CHAPTER II
LITERATURE REVIEW

2.1 Biofuel

Biofuel is a wide range of fuel which is derived from biomass. The term biofuel is referred to as solid, liquid, and gaseous fuel. Biofuel has gained more and more attention in both public and scientific point of view due to many factors, for example, increase in crude oil price and greenhouse gas emission from fossil fuel. Biofuel provided 1.8 % of the world's transport fuel in 2008 (Demirbas, 2009). Nowadays, there are two global biorenewable liquid transportation fuels: bioethanol and biodiesel which might replace gasoline and diesel fuel, respectively. According to the International Energy Agency (IEA), biofuel has the potential to meet more than a quarter of world demand for transportation fuel by 2050.

Bioethanol is an alcohol which is made by fermenting the sugar component of plant material. Mostly, bioethanol is made from sugar and starch crop; but, cellulosic biomass, such as tree and grass, can be used as feedstock for ethanol production by using advanced technology which is being developed. Bioethanol can be purely used as a fuel for flexi-fuel vehicle (FFV); however, it is usually used as a gasoline additive to increase octane number and improve vehicle emission (Larson, 2006). Bioethanol can also serve as feedstock for ethyl tertiary butyl ether (ETBE) which is easier to blend with gasoline. Bioethanol is widely used in the United States and in Brazil.

Biodiesel has become more attractive recently because of its environmental benefit. Biodiesel is made from vegetable oil, animal fat, and recycled grease through transesterification. Biodiesel can be purely used as a fuel for vehicle with minor engine modification; however, it is usually used as a diesel additive to reduce particulate matter, carbon monoxide, and hydrocarbon from diesel-powered vehicle (Larson, 2006). Biodiesel is the most common biofuel in European countries.

Moreover, there is another niche biofuel: biogas or biomethane, which has been derived by anaerobic digestion of manure and other digestible biomass materials. Biogas can be used in gasoline vehicle with slight adaptation. However,

the volume of biogas used for transportation is relatively small today (Girard and Fallot, 2006).

2.1.1 History of Biofuel

Biofuel has been used in the form of solid since human discovered fire. Wood is the first form of biofuel that was used by ancient people for heating and cooking. Sugarcane has been used in the production of ethanol since 6000 BC. Ethanol was first prepared synthetically by Henry Hennel in 1826. Rudolf Diesel, German inventor, designed diesel engine to run in peanut oil and Henry Ford later designed the Model T car which was produced from 1903 to 1926 (Demirbas, 2009). In the period of World War II, from 1939 to 1945, the high demand of biofuel was due to the serious shortage of fossil fuel. In 1970s, Organization of the Petroleum Exporting Countries (OPEC) also made a heavy cut in export especially to the non-OPEC nations because of the geopolitical conflict (Biofuel.org.uk, 2010). This energy crisis attracted the attention of people towards the use of biofuel in the twentieth century. At the present, the main reason for people shifting their interest to biofuel is the rising price of crude oil and emission of greenhouse gases.

2.1.2 Classification of Biofuel

Biofuel can be classified based on their production technology: first generation biofuel, second generation biofuel, third generation biofuel, and fourth generation biofuel (Demirbas, 2009).

2.1.2.1 First Generation Biofuel

First generation biofuel is biofuel that is made from sugar, starch, vegetable oil, or animal fat using conventional technology (Demirbas, 2009). Although the production of the first generation biofuel (i.e. bioethanol, biodiesel, and biogas) is now commercial with almost 50 billion liters produced annually (Naik *et al.*, 2010), it is produced from feedstock which is used for food. As a result of mass production of biofuel, the food price tends to rise more and more. In addition, the concern about the competition of biofuel with food crop, especially for land use, starts to exist.

Currently, about 1 % (14 million hectares) of the world's available arable land is used for the production of biofuel, providing 1 % of global transport fuel (Brennan and Owende, 2010). That means increasing the share to anywhere near 100 % is impractical owing to the severe impact on the world's food supply and the large area of the production land required. Therefore, the first generation biofuel which is produced from food crop is limited in its ability to achieve the target for petroleum substitution.

However, there is a possible exception that appears to meet many of the acceptable criteria which are bioethanol produced from sugarcane and corn in Brazil and the United States, respectively (Thamsiriroj and Murphy, 2011). For biodiesel production, rapeseed oil biodiesel in Germany and palm oil biodiesel in Malaysia are also characterized by commercial market. However, it is still difficult to use the agricultural food crop for biofuel production in most of developing countries including Thailand.

2.1.2.2 Second Generation Biofuel

Second generation biofuel is biofuel that is made from non-food crops using advanced technology. It refers largely to lignocellulosic material including cereal straw, forest residue, bagasse, and purpose-grown energy crop such as vegetative grass and short rotation forest (Demirbas, 2009). In addition, the organic fraction of municipal solid waste can also be used as feedstock for the second generation biofuel. The second generation biofuel can avoid many concerns facing in the first generation biofuel. Therefore, many problems associated with the first generation biofuel can be addressed by biofuel manufactured from this kind of sustainable feedstock. It is anticipated that the second generation biofuel will not compete with food crop anymore. For production, the lignocellulosic biomass can be burned directly or converted to intermediate solid, liquid or gaseous form for the production of heat, electricity, chemicals, or gaseous and liquid fuel. Main biomass conversion processes include thermochemical conversion, physicochemical conversion, and biochemical conversion (Naik *et al.*, 2010). Table 2.1 summarizes biomass conversion processes and corresponding end-uses, together with an indication of the status of respective technologies.

Table 2.1 Summary of biomass conversion processes (Bauen, 2005)

	Conversion technology	Resource type	Examples of fuel	Product	End-uses	Technology status
Themochemical	Combustion (excess air)	Mainly solid biomass	▪ Wood ▪ Agricultural residues ▪ Chicken litter	Heat	▪ Heat ▪ Electricity	Commercial
	Gasification (partial air)	Mainly solid biomass	▪ Wood ▪ Agricultural residues	Syngas	▪ Heat ▪ Electricity ▪ Transport fuels (methanol, hydrogen)	Demonstration/ Early commercial
	Pyrolysis (no air)	Mainly solid biomass	▪ Wood ▪ Agricultural residues	Bio-oil, Syngas, Charcoal	▪ Heat ▪ Electricity ▪ Transport fuel	Demonstration
	Liquefaction (no air)	Mainly solid biomass	▪ Wood ▪ Agricultural residues	Bio-oil	▪ Heat ▪ Electricity ▪ Transport fuel ▪ Chemicals	Demonstration
Physicochemical	Pressing or extraction and Trans-esterification	Mainly solid and liquid biomass	▪ Rapeseed ▪ Soybean ▪ Oil or fat ▪ Waste	Liquid fuel (biodiesel)	▪ Heat ▪ Electricity ▪ Transport fuel	Demonstration/ Early commercial
Biochemical	Hydrolysis and fermentation	Mainly solid biomass	▪ Wheat ▪ Maize ▪ Sugar beet ▪ Cassava	Liquid fuel (biocthanol)	▪ Transport fuel	Commercial
	Anaerobic digestion	Wet biomass	▪ Manure ▪ Sewage sludge	Biogas or Biomethane, Biohydrogen	▪ Heat ▪ Electricity ▪ Transport fuel	Commercial

The lignocellulosic biomass can simply be burned in order to produce heat and electricity. Moreover, sugar can be extracted from the lignocellulosic material through hydrolysis and then fermented into bioethanol. Transesterification can also be applied to produce biodiesel. The lignocellulosic biomass can be gasified in gasification process to produce syngas as well. To be technically and economically viable biofuel resource, it should be competitive or cost less than petroleum fuel (Brennan and Owende, 2010). However, the production of the second generation biofuel suffers with cost effectiveness due to technological barrier and feedstock collection network (Singh and Olsen, 2011). In other words, the second generation biofuel is still not commercial now.

2.1.2.3 Third Generation Biofuel

Biofuel produced from algae is considered the third generation biofuel and sometimes called oilgae. Biofuel production from algae is low cost and high yield since algae require only sunlight, together with water and CO_2 during the process of photosynthesis in order to convert to lipid or fatty acid (Dismukes *et al.*, 2008). Fatty acid includes medium chain (C_{10}–C_{14}), long chain (C_{16}–C_{18}) and very long chain ($\geq C_{20}$) species of fatty acid derivative. Hu *et al.* (2008) shown that *Bortyococcus braunii* can produce large quantity of very long chain hydrocarbon (C_{20}–C_{23}) up to 80 % which is similar to those found in petroleum. Moreover, oil content of some algae species exceeds 80 % of their dry cell weight.

Algae have high growth rate and tolerance to varying environmental conditions. Algae can double their mass several times a day and produce 5,000 to 15,000 gallons of oil per acre, per year as shown in Table 1.1 (Riesing, 2009). Algae can also grow in freshwater, seawater or even wastewater and on marginal land which is not suitable for food production. This feature has allowed algae to be used in wastewater treatment plant for sludge treatment. Nutrients for microalgae cultivation, especially nitrogen and phosphorus can be obtained from wastewater as well. However, in wastewater, medium needs to be treated in advance via anaerobic digestion to eliminate algae contamination. Unlike terrestrial crops, algae cultivation does not require any herbicides or pesticides. They also need less water than the terrestrial crops, so they can reduce the load on freshwater sources.

Additionally, since algae have high CO_2 tapping and fixation ability, they can be utilized to reduce CO_2 emission from power plant and other industries with high CO_2 emission. Microalgae can fix CO_2 from three different sources, namely CO_2 from atmosphere, CO_2 in discharge gases from industry, and CO_2 from soluble carbonates such as Na_2CO_3 and $NaHCO_3$ (Brennan and Owende, 2010). Algal biomass can be used for oil extraction and biodiesel production. The biomass left over from oil pressing can also either be fed to cattle as a protein supplement or fermented into ethanol. An overview of potential products of algae biorefinery is shown in Fig. 2.1.

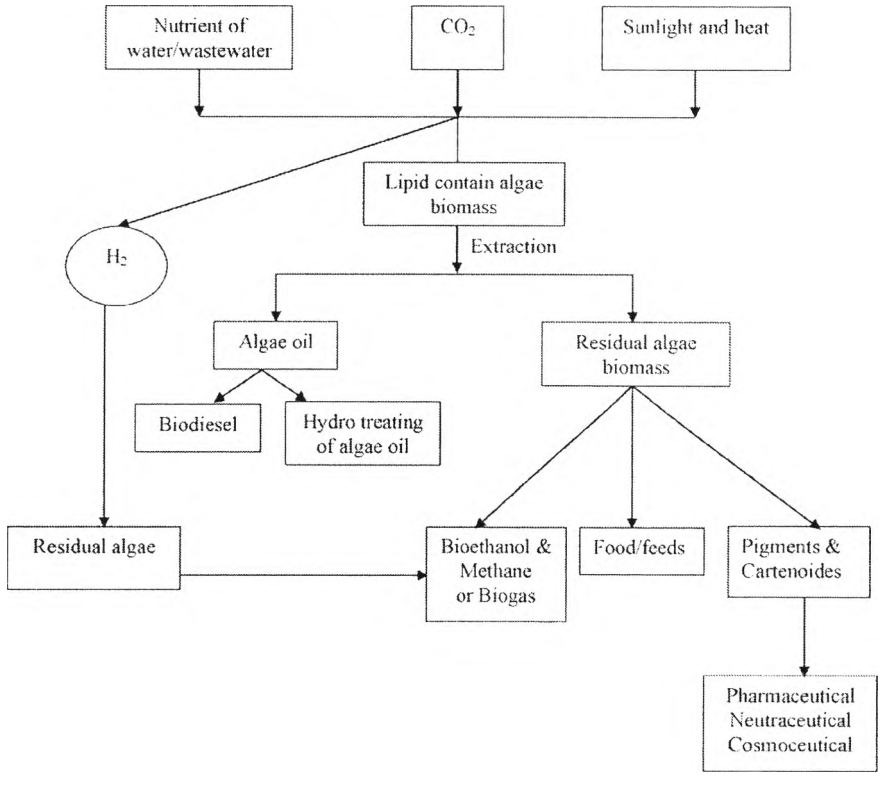


Figure 2.1 Schematic of algae biorefinery (Naik *et al.*, 2010).

Hossain and Salleh (2008) reported that the best algae for biodiesel production is microalgae. Macroalgae, like seaweed, are not as widely used in biodiesel production as microalgae because microalgae contain oil more than macroalgae and they are much faster and easier to grow. Microalgae can grow easily in every place where there is enough sunlight. Microalgae convert solar energy into

chemical energy via photosynthesis and then store it in the form of lipid, carbohydrate, and protein (Demirbas, 2011). The significant characteristics of microalgae are as follows:

- High Productivity

Microalgae have the potential to produce more oil per unit area than terrestrial plants due to high lipid content and high photosynthetic yield. In addition, different species of microalgae contain different quantity of lipid content.

- No Food-Fuel Competition

Microalgae have the ability to cultivate on non-arable land, so they do not compete directly with food crops. Moreover, some algae can grow in saline water and on non-agricultural land such as desert, arid and semi-arid land.

- Fast Growing

Microalgae are the fastest growing photosynthesizing organisms (Demirbas, 2011). They can complete the entire growing cycle every few days, so it is possible to meet the global demand, especially for transport fuel.

- CO_2 Sequestration

Microalgae have the ability to absorb CO_2 directly from industrial emission as a source of carbon for their growth. Chisti (2007) found that 1 kg of dry algal biomass utilizes about 1.83 kg of CO_2. Thus, they can reduce greenhouse gas emission in order to solve global warming and climate change problems.

According to the advantages of microalgae, they seem to be a very promising source of biofuel that have attracted considerable attention from researchers around the world to study the production of biofuel from microalgae. Biofuel from microalgae is more sustainable than other available biofuels (Chisti, 2007). That means using microalgae to produce biofuel would be the only viable method to replace the need of fuel used for automotive today. Moreover, processing

of biofuel from microalgae has been investigated that it captures large amounts of CO_2 and N_2O available in the atmosphere (Sobczuk *et al.*, 2008). With experiments being conducted all over the world, it is a good bet that microalgae will become an increasingly important source of renewable energy. Since microalgae are high productivity, easy to grow, and not food crop, it makes sense that algae seem to be the most promising fuel feedstock for the future.

2.1.2.4 Fourth Generation Biofuel

Fourth generation biofuel refers to genetically modified carbon negative crop. The fourth generation biofuel is based on genetic engineering or breeding of energy feedstock which is specifically designed to capture large amount of carbon and absorb high level of CO_2, for example, eucalyptus tree. The key process shown in Fig. 2.2 is the capture and sequestration of CO_2. In the fourth generation biofuel production system, biomass crop is seen as efficient carbon capturing machine that takes CO_2 out of the atmosphere and lock it up in its branches, trunks, and leaves. The carbon-rich biomass is then converted into fuels and gases by means of the second generation biofuel conversion techniques. Crucially, before, during or after the bioconversion process, CO_2 is captured by utilizing either pre-combustion or post-combustion processes. The greenhouse gas is then geo-sequestered and stored in depleted oil and gas fields, in unmineable coal seams or in saline aquifers, where it stays locked up for hundreds or thousands of years.

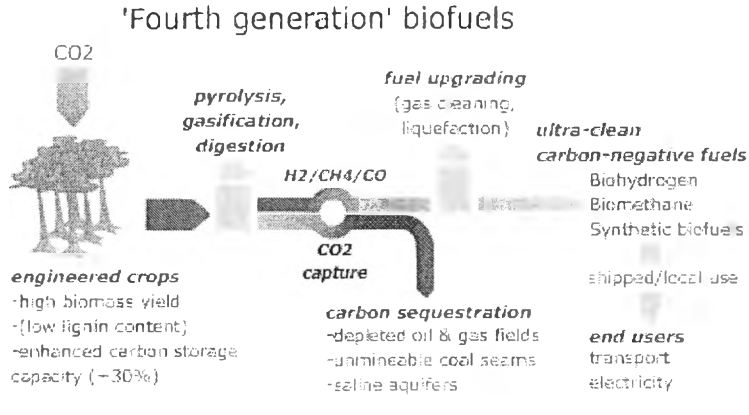


Figure 2.2 Fourth generation biofuel process (Rubens, 2008).

The resulting fuels and gases are not only renewable but also effectively carbon-negative. Only the utilization of biomass allows for the conception of carbon-negative energy; all other renewables (e.g. wind, solar, etc.) are all carbon-neutral at best, carbon-positive in practice. The fourth generation biofuel instead takes historic CO_2 emission out of the atmosphere. In other words, more carbon removed from the atmosphere than released.

2.2 Production of Algal Biofuel

Algae-to-biofuel production is divided into four stages, including algae cultivation, biomass harvesting, algal oil extraction, and oil and residue conversion as shown in Fig. 2.3 (Brennan and Owende, 2010).

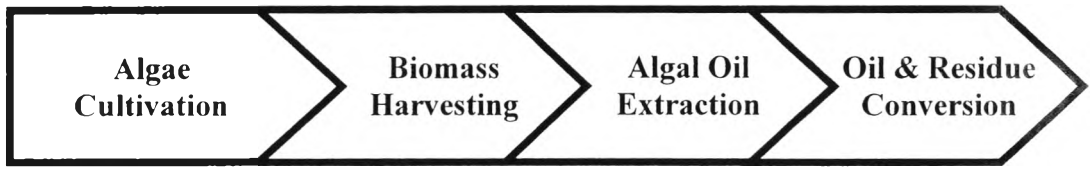


Figure 2.3 Algae-to-biofuel production pathway.

2.2.1 Algae Cultivation

Algae cultivation is an eco-friendly process for the production of organic material by photosynthesis from carbon dioxide, light, and water. The water used by algae can be low quality water, including industrial process water, effluent of biological water treatment and other wastewater streams. The technical viability of algae cultivation is influenced by intrinsic properties of the selected algae strain used as well as climatic condition and the cost of land and water. There are several factors to determine the growth rate of algae: light, temperature, nutrient, pH, algae type, aeration, mixing, etc. Table 2.2 shows the optimum conditions for microalgae cultivation. Microalgae can be cultivated by several systems (Scragg *et al.*, 2002). For large scale, algae can be grown either in open system or closed system (Ugwu *et*

al., 2008). For small scale or laboratory scale, a small fermenter, internally illuminated photobioreactor, or box type water tank can be used (FAO, 1996).

Table 2.2 A generalized set of conditions for culturing microalgae (FAO, 1996)

Parameters	**Range**	**Optima**
Temperature (°C)	16-27	18-24
Salinity (g/l)	12-40	20-24
Light intensity (lux)	1,000-10,000 (depends on volume and density)	2,500-5,000
Photoperiod (light:dark, hours)	-	16:8 (minimum) 24:0 (maximum)
pH	7-9	8.2-8.7

2.2.1.1 Open Pond System

Open pond can be classified into natural water and artificial pond or container. The most commonly used system includes shallow big pond, circular pond, raceway pond, and tank (Jiménez *et al.*, 2003). One of the major advantages of open pond is that it is easier to construct and operate than closed system. However, major limitations in open pond include poor light utilization by cell, loss of evaporation, fluctuation of temperature, diffusion of CO_2 to atmosphere, and requirement of large area of land (Chisti, 2007). Furthermore, contamination by other species has restricted the commercial production of algae in open culture system (Pulz and Scheibenbogen, 1998). Additionally, due to inefficient stirring mechanism in open cultivation system, mass transfer rate is very poor resulting to low biomass productivity.

The pond which the algae are cultivated is usually a raceway pond which is typically made of a closed loop, oval shaped recirculation as shown in

Fig. 2.4. It is generally between 0.2 and 0.5 m deep, with mixing and circulation required to stabilize algae growth and productivity (Chisti, 2007). It is also usually built in concrete; but, compacted earthlined pond with white plastic has been used as well. In this pond, the algae, water, and nutrients circulate around a racetrack. Algae are kept suspended in the water and circulated back to the surface on a regular frequency with paddlewheels providing the flow in order to prevent sedimentation. The pond is usually kept shallow because the algae need to be exposed to sunlight, and sunlight can only penetrate the pond water to a limited depth. The CO_2 requirement of algae is usually satisfied from the surface air; however, submerged aerator can be installed to enhance CO_2 absorption (Terry and Raymond. 1985). The pond is operated in a continuous manner, with CO_2 and nutrients being constantly fed to the pond, while algae containing water are removed at the other end.

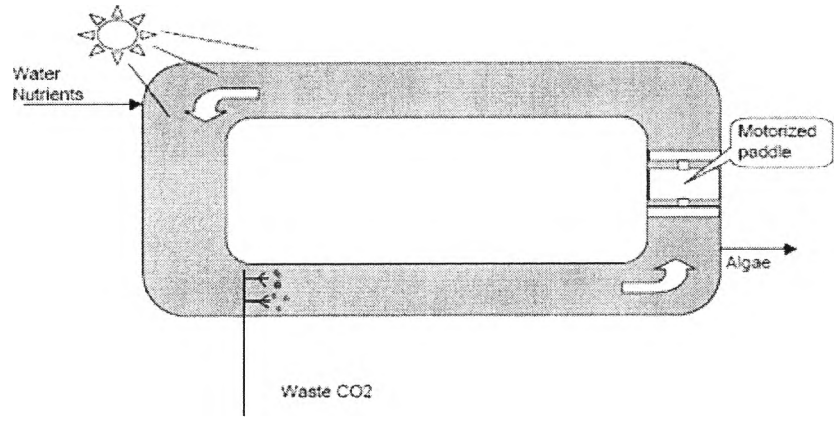


Figure 2.4 Plan view of raceway pond (Clixoo, 2010).

The biggest advantage of raceway pond is simplicity, resulting in low production cost and low operating cost. It also has low energy input requirement, so it may have the potential to return large net energy production (Ugwu *et al.*, 2008). Although this is the simplest growing technique, there are some drawbacks owing to the fact that the environment in and around the pond is not completely under control. Bad weather can disturb algae growth. Contamination from strains of bacteria or other outside organisms often results in undesirable species taking over the desired algae growing in the pond. The water in which the

algae grow also has to be kept at a certain temperature, which is difficult to maintain. Another drawback is the uneven light intensity and distribution within the pond.

2.2.1.2 Closed Pond System

An alternative to open pond is closed pond where the control over the environment is much better. As a variation of the open pond system, the idea behind the closed pond is to close it off, to cover a pond or pool with a greenhouse. Therefore, it does take care of many problems associated with the open system. It allows the species that are being grown to stay dominant. It is also possible to increase the amount of CO_2 in this quasi-closed system, thus the rate of growth of algae will increase. However, the closed pond system costs more than the open pond system, and considerably less than photobioreactor for similar area of operation.

2.2.1.3 Photobioreactor

A photobioreactor (PBR) is a closed equipment which provides a controlled environment and enables high productivity of algae in order to overcome some of the major problems associated with the described open pond production system (Ugwu *et al.*, 2008). As it is a closed system, all growth requirements of algae are introduced into the system and controlled according to the requirements. The photobioreactor facilitates better control of culture environment, for example, CO_2 supply, water supply, optimal temperature, efficient exposure to light, culture density, pH level, gas transfer, mixing regime, larger surface area-to-volume ratio, etc. As a result, an enclosed photobioreactor will enhance commercial algal biomass production by keeping algae genetics pure and reducing the possibility of contamination. Owing to the higher biomass production, harvesting cost can be significantly reduced. However, the investment cost of photobioreactor is substantially higher than open pond system and closed pond system (Carvalho *et al.*, 2006). Table 2.3 shows advantages and limitations of open pond system and photobioreactor. Various types of photobioreactor include tubular reactor (i.e. horizontal, vertical, and inclined), flat-plate reactor, vertical column reactor, bubble column reactor, airlift reactor, stirred tank reactor, immobilized reactor. In addition, tubular photobioreactor is widely used for the mass cultivation of algae.

Table 2.3 Advantages and limitations of open pond system and photobioreactor (Brennan and Owende, 2010)

Production system	Advantages	Limitations
Raceway pond	▪ Relatively cheap ▪ Easy to clean ▪ Use non-agricultural land ▪ Low energy input ▪ Easy maintenance	▪ Low biomass productivity ▪ Large area of land required ▪ Limited to a few strains of algae ▪ Poor mixing, light and CO_2 utilization ▪ Culture is easily contaminated
Tubular photobioreactor	▪ Large illumination area ▪ Suitable for outdoor cultures ▪ Relatively cheap ▪ High biomass productivity	▪ Some degree of wall growth ▪ Fouling ▪ Requires large land space ▪ Gradients of pH, dissolved oxygen and CO_2 along the tubes
Flat-plate photobioreactor	▪ High biomass productivity ▪ Easy to sterilize ▪ Low oxygen build-up ▪ Readily tempered ▪ Good light path ▪ Large illumination area ▪ Suitable for outdoor cultures	▪ Difficult scale-up ▪ Difficult temperature control ▪ Small degree of hydrodynamic stress ▪ Some degree of wall growth
Column photobioreactor	▪ Compact ▪ High mass transfer ▪ Low energy consumption ▪ Good mixing with low shear stress ▪ Easy to sterilize ▪ Reduce photoinhibition and photo-oxidation	▪ Small illumination area ▪ Expensive compared to open pond ▪ Shear stress ▪ Sophisticated construction

- Tubular Photobioreactor

Among proposed photobioreactors, tubular photobioreactor shown in Fig. 2.5 is one of the most suitable types for outdoor mass culture of algae according to large illumination surface area. It also seems to be the most satisfactory for producing algal biomass on the scale needed for biodiesel production (Patil *et al.*, 2008). For capturing sunlight, it consists of an array of straight, coiled, or looped transparent tubes which are generally 0.1 m or less in diameter (Chisti, 2007). They can be aligned horizontally (Molina *et al.*, 2001), vertically (Mirón *et al.*, 1999), inclined (Ugwu *et al.*, 2002), or as a helix (Watanabe and Saiki, 1997). Most outdoor tubular photobioreactors are usually constructed with either glass or plastic tubes. Aeration and mixing of the culture in tubular photobioreactor are usually done by air-pump or airlift system. Properly designed tubular photobioreactor completely isolates the culture from contamination as well.

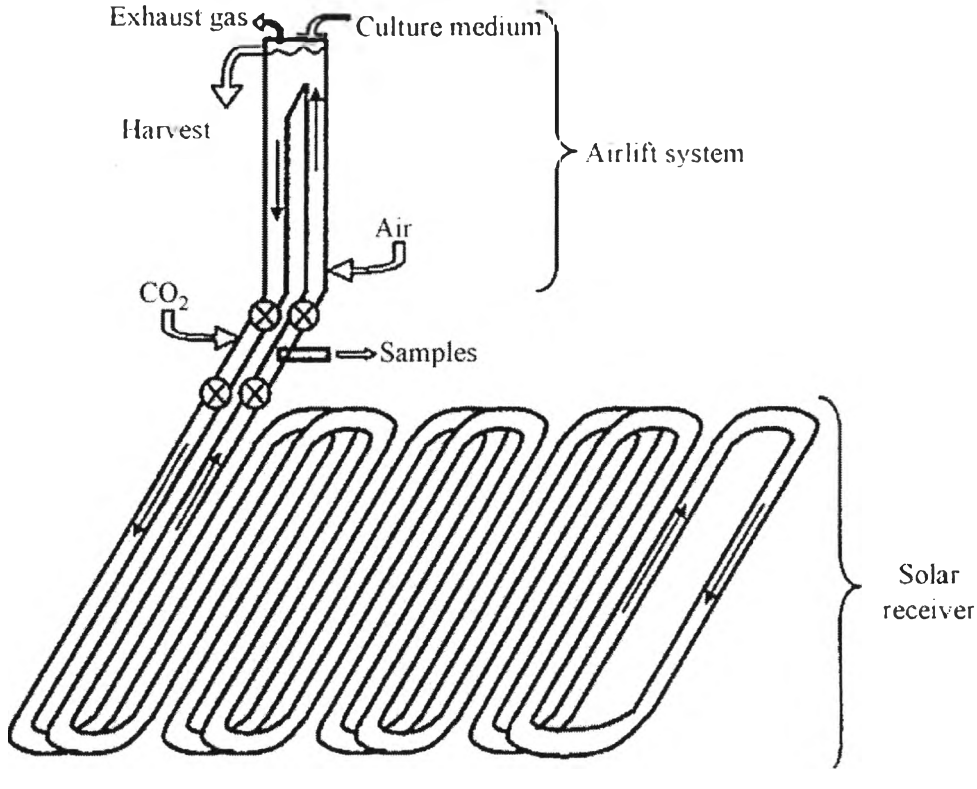


Figure 2.5 Schematic drawing of tubular photobioreactor (Kin, 2010).

However, one of major limitations of tubular photobioreactor is poor mass transfer. Mass transfer becomes a problem when tubular photobioreactor is scaled up because the length of tubes is dependent on oxygen accumulation and carbon dioxide depletion (Eriksen, 2008). Additionally, photoinhibition is a common concern in outdoor tubular photobioreactor. When a tubular photobioreactor is scaled up by increasing the diameter of the tubes, the illumination surface to volume ratio would decrease. On the other hand, the length of the tubes can be kept as short as possible while a tubular photobioreactor is scaled up by increasing the diameter of the tubes. In this case, cells at the lower part of the tubes will not receive enough light for cell growth due to light shading effect, unless there is a good mixing system.

Moreover, it is difficult to control culture temperature in most tubular photobioreactors. Although they can be equipped with thermostat to maintain the desired culture temperature, this could be very expensive and difficult to implement. Furthermore, a long tubular photobioreactor is characterized by gradients of oxygen and carbon dioxide transfer along the tubes. Therefore, large-scale production plant is based on integration of multiple photobioreactor units. The largest closed photobioreactors are tubular, e.g. the 25 m^3 plant at Mera Pharmaceuticals, Hawaii (Olaizola, 2000), and the 700 m^3 plant in Klötze, Germany (Pulz, 2001).

- Flat-Plate Photobioreactor

Flat-plate photobioreactor shown in Fig. 2.6 has received much research attention for cultivation of photosynthetic microorganism due to its large illumination surface area (Samson and Leduy, 1985) and high density of cell (Hu *et al.*, 1998). Generally, flat-plate photobioreactor is made of transparent material for maximum utilization of solar light energy (Richmond *et al.*, 2003). Accumulation of dissolved oxygen concentration in the flat-plate photobioreactor is relatively low compared to the horizontal tubular photobioreactor. However, high photosynthetic efficiency can be achieved in flat-plate photobioreactor. The flat-plate photobioreactor is very suitable for mass culture of algae (Richmond, 2000).

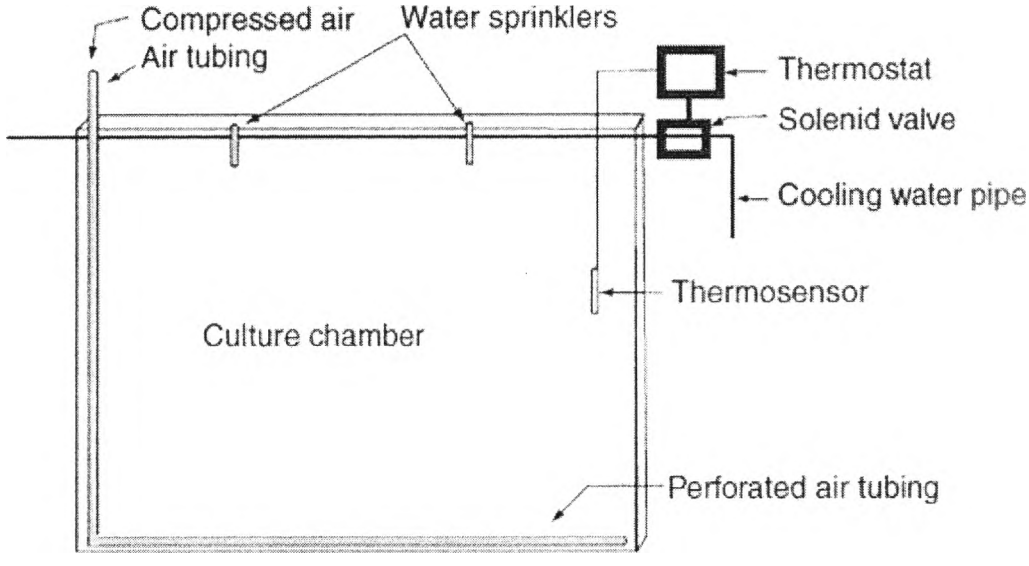


Figure 2.6 Schematic drawing of flat-plate photobioreactor (Oilgae, 2011).

- Column Photobioreactor

Column photobioreactor offers the most efficient mixing, the highest volumatic mass transfer rate, and the best controllable growth condition (Eriksen, 2008). Various designs and scales of vertical column photobioreactor have been investigated for cultivation of algae, for example, aerated vertical column photobioreactor and vertical bubble column photobioreactor shown in Fig. 2.7 and Fig. 2.8, respectively. The vertical column photobioreactor is aerated from the bottom and illuminated through transparent wall or internally (Suh and Lee, 2003). Its performance compares favorably with the tubular photobioreactor (Mirón *et al.*, 2002). The vertical column photobioreactor is compact, low cost, and easy to operate. Furthermore, it is very promising for large scale cultivation of algae.

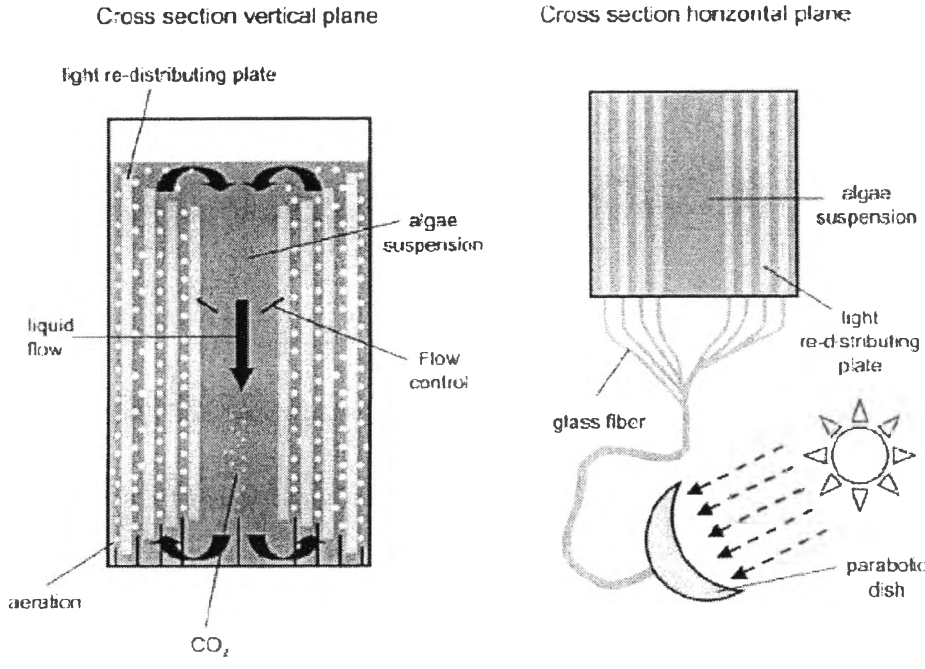


Figure 2.7 Schematic drawing of aerated vertical column photobioreactor (Kin, 2010).

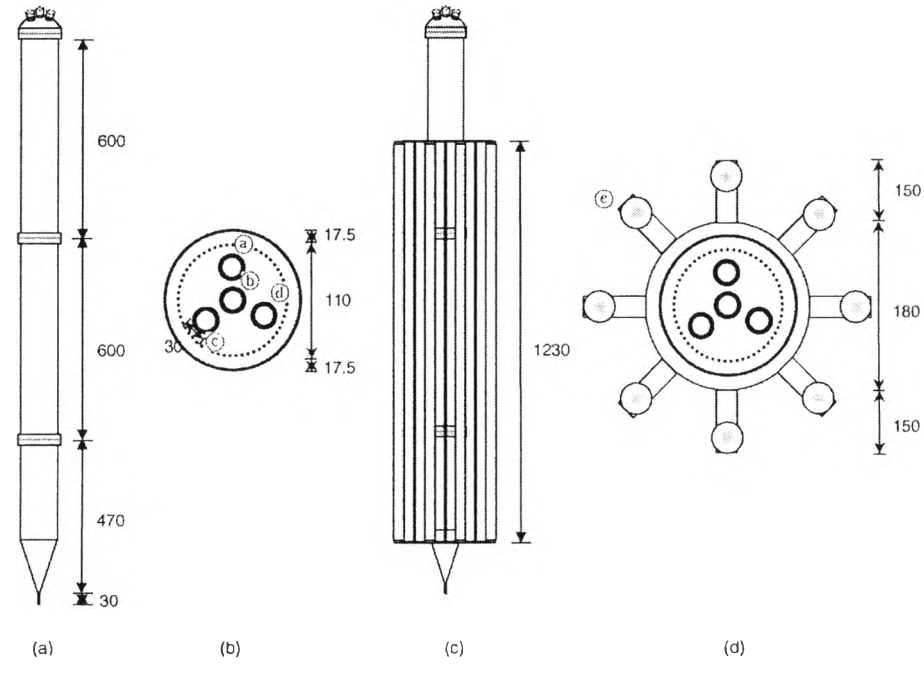


Figure 2.8 Schematic drawing of vertical bubble column photobioreactor (Kin, 2010).

2.2.2 Biomass Harvesting

Harvesting is a separation of algae from growing medium. The harvesting process is a process that concentrates a diluted algae suspension to become a thicken algae paste. The selection of harvesting technology is crucial to economic production of microalgal biomass (Schenk *et al.*, 2008). Choosing the effecting harvesting process depends primarily on characteristics of microalgae, e.g. size, density, type of algae, and value of target product (Olaizola, 2003). Normally harvesting of microalgae can be a single step process or two step process which involves harvesting and thickening/dewatering. The aim of thickening/dewatering is to concentrate the slurry. However, thickening/dewatering process is an energy intensive step. The most common harvesting processes for microalgae are filtration, centrifugation, flocculation, and flotation (Brennan and Owende, 2010).

2.2.2.1 Filtration

Filtration is carried out commonly on membranes with the aid of a suction pump (Grima *et al.*, 2003). The greatest advantage of this method as a concentrating device is that it is able to collect microalgae or cells of very low density. However, concentration by filtration is limited to small volume and leads to the eventual clogging of the filter by the packed cells when vacuum is applied. There are several methods to avoid these problems. One involves the use of a reverse-flow vacuum in which the pressure operates from above, making the process more gentle and avoiding the packing of cells. This method itself has been modified to allow a relatively large volume of water to be concentrated in a short period of time. Another process uses a direct vacuum but involves a stirring blade in the flask above the filter which prevents the particles from settling during the concentration process. Sometimes they may be collected very well with microstrainer. When the microstrainer is used to collect algae, the original suspension may be faintly green, which could be further concentrated.

2.2.2.2 Centrifugation

Centrifugation is a method of separating algae from their medium by using a centrifuge to cause algae to settle to the bottom of a flask or tank.

A Centrifuge is a useful device for both biolipid extraction from algae and chemical separation in biodiesel. It is a piece of equipment, generally driven by a motor that puts an object in rotation around a fixed axis, applying a force perpendicular to the axis. The centrifuge works using the sedimentation principle, where the centripetal acceleration is used to evenly distribute substances of greater and lesser density. Coupled with a homogenizer, one may be able to separate biolipid and other useful materials from algae.

Centrifugation is preferred for harvesting of high value metabolites (Heasman *et al.*, 2000). Biomass recovery depends on the settling characteristic of cell, slurry residence time in the centrifuge, and settling depth (Grima *et al.*, 2003). The disadvantages of the process are high energy cost and potentially high maintenance requirement due to freely moving parts (Bosma *et al.*, 2003). Centrifugation and drying are currently considered too expensive for small scale, but they are useful on a commercial and industrial scale.

2.2.2.3 Flocculation

Flocculation is a method of separating algae from the medium by using chemicals to force the algae to form lump. Flocculants or flocculating agents are chemicals that promote flocculation by causing colloid and other suspended particles in liquid to aggregate and then form a floc. Aluminium sulphate ($Al_2(SO_4)_3$), ferric chloride ($FeCl_3$), and ferric sulphate ($Fe_2(SO_4)_3$) are chemical flocculants which are used to harvest algae (Brennan and Owende, 2010). Since microalgae cells carry a negative charge that prevents natural aggregation of cells in suspension, addition of flocculant such as multivalent cation and cationic polymer neutralizes or reduces the negative charge. It may also physically link one or more particles through a process called bridging in order to facilitate the aggregation (Grima *et al.*, 2003).

However, the main disadvantage of this separation method is that the additional chemicals are difficult to remove from the separated algae. Additionally, the cost to remove these chemicals is too expensive to be commercially viable. Therefore, harvesting by chemical flocculation is a method that is often too expensive for large operation, but may be practical for small scale.

2.2.2.4 Flotation

Flotation is usually used in combination with flocculation for algae harvesting in wastewater. It is a simple method by which algae can be made to float on the surface of the medium and removed as scum.

- Froth Flotation

Froth flotation is a method of separating algae from the medium by adjusting pH and bubbling air through a column to create a froth of algae that accumulates above liquid level. The algae collect in froth above the liquid level and may be removed by suction. The pH required depends on algal species. Froth flotation and drying are currently considered too expensive for commercial use.

- Dissolved Air Flotation

Dissolved Air Flotation (DAF) separates algae from their culture using features of both froth flotation and flocculation. It uses alum to flocculate an algae/air mixture, with fine bubbles supplied by an air compressor. Alum is a common name for several trivalent sulfates of metal such as aluminum, chromium, or iron and a univalent metal such as potassium or sodium, for example, $AlK(SO_4)_2$.

2.2.3 Algal Oil Extraction

Oil extraction from algae is one of the most costly processes which can determine the sustainability of algae-based biofuel. Before extraction, dehydration or drying is commonly applied (Brennan and Owende, 2010). Dehydration methods that have been used include sun drying (Prakash *et al.*, 1997), low-pressure shelf drying (Prakash *et al.*, 1997), drum drying (Prakash *et al.*, 1997), spray drying (Desmorieux and Decaen, 2006), fluidized bed drying (Leach *et al.*, 1998), freeze drying (Grima *et al.*, 1994), and Refractance Window™ technology drying (Nindo and Tang, 2007). Sun drying is the cheapest dehydration method; however, main disadvantages include long drying period, the requirement for large drying surface, and the risk of material loss (Prakash *et al.*, 1997). Spray drying is commonly used for extraction of high value product, but it is relatively expensive

and can cause a significant deterioration of some algal pigments (Desmorieux and Decaen, 2006). Freeze drying is also equally expensive, especially for large scale operation, but it eases extraction of oil (Grima *et al.*, 1994). Extraction can be broadly categorized into two methods: mechanical and chemical method.

2.2.3.1 Mechanical Method

The simplest method is mechanical crushing. Mechanical crushing is often used in conjunction with chemicals. However, this method generally requires drying process which is energy intensive.

- Expression/Expeller Press

Algae are dried and retain its oil content, which then can be pressed out with an oil press shown in Fig. 2.9. Since different strains of algae vary widely in their physical attributes, various pressing configurations (e.g. screw, expeller, piston, etc.) work better for specific algae types. Many commercial manufacturers of algal oil use a combination of mechanical pressing and chemical solvents in extracting oil.

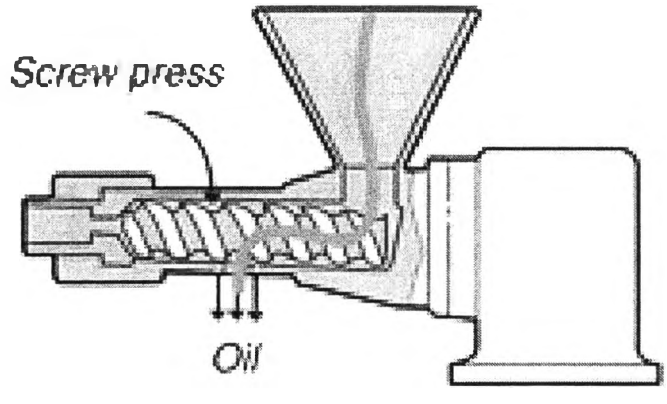


Figure 2.9 Screw press (Gilbert, 2011).

- Ultrasonic-assisted Extraction

Ultrasonic extraction, a branch of sonochemistry, can greatly accelerate extraction process. Using an ultrasonic reactor, ultrasonic waves are used

to create cavitation bubbles in a solvent material. When these bubbles collapse near the cell walls, it creates shock waves and liquid jets that cause those cells walls to break and release their oil contents into the solvent. OriginOil, a biofuel company based in Los Angeles, developed a wet extraction process that combines ultrasound and electromagnetic pulse induction to break the algae cell wall as shown in Fig. 2.10 (Heger, 2009). Carbon dioxide is also added to the algae solution in order to lower pH and separate biomass from oil.

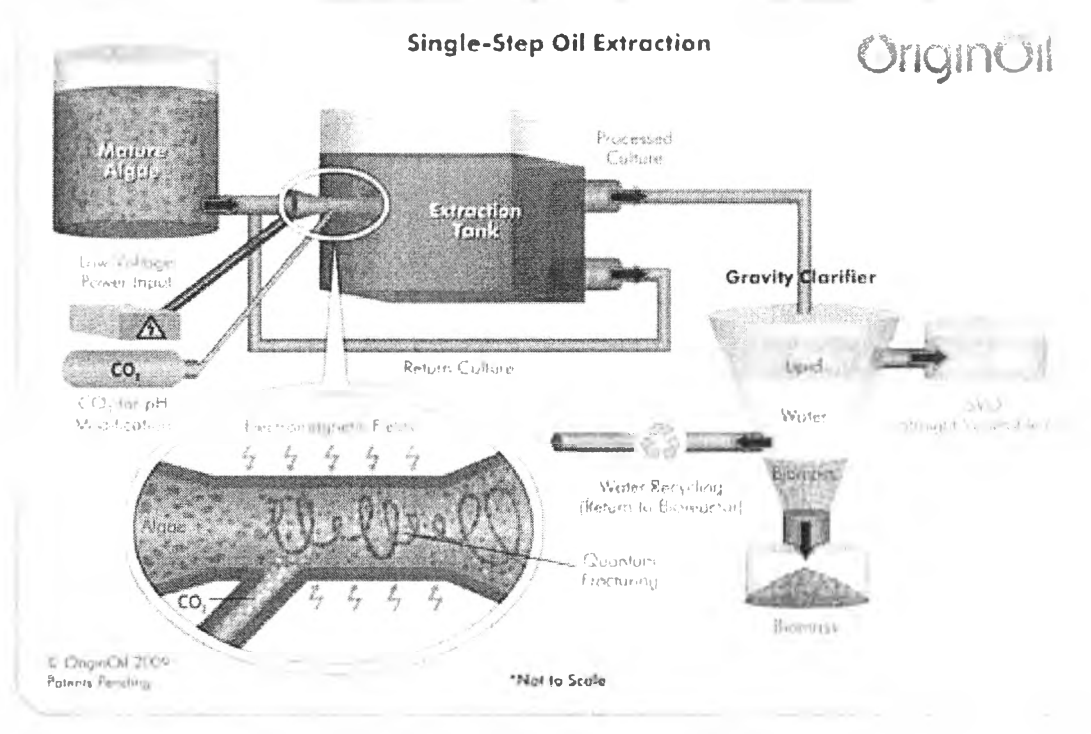


Figure 2.10 OriginOil's Single-Step Algal Oil Extraction (OriginOil, 2009).

2.2.3.2 Chemical Method

Algal oil can be extracted by using chemicals, for example, benzene, ether, and hexane. However, the downside of using solvent for oil extraction is the danger involved in working with the chemicals. Care must be taken to avoid exposure to vapor and direct contact with the skin, either of which can cause serious damage. For instance, benzene is classified as a carcinogen. Chemical solvent can also cause the explosion hazard.

- Solvent Extraction

In solvent extraction, benzene and ether have been used, but a popular chemical is hexane, which is relatively inexpensive. Hexane solvent extraction can be used in isolation or it can be used along with the oil press/expeller method. After the oil has been extracted using an expeller, the remaining biomass can be mixed with cyclohexane to extract the remaining oil content. The oil dissolves in the cyclohexane, and the biomass is filtered out from the solution. The oil and cyclohexane are separated by means of distillation. These two stages, which are mechanical and chemical extraction, are able to derive more than 95 % of the total oil present in the algae (Amin, 2009). Additionally, soxhlet extraction shown in Fig. 2.11 is a dynamic extraction method that uses chemical solvent. Oil from algae is extracted through repeated washing with an organic solvent such as hexane or petroleum ether, under reflux in special glassware.

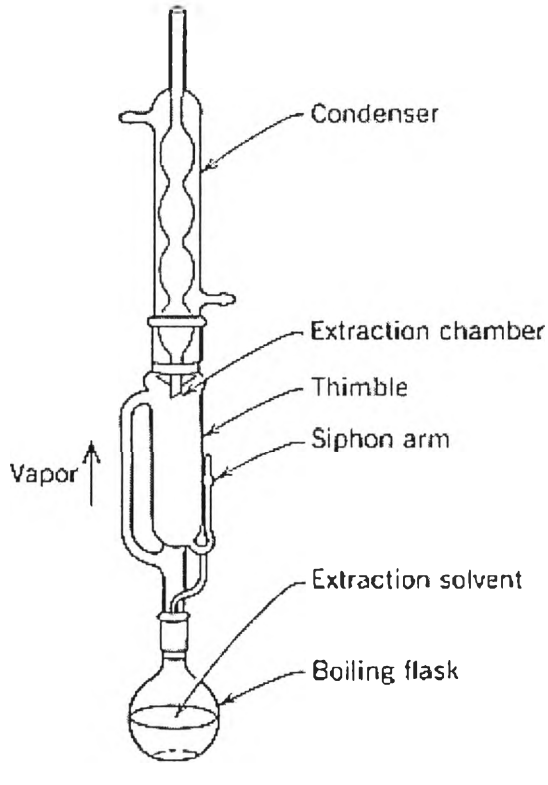


Figure 2.11 Soxhlet extractor.

- Supercritical Fluid Extraction

In supercritical fluid extraction, CO_2 is liquefied under pressure and heated to the point that it has the properties of both liquid and gas (Amin, 2009). This liquefied fluid then acts as the solvent for the extraction. A main drawback is that supercritical fluid extraction requires high pressure equipment that is both expensive and energy intensive. The scheme of a supercritical fluid extraction plant for solid-liquid extraction is shown in Fig. 2.12.

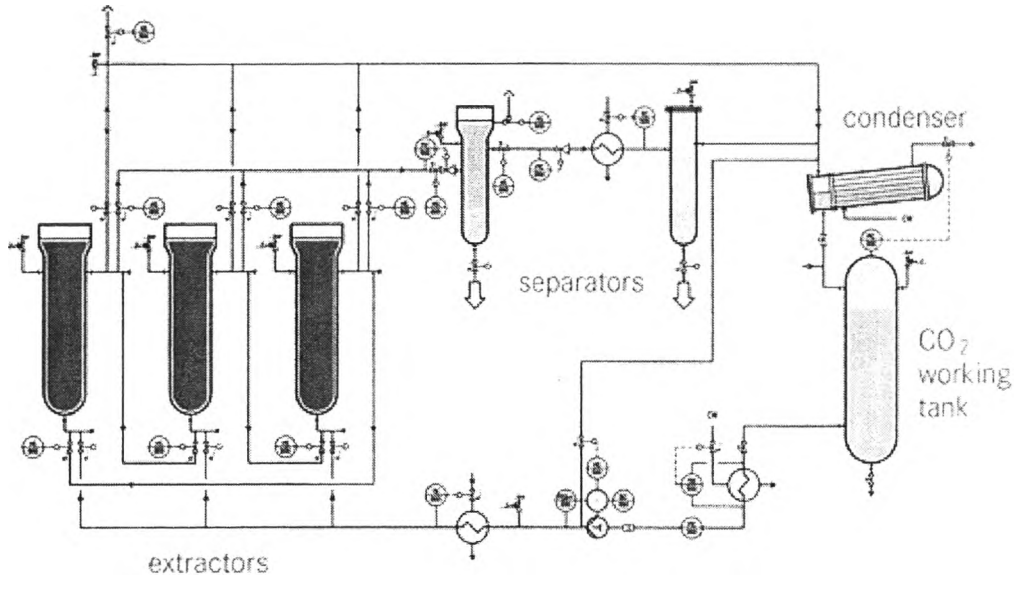


Figure 2.12 Scheme of a supercritical fluid extraction plant (NATEX, 2009).

2.2.4 Oil and Residue Conversion

The conversion of algal biomass-to-energy encompasses the different processes ordinarily used for terrestrial biomass like second generation biofuel. The conversion technologies for utilizing microalgae biomass can be separated into three main categories: thermochemical conversion, physicochemical conversion, and biochemical conversion as shown in Table 2.1. Factors that influence choice of conversion process include type and quantity of biomass feedstock, desired form of energy or product, economic consideration, etc (Brennan and Owende, 2010).

2.2.4.1 Thermochemical Conversion

Thermochemical conversion is the thermal decomposition of organic component in biomass to liquid or gaseous form for the production of heat, electricity, chemicals, and fuel. Main thermochemical conversion processes are direct combustion, gasification, pyrolysis, and liquefaction. Fig. 2.13 shows types and classification of biomass thermal conversion processes.

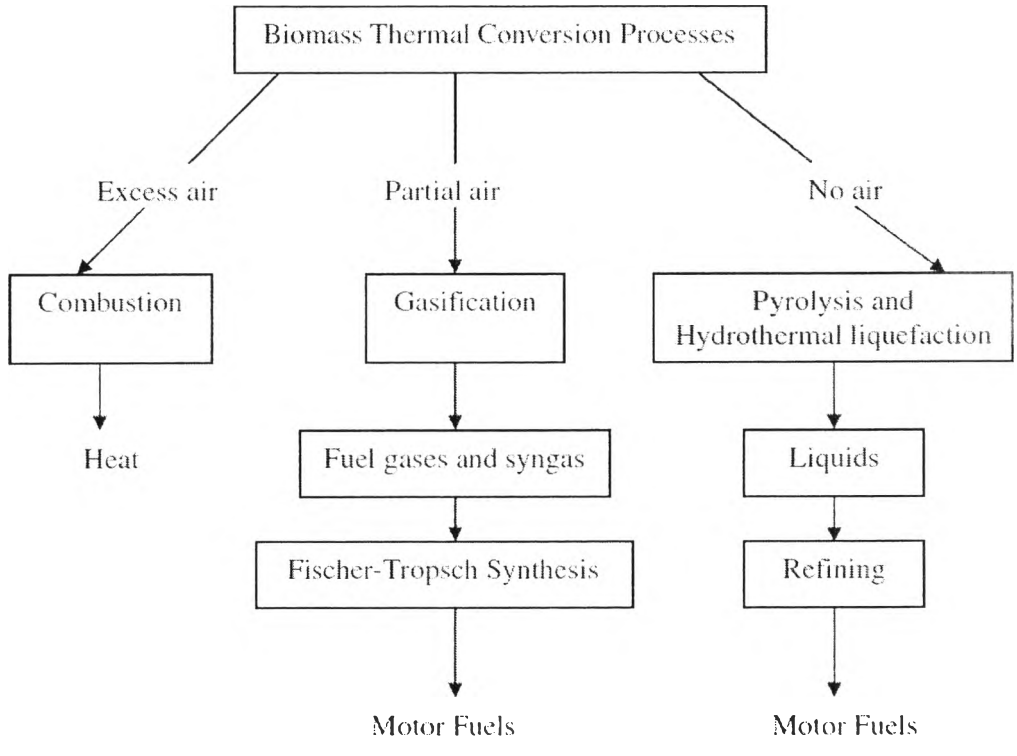


Figure 2.13 Biomass thermal conversion processes (Demirbas, 2009).

- Direct Combustion

In direct combustion process, biomass is burned in the presence of air to convert a stored chemical energy in biomass into hot gases which can be further used as heat and electricity. The heat produced must be used immediately as storage is not a viable option. This process usually occurs in furnace, boiler, or steam turbine at temperature above 800 °C. Biomass combustion system is now in commercial use around the world. It can burn any types of biomass; however, the combustion is only feasible for biomass with moisture content less than 50 % of

dry weight. Therefore, a main disadvantage of the direct combustion is that it generally requires pre-treatment process such as chopping, grinding, and drying which costs more. Kadam (2002) conducted a life cycle assessment of coal-algae-co-firing and suggested that coal-algae-co-firing could lead to lower greenhouse gas emission and air pollution.

- Gasification

Gasification is the conversion of a carbonaceous feedstock into a synthesis gas (syngas), a mixture of CO and H_2, together with CH_4, C_2H_4, CO_2, and other impurities such as nitrogen, sulfur, alkali compound, and tar. The process is a partial oxidation at high temperature, from 800 °C to 1000 °C. Syngas is a low calorific gas that can be burned directly or used as a fuel for gas engine or gas turbine. Gasification can use air, oxygen, steam or mixture of these as the gasifying agent (Damartzis and Zabaniotou, 2011). Air gasification results to a product with low to medium heating value, while gasification with oxygen or steam leads to a product with medium heating value. When steam is used, more hydrogen is produced from the reaction of methane reforming which leads to a product stream with higher heating value. However, gasification with steam requires higher operating temperature for the vaporization of water which makes it more expensive. Therefore, the use of a mixture of air and steam is recommended. The possible products which can be obtained from gasification process are given in Fig. 2.14.

Gasification characteristics of microalgae biomass have been studied by many researchers. Hirano *et al.* (1998) partially oxidized *Spirulina* at temperature of 850 °C, 950 °C, and 1000 °C. The composition of produced gas was also determined in order to evaluate the theoretical yield of methanol from the gas. They concluded that the gas composition depended on temperature, and gasification at 1000 °C gave the highest theoretical yield of 0.64 gram of methanol from 1 gram of biomass. Minowa and Sawayama (1999) gasified the microalgae *Chlorella vulgaris* in a novel energy production system with nitrogen cycling in order to obtain methane-rich fuel gas. All nitrogen in the microalgae was converted to ammonia during the reaction. A flow diagram of microalgal system for fuel production by low temperature catalytic gasification of biomass is shown in Fig. 2.15.

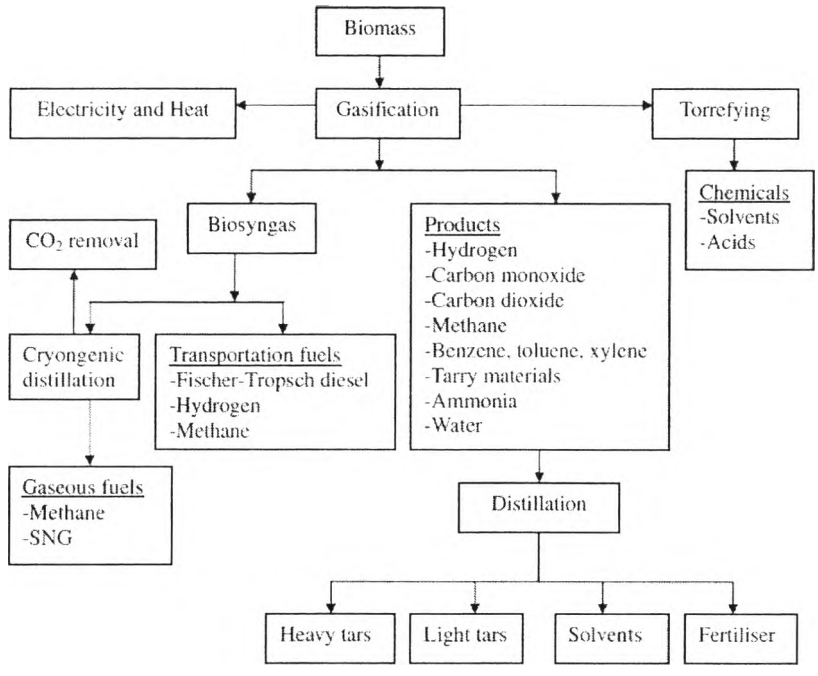


Figure 2.14 Products from gasification process (Demirbas, 2009).

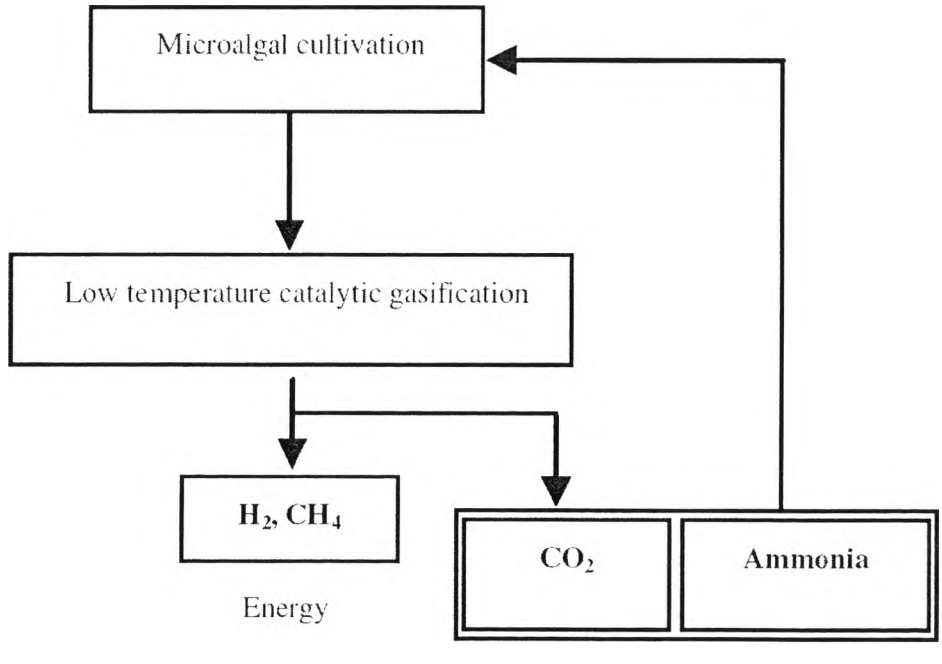


Figure 2.15 Flow diagram of microalgal system for fuel production by gasification (Amin, 2009).

- Pyrolysis

Pyrolysis is the conversion of biomass to bio-oil, syngas, and charcoal at medium to high temperature, from 350 °C to 700 °C, in the absence of oxygen. Table 2.4 outlines the characteristic and expected yield of different modes of pyrolysis. According to Table 2.4, flash pyrolysis is seemed to be a viable technique for future replacement of fossil fuel because of the high biomass-to-liquid conversion ratio that can be achieved.

Table 2.4 Operating parameters and expected yields for pyrolysis processes (Brennan and Owende, 2010)

Mode	Conditions	Liquid (%)	Char (%)	Gas (%)
Flash pyrolysis	▪ Moderate temperature (500 °C) ▪ Short hot vapor residence time (about 1 second)	75	2	13
Fast pyrolysis	▪ Moderate temperature (500 °C) ▪ Moderate hot vapor residence time (about 10 second to 20 second)	50	20	30
Slow pyrolysis	▪ Low temperature (400 °C) ▪ Very long solid residence time	30	35	35

For fast pyrolysis, a main advantage is that it can directly produce a liquid fuel. A conceptual fluidized bed fast pyrolysis system is shown in Fig. 2.16. Since algae usually have high moisture content, a drying process is required. Microalgae are subjected to pyrolysis in the fluidized bed reactor. After that, the result of the reaction flows to a cyclone and then is separated into bio-oil, gas, and char. Gas product can be used for drying the raw material and for the pyrolysis process.

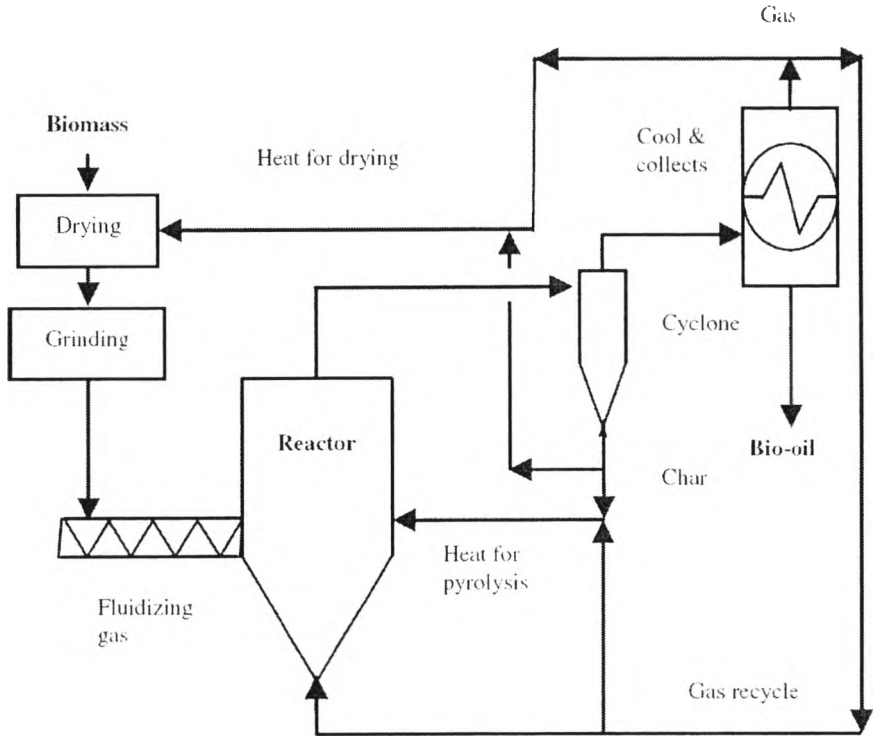


Figure 2.16 Fast pyrolysis process principles (Amin, 2009).

For conventional pyrolysis or slow pyrolysis which was performed under a low heating rate and a long residence time, the longer residence time can cause secondary cracking of the primary product, reducing yield and adversely affecting the biofuel property. In addition, the low heating rate and long residence time may increase the energy input as well. However, pyrolysis oil is acidic, unstable, and viscous. Therefore, upgrading hydrogenation and catalytic cracking are required to lower oxygen content and remove alkali. As a result, the preferred technology is now fast pyrolysis or flash pyrolysis at high temperature with very short residence time.

Miao *et al.* (2004) performed a fast pyrolysis of microalgae in the fluidized bed reactor to produce renewable fuel. He achieved the liquid product yield of 18 % and 24 % from *Chllorella protothecoides* and *Microcystis aeruginosa*, respectively. Miao and Wu (2004) also applied fast pyrolysis to improve the quality of bio-oil from microalgae *Chlorella prothothecoides*. The bio-oil was characterized by much lower oxygen content, with a high heating value, lower density, and lower

viscosity. These properties are comparable to fossil oil. Demirbaş (2006) studied the effect of pyrolysis temperature on the yield of bio-oil from mosses and algae. He founded that the yield increased exponentially with temperature. The bio-oil yield for *Chlorella protothecoides* rose from 5.7 % to 55.3 % as the temperature rose from 525 K to 775 K.

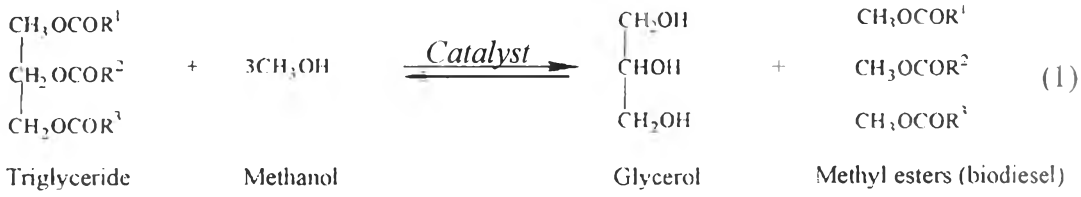
- Liquefaction

Thermochemical liquefaction is a process to convert wet algal biomass into liquid fuel. This process is occurred by the aid of catalyst at low temperature (300 °C to 350 °C) and high pressure (5 MPa to 20 MPa) in the presence of hydrogen to yield bio-oil. The bio-oil is a mixture with a wide molecular weight distribution which contains 10 % to 13 % oxygen and consists of various kinds of molecules. For upgrading, the process also utilizes the high water activity in sub-critical condition to decompose biomass down to shorter and smaller molecular material with a higher energy density.

Dote *et al.* (1994) performed a liquefaction of hydrocarbon-rich microalgae *Botryococcus braunii* to recover liquid fuel with sodium carbonate as a catalyst. A greater amount of oil than the content of hydrocarbon in *Botryococcus braunii* was obtained in a maximum yield of 64 % of dry weight at 300 °C. In a similar study, Minowa *et al.* (1995) converted algal cell of *Dunaliella tertiolecta* with a moisture content of 78.4 % directly into oil by thermochemical liquefaction at 300 °C and 10 MPa. The oil yield was about 37 % on an organic basis. These results indicate that thermochemical liquefaction is a viable option for the conversion of algal biomass-to-liquid fuel.

2.2.4.2 Physicochemical Conversion

After the extraction process, the resulting product algal oil can be converted to biodiesel through a process called transesterification. Transesterification shown in Eq. (1) is a reversible chemical reaction between triglyceride and alcohol in the presence of catalyst to produce methyl esters which are known as biodiesel, and glycerol, which is a high value co-product. In addition, to get high yield of ester, alcohol has to be used in excess (Schuchardt *et al.*, 1998).



According to the process of biodiesel production shown in Fig. 2.17, water is firstly removed from oil by increasing temperature to 120 °C for about 5 minutes to 10 minutes. After that, it is allowed to cool and sodium methoxide is produced by using a stirring catalyst tank with mixed sodium hydroxide and methanol. At the same time, clean oil is heated to 60 °C for 5 minutes and mixed with the sodium methoxide. Then the mixture is transferred to ultrasonic or mixer equipment. This equipment agitates the solution for 30 minutes. After the mixing process, the solution is allowed to cool and separate. The separation process takes approximately from 15 minutes to 60 minutes. The methyl ester (ME) or biodiesel would float on the top layer, while the denser glycerin would be in the bottom layer. Finally, the biodiesel is washed, dried, and then quality tested.

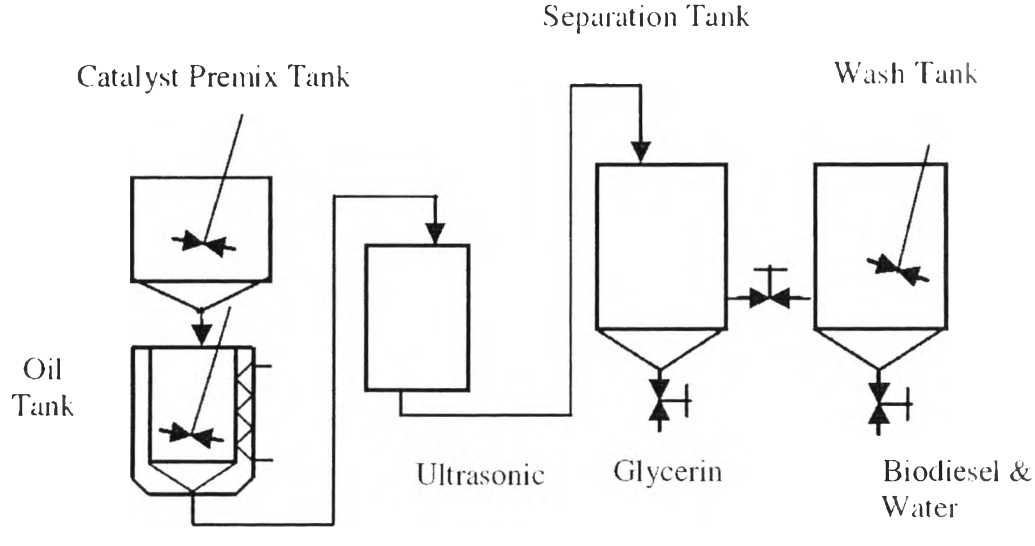


Figure 2.17 Schematic process of biodiesel production (Amin, 2009).

2.2.4.3 Biochemical Conversion

Biochemical conversion proceeds at lower temperature and lower reaction rate. This process is able to offer high selectivity of product. The biochemical process includes alcoholic fermentation and anaerobic digestion.

- Fermentation

Alcoholic fermentation is a conversion of biomass which contains sugar, starch or cellulose into ethanol. Firstly, starch is converted to sugar which is mixed with water and yeast and then kept warm in the fermenter. After that, the yeast breaks down the sugar and converts it to ethanol. Finally, a purification process of ethanol by distillation is required to remove the water and other impurities. In addition, the solid residue from the process can be used for cattle feed or for gasification.

The principle of ethanol production from microalgae is shown in Fig. 2.18. It consists of microalgae cultivation, algal cell harvesting, slurry preparation, fermentation and ethanol separation process. After cultivation and harvesting, the starch of microalgae is released from the cells with the aid of mechanical equipment or enzyme. When the cells begin to degrade, yeast is added to the biomass to start the fermentation. The product of fermentation is ethanol which is drained from the tank and then pumped to a holding tank in order to be fed to a distillation unit.

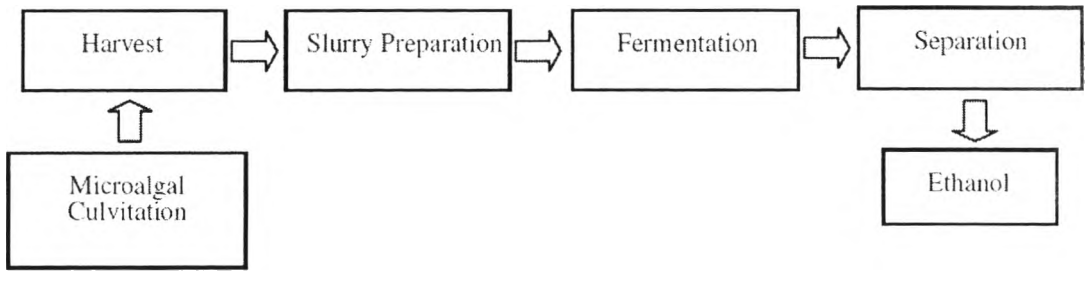


Figure 2.18 Fermentation process of microalgae (Amin, 2009).

Hirano *et al.* (1997) reported that microalgae such as *Chlorella vulgaris* are a good source of ethanol due to the high starch content. Up to 65 % of ethanol conversion efficiency has been recorded. Ueno *et al.* (1998) investigated ethanol production from marine green algae *Chlorococcum littorale* via dark fermentation process. Ethanol, acetate, hydrogen and carbon dioxide were obtained as fermentation products.

- Anaerobic Digestion

Anaerobic digestion (AD) is a conversion of organic waste into biogas in the absence of oxygen. The product gas consists primarily of methane (CH_4) and carbon dioxide (CO_2), with traces of other gases such as hydrogen sulfide (H_2S). The solid and liquid residue from the anaerobic digestion process can be used as compost and fertilizer. This process is appropriate for high moisture content (80 % to 90 %) organic waste, which can be useful for wet algal biomass. The anaerobic digestion process occurs in three sequential stages: hydrolysis, fermentation and methanogenesis. In hydrolysis, the complex compound is broken down into soluble sugar. Then fermentative bacteria convert sugar into alcohol, acetic acid, volatile fatty acid (VFA), and gas containing H_2 and CO_2, which is metabolized into primarily CH_4 (60 % to 70 %) and CO_2 (30 % to 40 %) by methanogenesis.

Yen and Brune (2007) achieved a significant increase in methane production with the addition of waste paper to algal biomass. They obtained double methane production rate compared to anaerobic digestion of pure algal biomass. Additionally, high protein content in algae can result in increase ammonium production, which inhibits anaerobic microorganisms.

2.3 Life Cycle Assessment (LCA)

Achieving sustainable development requires methods and tools to quantify and compare the environmental impacts of each product. Every product has a life, starting with design or development of the product, followed by production and consumption, and finally end-of-life activities including collection, waste disposal, reuse, and recycling (Rebitzer *et al.*, 2004). All of the processes throughout the

product's life result in the environmental impacts due to consumption of resources, generation of wastes, and emission of substances. Fig. 2.19 shows a simplified scheme of the product life concept which is usually referred to as a ''life cycle''.

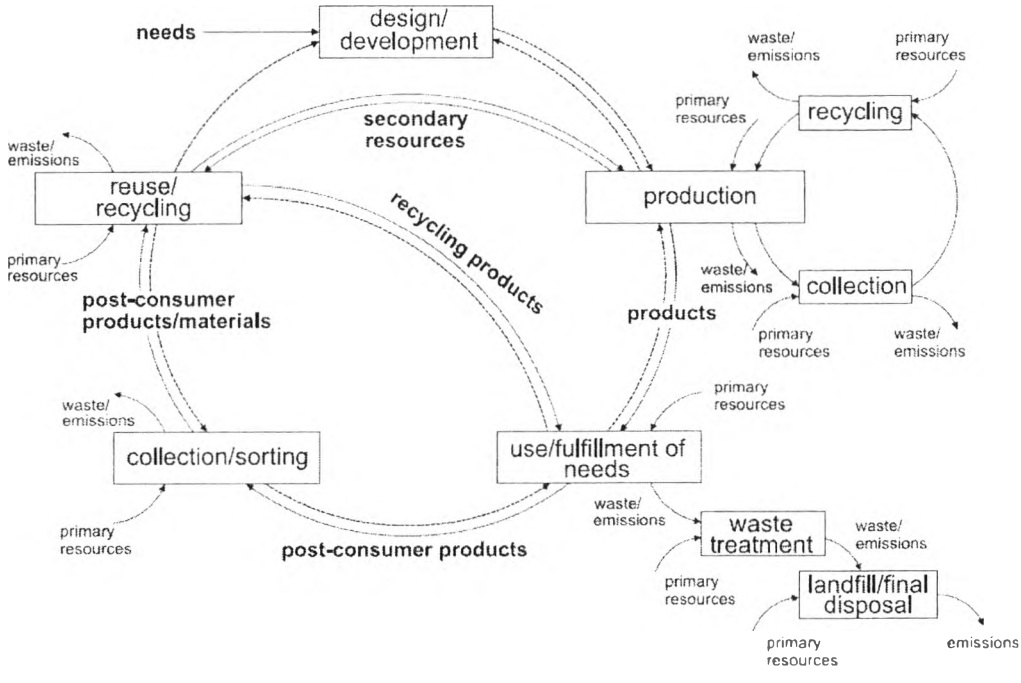


Figure 2.19 Schematic representation of a generic life cycle of a product (Rebitzer *et al.*, 2004).

2.3.1 History of LCA

Life cycle assessment (LCA) was developed around the late 1960s and early 1970s, a period in which oil crisis and environmental issue became a broadly public concern (Russell *et al.*, 2005). It became obvious that the petroleum resource will last forever and the exponential economic growth might result in both environmental and social disaster. Therefore, the concept of energy and environmental analysis, which had been conducted for several years, was later broadened to encompass resource requirement, waste generation, and emission loading.

2.3.1.1 Decades of Conception (1970-1990)

Decades of conception are the beginning period of LCA with widely diverging approaches, terminologies, and results. LCA was performed by using different methods and without a common theoretical framework in this period. In 1969, the first LCA study was conducted by Midwest Research Institute (MRI) in the United States for the Coca Cola Company about different beverage containers (Guinée *et al.*, 2010). In Europe, early LCA-like work started soon afterwards in Germany, England, Switzerland, and Sweden (Klöpffer, 1997). The main topic was the comparative analysis of packaging under environmental aspects, especially with regard to resource conservation and energy saving. The Swiss Federal Laboratories for Materials Testing and Research (EMPA) published a report that presented a comprehensive list of the data needed for LCA study in 1984 (Guinée *et al.*, 2010). In the late 1980s, not only packaging, but also many other systems were gradually studied and analyzed from "cradle to grave" (Klöpffer, 1997). Then a shift can be observed from comparative studies toward system optimization and benchmarking. It has been recognized that a large share of the environmental impacts of many products is not in the utilization of the product, but in its production, transportation, and disposal process.

2.3.1.2 Decade of Standardization (1990-2000)

The number of LCA research works and handbooks has been produced since the beginning of the 1990s (Russell *et al.*, 2005). Many scientific journal papers have also been published. In the early 1990s, through its North American and European branches, the Society of Environmental Toxicology and Chemistry (SETAC) shaped the development of LCA in a series of important workshop resulting in the "Code of Practice" in 1993 (Perriman, 1993; Ekvall, 2005). This document describes a procedural framework for LCA and also includes some methodological recommendations. Next to SETAC, the International Organization of Standardization (ISO) has been involved in LCA since 1994 in order to start a standardizing process (Arvanitoyannis, 2008). Therefore, this period can be characterized as a period of convergence between SETAC's coordination and ISO's standardizing activity.

Nowadays, LCA becomes increasingly important due to awareness of the environmental impacts caused by products. Governments and corporations all over the world also encouraged the use of LCA (Reap *et al.*, 2008). As a result, LCA has become a core element in environmental policy as well as voluntary action.

2.3.2 Definition of LCA

Two of the most widely accepted definitions of LCA are presented below as they have been chronologically formulated to date.

2.3.2.1 Definition of LCA by SETAC

"*The life cycle assessment is an objective process to evaluate the environmental burdens associated with a product, process or activity by identifying and quantifying energy and materials used and wastes released to the environment; to assess the impact of those energy and material uses and releases to the environment; and to identify and evaluate opportunities to effect environmental improvements. The assessment includes the entire life cycle of the product, process or activity, encompassing extracting and processing raw materials; manufacturing, transportation and distribution; use, re-use, maintenance; recycling; and final disposal.*"

2.3.2.2 Definition of LCA by ISO 14040

"*LCA is a technique for assessing the environmental aspects and potential impacts associated with a product by:*

1. *Compiling an inventory of relevant inputs and outputs of a product system;*
2. *Evaluating the potential environmental impacts associated with those inputs and outputs;*
3. *Interpreting the results of the inventory analysis and impact assessment phases in relation to the objectives of the study.*

LCA studies the environmental aspects and potential impacts throughout the product's life (i.e. cradle to grave) from raw materials acquisition through production, use and disposal. The general categories of environmental

impacts needing consideration include resource use, human health, and ecological consequences".

2.3.3 LCA Methodology

The Society of Environmental Toxicology and Chemistry's (SETAC) "Code of Practice", which can be illustrated by the famous SETAC triangle shown in Fig. 2.20, originally distinguished four methodological components within LCA: goal and scope definition, inventory analysis, impact assessment, and improvement assessment (Rebitzer *et al.*, 2004).

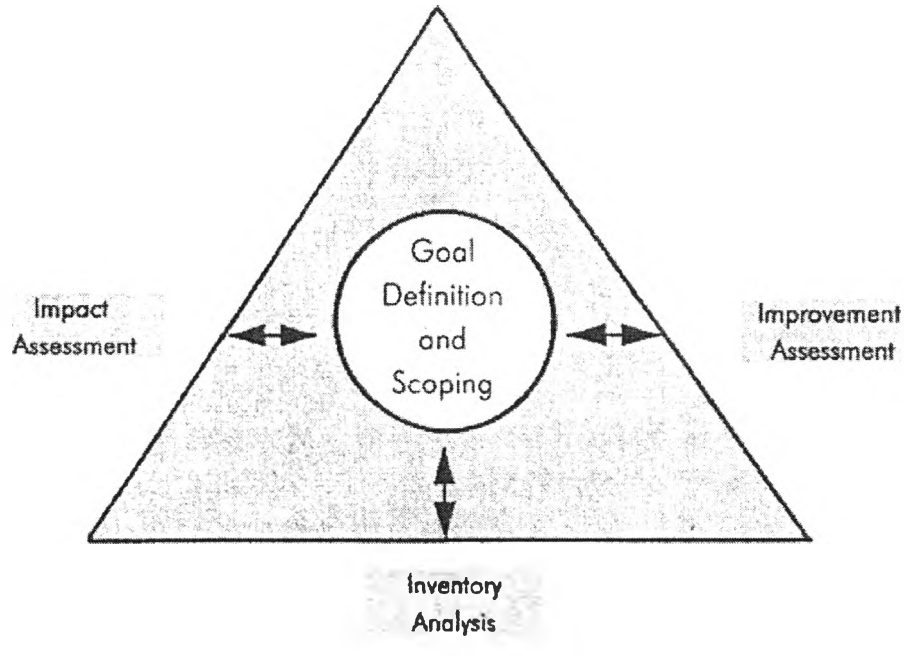


Figure 2.20 SETAC triangle (Klöpffer, 1997).

According to ISO 14040, improvement assessment is no longer regarded as a phase on its own, but rather as having an influence throughout the whole LCA methodology (Rebitzer *et al.*, 2004). Moreover, interpretation which is a phase that interacts with all other phases in the LCA has been introduced as illustrated in Fig. 2.21. In practice, LCA is often conducted iteratively, repeating some of the phases several times in order to eliminate uncertainties (Widheden and Ringström, 2007).

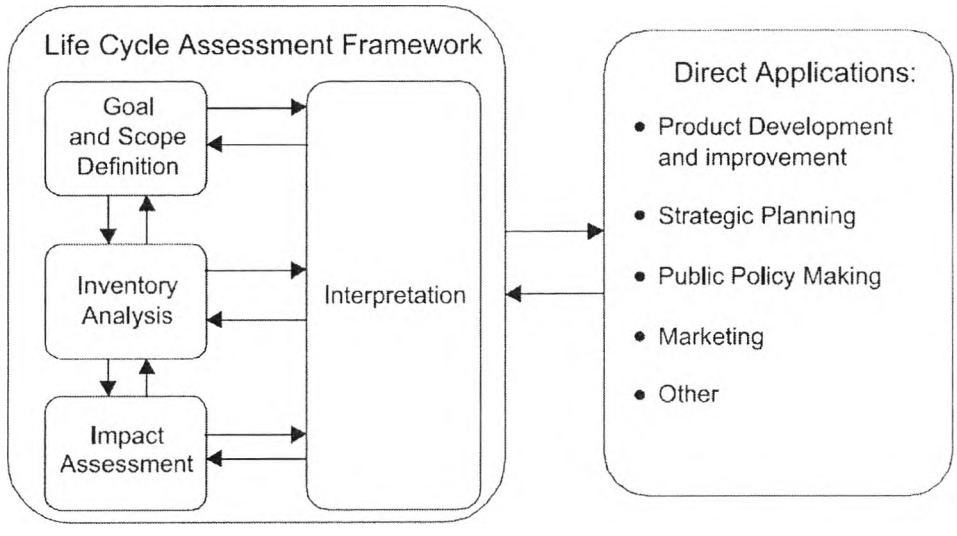


Figure 2.21 General methodological framework of LCA.

2.3.3.1 Goal and Scope Definition

Goal and scope definition phase in LCA is a planning phase which attempts to set the extent of the inquiry and provides the following descriptions of the product system (Widheden and Ringström, 2007):

- Objectives

The ISO 14040 standard states that the goal definition shall unambiguously state the intended application, the reason for carrying out the study and the intended audience.

- System Boundaries

The scope defines the boundary of the study, including the products and unit processes for which data are to be collected, and the geographical locations and technological levels of these processes, resulting in a strategy for data collection.

- Functional unit

Functional unit, which is a basis for calculation, is a measure of performance that the system delivers and also enables alternative products to be compared and analyzed.

- Assumptions and limitations

Assumptions and limitations are very important to each LCA in case of the internal consistency of the study.

- Allocation methods

Allocation methods are used to partition the environmental load of a process when several products or functions share the same process.

- Impact categories

Impact categories represent environmental issues of concern to which LCI results may be assigned. The impact categories which are selected in each LCA study have to be able to describe the impacts caused by the products being considered or the product system being analyzed.

2.3.3.2 Inventory Analysis

Life cycle inventory (LCI) is a methodology for quantifying the flow of material and energy attributable to a product's life cycle (Rebitzer *et al.*, 2004; Reap *et al.*, 2008). The implication of the inventory analysis is that all activities related to the production of one functional unit have to be analyzed concerning about raw material, intermediate, product, usage, and waste removal (Klöpffer, 1997). An LCI analysis includes (Widheden and Ringström, 2007):

- Flowchart

Flowchart represents the product system according to the system boundary decided in the goal and scope definition. All material flows are traced from the extraction of raw materials to their release into the environment. All transport operations are also included.

- Data

Data for all activities in the product system are collected, followed by data quality assessment and documentation of the collected data. Both numerical and qualitative/descriptive data need to be collected. The numerical data include: input (e.g. raw material), output (e.g. product and co-product), and emission to air, water, and soil as well as waste. The qualitative/descriptive data are for example geographical location of process, technology of process, where inflows come from and outflows go to, how and when emissions were measured and their uncertainty, etc.

- Calculation based on functional unit.

The numerical data have to be recalculated to fit the functional unit and summarized into a list of parameters representing the entire life cycle of the product. The result of the inventory analysis is the inventory table which is a list of all inputs and outputs per functional unit.

2.3.3.3 Impact Assessment

Since life cycle inventory (LCI) provides hundreds of parameters, it is difficult to draw any conclusions from LCI. Therefore, a formal impact assessment has to be performed. Life cycle impact assessment (LCIA) provides indicators and the basis for analyzing the potential contributions of the resource consumptions, waste generations, and emissions in an inventory analysis to a number of potential impacts (Rebitzer *et al.*, 2004). The result of the LCIA is an evaluation of a product life cycle, on a functional unit basis, in terms of several impact categories. According to the ISO 14040 standard for LCIA, the following steps have to be performed in order to convert the inventory data into the environmental impact estimates (Widheden and Ringström, 2007):

- Impact category definition

Some baseline examples of impact category considered in most of the LCA studies are illustrated in Table 2.5.

Table 2.5 Baseline examples of impact category (Iuga, 2009)

Impact category	Category indicator	Characterization model	Characterization factor
Abiotic depletion	Ultimate reserve, annual use	Guinee and Heijungs 95	ADP[9]
Climate change	Infrared radiative forcing	IPCC model[3]	GWP[10]
Stratospheric ozone depletion	Stratospheric ozone breakdown	WMO model[4]	ODP[11]
Human toxicity	PDI/ADI[1]	Multimedia model, e.g. EUSES[5], CalTox	HTP[12]
Ecotoxicity (aquatic, terrestrial, etc)	PEC/PNEC[2]	Multimedia model, e.g. EUSES, CalTox	AETP[13], TETP[14], etc
Photo-oxidant formation	Tropospheric ozone formation	UNECE[6] Trajectory model	POCP[15]
Acidification	Deposition critical load	RAINS[7]	AP[16]
Eutrophication	Nutrient enrichment	CARMEN[8]	EP[17]

[1] PDI/ADI Predicted daily intake/Aceptable daily intake

[2] PEC/PNEC Predicted environmental concentrations/Predicted no-effects concentrations

[3] IPCC Intergovernmental Panel on Climate Change

[4] WMO World Meteorological Organization

[5] EUSES European Union System for the Evaluation of Substances

[6] UNECE United Nations Economic Commission For Europe

[7] RAINS Regional Acidification Information and Simulation

[8] CARMEN Cause Effect Relation Model to Support Environmental Negotiations

[9] ADP Abiotic depletion potential

[10] GWP Global warming potential

[11] ODP Ozone depletion potential

[12] HTP Human toxicity potential

[13] AETP Aquatic ecotoxicity potential

[14] TETP Terrestrial ecotoxicity potential

[15] POCP Photochemical ozone creation potential

[16] AP Acidification potential

[17] EP Eutrophication potential

- Classification

Assignment of LCI result parameters to their respective impact categories, e.g., classifying CO_2 emission to global warming.

- Characterization

Modeling LCI impacts within impact categories using science-based conversion factors, e.g., modeling the potential impact of CO_2 and methane on global warming.

- Normalization

Relating the characterization results to a reference value in order to be compared, e.g. relating the impacts of the studied product to the impacts of the total amount of pollutants emitted in a region.

- Grouping

Sorting and possibly ranking of the indicators, e.g. sorting according to global, regional or local impact or sorting according to high, medium or low priority.

- Weighting

Aggregation of characterization results across impact categories into one total environmental impact value in order to generate a single score and also emphasize the most important potential impact.

2.3.3.4 Interpretation

Life cycle interpretation, which occurs at every stage in an LCA, is a process of assessing results in order to draw conclusions. It is a critical evaluation of the whole LCA using mathematical tool such as sensitivity analysis and dominance analysis (Klöpffer, 1997). For example, if two product alternatives are compared and one alternative shows higher consumption of resource and emission of CO_2, an interpretation purely based on the LCI and LCIA data can be conclusive. In other words, the interpretation phase is desirable to prioritize areas of concern within

a single life cycle study (Rebitzer *et al.*, 2004). Moreover, it also links the LCA with the applications which are not part of LCA. The interpretation should include results, conclusions, limitations, and recommendations in accordance with goal and scope of the study (Widheden and Ringström, 2007).

2.3.4 Application of LCA

As mentioned, LCA is a method to help quantify and evaluate the potential environmental impacts of product. This implies that LCA can be applied to any applications where the environmental impacts of the complete or part of the product's life cycle are of interest. For instance, LCA can be used in order to identify significant environmental aspects and also provide a baseline for decision about product improvement in product development project.

Governmental organizations, non-governmental organizations, and industries have applied LCA in a wide variety of sectors, either autonomously or with the help of research institutes or consultants (Rebitzer *et al.*, 2004). For example, LCA can be used for identifying and improving waste treatment strategy in the nation level. Another application area is marketing. The LCA results can be used to communicate the environmental benefits of a product to customers, e.g., through the LCA-based communication tool environmental product declaration (EPD) (Widheden and Ringström, 2007). It also shows that changes in consumer behavior are ultimately the most crucial factors for reducing the environmental impacts associated with products.

2.3.5 LCA Studies of Algal Biofuel

Many research works have been conducted to investigate the utilization of algal biomass as an energy feedstock for the production of different types of biofuel: biodiesel, bioethanol, biogas, and biohydrogen (Singh and Olsen, 2011). The different life cycle stages are presented in Fig. 2.22.

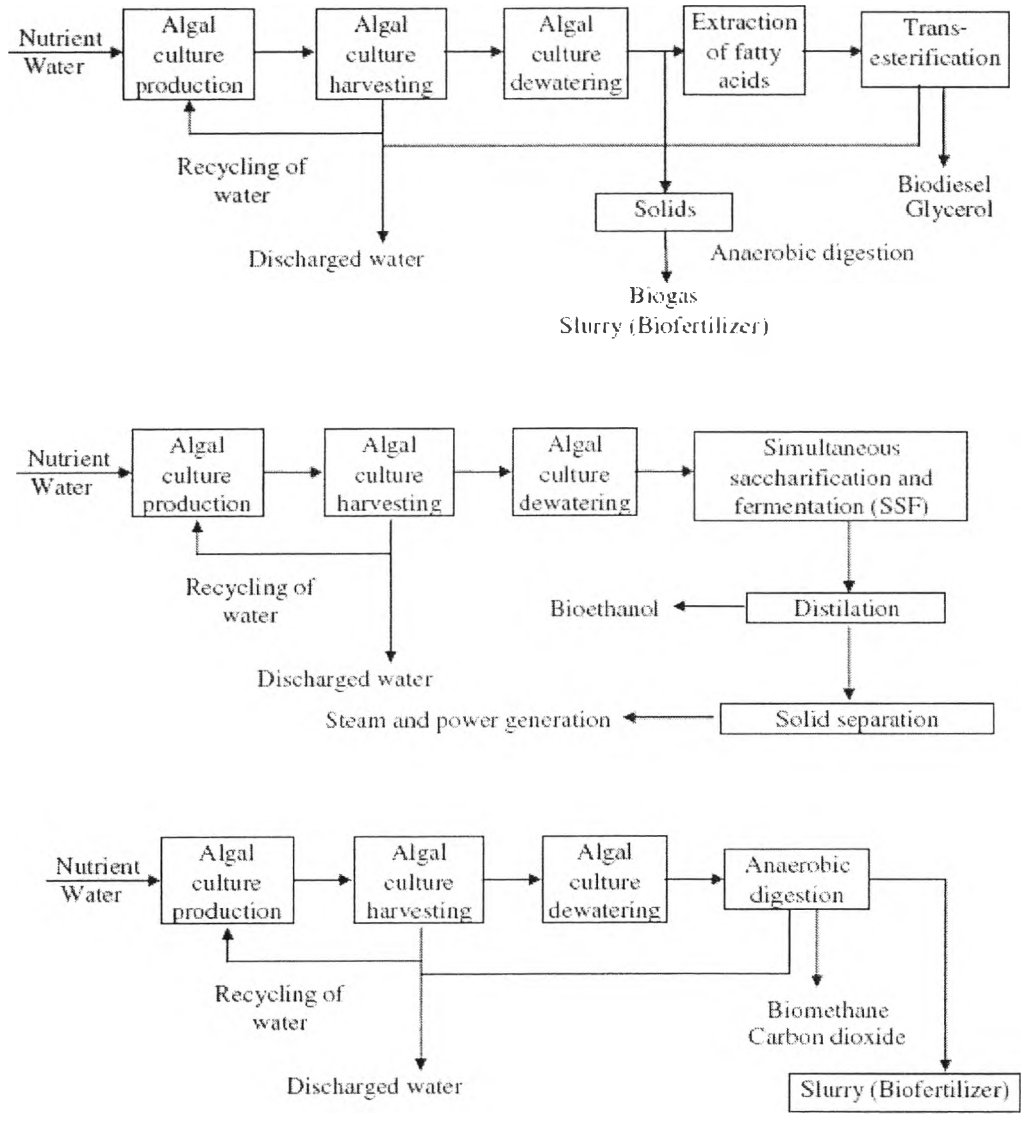


Figure 2.22 Life cycle stages of biodiesel, bioethanol, and biomethane production from algal biomass (Singh and Olsen, 2011).

In one of LCA studies on evaluation alternative energy routes, Rodríguez *et al.* (2011) concluded that LCA based indicator is an effective tool to compare alternative energy routes in terms of environmental impacts towards different products. Aresta *et al.* (2005) carried out an LCA for evaluating the potential of utilizing macroalgae to enhance CO_2 fixation and biofuel production. The result demonstrates that the net energy gain depends on the conversion technology. However, macroalgae can recycle carbon via CO_2 fixation which is a

potential energy benefit. Additionally, macroalgae can use the effluent water as a source of nutrient. In this study, different techniques (i.e. supercritical CO_2, organic solvent, and pyrolysis) were also used for the extraction of biofuel. Supercritical CO_2 appears to be the most effective way.

Sander and Murthy (2010) performed a well-to-pump LCA to investigate the overall sustainability and net energy balance of an algal biodiesel process. The objective is to provide baseline information for this process. The result showed that the largest energy input is in the drying process of the algal cake by using natural gas. Thermal dewatering process also requires high amount of fossil fuel derived energy (3,556 kJ/kg of water removed). While CO_2 emissions are positive for the centrifuge process, while they are negative for the filter press process. Additionally, 20.4 m^3 of wastewater per functional unit is lost from the growth ponds during the 4-day growth cycle due to evaporation.

Campbell *et al.* (2011) recently conducted a comparative LCA study of a production system designed for Australian conditions to compare biodiesel production from microalgae in ponds (with three different scenarios for carbon dioxide supplementation and two different production rates) with canola and ULS (ultra-low sulfur) diesel. Comparisons of greenhouse gas (GHG) emissions (g CO_2-eq/t km) and costs ($/t km) are given. Algae GHG emissions (-27.6 to 18.2) compare very favorably with canola (35.9) and ULS diesel (81.2). However, costs are not so favorable, with algae ranging from 2.2 to 4.8, compared with canola (4.2) and ULS diesel (3.8). This highlights the need for a high production rate to make algal biodiesel economically attractive. Additionally, new technology related to biofuel industry should be introduced to the system in order to reduce the economic and energy cost of harvesting and processing the algae, making it even more attractive from both GHG emission and economic point of view.

Yang *et al.* (2011) recently examined a life cycle water and nutrients usage of biodiesel production from microalgae. This study quantifies the water footprint and nutrients usage during the production. The influences of water type as well as operation with and without recycling were analyzed. The results shown in Fig. 2.23 highlight the necessity of recycling harvest water and using seawater or wastewater as a water source. If freshwater is used without recycling, 3726

kilograms of water, 0.33 kilogram of nitrogen, and 0.71 kilogram of phosphate will be required to generate a kilogram of biodiesel. However, if harvest water is recycled, the water and nutrients usage will be reduced by 84 % and 55 %, respectively. Moreover, no need of all nutrients except phosphate and 90 % water reduction can be achieved by applying seawater or wastewater to the process.

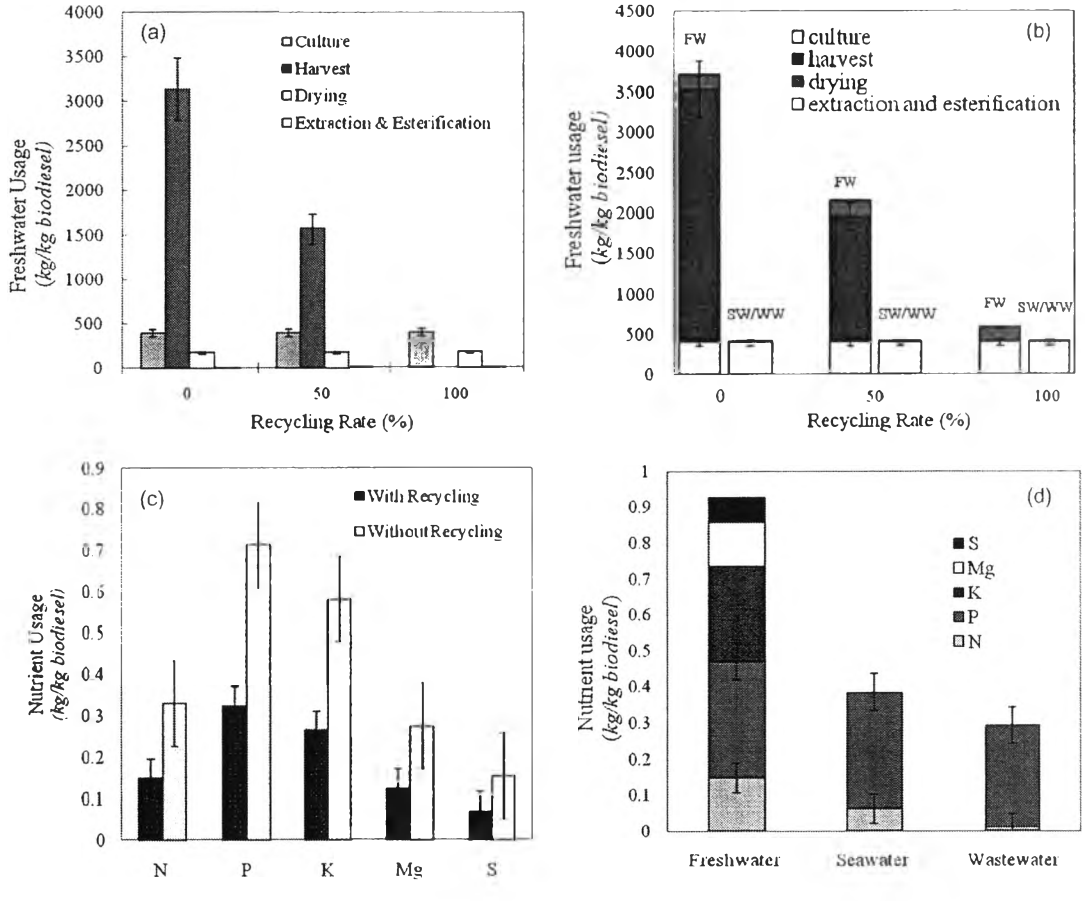


Figure 2.23 For producing 1 kg biodiesel from microalgae, (a) water footprint using freshwater (FW) medium; (b) water footprint using seawater (SW) or wastewater (WW) as the culture medium; (c) life cycle usage of nutrients in FW medium with/without harvest water recycling; and (d) life cycle usage of nutrients in SW or WW medium with 100 % harvest water recycling (Yang *et al.*, 2011).

Lardon *et al.* (2009) provided an analysis of the potential environmental impacts of biodiesel production from microalgae *Chlorella vulgaris*. A comparative LCA study has been undertaken to assess the energy balance and the

potential environmental impacts of the whole process chain, from the biomass production to the biodiesel combustion. Two different culture conditions, nominal fertilizing or nitrogen starvation, as well as two different extraction options, dry or wet extraction, have been experimented. Eventually, the best scenario, which is low nitrogen and wet extraction, has been compared to the first generation biodiesel and conventional diesel as shown in Fig. 2.24. The result confirms the potential of microalgae as an energy source but highlights the imperative necessity of decreasing the energy and fertilizer consumption. Therefore, control of nitrogen quantity and optimization of wet extraction seem to be valuable options. This study also emphasizes the potential of anaerobic digestion of oilcake as a way to reduce external energy demand and to recycle a part of mineral fertilizer.

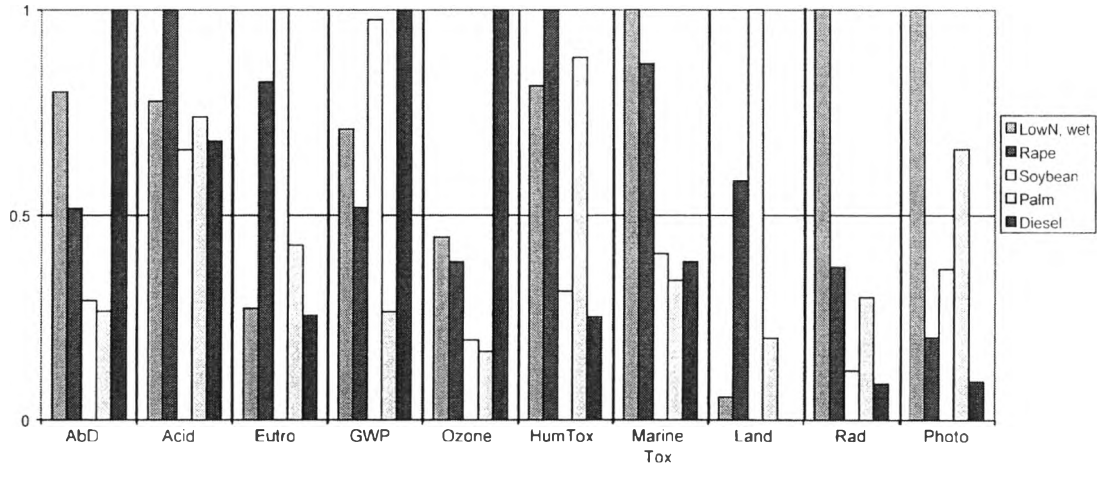


Figure 2.24 Comparison of impacts generated by the combustion of 1 MJ of different biodiesel and conventional diesel (Lardon *et al.*, 2009).

Jorquera *et al.* (2010) performed an analysis of the energy life cycle for biomass production using oil-rich microalgae *Nannochloropsis* sp. This is a comparative study among raceway pond, tubular, and flat-plate photobioreactor for algal cultivation. The net energy ratio (NER) for each process was calculated. The results showed that the use of horizontal tubular photobioreactor is not economically feasible (NER < 1) while NER of both raceway pond and flat-plate photobioreactor is greater than 1 (NER > 1) which is considered economically feasible. Moreover, the

NER for raceway pond and flat-plate photobioreactor could be raised to significantly higher values if the lipid content of the biomass were increased.

Stephenson *et al.* (2010) used an LCA to investigate the global warming potential (GWP) and fossil-energy requirement for biodiesel production from the freshwater algae *Chlorella vulgaris*, grown using flue gas from a gas-fired power station as a carbon source. They also considered a two stage method for cultivation, whereby the cells were initially grown to a high concentration of biomass under nitrogen-sufficient condition, before the supply of nitrogen was discontinued in order to let them accumulate triacylglyceride. Cultivation in typical raceway and air-lift tubular bioreactor was investigated. The results showed that cultivation in typical raceway is significantly more environmentally sustainable than in closed air-lift tubular bioreactor. Based on the basis of the net energy content, algal biodiesel cultivated in raceway pond has GWP lower than fossil-derived diesel approximately 80 %. While GWP of algal biodiesel cultivated in air-lift tubular bioreactor is significantly greater than an energetically equivalent amount of fossil-derived diesel.

Luo *et al.* (2010) calculated a life cycle energy and greenhouse gas emissions for an ethanol production process, using cyanobacteria (blue-green algae). The results show that the energy required for ethanol separation increases rapidly for low initial concentration of ethanol, and ethanol purification process is a major consumer of energy and a significant contributor to the carbon footprint. The optimum value of initial ethanol concentration ranges from 0.5 wt % to 5 wt %. Based on an energy equivalent basis, the net life cycle energy consumption, excluding photosynthesis, ranges from 0.55 MJ down to 0.20 MJ, and the net life cycle greenhouse gas emissions range from 29.8 g CO_2 equivalent down to 12.3 g. CO_2 equivalent. This ethanol fuel represents 67 % and 87 % reduction in the carbon footprint compared to gasoline. However, unlike other biofuel systems, there is little waste biomass available to provide process heat and electricity in order to offset the energy requirement.

Collet *et al.* (2011) recently performed an LCA of biogas production from microalgae *Chlorella vulgaris*. They focus on a simplified process where methane is the only recovered product. The results highlight the main bottleneck in this process. These results show that the impacts generated by the production of

methane from microalgae are strongly correlated with the electricity consumption as shown in Fig. 2.25. However, progresses can be achieved by decreasing the mixing cost and circulation between different production steps, or by improving the efficiency of the anaerobic process under controlled conditions.

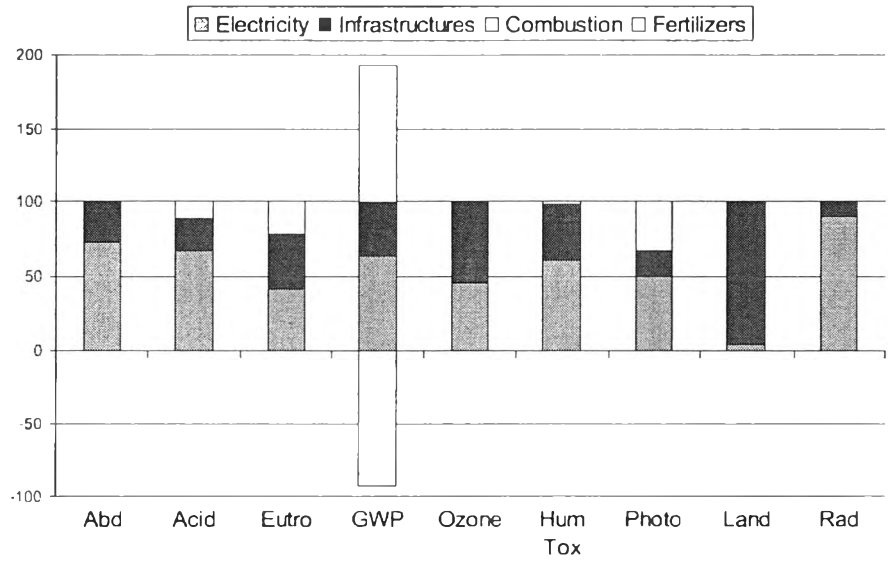


Figure 2.25 Processes contribution of the production of 1 MJ by algal methane combustion (Collet *et al.*, 2011).

In another study, Romagnoli *et al.* (2011) carried out an LCA of biohydrogen production from photosynthesis processes to increase the production yield and optimize the process in order to lessen the negative impacts on the environment and climate change. The analysis gives the possibility to compare different biohydrogen production approaches using different photosynthesis methods and identify the environmental hot spots of the whole process. The results show that using biohydrogen to produce electricity offers more environmental benefits than using a fossil fuel. Moreover, if sulfur deprivation is applied to the production, some CO_2 emissions from fossil fuel can be avoided. At this stage, the positive result can be clearly seen in terms of the climate change and human health categories.