CHAPTER 4

DISCUSSION

4.1 1-NP and $PM_{2.5}$ emissions in exhausts of tested fuels and their toxicity

Determination of 1-NP, absorbed on the soot or particle-phase was shown in Table 3.4. This study used CD(B2) as a reference fuel because CD(B2) is generally used as known as diesel in Thailand and pure diesel has not provided. The emission of 1-NP in CD(B2) is 208.23 ± 34.59 $\mu g/m^3$. The variation of 1-NP are high due to the process of fuel combustion in diesel engine. The emission of 1-NP in biodiesel fuels are decreased when those compared to diesel fuel CD(B2). The percentage of tested fuel emissions are 45.52 – 78.43 decreased from diesel fuel. Biodiesel was such an oxygenated fuel that can improve combustion efficiency in diesel engine, but adding too much biodiesel fraction to diesel fuel would cause incomplete combustion in the diesel engine generator and impede the release of energy from the fuel [9]. In 1-NP generating process, pyrolysis in diesel engine's combustion chamber is lower when biofuels were used because of their ester structure contained oxy-group. The oxy-group in ester contributes complete combustion in combustion chamber and reduce NO_x transformation [15].

Determination of $PM_{2.5}$ was measured by calculation of filter samples from agricultural diesel engine fuel with tested fuel. The results show using tested fuels reduced PM concentration from reference fuel (CD(B2)). When CBU and CBS were using, the emission reduced. In CD(B5), Emission change show better than CBU and CBS blends because the purification of mixing process and source of biodiesel are different. The source of biodiesels in community biodiesel didn’t pass intermediately purification process as biodiesel sources from PTT company [28]. According to the chemical structure and purification, biodiesel activate and make complete combustion in diesel engine combustion chamber [32].

1-Nitropyrene is one of the major nitroarenes in primary particulate emissions of diesel engines [33]. Substantially decreased amounts of 1-NP were reported in exhausts emitted from a single cylinder when nitrogen-free air was used in the diesel engine [34]. 1-NP has also been identified in used oil from a light-duty diesel engine at levels of 0.2 mg/l and 0.5 mg/l [35], and Manabe *et al.* found 0.4 mg/l in used diesel engine oil and 0.2 mg/l in used gasoline engine oil [36]. Jensen *et al.*[35] reported that oil was the source of a significant amount (16-80% depending on engine load) of extractable organic materials in diesel particulate emissions. Since 1 -nitropyrene was not detected in new oil (on the basis of a detection limit of 0.1 ng/ml).

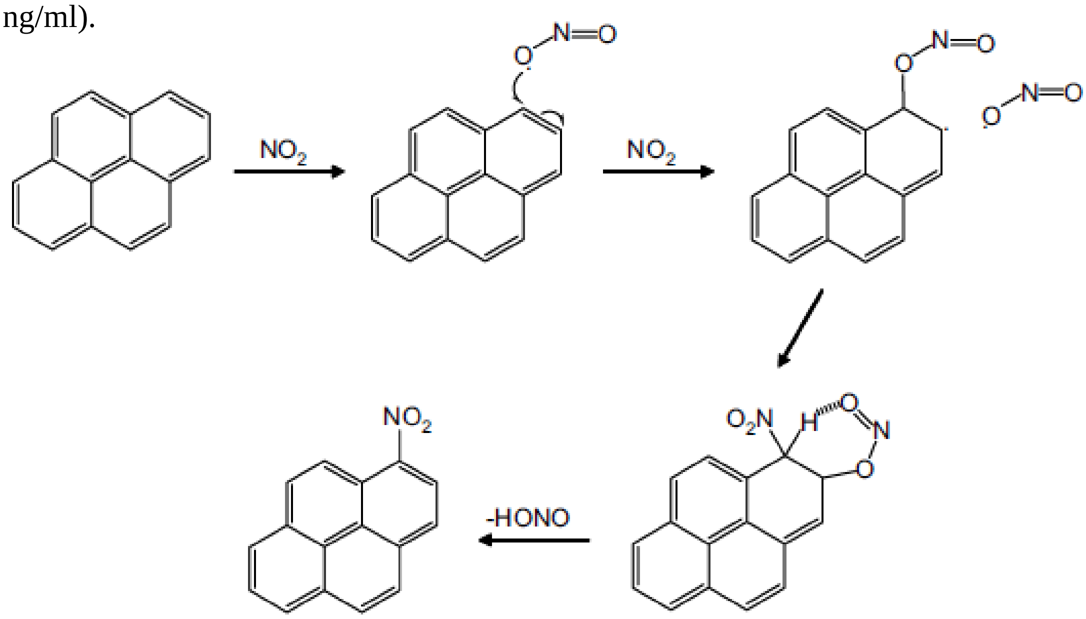

Figure 4.1 Mechanism proposed for the nitration of pyrene [37]

Toxiciy of 1-NP are previously shown in the introduction. Moreover, not only carcinogenicity and mutagenicity in Hepa1C1C7 cells are investigated [16-19] but another cells system also found the effect from 1-NP. 1-NP, induced DNA damage, increased intracellular reactive oxygen species (ROS) levels and ER stress in human umbilical vein endothelial cells (HUVEC). The 1-NP induced DNA damage, ROS production and endoplasmic reticulum stress were reduced by simultaneous treatment with dicoumarol suggesting that these effects were mediated by 1-NP metabolites mainly formed at nitroreduction. This data suggested that HUVEC represents a sensitive model system for elucidating the vascular effects of nitro-PAHs and that the human blood vessel endothelium is a sensitive target site for 1-NP induced effects [38].

In lungs, nitro-PAHs can be metabolized through both oxidative (C-ring) and reductive (nitro group) reactions prior to further conjugation. Some of these reactions can lead to the formation of electrophilic metabolites such as epoxides that can react with vital intracellular molecules [39]. Importantly, nitro reductions catalyzed by enzymes such as nitric oxide synthase (NOS), NADPH: quinone oxidoreductase (NQO1), xanthine oxidase and aldehyde oxidase may also result in the formation of reactive oxygen species (ROS), while acetylation or sulfate conjugations can lead to the formation of reactive nitrenium ions that can bind covalently to DNA and other macromolecules [40]. Ovrevik *et al.* investigated that 1-NP is the most striking in cytokine/chemokine gene expression profiles induced by 1-NP and 3-NF [41].

4.2 Correlation of 1-NP PAHs and pyrene emissions in community biodiesel fuel exhausts

The emission concentrations of 10 PAHs: Frt, Pyr, BaA, Chr, BbF, BkF, BaP, BghiPe, DBA and IDP in previous study [28, 29] were shown and compared with 1-NP concentration in Table 3.4. The previous results of pyrene emissions were compared with 1-NP because pyrene in diesel engine exhaust particle is source of 1-NP [30] thus, the comparison showed in Table 3.5.

Reduction percentage of PAHs, pyrene and 1-NP from the use of various tested fuels, in comparison with CD(B2) is shown in Figure 4.2. Significant decrease of 1-NP emission by using community-scale biodiesel reduce the toxicities of the exhaust. From Figure 4.2, PAHs, pyrene and 1-NP in this study showed significantly decrease from tested fuels compared to reference fuel. However, the gas emission results in previous study [28, 29] are not show of reduction as PAHs and 1-NP. Especially in NO_x emission, it showed the reductions of NO, NO_x and SO_2 in all CBFs, despite NO_2 which increasing less than 30% of base CBD. Whereas CO and CO_2 of almost CBF samples were found lower than those of CBD. The occurrences of these gases were typical produced in combustion process of diesel engine [42]. In addition, the use of ethanol as an additive to biodiesel–diesel oil blends can be an ally to control NO_x emissions and global warming though CO_2 concentration reduction, but is unfavorable to CO, HC and PM emissions. Optimization of fuel injection parameters may bring further benefits.

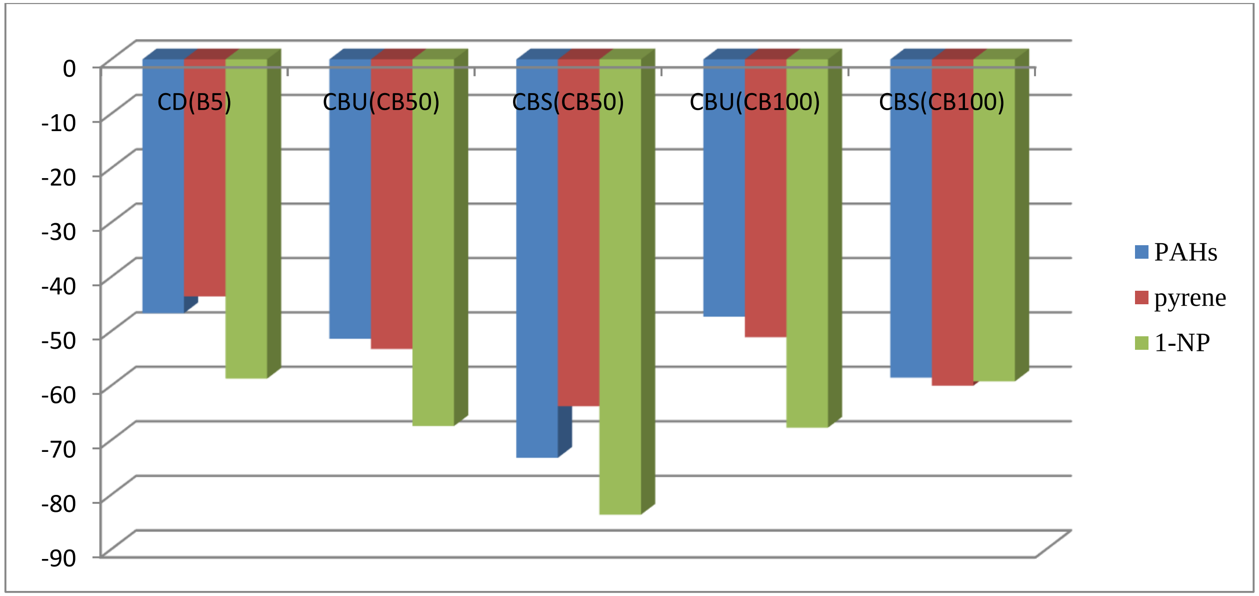

Figure 4.2 Percentage reduction of PAHs, pyrene and 1-NP from the use of various tested fuel, in comparison with CD(B2)

4.3 Fuel properties impact on 1-NP and PM emissions

Fuel properties have an effect on emissions from diesel engine. Fuel density, for instance, may affect the mass of fuel injected into the combustion chamber and thus, the air-fuel ratio. This was because fuel injection pumped fuel by volume not by mass, and a denser fuel contains a greater mass in the same volume. Fuel viscosity could also affect the fuel injection characteristics. The fuel with high viscosity caused poor fuel atomization during the spraying, increased the engine deposits, and needed more energy to pump the fuel into the combustion chamber [43].

From Table 3.4., CBU(CB100) and CBS(CB100) can produce higher 1-NP concentration than their blends (CBU(CB50) and CBS(CB50)). He *et al.* noticed that, with increasing ethanol concentration in diesel fuel, fuel density, cetane number, kinematic viscosity, heating value and aromatic fraction are reduced [44]. Under high load operation, smoke, NO_X and CO_2 emissions are reduced with the addition of ethanol to diesel oil, while CO, HC and acetaldehyde (C_2H_4O) are increased. Under low load operation, the use of ethanol blended to diesel oil reduced smoke emission, specific energy consumption and combustion period, but heat release rate, ignition delay and SFC were increased. According to Hansen *et al.* increased fuel consumption can be expected when using ethanol blended to diesel oil [45]. No difference on engine performance occurs for ethanol concentration in diesel oil below 10%. Durability tests should confirm that ethanol does not have an adverse effect on engine wear, in comparison with diesel oil. It is accepted that the use of ethanol blended with diesel oil help to reduce PM emission. The amount of emission reduction depends on engine design, but adjustments of the fuel injection system can bring further gains. Merritt *et al.* found that smoke and PM emissions were reduced with increasing ethanol content in diesel oil, while changes on CO and NO_X emissions varied with engine design [46]. Acetaldehyde and heavy PAH emissions were higher with increasing ethanol concentration, but benzene, 1,3-butadiene, 1-nitropyrene and light PAH emissions were lower.

However, fuel ageing ,properties and storage condition could effect to the biodiesel quality [47]. It was due to nature of biodiesel that makes it more susceptible to oxidation or autoxidation during long-term storage. The autooxidation process takes place during the storage of fatty acid methyl esters. In the primary stage of oxidation process peroxides and hydroperoxides are formed. Further reactions of the unstable hydroperoxide species with another fatty acid chain may form high molecular weight materials, such as dimer or trimer acids, polymerization products and cyclic acids. Storage conditions of biodiesel with sunlight and occasional shaking in presence of air could enhance the oxidation occurrences [47, 48].

The feedstocks of tested fuels were derived from the used palm oil and mixed used oil. The used palm oil was obtained from the food industry, which was located nearby the community, while the latter was obtained from local markets, restaurant or household. The mixed used oil might be comprised with vegetable oil, pork tallow or grease yellow oil and so on that could lead to the divergent emissions among various tested fuels and their blends.

4.4 Engine performance

Accoring to Table 3.6, BSFC from tested fuels are varied from 0.34 to 0.36 kg/kW. The mean increasing of BSFCs for tested fuels are varied from +6.25% to +13.25%, respectively, compared with that of CD (B2) (CD (B2) = 0.32 kg/kWh). The TE of all tested fuels were lower than that of CBD. The mean reduction of the TE values for tested fuels are -2.7% to -9.3% respectively, compare with that of CD (B2) (CD (B2) = 28% TE). The useing of community biodiesel on agricultural diesel engine were found higher for fuel consumption and quite lower in thermal efficiency when compared to that of CBD. According to the results were found in many studies, reported that when the engine was kept at constant speed and torque, the peak heat release rate of biodiesel in premixed combustion duration was evidently lower than that of diesel operations [49]. However, during the diffusion combustion duration, heat release rates of diesel and biodiesel were quite close to each other. Likewise, Lin *et al.* found that BSFC value from using palm-biodiesel on diesel generator under 75% of total torque load was 5.35% higher than that of petroleum diesel [50]. They mentioned that this evident was due to the low heating value of biodiesel that led to high fuel consumption [50]. Moreover, Lin *et al.* indicated that although the use of palm-biodiesel (bio/petroleum diesel ratio = 10% and 20%) could enhance the energy efficiency of diesel engine, the fuel blends with bio/petroleum diesel ratios from 20% to 100% resulted in incomplete combustion and obstruction of energy release, subsequently reducing the energy efficiency [51].