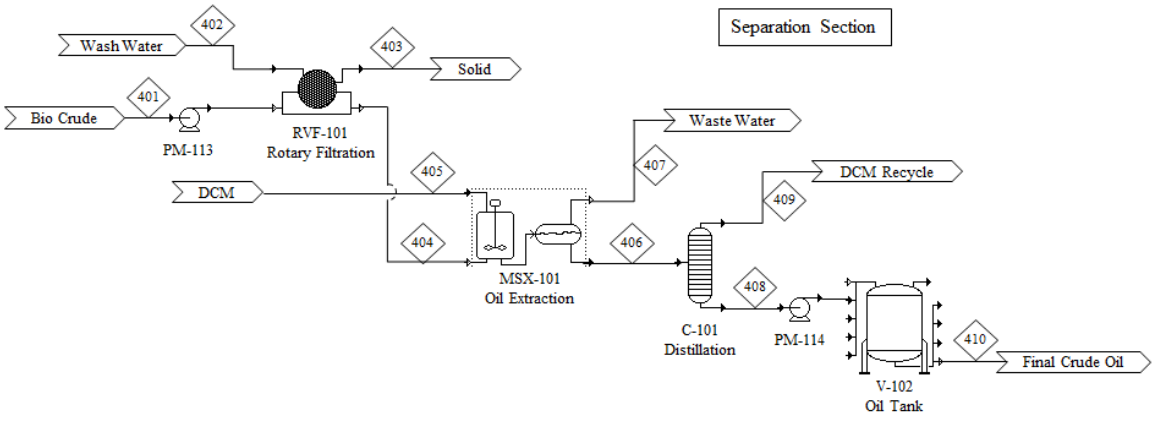


Figure A.5. Flow diagram of the separation section

A rotary vacuum filter was designed to perform the filtration operation. The material balances were based on the removal percentage of solids and the cake dryness which determined the amount of water retained in the cake before washing. The filter area (A) of was calculated using the following equation:

$$A = \frac{V_{slurry}}{Jt_p} \qquad \text{Eq (A.6)}$$

Where V_{slurry} is the volume of slurry processed, J is the average filtrate flux and t_p is the filtration time. The slurry volume only accounted for the feed volume, not including the wash water volume. The average filtrate flux rate was assumed to be 250 $L/m^2 \cdot h$ and the cake porosity was designed as 0.4 v/v with the solid removal rate of 99%.

For the oil extraction process, a mixer and settler combined unit was utilized. DCM was added as a solvent with the ratio of 39.54 g/g crude oil to mix with the stream, conducting the liquid-liquid extraction which was designed as single stage. The mixer and settler residence time were set as 10 and 30 min respectively and the extraction occurred at the temperature of 40 ℃. The mass balance was obtained from the following equation.

$$Hx_2 = H\left[\frac{(KL/H)^2-1}{(KL/H)-1}\right]x_1 - Ly_0 \qquad \text{Eq (A.7)}$$

Where L and H are the volumetric flow rates of the light and heavy phase respectively, yi and xi is the product composition at stage i in the light and heavy phase respectively, and K is the partition coefficient of a certain component, which equals to yi/xi. The number of stages was specified to calculate the upgraded crude oil recovery and the composition of the outlet streams. The partition coefficient of crude oil was assumed as 0.1 and the fraction of DCM in the water phase was specified as 0.001. The sizing of the extraction equipment was based on the residence time specified.

After extraction, crude oil was in the heavy phase with DCM which could be separated and recycled via distillation process due to its volatility. Feeding stream was coming into the middle of the vessel with DCM vaporizing and moving upward while crude oil going downwards. The oil leaving the main vessel was re-boiled and the produced DCM vapor entered the distillation drum again to meet the downwards liquid phase to condense the oil compounds that might be contained in the vapor. The boiler temperature was set as 40.55 ℃ which is the normal boiling point of DCM and the cooling temperature was set as 35 ℃. The percentages of DCM and upgraded oil that ended up in the distillate were assumed to be 99.5% and 0.1% respectively. The overall material balances were calculated based on these percentages. The equipment sizing was dependent upon the theoretical stages (N) using the following equation.

$$\frac{N-N_{min}}{N+1} = 0.75 - 0.75\left(\frac{R-R_{min}}{R+1}\right)^{0.5668} \qquad \text{Eq (A.8)}$$

Where N_{min} is the minimum number of stages, R is the desired reflux rate and R_{min} is the minimum reflux rate. The number of actual stages was calculated by dividing the number of theoretical stages by the stage efficiency which was 80% as default. The final upgraded crude oil was then pumped into a storage tank with a residence time of 24 hr before transportation.

1.5 Common Process Equipment

Centrifugal pumps were used in all sections in the model. Typically for centrifugal pump, the max system pressure is 48 MPa and the approximate capacity limit is 10 m^3/s. The efficiency of the pumps is ranging from 40-80% and the limitation of the viscosity is less than 0.1 Pa·s (Peters et al., 1991). According to these specifications, algae slurry can be sent by the centrifugal pumps. It was assumed the pump efficiency was 80% in the

simulation model. The required power was calculated from the following equation. Where Q is the volumetric flow rate, ΔP is the desired pressure change and η is the efficiency.

$$\text{Power} = Q\Delta P/\eta \qquad \text{Eq (A.9)}$$

Table A.10. Stream details of separation

Stream No.	401	402	403	404	405	406	407	408	409	410
Total (kg/hr)	9,043	200	537	8,707	7,802	8,014	8,495	258	7,756	258
T (℃)	350	25	113.48	113.48	25	40	40	40.55	32	40.57
P (bar)	200	1.013	1.103	201	1.013	1.013	1.013	1.013	1.013	1.013
2HTL tar (kg/hr)	188	0	186	2	0	2	0	2	0	2
2HTL water	1	0	0	1	0	0	1	0	0	0
Amino Acids	0	0	0	0	0	0	0	0	0	0
Bio-crude	5	0	0	5	0	5	0	5	0	5
CO_2	0	0	0	0	0	0	0	0	0	0
Carbohydrate	0	0	0	0	0	0	0	0	0	0
CO	0	0	0	0	0	0	0	0	0	0
DCM	0	0	0	0	7,802	7,795	8	39	7,756	39
DG	161	0	0	161	0	0	161	0	0	0
Ethane	0	0	0	0	0	0	0	0	0	0
Fatty Acids	137	0	0	137	0	0	136	0	0	0
Glucose	0	0	0	0	0	0	0	0	0	0
Glycerol	6	0	0	6	0	0	6	0	0	0
HDO Solid	108	0	107	1	0	1	0	1	0	1
HDO water	6,916	0	15	6,901	0	11	6,890	11	0	11
Hydrogen	0	0	0	0	0	0	0	0	0	0
K2HPO4	0	0	0	0	0	0	0	0	0	0
Lipid	48	0	48	0	0	0	0	0	0	0
Methane	0	0	0	0	0	0	0	0	0	0
MG	8	0	0	8	0	0	8	0	0	0
NaNO3	0	0	0	0	0	0	0	0	0	0
Nitrogen	0	0	0	0	0	0	0	0	0	0
Protein	0	0	0	0	0	0	0	0	0	0
Upgraded Oil	198	0	0	198	0	198	0	198	0	198
Water	1,267	200	179	1,288	0	2	1,286	2	0	2
2HTL tar (% wt.)	2.1	0.0	34.7	0.0	0.0	0.0	0.0	0.7	0.0	0.7
2HTL water	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Algae	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Amino Acids	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Bio-crude	0.1	0.0	0.0	0.1	0.0	0.1	0.0	1.8	0.0	1.8
CO_2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Carbohydrate	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CO	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
DCM	0.0	0.0	0.0	0.0	100.0	97.3	0.1	15.1	100.0	15.1
DG	1.8	0.0	0.1	1.9	0.0	0.0	1.9	0.1	0.0	0.1
Ethane	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Fatty Acids	1.5	0.0	0.1	1.6	0.0	0.0	1.6	0.1	0.0	0.1
Glucose	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Glycerol	0.1	0.0	0.0	0.1	0.0	0.0	0.1	0.0	0.0	0.0
HDO Solid	1.2	0.0	20.0	0.0	0.0	0.0	0.0	0.4	0.0	0.4
HDO water	76.5	0.0	2.8	79.3	0.0	0.1	81.1	4.3	0.0	4.3
Hydrogen	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
K2HPO4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Lipid	0.5	0.0	8.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Methane	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
MG	0.1	0.0	0.0	0.1	0.0	0.0	0.1	0.0	0.0	0.0
NaNO3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.1
Nitrogen	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Protein	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Upgraded Oil	2.2	0.0	0.1	2.3	0.0	2.5	0.0	76.5	0.0	76.5
Water	14.0	100.0	33.4	14.8	0.0	0.0	15.1	0.8	0.0	0.8

Storage Tank is common equipment in the model as well. Two types were used: one was vertical on legs tank and the other was the blending tank which was considered for the liquid required stirring such as algae slurry. The vessel sizing was calculated based on the equations below.

$$V_w = Ft_R \qquad \text{Eq (A.10)}$$

Where V_w is the working volume, F is the feed volumetric flow rate and t_R is the residence time. Finally, vessel volume was obtained by the working volume and the working to vessel volume ratio which was assumed as 90%.

1.6 Utilities

Steam with high pressure was used as heat agent in the first stage HTL which reacted at the temperature of 225 ℃. Chilled water was to cool down the hot stream of upgraded crude oil from the temperature around 100 ℃ to the 38 ℃ in the extraction process using DCM to prevent the solvent evaporation because DCM has low boiling temperature of 40.55 ℃. Steam and cooling water were used in the distillation column to recycle the DCM solvent. The feed stream was coming into the distillation column in the middle and the steam heated liquid flowing downwards to re-vaporize with the temperature of 40.55 ℃ while the cooling water condensed the DCM vapors moving to the top to 35 ℃.

Table A.11. Features of heat transfer agents

Heat Transfer Agents	Supply Temp. (° C)	Return Temp. (° C)	Mass to Energy Factor (kcal/kg)
Chilled Water	5	10	5.022
Cooling Water	25	30	4.997
Steam	152	152	503.683
Steam (High P)	242	242	419.632

2. Cost Analysis

Table A.12. Basis of purchased costs of main equipment of the algae liquefaction plant

Equipment	Base Cost	Base Capacity	Ref. Year	Scale Factor	Install Factor	Reference
Storage Tank	$157,800	1893 m^3	1998	0.6	0.4	Loh et al. (2002)
Raceway pond	$136,000	12140 m^3	2010	0.6	0.3	Lundquist et al. (2010)
Thickener	$10,240	133 m^2	2010	0.6	0.2	Lundquist et al. (2010)
Flotation Tank	$44,000	10 m^3/h	2004	0.6	0.1	Matis et al. (2005)
Bowl Centrifuge	$1,311,000	884 m^3/h	2011	0.6	1.7	Knorr et al. (2013)
PFR	$272,788	4.74 m^3	2013	1.0	2.0	Knorr et al. (2013)
CSTR	$272,788	4.74 m^3	2013	1.0	2.0	Knorr et al. (2013)
Heat Exchanger	$13,200	9 m^2	1998	0.7	0.5	Loh et al. (2002)
Disk Centrifuge	$3,565,000	884 m^3/h	2011	0.7	2.0	Knorr et al. (2013)
Rotary Vacuum Filter	$3,294,700	384 m^2	2010	0.8	1.7	Humbird et al. (2011)
Distillation Column	$486,746	811 m^3	2010	0.6	2.8	Humbird et al. (2011)

Table A.13. Labor distribution in the algae liquefaction plant

Labor Type	Cultivation	Harvesting	HTL	Separation	Total
Plant Manager	0.25	0.25	0.25	0.25	1
Engineer	0.25	0.25	0.25	0.25	1
Supervisor	1	1	1	1	4
Operator	8	3	5	4	20
QC Analyst	1	1	1	1	4
Secretary	0.25	0.25	0.25	0.25	1
Total	10.75	5.75	7.75	6.75	31

Table A.14. Labor costs of the algae liquefaction plant

Labor	Number	2007 Salary[a] ($)	2014 Salary[b] ($)	2014 Cost ($)
Plant Manager	1	147,000	171,000	171,000
Engineer	1	70,000	81,000	81,000
Supervisor	4	57,000	66,000	264,000
Operator	20	48,000	56,000	1,120,000
QC Analyst	4	40,000	46,000	184,000
Admin/Secretary	1	36,000	42,000	42,000

a. Data collected from Dutta et al. (2011)
b. The salaries of labor of 2014 were calculated based on the employment cost index from the US. Bureau of Labor Statistics

Table A.15. Feedstock cost of the algae liquefaction model

Feedstock	Cost	Reference
Water	0.0015, $/gallon	Estimated USA average
Sodium nitrate	0.45, $/kg	Estimated average market price
Dipotassium phosphate	1.50, $/kg	Estimated average market price
Carbon dioxide	0.04, $/kg	Davis et al. (2011)
Hydrogen	1.5, $/kg	Davis et al. (2011)
Dichloromethane	0.5, $/kg	Estimated average market price

Table A.16. Utilities costs of the algae liquefaction plant

Utility	Basis Unit	Unit Cost ($)	Usage (per yr)	Total Cost ($/yr)
STD Power	kWh	0.06	37,988,575	2,279,315
Chilled Water	MT	0.40	760,068	304,027
Cooling Water	MT	0.05	1,124,004	56,200
Steam	MT	12.00	21,414	256,968
Steam (High P)	MT	20.00	12,604	252,080

Table A.17. Utilities usage and cost of the algal bio-crude plant

Procedure Name	Type	Unit Cost ($/kW-h) /($/MT)*	Amount (kW-h/year) /(MT/year)	Cost ($/year)
Feeding Tank	Electricity	0.06	23,028	1,382
Raceway Pond	Electricity	0.06	13,153,156	789,189
Thickener	Electricity	0.06	215,238	12,914
Bowl Centrifuge	Electricity	0.06	309,959	18,598
Recycle Tank	Electricity	0.06	203,854	12,231
Harvest Tank	Electricity	0.06	611	37
1st HTL rector	Steam (High P)	20	12,604	252,083
Disk Centrifuge	Electricity	0.06	110,335	6,620
2nd HTL rector	Electricity	0.06	7,244,059	434,644
HDO reactor	Electricity	0.06	8,156,809	489,409
Filtration Drum	Electricity	0.06	2,362,378	141,743
Extractor	Electricity	0.06	9,716	583
Extractor	Chilled Water	0.4	759,977	303,991
Distillation Column	Steam	12	21,414	256,968
Distillation Column	Cooling Water	0.05	1,124,003	56,200
Pumping	Electricity	0.06	1,681,608	100,897
Unlisted Equipment	Electricity	0.06	1,129,456	67,767
General Load	Electricity	0.06	3,388,366	203,302
TOTAL				3,148,557

*The unit of electricity is kW-h and the unit of other utilities is MT.

Table A.18. Individual equipment cost summary

EQPT NO.	EQUIPMENT	No.	DESCRIPTION	Size	Units	Material	Ref. Cost	Ref. Year	Scaling Variable	Scaling Value	Units	Scal. Factor	Inst Factor	PC in Proj yr	Inst Cost in Proj yr
PM-104	Centrifugal Pump	1		0.00	kW	SS316							0.5	$10,000	$15,000
PM-105	Centrifugal Pump	1		0.00	kW	SS316							0.5	$10,000	$15,000
PM-108	Centrifugal Pump	1		1.26	kW	SS316							0.5	$21,000	$31,500
V-103	N Tank	1	0.61 m wide(diameter) × 1.82 m high	0.52	m3	SS316							0.4	$19,000	$26,600
V-104	K&P Tank	1	0.33 m wide(diameter)×0.99 m high	0.08	m3	SS316							0.4	$19,000	$26,600
V-105	Water Tank	1	7 m wide(diameter)×20.99 m high	807.06	m3	Concrete	$157,800	1998	Volume	500,000	gal	0.6	0.4	$157,000	$219,800
PM-106	Centrifugal Pump	1		1.26	kW	SS316							0.5	$21,000	$31,500
V-101	Feeding Tank	1	7 m wide(diameter) × 21 m high	807.67	m3	Concrete	$157,800	1998	Volume	500,000	gal	0.6	0.4	$157,000	$219,800
PM-102	Centrifugal Pump	1		1.26	kW	SS316							0.5	$21,000	$31,500
M-101	Centrifugal Fan	1		2341.16	m3/h	CS							0.5	$5,000	$7,500
R-101	Raceway Pond	38	60 m wide × 960 m long × 0.30 m high	12140.00	m3	Concrete	$136,000	2010	Volume	12,140	m3	0.6	0.3	$159,000	$206,700
PM-103	Centrifugal Pump	4		11.21	kW	SS316							0.5	$55,000	$82,500
TH-101	Thickener	14	24.23 m wide(diameter) × 3 m high	461.01	m2	Concrete	$10,240	2010	Surface Area	134	m2	0.6	0.2	$25,000	$30,000
FL-101	Flotation Tank	3	2.48 m wide × 15.87 m long × 0.67 m high	52.33	m3/h	CS	$44,000	2004	Throughput	10	m3/h	0.6	0.1	$172,000	$189,200
BC-101	Bowl Centrifuge	3		8.37	m3/h	SS316	$1,311,000	2011	Throughput	3894	gal/min	0.6	1.7	$90,000	$243,000
PM-107	Centrifugal Pump	1		0.34	kW	SS316							0.5	$12,000	$18,000
V-106	Harvest Tank	1	2.09 m wide(diameter)×6.26 m high	21.44	m3	SS316	$157,800	1998	Volume	500,000	gal	0.6	0.4	$18,000	$25,200
PM-101	Centrifugal Pump	4		11.17	kW	SS316							0.5	$55,000	$82,500
V-107	Recycle Tank	4	9.12 m wide(diameter) × 27.36 m high	1787.44	m3	Concrete	$157,800	1998	Volume	500,000	gal	0.6	0.4	$252,000	$352,800
PM-109	Centrifugal Pump	1		67.00	kW	SS316							0.5	$113,000	$169,500
HX-101	Heat Exchanger	1		15.89	m2	CS	$13,200	1998	Area	100	ft2	0.7	0.5	$32,000	$48,000
PFR-101	1st HTL Reactor	1	0.68 m wide(diameter) × 6.84 m long	2.51	m3	SS316	$272,788	2013	Volume	4.74	m3	1.0	2.0	$151,000	$453,000
DS-102	Disk Centrifuge	1		9.87	m3/h	SS316	$3,565,000	2011	Throughput	3894	gal/min	0.7	2.0	$172,000	$516,000
PM-110	Centrifugal Pump	1		0.26	kW	SS316							0.5	$11,000	$16,500
PM-111	Centrifugal Pump	1		81.80	kW	SS316							0.5	$122,000	$183,000
HX-103	Heat Exchanger	1		35.03	m2	CS	$13,200	1998	Area	100	ft2	0.7	0.5	$55,000	$82,500
PFR-102	2nd HTL Reactor	1	1.17 m wide(diameter) × 11.72 m long	12.63	m3	SS316	$272,788	2013	Volume	4.74	m3	1.0	2.0	$756,000	$2,268,000
PM-112	Centrifugal Pump	1		36.34	kW	SS316							0.5	$88,000	$132,000
M-102	Centrifugal Fan	1		6.56	m3/h	CS							0.5	$4,000	$6,000
HX-102	Heat Exchanger	1		26.00	m2	CS	$13,200	1998	Area	100	ft2	0.7	0.5	$45,000	$67,500
R-102	HDO Reactor	1	2.93 m wide(diameter) × 7.32 m high	49.22	m3	SS316	$272,788	2013	Volume	4.74	m3	1.0	2.0	$2,946,000	$8,838,000
PM-113	Centrifugal Pump	1		0.34	kW	SS316							0.5	$12,000	$18,000
RVF-101	Rotary Filter	1		36.97	m2	CS	$3,294,700	2010	Filter Area	384	m2	0.8	1.7	$593,000	$1,601,100
MSX-101	Oil Extractor	1	Mixer 2.45 m3 Settler 7.36 m3	14.72	m3/h	SS316							0.5	$40,000	$60,000
C-101	Distillation Column	1	0.56 m wide(diameter) × 5.2 m high	1.29	m3	CS	$486,746	2010	Volume	811	m3	0.6	2.8	$12,000	$45,600
PM-114	Centrifugal Pump	1		0.01	kW	SS316							0.5	$10,000	$15,000
V-102	Oil Tank	1	1.41 m wide(diameter) × 4.23 m high	6.60	m3	SS316							0.4	$30,000	$42,000

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APPENDIX B

Supplementary Information for Chapter 5:

"Life cycle assessment of biochar production from southern pine"

This supplementary document includes tables and descriptions with details on the process and results data for the life cycle assessment of biochar production from southern pine.

Table B.1. Forestry machinery data

Operation	Machine model	Weight (kg)	Data Source
Shearing	Crawler Dozer 700K XLT	13710	John Deere company
Piling	Crawler Dozer 700K XLT	13710	John Deere company
Planting	Utility Tractor 5083E	7385	John Deere company
Felling	Wheeled feller buncher 643K	12696	John Deere company
Skidding	Grapple Skidder 548G-III	10746	John Deere company
Delimbing	Forestry swing machine 2154D processor	27864	John Deere company
Loading	Forestry swing machine 2454D power clam	35370	John Deere company
Debarking	Nicholson R2 Sliding Ring Debarker	11818	Nicholson Manufacturing
Chipping	CAT Vermeer|BL1000XL	2091	Caterpillar Inc.

The data presented in Table B.1 was used in the LCA model to represent indirect use of machinery in the production of biochar.

Table B.2. Inputs of manufacturing to produce 1kg of forestry machinery

Inputs*	Values	Units
Aluminum ingot, production mix, at plant/US	3.30E-03	kg
Copper, primary, at refinery/RNA U	8.30E-04	kg
Diesel, at refinery/I/US	4.24E-02	l
Dummy_Lubricants, unspecified, at plant/US	6.72E-03	kg
Flat glass, uncoated, at plant/RER U	2.00E-03	kg
Cast iron, at plant/RER U	6.70E-01	kg
General purpose polystyrene, at plant/RNA	8.50E-03	kg
Cold rolled sheet, steel, at plant/RNA	1.10E-01	kg
Polybutadiene, at plant/RNA	1.60E-01	kg
Dummy_Energy, unspecified/US	2.60E+01	MJ

*Data were collected and modified from. (Heller, 2003)

Table B.3. Pyrolysis infrastructure construction inputs to produce 1 metric ton of biochar

Type	Material	Values	Units
*Pyrolysis plant	Portland cement, at plant/US	2.01E+00	kg
	Iron and steel, production mix/US	6.38E-01	kg
	Iron , sand casted/US	8.38E-03	kg
	Aluminum, cast, precision sand casting/kg/US	4.19E-03	kg
Missouri kiln	Concrete, sole plate and foundation, at plant/CH U	1.34E-03	m3
	Cold rolled sheet, steel, at plant/RNA	1.04E-01	kg
	Blast furnace slag cement, at plant/CH U	1.55E+01	kg

* Pyrolysis plant inputs data were gethered and calculated from Roberts et al. (2009)

Table B.4. Biochar and bio-oil yield per acre

Scenarios	Yield (t/ac)	
	Biochar	Bio-oil
Fast pyrolysis, clean chips	3.52	15.39
Fast pyrolysis, whole chips	4.07	17.80
Slow pyrolysis, clean chips	7.04	11.37
Slow pyrolysis, whole chips	8.14	13.15
Missouri kiln, small logs	15.50	-

Table B.5. Energy consumptions of biochar production from different scenarios

Scenario	Biochar GJ/t	% Change
Fast pyrolsis, clean chips	9.08	0.00%
Fast pyrolsis, clean chips, without machinery	8.93	-1.65%
Slow pyrolsis, clean chips	5.89	0.00%
Slow pyrolsis, clean chips, without machinery	5.73	-2.72%
Missouri kiln, small logs	2.19	0.00%
Missouri kiln, small logs, without machinery	1.97	-10.05%

Table B.6. Sensitivity analysis of biochar production

Category	Units	Fast pyrolysis			Slow pyrolysis			Missouri kiln		
Allocation methods		mass(base)	economic	energy	mass(base)	economic	energy	mass(base)	-	-
total energy	GJ/t	9.08	13.9	30.5	5.89	4.41	9.62	2.19	-	-
net energy	GJ/t	18.92	14.1	-2.5	24.11	25.59	20.38	24.81	-	-
Global warming	kg CO_2 eq	651.05	998.96	2185.33	416.76	311.92	681.16	1726.00	-	-
Smog	kg O_3 eq	89.41	137.19	300.13	65.25	48.84	106.65	76.10	-	-
Acidification	mol H^+ eq	341.55	524.07	1146.45	221.46	165.75	361.96	72.08	-	-
Eutrophication	kg N eq	0.59	0.90	1.97	0.41	0.31	0.67	0.24	-	-
Distance		-15%	0	15%	-15%	0	15%	-15%	0	15%
total energy	GJ/t	9.02	9.08	9.13	5.83	5.89	5.94	2.12	2.19	2.25
net energy	GJ/t	18.98	18.92	18.87	24.17	24.11	24.06	24.88	24.81	2.19
Global warming	kg CO_2 eq	647.39	651.05	654.72	413.00	416.76	420.53	1721.53	1726.00	1730.47
Smog	kg O_3 eq	88.86	89.41	89.97	64.68	65.25	65.83	75.42	76.10	76.78
Acidification	mol H^+ eq	340.38	341.55	342.73	220.26	221.46	222.67	70.64	72.08	73.51
Eutrophication	kg N eq	0.58	0.59	0.59	0.41	0.41	0.41	0.24	0.24	0.24
Yield (t/ac)		-15%	0	15%	-15%	0	15%	-15%	0	15%
total energy	GJ/t	10.70	9.08	7.89	6.93	5.89	5.12	2.57	2.19	1.90
net energy	GJ/t	17.30	18.92	20.11	23.07	24.11	24.88	24.43	24.81	25.10
Global warming	kg CO_2 eq	765.95	651.05	566.13	490.43	416.76	362.49	2030.59	1726.00	1500.87
Smog	kg O_3 eq	105.19	89.41	77.75	76.79	65.25	56.76	89.53	76.10	66.17
Acidification	mol H^+ eq	401.83	341.55	297.00	260.61	221.46	192.62	84.79	72.08	62.67
Eutrophication	kg N eq	0.69	0.59	0.51	0.48	0.41	0.36	0.28	0.24	0.21
Pyrolysis energy (GJ)		-15%	0	15%	-15%	0	15%	-15%	0	15%
total energy	GJ/t	8.38	9.08	9.78	5.35	5.89	6.42	2.11	2.19	2.26
net energy	GJ/t	19.62	18.92	18.22	24.65	24.11	23.58	24.89	24.81	24.74
Global warming	kg CO_2 eq	599.58	651.05	702.53	377.64	416.76	455.88	1483.18	1726.00	1968.83
Smog	kg O_3 eq	84.21	89.41	94.62	61.44	65.25	69.07	69.40	76.10	82.80
Acidification	mol H^+ eq	315.64	341.55	367.46	202.06	221.46	240.87	70.99	72.08	73.16
Eutrophication	kg N eq	0.55	0.59	0.62	0.39	0.41	0.43	0.24	0.24	0.24
Preprocessing methods		clean chips	whole chips	-	clean chips	whole chips		-	-	-
total energy	GJ/t	9.08	8.45	-	5.89	5.24	-	-	-	-
net energy	GJ/t	18.92	19.55	-	24.11	24.76	-	-	-	-
Global warming	kg CO_2 eq	651.05	607.64	-	416.76	371.80	-	-	-	-
Smog	kg O_3 eq	89.41	85.38	-	65.25	60.72	-	-	-	-
Acidification	mol H^+ eq	341.55	323.34	-	221.46	202.38	-	-	-	-
Eutrophication	kg N eq	0.59	0.56	-	0.41	0.38	-	-	-	-
Harvesting Energy (GJ)		-15%	0	15%	-15%	0	15%	-15%	0	15%
total energy	GJ/t	8.91	9.08	9.42	5.72	5.89	6.06	1.99	2.19	2.39
net energy	GJ/t	19.09	18.92	18.58	24.28	24.11	23.94	25.01	24.81	24.61
Global warming	kg CO_2 eq	640.04	651.05	662.07	405.45	416.76	428.08	1712.56	1726.00	1739.44
Smog	kg O_3 eq	85.84	89.41	92.99	61.59	65.25	68.92	71.74	76.10	80.46
Acidification	mol H^+ eq	334.86	341.55	348.24	214.59	221.46	228.34	63.91	72.08	80.24
Eutrophication	kg N eq	0.58	0.59	0.60	0.40	0.41	0.42	0.23	0.24	0.25

Reference

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