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Feasibility of Steam Hydrogasification of Microalgae for Production of Synthetic Fuels

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Feasibility of Steam Hydrogasification of Microalgae for Production of Synthetic Fuels

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by

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Amornrat Suemanotham

ABTRACT OF THE DISSERTATION

Feasibility of Steam Hydrogasification of Microalgae for Production of Synthetic Fuels

by

Amornrat Suemanotham

Doctor of Philosophy, Graduate Program in Chemical and Environmental Engineering
University of California, Riverside, June 2014
Dr. Joseph M. Norbeck, Chairperson

The development of sustainable fuels from biomass has become important due to the depletion of fossil fuels and concerns of global climate change. Microalgae offer several advantages as sources for bioenergy; their rapid growth rate, high productivity and lipid content, ability to cultivate in places other than on farmlands, or arable land, and their ability to capture CO_2 from flue gas which can be used as a source for photosynthesis. Microalgae are able to produce a wide range of biofuels including biodiesel, methane, ethanol, hydrogen, and synthetic fuels using different conversion technologies. High energy requirements and the cost for dewatering/drying and extraction are major drawbacks. The steam hydrogasification (SHR) process is attractive as an alternative for the conversion of microalgae to biofuels because the SHR can handle wet microalgae biomass without drying or extraction and been shown to have high carbon conversion efficiencies.

The overall objective of this thesis is to investigate the feasibility of using whole microalgae directly (wet biomass) and/or using the microalgae residue after lipid extraction to produce low carbon sustainable fuel using the CE–CERT process. Steam hydrogasification can convert microalgae to a high energetic synthesis gas in the presence of steam and hydrogen. The carbon in the synthesis gas then can be converted to synthetic fuels and electricity. The performance of steam hydrogasification of microalgae was investigated by varying parameters including gasification temperature, H_2/C and steam/biomass ratios. It was found that the operating conditions at a gasification temperature 750 °C, a steam/biomass ratio of 2 and a H_2/C ratio of 1 could provide richer in methane production and high carbon conversion (65%) using microalgae as a feedstock. The hydrogen in the product gas was sufficient to maintain a self–sustained supply back to the SHR. One ton per day of microalgae biomass is expected to produce 1.06 barrel of FT product with an overall thermal efficiency of 27%.

The utilization of the microalgae residue from traditional transesterification and the effect of different lipid content of different microalgae using the steam hydrogasification process was investigated also. It was found that the SHR could use microalgae residue to reduce the algae waste and recover energy of about 4.9 MJ/kg of dry microalgae residue. A higher lipid content would enhance the performance of the SHR in terms of carbon conversion and production of methane that resulted in more FT fuel.

Life cycle energy and greenhouse gas (GHG) emissions for the production of Fischer–Tropsch (FT) fuel derived from microalgae using the CE–CERT process were calculated and compared to microalgae to biodiesel production using transesterification. It was found that life cycle energy requirements for the microalgae biofuel production using the CE–CERT process were significantly lower (approximately 50%) compared to the transesterification process. The life cycle analysis showed that the lowest energy consumption to be 1.96 MJ/MJ of fuel (40 wt% of lipid content) compared to microalgae to biodiesel production. The CE–CERT technology reduces the GHG emissions by 50–64% compared to production of conventional diesel fuel.

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1. Introduction

Concerns about sustainability and the environment have motivated interest in the production and utilization of renewable alternative forms of energy. Biofuels have become an important alternative fuel to reduce global warming caused by fossil fuels. The production and utilization of biofuels contribute to carbon neutrality and reduction of sulfur into the atmosphere [1-3]. The first–generation biofuels are produced from terrestrial crops like corn or sugarcane for ethanol production, and vegetable oils such as soybean, rapeseed, and palm oil for producing biodiesel. The second–generation biofuels comprise of lignocellulosic biofuels from non–food crops and waste biomass. The products from the second-generation feedstock include bio-oil, liqnocellulosic ethanol, hydrotreating oil [4-6]. First and second–generation feedstocks are not able to achieve targets for biofuel production due to insufficient biomass feedstocks, land limitations, increased concerns of water usage and the potential of an increase in greenhouse gas (GHG) emissions [4, 7-10]. These concerns have stimulated attention toward the production of biofuels from rapidly growing natural biomass that can provide high efficiency in the conversion to sustainable renewable transportation fuel as well as minimize GHG emissions. So, microalgae biomass is an attractive source of carbon for third–generation biofuel compared to conventional terrestrial biofuel feedstock. The advantages of microalgae are numerous [11-17].

- Microalgae have higher photosynthesis efficiency than other biomass, high productivity yields and high growth rates.
- Microalgae have ability to be cultivated in wastewater, saline/brackish water and coastal sea water, thus reducing freshwater use.

- Microalgae can utilize nitrogen and phosphorus from wastewater sources.
- Microalgae use marginal areas unsuitable for agricultural crops, and thus do not complete with arable land for conventional energy crops.
- Microalgae produce nontoxic and highly biodegradable biofuels.
- Microalgae can recycle carbon from carbon dioxide (CO_2) rich flue emissions from power plants, industrial and other sources, thereby reducing GHG emissions.

1.1. Microalgae to biofuel production

1.1.1. Microalgae feedstock

Microalgae are unicellular plant like microorganism that can be generated through photosynthesis. Microalgae require light, carbon dioxide, water, and nutrients such as nitrogen (N) and phosphorous (P) for photosynthesis. Photosynthesis converts light energy into chemical energy by fixing atmospheric carbon dioxide in a similar manner as done in plants. The sugar formed by photosynthesis is converted to macromolecules, namely, lipids, proteins and carbohydrates that make up the biomass. A simplified equation for photosynthesis is given as below (Eq. 1.1).

$$6H_2O + 6CO_2 + light\ energy \rightarrow C_6H_{12}O_6\ (sugar) + 6O_2 \tag{1.1}$$

Microalgae consume carbon which they can get from dissolved CO_2 and nutrients and in the process release O_2. In general, microalgae biomass contains approximately 50% of carbon by dry weight. A mole of CO_2 has a mass of 44 grams and 12 of these grams come from carbon. So, one gram of microalgae can utilize 1.83 grams of CO_2 [12, 18]. Microalgae biomass contains three main components: carbohydrates, proteins, and lipids (oil). The biomass compositions of various microalgae strains are shown in Table 1.1. One microalgae sample (*Chlorella vulgaris*) is one of the most studied and is used as microalgae feedstock for biofuel production in many instances. Chlorella vulgaris is a unicellular green type fresh water microalgae and roughly spherical in shape. It is already in commercial cultivation for the production of nutriceutricals and animal feed [19, 20].

Table 1.1 Biomass composition of microalgae on a dry mass basis [21-23]

Strain	Protein (%)	Carbohydrate (%)	Lipid (%)
Anabena cylindrical	43-56	25-30	4-7
Botryococcus braunii	40	2	33
Chlamydomonas rheinhardii	48	17	21
Chlorella pyrenoidosa	57	26	2
Chlorella vulgaris	41-58	12-17	10-22
Dunaliella bioculata	49	4	8
Dunaliella salina	57	32	6
Dunaliella tertiolecta	29	14	11
Euglena gracilis	39-61	14-18	14-20
Porphyridium cruentum	28-39	40-57	9-14
Prynesium parvum	28-45	25-33	22-39
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 platensis	42-63	8-14	4-11
Synechoccus sp.	63	15	11
Tetraselmis maculata	52	15	3

1.1.2. Microalgae cultivation

The cultivation systems for microalgae biomass production include two primary systems: open ponds systems including shallow, circular tanks and raceway agitated by paddle wheel as shown in Figure 1.1, and closed systems (photobioreactors, PBR) such as tubular and flat plate as shown in Figure 1.2. Open pond systems are the oldest and simplest systems for microalgae farming and large commercial system exist [21]. Systems such as raceway ponds are simple to construct, normally less expensive to build and operate, and have a larger production capacity than closed systems. Open ponds have a variety of shapes and sizes but the most commonly used design is a raceway pond. Open ponds are typically made of closed loop, oval shaped recirculation channels, generally between 0.2 and 0.5 m deep, with mixing and circulation required to stabilized algae growth and productivity. Paddlewheels are typically used to mix open pond systems. Although these systems are the most widely used at the industrial level, the systems still present significant technical challenges. Open ponds are susceptible to weather conditions, evaporation, and lack controls of water, temperature, lighting and contamination by unwanted species or bacteria [14, 24, 25].

Figure 1.1 Open ponds system, pictures courtesy of Seambiotic, Ltd. (left) and pictures courtesy of energybiosciencesinstitute.org (right)

Another option for cultivation microalgae is to use a closed system or photobioreactors. There exist in many shapes, design and forms such as tubular reactors, plate reactors, or bubble column reactors. Closed bioreactors have many advantages and are able to control culture conditions, growth parameters (pH, temperature, sunlight, carbon dioxide, mixing, nutrients and oxygen level) as well as prevent outside contamination and evaporation. This method is easy to manage the growth of microalgae, improves productivity and ensures a high yield of algae. Some designs use natural light while others use artificial light for continual growth. The drawbacks of closed bioreactors; they are much more expensive to build than open ponds and require complex control systems and monitoring [24, 26, 27].

Both open ponds and photobioreactors, are used in hybrid systems to improve the yields and productivity, as well as cost–effective cultivation. A comparative of open and closed systems are summarized in Table 1.2.

Figure 1.2 Closed photobioreactors system, pictures courtesy of phytolutions (left) and www.oilgae.com (right)

Table 1.2 Comparison of open versus closed systems [7, 28-30]

Parameters	Open systems	Closed systems
Land required	High	Low
Water loss	Very high	Low
CO_2 loss	High	Low
CO_2 transfer rate	Poor	Excellent
O_2 concentration	Low due to continuous spontaneous outgassing	Exchange device
Light utilization efficiency	Poor	High
Temperature	Highly variable	Required cooling
Temperature control	None	Excellent
Controlling of growth conditions	Very difficult	Easy
Shear	Low	High
Mixing efficiency	Poor	Excellent
Cleaning	None	Required due to wall growth and dirt
Contamination control	Difficult	Easy
Contamination risk	High	Low
Species control	Difficult	Easy
Biomass quality	Variable	Reproducible
Biomass productivity	Low	High
Population (algae cell) density	Low	High
Capital cost	High	Very high
Operating cost	Lower	Higher
Harvesting cost	High	Lower
Harvesting efficiency	Low	High

Carbon dioxide is the major greenhouse gas emission and results from the combustion of fossil fuels. So, reducing the use of fossil fuels or promoting CO_2 sequestration seems to be the method for mitigating CO_2 emissions. One of the advantages of using microalgae for biofuel production is; one is able to tolerate and capture CO_2 from different sources including atmospheric CO_2, CO_2 emissions from power plants and industrial processes, and CO_2 from soluble carbonate [31-33]. Hence, microalgae have the advantage to fix CO_2 efficiently through photosynthesis. Flue gases that can be obtained from the power plants or industrial processes also provide a CO_2–rich source for microalgae cultivation. The concentration of CO_2 in flue gases ranges from 12 to 20% depending on the sources [34, 35]. CO_2 from industrial flue gases is supplied to the ponds in several methods such as direct injection and using chemical absorption (monoethanolamine, MEA) [34, 36, 37].

Nutrients are also an important factor for microalgae growth. Nutrients include nitrogen (N), phosphorus (P), Iron (Fe) and silicon (Si). Most algae require nitrogen a soluble form such as ammonium, urea or nitrate. Phosphorus is required in lesser amounts, and must be supplied in excess of the normal requirement amounts. The amounts of nutrients depend on cultivation conditions of microalgae. In addition, recycling nutrients from wastewater like municipal, agricultural and industrial sources could important reduce addition of nutrients by approximately 55% and significant reduce the operation costs [38, 39].

1.1.3. Microalgae harvesting and dewatering

Biomass concentration obtainable in microalgae cultivation systems are typically in the range of 1–5 g/L. Microalgae cells are usually extremely small, normally between 2 and

20 micron (μm). Microalgae typically have high water content, approximately 80–90%. Thus, harvesting and dewatering steps also require to remove the large quantities of water and increase the microalgae biomass concentration. Energy consumption and costs for biomass harvesting and dewatering are a significant concern and need to be addressed appropriately.

Microalgae harvesting can be divided into a two–step process, including: (1) Primary harvesting (Bulk harvesting): this is to separate microalgae biomass from the bulk suspension using flocculation, flotation or gravity sedimentation [40]; (2) Secondary dewatering (Thickening): the purpose is to concentrate the slurry using centrifugation, filtration or other techniques. This generally needs more energy than primary harvesting [40]. The desired microalgae concentration is achieved by a one or two step harvesting process. A primary harvesting step contains the microalgae slurry of 2–7% total suspended solids (TSS) and a secondary dewatering step to form a microalgae paste of 15–25% TSS. A diagram of microalgae harvesting is shown in Figure 1.3.

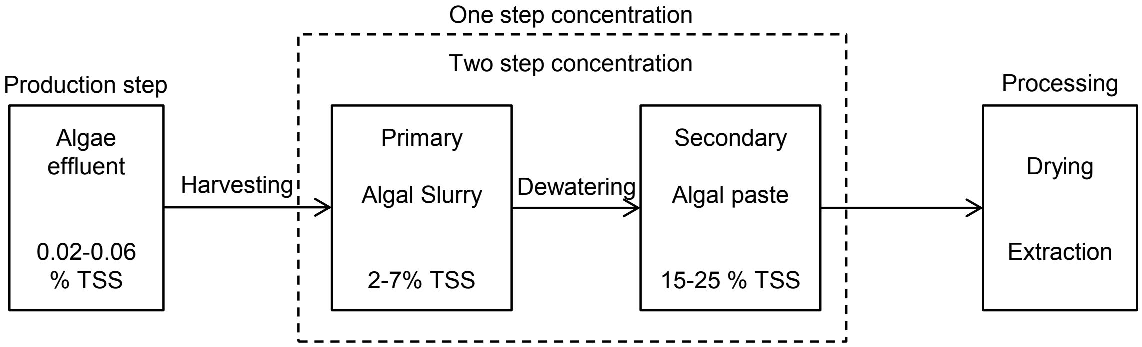

Figure 1.3 Schematic of microalgae production and processing [41]

The most common harvesting and recovery methods include gravity sedimentation, flocculation, air–flotation, centrifugation, filtration and screening, and electrophoresis techniques. The selection of suitable harvesting technique depends on the properties of microalgae such as size, density and the value of target products [41-43]. Some of microalgae harvesting are described below:

Sedimentation is one of the simplest processes to separate microalgae in water. The solid removal by gravity sedimentation depends on the size, shape and density of microalgae particles and the rate of microalgae sedimentation. Microalgae particles with low density do not settle well by sedimentation [41, 44]. Therefore, flocculation is frequently used in order to increase the particle size, density, and the efficiency of the rate of sedimentation.

Flocculation is an effective method to involve the aggregation of microalgae cells to form large particles for settling. Flocculation is a common primary harvesting method to increase particle size and improve the solid–liquid separation. The increased particle size will lead to faster sedimentation or easier centrifugal recovery, filtration and interaction with flotation bubbles. Flocculants are chemicals that are usually added to induce flocculation. Flocculants can be divided into two types: inorganic such as aluminium sulphate ($Al_2(SO_4)_3$, alum), ferric chloride ($FeCl_3$) and ferric sulphate ($Fe_2(SO_4)_3$), or organic like chitosan [40, 45]. Alum is widely used in wastewater treatment.

Flotation is a method of removal of microalgae from aqueous solutions based on fine air and gas bubbles adhering to the particles which will float to the surface of water and then they are separated by skimming. Dissolved air flotation (DAF) is the most widely used flotation technique in industrial treatment. DAF involves the generation of fine bubbles produced by decompression of a pressurized fluid. So, it is expensive to operate because of energy cost of air compression. The fine bubbles often 60–200 μm adheres to the particles making them to float to the surface rapidly [46]. DAF is commonly combined with chemical flocculation and it is possible to obtain a microalgae slurry of up to 7% TSS.

Centrifugation is widely used in industrial suspension separations. This process relies on the centrifugal force to accelerate and separate the suspended solids from liquids based on a density difference. Centrifugation is suitable for secondary dewatering method to concentrate initial slurry (10–20 g/L) to algal paste (100–200 g/L). Most types of centrifuges used in the industrial application are decanter, disc stack centrifuges, basket centrifuge and hydrocyclones. Centrifugation is an effective and fast recovery technique for microalgae but the major disadvantage is the high capital and operational costs required due to energy needed [13, 47]. However, dewatering performance, energy consumption, and costs depend on the centrifuge design and operational parameters. Centrifugation can possibly be used in combination with oil extraction.

Filtration is a process using a filter under gravity, pressure or vacuum operation to separate solid from liquid. Conventional filtration is most appropriate for recovering large quantities of microalgae and operates under pressure or suction. It cannot be used to harvest small microalgae cells. Membrane microfiltration and ultrafiltration are possible options for recovering small microalgae particles. The filtration process is highly expensive due to the replacement of membranes and energy requirement for pumping [7, 30, 48, 49].

1.1.4. Microalgae extraction

The microalgae biomass must typically be dried in order to remove high water content and increase the concentration to 80–90% (w/w) prior to lipid extraction. Several methods have been employed to dry microalgae that include solar drying, drum drying, spray drying, cross–flow drying, and freeze drying [40, 50]. Natural drying (solar or wind) is probably the cheapest and simplest option but it is not an effective method and takes long drying times as well it requires large space [14]. The drawbacks of most drying process; they are energy intensive and costly. Therefore, selection of the drying method should depend on the algae species, the scale of operation and the final desired product. It is critical to establish a balance between the cost effectiveness and drying efficiency for maximizing the net energy of fuels, as well as the impact on the final product.

Cell disruption of microalgae follows drying. Cell disruption methods are used to open the cells and improve the penetration of solvent to enhance the lipid yield. Cell disruption is often necessary for recovering intracellular products from microalgae, such as oil and starch for biodiesel or ethanol production. Some techniques of cell disruption are high pressure homogenizer, bead mills (agitation with glass or ceramic beads), autoclave, freezing, microwave, and osmotic shock [42].

There are several methods of oil extraction from microalgae such as solvent extraction, mechanical expulsion, supercritical fluid extraction (SFE) and ultrasound techniques [51-54]. One need to consider the energy inputs, potential environmental toxicity and safety concerns of chemical solvent with suitable oil extraction [30, 35].

1.1.5. Conversion Technologies

Microalgae can provide several different types of renewable biofuels by several conversion technologies. The conversion technologies for microalgae biomass can be divided into four basic categories: biochemical, thermochemical, chemical reaction and direct combustion. Figure 1.4 shows the energy conversion processes from microalgae. Three major components can be separated from microalgae biomass: lipids (including triglycerides and fatty acids), carbohydrates and proteins. Lipids and carbohydrates are fuel precursors for biodiesel, ethanol, and jet fuel while the proteins can be used for animal feed or fertilizers. Different conversion technologies will be used to produce biofuel depending on the final product desired.

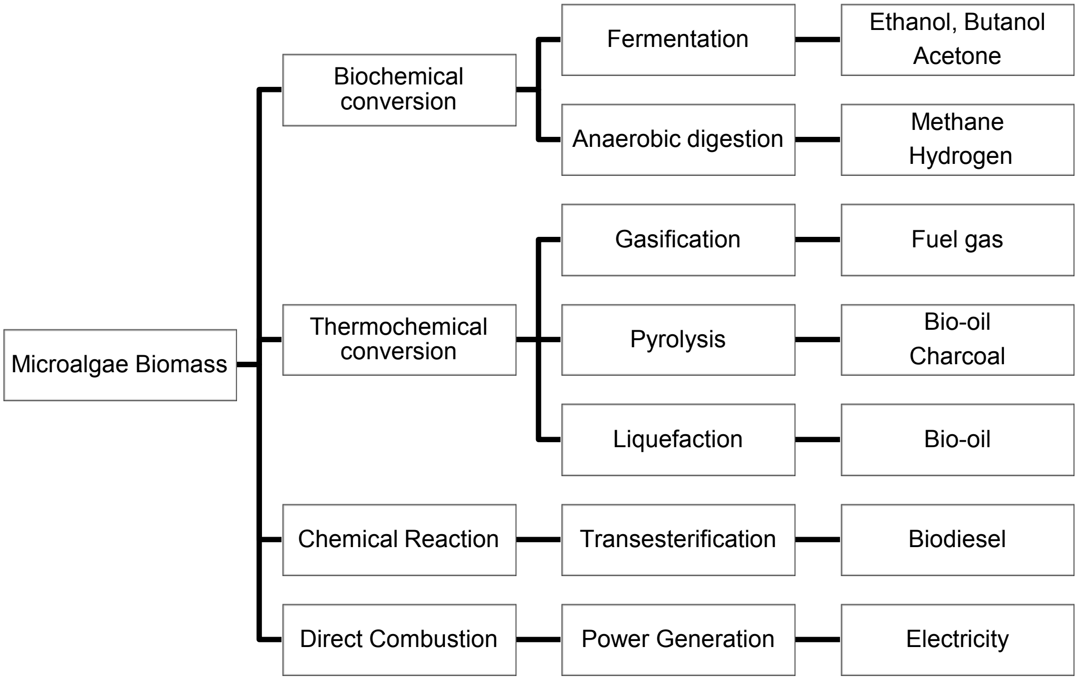

Figure 1.4 Energy production by microalgae biomass conversion using biochemical, thermochemical, chemical and direct combustion processes [35]

Biochemical technologies to process microalgae include fermentation and anaerobic digestion. Fermentation is used commercially to produce ethanol from sugar and starch crops. Ethanol can be used as fuel (100% ethanol) or as gasohol (a mixture of 90% gasoline and 10% ethanol). Organic material such as biomass or microalgae can be used to produce mainly methane (biogas) by anaerobic digestion while the rest component is mainly carbon dioxide which can be fed back for growing algae. Biogas combustion is carried out in combined heat and power plants. The major advantage of this process is the handling of wet biomass and the cost related to drying and extraction.

After extraction, the microalgae oil can convert to biodiesel by a transesterification process. Transesterification is a chemical conversion between triglycerides and alcohol (most commonly methanol or ethanol) in the presence of a catalyst (acid, alkali or lipase enzyme) [55-57] to produce biodiesel and the by–product glycerol as illustrated in Figure 1.5. The yield of methyl ester is approximately 98% on weight basis. Alkali catalyzed is approximately 4,000 times faster than acid catalyzed reaction [58]. The properties of microalgae based biodiesel must match or exceed the International Biodiesel Standard for vehicles such as ASTM biodiesel standard D 6751 (United States) or standard EN 14214 (European Union).

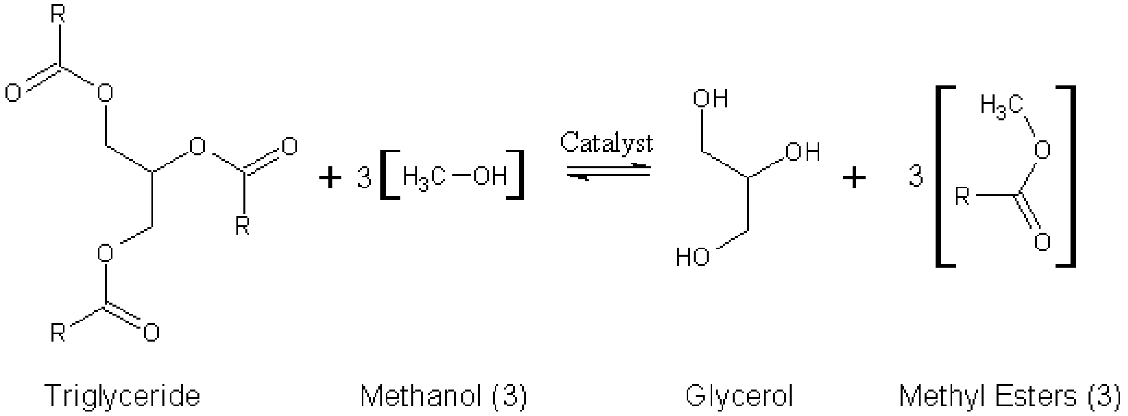

Figure 1.5 Transesterification reaction of triglyceride and methanol to biodiesel. R1, R_2 and R_3 are long chain hydrocarbons

Thermochemical conversion technology can be divided into gasification, pyrolysis and liquefaction [59-62]. These methods do not require the lipid to be extracted, and can convert the whole biomass into fuels. Gasification involves the partial oxidation with air, oxygen and/or steam of carbonaceous material into a combustible gas such as hydrogen (H_2), methane (CH_4), carbon monoxide (CO), carbon dioxide (CO_2) and ammonia (NH_3) at high temperature, typically in the range from 600 to 1500 °C [63]. The combustible gas can be burned directly and used as a fuel for gas engines and gas turbines. Gasification of the biomass also provides a flexible way to produce different liquid fuels such as through Fisher–Tropsch synthesis or mixed alcohol synthesis of the resulting syngas. Pyrolysis is a thermochemical process that converts biomass into biofuel by heating the biomass to around 500 °C. Three phase products are produced via pyrolysis: vapor phase, liquid phase and solid phase. The liquid phase is a complex mixture called bio–oil. The bio–oil can upgrade with hydrotreating or hydrocracking process for generating liquid diesel fuel. Liquefaction is a technology that can be employed to convert wet algae biomass to bio–oil. A direct combustion, microalgae are burned directly in the presence of air to convert the chemical energy in the microalgae biomass into hot gases that are used to generate heat and electricity.

1.2. Description of the CE–CERT process

The CE–CERT technology is a thermochemical process to convert carbonaceous material into synthetic liquid fuels or electricity. It is based on steam hydrogasification (SHR) and is referred to as a CE–CERT process. It has been shown to have increased conversion rate for the formation of methane [64]. It can utilize high moisture feedstock such as lignite, biomass, biosolids, as well as microalgae. The details and several advantages of the CE–CERT process have been published earlier [64-68]. In 2010, the U.S. Department of Energy, National Energy Technology Laboratory (NETL) completed an independent technical and economic assessment of the CE–CERT technology for Fischer–Tropsch (FT) liquid fuel and co–production of the power. The report summarized that the CE–CERT process has the potential to offer 3–5% higher efficiency with 14% less capital costs compared to conventional gasification technologies [69].

The schematic diagram of the CE–CERT process is shown in Figure 1.6. This is a three–step process that converts carbonaceous feedstocks such as coal or biomass into synthetic fuel. First step of the CE–CERT process is steam hydrogasification reaction and is followed by steam methane reforming (SMR). The final step of liquid fuel synthesis shown here is the Fischer–Tropsch Reaction (FTR). Initially, the carbonaceous feedstock is made into the slurry with water in a pretreatment unit. The steam hydrogasification combines hydrogen with the carbonaceous feedstock slurry and converts to a methane (CH_4) rich output gas along with carbon monoxide (CO) and carbon dioxide (CO_2) (Eq. 1.2). The product gases from the SHR are then subjected to a warm gas cleanup unit in order to remove contaminants such as sulfur species, chloride, ammonia and solid particles. These contaminants can lead to corrosion and poison to catalysts in the downstream gas processing. Then, most of methane is reformed to generate the synthesis gas, a mixture of H_2 and CO, in the SMR (Eq. 1.3). The SMR is used widely in commercial for syngas production. The partial H_2 is separated and fed back to the SHR to meet the system H_2 internal requirement. The syngas is fed into the FTR to produce synthetic liquid fuels and process heat (Eq. 1.4). The light hydrocarbons (C1–C4), unconverted syngas from FTR and surplus H_2 are burned for heat and power generation.

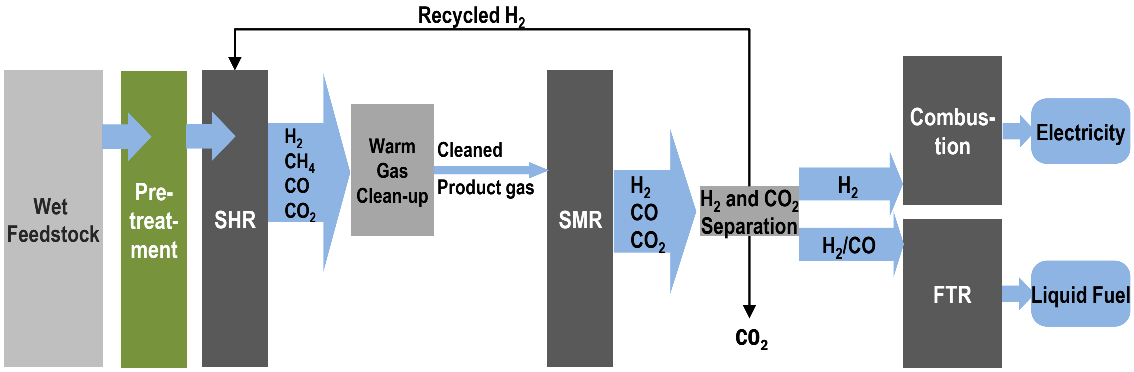

Figure 1.6 A block diagram of the CE-CERT process

The basic overall reaction taking place during the three–step process is represented in the Eq. 1.2–1.4. Cetane ($C_{16}H_{34}$) is represented as a liquid hydrocarbon in Fischer–Tropsch reaction. These reactions represent the basic concept of the process but the details vary widely, depending on the feedstock available and the final product desired.

Steam Hydrogasification Reaction:

$$C + H_2O + 2H_2 \rightarrow CH_4 + H_2O + others\ (CO, CO_2, C_{2+}) \qquad + 75\ kJ/mol \qquad (1.2)$$

Steam Methane Reforming:

$$CH_4 + H_2O \rightarrow 3H_2 + CO \qquad - 206\ kJ/mol \qquad (1.3)$$

Fischer–Tropsch Reaction:

$$33H_2 + 16CO \rightarrow C_{16}H_{34}(l) + H_2O(l) \qquad + 4004\ kJ/mol \qquad (1.4)$$

The steam hydrogasification plays an important role in the CE–CERT process. The main features and advantages of the CE–CERT process are summarized below:

1. SHR is able to handle wet feedstock and can utilize the slurry feed that contains high moisture content such as biosoilds, sewage sludge and microalgae. It reduces the drying cost of feedstock.
2. SHR does not need oxygen as the gasification medium which it eliminates the need for an expensive oxygen plant production. The SHR does not need a catalyst and can be operated at moderate temperature and pressure conditions. This reduces the capital and operational cost compared to competitive technologies.
3. Addition of hydrogen in the SHR process not only increases the yield of the product gas but also decreases the fraction of gas with higher carbon number which is the precursor for the tar formation. Tar is a major concern for biomass gasification processes.

4. The H_2/C and steam/feedstock ratios in the SHR can be adjusted to achieve a desired H_2/CO ratio of the syngas. The syngas ratio is a key parameter in the production of different hydrocarbon fuels.
5. The CE–CERT technology is self–sustainable in term of H_2 supply with a closed–loop cycle.

The CE–CERT process via steam hydrogasification as the thermochemical conversion is selected in this research to gasify microalgae as a feedstock for the production of synthetic liquid fuel. In addition, microalgae are a favorable feedstock because they can be gasified directly and continuously in the SHR to produce the product gases without oil extraction and drying. The CO_2 that is generated from the CE–CERT process can be captured and recycled back to use as a carbon source for growing microalgae. The residual microalgae after lipid extraction can be used as a feedstock in steam hydrogasification process for producing synthesis gas and then the synthetic liquid fuel through Fischer–Tropsch (FT) process.

1.3. Life cycle analysis

Life cycle analysis (LCA) is a fundamental tool to evaluate the environmental impact associated with products and processes. In this study, LCA has been performed using the GREET (Greenhouse gases, Regulated Emissions, and Energy use in Transportation) model [70]. The GREET model was developed at the Argonne national laboratory and is widely acknowledge as an excellent tool for evaluating the life cycle of different fuels and pathways. The LCA is performed in two parts, the well–to–pump (WTP) and pump–to–wheels (PTW). The final full life cycle emissions and energy consumption information i.e., well–to–wheels (WTW) results is obtained by adding the two parts. The WTP section accounts for all the fuel production steps such as resource extraction, fuel production, transport, storage, distribution and marketing. Facility fabrication and facility decommissioning during these steps are not taken into account. The PTW section takes into account the emissions during the vehicle operation. GREET is used to compute total energy, fossil fuel energy, petroleum, and natural gas, emissions of carbon dioxide (CO_2) equivalent greenhouse gas emissions, including CO_2, methane (CH_4), and nitrous oxide (N_2O), and six criteria pollutants: carbon monoxide (CO), volatile organic compounds (VOC), nitrogen oxide (NO_x), sulfur oxide (SO_x), particulate matter with diameters smaller than 10 μm (PM_{10}), and particulate matter with diameters smaller than 2.5 μm ($PM_{2.5}$).

GREET contains many fuel and vehicle systems. Fuels include gasoline, diesel, biofuels, hydrogen, natural gas, and electricity. The fuel production option in GREET is illustrated in Figure 1.7. Vehicle technologies include gasoline engines, diesel engines, hybrid electric vehicles with gasoline and diesel engines, plug–in hybrid electric vehicles with gasoline and diesel engines, battery–powered electric vehicle, and fuel cell vehicles.

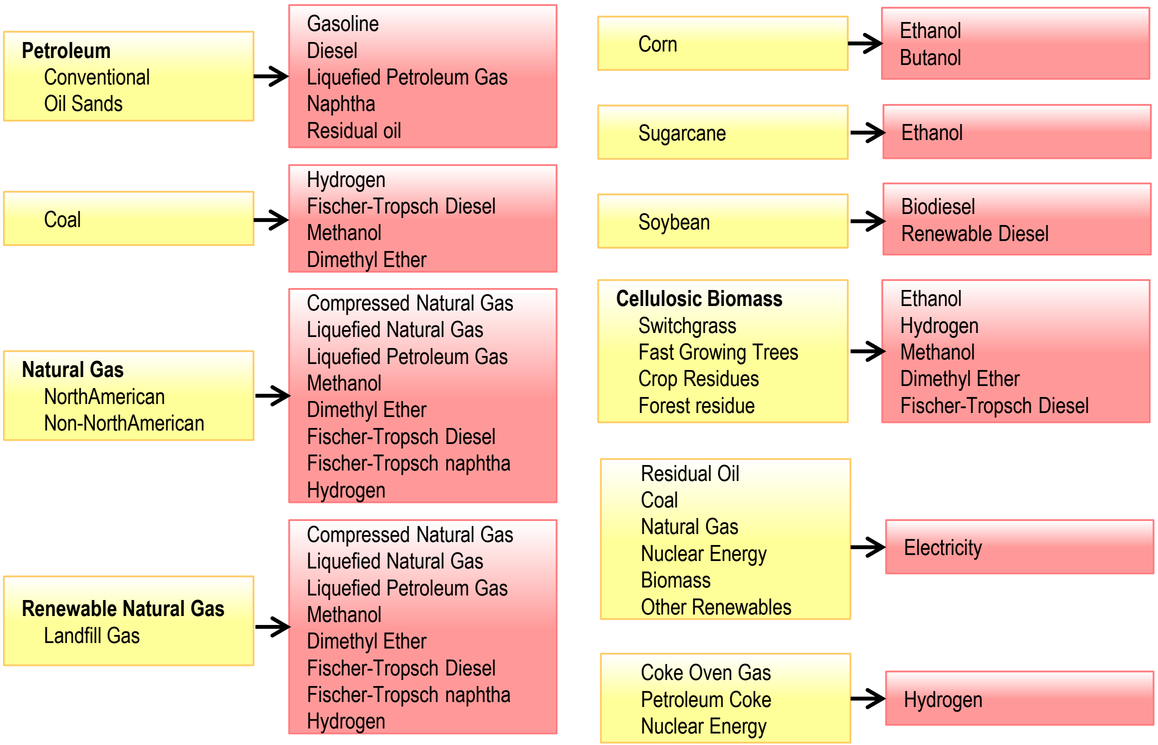

Figure 1.7 The fuel production options from various feedstocks in GREET model [71]

Figure 1.8 depicts the system boundary for algae–based fuels. The boundary defines well–to–wheels fuel cycle analysis. The GREET microalgae is comprised of two main LCA stages; well–to–pump (WTP) and pump–to–wheels (PTW). The WTP component analyses the total energy and emissions due to the production of microalgae fuel including cultivation, microalgae production including harvesting, dewatering and extraction processes, and conversion. The combustion of fuel during vehicle operation constitutes the PTW stage. Vehicle considered only compression ignition, direct injection (CIDI) engines for diesel fuels and spark ignition (SI) engines for renewable gasoline fuels. The combination of these two stages comprise the well–to–wheels (WTW) fuel cycle.

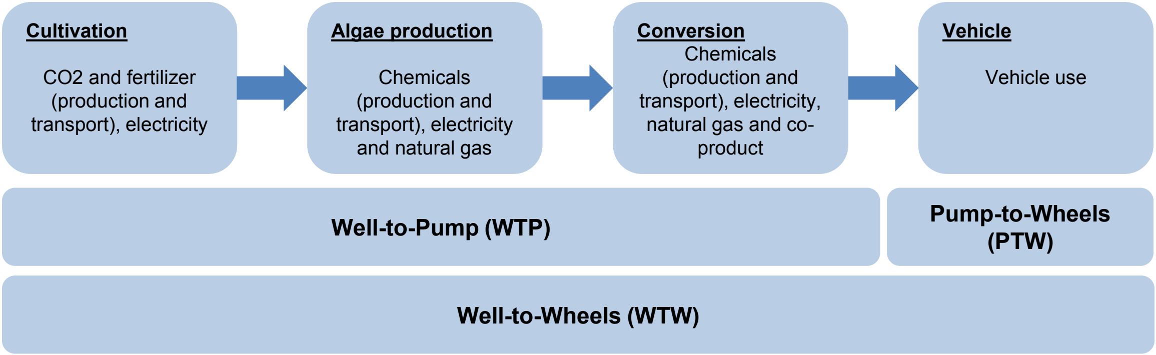

Figure 1.8 Illustration of “Well-to-Pump” and “Pump-to-Wheels” boundaries [71]

The algae process description (APD) model was built to facilitate the description of various algae pathways and transfer the selected operations to GREET. The information for each process included inputs, outputs, and yields, as well as material and fuels consumed are transferred. GREET and APD cover all five life cycle stages: feedstock cultivation, feedstock transportation, biofuel production, biofuel transportation, and biofuel end use in vehicle. APD and GREET were used in this study and details on this helper tool, the GREET modifications, and the GREET/APD interface are provided in Argonne publications [71, 72].

The fuel pathway considered in this research includes biodiesel from conventional transesterification from microalgae oil and FT fuel from the CE–CERT process via steam hydrogasification of the whole microalgae. Figure 1.9 shows the key stages and major product associated with biodiesel production from microalgae. The energy and GHG emissions associated with the growth and dewatering of algae, extraction of oil from algae biomass and the subsequent transesterification conversion and combustion in vehicle are examined. This pathway focused on open pond mixed by paddle wheel. There are several method for harvesting and dewatering microalgae such as bio–

flocculation, dissolved air flotation, centrifuge, filtration, or drying that depend on the assumption and the desired of final product. Microalgae biomass must be dried to remove high water content before extraction. Lipid (oil) is then extracted by solvent extraction. The residual microalgae, a co–product of the extraction process, can be used for methane production using anaerobic digestion and/or for electric power generation. Biodiesel from microalgae oil is produced by transesterification.

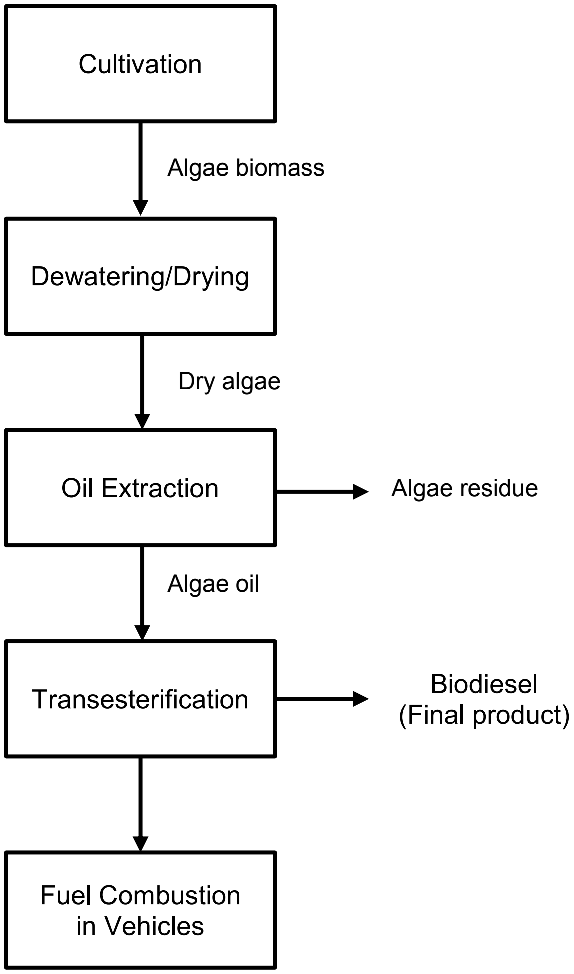

Figure 1.9 Energy pathway using transesterification

Figure 1.10 illustrates the system boundary and activities associated with FT fuel production using steam hydrogasification of microalgae. The fuel cycle energy and GHG emissions for FT fuel produced from microalgae and combustion in vehicle are investigated. The whole microalgae after cultivation, harvesting, and dewatering can be used directly in the CE–CERT process. The wet feedstock without drying is fed in steam hydrogasification in the presence of hydrogen to obtain a methane–rich output gas. The reaction between methane and steam in steam methane reforming generates the mixture of hydrogen and carbon monoxide called syngas. Syngas produced is converted via the FT process usually produce three groups of hydrocarbons: FT naphtha (C5–C9), FT middle distillates (C10–C20), and FT wax (>C20). Wax is further cracked into middle distillates. The unconverted syngas or flue gas can be used to generate electricity. The CE–CERT process is expected as another conversion technology for producing the FT fuel and electricity using the whole microalgae without drying that was capable of reducing the cost and energy consumption.

The results in terms of life cycle energy and net GHG emissions of FT liquid fuel of microalgae are compared to biodiesel from algae oil through transesterification and conventional diesel.

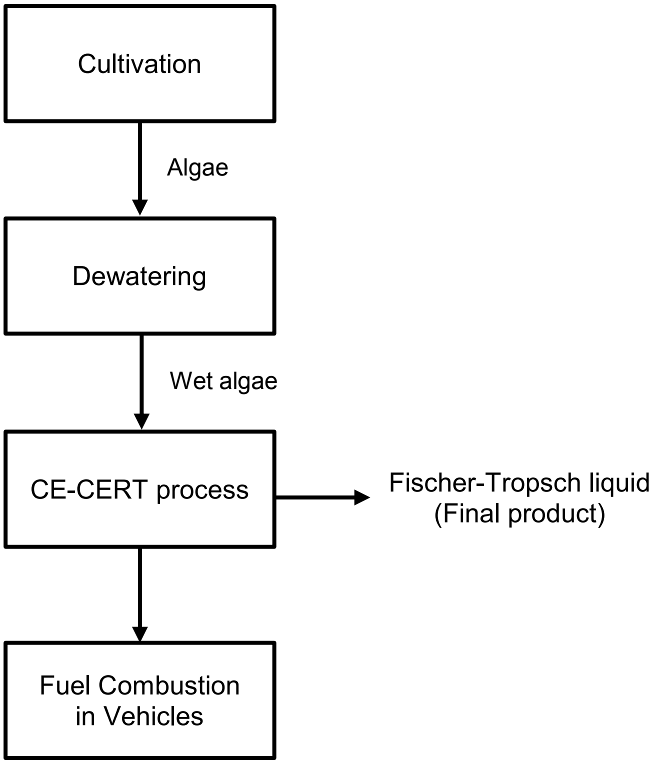

Figure 1.10 Energy pathway using the CE-CERT process via steam hydrogasification

1.4. Research objectives

The overall goal of thesis research is to evaluate the feasibility of implementing the CE–CERT technology through the steam hydrogasification process for production of Fischer–Tropsch (FT) liquid fuel from microalgae. This research involved studying the SHR process using both whole microalgae directly and/or using the microalgae residue after lipid extraction. The research also included life cycle analysis of production of synthetic fuel using the CE–CERT process compared to conventional transesterification from microalgae feedstock. The research objectives of thesis are described as follows.

1. Chapter Two is focused on studying the chemical conversion and compositions of the product gas during the steam hydrogasification process for whole microalgae biomass. The reaction condition variables are optimized for achieving a high gasification efficiency. Experiments are performed under varied reaction conditions such as temperature, steam to biomass ratio, and hydrogen to carbon ratio. The performance of steam hydrogasification of microalgae biomass was investigated from the mainly product gas: CH_4, CO, CO_2, and H_2 as well as carbon conversion efficiency. In addition, the simulation of the CE–CERT process using Aspen plus developed [73] is applied to estimate the combustible gas, FT liquid fuel, electricity as well as the mass and energy balances of the process.
2. Chapter Three contains the results of the chemical conversion and compositions of product gas during the steam hydrogasification process for microalgae residue after lipid extraction. The soxhlet extraction is used to separate the microalgae oil from microalgae biomass. The experimental results from steam hydrogasification of microalgae residue are investigated in terms of carbon conversion efficiency and the product gas compositions. Microalgae with different lipid content are also

investigated as feedstock for the gasification experiment. The effect of lipid content of microalgae in the gasification reaction is examined in terms of carbon conversion. The mass and energy balances of the CE–CERT process for FT liquid fuel of the residual microalgae are calculated using Aspen plus simulation.

3. Chapter Four contains the results of well–to–wheels life cycle analysis of the proposed process using the GREET model. This research evaluated the energy efficiency and greenhouse gas (GHG) emission (CO_2 equivalent) on the production of FT liquid fuel through the implementation of the CE–CERT technology. The fuel life cycle energy and GHG emissions that impact on the environment include microalgae cultivation, microalgae production, conversion, and vehicle operation. Detailed information on the assumptions and calculation methods are provided in this chapter. This gasification pathway results have been compared to the similar life cycle analysis for the production of biodiesel from the conventional transesterification of microalgae oil.

2. Steam Hydrogasification of Microalgae

This chapter addresses gasifying microalgae using the steam hydrogasification process. The main technical objective is to optimize the operating conditions to obtain a high conversion efficiency in the steam hydrogasification process. Experiments were done using a stirred batch reactor. The design details, features and operation of the stirred batch reactor are described in this chapter. The effect of operating parameters such as the reaction temperature and feed compositions (hydrogen/carbon ratio and steam/ biomass ratio) on the performance of the steam hydrogasification was investigated. The performance metrics are the carbon conversion and the compositions of the product gas. In addition, the mass and energy balance was done using Aspen plus® software and subsequent determination of the synthetic liquid fuel produced.

2.1. Introduction

Gasification generally refers to the thermochemical conversion of carbonaceous materials to combustible gases with a useable heating value. The detailed chemistry of biomass gasification is a relatively complex process. In the most basic form, biomass gasification can be divided into a two–step process: an initial devolatilization or pyrolysis step followed by gasification. The gasification process for biomass is illustrated in Figure 2.1. Drying process uses to remove the moisture content in the biomass. The drying occurs on the outside surface of a biomass particle and progresses toward the center. The biomass is heated and the moisture in biomass is converted to steam. Steam can also react with biomass and the volatile gases. Pyrolysis is the thermal decomposition of biomass called devolatilization. This step produces mainly volatile materials in forms of gases and the solid residue. The amount of volatile compounds depends on the temperature, type, and characteristic of the feedstock. The remaining solid residue containing the carbon material is referred to char residue. The volatile hydrocarbons and char are converted to combustible gas in the second step called gasification [63, 74, 75].

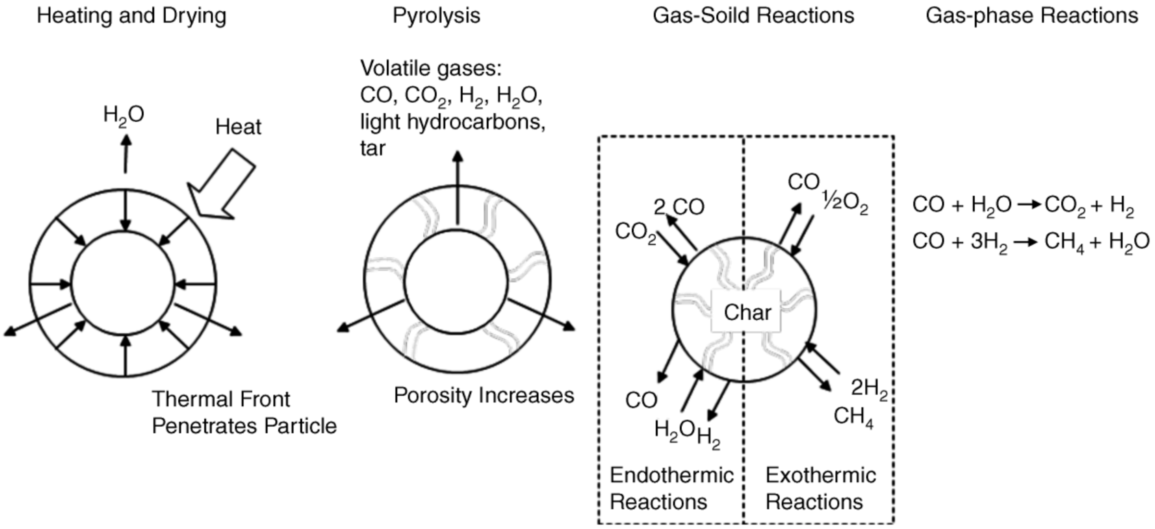

Figure 2.1 The process of thermal gasification [75]

There are several chemical reactions during gasification. A simplified representation of these reactions is presented in Table 2.1.

Table 2.1 The chemical reactions in biomass gasification

Reaction	Chemical Equation		
Pyrolysis	$Biomass \rightarrow gases\ (H_2, CO, CO_2, CH_4, C_nH_m) + tar + Char$		(2.1)
Combustion	$C + \frac{1}{2}O_2 \leftrightarrow CO$	$-111\ kJ/mol$	(2.2)
Boudouard	$C + CO_2 \leftrightarrow 2CO$	$+173\ kJ/mol$	(2.3)
Water gas	$C + H_2O \leftrightarrow CO + H_2$	$+131\ kJ/mol$	(2.4)
	$C + 2H_2O \leftrightarrow CO_2 + 2H_2$	$+90\ kJ/mol$	(2.5)
Hydrogenation	$C + 2H_2 \leftrightarrow CH_4$	$-75\ kJ/mol$	(2.6)
Water gas shift	$CO + H_2O \leftrightarrow H_2 + CO_2$	$-41\ kJ/mol$	(2.7)
Methane reforming	$CH_4 + H_2O \leftrightarrow 3H_2 + CO$	$+206\ kJ/mol$	(2.8)
	$CH_4 + 2H_2O \leftrightarrow 4H_2 + CO_2$	$+165\ kJ/mol$	(2.9)
Tar cracking and reforming	$Tar + H_2O \leftrightarrow H_2 + CO + CO_2 + CH_4 + hydrocarbon + \cdots$		(2.10)

The gasification process of biomass involves different reactive agents like air, oxygen, or steam to convert carbonaceous materials into gaseous products. Gasification is classified according to the gasifying agents: partial oxidation, hydrogasification, steam gasification and gasification with other agents such as CO_2 and there are shown in Figure 2.2.

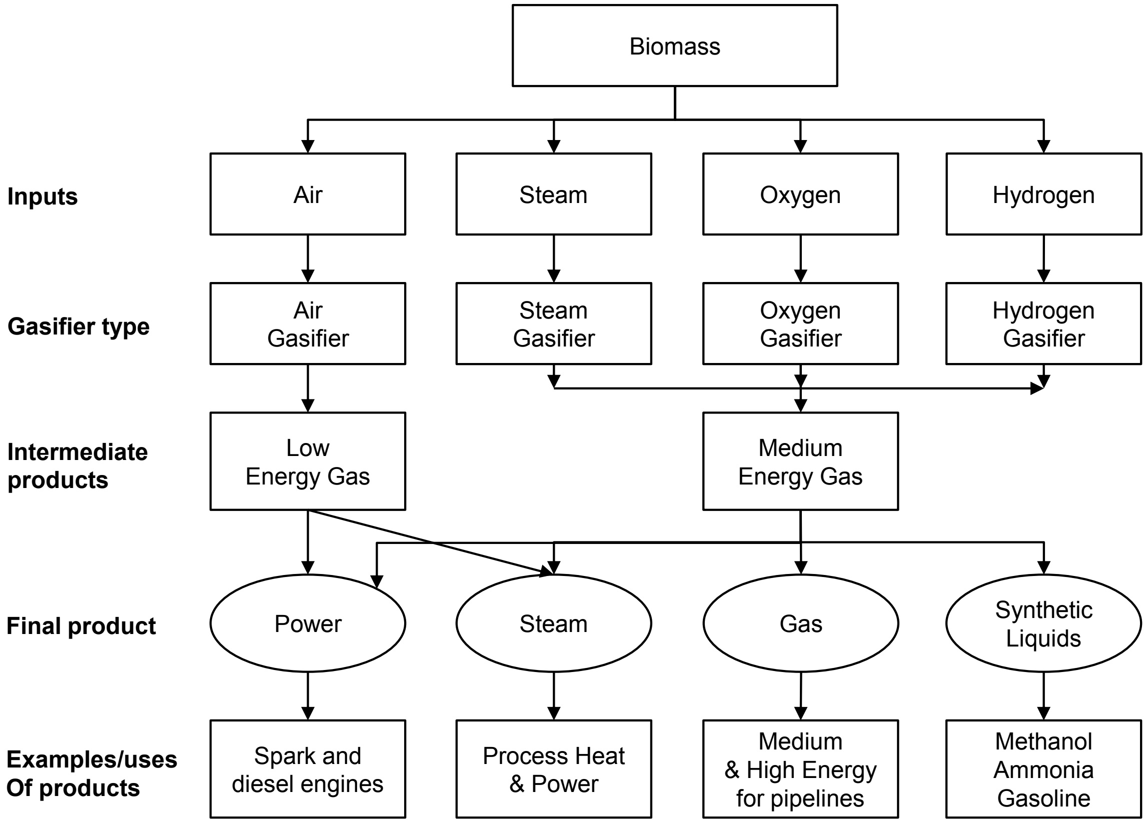

Figure 2.2 Gasification processes and their products [74]

The gasification process is performed at relative high temperature range from 600 to 1500 °C. Biomass gasification is predominantly converted into a mixture of hydrogen (H_2), carbon monoxide (CO), methane (CH_4) and other non–combustible gas such as carbon dioxide (CO_2), water vapor and nitrogen [75]. The product gas also contains particulates such as char, ash, soot, etc. The composition of the product gas and yield can vary significant by depending on the gasification agent, the gasifier operating conditions such as temperature, pressure, and feedstock characteristic [75]. The producer gas can be used for generate heat and electricity, as well as the production of liquid fuels and chemicals production such as methanol, ethanol, pure hydrogen, dimethyl ether, and synthetic diesel and gasoline [75].

Steam hydrogasification is a thermochemical process that converts the carbonaceous materials in the presence of steam and hydrogen into gaseous products. Steam hydrogasification enhances the rate of the hydrogasification reaction and methane formation [64]. Steam hydrogasification is an attractive process for the conversion of feedstocks contained high water content such as biosolids or microalgae into biofuels. Further details of steam hydrogasification reaction were described in Chapter 1.

Microalgae have been considered as a promising renewable and alternative feedstock source for biofuel production, especially biodiesel production. Compared with terrestrial plants, microalgae have a high oil content and growth rate. Microalgae contain high water content so a drying step is necessary to remove high amount of water before lipid extraction or conversion. The drying process is costly and energy intensive [41, 76]. Therefore, steam hydrogasification appears attractive for microalgae because gasification occurs directly and continuously without drying and lipid extraction. The water content in microalgae can serve as a source of steam in the steam hydrogasification process. The output can be used to produce the synthetic liquid fuel via Fischer–Tropsch reaction and/or generate electricity.

The production of liquid fuels using microalgae biomass using the CE–CERT technology will be studied. The results of experimental and modeling work of microalgae biomass will be presented and summarized below.

2.2. Experimental section

2.2.1. Feedstock material

The feedstock used is *Chlorella vulgaris* microalgae obtained from University of California, Merced and is shown in Figure 2.3. *Chlorella vulgaris* is a green type freshwater algae and it is already in commercial cultivation for the production of nutriceutricals and biofuels [19, 20, 77, 78].

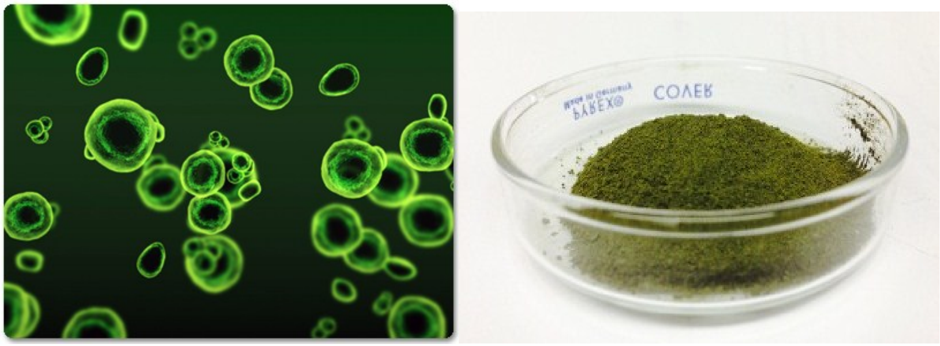

Figure 2.3 *Chlorella vulgaris* microalgae feedstock, picture courtesy of Wellstar company (left)

The microalgae were dried in a vacuum oven at a temperature 105 °C to get rid of its inherent moisture before test. It should be noted that in this study we used dried microalgae for controlling the experiment accuracy and eliminating uncertainly factors. All the experiments were repeated at least three times to eliminate operation and system error. The proximate and ultimate analysis of the microalgae sample is given in Table 2.2. Proximate analysis classified in terms of the contents of moisture, volatile matter, ash, and fixed carbon whereas ultimate analysis was corresponding to the element compositions of sample included C, H, N, S and O (by difference).

Table 2.2 Proximate and ultimate analysis of the *Chlorella vulgaris* sample

Proximate Analysis (wt%)	
Moisture	6.11
Volatile Matter	71.83
Fixed Carbon	22.30
Ash	5.87
Ultimate Analysis (wt%)	
Carbon	47.84
Hydrogen	6.29
Nitrogen	8.12
Sulfur	0.568
Oxygen by different	31.31
Higher heating value (MJ/kg)	22.8

2.2.2. Experimental apparatus

The experimental work was carried out using a stirred batch reactor. A schematic diagram of the reactor is presented in Figure 2.4. The reactor volume is 260 cc and has a maximum operating temperature of 800 °C and pressure of 500 psi. The system is comprised of a reactor vessel that is made of Inconel® alloy, an electrical furnace which provided the heat for the reaction, a magnetically driven impeller system, and gas inlet/outlet that the product gas is collected by a Tedler gas bag. All data were monitored and recorded using Labview software.

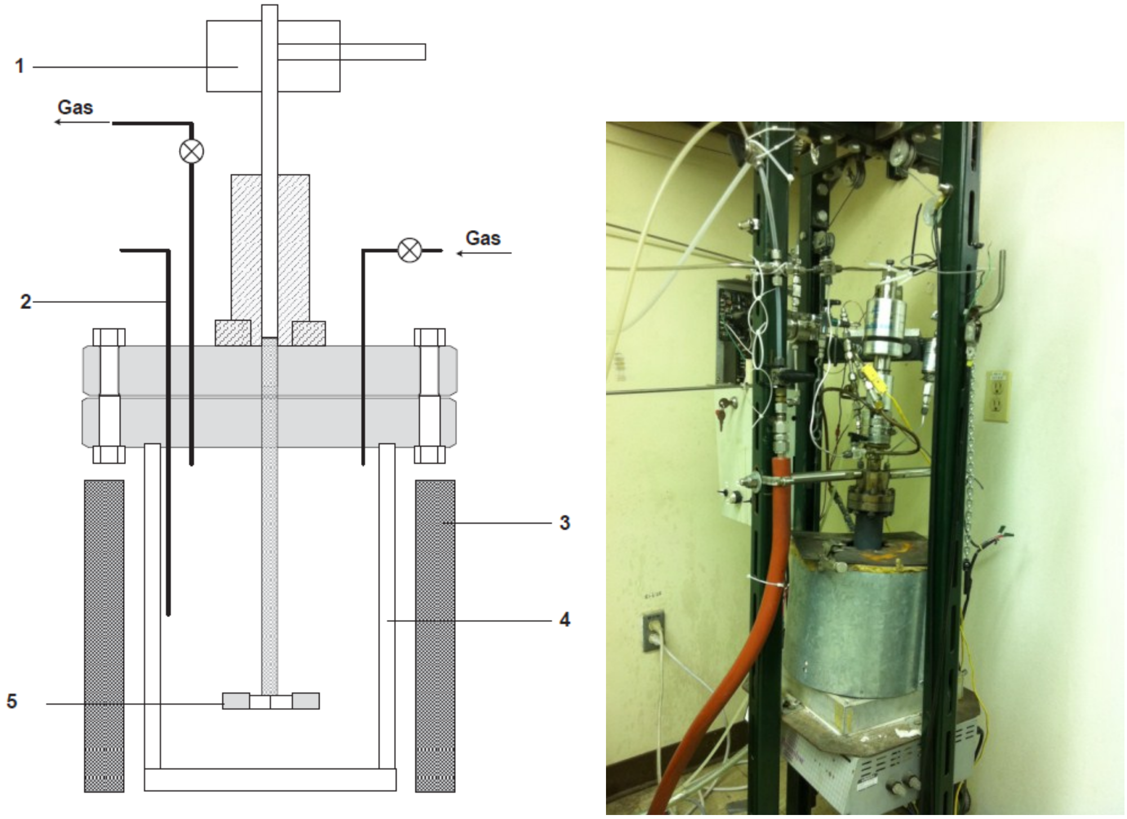

Figure 2.4 A schematic diagram and photo of the stirred batch reactor (1. Magnetic agitator 2. Thermocouple 3. Electrical furnace 4. Inconel reactor 5. Impeller coupled with agitator)

2.2.3 Experimental procedure

The experiments were carried out on three experiment series: varying the temperature, varying the hydrogen/carbon (H_2/C) ratio and varying the steam/biomass (S/B) ratio. The main purpose of these tests was to determine the carbon conversion and the product gas composition. The experimental parameters are shown in Table 2.3. The experimental procedure was discussed in the detail as follows.

All of the experiments were conducted using 0.5 g of microalgae. The microalgae were loaded into the reactor with the desired amount of water. The reactor was connected to the magnetic driven impeller, tightened by means of the flange and placed inside an electrical furnace, which provided the heat for the reaction. Afterwards, the reactor was then tested for leaking, flushed and purged with hydrogen gas three times using a vacuum pump. The reactor was then pressurized with hydrogen to the desired pressure. Cooling water was circulated during the test between the reactor and motor driver in order to avoid damage due to high temperature. Then, the reactor was heated by an electrical furnace to the desired temperature and the reaction was carried out until the pressure inside the reactor was constant. The temperature, pressure and heater duty information were recorded through the Labview data acquisition system. Finally, the reactor was cooled down to below 100 °C and the product gas was collected by Tedler gas bag and off – line analyzed by a Residual Gas Analyzer (RGA). The compositions of the gas produced; mainly H_2, CH_4, CO and CO_2 were documented (discussed in next section).

Table 2.3 Experimental parameters

Item	H_2/C ratio	Steam/biomass ratio	Temperature (°C)
Effect of temperature	1	2	650,700, 750, 800
Effect of Steam/biomass ratio	1	0, 1, 1.5, 2, 2.5	750
Effect of H_2/C ratio	0.5, 1, 1.5	1.5, 2, 2.5	750

2.2.4 Analysis method

A Cirrus^{TM} atmospheric pressure residual gas analyzer (referred to as RGA) is used for analysis of gaseous product and is shown in Figure 2.5.

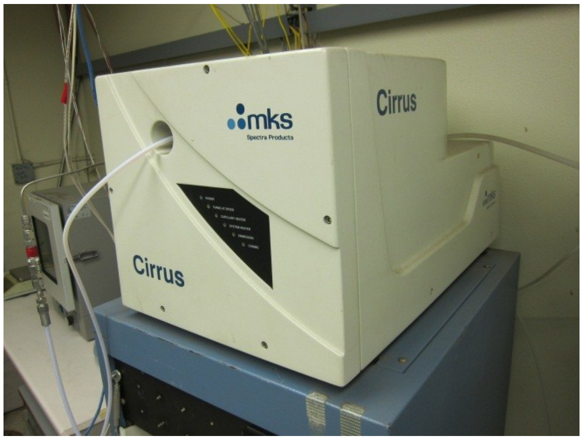

Figure 2.5 A photograph of Cirrus^{TM} atmospheric pressure residual gas analyzer

The RGA records the mass spectra data as intensity in units of torr. The major gases produced from the steam hydrogasification analyzed with the RGA are CH_4, CO, CO_2 and H_2. The relative concentration of a gas species in the mixture gases is proportional to the intensity of a gas species (Eq. 2.11) based on a constant sensitivity. The sensitivity of a gas species in mixture gases can be obtained by RGA calibration using certified calibration gas.

$$S_c = \frac{I_c}{P_c} \quad (2.11)$$

Where S_c is RGA sensitivity to gas species, I_c (torr) is major intensity of a gas species in mass spectra, P_c (torr) is partial pressure of a gas species in mixture gases.

The evolution of gas products during the SHR was analyzed by the RGA. The gases progressed were identified by detecting the key fragment ions produced. Therefore, analysis for CH_4, CO and CO_2 are taken for the molecular peak of m/z = 16, m/z = 28 and m/z = 44 in the mass spectra pattern.

Carbon conversion is defined as the ratio between the carbon present in the produced gas and the carbon that enters with the biomass (Eq. 2.2). The carbon conversion is used as key input assumption in simulation that affects the downstream steam methane reforming and Fischer–Tropsch outputs directly.

$$Carbon\ conversion\ (\%) = \left(\sum N_{c,i}/N_{c,feed}\right) \times 100 \tag{2.12}$$

where $N_{c,i}$ (mole) is number of moles of carbon in the gaseous products and $N_{c,\ feed}$ (mole) is number of moles of carbon in feed.

2.2.5 Process modeling methodology

Aspen Plus version 7.2 was used to predict process performance, mass and energy balances. Aspen Plus is well known as a simulation tool for handling non–conventional feedstock and process streams with built–in process models and physical/chemical property databases. Thermodynamics for the gasification and downstream unit operations are estimated by the Peng–Robinson equation for high temperature and pressure phase hydrocarbon behavior. A brief description of the process model used to simulate the CE–CERT technology is given below.

Steam hydrogasification is the core part of the CE–CERT process. The steam hydrogasification is simulated using decomposition and gasification units. These units are based on built–in Aspen reactor blocks and used to calculate the equilibrium composition in the reactor under any given conditions by means of Gibbs free energy minimization. The decomposition block converts the microalgae feedstock into its basic elements such as C (solid), H_2, O_2 and N_2. Using the RYIELD block and the gasification block Aspen calculates the equilibrium product gas composition using the RGIBBS block. The sulfur species such as H_2S, and impurities are removed from the product gas via a warm gas cleanup unit. The clean gas is then sent to the steam methane reforming (SMR) unit. The SMR is based on a built–in equilibrium block. The partial hydrogen is separated and recycled back to gasification unit to make the process self–sustainable. Any carbon dioxide is separated and removed from the syngas products. The Fischer–Tropsch (FT) block is simulated using an external model called through FORTAN module. This external model is empirically developed to predict the selectivity of the FT process [79]. The FT product contains fuel gas (C1–C4), naphtha (C5–C11), middle distillate (C12–C20), and wax (C20+). Wax can be converted into high quality diesel by the hydrocracking process. The fuel gas from the FT reactor is combusted for generating heat and electricity.

The FT product is evaluated in terms of overall thermal efficiency. The thermal efficiency based on the higher heating value (HHV) is defined as below (Eq. 2.13):

$$Thermal\ efficiency = {HHV_{FT\ product}}\Big/{HHV_{microalgae}} \tag{2.13}$$

where, $HHV_{\text{FT product}}$ is the higher heating value of FT naphtha and FT diesel in MJ/kg, and $HHV_{\text{microalgae}}$ is the higher heating value of microalgae feedstock. This value is 22.8 MJ/kg.

2.3 Result and discussion

2.3.1 Effect of temperature

Temperature is one of the most important operating parameter on the carbon conversion and the composition of the product gas for the gasification reaction. In this research, the effect of reaction temperature varied from 650 to 800 °C in the steam hydrogasification of microalgae was investigated. The experiments were carried out with a steam/biomass ratio of 2 and a H_2/C ratio of 1. The results for the product gases (H_2, CH_4, CO, and CO_2) are presented in Figure 2.6. An increase in temperature was found to increase the CH_4 production and decrease H_2 content, as expected. The increased in the CH_4 formation and H_2 production decreased with enhanced temperature are the result of a higher contribution of the chemical reaction of hydrogenation (Eq. 2.6), the reversible methane reforming called methanation (Eq. 2.8), and tar thermal cracking and reforming (Eq. 2.10). The small decrease in the production of CO with an increase temperature is the consequence of water gas shift reaction (Eq. 2.7).

The effect of gasification temperature on carbon conversion was also studied and the results are shown in Figure 2.7. The carbon conversion increased dramatically with increased temperature. The carbon conversion increased with increased temperatures, from 52% at 650 °C to 82% at 800 °C.

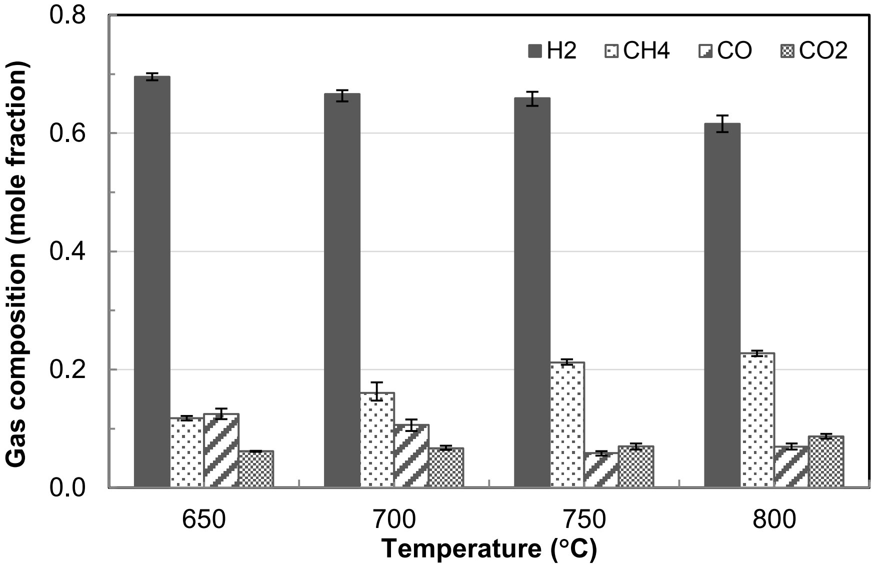

Figure 2.6 The effect of temperature on gas production (H_2/C = 1, S/B = 2)

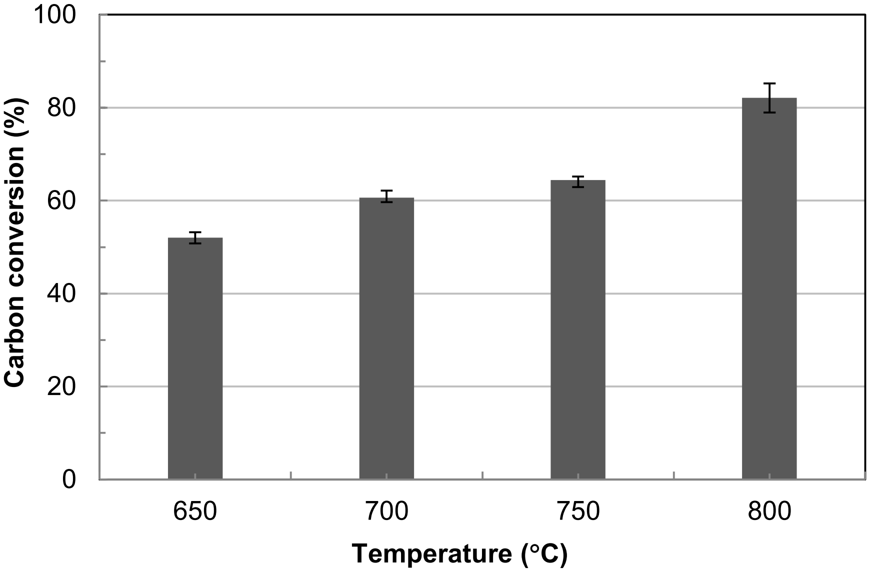

Figure 2.7 The effect of temperature on carbon conversion (H_2/C = 1, S/B = 2)

To summarize, temperature plays an important role in the overall efficiency of the gasification process that involve all the gasification reactions (Eq. 2.3–2.10). Higher temperatures in steam hydrogasification promote the decomposition of biomass. The hydrogenation, methanation, and water gas shift reactions appear to be more sensitive to the rise in temperature in steam hydrogasification. It leads to more methane–rich gas and an increase carbon conversion. It is recommended that the steam hydrogasification should operate at a temperature of 750 °C or higher to promote methane formation, which leads to higher gas yield and carbon conversion. The drawback of using high gasification temperatures could be higher operational cost and higher energy cost due to the increased requirement of heat needed for the steam hydrogasification process. Temperatures less than 750 °C would be low carbon conversion and production of methane. The gasification temperature was set at 750 °C and used in the rest of the experiments in this thesis but more research is needed to select the optimum reactor temperature.

2.3.2 Effect of steam/biomass ratio

The influence of steam/biomass ratio was investigated in the range of 0–2.5 at a temperature 750 °C with a H_2/C ratio of 1. The effect of the S/B ratio on the gas product composition is shown in Figure 2.8. It is found that the production of H_2 and CO_2 increased slightly with an increase the S/B ratio, whereas CH_4 and CO decreased slightly. This implies that the solid carbon and methane were formed with low steam content. An excess of steam, solid carbon and methane reduced further whereas H_2 and CO_2 production increased. Thus, the addition of steam favored the water gas reaction (Eq. 2.4 and 2.5) and methane reforming reaction (Eq. 2.8 and 2.9).

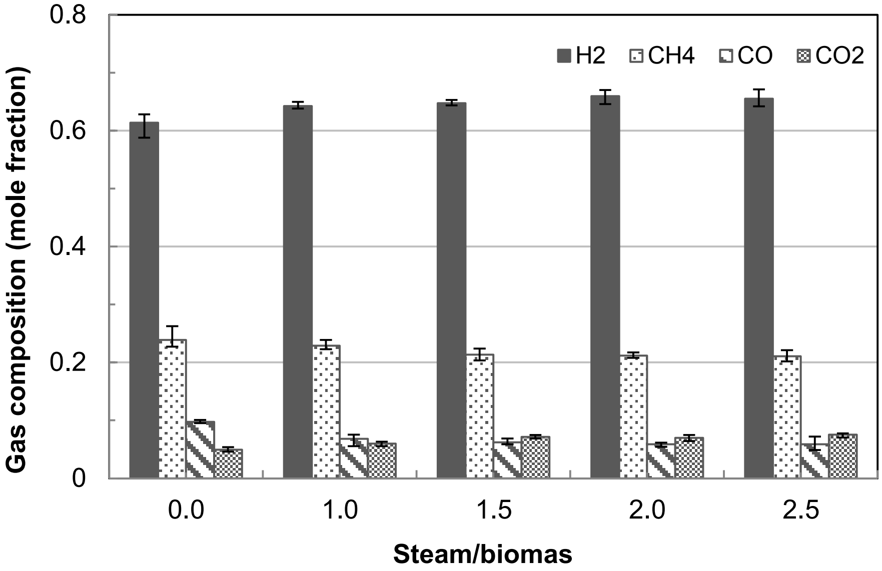

Figure 2.8 The effect of steam/biomass ratio on gas production at 750 °C and H_2/C =1

The product gas composition did not significantly change with S/B ratio in the range of 1.5–2.5. The excessive steam could result in temperature drop on the surface of biomass, which led to the reduction of decomposition of steam and the rate of gasification reactions [80-82].

The effect of S/B ratio on the carbon conversion efficiency is shown in Figure 2.9. The carbon conversion increased a little from 64% to 67% with the introduction of steam. The varied S/B ratio had no obvious effect on carbon conversion.

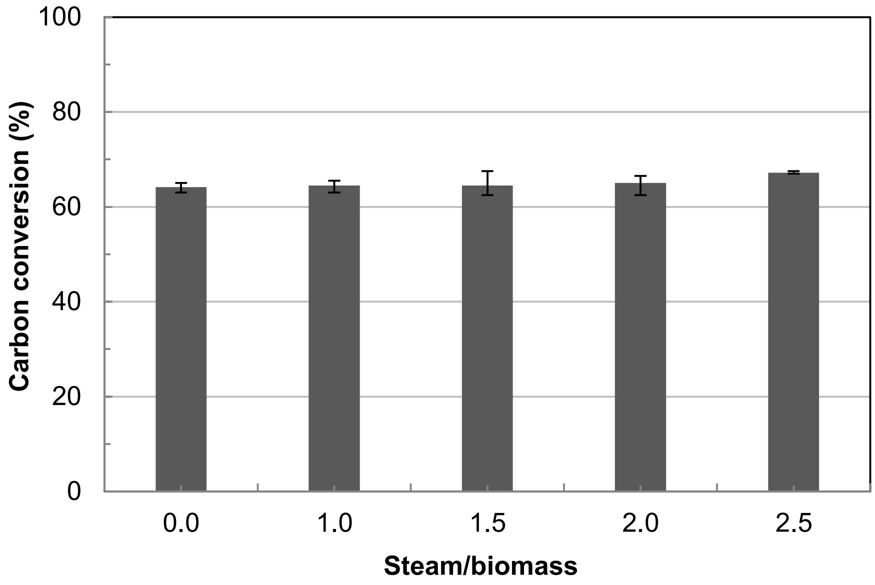

Figure 2.9 The effect of steam/biomass ratio on carbon conversion at 750 °C and H_2/C =1

The H_2/CO ratio increased with an increase of S/B ratio, while CO/CO_2 ratio showed an opposite trend. This is shown in Figure 2.10 and 2.11. It can be observed that the water gas (Eq. 2.4 and 2.5), water gas shift (Eq. 2.7) and steam reforming (Eq. 2.8 and 2.9) reactions play an significant role in steam hydrogasification process to promote the product gas mainly H_2 and CO_2 formation. Similar results have been report in other studied [60, 83, 84]. In contrast, the production of CH_4 and CO reduced as the same reactions that are promoted by steam.

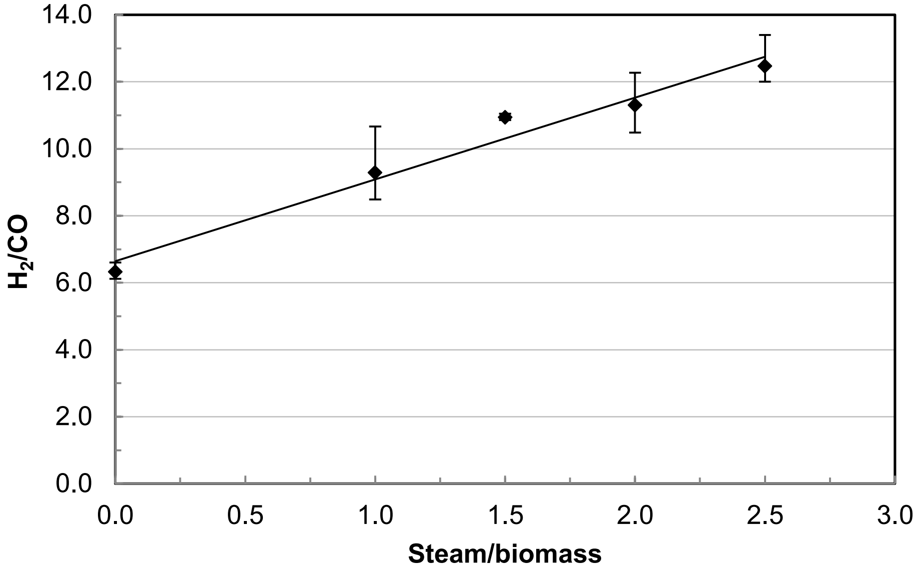

Figure 2.10 The effect of steam/biomass ratio on H_2/CO ratio at 750 °C and $H_2/C = 1$

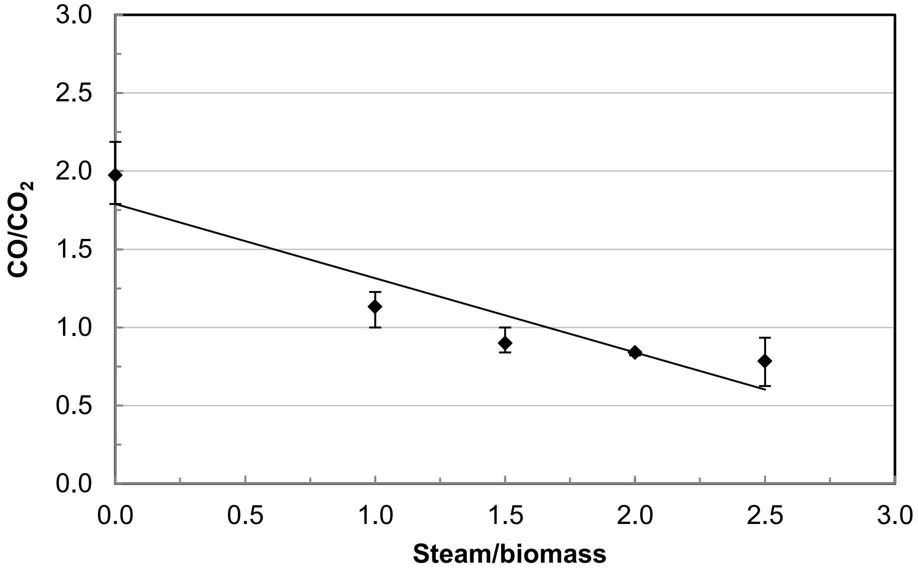

Figure 2.11 The effect of steam/biomass ratio on CO/CO_2 ratio at 750 °C and $H_2/C = 1$

The value of S/B ratio to achieve the product gas especially H_2 and CH_4 according to the data obtained in this study at range of 1.5–2.5. The maximum H_2 and CH_4 content can be obtained at about S/B ratio of 2. However, the main disadvantage of using higher S/B ratio values was the energy penalty in the initial devolatilization or pyrolysis step. It is significant to balance the operating cost and energy consumption between the upstream and downstream processes when using microalgae as feedstock. The upstream process includes harvesting and dewatering as well as drying or extraction while the downstream process consists of conversion technology like transesterification, gasification and anaerobic digestion processes.

2.3.3 Effect of H_2/C ratio

A H_2/C ratio range from 0.5 to 1.5 was used to investigate of hydrogen impact on the product gas composition. Figure 2.12 shows the combined effect of S/B and H_2/C ratios on the H_2 production. At each S/B ratio of 1.5, 2.0, and 2.5, the H_2 production was enhanced with an increase of H_2/C ratio.

One of the main advantages of the CE–CERT process is the internal hydrogen feedback by means of recycling the excess H_2 produced. The H_2 available must be higher than H_2 input for the process to be self–sustained in terms of H_2 supply. The H_2 available is defined as Eq. 2.14.

$$H_2\ available = Total\ H_2 - H_2\ input \tag{2.14}$$

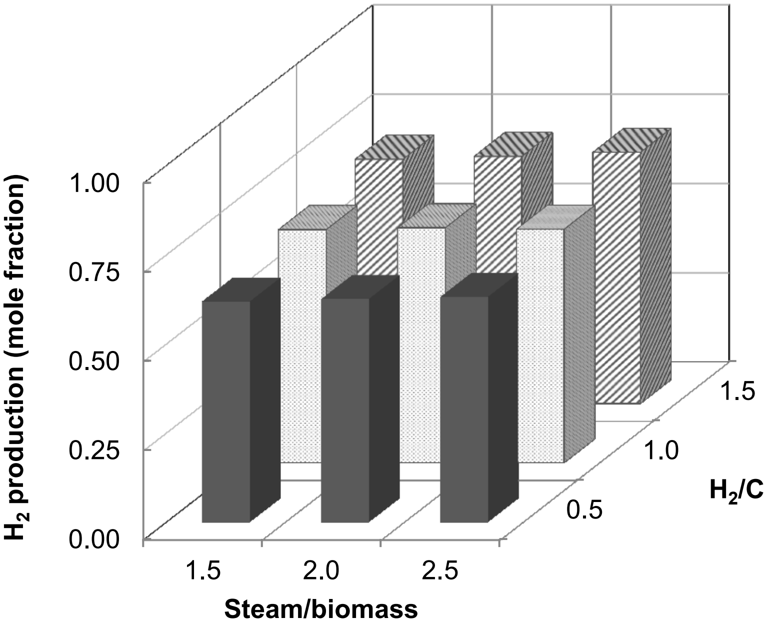

Figure 2.12 The effect of H_2/C and steam/biomass ratios on H_2 production at 750 °C

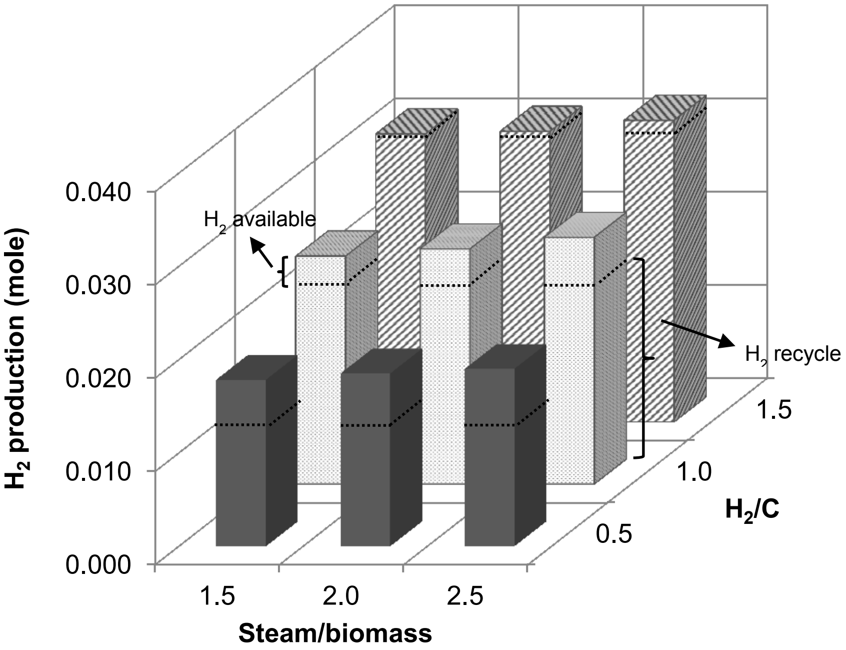

Figure 2.13 The effect of H_2/C and steam/biomass ratios on H_2 available at 750 °C

The H_2 available with H_2/C and S/B ratios at a temperature of 750 °C is shown in Figure 2.13. It can be seen that H_2 produced was enough for recycle to the gasifier and excess H_2 could be used for downstream process such as FT synthesis. The increase of S/B ratio enhanced the H_2 production (explained in section 2.3.2) and resulted in more H_2 available for recycle. On the other hand, the increase of H_2/C ratio decreased the H_2 available caused by the favorable hydrogenation reaction (Eq.2.6). Nevertheless, the amount of hydrogen was sufficient for recycle back to gasifier. It clearly indicated that the microalgae biomass can be gasified using steam hydrogasification process to generate sufficient amount of hydrogen for all experiment conditions in this research. The hydrogen produced can be supplied to the gasifier and the partial hydrogen can be used in downstream process in contrast to some cases for coal [67].

It can be concluded that steam plays an important role in H_2 production while hydrogen had influence on hydrogenation and methanation. However, the hydrogenation reaction is much slower reactivity compared to other gasifying agents. The reactivity of carbon with different species is presented below [85]. The presence of hydrogen with steam in the gasification process of carbon with high temperature favored to promote the methane formation and lead to the reduction of tar formation [86, 87].

$$\begin{array}{ccccccc} r_{O_2} & \gg & r_{H_2O} & > & r_{CO_2} & > & r_{H_2} \\ 10^5 & & 3 & & 1 & & 3.1^{-3} \end{array}$$

The combined effect of H_2/C and S/B ratios on the formation of methane is shown in Figure 2.14. At each S/B ratio, the production of CH_4 increased with the presence of hydrogen due to the favorable of hydrogenation reaction (Eq. 2.6). The maximum CH_4 formation can be obtained at S/B ratio of 2. On the other hand, at each H_2/C ratio, the CH_4 formation was decreased with an increase the S/B ratio. This effect was highly influence on methane reforming reaction (Eq. 2.8 and 2.9) that was explained in section 2.3.2.

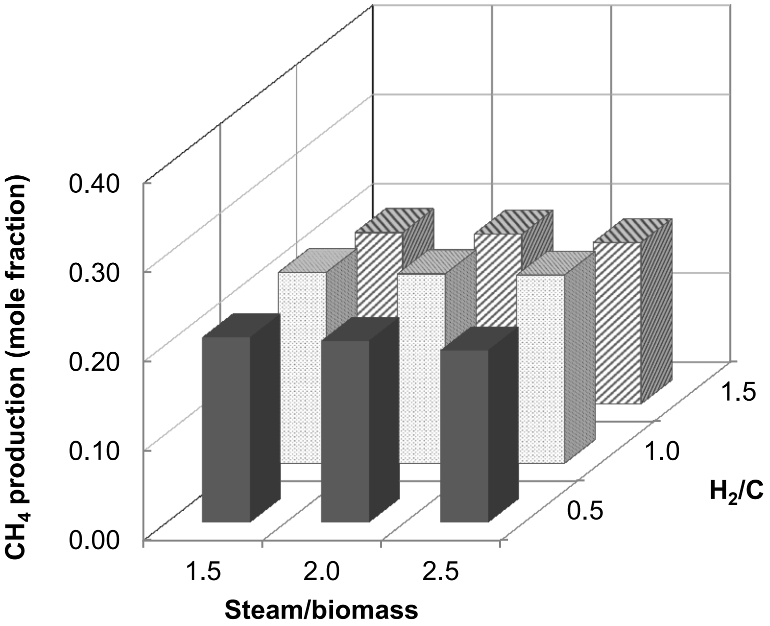

Figure 2.14 The effect of H_2/C and steam/biomass ratios on CH_4 production at 750 °C

The production of CO and CO_2 are presented in Figure 2.15 and Figure 2.16, respectively. The increase of H_2/C ratio reduced the production of CO and CO_2 at each S/B ratio. It can be indicated that some CO and CO_2 related methanation reactions (Eq. 2.8 and 2.9) that enhanced the CH_4 formation with the presence of excess H_2 in the reaction environment. On the other hand, at each H_2/C ratio, the production of CO did not significant change whereas the CO_2 formation slightly increased with higher S/B ratio. The more detailed were discussed in section 2.3.2.

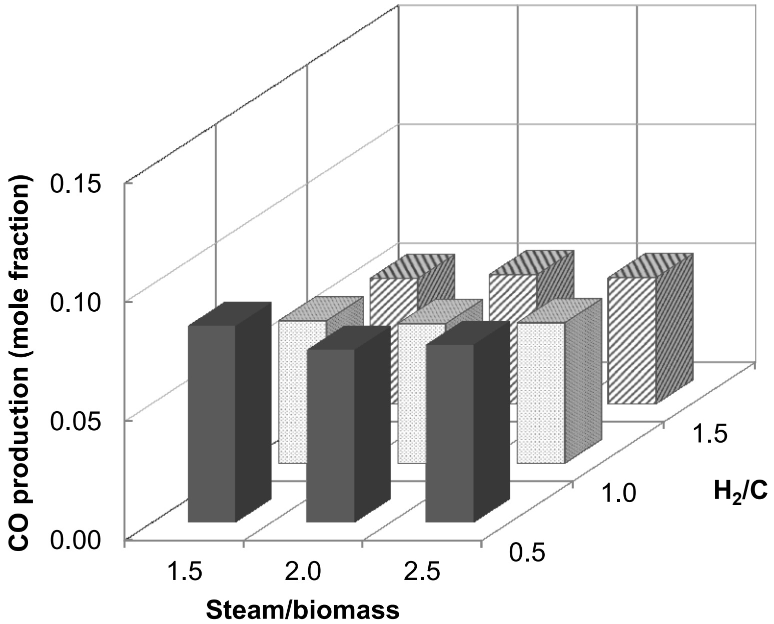

Figure 2.15 The effect of H_2/C and steam/biomass ratios on CO production at 750 °C

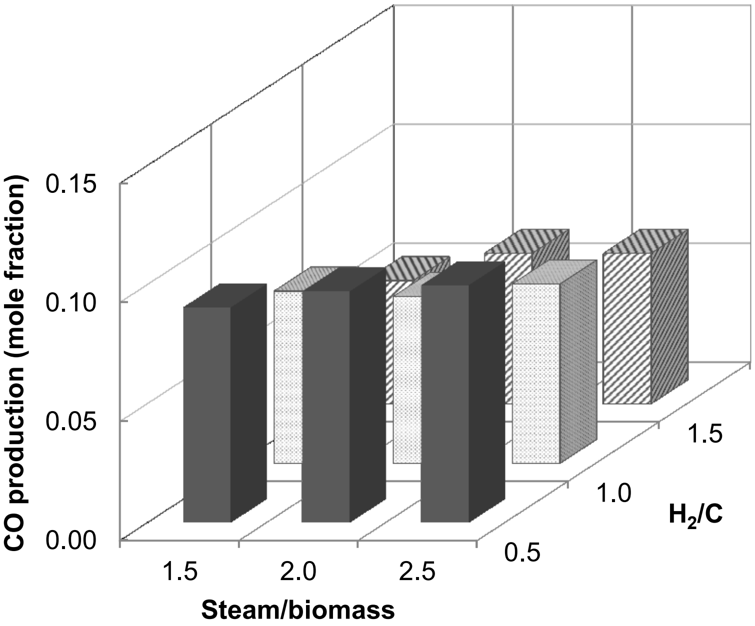

Figure 2.16 The effect of H_2/C and steam/biomass ratios on CO_2 production at 750 °C

The combined effect of H_2/C and S/B ratios on the carbon conversion is shown in Figure 2.17. At each S/B ratio, the carbon conversion enhanced with higher of H_2/C ratio due to the improvement of the gas production yield. However, an excess of hydrogen content (H_2/C=1.5), the carbon conversion is similar to H_2/C ratio of 1. On the other hand, at each H_2/C ratio, the carbon conversion slightly increased with higher S/B ratio.

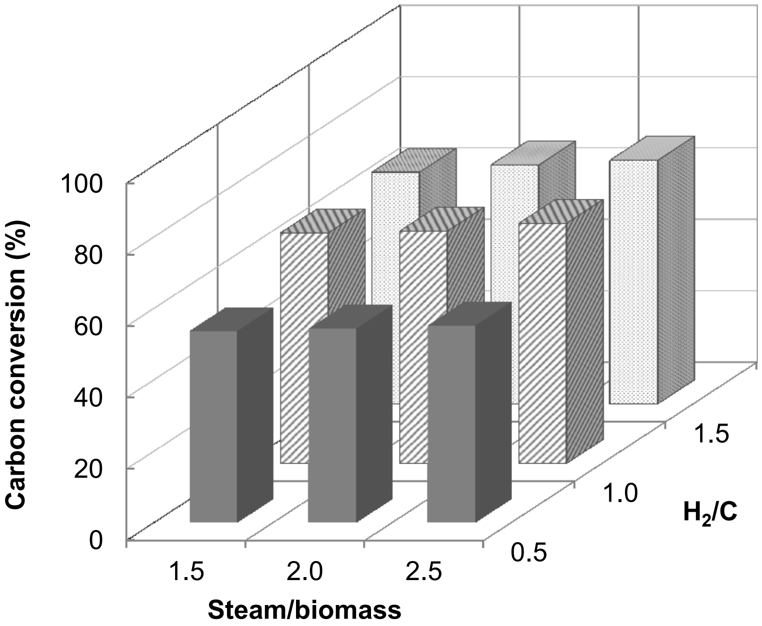

Figure 2.17 The effect of H_2/C and steam/biomass ratios on carbon conversion at 750 °C

In brief, at each S/B ratio, the production of H_2 and CH_4, and carbon conversion was enhanced while production of CO and CO_2 decreased with higher H_2/C ratio. The H_2/C ratio should be set at 1 in order to obtain the maximum methane formation and carbon conversion. In addition, the presence of hydrogen in the gasification reaction is more important not only to improve the rate of methane and reduce the tar formation but also make the process to be self–sustained in terms of H_2 supply.

2.3.4 Results of simulation

The Aspen plus model [73] was used to calculate the material and energy balance, and the product composition based on user defined input parameters such as the feedstock composition, temperature, pressure, flow rates, etc. These results can be used to estimate the overall process efficiency based on both the carbon converted to useful products and also the energy content of the feedstock. It should be noted that the experimental and simulation results were largely in agreement with each other.

In order to simplify the simulation process, the microalgae feedstock used in the simulation was a dry feedstock. The feedstock was first pretreated at a temperature 220 °C to make a slurry before it was sent to the gasification process. Based on the previous experiment, the H_2/C and steam/biomass ratios were determined as 1 and 2, respectively. This resulted in high CH_4 formation with 65% of carbon conversion. The gasification temperature and pressure was set at 750 °C and 400 psi, respectively. After gasification, the mixture gas passed through a warm gas cleanup unit to remove impurities. Then, the clean gas entered a steam methane reformer in order to generate syngas (a mixture of H_2 and CO). The reaction condition in the SMR was set at a temperature 850 °C and a pressure 400 psi. Partial H_2 was separated from the product gas for recycle back to the SHR. The syngas ratio used in the FT process was determined as 2.1 since cobalt was used as a catalyst in the reactor. The FT synthesis was set at a temperature 220 °C and a pressure 400 psi. The product distribution was determined by an external empirical model. Steam and CO_2 were removed from the final product. The FT fuel produced in the reactor comprised of FT liquid and wax. Wax can be converted into high quality diesel by hydrocracking. The fuel gas from the FT reactor is then combusted for generating heat and electricity.

The detailed mass and energy analysis for the overall CE–CERT process for FT liquid fuel production is shown in Figure 2.18. The calculations were performed for a feed rate one metric ton per day on dry basis. It can be seen in Figure 2.18(a) that one ton of dry microalgae produced 167 kg of char and 480 kg of CO_2. Char could be burned to generate heat for the process whereas CO_2 could be captured and used for growing microalgae. The CE–CERT process via steam hydrogasification from microalgae produced 153 kg of FT liquid fuel (approximately 1.06 barrel or 190 liters) that can be distributed into 102 kg of FT diesel and 51 kg of FT naphtha. In addition, wax is also produced and can be used in hydrocracking process to produce diesel fuel or sold as high value products that are able to use in the cosmetics industries. The energy consumed or generated during each step of the CE–CERT process is also presented in Figure 2.18(b). The heating of the slurry feed to the high temperatures and highly endothermic SMR reaction consume a large amount of energy. However, large amount of energy that generated by cooling down the SMR product gas and also from the exothermic FT reaction could be utilized for the SHR and SMR units. Based on the process simulation results, one ton per day of microalgae to liquid fuel produced 1.06 barrel of FT product with thermal efficiency of 27% using the CE–CERT process that is calculated from Eq. 2.13. In addition, the electricity that produced from the combustion of flue gas and char could enhance the overall thermal efficiency. The value of electricity obtained from the combustion was 24 kW.

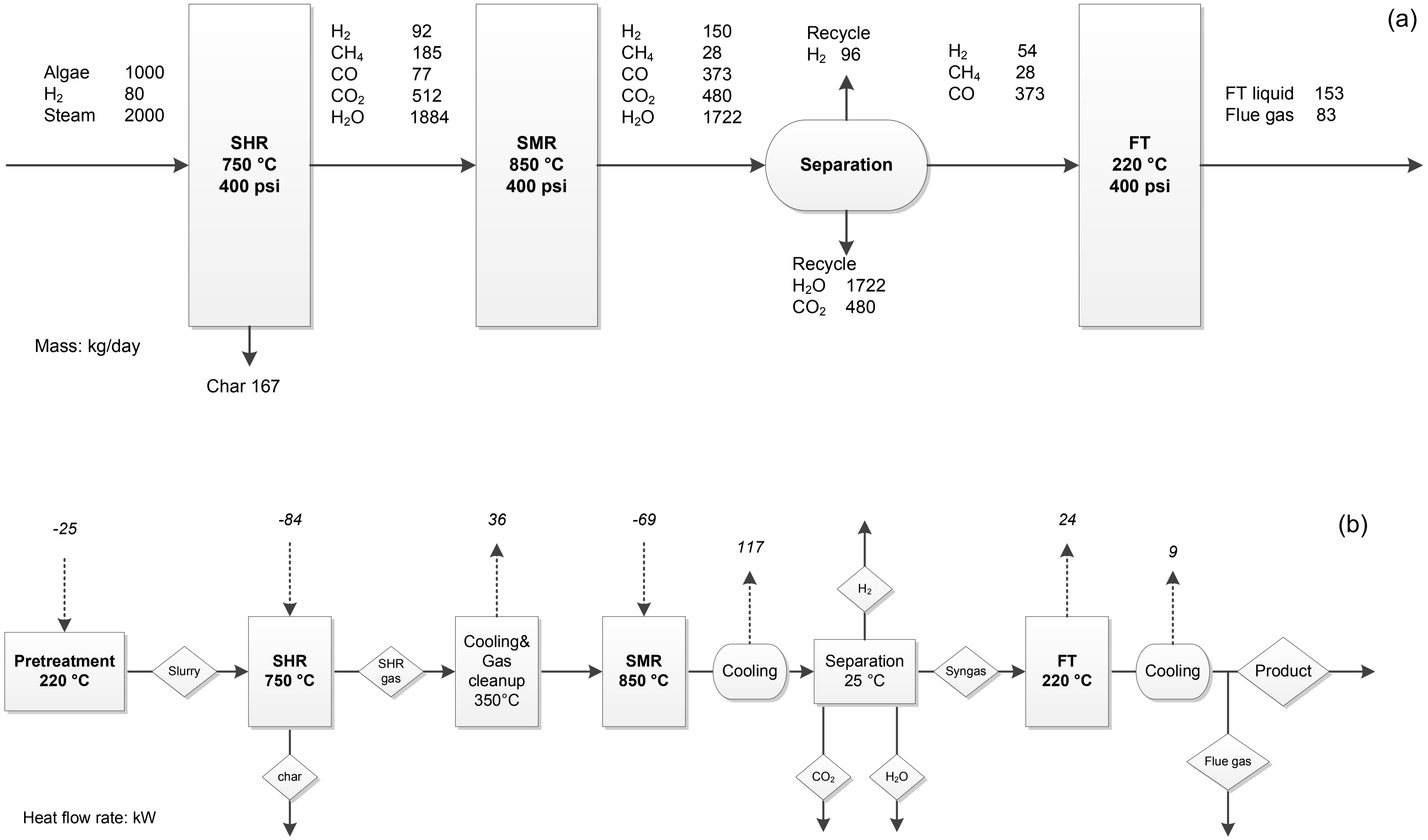

Figure 2.18 The overall mass and energy balance of the CE–CERT process for FT fuel production

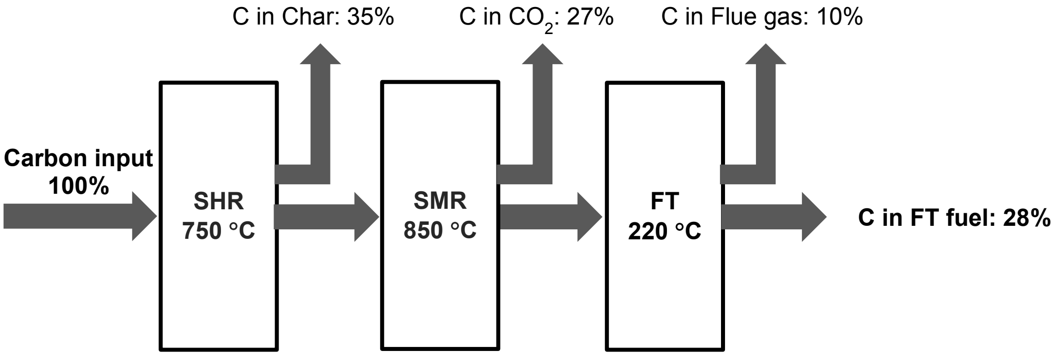

Figure 2.19 The carbon balance of the CE–CERT process for FT fuel production

The carbon balance of the overall CE–CERT process for FT fuel production is present in Figure 2.19. It can be seen that approximately 28% carbon was distributed to FT liquid fuel and 10% carbon in the flue gas. There is about 27% carbon in CO_2 generated that can be captured and recycled back to the pond and used as a carbon source for growing microalgae. However, about 35% of carbon in char can be burned to provide the heat for the process. Most carbon was formed in terms of char and CO_2 about 60% that mainly occurred in the SHR process. Therefore, the reduction of char and CO_2 could enhance the FT production as well as the performance of the SHR.

2.4 Conclusion

Steam hydrogasification process is an interesting technology for handling wet feedstocks like microalgae biomass. Microalgae biomass was gasified in a stirred batch reactor with steam and hydrogen environment in order to investigate the performance of steam hydrogasification in terms of the product gas composition and carbon conversion at different operating parameters. The following results were obtained:

1. An increase in gasification temperature showed the improvement on the product gas composition and carbon conversion efficiency. An increase in temperature also had a positive effect on the product gas rich in methane and the reduction of thermal cracking and reforming of tar. However, higher temperatures could result in higher energy and operational costs.
2. An increase in steam/biomass ratio had significant influence on both the product gas composition and carbon conversion. Consequently, the addition of steam significant promoted hydrogen formation. The influence of steam affected the water gas, water gas shift, and methane reforming reactions. Moreover, the introduction of steam also had a positive effect on a H_2/CO ratio that was interesting for the applications of syngas produced. Nevertheless, the excessive of steam could also adversely to lower hydrogen production.
3. An increase in hydrogen/carbon ratio found to enhance the hydrogen and methane formation. The influence of hydrogen affected the hydrogenation and methanation reactions. Methane rich gas could be used in the SMR for generating more syngas (a mixture of H_2 and CO) and then syngas could be utilized to produce synthetic liquid fuel through FT synthesis.

4. Steam hydrogasification of microalgae biomass can be self–sustained with no need for external H_2 or added catalysts. In addition, the excess hydrogen could be used further for FT fuel production.

5. Microalgae are an attractive biomass for FT fuel production using the CE–CERT process. Modeling indicates that at a temperature 750 °C with a H_2/C ratio of 1 and a S/B ratio of 2 provided the maximum methane formation in the product gas and obtained 65% carbon conversion. Based on these conditions, the process simulation results showed that the one ton per day of microalgae to liquid fuel was expected to produce 1.06 barrel of FT liquid with overall thermal efficiency of 27%.

3. The Utilization of Residual Microalgae after Lipid Extraction and Influence of Lipid Content in Microalgae using Steam Hydrogasification

This chapter addresses the potential to efficiently convert a co–product (the residual microalgae) after lipid extracted using the steam hydrogasification process to produce bioenergy. The effect of using microalgae with varied lipid content in steam hydrogasification is also addressed. A stirred batch reactor was used for the steam hydrogasification in this work. The design details, features and operation of stirred batch reactor were presented in the Chapter 2. Experiments of the residual microalgae were conducted at a temperature 750 °C and a pressure 400 psi with the steam/biomass ratio of 2 and H_2/C ratio of 1. The effect of different lipid content in microalgae was investigated at these same conditions.

3.1 Introduction

3.1.1 Availability of microalgae for biofuel production

Microalgae consist of three main components: lipids (including triglycerides and fatty acids), carbohydrates, and proteins. Most current research focused on lipids from microalgae that can be used for biodiesel production [11, 12, 55, 88-90]. The process of microalgae oil to biodiesel is similar to the process of oil derived from terrestrial crops. Thus, lipids are an important component as energy source for making biodiesel. However, the lipid content of microalgae varies in accordance with culture conditions and/or depending on species [91-93]. Several different lipids content are listed in Table 3.1. *Botryococcus braunii* can reach 75% of lipid in microalgae while the most common microalgae like *Chlorella*, *Dunaliella*, *Nannochloris*, *Nannochloropsis*, and *Spirulina* contain amount of lipid between 10 and 30%. Some species of microalgae have high lipid content but are associated with a low productivity. Moreover, the high productivities and growth rates of microalgae should be considered because the production of microalgae biodiesel also requires large quantities of microalgae biomass.

Lipids by means of fatty acid compositions can be divided in two types: saturated and unsaturated fatty acids. Microalgae oil has a lot of polyunsaturated fatty acids, which affect to low stability of biodiesel but have lower melting points than saturated and monounsaturated fatty acids. For example, the unsaturated and saturated fatty acids of *Chlorella vulgaris* are 70% and 28%, respectively [94].

Hence, it is too difficult to find the best species of microalgae that have high lipids content and productivity yields for producing biodiesel. In this chapter proposed the steam hydrogasification process as an alternative method for dealing with microalgae that comprise low, or high in lipid content. The experiments of steam hydrogasification of microalgae with different lipid content were investigated. The effect of lipid content on the product gas and carbon conversion was presented and summarized.

Table 3.1 Lipid content of some microalgae [12, 51]

Microalgae	Lipid content (%wt)
Anabena cylindrical	4-7
Botryococcus braunii	25-75
Chlamydomonus rheinhardii	21
Chlorella vulgaris	14-22
Crypthrcodinium cohnii	20
Cylindrotheca sp.	16-37
Dunaliella bioculata	8
Dunaliella primolecta	23
Isochrysis sp.	25-33
Monallanthus salina	>20
Nannochloris sp.	20-35
Nannochloropsis sp.	31-68
Neochloris oleoabundans	35-54
Nitzschia sp.	45-47
Phaeodactylum tricornutum	20-30
Scenedesmus dimorphus	16-40
Scenedesmus obliquus	12-14
Scenedesmus quadricauda	19.9
Skeletonema costatum	13-51
Spirulina maxima	6-7
Spirulina platensis	4-11
Tetraselmis sueica	15-23

3.1.2 Application of microalgae remnants after lipid extraction

Many researchers are interested in the potential of using microalgae as a feedstock for biofuel production. Microalgae–derived biodiesel is one of the noticeable preferences. Microalgae as a biodiesel feedstock have several advantages over other terrestrial crops; for instance, high growth rate, high productivity yields and photosynthesis efficiency, and high oil content. Moreover, microalgae have the ability to cultivate under varied conditions and locate on non–arable land and thus it does not complete with agricultural crops [3, 16, 17, 22, 95]. In order to achieve microalgae biodiesel production, the lipid must be extracted from microalgae biomass. Then, lipids are typically converted into biodiesel via transesterification. Biodiesel production from microalgae requires the energy and chemical intensive of current harvesting, drying and lipid extraction methods [96-98]. There are large quantities of co–products (residuals microalgae after lipid extraction) left over that are mainly carbohydrates and proteins. The residual microalgae that contain high remaining carbohydrates are appropriate feedstock for bioethanol production whereas co–products that consist of high remaining proteins are able to use for animal feed or fertilizers. So, the recovery of co–products can significantly improve the sustainability of microalgae biofuels. In addition, transesterification of algae lipids also generates glycerin as a by–product. Glycerin can also be burned for providing heat source or used as precursor for industrials such as polymers, paints, adhesives, etc. [99, 100].

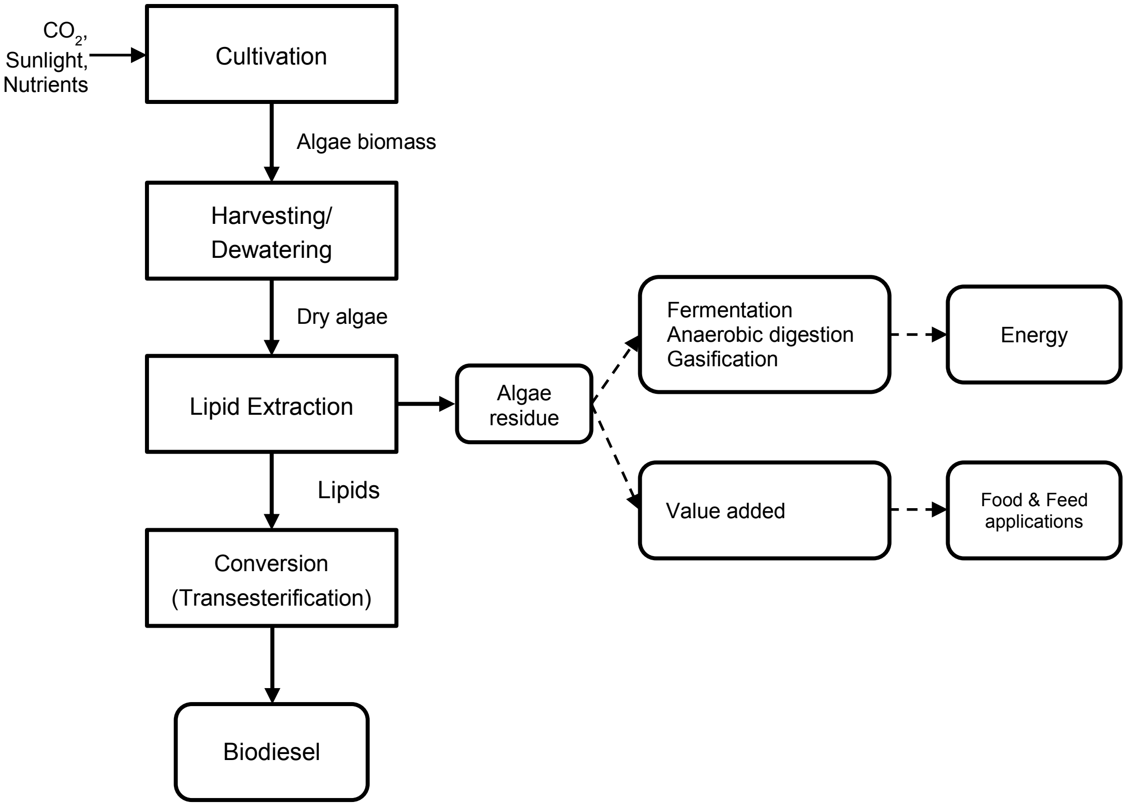

Figure 3.1 An integrated microalgae biodiesel production with utilization of microalgae residue

The microalgae biodiesel production integrated with the method for utilizing co–products after lipid extraction is shown in Figure 3.2. Lipids are usually major product after lipid extraction and then are used for producing biodiesel. The left over biomass that is obtained after lipid extraction can be utilized further for bio–energy production through anaerobic digestion, fermentation, combustion, and gasification etc. as well as for value added involved in food and feed applications. This can serve as a method to maximize energy production from microalgae and leads to the reduction of overall wastes and costs.

Lipid extraction is defined as the process of separating triglyceride lipids from the whole microalgae biomass after harvesting and dewatering. Whole microalgae typically must be dried to about 80–90% (w/w) solids in order to remove the remaining water before extraction. There are several methods for microalgae lipid extraction that can be roughly divided into two methods: (1) mechanical methods such as expeller press and ultrasonic (2) chemical methods like solvent extraction, and supercritical fluid extraction [101-103]. The advantages and limitations of extraction method are shown in Table 3.2. The mechanical method requires large quantity of biomass and energy intensive but it does not use solvent as well as is easy operation.

Solvent extraction technique is one of the most commonly methods of separating lipids from microalgae. The solvents that have been studied in the lipid extraction from microalgae are hexane, ethanol, dimethyl ether, and the mixtures chloroform/methanol, hexane/ethanol, hexane/isopropanol etc. [89, 102, 104-106]. Though chloroform or chloroform/methanol is highly effective for lipid extracted due to its fast and quantitative extraction but it has high toxicity [105]. So, hexane/isopropanol mixture or hexane is preferred due to its low toxicity, minimal non–lipid contaminations and is commonly used in many industries [105-107].

Supercritical fluid extraction is a green technology that has low toxicity compared to organic solvent extraction. However, the main drawback of the process is high cost and energy in terms of equipment and operation [54, 108, 109].

Table 3.2 Comparison of extraction method [7, 30, 110]

Extraction method	Advantages	Limitations
Expeller press	Easy operation No solvent	Slow process Need dried biomass Large amount of biomass required
Ultrasound	Reduced operation time Reduce solvent use	High energy consumption Difficult to scale-up
Solvent extraction	Reproducible Inexpensive solvent Solvent recycling possible	Solvent highly flammable/toxic Solvent recovery is energy/cost intensive
Supercritical fluid extraction	No toxicity solvent Nonflammable Simple in operation	High pressure equipment Energy intensive expensive

The residual biomass obtained after lipid extraction contains proteins and carbohydrates, plus nutrients (nitrogen and phosphorus) that are used for growing microalgae. There are several options for utilizing the remaining biomass such as anaerobic digestion, fermentation, combustion, animal feed or fertilizers. Many researchers have studied utilization of co–products after lipid extraction of microalgae using anaerobic digestion [98, 111, 112]. The residual microalgae are anaerobically digested to produce biogas, which can be used to generate electricity. The biogas typically is a mixture of methane and carbon dioxide. CO_2 can be captured and used as a carbon source for growing microalgae. The residuals remaining after anaerobic digestion are rich in nitrogen and phosphorus and can be recovered for microalgae cultivation or can be sold as soil fertilizers. In addition thermochemical conversion technologies, such as pyrolysis, gasification, and combustion, can also be considered for the energy recovery from the residual biomass. These technologies are able to convert the residual biomass into biofuels as well as have a potential advantage for recycling the nitrogen containing in ammonia or nitrous oxides into the algae ponds, thereby reducing the expense for nitrogen fertilizer.

The residual microalgae that are rich nutrients can be used for food, fertilizer and feed applications [19] in many industries such as fish, shrimps aquaculture and poultry as well as nutraceuticals market and animal consumption.

The steam hydrogasification process is an alternative method for handling the residual microalgae. Syngas is produced from steam hydrogasification and plays an important role as an intermediate in the production of Fischer–Tropsch liquid fuels. This process not only produces synthetic liquid fuel but also generates heat or electricity for energy recovery. The potential of energy recovery from co–products (the residual microalgae) after lipid extraction using steam hydrogasification process was studied in this work. The experimental and simulation work on the steam hydrogasification of microalgae residue are presented and summarized in the following section.

3.2 Experimental section

3.2.1 Feedstock material

The feedstock is *Chlorella vulgaris* microalgae also used in Chapter 2. The extraction method of the microalgae biomass is the solvent extraction using hexane as solvent. The product after extraction is mainly lipid (algae oil) and the residual microalgae. The microalgae residue is used as the feedstock for the steam hydrogasification process.

3.2.2 Experimental apparatus

1) Lipid extraction by Soxhlet method

Lipids were extracted from *Chlorella vulgaris* in order to imitate and obtain the residual microalgae that were used as feedstock in the experiments. Extraction of lipids from microalgae biomass was performed by solvent extraction using the Soxhlet method. The Soxhlet apparatus consists of extraction thimble and glass wool, condenser, flat–bottom flask with boiling chip, heating mantle and Soxhlet extractor. The Soxhlet apparatus was set up and shown in Figure 3.2.

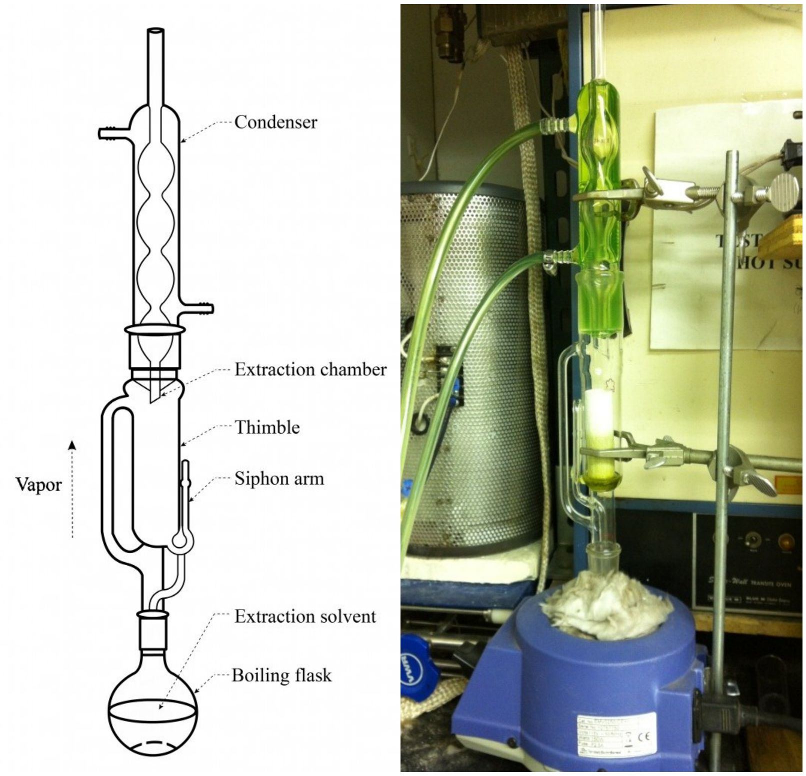

Figure 3.2 Soxhlet extraction unit used for lipid extraction, picture courtesy of technology lodging.com (left)

2) Steam hydrogasification using a stirred batch reactor

The experiments of steam hydrogasification were carried out in a stirred batch reactor. A schematic diagram of the experiment set up for steam hydrogasification is described in section 2.2.2.

3.2.3 Experimental procedure

1) Soxhlet method

The microalgae sample was dried, ground into small particles. A sample of 10 g of microalgae was placed in an extraction thimble and then covered at the top with glass wool to prevent floating. The thimble was placed in a Soxhlet extractor, which was suspended above a flat–bottom flask containing the solvent and below a condenser. A hotplate was used for heating for the extraction. The Soxhlet apparatus was set up, and 100 ml of solvent was added. The solvent was hexane. The flat –bottom flask was heated and the solvent evaporated and moved up into the condenser. The solvent was evaporated and converted into liquid that dropped into the Soxhlet extractor containing the sample. The Soxhlet extractor was designed so that when the solvent surrounding the sample exceeds a certain level it overflows and trickles back down into the boiling flask. As the solvent passes through the sample it extracted the lipids and carried them into the flat–bottom flask. The process continued for 7 hrs. The hotplate was turned off and the solvent cooled and collected in a flat–bottom flask. The flat–bottom flask containing the solvent and lipid was removed from the Soxhlet apparatus, the solvent was then evaporated. The lipids were collected and dried. The mass of lipid remaining was taken to determine the percentage of lipids extracted from the microalgae sample. The final residual microalgae biomass was dried in a vacuum oven at a temperature 105 °C in preparation for gasification experiment. Soxhlet extraction was assumed to be method for completely extracting all lipids existing in microalgae. Hence, the microalgae residue was assumed to have no lipids remaining and then used as feedstock in the steam hydrogasification process.

The amount of lipid and the percentage of lipid are calculated by formula below:

Mass of lipid:

$$Mass\ of\ lipid\ (g)\ = (weight\ of\ flask + boiling\ chips + extracted\ oil) - (weight\ of\ flask + boiling\ chips)$$

Lipid content:

$$Lipid\ content\ (\%) = \frac{mass\ of\ lipid\ extracted\ (g)}{sample\ weight\ (g)} \times 100$$

2) Steam hydrogasification of residual microalgae after lipid extraction

Steam hydrogasification of microalgae residue after lipid extraction was performed at a temperature 750 °C with H_2/C ratio of 1 and steam/biomass ratio of 2. Steam hydrogasification were carried out using a stirred batch reactor and the experimental procedure was explained in the section 2.2.3. A brief description is given as follows.

A 0.5 g of microalgae residue and 1.0 g of water was loaded into the reactor and then was connected to the system. The reactor was pressurized with hydrogen to the desired pressure. Then, the reactor was heated to reach a temperature 750 °C. After the reaction, the product gas was collected by a Tedler gas bag and off–line analyzed by the residual gas analyzer (RGA). The product gas and carbon conversion were examined. The experiments have been repeated at least three times to eliminate operation and system error. The results from experiment were used further in the simulation work. The simulation methodology was elucidated in section 2.2.5.

3) Steam hydrogasification of microalgae with different lipid content

The sample of microalgae with varied lipid content was prepared by mixing the residual microalgae with olive oil. The olive oil represents a microalgae oil. Microalgae residue was assumed no lipid remaining. The microalgae samples (a mixture microalgae residue and olive oil) were varied between 0 and 100 wt% in 20% increment. The olive oil contains approximately 78% of carbon, 12% of hydrogen and 10 % of oxygen that is calculated based on fatty acid composition [113] .

The prepared samples (microalgae residue mixed with olive oil) are performed in the steam hydrogasification at a temperature 750 °C with a H_2/C ratio of 1 and a steam/biomass ratio of 2 as those. Steam hydrogasification were carried out using a stirred batch reactor and the experimental procedure was elucidated in the section 2.2.3. A brief description is given as follows.

A 0.5 g of microalgae sample (a mixture of microalgae residue and olive oil) and 1.0 g of water was loaded into the reactor and then was connected to the system. The reactor was pressurized with hydrogen to desired pressure. Then, the reactor was heated to reach a temperature 750 °C. After the reaction, the product gas was collected by a Tedler gas bag and off–line analyzed by RGA. The compositions of the gas produced; mainly H_2, CH_4, CO and CO_2 were investigated. The experiments have been repeated at least three times to eliminate operation and system error.

3.3 Result and discussion

3.3.1 Utilization of residual microalgae after lipid extraction

The amount of lipids extracted using Soxhlet method (hexane as solvent) was about 15 wt% and the residual microalgae gasified at a reaction temperature of 750 °C, H_2/C ratio of 1 and steam/biomass ratio of 2. The gas production is shown in Figure 3.3. It is found that the final gas products consisted of H_2 mole fraction of 0.7, CH_4 mole fraction of 0.2, and small amount of CO and CO_2 production. The carbon conversion efficiency was 57%. So, it was assumed that carbon left over is presented in terms of char (43%). From the results obtained, the residual microalgae can be gasified to produce combustible gas that is an intermediate for the production of FT liquid fuel using the CE–CERT process. The experimental data was used further in the simulation work.

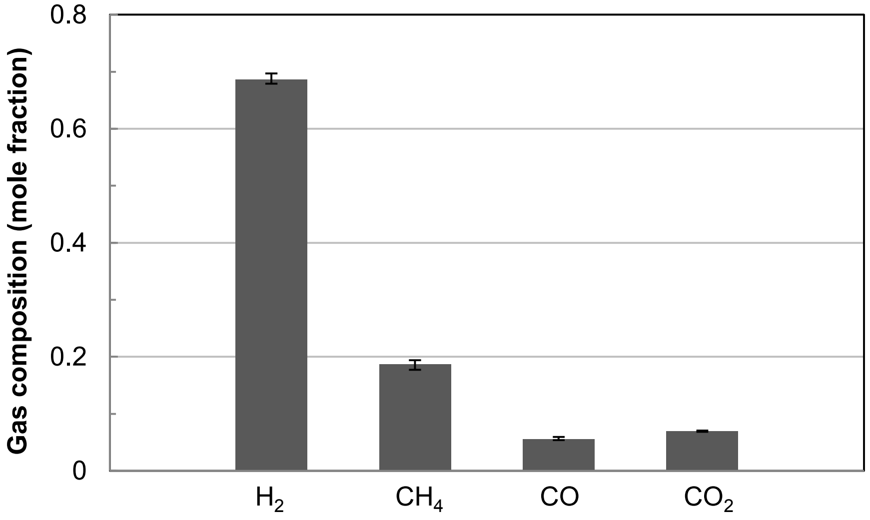

Figure 3.3 The product gas from the SHR of microalgae residue at 750 °C, H_2/C = 1, and S/B = 2

Based on the experiment, the H_2/C and S/B ratios were determined as 1 and 2, respectively and obtained 57% of carbon conversion efficiency. In the simulation, the percentage of char was set at 43 that obtained from previous experiment. The results of mass and energy of the overall CE–CERT process for FT liquid fuel production is shown in Figure 3.4. It can be seen in Figure 3.4(a) that one ton of dry microalgae residue produced 200 kg of char and 432 kg of CO_2. The CE–CERT process using the residual microalgae produced 126 kg of FT liquid fuel (approximately 1.0 barrel or 157 liters), a recoverable energy of 4.9 MJ/kg of microalgae residue. The energy consumed or generated during each step of the CE–CERT process is also presented in Figure 3.4(b). It is found that the thermal efficiency obtained from this process was 24%. In addition, the electricity that generated from the combustion of flue gas and char could enhance the energy recovery for the system. The value of electricity obtained from the combustion was 26 kW.

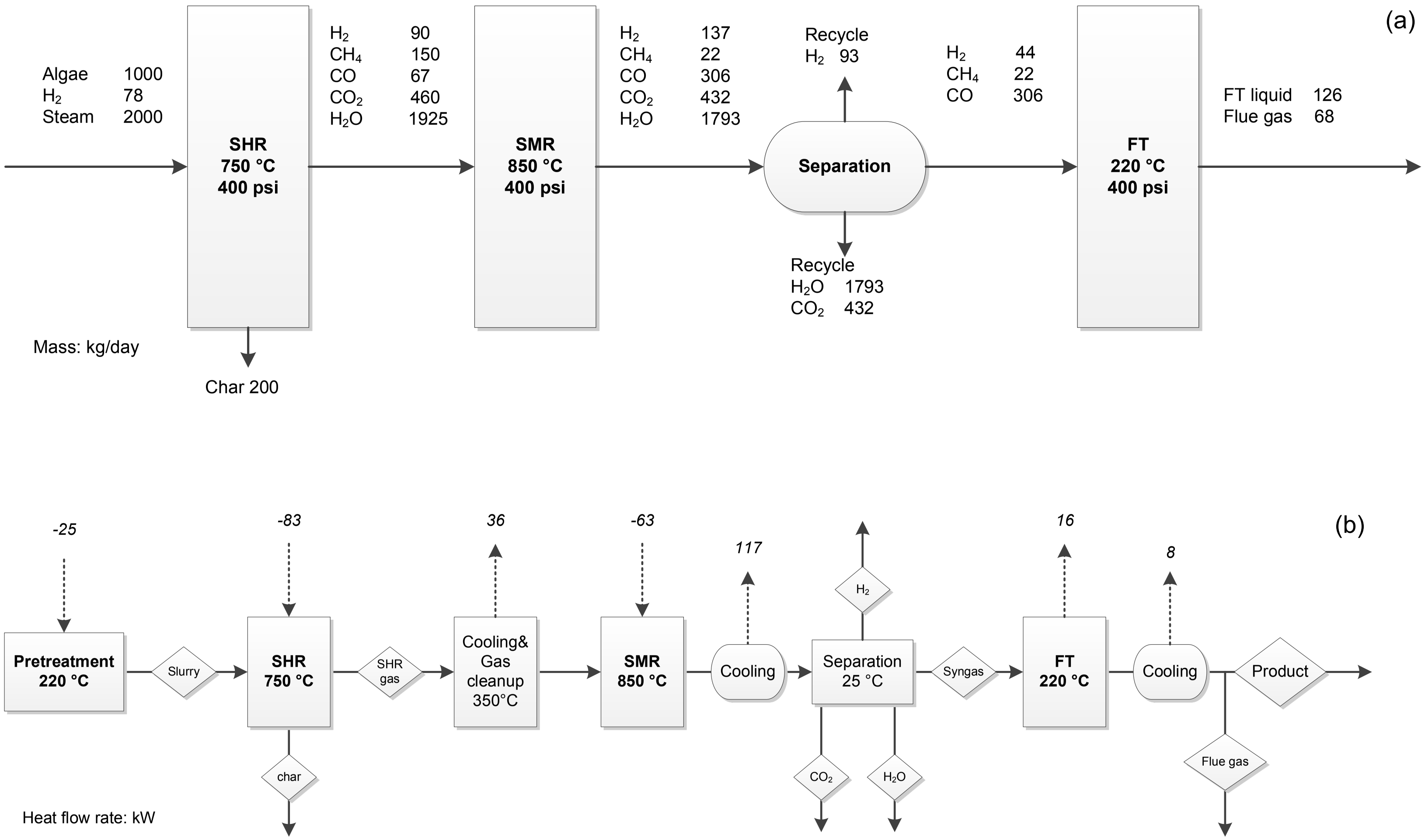

Figure 3.4 The overall mass and energy balance of microalgae residue using the CE–CERT process for FT fuel production

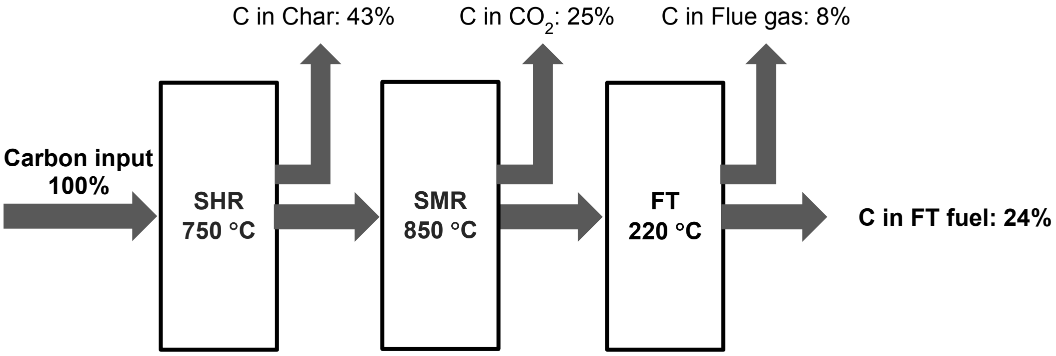

Figure 3.5 The carbon balance of microalgae residue using the CE-CERT process for FT fuel production

The carbon balance of the overall CE–CERT process of microalgae residue for FT fuel production is present in Figure 3.5. It can be seen that about 24% of carbon was distributed to FT liquid fuel and 8% of carbon in the flue gas. There is about 25% of carbon in CO_2 generated and 43% of carbon in char. Char is burned for supplying heat or electricity to the process and CO_2 can be captured and recycled back to the pond. Therefore, the residue microalgae after lipid extraction has potential as energy source for producing FT liquid as well as providing electricity using the CE–CERT process

3.3.2 Effect of different lipid content in microalgae

The effect of microalgae with varied lipid content in the steam hydrogasification was investigated in the range of 0–100 wt% in 20% increment. The mixture of microalgae residue and olive oil were prepared and used as the feedstock in this experiment due to difficulty for collecting various species of microalgae. The experiment was performed at a reaction temperature of 750 °C, H_2/C ratio of 1 and S/B ratio of 2. The product gas composition from steam hydrogasification with increase lipid content is shown in Figure 3.6. An increase in lipid content led to increase obviously in methane formation and showed the opposite trend in hydrogen production. The increase of lipid percentage in the feedstock from 0 to 100 wt% led to an increase of mole fraction of methane from 0.2 to 0.4. It can be observed that the lipid can be easily volatilized and subsequently went through cracking and reforming reactions as well as favored the hydrogenation reaction ($C+2H_2 \rightarrow CH_4$), thus resulting in higher hydrocarbon concentration, especially methane. The CO and CO_2 production have a small variation with increase in lipid amount in the feedstock.

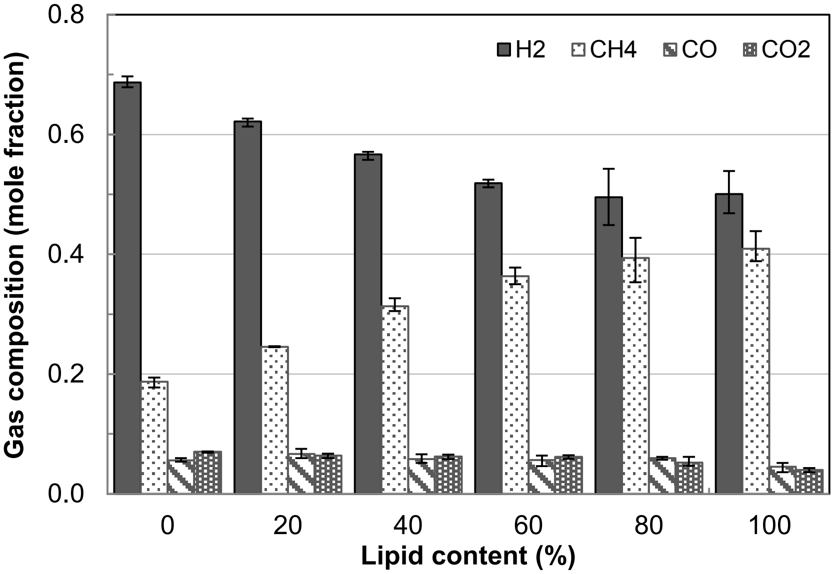

Figure 3.6 The effect of lipid content on gas production at 750 °C, $H_2/C = 1$, and S/B = 2

The effect of lipid content on carbon conversion was also studied and the results are shown in Figure 3.7. It is observed that an increase in lipid content from 0 to 100 wt% led to dramatic increase in carbon conversion (from 57% to 79%). The result showed that an increase of lipid content favored the carbon conversion and formation of methane.

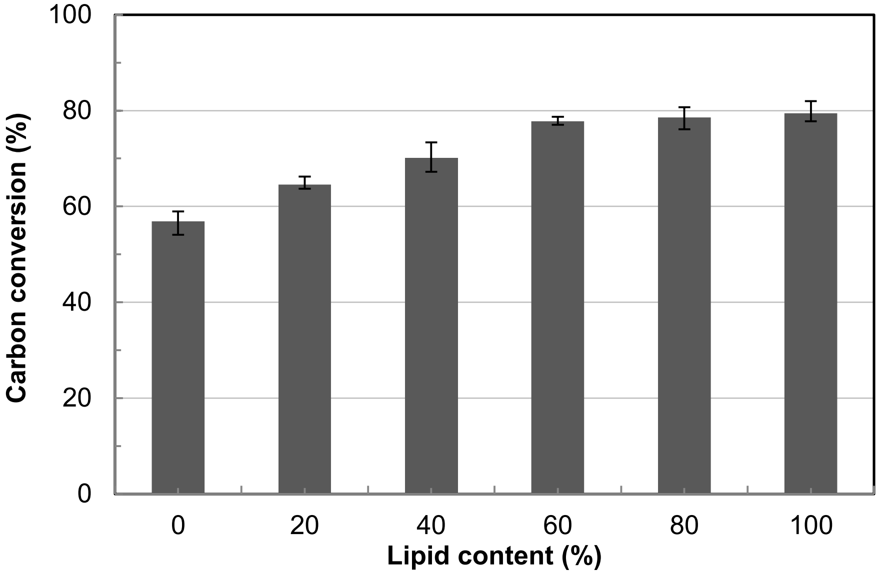

Figure 3.7 The effect of lipid content on carbon conversion at 750 °C, $H_2/C = 1$, and $S/B = 2$

The H_2 available was defined as total H_2 from the SHR minus the H_2 input to SHR. The equation was presented in section 2.3.3. The H_2 available with varied lipid content in microalgae at a temperature of 750 °C with H_2/C ratio of 1 and S/B ratio of 2 is shown in Figure 3.8 and 3.9. It can be seen that H_2 produced was enough for recycle to gasifier when the lipid content in feedstock did not exceed 25 wt% at this operating condition. However, high methane formation could be used to produce more hydrogen further through steam methane reforming ($CH_4+H_2O \rightarrow 3H_2+CO$) that resulted in the sufficient of H_2 available for recycle.

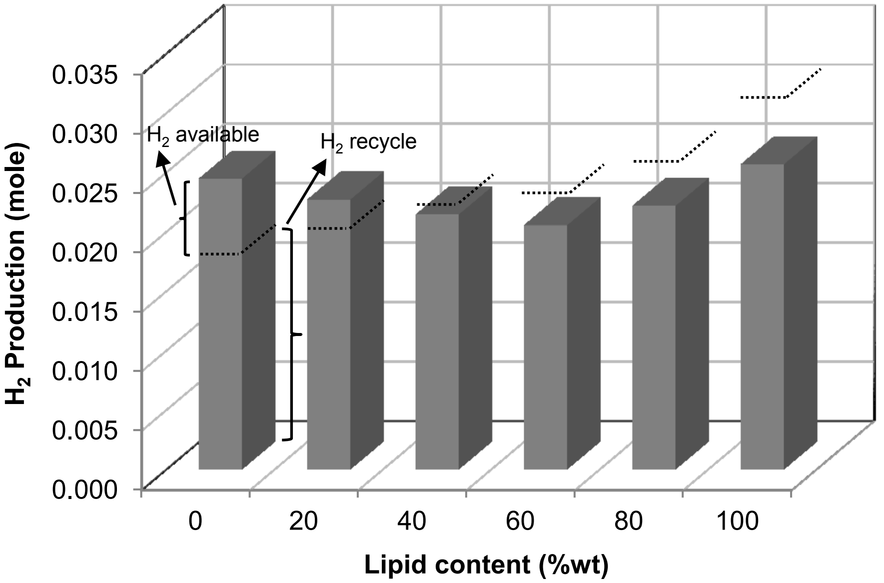

Figure 3.8 The amount of H_2 available at 750 °C, H_2/C = 1, and S/B = 2

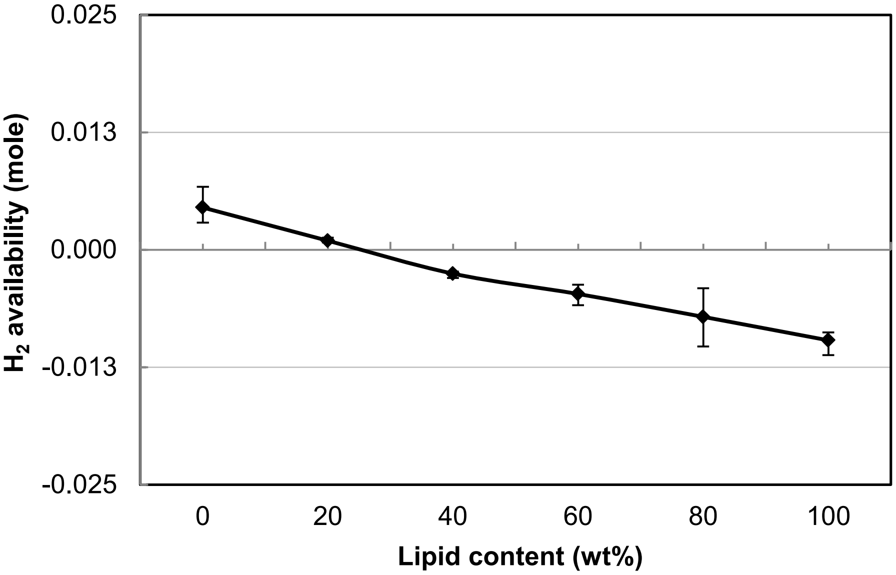

Figure 3.9 The H_2 available at 750 °C, H_2/C = 1, and S/B = 2

According to the data obtained in this study, it was expected that an increase of lipid content led to increase in the rate of several reactions during gasification process listed in Table 2.1. The hydrogenation, reforming and cracking reactions favored for obtaining higher methane and lower hydrogen concentration. However, the amount of lipid in the feedstock should not exceed 25 wt% in order to accomplish the H_2 available for recycling back to gasifier at this condition. The steam hydrogasification integrated with steam methane reforming process could help to enhance the H_2 available involved in conversion of CH_4 to syngas (a mixture of H_2 and CO). Moreover, the H_2 available could be controlled by modifying the H_2/C ratio or S/B ratio in the steam hydrogasification step.

3.4 Conclusion

Steam hydrogasification of microalgae residue and microalgae with different lipid content were performed in a stirred batch reactor at 750 °C with steam/biomass ratio of 2 and H_2/C ratio of 1. The prominent results are as follows.

1. Approximately 4.9 MJ/kg of microalgae residue was recovered using the CE–CERT process. The combustion of flue gas and char left over could generate heat and electricity for the system or upstream process. The CE–CERT technology via steam hydrogasification could assist in dealing with microalgae residue in order to reduce algae waste and produce FT liquid fuel and energy recovery as well as develop the sustainability for microalgae biodiesel production.
2. An increase of the lipid amount in microalgae resulted in the enhancement of carbon conversion and methane formation. It can be concluded that lipid was easily volatilized and produced a rich gas hydrocarbon, especially methane as well as led to higher carbon conversion. Higher lipid content resulted in increase the product gas and FT liquid fuel. The lipid content in microalgae can be as low as 25 wt% at this condition to achieve the sufficient of H_2 for making the process self–sustained.
3. Steam hydrogasification can be used to gasify all species of microalgae and residuals microalgae after lipid extraction to produce combustible gas and generate synthetic liquid fuel further using the CE–CERT process. It is not necessary to have a high lipid content in microalgae in the steam hydrogasification process.

4. Life Cycle Analysis of the Production of Microalgae–Derived Biofuel

The well–to–wheels (WTW) greenhouse gas GHG) emission and energy consumption of the production of biodiesel and Fischer–Tropsch (FT) fuel derived from microalgae biomass is presented in this chapter. The conversion technologies for microalgae biofuel to be compared are transesterification of microalgae oil and the CE–CERT process of whole microalgae biomass. Both dry and wet microalgae were considered. Anaerobic digestion (AD) and the CE–CERT process were compared for the conversion of the residue after oil extraction. The utilization of the microalgae residue as a co–product for energy credit was also investigated.

4.1 Introduction

Life cycle analysis has been used to investigate the energy requirement and the global warming potential of various processes. The GREET (Greenhouse gases, Regulated Emissions, and Energy use in Transportation) model developed by the Argonne National Laboratory [70] will be used. This study used GREET version GREET 1_2012 [114]. LCA evaluates all stages of a product from the raw material through material processing, manufacture, distribution, use, and disposal or recycling. The life cycle of microalgae biofuel includes feedstock production and feedstock transportation, fuel production and fuel transportation, and fuel consumption. GREET consists of two main LCA stages; well–to–pump (WTP) and pump–to–wheels (PTW). The WTP component of the module analyzes the total energy and emissions due to the production of microalgae biofuel and their delivery to the pump. WTP activities include feedstock production, conversion, and transportation of the fuel to pump. Facility fabrication and facility decommissioning during these steps are not taken into account. The combustion of fuel during vehicle operation constitutes the PTW stage. Vehicle manufacturing and vehicle decommissioning are not taken into account during this stage. The combination of the WTP and PTW stages results in the full life cycle well–to–wheels (WTW). The WTW stages for microalgae biofuel pathway are summarized in Figure 4.1.

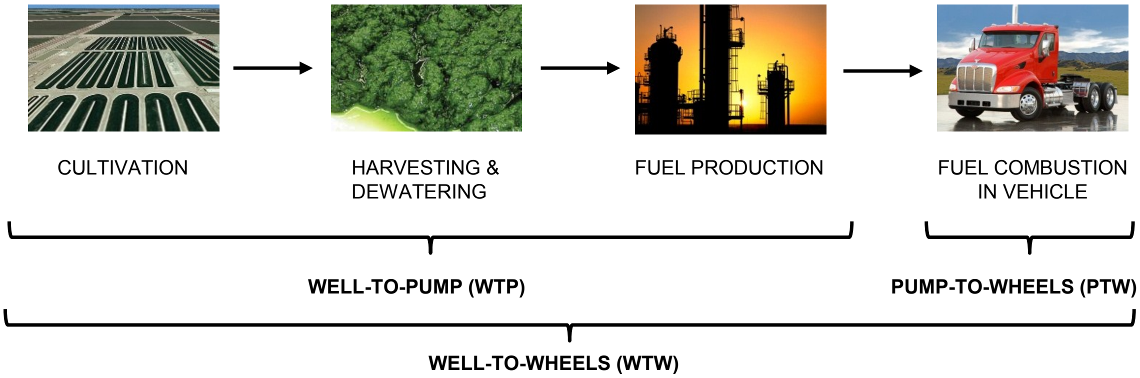

Figure 4.1 WTW pathway for microalgae–based biofuel

4.2 Methodology and assumption

The main interest of this LCA is well–to–wheels. The functional unit chosen is as one mega joule (MJ) of fuel product. The GREET calculates the total energy during the full life cycle in MJ/MJ of fuel and the total greenhouse gas emissions in g of CO_2 equivalent /MJ of fuel. The three main greenhouse gases considered are carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O). The global warming potential (GWP) is used to express the net GHG emissions on a CO_2 equivalent. The GWP is applied to CH_4 and N_2O emissions to calculate the CO_2 equivalent emissions. The GWP factors are 1 for carbon dioxide, 25 for CH_4 and 298 for N_2O [115]. The total energy is defined as the total energy consumed and also the fossil energy required which is further divided into petroleum fuel, natural gas and coal.

The fuel pathways considered in this analysis include conventional diesel fuel from crude oil, biodiesel fuel derived from microalgae oil and FT fuel derived from whole microalgae. The GHG emissions and the energy consumption are calculated based on the vehicle technology used and the efficiency of the specific vehicle type. The vehicle chosen is a light duty truck. The fuels (conventional diesel fuel, FT fuel and biodiesel fuel) are all used in compression ignition direct injection (CIDI) engines.

The production of conventional diesel fuel is based on the standard input assumptions of the GREET model. The production of biodiesel is the conventional transesterification of microalgae oil. The engine technology is assumed to be CIDI engine running on 100% of biodiesel (BD100). The FT fuel pathway assumes the production of FT fuel using the CE–CERT technology with whole microalgae feedstock. The engine technology is assumed to be CIDI engine running on 100% of FT fuel (FT100). The efficiency of microalgae to FT fuel using the CE–CERT process and electricity export as a co–product are obtained from the experiments and simulation results in Chapter 2 and 3.

The data for transportation and distribution for conventional diesel fuel, biodiesel fuel and FT fuel are based on the standard assumption of the GREET model. The crude oil for use in U.S. refineries is assumed to come from domestic wells (Alaska -7%, other states -35%), offshore countries (50%) and Canada and Mexico (8%). The Alaska crude oil is shipped directly to refinery by ocean tanker (2,100 miles) while the crude oil form the other sources are shipped to a bulk terminal by ocean tankers (5,500 miles) and pipeline (750 miles). The transport from the bulk terminal to the refinery is accomplished using barge (1%, 500 miles) and pipeline (92%, 750 miles). The microalgae biomass is transported to plant by rail (100%, 600 miles). The biodiesel is transported to bulk terminals by barge (8%, 520 miles), rail (29%, 800 miles), and Heavy Heavy–Duty Diesel Trucks (HHDDT) (60%, 50 miles). The transportation of fuel from bulk terminal to refueling station is assumed to be by HHDDT (30 miles). FT fuel, the microalgae biomass is transported to plant by rail (100%, 600 miles). The FT fuel produced is transported from the plant to a bulk terminal using barge (33%, 520 miles), pipeline (60%, 400 miles), and rail (7%, 800 miles). HHDDT is also used for transporting FT fuel from the bulk terminal to the refueling station, assumed to be 30 miles.

4.3 Alternative microalgae fuel production pathway

In the LCA, the boundaries include cultivation, harvesting, dewatering, extraction, conversion and use in the engine. An algae process description (APD) and GREET were used to study the biofuel production and biofuel end use in vehicles. APD consists of CO_2 transport and transfer to ponds, algae growth, harvesting, dewatering, extraction and recovery processes. GREET is then used to consider the conversion of microalgae biomass or microalgae oil into fuel, transportation, a co–product treatment, and emissions calculation to assess the WTW energy use and emissions associated with microalgae fuel pathways.

The system boundary for biodiesel production is shown in Figure 4.2. The process consists of cultivation, harvesting and dewatering, lipid extraction and finally biodiesel production. Briefly, biodiesel is produced via a transesterification process of the microalgae oil. Microalgae oil is combined with alcohol in the presence of a catalyst to form methyl ester (biodiesel) and glycerin as a by–product in the transesterification process. The remnant, or microalgae residue, a co–product of the extraction process, can be utilized in two ways. One is anaerobic digestion (AD) to produce biogas which is used to generate heat and electricity for the process. Another option for utilizing microalgae residue is to use the CE–CERT technology to produce FT fuel and electricity as a co–product.

The system boundary for FT fuel production is shown in Figure 4.3. The system is divided into four process steps: microalgae cultivation, harvesting, dewatering and conversion into fuel. The wet microalgae without drying and extraction are used directly in the CE–CERT process. The wet microalgae are gasified using the steam hydrogasification to produce the combustible gas rich in methane. The methane and steam are converted into syngas (a mixture of hydrogen and CO) in steam methane reforming step. Syngas can subsequently react over a catalyst in the FT synthesis process to produce hydrocarbons of varying carbon chain length. In a typical FT plant three groups of hydrocarbons are produced: FT naphtha (C5–C9), FT middle distillates (C10–C20), and FT wax (>C20). The unconverted syngas or flue gas and char left over can be burned to generate electricity.

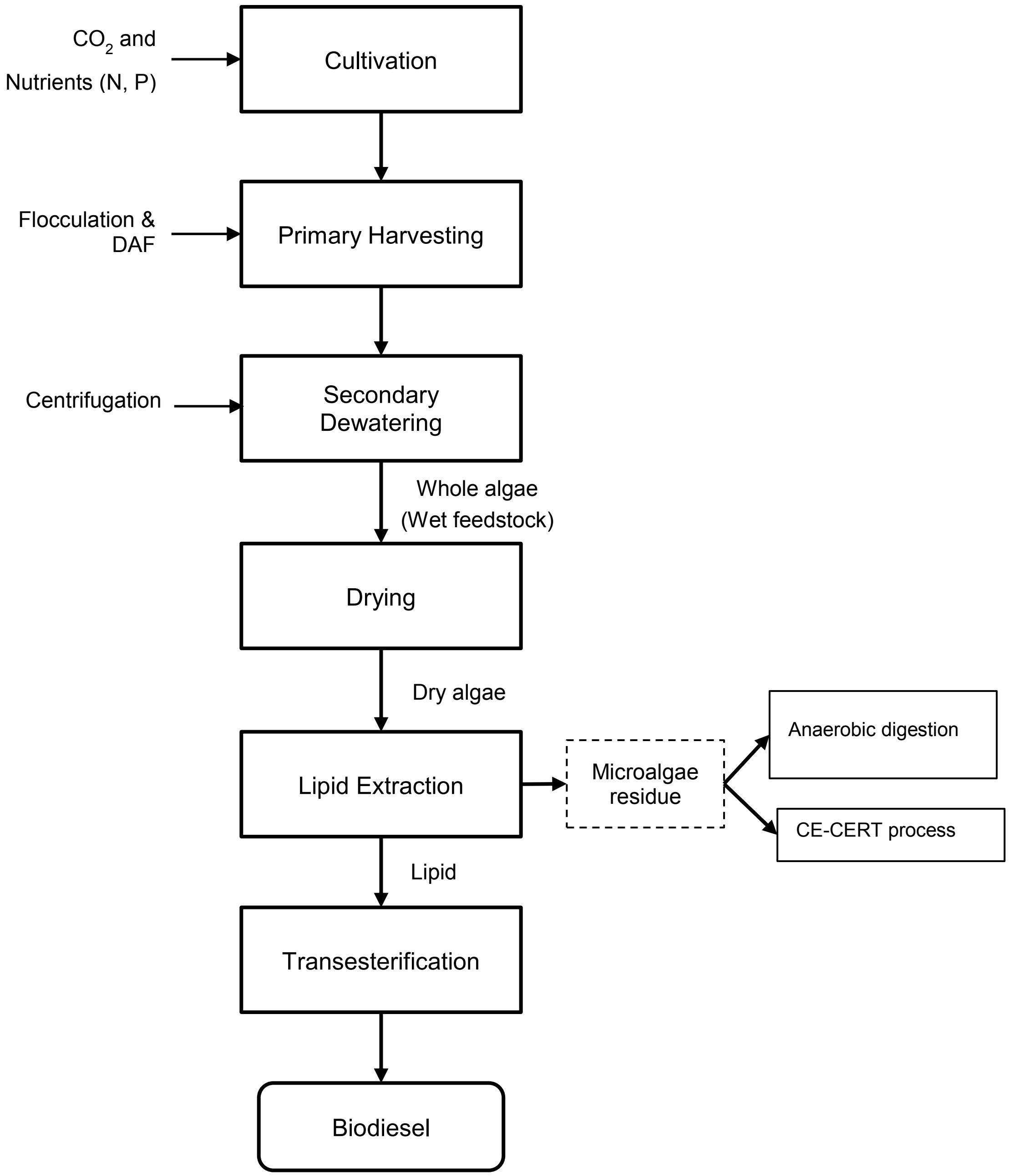

Figure 4.2 System boundary for biodiesel fuel production

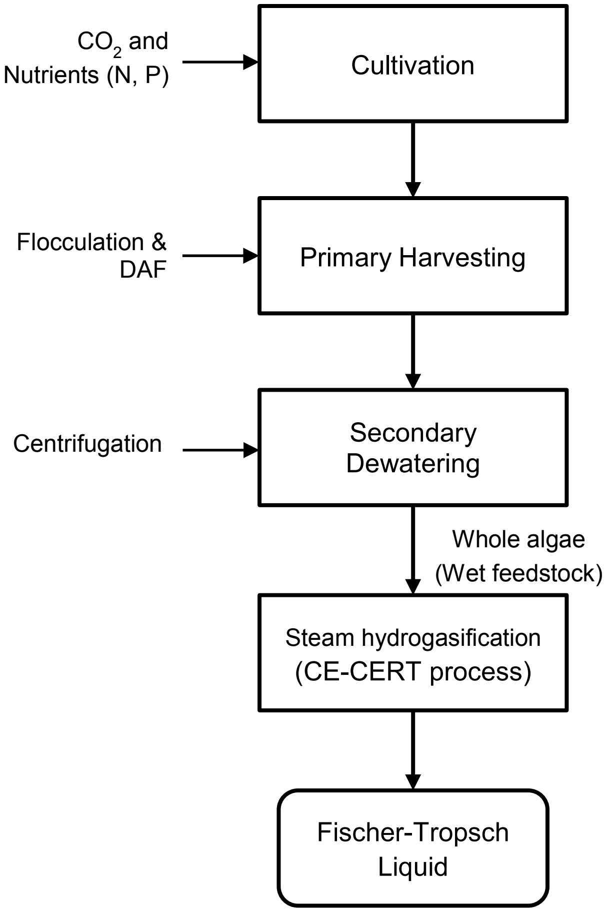

Figure 4.3 System boundary for FT fuel production

The details for the production of wet and dry microalgae, microalgae oil and utilization of the residual microalgae are described next.

Chlorella vulgaris will be used to represent microalgae in this model. Cultivation of the fresh water algae species *Chlorella vulgaris* is modeled using an open pond raceway systems with paddlewheels mixing. Mixing by paddlewheel is the most common method for the circulation. The raceway pond is circulated by paddlewheels which are a proven technology and appear to be the most effective method for circulating the microalgae in ponds. The mixing velocity is assumed at 25 cm/s [116, 117]. Carbon source is provided from CO_2 in a flue gas from power plant. Typically the flue gas contains 20 vol% of CO_2. CO_2 is delivered (transport from the power plant to microalgae farm and transfer into the cultivation ponds) by a low pressure gas pipeline with a utilization efficiency of 82%. A low pressure pipeline transport method is used due to its lower energy cost compared to other methods such as pressurized pipelines and supercritical pipeline [118]. Nutrients are based on carbon: nitrogen: phosphorus (C:N:P) composition of 175:21:1. Urea and ammonium phosphate are used as nutrient in this study. The microalgae productivity and oil content depend on several factors such as algae strain, solar irradiance, growth system etc. The algae growth rate used here is assumed to be 25 $g/m^2/day$ which is used in many studies [97, 119-122].

There are several techniques for recovering algae biomass. Microalgae are harvested by flocculation combined with dissolved air flotation (DAF) in this study. Flocculation is assumed to achieve an algae concentration range of 6% total suspended solids (TSS) The energy consumption for DAF is $1.33x10^{-4}$ kWh/g–algae with the harvesting efficiency of 90%. The microalgae slurry is further dewatered by a centrifugation process. A disc–stack centrifuge is selected to increase the microalgae concentration to 25% TSS before drying. The algae concentration of 33% TSS is assumed for the production of FT fuel using the CE–CERT process. The electricity consumption of centrifuge is $1.83x10^{-5}$ kWh/ g–algae with the recovery efficiency of 95%. Both DAF and centrifugation are matured technologies for liquid–solid separation [96].

The algae paste generated by secondary dewatering is dried to a solid content of 90% (w/w). A thermal drying model multiplies the latent heat of vaporization for water by vaporization efficiency coefficient to obtain the heat for drying used. The lipids are extracted by the commonly used hexane extraction method. The process heat and electricity requirement for lipid extraction process are 1.38×10^{-3} and 5.4×10^{-4} kWh/ g–lipid produced, respectively.

There are two conversion pathways considered in this analysis: transesterification and the CE–CERT process. The microalgae oil can be converted into biodiesel using transesterification by the reaction of fatty acids with methanol in the presence of catalyst and would have methyl ester and glycerin as a co–product. The CE–CERT technology can be used to gasify both the whole microalgae as a wet feedstock and the residual microalgae to produce a combustible gas that can be subsequently fed to SMR and FT reactors to produce FT fuel and electricity. The gasification efficiency and export electricity are key factors to estimate the life cycle energy and GHG emissions and these values are obtained from the experiments and simulation presented in Chapter 2 and 3.

There are several options for utilizing the remaining biomass after oil extraction: anaerobic digestion to produce biogas (methane) for generating power and heat, direct combustion to produce heat and/or electricity, and use as animal feed [111, 123, 124]. In this analysis, anaerobic digestion and the CE–CERT process are considered for the conversion of residual microalgae. The residual microalgae can be used for producing biogas (a mixture of CH_4 and CO_2) from anaerobic digestion. The methane yield 0.33 L-CH_4/g–total solids at standard temperature and pressure. The biogas volume is assumed 67 vol% of CH_4 and 33 vol% of CO_2 [122]. The combustion of biogas produces heat and electricity. The residual microalgae can be gasified using the steam hydrogasification and generate the FT fuel and electricity by the CE–CERT process.

The assumptions and details for life cycle analysis are given in Table 4.1. There are two major fuel pathways in this analysis: biodiesel pathway by transesterification and FT fuel pathway by the CE–CERT process. The production of microalgae–derived biodiesel consists of several steps: algae cultivation, dewatering, drying, oil extraction, oil transesterification and process for energy recovery from the microalgae residue. The conversion of microalgae residue in scenario 1–3 is anaerobic digestion whereas scenario 4–6 use the CE–CERT process to utilize the residual. The conversion process of whole microalgae biomass consists of algae cultivation, dewatering and the CE–CERT process (steam hydrogasification–steam methane reforming–FT synthesis) and presented in scenario 7–9.

The input parameters to the LCA model have been assigned to three main groups that are discussed earlier by scenario 1–3, 4–6 and 7–9 .The parameters in each groups are fixed except the lipid content varied as 15, 20 and 40 %wt, respectively. The key input parameters for the CE–CERT technology are gasification efficiency and the electricity export. In this study, the efficiency of microalgae steam hydrogasification in scenario 7, 8 and 9 is 35.8%, 40% and 49%, with the electricity export of 143, 133 and 103 kWh/mmBtu of FT product, respectively depending on different lipid contents.

Table 4.1 The detail and assumption for each scenario

Scenario	1	2	3	4	5	6	7	8	9
Productivity, $g/m^2/d$	25	25	25	25	25	25	25	25	25
Lipid content, wt%	15	20	40	15	20	40	15	20	40
DAF, output solids content	6	6	6	6	6	6	6	6	6
Centrifugation, output solids content	25	25	25	25	25	25	33	33	33
Drying, output solids content	90	90	90	90	90	90	-	-	-
Lipid extraction	Hexane	Hexane	Hexane	Hexane	Hexane	Hexane	-	-	-
Conversion	TE	TE	TE	TE	TE	TE	CE-CERT	CE-CERT	CE-CERT
Recovery process	AD	AD	AD	CE-CERT	CE-CERT	CE-CERT	-	-	-

DAF – Dissolved air flotation, TE – Transesterification, AD – Anaerobic digestion

4.4 Result and discussion

The life cycle simulation of energy and GHG emissions were conducted using GREET1_2012 model. GHG emissions are the sum of emissions of three gases (CO_2, CH_4 and N_2O) weighed by their global warming potentials. The total energy consumption over the entire life cycle has the unit of MJ/MJ of fuel product.

4.4.1 WTP total energy

The result of WTP total energy for 1 MJ of conventional diesel and microalgae derived biofuel is presented in Figure 4.4. The WTP stage of the conventional diesel consumed the lowest energy at 0.12 MJ/MJ of fuel product. This is followed by the energy requirement for FT fuel derived from wet microalgae with lipid of 40 wt% using the CE–CERT process (scenario 9). The energy requirement for scenario 9 is 1.16 MJ/MJ of fuel product. It is noted that the efficiency of the CE–CERT gasification is 49% with electricity export of 103 kWh/mmBtu of fuel produced. Energy need for the production of biodiesel by transesterification (scenario 1–6) is in the range of 2.11–4.57 MJ/MJ of fuel product which is significantly higher than energy required for FT fuel from the CE–CERT and conventional diesel fuel. It can be concluded the energy consumed for FT fuel derived from wet microalgae is less than biodiesel derived from microalgae oil (dried microalgae) at the same lipid content. The energy requirement for the production of biodiesel (scenario 3 and 6) could significant reduces due to effect of increasing amount of lipid (40 %wt).

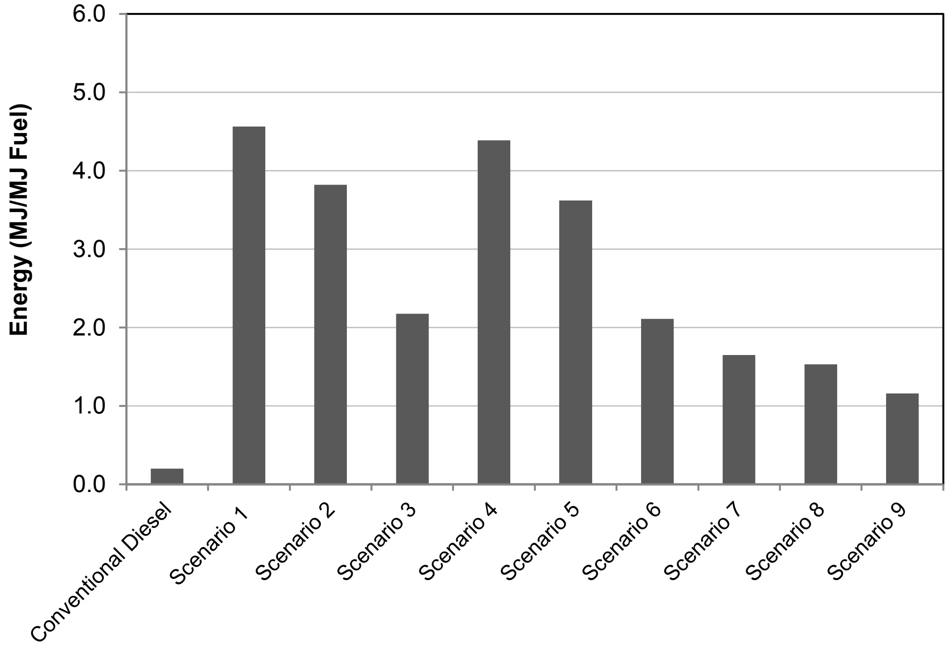

Figure 4.4 WTP total energy

The total energy consumption for biodiesel and FT fuel derived from microalgae is higher than conventional diesel due to the upstream process for producing both wet and dried microalgae biomass. The method for producing microalgae biomass includes CO_2 utilization, cultivation, harvesting, dewatering/drying and extraction processes and shown in Figure 4.5. The extraction process required very high energy followed by harvesting and dewatering process which is reported by others in the literatures [97, 125, 126]. Flocculation, dissolved air flotation, centrifuge and drying are included in harvesting and dewatering process. Extraction is energy intensive due to the extended time for extracting lipid and energy for recovery of hexane. Energy in these methods is required to remove high amount of water to achieve a dried feedstock. The lipid content in microalgae affected to the energy consumption for microalgae biomass production as well. The energy requirement substantially decreases by increasing the amount of lipid in microalgae. Higher lipid contents require fewer microalgae biomass (per kg) of lipid produced.

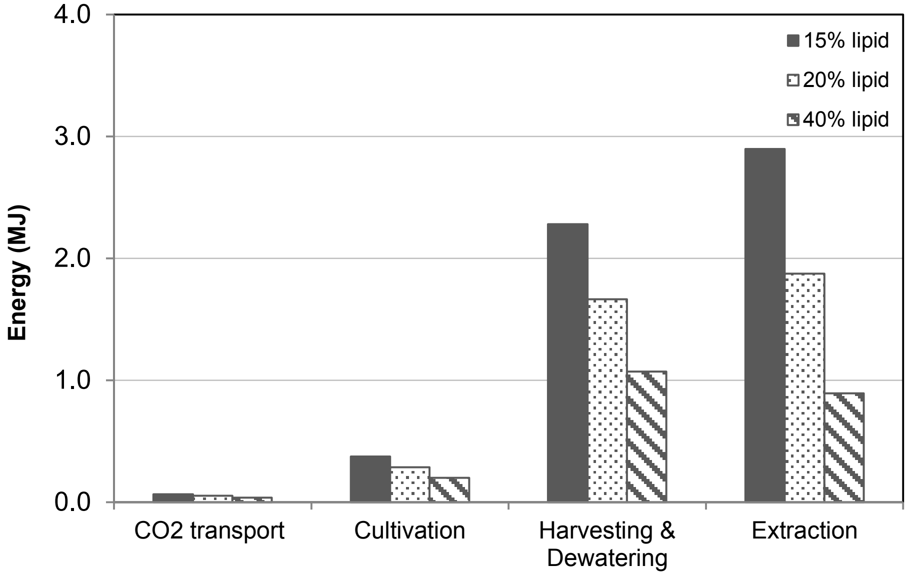

Figure 4.5 The effect of different lipid content on energy use for unit process

4.4.2 WTW total energy

The WTW total energy in unit MJ/MJ fuel is shown in Figure 4.6. It can be seen that the total energy for microalgae biodiesel and FT fuel is higher than it is for conventional diesel because the production of both wet and dried microalgae and oil extraction requires energy. The result showed the similar trend to WTP total energy. However, FT fuel from the CE–CERT process consumed less energy than the production of biodiesel because it uses wet microalgae as feedstock that is not required energy intensive for drying and extraction process. The energy requirements using the CE–CERT process (scenario 7) dropped significantly by approximately 50% compared to transesterification integrated with AD (scenario 1).

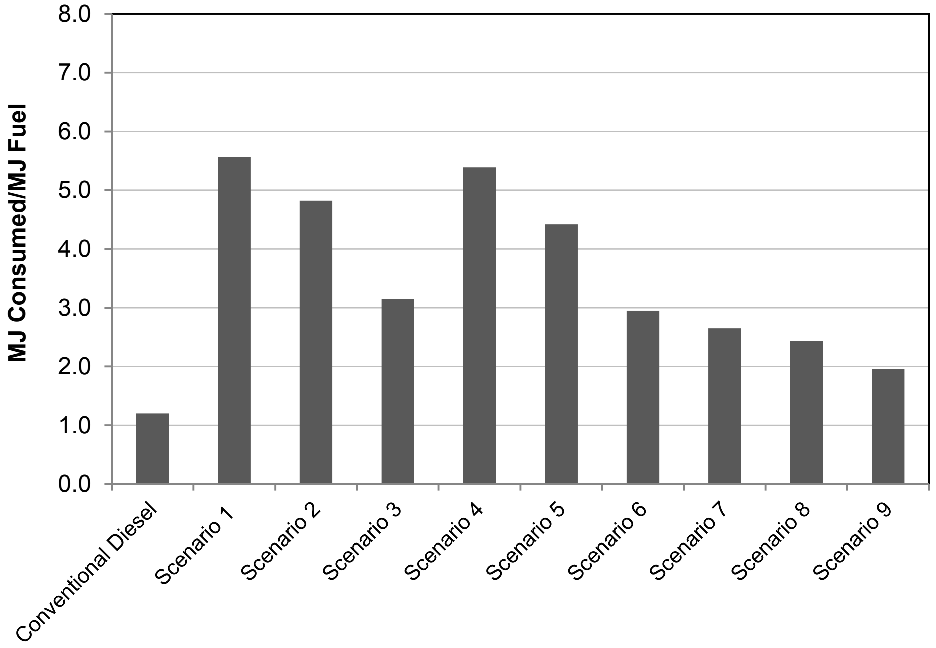

Figure 4.6 WTW total energy

4.4.3 WTW fossil fuel energy

The WTW fossil energy of microalgae biofuels and conventional diesel is shown in Figure 4.7. Fossil energy includes petroleum, natural gas, and coal. The WTW of FT fuel from the CE–CERT process (scenario 9) consume the least amount of fossil fuel (0.46 MJ/MJ of fuel) compared to all scenarios and diesel fuel. FT fuel using the CE–CERT process shows a significant reduction in fossil energy use and offered substantial saving in the fossil energy consumption. Microalgae oil (40 wt%) derived biodiesel integrated the CE–CERT process (scenario 6) also requires lower fossil fuel than conventional diesel. In contrast, the requirement of fossil energy for production of biodiesel derived from microalgae oil (scenario 1–5) is higher than FT fuel from the CE–CERT process. So, the CE–CERT technology offered an attractive option as it primarily relies on sustainable resources and generates liquid fuels.

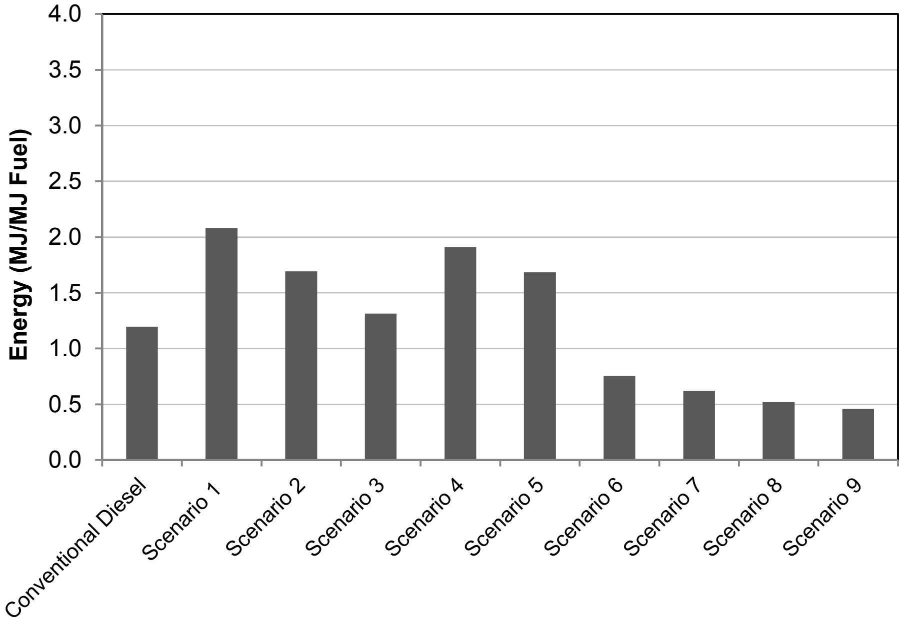

Figure 4.7 WTW fossil energy

4.4.4 Greenhouse gas emissions

The GREET model calculated the emissions of CO_2, CH_4 and N_2O in terms of CO_2 equivalent. These gases are called direct GHGs that have an impact on climate directly. The change in GHG emissions of nine scenarios relative to conventional diesel is presented in Figure 4.8. FT fuel derived from whole microalgae (wet feedstock) using the CE–CERT process offers the best GHG reduction benefit. The CE–CERT technology (scenario 7–9) and microalgae–derived biodiesel integrated with the CE–CERT process (scenario 6) can reduce GHG emissions by 32–64%. Microalgae–derived biodiesel integrated with anaerobic digestion (scenario 1–3) and microalgae–derived biodiesel integrated with the CE–CERT process (scenario 4 and 5) have GHG emissions higher than conventional diesel derived from crude oil. The GHG emissions for microalgae biodiesel originate from upstream usage of the energy use for dewatering, extraction and drying to obtain a dried feedstock. The electricity or heating from coal combustion, and the extraction and utilization of natural gas is accompanied by high CO_2 and methane emissions. The CE–CERT technology provides the most attractive sustainable option in terms of GHG emissions for the production of FT fuel derived from microalgae biomass.

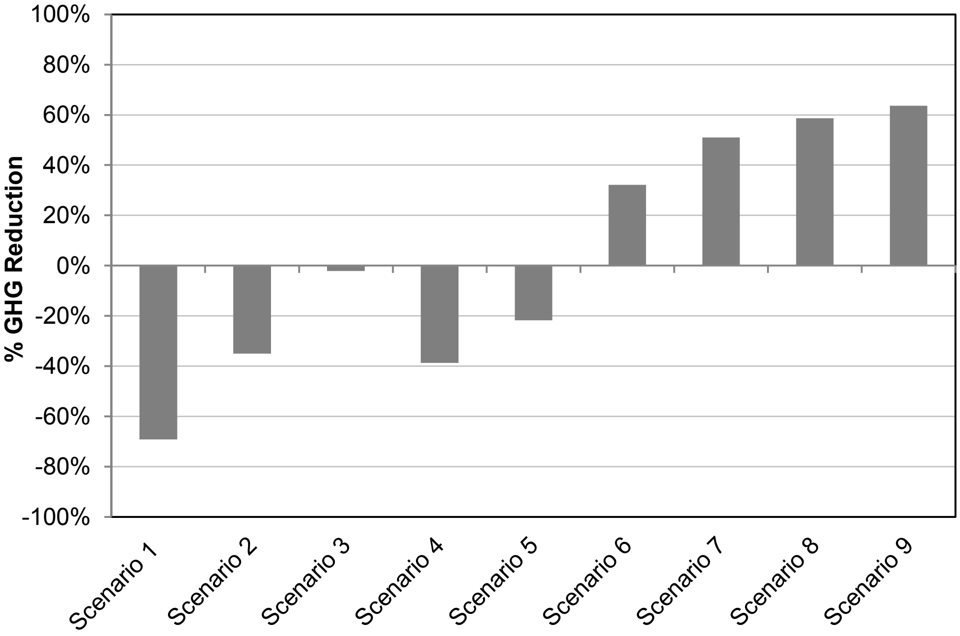

Figure 4.8 %GHG reduction

4.5 Comparatives life cycle analysis of microalgae fuels with existing literatures

Microalgae have significant potential compared to other biomass feedstocks to produce biofuel, especially biodiesel that can be supplied current transportation fossil fuel usage. There are many researchers who studied life cycle analysis for microalgae–derived biofuel. Life cycle analysis with parameters of productivity, culturing, CO_2 mitigation, nutrient loading, water use, lipid content, biomass harvesting and dewatering, lipid extraction and energy conversion was explored for biofuel production. It is know that the production of biodiesel requires high energy for cultivation, harvesting and dewatering, and lipid extraction. A wide range of these technologies is currently under development. The improvement of productivity, growth rate and lipid content can reduce the energy consumption. The wet extraction and the conversion of wet feedstock are alternative options to reduce high energy required for drying of microalgae slurry as well. Moreover, the utilization of microalgae residue after the extraction are also considered as the recovery of energy. The production of electricity and heat can be generated from the conversion of microalgae residue via anaerobic digestion, combustion, or hydrothermal liquefaction.

In this section, the life cycle energy and GHG reduction of this research and the existing published literature was presented. The details of the input parameters and results of life cycle energy and GHG emissions of some previous studies are given in Table 4.2. The microalgae fuel pathways in the published literatures is mainly biodiesel fuel except case 21 using hydrothermal liquefaction. Briefly, three main systems for cultivating microalgae: open pond, photobioreactor (PBR) and hybrid system are considered. CO_2 is obtained from flue gas. Many strains of microalgae (*Chlorella vulgaris, Schizochytrium limacinum, Pleurochrysis carterae* and *Nannaochloropsis sp.)* with a wide range of lipid content are selected for this case study. Microalgae are harvested and dewatered via a combination of autoflocculation, dissolved air flotation, centrifugation and thermal drying (if needed). The microalgae residue after lipid extraction is utilized by anaerobic digestion and animal feed. Two systems boundary: WTP and WTW are considered. In case of WTP is focused on the production of biodiesel excluded the combustion of biofuel in vehicle operation.

Figure 4.9 presents the total energy for microalgae–derived biofuels. Most of case study requires more energy than diesel fuel especially the case that relates to dry extraction. In the contrast, in some case consumes energy lesser than diesel fuel due to high amount of lipid content and usage of wet extraction instead of dry extraction. So, the lipid content and method for extracting microalgae oil have significant impact on the reduction of energy consumption in this case study.

Total GHG emissions can provide a comparison of the environmental impact of the production of microalgae biofuels. Figure 4.10 presents %GHG reduction relative to conventional diesel. It can be seen that most of case study for biodiesel production and FT liquid using the CE–CERT technology in scenario 7 can realize GHG reductions relative to a conventional diesel baseline. A negative CO_2 output results from the CO_2 sequestration in the production of microalgae biomass during the photosynthesis and utilization of co–products for energy recovery.

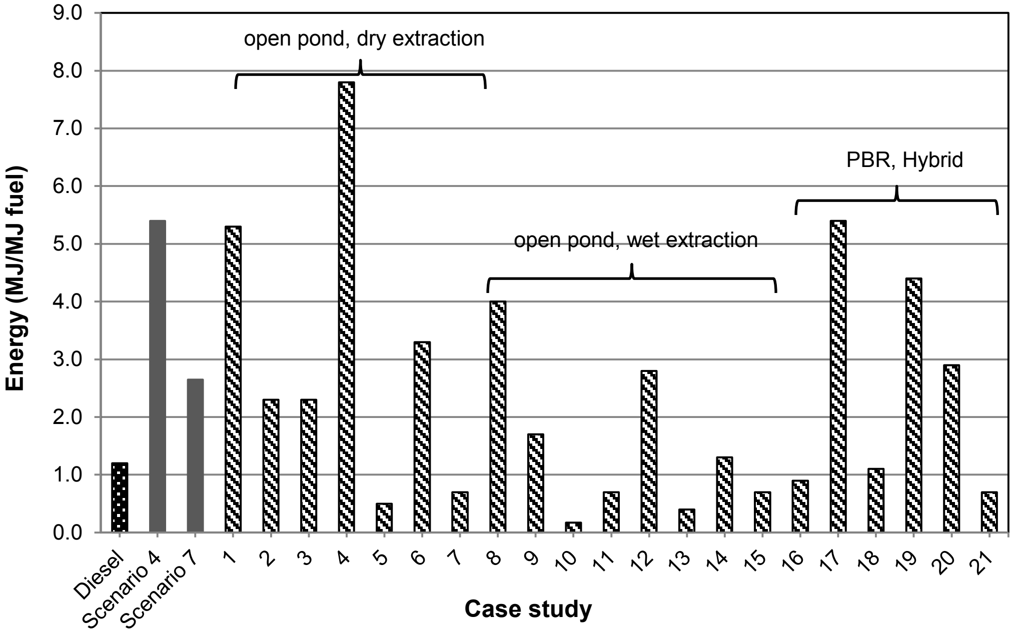

Figure 4.9 Energy for microalgae–based biofuel with other published studies

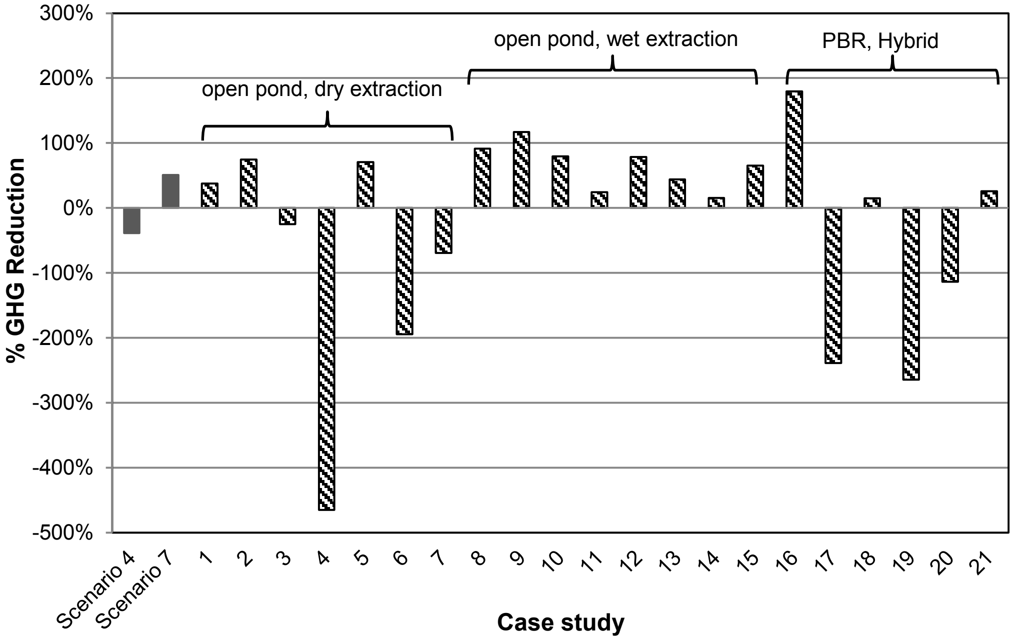

Figure 4.10 %GHG reduction for microalgae–based biofuel with other published studies

Table 4.2 Life cycle energy and GHG emissions with other published studies

Case	Algae species	Growth rate ($g/m^2/day$)	Lipid content (wt% DW)	Cultivation system	Energy (MJ/MJ fuel)	GHG emissions (g CO_2 eq/MJ fuel)	Notes	Reference
Diesel	-	-	-	-	1.2	94.5	Conventional diesel (this work)	-
Scenario 4	Chlorella vulgaris	25	15	OP	5.4	131.1	Scenario 4 (this work) dry extraction co-product utilization-CE-CERT boundary WTW	-
Scenario 7	Chlorella vulgaris	25	15	OP	3.1	57.5	Scenario 7 (this work) CE-CERT process boundary WTW	-
1	Chlorella vulgaris	24.75	17.5	OP	5.3	58.9	normal N, dry extraction boundary WTP	[97]
2	Chlorella vulgaris	19.25	38.5	OP	2.3	24.1	low N, dry extraction boundary WTP	[97]
3	Chlorella vulgaris	20	18	OP	2.3	118	dry extraction co-product utilization-animal feed boundary WTW	[127]
4	Not specified	Not specified	Not specified	OP	7.8	534	Base case dry extraction co-product landfilling boundary WTP	[128]
5	Schizochytrium limacinum	20	50	OP	0.5	27.8	dry extraction co-product utilization-AD boundary WTP	[129]
6	Not specified	20	25	OP	3.3	278	dry extraction co-product utilization-AD boundary WTW	[130]
7	Chlorella vulgaris	30	40	OP	0.7	160	dry extraction co-product utilization-AD boundary WTW	131]

Table 4.2 Life cycle energy and GHG emissions with other published studies (Continued)

Case	Algae species	Growth rate (g/m^2/day)	Lipid content (wt% DW)	Cultivation system	Energy (MJ/MJ fuel)	GHG emissions (g CO_2 eq/MJ fuel)	Notes	Reference
8	Chlorella vulgaris	24.75	17.5	OP	4	8	normal N, wet extraction boundary WTP	[97]
9	Chlorella vulgaris	19.25	38.5	OP	1.7	-16.1	low N, wet extraction boundary WTP	[97]
10	Chlorella vulgaris	30	40	OP	0.17	19.3	wet extraction co-product utilization-AD boundary WTW	[132]
11	Not specified	26.7	17.4	OP	0.7	71.7	wet extraction co-product utilization-AD boundary WTW	[133]
12	Not specified	25	25	OP	2.8	20.4	wet extraction co-product utilization-AD boundary WTW	[134]
13	Not specified	20	25	OP	0.4	53	wet extraction co-product utilization-AD boundary WTW	[130]
14	Pleurochrysis carterae	22	14.6	OP	1.3	80	wet extraction co-product utilization-AD	[120]
15	Pleurochrysis carterae	22	14.6	OP	0.7	33	wet extraction co-product utilization-hydrothermal liquefaction	[120]
16	Nannaochloropsis salina	25	50	PBR	0.9	-75.3	dry extraction co-product utilization-animal feed boundary WTP	[135]
17	Chlorella vulgaris	30	40	PBR	5.4	319.9	wet extraction co-product utilization-AD boundary WTW	[132]
18	Not specified	Not specified	Not specified	PBR	1.1	80.5	Best case Supercritical methanol extraction co-product utilization-AD boundary WTP	[128]
19	Nannaochloropsis sp.	Not specified	Not specified	Hybrid	4.4	344.3	wet extraction boundary WTP	[126]
20	Not specified	25	34	Hybrid	2.9	201.9	dry extraction co-product utilization-animal feed	[136]
21	Not specified	25	34	Hybrid	0.7	70	hydrothermal liquefaction co-product utilization-AD	[136]

OP-Open pond, PBR-Photobioreactor, AD-Anaerobic digestion, WTP-Well-to-Pump and WTW-Well-to-Wheels

4.6 Conclusion

WTW analysis has been performed for biodiesel and FT fuel as an alternative biofuel from microalgae biomass. The results of life cycle energy and greenhouse gas emissions performance were studied using GREET1_2012 model. The vehicle technology with a compression ignition direct injection, light duty truck was used as the vehicle operation. The most prominent results are as follows.

1. The life cycle analysis revealed that WTW energy consumption for the production of biodiesel derived from microalgae oil was substantially higher than the FT fuel derived from wet microalgae by the CE–CERT process. The higher lipid content could affect to the reduction of energy requirement. The lowest total energy for FT fuel from microalgae with 40 wt% of lipid using the CE–CERT process was 1.96 MJ/MJ of fuel. However, the energy demand also depends on other key factors such as the technologies advantage and highly optimized production system.
2. FT fuel from the CE–CERT process resulted in significantly lower GHG emissions compared with the biodiesel from conventional transesterification. FT fuel from the CE–CERT technology could reduce the environmental impact in terms of GHG emissions by 50–64% relative to a conventional diesel baseline on the basis of the assumptions made in this study.
3. The results from the existing published indicated that biodiesel derived from microalgae oil contained high lipid content and wet extraction method could reduce the energy consumption and GHG emissions similar to the CE–CERT technology for handling the wet microalgae biomass to produce FT fuel.

4. The results of this study indicate that the CE–CERT process is usable an alternative option for producing microalgae–based biofuel and utilizing the microalgae residue after lipid extraction. One unique advantage of the CE–CERT process is the ability to process wet microalgae that does not require drying and FT fuel production from the CE–CERT technology can prove sustainability in terms of environmental impact and energy security.

5. Conclusion and Future Work

5.1 Conclusion

The experimental results and conclusions of this thesis are summarized in this chapter. This chapter will also include some suggestion of research in the future. The feasibility of using steam hydrogasification of microalgae (both wet and/or dry biomass) for the production of biofuel was the main objective of this thesis. The entire life cycle energy and greenhouse gas emissions for Fischer–Tropsch (FT) fuel and biodiesel derived from microalgae are presented. The main tasks completed are summarized as follows.

1. Chapter Two, the steam hydrogasification of whole microalgae was determined the performance including carbon conversion and the formation of product gas. The experiments were performed at different operating parameters; temperature ranging of 650–800 °C, steam/biomass (S/B) ratio of 0–2.5 and H_2/C ratio of 0.5–1.5.

    1) Temperature has a significant influence in the steam hydrogasification process. Higher temperature showed an increase in product gas and increased carbon conversion efficiency. A rise in temperature from 650 to 850 °C resulted in approximately 30% increase in carbon conversion.

    2) An increase in the steam/biomass ratio promoted the production of hydrogen. This indicated that the water gas shift and steam reforming reactions were favored with the addition of steam.

    3) An increase in the H_2/C ratio resulted in increased the production of hydrogen and methane while the production of CO and CO_2 decreased. The steam hydrogasification of microalgae performed at a temperature 750 °C, H_2/C ratio of 1 and S/B ratio of 2 could achieve about 65% carbon conversion

    and further produce 1.06 barrel of FT fuel/ton microalgae. The steam hydrogasification of microalgae also generated sufficient hydrogen for recycle to the gasifier and excess hydrogen could be used for the FT fuel in the downstream process.

2. Chapter Three, the utilization of the microalgae residue was investigated as a means of further energy recovery for the upstream process. The effect of lipid content on steam hydrogasification was also studied.
    1) Steam hydrogasification was used to convert the microalgae residue after lipid extraction into energetic gas. The result showed that the microalgae residue have the potential to produce the FT fuel using the CE–CERT process as energy recovery about 4.9 MJ/kg of microalgae residue which would contribute to the microalgae production and fuel processing.
    2) It was shown that the addition of lipids in microalgae dramatically improved steam hydrogasification efficiency not only in the carbon conversion but also in the methane formation. The steam hydrogasification can be used to gasify all strains of microalgae even the residual microalgae.
3. Chapter Four, the overall life cycle energy and greenhouse gas emissions (GHG) of microalgae derived biofuel from the CE–CERT process was evaluated. The life cycle analysis of production of microalgae biofuel using the CE–CERT process was compared to biodiesel production using transesterification process.
    1) The production of FT fuel using the CE–CERT technology consumed less total energy than biodiesel production. The energy requirement was reduced about 50% when using 20 wt% of lipid content in microalgae. It could be explained that the CE–CERT technology could handle the wet microalgae

biomass without drying or lipid extraction resulted in lowering the energy required. While transesterification required higher energy for removing high amount of water and extracting the lipid.

2) The CE–CERT pathway released significant lower GHG emissions compared to the transesterification pathway for the production of microalgae biofuel. The CE–CERT process could reduce the GHG emissions by 50–64% compared to conventional diesel. This could be described that the CE–CERT process required lower fossil fuel than biodiesel and conventional diesel.

4. Microalgae biomass appears to be an attractive biomass feedstock for the CE–CERT steam hydrogasification process for the efficient production of low carbon synthetic fuels. Microalgae biofuel derived from the CE–CERT technology not only improves the energy security to replace fossil fuel but also reduces the GHG emissions and slowing global climate change.

5.2 Future work

There are several topics which can be addressed to enhance the production of microalgae biofuel in the future.

1. Determine the performance of steam gasification and carbon conversion efficiency using other types of reactor and scale–up for microalgae to the production of FT liquid fuel.
2. Investigate the effect of mineral and contaminants when using microalgae that grow in different water such as saline water, industrial or municipal wastewater etc.
3. Evaluate the life cycle analysis using various microalgae biofuel pathways (both wet and dry feedstock) such as fermentation, anaerobic digestion, and wet extraction for transesterification and input parameters for a commercial scale facility.
4. Evaluate economic feasibility of microalgae biofuel for commercial scale. Economic tests should be done based on cost of cultivation, dewatering, lipid extraction and conversion. It should be noted that costs are mainly associated with the energy requirement.

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