CHAPTER 1

INTRODUCTION

1.1 Energy in Thailand

From the problem of rised rapid population growth, not only food crisis but also energy crisis that already happened. One of the global energy crisis is petroleum crisis because petroleum using is rapidly increase while their reserves are rapidly declining. Many countries concern about petroleum crisis and try the ways to reduce consuming to make petroleum fuel sustained as long as possible.

In fact, Thailand is a country that can provide petroleum fuel (406,800 bbl/day) more than some OPEC's countries such as Brunei (159,400 bbl/day). However, the ratio of using is much more than providing rate (Thailand's consumption 807,100 bbl/day, Brunei's consumption 17,000 bbl/day) [1]. That problem leads to the petroleum cost in Thailand is higher when consumption rate is increasing. The most volume of petroleum fuel is petroleum diesel because main engine in the transportation sector is diesel engine. Diesel engine and petroleum diesel are mostly used because low price and low tax rate. Increasing the daily use of diesel fuel leads more import of petroleum especially in diesel fuel.

Table 1.1 List of fuel activity in Thailand [1]

Fuel activity	Volume (bbl/day)	World ranking
Production	406,800	33
Consumption	807,100	22
Exports	269,100	43
Imports	807,100	17

Table 1.2 Percentages of diesel and diesel B5 using in Thailand calculated from commercial energy

Type/Year	2008	2009	2010	2011	2012
Diesel	22.2	16.4	17.3	27.7	29.6
Diesel B5	6.1	13.7	10.7	1.0	0.0

Thailand Energy Statistic (2012) [2]

Table 1.3 Quantity of diesel using in Thailand

	2008	2009	2010	2011	2012
Diesel(Ml.)	13,813	10,293	11,404	18,484	20,544

Thailand Energy Statistic (2012) [2]

From Table 1.2 and Table 1.3, the qualitative and quantitative data are shown that energy consumption especially from diesel fuel are increasing. Thus, Thailand government attempts to reduce fuel import since 2008 by added 2% of biodiesel in diesel fuel and promoted productions, materials, researches and developments until

2022 [3]. Nowadays, diesel fuel in petroleum stations were added 4.5-5% of biodiesel followed the previous plans (Appendix A).

One of the promoting on researches and development from Department of Alternative Energy Development and Efficiency (DEDE) is community-scale biodiesel. The government planned for biodiesel and their sustainable system cooperated with economic and agricultural benefits. They promoted using biodiesel and also planned for small-scale community. Community-scale biodiesel's project has been started from 2006 and carried on with community participation and financial support by the Thai government. The production process at the community-scale was designed on the basis of a simple operation with a low capital and production costs and the products of community-scale biodiesel can use directly in agricultural engine such as water pump, cultivator engines, trailer mounted engines, dump trucks and farm vehicles with single-cylinder, 4-stroke diesel engine without operational problem [4].

1.2 Biodiesel

Biodiesel is a renewable fuel produced from various oil such as palm oil, rape seed oil, jatropha oil, soybean oil and also animal fat. Using biodiesel have many advantages in many parts. For example, biodiesel can promotes agricultural and economic parts by increase prices of fuel plants and biodiesel are also shown environmental benefits in term of decrease global warming impacts, reduce emissions, greater energy dependence and positive impacts on agriculture [5]. Biodiesel also separate to 3 types [6] including as follow :

1.Biodiesel from straight vegetable oil or animal fat added directly to diesel engine without chemical added. However, adding vegetable oil or animal fat need

worm up to 70 degree celsius because viscosity of vegetable oil is 11-17 times higher than diesel fuel and pour point is high compared to diesel fuel. This type of biodiesel also made problems of the incomplete combustion, slow and low volatility, difficult on engine start and make soot remaining in diesel engines.

2.Biodiesel from veggie/kero mix using vegetable oil or animal fat mixed with diesel or kerosene to reduce viscosity for getting nearly fuel property of diesel fuel as possible such as “cocodiesel”. The ratio of mixing is available from 10% vegetable oil mixed with 90% kerosene to 40% vegetable oil mixed with 60% kerosene. However, kerosene has high price and mixing with low ratio of kerosene also make problems similar to biodiesel from straight vegetable oil or animal fat.

3.Ester biodiesel or true biodiesel using worldwide such as Germany or United State because fuel properties are similar to diesel fuel. Biodiesel can start from ratio 5:95 to B100(pure biodiesel). Using of biodiesel also use by mixing with diesel to reduce production cost. However, many research showed positive impact of this fuel type so, ester biodiesel is now widespread using because of the safety of fuel also show in gas station by “cetane number”.

In Thailand, biodiesel has been promoted to community-scale biodiesel. Mostly products processed by tranesterification reaction (Figure 1.1) passed with cleaning processes and other processes (Figure 1.2). However, the variation of processes are different depended on various factors not only biodiesel product in Thailand but also worldwide.

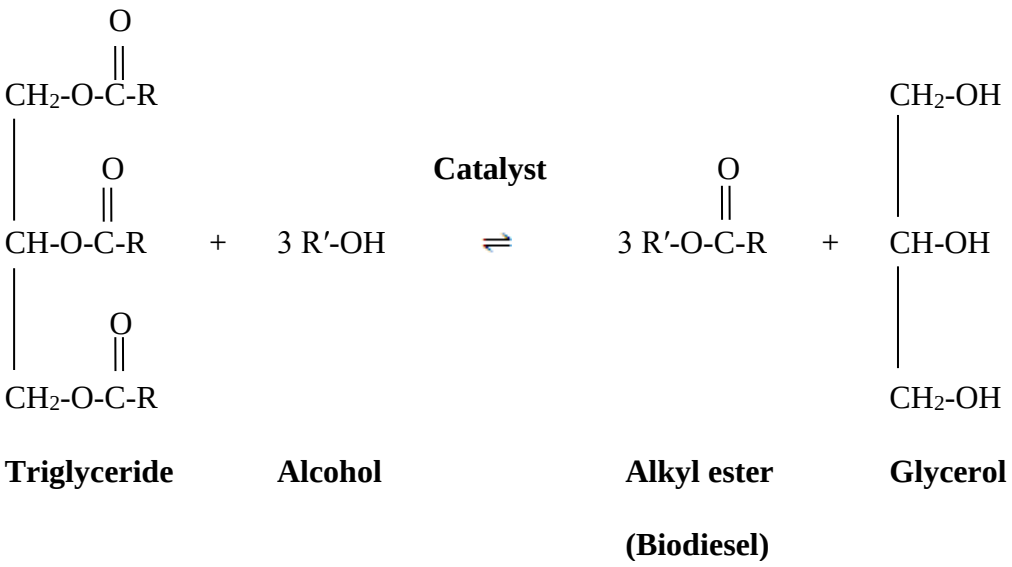

Figure 1.1 Transesterification reaction of biodiesel

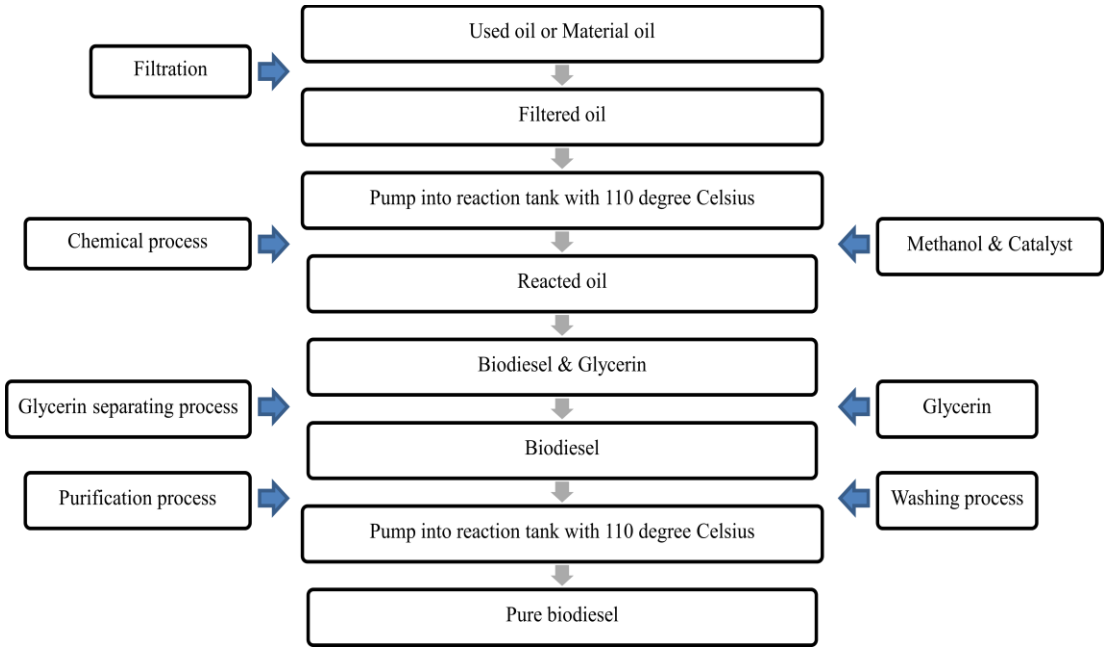

Figure 1.2 Schematic diagram of the community biodiesel production system in Sankampaeng, Chiang Mai Province, Thailand

In Thailand, there are 72 community-based small scale plants which are producing biodiesel 100 liters per day each. These small scale plants use palm oil, waste cooked oil as well as jatropha oil as raw material [7]. The production rates on each community depends on material sources, materials price fuel price and volume of using.

Figure 1.3 Community biodiesel production plant in Sankampaeng district, Chiang Mai Province, Thailand

1.3 Diesel and Biodiesel Emission

In many research, biodiesel also showed benefits on environmental effects such as biodiesels, made from palm oil and jatropha oil, can reduce carbon dioxide (CO_2) emissions, carbon monoxide (CO) emissions and total hydrocarbon (THC) emissions.

However, nitrogen oxides (NO_x) and soluble organic fraction (SOF) emissions are higher than diesel fuel using [8]. Unregulated emissions such 4,5 rings polycyclic aromatic hydrocarbons (PAHs), the most effected on carcinogenicity, are also observed that biodiesel cans reduce PAHs emissions [9]. However, the variation of emissions with the use of biodiesel found in the literature depends on several variables such as the type of engine, its regime (transient or steady-state), the biodiesel blendstocks (palm oil, rape seed, etc.) [10].

PAHs is the most abundance in diesel exhaust particulates (DEP) that formed during incomplete combustion of organic material. NPAHs are an important subgroup of PAHs found on DEP. Garshick *et al.* reported that NPAHs have been suggested to be related to the development of lung cancer [11]. Tokiwa and Ohnishi studied on several NPAHs and the results of NPAHs were showed highly mutagenic in bacterial systems and that they are found to cause mutations and tumors in animal models [12]. Yamazaki *et al.* reported that NPAHs may be metabolized by ring oxidation, nitroreduction, as well as conjugation reactions. Some of these reactions may lead to reactive metabolites that can covalently bind to macromolecules including DNA. Reactive epoxides may be formed by various CYP enzymes [13]. Bamford *et al.* studied about determination and comparison of NPAHs measured in air and diesel particulate and founded that 1-Nitropyrene is the most abundance NPAHs in the atmosphere and in diesel exhaust particles [14].

1.4 1-Nitropyrene and other NPAHs distribution and toxicity

1-Nitropyrene (1-NP) is a by-product of combustion. It is the predominant nitrated polycyclic aromatic hydrocarbon emitted in diesel engine exhaust and has

been found at concentrations of up to 357 pg/m^3 in the air over urban and suburban areas.

1-NP is detoxified mainly to 1-aminopyrene by nitro reduction. 1-NP can also undergo ring oxidation, depending on the concentration of oxygen. Aryl nitrenium ions generated by nitro reduction or K-region nitropyrene epoxides generated by ring oxidation can react with DNA, forming adducts [15].

1-NP is one of the hazardous environmental pollutants. There are many researches on their carcinogenicity and mutagenicity. Hatanaka *et al.* investigated on metabolic activation of 1-NP by human cytochrome P450 (CYP450) family 1 enzymes co-expressed with NADPH-cytochrome P450 reductase in *Escherichia coli* membranes and found that 1-NP induced umu gene expression in *Salmonella typhimurium* TA1535/pSK1002 in the absence of any P450 system, but the activities were influenced by the levels of bacterial O-acetyltransferase and nitroreductase [16]. Landvik *et al.* studied on the effects of NPAHs and DEP extracts on cell signaling related to apoptosis and found that 1-NP induced apoptosis characterized by several parameters as well as necrosis in Hepa1c1c7 cells [17].

The studies on 1-NP and NPAHs in diesel fuels are various in many countries. Sheepers *et al*. studied about NPAHs in airborne particulate matters from workplace atmosphere contaminated with diesel exhaust. They investigated 1-NP and 2-nitrofluoranthene (2-NF) in the different sources of diesel exhaust and found that 1-NP levels are higher than 2-NF (25 times) and 1-NP in DEP can be collected by low-volume air sampler [18]. Bamford *et al.* studied on NPAHs measured in air and diesel particulate reference materials and the results showed that 1-NP was dominant NPAHs present in the diesel particulate samples, while 2-NF was the highest NPAHs

concentration measured in air particulates samples [14]. Kameda *et al.* studied on the concentration of NPAHs in diesel exhaust particulate and in ambient airborne particles. They found that 1-NP is a major compound of NPAHs in DEP and airborne particulates (32 pmol/m^3 in DEP, 75.3 fmol/m^3 in airborne particle) [19]. Landvik *et al.* studied on the effects of NPAHs and DEP extracts on cell signaling related to apoptosis. They found 1-NP was a major compound in diesel exhaust particle extracts and 1-NP was also induced apoptosis characterized by several parameters as well as necrosis in Hepa1C1C7 cells [17].

Some researchers also investigated on NPAHs in biodiesels, Baldassarri *et al.* studied on the chemical and toxicological characteristics of emissions from an urban bus engine fueled with diesel and biodiesel blend. They found regulated and non-regulated pollutants in terms of PAHs and NPAHs were small reductions of them in biodiesel blend compared with diesel-using [9]. Karavalakis *et al.* studies on the effects of low concentration biodiesel blends in terms of PAHs, NPAHs and oxy-PAHs. The results showed biodiesel blends (10% v/v) can reduce PAHs and NPAHs and oxy-PAHs. Moreover, engine types, engine speed and tested method affected quantification of PAHs and their derivatives [20].

However , the study on 1-NP in Thailand is rarely found especially in source of 1-NP pollutions such as diesel engines. Moreover, 1-NP concentration data could be used as indicator for environmental impacts in terms of hazardous toxicity from using engines or fuels. In Thailand, no data observed on 1-NP in agricultural engines that could be used for improve quality to fuels for environmental impacts.

1.5 Research objectives

The purpose of this study is to determine and compare the results from $PM_{2.5}$ exhaust emissions of 1-nitropyrene concentration level from an agricultural diesel engine with community biodiesel and conventional diesel.