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# Quality and Trends of Automotive Fuels

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## Abstract

Automotive engines are designed to convert chemical energy to mechanical energy. The efficiency of this conversion is governed by thermodynamics. The two most common engines utilize gas oil and gasoline fuels for this purpose. However, the combustion processes are radically different. The combustion sequence and relative characteristics for both engine types will be discussed. Due to different combustion requirements, the fundamental properties of both fuels will also be examined as these are significantly different for the two fuel types. The main fuel properties discussed are energy density, stability, fluidity, corrosion, contaminants, safety, wear and environmental aspects. Also, with the advent of various renewable components in both fuels, new trends are emerging for both fuel quality assessments as these are molecularly distinct from their crude oil counterparts.

**Keywords:** combustion process, fuel properties, emerging trends

## 1. Introduction

Automotive engines are designed to convert chemical energy stored in the fuel to mechanical energy through combustion. Thus, the working fluids in the engine are the fuel and air with which it is mixed. The combustion process can be viewed to convert chemical energy of the reactants to thermal energy of the products. The thermal energy translates into higher temperature and pressure in the combustion chamber which in turn is converted to work by the engine.

There are two main types of automotive engines which are classified according to how the ignition in the combustion chamber is induced. These are the spark ignition (SI) engine and the compression ignition (CI) engine which determine which fuel is fit for purpose.

It is worth noticing that the combustion of both types of engines are governed by the laws of thermodynamics. The first law states that internal chemical energy in the reactants is converted in heat added to the system and work done by the system. The second law precludes the possibility of a perfect engine where all the internal chemical energy is converted to work as some heat must be exhausted to the environment. Thus, engines are designed to extract the maximum amount of work and minimizes the heat release which improves efficiency.

In this chapter the two types of engines will be discussed which leads to the desired combustion characteristics of the fuels. However, combustion is not the only aspect to be tested for automotive fuels. In fact, the quality assessment performed on the fuels to ensure that, in addition to combustion, other aspects

of the fuel are properly measured such as energy density, stability, fluidity, corrosion, contaminants, handling, wear, composition and environmental aspects will be illustrated. Impact of additives and renewable components will also be discussed.

## 2. Gasoline automotive engines

The gasoline automotive engine works by injecting a mixture of gasoline and air in the combustion chamber and after compressing them the timing of the combustion is just as the piston arrives at the top dead centre (highest point in the combustion chamber). The combustion timing is induced by a spark which causes a rapid rise in temperature and pressure which in turn push the piston down again turning the camshaft which translates this rotational motion into linear motion used by the vehicle. Thus in an ideal engine the reactants would all ignite with the spark instantaneously and thus it is called the spark ignition engine.

This cycle is called the Otto-cycle which is shown as follows together with the relative P-V diagrams:

Intake stroke is performed by an isobaric (same pressure) expansion of fuel/air mixture represented by point 1 to point 2 (**Figure 1**).

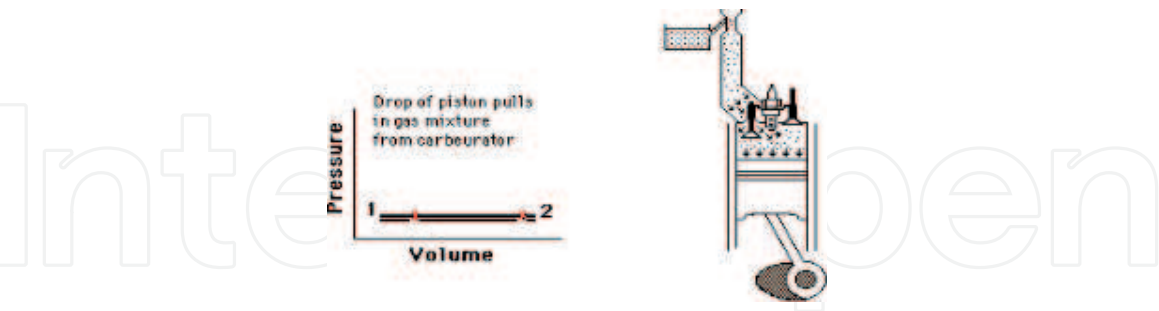
Followed by an adiabatic (no heat exchange) compression stroke represented by point 2 to point 3 (**Figure 2**).

Ignition starts power stroke isochoric (same volume) process shown by point 3 to point 4 (**Figure 3**).

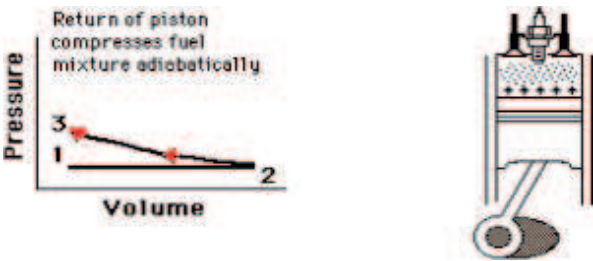
Adiabatic expansion process follows, characterizing the power stroke as per point 4 to point 5 (**Figure 4**).

The exhaust stroke is characterized by isochoric (constant volume) cooling compression processes as per point 5 to point 6 (**Figure 5**).

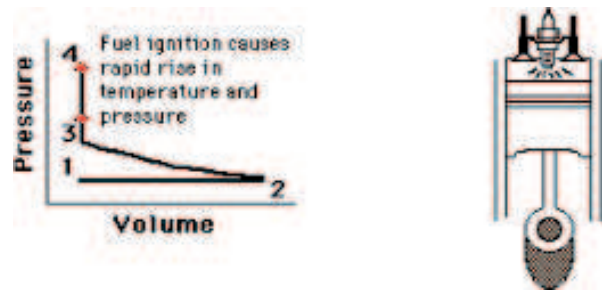
And the cycle is completed by an isobaric compression as represented from point 6 to point 1 (**Figure 6**).



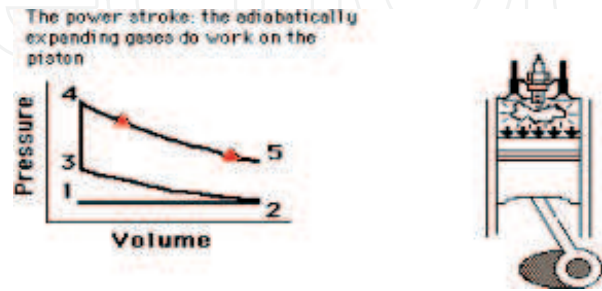
**Figure 1.**  
*Drop of piston pulls in gas mixture from carburettor.*



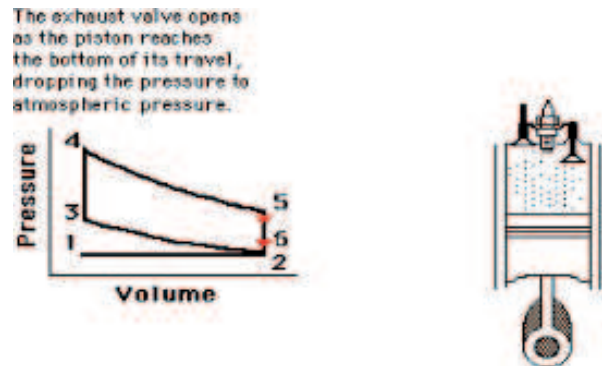
**Figure 2.**  
*Return of piston compresses fuel mixture adiabatically.*



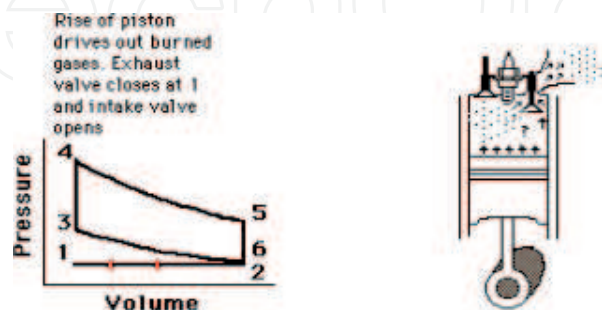
**Figure 3.**  
*Fuel ignition causes rapid rise in temperature and pressure.*



**Figure 4.**  
*The power stroke: the adiabatically expanding gases do work on piston.*



**Figure 5.**  
*The exhaust valve opens as the piston reaches the bottom of its travel dropping the pressure to atmospheric pressure.*



**Figure 6.**  
*Rise of piston drives out burned gases. Exhaust valve closes at 1 and intake valve opens.*

### 3. Gas oil automotive engine

The gas oil automotive engine injects only air at the start of the cycle. This is compressed and consequently the temperature also rises. Ignition is induced by timing of the fuel injection in the hot air already in the combustion chamber. The

fuel can be heated by a glow plug before injection to enhance efficient combustion. As the air temperature and pressure inside the combustion chamber are designed to be above the fuel's ignition point, spontaneous ignition of the most combustible components commences. This in turn induces combustion in the balance of the components. This is called compression ignition engine and relies on the spontaneous combustion as given temperatures and pressures.

Note that while spontaneous ignition is not desirable in spark ignition engine, it is the basis of compression ignition engines. The ideal diesel cycle is shown as follows together with the relative P-V diagrams:

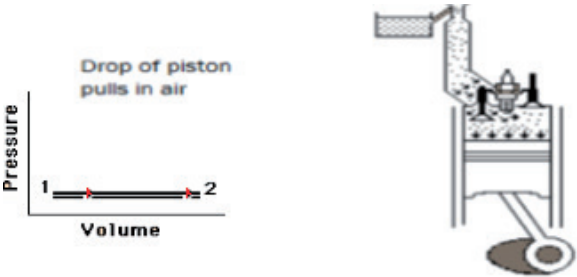
Intake stroke is performed by an isobaric (same pressure) expansion of air represented by point 1 to point 2 (**Figure 7**).

The air is compressed adiabatically (no heat loss) causing a rise in pressure and temperature from point 2 to point 3 (**Figure 8**).

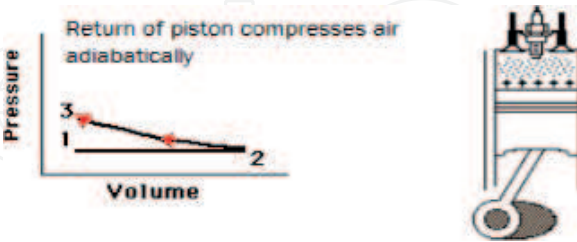
The fuel is injected and point 3 to point 4 represents a constant pressure heating following injection. This is caused by the initial combustion of the fuel which is a slow process compared to gasoline in the Otto cycle. Thus, an isobaric process is observed as opposed to isochoric in Otto cycle (**Figure 9**).

When the remainder of the fuel ignites the products force the volume in the combustion chamber to increase leading to the power stroke. This is shown in point 4 to point 5 (**Figure 10**).

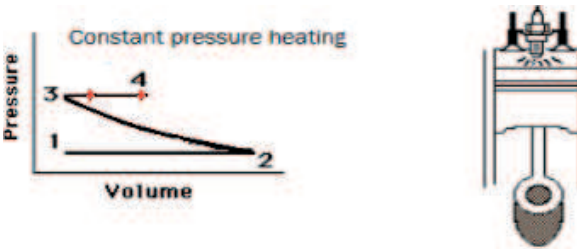
The exhaust stroke is characterized by isochoric (constant volume) cooling compression processes as per point 5 to point 6 (**Figure 11**).



**Figure 7.**  
*Drop of piston pulls in air.*

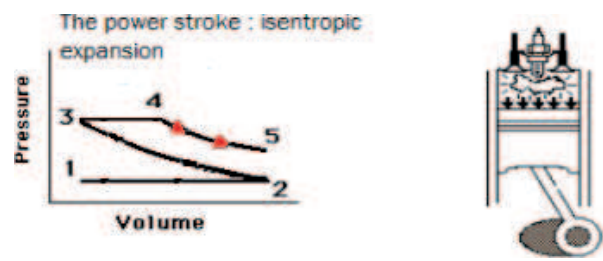


**Figure 8.**  
*Return of piston compresses air adiabatically.*

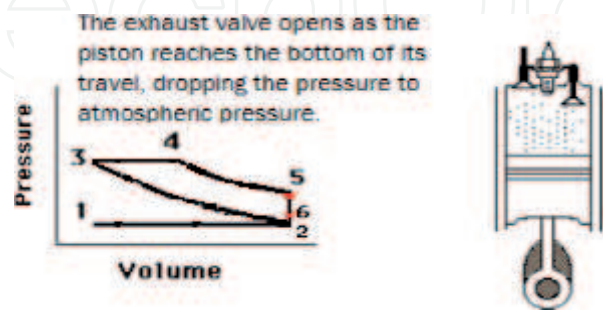


**Figure 9.**  
*Constant pressure heating.*

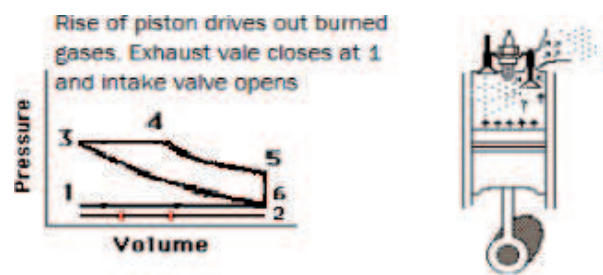




**Figure 10.**  
*The power stroke: isentropic expansion.*



**Figure 11.**  
*The exhaust valve opens as the piston reaches the bottom of its travel, dropping the pressure to atmospheric pressure.*



**Figure 12.**  
*Rise of piston drives out burned gases. Exhaust valve closes at 1 and intake valve opens.*

And the cycle is completed by an isobaric compression as represented from point 6 to point 1 (**Figure 12**).

#### 4. Combustion characteristics

As seen in the previous section, the main fuel characteristic which dominates both spark ignition engines and compression ignition engines is auto-ignition. Note that other engine design factors also come into play for auto-ignition such as combustion chamber pressure, temperature and compression ratio but we will focus on the fuel factors.

Auto-ignition is responsible for knocking in spark ignition engines. Two types of auto-ignition are known. Knocking is defined when the fuel spontaneously starts to combust in another area of the combustion chamber and the flame front clashes with the spark plug induced advancing flame front while pre-ignition is caused by hot surfaces in the combustion chamber rather than the spark plug. While knocking is the more common of the two auto-ignition types they both lead to uncontrolled combustion which, if severe, can cause major engine damage in a spark ignition engine utilizing gasoline fuel.

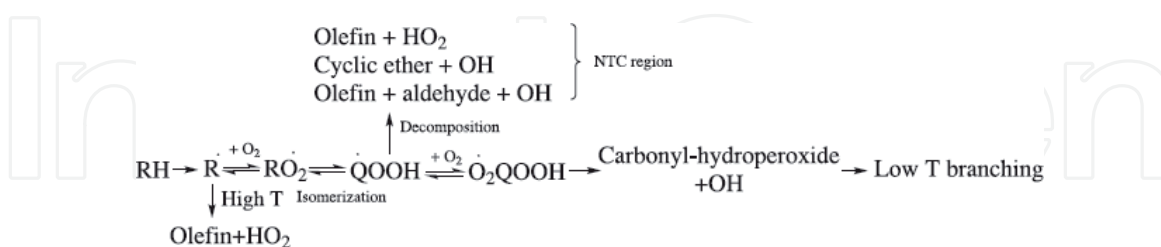
On the other hand, auto-ignition is a desired quality for compression engine using gas oil fuels. As the fuel is injected the faster the fuel starts combustion the more time it will have to completely burn. The time needed from when the fuel is injected in the combustion chamber to when it starts burning is called the ignition delay. The shorter the ignition delay the easier it is to start the engine, the lower the combustion generated noise and the lower the exhaust emissions of a compression ignition engine using gas oil fuel.

As fuels are composed of a mixture of hydrocarbons, the auto-ignition characteristics of each class will determine if they are more adequate to be used in a spark ignition engine or a compression ignition engine. The classes of hydrocarbons which mostly make up gasoline and gas oil fuels are paraffins (including n-paraffins, iso-paraffins and cycloparaffins), olefins and aromatics.

Based on the reaction mechanisms presented by Curran, Gaffuri, Pitz and Westbrook [1], the main reaction pathways for long chained paraffins can be drawn schematically as shown below (**Figure 13**):

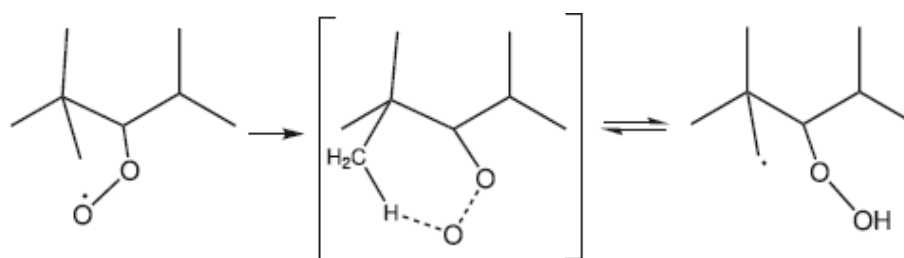
The main pathways are as follows (**Figure 14**):

1. Alkyl radicals  $R^\cdot$  are initially formed via hydrogen abstraction due to low activation energy.
2. This is followed by oxygen addition to produce alkylperoxy radicals  $RO_2^\cdot$
3. Next is the rate determining step where an internal hydrogen migrates to produce peroxyalkyl radicals  $Q^\cdot OOH$  isomers via a transition state composed of five to seven membered ring structures as shown below:
4. Peroxyalkyl radicals  $Q^\cdot OOH$  radicals subsequently react further with oxygen to form peroxyalkylhydroperoxide radicals ( $O_2Q^\cdot OOH$ ) at temperatures below 850 K or decomposes at higher temperatures up to 1200 K.
5. Decomposition reactions from 850 K to 1200 K lead to stable products such as hydrogen peroxide  $H_2O_2$  which slow down the reaction. At temperatures approach 1200 K  $H_2O_2$  decomposes into two reactive hydroxyl OH radicals. This



**Figure 13.**

Reaction mechanisms presented by Gurrán, Gaffuri, Pitz and Westbrook.



**Figure 14.**

Main paths of reaction mechanisms.

is called the negative temperature coefficient where the rate of reaction slowly increases in this temperature range.

6.  $O_2Q^{\cdot}OOH$  radicals, in turn, tend to abstract H atoms from the C atom which attached to the OOH group, producing  $Q^{\cdot} (OOH)_2$  radicals.
7.  $Q^{\cdot} (OOH)_2$  radicals yield OH radicals and carbonyl hydroperoxide species via isomerization and decomposition reactions as shown below.
8. OH and carbonyl radicals, accelerate the overall reaction rate leading to rapid low temperature chemistry.

Note that point 3. of this pathway requires a transition state of 5 to 7 membered structure. Thus iso-paraffins and cycloparaffins are less likely to form these transition states leading to longer ignition delays compared to n-paraffins (**Figure 15**).

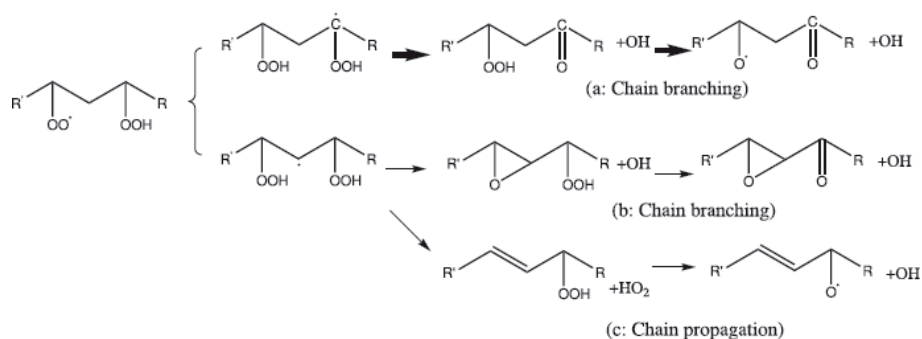
Olefins tend to have a slower combustion reaction rates than corresponding paraffins. In fact at low temperatures the double bond induces an addition reaction first which slows down the overall rate. At higher temperatures hydrogen abstraction tends to occur in an allyl site which leads to stable allyl radicals which also slows down the reaction. The rate decrease with respect to n-paraffins depends on the chain length and position of the double bond.

Aromatics' combustion rates are even slower than olefins. This is due to the delocalization stability of the  $\pi$  bond ring which makes addition, substitution and extraction of a hydrogen (as per point 1) tough. Thus low temperature combustion reactions are not observed for aromatics. At sufficiently high temperatures, electrophilic substitution and H abstraction reactions create a phenyl radical. This reacts with  $HO_2$  radical,  $O_2$  or O atom, to produce phenoxy radicals. This is a stable radical due to resonance but it is an intermediate for ring opening reactions at high temperatures. Note that low temperature combustion reactions increases for aromatics with side chains as paraffinic reactions occur in the side chain.

Thus the auto-ignition characteristics for the most common classes of corresponding hydrocarbons can be summarized as follows starting from the most prone to least prone:

Paraffins > iso – paraffins > cycloparaffins > Olefins > Aromatics.

Thus paraffins are the most adequate for combustion ignition engines due to their propensity for auto-ignition. In fact gas oil fuel tend to have a significant proportion of this class of hydrocarbons. Aromatics are the most adequate for spark



**Figure 15.**  
Main paths or reaction mechanisms – Carbonyl and -OH radicals.



ignition due to the lack of susceptibility of auto-ignition which make it ideal for gasoline fuel.

The cetane number test as per ASTM D613 is used for gas oils to measure the auto-ignition tendency. In fact a high cetane number indicates a short ignition delay from the start of injection to start of combustion. The higher the cetane number the longer the time available for complete combustion. Thus particulate matter and carbon monoxide emissions decrease.

Various derived cetane number equipments are available today (ASTM D6890, D7170, D7668 and D8183) which mostly exhibit improved precision limits. The cetane index is an estimation of the cetane number by calculation from distillation and density. Note that cetane number additives are not detected by cetane index calculations as the distillation and density are not altered.

Cetane number additives are thus promoting auto-ignition. They are organic nitrates (mostly 2-ethylhexyl nitrate and alkyl nitrate) or peroxides which start to auto-ignite early and thus induces the hydrocarbons to follow suit [2]. This reduces the overall ignition delay and thus increases the cetane number.

On the other hand, the RON by ASTM D2699 and MON by ASTM D2700 are used for gasolines in order to measure the resistance for auto-ignition. RON is the anti-knock performance at lower engine speed and typical acceleration conditions while MON reflects the anti-knock performance of a fuel under high engine speed and higher load conditions.

RON and MON additives are intended to inhibit auto-ignition which cause knocking. These additives decompose in the combustion chamber into a metal, metal oxides and hydrocarbon radicals which have a very limited lifetime. The metal and metal oxides role are to scavenge any radical intermediates which stops the auto-ignition in its tracks. Most common additives are based on lead, manganese and iron. Nowadays however the use of these additives is being limited on health grounds and are replaced by higher octane oxygenated components in the gasoline pool.

## **5. Energy density**

Energy density is the amount of energy stored per unit volume when the fuel is burned. The most influential factor for the determination of net calorific value for both gas oil and gasoline fuels is the density as this determines how much mass is available per unit volume. In fact, the fuel's density has a direct effect on engine maximum power output and volumetric fuel consumption. If density is reduced, heating value per volume decreases and engines need higher fuel volume in order to provide the same energy output.

Densities of different classes of hydrocarbons are influenced by:

- Intermolecular attractions (including polarizability)
- The three dimensional structure

Intermolecular attractions in n-paraffins are the relatively weak Van der Waals forces. These increase with chain length as there is more surface area per molecule and thus the density increases with carbon number.

Isoparaffins also have Van der Waals forces. These tend to be weaker than in n-paraffins as for an equivalent carbon number they have less surface area. Thus the densities of iso-paraffins are lower than for n-paraffins due to their three dimensional structure.

Hydrocarbon density at 20°C for comparison												
Carbon number	5	6	7	8	9	10	11	12	13	14	15	16
N-paraffin	0.630	0.664	0.683	0.702	0.719	0.730	0.740	0.750	0.756	0.760	0.769	0.773
Iso-paraffin: 2,2-dimethylalkane	0.590	0.648	0.674	0.691	0.711	0.724						
Cycloparaffins (no side chains)	0.746	0.777	0.810	0.831	0.849	0.857						
Alkylcyclohexane			0.770	0.788	0.794	0.800	0.804	0.808	0.811	0.814	0.816	0.819
Olefins: 1-alkene	0.641	0.673	0.697	0.715	0.733	0.741	0.751	0.758	0.766	0.779	0.776	0.781
Aromatics: n- alkylbenzene		0.880	0.866	0.866	0.863	0.860	0.859	0.858	0.857	0.856	0.858	0.855

**Table 1.**  
*Densities for comparison for the hydrocarbon classes discussed.*

Cycloparaffins also have similar forces to n-paraffins but they exhibit higher densities. This is due to stronger Van der Waals forces caused by their ring structure which allows for a larger area of contact. Their locked conformations also give an increased plane of intermolecular contact.

Olefins are characterized by the double bond. Since the relative  $\pi$  bond is more polarizable than the  $\delta$  bonds, the Van der Waals attractions in olefins are augmented by polarizability. Thus, olefin densities are higher than n-paraffins but still lower than cycloparaffins which are enhanced by their structure.

Aromatics have a delocalized  $\pi$  bond system which further increases the polarizability and thus intermolecular attractions. Also, benzene rings must be flat in order to allow the p orbital overlap for all six carbons. This is a more compact structure than other hydrocarbons and contributes to increased density (**Table 1**).

Even though gasoline has got more aromatics (the highest density hydrocarbon) than gas oil the densities are lower due to the shorter chains. In fact, gasoline cuts typically range between C5 and C12 while gas oils range from C10 to C25. The requirement to narrow the density range of automotive fuels is driven largely by engine manufacturers to improve fuel economy and combustion through fuel management systems by regulating the fuel to air mixture to values at least 20% lean of stoichiometric. Lower density would imply a lower energy density and thus poor fuel economy and rough engine idle. A higher density would result in increased emissions due to incomplete combustion. Reductions in the upper limit have generally been for the purposes of limiting heavier aromatic components, thereby reducing emissions, principally particulates. This effect is also achieved to some extent by control of the high end of the distillation curve. The higher content in aromatics in gasolines lead to higher octane numbers (better combustion) and in contrast the higher content in paraffins leads to higher cetane numbers (better combustion and less harmful emissions in general).

## 6. Stability

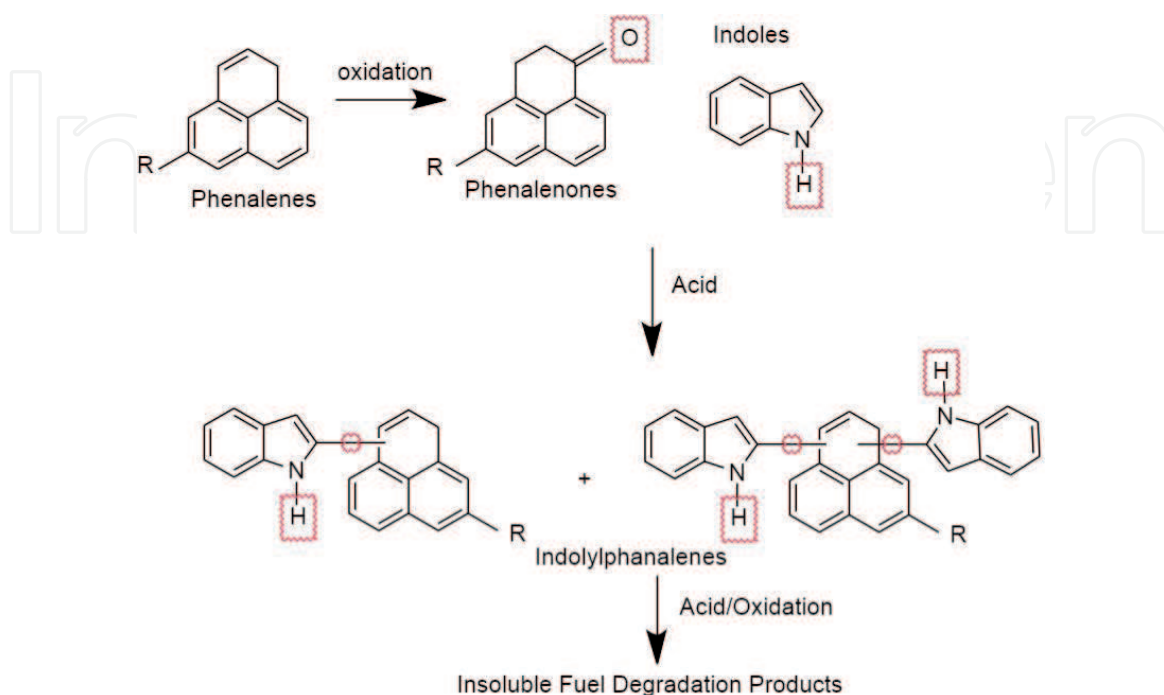
All petroleum products will degrade when exposed to certain environmental conditions such as high temperatures, oxygen, mechanical shear, and UV exposure. This degradation will often cause plugging of filters and engine deposits. Instability involves the chemical conversion of precursors to species of higher molecular weight with limited fuel solubility and tend to be nitrogen- and sulfur containing compounds, organic acids, and reactive olefins. The number and rate of these deleterious reactions depends on the concentration of reaction precursors, the concentration of oxygen, catalytic species presence (such as metals), the light intensity and storage temperature.

Oxidation stability is a measure of the fuel's resistance to degradation by oxidation. In the oxidation stability test, the automotive fuel is subjected to conditions which promote oxidation (by subjecting the fuel to oxygen and an elevated temperature for a fixed time). The pressure is monitored for gasoline by ASTM D525 (or equivalent ISO7536 [3] and IP40 [4]) as pressure drops when smaller gasoline molecules oxidize to form larger and less volatile ones. As gas oils are not so volatile, the product after oxidation is cooled and the total insolubles are measured by ASTM D2274, D4625, D5304 and UOP413. These methods differ in oxygen administration technique (continuous bubbling or by pressure vessel), oxidation time and testing temperature. ASTM D2274, D5304 and UOP413 are rapid screening tests used for comparative purposes for evaluation of the tendency to form sediment in storage. In order to accelerate the oxidation process the testing temperatures used are 95°C, 90°C and 100°C respectively. ASTM D2274 tends to be mostly used in current

specifications even though screening tests may not be fully representative of the aging process. ASTM D4625 is a much slower technique which takes up to 24 weeks at a temperature of 43°C. The degradation observed is much closer to real life conditions but is not adequate to be used in specifications due to the length of time required.

A myriad of chemical reaction pathways could be derived from various functional groups in the following mechanisms (**Figure 16**):

- In gasoline fuel, hydroperoxide initiated polymerization oxidation reactions with olefins to produce gums are the most common oxidation mechanism. Chain radical reactions generate oxygenated products such as hydroperoxides, polyperoxides, and carbonyls that have the potential to deposit gums. These reactions can be stopped with antioxidants which are essentially are radical scavengers that react with peroxy radicals and hydroperoxides.
- In gas oil fuel soluble macromolecular oxidatively reactive species (SMORS) may cause two fuels that, individually have good stability, to form a less stable blend when they are combined [5] (**Figure 16**). In this case, each fuel contains some of the precursors needed for the formation of higher molecular weight species. Only when the fuels are mixed are all the precursors available, enabling the conversion to proceed.
- The hydroperoxide oxidization of organo-sulfur compounds such as mercaptans to sulphonic acids. Sulphonic acids then subsequently catalyze reactions such as condensations between organo-sulfur and nitrogen compounds and esterification reaction leading both to incorporation of heteroatoms and a simultaneous increase in polarity and molecular weight and thus precipitation from the fuel. This is the slowest of the oxidation reactions because of the hydroperoxide induction period and the subsequent oxidation of the organo-sulfur compounds. Also, since sulfur is heavily restricted due to environmental concerns, this marginally contributes to instability in automotive fuels.



**Figure 16.**  
 Path mechanisms for insoluble fuel degradation products.



- A well-known oxidation mechanism in gas oil fuels is the acid-catalyzed conversion of phenalenones and indoles to complex indolylphenalene salts. Phenalenones are formed by oxidation of certain reactive olefins; indoles occur naturally in certain blend components of diesel fuel. The required organic acid is either present in a blend component or is generated by the oxidation of mercaptans to sulfonic acids as shown below.

ASTM D 6748 test method can be used for gas oil fuels to determine potential instability caused by phenalenes and phenalenones to determine the potential for storage instability.

## **7. Fluidity**

Fluidity encompasses all aspects of the ability of the automotive fuel to flow. This encompasses the fuel's characteristics when it is moved when in liquid state and what happens when it is cooled. These properties are measured by viscosity (ASTM D445) and cold flow properties where viscosity is a measure of the fuel's resistance to flow and cold flow properties (cloud point, CFPP and pour point) describe the fuel's reaction on cooling.

Viscosity is determined by the intermolecular structure. Thus, the same considerations for density apply where viscosity is dependent on composition and temperature at which it is measured. N-paraffins have the lowest viscosity (as intermolecular interactions are the weakest Van der Waals forces) while the aromatics have the highest viscosity (as they are polarizable). Also, the longer the chains the greater the intermolecular forces, and thus the higher the viscosity. As gas oil fuel typically is in the C10 to C25 range compared to gasoline fuel, which is C5 to C12, gas oil fuels have a higher viscosity. In fact, gasoline's viscosity is so low that it is not normally requested in specifications.

Both a minimum and maximum are normally specified for viscosity at 40°C for gas oil fuel. This is done as the pump which carries the fuel from the fuel tank to the combustion chamber are either mechanical pumps (such as a diaphragm pump) or electrical pumps which deliver a constant pressure on the fuel. Thus if the viscosity is too low excessive fuel may be delivered resulting in incomplete combustion. This would increase the fuel consumption and result in harmful exhaust emissions. On the other hand, if the viscosity is too high flow rates can reduce to an extent where insufficient fuel is being delivered to the engine resulting in difficulty in start-up.

Cold flow properties measure the characteristics when the sample is cooled. In addition to intermolecular forces, these are also greatly determined by molecular symmetry. Since molecules in the liquid state are crystallizing into a solid, ability to pack well into a crystalline lattice is of fundamental importance. In fact, n-paraffins tend to be the main contributors to cold flow properties as they are symmetrical when compared to iso-paraffins or cycloparaffins and aromatics with side chains.

Once again the short molecular structures of gasoline fuel precludes cold flow issues while there are three cold flow properties which can be performed for gas oil fuel. These are:

- Cloud point by ASTM D2500, D5771, D5772, D5773 and D7689 where the wax crystals first appear out of the fuel.
- CFPP by IP309 [4], EN116 or ASTM D6371 where the wax crystals continue to increase in size on progressive cooling and block a 45 µm filter up to specified conditions. This is intended to mimic clogging of fuel lines.



- Pour point by ASTM D97, D5949, D6749 or D7346 where the wax crystals forms an interlocked 3D network lattice big enough to trap the remaining liquid. This prevents the fuel from moving and thus no fuel can be transported.

Cold flow improvers can be added to improve low temperature performance of the gas oil fuels. These consist of different types of polymeric materials of hydrocarbon chains and polar segments. The polymers' hydrocarbon chains provide interactions with the gas oil's paraffin segment while the polymers' polar groups are responsible for modifying the wax crystals. This results in a sort of scaffolding where wax crystals are not allowed to agglomerate resulting in crystal morphological changes. There is no universal additive for all gas oils and the choice of additive would depend on the interaction of the additive with the particular fuel.

## 8. Corrosion

Corrosion in automotive fuels is normally caused by acids. An important distinction is that weak organic acids can be present in the crude oil itself and thus carried over to automotive fuels. However strong inorganic acids are not found in crude oils. These are used by various refinery processes and should be removed thereafter. Thus, detection of strong acids is a clear sign of contamination while weak acids could originate from the crude oil.

Total acid number (TAN) by ASTM D974 is defined as the amount of milligrams potassium hydroxide (KOH) required to neutralize all acid compounds in 1 g of oil sample. This test determines the amount of soluble or nearly soluble acids in a sample dissolved in a toluene and 2-propanol mixture. The higher the TAN, the more corrosive the fuel possibly is. However, TAN does not distinguish between different acid strengths and further investigation related to the proportion of acids molecules which have dissociated into cations and anions could be required if a fuel is found to have high TAN.

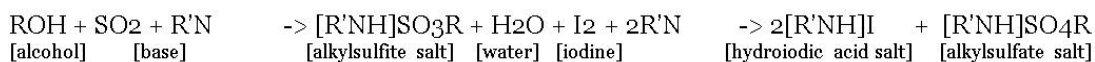
Normally corrosiveness in both automotive fuels is measured by copper strip corrosion measured by ASTM D130. Corrosion can affect metallic components in vehicle fuel systems, dispenser pumps and fuel storage systems and is related to the fuels' acidity. The test procedure uses a strip of polished copper which is immersed in a sample of the fuel and heated to a stated temperature for a prescribed time. The degree of corrosion is measured by comparing the staining with a reference sample.

## 9. Contaminants

The most common contaminants for automotive fuels are water and particulate matter which can be picked up in the distribution system.

Water can accumulate in the fuel due to leaks or condensation in pipelines. Since liquids are held together by intermolecular forces the hydrocarbon solvent molecules would have to overcome these forces in the water solute in order to find their way between the solute molecules. This process is most efficient when the intermolecular forces of solvent and solute are similar. As water is a polar molecule (while hydrocarbons are not polar) its solubility in hydrocarbons is limited. In fact, oil and automotive fuels do not mix well because the water molecules are strongly attracted to each other and will not allow the weakly attracted oil molecules between them.

Although the degree of water solubility depends on composition, the bigger the density variance the lower the solubility is expected. For example, water solubility in unoxxygenated gasoline fuel is expected to be lower than gas oil fuel with

**Figure 17.**

Main paths of reactions for water detection in fuels.

no biofuel as the hydrocarbon molecules are smaller and thus have less intermolecular forces when compared to the polar water. Water is thus not a contaminant which greatly effects gasoline, but it must be monitored for gas oil fuels as it may cause injector and piston groove deposits and corrode engine components. This is achieved by Karl Fisher technique where the reaction below is used to measure water. As water and iodine are consumed in a 1:1 ratio in the below reaction, when all of the water present is consumed, the presence of excess iodine is detected volumetrically by the titrator's indicator electrode. That signals the end-point of the titration (**Figure 17**).

Another source of contamination is particulate matter. This encompasses any solid material which finds its way to the automotive fuel during transportation. The most common would be rust particles which could plug filters and injectors and thus starves the engine of the required combustion energy for optimal operation. This parameter is tested in gas oil fuels gravimetrically by EN12662 or IP440 [4] where the fuel is filtered through a glass fiber filter of 0.7  $\mu\text{m}$  porosity. Thus, particles larger than 0.7  $\mu\text{m}$  are trapped and weighed in percentage of the fuel filtered.

Appearance by ASTM D4176 is quick indicator of water and particulate matter. A rough indication is that 200 ppm of water at 20°C is expected to be the threshold for water retention in gas oil fuel not containing biofuels. The test method also specifies to observe and report any particulates in the sample.

It is worth noticing that when oxygenates are added to hydrocarbon based mineral fuels the water retention is greatly increased. This is due to the increased polarity of the oxygenates such as esters (biodiesel) in gas oil which are better suited to interact with the water molecules. This increased interaction leads to a much higher water retention threshold for biodiesel to about 1500 ppm at 20°C. When the biodiesel is then mixed with mineral gas oil the overall blend could become hazy as the water retained in the biodiesel is not soluble in the mixture.

## 10. Safety

During storage and transportation one of the main concerns is the volatility of the fuels. This is directly linked with the intermolecular forces acting on the various classes of hydrocarbons. As discussed in the Energy density section, aromatics have the strongest forces. However, gasolines are very volatile when compared to gas oil fuels due to their shorter chains.

At ambient temperature gasoline fuels are considered as volatile products. Thus, gasoline fuels are stored and transported in an inert atmosphere by removing oxygen and preventing combustion. The test which controls the volatility of gasoline fuels is the RVP which is normally tested by ASTM D5191. ASTM D5191 determines the total vapor pressure exerted in a vacuum by air-containing chilled, air-saturated, volatile, liquid petroleum products. This test method is performed at 37.8°C (100°F) at a 4:1 vapor-to-liquid ratio (internal volume that is five times that of the total test specimen introduced into the chamber). The sum of the partial pressure of the sample and the partial pressure of the dissolved air is obtained. The dry vapor pressure equivalent (DVPE) is calculated by removing the partial pressure exerted by the water vapor in the air.

Alternative methods are available such as ASTM D323, D4953, D5190, D5482 and D6378. D323 is a manual procedure where a chamber is filled with air saturated sample and immersed in a bath at 37.8°C (100°F) until a constant pressure is observed. D4953 is a modification of D323 where the interior surfaces of the liquid and vapor chambers be free of water. Hence, this method is often referred to as the Dry Reid method. D5190 and D5482 are very similar to D5191, with the exception that the test chamber is not evacuated at the start of the test. D5482 employs a small volume test chamber. D6378 is also similar to D5191 with the exception is the fact that air-saturation and chilling of the sample is not required. The relative bias correlating D6378 to D5191 is also known.

RVP also affects starting gasoline fuels performance, warm-up, and tendency to vapor lock with high temperature or high altitudes. The RVP results can be converted to the true vapor pressure at ambient conditions by API MPMS Ch 19.4 or AP-42 by EPA formulae which is a prerequisite to determine if a storage tank or vessel tank are adequate for storing a volatile product.

As gas oil fuels are less volatile, the temperature at which they can ignite when exposed to a flame is tested. This is the definition of the flash point which is normally tested by closed cup Penske Martens by ASTM D93. Note that flash point has no relationship with the combustion characteristics and is used only as a safety measure. In general the temperature of the product is kept at least 10°C below the flash point during storage and transportation in order to ensure that the product cannot combust.

Other concerns are also addressed by limiting the total aromatics in gasoline. Benzene is the simplest aromatic compound but others common in gasoline include toluene and xylene. As aromatics, particularly benzene, are known to be carcinogenic. They are limited in gasoline fuel and not in gas oil since aromatics are resistant to auto-ignition and cetane number specifications would not be met for highly aromatic gas oils. For the same reason they are desirable for gasoline fuels and thus they are limited as this is the most practical way of limiting human exposure to these substances from evaporative losses and in exhaust emissions.

Alternative high octane products are used in substitution of aromatics such as oxygenates and olefins. Both come with limitations though as olefins induce instability and thus adversely affect oxidation stability test while oxygenates can impact RVP. In fact mixing ethanol and mineral gasoline may increase evaporative emissions. The relationship between vapor pressure and ethanol content of a blend is non-linear as the hydrogen bonding previously holding the ethanol molecules together are greatly reduced when the ethanol is blended as mineral oil gasoline is devoid of oxygen. Thus, the mixture may have a higher vapor pressure than either product alone.

## 11. Wear

Automotive fuels protect some moving parts such as fuel pumps and injectors from wear. This is achieved by forming a layer between the moving parts thus not allowing the metal to metal contact which would otherwise result, and it is measured by the lubricity test. As gasoline fuel is composed of shorter chains this ability to form a layer between moving surfaces is less efficient. However, spark ignition engines inject the gasoline fuel and air mixture upstream of the combustion chamber and thus operates at low pressures. However, gas oil fuel is injected directly in the combustion chamber containing compressed air. Thus, compression ignition engines require a much higher degree of lubricating property. In fact lubricity is only tested for gas oil fuels with ASTM D6079 using a high frequency reciprocating



rig (HFRR) technique. This uses a laboratory rig to measure the effective wear than can be expected by determining a wear scar diameter in microns ( $\mu\text{m}$ ). The specification is a maximum wear scar diameter of 460  $\mu\text{m}$  (microns) at 60°C.

The ability of automotive fuels to form a protective layer is given by their propensity to stick to the metal surfaces. Therefore it is only natural to expect polar compounds to have this property as non-polar hydrocarbons would not have any means to interact with the metal surface. In gas oils the most polar compounds are oxygen and nitrogen containing compounds. Lubricity does not tend to be an issue for high sulfur gas oil fuels derived from atmospheric crude oil distillation as these compounds were providing adequate protection.

However lubricity issues were first noted when ULSD was first used in 1991 by sulfur removal via hydrodesulphurization (HDS) in Sweden. It was discovered that while HDS removed sulfur (to the benefit of the environment) it also attacked these oxygen and nitrogen containing compounds which imparted lubrication resulting in pump and injector failures. This required suitable additives to be added to the gas oil to restore the lubrication. It is to be noted that these polar additives must be injected at moderate doses to reach the specification limit as if their concentration is too high they can have adverse effects such as fuel injector deposits, water separation problems, or premature filter plugging.

Gasoline fuel is a blended product from a variety of sources such as isomerase, reformate, alkylate, dimate or polygasoline and catalytic naphtha which do not contain polar molecules. Thus, such blends are bound to have a lubricity higher than the gas oil specification mentioned. Even though lubrication is less important for spark ignition engines it could still cause long term wear. However, antiknock properties is conveyed by metal containing additives or by oxygenates. Both of these also impart the minimum lubricity needed. This parameter was tested in gasoline fuel and found that anti-knock additives like the ones used in LRP gasolines in 2000 enhanced the lubricating ability of these gasoline fuels (lower wear characteristics than bulk gasoline samples). Also, MTBE and ETBE lower the wear with optimum percentage in commercial gasolines around 8 to 9% per volume. Gasoline lubricity is a complex phenomenon, involving many complicated and interrelated factors, such as the presence of water, oxygenates diolefins, diaromatics, the effect of viscosity and the synergistic effect of different wear mechanisms. The lubricity mechanism of gasoline is quite different from that of diesel fuels that leads to severe adhesive wear. With low-sulfur fuels, adhesive wear is observed instead of corrosive and mild oxidative wear, and deposits build up on top land.

Metallurgy and mechanical properties of test specimens have important effects on the lubricating mechanisms of fuels. When the hardness of the lower specimen in an HFRR test is not enough to support the generated oxide films formed by the reaction between surfaces and dissolved oxygen and the adsorption films formed on top of the oxide films by gasoline polar impurities, severe adhesion and metal transfer occur.

Lubricating properties are also influenced by the relationship of viscosity to applied pressure termed as ' $\alpha$ '. The  $\alpha$ -values of toluene and normal alkanes in gasoline boiling range are significantly lower than those of corresponding diesel fuel components. The  $\alpha$ -values of these gasoline components are almost temperature independent in moderate temperature. In contrast, the  $\alpha$ -values of long chain hydrocarbons (diesel fuel components) decreases significantly with increasing temperature. In general, the  $\alpha$ -values of gasoline and diesel fuel obtained using film thickness results are about 20 percent lower than corresponding average  $\alpha$ -values of their main components.

Although the variation of film does not seem to be related to the value of the corrected wear scar diameter in the case of the mixtures of gasoline refinery streams, some of the categories of the refinery streams separately present the value of the corrected wear scar diameter (CWSD1.4) to decrease exponentially with increasing

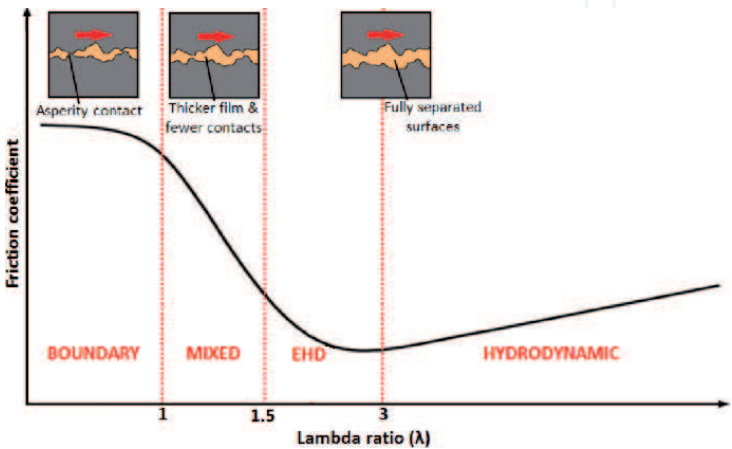
of the lubricating film, such as the refinery streams from the isomerisation, reformation and dimerization unit. Generally there are two areas of film variation with the corrected wear scar diameter, where in the first region is observed a relative reduction in film increasing the corrected wear scar diameter to 900  $\mu\text{m}$ , while for higher values of the corrected wear scar diameter is observed a relative increase of film, but there is not a sufficiently high correlation observed. It was carried out numerical analysis for finding the optimum rate of addition for the 7 different refinery streams according to the maximum and minimum addition, as it was obtained from the data of 36 gasoline blends. The optimum addition rate is following the mixing rules that prevail in modern refineries and specifically an optimum rate of 35% for the stream of catalytic cracking FCC unit and 26% for the stream of catalytic reformer unit were observed. The methodology used to measure gasoline lubricity is the ASTM G133 standard test method for linearly reciprocating ball-on-flat sliding wear [6] (**Figure 18**).

The lambda ratio ( $\lambda$ ) is the ratio of minimum lubricant film thickness ( $h$ ) to composite surface roughness ( $\sigma$ ) which correlates with surface contact fatigue. The interface between mixed and boundary lubrication is far more questionable. In 1990, Schipper demonstrated that some micro-EHD (elastohydrodynamic) occurs in lubricated concentrated contacts even down to a lambda ratio value of 0.03. More recently ultra-thin film interferometry in conjunction with friction measurements have demonstrated that the transition from mixed to boundary lubrication can occur at even lower lambda ratio value, probable approaching to 0.01.

For the diesel fuels, friction/film thickness shows the classical Stribeck behavior and illustrates that full, speed-independent friction is reached with in the film thickness range studied. (The further drop in friction at high speed is generally considered to result from heating of the EHD film in the contact). For gasolines, the friction/film thickness plots show no sign of leveling at high film thickness.

The composite surface roughness in the MTM test was approximately 30 nm, so the maximum film thickness reached of 20 nm corresponding to lambda ratio of about 0.7. This indicates that the gasolines are probably not reaching full boundary lubrication even at the highest speed -they are still in the mixed regime [6, 7].

From 1990's fuel quality improvement has become the most important subject for automobile industry, because it is the key factor for the energy saving and the reduction of  $\text{CO}_2$ , one of the most harmful greenhouse effect gas. In order to meet this requirement, energetic research activities started to establish the direct injection gasoline engine technologies that can be applied to the practical engines in the real world. It has been a common target of research activities to develop a direct



**Figure 18.**  
*Variation of friction coefficient with film parameter ( $\lambda$ ).*



injection gasoline engine realizing greater fuel economy compared with a diesel engine at partial loads and to realize better performance than the conventional MPI (Multi Point Injection) engines at high loads. In order to realize its fuel economy potential, the direct injection gasoline engine should be operated unthrottled in an extremely lean condition by distinctively stratifying the charge. In order to achieve its higher performance potential at high loads, the direct injection gasoline engine should be operated under stoichiometric or slightly rich conditions. When the charge is stratified, soot is generated in the rich zone. Sufficient excess air should be provided around the combustion zone containing soot, in order to burn-up the generated soot. Therefore, when the average mixture strength is stoichiometric or slightly rich, that is when the equivalence ratio is larger than unity, the mixture should be homogenous to suppress the soot formation. Additional pressure through pump and injection might generate issues on gasoline lubricity in the future [8].

## 12. Composition

In a refinery process the atmospheric and vacuum distillation are the first steps for separation of crude oil into various fractions or “cuts” which are composed of large numbers of hydrocarbons. These cuts have specific boiling-point ranges and can be classified in order of decreasing volatility into gases, light distillates, middle distillates, gas oils, and residuum. Modern refineries are much more complex and are able to extract a variety of streams from cracking processes. These are carefully distilled to fit into the required cut boiling points making this parameter as a primary selection criteria for automotive fuels.

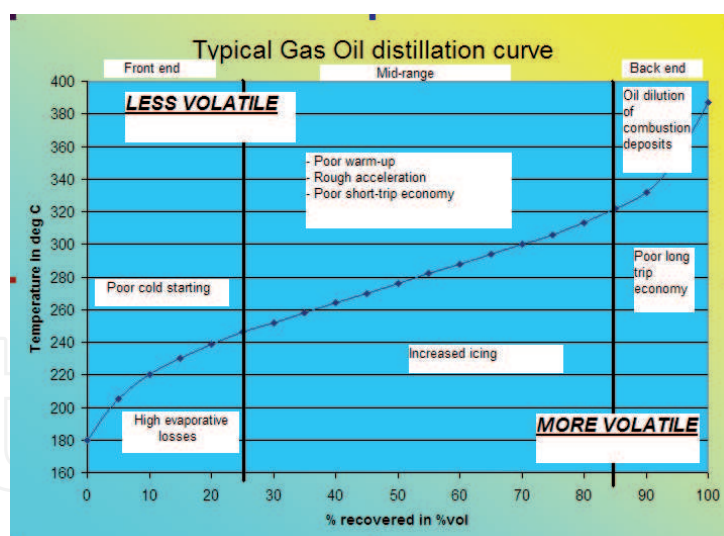
Both the volatile and heavy components in automotive fuels are needed and thus a distillation curve is tested by ASTM D86 to ensure that all the requirements are met. The distillation curve is the temperature vs. percentage volume recovered. It is related with the volatility and flash point of the fuel initially and with density at the back end as the high boiling point components tend to be long chain and/or aromatic which increases the density.

The distillation curve can be split in three for a better understanding [9]. The front end is typically the first 25% recovered, the next 60% is the mid-range while the final 15% is the back end which are all regulated (**Figure 19**).

If the front end is too volatile it would incur evaporative losses and flash point issues for gas oil fuel and high RVP for gasoline fuel. If gasoline fuels are too volatile they could also vaporize in the fuel lines when the engine is hot impeding fuel flow (known as vapor lock). If less volatile combustion on a cold day would be problematic as the fuel would not vaporize easily.

The bulk of the curve is the mid-range. If this section is too volatile the majority of the chains would be composed of shorter chain molecules and thus would tend to have poorer cold properties for gas oil fuels and increased icing tendency for gasoline fuels. If it is not volatile enough it would release less chemical energy and it would incur in poor warm-up time, rough acceleration and poor short trip economy.

The last section deals with the heaviest components. If these are too volatile poor long trip economy would result as these give the highest combustion chemical energy release. If this is not volatile enough these heavy components would result in increased incomplete combustion that would give soot or smoke in the exhaust emissions. These heavier components have more potential for incomplete vaporization and combustion and limiting the high-end temperatures reduces their proportion giving cleaner burning. The products left after incomplete combustion can cause oil dilution and increased cylinder wear and may lead to combustion chamber and inlet system deposits and spark plug fouling in spark ignition engines and injector deposits in compression



**Figure 19.**  
Chart illustrating the effects of having more or less volatile components in the gas oil pool.

ignition engines. Note that the end point in a gas oil fuel is related to the polyaromatic hydrocarbon content which typically have the highest boiling points.

### 13. Environmental aspects

Environmental specifications include RVP in gasoline to control evaporative emissions. The specifications recognize that the ambient temperatures varies in different regions and thus allows for various ranges.

Another environmental aspect which has been regulated is the sulfur content. Sulfur in automotive fuels is converted to sulfur dioxide and small amount of sulfur trioxide. If released to the atmosphere, they will form acid rain. Sulfur trioxide and dissolve in water to form sulfuric acid that will cause engine corrosion. However, the main contributor to sulfur reduction in automotive fuels is environmental as only 1 to 3% of sulfur dioxide is oxidized to sulfur trioxide in the combustion chamber. Sulfur occurs naturally in crude oils and must be removed to an acceptable level during the refining process by hydrodesulphurization (HDS) as previously discussed for effects on lubricity. The current specification for both automotive fuels is set at 10 ppm.

Sulfur in automotive fuel reduces the efficiency of catalytic converters as sulfur dioxide inhibits most gaseous heterogeneous catalytic reactions by strongly competing with the exhaust pollutants for space on the active catalyst surface [10].

Developing gasoline engine technologies such as gasoline direct injection (GDI) and lean burn will require advanced catalyst technology in order to control of hydrocarbons (HC), carbon monoxide (CO) and oxides of nitrogen (NO<sub>x</sub>) exhaust emissions [11]. Sulfur inhibition varies in degree according to the gasoline sulfur level, the catalyst formulation, catalytic function, combustion products from various air/fuel mixtures, and exhaust temperature range.

In compression ignition engines the diesel oxidation catalyst (DOC) is a fundamental device of exhaust after-treatment. Reduction of the NO<sub>x</sub> emission is achieved mainly by a significant delay of the fuel injection and using the high rates of the exhaust gas recirculation. However, these cause a significant increase in the emission of products of the non-complete combustion process i.e. carbon monoxide, hydrocarbons and particulate matter. In order to keep the emissions low it is necessary to eliminate such compounds by using the catalyst DOC which is able to oxidize CO and HC and the soluble organic fraction (SOF) of the particulate matter.

Thus, apart from its direct environmental detrimental effects, sulfur also contributes to formation of particulate matter (PM) in engine exhaust and affects the performance of vehicle emissions control equipment. It therefore has an indirect effect on emissions of carbon monoxide, hydrocarbons and NO<sub>x</sub>.

In gas oil fuels another environmentally regulated parameter is the polyaromatic hydrocarbons. These aromatics contain multiple benzene rings and their boiling points are in the gas oil range. PAHs contribute to particulate emissions while some PAHs such as benzo(a)pyrene are known to be carcinogenic. These tend to be the heaviest components in gas oil and are the slowest to burn due to their extended delocalization over several benzene ring systems. Thus, they contribute the most to incomplete combustion and thus to hydrocarbon and particulate matter emissions. The current specification has reduced the limit for PAH from 11mass% to 8mass% maximum which are tested using an HPLC technique. An additional indirect way to control PAH in gas oils is to limit the end point of the distillation curve. In fact, as PAH are the heaviest components in gas oil fuel, limiting the end point will also reduce the PAH content.

## 14. Renewable components

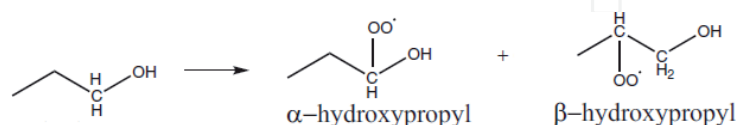
Mineral oil gas oil and gasoline fuels are derived from crude oil. This is a fossil fuel because it was formed from the remains of tiny sea plants and animals that died millions of years ago and thus cannot be regenerated. On the other hand, renewable components are any type of fuel with can be replenished and thus will not be depleted within the foreseeable future. They are part of a closed cycle and do not create a net surplus of carbon dioxide greenhouse gases when used. The most common are biodiesel and ethanol. Biodiesel is blended with gas oil fuel while ethanol and MTBE (as well as other oxygenates) are blended with gasoline fuel.

All renewable fuels contain oxygen. Thus, their combustion characteristics are significantly different from mineral oil derived fuels.

### Ethanol

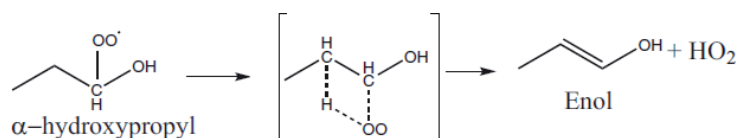
Ethanol is one of the main octane boosters used due to its high knock resistance. The presence of a hydroxyl group on the chain affects otherwise paraffinic chemistry scheme. The main combustion pathways are (**Figure 20**):

Hydroperoxyalkyl (RO<sub>2</sub>) radicals can now, besides isomerization to QOOH and subsequent low temperature branching reactions as for paraffins, also react via three other routes that compete with the chain branching reactions (**Figures 21–23**).



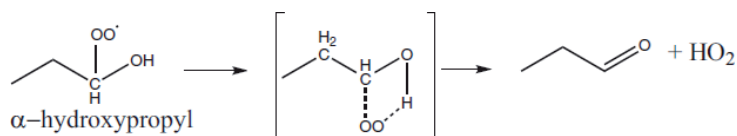
**Figure 20.**

*H atom abstraction favors C $\alpha$ -H, forming  $\alpha$ -hydroxypropyl sites radicals.*



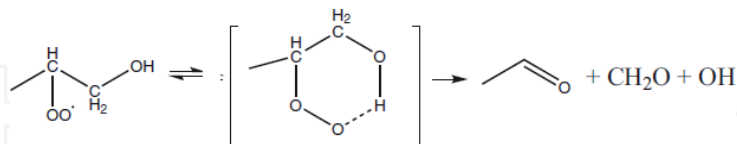
**Figure 21.**

*The first involves HO<sub>2</sub> concerted elimination of  $\alpha$ -hydroperoxyalkyl radicals, including one via a 5-membered transition ring, forming enol and HO<sub>2</sub>.*



**Figure 22.**

The second reaction concerns the formation of  $\alpha$ -hydroperoxyalkyl directly from carbonyl and  $\text{HO}_2$ .



**Figure 23.**

The third and final route occurs via Waddington type chemistry for  $\beta$ -hydroperoxyalkyl and involves H atom transfers from C-OH to C $\beta$ -OO radical sites, thereby producing two aldehydes and an OH radical.

Thus, low temperature reactivity of alcohols is greatly reduced by the presence of the hydroxyl group as radicals first have to form the enol or aldehyde/ketone intermediates. As for olefins this slows down the overall reaction rate. Branched alcohols with less paraffinic chain will have longer ignition delays and thus be the preferred octane booster.

When blending ethanol in gasoline particular attention must be given to RVP. Ethanol has a relatively low RMM but it is a liquid at ambient temperature due to a type of intermolecular force that is possible due to the hydroxyl radical. This is the hydrogen bonding where a hydrogen on one molecule is attracted to the lone pairs of an oxygen on another molecule. This is clearly seen when comparing the RVP of ethanol (having a molar mass of 46.07 and an RVP of about 2 psi) to a paraffin such as butane (having a molar mass of 58.12 and RVP of 51.7 psi). However, when blending ethanol in gasoline below 10%vol, the ethanol molecules are now separated by hydrocarbons and are thus unable to interact via the hydrogen bonding. Thus, ethanol molecules become very volatile and the RVP of the blend is higher than the highest component. When the ethanol percentage increases above 10%vol the ethanol molecules start encountering each other more often and hydrogen bonding starts to be restored thus lower the RVP again.

In order to accommodate increased ethanol use as an octane component both EPA and EN228 introduced ethanol waivers. These give RVP allowances on the upper limit in view of this occurrence. As RVP is related to the distillation, ethanol will also decrease the distillation points mostly up to the back-end section. Because of its effect on distillation it affects the driveability index (intended to control cold start and warm-up driveability) and the vapor lock index (intended to protect against excessive volatility in the lines, pumps and carburetors impeding flow).

Also, ethanol has an affinity for water as both molecules interact with hydrogen bonding. Thus care must be taken not have excessive water in the distribution system and storage [12]. If a gasoline/ethanol blend encounters excessive water, it can pull the ethanol out of the blend resulting in tank bottoms comprised of water, ethanol, and some hydrocarbon content. When the water is drained out this will result in a volume loss as well as an octane loss.

Finally ethanol in gasoline blends may cause the elastomers (namely Neoprenorubber, Nitrilerubber, hydrogenatedNitrilebutadienerubber (HNBR), and Polyvinylchloride/Nitrilebutadienerubber blend (PVC/NBR)) and two types of plastic materials (namely Nylon-66 and Polyoxymethylene) in vehicle fuel systems to swell and lose strength [13]. This would lead to failures of critical components such as fuel pumps, engine seals, gaskets, fuel system seals and hoses and promote risk of fire.



## Biodiesel

Biodiesel refers to the esters obtained by transesterification of triglycerides found in oils and fats. Biodiesel can be produced from different triglyceride sources such as vegetable oils (that can be edible, non-edible or waste oils [14]), animal fats (mostly edible fats or waste fats) and microalgae oil. The crops identified for biodiesel production are corn, sunflower, palm, olive, canola, soybean, rape and peanut oils. The main transesterification reaction for biofuel production is as follows (**Figure 24**):

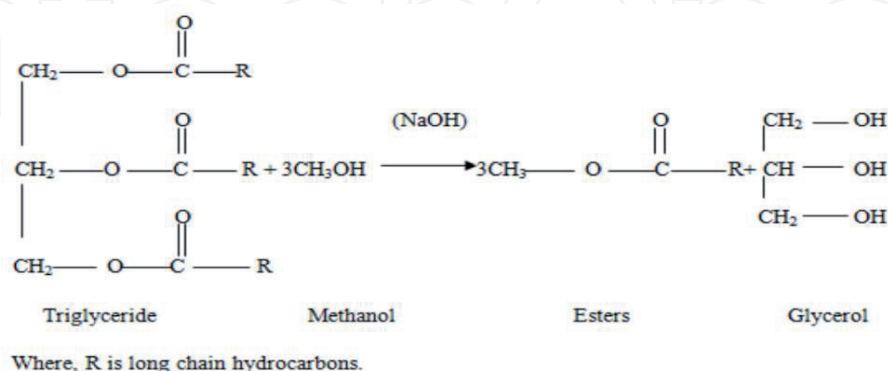
This conversion goes in three steps where triglycerides react with methanol to give diglycerides. These react with another methanol to monoglycerides. Finally monoglycerides react with a third methanol to five long chain esters (also called fatty acid methyl esters - FAME) and glycerol. European EN 590 specifications require gas oil fuel to contain a maximum of 7%vol biodiesel which must be compliant with the standard EN 14214 while US specifications ASTM D975 allows mixing commercial diesel oil with 5%vol biodiesel that meets the requirements of ASTM D6751.

Long chain esters (where the triglyceride R chain is from C8 to C20) are used as a blending component for gas oil fuels since the combustion ignition delay is generally long enough to be used for this application. In fact, esters display a paraffin-like reaction chemistry as their functional group provides an attractive site for H atom abstraction. These radicals are stabilized by resonance which slows down the reaction to yield an unsaturated ester which is resonance stabilized and thus has poor low temperature reactivity as follows:

Another reaction path is an elimination reaction involving a six-membered transition state producing olefins, small esters or acids. However, this is the preferred route only when the O-alkyl side is long. This clearly not the case for FAME as the O-alkyl side is the shortest possible (a methyl) (**Figures 25 and 26**).

Thus, the slow H atom abstraction is the predominant route for FAME which increase their ignition delay and consequently increase the cetane number. Note that branching effect reduces the activation energy needed for the six-membered transition state and thus straight chain and saturated R chains promote higher cetane numbers.

The main quality concerns for biodiesel are cetane number, cold properties and stability. As discussed, unbranched and saturated alkyl chains promote

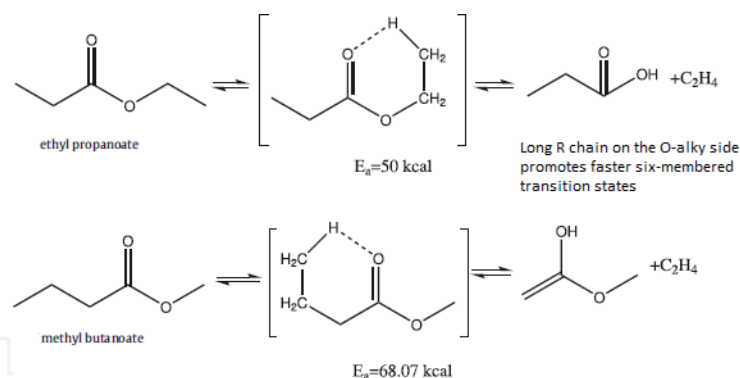


**Figure 24.**  
Transesterification reaction.

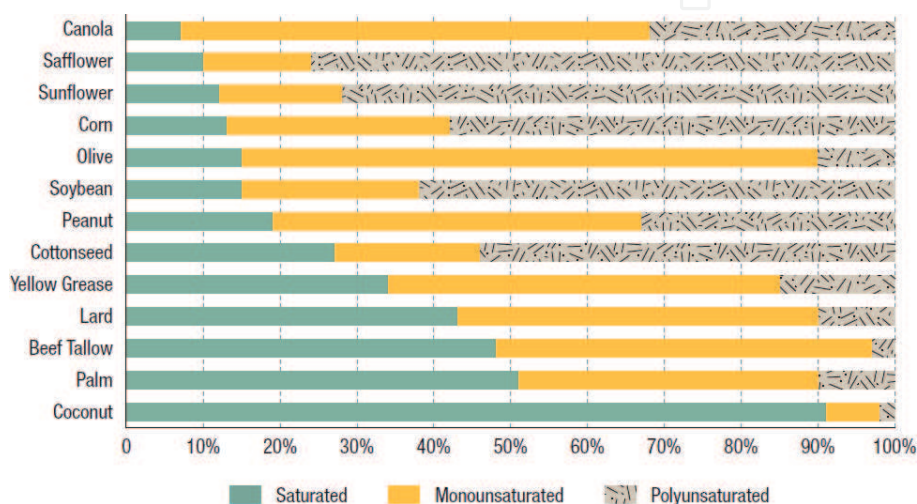


**Figure 25.**  
Stabilized resonance and poor low temperature reactivity.





**Figure 26.**  
Reaction paths for producing olefins, small esters or acids.



**Figure 27.**  
Each feedstock is set apart from the others because it is made of different proportions of saturated, monounsaturated, and polyunsaturated fatty acids.

cetane number. Saturation also promotes stability as olefinic sites promote oxidation reactions. However, saturation also promotes high melting points and thus leads to high cold properties. The middle ground is to have a monounsaturated FAME such as rape seed oil methyl ester which is composed of 63.9mass% C18:1 (alkyl group is 18 carbon atoms long having one double bond). However, as shown below (**Figure 27**):

Advantages of biodiesel are cleaner burning of engines, lower emissions, better lubrication of fuel injection pumps, safe due to high flash points, non-toxic and low volatility, spills are biodegradable, mixes well with mineral diesel and needs little engine adaptations [15]. However, disadvantages are cost, restricted shelf life, season sensitive, hygroscopic, housekeeping critical, filterability issues and could be foodstuff competitive.

Hydrotreating of oils and fats is a novel process for producing renewable paraffinic diesel, abbreviated HVO. In production, hydrogen is used to remove oxygen from the triglyceride vegetable oil or animal fat molecules. Hydrogen needed for the HVO process is today made from natural gas, but it could also be made from biogas or other renewable sources. When comparing HVO and biodiesel (FAME) production processes it can be concluded that both need about the same amount fossil feed i.e. hydrogen for HVO and methanol for FAME. However, HVO production is even more expensive than biodiesel.

According to research the latest twenty years the maximum allowable limit of biodiesel in gasoil fuels is 20% v/v named B20 without engine or other issues.

## 15. Conclusion

Internal combustion engines are still the most common means of imparting vehicular power even though lately electric and hybrid systems have emerged. Thus legislation is progressively becoming more stringent on various aspects regulating polluting exhaust and environmental impact which incentivize manufacturers to produce ever more clean and fuel efficient vehicles. As discussed direct injection gasoline technology has already been successfully employed to reduce fuel consumption and carbon dioxide emissions for the same power output. Further research on both fuels and combustion technology is currently underway to continue improving the environmental impact. Future work in LNG powered vehicles and homogeneous charge compression ignition (HCCI) are two areas where vehicles' power units can continue reducing environmental impact.

## Conflict of interest

The authors declare no conflict of interest on the information delivered in this chapter.

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