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Chapter

Fuels of the Diesel-Gasoline Engines and Their Properties

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Abstract

Hydrocarbon-based fuels which are gasoline, diesel, natural gas, and liquefied petroleum gas (LPG) have been generally used in the diesel and gasoline engines as a fuel. In this study, hydrocarbon-based fuels such as alkanes (paraffins), naphthenes (cycloparaffins), alkenes (olefins), alkynes (acetylenes), and aromatics (benzene derivatives) have been classified. Their molecular structure and properties have been comprehensively explained. In addition to this, some of the important fuel properties of the commonly used fossil-based fuels such as gasoline and diesel in the internal combustion engine have been evaluated. Thus, hydrocarbon derivative fuels which are diesel, gasoline, natural gas, and liquefied petroleum gas (LPG) have been investigated as an internal combustion engine fuel. Their physical and chemical properties were explained and compared to each other. Octane number and cetane number substantially affect the fuel ignition delay period and selfignition temperature properties. Therefore, the gasoline and diesel engine running is dominantly affected by the octane and cetane numbers, respectively. As a result, fossil-based fuel's physical and chemical properties, advantages, and disadvantages have been comprehensively explained and compared to each other. The fuels, which are commonly used in the diesel and gasoline engine, have been investigated, and their important properties have been revealed.

Keywords: fuels, hydrocarbons, diesel fuel, gasoline fuel, diesel and gasoline engine

1. Introduction

Fuels can be classified into three groups as solid, liquid, and gas. Although liquid hydrocarbons are generally used in internal combustion engines, in urban transportation where air pollution is a problem, biofuels such as alcohols and biodiesel or gaseous fuels, which are liquefied petroleum gas (LPG) or natural gas, have been rarely used as a fuel. The importance of using alternative fuels in internal combustion engines emerges because of limited oil resources and decreasing reserves, increasing oil prices, and increasing environmental problems. In order to reduce dependence on oil, alternative engine fuels such as vegetable oils, biofuels (alcohols, biodiesel, biogas), and liquefied hydrogen gas have been of particular interest to researchers [1, 2].

2. Hydrocarbon-based fuels

Fuel compounds containing carbon and hydrogen atoms in their basic molecular structure are called hydrocarbon-based fuels. Hydrocarbons can be divided into two main groups, aliphatic and aromatic. Aliphatic hydrocarbons are divided into two subclasses as saturated and unsaturated hydrocarbons. The carbon atom in hydrocarbon is called saturated if it has bonded with four hydrogen atoms and unsaturated if the carbon atoms have made double or triple carbon-carbon bonds. Saturated hydrocarbons are classified as alkanes; unsaturated hydrocarbons are classified as alkenes or alkynes [3, 4]. Hydrocarbons can be in the solid, liquid, and gas phases according to the number of carbons in the chemical structure. Generally, hydrocarbons with carbon atoms 1–4 are in gas, 5–19 are liquid, and molecules with 20 and more carbon atoms are in the solid phase [5]. C_nH_m is the general closed chemical formula of liquid hydrocarbons used as a fuel in the internal combustion engines. However, hydrocarbons consist of hydrogen and carbon and also small amounts of O₂, H₂, S, H₂O, and some metals containing crude oil derivatives [2]. **Figure 1** gives the classification of the compounds of hydrocarbons.

2.1 Alkanes (paraffins)

Alkanes are saturated hydrocarbons with the general closed formula C_nH_{2n+2}, also known in the literature as paraffins, which add the suffix "-an" at the end of the Latin carbon numbers. Alkanes contain more hydrogen in their chemical structure compared to other hydrocarbons, this high number of hydrogen atoms lead to be higher thermal values and lower density than other hydrocarbons (620–770 kg/m³). As the number of carbon atoms in the hydrocarbon chain increases, the properties of the alkanes such as autoignition tendencies, molecular weights, and melting and boiling points increase. Each increase in carbon number in the hydrocarbon chain causes the boiling point to rise by about 20–30°C. Alkanes are insoluble in water because they are apolar. Among the apolar molecules such as hydrocarbons and inert gases are Van der Waals forces, in other words, London dispersion forces. Dispersion force is as a weak intermolecular force between all molecules by means of temporary dipoles induced in the atoms or molecules. The dispersion forces are commonly expressed as London forces. Electron numbers and surface area of the molecules are the most important affecting factors of the magnitude of dispersion forces. These tensile forces directly affect the boiling point of these materials. The alkanes may exist in a straight chain, branched chain, and cyclic form depending on

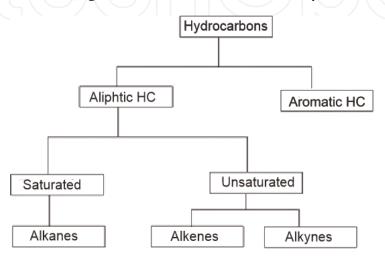
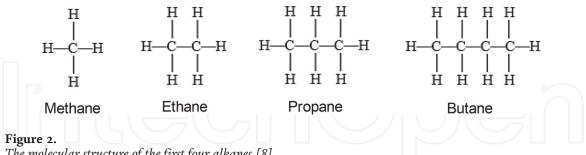


Figure 1. Classification of hydrocarbons [3].

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the arrangement of the carbon atoms. Van der Waals forces are more effective than branched ones because the molecular surfaces of the straight-chain alkanes are more in contact with each other. Thus, the boiling point of the straight-chain alkanes having the same molecular weight is higher than the branched ones. In other words, as the branching increases, the boiling point decreases, because the branched structure makes the molecule tighter. However, the increasing of branching has led to the surface area of the molecule to become narrow, and the boiling point decreases with the reduction of Van der Waals forces between itself and neighboring molecules. The ignition tendencies of straight-chain alkanes are generally higher than the branched chain ones due to it being more easily broken down. Unlike straight-chain molecule structures, branched chain and ring structures have higher ignition resistance. Therefore, straight-chain alkanes are more suitable for use as diesel fuel rather than as gasoline fuel. However, alkane isomers which are of the same closed formula but with different branched chains and rings are more suitable for use as a gasoline engine fuel since they have higher engine knocking resistance. The property that defines whether the fuel ignites spontaneously is called the octane number. In other words, it is defined as ignition resistance. Straight long chain fuels generally have a lower octane number, whereas branched structures have a higher octane number. To summarize this briefly, the octane number is usually inversely proportional to the chain length of the molecules of the fuels. The shorter the chain structure of the fuel molecules, the higher the octane number. The octane number is directly proportional to the branched side chain components. Besides, having a ring molecular structure of fuels leads to high octane numbers. Alkanes are present in solid, liquid, and gaseous form according to their carbon number. The carbon number 1–4 is present in gas, 5–25 in liquid form, and more than 25 in solid form. Alkanes contain less than 4 carbon atoms in their natural gas and petroleum gases, 5–12 atoms in gasoline, 12–20 atoms in diesel fuels, and 20–38 atoms in lubricating oils [1–8]. Figure 2 shows the molecular structure of the first four alkanes.



The molecular structure of the first four alkanes [8].

2.2 Naphthenes (cycloparaffins)

Another type of alkanes is cyclic structures which demonstrate as the general formula C_nH_{2n}. Two hydrogen atoms are missing from normal alkanes because their structures are cyclic-shaped and in closed form. As the number of hydrogen atoms is low compared to normal alkanes, they have lower thermal values but higher densities (740–790 kg/m³). Cycloalkanes are difficult to break up because of their closed cycle structure and have higher ignition resistance than straight-chain alkanes. However, they are also suitable for use as both petrol and diesel fuel due to that they have lower ignition resistance than branched ones. Thermal values of naphthenes are lower than alkanes and higher than aromatics [2]. Figure 3 shows the cyclic molecular structure of cyclohexane.

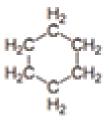


Figure 3. *The cyclic molecular structure of cyclohexane* [5].

2.3 Alkenes (olefins)

Alkenes are unsaturated hydrocarbons that have double bond between carbon atoms shown as the general formula C_nH_{2n} . The olefins with one double bond in the molecular structure are called monoolefins (C_nH_{2n}) , and those with two double bonds are called die-olefins (C_nH_{2n-2}). Monoolefins are entitled after the "en" or "ilen" suffix at the end of the carbon number, while die-olefins are entitled by attaching the "dien" suffix to the roots showing the carbon number. Many isomers are formed by displacement of the double bonds of alkenes. Alkenes' thermal values are lower than alkanes, and their density is between 620 and 820 kg/m³ due to that the ratio of carbon atoms to hydrogen atoms is higher in the molecular structure of alkenes. Alkenes have high ignition resistance. Alkenes are less resistant to oxidation than alkanes so that they can easily react with oxygen. Thus, oxygen causes to be gummed to alkenes and consequently block the fuel pipeline. Alkenes contain double bonds between carbon atoms, one of which is sigma (δ) and the other is pi (*n*). For this reason, it breaks down more difficult than alkanes with a single sigma bond. Alkenes can be used as fuel for gasoline engines due to high ignition resistance. Besides, it can be used as a diesel fuel by increasing autoignition temperature. The most important properties of alkenes give addition reactions with H₂, X₂, HX, and H₂O compounds. Carbon atoms of alkenes are not fully saturated with hydrogen. Therefore, alkenes can be more easily associated with elements such as hydrogen, chlorine, and bromine due to it being more chemically reactive than alkanes and naphthenes. With this reactive structure, they are used as raw materials to obtain better quality fuels by methods such as hydrogenation, polymerization, and alkylation. While alkenes are present in very small amounts in crude oil, generally they can be obtained by thermal and catalytic cracking methods which are heat or catalyst by means of large molecular product decomposition. Alkenes are present in large quantities in the gasoline obtained by these methods. The high ignition resistance of the alkenes makes them a good gasoline engine fuel, but they can also be diesel engine fuel by increasing the ignition tendencies [1-3, 5, 9]. Figure 4 shows the molecular structure of some alkenes.

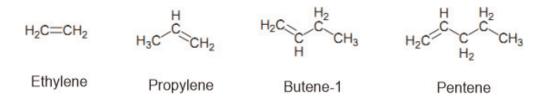


Figure 4. *The molecular structure of some alkenes* [5].

2.4 Alkynes (acetylenes)

Alkynes are compounds which having the general closed formula C_nH_{2n-2} and having at least one triple bond ($C \equiv C$) between carbon atoms. Alkynes are unsaturated hydrocarbons due to all carbon atoms not having enough bonds with hydrogen. Besides, alkynes have "-in" suffix which is added to the end of the compound and entitled according to the number of carbon atoms in the longest chain. The simplest and most known compound is acetylene (C_2H_2) . Alkynes may also be referred to as acetylene derivatives. Alkenes are more reactive than alkanes and naphthenes because they are unsaturated. Thus, they can be more easily reacted with elements such as hydrogen, chlorine, and bromine to form a compound [3, 5, 9]. **Figure 5** gives the molecular structure of some alkenes.

> H3C-C=C-H H-C=C-H Acetylene Methylacetylene

Figure 5. The molecular structure of some alkynes [5].

2.5 Aromatics (benzene derivatives)

At the end of the nineteenth century, organic compounds were divided into two classes as aliphatic and aromatics. Aliphatic compounds meant that the compounds exhibited "liparoid" chemical behavior, while aromatic compounds meant low hydrogen/carbon content and "fragrant." Aromatics are unsaturated hydrocarbons having double bonds between carbon atoms that have a closed general formula C_nH_{2n-6} . Aromatic compounds are bonded to each other by aromatic bonds, not single bonds. In other words, aromatics are also called arenes. Although aromatics are unsaturated compounds, they have different chemical properties than other aliphatic unsaturated compounds. Unlike alkenes and alkynes, aromatics do not give an addition reaction which is the characteristic reaction of unsaturated compounds. Furthermore, aromatics carry out displacement reactions especially specific to saturated hydrocarbons. Because of these reasons and aromatics are more stable than other unsaturated compounds, aromatics have been categorized as a separate class of hydrocarbons. Due to the presence of more than one double bonded carbon atoms and cyclic structure, they have strong bond structures and highly resistant to ignition. Densities of aromatics range between 800 and 850 kg/m³. Higher densities in the liquid state cause them to have a high-energy content per unit volume but have a low thermal value per unit mass. The bonds between carbon atoms are strong; aromatics have a high resistance to knocking. Therefore, because of the high octane number of aromatics, they can be a good gasoline fuel with the addition of gasoline to increase knocking resistance, but they are not suitable to use as diesel engine fuel because of their low cetane numbers. The simplest aromatic compound is benzene with the chemical formula C_6H_6 . The main structures of other aromatics are also constituted by benzene. Generally, they can be obtained artificially from coal and can be used as a gasoline additive to improve the knocking resistance of gasoline. The aromatics must be used carefully because they are carcinogenic, cause exhaust pollution, have high solubility, and have corrosive effects on fuel supply systems [1–3, 5, 6, 9]. Figure 6 shows the molecular structure of some important aromatics.

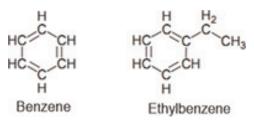


Figure 6. Molecular structure of some aromatics [5].

3. Fuels of internal combustion engine

Gasoline and diesel fuels, which are derivatives of crude oil, are generally used in internal combustion engines. The approximate elemental structure of an average crude oil consists of 84% carbon, 14% hydrogen, 1–3% sulfur, and less than 1% nitrogen, oxygen atoms, metals, and salts. Crude oil consists of a wide range of hydrocarbon compounds consisting of alkanes, alkenes, naphthenes, and aromatics. These are very small molecular structures such as propane (C_3H_8) and butane (C_4H_{10}) but can also be composed of mixtures of various structures with very large molecules such as heavy oils and asphalt. Therefore, crude oil needs to be distilled to be used in internal combustion engines. As a result of heat distillation of crude oil, petroleum derivatives such as petroleum gases, jet fuel, kerosene, gasoline, diesel, heavy fuels, machine oils, and asphalt are obtained. In general, the distillation of crude oil resulted in an average of 30% gasoline, 20–40% diesel, and 20% of heavy fuel oil, and heavy oils from 10 to 20% are obtained [2, 5].

During the distillation of crude oil, gasoline is obtained between 40 and 200°C, and diesel fuel is obtained between 200 and 425°C. In order to use these fuels in engines, some of the important physical and chemical properties such as specific gravity of the fuel, structural component, thermal value, flash point and combustion temperature, self-ignition temperature, vapor pressure, viscosity of the fuel, surface tension, freezing temperature, and cold flow properties are required. The specific mass, density of the fuel decreases with increasing hydrogen content in the molecule. The density of gasoline and diesel fuels is generally given in kg/m³ at 20° C. The American Petroleum Institute (API) number is an international measurement system that classifies crude oil according to its viscosity according to the American standards. The specific gravity can be defined as the ratio of the weight of a given volume of a given substance at 15.15°C (60°F) to the weight of the water at the same volume and temperature. The relationship between API number and specific gravity is expressed as follows [1, 2, 5]:

Specific weight
$$(15.15^{\circ}C/15.15^{\circ}C) = \frac{\rho_{\text{specimen}}(15.15^{\circ}C)}{\rho_{\text{water}}(15.15^{\circ}C)}$$
 (1)

$$API = \frac{141.5}{Specific weight (15.15^{\circ}C/15.15^{\circ}C)} - 131.5$$
(2)

According to the API number, crude oil is divided into three groups as heavy, medium, and light, and as the number of the API increases, crude oil becomes thinner. The API degree of diesel fuels varies between about 25 and 45. The viscosity, color, main component, and definition of crude oil according to the API grade are given in **Table 1** [1, 5].

API grade	Definition	Viscosity	Color	Composition
0–22.3°	Heavy	Too viscous	Dark	Asphalt
22.3–31.3°	Medium	Medium	Brown	Diesel + gasoline
31.3–47°	Light	Fluid	Light yellow	Gasoline

Table 1.

Classification of crude oil according to API grade [5].

While the density of gasoline is $\rho = 700-800 \text{ kg/m}^3$, it varies between $\rho = 830-$ 950 kg/m³ for diesel fuel. While the carbon content in alkane and naphthene fuels is 86%, it is around 89% for aromatics. In addition to carbon and hydrogen atoms, sulfur, asphalt, and water can be found in gasoline and diesel fuels. In particular, sulfur can cause corrosion in engine parts, and the combustion products of sulfur have a negative impact on the environment. The asphalt adheres to the valve on the piston surfaces and causes wear. The water causes corrosion and reduces the thermal value of the fuel. These are undesirable components in the fuel. The thermal values of liquid fuels are given as unit mass energy (kJ/kg or kcal/kg), while the thermal values of gas fuels are given as unit energy (kJ/l, kJ/m³ or kcal/m³). Thermal values of fuels are expressed in two ways as lower and higher heating value. If the water in the fuel is in the vapor state at the end of the measurement, it gives the lower thermal value of this fuel. When the water in the fuel condenses at the end of the measurement, it gives the evaporation heat to the system, and the measured value gives the higher heating value of the fuel. As a result, the single-phase steam is obtained in the calorimeter capsule as a result of the thermal value measurement so that the lower heating value is measured. The dual phase (liquid-vapor phase) is obtained so that the higher heating value is measured. When the temperature of an air-fuel mixture is sufficiently heated, the fuel starts to ignite by itself without external ignition. This temperature is referred to as the self-ignition temperature (SIT) of the fuel and the delay time for the combustion of the fuel to be the ignition delay (ID). The terms SIT and ID are important features of engine fuels. SIT and ID values vary depending on variables such as temperature, pressure, density, turbulence, rotation, air-fuel ratio, and presence of inert gases. Self-ignition is the basic rule of the combustion process in diesel engines. SIT value is desired to be high in gasoline engines and low in diesel engines. The autoignition temperature of the gasoline is 550°C and higher temperatures [1, 2, 4].

Depending on the type of gasoline or diesel engine, the desired properties of fuels vary. The most important properties of gasoline fuels are properties such as volatility and knocking resistance, whereas diesel fuels are required to have important fuel properties such as viscosity, surface tension, and ignition tendency. In gasoline fuels, volatility and knock resistance are one of the most important parameters affecting engine performance. The volatility of gasoline fuel affects the rate and amount of evaporation of the fuel in the intake channel and in the cylinder. The low volatility of the fuel influences the formation of sufficient air-fuel mixture, but when it is very volatile, it can prevent the flow of fuel by creating vapor bubbles in the suction channel with the local temperature increases. When the flame front advances during combustion, with the increasing temperature and pressure inside the cylinder, it compresses the air-fuel fill which the flame front cannot yet reach. Thus, the fuel can constitute another combustion front due to the fuel spontaneously reaches the ignition temperature to heat and radiation. The combustion speeds of the flame fronts at these different points can be 300–350 m/s, and cylinder pressures may reciprocate to as high as 9–12 MPa. At these high speed and pressure values, the flame fronts are damped by hitting each other or against the walls of the combustion chamber. These damping are not only cause loss of energy but also increase the local heat conduction. As a result of this situation, engine performance decreases. This phenomenon is called a knock in gasoline engines and is an undesirable situation. The chemical structure of the fuel has a considerable effect on the autoignition temperature. Octane number (ON) is defined as the property of fuel to knocking resistance or how well the fuel itself ignites. The octane number is inversely proportional to the chain length of the fuel molecules. The shorter the molecular chain length of the fuels has, the higher the octane number is. However, the octane number is directly proportional to the branched side chain component. The higher the branching in the molecule chain leads to the higher octane number of the fuel. In other words, it causes higher knocking resistance of fuels. Generally, increasing the number of carbon atoms in the composition of the fuel has higher impact resistance. However, the octane numbers of cyclic molecules, naphthenes, alcohols, and aromatics are high. In order to scale the octane number of gasoline, two reference points are taken, which represent points 0-100. The octane number of normal heptane (C_7H_{16}) is assumed to be 0, while the octane number of isooctane (C_8H_{18}) is considered to be 100. The reason of these two fuels as a reference point is that both fuel compounds have almost the same volatility and boiling point values. The reason as a reference point of these two fuels is that both fuel compounds have almost the same volatility and boiling point values. Fuels such as alcohols and benzenes with an octane number higher than the top octane number of this measure are also available. In gasoline engines, additives are used to increase the knocking resistance of the fuel to prevent knocking. The two most commonly used methods for determining the octane number of fuels are engine method and research method. The octane numbers determined by these methods give the values of motor octane number (MON) and research octane number (RON), respectively. Table 2 gives the test conditions for determining the octane number of fuel [1, 2, 4, 5].

Properties	RON	MON		
Engine speed (rpm)	600	900		
Intake air temperature (°C)	52 (125°F)	149 (300°F)		
Cooling water temperature (°C) 100 (212°F)		100		
Oil temperature (°C)	57 (135°F)	57		
Ignition time	13°KMA (before TDC)	13–19°KMA (before TDC)		
Spark plug nail range	0.508 (0.020 inç)	0.508		
Intake air pressure	Atmospher	ic pressure		
Air-fuel ratio	Adjusted for maximum knock			
Compression ratio	Adjusted to achieve a standard knock			

Table 2.

Test conditions for octane number measurement [4].

Since the inlet air temperature of the MON method is higher than the RON method, the post-combustion temperature reaches higher values. Thus, the fuel spontaneously ignites and knocks. Therefore, the octane number obtained by the MON method is lower than the octane number obtained by the RON method because it is operated at lower compression ratios in the MON method. The value difference between these two octane number determination methods is called fuel sensitivity (FS). When the number of fuel sensitivities is between 0 and 10, it is stated that the knock characteristic of the fuel does not depend on engine geometry,

and if it is higher than these values, the knock characteristic of the fuel is highly dependent on the combustion chamber geometry of the engine. YD is calculated as in Eq. (3):

$$FS = RON - MON \tag{3}$$

Combustion chamber geometry, turbulence, temperature, and inert gases are the parameters that affect the octane number. The octane number is highly dependent on the flame velocity in an air-fuel charge. As the flame velocity increases, the air-fuel mixture above the spontaneous ignition temperature immediately burns during the ignition delay. Thus, there is a direct correlation between the flame speed and the octane number, as the flame speed will allow the fuel to run out without knocking. Alcohols have high flame speeds, so their octane numbers are high. The ID period does not depend on the physical properties of the fuel such as density and viscosity in a hot engine at steady state. It is strongly dependent on the components of the fuel chemistry. Therefore, additives such as alcohols or organic manganese compounds are added to increase the octane number of the fuel [4, 5]. It is possible to work at higher compression ratios by increasing the octane number of fuels. Thus, high compression ratio increases engine power and provides fuel economy [10].

Diesel fuels are divided into two main categories as light diesel and heavy diesel fuels. The chemical formula of light diesel is approximately $C_{12.3}H_{22.2}$, while heavy diesel is considered as $C_{14.06}H_{24.8}$. The molar weights of light and heavy diesels are approximately 170 and 200 g/mol, respectively. Viscosity, surface tension, and ignition tendency of fuel are important fuel property parameters in diesel fuels. Light diesel fuel has a lower viscosity and requires less pumping work. Since low viscosity also reduces the surface tension of the fuel, the fuel has a smaller droplet diameter during spraying. In contrast to gasoline engines, it is desirable to have a high ignition tendency in diesel engines, since combustion in the diesel engines is based on the spontaneous combustion of the air-fuel mixture. At this point, the cetane number, which is a measure of the fuel's ignition ability, emerges as a fuel feature. In other words, it is a quantity that quantifies the ignition delay period. Hexadecane $(C_{16}H_{34})$, a straight-chain fuel of the alkane group, is considered to be the highest reference point of the cetane number, which is the measure of the ignition tendency. The other reference point is cetane number 15 as heptamethylnonane (HMN) $C_{12}H_{34}$, or the lowest reference point was accepted zero as the cetane number value of alpha-methyl naphthalene $C_{11}H_{10}$ fuel. First of all, fuel with unknown cetane value is run in the adjustable compression ratio engine. Then, the engine test is carried out until the compression rate at which the first knock starts for determining compression ratio of the fuel. Then, the mixture of these two reference fuels in various ratios is tested at the specified compression ratio, and the reference fuels are mixed until the knocking begins. The percentage of hexadecane at the moment of the knock, in the heptamethylnonane or alphamethyl naphthalene fuel mixture, gives us the cetane number of the measured fuel. Several empirical equations have been developed by using the physical properties of the fuel since the engine tests are very laborious and costly in determining the cetane number. These methods, which measure the fuel propensity to ignite, are called cetane index, aniline point, or diesel index. Aniline is an aromatic compound which is very easily mixed with compounds of its group even at low temperatures, while it is more difficult to form mixtures with alkanes (paraffins). Therefore, hexadecane $(C_{16}H_{34})$ which is an alkane group and has a high ignition tendency has a high mixing temperature with the aniline. The mixture of the sample fuel with the same amount of aniline is heated to find the diesel index. Then, all of the aniline is dissolved in the fuel. After that the mixture is cooled for allowing to aniline to separate from the fuel. This temperature, where the aniline is separated from the

fuel, is called the aniline point. The diesel index is calculated with the aniline point and API grade specified in Eq. (4):

Diesel index =
$$\frac{\text{Aniline point}(^{\circ}\text{F}) \times \text{API (at 60^{\circ}\text{F})}}{100}$$
 (4)

The higher the diesel index value, the fuel is more alkane (in paraffinic structure), and it has the higher ignition tendency. Increasing volatility in diesel fuels causes acceleration of fuel evaporation and decrease in viscosity. This is generally undesirable since the fuel causes a reduction in the cetane number [1, 2, 4].

Some fuels commonly used in engines are presented in **Table 3**. Some of the important properties of fuels such as the closed formulas, molar weight, lower heating value and higher heating value, stoichiometric air/fuel and fuel/air ratios, evaporation temperature, motor octane number (MON), research octane number (RON), and cetane number are given.

The cetane index can be calculated from Eq. (5) which is shown by distilling the fuel. It is calculated from the temperatures and the density of the vaporized fuel at 10, 50, and 90% volumetric ratios by the distillation of the fuel:

$$SI = 45.2 + 0.0892(T_{10} - 215) + 0.131(T_{50} - 260) + 0.523(T_{90} - 310) + 0.901B(T_{50} - 260) -0.420B(T_{90} - 310) + 0.00049(T_{10} - 215)^2 - 0.00049(T_{90} - 310)^2 + 107B + 60B^2$$
(5)

The values of T_{10} , T_{50} , and T_{90} are the temperatures at which the fuel evaporates in volume ratios of 10, 50, and 90%, respectively. $B = -\exp[-3500(\rho - 850)] - 1$, where ρ = density in kg/m³ at 15°C. This formula is related to the number of cetane, unless cetane-enhancing additives are added to the fuel. Otherwise, the cetane number of doped fuels can be measured by engine test experiments. Another method used to calculate the cetane index is the empirical equation given in Eq. (6), which is calculated using some physical properties of the fuel [5]:

$$SI = -420.34 + 0.016G^{2} + 0.192G(\log_{10}T_{gn}) + 65.01(\log_{10}T_{gn})^{2} - 0.0001809T_{gn}^{2}$$
(6)

where $G = (141.5/S_g) - 131.5$ is the API degree of the fuel. S_g and T_{gn} are the relative boiling point temperature in °F and relative density, respectively.

The semiempirical expression that predicts ID duration based on cetane number and other operating parameters is as follows:

$$ID = (0.36 + 0.22U_p) \exp\left(E_A\left[\left(1/R_u T_{em} \varepsilon^{k-1}\right) - (1/17.190)\right]\left[(21.2)/\left(P_{em} \varepsilon^{k} - 12.4\right)\right]^{0.63}\right)$$
(7)

ID (°CA) is a time in crankshaft angle, $E_A = (618.840)/(\text{cetane number + 25})$ activation energy, $R_u = 8.314$ kJ/kmol K universal gas constant, T_{em} and P_{em} temperature at the beginning of compression time, respectively, (K) and pressure (bar), $\varepsilon = \text{compression ratio}$, and k = cp/cv = 1.4 are the values used in air standard cycle analysis. ID is calculated by the formula given in Eq. (8). It is expressed in milliseconds for an engine at n rpm [4]:

$$ID(ms) = D(\circ CA) / (0.006 n)$$
 (8)

The low cetane number of diesel engines leads to an increase in ID time, which in turn reduces the time required for combustion and CA. An increased TG time

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Fuel	Closed formula	Mole weight	Heatin HHV (kJ/kg)	g value LHV (kJ/kg)	(A/F)s	ometric (F/A)s	MON	number RON	Evaporation temperature (kJ/kg) —	CN
Gasoline	C ₈ H ₁₅	111	47,300	43,000	14.6	0.068	80–91	92–99	307	_
Light diesel	C _{12.3} H _{22.2}	170	44,800	42,500	14.5	0.069	_		270	40–55
Heavy diesel	$C_{14.6}H_{24.8}$	200	43,800	41,400	14.5	0.069	_	_	230	35–50
Isooctane	C ₈ H ₁₈	114	47,810	44,300	15.1	0.066	100	100	290	
Heptane	C ₇ H ₁₆	100	48,070	44,560	15.2	0.066	0	0	316	
Cetane	$C_{16}H_{34}$	226	47,280	43,980	15	0.066	_	_	292	100
Heptamethylnonane	$C_{12}H_{34}$	178		_	15	0.063	_	_		15
Alpha-methyl naphthalene	$C_{11}H_{10}$	142		_	13.1	0.076	_	_		0
Isodecane	$C_{10}H_{22}$	142	47,590	44,220	15.1	0.066	92	113		_

Table 3.Common fuels and their properties [4].

leads to accumulate more fuel in the combustion chamber than required. Thus, this excess fuel causes sudden and high-pressure increases during the onset of combustion. These sudden pressures increase cause mechanical stresses and hard engine operation, which is known as diesel knocking [2, 4].

In brief, the number of cetane and the number of octane refer to the spontaneous combustion of fuels. A higher cetane number indicates that diesel fuel burns suddenly and easily. The high octane number defines the resistance of gasoline to sudden ignition. Generally, if the cetane number is high, the octane number is low. There is an inverse relationship between these two properties, so that the cetane number is low if the octane number is high [5].

4. Natural gas and liquefied petroleum gas (LPG)

Natural gas is a gas mixture containing methane, ethane, propane, pentane, and hexane in a lighter content than air, without color, smell, and taste. However, it contains a small amount (0–0.5% by volume) of carbon dioxide, nitrogen, helium, and hydrogen sulfide gas. Generally, this gas composition contains about 70–90% of methane, 0–20% ethane, and slightly less propane than ethane. The natural gas used in the market is refined and separated from other gases and used as almost pure methane gas (CH₄) [5]. Natural gas can be stored as compressed natural gas (CNG) at high pressures such as 16–25 MPa or liquid natural gas at low pressures such as 70–210 kPa and at very low temperatures such as -160°C. Natural gas can be stored by these methods and generally used as compressed natural gas (CNG) in internal combustion engines with a single-point spray system. The single-point spraying system allows for the most efficient use of natural gas as it provides a longer mixing time than required for natural gas [4]. **Table 4** shows the compounds that form natural gas and boiling points.

Composition	Boiling point (°C)	Composition	Boiling point (°C)
Methane	-161.6	Isopentane	28
Ethane	-88.6	n-Pentane	36.1
Propane	-42.1	Hexane	69
Isobutane	-11.7	Heptane	98.4
n-Butane	-0.5		
Table 4.			

Compounds and boiling points in natural gas [5].

There are dual fuel diesel engines in which natural gas and diesel fuels work together. Natural gas is supplied to the combustion chamber at approximately sound speed. This leads to high turbulence and high flame speeds. Natural gas has lower combustion temperatures than diesel fuel, and with late spraying, the combustion chamber temperature can be further reduced. Decrease in combustion chamber temperature significantly reduces NO_x formation. However, the low carbon content in natural gas leads to less CO₂ emissions and much less solid particulate matter [4].

Dump gas engines, converting methane gas into energy, are one of the most common natural gas applications. Gases produced in landfills generally contain between 45 and 65% methane. In addition to methane, these landfill gases contain highly polluting and variable quality gases such as fluorine, chlorine, silicon, and solid particles. Especially due to the corrosive and abrasive effect of these gases, special piston and valve materials must be used in the engines. The thermal value of natural gas is between 33.4 and 40.9 MJ/m^3 . CO₂, H₂O, and 891 kJ of energy are obtained when 1 mol of methane gas is fully combusted. The combustion equation of 1 mol of methane is as described in Eq. (9) as follows:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2 H_2O(l) + 891 \text{ kJ}$$
 (9)

The high flame velocity and octane number 120 of the natural gas enable the natural gas to operate at high compression rates. This ensures that natural gas is a good gasoline engine fuel. Furthermore, natural gas has low exhaust emissions. In addition, the most important advantage of natural gas fuel is that natural gas can be produced from a source such as coal that has a lot of reserves all over the world. However, since the low-energy capacity of natural gas is in the form of gas, its low volumetric efficiency leads to reductions in engine performance. The disadvantages of this fuel are that natural gas requires high-pressure fuel storage tanks; refueling takes time and has variable fuel components in the content of natural gas [4]. **Table 5** presents the properties of natural gas and its comparison with other fuels as thermal values.

Properties	Natural gas Fuel types		Heating value (kcal/kg)	
Volume by composition (%)	95–98	1 kg of diesel oil	10,200	
Mole weight (kg/mol)	16.04	1 kg no: six fuel oil	9200	
Density (kg/m ³)	0.82	1 kg LPG	11,000	
Thermal value (MJ/m ³)	36.14	1 kg imported lignite coal	4700/6500	
Highest flame speed (m/s)	0.39	1 m ³ natural gas	8250	

Table 5.

The properties of natural gas and its comparison with other fuels [11].

LPG, a liquefied petroleum gas, is produced as a by-product from natural gas production processes or during the distillation of oil in refineries. In general, it contains 90% propane, 2.5% butane, and a small amount of ethane and propylene with heavy hydrocarbons. These propane and butane gas ratios in LPG may vary according to the regions and areas of use [5]. In recent years, propane-butane mixtures in different ratios (80% propane/20% butane, 70% propane/30% butane, 50% propane/0% butane) have been tested as fuel in vehicles. LPG gas used in Turkey consisted of 30% propane and 70% butane. LPG is the most preferred fuel type after gasoline and diesel fuels, since LPG is much easier to store and transport than natural gas [1, 4].

LPG is a colorless, odorless, nontoxic, and easily flammable gas. LPG is a mixture of propane and butane gas, which is gas at normal pressures and temperatures. However, LPG is a liquid at moderate pressure. Besides, it is two times heavier than air and half weight of water. Therefore, LPG leaks to the floor in case of leakage. LPG in liquid state expands to approximately 273 times its liquid volume. This is called sudden expansion and cooling of the sudden temperature drop with the very rapid evaporation of the liquid fuel as it passes into the gaseous state. Since this can cause cold burns, the gas should not be touched with bare hands. Although LPG is a noncorrosive gas, it can melt paint and oil and also inflate natural rubber materials, causing them to lose their properties. Therefore, the use of LPG compatible materials in autogas systems using LPG is very important for safety [1, 5]. LPG system is widely used in gasoline vehicles. With respect to this, the comparison of physical and chemical properties of propane and butane gases which are components of LPG and the gasoline fuel is given in **Table 6**.

Properties	Propane	Butane	Gasoline
Volumetric mass at 15 °C (kg/l)	0.508	0.584	0.73–0.78
Gas pressure at 37.8 °C (bar)	12.1	2.6	0.5–0.9
Boiling temperature (°C)	-42	0.5	30-225
RON	111	103	96–98
MON	97	89	85–87
Lower heating value (MJ/kg)	46.1	45.46	44.03
Lower heating value (MJ/l)	23.4	26.5	32.3
Stoichiometric ratio	15.8	15.6	14.7
le 6.			

5. Conclusions

Fossil-based fuels such as diesel, gasoline, natural gas, and LPG have been commonly used in engines as a fuel. However, the internal combustion engines show differences in the fuel types depending on the thermodynamic cycles. Therefore, fuels can be demonstrated in different properties with each other. For example, gasoline fuels should have a high ignition resistance, while diesel fuels should have well self-ignition. For these reasons, hydrocarbon fuels can be converted by some chemical process depending on the engine types or by improving fuel properties. Thus, new fuel formulas or various fuel properties can be improved by converting hydrocarbons each other via some of the chemicals process.

Diesel and gasoline engine fuel properties such as cetane number, octane number, viscosity, and density can be improved by fuel additives. One of the most promising fuel additives are alternative fuels in the future. High octane number and low density propensities of the alcohols lead to be improved the fuel properties such as increases the octane number of gasoline and decreased the viscosity, density properties of the diesel fuel. Besides, the diesel fuel cetane number can be improved by biodiesel, which has a high cetane number.

Nomenclature					
API bTDC CN HHV FS ID LHV LPG MON n RON rpm SI SIT θ γ ρ	American Petroleum Institute before top dead center cetane number higher heating value (kJ/kg) fuel sensitivity ignition delay (ms) lower heating value (kJ/kg) liquefied petroleum gas motor octane number engine speed (rpm) research octane number revolution per minute cetane index self-ignition temperature crank angle (°CA) specific heat ratio density (kg/m ³)				
,	7 (0)				

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