

CHAPTER II

THEORY AND LITERATURE REVIEW

The idea of using vegetable oil as a substitute for diesel fuel was demonstrated by the inventor of the diesel engine, Rudolph Diesel, around the year 1900. Since then, research in this area has continued with various vegetable and animal fat-derived biofuels having been widely tested as alternative diesel fuels.

To overcome problems (high viscosity and fuel injector fouling) associated with the use of intact triglycerides as diesel fuels, the oil and/or fat is converted to simple alkyl esters (primarily methyl and ethyl esters). Today, “biodiesel” is the term applied to simple alkyl fatty acid esters used as alternatives to petroleum-based diesel fuels [7].

2.1 Transesterification of Vegetable Oils [8]

Transesterification is the general term used to describe the important class of organic reactions where an ester is transformed into another through interchange of the alkoxy moiety. When the original ester is reacted with an alcohol, the transesterification process is called alcoholysis (Figure 2.1). In this review, the term transesterification will be used as synonymous for alcoholysis of carboxylic esters, in agreement with most publications in this field. The transesterification is an equilibrium reaction and the transformation occurs essentially by mixing the reactants. However, the presence of a catalyst (typically a strong acid or base) accelerates considerably the adjustment of the equilibrium. In order to achieve a high yield of the ester, the alcohol has to be used in excess.

In the transesterification of vegetable oils, a triglyceride reacts with an alcohol in the presence of a strong acid or base, producing a mixture of fatty acids alkyl esters and glycerol. The overall process is a sequence of three consecutive and reversible reactions, in which di- and monoglycerides are formed as intermediates. The stoichiometric reaction requires 1 mol of a triglyceride and 3 mol of the alcohol. However, an excess of the alcohol is used to increase the yields of the alkyl esters and to allow its phase separation from the glycerol formed.

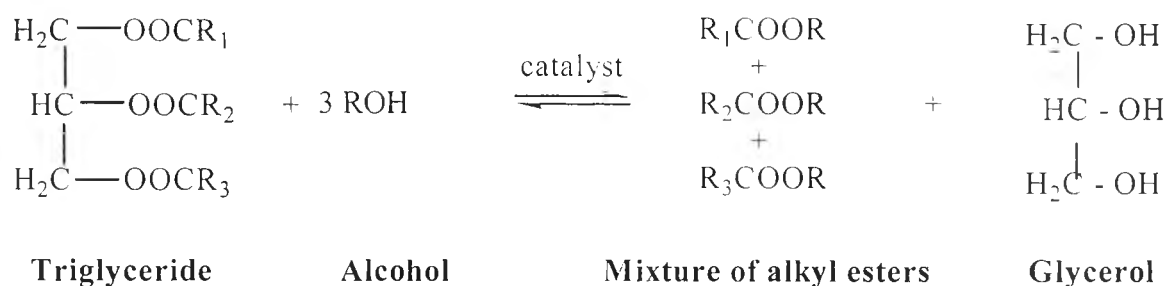


Figure 2.1 Transesterification of vegetable oils.

Several aspects, including the type of catalyst (alkaline or acid), alcohol/vegetable oil molar ratio, temperature, purity of the reactants (mainly water content) and free fatty acid content, have an influence on the course of the transesterification and will be discussed below, based on the type of catalyst used.

2.1.1 Acid-Catalyzed Processes

The transesterification process is catalyzed by Bronsted acids, preferably sulfonic and sulfuric acids. These catalysts give very high yields in alkyl esters, but the reactions are slow, requiring typically temperatures above 100 °C and more than 3 hours to reach complete conversion.

The alcohol/vegetable oil molar ratio is one of the main factors that influences the transesterification. An excess of the alcohol favors the formation of the products. On the other hand, an excessive amount of alcohol makes the recovery of the glycerol difficult, so that the ideal alcohol/oil ratio has to be established empirically, considering each individual process.

The mechanism of the acid-catalyzed transesterification of vegetable oils is shown in Figure 2.2, for a monoglyceride. However, it can be extended to di- and triglycerides. The protonation of the carbonyl group of the ester leads to the carbocation I which, after a nucleophilic attack of the alcohol, produces the tetrahedral intermediate III, which eliminates glycerol to form the new ester IV, and to regenerate the catalyst H^+ .

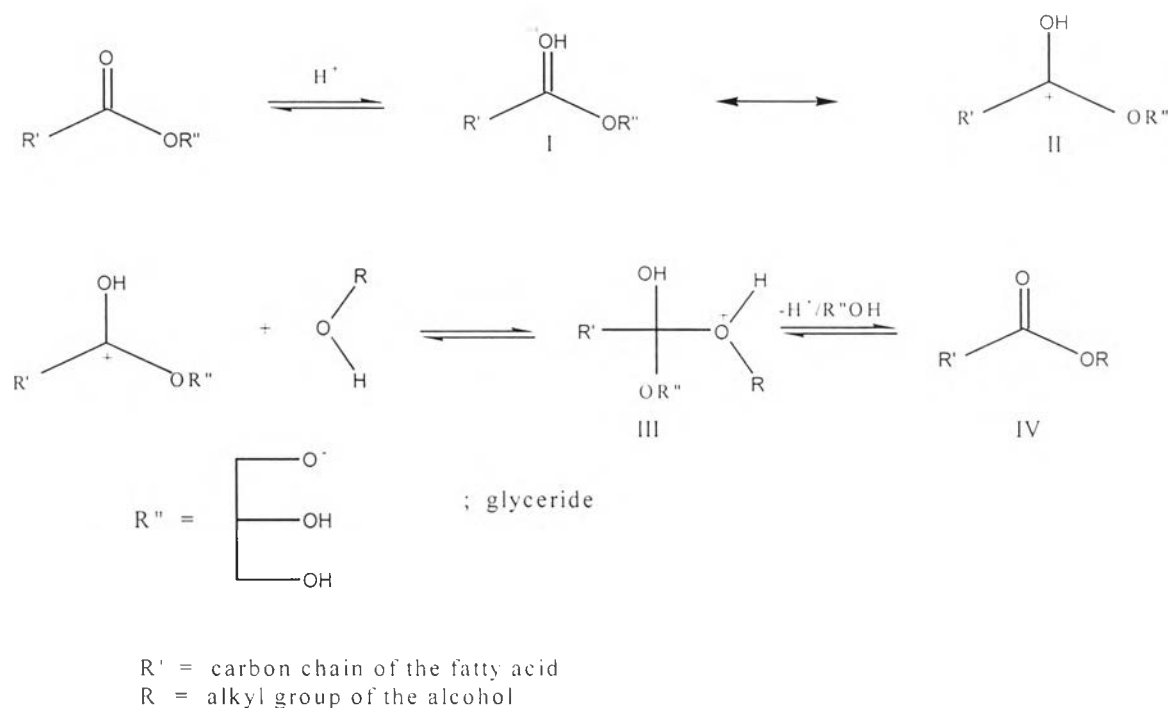


Figure 2.2 Mechanism of the acid-catalyzed transesterification of vegetable oils.

According to this mechanism, carboxylic acids can be formed by the reaction of the carbocation II with water present in the reaction mixture. This suggests that an acid-catalyzed transesterification should be carried out in the absence of water, in order to avoid the competitive formation of carboxylic acids which reduce the yields of alkyl esters.

2.1.2 Base-Catalyzed Processes

The base-catalyzed transesterification of vegetable oils proceeds faster than the acid-catalyzed reaction. Due to this reason, together with the fact that the alkaline catalysts are less corrosives than acidic compounds, industrial processes usually favor base catalysts, such as alkaline metal alkoxides and hydroxides as well as sodium or potassium carbonates.

The mechanism of the base-catalyzed transesterification of vegetable oil is shown in Figure 2.3. The first step (Eq. 1) is the reaction of the base with the alcohol, giving an alkoxide and the protonated catalyst.

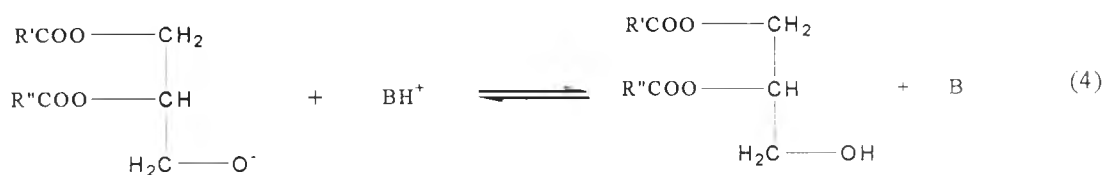
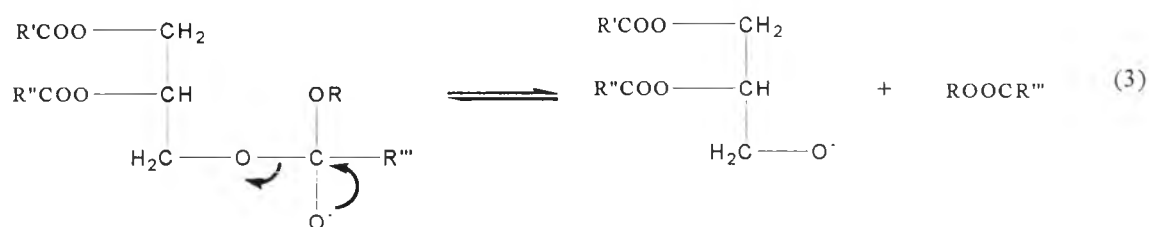
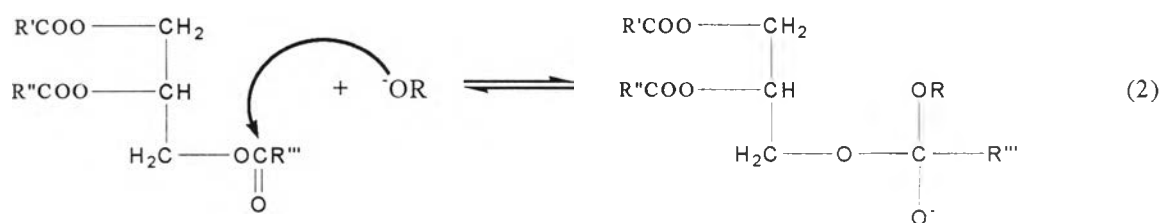


Figure 2.3 Mechanism of the base-catalyzed transesterification of vegetable oils.

The nucleophilic attack of the alkoxide at the carbonyl group of the triglyceride generates a tetrahedral intermediate (Eq. 2), from which the alkyl ester and the corresponding anion of the diglyceride are formed (Eq. 3). The latter deprotonates the catalyst, thus regenerating the active species (Eq. 4), which is now able to react with a second molecule of the alcohol, starting another catalytic cycle. Diglycerides and monoglycerides are converted by the same mechanism to a mixture of alkyl esters and glycerol.

Alkaline metal alkoxides (as CH_3ONa for the methanolysis) are the most active catalysts, since they give very high yields (>98 %) in short reaction times (30 min) even if they are applied at low concentrations (0.5 mol %). However, they require the absence of water which makes them inappropriate for typical industrial processes. Alkaline metal hydroxides (KOH and NaOH) are cheaper than metal alkoxides, but less active. Nevertheless, they are a good alternative since they can give the same high conversions of vegetable oils just by increasing the catalyst concentration to 1 or 2 mol %. However, even if a water-free alcohol/oil mixture is used, some water is produced in the reaction of the hydroxide with the alcohol. The presence of water gives rise to hydrolysis of some of the produced ester, with consequent soap formation. This undesirable saponification reaction reduces the ester yields and considerably disturbs the recovery of the glycerol due to the formation of emulsions.

Potassium carbonate, used in concentration of 2 or 3 mol %, gives high yields of fatty acid alkyl esters and reduces the soap formation. This can be explained by the formation of bicarbonate instead of water, which does not hydrolysis the esters.

2.1.3 Fatty Acid Alkyl Esters as Biodiesel

With exception of hydroelectricity and nuclear energy, the major part of all energy consumed worldwide comes from petroleum, charcoal and natural gas. However, these sources are limited, and will be exhausted by the end of the next century. Thus, looking for alternative sources of energy is of importance.

Vegetable oils are a renewable and potentially inexhaustible source of energy with and energetic content close to diesel fuel. Historically, it is believed that Rudolf Diesel himself started research with respect to the use of vegetable oils as fuel for diesel engines.

In the following decades, the studies became more systematic and, nowadays, much is known about its use as fuel. Despite energetically favorable, the direct use of vegetable oils in fuel engines is problematic. Due to their high viscosity (about 11 to 17 times higher than diesel fuel) and low volatility, they do not burn completely and form deposits in the fuel injector of diesel engines. Furthermore, acrolein (a highly toxic substance) is formed through thermal decomposition of glycerol. Different ways have been considered to reduce the high viscosity of vegetable oils:

- dilution of 25 parts of vegetable oil with 75 parts of diesel fuel;
- microemulsion with short chain alcohols (e.g. ethanol or methanol);
- thermal decomposition, which produces alkanes, alkenes, carboxylic acids and aromatic compounds;
- catalytic cracking, which produces alkanes, cycloalkanes and alkylbenzenes, and
- transesterification with ethanol or methanol.

Among all these alternatives, the transesterification seems to be the best choice, as the physical characteristics of fatty acid esters (biodiesel) are very close to those of diesel fuel and the process is relatively simple. Furthermore, the methyl or ethyl esters of fatty acids can be burned directly in unmodified diesel engines, with very low deposit formation.

Several types of vegetable oils, with a diversified composition in fatty acids, can be used for the preparation of biodiesel. Soybean, rapeseed, sunflower and palm oils are most studied. However, there are no technical restrictions to the use of other types of vegetable oils. Considering the type of the alcohol, the use of methanol is advantageous as it allows the simultaneous separation of glycerol. The same reaction using ethanol is more complicated as it requires a water-free alcohol, as well as an oil with a lower water content, in order to obtain glycerol separation.

Normally, methanol is used as it is the cheapest alcohol in most countries. However, in Brazil it is advantageous to use anhydrous ethanol, which is already produced in large quantities to be mixed with gasoline.

2.2 Biodiesel [3]

Biodiesel is a diesel fuel substitute produced from renewable sources such as vegetable oils, animal fats, and recycled cooking oils. Chemically, it is defined as the mono alkyl esters of long chain fatty acids derived from the renewable lipid sources. Biodiesel is typically produced through the reaction of a vegetable oil or animal fat with methanol or ethanol in the presence of a catalyst to yield glycerin and biodiesel (chemically called fatty acid methyl or ethyl esters). Biodiesel can be used in neat form, or blended with petroleum diesel for use in diesel engines. Its physical and chemical properties are similar to petroleum based diesel fuel, non-hazardous and biodegradable as it relates to operation of diesel engines.

2.2.1 Biodiesel's Attributes

Across the globe environmental concerns and energy security issues have prompted legislation and regulatory actions spurring demand for alternative fuels such as biodiesel. However, the greatest driving force for the use of biodiesel and biodiesel blends is the need to have a fuel that fulfills all of the environmental and energy security needs previously mentioned which does not sacrifice operating performance. One of the largest roadblocks to the use of alternative fuels is the change of performance noticed by users. Biodiesel has many positive attributes associated with its use, but by far the most noted attribute highlighted by fleet managers is the similar operating performance to conventional diesel fuel and the lack of changes required in facilities and maintenance procedures. Other attributes of biodiesel and biodiesel blends are detailed below:

2.2.2 Biodegradability

Biodiesel has desirable degradation attributes which make it the fuel of choice by environmentally conscious boaters. Studies at the University of Idaho compared the biodegradation of biodiesel in an aqueous solution to diesel fuel and dextrose (sugar). Biodiesel samples degraded more rapidly than dextrose, and were 95 percent degraded at the end of 28 days. The diesel fuel was approximately 40 percent degraded after 28 days.

It should also be noted that blending biodiesel with diesel fuel accelerates its biodegradability. For example blends of 20% biodiesel and 80% diesel fuel degrade twice as fast as No.2 diesel. Thus, biodiesel use has demonstrated biodegradability benefits at levels lower than 100%. Simply stated, neat biodiesel degrades as fast as sugar and a B20 blend will degrade twice as fast as petroleum based diesel fuel.

2.2.3 Flash Point

The flash point of a fuel is defined as the temperature at which the fuel becomes a mixture that will ignite when exposed to a spark of flame. The flash point of biodiesel has been tested and reported by various sources. Specific testing at Southwest Research Institute concluded that the flash point of biodiesel blends increases as the percentage of biodiesel increases. Therefore pure biodiesel and blends of biodiesel with petroleum diesel are safer to store, handle, and use than conventional diesel fuel. Neat biodiesel has a flash point over 300 Fahrenheit, well above the flash point of petroleum based diesel fuel [3].

2.2.4 Toxicity

The impact on human health is a significant criteria when considering the suitability of a fuel for commercial applications. Health effects can be measured in terms of the fuel's toxicity to the human body of health impacts due to exhaust emissions. Tests conducted by Wil Research Laboratories, Inc. investigated the acute oral toxicity of pure biodiesel fuel as well as B20 in a single-dose study on rats. The median lethal dose (LD_{50}) of pure biodiesel, as well as B20, was found to be greater than 5000 mg/kg. The acute dermal toxicity of neat biodiesel was evaluated in a single dose study involving rabbits. The LD_{50} of biodiesel was found to be greater than 2000 mg/kg and the 2000 mg/kg dose level was found to be a no observable effect level (NOEL) for systematic toxicity. There were no deaths, remarkable body weight changes or gross necropsy findings for the LD_{50} dose levels for each of the studies.

Acute aquatic toxicity tests with *Daphnia Magna* have also been conducted. Table salt (NaCl), diesel, and biodiesel were compared to each other. The LC₅₀ count (the concentration where 50 percent of the *Daphnia Magna* have died and 50 percent were still alive) for table salt was 3.7 parts per million (ppm), 1.43 ppm for diesel fuel, and 23-332 ppm for biodiesel. Therefore, biodiesel is less toxic than diesel fuel and table salt.

2.2.5 Emission Reductions

The use of biodiesel in a conventional diesel engine results in substantial reduction of unburned hydrocarbons, carbon monoxide, and particulate matter. Emissions of nitrogen oxides are either slightly reduced or slightly increased depending on the duty cycle of the engine and testing methods employed.

The use of biodiesel decreases the solid carbon fraction of particulate matter (since the oxygen in biodiesel enables more complete combustion to CO₂), eliminates the sulfate fraction (as there is no sulfur in the fuel), while the soluble, or hydrocarbon, fraction stays the same or is increased. Therefore, biodiesel works well with new technologies such as catalysts (which reduces the soluble fraction of diesel particulate but not the solid carbon fraction), particulate traps, and exhaust gas recirculation.

2.2.6 Health Effects

Evidence does exist which indicates that diesel particulate matter is a potential carcinogen. In 1988, the National Institute for Occupational Safety and Health (NIOSH) recommended that whole diesel exhaust be regarded as “a potential occupational carcinogen,” as defined in the Cancer Policy of the Occupational Safety and Health Administration. The use of biodiesel decreases most regulated emissions. Research results indicate that particulate matter (specifically the carbon or insoluble fraction), hydrocarbons, and carbon monoxide are significantly reduced.

In addition to reducing the overall levels of pollutants and carbon, the compounds that are prevalent in biodiesel and diesel fuel exhaust are different. Research conducted by Southwest Research Institute on a Cummins N14 engine indicates that biodiesel exhaust has a less harmful impact on human health than petrodiesel. Biodiesel emissions have decreased levels of all target polycyclic aromatic hydrocarbons (PAHs) and nitrated PAHs compounds, as compared to petroleum diesel exhaust. PAHs and nPAHs compounds have been identified as potential cancer causing compounds. All of the PAH compounds were reduced by 75 to 85 percent, with the exception of benzo(a)anthracene, which was reduced by roughly 50 percent. The target nPAH compounds were also reduced dramatically with biodiesel fuel, with 2-nitrofluorene and 1-nitropyrene reduced by 90 percent, and the rest of the nPAH compounds reduced to only trace levels. All of these reductions are due to the fact the biodiesel fuel contains no aromatic compounds of any kind, including PAHs.

In addition, the total speciated hydrocarbon mass of biodiesel is nearly 50 percent less than that measured for conventional diesel fuel, and the associated ozone potential is reduced by the same amount. Significant reductions in most aldehyde compounds were also observed with biodiesel, with formaldehyde and acetaldehyde 30 percent lower than the levels observed for conventional diesel fuel.

2.2.7 Lubricity

In the United States the sulfur level of diesel fuel that is used for on-road purposes is limited to 0.05 % by weight. This limit was mandated in October 1993 as a method to decrease particulate matter emitted from diesel powered vehicles. With the introduction of mandated Environmental Protection Agency (EPA) low-sulfur diesel fuel, fleet operators began to encounter premature wear and/or failure of injector pumps in increasing numbers. Pump manufacturers such as Stanadyne and Bosch began recommending the use of lubricity additives to alleviate the serious damage that the reduced sulphur content of low sulfur diesel was causing to their injection pumps.

Many petroleum distributors are only marketing low-sulfur diesel even though it remains legal to sell high-sulfur diesel in off-road markets. Testing at labs such as Southwest Research Institute, Stanadyne Automotive, and Engineering Testing Services have demonstrated that biodiesel provides significant lubricity improvement over petroleum diesel fuel. Lubricity results of biodiesel and petroleum diesel using the High Frequency Reciprocating Rig test indicate that there is a marked improvements in lubricity when biodiesel is added to conventional diesel fuel, even at blend levels below 1%.

2.2.8 Infrastructure

In general, the standard storage and handling procedure used for petroleum diesel can be used for biodiesel. The fuel should be stored in a clean, dry, dark environment. Temperature extremes should be avoided. Acceptable storage tank materials include stainless steel, fluorinated polyethylene, and fluorinated polypropylene. Biodiesel has a solvent effect which may release deposits accumulated on tank walls and pipes from previous fuel storage. The release of deposits may clog filters initially and precautions should be taken.

2.3 Diesel Engine

Typical diesel engines and gasoline engines are reciprocating engines that operate with four strokes of the piston in the cylinder:

- 1) Induction (intake)
- 2) Compression
- 3) Power (ignition and expansion)
- 4) Exhaust

The gasoline engines draw in a pre-mixed combustible charge of air and fuel, whereas the diesel unit is supplied with air and fuel separately. Power control over gasoline engine is effected by throttling the flow of the air/fuel mixture into the cylinder, whereas the diesel engine is controlled by adjusting the quantity of fuel injected per induction stroke into the cylinders [9].

Specifically, the diesel engine takes in and compresses air. The air compression increases the pressure and temperature inside the cylinder to values in the range of 3-5 MPa and 500-600 °C, respectively. Shortly before the end of the compression stroke, one or more jets of fuel are injected into the cylinder. The fuel droplets absorb heat from the compressed air and vaporize, and then ignition of the fuel begins by auto-ignition in one or several zones in the marginal operating conditions such as cold starting, a high compression ratio is necessary, generally between 14 and 25. The delay time between injection (vaporization) and ignition must be kept short. If the ignition delay is too long too much fuel accumulates in the cylinder before combustion. The rapid burning of a large quantity of fuel can cause diesel knock, which is noisy and can cause damage to the engine.

In a high-speed diesel engine, the delay time between fuel injection and ignition is only about 0.5-0.6 ms. After ignition, fuel injection continues for a portion of the power stroke; the additional fuel burns as a diffusion flame (almost instantly) as it mixes with the remaining air and combustion products in the cylinder. Fuel injection is terminated partway through the power stroke. The rate of injections is carefully controlled during fuel injection to provide smooth engine operation. The temperature and pressure of gases inside cylinder of diesel engines during combustion can reach as high as 1600-2000 °C and 6-10 MPa, respectively. The temperatures inside the cylinder after the exhaust could still be 500-600 °C. Power output is controlled, not by adjusting the quantity of air/fuel mixture as in the case of spark ignition engines, but by changing the mass (flow) of diesel fuel introduced into a fixed volume of air.

By its concept, the diesel engine operates at variable fuel-air ratios. It is not possible to attain the stoichiometric ratio because the fuel does not diffuse in an ideal manner into the air. A large part of combustion occurs (after the auto-ignition) in a diffusion-type flame. The equivalence ratio is defined as the actual fuel-air ratio divided by the stoichiometric fuel-air ratio. For an average equivalence fuel-air ratio of 1.00, the combustion chamber may contain zones that are too fuel rich leading to incomplete combustion accompanied by smoke and soot formation. Finally, at full load, the overall equivalence ratio in a diesel engine is between 0.70 and 0.85.

For the gasoline engine, auto-ignition is highly undesirable and is minimized as much as possible by design and by fuel formulation, to avoid engine knock. It seems surprising at first glance that auto-ignition should be so highly desirable and preferred in the diesel engine. This is because auto-ignition in diesel engine occurs in very localized zones and concerns only a small fraction of the total amount of fuel introduced. Thus there are one or more ignition centers instead of auto-ignition of one massive homogeneous system which characterizes knocking. Furthermore, the sturdy structure of the diesel engine provides good resistance to damage which might be caused by a rapid release of energy at the moment of auto-ignition.

2.3.1 The Diesel Combustion Process

The process of combustion in diesel engines is a complex sequence of events consisting of 3 phases [9]. *The first phase* is the ignition delay period during which the fuel must vaporize, mix with air, and undergo pre-flame chemical reactions that produce the chemical species necessary for spontaneous combustion. *The second* is the premixed burning phase (chemically controlled), which is spontaneous combustion in regions of fuel-air mixtures formed (prepared) during the ignition delay period. The rapidly rising temperature and pressure in the cylinder accelerate the combustion in an uncontrolled manner until the backlog is depleted. *The third phase* is the diffusion burning phase (controlled by mixing rate). After the second phase, the fuel in the spray core is too rich to burn, and the fuel in the periphery of the spray is too lean to burn. As a result, combustion slows down and is controlled by the rate at which the air is entrained and a combustible mixtures formed.

The rate of burning during the mixing-controlled phase depends on the air motion and fuel spray momentum. The burning rates starts quite high because there is considerable excess air and the fuel spray entrains air rapidly. After the end of fuel injection, particularly at high loads when there is not as much excess air as with light loads, the burning rates decreases gradually [9].

2.3.2 Combustion of Diesel Fuel Oils

Both physical and chemical processes are involved to any combustion process. In the diesel engine, the physical processes include transportation of the fuel and air into the combustion chamber, mixing of fuel and air, and provision of environmental conditions favorable to chemical reaction. The chemical processes involve self-ignition or auto-ignition of the fuel and finally extensive chemical reaction that liberates the potential energy in the fuel.

2.4 Composition of Diesel Fuels

2.4.1 Type of Diesel Fuels

Compositions of fuels for diesel engines are generally different from those for gasoline and jet engines, as seen from table 2.1.

Table 2.1 Comparison of diesel fuels with gasoline and jet fuels.

Fuel	Distillate Fraction	Boiling Range, °C	Sulfur wt%	Engine for Use ^a	Quality Indicator
Gasoline	Gasoline	30-225	0.035	S.I.	Octane No.
Jet Fuel	Kerosene	160-300	0.1-0.4	Gas Turbine	Specs
Diesel	L Gas Oil	160-380	0.05	C.I.	Cetane No.

a): SI: spark ignition; CI: compression ignition; Specs: specifications.

There are three classes of diesel engines [9], those for high-speed diesels—trucks, cars, locomotive; those for medium-speed diesels—marine auxiliaries, stationary power generators, and those for low speed diesels (marine diesels) – ships, fishing boats, farm tractors, and electric power generators. The fuels for high-speed diesel engines are mainly lighter and higher-quality diesel fuels. The low-speed diesel engines can operate on fairly-poor quality fuel such as marine diesel, heavy fuel oil and home heating oils. In some cases they can even operate on crude oils. Typical ranges of diesel engines are listed below:

Type	Range	Conditions and applications
High Speed	> 1000 rpm	Frequent variation in load and speed Road transportation vehicles Diesel locomotives; construction equipment
Medium Speed	300-1000 rpm	Fairly high load, relatively constant speed Marine auxiliaries; Pumping units Stationary power generation
Low Speed	< 300 rpm	Heavy load, constant speed; Marine main propulsion; Electric power generation

There are several types of diesel fuels specified in the U.S. ASTM D975-91 (No.1-D, No.2-D, and No.4-D). No.1-D diesel fuel is generally made from virgin or hydrocracked stocks having cetane numbers above 45. It is a relatively volatile distillate fuel oil for engines requiring frequent speed and load change. It has a narrow boiling range of about 182 to 316 °C (maximum T₉₀: 288 °C) and is used in high-speed engines in automobiles, trucks, and buses. Such fuel is required for use at very low temperatures. No.2-D diesel fuel has a wide boiling range and lower volatility than No.1-D, and it is similar to No.2 fuel oil. It usually contains cracked stocks and may be blended from naphtha, kerosene, and light cracked oil from the coker and the fluid catalytic cracking unit. No.2-D fuels are transportation diesel fuels. They are used for applications that do not require a high-volatility fuel. They can also be used for engines in industrial and heavy mobile services. The specification for No.1-D diesel fuel overlaps with kerosene and jet fuel, and all three are commonly produced from the same base stock. One major use of No.1-D diesel fuel is to blend with 2-D during winter (in cold regions) to provide improved cold flow properties. No.4-D diesel fuels are generally low-quality fuels for low- and medium-speed engines in non-automotive applications. The focus of this article is automotive diesel fuels.

The heating values for 1-D, 2-D and 4-D diesel fuels are around 134,000, 138,000 and 148,000 Btu/gal, respectively [10]. In addition, No.2-D diesel fuel is similar to No.2 fuel oil which is made from blended naphtha, kerosene, diesel and cracked gas oils. No.2 fuel oil may have higher final boiling point (FBP) than No.2-D. Similarly, No.4-D diesel fuel and No.4 fuel oil have similar specifications.

Railroad diesel fuels also have markets worldwide. For example, there are approximately 25000 diesel locomotives in the U.S. alone. Railroad diesel fuels are generally similar to the heavier automotive diesel fuels but they have higher boiling ranges up to 400 °C and lower cetane numbers (30 minimum).

Military diesel fuels are generally lighter fuels; they typically consist of distillate fractions having narrower boiling range with more lower boiling components than commercial automotive diesel fuels for high-speed diesel engines.

2.4.2 Molecular Components of Diesel Fuels

The compound classes and molecular components of diesel fuels are described below. Diesel fuels consist mainly of saturate (paraffins and naphthenes) and aromatic hydrocarbons. Their relative distribution depends on the feedstocks and fuel processing schemes. It should be noted that refineries of oil companies generally vary the mix of hydrocarbons in the fuels they supply to suit the demand, climate and the season of the year. They include more components of low boiling range in cold climates and in winter, and vice versa in hot weather.

2.4.2.1 Saturate Hydrocarbons

Generally, long-chain alkanes with carbon numbers in the range of C₁₀-C₂₀ are the major paraffinic components. The corresponding lower and upper boiling points for the n-alkanes are 174 °C (n-C₁₀) and 344 °C (n-C₂₀), respectively. The boiling range in the distillation curve of a diesel fuel could cover the range from about 160 to 380 °C. There can be some lighter (C₉-) and heavier (C₂₀₊) components, but they exist in small quantities in most high-way diesel fuels.

The contents of heavier components in fuel oils for low-speed diesel engines are higher than those in automotive diesel fuels. Long-chain paraffins have excellent cetane numbers and show good combustion performance, but higher-boiling n-alkanes tend to have higher cloud points and do not have good cold-flow properties.

Alkylated cycloalkanes are also present in diesel fuels. Alkylcyclohexanes, decahydronaphthalenes and perhydrophenanthrenes are typical examples of one to three ring cyclohexanes in diesel fuels, and in hydrotreated light cycle oil. The contents of naphthenic components depend on both the nature of the crude and the blending stocks as well as processing parameters.

2.4.2.2 Aromatic Components

While aromatic compounds can be identified by GC-MS (gas chromatograph coupled with mass spectrometer), the contents of aromatic and saturate compounds in diesel fuels can also be quantitatively determined by HPLC (high-performance liquid chromatograph). The aromatic compounds can be separated into monoaromatics, diaromatics, and polyaromatics by HPLC with a refraction index detector using amino column made with the silica gel modified by NH_2 groups. Alternatively, a tetrachlorophthalimidopropyl bonded silica as the normal-phase column with photo diode array detector can be used.

The aromatic compounds in diesel fuels include alkylated benzenes, indanes, naphthalenes, tetralins, biphenyls, acenaphthenes, phenanthrenes, chrysenes, and pyrenes. Diaromatic hydrocarbons with naphthalene-type structure are more abundant aromatic components in diesel fuels [10].

Straight-run gas oils (SRGO) or middle distillates generally have between 20 to 35 wt% aromatics while light cycle oil (LCO) from fluid catalytic cracking (FCC) may contain from 50 to 80 wt% aromatics that can be determined by HPLC, with the following distribution:

Aromatics in SRGO	20-35 wt%
Monoaromatics	15-25 wt%
Diaromatics	5-15 wt%
Polyaromatics	0-5 wt%

Aromatics in LCO	50-80 wt%
Monoaromatics	10-35 wt%
Diaromatics	30-50 wt%
Polyaromatics	5-15 wt%

Retention indices for temperature-programmed GC and GC-MS analysis of aromatic and saturate as well as polar compounds in hydrocarbon fuels have been determined for over 150 compounds [11]. The indices for different compound classes respond to the changes in GC column temperatures in a different fashion, which can also be used to identify different compounds and distinguish different isomers, as has been demonstrated for petroleum derived and coal-derived middle distillates [11].

2.4.2.3 Heteroatom-Containing Compounds

Due to higher boiling range, the sulfur compounds in diesel fuels have higher molecular weights and larger ring sizes than the sulfur compounds in gasoline. Typical feedstocks for making diesel fuels in the U.S. include straight-run gas oil, LCO from FCC, vacuum gas oil, coker distillates, and visbreaker distillates; their sulfur contents may range from 0.4 wt% to 2.4 wt%. Most sulfur compounds are alkylated benzothiophene-type and dibenzothiophene-type species in diesel fuels, as compared to thiophene-type and some benzothiophene-type cyclic sulfur species in gasoline.

Kabe and coworkers analyzed the sulfur compounds in light gas oil and hydrotreated gas oils using gas-chromatography with an atomic emission detector (GC-AED) and GC-mass spectrometry (GC-MS). Forty two alkylated benzothiophene compounds and twenty nine alkylated dibenzothiophene compounds were identified. Among them the 4,6-dimethyl dibenzothiophene was found to remain even after deep hydrodesulfurization.

Ma et al. analyzed polycyclic sulfur compounds in a non-polar fraction of vacuum gas oil. Hsu and coworkers performed mass spectrometric analysis of many diesel fuels and petroleum fractions. The major compounds in all classes and trace amounts of heteroatom-containing compounds were found.

Trace amounts of nitrogen compounds in diesel fuels include indoles, carbazoles, quinolines, acridines, and phenanthridines. The oxygen compounds are alkylated phenols and dibenzofurans. Formulated diesel fuels also contain trace amounts of additives.

2.5 Properties of Diesel Fuels

Although diesel engines vary widely in size, speed, power output, and mechanical design, their fuel requirements are quite similar in many respects. Performance features desired of all diesel fuels, and the physical properties most directly related to them are summarized below. Fuel properties are presented in the order in which they are seen by the engine as the fuel flows from the storage tank, through the fuel system, to the combustion chamber. No attempt is made in the table to indicate relative importance [9].

<i>Performance Feature Desired</i>	<i>Indicated By</i>
1. Safety in handling	Flash point
2. Pumpability at low temperatures	Pour or Cloud point, Viscosity
3. Freedom from all suspended matter	Storage stability, Suspended sediment tests
4. Readily atomized	Viscosity
5. Readily ignitable	Cetane No.
6. Clean burning	Volatility, Cetane No.
7. Good fuel economy	API Gravity
8. Major effect on engine wear and deposits	Sulfur

Except for the calorific value or energy content, the required properties of hydrocarbon in fuel for use in diesel engines differ significantly from those in gasoline engines. Cetane number, density, viscosity, low-temperature property, sulfur content, aromatic content, volatility and boiling range make up the essential characteristics of diesel fuel necessary for satisfactory operation of the diesel engine.

2.5.1 Cetane number (CN) is a measure of ignition quality or ignition delay, and is related to the time required for a liquid fuel to ignite after injection into a compression ignition engine. A high cetane number is representative of a short ignition delay. This property is related to the fuel composition. The two standards, cetane (n-hexadecane) and 1-methylnaphthalene (1-MN) are assigned CN values of 100 and 0, respectively. The operating definition of CN represents the volume percentage of cetane which must be mixed with 1-MN to give the same ignition performance as a given real diesel fuel. Due to the difficulty to obtain large supplies of pure 1-MN (partly due to oxidative degradation during storage), there is now a secondary standard in use, heptamethylnonane (2,2,4,4,6,8,8-heptamethylnonane), which is assigned a CN = 15, and the corresponding equation for CN is as follows.

$$\text{CN} = \text{vol\% of cetane} + 0.15 (\text{vol\% of heptamethylnonane})$$

The auto-ignition phenomenon is the basis of the physical meaning for cetane number. In the compression stroke, the air is precompressed until its temperature exceeds that necessary for auto-ignition or spontaneous combustion of the fuel. Near the end of compression stroke, the diesel fuel is injected into the cylinder in atomized form and is vaporized in the air. Auto-ignition temperature (AIT) is defined as the lowest temperature at which a substance will ignite in the absence of a spark of flame. Auto-ignition is initiated at elevated temperatures where the oxygen in the air can begin to interact with the hydrocarbons, resulting in an exothermic oxidation reaction. When the rate of heat production exceeds the rate at which the heat can be dissipated to the surroundings, auto-ignition occurs. Auto-ignition is believed to proceed through a free radical mechanism. The ease of auto-ignition generally increases, and thus AIT decreases in the order of aromatics < branched alkanes < cycloalkanes < n-alkanes.

2.5.2 Cetane Index (CI). Cetane index is a calculated value, derived from fuel density (see below) and volatility. Cetane index usually gives a reasonably close approximation to real cetane number, which is derived from measurement in a real engine. Cetane index is widely used for routine monitoring of diesel fuel ignition quality. The calculated cetane index has mainly served as an alternative method of determining

the ignition quality of diesel fuel to minimize the need for engine tests. The method D4737-1988 by ASTM (American Society for Testing and Materials) gives the relatively new equation for calculating the cetane index that uses density and three distillation points as shown below:

$$\begin{aligned} \text{CI} = & 45.2 + 0.0892 (T_{10} - 215) + 0.131 (T_{50}-260) + 0.0523 (T_{90} - 310) \\ & + 0.901 B (T_{50} - 260) - 0.420 B (T_{90} - 310) + 0.0049 (T_{10} - 215)^2 \\ & - 0.0049 (T_{90} - 310)^2 + 107.0 B + 60.0 B^2 \end{aligned}$$

where T10, T50 and T90 are the 10%, 50%, and 90% recovery temperatures in °C, respectively, according to the distillation curve, corrected to standard barometric pressure, and D the density in kg/l at 15 °C and

$$B = e^{[-3.5(D-0.85)]} - 1$$

2.5.3 Density Density is the mass per unit volume of diesel fuel at a given temperature. It can provide useful indications about a fuel's composition and performance-related characteristics. Density has an importance in diesel engine performance, since fuel injection operates on a volume metering system. A change in density will influence engine output due to different mass of fuel injected, and a higher density fuel will tend to produce more smoke as well as more power. The densities of fuels obtained by different refining processes are approximately as follows:

Straight-run distillates	0.805-0.870 g/ml
Hydrocracked gas oil	0.815-0.840 g/ml
Thermally cracked gas oil	0.835-0.875 g/ml
Catalytically cracked gas oil	0.930-0.965 g/ml

A limit to maximum density is set to avoid smoke formation at full load. Therefore, the density of diesel fuels should be in the range of 0.80-0.86 g/mL (800-860 kg/m³). A related unit is API gravity developed by the American Petroleum Institute.

$$\text{API Gravity (}^\circ\text{)} = [141.5/(\text{specific gravity at } 60^\circ\text{F}(15.6^\circ\text{C}))] - 131.5$$

It may be noted that water has a specific gravity of 1.0 g/mL and an API gravity of 10.0°. API gravity is a useful measure of density for liquids lighter than water. Diesel fuels have API gravity of 33-45°. Density differs from API gravity in that the higher the number in degrees API, the lighter is the fuel.

2.5.4 Viscosity. Viscosity is a measure of the internal fluid friction, which tends to oppose any dynamic change in the fluid motion. It reflects on the extent of intermolecular (attractive) forces and decreases with increasing temperature. Therefore, the viscosity of a fluid indicates its resistance to flow; the higher the viscosity, the greater the resistance to flow. The viscosity of diesel fuels is important for fuel flow and engine operation. The unit of viscosity is the poise, which is the force required to move an area of 1 cm² at a speed of 1 cm/sec past two parallel surfaces that are separated by the fluid. The kinematic viscosity is the ratio of the viscosity to the density. The unit of kinematic viscosity is the Stoke (St), measured in cm²/s but often reported in centistoke (cSt).

For convenience, the two figures are often expressed in centipoises (cP) and centistokes (cSt), and the two are related in that cP = cSt x density of the fluid. The term centistokes is being replaced by the preferred SI (System International) unit mm²/s. A widely used laboratory method for determining the kinematic viscosity of diesel fuels is ASTM D445, which measures the time taken for a fixed volume of the fuel to flow under gravity through a capillary tube viscometer immersed in a thermostatically controlled bath.

Viscosity is an important property of diesel fuel because of its relevance to the performance of the fuel injection equipment, particularly at low temperatures when the increase in viscosity affects the fluidity of the fuel. Increasing viscosity reduces the injector spray cone angle and fuel distribution and penetration while increasing the droplet size.

If the viscosity is too high, poor atomization of fuel spray results, which leads to poor combustion and loss of power, and thus poor fuel economy. If the viscosity is too low, the lack of lubricity leads to injector pump wear. Very low viscosity can also result in significant leakage of fuel from pumping elements, particularly at low pumping speeds.

2.5.5 Boiling Range. Boiling range is defined by the initial boiling point (IBP) and final boiling point (FBP) in the distillation curve. Most diesel fuels contain hydrocarbons with boiling points within the range of 150 to 380°C. For typical transportation diesel fuels in the U.S., boiling range is between 177 °C (350 °F) to 343 °C (650 °F) [10].

2.5.6 Distillation Curve. It is necessary to obtain values for T10, T50, and T90 to meet fuel specifications and to calculate the cetane index. The development of simulated distillation gas chromatography (SimDis GC) has resulted in a newer and simpler method for determining the distillation curve in addition to the boiling range of hydrocarbon fuels. ASTM D 2887 method can be used for measuring the boiling range of diesel fuels with GC. ASTM D 2887 method is much more efficient than the old distillation method ASTM D86. SimDis GC can be used for evaluating boiling range of light oils, heavy oils and even residual oils and their upgrading products. SimDis GC method generally uses a non-polar stationary phase (such as polymethylsiloxane) for the GC column where the compounds are separated based on their differences in boiling points. Thus the retention times of fuel components give their equivalent boiling points after calibration with standards. Fuel oils used for low- and medium-speed engines have more higher boiling components that used to require high- temp of vacuum distillation for analysis, but they all can be easily analyzed now by using 1 µl injection of the sample into SimDis GC. The extent of deviation from true boiling points depends on the contents of different compound classes in fuels as well as the polarity of GC column [11].

2.5.7 Volatility. Volatility of the fuel influences many other properties including density, auto-ignition temperature, cold-flow, flash point, viscosity, and cetane number. Volatility depends on the boiling range and the content of light fractions, which can be measured by distillation with SimDis GC. Increasing the contents of lower boiling fractions increases the volatility of fuels.

2.5.8 Flash Point. Flash point is the temperature to which fuel must be heated to produce a vapor-air mixture (above the liquid) that will ignite and spread over the liquid surface when a small flame is applied. It can be measured by ASTM D93 method using a Pensky-Martens closed cup tester, where the lowest temperature at which a small flame of a specified size causes the vapor above the sample to ignite and be self sustaining is recorded as the flash point. Flash point is roughly proportional to boiling range and volatility, and relates to the front-end volatility of the fuel. Typical minimum values of flash points for automotive diesel fuels range from 38-52 °C in the U.S. to 56 in some European countries. As far as performance in an engine is concerned, the flash point of a diesel fuel has no significance. It is solely concerned with fuel storage safety.

2.5.9 Pour Point. Pour point is the temperature at which the amount of wax precipitated out of the solution is sufficient to gel the fuel. It is the lowest temperature at which the fuel is observed to flow. Definition from ASTM is the temperature at which a measured volume of fluid does not flow for 5 seconds when tilted horizontally. It is usually the lowest temperature at which a fuel can be pumped. The pour point is generally 5-11 °C below cloud point [12]. No wax precipitation problems are encountered above the cloud point. Pour points for most automotive diesel fuels are usually between -15 and -35 °C.

2.6 PAHs in Exhaust Emission

Two major pathways are recognized as sources of PAHs recovered in the exhaust emissions : (i) survival of PAHs from the fuel; (ii) combustion reactions in which fragments of fuel or lube oil are pyrosynthesized to produce the PAHs. In (i) the carbon skeleton of the PAHs remain unchanged, while in (ii) it is newly formed in the combustion chamber. The emission rates of PAHs by an internal combustion engine are related to a number of factors such as composition of both fuel and lubricating oil, mileage of engine, number of revolutions per minute (rpm), change of speed, and load under which the engine is running [13].

Due to their low vapour pressures, most PAHs will immediately condense and form a thin film (adsorb) onto soot particles or form as very small particles themselves [14]. However, the dominant amount of the low molecular weight PAHs was found in the vapour phase [15].

2.6.1 Exhaust Sampling Systems

There are two standard methods in exhaust sampling for determination of PAHs in exhaust emission : the U.S. EPA dilution tunnel and filtering system, and the total exhaust solvent scrubbing apparatus (TESSA).

2.6.1.1 The Dilution Tunnel [16]

This method was devised to mimic the natural dilution and cooling of exhaust as it leaves the tailpipe. The schematic of exhaust gas dilution tunnel is shown in Figure 2.4. After combustion in the engine, particulate carbon scavenges organic components from the vapour phase. These include the PAHs which may originate from unburned fuel and lubricating oil or from pyrosynthetic reactions involving the incomplete combustion of fuel. The PAHs adsorbed onto particulate carbon are sampled by a filter and may be extracted, usually using Soxhlet extraction, into solvents to produce a soluble organic fraction (SOF), however, the filter will not efficiently sample those hydrocarbons and PAHs which have remained in the vapour phase.

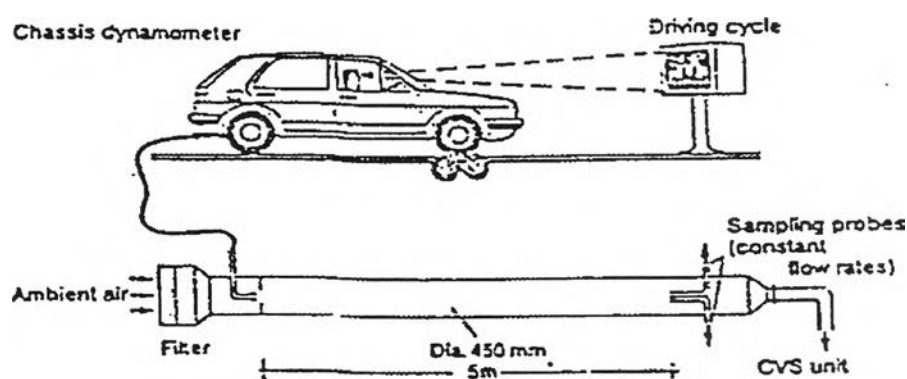


Figure 2.4 Schematic of exhaust gas dilution tunnel. Reproduced from [4].

The filter method suffers from the disadvantage that artifacts may be formed on the carbon particles as the diluted exhaust continues to pass through the filter.

2.6.1.2 The Total Exhaust Solvent Scrubbing Apparatus (TESSA) [17]

The TESSA system consists of a vertical stainless steel tower ($\sim 1.5 \times 0.3$ m) connected by a short (50 cm) heated transfer line to the engine. The tower comprises two sections. Collection of the exhaust organics occurs in the lower section, which is filled with graded-glass tubing to maximize the area of contact between solvent and exhaust gases. The upper section is used to cool the exhaust effluent and contains a series of cooling baffles. The exhaust is sampled using a pressure-controlled countercurrent flow of solvent (dichloromethane-methanol 1:1) which strips the organic species from the exhaust gases as they enter the apparatus. The exhaust sample is collected in large flask at the base of the tower. Figure 2.5 shows the schematic of the total exhaust solvent scrubbing apparatus.

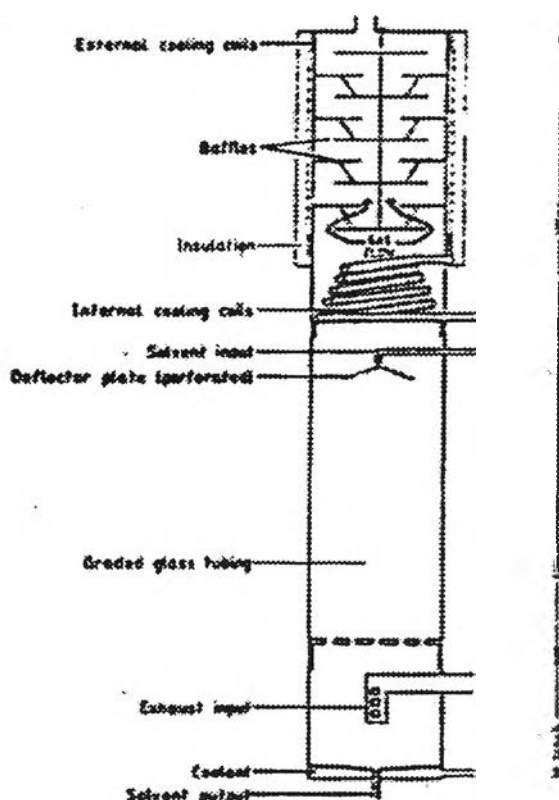


Figure 2.5 Schematic of the total exhaust solvent scrubbing apparatus (TESSA).

Reproduced from [4].

In addition to the both systems, filtration and condensation-filtration systems were employed in many studies [18,19]. Glass fibre filter has been used for trapping particulate matter formed in the exhaust and polyurethane foam has been used for trapping the semivolatile phase. The particulate and semivolatile samples were then subjected to the extraction, usually using Soxhlet extraction, and separation procedures. The most commonly used solvents for the extraction of PAHs from particulates are dichloromethane, cyclohexane and mixtures of benzene with and alcohol.

2.6.2 Sampling of PAHs [20]

The standard method of sampling particulate carbon from a diesel engine involves cooling and diluting the exhaust with air before passing a sample through a filter. This method (EPA dilution tunnel) was devised to mimic the natural dilution and cooling of exhaust as it leaves the tailpipe. After combustion in the engine, particulate carbon scavenges organic components from the vapour phase. These include the PAC which may originate from unburned fuel and lubricating oil or from pyrosynthetic reactions involving the incomplete combustion of the diesel fuel. The PAC that is adsorbed onto particulate carbon is sampled by the filter and may be extracted, usually using a Soxhlet extraction technique, into solvents to produce a soluble organic fraction (SOF) [21]. Particulate-associated PAH emission samples were taken in dilution exhaust with Teflon-coated glass fiber filters (Pallflex T60A20) or Whatman glass fibre filter. However, the filter will not efficiently sample those hydrocarbons and PAH which have remained in the vapour phase. Downstream of the filter, semivolatile PAH compound were trapped on polyurethane foam plug (PUF). However, the filter will not efficiently sample those hydrocarbons and PAC which have remained in the vapour phase.

The filter method suffers from the disadvantage that artifacts may be the formed on the carbon particles as the diluted exhaust continues to pass through the filter. This is especially true when mutagenicity tests are undertaken because a relatively prolonged exposure time may be needed to obtain the sufficient weight of sample that these kinds of bio-assays require. A method which overcomes this objection involves the use of a stainless-steel tower placed immediately after the engine in which the exhaust passed countercurrent to a solvent stream. The solvent rapidly cools and strips the exhaust of all

hydrocarbons which are not gaseous at standard temperatures and pressures and including any PAC present, before these can adsorb onto the carbon particles. Figure 2.5 shows a schematic representation of the total exhaust solvent scrubbing apparatus (TESSA).

2.6.3 Analytical Methods [4]

Because of the environmental concerns over PAHs, a wide variety of analytical methods have been used, with various sample extraction, cleanup. And concentration procedures. Analysis is commonly either by capillary GC with FID or MS detection, or by HPLC with detection by UV diode array and fluorescence. Gas chromatography has been widely applied to the analysis of PAHs. High-efficiency separation and resolution can be obtained by using capillary GC column.

2.7 Health Hazards of PAHs

The U.S. Department of Health and Human Services (DHHS) has determined that PAHs may reasonably be anticipated to be an important group of chemical carcinogens. Several of PAHs, including benz(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, chrysene, dibenz(a,h)anthracene, indeno(1,2,3-cd)pyrene, have caused tumors in laboratory animals when they ate them, when they were applied to their skin, or when they breathed them in the air for long periods of time. Reports on humans show that individuals exposed by breathing or skin contact for long periods of time to mixtures of other compounds and PAHs can also develop cancer [22].

Studies on animals have also known that PAHs can cause harmful effect on skin, body fluids, and the body's system for fighting disease after both short- and long-term exposure. These effects have not been reported on humans. As can be seen, no information is available from human studies to determine health effect resulting from exposure to specific levels of the individual PAHs, although inhalation and skin exposure to mixtures containing PAHs has been associated with cancer in humans.

Several investigations have studied the mechanism of carcinogenic action of a wide range of PAHs in the biological systems and animal tumor bioassay systems. The key event of chemical carcinogenesis is the covalent binding of the carcinogen to macromolecules, especially to DNA, in the cell. PAHs are large, flat compounds that are similar to benzene in structure. Many aromatic compounds, including PAHs are carcinogenic as a result of their structure. The flat hydrophobic shape of PAH makes it difficult to excrete from the body. In addition, this shape allows PAH to insert into the structure of DNA where it interferes with the proper functioning of the DNA and can lead to cancer.

In addition, during their migration through the environment, PAHs may be transformed, by interaction with oxidants and sunlight, into products which, in some cases, are much more mutagenic than the compounds from which they were derived.

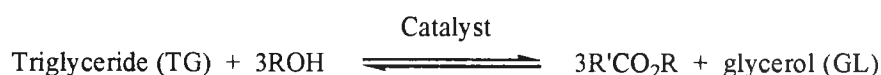
2.8 Literature reviews

Oxygenated fuels are well-known to reduce exhaust emissions from motor vehicles. In particular, methyl-tertiary-butyl ether (MTBE) and ethanol reduce emissions from gasoline engines. In high polluting automobiles, oxygenated gasoline can decrease carbon monoxide (CO) up to 50%. Oxygenated are now mandated under the Clean Air Act for use in reformulated and CO control gasoline. This success of oxygenated gasoline has led to interest in the use of oxygenated compounds as emissions reducing additives in diesel fuel. Numerous oxygenated compounds have been investigated as either diesel fuel additives or replacements and have shown emissions reducing properties. Oxygenated fuels are also of special interest since they are a potential source of renewable energy. Biodiesel is an oxygenated diesel fuel made from vegetable oils and animal fats by conversion of the tri-glyceride fats to esters via transesterification [23].

Many studies have examined emissions from biodiesel. Studies employing heavy-duty transient testing showed that emissions of PM and CO are reduced and NO_x emissions are increased relative to petroleum diesel. PM can be viewed as being made of carbon or soot, a soluble organic fraction (SOF) and sulfate. Biodiesel causes a reduction in the soot fraction of PM [23].

In 1986, Freedman, *et al* [24] studied transesterification of soybean oil (SBO) with alcohols, in the presence of a catalyst, yields fatty esters and glycerol. Di- and monoglycerides were used as intermediates. Reactions are consecutive and reversible. A computerized kinetic program was used to determine whether a proposed kinetic order appeared possible. Forward reactions appear to be pseudo-first order or second order depending upon conditions used. Reverse reactions appear to be second order. The reactions studied are shown in Figure 2.7.

Overall Reaction :



Stepwise Reactions :

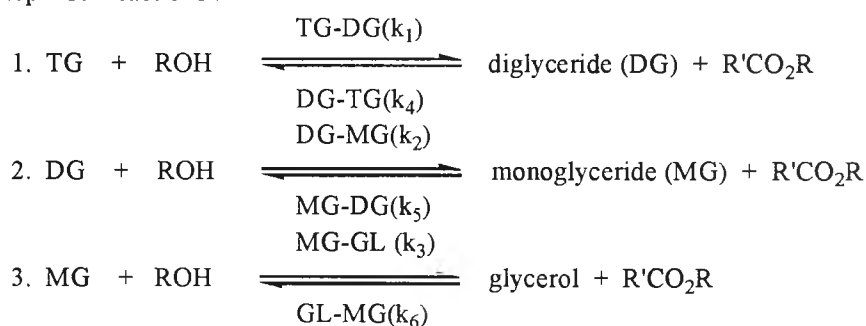


Figure 2.7 Chemistry of transesterification of vegetable oils.

In 1988, Mittelbach and Tritthart [25] described the preparation of methyl ester of used frying oil. Methanol and potassium hydroxide were used to transesterify vegetable oil collected from different households and restaurants over a period of one year. The emission tests were carried out with direct-injection diesel engine which was tested under the US Federal Test Procedure (US-FTP) and in the High-Way-Fuel-Economy-Test (HWFET).

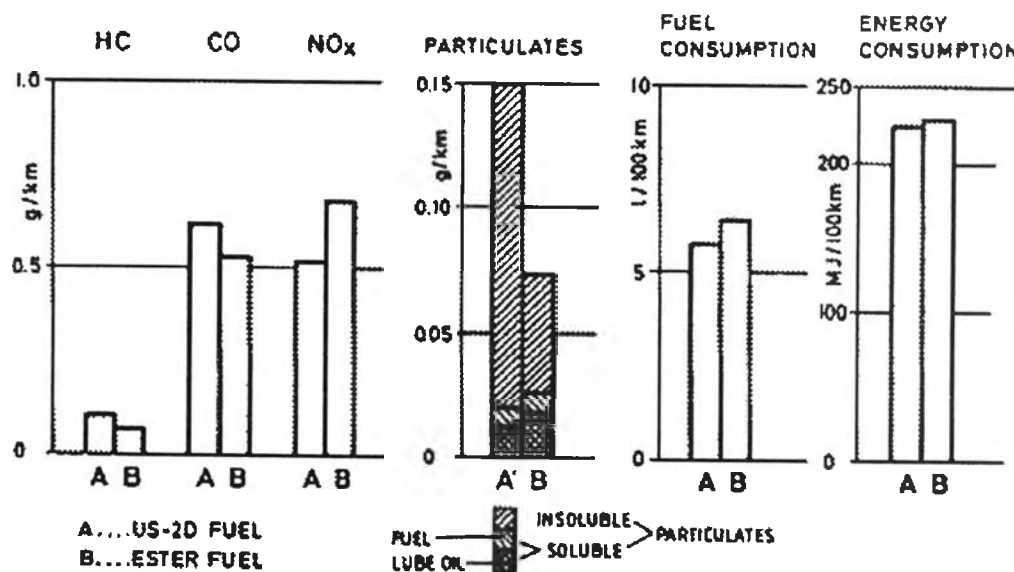


Figure 2.8 HC, CO, NO_x and particulate emissions. Fuel consumption US-FTP 72 test (four-cylinder, four-stroke, DI/TC diesel engine with EGR, 2.3 l displacement, 1360 kg inertia weight). Reproduced from [25].

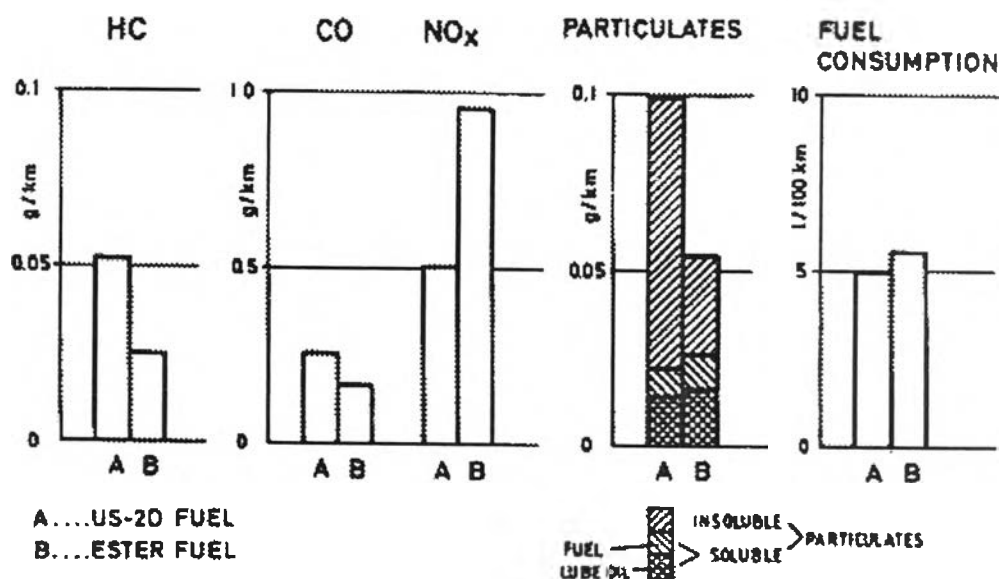


Figure 2.9 HC, CO, NO_x and particulate emissions. Fuel consumption HWFET test (four-cylinder, four-stroke, DI/TC diesel engine with EGR, 2.3 l displacement, 1360 kg inertia weight). Reproduced from [25].

The ester fuel, compared with the US-2D fuel, shows slightly lower HC and CO emissions but increases NO_x values under the US-FTP 72 (Figure 2.8) and almost doubled NO_x values under the HWFET Test (Figure 2.9). The particulate emissions are significantly reduced with the ester fuel under both tests, especially the insoluble portion of particulates.

In 1991, Westerholm, *et al* [26] reported that the PUF technique gave the highest recovery of polycyclic aromatic hydrocarbons (PAHs) and mutagenic activity. The amount of PAHs, mainly three-ringed PAHs, emitted in the semivolatile phase was approximately 3 times higher than that emitted in the particulate phase. Emissions of PAHs in the particulate phase are presented in Table 2.2.

In 1995, Collier, *et al* [1] studied polycyclic aromatic hydrocarbons emissions from a light-duty direct-injection diesel engine. The exhaust from the engine was sampled for PAHs at three constant speeds and five load settings for each speed, using a total-exhaust solvent-stripping apparatus. The PAHs recoveries (percent of fuel PAHs) were highest at low loads and progressively declined with increasing load as shown in Figure 2.10.

Table 2.2 Emission of particulate-associated PAHs ($\mu\text{g}/\text{m}^3$)^a[26]

PAHs	X ^a	RSD (%)
2-methylfluorene	<0.04	
phenanthrene	29	48
anthracene	3.3	13
3-methylphenanthrene	30	27
2-methylanthracene	40	24
4-+9-methylphenanthrene	48	21
1-methylphenanthrene	41	20
fluorene	17	11
pyrene	11	14
benzo[a]fluorene	2.4	32
2-methylpyrene	2.0	19
1-methylpyrene	0.75	35
benzo[ghi]fluoranthene	1.5	19
cyclopenta[cd]pyrene	0.18	30
benz[a]anthracene	0.47	54
chrysene/triphenylene	2.8	18
benzo[b and k]fluoranthene	0.29	31
benzo[e]pyrene	0.15	28
benzo[a]pyrene	<0.06	
perylene	<0.01	
indeno[1,2,3-cd]fluoranthene	<0.09	
indeno[1,2,3-cd]pyrene	<0.04	
picene	0.01	
benzo[ghi]perylene	<0.13	
coronene	<0.01	
SUM of PAH(25)	<230	22

^a n = 6, mean value (X) +/- relative standard deviation (RSD) (%)

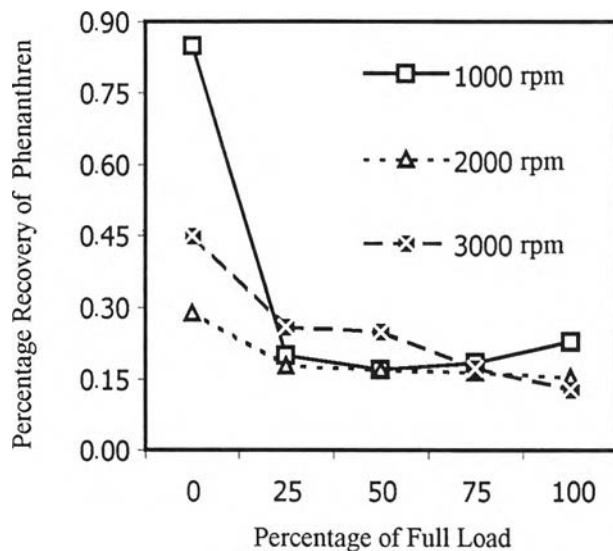


Figure 2.10 Effect of engine speed and load on percentage recovery of phenanthrene.

Adapted from [1].

The recovery of all PAHs converged at high load, indicating survival of fuel PAHs unchanged. A greater range of PAHs recoveries was found at low load. The increased range of recoveries at high speed may be due either to pyrosynthetic contributions or to a range of combustion efficiencies of individual PAHs structures.

In 1996, Septhum [27] studied the effect of a cetane improver on polycyclic aromatic hydrocarbons in diesel exhaust, operating the diesel engine at different loads and speeds. Main PAHs found in diesel exhaust were naphthalene, methylnaphthalene, diemethylnaphthalene, acenaphthene, phenanthrene, methylphenanthrene, fluoranthene and pyrene. Addition of cetane improvers, 2-ethylhexyl nitrate and di-t-butyl peroxide, reduced PAHs in diesel exhaust. For the engine load test, it was found that the amount of PAHs in diesel exhaust was lowest at load of 50% and highest at load of 80% of full load. The amount of PAHs in diesel exhaust at the engine speed of 2500 rpm was found to be slightly higher than that at the engine speeds of 1500 and 3500 rpm.

Additional studies [27] also reported that the two-ringed PAHs were emitted into the semivolatile phase rather than into the particulate phase because over 90 percent of PAHs in semivolatile phase were trapped in PUF. Mainly higher molecular weight PAHs were trapped in GF. Moreover, some of the low molecular weight PAHs, naphthalene, methylnaphthalene, and dimethylnaphthalene, contaminated the blank of the PUF.

Furthermore, the results of repeatability of analytical method showed that high molecular weight PAHs had better precision than low molecular weight PAHs because the low molecular weight PAHs could easily be lose during sampling, extraction and sample storage.

In 1997, Tuntipisit [20] studied the effect of oxygenated compounds on the emission of polycyclic aromatic hydrocarbons (PAHs) from diesel engine. Exhaust samples were sampled at no load and at engine speeds of 800, 1600 and 2400 rpm. Base diesel fuel was blended with isoamyl alcohol at 4, 6, 8 and 10% by volume. The concentrations of PAHs in diesel exhaust decreased with an increase of the concentration of isoamyl alcohol from 4 to 10% by volume. Besides, the concentration of PAHs in diesel exhaust emission at the engine speed of 1600 rpm was slightly lower than that of the engine speeds of 800 or 2400 rpm.

In the same year, Starr [28] examined the transient emissions of a 260 kW DDC Series 60 heavy-duty diesel engine when using various untreated and treated high cetane, low aromatic diesel fuel and typical low-sulfur type 2D diesel served as base fuel. The base fuel was then treated with the two different cetane improvers ethyl hexyl nitrate (EHN) and di-tertiary butyl peroxide (DTBP). The base fuel was also blended with soy methyl ester in a ratio of 80:20, known as B20. It was found that the 2D base fuel resulted in the highest NO_x and PM levels at each test. However, increasing cetane number reduced the volatile organic fraction (VOF) and hence total particulate, and also reduced NO_x at all testes. With the oxygenate present in soy methyl ester, the bio-diesel fuels had the lowest PM emissions compared to all other fuels tested.

In 1998, Buravannint [29] studied the effect of fusel oil, by-product from alcoholic fermentation, on PAHs from exhaust emission of diesel engine. A base diesel oil was blended with 2, 4, 6, 8 and 10% v/v of fusel oil. The engine speed was varied at 800, 1600 and 2400 rpm. The results demonstrated that the engine speed of 800 rpm resulted in large amounts of PAHs; while that of 2400 rpm in the lowest PAHs. The addition of fusel oil into diesel fuel resulted in a decrease in the amount of PAHs in the diesel exhaust. Moreover, the major 9 species of PAHs including naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene and benzo(b)fluoranthene were found.

In 2001, McCorMick, *et al* [30] examined biodiesels produced from a variety of real-world feedstocks as well as pure (technical grade) fatty acid methyl and ethyl esters for emission performance in a heavy-duty truck engine using the U.S. heavy-duty federal test procedure (transient test). Many studies examined emissions from biodiesel and it was found that emissions of PM and CO are reduced and NO_x emissions are increased relative to petroleum diesel. PM can be viewed as being made of carbon or soot, a soluble organic fraction (SOF) and sulfate. Biodiesel causes a reduction in the soot fraction of PM. For 100% biodiesel, the composite NO_x increased by 11% while PM was decreased by 66%. More recent studies have shown similar levels of PM reduction and NO_x increase. The studies cited above clearly indicate that substantial reduction in particulate emissions can be obtained through the addition of biodiesel to diesel fuel.