CHAPTER II

THEORETICAL CONSIDERATIONS

PETROLEUM REFINING : Distillation [2,3]

Refining consists of a series of steps by which the original crude oil is eventually converted into salable products in the amouts dictated by the market

A refinery is a variety of process (Scheme 2.1) which vary in number depending on the crude oil and the products required. The process must be selected and products manufactures to give balanced operation. A refinery must be flexible and have the ability to change operation as needed.

A refinery installation must also incrude all necessary non processing facilities; adequate tankage for storing crude oil, intermediate and finish products; a depenable source of electric power; materials handing equipment, workshops and supplies for maintaining continuous 24 hours a day, 7 days a week operation; waste disporsol and water treatment equipment; and products bleding facilities.

In the eary stage of refinery development, when illuminating and lubricating oils were the main products, distillation was the major, creased, conversion process were developed because distillation could not longer supply the necessary quantities.

Distillation has remained a major refinery process and it is a process to which just about every crude which enters the refinery is subjected. The most important and primary function of distillation in the refinery is its use for the separation of crude oil into component fractions (Table 2.1).

(a)

(b)
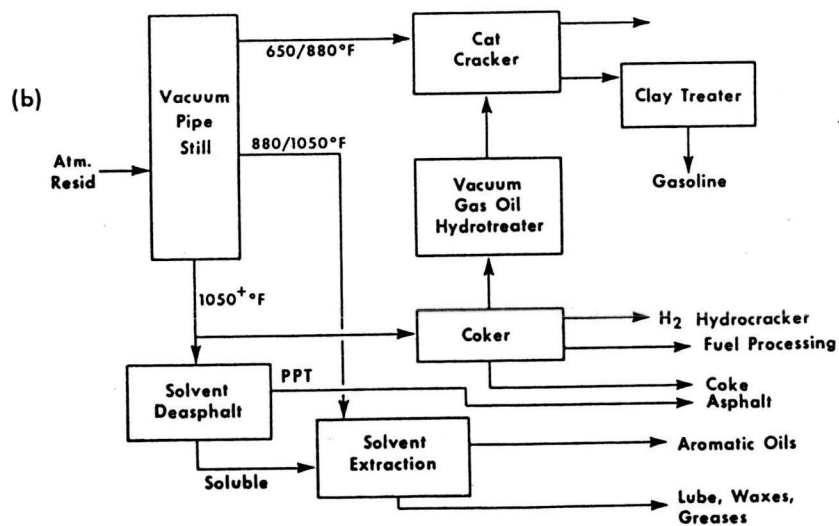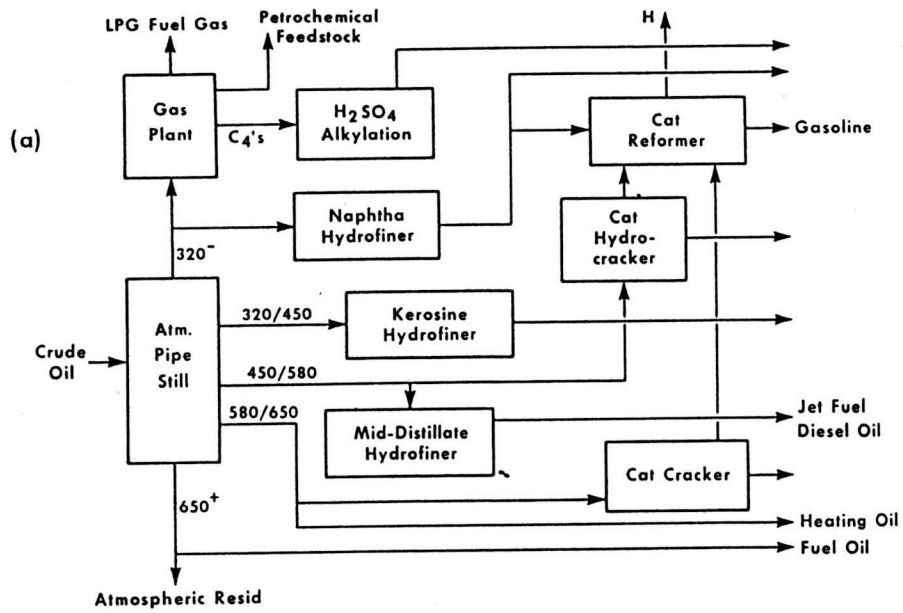
Scheme2.1 Schemetic representation of the interrelationship of the various refinery processes

It is possible to obtain products which range from low boiling materials to a heavy 'nonvolatile' residue or 'bottom' with lighter material taken off at intermediate points. The bottom (or reduce crude) may then be processed by vacuum distillation in order to separate the high boiling lubricating oil fraction without the danger of decomposition which occurs at high temperatures ($>350^0$C; $>660^0$F). Atmospheric distillation can be terminated with lower boiling fraction if it is felt that vacuum or stream distillation with yield a better quality product or if the process appears to be economically more favorable.

Table 2.1 Nomenclature and boiling range of the various distillation
fractionsof petroleum [2]

Fraction	Boiling range	
	(^{0}C)	(^{0}F)
Light naphtha	-1 - 150	30 - 300
Heavy naphtha	150 - 205	300 - 400
Gasoline	-1 - 180	30 - 355
Kerosene	205 - 260	400 - 500
Stove oil	205 - 290	400 - 550
Light gas oil	260 - 315	400 - 600
Heavy gas oil	315 - 425	600 - 800
Lubricating oil	>400	>750
Vacuum gas oil	425 - 600	800 - 1100
Residuum	>600	>1100

GASOLINE [2,3]

Gasoline is a complex mixture of hydrocarbons that boil below 200^0C (390^0F). The hydrocarbon constituents in this boiling range are those that have 4 - 12 carbon atoms in their molecular structure. Gasoline can very widely in composition even those with the same octane number may be quite difference. For example, low boiling distillates with high aromatics content (above 20 %) can be obtained from some crude oils. The variation in aromatics content as well as the variation in the content of normal paraffins, branch paraffins, cyclopentanes, and cyclohexanes all involve characteristics of any one individual crude oil and influence the octane number of the gasoline,

Up to and during the first decade of the twentieth century, the gasoline produced was that which was originally present in crude oil or which could be condensed from natural gas. However it was soon discovered that if the heavier portions of petroleum (such as the fraction which boiled higher than kerosene, e.g., gas oil) were heated to more severe temperatures. Therefore, gasoline that was not originally in the crude petroleum could be manufactured.

At first cracked gasoline was regarded as in interior product because of its comparative instability on storage, but as more gasoline was required the petroleum industry revolved around processes by which the material could be produced (e.g., catalytic cracking, thermal and catalytic reforming, hydrocracking, alkylation and polymerization) and the problem of storage instability was addressed and resolved.

Because of the differences in composition of various gasolines, gasoline blending is necessary. The physical process of blending the components is simple but determination of how much of each component to include in a blend is much more difficult. The operation is carried out by simultaneously pumping all the components of a gasoline blend into a pipeline that leads to the gasoline storage, but the pump must be set to automatically delivery the proper portion

of each component. Baffles in the pipeline are often used to mix the components as they travel to the storage tank.

Selection of the components and their proportions in a blend are the most complex problems in refinery. Blending of up to a dozen different hydrocarbon streams may be needed to produce quality gasoline (table 2.2) Each property of each stream is a variable and the effect of the product gasoline can be considerable. For example of the low octane number of straight run naphtha limits its use as a gasoline component although its other properties of the component streams due to processing changes. For example, an increase in cracking temperature will produce a smaller volume of a higher octane cracked naphtha can be included in blend, adjustments must be made in the proportions of the other hydrocarbon components. Similarly, the introduction of new processes and changes in the specifications of the finish gasoline dictate reevaluation of the components that make up the gasoline.

Aviation gasolines now usually found in use in light aircraft and older civil aircraft have narrower boiling range than conventional (automobile) gasoline, i.e., 38-170 °C (100-340 °F), compare to -1 to 200 °C (30 to 390 °F) for automobile gasoline. The narrower boiling range ensures better distribution of the vaporized fuel through the more complicated induction systems of aircraft engines. Since aircraft operate altitudes where the prevailing pressure is less than the pressure at the surface of the earth [pressure at 17,000 ft is 7.5 psi(0.5 atmosphere) compared to 14.8 psi (1.0 atmosphere) at the surface of the earth], the vapor pressure of aviation gasolines must be limited to reduce boiling in the tanks, fuel lines, and carburetors.

Table 2.2 Component stream for gasoline

Stream	Producing process	Boiling range	
		(^{0}C)	(^{0}F)
Paraffinic			
Butene	Distillation	0	32
	Conversion		
Isopentane	Distillation	27	81
	Conversion		
	Isomerization		
Alkylate	Alkylation	40-150	105-300
Isomerate	Isomerization	40-70	105-160
Straight-run naphtha	Distillation	30-100	85-212
Hydrocrackate	Hydrocracking	40-200	105-390
Olefinic			
Catalytic naphtha	Catalytic cracking	40-200	105-390
Stream-cracked naphtha	Stream cracking	40-200	105-390
Polymer	Polymerization	60-200	140-390
Aromatic			
Catalytic reformate	Catalytic reforming	40-200	105-390

DIESEL [3,4]

The largest single market for diesel is for railroad diesel engines, this market accounted more than one - third of all diesel fuel sales. The diesel engine is a high compression, self - ignition engine. The fuel is ignited by the heat of the high compression and no spark plug is used. The diesel cycle consists of charging the combustion chamber with air, compressing the air,

injecting the fuel, which ignites spontanously, expanding the burn gas and expelling the products of combustion.

Diesel fuel has a widely boiling range (150 to 400^{0}C).It usually contains some cracked stocks and may be blended from naphtha, kerosene and light cracked cycle oils. Limiting specifications are flash point (52^{0}C min), sulfur content (0.25% max), distillation range, cetane number (47 min) and pour point (10^{0}C max)

The ignition properties of diesel fuel are expressed in term of cetane number. this is very similar to the octane number in gasoline and expresses the volume percentage of cetane ($C_{16}H_{34}$, high ignition quality) in a mixture with alpha- methyl-naphthalene ($C_{11}H_{10}$ low ignition quality). The fuel is used to operate a standard diesel test engine according to ASTM test method D-613 or IP 41

Table 2.3 The Diesel properties of optimum condition product

Properties	Method	High Speed Diesel	Low Speed Diesel
Kinematic Viscosity @ 40 °C, cSt	ASTM D445	1.8-4.1	max 8.0
Specific Gravity @ 15.6/15.6 °C	ASTM D1286	0.81-0.87	max 0.92
Color	ASTM D1500	max 4.0	4.5-7.5
Pour Point, °C	ASTM D97	max 10	max 16
Flash Point, °C	ASTM D93	min 52	min 52
Sulfur Content, %wt	ASTM D129	max 0.25	max 1.5
Distillation, °C	ASTM D86	max 357	-
Calculated Cetane Index	ASTM D976	min 47	min 45

The cetane number of a diesel fuel is the numerical result of and engine test designed to evaluate fuel ignition delay. To establish the cetane number scale, two reference fuels were selected. One, normal cetane, has excellent ginition qualities and, consequently, a very short ignition delay. A cetane number 100 was arbitrarily assigned to this fuel. The second fuel, alphamehylnaphthalene, has poor ignition qualities and was assigned a cetane number of 0. In 1962, alphamethylnaphthalene was replaced as a primary reference fuel by heptamethylnonane, which has a cetane number of 15 as determined by use of the two original primary reference fuels.

The cetane number of a diesel fuel is defined as the whole number nearest to the value determined by calculation from the percentage by volume of normal cetane (Cetane No. =100) in a blend with haptamethylnonane (Cetane No. 15) which matches the ignition quality of the test fuel when compared by this method. The matching blend percentages to the first decimal are inserted in the following equation to obtain the cetane number:

Cetane No.   =   % n - cetane + 0.15 (% heptamethylnonane)

The shorter the ignition delay period the higher the cetane number of the fuel and the smaller the amount of fuel in the combustion chamber when the fuel ignites. Consequently, high cetane number fuels generally cause lower rates of pressure rise and lower peak pressures, both of which tend to lessen combustion noise and to permit improved control of combustion, resulting in increased engine efficiency and power output.

In addition to the above, higher cetane number fuels tend to result in easier starting, particularly in cold weather, and faster warm-up. The higher cetane number fuels also usually form softer and hence more

readily purged combustion chamber deposits and result in reduced exhaust smoke and odour.

High speed diesel engines normally are supplied with fuels in the range of 47 to 55 cetane number. Gasoline and diesel fuel additives are more important today than they have ever been. This is because there has been a very significant change in the composition of both gasoline and diesel fuel over the past ten years resultingfrom the phasing out of lead alkyls from gasoline and the depression of the fuel oil market. Both gasoline and diesel fuel now contain more cracked components than in the past, which means that the olefin content of these fuels has increased. Olefins are less stable to oxidation and hence more likely to form deposits in a vehicle fuel system than are the paraffinic and aromatic components. They are also poorer in cetane quality. Thefuels therefore need additives in order to overcome these deficiencies. Oxygenated components are also now widely used in gasoline as an extender and to compensate for the loss of lead alkyls. This can cause a number of difficulties which can be overcome by use of appropriate additives.

Another factor which has increased the importance of additives is the pressure on vehicle manufacturers to improve exhaust gas quality and fuel economy. Deposit formation can steadily worsen and engine's performance in these respects, and many new models are particularly sensitive to performance by preventing deposit build-up.

A third factor is the wish for product differentiation on the part of oil companies, who need to demonstrate that their gasoline or diesel fuel has special features that makes it more desirable than competitive materials. The widespread practice of exchanging fuels between companies to minimize distribution costs means that the use of additives is often the only way that a company can cahieve this product differentiation, since such additives can be injected into the road tanker during loading prior to delivery to the

service station. There are a large number of examples of the use of additives to proivde a strong basis for advertising 'new' gasolines, and the potential for market share improvement by this means has been demonstrated many times.

GASOLINE AND DIESEL ADDITIVES

1. Detergent and Dispersant

These are the additives commonly used in gasoline and diesel fuel to disperse the particles of contamination created by combustion and help prevent the formation of harmful deposits, such as sludge and vanish. Regular drain intervals and filter changes are essential to the prevention of the particles depositing in the engine. The filter removes many of these particles and products of oxidation which would tend to accelerate the rate of oxidation. Over-extended drain intervals or excessive by-products of combustion can cause the depletion of these additives and allow the contaminants to deposit themselves throughout the engine. Detergent-dispersant additives are used more to keep and engine clean than to clean up deposits already in the engine.

Calcium, magnesium, or barium soaps of petroleum sulfonic acids or synthetic sulfonic acids are some of the materials which may be used. Various compounds of barium, sulfur, and phosphorus-containing polymeric and ashless detergents are also used. They are commonly found in motor oils and, to a lesser degree, some hydraulic oils. the detergent polar substrate is make up basically of two part as illustrated in Figure 2.1. The hydrocarbon tail or the oleophilic group is the portion of the detergent polar substrate that act as the solubilizer to anable to detergent to be fully compatible and soluble in base oil. The other part of the detergent polar

substrate is the polar head containing a metal cation. Many metal have been incorporated into detergents but currently, based on cost/performance, the three most commonly used metal are calcium, magnesium, and sodium. These metals have largely replaced the less cost/performance effective barium materials. In addition, barium compounds may have toxic properties. Some countries limit the amount of barium allowed in consumer goods like motor oils.

Hydrocarbon Tail   Polar Head

Oleophilic Group   Metal Attachment

Solubilizer   Point

**Figure 2.1** Detergent Polar substrate

The addition of ash-type detergent additives will increase the ash residue and can be detrimental in applications where increased ash can cause increased maintenance. In engine application, where acidic condition can easily occur, ash-type additives provide a higher and more stable TBN (total base number) to more effectively combat corrosive wear of the engine components. Detergent polar substrate types consist of four major classes: sulfonates, phenates, salicylates, and phosphonates. Sulfonates are the most widely-used detergent additives followed by phenates, salicylates, and phosphonates. Detergents have varying capacity to provided engine rust protection when the engine is not in use. Sulfonates in particular provide excellent engine anti-rust properties. Phenates, in addition to detergency characteristics, provide oxidation inhibition properties and a somewhat lower sulfated ash content at equal alkalinity when compared with

sulfonates. Some diesel engine builders include a maximum sulfates ash level in their engine oil specifications. The use of salicylates is limited while phosphonate use is minimal. These additives structure are shown in Figure 2.2.
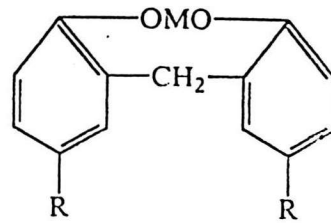
$$RSO_3M$$

$$R = alkyl, aryl$$
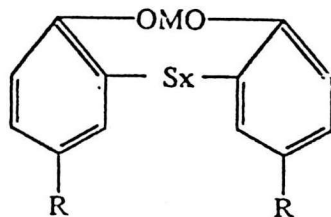
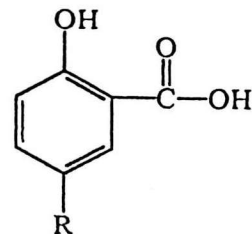**Figure 2.2** Neutral sulfonate
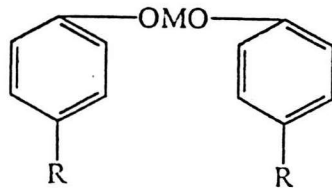
Normal phenate   Methylene coupled phenate

Phenate sulfide   Alkyl salicylic acid

Figure 2.3 Some types of detergents

Overbased sulfonates are formed by a complex reaction between a neutral sulfonate and a metal hydroxide. This complex reaction takes place using carbon dioxide in the presence of a promoter, which is generally an alcoholic-type material. The promoter dissolves a small amount of metal hydroxide, which is subsequently reacted with carbon dioxide to form a metal carbonate. The advantage of the basic sulfonates is their greater ability to neutralize acidic bodies.

Dispersants are very effective and used in many gasoline and diesel oils today. Dispersants are non-metallic or ashless cleaning agents. Figure 2.4 shows the stylized structure of and ashless dispersant. The structure of an ashless dispersant is similar to the structure of a detergent in that the dispersant has a hydrocarbon tail or oleophilic group which enables the dispersant to be fully soluble in the base oil used. The dispersant also has a polar head. The polarity of a dispersant is derived from the inclusion of oxygen, phosphorus, or nitrogen into the molecule.

Hydrocarbon Tail   Polar Head
Oleophilic Group   Oxygen and/or
Solubilizer   Nitrogen Atoms

Figure 2.4 Stylized dispersant

The sludge and vanish-forming precursors, resulting as a by-product engine fuel combustion, contaminate the engine oil as blow by the piston rings into the engine crankcase. Prior to introduction of dispersants, these contaminants would settle out on critical parts of the engine hampering operation and eventually requiring engine overhaul. Ashless dispersants are

designed to have their polar chemical heads attached to rather large hydrocarbon groups. As shown in Figure 2.4 these polar heads interact with sludge. The hydrocarbon groups provide the solubilizing acting which maintains the potentially harmful debris in suspension in the oil. Most dispersants currently in use are prepared from polyisobutylenes of 1000 to 10000 molecular weight. They are four different types of ashless dispersants: (1) succunimides, (2) succinate esters, (3) Mannich types, and (4) phosphorus types. Their structures are shown in Figure 2.5
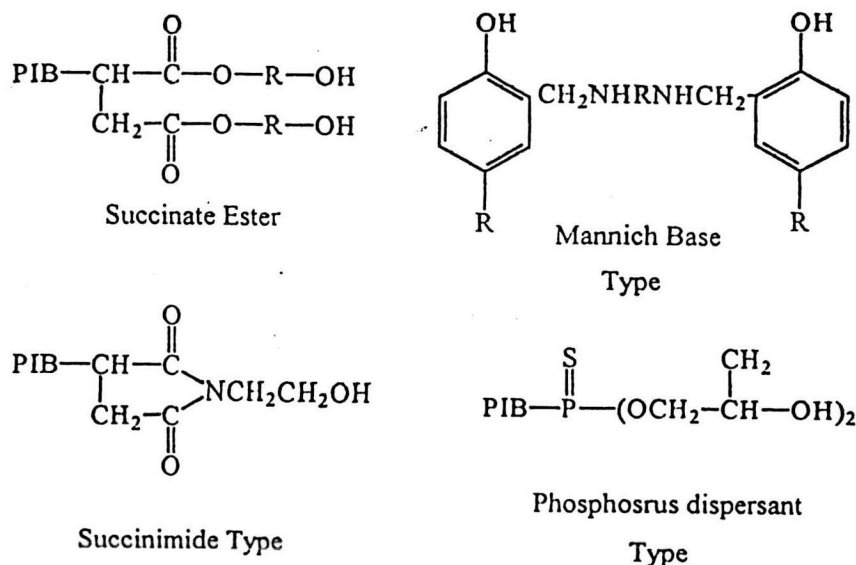

Figure 2.5 Structure of some dispersants

2. Antioxidant

Gasoline and diesel, in common with most organic materials, are subjects to deterioration due to oxidation, and this occurs both during storage and in use in and engine. Oxidation gives rise to the formation of

gums which can seriously influence the performance of the gasoline and diesel.

Gum formation first became a problem with the introduction of commercial cracking processes, since the olefinic compounds produced by cracking are more susceptible to oxidation than the other hydrocarbons present. The use of these processes is still increasing quite rapidly due to the surplus of the heavy fractions from curde oil.

Of the olefins formed, the presence of diolefins is particularly undesirable, since these compounds are highly reactive and form gums and polymers very readily indeed. when gums are formed, they initially remain dissolved in the gasoline but, as the amount increases, they begin to separate out of solution. The problems that can then occur are blockages of lines and filters, high sludge levels in storage tanks, cloudy gasoline and diesel and deposits in various parts of and engine fuel system which can give rise to vehicle malfunctions.

Changes can be made in refinery processing to overcome these problems, such as the use of hydrogen treatment, but are usually relatively expensive since they often reduce yield and lower octane or cetane quality. Additives known as antioxidants or oxidation inhibitors retard oxidation, and these are now universally used as a cost effective alternative or supplement to processing modifications.

Types of antioxidant

The effectiveness of an oxidation inhibitor depends upon its chemical structure, the composition of the gasoline and diesel to be protected and the conditions under which the gasoline is to be stored. It is important for the antioxidant to be readily soluble in gasoline and diesel at all temperatures and to be as insoluble as possible in any aqueous layer that may be present

in the bottom of a gasoline or diesel storage tank. It should now react with any of the fuel componets or ther additives, and it should be capable of complete combustion without leaving any residual deposit in the combustion chamber.

(1) *Aromatic diamines.*

Paraphenylenediamines are extremely effective antioxidants, particularly for gasolines and diesel having a high olefin content, A number of compounds of this type are used commercially and have the general formula :

$$R-NH-C_6H_4-NH-R'$$

The groups R and R' can be the same or different and are commenly sec-butyl, isopropyl, 1,4-dimethylpentyl or 1-methylheptyl. One of this class of antioxidant that is frequently used is NN'-di-sec-butyl-p-phenylenediamine. It has a freezing point of about 14°C and , although it often supercools, it is best used with a diluent at low ambient temperatures.

(2).Alkylphenols This type of antioxidant is most effective in gasoline and diesel having a low level of olefins. The most important phenols having good antioxidant activity in gasoline and diesel have sterically hindered hydroxyl groups due to the presence of alkyl groups in the 2,6 positions. The most commonly used are probably 4-methyl-2,6-di*tert*-butylphenol, 2,4-dimethyl-6-*tert*-butylphenol and 2,6-di*tert*-butylphenol. These can be supplied either alone or mixed with other alkyl phenols. The mixtures have the advantages that they have lower freezing points than the pure materials and can be more cost effective.

3. Dye and markers

The most common reasons for using dyes are first, to meet legal requirements, as in the USA, where all leaded gasoline must be coloured, and second, to be able to distinguish one product or brand from another. The are also used, with or without special marker chemicals, to supply evidence in cases of theft, tax evasion , fuel adulteration, etc. and for identifying the source of leaks.

The dyes are usually red, orange, blue or green, and are mainly azo compounds although, in the case of the blue dye, this is often an anthraquinone. Treat levels are very low and normally in the range of 2-10 ppm, since it is important that gasolines containing them do not stain the sides of light-coloured vehicles if there is a spill during filling. Dyes supplied as concentrated solutions are preferred by refiners because they are easier to handle.

Marker chemicals are particularly important for security purposes since they impart no colour to the fuel but are detected either by a colour reaction with another chemical or by other means. Such markers must be detectable without interference by lead alkyls, dyes and other gasoline and diesel additives. Furfural or diphenylamine are often used as markers and are detected by mixing the gasoline or diesel with another chemical to give a colour. The presence of marked fuels can generally be detected in concentrations as low as 5 per cent in other fuels.

4. Corrosion inhibitors

Internal corrosion of pipelines is a serious problem, since it reduces flow rates and can give rise to suspended rust in the gasoline and diesel. The main purpose of rust inhibitor is to minimize corrosion in pipelines,

although the remainder of the fuel system and storage tanks also benefit. For this purpose, these additives are used at comparatively low treat rates typically, below 20 ppm.

The additives themselves are surfactant materials that attach themselves as a monomolecular layer to the internal surface of the pipeline, thereby protecting it from attack. Many different chemical types are used but all have a polar or hydrophilic group at one end of the molecule and an oleophilic/hydrophobic group such as a long chain alkyl group at the other. The polar group attaches it self to the metal surface and the non-polar tail sticks into the hydrocarbon phase and provides an oily layer that repels water.

The most effective polar groups are acidic (e.g. carboxylic, phosphoric and sulphonic acids). The amines salts of these acids are also effective. The use of additives containing phosphorus has, however, now almost disappeared because of their adverse effect on exhaust gas catalysts.

In recent years the widespread use of alcohols as gasoline octane or diesel cetane boosters have increased the corrosivity of gasoline and diesel, and this has raised the need for distribution system corrosion inhibitors. Usually, higher concentrations of additive are required to prevent corrosion when alcohols are present, not only because the solvent action and polarity of the hydrocarbon/alcohol blend reduces the ability of a surfactant to attach itself to the pipeline walls.

5. Biocides

One of the beneficial side effects of the use of lead alkyls in gasoline and diesel are their biocidal properties, i.e. they prevent micorbial growth. However, the ever-increasing usage of unleaded gasoline and diesel could mean that this problem will become very much more common- as it is with

middle distillates-so that the use of biocides in gasoline and diesel could grow very significantly.

When microbial activity commences in a gasoline or diesel tank the colour and clarity of the gasoline and diesel and the tank water bottoms change. The colour becomes somewhat darker and suspended matter develops at the fuel/water interface which can block filters, etc. Once it has started, it can be quite difficult to stop, but there are a number of actions that should be taken in addition to considering the use of a biocide. These can include the following:

1. The fuel should be made less susceptible to microbial activity by avoiding the use of additives containing nitrogen or phosphorus;

2. The pH of the water bottoms in tankage should be adjusted to minimize the solubility of any gasoline additives present that contain nitrogen or phosphorus;

3. Free water should be removed by regular and frequent draining of water bottoms from storage tank. It is in this free water that micro-organisms proliferate and from which they obtain some of their nutrients.

When juels of low electrical conductivity are pumped through pipes, etc., particularly at high velocities, a charge of static electricity can build up in the fuel. this can give rise to sparking as it discharges, and if this happens within a flammable mixture of hydrocarbon vapour and air a fire or explosion can take place. Fortunately, when filling a vehicle with gasoline and diesel the vapour/air mixture coming from the tank is usually much too rich to burn or explode, and , in addition, the conductivity of gasoline and diesel are often high enough to dissipate the charge.

This problem of static electricity is particularly acute with aviation kerosine, which has a very low conductivity and is handled at high pumping rates. Anti-static additives have been added to this material for many years in order to increase its conductivity. The additive used has been mainly a

chromium-based or ganometallic material, although totally organic additives are now available.

Concern is now being expressed over the possibility of static discharge problems with gasoline and diesel, since in some cases high pumping rates are being used. Some conventional surfactant additives are effective in reducing the conductivity, as are many oxygenates.

6. Drag-reducing agents (DRAs)

When pipelines become limiting in capacity one possibility to increase the throughput is to use drag-reducing additives in the products going through the pipeline. These additives are extremely high molecular weight polymers which shear very readily and reduce drag be smoothing turbulent bursts off the walls of the pipeline and so allow more product to flow. They have been used in some countries at concentrations of up to about 50 ppm. There are concerns about their long-term use and possible effect on fuel intake system deposits such as on valves and injectors, but it is probable that a properly forulated additive package containing is probable that a properly formulated additive package conaining is probable that a properly formulated additive package containing appropriate detergents/dispersants will overcome any adverse influences.

7. Demulsifiers and dehazers

Water can find its way into fuel during refinery processing and distribution and can be present both as free and as dissolved water. Dissolved water can be forced out of solution by a sudden drop in temperature and will appear as a haze that can often take a long time to clear if the gasoline and diesel are simply left to stand on its own. Water can

also come out of solution during blending if there is a temperature difference between components or if two saturated components having different water solubilities are blended together. Aromatic components tend to be able to dissolve more water than paraffinic ones.

The ease with which the water haze clears depends mainly upon whether emulsion-stabilizing materials are present such as some surfactant additives, finely divided solids, etc. Special anti-haze additives are available which are extremely effective in accelerating the rate at which the gasoline and diesel clear by promoting coalescence of small droplets. They are themselves surface-active materials which have limited solubility in both oils and water, and so tend to concentrate at the fuel/water interface.

When free water is present in the tank it can sometimes be entrained with gasoline and diesel during pumping and the shearing forces involved can give rise to quite stable emulsions that, in severe cases, gives the oil a milky appearance and can plug filters This will normall only happen when excessive amounts of surfactant additives are used or when such additives have been improperly formulated. Anti-haze type additives can also help to avoid these problems, and are generally used in the range of 1-30 ppm.

Chemically, the anti-haze additives used in gasoline and diesel can be very complex, and often consist of a mixture of several different compounds. The composition is almost always proprietary. The selection of the most suitable additive and concentration to use is a matter of considerable skill and experience, since their effectiveness depends upon what other additives are present, the composition of the gasoline and diesel themself (including the use of oxygentaes) and on the storage conditions. Because the anti-haze additives are themselves surfactants they can interfere with the effectiveness of other surfactants present in terms of detergency, etc. For this reason, if such additives are frequently found to be necessary to

ensure consistently clear and bright gasolines or diesel it is advisable to check that the benefits of any other surfactants being used are still valid.

8. Anti-knock additives

Very early in the evolution of the spark-ignition engine the phenomenon of knock was encountered. The phenomenon needed to be properly defined and measured, and in the years between World Wars I and II the engine-testing procedures were set in place with the adoption of the CFR (Cooperative Fuels Research) single-cylinder test engine. At this time the role of hydrocarbon composition came to be recognized and the octane or cetane scale was invented. The relationship of fuels behaviour in the CFR engine to that in a vehicle on the road were also explored.

The mechanism of knock can be attributed to an end-gas explosion or auto-ignition before the normal flame can reach it. Therefore for fuel design or additives to affect the situation they must act either to increase the speed of the flame or to decrease the propensity of the end-gas mixture to auto-ignite. Since the flame is a turbulent flame process owing much of its speed to the physical processes of heat transfer from the burnt to the unburnt gases rather than to any chemical ones, the likelihood of finding chemical additives that increase this flame speed is rather remote. However, the process of auto-ignition is different, it being mechanistically a free-radical chemical chain reaction whose rate can be readily controlled by appropriate chemical radical inhibitors or traps

It is well known that lead alkyls have provided the most cost-effective anti-knock additives for the last 60 years. However, it is less well know that other metallic-based materials have also been used (and in some cases still are). Much early research was undertaken on organic material

(e.g. amines), and more recently searches for ashless anti-knocks have again been attempted.

9. Anti-run-on additives

Run-on (or afterrun, as it is sometimes known) is an occasional occurrence in modern engines, and can be regarded as a driveability 'nuisance'. It occurs when the engine 'diesels' after the ignition is switched off.

The engine and fuel factors controlling this phenomenon have been well researched and understood. Engine speed at idle was found to be the most important engine factor of all, so throttle-stop settings are of practical importance. As far as the fuel is concerned, octane quality, governed by the RON, is the predominant property. Engines are tuned such that they almost invariably reach a knock limit before they reach a run-on one (although it is conceivable that the reverse could be the case; e.g. in a heavily spark-retarded engine).

The additives that are effective to control this phenomenon are therefore the same that are used for anti-knock purposes (e.g. lead alkyls or others). Similarly, it might be expected that anti-ORI additives would also show anti-run-on capability. The Techron additive was indeed tested in this regard and positive evidence was adduced in a 5.0-litre V8 bench engine with unleaaded gasoline. For a given RON level, run-on was found to greatly increase in the presence of equilibrium fuel deposits compared with the clean engine, and was decrease somewhat after use of the octane requirement decreasing additive treatment.

10. Anti-pre-ignition additives

In the 1950s as compression ratios first increased up to 9:1 or more the phenomenon of pre-ignition was encounterd. The problem showed itself as noisy and sometimes damaging combustion behaviour, and attracted such descriptive titles as 'wild ping', 'rumble' or 'picket-fence rattle'. It was attributed to the presence of growing amounts of combustion chamber depposits arising from the presence of large amounts of lead in the high-octane fuels of the day. These deposits became hot enough to ignite an incoming carge before the moment of spark-ignition, so the event can properly be termed surface pre-ignition. The point of ignition can vary; sometimes it would be the piston top, often the spark plug tip itself. It is a very dangerous phenomenon because of its propensity to lead to runaway damage. However, sometimes the violence of the process is sufficient to detach the offending deposits, in which case the effect is transitory and self-correcting.

The action of the deposits needs further elucidation. Carbonaceous deposits need to be heated to above 700°C in air before they start to combust and glow. However, the presence of lead salts catalyses this process such that the glow temperature is much reduced, and so these deposits became a more ready source of pre-ignition. It was discovered in the mid-1940s that phosphorus compounds can raise this glow temperature by converting the lead halides and oxyhalides to less catalytic lead phosphate salts. Anumber of materials were shown to be effective. Two of the most cost-effective additives were tricresyl phosphate (TCP) and cresyldiphenyl phosphate (CDP). The dose rate was typically 0.2-0.5. Theories of phosphorus relative to lead, calculated on the basis that the two materials combine to form lead phosphate. These materials were in much commercial use in the mid-1950s, but as lead contents have decreased

steadily in the succeeding 30 years, so too has the use of these phosphorus additives.

11. Anti-VSR (valve seat recession) additives

A well-known problem of unleaded gasoline is that for certain 'soft' metallurgies of the exhaust valve seat a significant wear problem occurs. The high temperatures of the environment together with the absence of semi-solid or solid-lubricant materials in the combustion products of leaded gasoline make for a very hostile environment. Valve seat recession (or sinkage) can occur in such engines at a great rate; sufficiently large, for example, for the engine to use up all its valve-tappet clearance in a period of, say 10,000 km if it is driven under severe road conditions.

12. Addition that improve lubricant performance

Some gasoline or diesel additives are designed to function by helping the lubricant after surviving unchanged in the combustion chamber. They do this in two ways. First, when an engine is switched on or off it rotates for a few cycles before or after ignition, and this means that gasoline or diesel containing the additive are brought into the combustion chamber and not combusted. These fuels flow down the bores into the crankcase, diluting the areas and in the lubricant itself. Second, if the additives are reasonably stable to oxidation a small percentage of them will survive the combustion process and again reach the bores and the lubricant.

13. Miscellaneous additives

The patent literature if full of inventors' additives with a wide variety of claims, and a review of this disparate source cannot be given here. The fact that few (if any) of these have come to market probably speaks for itself.

There have been similar claims of additives promoted by smaller commercial companies, many of these exagerated and often of the 'cure-all' variety. Such additives seldom stay in the market for long, although it should be said that it can be a very difficult and expensive matter to prove or disprove claims made in this way.

Lastly, there have been certain additives developed by the more important oil or additive companies that have been produced for a short time (e.g. combustion catalysts) or for which research findings have been fairly well documented but which, for some reason, have not been commercialized.

14. Cetane number improvers

Cetane number or cetane index requirements are present in most diesel fuel specifications, significant variation in the quoted values is evident. Within Europe the cetane quality of diesel fuel has traditionally been high, and importance is attached to the performance benefits this offers in terms of :

1. Improved cold starting
2. Reduced smoke emission during warm-up
3. Reduced noise
4. Reduced fuel consumption and exhaust emission
5. Improved engine durability.

DETECTION OF DISPERSANT IN GASOLINE AND DIESEL OIL

It is sometimes necessary or desirable to be able to analyse a gasoline and diesel fuel to see what type and concentration of dispersant additive is present. This may be in order to check on the accuracy of the injection equipment used or to establish the losses of additive that might be occurring during distribution due to adsorption on to rust, losses to tank water bottoms, etc.

It must be said that it is extremely difficult to carry out such analyses, particularly if one is attempting to identify the nature and concentration of an unknown additive. Additives are commonly ashless, and today, because of concern for exhaust catalyst poisoning, most commercial additives contain only carbon and hydrogen together with other pounds at low concentrations from other materials present in gasoline and diesel presents a challenge.

There are no commonly available test procedures for this purpose, although it is usual to evaporate off the bulk of the gasoline and diesel at a low temperature and reduced pressure and then to investigate the residue by extraction with different solvents followed by the use of such techniques as infrared spectroscopy, liquid chromatography, etc.

Additive manufacturers will often be able to supply procedures for identifying and quantifying their own additives in gasoline and diesel, and these will normally involve thin layer chromatography (TLC) and high-performance liquid chromatography (HPLC). In these cases, where the neat additive is available it is possible to make up standard strength solutions of the additive in gasoline and diesel to compare with the results obtained on the test sample.

It must be remembered that, in many cases, additive package can contain several different dispersants. These can be lost in the distribution.

LITERATURE REVIEWS

Many determination methods had been used for determined the dispersant additive in gasoline and diesel fuel.

In 1986, Gilbert R. Malone et al. [10] studied the method of analysing high molecular weight dispersants in motor oils by GPC and VPO determinations.

In 1989, Menez H.R. and Perez C.L. [11] determined of alkyl chain distribution in lubricating oil additives of the type alkyl aryl sulfonates by HPLC.

In 1992, Ashraf S. et al. [12] studied the analysis of lubricating oil additives by supercritical fluid chromatography with packed and open tubular capillary columns. Carbondioxide and modifdied carbondioxide were used as mobile phase and detector was accomplished by flame ionization and micro UV.

In 1992, Myers and Helane [13] studied the determination of aromatics in hydrocarbon by near infrared spectroscopy.

In 1992, Fields and Carolyn E. [14] studied the process and apparatus for analysis for hydrocarbons by near infrared spectroscopy.

In 1996, Ethyl Petroleum Additives, Inc. [15] has been determined the concentration of Hitech 4961A additive in gasoline by UV-Visible.

1996, Lubrizol Corporation, [16] has been determined the concentration of LZ 8195 additive in fuel oil by UV-Visible (two phase).