CHAPTER II
LITERATURE REVIEW

2.1 Microemulsion Biofuel

Microemulsion-based biofuel is an emerging biofuel production technology, produced by microemulsification of mixed liquid fuels such as vegetable oils and bio-alcohols. Therefore, the microemulsion fuels have been considerable interest in an alternative fuel to replace petroleum-based transportation fuels. Microemulsion biofuels can be typically formulated by stabilizing polar phase (e.g., ethanol) in reverse micelles which all disperse in non-polar phase (vegetable oil and/or diesel blend) which known as water in oil microemulsion formation. The unique characteristics of microemulsion fuel are isotropic, transparent, thermodynamically stable mixtures consisting of non-polar phase, polar phase and stabilized by an appropriate surfactant system in sufficient concentration. Furthermore, microemulsion biofuel contains about at least five components (vegetable oil/diesel, ethanol and surfactant and/or cosurfactant). Surfactant is one of the key parameters to formulate the microemulsion fuel with single phase system. Several surfactants have been used for formulating of microemulsion based biofuels from vegetable oil feedstock. Selecting an appropriate surfactant is a challenge for formulating thermodynamically stable mixture of microemulsion fuel (Arponpang *et al.*, 2014).

2.2 Benefits of Microemulsion Biofuel

Microemulsion biofuel production which is the concept of blending vegetable oil and/or diesel with ethanol, has been receiving interest in order to overcome the limitations of biodiesel production by transesterification process. Microemulsions are homogenous, transparent, thermodynamically stable colloidal dispersions of immiscible water and oil combination between surfactant with co-surfactant (Al Sabagh, 2012). It has been receiving increased attention for biofuel production since this technique can reduce the high viscosity of vegetable oil without large amount of wastewater (Balat, 2008)

2.3 Raw Materials Used in Microemulsion Formulation

2.3.1 Surfactant

Theoretically, surfactants (*Surf*ace *act*ive *agent*) contain two parts (hydrophilic and hydrophobic part) in a molecule or known as an amphiphile molecule; hydrophilic part soluble in polar phase (e.g. water, ethanol) and hydrophobic part soluble in the non-polar phase (e.g. oil) (Rosen, 1988). The polar part of the surfactant molecule (e.g., SO_4 -, COOH-, EO-ethylene oxide group) is referred as head, and the non-polar part of the molecule is referred as a tail. The polar nature of the head group of surfactants varies from non-ionic to ionic character. Depending on the nature of head group, the surfactants are classified into four types; anionic, cationic, non-ionic, and zwitterionic surfactants. Surfactant monomer and micelle structures are shown in Fig. 2.1 (Arpornpong *et al.*, 2014).

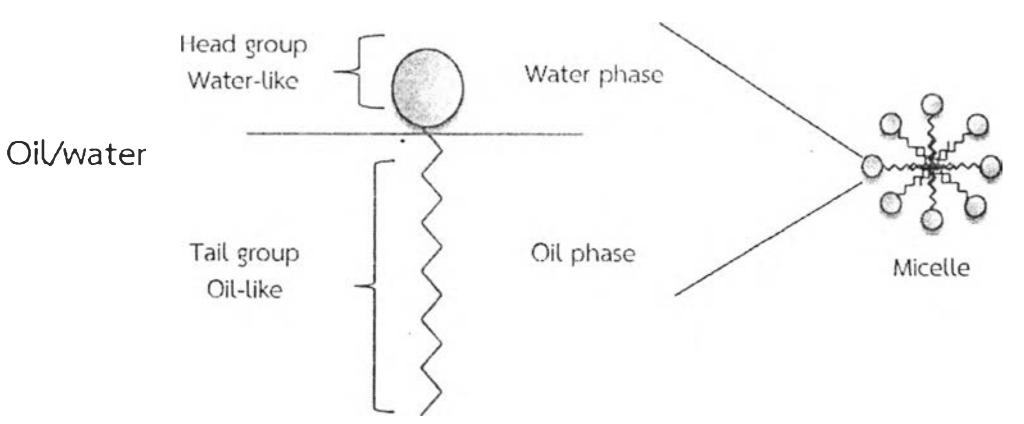


Figure 2.1 Structure of surfactant and micelle (Arpornpong *et al.*, 2014).

2.3.2 Cosurfactant

Short-chain alcohols or alkanols (C_2-C_{12}) act as cosurfactants, directly influencing the properties of the aggregates, while alcohols with longer hydrocarbon chains perform as cosolvents, altering the properties of the solvent (Naresh *et al.*, 2005).

Short-chain alcohols were found to concentrate in the surfactant layer of the aggregates, replacing surfactant molecules and leading to a strong decrease of the aggregation number. On the other hand, only a small number of alcohol molecules with longer chain length were found in the aggregates, leading to a slight increase in the aggregation number.

2.3.3 Alkanol as Fuel Additives

The use of ethanol in bio-based fuel has been receiving much attention since ethanol can be converted from renewable resources. In general, ethanol can be produced from petrochemical based process with low cost. In microemulsion biofuel system, ethanol acts as a viscosity reducer. Bioethanol, on the other hand, can be produced from sugar-based alcoholic fermentation derived from plant or biomass materials (e.g., corn, cassava, sugar cane, molasses and agricultural residuals). The use of ethanol in diesel blend is known as diesohol or ethanol diesel blend. Although blending diesel fuel with ethanol has notable advantages in terms of renewable nature as well as emission reduction, the major problem is that ethanol is insoluble in diesel over a wide range of temperatures. Therefore, a suitable emulsifying agent or surfactant is required to formulate an emulsion of homogeneous mixture.

However, the critical issues of using ethanol in either diesel blend or microemulsion biofuel blend have been debating. Because ethanol has lower heating value than those of regular diesel as well as possess a very low cetane number that can reduce overall cetane level in ethanol-diesel blends. To overcome this problem, butanols are required in order to improve not only phase separation of microemulsion system but also its energy content. Due to butanol having higher energy configuration and higher immiscibility than ethanol, it has been being an interest for cetane enhancing additives in diesel fuel. Furthermore, similar to bio-ethanol, butanol can be derived from biomass or agricultural crop (Arpornpong *et al.*, 2014).

In addition, bioethanol is usually made by fermentation of plant materials. First generation bioethanol is produced from various common crops such as sugar cane, sweet sorghum and sugar beet. It can also be produced from starchy crops such as wheat, potatoes, cassava and maize. Second generation bioethanol (Cellulosic bioethanol) is derived from non-food sources, such as trees, grasses and agricultural residues. More specifically, the production process of bioethanol from lignocellulosic materials consists of the feedstock pre-treatment, hydrolysis, fermentation, product separation by distillation and post-treatment of the liquid fraction (Balat, 2008). Ethanol can be used as a fuel for vehicles in its pure form as a gasoline additive to increase octane number and improve vehicle emissions.

2.3.4 Vegetable Oils

2.3.4.1 Palm Oil Production

Palm oil presents an attractive feedstock for biodiesel production compared to other feedstock. Because of its high oil yield (averagely 8.6 tons per hectare of land), it is almost three times more than that of coconut, 12 times more than that of soybean oil yield, and seven times more than that of rapeseed (Schmidt, 2007).

Currently, palm oil is the second largest edible oil source after soybean oil, which forms approximately 34 percent of the global vegetable oil supply (Schmidt, 2007). In 2009, both palm oil and palm kernel oil accounted for 5 percent of the total cultivated land for vegetable oil production globally. In year 2010, the global palm oil production was 47.9 million tons of which 11 percent were used for biodiesel production. For the production in year 2010, Malaysia and Indonesia together contributed about 87 percent of the total palm oil produced in the world , accounting for 19.5 and 22.5 million tones, respectively (MPOB, 2010).

In Thailand, palm oil production has been accelerated in recent years. Currently, fourteen bio-diesel plants, twelve oil palm refineries and more than sixty oil palm crushing mills are in operation in Thailand. In year 2010 production of crude palm oil (CPO) reached 1,287,509 tons of which 65,942 tons were exported. Exports made up 5.1 percent of total production. This is a usual share for the palm oil exported from Thailand. As the average annual export of palm oil has remained at around 6 percent over the last twenty years, peak occured at around 20 percent of total production in a few specific years (Singh *et al.*, 2013).

Fig. 2.2 illustrates the production of biodiesel from various feedstocks in which oil palm is mainly used for biodiesel production in year 2010.

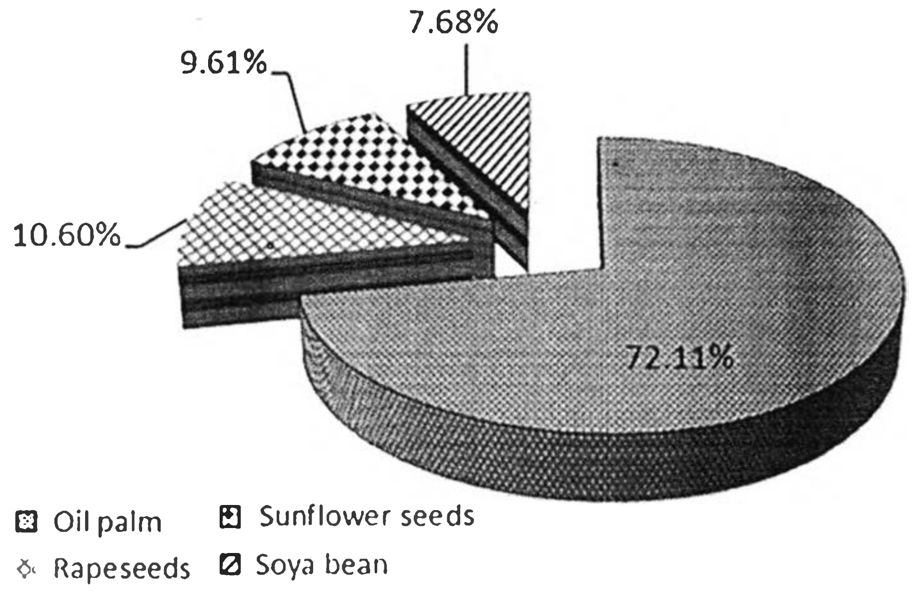


Figure 2.2 Biodiesel production from various feedstocks commonly used in the world (Singh *et al.*, 2013).

2.3.4.1.1 Oil Palm Plantation

More than 70 percent of the oil palm plantations are located in the southern provinces of Thailand such as Krabi, Chumporn and Suratthani where the climate conditions are suited for growing oil palm. Cultivation of oil palm consists of two major stages i.e. growing at the nursery and planting in the field. In the nursery, the seeds are sown in small polyethylene bags until the seedlings are approximately three to four months old. After that, the seedlings are transferred to larger bags until they are 12 to13 months old and ready for planting.

Oil palm starts bearing fruits after 2.5 to 3 years and the first harvest is possible after five years. Estimated plant lifetime is more than 30 years, however, it is generally replanted after 25 years because it starts getting to tall for convenient harvesting. The plantation has occupied about 131 to137 trees per hectare. The average fresh fruit bunches (FFB) yield in Thailand is 17.5 ton /ha/yr. The applied fertilizers are 151, 72 and 307 kg /ha/yr for N, P_2O_5 and K_2O fertilizer, respectively. Herbicides such as glyphosate and paraquat are applied at 4.8 and 1.6 kg ha/yr, respectively.

In addition, biomass residues such as fronds and trunks are also generated in the plantation. Each palm tree produces 20 to 30 fronds per year. The fronds cut down regularly from the palm trees over the service life of the plantation, are estimated to be around 12 ton of dry matter per hectare and year. However, the trunks will be available only one time (when cutting down for re-planting) over the 25 years; the total dry mass of these trunks was estimated to be around 57 ton / ha/yr. (Silalertruksa, 2012).

The production of FFB involves six main processes which are summarized in Fig. 2.3. The planning stage involves the feasibility studies of the proposed area for plantation.

Oil palm nursery proceeds after confirmation of the suitability of area for plantation which is normally endorsed by respective bodies for development. The seedlings are raised in polybags as nursery for about a year with adequate irrigation with manuring.

Other field maintenance practices include pruning, pest and disease control, and mulching. After 24 to 30 months of transplanting depending on the nutritious value of the soil, harvesting of FFB may be due. Normally, harvesting is done manually with chisels and sickles mounted on bamboo or aluminum poles.

The FFB are then sent to the oil mill for oil extraction. In order to ensure the amount of free fatty acid (FFA) content of the oil, handling of FFB after harvesting must be done in a way to reduce bruises on the fruits. Also, since the quality of the oil produced depends on the time interval between harvesting and sterilization (the first stage of milling), FFB must be transported as soon as possible after harvesting and the distance from plantation to milling site must be close. Therefore, most oil mills are located near the cultivation area to minimize the cost of transportation (Singh *et al.*, 2013).

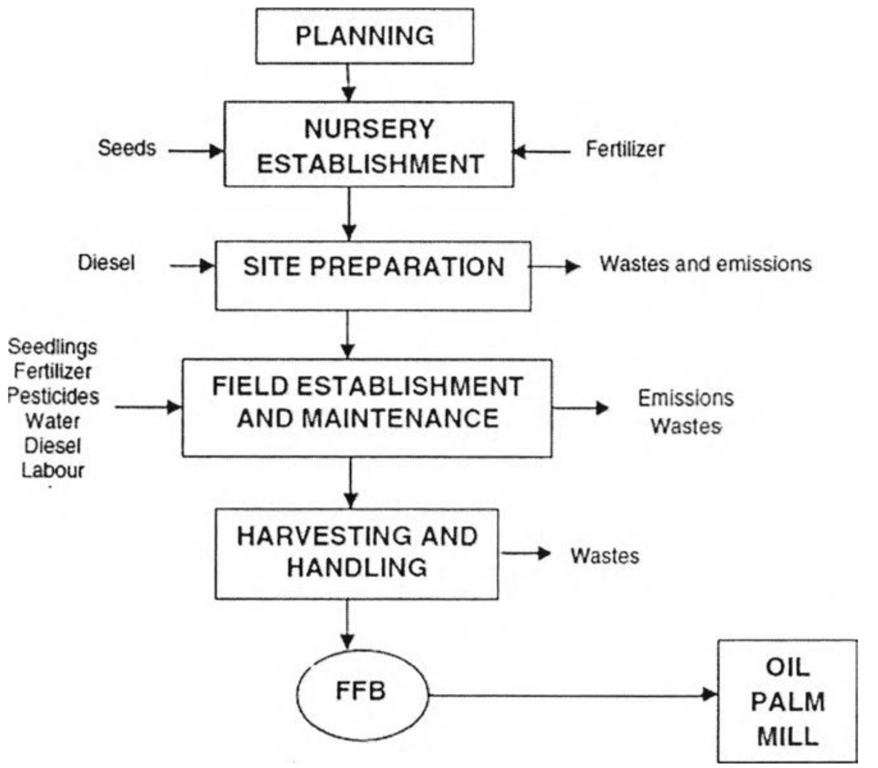
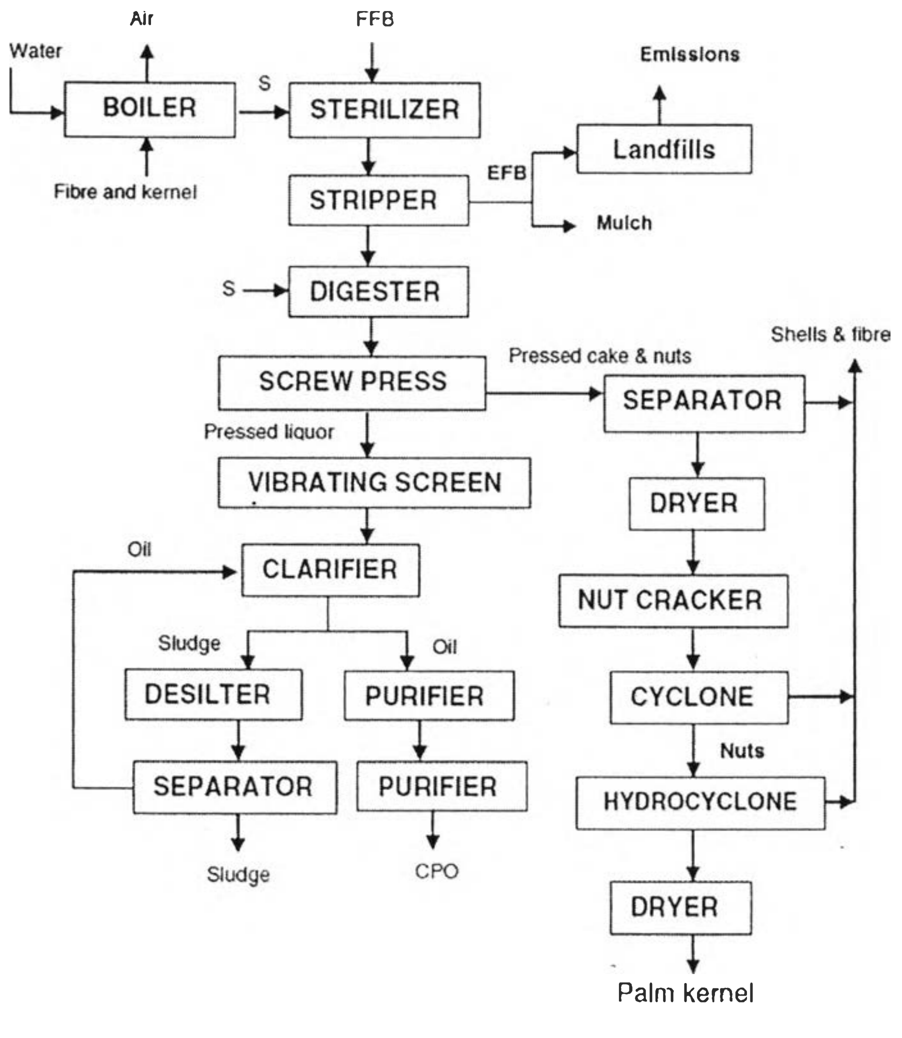


Figure 2.3 Process flow diagram for oil palm cultivation (Singh *et al,* 2013).

2.3.4.1.2 Palm Oil Extraction

Fig. 2.4 illustrates the main processes involved in the milling or extraction of palm oil from fresh fruit bunches (FFB). Sterilization of FFB is done in a steamer (pressurized cages) at about 2 to 3 bars to ameliorate the content of free fatty acid (FFA) which could reduce the quality of the oil. Therefore, this process requires the large amount of energy and water to make hot steam. A rotation drum stripper is used to thresh the fruitlets from the sterilized bunches and the fruitlets sent to the digester. The empty fruit bunches (EFB) are also used as organic fertilizer in the oil palm plantation.

The digester then removes the fruits' mesocarp from the nuts by continuous heating the fruits with steam which helps to open the oil cells in the mesocarp for effective oil extraction. The oil extraction is done with the help of screw press where the press cake and nuts are conveyed to the palm kernel crushing (PKC) plant and the pressed liquid oil also sent to a vibrating screen where it is diluted. The oil is then clarified and purified to remove dirt and moisture. The sludge from clarifier consists of mainly water soluble parts of the palm fruits and suspended materials. Then, it is desalted and further sent to the centrifuge to recover the excess oil which is recycled and return into the clarifier. The water–sludge mixture (palm oil mill effluent, POME) is then sent to the effluent treatment plant (ETP). Then, the crude palm oil (CPO) from the oil extraction process is then stored and transported to oil refinery. The palm kernel nuts are also cracked to separate the kernel from the shells. The oil palm fiber and kernel shells from the PKC plant are utilized as biomass fuel in the boiler which generates steam for oil milling processes.



S=steam

Figure 2.4 Flow diagram of palm oil milling processes (Singh *et al.*, 2013).

2.3.4.1.3 Palm Oil Refining

In the refining process, palm oil can be separated in fractions of liquid and higher melting-point (at room temperature) substances. Different grades of oleins and stearins are commercially usable. CPO from extraction mills has to be refined in order to obtain neat palm oil that is suitable for consumption or for use as raw material by down- stream industries. The main product is neat palm oil and the co-product is palm stearin. The pure palm oil yield is 0.71 kg/kg CPO and palm stearin yield is 0.29 kg/kg CPO (Papong *et al.*, 2009).

Palm and palm kernel oils consist mainly of glyceride and, like other oils in their crude form may consist of small and variable portions of non-glyceride components as well. In order to render the oils to an edible form, some of these non-glycerides need to be either removed or reduced to an acceptable levels.

The refining routes of palm oil and palm kernel oil are quite identical. There are two routes which can be taken to process crude oil into refined oil; chemical /alkali refining and physical refining shown in Fig. 2.5.

Chemical refining, which has a higher cost of refining and generally found in older refineries, utilizes an alkali to neutralize most of the fatty acids which are removed as soap. Physical refining, which eliminates the need for an effluent plant for the soap stock, involves subjecting the oil to steam distillation under high temperature and vacuum for removal of the free fatty acids (Singh *et al.*, 2013).

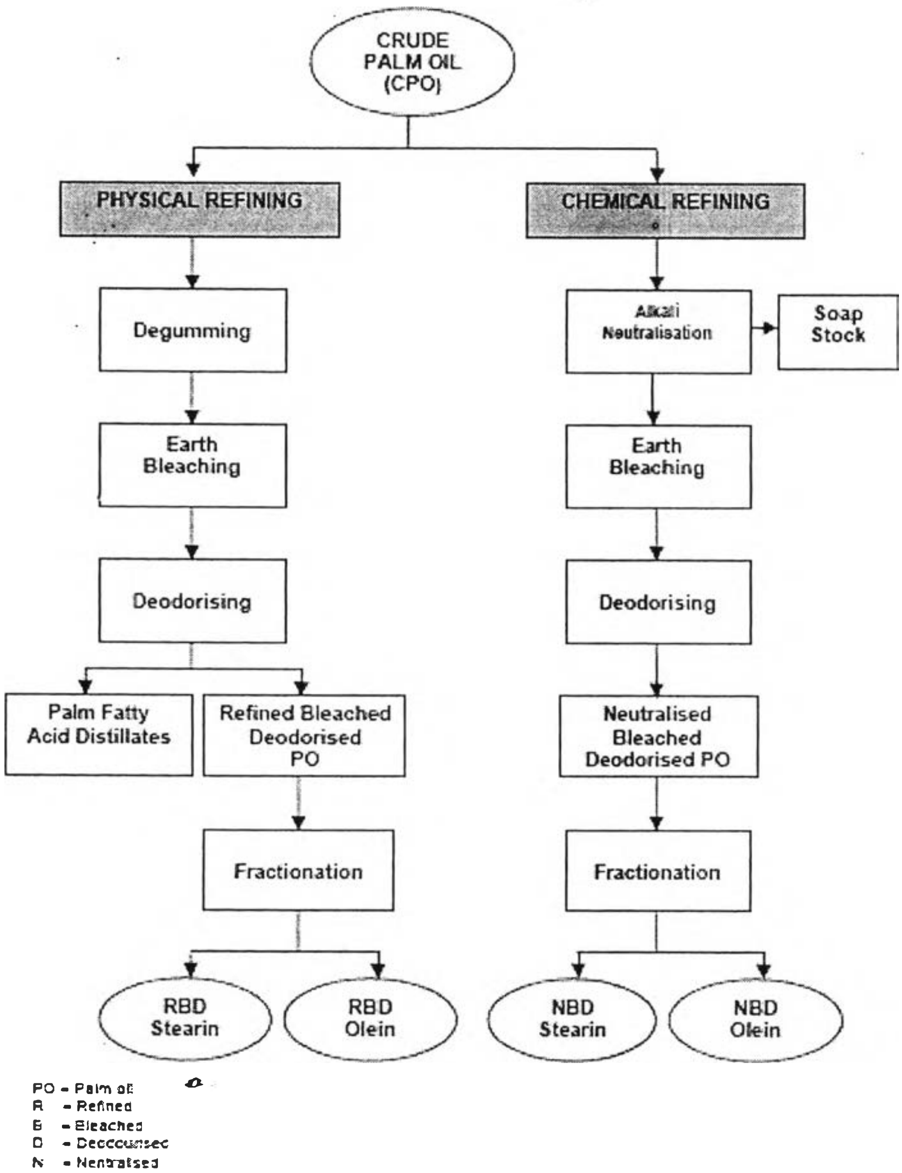


Figure 2.5 Flow diagrams of palm oil refining processes (Singh *et al.*, 2013).

2.4 Life Cycle Assessment (LCA)

LCA is defined as the "compilation and evaluation of the inputs, outputs and potential environmental impacts of a product system throughout its life cycle". Thus, LCA is a tool for the analysis of the environmental burden of products at all stages in their life cycle – from the extraction of resources, production of materials and use of the product for the management after it is discarded, either by reuse, recycling or final disposal. The total system of unit processes involved in the life cycle of a product is called the "product system". The environmental burden covers all types of impacts upon the environment, including extraction of different types of resources, emission of hazardous substances and different types of land use (Dr. Arnold, 2004).

2.4.1 LCA Metholodogy

LCA methodology used in this study followed the principles and framework of the International Organization for Standardization, ISO 14040 and 14044, which comprises four major steps that are summarized in Fig. 2.6.

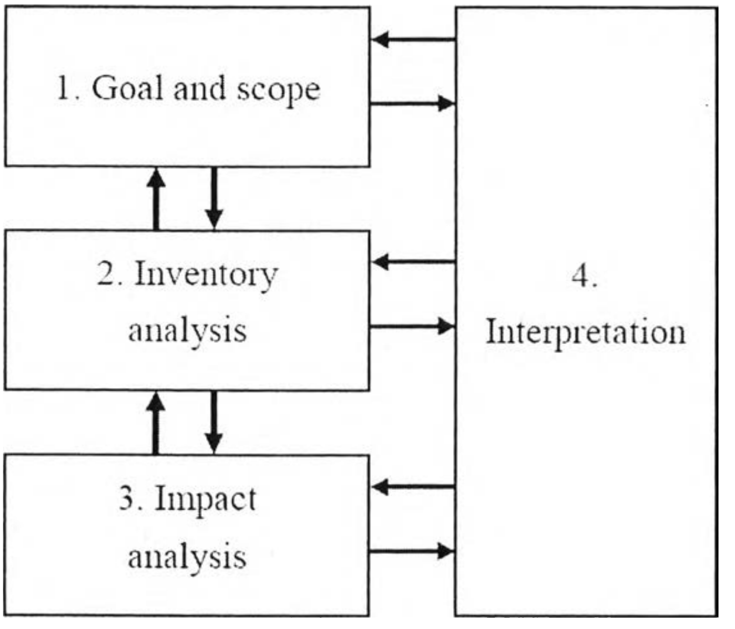


Figure 2.6 General methodological framework of LCA (ISO14040, 1997).

2.4.1.1 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.

- 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.

2.4.1.2 Inventory Analysis

Life cycle inventory (LCI) is a methodology for quantifying the flow of material and energy attributable to a product's life cycle. 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 (Wibul, 2012).

2.4.1.3 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 generation, and emissions in an inventory analysis to a number of potential impacts. The result of the LCIA is an evaluation of a product's 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 (Wibul, 2012).

2.4.1.4 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. 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. 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 (Wibul, 2012).

2.4.2 Application of LCA

The life cycle assessment (LCA) is a tool that can be used effectively in evaluating various renewable energy sources for their sustainability LCA can play a useful role in public and private environmental management in relation to products. This may involve both an environmental comparison between existing products and the development of new products.

LCA may well make an essential contribution concerned with eco-labeling (i.e. assigning a 'green label' to environmentally friendly product alternatives), enabling consumers to make comparisons between products.

Similar applications can be distinguished at a strategic level, dealing with government policies and business strategies for renewable and sustainable energy source. Furthermore, public sector uses of life-cycle methodologies include use as a tool for making procurement decisions and developing regulations. Policymakers report that the most important uses of LCA are for helping to develop long-term policy regarding overall material use, resource conservation and reduction of environmental impacts and risks posed by materials and processes throughout the product life-cycle, evaluating resource effects associated with source reduction and alternative waste management techniques, and providing information to the public about the resource characteristics of products or materials (Singh *et al.*, 2013).

2.4.3 LCA and Related Studies of Biofuel Production

Life cycle assessment studies have been carried out on various biofuel production technology.

In one of the LCA studies, Thapat and coworkers (2012) carried out the LCA to evaluate the potential environmental impacts associated with biodiesel production. The functional unit of the study was the production of 1000 L of palm biodiesel. In this study, oil palm plantation and palm oil milling were the two major contributors to global warming. N-fertilizer production and its application which induces N_2O emissions was the main source for agricultural stage shown in Fig. 2.7.

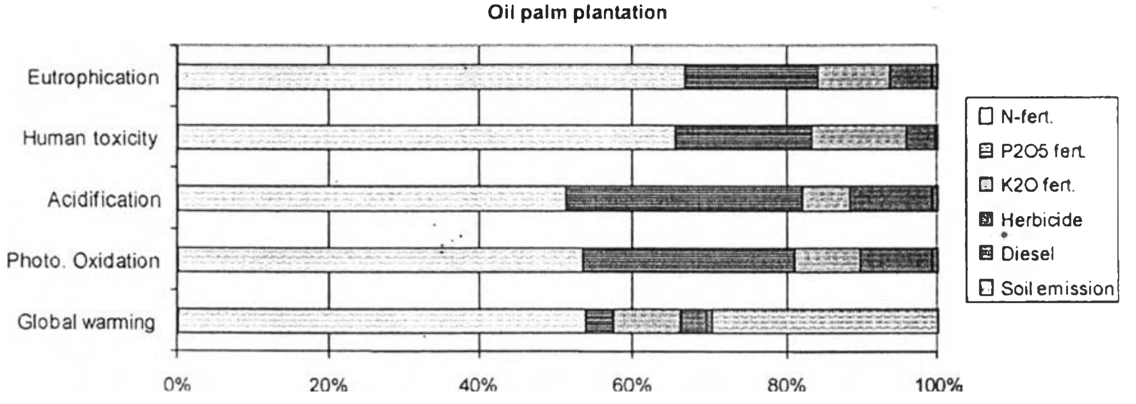


Figure 2.7 Environmental impacts of oil palm plantation (Silalertruksa, 2012).

For milling stage, methane generated from the treatment of palm oil mill effluent (POME) in open ponds was the biggest source of global warming potential (GWP) shown in Fig. 2.8. It contributes almost 100% of GWP in the milling stage. Moreover, palm oil milling is the major stage that results in high photochemical oxidation associated with the emissions of methane from POME in open ponds. The results indicated that oil palm plantation, in which SO_2 and NOx were generated during the production of N-P-K, also accounted for acidification potential. The stage contributing to human toxicity potential is the same as acidification potential mainly by N-P-K fertilizer production at the oil palm plantation stage. According to the results, POME is the major source of eutrophication impact followed by fertilizers used in the oil palm plantation.

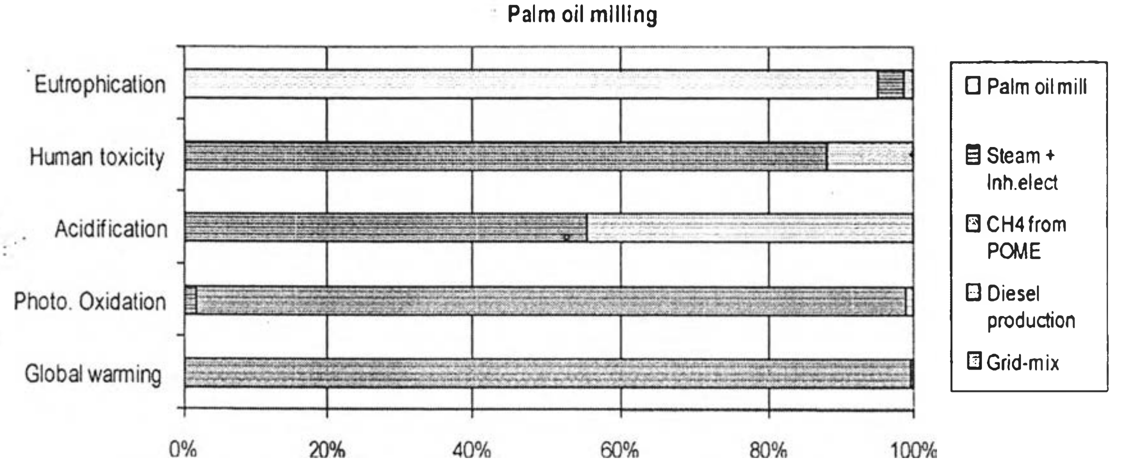


Figure 2.8 Environmental impacts of palm oil milling (Silalertruksa, 2012).

Silalertruksa and coworkers (2012) pointed out that production and use of the chemical fertilizers especially N fertilizer in palm cultivation is the major contributor to the various environmental impacts such as global warming, acidification and eutrophication. Usage of organic fertilizer produced from the co-compost (empty fruit bunches and palm oil mill effluent) can be a substainable way to reduce the environmental impacts.

Kaewmai and coworkers (2012) revealed that the averaged GHG emissions from palm oil mills with biogas capture and without biogas capture were 1,039 and 1,484 CO_2 eq per MT of CPO production respectively. Biogas capture system could reduce 30 percent GHG emission. The better the performance of a biogas recovery plant, the lower the values of GHG were emitted.

Arpornpong and coworkers (2013) recently performed the LCA of palm oil microemulsion-based biofuel (ME50). This study investigated the LCA of microemulsion biofuel production from palm oil-diesel blends with ethanol and compared it with alternative biofuels, neat biodiesel (B100) and biodiesel-diesel blends (B50). In this studies, one ton of microemulsion biofuel generated 1,140 kg of CO_2 equivalent. The results showed that palm oil production from cultivation stage to oil refining stage imparts greater environmental impacts on eutrophication and water depletion categories. According to results shown in Fig. 2.9, it can be observed that surfactants generate significant impacts on land use and ecotoxicity related categories.

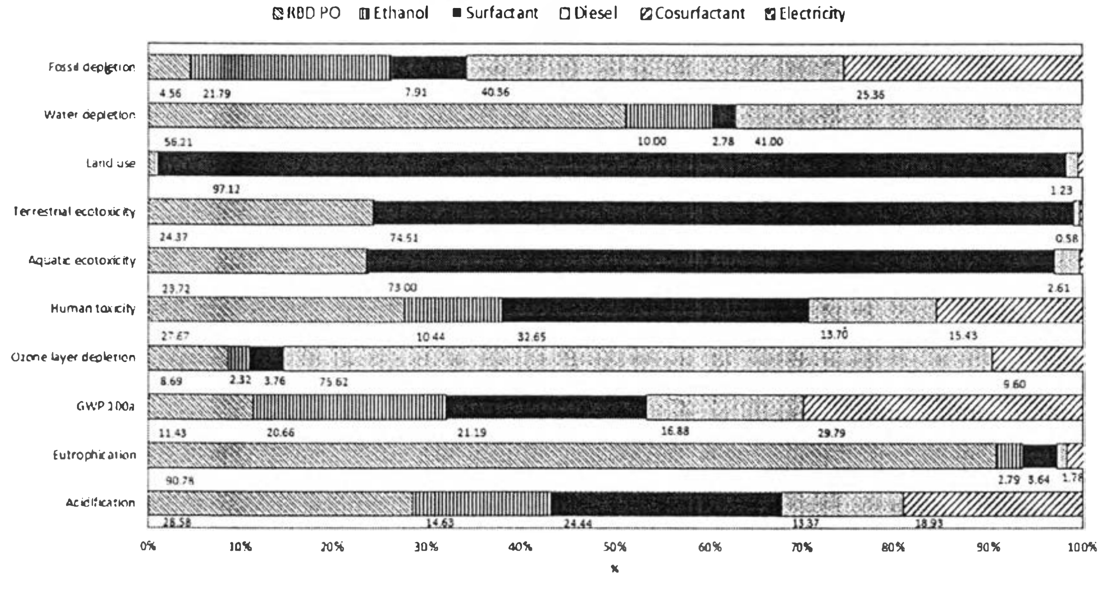


Figure 2.9 Environmental impact assessment of microemulsion biofuel production (Arpornpong *et al.*, 2013).

Fig. 2.10 illustrated the comparison of the ME50, B100 and B50. It was found that the production of microemulsion fuel offers more environmental benefits than those of B100 and B50 excluding in terms of land use and fossil depletion impact categories. Moreover, 99.6 % of the GHG emissions were generated from material usage in production of microemulsion biofuel production.

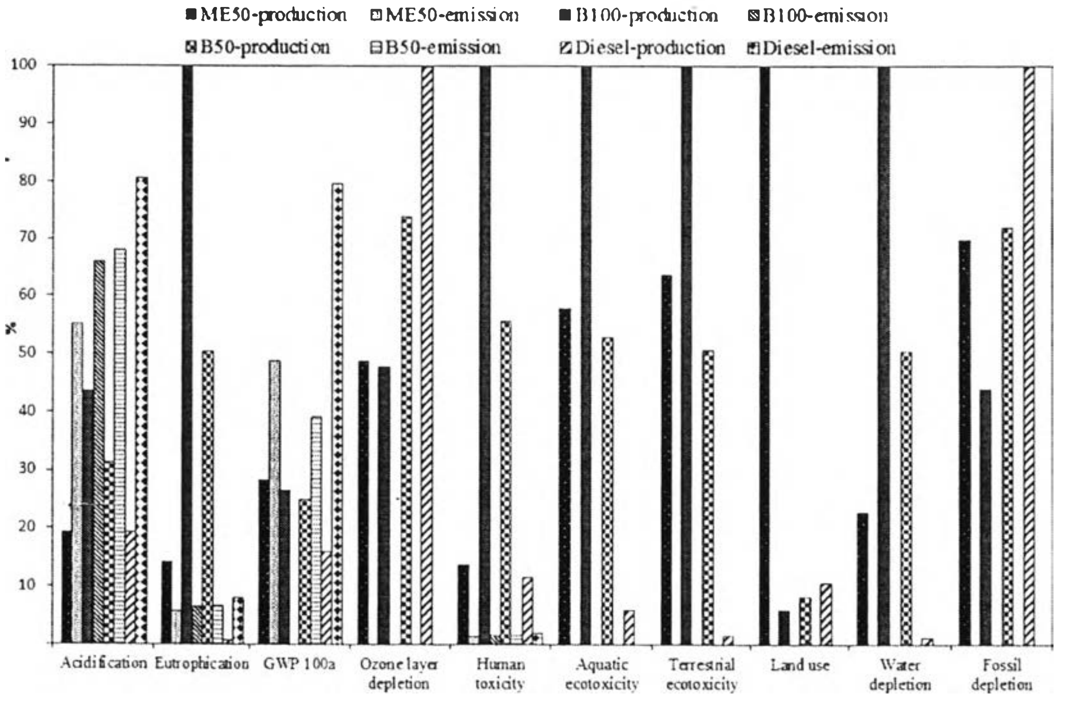


Figure 2.10 Comparison of environmental impact generated from different biodiesel and conventional diesel (Arpornpong *et al.*, 2013).