1

Fuels and Fuel Additives – Overview

1.1 Introduction

The fuels under consideration here are the liquid fuels obtained from crude oil by fractional distillation and other refinery processes, together with biofuels and synthetic Gas to Liquid (GTL) and related fuels. The gases methane, ethane, propane and butane are not covered as they generally need few, if any, additives other than odorants.

Coal is not considered here either. Most coal is burned in fluidised beds in electricity power stations, which provided about 38% of the world's electricity (22% in Europe) in 2017 [1]; overall, coal provided 28% of the world's energy and oil provided 34%, in 2017. Coal additives are added to reduce soot, fly-ash, bottom-ash, slag and clinker in power stations, but a European Commission research document concludes that only the use of lime or limestone effectively reduces deposits, fly-ash and sulfur oxides [2,3]. Magnesium additives are used in furnaces burning heavy fuel but are not effective in coal, so links with the additives used for petroleum derived fuels are almost non-existent.

This chapter will give a condensed explanation of the refinery operations that convert crude oil into fuels and compositions of the different fuels. Also, in this chapter are presented some of the statistics of quantities of various refinery products and global variations. The author's intention is to provide sufficient understanding of refining to support the discussions of the applications of fuel additives. Much has been written about refineries, specifications and internal combustion engines, so the reader is guided to some of the relevant literature for more detailed explanations – for an example of the engineers' perspective see the *Automotive Fuels Reference Book* [4].

Finished fuels are put together from the refinery components to provide the properties that they need to have and to meet fuel specifications. However, many of the properties that a fuel should have are difficult to achieve by blending

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refinery output streams. Fuel additives provide the additional necessary properties – usually in the most economical way and sometimes the use of additives is the only way for the different fuels to meet their specifications. This chapter introduces the reader to the range of fuel additives used in the different fuels.

When fuels reach the market and are sold, not surprisingly there is a whole tax regime, particularly for motor fuels. And, as in other areas of taxation, there are some concessions of low taxation on fuels for particular applications which carry the potential for criminal diversion of low-tax fuels into high-tax applications. So, it is here that we are first introduced a discussion of fuel additives: dyes and markers that are used to identify low-tax fuels.

While petroleum fuels and their production form a worldwide industry, most of the data referred to is from Europe and the USA because information of these markets is that which is most widely available. The oil industry started in the USA, followed closely by Europe [5] – the industry in other parts of the world followed in the footsteps of these two regions and still set specifications which are closely related to those in the USA and in Europe.

1.2 Refinery Operations and Processes

There is much literature on refineries, and useful, easy-to-follow descriptions and diagrams are provided in oil company websites [6–12]. A schematic of refinery operations helps to visualise how the different fuel components arise and how they are combined into the finished fuels (Figure 1.1) [8]; this will help in understanding the discussions of how particular fuel problems arise and the refinery limitations which lead to additives providing the best solutions.

1.2.1 Distillation

Crude oil coming into the refinery is preheated in the heat exchangers that, at the same time, cool the exiting refinery product streams. Steam is then injected into the crude which moves into a furnace (at about 500°C to 550°C) where it is heated to almost 400°C. The furnace is at the bottom of the atmospheric (pressure) distillation tower – more commonly known as the atmospheric pipestill or topping unit. Here, the more volatile fractions rapidly vaporise, and the hot vapours pass up the tower through a series of perforated metal trays – the perforations are holes with a collar and a supported cap known as a bubble cap. As the vapours cool to the lower temperatures higher in the tower, the less volatile components condense into liquids that collect on the trays and pass down the column. During this process, the bubble caps force the rising vapours to bubble through the condensing liquids, thus improving the efficiency of the fractional distillation: the cooler liquid condenses more of the less volatile

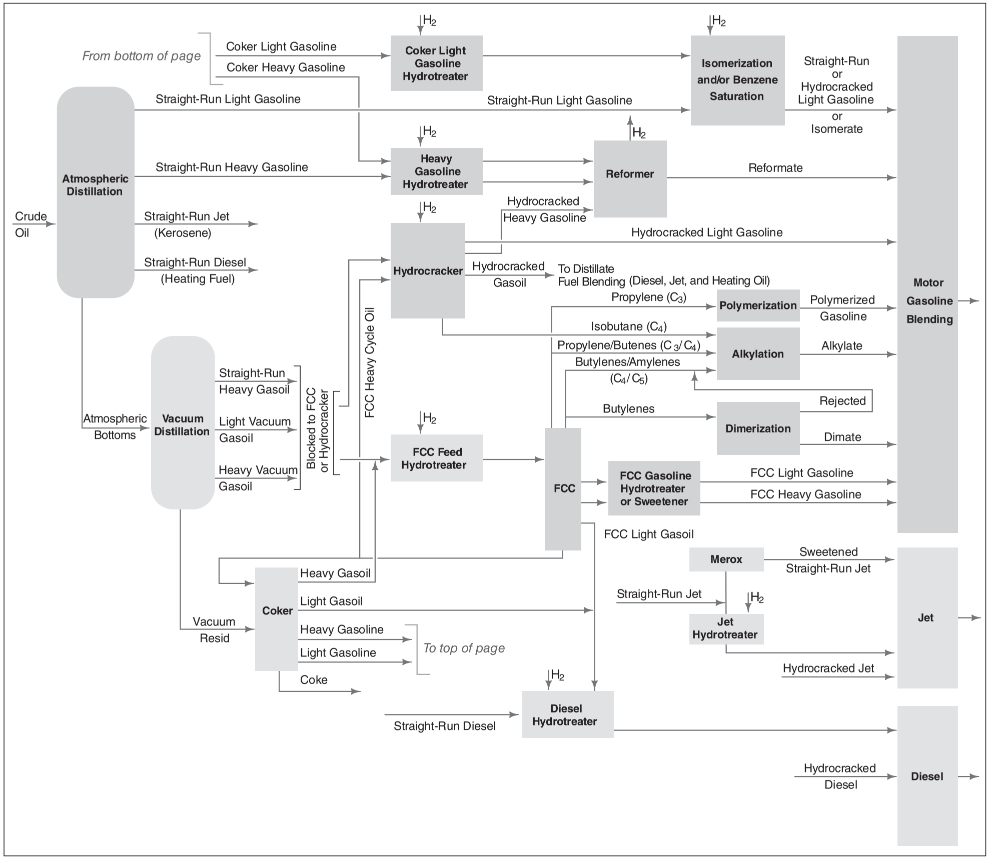


Figure 1.1 Refinery Operations. © 2019 Chevron. All rights reserved.

liquids from the vapour and the vapour takes out the more volatile components from the liquid. Every few trays, the condensed liquids are continuously removed as a 'side-stream' or 'cut'. These side-streams are collected and blended for use as the distillate fuels gasoline, jet, kerosene, diesel fuel and gas oil or are transferred to various conversion processes (Figure 1.1).

A steady, falling temperature gradient is established in the distillation tower. The most volatile components pass over at the top of the tower while the non-volatile material, known as atmospheric residual fuel, collects at the bottom of the pipestill, after removal of more volatile fractions with the help of a current of steam. Boiling temperatures of the side-streams are highest at the bottom of the tower – for example heavy gas oil (up to 380°C) – and lowest at the top (below 100°C) – such as the gasoline component light naphtha (up to 70°C). Exact boiling ranges of the side-streams and their degree of overlap (efficiency of separation) depend upon the exact details of operations at each refinery but the variations are not huge.

The proportions of side-streams, hence products, vary with type of crude oil. 'Light crudes' and 'heavy crudes', meaning low and high density, contain different proportions of lower and higher boiling material. West Texas Intermediate is a light crude which contains a relatively high proportion of the valuable low-boiling gasoline fractions and a low proportion of high-boiling residual fuel; in contrast, Arabian heavy crude has low proportions of the valuable light products and a large (about 60%) of low-value high-boiling material ('other' in Figure 1.2), of which half is vacuum distillable leaving half as an undistillable vacuum residual fuel [13]. More importantly, the distributions of products possible from

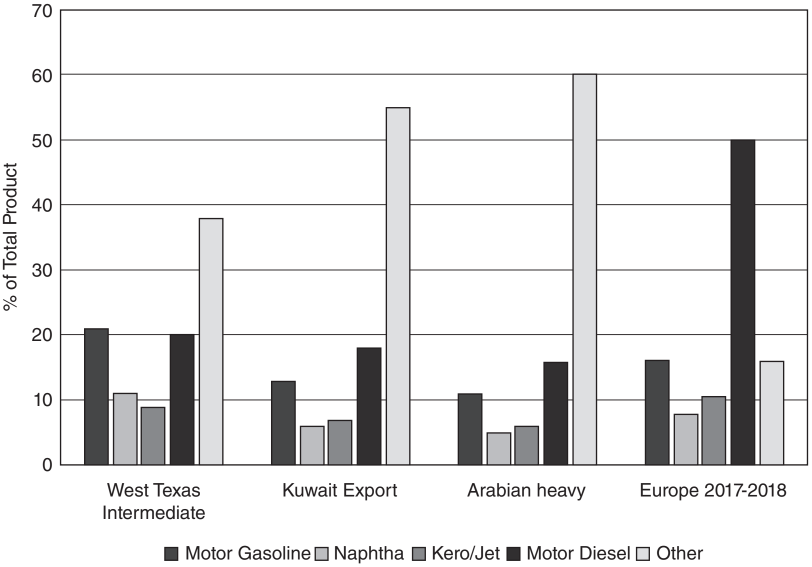


Figure 1.2 Straight-Run Yields (Wt.% of Total) of a Range of Crude Oils, Compared with European Union-28 Refinery Output 2017.

both crudes after atmospheric distillation, known as 'straight-run', and blending do not match that of the average refinery output. A region's average refinery output is designed to meet customers' needs (such as the EU-28 [14,15] in Figure 1.2), which is termed the demand barrel.

1.2.2 Balancing Production to the Demand Barrel

Distillate fuels are needed in larger proportions than are naturally present in crude oil. In Europe, this is particularly true for the middle distillates gas oil and diesel, while the USA needs more gasoline. The problem lies in the high proportions of atmospheric residual fuels, such as 32% to 54% of the crude oil ('other' in Figure 1.2), which outstrips demand for this fuel. Clearly, this excess cannot be treated as waste; the quantities are huge – the reality of refining is that all that comes into a refinery as crude oil must go out as products. For example, the Fawley refinery supplies 14% of the UK's oil products; it processed around 22 million tonnes of crude oil in 2019 (60 thousand tonnes per day[1]) [11]. If one-third of this came out as atmospheric residual fuel, that would pose an enormous problem of disposal.

Most refineries, then, have more complex operations than those providing only straight-run, atmospheric distillation. Through the second half of the twentieth century, almost all simple, straight-run only refineries (also known as 'hydroskimming' refineries) in Europe and North America have closed and the more complex refineries have expanded to meet demand. Atmospheric residual fuel is further refined first by being vacuum distilled up to a temperature equivalent[2] of 550°C. This takes place in a vacuum distillation pipestill, which has the same arrangement as for the atmospheric pipestill but with the addition of a partial vacuum (reduced pressure), provided by steam injectors. From this pipestill, a range of vacuum-distilled fractions (known as 'vacuum gas oils') are produced; some of these are converted into lubricating oils but most is used as feed for the crackers (section 1.2.3). Finally, left behind at the bottom of the vacuum pipestill is a certain proportion of a high-boiling, undistillable vacuum residue. Some of the vacuum residue is converted to bitumen or heavy lubricating oil, some is blended with low-value distillates into residual fuels and some is processed further to produce lighter products in cokers (section 1.2.5). Residual fuels are used in heavy marine diesel fuels, in refinery furnaces and in some power stations.

After the atmospheric and vacuum distillations, the refinery products are typically those shown in Table 1.1 [6] from a heavy Middle Eastern crude. For this Kuwait crude oil distillation, the proportion of vacuum residue is 26.7% while an assay of Kuwait export crude put the proportion of atmospheric residue at 54.5% (Figure 1.2) [13], i.e. 'fairly heavy'.

Refinery fuel products from complex European refineries are made up of higher proportions of non-residual, higher-value products than are possible by blending the straight-run distillation cuts of either the Kuwait or Arabian

Table 1.1 Side-streams in a typical modern refinery from Kuwait export crude.

Cut Number	Product Name	Cut Vol% of Whole	Distillation[3] End Point	Average NBP	Average Mol. Wt.
1	Gases	1.3	10	2.5	56
2	Light naphtha	7.3	70	44	71
3	Naphtha	16.6	180	132	112
4	Kerosene	10.1	240	210	160
5	Light diesel	7.8	290	264	200
6	Heavy diesel	7.0	340	314	244
7	Atmospheric gas oil	3.8	370	355	285
8	Vacuum gas oil	2.4	390	380	313
9	Vacuum distillate	18.3	550	467	435
10	Vacuum residue	26.7	–	689	1150

Table 1.2 Petroleum refinery products in Europe 2018.

Product	Refiney Output, Mtoe	Refinery Output, % of Total
Total output:	638.5	100
LPG	30.3	2.8
Naphtha	42.2	7.0
Gasoline	80.1	18.5
Kerosene + Jet	62.8	8.6
Gas oil /Diesel oil	292.6	39.4
Fuel oil	49.3	11.7
Other products	53.1	12.1
Refinery use/losses	27.7	–

crudes (Figure 1.2[4], cf. Table 1.2 [15]). The difference between total refinery output (638.5 Mtoe[5]) and the use as liquid fuel (transport plus heating, 508 Mtoe) is made up of other petroleum product applications such as heavy (marine) fuel, industrial use (many varied sectors), liquefied petroleum gases, lubricating oils, waxes and chemicals (Figure 1.3 [16]). Many refineries produce items such as solvents that contain aliphatic and aromatic hydrocarbons,

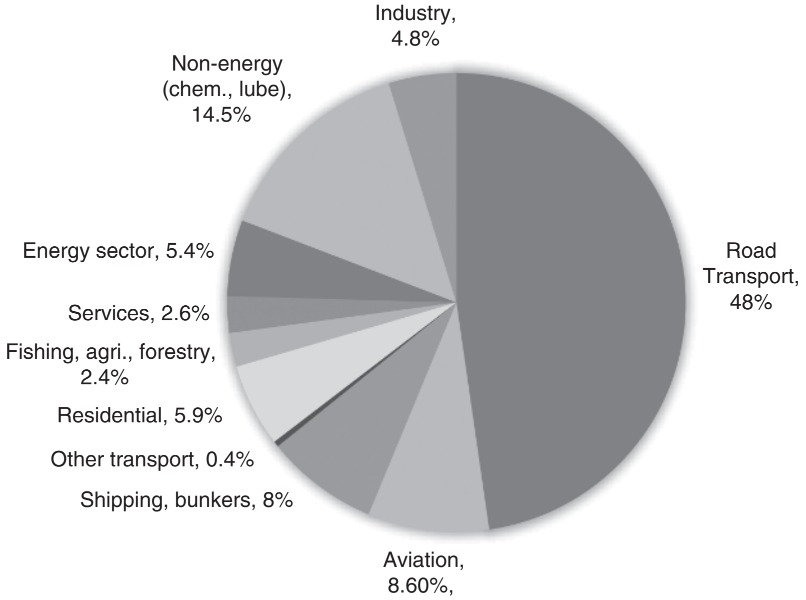


Figure 1.3 Distribution of End Uses for Petroleum Products in the EU-28, 2016.

ketones and alcohols; raw materials for the chemical and plastics industries such as ethylene, propylene and butylene, and higher alkenes, such as tetrapropylene, are other refinery products. These other products are made from both the liquid fractions and the gases. Diesel is also used for non-transportation engines such as generators. Import/export balances can confuse the quantities, and the counting of residual fuel may be short because sales are often private.

(Quantities in million tonnes oil equivalent (Mtoe) are close to actual tonnes as the factors for conversion of quantities, by weight, to tonnes oil equivalent are close to 1.0:1.01 for diesel and 1.105 for gasoline; residual fuel oil is 0.955.)

Imbalances between the supply and demand barrels vary between regions, seasonally and over years with macroeconomic changes, such as the adoption of fuel-efficient diesel in Europe and heating oil being replaced by natural gas. They are corrected, in part, by refinery conversion facilities such as crackers (section 1.2.3). Such facilities raise costs and prices but enable global refining to meet the global balance in demand. Regional imbalance is corrected by trade that reflects different regional needs. As a result, excess of a fuel in one region may be exported to a region that has a shortage of that fuel. The import/export effect is illustrated by the European and USA markets. A comparison between the two illustrates the differences between the USA and the European petroleum fuel markets. These differences in fuel consumption explain the differences in emphasis on additives that have developed in these two markets.

Transportation fuels, road, aviation and shipping, take up the major part of fuel consumption (Figure 1.3, in Europe [16]) so dominate refinery operations and trade. Europe and the USA have quite different distributions of transport fuel consumption – European transport relies heavily upon diesel while gasoline dominates in the USA [17] (Figure 1.4). In a worldwide comparison, while Europe depends upon middle distillates and the USA upon gasoline, the Asia-Pacific region depends somewhat evenly upon these two (Figure 1.5 [18]).

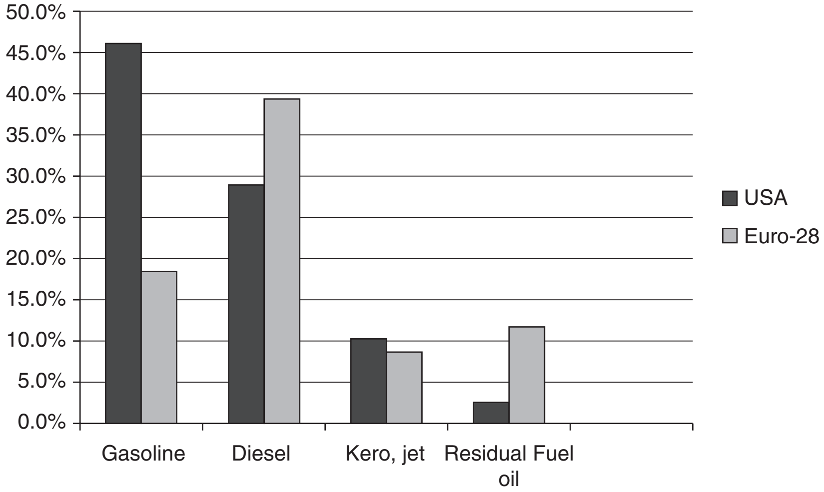


Figure 1.4 Distribution of Liquid Transport Fuels in the USA and Euro 28 Countries, 2018.

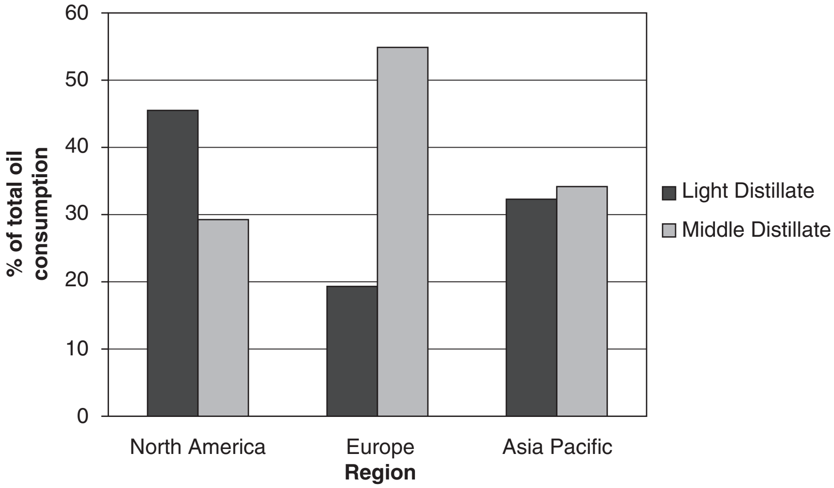


Figure 1.5 Distribution of Liquid Fuel Use by Type in Main Economic Blocs, 2018 [18][6].

As might be expected, import/export figures for these fuels show that Europe imports substantial quantities of middle distillates, while exporting similar quantities of gasoline [15] (Figure 1.6). Historically, the USA imported more gasoline than it exported, for example 25 Mtoe in 2011 [19]; however, since the recent resurgence of oil production in the USA, it has become a net exporter of both diesel (58 million tonnes ULSD in 2017) and gasoline (31 million tonnes) [17]. Europe's major supplier of diesel is now Russia, and the Middle East is its major supplier of jet fuel [15].

In the world of petroleum and petroleum products, such changes are not surprising given the background that over the ten years from 2008 to 2018, the total consumption of oil has changed little in North America (from 1105 to 1113 Mtoe) while falling in the European Union (731 to 647 Mtoe) and growing strongly in Asia Pacific (1250 to 1695 MT pa) [18].

Worldwide, the 4,474 million tonnes of petroleum products consumed in 2018 had a distribution of petroleum cuts [18] (Figure 1.7) most like that in the Asia Pacific. It is perhaps worth reminding the reader that diesel engines are used to propel buses, HGVs/trucks, ships and smaller boats, tractors, construction vehicles and back-up electricity generators as well as passenger cars and light vans. By reason of the greater fuel efficiency of diesel over gasoline engines (and the rising cost of oil), the growth in the demand for diesel was outstripping that for gasoline in the noughties, such that in 2012, 51% of new cars were diesel in the UK and 56% in Europe [20] – except in America. In fact, the USA had been dubbed 'Refiner to the World' because the high demand for diesel outside the USA was providing USA refineries with profitable production and sales of diesel for export [21].

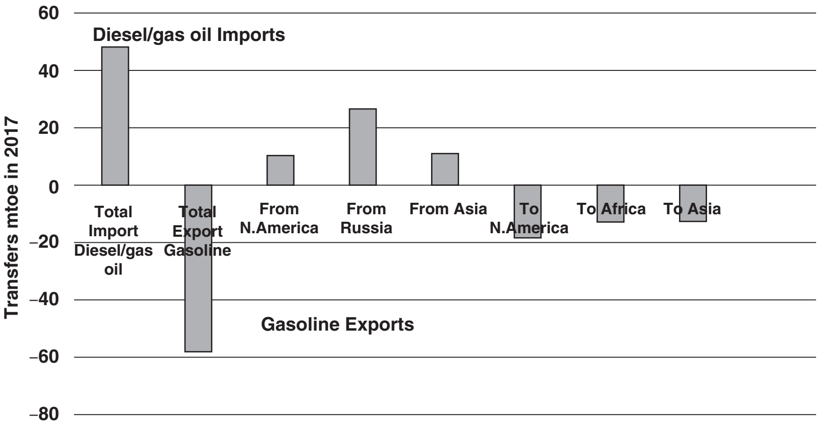


Figure 1.6 EU-28 Imports of Diesel/Gas Oil and Exports of Gasoline, Million Tonnes in 2017.

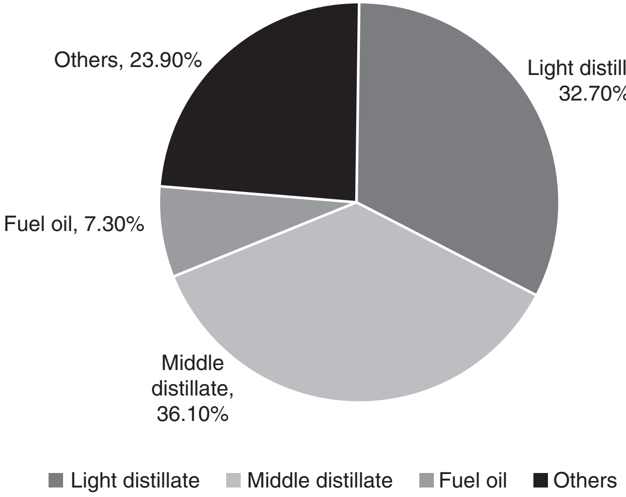


Figure 1.7 Distribution of Fuel Consumption by Refinery Description, Worldwide, 2018. Light distillate: aviation and motor gasoline with light distillate feedstock. Middle distillates: jet, heating kerosene, gas oils and diesel fuel, including some marine bunkers.[7] Fuel oil: marine bunkers (heavy fuel) and crude oil used as fuel. Others: refinery gas, LPG, solvents, bitumen, lubricants and other refinery products and losses.

Looking to the future, in a 2011 survey for the UK department of energy [19], the projection to 2030 was for a fall in the gasoline share of demand (to 10% of total petroleum products) and a corresponding rise in diesel fuel demand (to 40%), an increase in jet fuel consumption and continued fall in the demand for heavy fuels. The last two did occur but the continued rise in diesel demand was being limited by worries about its contributions to city pollution, inroads of biodiesel and decreasing energy intensity[8] as the new Asia Pacific economies mature.

In 2017, however, a break in the trend was underway, resulting from a combination of rising air pollution in cities, due to petroleum-driven motor transport, in particular diesel vehicles (particulates and NOx worries), and the rapid rise in electric vehicle technology. ACEA reported that of the new passenger cars sold in Western Europe, in 2016, 49.5% were diesel and 45.8 were petrol engine powered (2.1% hybrid electric, 1.5% rechargeable electric, 1.2% LPG) [22]. In June 2017, diesel passenger cars took only 39% of sales in Germany, and it was predicted that this could soon fall to 30% [23]; new passenger cars in Europe in 2018 showed a complete reversal to 36% diesel and 57% gasoline (electric rechargeable and hybrid 6%) [24]. As Yogi Berra said, ‘It is difficult to make predictions, especially about the future’.

1.2.3 Catalytic Conversions

As already discussed, there is not sufficient distillate fuel after straight-run, atmospheric distillation to meet customer demand. This mismatch between what is in crude oil, that may be separated by distillation, and the needs of the market for transportation is resolved by cracking the molecules in the higher boiling fractions – so converting the low-value high-boiling gas oil into valuable gasoline and diesel. Vacuum distillates are hydrotreated to remove the sulphur that would poison the catalysts, fed into the crackers, and redistilled to give the lower boiling cuts needed for automotive fuels.

There are two main types of cracker [6]. In one, the Fluid Catalytic Cracker (FCC), hydrotreated, liquid vacuum gas oils are passed through a bed of zeolite catalyst at about 500°C, under low pressure (1 to 5 bar). The FCC produces hydrocarbons with a high degree of unsaturation (alkenes and aromatics) as well as branched lower alkanes and hydrogen (which is used in the hydrotreaters). The product is then distilled to produce streams that are valuable, high octane blend components for gasoline, which is the primary purpose of the FCC. In addition, there are smaller amounts of aromatic-rich kerosene and middle distillate fractions.

The other is the hydrocracker, in which vacuum gas oils are cracked at 350°C to 450°C in the presence of hydrogen. There are degrees of hydrocracking: mild hydrocracking uses hydrogen at a pressure of 35 to 70 bar and a nickel-molybdenum catalyst to remove sulphur, nitrogen, and destabilising olefin unsaturation. Conventional hydrocracking uses hydrogen at 85 to 140 bar and a nickel-molybdenum on silica-alumina-zeolite catalyst to remove most of the sulphur and most of the aromatics; at the same time, hydrocracking[9] and hydroisomerising occur to produce distillation streams that have high cetane numbers, so are suitable for ultra-low sulphur diesel fuel [6].

For light distillates, there is a further catalytic process. Catalytic reforming is used to convert low octane naphtha into gasoline components that are rich in iso-alkanes and aromatics, which have high octane numbers. Catalytic reforming is carried out by passing the naphtha over a platinum-based catalyst, under moderate pressure (5 to 25 bar) at 500°C [6].

1.2.4 Alkylation

Alkylates are the products of the sulphuric acid-catalysed reactions of short chain alkenes, usually butylene or propylene, with isobutene[10]. Alkylates are highly branched and so have high octane numbers – for example, the isobutylene/isobutane product is iso-octane which has a 100 octane number [6].

1.2.5 Coking

Finally, there are the atmospheric and vacuum distillation residues. These may be converted to distillable liquids by 'coking' whereby the distillation residues are heated at a high temperature so that carbon is extruded, as coke, from the high molecular weight, carbon-rich molecules leaving liquid products of lower molecular weight that contain more hydrogen. The process also leaves much of the sulphur and metals in the coke. The chemistry of the process is thought to be that as the already high molecular weight molecules condense together into poly-aromatic structures, low molecular weight alkanes, alkenes and aromatics are split off. Eventually, the poly-aromatics have graphite-like structures and contain low proportions of hydrogen. The product liquids are distilled into a full range of products: gases such as methane and alkenes such as ethylene, propylene and butylene (valuable chemical intermediates); aromatic-rich (hence high octane) gasoline components; aromatic-rich kerosene and gas oils that need hydro-treatment to be useful as jet and diesel blend components [6].

In delayed coking, the residue is heated to about 500°C, at several bar pressure in a furnace. It is then kept in a '(heat) soak drum' at about 450°C to 480°C until about 20% to 30% of the residual fuel is converted to coke plus lower boiling liquids, which are then redistilled. In a flexicoker, the residual fuel is passed through a fluidised bed, at about 520°C and low pressure (under 1 bar), with a flow of steam; in this process, the extruded carbon is burned off (only 2% left behind) providing the heat needed for the endothermic coking process. Visbreaking is a similar but milder process in which 15% to 25% of the residue is converted to lower molecular weight components that lower the viscosity, which is often necessary in heavy fuel blending. In the visbreaker, the residue is passed over heat-exchange tubes at 425°C to 450°C, depending upon the severity of cracking required; for example, at 450°C, 75% may be cracked to lower boiling materials [6,7]. Alternatively, the heated residue may be kept in a soaker drum for some time (as in delayed coking but at a lower temperature and shorter time).

1.3 Finished Fuels

As the boiling point range of the fuel is raised, the molecular weights and densities of the fuel components also increase giving rise to the terms 'light' and 'heavy', which refer to lower and higher boiling fractions, respectively. Finished fuels from a refinery are usually made up by blending a range of distillate streams (plus residual fuel for heavy fuels) – a range that can be several streams in a complex refinery (Figure 1.1). Blending enables all of a refinery's production to be used. The process is guided by the need to meet a range of specifications for the products. Specifications are set by various industry and government bodies to ensure that fuels meet a minimum quality to provide the performance needed by the customer and minimise environmental pollution.

1.3.1 Gasoline

Several refinery streams may be combined to produce gasoline that meets the local specifications – the most important two are octane number and volatility. Octane number is the gasoline quality that indicates whether the fuel will work effectively in the engine; it is specified either as a Research Octane Number (RON) of at least 95 or a Motor Octane Number (MON) of at least 85[11] (EN228 specifications) [25,26]. A minimum octane rating is necessary to ensure that gasoline used in an engine with standard compression[12] does not cause the engine to knock. Such knocking is caused by auto-ignition of the gasoline/air mixture lower down the engine cylinder as the flame front moves through the cylinder. This causes an out-of-time spike in pressure accompanied by a sharp sound (knock or ping) that can lead to engine damage (section 6.2.1). Auto-ignition is a free radical process which is inhibited by compounds that form relatively stable radicals, such as highly branched alkanes as 2,2,4-trimethylpentane[13] and alkyl aromatics such as toluene (see Chapter 6).

In order that gasoline burns evenly and completely in the combustion chamber, it must vaporise readily – the volatility of a gasoline should also be sufficient to ensure easy starting. Volatility is specified, for example in Europe and the USA (Table 1.3 [9,26]), and it depends upon the distillation properties of a gasoline, so the specifications are met by blending streams of different distillation ranges. Laboratory distillations of refinery products (by a standardised distillation procedure, ASTM D86) provide the cumulated weight percentage collected at each distillation temperature (see section 4.2.5). For the European EN 228 gasoline specification, distillation is presented as the amount evaporated (same as collected distillate) at 70°C, 100°C and 150°C or 180°C, and at the final boiling point (Table 1.3a)[14]. In the USA, ASTM gasoline specification D4814 distillation requirements are presented as the distillation temperature at which 10%, 50% and 90% of the distillate is collected, together with the end point – the temperature at which the last of the distillate is collected, the final boiling point (Table 1.3b). In general, the carbon numbers of the hydrocarbons that make up gasoline are mostly C_4 to C_{11}, with small amounts of C_3 and C_{12} [9].

Different classes of volatility are set to allow for climatic variations owing to region and season. Vapour pressure is a balance between the need to avoid vapour lock (vapour bubbles in the fuel lines, inhibiting the pumping of the fuel in hot weather) and to provide easy starting in the cold (which needs the lower boiling material). Since the vapour pressure is measured at a fixed

Table 1.3a EN 228, European volatility class gasoline specifications (the first, fourth and sixth of the six classes have been selected).

Volatility/ Distillation	Unit	Class A	Class B	Class C	Class D	Class E
Vapour pressure	KPa at 38°C	45–60	45–70	50–80	60–90	65–95
Ambient temperature	°C	>15	5 to 15	−5 to + 5	−15 to −5	<−15
% Evaporated at 70 °C	Vol %	20–48	20–48	22–50	22–50	22–50
% Evaporated at 100 °C	Vol %	46–71	46–71	46–71	46–71	46–71
% Evaporated at 150 °C	Vol % maximum	75	75	75	75	75
Final boiling point	°C, maximum	210	210	210	210	210
MON/RON		85/95	85/95	85/95	85/95	85/95

Table 1.3b ASTM D4814, American volatility class gasoline specifications (the first, fourth and sixth of the six classes have been selected).

Volatility/Distillation	Unit	Class AA	Class C	Class E
Vapour pressure	Max. Kpa at 38°C	54	79	103
Temperature for 10% evaporated	°C, maximum	70	60	50
Temperature for 50% evaporated	°C, maximum	77–121	77–116	77–110
Temperature for 90% evaporated	°C, maximum	190	185	185
End point	°C, maximum	225	225	225
Anti-Knock Index, (MON + RON)/2		Regular 87	Mid-range 89	Premium 91–94

temperature, this figure rises along the series of fuel classes to reflect the lower temperatures at which these classes of fuels are used; class E fuels would be used when the ambient temperature is low (winter) and class A when it is high (summer) (Table 1.3). The variation in the distillation temperatures of the

Table 1.4 The refinery components (Streams) that may be blended into the gasoline.

Component	Vapour Pressure, Kpa at 38°C	RON
Butanes, iso/normal	483/354	93/93
Pentanes, iso/normal	132/100	93/72
Light straight run (LSR) gasoline	76	66
Heavy straight run (HSR) gasoline	7	62
Light hydrocracker gasoline	88	83
Heavy hydrocracker gasoline	7	68
Coker gasoline	24	67
FCC light gasoline	95	92
FCC heavy gasoline	10	83
Reformate 94 RON	19	94
Reformate 98 RON	15	98
Alkylate C3’	39	91
Alkylate C4’	31	97
Alkylate C5’	7	90

lowest boiling 10% (USA data) shows that the higher vapour pressure is a result of including more lower boiling material in the gasoline. The same higher boiling blend components are used in all grades so the amounts of distillate at higher test temperatures vary little across the class series.

To meet both the requirements of octane and volatility, a refiner blends together a range of components that depend upon their availability in his refinery. The range of components that may be used have varied octane numbers and volatilities (Table 1.4). Gasoline fractions are known either as light and heavy gasoline or as light and heavy naphtha. These are mostly volatile enough to be fed into the engine as a vapour mixed with air after passage through the carburettor. Modern gasoline engines now use fuel injection which provides much better, electronic control of the fuel/air mixture; however, when the gasoline enters the combustion chamber, it has been almost completely vaporised in the inlet port. The light and heavy gasolines make up the bulk of the final blend but, when straight run, these have relatively low RONs [6] (Table 1.4). However, in a complex refinery there are other gasoline blend components that have the similar boiling ranges but higher RONs; such components come from distillations of FCC and hydrocracker products, and from the reformer and alkylation (sections 1.2.3 and 1.2.4).

Volatile alkanes – butanes and isopentane – help raise the RON of the blend towards the specification minimum of 95 but their use is limited by their volatility. Using the calculation for vapour pressure contributions to a gasoline blend [6], just 1.0 volume % of iso-butane increases the vapour pressure by 23 kPa, so it must be used sparingly.

Clearly, with this range of components, given the limitations of availability in a refinery, achieving a 95 RON may be quite difficult. There are, however, several alternative blend components with significantly higher RONs that can provide a boost to the RON of the blend. For example, methyl-tert-butyl ether (MTBE) was a much-favoured blend component having a RON of 115; a textbook example [6] shows that 7% of MTBE raises the RON from 88 to 95. Other components that can be used are short chain alkylated benzenes, such as toluene and xylene (RONs of 120 and 118), isopropanol and ethanol (RONs 118 and 109) – ethanol is a favoured component as it is readily made in large quantities from natural, renewable resources and, for example, blending 30% ethanol with gasoline (RON of 91) gives E30 which has a RON of 101 [27].

The major change to gasoline since 1990 has been the reduction of sulphur in most parts of the world. Sulphur dioxide is harmful if inhaled, causing lung diseases such as asthma and bronchitis. Initially, sulphur in gasoline was reduced to low levels of below 100 ppm (from up to 0.5% in the worst case) but other emission controls were also introduced to minimise unburnt hydrocarbons and carbon monoxide, which required catalytic convertors in vehicle exhaust systems. Such catalyst are very sensitive to deactivation by sulphur, so ultra-low sulphur specifications of 10 to 15 ppm maximum have been introduced widely. Sulphur is removed by hydrogenation of the fuel over a catalyst.

1.3.2 Middle Distillates

Fuels with boiling points higher than those of gasoline are generally known as middle distillates: jet fuel, kerosene, diesel fuel and heating oil. Higher boiling fractions may be blend components for some diesel and heating oils, or they may be blended into heavy fuels; various proportions may not leave a complex, modern refinery at all but are, instead, converted to the more valuable lower boiling fractions in the crackers. Where there is an excess of heavy distillates, there is a market for these as lower cost fuels for heating, power generation, off-road vehicles (earth moving and farm equipment), and marine fuels.

Middle distillates, in general, can suffer from a problem which does not arise with gasoline – that is their tendency to produce wax in the cold. This wax results from the higher molecular weight n-alkanes present in middle distillate fractions crystallising out of the fuel. The higher molecular weight, least soluble n-alkanes are also the highest boiling, so wax formation can be the factor that limits the use of high-boiling fractions in a fuel blend (see Chapter 4).

1.3.2.1 Jet Fuel

Jet fuel is a kerosene stream with more clear-cut specifications than those of general kerosene. The main international jet fuel, Jet A-1, distils to give 10% recovered at 205°C and an end point of 300°C; hydrocarbons in jet fuel have carbon numbers C_8 to C_{16} [28]. The upper boiling limitation is to ensure complete vaporisation in the jet engine and to ensure no wax formation in the wing tanks; the lower boiling specification is to remove the fire risk and vaporisation losses that were problems with the early, broad-cut jet fuel, which contained gasoline fractions [28]. It is often taken from the straight run atmospheric distillation, but hydro-treated streams may also be blended in. It is not heavily de-sulphurised, having a sulphur maximum specification of 0.3%, but mercaptans are neutralised by conversion to the less corrosive disulphides in the Merox© process [6]. There are a number of items specified to ensure the suitability of a particular fuel for handling, storage and use [28,29]):

- Conductivity and flash point to avoid the risk of vapour/air explosions initiated by a static spark.
- Freeze point to avoid wax separation at −40°C to −55°C in wing-tanks and viscosity to ensure no problems in pumping the fuel from wing-tank to jet engine.
- Reliable combustion relies upon energy content, distillation to ensure vaporisation in the engine, and smoke point and aromatics content to ensure that no soot is produced.
- Acidity and sulphur content are limited to prevent corrosion of the fuel system and corrosion of turbine metal parts a by sulphur oxides.
- Stability against the formation of fuel-line-blocking degradation products during storage.
- Lubricity of the fuel to prevent wear in the fuel pump.

Since a jet fuel is, in fact, burned in air, it does not have to meet an octane- or cetane-like requirement, though it does need a minimum calorific value, as do gasoline and diesel fuels. A sooty flame would provide a number of problems such as erosion of turbine blades, build up and blockage of the air inlets inside the jet engine, and changes to heat absorption by the jet engine walls. The other controls on handling and storage, such as stability, corrosion, lubricity, and prevention of static sparks, are similar to those for gasoline and diesel fuels. Wax separation in jet fuel is avoided altogether by limiting higher boiling components to meet a freeze point specification, which is set below the lowest temperature that a jet fuel is expected to meet.

1.3.2.2 Diesel Fuel

Diesel engines all use fuel injection as most of the fuel components (usually C_{12} to about C_{30} hydrocarbons) have low volatility. Fuel is sprayed into the combustion chamber through very fine orifices under very high pressure (30,000 psi or 200 MPa [8]). This occurs at top dead centre of the piston-in-cylinder cycle. At top dead centre, maximum compression of the air, taken in on the first down stroke of the piston, produces a temperature that is high enough to cause the injected fuel to auto-ignite. Auto-ignition, a problem to be avoided in gasoline engines, is essential to the operation of diesel engines – if it does not occur at the right time on every stroke, 'diesel knock' occurs, which reduces engine efficiency and causes excessive wear. Auto-ignition fuel qualities are reported as cetane numbers[15], which respond to fuel component chemistries in a fashion contrary to the response of octane numbers (data here drawn from different references [8,9] [30,31]):

- n-Alkanes have low auto-ignition temperatures and a low tendency to form relatively stable radicals, which would slow down auto-ignition. This is desirable for diesel engines with the standard for a cetane number of 100 being cetane (hexadecane).
- Branched n-alkanes, such as iso-octane, form relatively stable free radicals via H-atoms donated from tertiary C–H positions. This is bad for auto-ignition, so branched n-alkanes have low cetane numbers: 2,2,4,4,6,8,8-heptamethyl nonane, known as iso-cetane, is used as a low cetane standard having a cetane number of 15.
- Alkyl-aromatics can form relatively stable radicals on the carbon attached to the aromatic ring. These also have low cetane numbers – for example xylene has a cetane number of 30 compared with a RON of 118; 1-methylnaphthalene is defined as having a zero cetane number. The aromatic-rich FCC gas oils and kerosenes have low cetane numbers but can be hydro-treated to make them more suitable for diesel blends. Severe hydrotreating is needed to provide ultra-low sulphur diesel (ULSD, maximum 10 ppm sulfur), so separate hydro-treating of a FCC component may not be necessary.

In the aerosol of injected diesel fuel, some of the fuel vaporises and some remains as small liquid droplets which have the potential to produce fine particulates of unburnt carbon in the exhaust – particularly if the fuel contains a high proportion of high boiling components that contain hydrocarbons above C_{30} and multi-ring aromatics, such as alkyl naphthalenes. To minimise particulate emissions by road vehicles, boiling ranges and polycyclic aromatics contents are controlled by the current diesel specifications, especially in the

European specification EN 590 [26,32]. The main EN 590 specifications, for on the road diesel, are listed below (Table 1.5). An additional control of the emission of harmful particulates is provided by diesel particulate filters that are now fitted to diesel vehicles (see section 6.2.4).

Other properties that are measured to agreed specifications are viscosity and corrosiveness; cloud point, pour point, and cold filter plugging point to protect against waxing problems in cold weather; oxidative stability to prevent the formation of insoluble particles on storage; lubricity as a measure of ability of the fuel to lubricate the fuel pump; and flash point to be > 55°C for safe handling [8].

Components with distillation ranges within the diesel fuel specifications that may be combined into a diesel fuel may be selected from the following list, depending upon the refinery concerned – different degrees of conversion and different product demands affect the availability of the components:

- Kerosene.
- Light gas oil (LGO, No. 1 fuel in the USA).
- Middle gas oil (MGO; No. 2 fuel in the USA).
- Heavy gas oil (HGO, while too high a boiling range for EN 590 diesel, they were allowed in off-road and marine diesel fuels until recently).
- Fluid catalytically cracked gas oils (FCC-GO) have low cetane numbers so their use is limited unless they are hydrotreated.
- Hydrocracked gas oils (HCGO).

The boiling ranges of LGO, MGO and HGO can vary from refinery to refinery or the refinery may have only two gas oils which cover this boiling range.

Table 1.5 Selected specifications for on the road auto diesel oil, EN 590.

Property	Units	Minimum Value	Maximum Value
Cetane Index (CI)[16]		46.0	–
Cetane Number (CN)		51.0	–
Density at 15°C	kg/m^3	820	845
Sulphur content	mg/kg	–	10.0
Water and sediment	mg/kg	–	200
Polycyclic aromatics	% Wt.	–	4.5
Distillation, vol.% recovered, at:			
250°C	% V/V	–	<65
350°C	% V/V	85	–
95% recovered at:	°C	–	360

1.3.2.3 Heating Oils

Heating oils, also known as furnace oils, cover a wide range of boiling points and aromatic contents and often provide a sink for lower value refinery streams that cannot be used in other fuels. Such streams include aromatic middle distillates (also known as cycle oils), which are by-products of the FCC (after gasoline production), high boiling atmospheric, and vacuum distillates and residual fuels. Different burners for heating systems have varied tolerances for aromatics which, when burned, have a high oxygen requirement and a tendency to produce a sooty flame, or 'smoke'. Specifications limit the amount of aromatics through the use of the aniline point and smoke point tests [6]. Kerosenes with low aromatic content are more valuable as jet or diesel blend components; however, low aromatic/low sulphur grades of kerosene, which burn with little smoke, are also necessary for small, free-standing domestic paraffin heaters – these were widely used from about 1900 to the late 1980s when grades such as Esso Blue and Shell Pink were widely advertised.

Currently, in the UK, domestic heating oil (EN 2869 Class C2 [33]) is now kerosene that contains aromatic fractions – the difference between this and diesel fuel is clear from its smell. Oil heaters are now somewhat like mini-jet engines and have assured ventilation and exhaust systems. The older domestic, free-standing paraffin heaters relied upon a drip-feed system and no special ventilation arrangement. In larger heating facilities, and in general in Europe and North America, heating oil is a gas oil, somewhat similar to diesel fuel; however, it may contain more aromatic fractions, so it has a lower cetane number (45 minimum) and often has a higher cloud point. It is also used as off-road diesel in tractors, construction equipment, and boats. Heating oil usually has no duty and a low VAT, so it also contains a chemical marker and a dye for identification. In North America, heating oils (furnace oils) vary widely with region and may be a kerosene-like fuel ('No. 1 fuel') or a blend of No. 1 fuel and No. 2 fuel (see ASTM D396 [34] for fuel oil specifications).

While some off-road and heating oils had high sulphur contents (0.2% and 0.5% for Classes C2 and D) before 2010 [35], since then, off-road ('Red') diesel has a maximum of 10 ppm sulphur – gas oil specification EN 2869 Class A2 – as for modern on-road diesel. The class D gas oil specification now allows sulphur contents up to 1000 ppm (0.1%, EN 2869 Class D) for use as marine red diesel and static uses. In many parts of the world, various higher boiling gas oils, some of which contain residual fuels, are burned to raise steam in large-scale heating facilities or power stations.[17]

1.3.2.4 Marine Diesel Fuels and Power Generation

Marine diesel engines used a wide range of blends and specifications – a list of the specifications shows 4 distillate categories and 11 residual fuel categories

[36]. These contain high-boiling, vacuum-distilled fractions that are not found in on-road diesel fuel. Distillate heavy fuels are known as marine gas-oils, or just gas-oils. Residual fuel categories also contain the various residual fuels that are found in a refinery. Fuel storage vessels on ships are termed bunkers and the loading of ships fuels is 'bunkering' [37].

Atmospheric residue is now less commonly available because, in most refineries, it is vacuum distilled. Residual fuels, from the vacuum still or visbreaker, contain low solubility compounds known as asphaltenes. To guard against the possibility that the asphaltenes may separate out and to control their high viscosities, residual fuels are usually blended with aromatic light and heavy cycle oils. The sulphur contents of these fuels have been much higher than those of on-road diesels but have recently been sharply limited: in 2015 the maximum of 1.0% was reduced to 0.1% in European coastal waters and, in 2020, the maximum was reduced from 3.5% to 0.5% in the open sea [38]. At the time of writing, the whole range of marine fuel specifications have been or are being rewritten to meet the new limitations on sulphur contents and it appears that it may take some time for them to be followed everywhere [39]. Residual fuels may also end up in cokers – a more likely destination now that the worldwide sulphur specification for the heaviest marine fuels is limited to a maximum of 0.5%.

Heavy fuel oil (HFO) may be blended from any or all of these components [36]:

- Light and heavy gas oils (LGO and HGO);
- Light and heavy cycle oils (LCO and HCO);
- Waxy distillate (WAXD);
- Atmospheric residue (ARES);
- Vacuum residue (VRES);
- Visbreaker residue (VisRES).

Any of the distillates could be straight-run or by-product from the cracker or coker streams – they are more likely to be the low-value, by-product streams that cannot be used in the high-quality and high-value distillate products, such as on-road diesel. Cost is a particularly important factor for shipping which burns huge quantities of fuel in a highly cost-competitive business.

The large engines that are used to propel the marine world have been adapted to the production of electricity. For example, Wartsila, one of the major producers of marine diesel engines, including some of the largest of such engines, also produces power plants that use these engines [40]. There is a full range of diesel generators up to major power stations that may burn the heavy fuels also found in bunkers. Alternatively, these heavy fuels may be found in power plants in which the fuels are burned to produce steam to drive steam turbines for the generation of electricity.

1.3.4 Coal, Gas or Biomass to Liquids

The fuels discussed so far have come from crude oil. However, liquid fuels can also be obtained from other sources using the Fischer-Tropsch (FT) process. This was invented in Germany in the 1920s to converts a mixture of carbon monoxide (CO) and hydrogen (H_2) into a range of paraffins, at moderate pressures and temperatures over a range of catalysts [41,42]. The reactant mixture, known generally as producer gas, may be produced by blowing steam through a bed of burning carbon, coal or coke. Coal-rich countries without access to oil have made the earliest use of this Coal To Liquids (CTL) process: Germany, in the Second World War, and South Africa in response to oil sanctions in the 1950s and onwards. Sasol (founded in 1950 in Sasolburg, South Africa) still makes full use of this process. Now, methane (natural gas) is used as the preferred source of producer gas in the gas-to-liquids (GTL) process. Sasol International licenses its technology and provides FT conversion units to other countries with large coal reserves, such as China, or with large methane reserves, such as Nigeria [43]. Any carbon-containing fuel can be used as a source for the producer gas, and processes have been developed to use biomass such as straw and wood chips for Biomass To Liquids (BTL).

FT products are n-alkanes, so the lower boiling liquids have low octane numbers and need to be cracked and reformed to produce iso-paraffins and aromatic compounds that are suitable for use as gasoline. n-Alkanes have high cetane numbers, but those with middle distillate volatility and carbon numbers are waxes. These waxes are selectively hydrocracked and isomerised to produce liquid alkanes that have some alkyl branching while retaining a high cetane, making them suitable for diesel or jet fuel [44]. In Qatar, Shell Global have been responsible for the building of the world's largest GTL plant which produces low-sulphur naphtha suitable as chemical feedstock, kerosene for jet fuel and heating oil, gas oil for diesel fuel and paraffin waxes [45].

1.3.5 Biofuels

There is now a further fuel category: biofuel. European biodiesel contains Fatty Acid Methyl Esters (FAMEs), which are derived from natural sources such as soya, sunflower, rapeseed (canola), and palm oils [46]; also, used from cooking oil, recovered from major users such as fast food outlets. FAME has good cetane properties and low sulphur content (specified as EN 14214 [47]). Biodiesel containing FAME is described by its B# – for example, B10 contains 10% FAME and 90% petroleum diesel. Another, less common version is Hydrotreated (hydrogenated) Vegetable Oil (HVO), which has the advantage of being pure hydrocarbon, with a good cetane number. These hydrocarbons are mainly n-alkanes which contribute to the wax content of the fuel (see Chapter 4) so, as for GTL, they may need catalytic reforming to be converted into more soluble iso-alkanes.

For gasoline, alcohols and ethers are used as blend components under the label 'Oxygenates' [46]. Ethanol is the main bio-alternative, though consideration has also been given to butanol; both ethanol and butanol are made by fermentation processes. MTBE, methyl-t-butyl ether, was popular for a time, but its use was discontinued on concerns over drinking water contamination. Butanol is less volatile and more fuel-like (C_4H_9OH), with a higher proportion of hydrocarbon than ethanol (C_2H_5OH), but ethanol is currently accepted as the biological gasoline source of choice. The mixture of ethanol and petroleum-derived gasoline is sometimes referred to as gasohol and rated with an E# – for example, E10 refers to a gasohol containing 10% ethanol and 90% petroleum gasoline.

Biofuels are often blended into petroleum-sourced fuel, and the blend must meet the same specification requirements as 100% petroleum fuel. Some refiners and writers refer to biofuels as oxygenates and as additives. However, those in the additive industry consider them to be blend components, as distinct from performance-enhancing additives used at, usually, less than 1% of the fuel [48,49]. Blend components add volume and calorific value to a fuel while additives are added at such low levels that they do not add significantly to the fuel [50]. This distinction is worth remembering when looking at the statistics of quantities of fuel additives in use because some citations have included oxygenate blend components in their figures while others have not.

1.4 Fuel Additives – Value and Need

1.4.1 Value

Fuel additives are, in the most part, not sold as finished products to the end user, such as motorists, ship or truck operators and home heating consumers, but to the producers and marketers of bulk fuels [48]. Additive packages, at levels that are adequate to provide at least the minimum needs for fuel to meet specifications or consumer handling, are usually added at the refinery. Premium grades of fuel will contain higher levels of some components, such as the fuel detergent, and may be added either at the refinery or at the fuel distribution terminal [4] [18]. Relatively small amounts of fuel additives are sold directly to consumers in small packages with promises of improving their vehicles performance or protecting it from harm. Certainly, in the developed world, commercial fuels have to meet tight specifications so contain the required additives and more, for competitive reasons: commercially available fuels usually have no need for further additives.

Of the worldwide petroleum consumption total of 4662 million tonnes in 2018, 76%, or 3543 million tonnes per annum (mtoa), were liquid fuels [18]. Fuel additives are used at a range of total concentrations depending upon need and fuel grade. For gasoline and middle distillates these can range from 1 to 1000 ppm (parts per million, 0.0001 to 0.1%, by weight) of undiluted, active ingredient [48] – with a reasonable average being 500 ppm, a total that is usually a combination of additives. Examples of additive concentrations, or 'treat rates', in automotive fuels are found in a paper from the Technical Committee of Petroleum Additive Manufacturers (the ATC) in Europe [48] and, in general, in many patents. For example, for heavy fuels, tests on an asphaltene dispersant (stabiliser) were carried out at 700 ppm [51] or 2000 ppm [52] while a combustion improver was said to be used at preferred 10 to 30 ppm [53]. The reader is directed to relevant sections in this book for each additive type.

Assuming that all the world's fuel is treated with 500 ppm of additive (on average), this would indicate a potential total worldwide fuel additive use of 1.8 mtoa (in 2018). 'ATC estimates ... that the EU-27 market for fuel additives is over 200,000 tonnes per annum' in 2013 [54], which would be to treat about 15% of the world's liquid petroleum products, giving an estimated potential of about 1.3 million tpa. A published estimate of fuel additive volumes expected in 2016 is 26.5 million tonnes, but 94% of this is made up of ether oxygenates for gasoline [55] – more generally considered to be blend components and without which this estimate is for 1.6 million tpa for performance additives. The European ATC estimated a worldwide turnover of €7 billion in 2013 [54] while more recent figures are of $7.5 billion in 2017 and an outlook of $8.7 billion in 2023 [56].

1.4.2 Need

Fuel additives are needed to provide fuels with properties that they do not have after the refining processes, or to provide those properties that would cost much more to provide by a refining solution. These fuel properties are often seen as being essential such as the ability of the fuel to lubricate the fuel injection pump (lubricity), inhibiting autoxidation to prevent the formation of filter-blocking particulates during storage and the ability of diesel fuel to flow in cold weather (cold flow). It may be possible to solve some of these problems during refining but at much higher cost. For example, cold flow in diesel fuel can be provided by adding more kerosene; however, about 5% additional kerosene is needed for one degree centigrade of cloud point reduction while ten degrees of cold flow improvement may be obtained by the addition of 100 to 500 ppm of additive[19].

A problem with refinery solutions is that the improvement in one property may lead to the degradation of another property. Take lubricity, this is not a problem if sulphur is not removed at the refinery, but desulphurization of gasoline and diesel is now written into legally binding specifications as an environmental measure, almost worldwide. The process to remove sulphur also removes naturally occurring lubricity-providing compounds – lubricity additives replace this loss. With cold flow, more n-alkanes in diesel are good for cetane but they produce more wax and, hence, poor low temperature handling. In this case, a cetane improver can help cetane and a cold flow improver solves the low temperature handling [57]. The availability of these additives to meet the necessary performance specifications enables a refiner to optimise distillations and fuel component blends and so match production with demand more efficiently.

Competitive marketing makes good use of valuable features that a fuel additive may provide. For example, an anti-foaming agent enables quick filling of a fuel tank at the pump – especially useful for a 200-litre tank on a 40-tonne truck. The need for safe, trouble-free distribution favours the use of anti-foam, anti-static, biocide, and demulsifier additives. Detergents in automotive fuels are now seen as being essential for keeping critical parts of the fuel systems clean, particularly injector nozzles, which have extremely fine orifices through which fuel is sprayed. The use of fuel detergents reduces maintenance problems, fuel consumption, emissions and ensures a smoothly running engine.

Some advantages may seem small to the private motorist, such as the evidence-backed 3% fuel-saving claim for Shell Advanced Diesel (1988 [57]), but the value of this 3% to a truck fleet operator was €1,350 per year per 40 T truck (Goodyear's estimated value of a 3% fuel saving in 2008 [47,58]). Such savings are even more valuable to a shipping company – a 7000 teu[20] container ship typically burns 217 tonnes of fuel per day! [59]. On the other hand, the private motorist or householder with oil-fired heating would be terribly upset if their car or heating did not work because fuel deposits blocked the fuel lines. Most people would consider it unacceptable to permit any risk of failure in an aeroplane jet engine due to deposits or corrosion.

Leakages from corroded large storage tanks have been either a minor inconvenience or catastrophic, with terrible fire risk and outstanding environmental effects. A recent example is that of the scale of such problems is provided by the Norilsk oil spill starting on the 29 May 2020, when a fuel storage tank collapsed, spilling around 21,000 cubic metres of diesel fuel into the local river which is a tributary to other rivers downstream [60]. The company involved referred to softening permafrost as a cause but this tank had been identified years earlier as needing treatment because of extensive corrosion. At time of writing, it is reported that the Russian government is fining the company, Norilsk Nickel, $2bn as the cost of cleaning up the affected rivers [61]. So, a corrosion problem can not only cause damage to the environment but can also cost an errant company dearly.

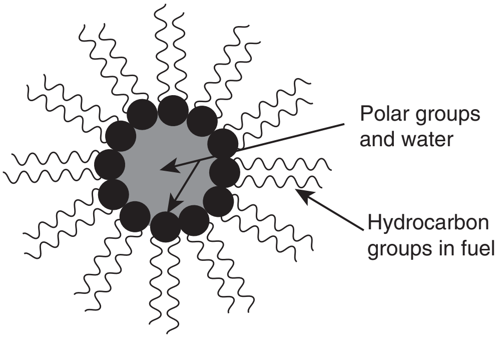
1.5 The Application of Fuel Additives

Additives for some applications, such as detergents, are used in most fuels though specific details vary from fuel type to fuel type. Cold flow improvers may be used in all fuels except gasoline, but jet, diesel, marine-distillate, and marine-residual fuels all require different, specific cold flow improvers. Others are quite fuel specific: octane improvers are used only in gasoline and cetane improvers only in diesel. However, the physical chemistries relating to the modes actions of a range of detergents, lubricity improvers, cold flow improvers, anti-foam additives, and the rest, are usually the same across the full range of fuels. Also, the chemical entities of the various versions of a additive type are usually related. For these reasons, the approach taken in this book is to classify by additive type, since that best relates to additive chemistries and their modes of action.

An aspect of fuel additives that is sometimes overlooked is that they are used in a hydrocarbon medium. The active parts of additives are usually polar so will tend to aggregate in hydrocarbons. Consequently, the individual molecules need to carry substantial non-polar groups to confer solubility – they are, in fact, surfactants [62]. Surfactant chemistry is mostly concerned with aqueous solutions, in which the hydrocarbon segments of surfactant molecules aggregate leaving the polar groups in contact with the water [63,64]. A fuel additive may be added at only a few hundred parts per million to a fuel but the polar groups, having no solvation, must aggregate together – their dipole-dipole and hydrogen-bonded interactions outweighing the entropic advantage of separation. With the polar groups and water from the fuel on the inside and the hydrocarbon groups on the outside (the long tails), such aggregates are known as reverse or inverse micelles [65] (Figure 1.8). This arrangement is likely to affect the activities and interactions of different fuel additives, both in the dilute state in fuel and in the concentrated fuel additive package.

Additives are supplied to an oil company as a concentrated solution that is then, usually, automatically injected into a fuel stream – either during refinery fuel blending or further down the supply-line between fuel terminal and tanker. An oil company needing to use several fuel additives will not wish to use several different storage and injection systems but just one, for a concentrate into which all the required additives have been blended. Such concentrates can

Figure 1.8 Diagrammatic Inverse Micelle.



suffer from physical instability, leading to undesirable phase separations with a different mix of additives in each separate phase – one objective of the development work of additives and their packages is to ensure the stability of the concentrates.

After decades of research, testing, development, and application of fuel additives, significant changes have occurred since the early 1990s. There has been a continual engineering push to improve engines for fuel efficiency and reduced emissions, aided by tightening of fuel specifications to help these improvements, backed by legislation. This progress has led to changes in fuels and more severe requirements in an engine. In addition, there has been the introduction of biofuels. These fuels, alcohols or esters (also known as oxygenates), provide significant levels of polarity and alter the solvency of the fuel, a factor that may affect the activity of the additives and which enables the fuel to absorb water. Other new fuels, such as GTL or HVO, are more petroleum-like and can provide high cetane numbers with little effect on the solvency or hydrophilicity of the fuel.

There are many fuel additive types available and their use may be optional or necessary, dependent upon fuel type. Also, some additive names vary depending upon the fuel in which an additive is used – for example, a friction modifier for gasoline is now termed lubricity improver when applied to diesel fuel. A summary of fuel additives and their applications to the different fuel types has been compiled as a guide (Table 1.6). It is worthwhile qualifying this list with a discussion by fuel type.

List compiled using references [7–9,50,57,66–72]. Heating oil is usually mentioned alongside diesel fuel but possible additives for heating oil are sometimes listed [73]. The Shell website [74] contains a list of additives that may be used in jet fuel (and 'Avgas'); the fuel additives sections of the Chevron [8,9], Lubrizol [68], Infineum [69] and Innospec [70] websites give descriptions of the problems that fuel additives solve in a range of fuels.

Table 1.6 Fuel additives and fuel type.

Additive Type	Gasoline	Jet Fuel	Diesel Fuel	Heating Oil	Heavy Fuel
Anti-icers	y	y	y	y	
Anti-static additives	y	Y	Y	y	
Biocides/Anti-foulant	y	y	y	y	y
Cold flow improver		(y)	y	Y	Y
Combustion improver	Octane improver		Cetane improver	Ferrocene	Y
Corrosion inhibitor	Y	y	Y	Y	Y
Particulate filter additives			Y		
De-/anti-foamers			Y	Y	
Demulsifiers/Dehazers	y		Y	y	
Detergent	Y		y		Y
Dispersant		y	y	Y	
Drag reducers	Y		y	y	
Dyes and markers	Y		y	y	
Emissions reduction	y		Y		
Friction modifiers	Y				
Lubricity additives		y	y	y	
Metal deactivators	y	y	y	Y	
Oxygenates/biofuel	Y		Y	y	
Re-odorant			y	y	
Silver corrosion inhibitors	Y				
Slag and ash inhibitors					Y
Stabiliser, antioxidants and metal deactivators	Y	y	Y	Y	y
Sulphur scavenger					Y

Additive use in jet fuel – also known as aviation turbine fuel – is particularly tightly controlled. Only specific additive types allowed and the individual, commercial compounds must be approved as additives for use in jet fuel (see Appendix D, Additives, in Aviation Fuel [29]). Jet fuels are specified internationally as Jet A-1 and, in N. America, Jet A; in addition, there are some national grades and several military grades. Here, use in Jet A-1 is taken as the major criterion: anti-oxidants and static dissipaters are required; anti-icing, corrosion and lubricity additives are used by agreement between jet fuel supplier and customer; metal deactivators and biocides are optional. Thermal stability additives are required in some special fuel grades that are used in USAF aeroplanes.

Both automotive fuels, gasoline and diesel, use most of the types of additives listed – especially detergents – with a few major exceptions. In gasoline, at one time octane improvers were widely used but, with the removal of lead anti-knock for environmental reasons, there is only a minor role for octane number improvers. Refiners usually depend upon blending together the right refinery components to attain the necessary octane number. Diesel fuel sometimes needs the addition of a cetane improver to meet the specification cetane number. Cold flow improvers are widely used in diesel fuel to modify the wax that separates in the cold, which is not a problem with gasoline.

Heating oil is often like diesel fuel but with a higher cloud point, so it also needs cold flow improvers. It often contains more aromatic compounds than does automotive diesel fuel and, since it is usually stored for many months before use, biocide and stability additives are needed. In some countries, such as the UK, domestic heating oil is usually kerosene – one containing much of the aromatic FCC by-product kerosene (also known as light cycle oil).

Heavy fuel, containing residual fuel, will have a relatively with high sulphur content (up to 0.5% from 2020) so has special problems of corrosiveness and may also need a hydrogen sulphide scavenger. While detergents may have some beneficial effect on the injectors, they are often added to stabilise the asphaltenes in the fuel, which may otherwise separate out on storage. When heavy fuels are burned in furnaces for steam generation in power stations, large heating installations or refineries, there is a need to control the build-up of ash in the form of a slag on the walls of the furnace, heat exchangers and exhaust systems, where it causes severe corrosion.

Certain problems apply to all fuels, such as the needs for corrosion inhibitors, biocides, and stabilisers, which are particularly necessary during long-term storage. Demulsifiers or dehazers are needed in any fuel that forms emulsions by agitation with any water that may be present in fuel tanks or lines. Distillate fuels usually need anti-static additives to prevent ignition from static sparks during the pumping of fuel through delivery hoses. Dyes and markers provide no technical advantage but are required to ensure tax is collected on motor fuel or that the correct grade of aviation gasoline is used.

1.6 Fuel Quality, Taxation, Dyes and Markers

1.6.1 The Need for Quality and Brand Recognition

Perhaps the earliest patent on the use of a dye to identify a fuel was in 1921, when there were concerns about the qualities of commercial motor fuels [75]. This early description of the problem to be addressed pointed to the fact that 'as is well known there are several grades of petrol' which may be of different qualities but were identical in appearance. Concern was that only the finest grades of petrol should be used in aeroplane engines, for there had been aeroplane crashes caused by engine problems attributed to the use of inferior grades of petrol. Not surprisingly, general concern was quickly raised by owners of the new internal combustion (IC) engines that powered their automobiles. To avoid the problem of being misled as to the quality of the petrol being supplied, it was proposed that an aniline dye should be added to the fuel to identify it as being of high quality. Some of the dyes suggested are still in use today, then referred to as Soudan 1, 2 or 3 or just 'Soudan[21] Red', to be applied at a low concentration of 2 ppm. Dyes are still used to visibly identify different grades of aviation gasoline that meet the varied requirements of different aircraft engines (Table 6.1). In 1931, invisible markers were proposed to enable a supplier to identify his grades of petrol or motor spirit; such markers would be detectable by some physical or chemical test [76].

Very soon in the history of internal combustion engine powered transport, the oil companies sold their motor fuels based on their trustworthy brands. As the private motor vehicle numbers expanded in the first two decades of the twentieth century, many gasoline-supplying companies appeared in the USA; the break-up of Rockefeller's Standard Oil company lead to the formation of six Standard Oil companies, Standard Oil of New Jersey became Esso, Standard Oil of New York became Mobil and so on, with others such as Gulf, Texaco and Atlantic-Richfield [5]. In the UK, the Anglo-American Oil company was another Standard Oil company, taking the name Esso in the 1930s. The Shell and BP brands also have their roots in this era. Brands took over as signs of quality so there was little need for dyes and markers to set them apart; there were very few patents on this subject until after the 1939–1945 war.

1.6.2 The Introduction and Growth of Fuel Taxation

In the early days of motor transport, motor fuel taxation was low and part of the total taxation of motor vehicles levied to pay for road building. In 1928, fuel tax amounted to 24% of the cost of petrol in the UK (at a price of 1s 6½d, now 8p, per imperial gallon) [77]. From 1937, UK motor taxes have been part of general taxation and, after the Second World War, began an inexorable rise to, now, 60% or more of the price paid at the pump. This is a universal picture, though European countries apply the highest rates with France, Britain and Germany at about \$3 per US-gallon, Asia-Pacific countries about \$2 per US-gallon and the USA about \$0.5 per US-gallon [78]. However, alongside of this, big exemptions were made for public transport, heating oils and off-road applications such as agriculture, mining, marine and construction. As a result, the big driver for the effective dying and marking of fuels across the western world became the protection of fuel taxation from the illegal use of fuels for which low rates of taxes are levied, such as the widely known 'Red diesel'. While dyes give an immediately visible identification of a low-taxed fuel, after its illicit removal such a fuel may pass as a fully taxed fuel. To counteract such a problem, further identification may be provided using markers that are not visible in dye-treated fuels but may be detected by some further physical or chemical analysis.

In the USA, Sudan Red and chemically similar red dyes have long been mandated to be added to heating oils and diesel fuel for off-road applications [50] to distinguish them from taxed motor diesel. More recently, the red dye has been applied to fuels with a high sulphur content to differentiate them from ultra-low sulphur automotive diesel fuels [79]. Red diesel was used in the UK and many European countries [80] for many years to indicate that it was for use in agricultural and off-road applications, for which there was a significant concession of reduced fuel taxation [81]. Around the world, shades of red are most widely used but yellow, blue and green are also used [81]. For example, in India there is concern about the quality of motor fuels, as indicated by the developments of their diesel and gasoline specifications (listed on the website of Indian Oil [82]) as these move to match the European specifications [83]. The Hindustan Petroleum Corporation has a fuel quality promise for its kerosene backed up by the use of a blue dye, which serves the dual purpose of identifying their quality kerosene and also enabling diesel or gasoline customers to check if their fuel has been adulterated by the blue-dyed kerosene [84]. The different grades of aviation gasoline are universally identified as red, purple, blue or green.

Taxes on motor fuels have risen over the years, particularly in European countries, since 1990 [85,86]. The difference in cost to a commercial transporter between fully taxed motor diesel (in the UK, 58p per litre of diesel fuel in 2012 [86]) and lowly taxed off-road red diesel (12p per litre) had made it worthwhile for some organisations to illegally remove the tagging dye from the cheaper fuel and share the cost saving with their customers[22]. The red dyes could be removed from the fuel by acid extraction, which leaves some acidity in the fuel and produces a potentially toxic waste that would be dumped illegally.

In 2002, following a proposal in 1995 to develop a suitable fuel marker to provide greater security [80], a European community mandate was made for the addition of solvent yellow 124[23] as the Euromarker to fuels for agriculture and marine use and for heating oil, at a concentration which does not add visible colour to the fuel [81]. Such fuels are often like highly taxed automotive diesel fuel for reasons of refinery efficiency. However, Solvent Yellow 124 can also be extracted from the fuel with aqueous acid as a bright red compound – the process by which it is detected (Figure 1.15 and Figure 1.16). To quote 'This has resulted in substantial losses of tax revenue' and many member states had pointed this out to the European Commission, leading to a detailed study and calling for new candidates in the search for a more secure fuel marker to work along with existing national dyes, in 2015 [87]. Clearly, the recognition of this major problem in Europe had not been lost on dye and marker manufacturers, whose patent activity in dyes, markers and their applications increased markedly in the 1990s, after a lull in the 1980s. In earlier years, dyes had been widely mentioned in patents for improved fuels but only as one of the many additives that come under the umbrella statement 'the fuel may also contain …'.

An example of the lack of an effective answer to the need to mark low-tax fuels was the illegal tax evasion in Ireland involving the removal of dye from off-road diesel fuel. After an extended period of identification of the properties needed for secure markers and careful evaluation of candidates [87], new markers were introduced. The new technology has been demonstrated as successful in the UK, both in a 2016 news article [88] and in a 2018 Dow report [89] that provides some details of the efficacy of the introduction of the new fuel marker ACCUTRACE™ S10 in 2015 by UK and Irish authorities. The Dow report [89], which is a summary of official reports, shows a reduction of fuel-laundering plants operating in Northern Ireland from 38 in 2013/14 to 6 in 2016/17 and of hazardous fuel-laundering waste, that was collected, from 1237 tons to 148 tons on the introduction of this new fuel marker.

There had also been a burst of patent activity in the 1960s and 1970s in realisation of the need for reliable marking of fuels for tax reasons and the rapid growth in the volumes of motor fuels used. In this period, most of the patents were concerned with the solubility of the dye in hydrocarbon solvents, not only in fuel itself to ensure that the dye formed no deposits, but also in solvents such as xylene in order that the liquid solutions sold to refiners were as concentrated as possible while being stable. As with all fuel additives, the more concentrated the solution, the better the savings in cost of solvent, in transportation and storage of lower volumes, plus greater ease of injecting lower volumes into the fuel line exiting the refinery.

1.6.3 The Use and Chemistries of Fuel Dyes

Dyes have light absorption bands, due to electronic transitions, in the visible spectrum. Without an absorption band in the visible, compounds reflect all light so appear white. With absorption bands in the short visible wavelength of 400 to 430 nm, a dye would absorb in the violet end of the spectrum leaving an overall yellow appearance by the remaining reflected or transmitted light [90]. Similarly, the appearances of compounds having other absorption bands are well known (Table 1.7).

Dyes have particularly strong absorptions, giving colours at extremely low concentrations. Differences between light absorptions by similar solutions of different dyes can be in the order of powers of ten, so their efficiencies as colouring agents can differ widely which is then reflected in the cost required to produce a colouration. In practical terms, the dyes that are used in fuels will give a noticeable colour at extremely low concentrations – as low as 0.5 ppm in some cases. However, though they would be added at up to 10 ppm in order to ensure that the colour would be obvious to the eye and to take into account the possibility that the low-tax fuel may be used to adulterate a taxed fuel at, perhaps, 20% of the blend.

Initially, synthetic dyes were discovered and widely developed for colouring textiles, then inks and paints, well before they were used for colouring fuels – the first synthetic dye, mauveine, was invented by Perkin in 1856 and commercialised the following year. Diazo dyes were discovered and began their proliferation in the mid-1870s [91]. One of the earliest patents for the use of established dyes, in particular Soudan Red, for colouring fuel was in 1921 [75]; this patent was a claim for the use of any petrol soluble and water insoluble dye, particular aniline/azo dyes, for the purpose of identifying a fuel of adequate quality.

The issue of solubility in a concentrate, rather than in a fuel at 10 ppm, was realised as necessary for supplying a fuel dye in as little solvent as possible for

Table 1.7 Dye absorption bands and colour.

Absorption Band (wavelength, nm)	Appearance, Colour
430–480	Orange
480–550	Red
550–600	Violet
600–700	Blue
400–450 and 580–700	Green

easy storage and injection into fuel, at a much lower concentration. When interest in patentable aspects of dying fuels re-emerged in the 1960s, it was often of known dyes that were derivatised to ensure that they had high solubilities in organic solvents such as xylene. The simple azo dye structure of aniline diazotised and coupled with N,N-diethylaniline gave N,N-diethyl-4-phenylazo-aniline, now known as Solvent Yellow 56 (Figure 1.9), which adds a yellow colour to petrol at only 2 ppm. The N,N-diethyl-4-phenylazo-aniline version had increased solubility (35% to 50% in xylene) [92,93] over the pre-existing N,N-dimethyl-4-phenylazo-aniline dye, enabling a more concentrated commercial solution[24]. A further improvement, to enable a concentrate of up to 60% in xylene, was claimed for the azo dye from the coupling of the benzene diazonium ion with N,N,N′,N′-tetraethyl-1,3-diaminobenzene [94].

For use in oils and fuels, red dyes became widely used – these were the Sudan Reds, or Solvent Reds, that are azo and diazo compounds. These dyes have a diazo link to a naphthalene molecule and usually have a hydroxyl, alkyl ether or alkylamino substituent on the benzene or naphthalene group, such as 1-(2-methoxyphenolazo)-2-naphthol, known as Sudan Red G, or solvent Red 1 (Figure 1.10) [95].

Bis(diazo) compounds have extended delocalisation and are variations of early Sudan Reds. They have improved fuel colouring properties, such as Solvent Red 23, 1-(4-(phenyldiazenyl)-phenyl) azanaphthalen-2-ol (Figure 1.11). More recent variations on this structure were made to provide better fuel solubility and better solubility in an aromatic solvent, to allow higher concentrations in commercial solutions. A methylated variation, Solvent Red 26 (Figure 1.11) was in use over many years, in the USA (at 11 ppm), for tagging low tax heating oil

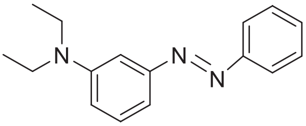


Figure 1.9 Solvent Yellow 56.

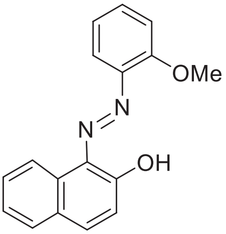


Figure 1.10 Sudan Red G.

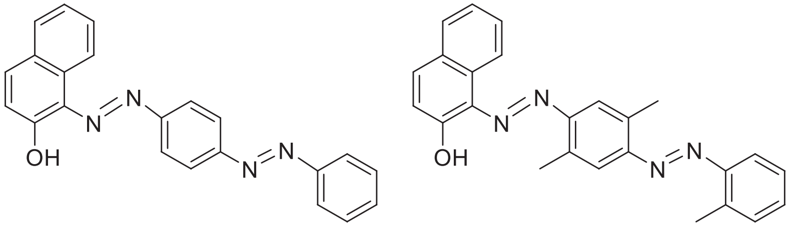


Figure 1.11 Sudan Reds, Solvent Red 23 and 26.

to prevent its being added to fully taxed diesel fuel [79]. A further variation, with a heptyl group on the naphthalene ring, solvent Red 164 [96], was introduced to tag high sulphur fuel when ULSD was introduced in the USA.

Such structures, widespread among the various versions of solvent red, are prepared by diazotising 4-amino-azobenzene and reacting it with 2-naphthol [97]. The various alkyl substitutions depend upon the alkyl anilines used to prepare the 4-amino-azobenzene and the alkyl naphthol used.

At the same time as there was a proliferation of azo dyes, a relative of an ancient red dye, madder, was brought into play as a fuel colourant. Madder contains alizarin, 1,2-dihydroxy-anthraquinone, but 1,4-dihydroxyanthraquinone is more easily synthesised from phthalic anhydride and hydroquinone, so this was the product, known as quinizarin or Solvent Orange 86 (Figure 1.12), used as a dye for fuel. However, the low solubility of quinizarin made its application difficult so the version alkylated with 2-ethylhexene was preferred for its good solubility in aromatic solvents (Figure 1.12) [98]. The 2-(2-ethylhexyl)-quinizarin may be used at very low concentrations in a distillate fuel, even as little as 0.2 ppm, when its colour is not apparent but it is readily extracted by alcoholic[25] aqueous caustic soda to give a deep purple aqueous layer [98]. In addition, quinizarins fluoresce under UV light so, with two methods of detection, they are among the earliest invisible markers.

Dyes that are green or blue are also based on the anthraquinone structure – the colour shift is obtained by amine substituents instead of the hydroxy substituents. For example, Sudan Blue II (Solvent Blue 35) is 1,4-bis(butylamino)anthracene-9,10-dione (Figure 1.13). Blue is in use in the republic of Ireland and Denmark [80] and is one of the dyes used to mark a grades of aviation gasoline [29].

A green dye is used in Norway for agricultural fuel [81] and in Italian gas oil [80]. The green dye used in fuel can be a combination of blue and yellow or Solvent Green 33, which is 1,4-bis(4-methylanilino) anthracene-9,10-dione (Figure 1.14).

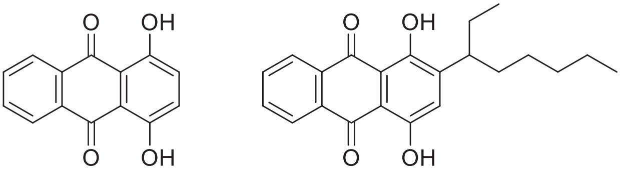


Figure 1.12 Quinizarin and 2-(2-Ethylhexyl)-Quinizarin.

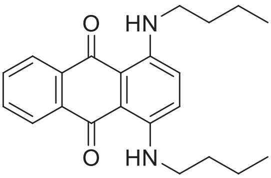


Figure 1.13 Solvent Blue 35.

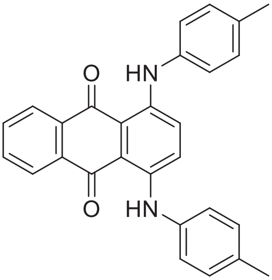


Figure 1.14 Solvent Green 33.

1.6.4 Invisible Fuel Markers

Solvent Yellow 124 (Figure 1.15) was mandated by the EU from 2002 for use as a common marker for fuels having concessionary low taxes [99]. Solvent Yellow 124 is N-ethyl-N-[2-(1-isobutoxyethoxy) ethyl]-4-(phenylazo)aniline, which is chemically stable, very oil soluble, easy to detect at very low levels and supposedly resistant to removal [80]. At the recommended concentration (6 ppm), Solvent yellow 124 is a colourless marker that is detected by extraction into dilute HCl, which hydrolyses the acetal group and protonates the product (Figure 1.16) to give an intense red colouration [99,100]. It is also detectable, quantitatively, in the presence of other commonly used fuel dyes, by its UV/visible absorption at 450 nm [101].

The use of Solvent Yellow 124 was not the first colourless marker (at its recommended concentration) to be used either alone or in combination with a

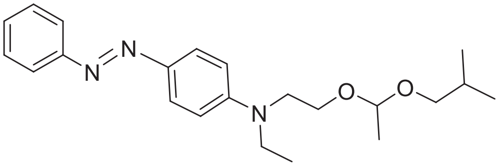


Figure 1.15 Solvent Yellow 124.

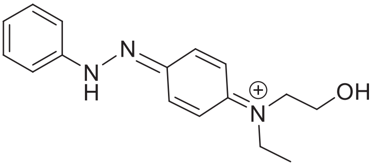


Figure 1.16 Hydrolysed Protonated Solvent Yellow 124.

visible dye. A variety of invisible markers, and means by which they should be detected, had been proposed in 1931 [76]: anthracene and its derivatives, which may be detected at low levels by their UV-fluorescence, and the indicator phenolphthalein, which turns bright pink when extracted into aqueous alkali. Furfural has been widely used in the past as a gasoline marker – it could be detected at extremely low concentrations by extraction with aniline in acetic acid to give an intense blue colour [98,102,103]. However, furfural fell out of use because of drawbacks: false positives due to low levels of contamination between fuels at the refinery, it decomposes on storage of the treated fuel and may be hidden by the coloration that fuels take up on ageing [102].

Another group of invisible markers that has been proposed [104] are those that rely upon a colour that develops on reaction with a diazonium salt. An invisible marker such as N-ethyl-N-(2-hydroxyethyl)-4-methylaniline is used to mark the fuel and is detected by contacting it with a diazonium salt of 1-aminoanthraquinone[26] in one of various forms (aqueous solution adsorbed onto titanium dioxide powder or onto a test paper) to give a dark blue-red colour (a wide range of options are described in the patent [104]).

The most recent development of invisible markers is from the Dow Chemical company. Dow® has been actively patenting many poly-aryls and their alkyl ethers, amine derivatives and others[27]. The basic concept is that the marker is a stable compound that behaves much like a fuel molecule, is not extractable but, being a compound that does not occur naturally, is readily detected by gas chromatography with a mass spectroscopy analyser [105–109]. The patents propose compounds such as 2,4,6-substituted-1,3,5-triazines, triphenylamines, bis-(aryl)-diaryl-ethers and trityl-phenol derivatives (such as those in Figure 1.17) – all of which may bear further substituents on any or all of the benzene rings. Their molecular weights can be varied to match the volatilities of

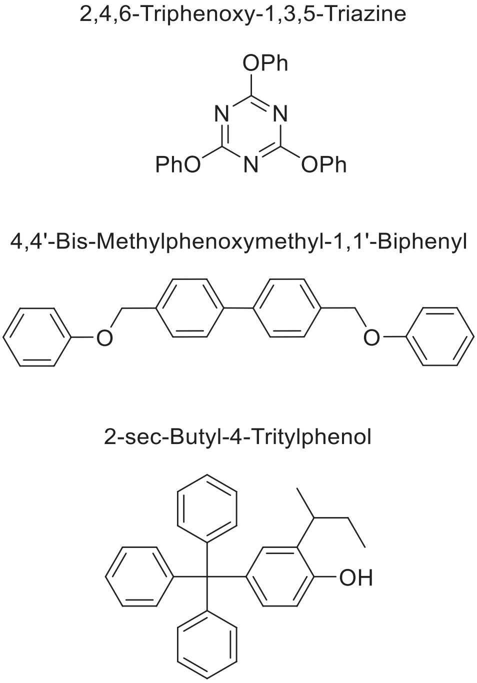


Figure 1.17 Some Markers in the Dow Technology. 2,4,6-Triphenoxy-1,3,5-triazine [105], 4,4′-bis(3-methylphenoxymethyl)-1,1′-biphenyl [106] and 2-(sec-butyl)-4-tritylphenol [108].

gasoline, kerosene or a middle distillate, as well as to provide a myriad of markers of different molecular weights.

The Dow® inventors have proposed that chosen combinations of these compounds could provide a wide range of fuel digital markers. Dow® has also patented a GC-MS method for detecting these compounds in petroleum fuels, singly or in mixtures, from their characteristic m/e mass spectroscopy signals to provide the digital markers [110]. For example, 2,4,6-triphenoxy-1,3,5 triazine in diesel fuel (7 ppm) was detected by its characteristics m/e signals by GC-MS at 264, 238, 145 and 121, which provide its digital signature [105]. The marker system that was reported to have been introduced in 2015 in the UK and Ireland, ACCUTRACE™ S10 [88,89], is probably an example of this chemistry and procedure. The digital marker system is also proposed to provide the identification of fuels in spills that, usually, end up contaminating water and are then untraceable.

1.7 Future Need for Fuel Additives

At the time of writing, the media are full of discussions about electric cars and trucks and their taking over from the traditional Internal Combustion Engine (ICE)- driven vehicles. One could be forgiven for the thought that this may mean the end of the market for petroleum liquid fuels and hence the demand for fuel additives. However, revolutions of this sort do not occur overnight. BP statisticians have made projections of the demand for the different fuels up to 2040 [111], based on current statistical data and trends. In summary, BP statisticians conclude that the demand for oil as a primary fuel will peak around 2030 and will be little changed between 2020 and 2040.

ExxonMobil have made similar projections [112]. Of total energy, electrical energy consumption is growing rapidly and is projected to continue to do so, while the demand for petroleum transport fuels is expected to peak around 2025 and remain steady until 2040. Oil demand for light-duty vehicles is expected to enter a slow decline from 2025, but this is balanced by the growth in the demand from commercial transport (trucks, aviation, marine and rail). The decline in light-duty use of oil is a combination of more fuel efficiency and a gradual displacement by electric vehicles, alongside an almost 50% increase in vehicle numbers between 2017 and 2040. Commercial transport energy demand is expected to increase by about 50% by 2040, driving the rise in oil demand from this sector, while the expectation is that 'Electrification plays a role in certain applications (e.g. short-haul trucks and buses) but electricity in commercial transportation grows slowly due to upfront costs, range limitations, payload requirements, and the pace of infrastructure development' [112]. The growth in the demand for energy and motor vehicles follows from the world's expanding population and its enrichment. At the same time, the energy efficiency of ICE vehicles will continue to grow, and their emissions will fall – as in the past, fuel additives will aid such developments.

It is worth remembering that over the most recent ten year period (2007–2017), that oil consumption has fallen by a small proportion in the west: little change in N. America, 1,105 Mtoe to 1,113 Mtoe, and a fall of 817 to 742 Mtoe in Europe[28]; while that in the Asia-Pacific region has increased dramatically, from 1,250 to 1,695 Mtoe [113]. In the ten years to 2018, the worldwide split between light and middle distillate fuels (mainly gasoline and diesel, respectively) has moved very little, from consumptions of about 33%/36% light/middle distillates in 2008 to about 31%/36% in 2018.

With respect to the electrification of the transport sector, the enormity of this is challenging: in 2017, for the EU-28, transport, mostly reliant upon oil products, took 31% of the total end use of energy (a total of 1,060 Mtoe) while electricity provided only 23% [14]; clearly, in order to convert the whole of transport's use of energy to electricity, the EU-28 would need to increase the production of electricity by 135%. While the richer countries currently have an excess of electricity-generation capacity over demand, it may be less when considering the reliance on sources that are productive for only part of the time (e.g. solar cells); this is allowed for by the 'de-rated supply' which has a relatively small margin over winter peak demand [114]. The effects of a major proportion of vehicles plugging-in on a winter evening – an event that may create double the current electricity demand – may be unwanted. However, while the proportion of electric vehicles is small, it is growing rapidly.

Many point to the rapid growth in the renewable energy sector, particularly wind-power and solar cells. However, these renewable power sources are, for years ahead, needed to replace the electricity lost by the closures of coal and oil-fired power stations. Combine these uncertainties with the current low level of investment in new oil production as major oil companies, such as Shell and BP, commit themselves to supporting the change to renewable, clean power, plus the growth in demand from the developing world, and the future decade or two may see a shortage of oil. This appeared to be Exxon's view [115]. It could be that, as it has before in its history [5], oil could still spring a few surprises.

Notes

1. The oil industry uses two measures of oil quantities, barrels per day and tonnes per annum. Switching between these is confusing, so quantities in this book are mostly in tonnes and tonnes per annum.
2. Meaning the vacuum distillation temperature being corrected to one atmosphere pressure.
3. °C, corrected to 760 mm Hg pressure, as a Normalised Boiling Point, NBP. For Kuwait export crude.
4. In Figure 1.2, the Kuwait example, the gasoline output would be a blend of the light naphtha and some of the heavier naphtha.
5. 'Mtoe' is million tonnes of oil equivalent – one toe is a common unit to compare quantities of other fuels, which are converted to an amount of oil that would contain the same calorific value, one toe defined as containing 10 gigacalories [1].
6. Light distillate are gasoline and naphtha cuts; middle distillates are jet, kerosene, diesel and gas oil.
7. Heavy distillate fuels are included as middle distillates while residual fuels are included in fuel oil.
8. How much the economy depends upon energy as processes and engines become more efficient and economies rely more upon services and less upon manufacturing. Measured as how much energy is needed to produce a unit of Gross Domestic Product.

9 While in the FCC, large molecules are cracked into smaller, unsaturated molecules with the loss of hydrogen, in the hydrocracker, the free radical ends of the smaller molecules produced are trapped by hydrogen to give saturated hydrocarbons. Ranges of catalysts that include other metals are also used.

10 The butylenes, propylene and isobutene are collected as by-products of the FCC and the coker.

11 RON and MON are measured in a gasoline test engine which has variable compression, in comparison with mixtures of iso-octane (octane number 100) and n-heptane (octane number 0). The same engine is run under different conditions for RON and MON and some specifications take an average of the two.

12 Gasoline engine compression ratios are usually between 10 and 14 times.

13 Also known as iso-octane which is defined as the standard for a RON of 100.

14 Other properties that are specified as measures of the quality of gasoline fuels are gum content, oxidative stability, water tolerance, sulphur content (10 or 15 ppm maximum USA and EU) and corrosiveness [9].

15 Cetane numbers are measured on a standardised diesel engine with variable compression. The compression ratio is varied until the delay between fuel injection and ignition is 2 milliseconds; the cetane number is then defined by the mixture of cetane and iso-cetane that gives the same delay.

16 Cetane Index is a cetane measure that is calculated from the density and distillation of a fuel.

17 More detail on this in the chapter 5 on Corrosion Inhibitors, as such fuels are more corrosive than ULSD.

18 Large quantities of bulk fuels are transported by pipeline from refineries to terminals, close to centres of population, at which tankers are loaded for local delivery.

19 Finding an additional 50% of kerosene would disrupt a refiner's ability to match the demand barrel.

20 TEU – Twenty-foot Equivalent Unit, a standard shipping container 20 feet long, 8 feet wide.

21 Early references spell this as Soudan [75] and recent documents (such as in Wikipedia [79]) use the spelling Sudan, though the most recent nomenclature format for non-aqueous soluble dyes is 'Solvent #', so Soudan (or Sudan) Red or Sudan 3 or Solvent 23 are the different names for the same dye.

22 In Germany, 2012, red fuels carried no duty [116] but the duty on motor fuels was 65.5-euro cents per litre on gasoline and 47 cents on ULSD [78].

23 Solvent Yellow 124 turns red if extracted from fuel into dilute hydrochloric acid.

24 The N,N-diethylaniline products were covered in both patents published in 1969 but the first application for BASF's patent [92] was in January 1967 (in Germany) while for ICI's patent [93] it was in September 1965.

25 Methanol or ethanol preferred.

26 The diazonium salt of 1-aminoanthraquinone is exceptionally stable at ambient temperatures, compared with diazotised aniline which decomposes above 10°C.

27 Initial patent applications were made by Angus Chemical company, then a subsidiary of Dow®, and Rohm and Haas, which was acquired by Dow in 2009, and were granted under Dow's name.

28 These are the figures for the whole of Europe, including Switzerland, Turkey, the Ukraine and 'other Europe' while the figures in section 1.2.2b were for the European Union only.

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