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INDUSTRIAL ECOLOGY APPROACH FOR BIODIESEL INDUSTRY IN THAILAND

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THANANUCH RAGHAREUTAI: INDUSTRIAL ECOLOGY APPROACH FOR BIODIESL INDUSTRY IN THAILAND. ADVISOR: ASSOCIATE PROFESSOR ORATHAI CHAVALPARIT, CO-ADVISOR: MANEERAT ONGWANDEE, PH.D., 163 PP.

Due to the Thai government policy to promote use of biodiesel as an alternative for diesel fuel since 2005, the biodiesel production capacity has been continuously increased. Its production process largely consumes both water and energy and also generates wastes and by-product. The objectives of this research were to study waste management in the biodiesel industry and to propose waste management options based on industrial ecology concept, which includes in-plant clean technology and external waste exchange, in order to improve the environmental performance of the industry. Five biodiesel factories that represented for 1-large, 3-medium, and 1-small scale factory were selected to study their production processes, natural resources consumption, wastes generation, and environmental impacts. The waste management options were proposed and analyzed with respect to technical, economic, and environmental considerations. The results from the survey showed that 1 m^3 of biodiesel consumes 900 kg of feeding oil, 160 kg of methanol, 10 kg of catalyst, and 0.47 m^3 of water. Its production process also generates 140 kg of crude glycerin as by-product, 8 kg of spent bleaching earth, and 0.47 m^3 of wastewater. The appropriate options are reusing the last methyl ester washing water as the first washing water, purifying crude glycerin as pharmaceutical grade, reusing crude glycerin as raw material of other industries such as bio-methanol and propylene glycol, and reusing spent bleaching earth in industrial or agricultural sectors. Generated wastewater can be used to produce biogas which is alternative energy for electricity generation.

Field of Study : Environmental Management Student's Signature T. Raghareutai
Academic Year : 2008 Advisor's Signature
Co-Advisor's Signature

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ABBREVIATION

ABR	Anaerobic Baffled Reactor
Al_2O_3	Aluminium oxide
B10	Blended diesel fuel with 10% of biodiesel
B2	Blended diesel fuel with 2% of biodiesel
B5	Blended diesel fuel with 5% of biodiesel
BOD	Biochemical Oxygen Demand
$C_3H_8O_3$	Glycerin
$CaSO_4$	Calcium sulfate
CCl_4	Carbon tetrachloride
CH_3ONa	Sodium methoxide
CHP	Co-production of heat and power
CO	Carbon monoxide
CO_2	Carbon dioxide
COD	Chemical Oxygen Demand
CPKO	Crude Palm Kernel Oil
CPO	Crude Palm Oil
CSTR	Complete Stirred Tank Reactor
DAF	Dissolved Air Floatation
DHA	Dihydroxyacetone
DME	Dimethyl ether
EIE	Eco-Industrial Estate
EIPs	Eco-Industrial Parks
FFA	Free fatty acid
FFB	Fresh Fruit Branch
FOG	Fat, Oil, and Grease
GTBE	Glycerin tri-butyl ether
H_2	Hydrogen
H_2SO_4	Sulfuric acid
H_3PO_4	Phosphoric acid

HCl	Hydrochloric acid
IE	Industrial Ecology
IEAT	Industrial Estate Authority of Thailand
KOH	Potassium hydroxide
LCA	Life Cycle Assessment
MeOH	Methanol
MTBE	Methyl tri-butyl ether
MTPIE	Map Ta Phut Industrial Estate
NaOH	Sodium hydroxide
NEIPS	The networked eco-industrial park system
NO_2	Nitrogen dioxide
O_2	Oxygen
PEA	Provincial Electricity Authority
PHA	Polyhydroxyalcanoate
Pt	Platinum
PVC	Poly Vinyl Chloride
RBD	Refined-Bleached-Deodorized
RBDPO	Refined-Bleached-Deodorized Palm Oil
RDF	Refuse Derived Fuels
SO_2	Sulfur dioxide
SS	Suspended Solid
wt	Weight

CHAPTER I

INTRODUCTION

1.1 Background and motivation

In recent times, the world has been confronted with an energy crisis due to depletion of resources and increased environmental problems. The situation has led to the search for alternative fuels such as natural gas, hydrogen, and biofuel, which should not only be sustainable but also environmental friendly. Among these alternative fuels, fuels of bio-origin have become increasingly important for developing countries due to their production capability. The bio-origin fuels include alcohol, vegetable oils, biomass, biogas, and synthetic fuels.

From the point of view of the global environmental protection and the concern of long-term supplies of conventional fossil fuels, development and use of alternative fuels to substitute conventional fossil fuels, such as diesel fuel, are necessary. Since diesel fuel is tremendously utilized in many industrial, agricultural and transport sectors, substitution of diesel fuel with a small fraction of alternative fuels can help to alleviate the economic and environmental problems. Of the alternative fuels, biodiesel obtained from vegetable oils has good potential to be an eco-friendly alternative to diesel fuel.

Biodiesel is an alternative fuel for diesel engines. It is produced by a chemical reaction of vegetable oil or animal fat with alcohols. The reaction, which is called transesterification, requires a catalyst and produces new chemical compounds called methyl esters and glycerin as a main product and by-product, respectively. These produced esters are well known as biodiesel (Gerpen, 2005).

The Thai government aims to promote the production and use of biodiesel in place of petrodiesel oil with purposes of reducing the country's dependence on imported oil, reducing air pollution, and enhancing people’s quality of life (Promotion policy, 2008).

One of the plans is to promote domestic production and use of biodiesel to replace 10% of diesel consumption in 2012. The government launched the programs for community-based biodiesel production and usage during 2005 – 2006, and commercial biodiesel production and B5 usage in 2007. It also enforces the nationwide usage of B2 and B5 in 2008 and 2011, respectively (Jencanitpanjakul, 2007).

Due to the governmental promotions of biodiesel production, several biodiesel factories have been established in Thailand, including community and commercial scales. An increasing number of factories have led to many environmental problems. For example, wastewater from the production processes is contaminated with both water-insoluble and water-soluble. It also contains significantly higher contents of COD, BOD, oil, and grease than the Thai effluent standards. Therefore, treatment of the wastewater is required before discharging to environment. Crude glycerin, which is a by-product of the biodiesel production, can be purified and sold as pharmaceutical product; however, most biodiesel factories have to store it in plant without purification or disposal due to high cost of process. This causes the problems to factory itself and nearby community such as effluent.

Although the environmental problems related to the biodiesel production are alleviated by many approaches such as “end-of-pipe” and cleaner production measures, these approaches still have disadvantages. “End-of-pipe”, for instance, is not adequate for efficient use of limited resources. It has a low environmental performance and is more costly and less sustainable than proactive and preventive environmental protection approaches (Dieu, 2003). Cleaner production is a preventive strategy to minimize the impact of production and products on the environment by applying clean technologies and organizational measures, but it is restricted to only one production process or one factory.

Industrial ecology is the one of environmental management approaches that is sustainable. It is considered as an industrial ecosystem, an industry or set of industries with its relations to other industries and actors (Chavalparit, 2006). The idea of industrial ecology application is to improve total environmental quality, whereas satisfying the economic demands of industry, in a win-win situation (Roberts, 2004).

This research is aimed to adopt industrial ecology approach to alleviate the environmental problems related to biodiesel production in the biodiesel industry in Thailand. The measures will involve the use of wastes/by-product, such as wastewater and glycerin, from the biodiesel processes as raw materials for itself and other industry.

1.2 Objectives

- To assess Thai biodiesel industries in terms of production processes, natural resources consumption and waste generations according to the factory-size variation: small-, medium-, and large- scale
- To analyze the material flows in the biodiesel production processes
- To generate the possible and appropriate options for minimization of the environmental impacts from biodiesel production using an industrial ecology concept

1.3 Hypothesis

- Wastes/by-product generated from biodiesel production processes could be deducted and utilized as raw material in the same or other sections.
- Generated options could improve environment performance of biodiesel industry in Thailand.

CHAPTER II

LITERATURE REVIEWS

Nowadays, the world has been confronted with an energy crisis due to depletion of fossil fuel resources and increased environmental issues such as global warming. Another concern is the rising prices of the crude oil which have continuously risen about 3 times of the price in 2003 (Other alternative fuels, 2008). In Thailand, cost of energy importation was increased up to 900,000 million Baht in 2007 and it tends to increase more.

Diesel fuel is largely utilized in the transport, agriculture, commercial, domestic, and industrial sectors for the generation of power/mechanical energy. Its consumption has been increasing. One of the measures to reduce the use of fossil fuel, especially diesel fuel, is substitution with alternative clean energy (Ophanonamata, 2008). The substitution of even a small fraction of total consumption by alternative fuels will have a significant impact on the economy and the environment. Of the alternative fuels, such natural gas, hydrogen, and biofuel, biodiesel obtained from vegetable oils holds good promises as an eco-friendly alternative to diesel fuel.

2.1 Biodiesel

2.1.1 Background

Biodiesel is an alternative fuel for diesel engines that is produced by chemically reacting a vegetable oil or animal fat with an alcohol such as methanol. Transesterification, the well-known reaction for converting vegetable oil to biodiesel, requires a catalyst and produces new chemical compounds called methyl esters and glycerin as main product and by-product, respectively (Gerpen, 2005).

Biodiesel is biodegradable and nontoxic fuel; has low emission profiles; and so is environmentally beneficial. Its characteristics are very close to those of diesel fuel; therefore, it is intended to be used as a replacement for petroleum diesel fuel, or can be blended with petroleum diesel fuel in any proportion.

Vegetable oils, also known as triglycerides, have the chemical structure given in figure 2-1 comprise of 98% triglycerides and small amounts of mono- and diglycerides. Triglycerides are esters of three molecules of fatty acid and one of glycerin and contain substantial amounts of oxygen in their structure. The fatty acids vary in their carbon chain length and in the number of double bonds (Barnwal and Sharma, 2005).

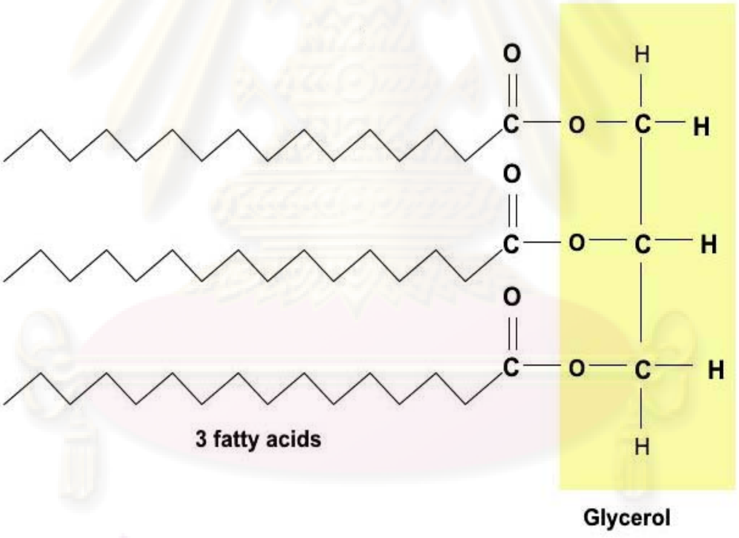


Fig 2-1 Structure of a typical triglyceride molecule (Barnwal and Sharma, 2005)

2.1.2 Biodiesel production process

Vegetable oils cannot be used as fuel directly because of their properties. The high viscosity of vegetable oils interferes with the injection process and leads to poor fuel atomization. The inefficient mixing of oil with air contributes to incomplete combustion, leading to heavy smoke emission, and the high flash point attributes to lower volatility characteristics (Barnwal and Sharma, 2005). These problems can be solved by converting oils to biodiesel through chemical process: microemulsions, pyrolysis, and transesterification. Among of these, transesterification is not complicated as the others (Srivastava, and Prasad, 2000) and is important step to produce the cleaner and environmentally safe fuel.

2.1.2.1 Transesterification reaction

Transesterification, also called alcoholysis, is the reaction of a fat or oil with an alcohol to form ester and glycerin (Ma and Hanna, 1999). It is reversible reaction, so excess alcohol is required to shift the equilibrium to the product side. Alcohols are primary and secondary monohydric aliphatic alcohols such as methanol and ethanol are used most frequently, especially methanol because of its low cost and shortest chain alcohol. The general equation of transesterification reaction is shown in figure 2-2.

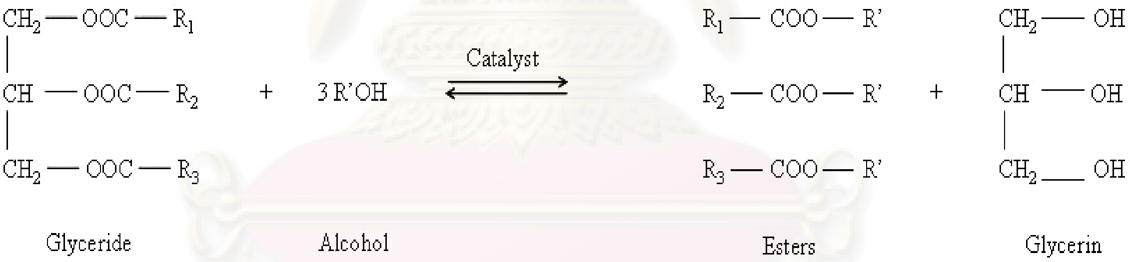


Fig 2-2 Transesterification of triglycerides with alcohol (Barnwal and Sharma, 2005)

In general, there are two methods of transesterification. One method simply uses a catalyst and the other is without a catalyst. The former method has a long history of development and the biodiesel produced by this method is now available in most countries around the world (Barnwal and Sharma, 2005).

Transesterification with a catalyst can be classified into 3 types upon catalyst used: alkali-catalyst, acid-catalyst, and enzyme catalyst. These catalysts are used to improve the reaction rate and yield. The comparison of each catalyst is shown in table 2-1.

Table 2-1 Comparison between acid-catalysis, alkali-catalysis, and lipase-catalysis methods for biodiesel fuel production

	Acid-catalysis process [1]	**Alkali-catalysis process** [2]	**Lipase-catalysis process** [2]
Reaction temperature	55 - 80 ºC	60 – 70 ºC	30 – 40 ºC
Free fatty acids in raw materials	Esters	Saponified products	Methyl esters
Water in raw materials	No influence	Interference with the reaction	No influence
Yield of methyl esters	Normal	Normal	Higher
Recovery of glycerin	Difficult	Difficult	Easy
Purification of methyl esters	Repeated washing	Repeated washing	None
Production cost of catalyst	Cheap	Cheap	Relatively expensive
Reaction time	Slow	Fast	Slow
Catalyst removal from the product	Needed	Needed	None
Wastewater treatment	Needed	Needed	None

Note: 1. Leungnareumitchai, 2006
2. Fukuda, 2001

Acid-catalyzed transesterification: Acids used for transesterification include sulfuric acid (H_2SO_4), phosphoric acid (H_3PO_4), hydrochloric acid (HCl), and organic sulfonic acids. Although transesterification by acid catalysis is much slower than that by alkali catalysis, acid-catalyzed transesterification is more suitable for glycerides that have relatively high free fatty acid and water contents (Srivastava and Prasad, 2000).

Alkali-catalyzed transesterification: Alkalis used for transesterification include sodium hydroxide (NaOH), potassium hydroxide (KOH), and alkoxides such as sodium methoxide (CH_3ONa). In a present of alkali-catalyst, the process is carried out faster than that catalyzed by the same amount of an acidic catalyst, approximately 4000 times (Cerveró et al., 2008). In the process, the glycerides and alcohol must be substantially anhydrous because water causes a partial reaction change to saponification, which produces soap (Mittelbach and Remschmidt, 2004). The soap consumes the catalyst and reduces the catalytic efficiency, as well as causing an increase in viscosity, the formation of gels, and difficulty in achieving separation of glycerin. Ma and Hanna (1999) suggested that the free fatty acid content of the refined oil should be as low as possible. Alkali-catalyzed transesterification is the most often used commercially.

Enzymatic transesterification: Although chemical transesterification using an alkali-catalysis process gives high conversion levels of triglycerides to their corresponding methyl esters in short reaction times, the reaction has several drawbacks: it is energy intensive, recovery of glycerin is difficult, the acidic or alkaline catalyst has to be removed from the product, alkaline wastewater requires treatment, and free fatty acids and water interfere with the reaction. Enzymatic tranesterification methods, using lipase as catalyst, can overcome the problems mentioned above. In particular, it should be noted that the by-product, glycerin, can be easily recovered without any complex process, and also that free fatty acids contained in waste oils and fats can be completely converted to methyl esters. On the other hand, in general the production cost of a lipase catalyst is significantly greater than that of an alkaline one. (Fukuda et al., 2001)

2.1.2.2 Technology of biodiesel production process

The biodiesel production technology can be classified into 4 types: batch technology, continuous transesterification technology, two stage technology, and micro wave technology (Biodiesel industry handbook, 2008). Table 2-2 shows the comparison of the biodiesel production techonology.

Batch technology

Batch technology is that all components are completed at a workstation before they move to the next one. Its cost is cheap, but the quality of products may be streaky and the production capacity per time is less than another technology.

Continuous transesterification technology

This technology is the consecutive reaction. The raw material and chemicals are heated and pumped to the pipe where transesterification reaction occurs. The quality of products is straight; however, its investment capital is high.

Two stage technology

The first stage of two stage technology is esterification reaction, which uses acidic catalyst to convert fatty acid in oil to ester. Next step is using alkali as catalyst, transesterification. This technology is suitable for all feeding oil, especially high containing free fatty acid oil.

Micro wave technology

The reaction can faster occur than another by using micro wave. It uses small space to set up the equipment. Nevertheless, this technology is applied only in pilot plant due to high investment capital.

Generally, biodiesel factories in Thailand usually apply batch technology and continuous transesterification technology.

Table 2-2 Comparison of biodiesel production technology

Technology	Advantage	Disadvantage
1. Batch technology	Cheap	Streaky quality of products
		Less production capacity
2. Continuous transesterification technology	Straight quality of products	High investment capital
3. Two stage technology	Suitable for all feeding oil	More complicated
	More product	High investment capital
4. Micro wave technology	Fast reaction	High investment capital
	Small space for equipments	

2.1.2.3 Biodiesel production by alkali-catalysis batch technology process

The biodiesel production process description is below and its simple production flow chart is shown as figure 2-3. (Bioener G Ltd., 2007)

Mixing of alcohol and catalyst

The catalyst is dissolved in the excess alcohol using a mixer in order to homogenization. The alcohol/catalyst mix is then charged into a closed reaction vessel. The system from here on is totally closed to the atmosphere to prevent the loss of alcohol.

Transesterification

The reaction mixing is kept around 70 °C, to speed up the reaction and the reaction takes place. A condenser may be used to prevent the evaporative losses of the alcohol. Care must be taken to monitor the amount of water and free fatty acids in the incoming oil or fat. If the free fatty acid level or water level is too

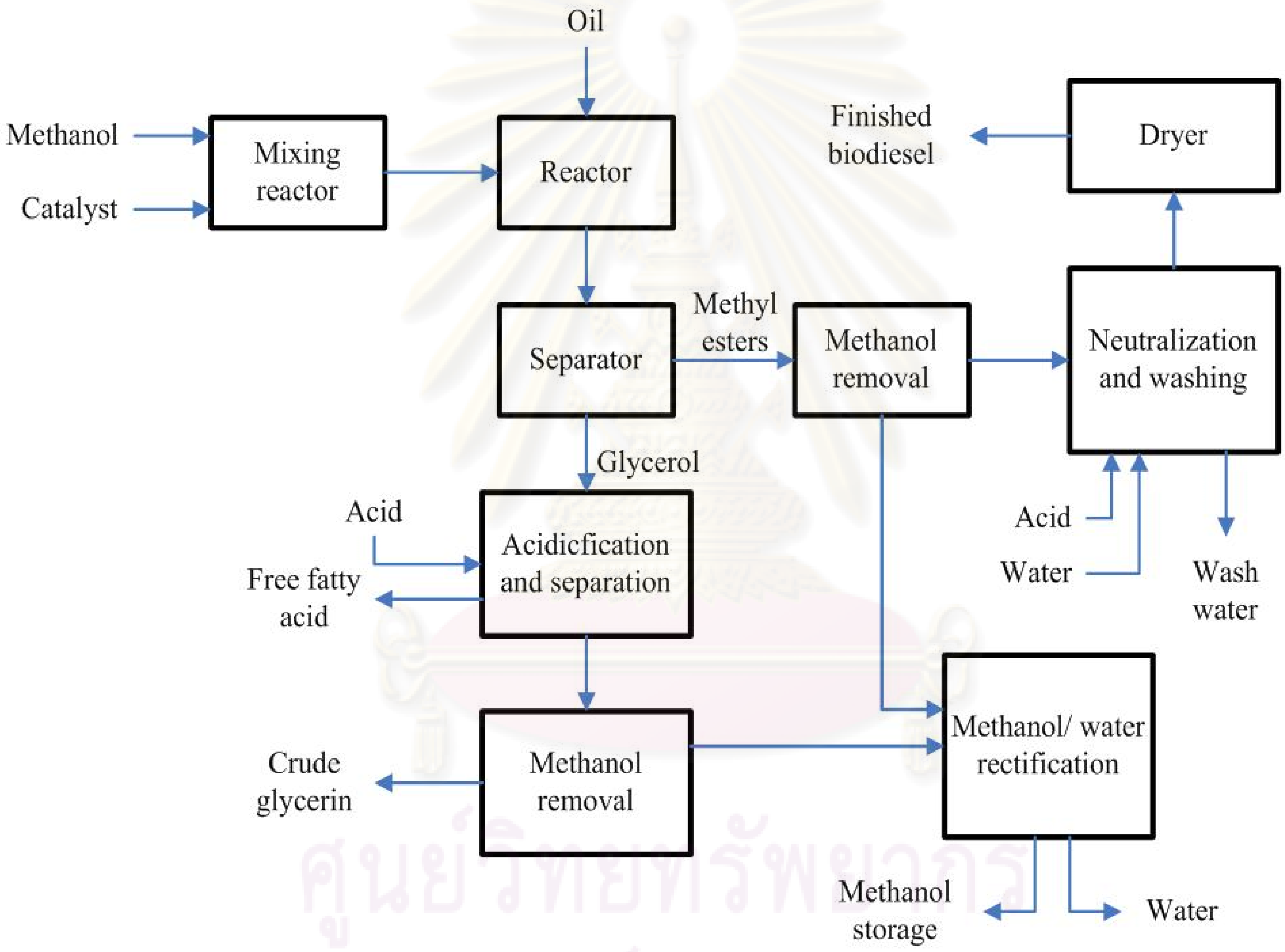


Fig 2-3 Simple biodiesel production flow chart (Adapted from Gerpen, 2005)

high it may cause problems with soap formation and the separation of the glycerin by-product downstream.

Separation

Once the reaction is complete, two major products exist: glycerin and biodiesel. Each has a substantial amount of the excess methanol that was used in the reaction. The reacted mixture is sometimes neutralized at this step if needed. The glycerin phase is much denser than biodiesel phase and the two can be gravity separated with glycerin simply drawn off the bottom of the settling vessel.

Alcohol Removal

After the glycerin and biodiesel phases have been separated, the excess alcohol in each phase is removed by distillation and then is reused in order to reducing the production cost. In others systems, the alcohol is removed and the mixture neutralized before the glycerin and esters have been separated.

Glycerin Neutralization

The glycerin by-product contains unused catalyst and soaps that are neutralized with an acid and sent to storage as crude glycerin. In some cases the salt formed during this phase is recovered for use as fertilizer. Water and alcohol are removed to produce 80 – 88% pure glycerin that is ready to be sold as crude glycerin. In more sophisticated operations, the glycerin is distilled to 99% purity and sold into the cosmetic and pharmaceutical markets.

Methyl Ester Washing

Once separated from the glycerin, the biodiesel is sometimes purified by washing gently with warm water to remove residual catalyst or soaps, dried, and sent to storage. This is normally the end of the production process resulting in a clear amber-yellow liquid with a viscosity similar to petrodiesel. In some systems the biodiesel is distilled in an additional step to remove small amounts of color bodies to produce a colorless biodiesel.

2.1.3 Environmental problems

Compare with diesel, biodiesel generates lower green house gas emission and has a very low toxicity. However, its production process may cause some environmental problems: waste generation, water pollution, and air pollutions. Table 2-3 shows types of waste from biodiesel production process.

2.1.3.1 Spent bleaching earth

Bleaching earth, or activated clay, is an adsorbent material made from activating bentonite by acid. It is used in vegetable oil industry to decolorize by removing color pigments like carotenoids, chlorophyll, and pheophytine; to remove gums, fatty acid, and trace metal; to reduce and control different oil parameters like peroxide value and anisidine value; and also to remove sulfur, acid-tars, acid-sludge, and sulfonic acid from vegetable oil (Baroda Earth).

The biodiesel industry which is the entire palm oil industry consisting of palm plantation, palm oil extraction plant, and palm edible oil refinery plant, uses bleaching earth to remove contaminants, such as gums and color, in section of palm edible oil refinery. The spent bleaching earth contains 30 – 40% of oil (Foletto et al., 2002) and is disposed directly in landfills without treatment.

2.1.3.2 Crude glycerin

In converting vegetable oils into biodiesel, about 10% of crude glycerin is produced as a by-product; that means for every 9 kg of biodiesel produced, about 1 kg of a crude glycerin is formed (Mohanprasad et al., 2005). Almost properties both in physical and chemical of crude glycerin are similar to pure glycerin except the purity. Figure 2-4 and table 2-4 show its molecular structure and properties, respectively.

Table 2-3 Types of waste from biodiesel production process

Types of waste	**Source**	**Characteristic**	**Quantity**
1. Spent bleaching earth	Palm oil refinery	Black powder containing gum and color pigment of crude palm oil	Approximate 1% of feeding oil
2. Crude glycerin	Methyl ester-glycerin separation	Solid or liquid phase	Approximate 10% of feeding oil
3. Wastewater	Methyl ester washing	Containing catalyst, soap, glycerin, and methyl ester	1 – 3 times of biodiesel product
4. Air pollution	Boiler	Dust and SO_2	
	Leaking pipe	Methanol vapor	

Source: Biodiesel industry handbook, 2008

Crude glycerin is 70 – 80% pure. In its raw state crude glycerin has a high salt and free fatty acid content and a substantial color, yellow to dark brown (Pagliaro and Rossi, 2008). Most crude glycerin is sent to water treatment for digestion but this process is slow, expensive and has a low yield (Nopharatana et al., 2007). Glycerin has been

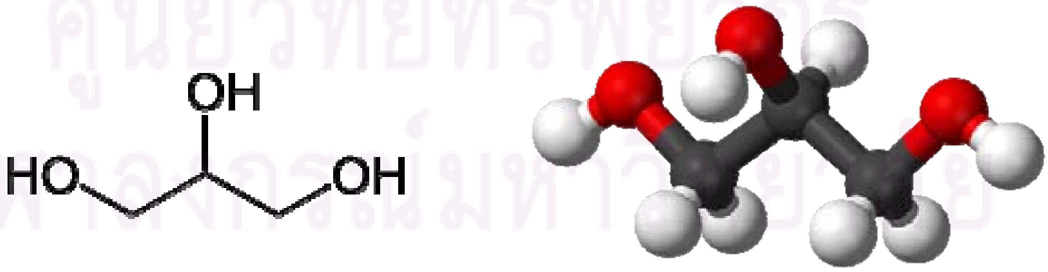


Fig 2-4 Molecular structure of glycerin

purified by distillation and used in both food and pharmaceuticals. However, distillation is a costly process and the low price of glycerin makes it uneconomic (Zhang et al., 2003). Therefore, crude glycerin is discharged through the environment or stored in plant without utilization, especially for small-scale factories.

2.1.3.3 Wastewater

Wastewater is one of important environmental problems. The major source of wastewater is from methyl ester washing step approximately 1-3 times of biodiesel product (Biodiesel industry handbook, 2008). It is contaminated with soap, methanol, catalyst, and product itself. Generally, wastewater treatment process employed in biodiesel plant is Dissolved Air Floatation (DAF) unit followed by biological treatment. Such treatment plant units could not remove contaminants in wastewater effectively. Effluent still contains high Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD) and Suspended Solids (SS) because soap and toxic substance in wastewater may harm microorganism. Moreover, sludge from wastewater plant generated bad smell and impact to surrounding.

Table 2-4 Properties of glycerin

Property	Value
Molecular formula	$C_3H_8O_3$
Molar mass	92.09 g/mol
Specific gravity	1.261
Melting point	17.8 °C
Boiling point	290 °C
Viscosity	1.5 Pa·s
Flash point (closed cup)	160 °C
Critical temperature	492.2 °C
Critical pressure	42.5 atm

Source: Material Safety Data Sheet of glycerin

2.1.3.4 Air pollution

Air pollution from biodiesel production process depends on fuel that used in boiler. The pollutants are dust and sulfur dioxide, including methanol vapor which is from reaction leaking pipe, and methanol recovery.

2.1.4 Biodiesel situation in Thailand

2.1.4.1 Choice of oil for biodiesel production

The choice of fats and oils for producing biodiesel depends on the climate, soil conditions, local availability and affordability. In Thailand, there are currently 3 types of oil that are used in biodiesel process, including used cooking oil, jatropha oil, and palm oil.

Used cooking oil

Used cooking oil is used about 74 million liters per annum, averaging 0.1 – 0.2 million liters per day. However, only 50 – 60 percent is used for the biodiesel production. Currently, used cooking oil is being gained more interest than other oils because of its low investment capital, availability, and ease of production by consumers (Biodiesel, an alternative fuel from used vegetable oil, 2007). Therefore, used cooking oil is considered to be an appropriate raw material for publics, but not to process commercially due to the limited amount available.

Jatropha oil

Jatropha oil is vegetable oil produced from the seeds of the *Jatropha curcas*, a plant that is a perennial poisonous shrub. *Jatropha curcas* can thrive on the poorest stony soil and grow in the crevices of rocks (Jatropha oil, 2008). When jatropha seeds are crushed, the resulting jatropha oil can be processed to produce a high-quality biodiesel that can be used in a standard diesel car. Jatropha oil is not suitable for human consumption, as its poison induces strong vomiting and diarrhea. Although jatropha oil seed is not yet cultivated on a large scale in

Thailand, jatropha oil is the major feedstock of the biodiesel program in India and other tropical countries.

Palm oil

Palm oil is obtained from the fruit of the oil palm tree. It may have now surpassed soybean oil as the most widely produced vegetable oil in the world. The palm fruit is the source of both palm oil, extracted from palm fruit; and palm kernel oil, extracted from the fruit seeds. (Oil palm, 2008) The largest producers of palm are Malaysia and Indonesia, accounting for 80% of the world's output.

Since oil palm can grow well in the south of Thailand, average around 5.5 million tones oil palm production per annum, (Database of biofuel, 2008) most of biodiesel are produced from palm oil. It also yields a higher amount of oil than does jatropha (Malaysian Palm Oil Council, 2008). Moreover, palm oil is nontoxic, while jatropha oil is poison and it may harm to human as glycerin, by-product of transesterification process, is transmuted to pharmaceutical products.

2.1.4.2 Governmental strategy on biodiesel in Thailand

In Thailand, the Government has promoted the production and the use of biodiesel in place of petrodiesel oil with purposes to reducing the country's importation oil, enhancing the country's energy security, and promoting the use of alternative energy made from domestic crops. After all, the use of plant energy reduces air pollution and enhances life quality of people. The government planned that in 2012, all diesel sold in Thailand will be 10% biodiesel, B10. They estimated that the consumption of blend would be 85 million liters per day, assume that blend is 10% biodiesel, so the biodiesel requirement would be 8.5 million liters per day (Gonsalves, 2006).

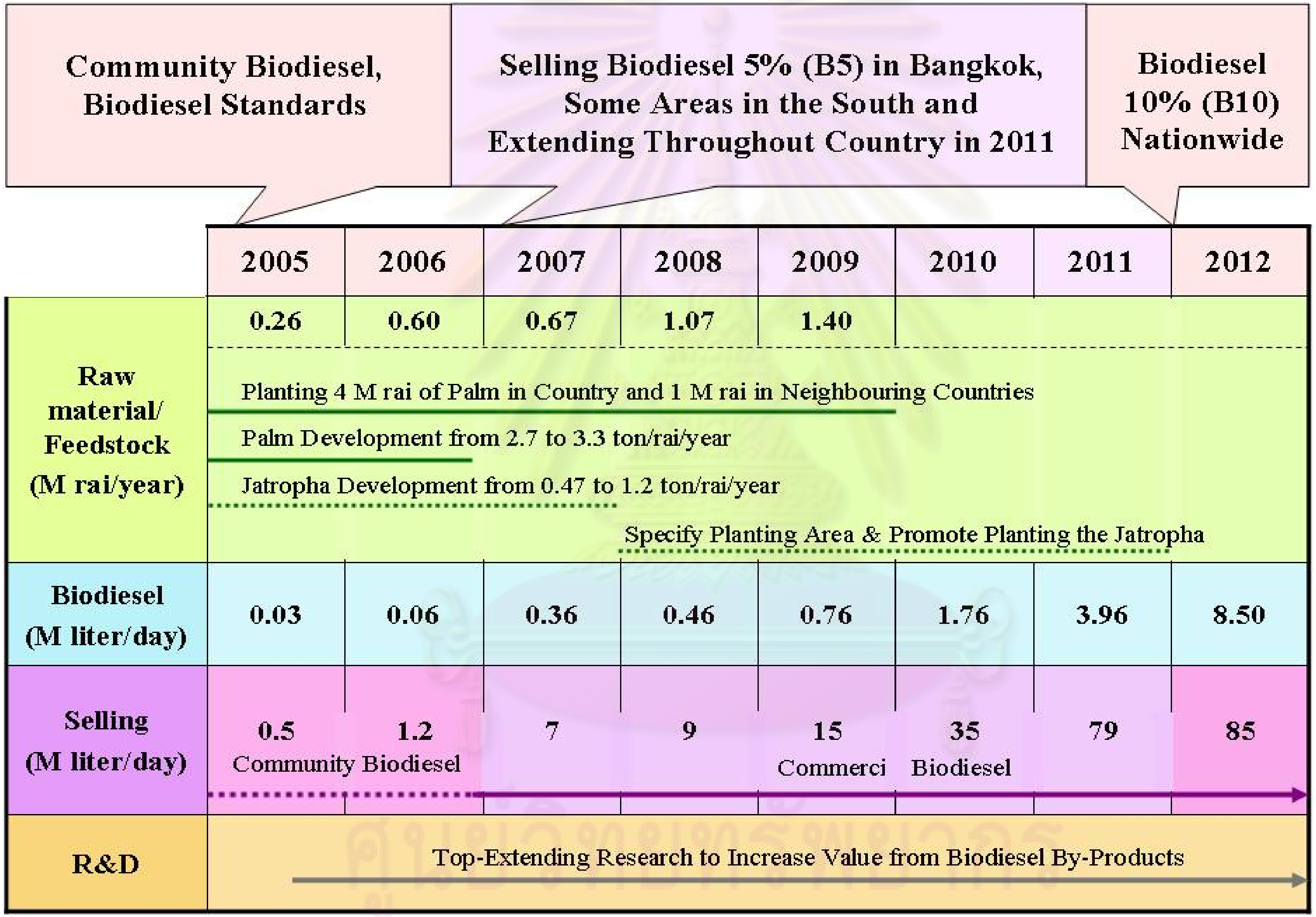
At present, the existing capacity of biodiesel production in Thailand is approximately 1.2 million liters per day (Department of Alternative Energy Development and Efficiency, 2008), lower from the targeted demand 7 times, so Thai Government highly supports biodiesel-manufacturing entrepreneurs by offering privileges granted such as the exemption of import duty of machines and the eight-year exemption of income tax. It creates biodiesel market through tax measures that can make biodiesel price cheaper than petrodiesel price (Promotion policy, 2008).

Biodiesel factories are classified by their investment capital into 3 scales, as shown in table 2-5: small scale where the investment capital is less than 50 million Baht; medium scale where the investment capital is between 50 – 200 million Baht; and large scale where the investment capital is more than 200 million Baht (Department of Industrial Work, 2008). Many large scale biodiesel plants are expected to be established in order to achieve strategic capacity. After all, a lot of environmental pollutions will certainly arise. So, environmental management is the key of control and reduction the pollution.

Table 2-5 The classified biodiesel-factory scale in Thailand

No.	Area	Amount of biodiesel factory	Scale of factory		
			Small scale	Medium scale	Large scale
1	Bangkok and its perimeter	14	10	3	1
2	East	6	4	2	-
3	Northeast	6	6	-	-
4	Center	7	5	2	-
5	North	1	1	-	-
6	South	9	5	1	3
	Total	43	31	8	4

Source: Department of Industrial Work, 2008



Community Biodiesel, Biodiesel Standards

Selling Biodiesel 5% (B5) in Bangkok, Some Areas in the South and Extending Throughout Country in 2011

Biodiesel 10% (B10) Nationwide

	2005	2006	2007	2008	2009	2010	2011	2012
Raw material/ Feedstock (M rai/year)	0.26	0.60	0.67	1.07	1.40			
	Planting 4 M rai of Palm in Country and 1 M rai in Neighbouring Countries							
	Palm Development from 2.7 to 3.3 ton/rai/year							
	Jatropha Development from 0.47 to 1.2 ton/rai/year							
				Specify Planting Area & Promote Planting the Jatropha				
Biodiesel (M liter/day)	0.03	0.06	0.36	0.46	0.76	1.76	3.96	8.50
Selling (M liter/day)	0.5	1.2	7	9	15	35	79	85
	Community Biodiesel				Commerci	Biodiesel		
R&D	Top-Extending Research to Increase Value from Biodiesel By-Products							

Fig 2-5 The government biodiesel implementation plan (Gonsalves, 2006)

2.2 Industrial environmental management

Many approaches to industrial environmental management have been tried and grown in complexity and coherence over time, for example, moving from end-of-pipe controls towards a life-cycle approach for products, and from local to global scale. At the same time, the design of industrial estates has been moved toward the concept of industrial ecosystem, by which industrial systems are models, at the global, industry sector and company levels, as a mirror of natural ecosystems. The implementation of industrial ecology has been recommended as the goal for industrial estates in environmental management. (Wiriyaumpaiwong, 2002)

2.2.1 End-of-pipe treatment

End-of-pipe treatment is an approach to pollution control which concentrates upon effluent treatment or filtration prior to discharge into the environment, as opposed to making changes in the process giving rise to the wastes (EIONET, 2009). The companies have to treat their waste to meet emission standards. This resulted in the installation of much end-of-pipe pollution control and waste clean-up technologies. A great number of treatment plants apply biological, physio-chemical or chemical process to treat different kinds of industrial wastewater, solid wastes and air pollutants.

This approach reduces the direct release of some pollutants to achieve regulatory compliance, but do not really solve the environmental problems. Many times it shifts pollution from one environment medium to another. Beside this, technology causes extra costs for investment and operation.

Although, the end-of-pipe approach is still one of the most used pollution treatment methods to handle unavoidable wastes and emission of pollutants, it is arguably curative, has a low environmental performance and is more costly and less sustainable than more proactive and preventive environmental protection approaches (Dieu, 2003).

2.2.2 Cleaner production

Cleaner production is the continuous application of an integrated preventive environmental strategy to processes, products, and services to increase overall efficiency and reduce problems and product risks to human beings and the environment. It is a preventive strategy to minimize the impact of production and products on the environment by applying clean technologies and organizational measures. It includes organizational changes, motivation and training for good housekeeping as well as changes in raw materials, process technology and internal recycling. It also refers to a mentality of how goods and services are produced with minimal environmental impact under present technological and economic limitations. Cleaner production protects the environment, the consumer and the worker, while improving industrial efficiency, profitability, and competitiveness (Chavalparit, 2006).

Cleaner production differs from end-of-pipe treatment in that it increases production efficiency, while it eliminates or minimizes wastes and emission at the sources. By introducing material and energy flow management into the companies instead of end-of-pipe measures, cleaner production aims to avoid the generation of wastes and emissions and uses materials and energy as efficiently as possible (Murphy and Gouldson, 2000). However, both end-of-pipe and cleaner production approaches are restricted to one factory that applies the approaches.

2.2.3 Industrial ecology

2.2.3.1 Concept of industrial ecology

Industrial Ecology, IE, is a new approach to the industrial design of products and processes and the implementation of sustainable manufacturing strategies. The industrial ecology concept certainly follows the principle hierarchy of environmental protection; for instance, first to reduce/avoid, followed by recycling and, if otherwise not possible treatment and disposal of the waste in an environmental friendly manner. It is a concept in which an industrial system is viewed not in isolation from its surrounding systems but in concert with them. (Jelinski et al., 1992) Industrial ecology focuses on the relations among companies in a direct waste/by-product exchange. It suggests several environmentally desirable changes in industrial production practices. These changes include improving the efficiency and productivity of industrial systems; minimizing waste by reducing raw materials consumption; reduction of the use of hazardous materials/substances by substitution with benign material/substances; developing useful applications for waste products; and reusing manufactured products at the end of their first life. (Erkman and Ramaswamy, 2001) Table 2-6 shows the difference between end-of-pipe treatment, cleaner production and industrial ecology approach.

Industrial ecology is linked intrinsically to the concept of clusters which focuses on the functional linkages and interdependencies among actors in value chains. (Enright and Robert, 2001) The clustering of firms with similar waste and by-product streams create opportunities to concentrate and minimize the collection costs of waste in one location. Achieving a critical mass of waste through geographic concentration offers opportunities to encourage the co-location of that can reprocess waste material, and then sell it to firms in a cluster who can mix this with virgin materials or make use of recycled water, flare gas or heat. This has the potential to reduce individual firm energy, materials delivery and utility service costs such as water. (Roberts, 2004)

Its ultimate goal is bringing the industrial system as close as possible to being a closed-loop system, with near complete recycling of all materials. (Lowe, 1993) The challenge of industrial ecology is to reduce the overall environmental burden of an industrial system that provides some service to society.

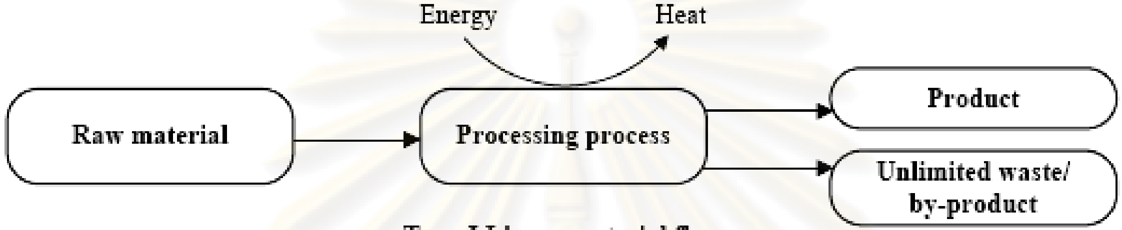
The concept of industrial ecology can be illustrated by considering three different models of systems, as shown in figure 2-6. (Garner and Keoleian, 1995)

Type I system is depicted as a linear process in which materials and energy enter one part of the system and then leave either as products or by-products/wastes.

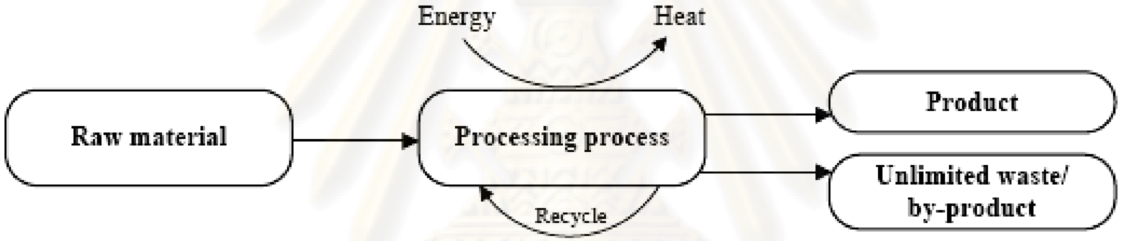
Table 2-6 The difference between end-of-pipe treatment, cleaner production, and industrial ecology approach

	End-of-pipe treatment	**Cleaner production**	**Industrial ecology**
Target of application	- Waste after generation from process	- Raw material, work practice and techonogy improvement, final product/by-product, production process and service	- Close loop system (zero waste discharge)
Objective	- Reduction of pollutant emission to the environment	- Reduce resource consumption and waste generation	- Optimize industrial metabolism, reduce environmental impacts
Innovation	- Technology only	- Techonology integrated with management	- Technology integrated with management
Production processes	- Concern on emissions from processes	- Concern on raw material and energy, climnate toxic raw materials, reducing the quantity of emissions and waste before they leave the process	- Concern on utilization of waste/by-product by other industries, waste exchange
Application level	- Single company	- Single company	- Community of business
Co-operative approach	- Industries	- Industries and commercial	- Industries, commercial and residence

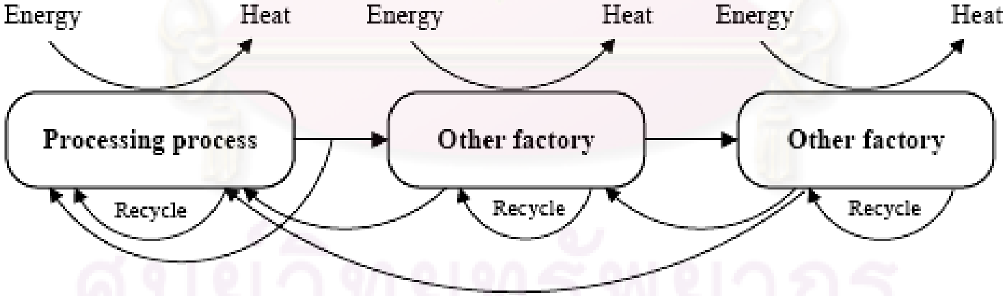
Source: Chavalparit, 2006



Type I Linear material flow



Type II Quasi-circular material flow



Type II Circular material flow

Fig 2-6 Type of industrial ecology models (Adapted from Chavalparit, 2006)

Because wastes and by-products are not recycled or reused, this system relies on a large, constant supply of raw materials. It resembles an end-of-pipe approach.

Type II system, which characterizes much of our present-day industrial system, some wastes are recycled or reused within the system while others still leave it. It is much more efficient than the type I, but it clearly is not sustainable over the long term because the flows are all in one direction, that is, the system is running down.

Type III system represents the dynamic equilibrium of ecological systems, where energy and wastes are constantly recycled and reused by other organisms and processes within the system. In a totally close industrial system, only solar energy would come from outside, while all by-products would be constantly reused and recycled within. A type III system represents a sustainable state and is an ideal goal of industrial ecology, zero discharge.

2.2.3.2 Material and energy flows in industrial ecology

Material and energy flows are two key aspects of industrial metabolism in industrial ecosystem, which is a conceptual model to apply industrial ecology to industrial development (Chiu and Yong, 2004). Material flow analysis is an important tool to identify and quantify the material and energy input and output in industrial ecosystems. These data can be used to assess the impact of material and energy use and release to the environment, in order to subsequently design optimized options for improving the environmental performance of the industry/industrial system. According to Manahan (1999) base on an as complete knowledge as possible of a system of industrial metabolism, it is possible to optimize the industrial system for maximum efficient production, minimum waste and minimum environmental pollution by internalization of the material cycle.

2.2.3.3 Boundaries of industrial ecosystems

To study the current state of an industrial ecosystem, it has to identify the system boundary and industrial metabolism to achieve the goals for the optimized use of materials and energy in an industrial ecosystem.

Roberts (2004) categorized the industrial ecology by concluding that it can be applied to eco-industrial on three levels: micro-level (firms), meso-level (eco-industrial parks), and macro-level (regional and wider global networks of manufacturing activity centers).

Firm level: Applying industrial ecology at the firm level can achieve significant operational saving; for example, it can help to supplement energy and raw material demand and reduce costs and overall levels of waste. However, there may be limitations related to scale and quality of waste or materials by-products that affect recovery costs.

Eco-industrial parks (EIPs): Its concept is trying to optimize the industrial metabolism of a group of companies found in industrial estate, with the focus on decreasing their environmental impact. It refers to areas where factories cooperate to make the most of resource use, namely through mutual recovery of the waste they generate or by reuse of waste generated by one firm as material in another. (Erkman and Ramaswamy, 2001) Such firms in eco-industrial parks can reduce operational costs through sharing common suppliers and services and at the same time reduce the collection and disposal costs. Firms can reprocess waste material or sell it to firms in an eco-industrial park who at their turn use these wastes as raw material or make use of recycled waster or energy.

Regional level: The networked eco-industrial park system, NEIPS, present EIPs macro-level developments that have strategic links or alliances with other EIPs across metropolitan regions or even global network structures. NEIPSs emerge where manufacturing industries actively seek opportunities for alliances and partnerships to encourage the development of synergies through networks as well as spatial association. NEIPSs are not just a waste exchange system or market. They can be designed to encourage synergies between industries that deal in waste or reprocessed products.

2.2.3.4 Industrial waste exchange

One industrial ecology opportunity for improved performance is industrial waste exchange, where collections of companies achieve material and energy efficiency through the reuse of by-product. (Erkman and Ramaswamy, 2001) The waste exchange process connects waste generators with waste reusers and recyclers. It naturally connects to waste minimization and cleaner production program. The benefits of waste exchange include: reduced disposal costs and quantities, reduced demand of natural resources, and a potential increase in waste value. (USEPA, 1994)

Chiu and Yong (2004) argue that unlike the usual way of applying industrial ecology as a technical tool, the Asian developing countries need to adopt industrial ecology as a strategic vision and a strategic approach to plan the economic, social, and ecological development of their national economies. Only then can Asian developing economies avoid the same problems that occurred when the developed countries experienced industrialization.

2.2.3.5 Industrial ecology potential in Thailand

In Thailand, the concept of an eco-industrial park is new and is considered by the national government as a way of achieving more sustainable industrial development. It has embraced industrial ecology as a potential approach to economic development. The Industrial Estate Authority of Thailand (IEAT), technically supported by the German organization GTZ, applied the industrial ecology concept in some industrial estates, such as estates of the Estate Authority of Thailand at Map Tha Phut, Lampoon, Bang Poo, and Amata Nakorn. At firm level, the industrial ecology concept is misunderstood and treated with suspicion in Thailand. In general, a major question still is how the industrial ecology concept and waste exchange can be successfully applied in Thailand, and under what conditions. (Chavalparit, 2006)

2.2.4 Kalundborg Estate, Denmark

Kalundborg's industrial symbiosis, as shown in figure 2-7, is the world's most well known example of industrial ecology in practice. The industrial symbiosis in the Kalundborg district was built as network cooperation between five industrial enterprises and the municipality of Kalundborg for mutual economic and environmental benefit. It is based on a series of bilateral commercial agreements on three different kinds of projects: recycling waste, exchange energy at different levels, and recycling waste products.

In this symbiosis, the five enterprises; Asnaes Power Station, the plasterboard manufacturer Gyproc, the pharmaceutical and biotechnology company Novo Nordisk/Novozymes, the soil renediating company A/S Bioteknisk Jordrens and the Statoil refinery trade their by-products as a valuable raw material to one or more of the others. For example, waste heat and steam from the Asnaes are used by Novo Nordisk. Where the Novo Nordisk distributes sludge from its manufacturing process to local farmers to fertilizer. These result in the reduction of both resource consumption and environmental impacts.

Following lists of material transfers in the system indicated flow of energy an materials between nodes in the symbiosis. Moreover, reduction of gaseous emission was also taken into account.

<u>For material and energy</u>

- 225,000 tons of steam was provides by Asnaes to the district heating system equivalent to 19,000 tons of oil.
- The Asnaes plant made use of its own excess heat to run a fish farm.
- The sludge from the fishponds was recovered and sold as fertilizer.

- 80,000 tons per year of gypsum (calcium sulfate, $CaSO_4$) recovered from the Asnaes power station's sulfur dioxide scrubber, was supplied to Gyproc.
- The power station also sold 170,000 tons per year of fly ash and clinker residues from coal burning for using in construction and road building.
- Ethane and methane from the Statoil refinery were supplied for Gyproc's drying ovens and for the power station's boilers. Gyproc consumed 900 kilograms per hour and the power station is able to avoid burning 30,000 tons of coal a year.
- Novo Nordisk shipped 400 tons of phosphorus to farmers in the form of bio sludge fertilizer.

For emission reduction

- CO_2 emissions have been reduced by 130,000 tons per year or about 3%.
- SO_2 emissions have declined 25,000 tons a year or roughly 58%.

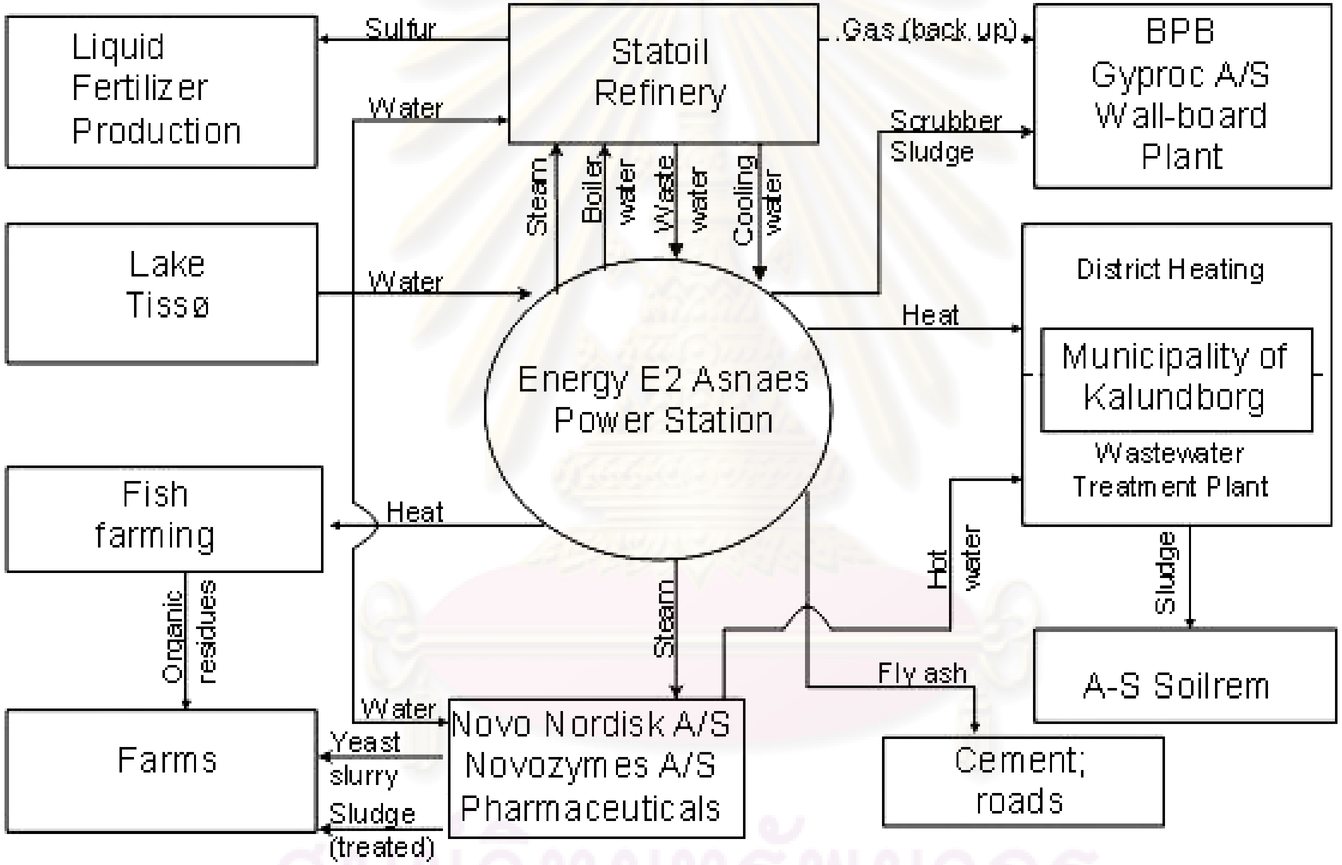


Fig 2-7 Kalundborg’s Industrial Symbiosis (Chertow, 2008)

2.2.5 Previous studies:

- Mortimer et al. (2003) researched in life-cycle assessment of biofuel. Their study aims were to provide an independent, comprehensive and rigorous evaluation of the comparative energy, global warming and socio-economic costs and benefits of producing biodiesel from oilseed rape in the United Kingdom. They reported that there are many sources of CO_2 associated with biodiesel production. Most of the emissions come from the esterification process, the production of fertilizer and the extraction of the oil from the seed. These CO_2 emissions are not always produced directly from the process but taken from the energy requirement. For example electricity used in the esterification process may come from a coal power plant, so the amount of electricity used can be related to the amount of CO_2 released from the plant. It was found that for every ton of biodiesel produced 916 ± 52 kg CO_2 was released into the atmosphere.

- Pleanjai et al. (2004) studied an environmental evaluation of biodiesel production from palm oil in order to assess the environmental implications of the proposed substitution. The goal of this study is to evaluate the environmental performance of biodiesel production from palm oil based on a life cycle perspective. The study was divided into 3 stages: oil palm plantation, palm oil production and transesterification into biodiesel. For the results, they found that the major water requirement for the production of biodiesel comes from oil palm agriculture. Nitrogen is the largest input from fertilizer although potassium and phosphorus are also significant contributors. In the steam generation step of palm oil production emissions are composed of particulate matter, NO_2, and CO (in flue gas), all of which contribute to photochemical ozone formation. In palm oil transesterification into biodiesel wastewater is produced from washing of methyl esters. Although the water is low in pollution, contaminants may include sodium hydroxide catalyst, methanol, glycerol, palm oil. This process also has the largest demand for electricity.

- Harding et al. (2007) studied in life cycle assessment (LCA) to compare the environmental impacts of various flowsheets which could be proposed for the production of biodiesel at the industrial scale. Five flowsheets options have been included in the study to investigate the alkali and enzyme catalyzed production routes from rapeseed oil, use of methanol or ethanol for transesterification, and the effect of efficiency of alcohol recovery. The LCA showed that the enzyme production route is environmentally more favorable. Improvements are seen in all impact categories, global warming, acidification, and photochemical oxidation are reduced by 5%; however, there are no industrial-scale processes for biodiesel based on enzymatic esterification. Although methanol is the most commonly used alcohol in the reaction because of its short chain length and low cost, they found that the methanol production impact is higher than the ethanol production impact and plays a large role in the overall LCA results in these scenarios. When methanol recovery in the alkali catalyzed process was lowed from 94 to 50%, impacts increased in all categories, abiotic depletion, ozone layer depletion, global warming; photochemical oxidation, and acidification.

- Sampattagul et al. (2007) researched to develop the life cycle inventory database of Jatropha biodiesel and analyze the environmental impacts by using the concept of life cycle thinking. They found that to generate biodiesel from Jatropha oil, the materials processing, energy input have been consumed and the emissions and wastes have been released to the environment, especially in cultivation and biodiesel production process. In transesterification and oil extraction, it not only intake much amount of chemical and electricity but also generate chemical waste to soil and water. Finally, they concluded that Jatropha biodiesel production in Thailand should be improved according to higher environmental impacts and total cost than conventional diesel fuel from life cycle aspects.

- Hu et al. (2008) studied life cycle energy, environment and economic assessment for conventional diesel and soybean-based biodiesel in China. The results of the assessment have shown that compared with conventional diesel, soybean-based biodiesel has about 4% higher feedstock and fuel production total energy consumption, about 76% lower feedstock and fuel production fossil energy consumption. Soybean-based biodiesel has 31%, 44%, 36%, 29% and 67% lower the source of fuel to fuel combustion hydrocarbon, carbon monoxide, particulate matter, sulfur dioxides (SO_x), and carbon dioxide (CO_2) emissions, respectively, and about 79% higher the source of fuel to fuel combustion NO_x emission. Soybean-based biodiesel is thus considered to be much more renewable and cleaner than conventional diesel. However, the retail price of soybean-based biodiesel at gas stations would e about 86% higher than that of conventional diesel without government subsidy according to the cost assessment and China had to import large amount of soybean to meet the demand in recent years. Therefore, although soybean-based biodiesel is one of the most promising clean and alternative fuels, currently it is not a good choice for China. It is strategically important for China to diversify the feedstock for biodiesel and to consider other kinds of alternative fuels to substitute conventional diesel.

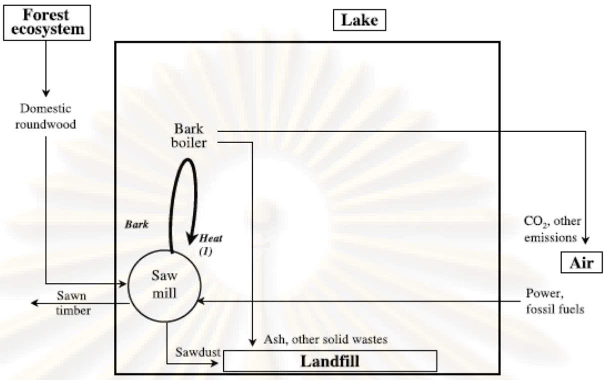
- Schwarz and Steizinger (1997) reported a self-evolved industrial recycling network in the Province of Styria, Austria. The complex network consists of more than fifty facilities. Industries participating include agriculture, food processing, plastics, fabrics, paper, energy, metal processing, woodworking, building materials, and a variety of waste processors and dealers. Flax refining residues from agricultural associations are fed to stone and ceramic industry, in the same time, it consumes textile waste and pine oil pitch from textile industry and chemical industry, respectively, as its raw material. Power plant produces crude ash which can be served as raw material of cement plant, construction material industry, and mining company. Iron manufacturing industry not only supplies blast furnace sand to cement plant and construction materials industry, but also provides LD dust to color industry as raw material. Saw mills provide wood residues to paper producing industry where its waste is sent to waste paper dealer through another paper producing industry. These industries found that they can save the costs on raw material and landfill disposal. In some cases the by-products are less expensive or of higher quality than primary materials would be. Moreover, resources of each raw materials and emissions are reduced and landfill lifetimes are extended.

- Wiriyaumpaiwong (2002) studied Eco-Industrial Estate (EIE) in Map Ta Phut Industrial Estate (MTPIE). This study aimed to assist in EIE development program at MTPIE by investigating existing environmental management activities, identifying industrial synergy linkages and analyzing the economic and environmental benefits. Six factories were chosen for detailed study with two waste recycling projects in material area. These projects are steel scrap recycling project, which is carried out by sending steel scrap directly to steel manufacturer, and used fluorescent lamp recycling at lamp manufacturer project. The result of this study showed that these projects would promote sustainable use of natural resources, reduce environmental impact, and save operating cost. Moreover, recycling process will decelerate the need for landfills. This will promote pollution prevention at its source, energy saving, and reducing greenhouse gas emission, and community development.

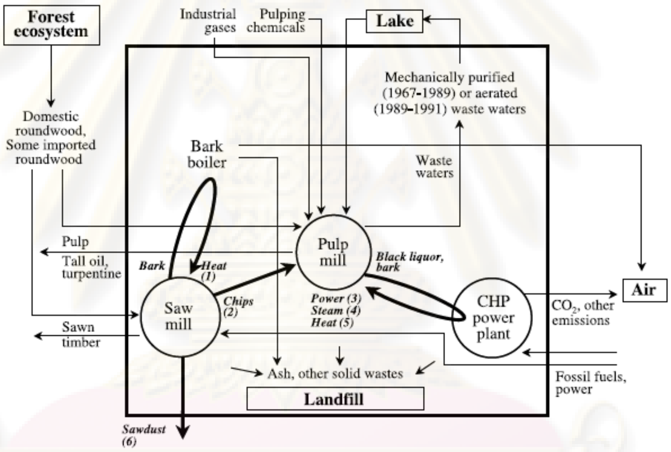
- Mirata (2004) reported the existing, planned and possible synergies in Humber region where is located on the East coast of England. There are chemical industries, oil refineries and power plant stations, processing of gas in the region. Food producers and agriculture are also included in this region. The wastes of food and fish processing are used as raw material in many industries; for example organic waste is fed to pet food, local farms, and gasifier. Its waste edible oils are served to out of the biodiesel production region. Furthermore, food and fish processing will plan to feed offal to protein extraction plant. Wastewater treatment plant receives wastewater from all industries, after treating the treated water is sent to co-production of heat and power (CHP) and refineries as cooling water. CHP receives refinery by-products as fuel to produce power. This process gets stream which is provided to chemical industry. These industries benefit from synergies by reducing their waste disposal costs.

- Korhonen and Snäkin (2005) studied Uimaharju Industrial Park, figure 2-8, located in the small municipality of Eno in Eastern Finland. During the 1950s and 60s, (A) the Uimaharju industrial area consisted only of a saw mill where the bark waste form saw logs was combusted for energy. In 1967–1991 (B), a pulp mill and a power plant were built alongside the saw mill (1). Since then heat derived from wood waste has been used in the saw mill. Waste wood chips serve as raw material for pulping (2), and pulping wastes, in turn, as fuels for energy production in the new power plant providing the pulp mill with some power (3), stream (4), and heat (5). The co-production of heat and power (CHP) was not efficient enough to produce the power required by the mills and this need was met by purchasing power from the national grid. Some sawdust (6) was supplied to other mills outside the park as resources with value. The pulp mill needed pulping chemicals and some industrial gases, O_2 and CO_2, for pulp bleaching. These were sourced from outside the system. In 1992–2003 (C) the newest actors are a waste ash treatment plant, a wastewater treatment plant and a gas plant. The new flows are waste ash utilization (9) for fertilizer, wastewater sludge (11) used as fuel, saw-mill bark (7) used as fuel in the power plant that applies CHP, recovery and reuse of pulping chemicals (10), and industrial gas recovery (8) in the gas plant. There are also some new flows between the system and its environment. The municipality of Eno runs its municipal wastewater (12) into the Uimaharju Park to be treated efficiently in the park's wastewater plant. The industrial park sells some of the unused wood wastes outside the park (13). And finally, some surplus electricity is sold to the international grid (14).

A. Type I Ecosystem 1955–1966



B. Type II Ecosystem 1967–1992



C. Type III Ecosystem 1992–2003

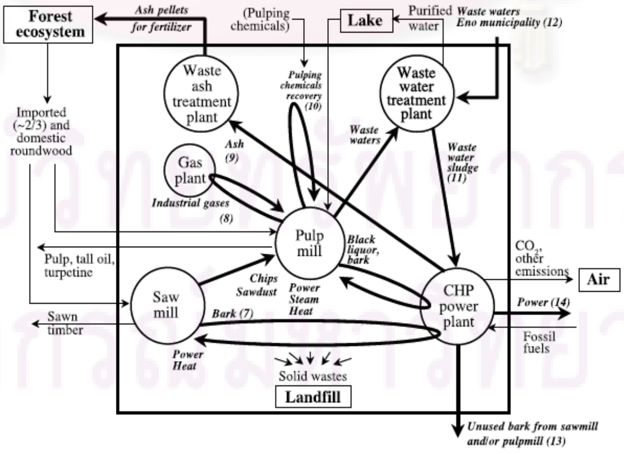


Fig 2-8 Flows of material and energy in the Uimaharju Industrial Park (Korhonen and Snäkin, 2005)

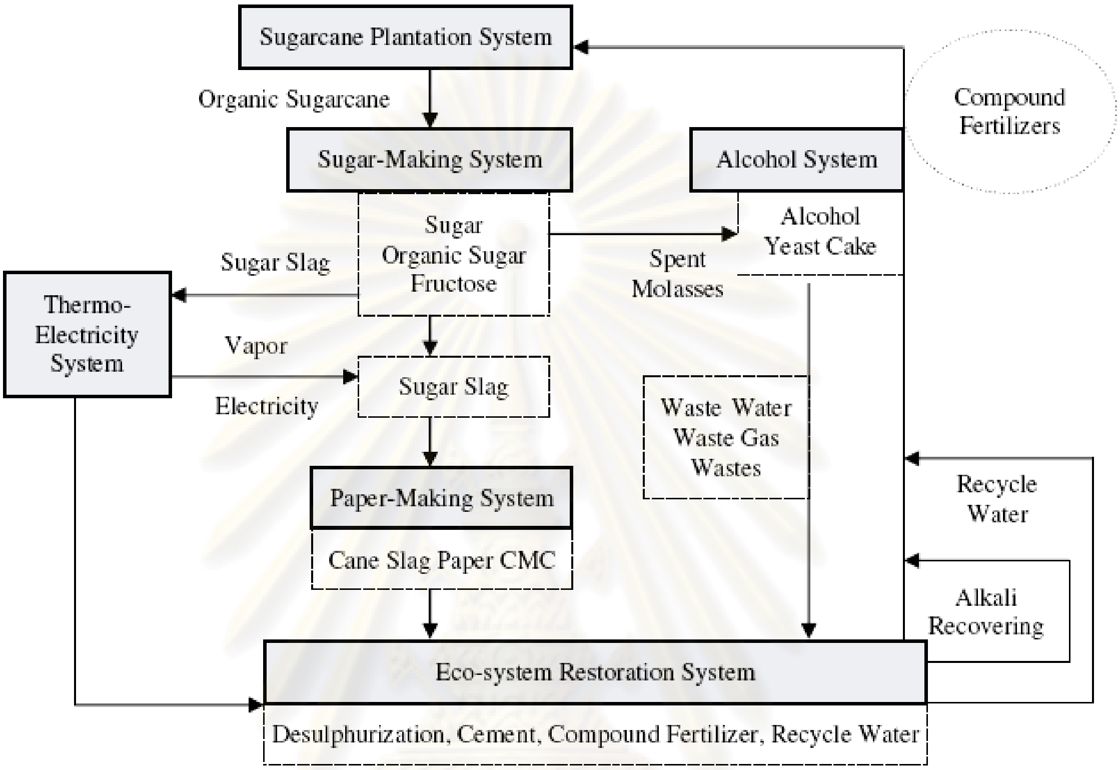


Fig 2-9 Industrial symbiosis and closed-loop supply chains for sugar-making industry in Guigang Park (Fang et al., 2007)

- Fang et al. (2007) investigated the application of industrial ecology concepts by reference to several case studies in China. In the case study, they found that each system has different characteristics and management concerns. These below are a few examples of their research.

  - Guigang group is now the largest stock company in the city of Guigang. Today it is the largest sugar-making industry in China and includes a pulp-making plant, a paper-making plant, an alcohol plant, a cement mill and a fertilizer plant. All these plants are based on by-products generated from the sugar-making industry. The web shaped by the Guigang group consists of two main chains, namely sugar and paper. The sugar chain consists of a sugar-processing plant, an alcohol-processing plant and a compound-fertilizer plant. Along this chain each down-stream plant uses as its raw material the by-product generated by the up-stream plant. The principle of using by-products from one plant as raw material for the downstream plant has also been adopted in the paper-making chain. The paper-making plant uses the sugar slag generated from the sugar-making plant, and the downstream cement mill uses its by-product, the sludge, as raw material for the production of cement, as shown in figure 2-9.

- The Lubei Group is now a large state-owned industrial group covering 12 industrial sectors such as building materials, light industry, electricity generation and production of machinery. It has been the largest producer of phosphate fertilizer in China as well as the largest manufacturer of ammonium phosphate, sulfuric acid and cement in the world since 2001. The Lubei integrated industrial system reveals synergy in the reuse of by-products both within and among the three production chains. Sulfuric acid and seawater are the basic material flows, steam and electricity are the energy flows, and gypsum and furnace slag are the main wastes flows.

CHAPTER III

METHODOLOGY

Methodology of this study involved 6 steps, i.e., biodiesel factories selection, analysis of the existing production process, analysis of the material flow, identifying and designing potential options and waste exchanges, analysis of possibly appropriate options for improvement of economic and environmental performance, and analysis of appropriate waste treatment, as shown in figure 3-1.

Step 1: Biodiesel factories selection

Currently, in Thailand, there are forty-three biodiesel factories that have registered to Department of Industrial Work. These can be classified by their capital investment into 3 scales: 31 small-scale factories; 8 medium-scale factories; and 4 large-scale factories (Department of Industrial Work, 2008). In this research five production capacity factories, which represent for small-, medium-, and large-scale biodiesel factory, were selected to study their production process, quantity of resources used and waste generation. However, the selection of the study factories also depended upon accessibility and cooperation of the factory owners.

Step 2: Analysis of the existing production process

The researcher did an observational survey, involving a walking-through method to collect data of all production processes, sources of waste generation, and environmental impacts. The objective of this step was mapping the technological profile of the production process.

Step 3: Analysis of the material flow

Each factory assessment started with an inventory of the process flow data to identify the flows of material and sources of waste generation and quality. The steps are as follows:

- *Investigating manufacturing process:*

  This step was to collect general information of the study factories and how they deal with the waste streams.

- *Mapping the production process:*

  The process started with drafting lists of unit operations and identifying raw material inputs and waste generation from each processing step.

- *Water use identification:*

  Water usage in the production lines was determined qualitatively and quantitatively. Data were collected mainly from the factory recording systems.

- *Wastewater generation in each processing step:*

  This step was similar to the water use identification step. The researcher characterized the sources of wastewater generation. Data were collected mainly from the factory recording systems.

- *Material balances:*

  The purpose of a material balance was to determine the consumption of raw materials in the process and to identify and estimate losses due to waste emissions.

- *Evaluation of the environmental impacts:*

  The environmental impacts were assessed in terms of both consumption of natural resources and generation of industrial pollution.

Step 4: Identifying and designing potential options and waste exchanges

Three main focusing factors were the prevention of waste generation, reuse and recycle waste, and minimization of waste and waste exchange. All data collected in the previous step were used as guidelines and inspiration to generate possible options for minimization of environmental impacts and to improve the environmental performance of biodiesel industry. The proposed options were also based on the results from many research projects both in Thailand and developed countries.

- *Clean technology options:*
  The options involved identifying, analyzing and designing potential internal recovery, recycling, and reuse options.

- *Waste exchange options:*
  The applications of biodiesel waste exchange options for reuse/recycling with other industrial sections were derived from the literatures. The aim was to achieve the goal of a zero waste discharge plant.

Step 5: Analysis of possibly appropriate options for improvement of economic and environmental performance

All improvement alternatives were analyzed for the appropriation and possibility of their technical, economic, and environmental considerations prior to implementation (Cleaner Technology Audit Manual for Food Industry, 2001).

Technical Evaluation: Its objective is to determine the technical feasibility of options. The impacts of the proposed options on process, product, production rate, and safety are evaluated. It is important to include all employees and departments affected by the implementation of these options.

Economic Evaluation: Economic viability is often the key parameter which determines whether or not an option will be implemented. Therefore, this objective is to evaluate the cost effectiveness of the proposed options. The economic evaluation is carried out using standard measures of profitability such as payback period.

Environmental Evaluation: Since one of the goals of industrial ecology is to improve the environmental performance, an environmental evaluation is therefore imperative to determine the positive and negative impacts of the options.

Step 6: Analysis of appropriate waste treatment

Sometimes, there are remaining wastes in the process that need to be treated before discharging into the environment. “End-of-pipe” technologies are helpful for a complete removal of remaining contaminants. The treatment technology should be selected based on emission standard requirements, final targets, available technologies, and economic efficiency.

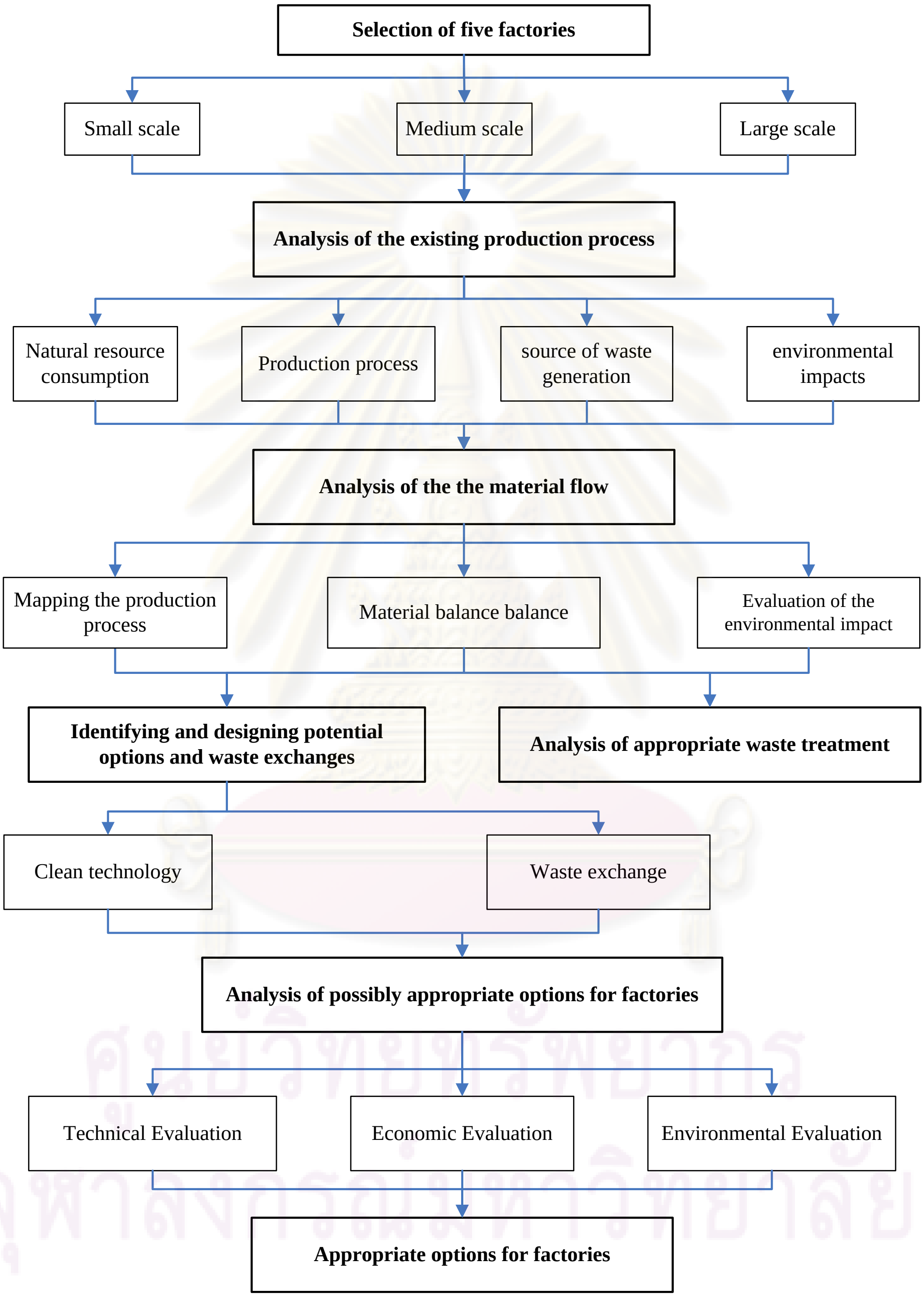


Fig 3-1 Flow chart of the research methodology

CHAPTER IV

RESULTS AND DISCUSSION

4.1 General information

Five biodiesel factories with different investment capital were selected from forty-three biodiesel factories that registered to Department of Industrial Work. These were represented for one small-, three mediums-, and one large-scale factory. The major reason of the selection was based on the cooperation and willingness of the factory owners.

Factory A represents for the small-scale factory with investment cost of 36 million Baht. Factories B, C, and D with investment cost of 60 – 65 million Baht are represented for medium-scale factory. Factory E, the large-scale factory, invested 300 million Baht for investment capital. Their production capacity varies from 20,000 to 800,000 liters per day. The comparison of general data of five selected factories is shown in table 4-1.

4.1.1 Biodiesel production process

The production process description is presented below and its production flow chart is shown as figure 4-1.

Degumming

If crude palm oil is used as raw material, refinery process is necessary in order to eliminate dirt, gum and crude palm oil color pigment. However, if crude palm oil is not used as raw material, this step is unnecessary. Gum and color pigment of palm oil are separated from crude palm oil by adding food grade phosphoric acid (H_3PO_4) and bleaching earth in the process. In some case if crude palm oil has high free fatty acid or water content, evaporation and condensation are necessary for pretreatment of the feed stock of biodiesel production.

Mixing of alcohol and catalyst

The catalyst is dissolved in the excess alcohol using a mixer in order to homogenization. The alcohol/catalyst mixture is then delivered into a closed reaction vessel. The system from here on is a totally closed system to prevent the loss of alcohol.

Transesterification

The mixed solution is fed to react with oil in this section. The reaction temperature is kept between 65 and 80 °C in order to speed up the reaction. A condenser may be used to prevent the evaporative losses of the alcohol.

Separation

After the reaction is complete, two major products are produced; i.e., glycerin and biodiesel. The products are settled to separate from each other. The glycerin phase is much denser than biodiesel phase so that glycerin can be simply drawn off the bottom of the settling vessel. Some factories use centrifuge to help separation which can save settling.

Alcohol removal

After the glycerin and biodiesel phases have been separated, the excessive methanol in each phase is removed by distillation and then is reused in the process. However, some of biodiesel factories, such as Factory B, does not remove excessive methanol from methyl ester phase because a little amount of methanol may be removed in the next step, methyl ester purification step.

Methyl ester purification

After separating, methyl ester contains methanol, catalyst, and glycerin. It is necessary to be purified before storage as biodiesel. From the survey of five selected biodiesel factories, the production process can be divided into 2 types upon the methyl ester purification process; i.e., washing and distillation.

Table 4-1 Comparison of general data of five selected biodiesel factories

	Factory A	Factory B	Factory C	Factory D	Factory E
Investment cost (million Baht)	36	60	61	65	300
Production capacity (lit/day)	200 000	80 000	800 000	20 000	200 000
Type of process	Batch	Batch	Batch	Batch	Continuous
Own palm oil refinery plant	No	Yes	Yes	No	Yes
Raw material	Palm stearin	Palm stearin and Palm kernel oil	RBD palm oil	Used cooking oil	RBD palm oil
Alcohol	MeOH	MeOH	MeOH	MeOH	MeOH
Catalyst	CH_3ONa	KOH	NaOH	NaOH	$NaOH/CH_3ONa$

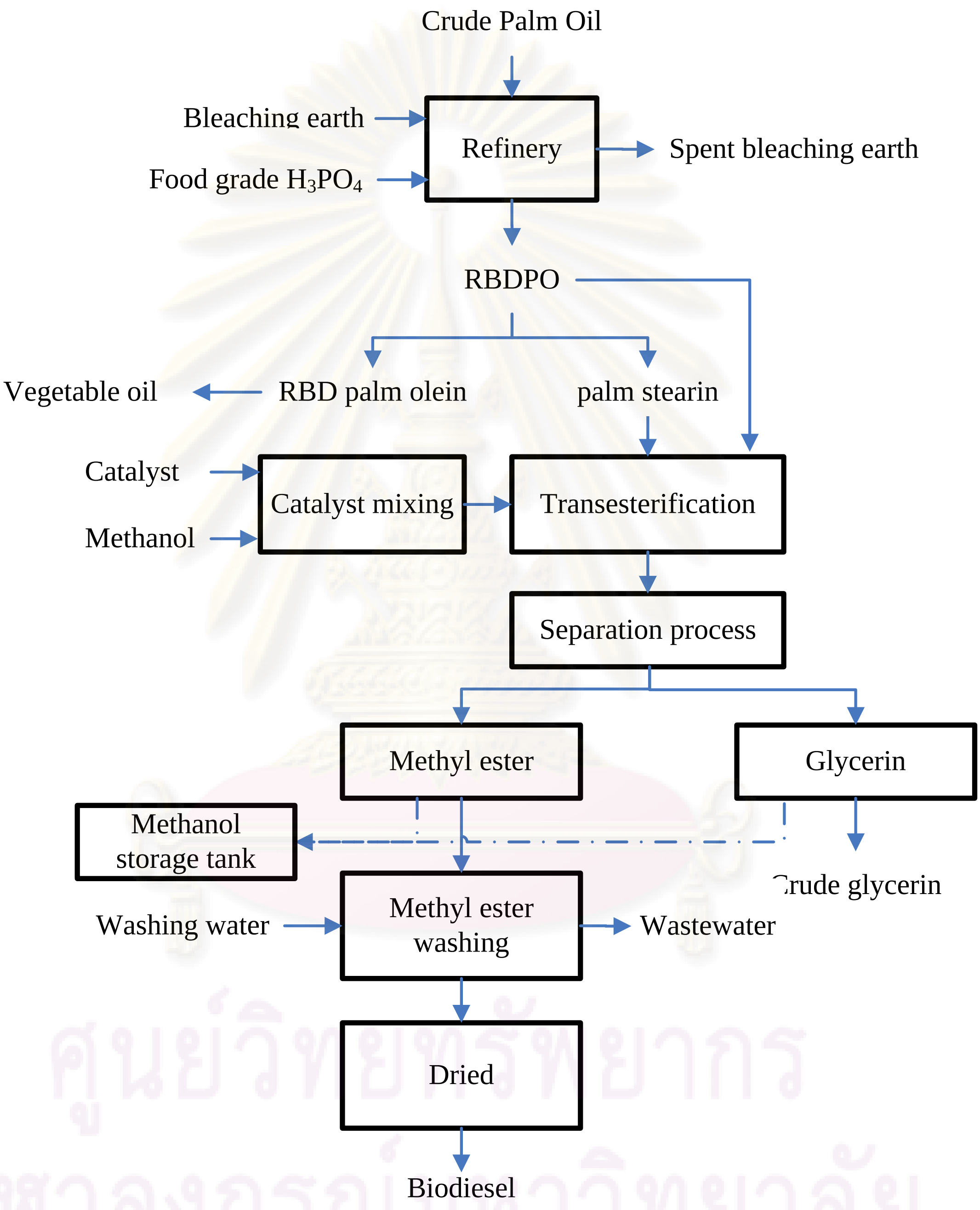


Fig 4-1 Biodiesel production process

Methyl ester washing process: Most of the selected factories purify the methyl ester by gently washing with warm water around 3 to 5 times to remove residual catalyst, soaps, and some glycerin. The methyl ester, which is known as biodiesel, from this purification step is clear amber-yellow liquid with a viscosity similar to petrodiesel. However, this step generates high volume of wastewater.

Methyl ester distillation process: From the survey, there is only Factory A that purifies methyl ester by distillation. Due to use of CH_3ONa as catalyst, less saponified product or soap occurs in the process. So this processing type does not need washing to remove soaps. The distillation process not only removes excessive alcohol from methyl ester, but also removes color to some degree. The product is a colorless methyl ester, which is higher quality and can be used for other purposes than being fuel. However, this process consumes high energy and leaves the dark brown biodiesel and tri-glyceride residues at the bottom.

The purified methyl ester is dried and storage as biodiesel.

Glycerin purification

After being removed methanol, the crude glycerin has purity of 80 – 85%, called. All of the biodiesel factories store it in plant, waiting for selling to glycerin purifying factories both in Thailand and other countries.

4.1.2 Inputs of biodiesel production process

4.1.2.1 Feeding oil

The selected factories can be classified into 2 types upon the existence of palm oil refinery process within the factories. This makes the different feeding oil used. From the survey of five studied factories, oil feedstock can be divided into refined-bleached-deodorized palm oil (RBDPO), palm stearin, and used cooking oil.

Refined-bleached-deodorized palm oil (RBDPO)

RBDPO is obtained from refining crude palm oil. Crude palm oil is degummed and bleached in order to adjust its quality by adding acid and then bleaching earth. After that the bleached palm oil is fed to the refinery column, producing RBDPO a light yellow liquid mixed semi-solid at room temperature, and fatty acid as a product and by-product, respectively. Biodiesel produced from RBDPO has higher quality, such as cloud point, than produced from palm stearin.

Palm stearin

Palm stearin is one of the products obtained from separation of RBDPO. Another is RBD palm olein, which is served as raw material for producing edible vegetable oil. Although most of stearin is used as raw material for soap-producing industry, some biodiesel factories having their own refinery process use stearin as oil feedstock to produce biodiesel. In contrast, the biodiesel factories that do not own refinery process have to purchase palm stearin, which is cheaper than RBDPO. The path way of palm oil is shown in the figure 4-2.

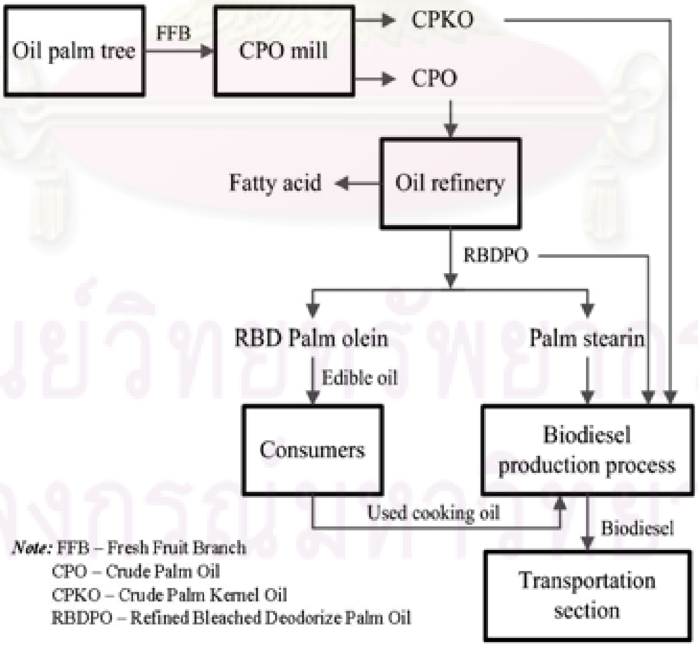


Fig 4-2 Path way of biodiesel produced from palm oil

Used cooking oil

The used cooking oil can also be used as raw material of biodiesel. However, it requires filtration for food residual, evaporation of moist, and addition of anti-oxidant before feeding to the biodiesel production process. Moreover, the amount of used cooking oil is insufficient for biodiesel production demand. Thus, most biodiesel factories do not use it to produce biodiesel for commercial.

From the survey of five selected factories, the production of 1 m^3 biodiesel uses the average feeding oil of 900, 870, and 1,000 kg for RBDPO, palm stearin, and used cooking oil, respectively.

4.1.2.2 Alcohol

The result from the survey shows that all factories use methanol in the process due to its low cost. The average alcohol consumption of five selected factories was 160 kg per 1 m^3 biodiesel.

4.1.2.3 Catalyst

The common catalysts used in transesterification are either NaOH or KOH. Even though NaOH is cheaper than KOH, the by-product, glycerin, is in a solid form at room temperature. In contrast, glycerin from using KOH as catalyst is in a liquid form. Therefore, some of biodiesel factories use KOH as catalyst because the by-product can be easily handled. From the survey, Factories C, D, and E use NaOH as catalyst, whereas Factory B uses KOH.

However, saponified product may occur in the production process when using NaOH and KOH as catalyst. Sodium methoxide is the other catalyst for producing biodiesel. It is colorless solid that is formed by deprotonation of methanol. Since it is anhydrous catalyst, less saponified product occurs in the process and the glycerin is easily separated from methyl ester. Moreover, the yield of product is greater than using NaOH or KOH. Nevertheless, Sodium methoxide is relatively expensive and highly caustic and more volatile as compared with NaOH catalyst. From the survey, Factory A uses CH_3ONa as catalyst, while Factory E only uses it when its price goes down.

The average use of catalyst in the selected factories was 10 kg per 1 m^3 produced biodiesel.

4.1.2.4 Water consumption

In the production process, the major source of water consumption is methyl ester washing step to remove residual catalyst, methanol, and some soap. From the survey, the production of 1 m^3 of biodiesel consumed potable water approximately 0.47 m^3.

4.1.2.5 Energy consumption

Steam and electricity are energy used in the biodiesel production processes. The factories that have their own crude palm oil process use palm fiber as fuel to produce steam, whereas the others without their own crude palm oil process have to purchase steam and electricity. From the survey, all of the selected factories had no energy collecting data. However, Gonsalves (2006) reported that the average consumption of steam and electricity were 680 kg and 26 kWh per 1 m^3 of biodiesel, respectively.

4.1.3 Outputs of biodiesel production process

4.1.3.1 Methyl ester

Methyl ester, biodiesel, is the major product of transesterification reaction. It is generated around 90% of the feeding oil. Its color is either golden or dark brown, depending on the production feedstock.

4.1.3.2 Glycerin

In theory, conversion of oil to biodiesel produces about 10 % by weight of glycerin as a by-product. However, more glycerin is practically generated around 15%. Crude glycerin contains alcohol, catalyst residue, carry-over fat/oil, and some esters. Results from the survey show that about 140 kg glycerin was generated from 1 m^3 of biodiesel production.

4.1.3.3 Spent bleaching earth

The biodiesel factories that have their own palm oil refinery process use bleaching earth, which is a clay adsorbent, to remove gum and color from crude palm oil, yielding refined palm oil. The bleaching earth after removing gum and color is called spent bleaching earth. The results show that the average amount of spent bleaching earth was 1%, 8 kg per 1 m^3 of produced biodiesel.

4.1.3.4 Residues of biodiesel and tri-glyceride

Residue of biodiesel and tri-glyceride occur in the methyl ester distillation process of Factory A. Methyl ester distillation process generates residue approximate 4 – 5% of biodiesel as finish product.

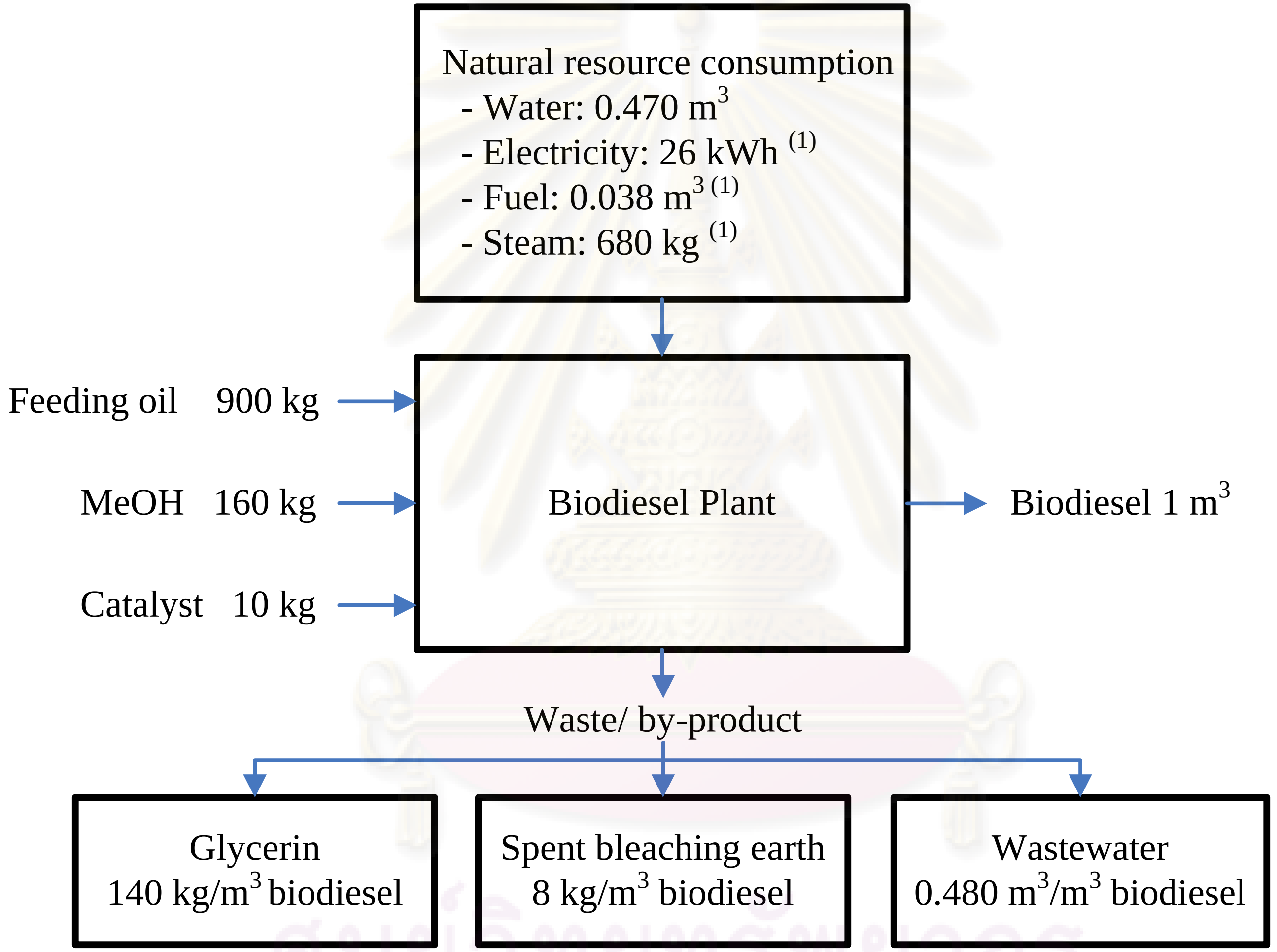
4.1.3.5 Wastewater

The major source of wastewater is from the methyl ester washing process. The wastewater contains methanol, catalyst, glycerin, and product itself. In this study, the average water consumption in the biodiesel production process was 0.47 m^3 per 1 m^3 of biodiesel.

The average values of raw material consumption and waste generation rate (per 1 m^3 biodiesel) from five selected biodiesel factories are shown in figure 4-3

4.2 Environmental impacts and existing waste management

The environmental impacts and existing waste management can be divided into 2 groups; i.e., biodiesel plants with their own palm oil refinery process and without refinery process.



Note: (1) Gonsalves, 2006

Fig 4-3 The average value of raw material and waste generation rate (per 1 m^3 biodiesel) from five selected biodiesel factories

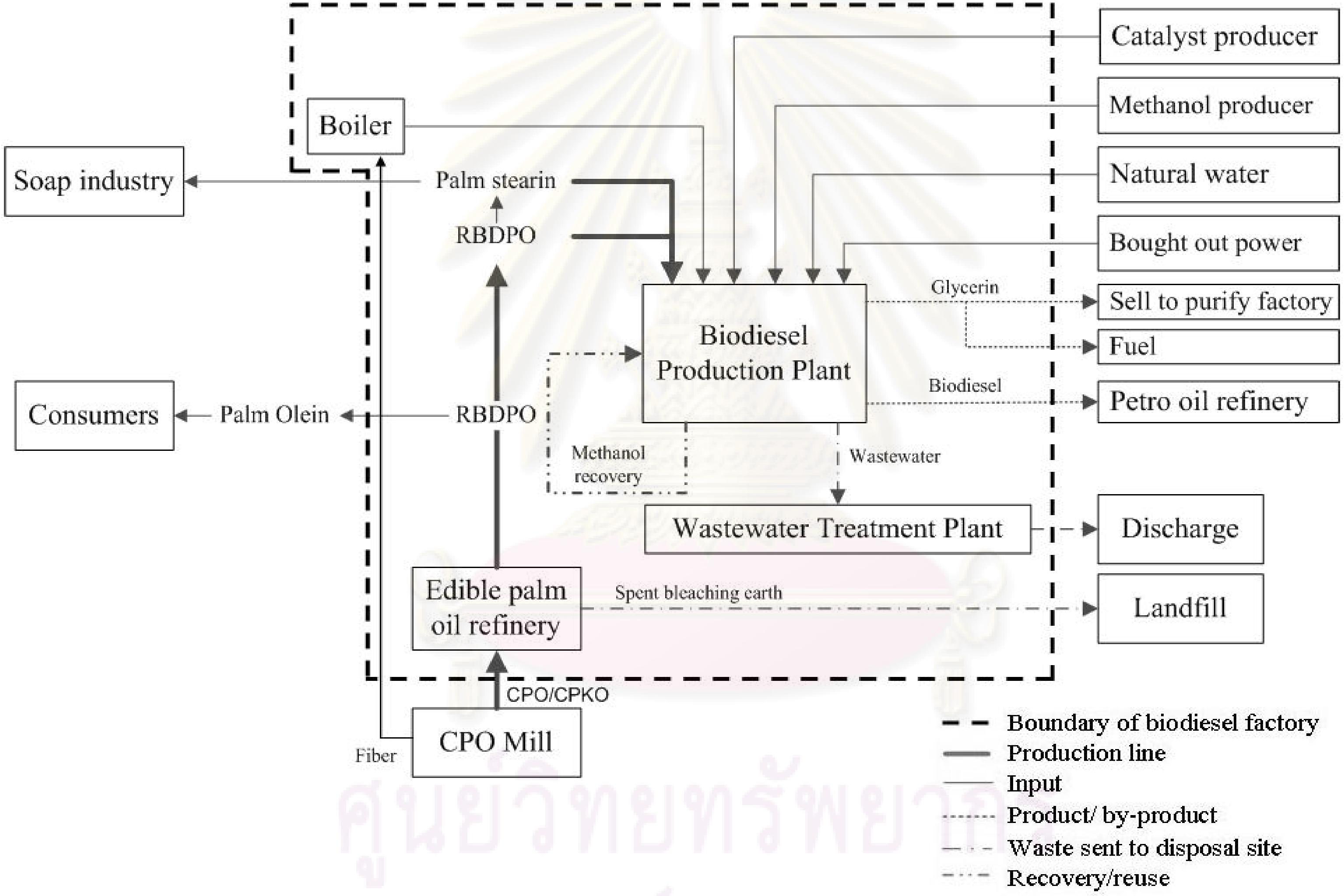


Fig 4-4 The existing waste management model of biodiesel industry which stand with own palm oil refinery plant

4.2.1 Biodiesel plants with their own palm oil refinery process

Three out of five studied biodiesel factories have their own palm oil refinery process; i.e., Factories B, C, and E. From surveying, these factories generated 3 types of waste: glycerin, spent bleaching earth, and wastewater. The existing waste management model of the biodiesel factories with their own palm oil refinery process is shown in figure 4-4.

4.2.1.1 Glycerin

Despite of the wide applications of pure glycerin in food, pharmaceutical, and cosmetics, refinery of crude glycerin for a high purity is considered to be costly and unworthy. Therefore, two of the studied factories store crude glycerin in their factories and sold it to purifying factories in other countries, such as China and India. Purification of glycerin can add the final product value. The other factories sell glycerin as fuel for other industries.

4.2.1.2 Spent bleaching earth

Factories B, C, and E with their own palm oil refinery process use bleaching earth in the step of crude palm oil refinery to remove gums, color pigment, and other contaminants. Spent bleaching earth contains gum, color pigment, oil, and some nutrient such as carotenoids and chlorophyll, which are the components of palm oil. The average amount of bleaching earth use was approximately 8 kg per 1 m^3 biodiesel. Spent bleaching earth is disposed to landfill without treatment.

4.2.1.3 Wastewater

The major source of wastewater is from the methyl ester washing step. Wastewater is contaminated with feeding oil, methyl ester, glycerin, methanol, and alkaline catalyst. It is characterized by high pH, high COD ranging from 37,419 to 117,419 mg/L, and high oil and grease ranging from 325 to 8,190 mg/L. The wastewater characteristics are shown in table 4-2.

In this study, each factory has wastewater treatment systems with a few different processes. For example, Factory C employs wastewater pH adjustment to an acidic condition in order to separate and remove oil from wastewater with grease trapping. After that wastewater is neutralized and drained to an anaerobic lagoon following by an aerobic system. Factories B and E use the similar wastewater treatment system as that of Factory C with some exception. Factory B has no grease trapping and employs only anaerobic treatment process, while Factory E has only an anaerobic lagoon.

4.2.2 Biodiesel plants without their own palm oil refinery process

Although the biodiesel plants without their own palm oil refinery process have different feeding oil from the plants with refinery process, their wastes are similar, except for spent bleaching earth. The figure 4-5 shows the existing waste management plan for the biodiesel plants without their own palm oil refinery process.

4.2.2.1 Glycerin

Similarly, one of the studied factories stores glycerin for sale to glycerin-purifying factories both in Thailand and other countries, whereas the others sell glycerin to nearby industries as fuel.

4.2.2.2 Residues of biodiesel and tri-glyceride

Approximate 4 – 5% of biodiesel and tri-glyceride residue, which are generated from methyl ester distillation process of Factory A, are used as fuel for energy in its plant.

4.2.2.3 Wastewater

The major source of wastewater is from the methyl ester washing step. Wastewater of Factory D is also contaminated like wastewater of Factories C and E. It is characterized by high pH, high COD of 170,100 mg/L, and high oil and grease of 9,032 mg/L as shown in table 4-3. From the survey, Factory D employs only aerobic process to treat wastewater, while Factory A has no wastewater treatment process because it employs methyl ester distillation process.

Table 4-2 Wastewater quality of biodiesel plant standing with palm oil refinery plant

	Size of factory	**Wastewater load (L/L biodiesel)**	**pH**	**COD (mg/L)**	**SS (mg/L)**	**FOG (mg/L)**	**Glygerin (mg/L)**	**Methanol (mg/L)**
Factory C	Medium	0.39	5.52	37,419	25	325	379	6,318
Factory E	Large	0.33	10.13	117,419	910	8,190	39	37,603

Note: * Wastewater after pre-treatment using CPI system
No collected wastewater of Factory B because of shutting down

Table 4-3 Wastewater quality of biodiesel plant standing without palm oil refinery plant

	Size of factory	**Wastewater load (L/L biodiesel)**	**pH**	**COD (mg/L)**	**SS (mg/L)**	**FOG (mg/L)**	**Glygerin (mg/L)**	**Methanol (mg/L)**
Factory D	Medium	0.77	10.00	170,100	4,251	9,032	9,602	66,267

Note: No wastewater from Factory A according to methyl ester distillation

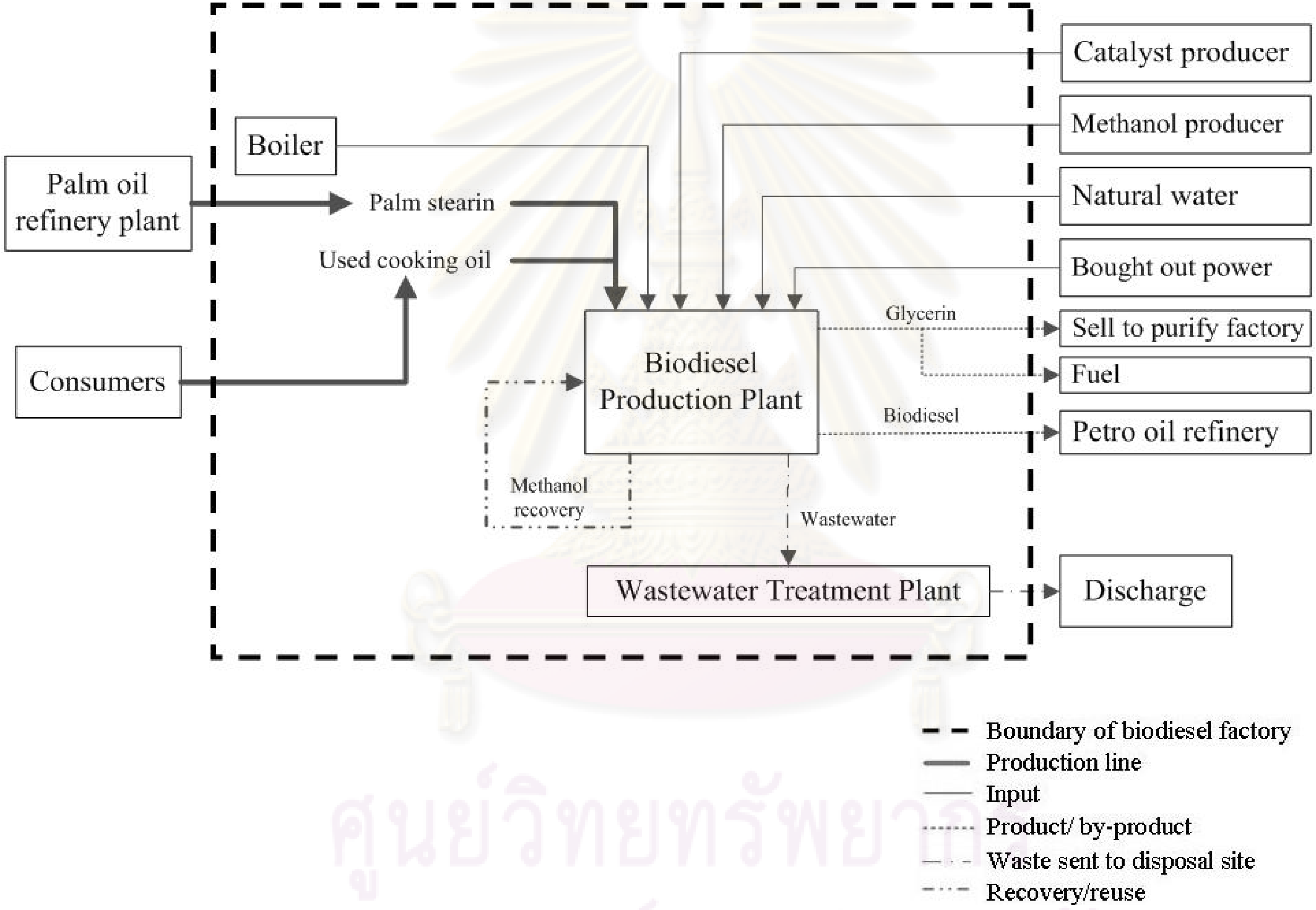


Fig 4-5 The existing waste management model of biodiesel industry which stand without own palm oil refinery plant

Table 4-4 Summary of proposed options waste management

Proposed options	**Technology**	**Products**	**Scale**	**Reference**
Reuse the last methyl ester washing water as the first washing water			Commercial scale	
Reuse of crude glycerin as fuel - Direct burning	Paten-pending burner system	Fuel	Commercial scale	Hassannia, 2009
- Hydrogen/syn gas fuel	Pyrolysis	Hydrogen and syn gas	Experimental scale	Chaudhari and Bhakshi, 2002; Valliyappan, 2004; Valliyappan et al., 2008
	Steam gasification	Syn gas	Experimental scale	Xu et al., 1996; Chaudhari and Bhakshi, 2002; Valliyappan, 2004;
	Catalytic steam reforming	Syn gas	Experimental scale	Czernik et al., 2000; Chaudhari and Bhakshi, 2002; Chaudhari and Bhakshi, 2002; Slinn et al., 2008

Proposed options	Technology	Products	Scale	Reference
	Fermentation	Methane and carbon dioxide	Commercial scale	Renewable Product and Energy Technology Centre, 2009a
- Pelletized fuel		Pelletized fuel	Experimental scale and household use	Clark, 2002; Chaiyaomporn, 2008; Brandy and Tam, 2009
Purify glycerin by the factory itself and sold as pharmaceutical grade	Distillation process	> 90% purity	Commercial scale	Matthys, 2003; K-Patents Process Instruments
	Chemical process	75 – 80% purity	Experimental scale and community scale	Zengwong and Kodkhamhan, 2001; Punyanun et al., 2006; Renewable Product and Energy Technology Centre, 2009b
Recycling of crude glycerin as raw material for other industries	Via biological process	Hydrogen and ethanol	Experimental scale	Nakashimada et al., 2002; Ito et al., 2005

Proposed options	**Technology**	**Products**	**Scale**	**Reference**
		1,3-propanediol	Experimental scale	Veiga da Cunha and Foster, 1992; Biebl et al., 1992; Biebl and Marten, 1995; Macis et al., 1998; Cheng et al., 2004; González-Pajuelo et al., 2006; Yang et al., 2007
		Citric acid	Experimental scale	Roukas and Kotzekidou, 1997; Papanikolaou et al., 2002
		Polyhydroxyalcanoate	Experimental scale	Bormann and Roth, 1999; Ashby et al., 2004; Ashby et al., 2005
		Dihydroxyaceton	Experimental scale	Wethmar and Deckwer, 1999; Bauer et al., 2005
		Succinic acid	Experimental scale	Lee et al., 2001; Lee et al., 2004

Proposed options	Technology	Products	Scale	Reference
		Propanoic acid	Experimental scale	Barbirato et al., 1997
		Biosurfactant	Experimental scale	Rahman et al., 2002; Nitschke et al., 2005; Zhang et al., 2005
		Pigment	Experimental scale	Kusdiyantini et al., 1998; Montaner et al., 2000; Campàs et al., 2003; Tao et al., 2005
	Via chemical process	Bio-methanol	Commercial scale	BioMCN, 2009
		Propylene glycol	Commercial scale	Senergy Chemical Holdings, Dow Haltermann Custom Processing, and Huntsman Corp. (Shelley, 2007)
		Epichlorohydrin	Commercial scale	Solvay Chemical, 2009
		Glycerin tri-butyl ether (GTBE)	Experimental scale	Malinavskii and Vvedenskii, 1953; Vijai and Berwyn, 1995; Noureddini et al., 1998

Proposed options	Technology	Products	Scale	Reference
		Mono- and dilaurins	Experimental scale	Nakayama et al., 2004; Mantri et al., 2005; Nakamura et al., 2008
Regeneration and utilization of spent bleaching earth			Experimental scale	Foletto et al., 2002; Chomphuchan and Chomphu, 2005; Vanichchareonngam and Muodchan, 2005; Chatchoochaikul and Phokha, 2006
Reuse of spent bleaching earth for both in industrial and agricultural sectors		Mould releasing agent Soil-improving substance Feedstuff	Commercial scale Commercial scale Commercial scale	

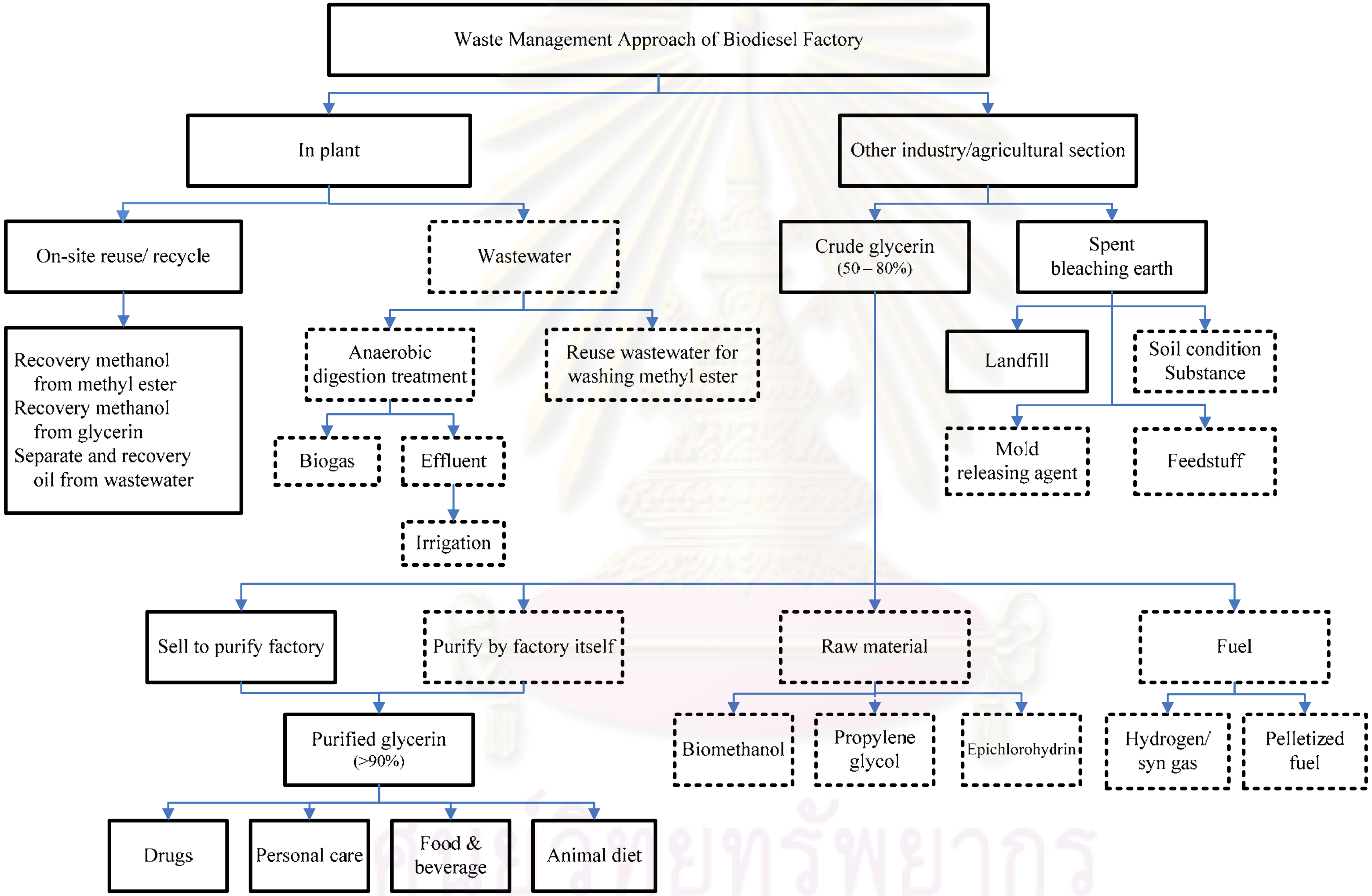


Fig 4-6 The waste management options (—— Existing waste management, - - - Proposed waste management)

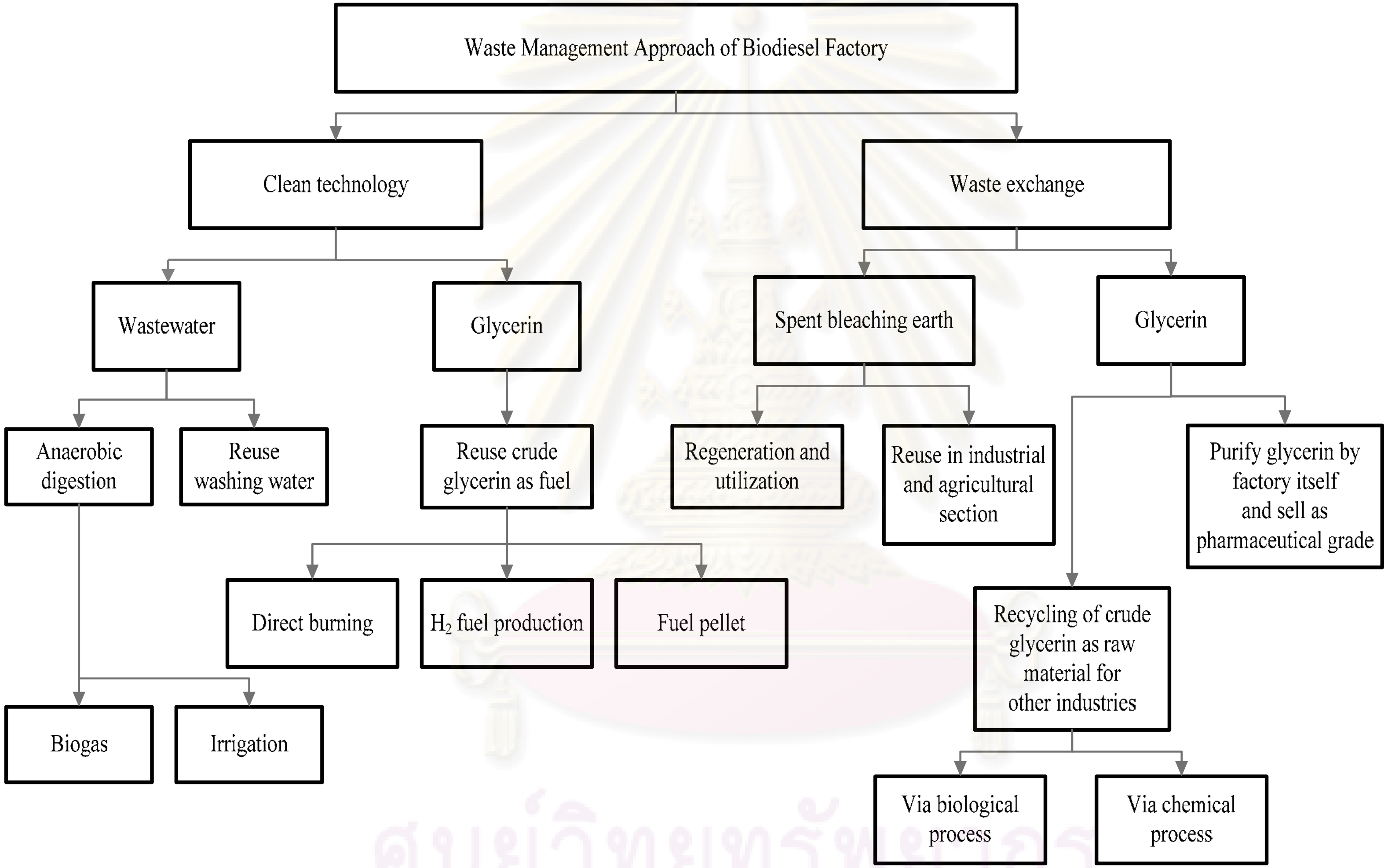


Fig 4-7 The proposed waste management classified into clean technology and waste exchange options

4.3 Proposed waste management options

Possible options are proposed in order to improve the environmental performance of the selected factories and also to make biodiesel production in Thailand more sustainable. The proposed waste management options which are summarized in table 4-4 can be classified into clean technology and waste exchange. The figure 4-6 shows the waste management options, both existing and proposed options, for improving environmental performance of biodiesel factories. The figure 4-7 shows the proposed waste management classified into clean technology and waste exchange.

4.3.1 Clean technology

4.3.1.1 Reuse the last methyl ester washing water as the first washing water

In methyl ester washing step of batch technology, there are usually 3 to 5 times of washing water. From table 4-5, showing the quality and quantity of washing water of Factory D, the last washing water contains less as amounts of suspended solid, COD, glycerin, and methanol. It can be reused as the first washing water.

The summary estimated revenue of this option for Factory D is shown in table 4-6. Factory D, an example of this practice, purifies 20,000-liters methyl ester by washing with water for 5 times.

Table 4-5 Quality and quantity of washing water of Factory D

Indicators	**Water consumption (m^3/time)**	**Concentration**					
		pH	**SS (mg/L)**	**COD (mg/L)**	**FOG (mg/L)**	**Glycerin (mg/L)**	**Methanol (mg/L)**
1st Washing water	3	9.62	20,450	712,800	17,880	42,237	257,917
2nd Washing water	3	10.33	675	107,950	10,880	3,126	56,016
3rd Washing water	3	9.12	60	19,483	9,100	952	14,406
4th Washing water	3	9.46	40	7,774	6,280	933	2,574
5th Washing water	3	7.68	30	2,495	1,020	764	421

Note: SS = Suspended Solid, COD = Chemical Oxygen Demand, FOG = Fat, Oil, and Grease

Table 4-6 Summary estimated revenue of reuse the last methyl ester washing water of Factory D

Production capacity	20 m^3 /day
Times of methyl ester washing (per 20 m^3 of biodiesel)	5 times
Total washing water consumption	15 m^3
Amount of reuse the 4th and 5th washing water	6 m^3/day
Estimated cost of potable water (Provincial Waterworks Authority, 2008)	24 baht/m^3
Total water saving cost	144 baht/day 43,200 baht/year

This practice can reduce not only the amount of water consumption and wastewater generation but also the cost of potable water purchasing, 43,200 baht/year, and wastewater treatment operation.

4.3.1.2 Reuse of crude glycerin as fuel

Direct burning

The combustion of crude glycerin offers an elegant solution for glut of glycerin. A kilogram of glycerin burned gives roughly 16 MJ of energy, which could be used in the biodiesel process or another collocated system with an optimal combination of heat and power. However, the combustion of glycerin has heretofore been challenging because of technical, safety, and cost obstacles. Due to its properties, glycerin has a high viscosity, high auto- ignition temperature and low heating value. This means that conveying glycerin along pipes to a burner is difficult; ignition of glycerin is hard, and it is even more challenging for an operator to maintain a flame. In addition, if the glycerin is incompletely combusted, it is possible to generate pollutants such as acrolein. Generally, biodiesel factories that associated with palm extraction and palm oil refinery plant usually use glycerin as fuel in the boiler.

The patent-pending burner system developed by Diversified Energy Corporation and North Carolina State University (DEC-NCSU) uses a novel spray atomization swirl burner architecture that overcomes technical and safety issues. This includes a unique approach to pre-heat the combustion chamber, maximize heat and radical retention, and carefully mix the air and fuel flows. Several forms of crude glycerin (from the transesterification of chicken fat, and virgin and waste soybean oil) have been successfully combusted in the burner. The crude glycerin does not require pre-treatment or blending with another fuel source. Preliminary emissions characterization has been completed to showcase the system's safety; for example, acrolein emissions have been shown at the few parts per billion level and other aldehyde emissions similar to that of methane, propane, or kerosene combustion. (Hassannia, 2009)

For commercial-scale, DEC demonstrated how the burner could be successfully integrated into such a boiler to allow for crude glycerin as the energy source for the boiler. The design will allow for the boiler to utilize natural gas or fuel oil, crude glycerin, and its combinations. At least ten varieties of crude glycerin will be demonstrated (including some from operational facilities) which showcase a variety of feedstocks, alcohol levels, catalysts, and water content, among other parameters.

Preliminary economic analyses, payback periods, and return on invested capital have been completed to characterize the potential value of this crude glycerin burner; however, it is not revealed to the public.

Hydrogen/syn gas fuel production

At present, almost 95% of the hydrogen (H_2) is being produced from fossil fuel-based feedstocks (Ewan et al., 2005) and most is used as a chemical ingredient in petrochemical, metallurgical, food, and electronics processing industries (Yang et al., 2006). Demand for hydrogen is growing due to the technological advancements in fuel cell industry (Dunn, 2002).

Glycerin is a potential feedstock to produce hydrogen because one mol of glycerin can theoretically produce up to 4 mol of hydrogen. Compared to ethanol, glycerin has more number of moles of hydrogen and it would be a logical substrate to produce hydrogen. The hydrogen production process from glycerin can be divided into pyrolysis, steam gasification, catalytic steam reforming, and fermentation technology.

Pyrolysis

Pyrolysis is a special case of thermolysis, and is most commonly used for organic materials which does not involve reactions with oxygen or any other reagents but can take place in their presence at high temperature. The pyrolysis process yields liquid fuels at 400 to 600ºC and gaseous products more than 750ºC.

Several research projects carried out pyrolysis of glycerin at high temperature, in range 350 – 800ºC (Chaudhari and Bhakshi, 2002; Valliyappan, 2004; Valliyappan et al., 2008). The maximum gas product yield was 71 wt % and volume of product gas was 1.32 L/g of glycerin. Heating value ranged from 13 to 22 MJ/m^3. There were some residue and char in the process.

Steam gasification

Gasification is a method for extracting energy from many different types of organic materials. Its process converts carbonaceous materials, such as coal, petroleum, biofuel, or biomass, into carbon monoxide and hydrogen by reaction the raw material at high temperatures with a controlled amount of oxygen. It is a process related to pyrolysis, but the major difference between is that gasification achieved in the presence of oxygen, in the form of air, pure oxygen or steam.

Many researchers carried out stem gasification of glycerin at temperature of 700 – 800 °C (Chaudhari and Bhakshi, 2002; Valliyappan, 2004). Glycerin was converted to the maximum gas yield of 94 wt% at 800 °C. The net energy recovered at 800 °C was 117.19 kJ/mol of glycerin fed. Xu et al., 1996 carried out gasification of glycerin with supercritical water at 600 °C. Glycerin was easily and completely gasified to a 54.3 mol % hydrogen-rich as in this condition.

Catalytic steam reforming

Catalytic steam reforming is one method of processes used to produce hydrogen from organic compounds in the presence of catalyst. The catalyst is mainly used to increase the reaction rate and to increase the selectivity of hydrogen. Catalytic steam reforming is the most energy efficient technology available, and it is the most cost-effective (U.S. Department of Energy, 2006). It is strongly endothermic, and ideally, it must be carried out at high temperatures, low pressure, and high steam to glycerin ratio to achieve higher conversion (Sehested, 2006). The steam reforming reaction of glycerin proceeds according to the following equations (Hirai et al., 2005):

Steam reforming of glycerin:

$$C_3H_8O_3 \xrightarrow{H_2O} 3CO + 4H_2$$

Water-gas shift reaction:

$$CO + H_2O \longrightarrow CO_2 + H_2$$

The overall reaction at ideal conditions can be given as follows:

$$C_3H_8O_3 + 3H_2O \longrightarrow 3CO_2 + 7H_2 \qquad (\Delta H^{o}_{298} = +346.4 \text{ kJ/mol})$$

Because of the excess steam used in the process, carbon monoxide further undergoes the water gas shift reaction to produce carbon dioxide and hydrogen. Research has been also carried out to produce hydrogen from biomass-derived oxygenated compounds such as methanol, glycerin and ethylene glycol using catalytic aqueous phase reforming reactions (Davda et al., 2003).

Catalytic steam reforming of crude glycerin was achieved in presence of several catalysts such as nickel based, HZSM–5, γ–alumina, Y–zeolite, and Pt/Al_2O_3. The temperature of crude glycerin was maintained at 60 – 80 °C because of its high viscosity which was difficult to pump and atomize. The results showed that Pt/Al_2O_3 was the best catalyst for converting crude glycerin to syn gas, almost 100% gas yield was reached and selectivities of up to 70% (dry basis) obtained at high temperature, while in presence of Ni based catalyst the hydrogen yield was around 77 wt%. Reactions using HZSM–5 catalysts produced 53 – 61 wt% of liquid product consisting of acetaldehyde and acrolein. As a result, gaseous product approximate 9 wt% yield was very low in which hydrogen concentration was around 57 – 64 mol%. γ–alumina and Y–zeolite performed poorly when compared to HZSM–5 catalyst. (Czernik et al., 2000; Chaudhari and Bhakshi, 2002; Chaudhari and Bhakshi, 2002; Slinn et al., 2008)

These results showed that a commercial value by-product from biodiesel production could become a viable renewable material for producing hydrogen and it could be potentially a better option than purification. The authors suggested that integration of the water-gas shift reaction and fluidized bed technologies would enhance the production of hydrogen and make it economically feasible.

Fermentation

Fermentation is the process of deriving energy from the oxidation of organic compounds, such as carbohydrates (Donald et al., 2005). Biogas, mainly methane and carbon dioxide, is the product of fermentation process.

Generally, glycerin fermentation process begins with methanol and moisture removal from crude glycerin. Then it is separated from the other contaminants, fatty acid and soap, by adding acid such as sulfuric acid. Glycerin, the bottom layer, is collected and neutralized with alkaline, always uses sodium hydroxide. After that glycerin is diluted to reach 10,000 to 20,000 mg/L of COD and then nutrients are added (see in appendix B-3). Before feeding glycerin to anaerobic digester, glycerin is mixed with water at mixing tank. In anaerobic digester, glycerin is degraded and biogas is produced (Renewable

Product and Energy Technology Centre, 2009a). Figure 4-8 shows the flow chart of biogas production process from glycerin.

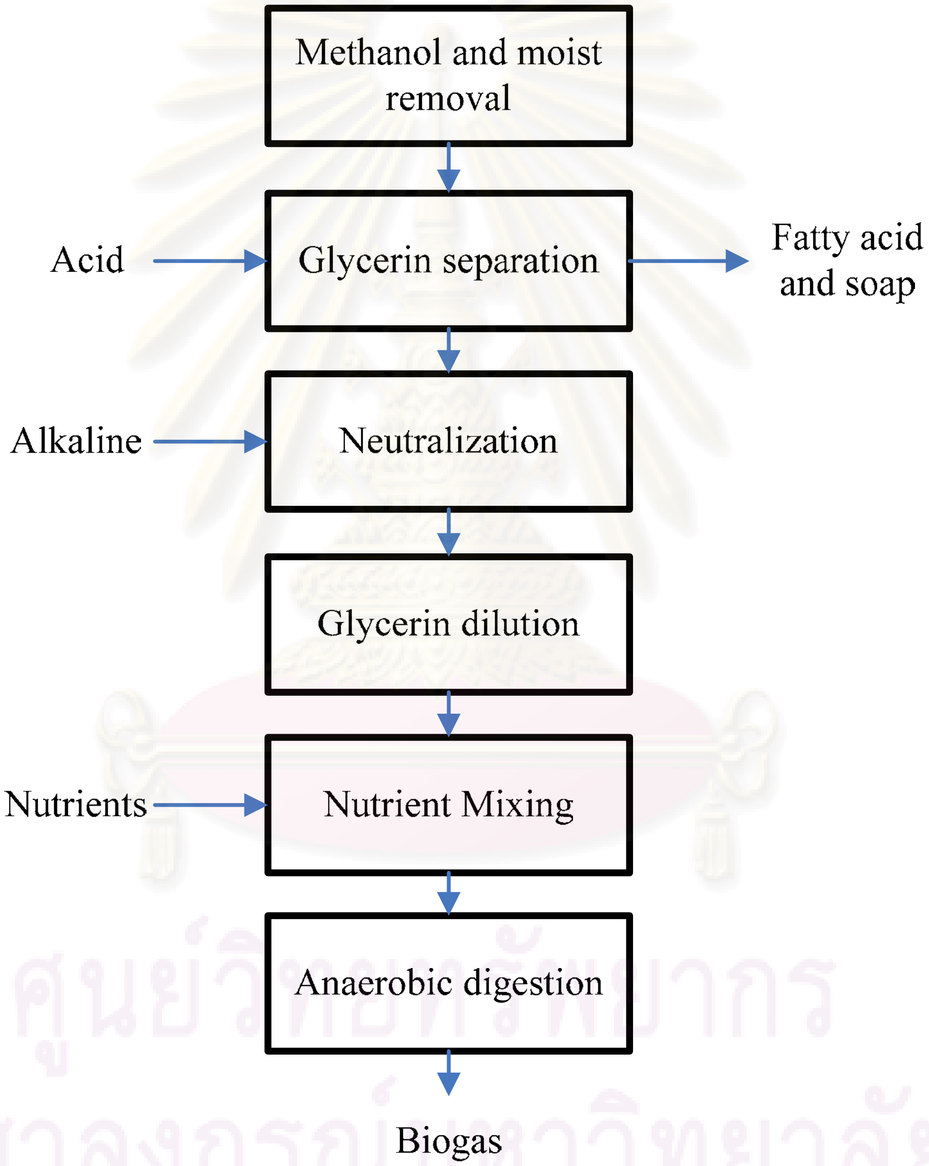


Fig 4-8 Biogas production process from glycerin

Pelletized fuel

The creation of waste pellets is already a significant industry in the developed world, converting waste from material and food industries to create compressed pellets suitable for combustion as an energy sources. The manufacture of a pellet is easy to automate. In addition, the process often does not require heat input or a chemical change, and as such can be manufactured quickly. Many of these pellets are used in combustion plants, and therefore do not need extremely costly food-grade processing.

There are a few research projects that produced the fuel pellet combined the waste glycerin from the biodiesel process with biomass. Using waste pellet as fuel would not only reduce the coal burned, but also lead to an increased use of biodiesel, thereby improving are quality and reducing the immediate health effects on the population.

The biomass glycerin fuel pellets will burn cleaner than the coal currently used as fuel in many industries. Additionally, two pre-existing waste streams will be used to make the pellets, requiring no new raw materials. Also the energy required to make the fuel pellets will be substantially less than the energy required to produce coal. Most importantly, the fuel pellets will be a nearly carbon- neutral fuel, meaning that the carbon that is released into the atmosphere when burned is carbon which has already been in the environment.

To pelletize fuel, the raw materials, waste glycerin and waste biomass such as food, paper, and agricultural waste are mixed and blended (Clark, 2002; Chaiyaomporn, 2008; Brandy and Tam, 2009). Then mixture is placed inside a mold, such as PVC pipe and milk box, which helps the pellet retain the shape like that used mold. Sometimes, pressure is applied to reduce the pellet size and also encourage the glycerin permeated the materials and form a single firm unit. The energy value for glycerin waste pellets and competing energy sources are shown in table 4-7, showing that theoretically and experimentally, the glycerin waste pellet is a very suitable source in replacing or supplementing low end coal.

Table 4-7 Energy content of fuel[1]

Literature Values: Fuel Source	Energy (kJ/g)
Coal [2]	15 – 27
Coke [3]	28 – 31
Dry wood [4]	14.4 – 17.4
Gasoline (octane) [5]	47
Diesel[5,6]	44.8 – 47
Biodiesel [2,5]	41.2
Natural gas (CH_4) [5]	56
Ethanol [5]	29.7
H_2 [5]	142
Tires	28.5 – 35
Glycerin[7]	16
Waste Plastic	29 – 40
Household waste (RDF)	12 – 16
Household (RDF)	13 – 16
Demolition waste (RDF)	14 – 15
Paper sludge (RDF)	12.5 – 22
Waste wood	15 – 17
Dried sewage	16 – 17
Animal waste	16 – 17
Commercial waste	16 – 20
Industrial waste	18 – 21
Theoretical Value: Fuel Source	
1:1.3 Biomass/glycerin (manure 60%, trimmings 35%, leafy material 5%) (theoretical)	11 – 24
1:1.3 Glycerin/sawdust pellet (theoretical)	16.94
1:1.6 Glycerin/sawdust pellet (theoretical)	17.1
Experimental Value: Fuel Source	
1:1.6 Glycerin/sawdust pellet (theoretical)	16.9
4:1:1:4 Palm fiber/palm shell/water/glycerin[8]	19.71

Source: [1] Brandy and Tam, 2009
[2] Herington, 2006
[3] Crumpler, 1996
[4] Cherry and Shorgun, 2002
[5] Fukuda et al., 2001
[6] Akers et al., 2006
[7] Hassannia, 2009
[8] Chaiyaomporn, 2008

From the table, energy content of fuel composing glycerin and biomass is in range 16.9 – 19.7 kJ/g of glycerin which is more than some another wastes such as dry wood, household waste, waste wood, animal waste and glycerin itself. To consider in cost effectiveness, Chaiyaomporn (2008), for example, estimated the cost of pelletized fuel from palm fiber and palm shell with glycerin at the optimum condition. It was 1.14 baht/kg of glycerin which was low cost, compared to 2 baht/kg of coal used in most industries.

Making pelletized fuel is a feasible idea that can be commercialized, easily. With further research and design, this concept for creating an effective source of energy from these waste streams can be applied and improved further to industry and eventually become a viable commercialized product.

4.3.2 Waste exchange

4.3.2.1 Purify glycerin by the factory itself and sold as pharmaceutical grade

The crude glycerin from transesterification process, containing alcohol, residual catalyst, water, fat/oil, and some esters, can be added value up by purifying to more than 90% purity.

Properties and utilization

Purified glycerin is the colorless, odorless, and non-poison liquid. Its structure is similar to sugar which has hydrogen bonds, so it is sweet and viscous liquid. Due to trihydric alcohol, it can well dissolve into water and $C_1 – C_5$ alcohol so that it is utilized as solvent in several industries (Sakkampung and Santhivarakorn, 2008). Moreover, it is high stability and friendly environmental substance.

Due to its properties, purified glycerin is utilized in many industries, especially in food and pharmaceutical industry. It is also used in personal care, agricultural sprays, tobacco, paper and printing, lubricants, electrical and electronics, and textiles, see also in appendix B-1. (Bonnardeaux, 2006 and Hoogendoorn et al., 2007). Glycerin is also used as ingredient in sport drink to reduce the dehydrating and to extend 20% of body duration. However, it is limited for diabetic person, pregnancy, including hypertension; heart disease; and kidney's patient (Surojchanamethakul, 2003).

Glycerin purification process

There are different processes to purify glycerin such as distillation and chemical process. However, all of them involve soap splitting followed by salt and methanol removal. Vacuum separation techniques may involve because glycerin is a heat sensitive agent that splits into water and decomposes at 180°C (Brockmann et al., 1987).

Distillation process:

The first step of glycerin purifying is oil splitting. Crude glycerin is acidified by an acid to remove catalyst and oils. After adding acid, free fatty acid and salt are formed. Since the free fatty acids are insoluble in the glycerin, they rise to the top and are skimmed off. Some insoluble salts also precipitate out. The glycerin fraction is neutralized to pH 7 by alkaline and then demethanol can start (Matthys, 2003). After removal of methanol the purity of glycerin will be approximately 85%.

The final purification of glycerin is completed using vacuum distillation with steam injection, followed by activated carbon bleaching (K-Patents Process Instruments) used to deodorize and remove color and some contaminants (Punyanun et al., 2006). Glycerin after this section is the pharmaceutical grade, 95 – 99%. By-products from glycerin purification process are soaps and alkali-salt which can be sold to soap industry and used as fertilizer, respectively, for more detail see in appendix B-2.

By enquiry a biodiesel factory, a 20-ton/day purifying-glycerin plant is planned with 40-ton/day of crude glycerin. All tanks in the process are made of stainless to avoid iron rust contamination. The example of a factory with 200-m^3/day production capacity on estimated investment capital of purifying-glycerin process by distillation and revenue from selling glycerin as pharmaceutical grade are summarized and shown in table 4-8.

Table 4-8 The example of Factory D on estimated revenue from crude glycerin purifying by factory itself and selling as pharmaceutical grade

Production capacity	200 m^3/day
Glycerin generation	20 m^3/day 25,200 kg/day
Investment capital of glycerin-purifying plant (production capacity of 20 ton/day)	18,000,000 baht
Total generated purified glycerin	12,600 kg
Average price of pharmaceutical-grade glycerin (per kg of glycerin)	20 baht
Cost of purifying glycerin (per kg of glycerin)	14 baht
Profit (per kg of glycerin)	6 baht
Total revenue from selling glycerin as pharmaceutical grade	75,600 baht/day 1,890,000 baht/month
Payback period	9.5 months

Note: Based on year 2008

Chemical process:

Although glycerin purification process by distillation obtains high purity, more than 90% glycerin, it consumes large amount of energy on the distillation column which represents approximately 75% of the total energy consumption (Hoogendoorn et al., 2007). It is hardly apply to small investment manufacturer or community scale to purify crude glycerin by distillation. Glycerin purification using chemical is the one purification process for reducing the energy consumption.

The overview of chemical process is shown in figure 4-9. It starts with methanol removal by evaporation at 70 – 80°C. Glycerin, still containing alkaline from catalyst, is neutralized with acid such as sulfuric acid. Due to low pH, the oil is separated and skimmed from glycerin. Afterward, color and odor of glycerin is removed by using activated carbon. The purity of glycerin is 75 – 80% which can be used as feedstuff.

(Zengwong and Kodkhamhan, 2001; Punyanun et al., 2006; Renewable Product and Energy Technology Centre, 2009b).

Renewable Product and Energy Technology Centre (2009) estimated the investment cost of 5 – 10 liters-capacity of glycerin-purifying pilot plant which all tanks in the process are made of stainless to avoid iron rust contamination. That estimation was 300,000 to 400,000 Baht.

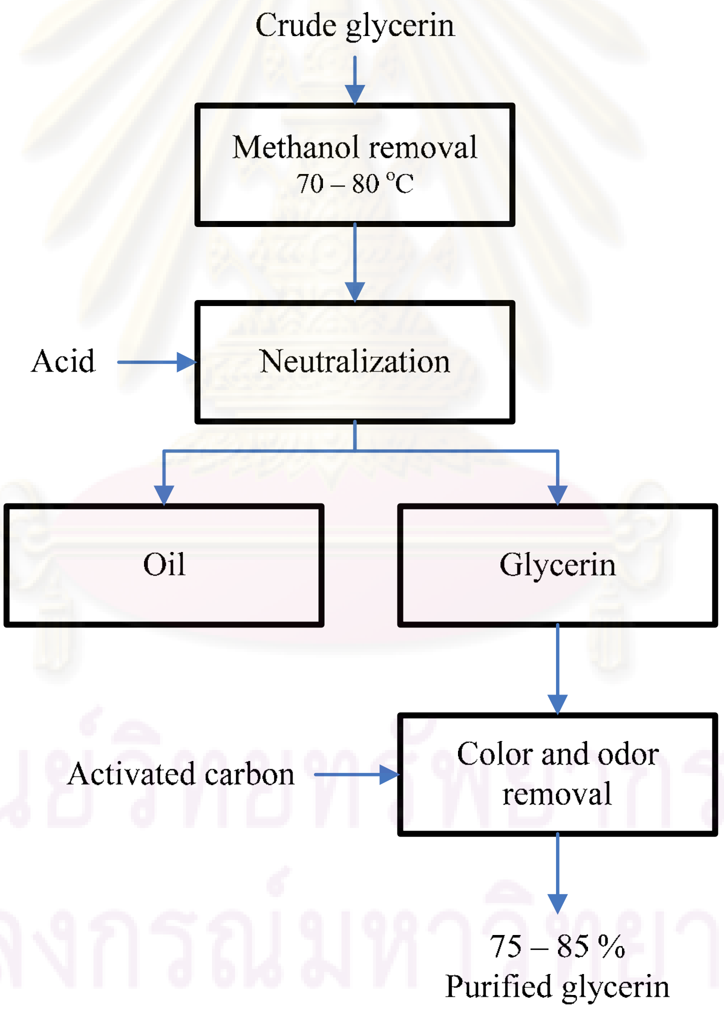


Fig 4-9 The overview of glycerin purification process using chemical

4.3.2.2 Recycling of crude glycerin as raw material for other industries

According to an overproduction of biodiesel, it would destabilize the glycerin market and may considerably reduce the current glycerin market value. Current glycerin uses involve high cost purification steps to produce a product of questionable value which is sold as low-grade glycerin (Noureddini et al., 1998). So, many researchers have found out the value added of crude glycerin via biological and chemical reaction.

Conversion crude glycerin to useful chemicals via biological process

The microbial conversion of glycerin to various compounds has been investigated recently with particular focus on the production of many products. The example of these products are hydrogen and ethanol, 1,3–propanediol, citric acid, polyhydroxyalcanoate, dihydroxyaceton, succinic acid, propanic acid, biosurfactant, and pigment (for more detail see in appendix C). Nevertheless, the conversion crude glycerin to useful chemicals via biological process is still in the experimental stage, further detail study should be carried out in commercial scale.

Conversion crude glycerin to useful chemicals via chemical process

The specialty chemicals from glycerin are due the fact that glycerin provides a C_3 building block for complex structures. It is easily modified by reacting –OH functional groups and it can produce water soluble, nontoxic, and nonflammable products. The following processes can be utilized in obtaining useful derivatives from glycerin: esterification, etherification, oxidation, reduction, amination, halogenation, nitration sulfaction, and phosphorylation (Hoogendoorn et al., 2007). The complete schematic flow sheet is given for the production and utilization routes for glycerin (Koseoglu, 2007) is shown in figure 4-10.

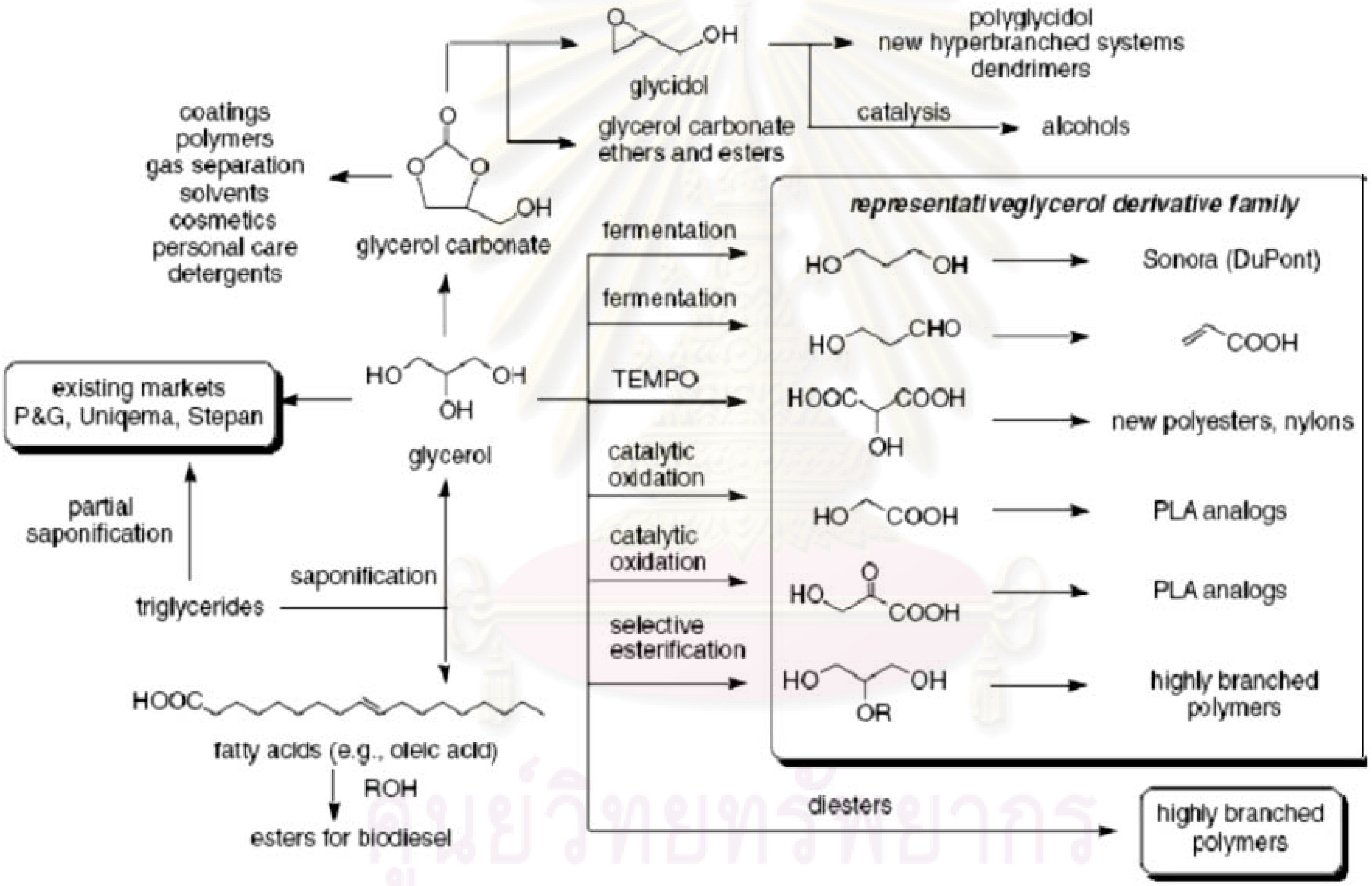


Fig 4-10 The schematic flow of production and utilization routes for glycerin (Koseoglu, 2007)

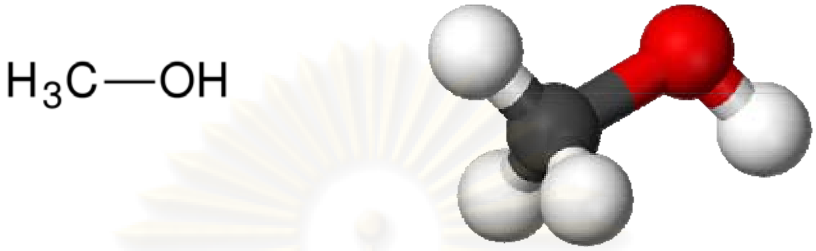


Fig 4-11 Molecular structure of methanol; 2-dimension (left), 3-dimension (right)

Converting glycerin to bio-methanol

Presently, methanol is usually produced using methane, the chief constituent of natural gas, as a raw material. It may also be produced by pyrolysis of many organic materials or by Fischer Tropsch from synthetic gas, so be called bio-methanol. Bio-methanol is an extremely versatile product, which can either be used as a fuel; it can either be blended with petro or as a feedstock for other environmentally friendly fuels. It is also used for a variety of non-fuel applications including plastics and paints. Bio-methanol can also be used as a chemical building block for a range of future-oriented products, such as bio-MTBE, bio-DME, bio-hydrogen and synthetic biofuels (BioMCN, 2009).

BioMCN is the first company in the world to produce high quality bio-methanol from renewable resources on an industrial scale. After BioMCN acquired a conventional methanol plant in Delfzijl in the north of the Netherlands using non-renewable natural gas as raw material, they have developed an innovative patented process that converts crude glycerin into bio-methanol.

The process closes the cycle by converting the by-product crude glycerin into methanol feedstock. The crude glycerin is then purified, evaporated and cracked to obtain syngas, which is used to synthesize the bio-methanol. Next, the bio-methanol is purified by distillation and is stored. Tankers delivering the crude glycerin collect a return load of methanol, thus optimizing the logistics in the chain. The bio-methanol production scheme is shown in figure 4-12.

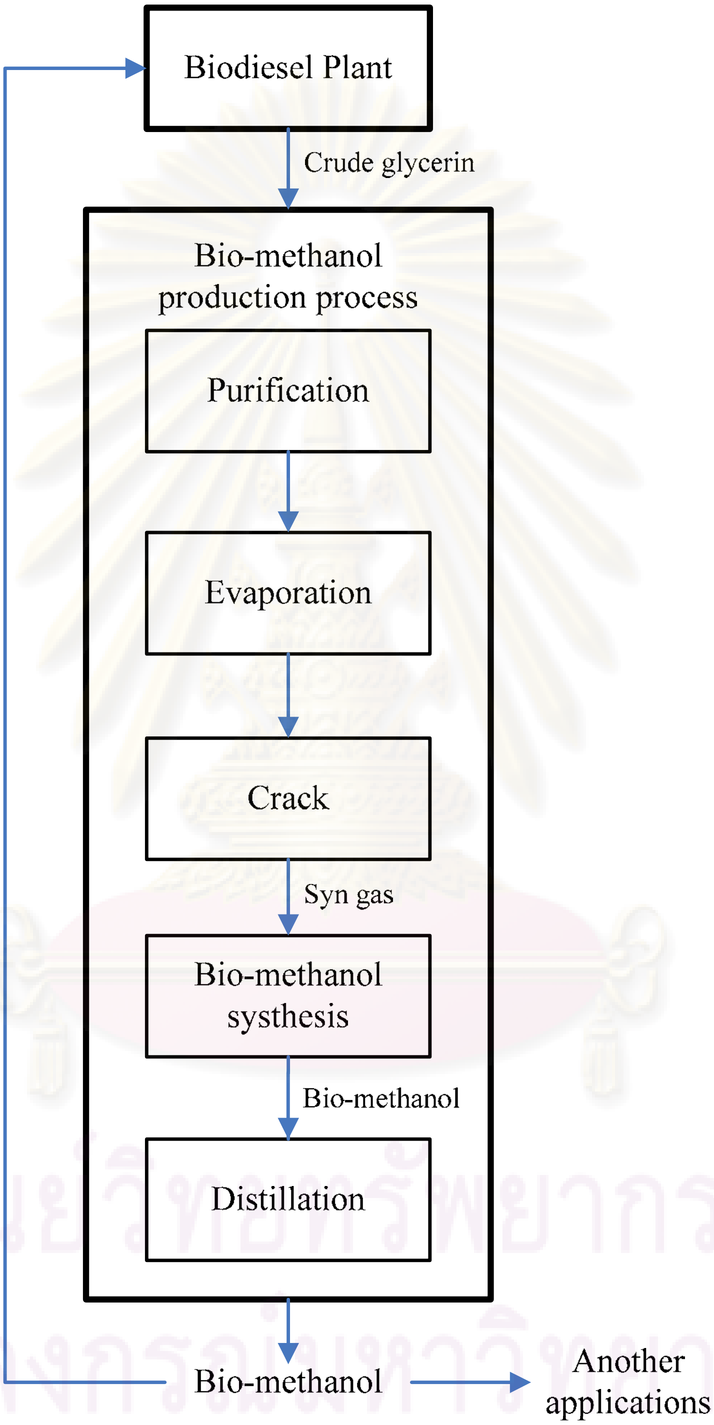


Fig 4-12 Bio-methanol production scheme

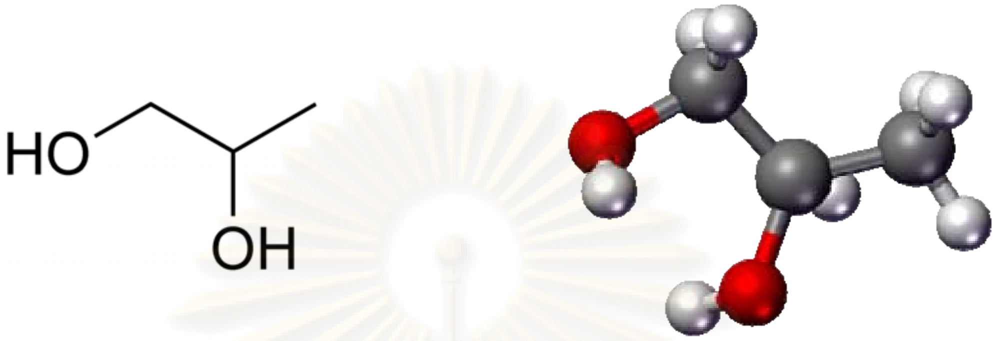


Fig 4-13 Molecular structure of propylene glycol; 2-dimension (left), 3-dimension (right)

Converting glycerin to propylene glycol

Propylene glycol, known also by the systematic name 1,2-propanediol, is an organic compound, usually a faintly sweet, and colorless clear viscous liquid that is hygroscopic and miscible with water, acetone, and chloroform. Propylene glycol, which has properties similar to those of ethylene glycol, is a widely used commodity chemical that plays a significant role in the manufacture of a broad array of industrial and consumer products, including unsaturated polyester resins, plasticizers and thermoset plastics, antifreeze products, heat-transfer and coolant fluids, aircraft and runway deicing products, solvents, hydraulic fluids, liquid detergents, paints, lubricants, cosmetics and other personal care products. The molecular structure of propylene glycol is shown in figure 4-13.

The commercial route to produce propylene glycol is by the hydration of propylene oxide derived from propylene by either the chlorohydrin process or the hydroperoxide process

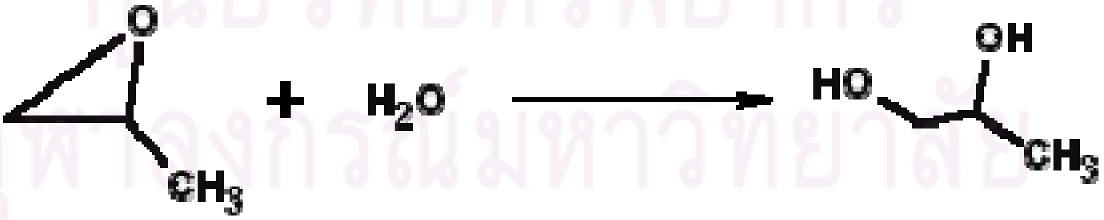


Fig 4-14 Hydration reaction of propylene oxide

(Trent, 1996), shown in figure 4-14. However, the other common route of production is in through hydrogenolysis of sugars or sugar alcohols at high temperatures and pressures the presence of a metal catalyst producing propylene glycol and other lower polyols.

In the presence of metallic catalysts and hydrogen, glycerin can be hydrogenated to propylene glycol, or ethylene glycol. In laboratory scale, many catalysts, such as copper, zinc, sulfided ruthenium, cobalt, manganese, molybdenum, nickel, palladium, platinum, and copper-chromite catalyst (Casale and Gomez, 1994; Ludwig and Manfred, 1997; Mohanprasad et al., 2005) were used to reach the optimal conditions. Copper-chromite catalyst was identified as the most effective catalyst for the hydrogenolysis of glycerin to propylene glycol because temperatures and pressures were lower than convention, 260ºC and 2,170 psi. Both of these advantages help to reduce capital and operating costs. In addition, the process has higher yields – in excess of 90% to produce a mixture of acetol and propylene glycol. The overall reaction of converting glycerin to propylene glycols is summarized in figure 4-15.

Nowadays, there are many companies run the commercial process of propylene glycol from glycerin; for instance, Senergy Chemical Holdings, Dow Haltermann Custom Processing, and Huntsman Corp (Shelley, 2007). One particular environmental benefit from using glycerin as raw material is that the production of propylene glycol consumes considerably less fresh water than the conventional, petroleum-based route for producing

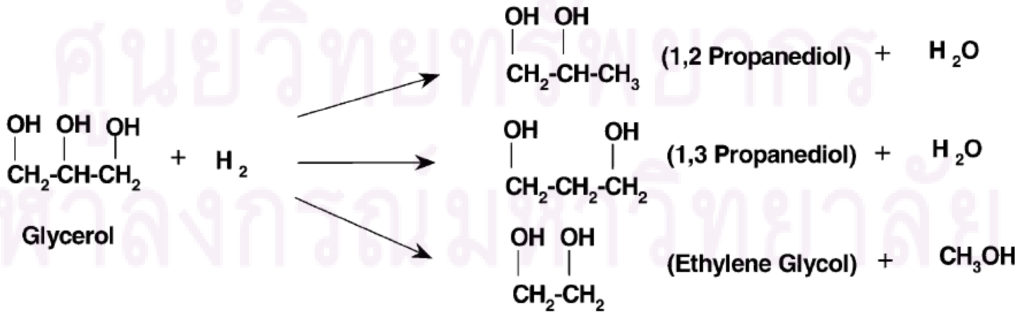


Fig 4-15 The overall reaction of converting glycerin to propylene and ethylene glycols

propylene glycol. Moreover, the renewable route to propylene glycol is a very clean process, which generates no appreciable emissions other than salts and water.

The technology used hydrogen as a co-reagent to perform a hydrogenolysis conversion of glycerin, in the presence of a copper-chromite catalyst. The process first involves the cleanup of the crude glycerin by removing a water molecule from the glycerin, and then adds a hydrogen molecule for hydrogenation. This yields two products – acetol and propylene glycol – as well as a water by-product. Distillation is then used to separate and purify the propylene glycol.

Converting glycerin to epichlorohydrin

Epichlorohydrin is an organochlorine compound and an epoxide. This a colorless liquid with a pungent, garlic-like odor is insoluble in water, but miscible with most polar organic solvents (USEPA, 2006). Epichlorohydrin is a highly reactive compound and is used in the production of glycerin, plastics, and elastomers. It is a building block in the manufacture of epoxy resins; for example by alkylation of bisphenol-A, and is also a precursor to monomers for other resins and polymers. Epichlorohydrin is used as a solvent for cellulose and paints; used in paper reinforcement; used in the food industry to manufacture tea bags, coffee filters, and sausage/salami casings; and water purification. It has found use as an insect fumigant, also (GroupPanorama, 2006). Its molecular structure is shown in figure 4-16.

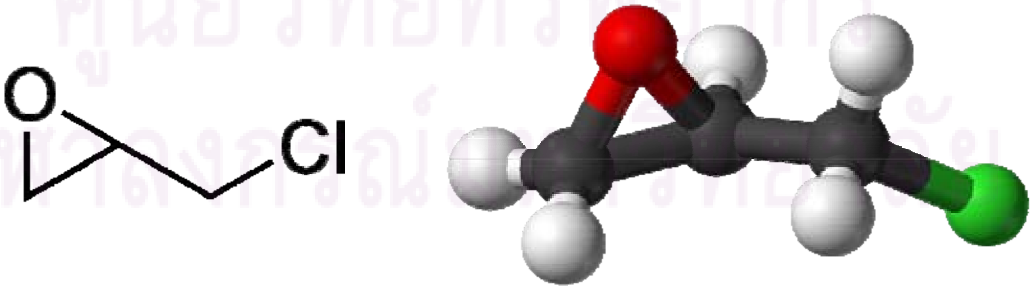


Fig 4-16 Molecular structure of epichlorohydrin; 2-dimension (left), 3-dimension (right)

Epicerol (Solvay Chemical, 2009) is a novel epichlorohydrin process developed by Solvay, based on the transformation of glycerin. The traditional epichlorohydrin process uses chlorine and propylene as raw materials while Epicerol technology is based on using hydrochloric acid and glycerin to form dichloropropanol as intermediate and then convert to epichlorohydrin. The novel technology not only utilizes renewable material, glycerin, but also largely reduces in chlorine consumption and consequently, less chlorinated organic compounds as by-products and lesser needs for effluent streams.

Converting glycerin to Glycerin tri-butyl ether (GTBE)

Although biodiesel is desired benefits of the improvements are cleaner air, a cheaper product, and better fuel properties, many problems inherent to biodiesel continue to exist. The cloud point, the temperature at which dissolved solids are no longer completely soluble, precipitating as a second phase giving the fluid a cloudy appearance, of neat soy oil methyl ester is 0ºC, as compared to -16ºC for diesel (Dunn and Bagby, 1995). The other problem with biodiesel has been reported with regard to emissions, most dramatically increased NO_x emissions. One potential solution of these problems is the use of glycerin or its derivatives as fuel additives.

Glycerin cannot be added directly to fuel due to its decomposition, polymerization and consequential engine problems at high temperatures. Glycerin must be modified to derivatives fat are compatible with diesel and biodiesel prior to being added to the fuel. GTBE is a mixture of di and tri butyl ethers of glycerin. It could similarly be used for diesel and biodiesel reformulation to reduce the emissions of particulate matter, NO_x and hydrocarbons.

Glycerin was reacted with isobutylene in the presence of catalyst, such as an acid and Amberlyst-15 catalyst, in a two-phase reaction to produce mono-, di-, and tri-tertiary butyl ethers of glycerin (Malinavskii and Vvedenskii, 1953; Vijai and Berwyn, 1995; Noureddini et al., 1998). However, it was reported that impurities in the crude glycerin appeared to poison the catalyst, which resulted in poor conversions. To minimize these effects, neutralization and methanol removal from the crude glycerin need to be performed prior to its use. A 20% blend of these additives with methyl esters resulted in a 5ºC reduction in cloud point and an 8% reduction in viscosity. The conversion of glycerin and isobutylene on acid catalysis to give mono, di, and tri glycerins is shown in figure 4-17.

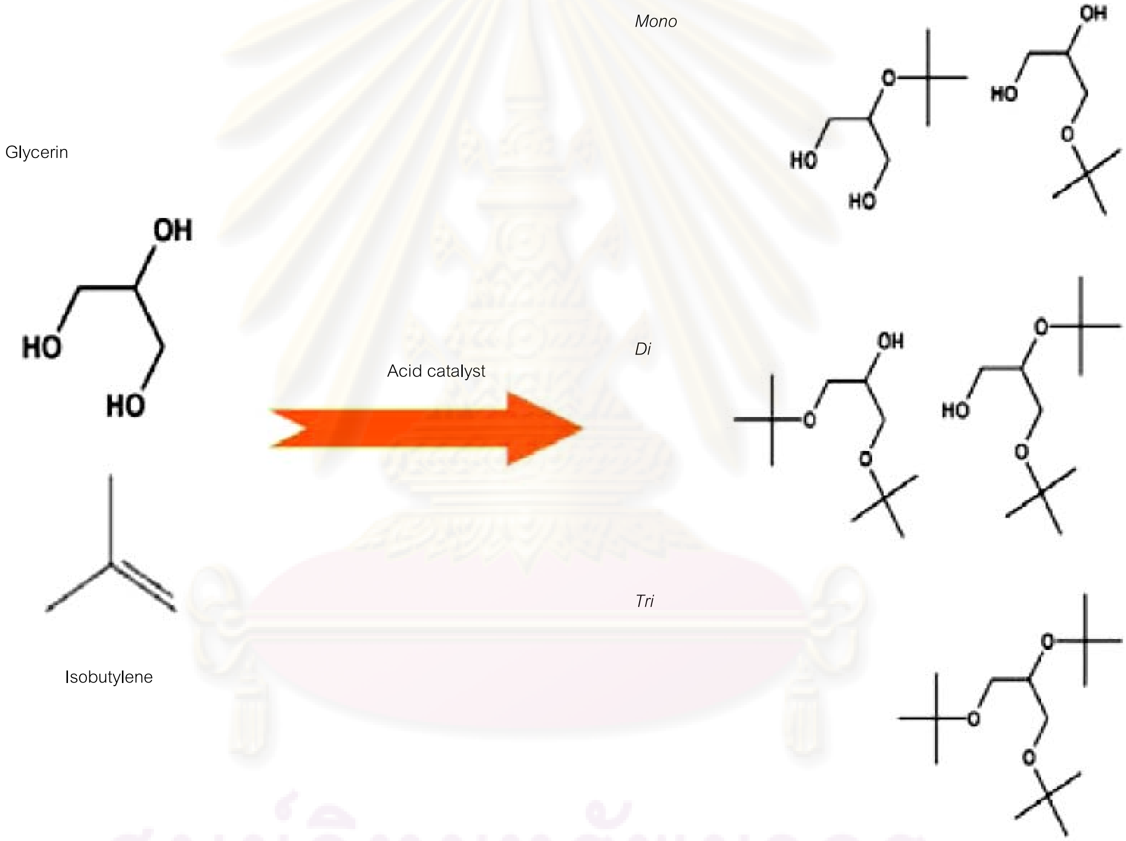


Fig 4-17 Conversion of glycerin and isobutylene on acid catalysis (Hoogendoorn et al., 2007)

Converting glycerin to mono- and dilaurins

The selective esterification of glycerin with long chain aliphatic acids has been of interest in the manufacture of functional materials for medicines, cosmetics, and surfactants. These esters have been manufactured by the esterification of glycerin with fatty acid or by transesterification of fatty acid triglyceride by glycerin. For the esterification, the strong acid such as sulfuric acid or a strong base such as cesium and sodium hydroxide has been conventionally used as the catalysts. However, there are some drawbacks from the environmental aspects, such as corrosiveness and hazards of waste catalysts (Otera, 2003). The development of alternative catalysts for the esterification, which have high activity, high productivity, and easy recovery without severe environmental pollution, is the emerging topics concerning the aspect of the green-chemical process.

Some multi-valent metal salts of chloride, sulfate, nitrate, and acetate of zirconium, aluminum, and iron were found that they had the catalytic activities for the esterification of glycerin with lauric acid. Among them, some chloride, $ZrOCl_2 \cdot 8H_2O$ and $AlCl_3 \cdot 6H_2O$, were active for the formation of monoluarin, and the sulfates, $Fe_2(SO_4)_3 \cdot nH_2O$ and $Zr(SO_4)_2 \cdot 4H_2O$ for dilaurin. The yields for them were in 70 – 80% even in the presence of excess glycerin (Nakayama et al., 2004; Mantri et al., 2005; Nakamura et al., 2008). The esterification reaction of glycerin with lauric acid is shown in figure 4-18.

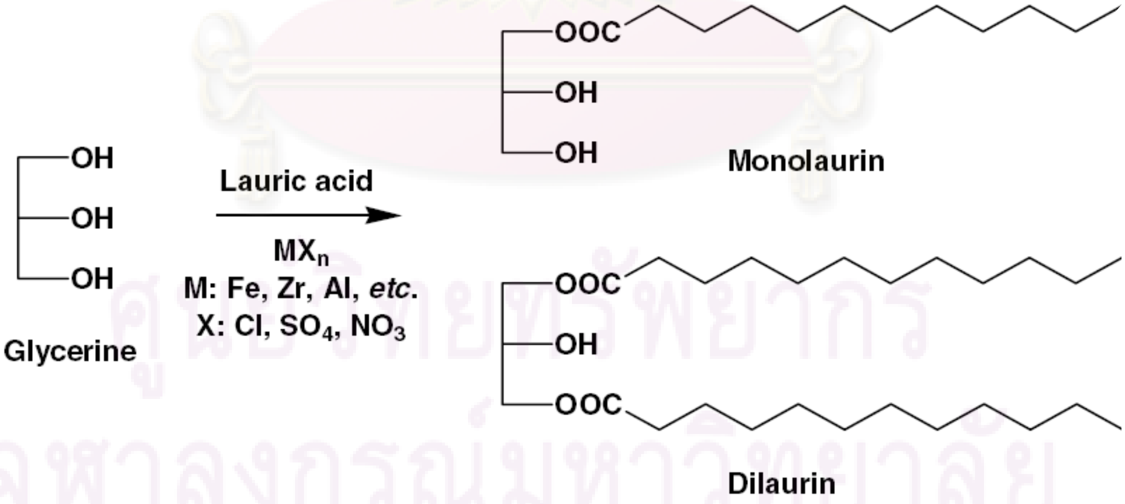


Fig 4-18 Esterification reaction of glycerin with lauric acid

4.3.2.3 Regeneration and utilization of spent bleaching earth

Bleaching earth, or activated clay, is bentonite or other clay, treated with acid to enhance its ability to absorb or bleach. After adsorption, it is called spent bleaching earth. There is no research that spent bleaching earth is utilized, reused, or recycled in the same and other sectors, because its price is cheaper than regeneration cost. However, there are a few experimental-scale projects that regenerate spent bleaching earth and utilize it as adsorbent.

To regenerate spent bleaching earth, organic solvents were used to remove residual oil, followed by reactivation through heat treatment. The solvents used showed the following order in the efficiency of oil extraction: methyl ethylketone > acetone > petroleum ether ≅ hexane. Results showed that extraction process, using just solvent, is insufficient to recover the bleaching powder of the spent clay. It needs treatment with (or only) high temperature treatment, 103ºC and 550ºC (Foletto et al., 2002; Vanichchareonngam and Muodchan, 2005; Chatchoochaikul and Phokha, 2006). After regeneration, a few research projects used spent bleaching earth to adsorb both dyes and heavy metal such as chromium, nickel, and zinc (Chomphuchan and Chomphu, 2005; Vanichchareonngam and Muodchan, 2005). The results showed that spent bleaching earth can adsorb these contaminants. Nevertheless, it took much retention time when compared with adsorption of bleaching earth.

4.3.2.4 Reuse of spent bleaching earth for both in industrial and agricultural sectors

Bleaching earth is used in vegetable oil industry to decolorize by removing color pigments like carotenoids, chlorophyll, and pheophytine and to remove gums and fatty acid. After removing unwanted contaminants, it contains gums, fatty acid, and pigments, including oil. Also in the entire palm oil industry, in this study were Factory B, C, and E, bleaching earth was used with the same purposes. They generate spent bleaching earth around 1% of feeding oil which is disposed to landfill. To reduce amount of disposal of spent bleaching earth, it should be reused in other sections such as industrial and agricultural sectors.

Industrial sectors

Mould releasing agent

According to containing gums and oil in spent bleaching earth, it can be used as mould releasing agent in tile and ceramic industry. Generally, tile and ceramic industry use oil and talcum in the production process to easily take off the product from the mould. The price of sale spent bleaching earth as mould releasing would be estimated approximately 1 – 2 baht/kg. Table 4-9 shows the revenue from selling spent bleaching earth as mould releasing agent of Factory B, the minimal generated spent bleaching earth.

Table 4-9 Revenue from selling spent bleaching earth as mould releasing agent of Factory B

Production capacity	80 m^3/day
Average spent bleaching earth generation (per m^3 of biodiesel)	8 kg
Total generated spent bleaching earth	640 kg/day
Average estimated price of selling spent bleaching earth	1.5 baht/kg
Total revenue	960 baht/day 288,000 baht/year

This option not only makes revenue to the factory approximate 288,000 baht/month but also lessens the impact of refuse on landfills.

Agricultural sectors

Soil-improving substance

Spent bleaching earth can be used to increase moisture and improve soil quality, especially for sandy soil in the north-east of Thailand, since it absorbs water and little dilates. Although its cost may be not effectiveness, this option can improve soil quality in order to growing plants for drought area.

Feedstuff

According to the interview with the expert of oil and biodiesel, he suggested that spent bleaching earth containing carotenoids, chlorophyll, and pheophytine can be feedstuff for sloping pigs. These nutrients make pigs grow up well and be healthy, since they compose some vitamin; for example vitamin A is in carotenoids. However, spent bleaching earth should be analyzed in acid value, and sometimes neutralized, before sloping because of using phosphoric acid in palm oil refinery step.

4.4 Appropriate waste treatment

From the survey, there were two kinds of wastes; i.e., spent bleaching earth and wastewater, that are need to be treated or disposed. Spent bleaching earth was disposed to landfill without any treatment; however, it should be value-added up by reusing in industrial and agricultural sectors. Wastewater is the important issue to find the appropriate treatment to reach the effluent standard and highest benefit from it.

4.4.1 Wastewater treatment

Wastewater treatment can be divided by complex treatment into primary, secondary, and final treatment (Metcalf and Eddy, 2004).

Primary treatment is the step of wastewater adjustment such as solid separation, neutralization, and precipitation, whereas secondary treatment focuses on removal organic soluble matters from wastewater. Even though, there are several types of organic matters removal, biological treatment is the most popularity due to low cost. Final treatment is employed to remove dissolved solid, heavy metals, or toxic substances such as phenol. For biodiesel wastewater, only primary and secondary treatment are employed to remove contaminants.

4.4.1.1 Primary treatment of biodiesel wastewater

Primary treatment is employed to biodiesel wastewater containing the high amount of oil and grease to separate oil and grease. In this research, oil and grease ranged from 320 to 9,000 mg/L.The wastewater is neutralized with acid, such as sulfuric acid or hydrochloric, prior to oil and grease separation. There are 3 types of oil separation techniques; i.e., coagulation-floatation, Dissolved Air Floatation and membrane filtration. Among of these, DAF is the most used and suitable method for biodiesel factories.

DAF is a flotation system where the air bubbles in the water are substantially smaller. These very fine bubbles guarantee higher separation efficiency. The air bubbles are generated by saturating a small continuous flow of clarified water with air from a small compressor at a pressure of approximate 6 bar. The pressurized air/water feed is then injected into the flotation tank and the sudden pressure drop causes the release of very fine air bubbles. They attach to the flocculated oil and solids, which then rise to the water surface in the flotation tank and form a floating layer. A skimmer removes the scum to the discharge hopper and the treated water is discharged to the next step (Wolterink, 2004). The system of DAF is shown in figure 4-19.

4.4.1.2 Secondary treatment of biodiesel wastewater

Secondary treatment employed in biodiesel wastewater is biological treatment which can be divided to anaerobic and aerobic treatment process. Generally, anaerobic process is employed following aerobic process to reduce the use of power for air pumping.

Anaerobic treatment process

Anaerobic digestion is a series of processes in which microorganisms break down biodegradable material in the absence of oxygen. It is widely used to treat wastewater sludge and organic waste because it provides volume and mass reduction of the input material (MONSAL advanced digestion technology, 2008). Anaerobic digestion reduces the emission of landfill gas into the atmosphere. It is a renewable energy source because the process produces a methane (CH_4) and carbon dioxide (CO_2) rich biogas suitable for

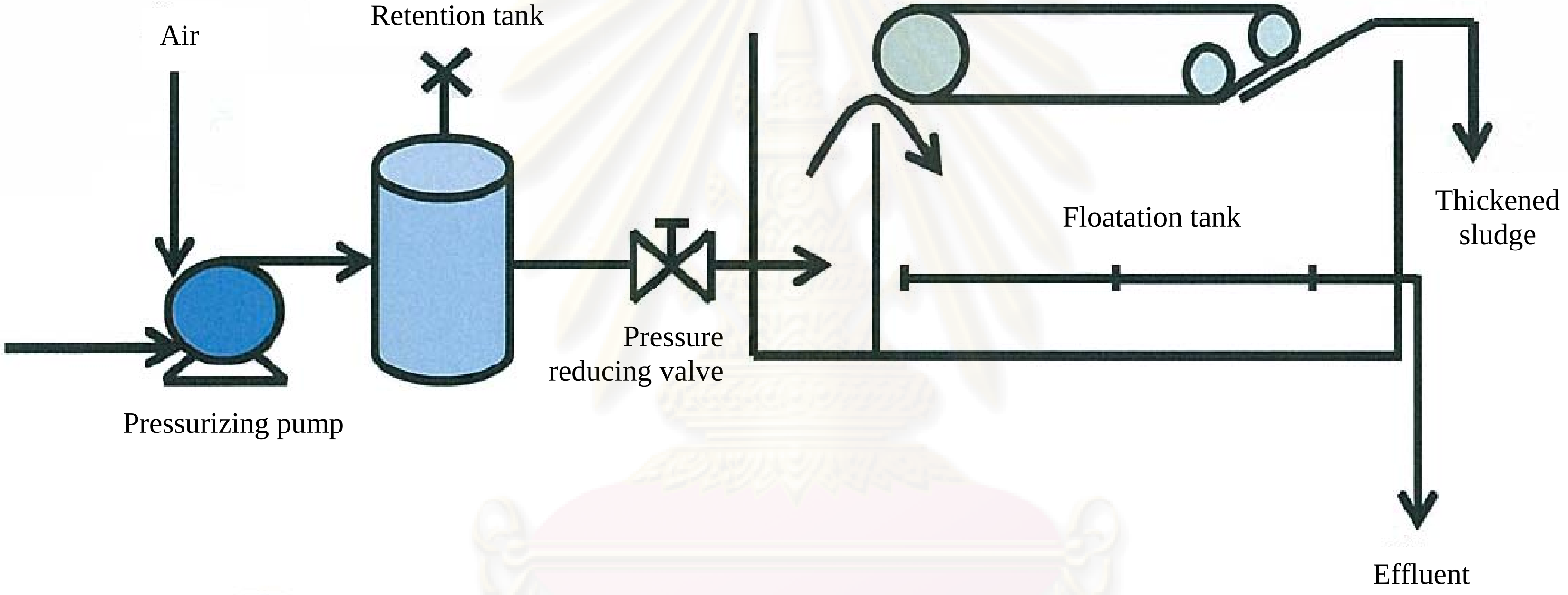


Fig 4-19 The system of Dissolved Air Floatation (Biodiesel Industrial handbook, 2007)

energy production helping replace fossil fuels. Also, the nutrient-rich solids left after digestion can be used as fertilizer, see also in appendix C for more detail.

Biogas produced from anaerobic digestion can be used as a low-cost fuel in any country for any heating purpose, such as cooking. It can also be used in modern waste management facilities where it can be used to run any type of heat engine, to generate either mechanical or electrical power. Biogas can be compressed, much like natural gas, and used to power motor vehicles. In the United Kingdom, for example, biogas is estimated to have the potential to replace around 17% of vehicle fuel (Biomethane fueled vehicles the carbon neutral option, 2008). Biogas is a renewable fuel, so it qualifies for renewable energy subsidies in some parts of the world.

Aerobic treatment process

Aerobic treatment is a biological process, the principle of which is the use of free or dissolved oxygen by microorganisms, called aerobes, in the degradation of organic wastes. It is suitable for low organic loading wastewater. Although, it is high efficiency to remove organic matters, uncomplicated, minimizing odor when properly loaded and maintained, and providing a good quality effluent, a lot of money is spent on the energy cost of aeration at an adequate rate to maintain the dissolved oxygen levels for aerobic growth. Moreover, biological aerobic treatment causes biosludge due to active aerobic growth powered by sufficient oxygen, potentially leading to reduction in storage capacity of lagoons or ponds (Zhu, 2002).

The wastewater after treatment containing low amount of oil, glycerin, methanol, and COD can be irrigated to nearby agricultural area, especially in drought. It reduces the water consumption for the agriculturists and activated sludge from the treatment reactor can be used as fertilizer for crops.

According to utilization of biogas produced from anaerobic process, there are several researches on biogas production potential. Phukingngam et al. (2008a) reported that 1 m^3

wastewater of biodiesel produced approximately 25 m^3 biogas in 15 – 17 days. To compare with other studies of biogas production from other wastewater sources, as shown in table 4-10, they found that biodiesel wastewater was the highest potential for biogas production

Table 4-10 Comparison of biogas production from other wastewater sources

Wastewater sources	Quantityl of wastewater (m^3)	Biogas production capability (m^3)
Livestock	1	3.5
Slaughterhouse	1	0.7
Rice flour factory	1	2.4
Cassava starch factory	1	7
Crude palm oil factory	1	15

Table 4-11 Wastewater quality of Factory D and E and its average values

Parameter	Factory D	Factory E	Average value of Factory D and E
pH	10.0	10.13	10.07
BOD (mg/L)	-	-	-
COD (mg/L)	170,100	117,419	143,760
SS (mg/L)	4,251	910	2,580
Oil and grease (mg/L)	9,032	8,190	8,611
Glycerin (mg/L)	9,602	39	4,820
Methanol (mg/L)	66,267	37,603	51,935
Flow (m^3/day)	15.2	66	40.6

Phukingngam et al. (2008b) also investigate the efficiency of biodiesel wastewater treatment by Anaerobic Baffled Reactor (ABR). Results showed that the removal efficiency of total COD, soluble COD, SS, methanol and glycerin were 97.81%, 98.31%, 38.02%, 84.36% and 86.55%, respectively, and treated wastewater contained total COD, soluble COD, SS, methanol and glycerin were 139, 77, 233, 391 and 156 mg/L, respectively. The biogas production and biogas yield were average 2,680 ml/day and 395 ml/g COD removed, respectively, which corresponded to the methane content of 58.9%.

A biodiesel factory with capacity of 110 m^3/day generates wastewater 40.6 m^3/day with COD loading of 5,840 kg/day, as shown in table 4-11. Biogas generation yield is approximate 25 m^3/m^3 of wastewater so that the average biogas production is 1,015 m^3/day. Each cubic meter of biogas can generate electricity on the average of 2.5 kWh (Board of Judge on ASEAN Renewable Energy Project Competition, 2007); therefore, total generated electricity is approximate 2,540 kWh/day. The electricity generation can be used within the factory and the rest can be sold to Provincial Electricity Authority (PEA).

In this study, based on the data of potential biogas production by the study of Phukingngam et al. (2008a) and investment capital of Asian Palm Oil Company on biogas and electrical generation plant, 40 million Baht (Board of Judge on ASEAN Renewable Energy Project Competition, 2007), the estimated revenue of selling electricity to PEA is shown in table 4-12.

Table 4-12 The estimated revenue of selling electricity to PEA

Average produced biodiesel from four factories	275 m^3/day
Average wastewater generation (per 1 m^3 of biodiesel)	0.47 m^3
Total wastewater generation	130 m^3/day
Biogas generation (per 1 m^3 of wastewater)	25 m^3
Total generated biogas	3,250 m^3
Electricity generated (per 1 m^3 of biogas)	2.5 kWh
Total generated electricity	8,125 kWh
Average price of electricity	2.02 baht/kWh
Total revenue from selling electricity to PEA	16,400 baht/day 4,920,000 baht/year
Investment capital on CSTR and electrical generation plant (overestimated)	40,000,000 baht
Payback period	8.13 years

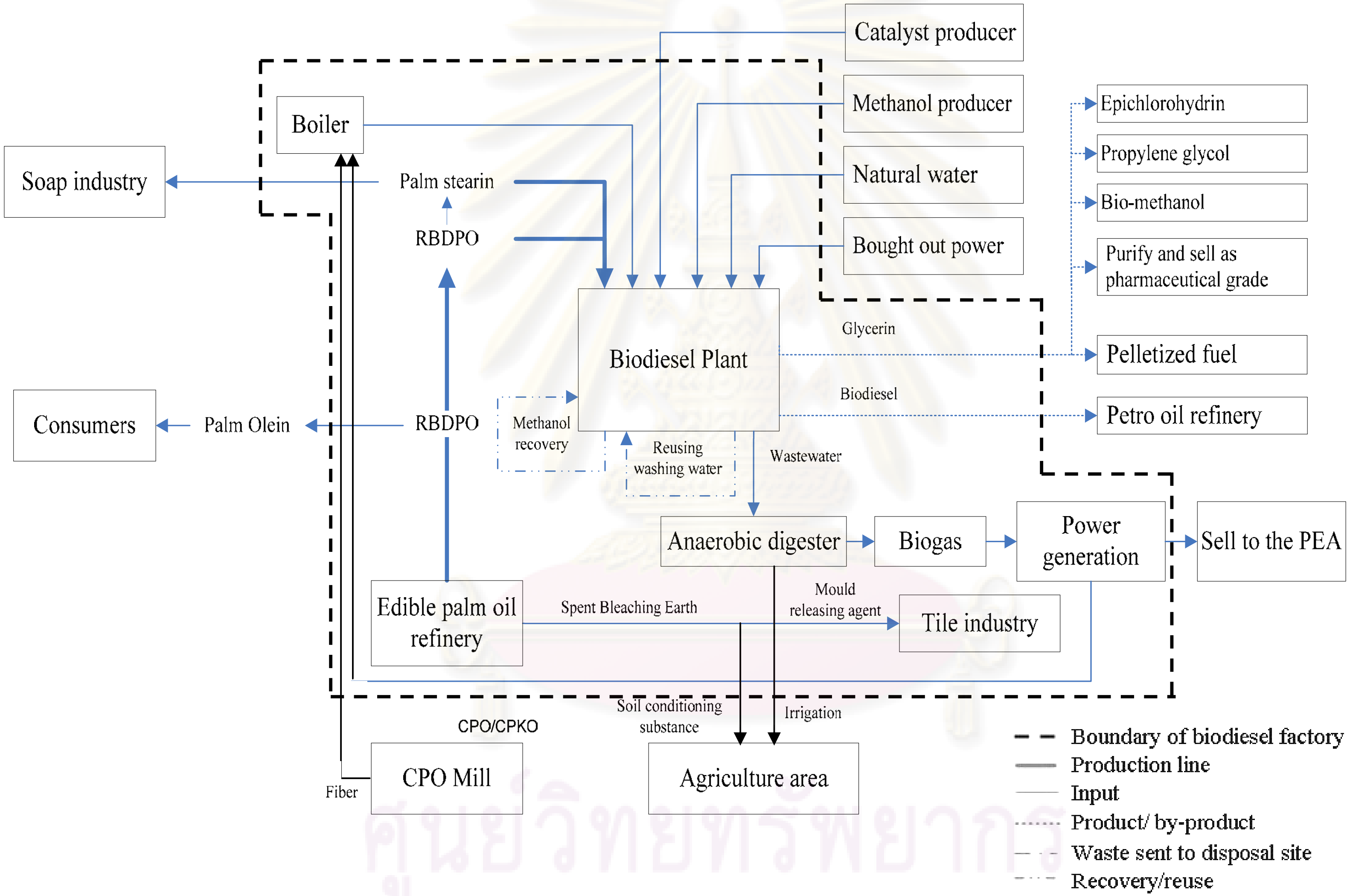


Fig 4-20 The possible and appropriate waste management model of biodiesel industry which stand with own palm oil refinery plant

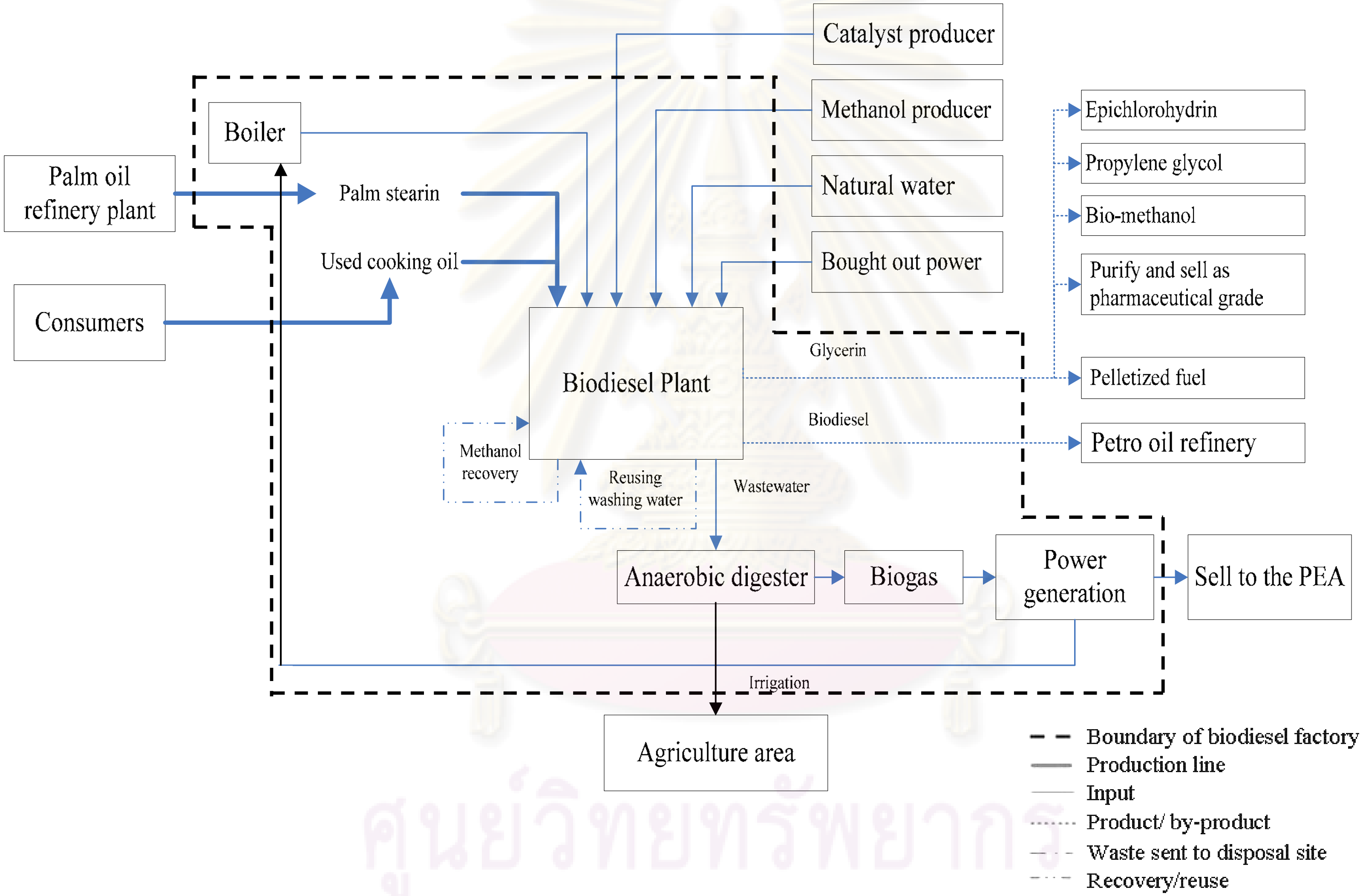


Fig 4-21 The possible and appropriate waste management model of biodiesel industry which stand without own palm oil refinery plant

4.5 Possible and appropriate waste management

From the above information, the possible and appropriate options were evaluated based on the considerations of technical, economic, and environmental aspects before implementation. Figures 4-20 and 4-21 show the appropriate and possible waste management models of biodiesel industry for both types; i.e., factories with and without refinery process.

4.5.1 Spent bleaching earth

Reuse of spent bleaching earth in industrial and agricultural sectors appears to be a better approach than regeneration or landfill disposal. For example, the spent bleaching earth can be used as mould releasing agent, soil-improving substance, and feedstuff. Although this option offers the less cost-benefit for the factory owners, which the revenue would be approximately 1 to 2 baht of each kg, it can help to alleviate the environmental impact. Reuse of spent bleaching earth can reduce the disposed waste to landfills, which in turn can increase capacity area and extend the life time of landfill.

4.5.2 Glycerin

The best option to add value to crude glycerin is to purify it by distillation process. The purified glycerin can be sold as pharmaceutical grade glycerin. Even though the investment capital of purification process is high, the revenue from selling pharmaceutical grade glycerin is highly lucrative.

Comparing among the possible options, establishment of glycerin purification process within the biodiesel factory offers the highest revenue. Eighteen million baht of investment capital of 20-ton/day production capacity plant would be returned within 8 years of payback period, based on the least crude glycerin generation, 2.5 ton/day, and 20 baht/kg of purified glycerin price.

However, small-scale biodiesel factories may be incapable to establish their own glycerin distillation purification process. Chemical purification process is the other option for purifying crude glycerin. Eighty-five percent purity of glycerin obtained from chemical process can be used as feedstuff. Selling crude glycerin to other industries can be the option for adding glycerin’s value. In commercial scale, the conversion crude glycerin to useful chemicals via chemical process is more possible than via biological process. Bio-methanol, propylene glycol, and epichlorohydrin seem the most possible chemicals for commercial scale as there are some factories producing them.

Other option is using crude glycerin as fuel. Since glycerin has low energy content as 16 MJ/kg; therefore, it should be mixed with biomass, such as palm fiber and palm shell, in order to increase its heating value before feeding to boilers. Its investment cost is very cheap, approximate 1 to 1.5 baht/kg.

4.5.3 Wastewater

Reuse of the last methyl ester washing water as the first washing water is the appropriate option which can reduce not only the water consumption and wastewater generation but also the cost of potable water purchasing, 21,600 baht/year, and wastewater treatment operation.

For the wastewater treatment process, the appropriate biodiesel wastewater treatment is oil separation from wastewater prior to anaerobic digestion. The anaerobic digestion is proved to effectively remove oil and grease, BOD, and COD from the wastewater. Moreover, its system produces biogas, which can be used as fuel for the boiler by direct burning or generating electricity. This closed treatment system can relieve the impact of odorous gases on communities around the factory, also. This treatment system followed by aerobic process can enhance pollutant removal efficiencies. Effluent after treatment can be also irrigated to nearby plantation, especially in drought.

The biogas produced from average wastewater generation of five biodiesel factories is estimated 3,250 m^3. This biogas generates electricity approximate 8,125 kWh/ day. Based on average price of electricity, 2.02 baht/kWh, the net value added from selling electricity to PEA would be 4,920,000 bath/year. According to the overestimated investment cost of Asian Palm Oil Company on the anaerobic digester and electrical generation plant, 40 million baht, payback period would be estimated in 8.13 years.

These appropriate options are suitable for each factory size. Table 4-13 shows the summary of appropriate options for each biodiesel factory scale.

Table 4-13 The summary of appropriate options for each scale factory

Appropriate options	**Small-scale factory**	**Medium-scale factory**	**Large-scale factory**
Reuse the last methyl ester washing water as the first washing water	✔	✔	✔
Reuse of crude glycerin as fuel			
- Direct burning			
o For factory standing with CPO mill	–	✔	✔
o For factory standing w/o CPO mill	✔	✔	✔
- Pelletized fuel	✔	✔	✔
- Hydrogen/syn gas	–	–	✔
Purifying crude glycerin by the factory itself and sold as pharmaceutical grade			
- Distillation process	-	✔	✔
- Chemical process	✔	✔	-
Recycling of crude glycerin as raw material for other industries	✔	✔	✔
Reuse of spent bleaching earth in industrial and agricultural sections	✔	✔	✔
Recovery biogas from wastewater	-	✔	✔

CHAPTER V

CONCLUSION

Production of biodiesel generates both by-product and wastes; i.e., glycerin and wastewater, including spent bleaching earth from palm oil refinery process. From the survey study of five selected biodiesel factories, the average in 1 m^3 of biodiesel generates 140 kg of glycerin, 8 kg of spent bleaching earth, and 0.47 m^3 of wastewater. Although the biodiesel wastes are handle by different approaches such as end-of-pipe and cleaner production, these are not considered to be the best approaches and sustainable. Industrial ecology approach combining with clean technology and waste exchange is proposed for biodiesel wastes handling in this research.

According to the results of numerous researches in Thailand and other developed countries, possible and appropriate solutions for improvement of the environmental performance of the biodiesel industry can be summarized as follows:

1. The existing managements of crude glycerin, biodiesel by-product, is either sold to glycerin-purifying factories in order to purify it as pharmaceutical grade or used as fuel for a boiler.

   Purification of glycerin within biodiesel factories appears to be more cost effective than selling to outside purifying factories. Distillation purifying process, producing more than 90% purity of glycerin, is suitable for high investment capability factories. This purified glycerin grade can be used as food ingredient, pharmaceutics, and personal care. On the other hands, low investment capability factories could purify crude glycerin by chemical process to produce 85% purity which is utilized as feedstuff. Also, the biodiesel plant can use crude glycerin as pelletized fuel by mixing it with biomass such as palm fiber and palm shell.

   Furthermore, crude glycerin can be used as raw material for other manufacture such as bio-methanol, propylene glycol, and epichlorohydrin. It not only adds value of crude glycerin, but also considers environmentally friendly chemical.

2. Wastewater is the important problem for biodiesel production process. Its existing handling is only in-plant wastewater treatment. Reuse of the final washing-step water of methyl ester as the first washing-step water is the effective option that can be implemented without any investment cost. It reduces both water consumption and wastewater generation in the biodiesel production process.

   The appropriate option for biodiesel wastewater treatment is dissolved air floatation to remove oil followed by biological treatment; i.e., anaerobic and aerobic processes. Anaerobic digester is considered to be the most suitable option because it reduces significant volume and mass of the wastewater and generates biogas, which can be used as fuel for a boiler or electricity generation. Aerobic treatment process may be employed for the need of higher quality of the effluent. The effluent can be also irrigated to nearby plantation.

3. The other waste is spent bleaching earth which is disposed by landfill. Reuse of spent bleaching in industrial and agricultural sectors as mould releasing agent and soil-improving substance can reduce waste regeneration and also lessens the impact of refuse on landfill.

Some options, such as reuse of spent bleaching earth in industrial and agricultural sectors, offer less cost effective, thus are making them not profit-driven options for the factory owners. However, these options should still be promoted based on the consideration of alleviation of the environmental impacts. Furthermore, the government should encourage and support the research associated with value-adding of the biodiesel waste/by-product for sustainability.

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APPENDICES

APPENDIX A-1

FACTORY A

Introduction to the factory

Factory A was established in 1991 with the crude fuel oil refinery plant. Fourteen years later, in 2007, the factory owner spent 36 million Baht in order to set up biodiesel plant to respond to government policy. It is a small-scale factory, covering 17,600 m^2. Its production capacity is 200,000 liters per day.

Inputs-outputs

According to standing without crude palm oil refinery process, Factory A uses palm stearin which is bought from nearby vegetable edible oil factories as feeding oil. In the process, sodium methoxide and methanol are used as catalyst and alcohol, respectively. To produce 1 m^3 of biodiesel, the amount of palm stearin, sodium methoxide, and methanol are approximate 870, 9, and 100 kg, respectively. Due to distillation of methyl ester, there is no wastewater in the process; however, it consumes large amount of energy, for distillation. The main energy, steam, used in the process obtains from fuel oil. The output of Factory A is only crude glycerin, approximate 100 kg. The mass balance of Factory A is shown in figure a-1.

Production process

The production process of Factory A is batch technology. It begins with heating palm stearin to 70 ºC in the reactor to convert solid phase to liquid phase. The mixed methanol and sodium methoxide solution is added to the reactor to react with palm stearin. In this step, transesterification reaction occurs for 1.50 hours. The products, methyl ester and glycerin, are settled to separate from each other for 5 hours. Then glycerin is drain from the bottom of tank. After that methanol in the methyl ester phase is removed and sold to the methanol recycle company where purifies methanol by distillation and sell it back to the factory in lower price. Methyl ester is purified by distillation to get 99.8% biodiesel. Biodiesel is the colorless and can be used not only as fuel oil, but it also can be used as cosmetic ingredient and solvent for pesticide and insecticide. For crude glycerin, the factory stores it in plant and sometimes sells it to neighbouring factories as fuel. The production process is shown in figure a-2.

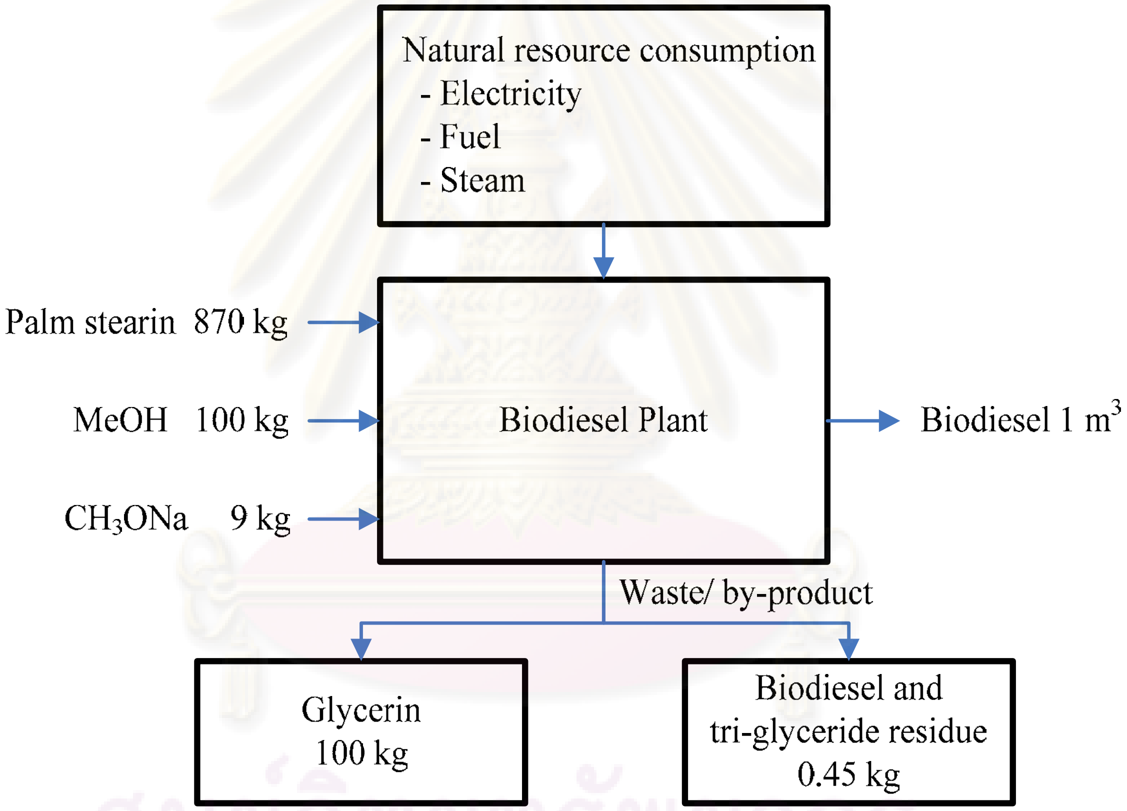


Fig a-1 Material balance of production process of Factory A (per 1 m^3 biodiesel)

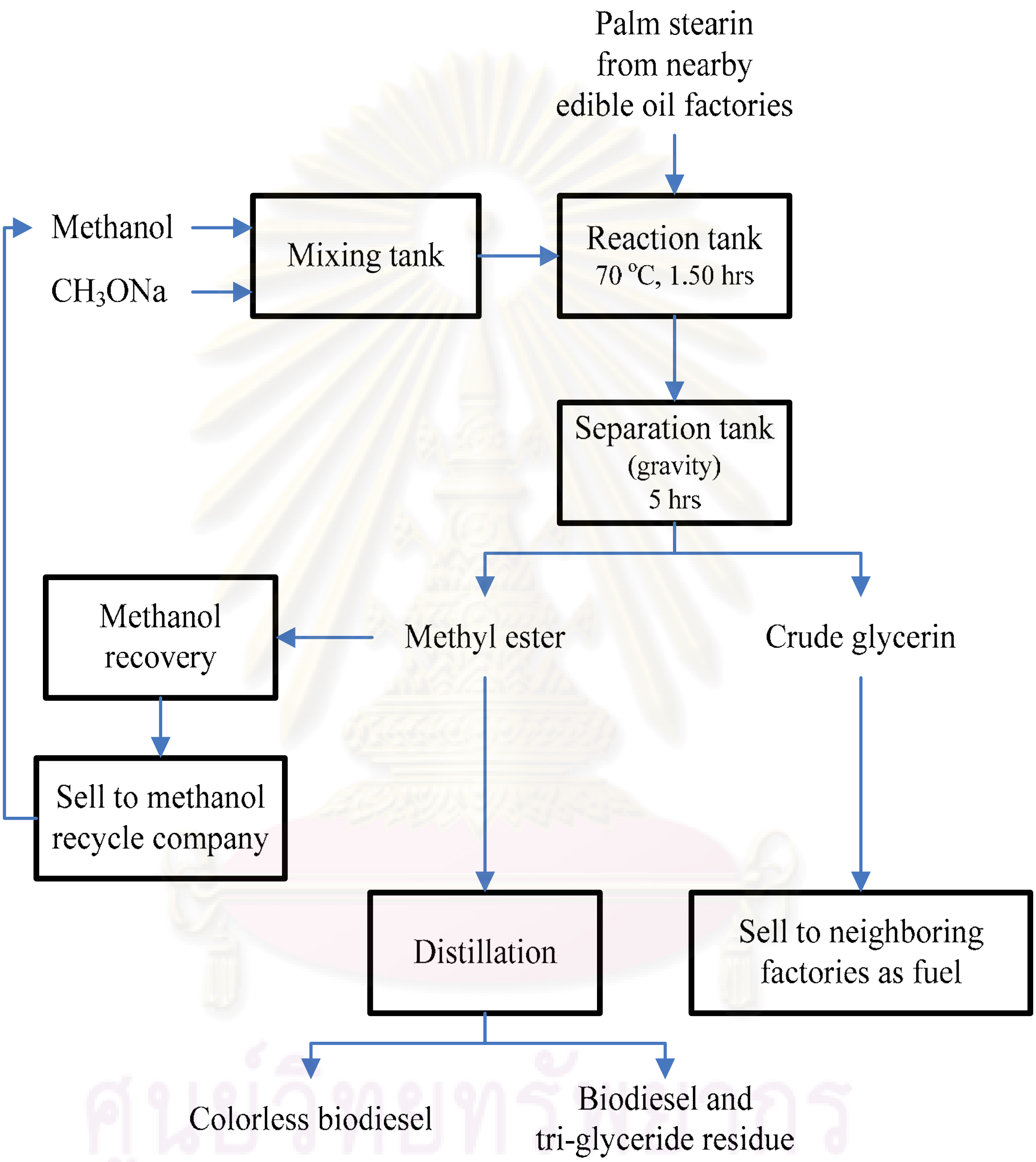


Fig a-2 The biodiesel production process of Factory A

APPENDIX A-2

FACTORY B

Introduction to the factory

Factory B is the entire palm oil industry which consists of palm plantation, palm oil extraction plant, palm edible oil refinery plant, and biodiesel plant. The biodiesel production plant was set up with 60 million Baht of investment capital. Its production capacity is around 80,000 liters per day.

Inputs-outputs

Factory B uses palm stearin, palm kernel oil obtained from palm oil refinery, and sometimes crude palm oil obtained from palm oil extraction as feeding oil. In the process, potassium hydroxide and methanol are used as catalyst and alcohol, respectively. To produce 1 m^3 of biodiesel, the amount of feeding oil, potassium hydroxide, and methanol are approximate 870, 20, and 100 kg, respectively. Moreover, it consumes water in amount of 0.39 m^3 in the methyl ester washing step. The production process also consumes steam produced from palm fiber and electricity. The outputs of Factory B are 100 kg of crude glycerin, 8 kg of spent bleaching earth, and 0.39 m^3 of wastewater. The mass balance of Factory B is shown in figure a-3.

Production process

The production process of Factory B is batch technology. Its production process starts with mixing of methanol and potassium hydroxide for 25 minute. Then the mixed solution is fed to reaction tank to react with oil at 65 ºC for 45 minute. After that the products are settled to split from each other. Methyl ester is purified by washing with water until the pH of washing water is approximate 7. Then it is heated up to evaporate the moisture; however, methyl ester still contains 1% of moisture which is over the standard of biodiesel production so it is centrifuged and dried. After drying, methyl ester contains 0.02% of moisture and the purity is 98%. Crude glycerin that is distilled to recover excess methanol is storage in liquid phase and sold to another factories as fuel. The biodiesel production process of Factory B is shown in figure a-4.

Wastewater treatment plant

Wastewater from biodiesel plant which is alkalinity is used as neutralizer to neutralize acidic wastewater from palm edible oil refinery plant before sending to anaerobic wastewater treatment plant.

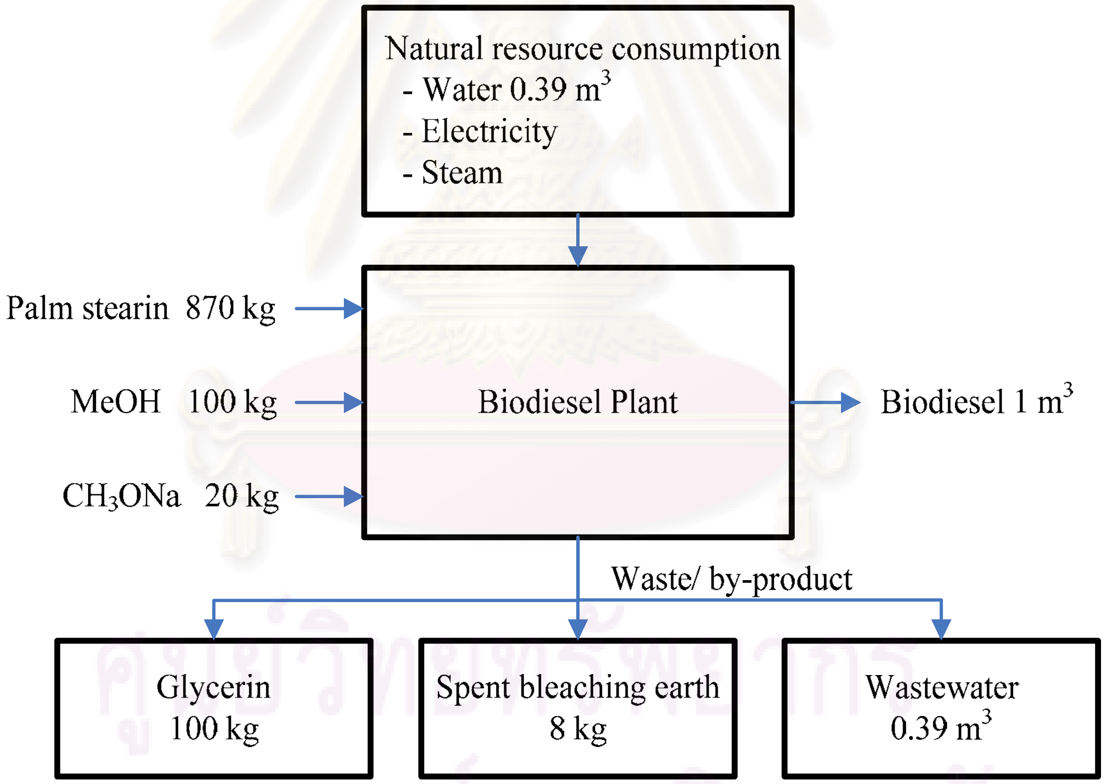


Fig a-3 Material balance of production process of Factory B (per 1 m^3 biodiesel)

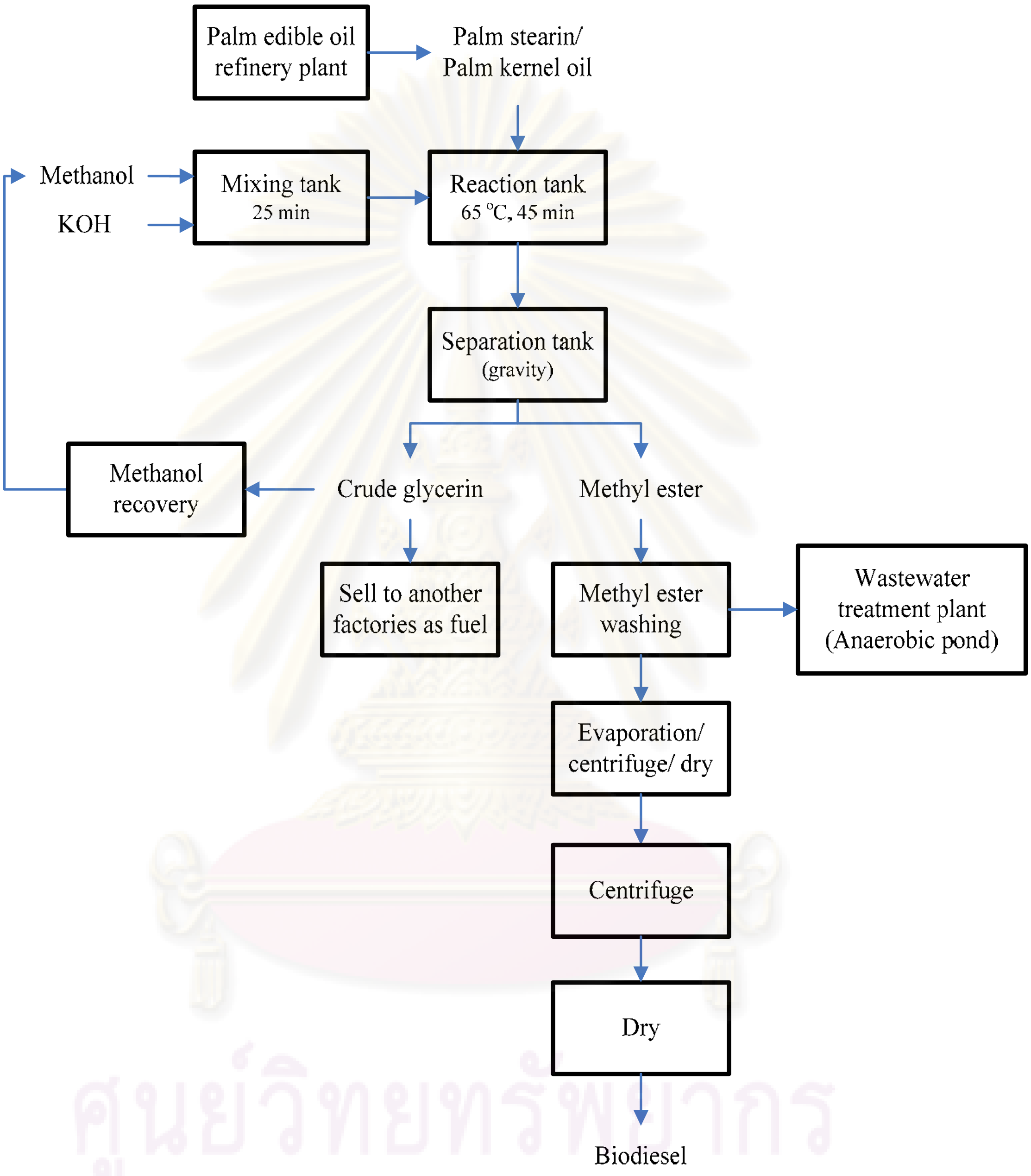


Fig a-4 The biodiesel production process of Factory B

APPENDIX A-3

FACTORY C

Introduction to the factory

Factory C commenced in 1975 with only edible oil refinery plant, until in early 2006 the Factory C entered the energy sector by establishing a biodiesel plant with 61 million Baht of investment capital in order to respond to government policy and to help reduce green house gas emission from fossil fuel. It is medium-scale factory which covers an area of 121,400 m^3. Nowadays, the production capacity of biodiesel plant is 800,000 liters per day.

Inputs-outputs

Factory C has no own palm plantation; therefore, it has to buy palm fruit from the South of Thailand to extract. Crude palm oil is refined by itself to get RBDPO as product which is used as biodiesel raw material. Sodium hydroxide and methanol are used as catalyst and alcohol, respectively. To produce 1 m^3 of biodiesel, the amount of RBDPO, sodium hydroxide, and methanol are approximate 920, 7, and 110 kg, respectively. Moreover, it consumes water in amount of 0.39 m^3 in the methyl ester washing step. The production process also consumes steam produced from coal and electricity. The outputs of Factory C are approximate 150 kg of crude glycerin, 8 kg of spent bleaching earth, and 0.39 m^3 of wastewater. The mass balance of Factory C is shown in figure a-5.

Production process

The biodiesel production process of Factory C is batch technology. The production process begins with mixing of methanol and sodium hydroxide then feeding to reaction tank to react with RBDPO. Methyl ester and glycerin are settled and centrifuged for separation. Excess methanol is recovered from methyl ester phase to reuse. After that methyl ester is purified by washing with acidic warm water for 3 times in order to converting soap in methyl ester to oil which is removed from washing water. Then methyl ester is dried. Crude glycerin is stored in the plant wait for selling to glycerin purified factories. Figure a-6 shows the biodiesel production process of Factory C.

Wastewater treatment plant

Wastewater from methyl ester washing step is drained to wastewater pre-treatment plant where wastewater from all sources are mixed. In this sector, alkaline chemical is added in order to increase pH value of wastewater to 5. After that, wastewater is drained to anaerobic pond following aerobic lagoon. Wastewater is also settled to sediment the activated sludge in next basin and drained to the cesspit.

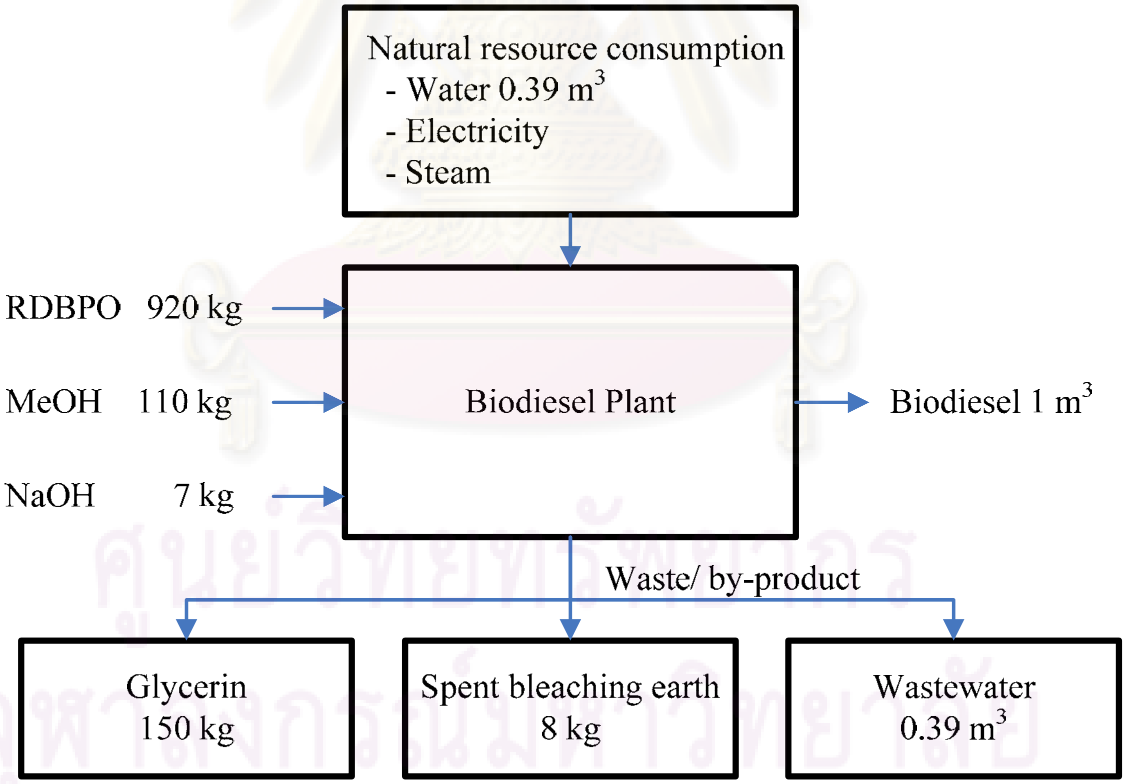


Fig a-5 Material balance of production process of Factory C (per 1 m^3 biodiesel)

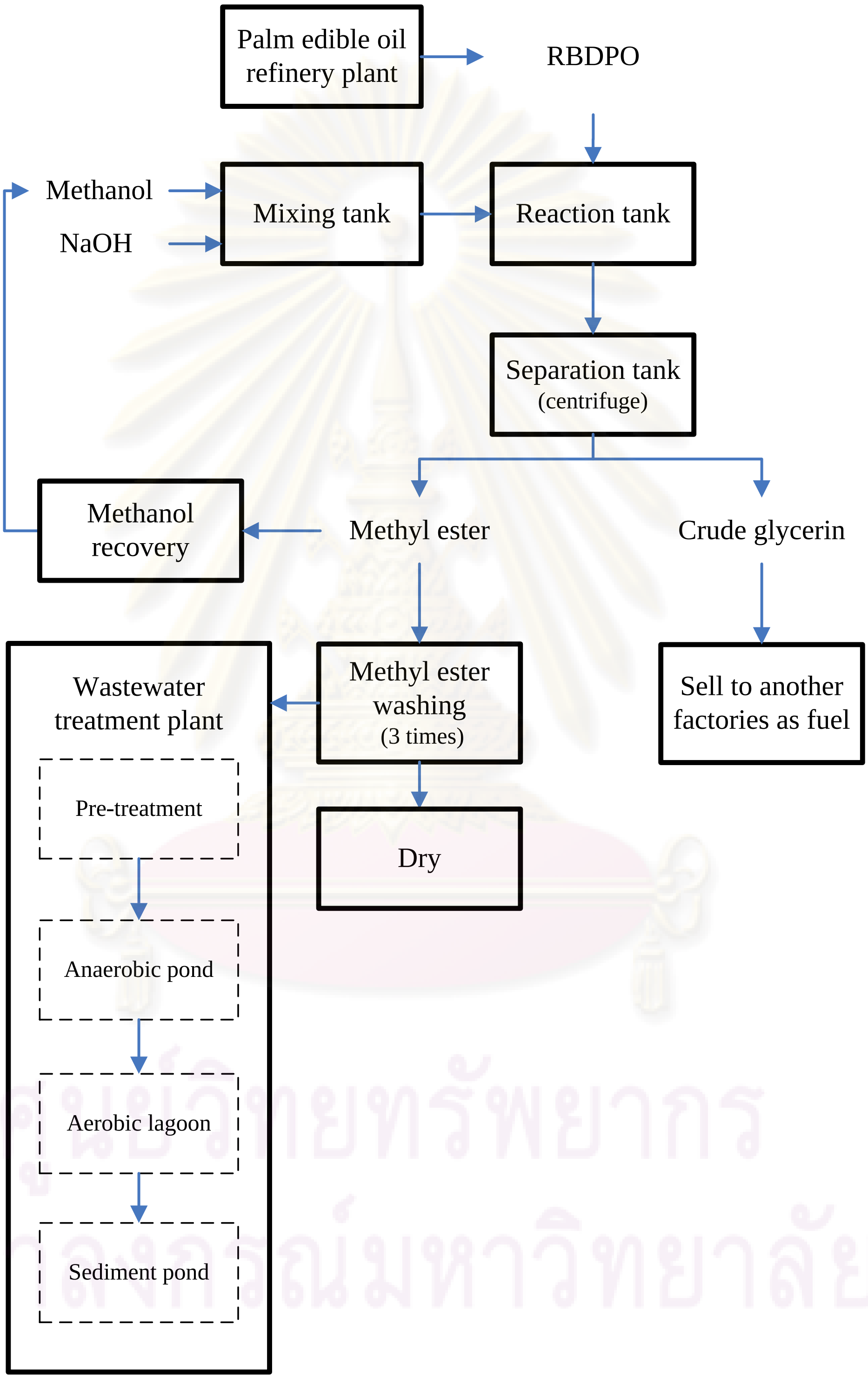


Fig a-6 The biodiesel production process of Factory C

APPENDIX A-4

FACTORY D

Introduction to the factory

Factory D has continuously supported the alternative clean energy project since 2004. Initially, it was the project that was extended from Chitrada biodiesel project. After that the owner extended the plant by investing 65 million Baht to establish 20,000 liters per day capacity biodiesel plant. Now it is going to expand capacity to 30,000 liters per day in 2009

Inputs-outputs

To reduce the dispose of used cooking oil problem and to reduce the people's health impact from cooking oil reusing problem, Factory D purchases used cooking oil from households to produce biodiesel. Sodium hydroxide and methanol are used as catalyst and alcohol, respectively, in the process. To produce 1 m^3 of biodiesel, the amount of used cooking oil, sodium hydroxide, and methanol are approximate 960, 9, and 220 kg, respectively. Furthermore, it consumes water in amount of 0.77 m^3 for 5 times of methyl ester washing step. The production process also consumes steam and electricity. The outputs of Factory D are approximate 260 kg of crude glycerin and 0.77 m^3 of wastewater. Figure a-7 shows the mass balance of Factory D.

Production process

The biodiesel production process of Factory D is batch technology. After adjusting quality of used cooking oil by filtering, removing moisture and free fatty acid, and adding antioxidant, it is fed to react with mixed solution of methanol and sodium hydroxide in the reactor at 60 ºC for 1 hour. The products are settled for 3 hours to separate from each other. Excess methanol in glycerin phase is recovered for reusing in the process while methyl ester is purified by washing with warm water for 5 times, and then it is dried and storage in the tanks. Crude glycerin of Factory D is stored in plant and sold to purified factory to add its value. Figure a-8 shows the flow chart of biodiesel production process of Factory D.

Wastewater treatment plant

The first methyl ester washing water that has very high COD is treated outside the factory, whereas other washing water is drained to wastewater treatment plant, aerobic lagoon.

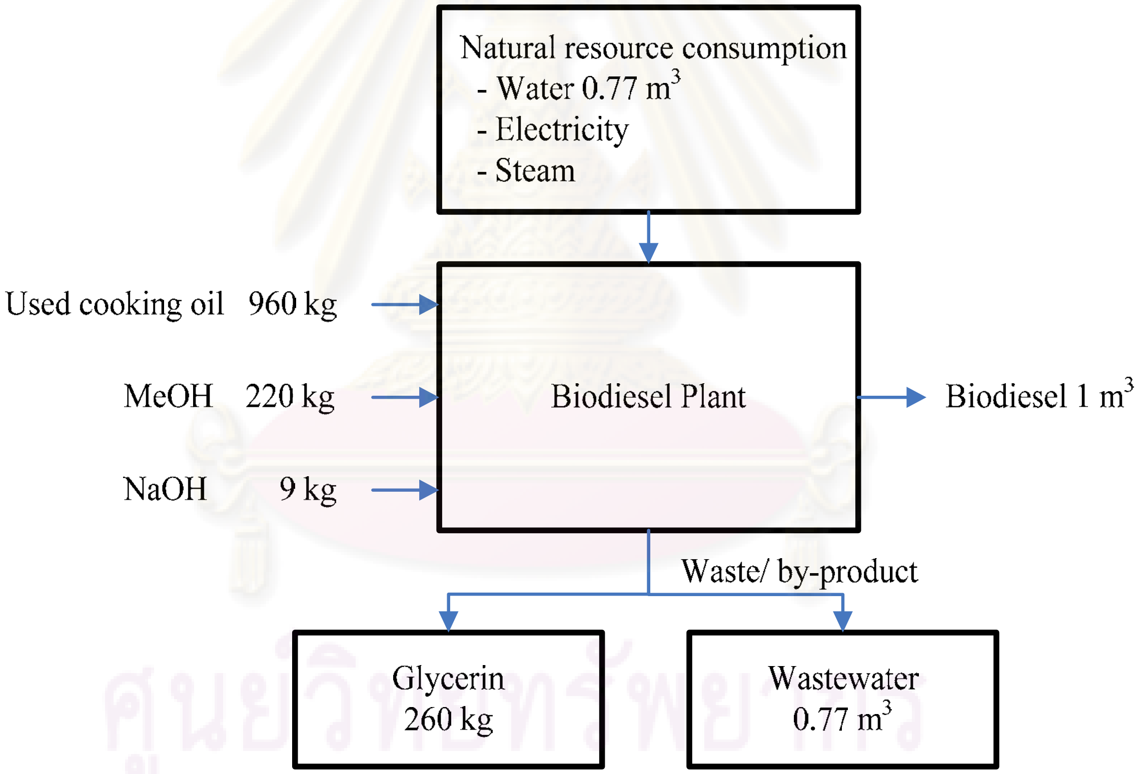


Fig a-7 Material balance of production process of Factory D (per 1 m^3 biodiesel)

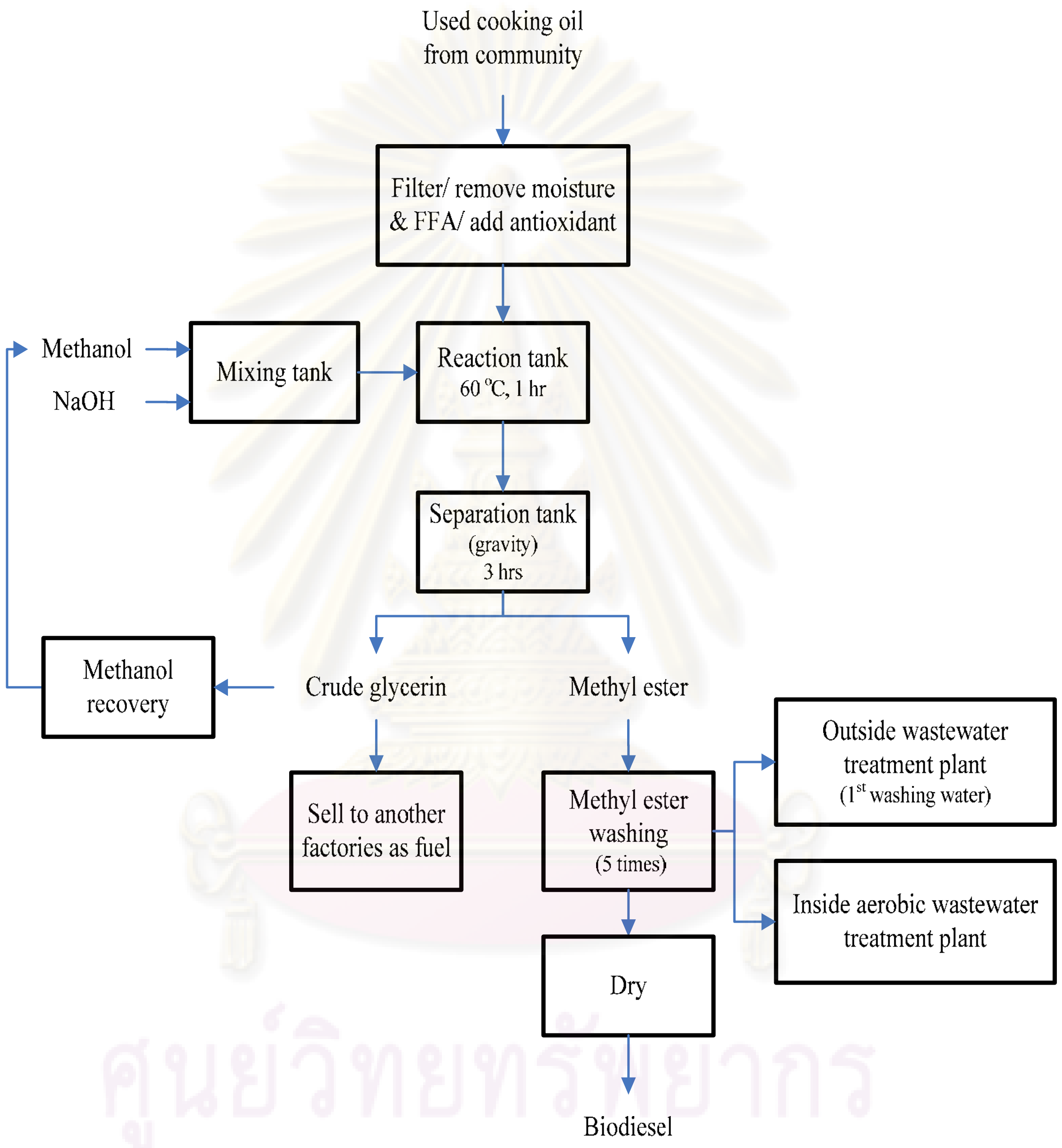


Fig a-8 The biodiesel production process of Factory D

APPENDIX A-5

FACTORY E

Introduction to the factory

Factory E was established to produce biodiesel from palm oil in 2006 with 300 million Baht of investment capital. It is the entire palm oil industry which consists of palm plantation, palm oil extraction plant, palm edible oil refinery plant, and biodiesel plant, covering 80,000 m^2. Its production capacity is approximate 200,000 liters per day.

Inputs-outputs

Factory E uses RBDPO obtained from palm oil refinery as feeding oil. In the process, sodium hydroxide and methanol are used as catalyst and alcohol, respectively. To produce 1 m^3 of biodiesel, the amount of feeding oil, sodium hydroxide, and methanol are approximate 870, 4, and 100 kg, respectively. Moreover, it consumes water for methyl ester washing in amount of 0.33 m^3. The production process also consumes steam and electricity. The outputs of Factory E are 100 kg of crude glycerin, 9 kg of spent bleaching earth, and 0.33 m^3 of wastewater. The mass balance of Factory E is shown in figure a-9.

Production process

The production process starts with methanol and sodium hydroxide mixing in the mixing tank. Then it is fed to react with RBDPO in reaction tank and fed to separation tank. According to continuous process, there are three sets of reaction and separation tank. The last separation tank is centrifuge to completely separate glycerin from methyl ester. After that excess methanol in methyl ester phase is recovered at 90 ºC for two times. Methyl ester is washed with warm water by in opposite directions and then is dried in vacuum condition and stored in tank, while crude glycerin is storage for selling to purified factories. Figure a-10 shows the biodiesel production process of Factory E.

Wastewater treatment plant

Oil in wastewater from methyl ester washing is trapped by grease trap before draining it to anaerobic pond.

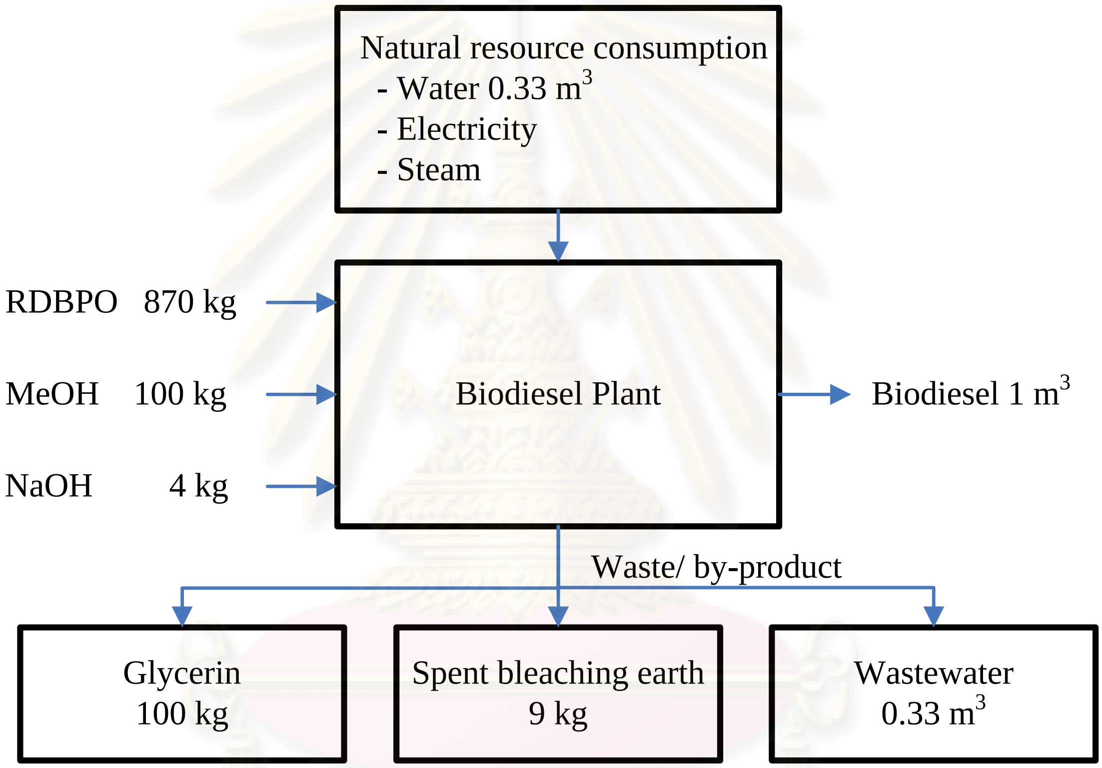


Fig a-9 Material balance of production process of Factory E (per 1 m^3 biodiesel)

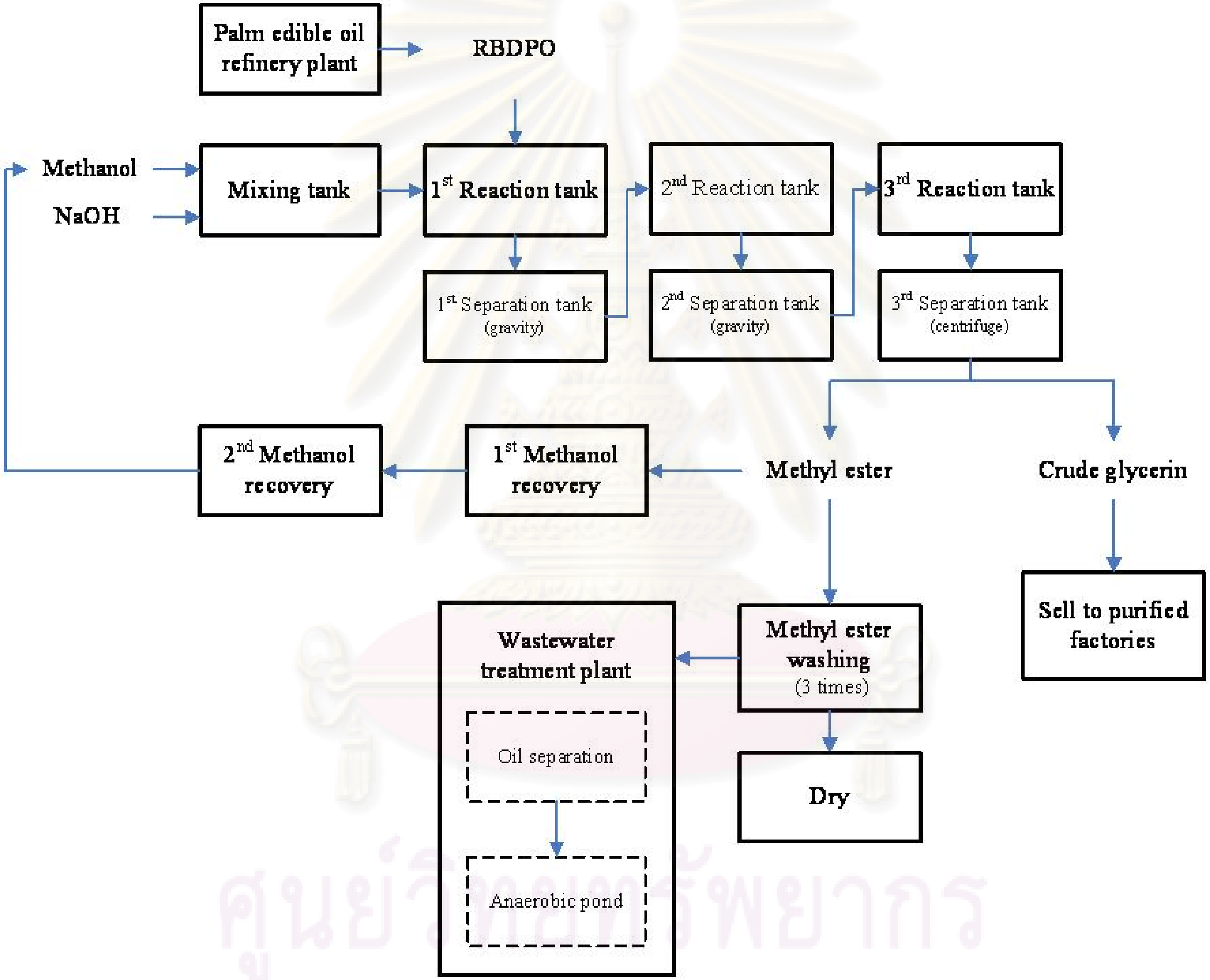


Fig a-10 The biodiesel production process of Factory E

APPENDIX B-1

PURIFIED GLYCERIN UTILIZATIONS

Purified glycerin can be divided into 4 grades: i.e., Chemical grade, Dynamite grade, Technical grade, Pharmaceutical grade. The properties of each grade are shown in table b-1. It is utilized in many industries, especially in food and pharmaceutical industry. These below express the detail of its utilizations.

Food and beverages:

Glycerin can serve as humectants, solvent, and sweetener which may help preserve foods; solvent for flavors such as vanilla and food coloring; used as filler in low-fat food products such cookies; used as humectants and softening agent in candy, cakes, and casing for meats and cheeses.

Pharmaceuticals:

It can be used in medical and pharmaceutical preparations, mainly as a means of improving smoothness, providing lubrication and as humectants. Also may be used to lower intracranial and intraocular pressures. The examples of the product are cough syrups, laxative, suppositories, ear infection remedies, and gargles.

Personal care:

Glycerin is used as an emollient in toothpaste, skin creams and lotions, shaving preparations, deodorants, soaps and makeup. It is not only non-allergic to human but also inhibits microorganism growth.

Agricultural sprays:

It can be used of as an adjuvant with humectants properties increasing herbicide activity in low humidity conditions. Used as a spreader or wetting agent–a material that increases the area that a droplet of a given volume of spray mixture will cover on a target. Used as an antifoaming agent in micronised wettable sulfur. This enables the product to be mixed in a tank effectively and sprayed on evenly.

Tobacco:

It can keep tobacco moist and soft to prevent breaking and crumbling during processing; ensures freshness in packaged cigarettes and other tobacco products.

Surface coating:

It can be used in the manufacture of alkyd resins; this is an important component of surface coatings.

Paper and printing:

It can be used as a plasticizer and lubricant in the manufacture of paper; used with other ingredients in specialty treatments such as grease-proofing; alkyd resins also an important constituent of many printing inks.

Lubricants:

Due to its non-toxic character, it can be used in lubricants for food and other machinery where product purity is essential.

Textiles:

It can be used as a conditioning agent used widely in lubricating, sizing, and softening yarn and fabric; lubricates many kinds of fibers in spinning, twist setting, knitting, and weaving operations.

Electrical and electronics:

It can be widely employed in manufacturing electrolytes for electrolytic condensers, which are used in radios and neon lights, and in processes for electrodeposition and treatment of metals.

Table b-1 The properties of each glycerin grade

No.	Property	Chemical grade	Dynamite grade	Technical grade	Pharmaceutical grade	Test reference
1	Glycerin (wt%)	99.0	99.0	99.0	95.0	BS 5711:Part3
2	Asinic (mg/kg)	< 2.0	-	-	< 1.5	TISI 1281
3	Sugar	Not found	-	-	-	BS5711:Part18
4	Lovibond color in 133 mm cell	-	< (5.0Y+1.2R)	< (5.0Y+1.2R)	< (5.0Y+1.2R)	BS 2821-5
5	Odor	Odorless	Odorless	Odorless	Odorless	ES 5711:Part19
6	Density					ISO 2099
	- at temp. 20 ºC	1.261 – 1.264	1.261 – 1.264	1.261 – 1.264	-	
	- at temp. 25 ºC	-	-	-	1.249	
7	Acidity-alkalinity (meq/100g)	< 0.064	< 0.32	< 0.32	-	BS 5711:Part5
8	Sulfate ash (mg/kg)	< 0.010	< 0.010	< 0.010	< 0.01	ISO 1616
9	Total heavy metal (mg/kg)	< 5.0	-	-	< 5	BS5711:Part15
10	Chloride (wt%)	-	<0.010	<0.010	<0.001	BS5711:Part12
11	Ferrous (mg/kg)	-	-	< 2.0	-	BS5711:Part16
12	Chlorine cpd. (wt%)	-	-	-	0.003	USP
13	Sulfate (wt%)	-	-	-	0.002	USP

Source: Thai Industrial Standards Institute, Ministry of Industry, 2002

APPENDIX B-2

GLYCERIN-PURIFYING BY DISTILLATION PROCESS

Purified glycerin obtained from chemical process has its purity 75 – 80% while purified glycerin obtained from distillation process has purity more than 90% which can be sold in high price. Therefore, most of glycerin-purifying factories employ distillation process to treat crude glycerin. However, the first step of this process starts with soap splitting, which similar to chemical process, and then purify glycerin by distillation.

Distillation process:

Soap splitting

Crude glycerin is acidified by an acid to remove catalyst and oils. The reaction of an acid with soap containing in glycerin gives free fatty acid (FFA) and salt while its reaction with the base catalyst gives salt and water. Since the FFA's are insoluble in the glycerin, they rise to the top and are skimmed off. Some insoluble salts also precipitate out. Next step involves removal of methanol. The methanol stream in the glycerin can be removed with flash evaporation. After removal of methanol the purity of glycerin will be approximately 85%. Next step, glycerin can be further purified up to 99.5%.

Glycerin purification

There are 2 technological processes of glycerin purification; i.e., conventional process and recent development process.

Conventional process

The conventional process for glycerin purification comprises of the following steps: pretreatment, concentration, purification and refining.

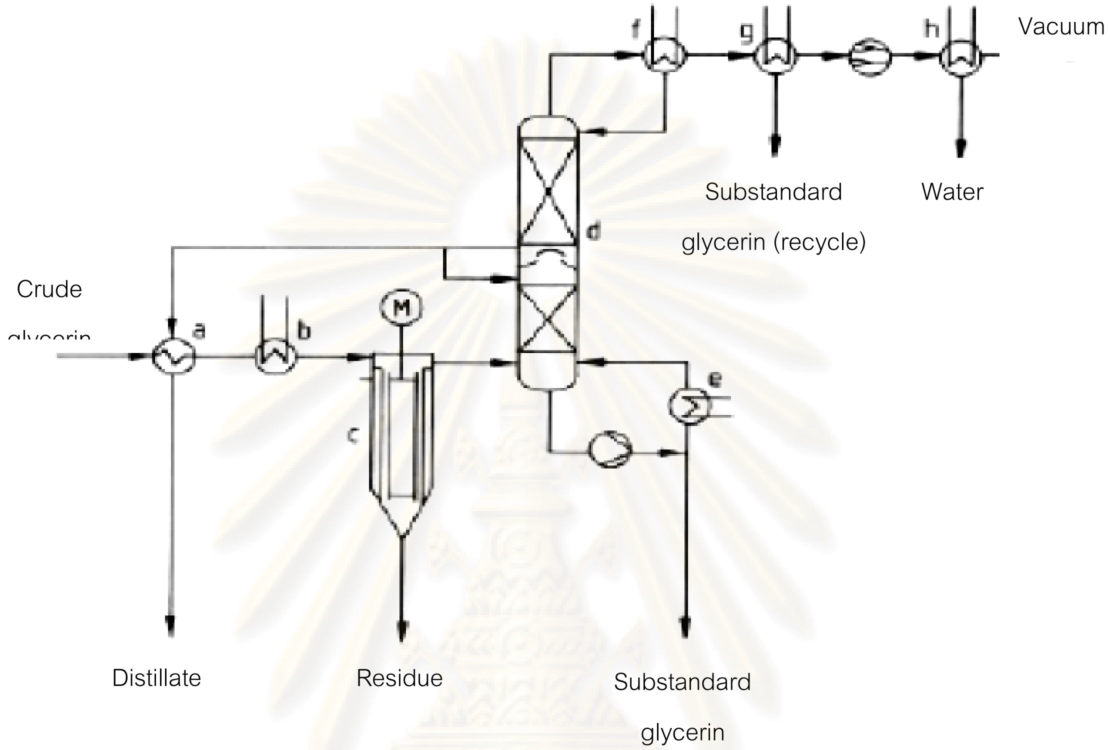
The pretreatment step is used to remove color and odor matters as well as any remaining fat components from crude glycerin. In the pretreatment step sodium hydroxide is used for the removal of fat components by saponification reaction whereas activated carbon is used for bleaching purpose.

The concentration step involves the removal of ionic substances using ion exclusion chromatography. In this process a bed filled with strongly acidic exchange resins is charged with a glycerin stream. Ionic substances are repelled from the resin surface remain in the liquid volume due to their charge while the non-ionic ones can be accommodated in the pores of the resins. Afterwards the column is rinsed with water which removes the ionic substances in the liquid first and the non-ionic ones later. In some cases when the concentration of ionic substances in the glycerin stream is very high, ion exchangers both cationic and anionic are used and they are exchanged for wash water.

The next step is purification which uses ion-exchangers. As mentioned before the exchangers are used in pairs, cationic and anionic. In cationic exchangers positive ions are exchanged for hydrogen ion while in anionic exchangers negative ions are exchanged for hydroxide ions. This purification step will remove inorganic salts, fat and soap components, color and odor causing matters. The subsequent step is treatment of glycerin in multiple vacuum flash evaporators, 10 – 15 kPa vacuum, which results in 90 – 95% concentration. An alternative way to do the same job is to use thin film distillation, shown in figure b-1. In thin film distillation the glycerin stream is distributed as a thin film on the wall of the evaporator and heated externally. The glycerin will fall down to the bottom as a residue while high volatile components like methanol and water are evaporated and collected at the top. The final concentration of glycerin to 99.5% is carried out in vacuum, 0.5 – 1 kPa, in forced circulation evaporators

Recent development process

Aiken and Monroeville (2006) has made some improvements in glycerin purification process, recent development process. He proposed five separation



Note: a) Economizer; b) End heater; c) Thin-film distillation; d) Fractionating column; e) Reboiler; f) Reflux condenser; g) Glycerin condenser; h) Water condenser

Fig b-1 Continuous glycerin distillation (SRI Consulting, 2006)

steps, which can be conducted in either batch or continuous mode, shown in figure b-2. This process is claimed to be able to produce glycerin of higher than 99.5% purity from typical crude glycerin.

i) First reactor

Crude glycerin is preheated then fed to the first reactor where is used to recover triglycerides by reacting entrained methyl esters and glycerin to produce glycerides and methanol, reversed biodiesel production reaction. Nitrogen is sparged to provide agitation and to remove methanol and water; thus, the reaction is shifted to glycerides formation. The temperature inside the reactor is maintained at 120 – 160 °C. Gas effluent

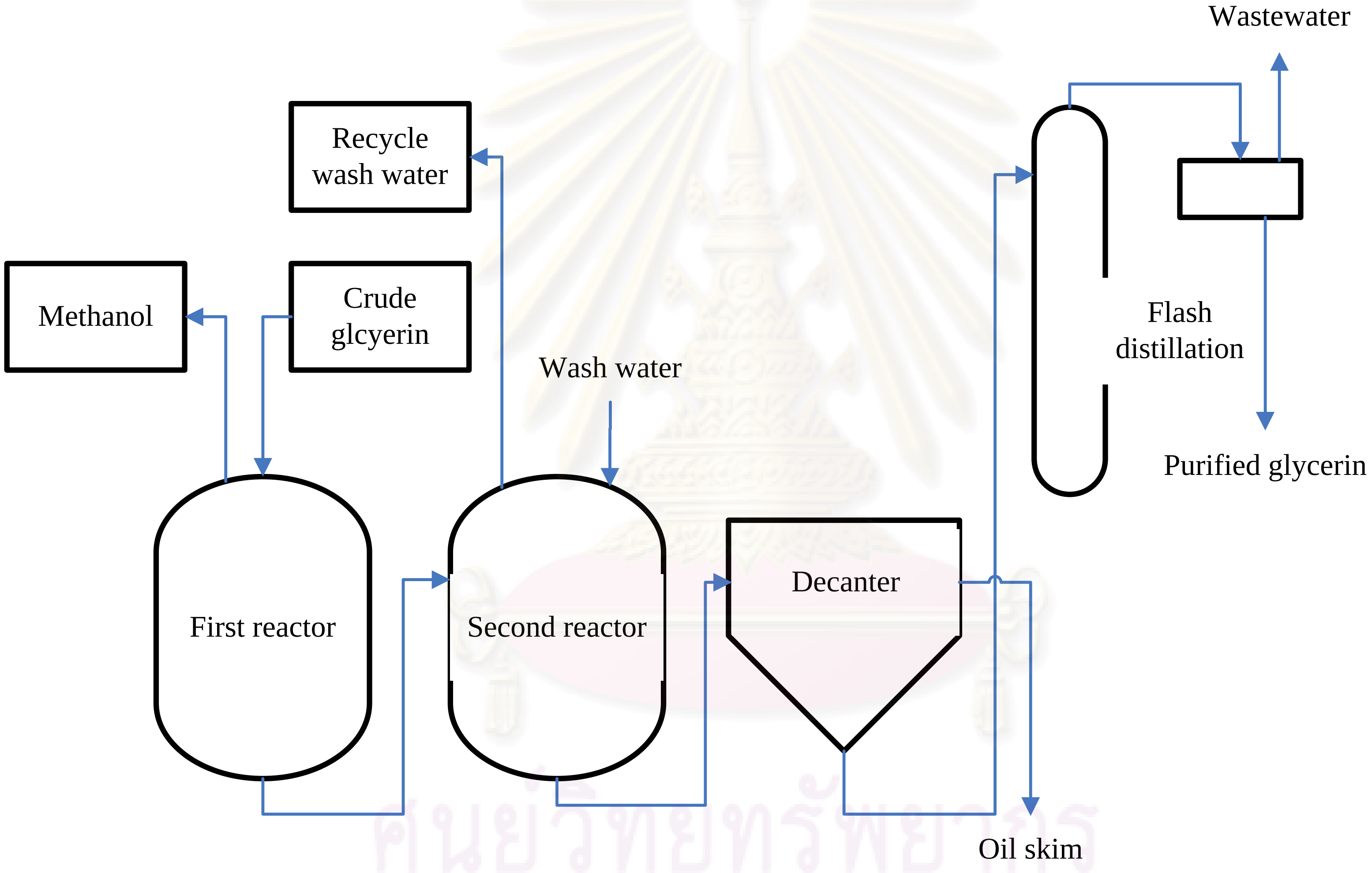


Fig b-2 Simplified flow diagram of the recent glycerin development process (Aiken J.E., 2006) stream is then passed through a condenser. After separated from condensed methanol and water in a condenser, nitrogen is recycled to the reactor.

ii) Second reactor

Liquid effluent stream from the first reactor is heated to maintain the second reactor at 120 – 160 °C. In this reactor, unreacted methyl esters are reacted to produce methanol and triglycerides. Wash water, which contains glycerin, is also added to the second reactor. Similarly, sparging nitrogen is used to agitate the mixture inside the reactor and to remove methanol and water. Entrained methanol and water are condensed. After being separated from nitrogen, wash water is recycled. The operating conditions are adjusted in such a way that glycerin effluent stream contains maximum 0.5 wt% of methanol and approximately 5 wt% of water.

iii) Decanter

A decanter is placed after the second reactor. It serves as a feed tank for the flash distillation column and a separator to remove oil layer of the glycerin stream by lowering the pH below 7 and skimming it from the glycerin layer. The recycle stream from the bottom of the flash distillation column is mixed with the glycerin stream in this tank.

iv) Flash distillation column

The flash distillation column consists of a packed bed column with a steam-heated reboiler. This column operates at a temperature of 185°C and a pressure of 5 – 20 mmHg. There is no reflux returned to the top of the column. About 80-90% of glycerin in the feed stream is drawn as overhead product, which is then condensed in two condensers in series. The first condenser is used to condense glycerin, while the second one is used to condense water which will be sent to waste water stream.

v) Adsorption columns

The last step of glycerin refining is the removal of color and trace impurities. There are lots of material that may be used as adsorbent, such as activated carbon, ion exchange resins and molecular sieves. The purified glycerin is then pumped to a storage tank.

The tables b-2 and b-3 show the energy balance calculations for the convectional process and the patent of Aiken, respectively. The conventional process consumes around 0.314 MJ/kg of glycerin, while the Aiken process consumes 0.55 MJ/kg of glycerin. That means the recent development for glycerin purification consumes higher energy than the conventional one. One reason could be the reverse transesterification reactions need high temperature to start which necessitates preheating of the feed streams.

Table b-2 Energy balance summary for a conventional process

Equipment	**Energy supplied, J/gram of glycerin**
First effect evaporator	297
Last effect evaporator	17
Total energy required	**314**

Table b-3 Energy balance summary for recent glycerin development process

Equipment	**Duty**	**Energy supplied, J/gram of glycerin**
Preheater 1	Feed heater	103
Compressor	Increase N_2 pressure	8
Preheater 2	Increase N_2 temp.	8.1
Reboiler	Heat need in distillation column	430
Total energy required		**550**

APPENDIX B-3

NUTRIENTS FORMULA FOR GLYCERIN FERMENTATION

Table b-4 The nutrients formula for mixing to crude glycerin in fermentation process

Chemical	**Concentration (mg/L)**
$NaHCO_3$	4,000
NH_4HCO_3	400
$(NH_4)_2SO_4$	200
K_2HPO_4	200
$CaCl_2$	200
Heavy metal solution	
$MgCl_2 \cdot 6H_2O$	4
$FeCl_3 \cdot 6H_2O$	5
$MnCl_2 \cdot 4H_2O$	2
$Al_2(SO_4)_3 \cdot 18H_2O$	4.23
$Ca(OH)_2$	3
$CoCl_2 \cdot 6H_2O$	0.4
$ZnCl_2$	0.2
$NiCl_2$	0.4
$CuCl_2 \cdot 2H_2O$	0.25

Source: Science and Technology Research Institute, 2009

APPENDIX C

CONVERSION CRUDE GLYCERIN TO USEFUL CHEMICALS VIA BIOLOGICAL PROCESS

Hydrogen and ethanol

The biological production of hydrogen and ethanol from glycerin is an attractive because hydrogen is expected to be a future clean energy source and ethanol can be used as a raw material and a supplement to gasoline.

Enterobacter aerogenes HU-101 (Nakashimada et al., 2002; Ito et al. 2005), an example of microorganism, can convert various carbohydrates, such as sugars and sugar alcohols, to hydrogen, ethanol, 2,3-butanediol, lactate and acetate. Using glycerin as carbon source, it was dilute with a synthetic medium to increase the rate of glycerin utilization and the addition of yeast extract and tryptone to the synthetic medium accelerated the production of hydrogen and ethanol. The yields of hydrogen and ethanol decreased with an increase in the concentrations of glycerin.

Although the result indicated that a higher concentration of glycerin decreased the yields of hydrogen and ethanol, it is necessary to increase glycerin concentration used in the production of hydrogen and ethanol because an excessive dilution of crude glycerin using the medium increases the cost for the recovery of ethanol and wastewater treatment.

1,3–propanediol

1,3-Propanediol, a colorless viscous liquid that is miscible with water, is mainly used as a building block in the production of polymers. 1,3-Propanediol can be formulated into a variety of industrial products including composites, adhesives, laminates, coatings, moldings, an antifreeze and wood paint. It can be used as a monomer for polyesters, polyether, and polyurethanes (Du et al., 2006; Yang et al., 2007). The molecular structure of 1,3-propanediol is shown in figure c-2.

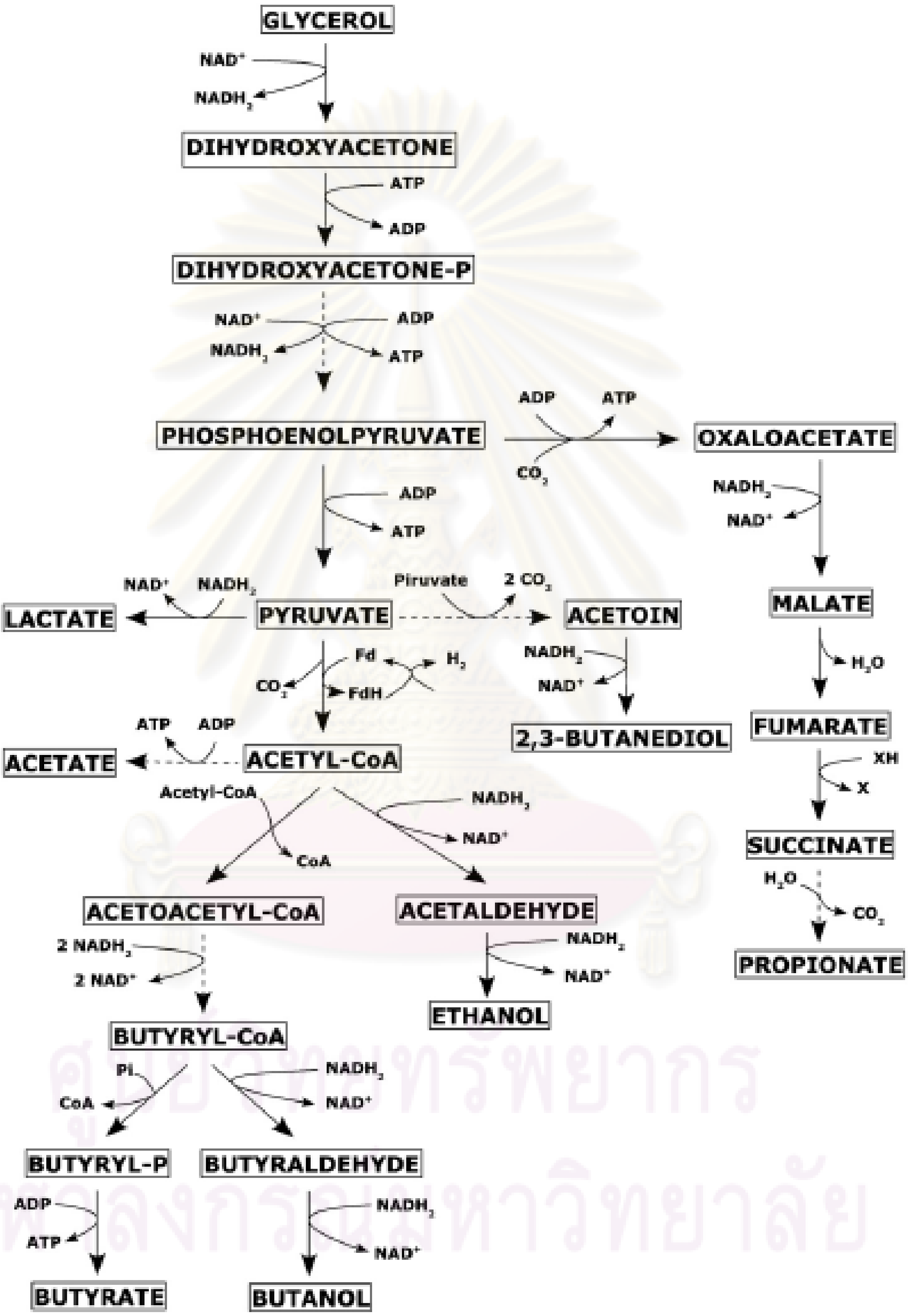


Fig c-1 Overview of some possible end products for different microorganisms during glycerin degradation (Silva et al., 2009)

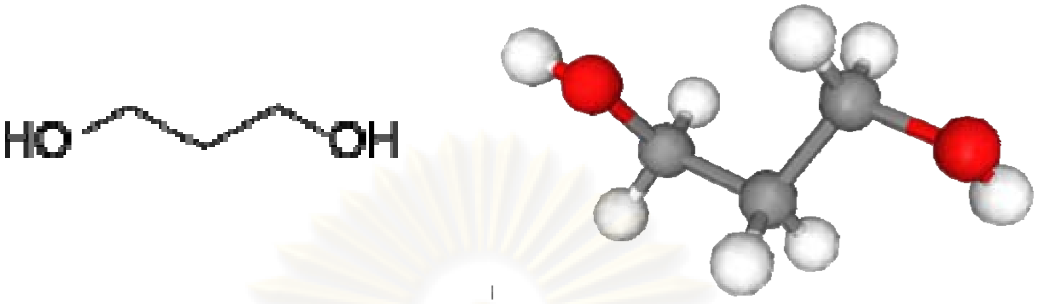


Fig c-2 Molecular structure of 1,3-propanediol; 2-dimension (left), 3-dimension (right)

There are currently two processes for the chemical synthesis of 1,3–propanediol: hydration of acrolein and hydroformylation of ethylene oxide (Hao et al., 2006; Yang et al., 2007); however, both of these processes produce toxic intermediates and require a reduction step under high hydrogen pressure (Sullivan, 1993). The biological production of 1,3–propanediol from glycerin was demonstrated for several bacterial strains, such as *Lactobacillus brevis*, *Lactobacillus buchnerii*, *Bacillus welchii*, *Citrobacter freundii*, *Klebsiella pneumoniae*, *Clostridium pasteurianum*, *Clostridium butyricum*, *Clostridium acetobutylicum* and *E. agglomerans* (Veiga da Cunha and Foster, 1992; Biebl et al., 1992; Biebl and Marten, 1995; Macis et al., 1998; Cheng et al., 2004; González-Pajuelo et al., 2006; Yang et al., 2007). Among these microorganisms, *C. butyricum* is the best ‘‘natural producer’’ both in terms of yield and titer of 1,3-propanediol produced (Saint-Amans et al., 1994).

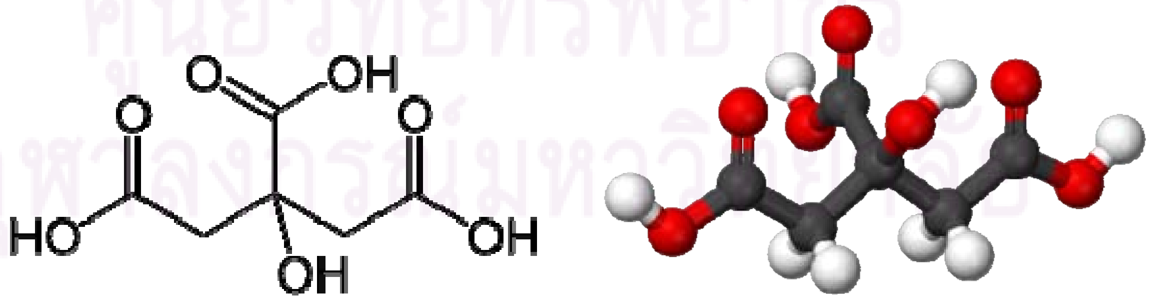


Fig c-3 Molecular structure of citric acid; 2-dimension (left), 3-dimension (right)

Citric acid

Citric acid, a weak organic acid and a natural preservative, is used to add an acidic, or sour, taste to foods and soft drinks. It also serves as an environmentally benign cleaning agent and acts as an antioxidant and a lubricant. The molecular structure of citric acid is shown in figure c-3.

Citric acid can be added to ice cream to keep fat globules separate, and can be added to recipes in place of fresh lemon juice as well. It is used along with sodium bicarbonate in a wide range of effervescent formulae, both for ingestion and for personal care, such as bath salts, bath bombs, and cleaning of grease. Citric acid is commonly employed in wine production as a substitute or improver where fruits containing little or no natural acidity are used (Robinson, 2006).

Crude glycerin seems an efficient substrate for citric acid production by *Yarrowia lipolytica* LGAM S(7)1 (Roukas and Kotzekidou, 1997; Papanikolaou et al., 2002). The growth of these micro-organisms on sugars is followed by a significant citric acid accumulation in the culture medium. The use of glycerin substrate in high concentrations resulted in a significant increase in citric acid production up to 33 – 35 g/L, yield 0.42 – 0.44 g acid/g glycerin consumed. Relatively large amounts of this acid have been produced, although it is plausible to wait for improved productivities with an optimization of the operating conditions, use of bioreactors, growth on a constant medium pH, increase of agitation and aeration rate.

Polyhydroxyalcanoate

Polyhydroxyalcanoate (PHA), figure c-4, represents a complex class of naturally occurring bacterial polyesters that are synthesized intracellularly as carbon and energy reserve materials (Ashby et al., 2004) by microorganisms under nutrient-limiting conditions with excess carbon (Valappil et al., 2007). Since PHAs are biodegradable, biocompatible and exhibit thermo-plastic properties, they may replace petroleum-derived polymers, which are widely used in medicine, drug delivery, agriculture/horticulture, the

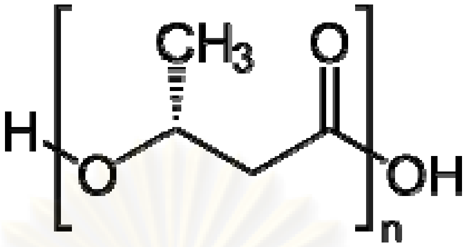


Fig c-4 Molecular structure of polyhydroxyalkanoates (polyhydroxybutyrate)

fiber industry and the consumer care branch (Solaiman et al., 2006) including biomedical application such as tissue engineering (Misra et al., 2006).

Methylobacterium rhodesianum, Ralstonia eutropha, Pseudomonas sp., Pseudomonas oleovorans, and *Pseudomonas corrugate* (Bormann and Roth, 1999; Ashby et al., 2004; Ashby, et al., 2005) are the example of microorganism for producing PHA. Crude glycerin can be used for PHA production by *Pseudomonas sp.* without the need for separating and recovering glycerin and other components. Up to 5% glycerin (v/v) could be used for the production of both PHB by *P.oleovorans* and medium-chain length PHA by *P. corrugata* under identical growth conditions, allowing mixed culture fermentations to be used in the formation of PHA polymer blends with varying blend ratios (Ashby et al., 2005).

Dihydroxyaceton

Dihydroxyacetone, also known as DHA, is a hygroscopic white crystalline powder. It has a sweet cooling taste and a characteristic odor. It is frequently used in the cosmetic industry and serves as a versatile building block for the organic synthesis of a variety of fine chemicals (Hekmat et al., 2003; Bauer et al., 2005). The molecular structure of DHA is shown in figure c-5.

Due to rigorous safety requirements, the chemical production of DHA is rather expensive. Thus, DHA synthesis is performed more economically using a microbial

Fig c-5 Molecular structure of dihydroxyacetone; 2-dimension (left), 3-dimension (right)

process (Hekmat et al., 2003). It is produced via the oxidation of glycerin using the acetic acid bacterium *Gluconobacter oxydans* (Wethmar and Deckwer, 1999; Bauer et al., 2005) in a process that requires good oxygenation and a medium containing yeast extract (Flickinger and Perlman, 1977). Wethmar and Deckwer (1999) developed a semi-synthetic medium that allows increased specific DHA production, significantly reducing the yeast extract in the medium.

One of the main problems of microbial DHA synthesis is the fact that both the substrate and product have an inhibitory effect on bacterial growth (Hekmat et al., 2003; Bauer et al., 2005). *G. oxydans* lost its regeneration capability at DHA concentrations above 160 kg/m^3, but product formation was observed up to a maximum DHA concentration of 220 kg/m^3 because intact membrane-bound glycerin dehydrogenase was still active both in the irreversibly growth-inhibited cells as well as in the cell debris.

Succinic acid

Succinate or butanedioic acid has a specialty chemical market in industries producing food and pharmaceutical products, surfactants and detergents, green solvents, biodegradable plastics and ingredients to stimulate animal and plant growth. Due to its structure as a linear saturated dicarboxylic acid, shown in figure c-6, succinate can be used as an intermediate chemical and be converted to 1,4-butanediol, tetrahydrofuran, γ-butyrolactone, adipic acid, n-methylpyrrolidone and linear aliphatic esters (Zeikus et al.,

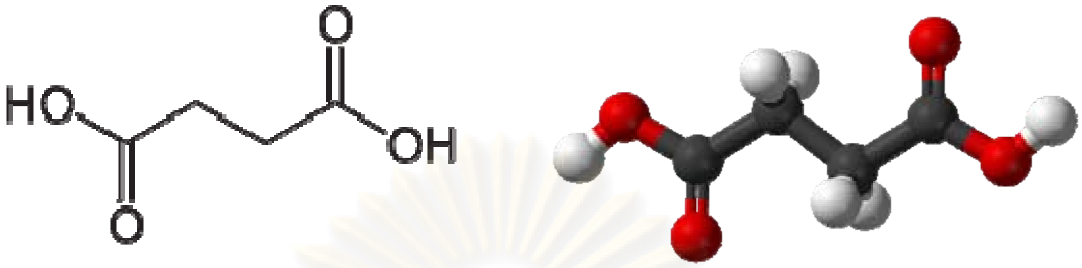


Fig c-6 Molecular structure of succinic acid; 2-dimension (left), 3-dimension (right)

1999). An increasing demand for succinic acid is expected as its use is extended to the synthesis of biodegradable polymers such as polybutyrate succinate and polyamides (Song and Lee, 2006).

Succinate is currently produced petrochemically from butane through maleic anhydride; only natural succinic acid sold in the food market is produced by fermentation (Zeikus et al., 1999). Succinate is normally produced under anaerobic conditions through several different metabolic pathways, such as PEP and pyruvate carboxylation. *Anaerobiospirillum succiniciproducens* (Lee et al., 2001; Lee et al., 2004) is one of the most efficient succinate producers and uses the PEP carboxylation pathway, as shown in figure 4-17, catalyzed by PEP carboxykinase or PEP carboxylase.

Succinic acid production from glycerin presents several advantages over glucose, such as high succinic acid yield with reduced acetic acid formation. This is advantageous because acetic acid imposes difficulties with respect to downstream processes for the recovery of succinic acid (Song and Lee, 2006).

Propanoic acid

Propanoic acid, figure c-7, is derived directly from a metabolic pathway balanced with regard to redox-equivalents. Propanoic acid is used as an antifungal agent in food and as a basic chemical to produce cellulose-based plastics, herbicides, solvents and perfumes

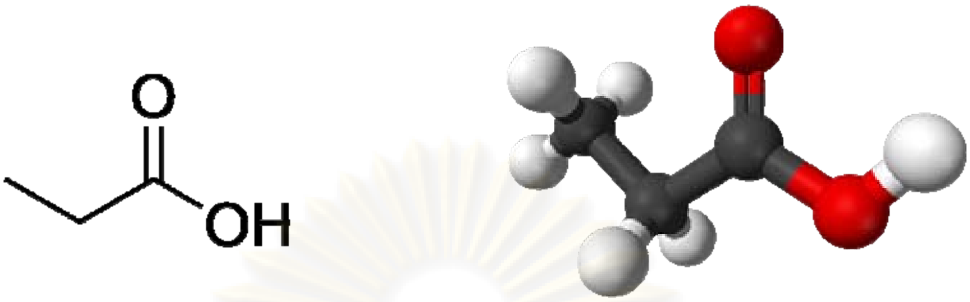


Fig c-7 Molecular structure of propanoic acid; 2-dimension (left), 3-dimension (right)

(Barbirato et al., 1997a), arthritis drugs, flavors and thermoplastics (Himmi et al., 2000). The numerous industrial applications of propanoic acid account for an increasing interest in the development of a biotechnological production process based on the renewable resource glycerin (Barbirato et al., 1997a, Himmi et al., 2000).

Propanoic from glycerin is produced by three bacterial strains: *Propionibacterium acidipropionici*, *Propionibacterium acnes*, and *Clostridium propionicum* (Barbirato et al., 1997). Considering fermentation time and conversion yield, the best strain for glycerin conversion to propionate was *P. acidipropionici*. Glycerin is a promising substrate for propanoic acid production both in terms of conversion yield and productivity. Better efficiency for propanoic acid production from glycerin could be expected because of its higher reduction level over conventional substrates.

Biosurfactants

Biosurfactants are surface-active substances synthesised by living cells. They have the properties of reducing surface tension, stabilizing emulsions, promoting foaming and are generally non-toxic and biodegradable. Biosurfactants enhance the emulsification of hydrocarbons, have the potential to solubilize hydrocarbon contaminants and increase their availability for microbial degradation. The use of chemicals for the treatment of a hydrocarbon polluted site may contaminate the environment with their by-products,

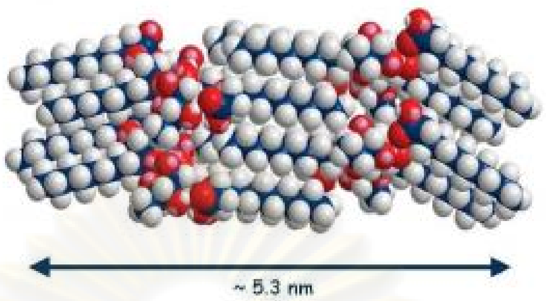


Fig c-8 A rhamnolipid biosurfacant model

whereas biological treatment may efficiently destroy pollutants, while being biodegradable themselves. Hence, biosurfactant producing microorganisms may play an important role in the accelerated bioremediation of hydrocarbon contaminated sites.

Biosurfactants have many advantages over chemically manufactured surfactants (Bognolo, 1999). They are environmentally friendly nature, possibility of large-scale production, selectivity, performance under extreme conditions and potential applications in environmental protection. Research in the field of biosurfactants has expanded quite a lot in recent years, due to their potential use in areas such as the food industry, agriculture, pharmaceutical industry, crude oil recovery and bioremediation of contaminated sites (Bannat et al., 2000).

Pseudomonas aeruginosa (Rahman et al., 2002; Nitschke et al., 2005; Zhang et al. 2005) can synthesize rhamnolipids from glycerin as the sole carbon source. Approximate 15.4 g/L rhamnolipids were produced using *P. aeruginosa* growing on a basal mineral medium containing glycerin. These results show that glycerin can be used for the production of biosurfactants. Figure c-8 shows a rhamnolipid

Pigment

Some studies have been made using glycerin as carbon source for pigment production, such prodigiosin and astaxantin which their molecular structure are shown in figure c-9 and c-10, respectively.

Prodigiosin is a deep red pigment formed by the Gram-negative bacterium *Serratia marcescens* (Montaner et al., 2000; Campàs et al., 2003; Tao et al., 2005) when cultivated on rich solid media. This pigment is an immunosupressor and has been reported to induce apoptosis of several cancer cell lines, such as hematopoietic cancer cells, colon cancer cells, B-lymphatic cancer cells and chronic lymphocytic leukemia cells, but not in nonmalignant cells, which indicates that prodigiosin may have potential as new antineoplastic candidate. In a two-step feeding strategy using glucose for growth and then glycerin for prodigiosin synthesis, *S. marcescens* mutant produced about 583 mg prodigiosin/L in 30 hours, with glycerin as the sole carbon source in a 5-l bioreactor.

Astaxanthin, 3,3´-dihydroxy-β,β´-carotene-4,4´-dione, is a red or orange pigment found in marine environments. It is used to feed animals such as salmon, trout (freshwater) and crustaceans in order to give them a color that appeals to consumers.

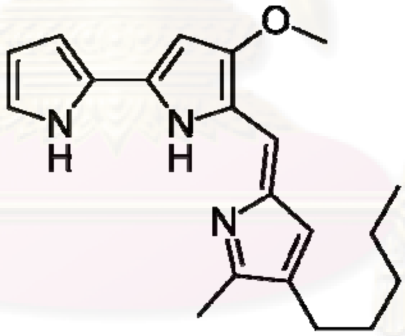


Fig c-9 Molecular structure of prodigiosin

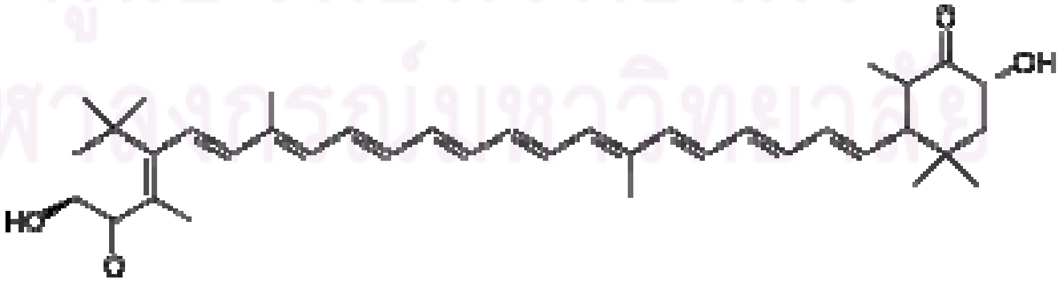


Fig c-10 Molecular structure of astaxanthin

Glycerin is a potential substrate for astaxanthin production in *P. rhodozyma*, obtaining a maximum total volumetric astaxanthin concentration of 33.7 mg/L (Kusdiyantini et al., 1998).

APPENDIX D

CALCULATION

Table d-1 The revenue calculation of reuse the last methyl ester washing water of Factory D

List	Value	
Production capacity	20	m^3/day
Times of methyl ester washing	5	times/day
Washing water consumption	3	m^3/time
Total washing water consumption	15 (3 x 5)	m^3/day (m^3/time) x (time/day)
Amount of reuse the 4th and 5th washing water	6	m^3/day
Estimated cost of water	24	baht/m^3
Average working day	300	day/year
Total water saving cost	144 (24 x 6) 43,200 (144 x 300)	baht/day (baht/m^3) x (m^3/day) baht/year (baht/day) x (day/year)

Table d-2 The revenue calculation of crude glycerin purifying by factory itself and selling as pharmaceutical grade of Factory D

List	Value	
Production capacity	200	m^3/day
Crude glycerin generation	20 25,200 (20,000,000 x 1.261)/1000	m^3/day kg/day (cm^3/day) x (g/cm^3)/ (kg/g)
Investment capital of glycerin-purifying plant (production capacity of 20 ton/day)	18,000,000	baht
Total generated purified glycerin	12,600 (25,200 / 2)	kg/day (kg/day)
Average price of pharmaceutical-grade glycerin	20	baht/kg
Cost of purifying glycerin	14	baht/kg
Profit	6 (20 – 14)	baht/kg baht/kg
Average working day	25	day/month
Total revenue from selling glycerin as pharmaceutical grade	75,600 (12,600 x 6) 1,890,000 (75,600 x 25)	baht/day (kg/day) x (baht/kg) baht/month (baht/day) x (day/month)
Payback period	9.5 (18,000,000 / 1,890,000)	months baht/ (baht/month)

Note: based year 2008

Table d-3 The revenue calculation of selling spent bleaching earth as mould releasing agent

List	Value	
Production capacity ranging of three factories that using bleaching earth	80 – 800	m^3/day
Average spent bleaching earth generation	8	kg/m^3
Total generated spent bleaching earth	640 – 6,400 (8 x 80, 8 x 800)	kg/day (kg/m^3) x (m^3/day)
Average estimated price of selling spent bleaching earth	1.5	baht/kg
Average working day	300	day/year
Total revenue	960 – 9,600 (1.5 x 640, 1.5 x 6,400) 288,000 – 2,880,000 (960 x 300, 9,600 x 300)	baht/day (baht/kg) x (kg/day) baht/year (baht/day) x (day/year)

Table d-4 The revenue calculation of selling electricity to PEA

List	Value	
Average produced biodiesel from five factories	275	m^3/day
Average wastewater generation	0.47	m^3/m^3 of biodiesel
Total wastewater generation	130 (275 x 0.47)	m^3/day (m^3day) x (m^3/m^3 biodiesel)
Biogas generation	25	m^3/m^3 wastewater
Total generated biogas	3,250 (130 x 25)	m^3/day (m^3 wastewater/day) x (m^3/m^3 wastewater)
Electricity generation	2.5	kWh/m^3 biogas
Total generated electricity	8,125 (3,250 x 2.5)	kWh/day (m^3 biogas/day) x (kWh/ m^3 biogas)
Average price of electricity	2.02	baht/kWh
Average working day	300	day/year
Total revenue from selling electricity to PEA	16,400 (8,125 x 2.02)	baht/day (kWh/day) x (baht/kWh)
	4,920,000 (16,400 x 300)	baht/year (baht/day) x (day/year)
Overestimated investment capital on anaerobic digester (CSTR) and electrical generation plant	40,000,000	baht
Payback period	8.13	years

BIOGRAPHY

Miss Thananuch Raghareutai was born on 15th March, 1984 in Bangkok. She finished her higher secondary course from Satriwithaya School, Bangkok in March 2003. After that, she studied in the major of Chemistry in Faculty of Science at Chulalongkorn University and got Bachelor’s degree in April 2007. She continued her further study for Master’s degree in Environmental and Hazardous Waste Management and achieved her Master’s degree in May, 2009.