CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Formation of PAHs

PAHs are produced in combustion sources through the condensation of ethylenic radicals in the gas phase to form the larger polycyclic compounds. The formation of mono- and polyaromatic species in pyrolysis of alkanes to produce olefins which are subsequently aromatized by Diels-Alder reaction. Pyrolysis cracking of the olefins between 600 °C and 900 °C showed their formation of single ring aromatic compounds, such as benzene, toluene and alkylaromatics by Diels-Alder reactions.

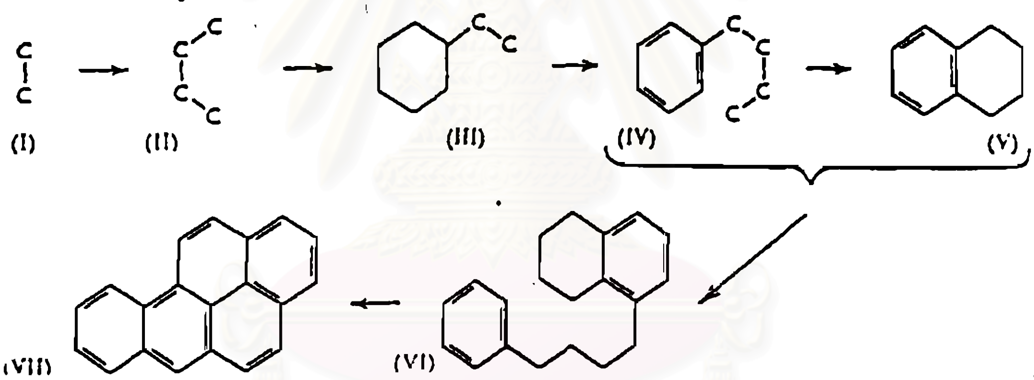
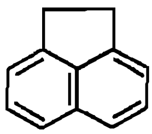
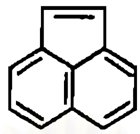


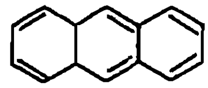
Figure 2.1 Schematic of stepwise synthesis of benzo(a)pyrene

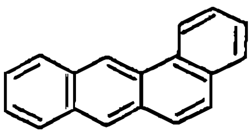
Pyrolysis of acetylene(I) is known to give aromatic hydrocarbons, incomplete combustion of organic compounds often gives acetylene. A four-carbon unit(II) such as vinylacetylene or butadiene, especially, butadiene undergoes diene synthesis with itself to give vinylcyclohexene, and pyrosynthesis of butadiene yields relatively large amounts of ethylbenzene and styrene(III). Naphthalene and tetralin(V) were also formed in this pyrolysis and complex mixture of polycyclic compounds contained benzo(a)pyrene.[7]

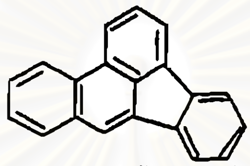
In addition, naphthalene and alkylnaphthalenes are formed, and condensation reaction may continue to produce higher PAHs[8]. During the incomplete combustion of organic fuel, the formation of oxygenated and nitrated PAHs may also occur. Interested PAHs have 16 species which classifies as priority pollutants by U.S. Environmental Protection Agency (U.S. EPA), as shown in Figure 2-2

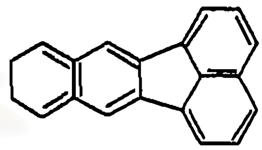

Acenaphthene

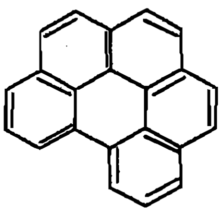

Acenaphthylene

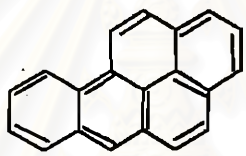

Anthracene

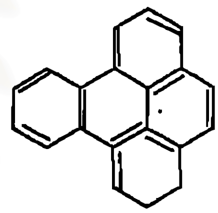

Benzo(a)anthracene

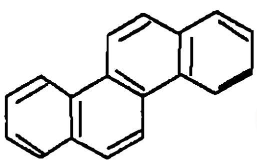

Benzo(b)fluoranthene

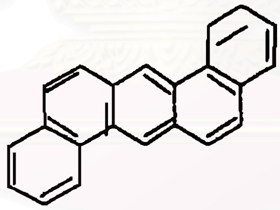

Benzo(k)fluoranthene

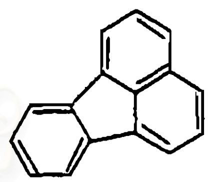

Benzo(g,h,i)perylene

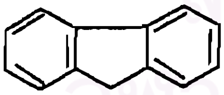

Benzo(a)pyrene

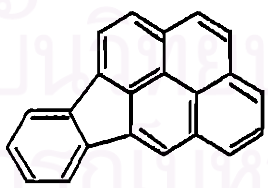

Benzo(e)pyrene

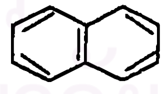

Chrysene

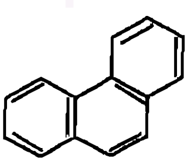

Dibenz(a,h)anthracene


Fluoranthene


Fluorene


Indeno(1,2,3-c,d)pyrene


Naphthalene


Phenanthrene

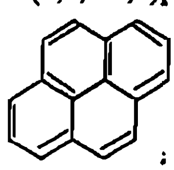

Pyrene

Figure 2-2 Ring Structure of Classified PAHs

2.2 Analysis of PAHs from Exhaust Emission

There are various methods for the determination of PAHs from exhaust emission, including HPLC(EPA method 8310), GC(610, 8100), and GC-MS (625, 8270). Each method has advantages and disadvantages[11]. HPLC is generally the most sensitive, but is subject to interference and not as widely available as other techniques. GC is also subject to interference and is not as sensitive, but is relatively inexpensive and a good screening too. GC-MS is also not as sensitive as HPLC , and is relatively expensive, but the MS gives positive identification with the use of selected ion monitoring(SIM). The detection limit can be reduced by 5-10X.

2.3 Literature review

In 1985, W. M. Sweeney [12] reported the low flash point diesel fuel of increased conductivity containing amyl alcohol. It is apparent that the flash point of the mixed fuel is lower, but the conductivity desirably increased when added 0.5 parts of a mixture of pentanols in diesel oil. There is a result in a tendency for the static electricity to build up during use. This may discharge sparking and can cause an ignition, fire, or explosion.

In 1987, I. S. Myburg [13] reported the performance and durability testing of a diesel engine fuelled with propanol-plus/diesel blend. Operation on the propanol-plus/diesel blend resulted in lower exhaust gas, and gave the lower viscosity which resulted in reduced fuel delivery and retarded injection timing.

In 1992, C. I. McCarthy and coworkers [14] studied the effect of diesel fuel property on exhaust emissions from a heavy duty diesel engine. The raising cetane number reduced all regulated diesel emission species and the decreasing aromatic content reduced NO_x and particulate emissions. An economic analysis indicated that the cost to reduce NO_x through the reduction of aromatic contents are higher than the cost to achieve similar emission reductions by raising the fuel cetane number.

In 1993, D. M. Montalvo and F. J. Liotta Jr [15] studied the effect of oxygenated fuels on emission from a modern heavy-duty diesel engine. aromatic alcohol, aliphatic alcohol, glycol ether, polyether polyol, methyl soyate and diglyme were selected as fuel oxygenating additive on a basis of their fuel bending properties, toxicity, and potential costs. The addition of oxygen to diesel fuel reduces particulate matter emission which is directly related to the oxygen content of the fuel and has lower total aldehyde and ketone emissions than an untreated fuel.

In 1995, Amoco and Haldor Topsoe Inc [4,5,6] joined to develop dimethyl ether as alternative diesel fuel. 99% Dimethyl ether was used in the 0.273 liters direct injection diesel engine which resulted in reducing particulate material, NO_x , and higher thermal efficiency. Exactly, The use of dimethyl ether gave an ultralow emissions and a smokeless operation. It found that a diesel engine which used with dimethyl ether has a quiet combustion, low-pressure, and low-noise. However, the high vapor pressure is the main problem of operation in the common diesel engine which is modified to the available engines.

In 1996, Mike Osenga [16] reported that Caterpillar developed the advanced fuel for the 21st century (A-21) as alternative diesel fuel which is a proprietary fuel emulsion made up of naphtha, water and an additive package that includes a surfactant. A-21 is also demonstrating low flammability outside of the combustion chamber and showing in reducing NO_x and particulate material which depending on the content of water is increasing. Looking the

Numtip [17] studied the effect of improved fuel on toxic substance from diesel engine. The distillation point has slightly effect to the quantity of hydrocarbon, carbon monoxide, benzene, toluene, xylene. Raising cetane number 52 to 58 shows that the hydrocarbon and carbon monoxide decreased.

Septhum [18] studied the effect of cetane improver on the quantity of PAHs. It was reported that 2-ethyl hexyl nitrate or di-t-butyl peroxide was used as cetane improver with cetane number 61-62, the amount of PAHs decreased.

In 1997, Tuntipisit [19] studied the effect of isoamyl alcohol on PAHs emission from diesel engine. The amount of PAHs decreased, but isoamyl alcohol did not increase of cetane number. The additon of isoamyl alcohol significantly decreased the flash point of blended fuel.