

# Hydrocarbons

Physical Properties and their Relevance to Utilisation

Prof. Dr J. Clifford Jones



Dr Clifford Jones

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Hydrocarbons – Physical Properties and their Relevance to Utilisation

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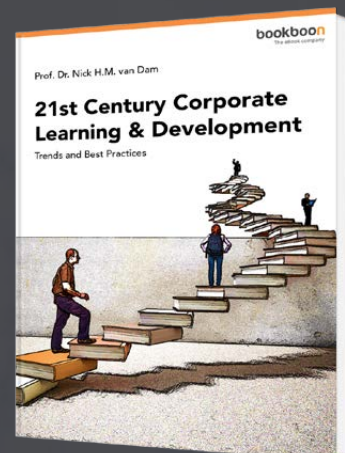
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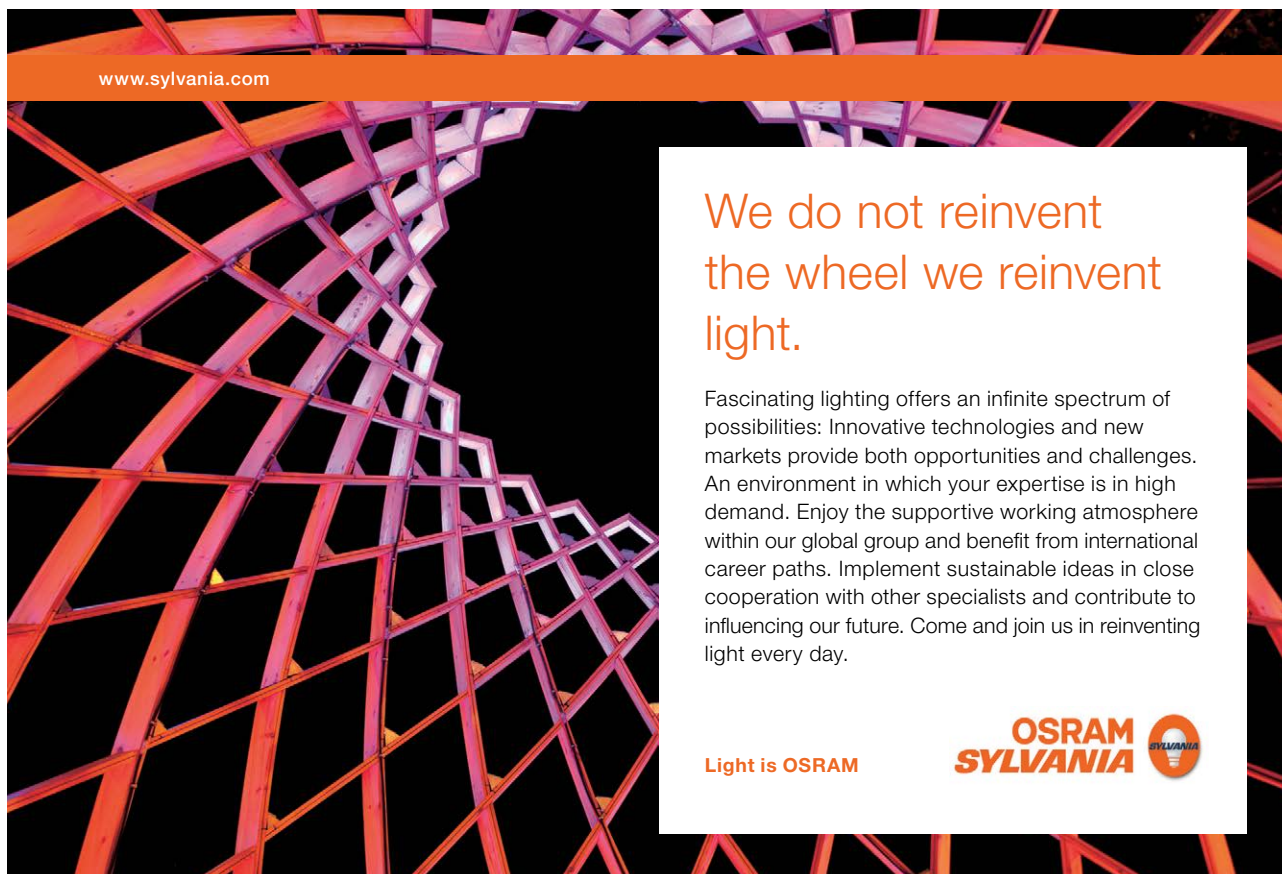
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# Author's Preface

The 'electronic book' is a feature of this early 21<sup>st</sup> Century. I have been in academic life for several decades, and have I hope responded with flexibility to changes over that time. I have been using a word processor on a daily basis for twenty years and am deeply conscious of the advantages over even the most advanced typewriters. The first time I gave a presentation using Microsoft PowerPoint was in India about six years ago. I have with enthusiasm used PowerPoint for every invited talk or conference contribution I have given since. Such talks and contributions have been in countries including Australia, Bahrain, Trinidad and Tobago, Kuwait and Armenia.

About a year ago I published, by invitation from Ventus, 'Atmospheric Pollution'. This was my eighth book, and my first electronic one. Once it became available I was quite delighted with the result, and sent a link to it to friends and professional associates around the world. I used the book as the recommended text in an MSc course at Aberdeen and student response was very positive. I hasten to add that I do not believe that the positive response was due solely to the fact that the book, unlike a 'conventional' book, was available free of charge. University students are too shrewd and perceptive to extend their acceptance to something simply because it comes for nothing. Even so, the endeavours of Ventus Publishing and Boon Books in making quality texts available at no cost deserve support. I was therefore pleased to respond in the affirmative to an invitation to write a second book for Ventus. The result is this tome on the physical properties of hydrocarbons.

I expect that this book will be of interest to students and professionals in chemical engineering, fuel technology and mechanical engineering. I have myself used bits of it, prior to publication, in the newly set up chemical engineering degree course at the University of Aberdeen. I shall be pleased to receive feedback from readers.

J.C. Jones

Aberdeen, February 2014.

In 'Atmospheric Pollution' the author made the following statement in the Preface:

To have acknowledged each and every one of the electronic sources I have drawn on would not only have lengthened the book to no real purpose but, more seriously, might even have been a distraction to a reader. I am hopeful that this acknowledgement in the preface of such sources will suffice.

The statement applies equally to this volume.

Having regard to the time which has elapsed since the book was written it is inevitable that some of the links to references are no longer active. A reader unable to find an equivalent for an inactive link may if he or she wishes contact the author for advice.

J.C. Jones

Aberdeen, January 2014

# 1 Physical properties of organic liquids

## 1.1 Introduction

This chapter will provide background on some of the properties of hydrocarbons which are prevalent in discussion and in quality control. The respective properties will be discussed for particular hydrocarbon products in the subsequent chapters where, as necessary, other properties including density will be introduced.

## 1.2 Viscosity

### 1.2.1 Definitions, dimensions and units

Viscosity, usually qualitatively described as ‘resistance to flow’, has dimensions:

$$M L^{-1}T^{-1}$$

hence in SI the units are  $kg m^{-1} s^{-1}$ . Now the SI unit of pressure is the Pascal which is:

$$\text{force/area} = kg m s^{-2}/m^2 = kg m^{-1}s^{-2}$$

Hence the units of viscosity are those for pressure multiplied by seconds, so Pa s has become the terminology for the SI unit of viscosity, where:

$$1 Pa s = 1 kg m^{-1} s^{-1}$$

The viscosity so expressed is the dynamic viscosity, usual symbol  $\mu$ , and the following applies:

$$\text{kinematic viscosity (usual symbol } \nu) = \mu/\rho$$

where  $\rho$  is the density. The kinematic viscosity therefore has units:

$$kg m^{-1} s^{-1}/kg m^{-3} = m^2s^{-1}$$

and a reader is asked to note the following in relation to kinematic viscosities.

First, the units and dimensions of kinematic viscosity are the same as those of diffusion coefficients and of thermal diffusivities. Kinematic viscosities therefore feature in dimensionless groups including the widely used Prandtl number (symbol  $Pr$ ) which is simply:

$$Pr = \nu/\alpha$$

where  $\alpha$  is the thermal diffusivity. The kinematic viscosity also appears in the Lewis number (symbol  $Le$ ).

Secondly, noting the definition of the kinematic viscosity the numerator changes with temperature much more rapidly than does the denominator; that is, the dynamic viscosity of a liquid is a much stronger function of the temperature than is the density. The latter can for engineering purposes often be taken to be constant over quite a wide temperature range, therefore in the calculation of kinematic viscosities at different temperatures only changes in the dynamic viscosity need to be considered.

### 1.2.2 Benzene as a model compound

The above ideas and extensions of them are best examined with reference to a pure organic compound and benzene, which is very important in hydrocarbon technology, is the obvious choice.

The increased mobility of molecules as temperature increases and viscosity decreases involves loss of intramolecular forces and is an activated process [1]. The temperature dependence of the dynamic viscosity therefore conforms to an expression of the form [1]:

$$\mu = A \exp(\Delta E/RT)$$

where  $A$  is a constant,  $R$  the universal gas constant ( $= 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ ) and  $T$  the absolute temperature. The constant  $A$  is given by [2]:

$$A = hN_o/V_m$$

where  $h$  = Planck's constant ( $= 6.626 \times 10^{-34} \text{ Js}$ ),  $N_o$  the Avogadro number ( $= 6.02 \times 10^{23} \text{ mol}^{-1}$ ) and  $V_m$  ( $\text{m}^3 \text{ mol}^{-1}$ ) is the molar volume of the liquid. The units of  $A$  are examined in the boxed area below.

$$\text{J} \times \text{s} \times \text{mol}^{-1} / \text{m}^3 \text{ mol}^{-1} = \text{kg m s}^{-2} \text{ m m}^{-3} = \text{kg m}^{-1} \text{s}^{-2} = \text{Pa s}$$

'A' needs to have units  $\text{Pa s}$  for dimensional correctness as the exponential of course has no units.

Now at  $20^\circ\text{C}$  ( $293 \text{ K}$ ) the density of benzene is  $0.879 \text{ g cm}^{-3}$ . In the boxed area below this is converted to molar volume in SI units.



$$0.879 \text{ g cm}^{-3} \equiv 879 \text{ kg m}^{-3}$$

$$\text{molar mass of benzene (C}_6\text{H}_6) = 0.078 \text{ kg}$$

$$\text{density on a molar basis} = 879 \text{ kg m}^{-3} / 0.078 \text{ kg mol}^{-1} = \rho_m$$

$$V_m = 1 / \rho_m = 8.87 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$$

Using this and the values for  $h$  and  $N_o$  given furnishes a value of  $4.5 \times 10^{-6} \text{ Pa s}$  for  $A$ . We lack a value for  $\Delta E$ . The way forward is therefore to use a literature value for the dynamic viscosity and find  $\Delta E$ . This should conform to the general rule [2] that  $\Delta E$  is 30 to 40% of the heat of vaporisation. At  $20^\circ\text{C}$  the dynamic viscosity of benzene is:

$$0.652 \text{ cPa s} = 0.00652 \text{ Pa s}$$

Putting this into:

$$\mu = A \exp(\Delta E / RT)$$

and solving for  $\Delta E$  gives:

$$\Delta E = 17.7 \text{ kJ mol}^{-1}$$

Now the heat of vaporisation of benzene at its boiling point is  $44.3 \text{ kJ mol}^{-1}$  and  $\Delta E$  is precisely 40% of this. Reference [2] does in fact give the equation as:

$$\mu = (hN_o/V_m) \exp(0.4L/RT)$$

where  $L$  ( $\text{J mol}^{-1}$ ) is the heat of vaporisation at an unspecified temperature. Variation of the heat of vaporisation with temperature is not a source of major error in this analysis. It is common for example not only in such disciplines as fuel technology but also amongst 'purist' physical chemists to integrate the Clausius-Clapeyron equation with the enthalpy change for whatever phase transition is being considered outside the integral. Only where a very high degree of precision is required would the enthalpy change be taken inside the integral, usually as a power series in temperature obtainable from such sources as the JANAF<sup>1</sup> tables.

Our equation for the temperature dependence of the viscosity of benzene can easily be used to estimate by how much the temperature would need to rise above the reference temperature of  $20^\circ\text{C}$  which we have used for the viscosity:

- a) to halve
- b) to decrease by an order of magnitude.

The interested reader can easily confirm that the answer to (a) is an increase to 324 K (51°C). The answer to (b) is an increase to 429 K (156°C).

### 1.2.3 Extension to other organic compounds

The table below gives values of the dynamic viscosity for a selection of hydrocarbons and oxygenated hydrocarbons. Viscosity values are usually in the literature in units cP – centipoise – where 1 cP =  $10^{-3}$  Pa s.

Compound (temperature)	Dynamic viscosity/Pa s
n-octane (20°C)	0.00054
n-hexane (25°C)	0.00029
toluene (20°C)	0.00059
meta xylene (20°C)	0.00062
ethanol (20°C)	0.0012
acetone (20°C)	0.00032
ethylene glycol (25°C)	0.0161
glycerine (20°C)	1.42

In the table following are given results of a calculation for each of the compounds to determine the factor by which in the exponential the heat of vaporisation must be multiplied in order for the viscosities in the table and calculated ones to match.

Compound (Temperature)	Density /kg m <sup>-3</sup>	Molar volume/ m <sup>3</sup> mol <sup>-1</sup>	Heat of vaporisation/ kJ mol <sup>-1</sup>	Factor by which <i>L</i> must be multiplied
n-octane (20°C)	780	0.000146	34	0.38
n-hexane (25°C)	655	0.000131	29	0.39
toluene (20°C)	867	0.000106	38	0.32
meta xylene (20°C)	870	0.000122	36	0.35
ethanol (20°C)	789	0.0000583	39	0.32
acetone (20°C)	790	0.0000734	31	0.32
ethylene glycol (25°C)	1113	0.0000557	53	0.36
glycerol (20°C)	1261	0.0000730	75	0.40

Values of  $L$  used in the calculations are those at the boiling point rounded to the nearest whole number in units  $\text{kJ mol}^{-1}$ . There is good agreement with the general rule [2] that the heat of vaporisation in the exponential is multiplied by a factor of 0.3 to 0.4. Having regard to the fact that the liquids in the table range in viscosity by a factor of almost 5000 the treatment can be judged to be remarkably robust. To extend this treatment to petroleum fractions, which are of course mixtures of very many organic compounds, is a challenge which later parts of the book will address. One difficulty will however at this stage be anticipated: such a fraction does not have a single boiling point, only a boiling *range*.

In the table below the kinematic viscosities ( $\nu$ ) of the respective hydrocarbons are given. They were obtained by dividing the dynamic viscosity by the density to give a value for  $\nu$  in  $\text{m}^2\text{s}^{-1}$ . Values are also given in centistokes (cSt) where:

$$1 \text{ centistoke} = 10^{-6} \text{ m}^2 \text{ s}^{-1}.$$

Compound (Temperature)	kinematic viscosity/ $\text{m}^2\text{s}^{-1}$
n-octane (20°C)	$6.9 \times 10^{-7}$ (0.69 cSt)
n-hexane (25°C)	$4.4 \times 10^{-7}$ (0.44 cSt)
toluene (20°C)	$6.8 \times 10^{-7}$ (0.68 cSt)
meta xylene (20°C)	$7.1 \times 10^{-7}$ (0.71 cSt)
ethanol (20°C)	$15.2 \times 10^{-7}$ (1.52 cSt)
acetone (20°C)	$4.0 \times 10^{-7}$ (0.40 cSt)
ethylene glycol (25°C)	$144 \times 10^{-7}$ (14.4 cSt)
glycerol (20°C)	$11260 \times 10^{-7}$ (1126 cSt)

Brent crude oil, North Sea (40°C)	3.87 cSt
Brent crude oil, North Sea (50°C)	3.25 cSt

Values for Brent crude – a benchmark crude from the North Sea – at two temperatures are also given. These values are straddled by those for ethylene glycol and ethanol.

#### 1.2.4 Further remarks

What has been learnt in this introductory chapter about the viscosities of simple organics will be carried forward to subsequent chapters in which crude oil and fractions therefrom will be discussed. The range of viscosities in the tables is sufficient for direct comparison with crude oils or any distillate.

## 1.3 Acoustic impedance

### 1.3.1 Introduction

The most obvious importance of this topic is its application to exploration. The principles will be given in this chapter and examples of application to crude oil in the next. The acoustic impedance is defined:

pressure applied/speed of pressure wave resulting

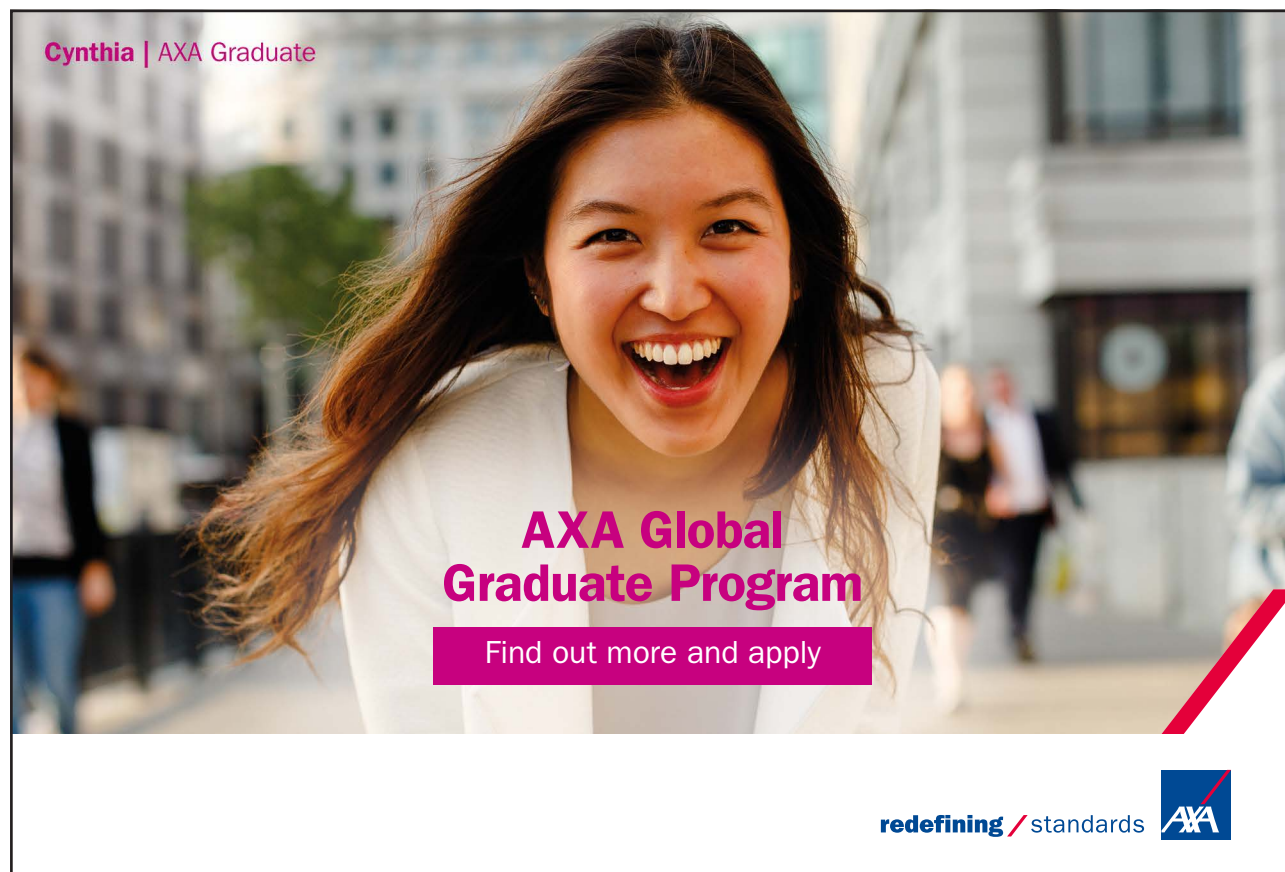
Hence in SI the quantity has units:

$$\text{Pa/m s}^{-1} \equiv \text{Pa s m}^{-1}.$$

$$1 \text{ Pa s m}^{-1} = 1 \text{ rayl (so named after Rayleigh).}$$

### 1.3.2 Examples of values for organic liquids

Most liquids have acoustic impedances of the order of 1 megarayl (Mrayl). Values for selected liquid organic compounds, taken from [3], are given below together with values for water and mercury.



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Liquid	Acoustic impedance/Mrayl
Acetone	1.07
Ethanol	0.95
Glycerol	2.34
Diethyl ether	0.70
Ethylene glycol	1.51

Water at 20°C	1.48
Water at 60°C	1.55
Mercury at 25°C	19.58

Note that the ratio of the values at room temperature for water and mercury (13.2) is almost exactly the ratio of their densities (13.6). In their **thermal** properties (e.g., Prandtl numbers) liquid metals tend to differ widely from organic liquids because of their high thermal conductivities but clearly the very high value for the acoustic impedance of mercury is a density effect.

The unit of rayl breaks down to:

$$1 \text{ rayl} = 1 \text{ kg m}^{-2}\text{s}^{-1}$$

and these are also the units of the product:

$$\text{density} \times \text{velocity}$$

The significance of this identity will become clearer when applications of the acoustic impedance are discussed.

## 1.4 Thermal conductivities

Values of the thermal conductivities of selected liquids at room temperature are given below having been taken from [4].

Liquid	Thermal conductivity ( $\lambda$ ) /W m <sup>-1</sup> K <sup>-1</sup>
Acetone	0.180
Methanol	0.202
Benzene	0.167
Toluene	0.151
Hexane	0.124

Water	0.609
-------	-------



We note the significantly higher value for water than for the organics. Thermal conductivities of organic liquids decrease in a linear fashion with temperature though quite weakly. It is seldom if ever necessary to incorporate the thermal conductivity as a function of temperature in heat transfer calculations in engineering practice. A single value at a suitably representative temperature will suffice. As will be seen in subsequent chapters the thermal conductivities of petroleum fractions do not differ hugely from each other.

## 1.5 Electrical properties

### 1.5.1 Introduction

The electrical properties of any hydrocarbon have direct relevance to fire safety. If in movement or in tank filling a hydrocarbon liquid is splashed, static electricity will be generated. No hydrocarbon liquid is a 'conductor', but the lower the resistance to conduction of any static so generated the better as such static can become an ignition source for vapours.

The resistivity of pure water at 20°C is 18.6 megaohm cm. The conductivity is the reciprocal of the resistivity, units  $\text{ohm}^{-1} \text{cm}^{-1}$  or  $\text{S cm}^{-1}$  where S denotes the unit Siemen which has replaced the old 'reciprocal ohm' (mho). Hence the conductivity of pure water is:

$$1/(18.6 \times 10^6) \text{ S cm}^{-1} = 5.4 \times 10^{-8} \text{ S cm}^{-1} \equiv 5.4 \times 10^{-6} \text{ S m}^{-1}$$

The final figure in the above row can be re-expressed  $5.4 \mu\text{S m}^{-1}$ . As an example of an organic liquid, ethylbenzene has a value of  $123 \text{ pS m}^{-1}$ , many orders of magnitude lower. Even though there are very few ions in 'pure' water, the polar structure of the molecules provides for some enhancement of electrical conductivity.

Another electrical property of interest in hydrocarbon technology is the capacitance. The capacitance of a dielectric is the amount of charge it can hold per unit potential difference across it. The units are thus:

$$\text{coulomb/ volts} = \text{farad}$$

In [5] the capacitances of benzene and n-pentane are given as 120 and 98 picofarads (pF) respectively. Capacitance provides a basis for tank level gauging in particular with jet fuel, as will be described in Chapter 4.

## 1.6 Optical properties

The refractive index of a medium is of course dependent upon the wavelength of the incident light and 589.3 nm, corresponding to the sodium D lines, is a common choice. The refractive indices of some organic compound on this basis measured at 20°C are given below having been taken from [6].

Liquid compound	Refractive index
Benzene	1.501
Toluene	1.497
Aniline	1.586
Glycerol	1.470
Water	1.333

It is shown in [2] that for non-polar liquids the following approximate relationship applies:

$$\text{refractive index} = (\text{dielectric constant})^{0.5}$$

and of the liquids in the table above only benzene and toluene are non-polar. The dielectric constant of benzene at 20°C is 2.3 [7] giving refractive index 1.517 only 1% higher than the value in the table. The dielectric constant of toluene at 20°C is 2.4 giving a refractive index of 1.549. This is a greater discrepancy than for benzene (3.5%) but still not a huge one. The correlation above will be re-examined when petroleum distillates are considered. (The reader can easily satisfy him/herself of the folly of attempting to apply the correlation to polar compounds such as glycerol.)

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The quotient:

$$(n^2 - 1)/(n^2 + 2)$$

where  $n$  is the refractive index is called the refractive index parameter usual symbol  $I$ . For water then:

$$I = [(1.333^2 - 1)/(1.333^2 + 2)] = 0.206$$

In the correlation of refractive index with other thermodynamic properties this parameter often features. For example, Riazi and Roomi [8] determined the dynamic viscosity ( $\mu$ , units centipoise) of n-pentane and cyclopentane across a temperature range and the refractive index of each across the same temperature range. For each a plot of  $1/\mu$  against  $1/I$  gave a good straight line. The lines for the two closely similar organic compounds were widely separated.

When a binary liquid is being distilled the composition of distillate can be determined from its refractive index provided that the refractive indices of the two liquids when pure are sufficiently spaced. Similarly, in complex mixtures of hydrocarbons the refractive index has some diagnostic potential and this will be discussed in subsequent chapters.

## 1.7 Concluding remarks

The author has in mind that readers will refer back to this chapter when encountering in the later ones the respective properties for hydrocarbon products. Such properties are frequently encountered in the most up-to-date research literature on liquid fuels.

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## 2 Physical properties of crude oils

### 2.1 Classifications of crude oil by density

Density is an important property in the pricing of a particular crude oil. Lighter crudes are preferred because they are richer in the lowest boiling distillate, namely gasoline, which remains the most saleable product of oil refining. Consequently the usual index of quality, the API gravity, is defined in such a way that it is higher for light crudes and lower for heavy crudes having therefore the reciprocal of the density in its definition. The API gravity is given by:

$$\text{degrees API} = 141.5/\rho_r - 131.5$$

where  $\rho_r$  is the density relative to that of water at 60°F (15.6°C). Hence water itself has an API gravity of 10 degrees. The API gravity has been in international use as an indicator of crude oil quality for over a century and also applies to fractionated material. The following definitions are widely used:

Light Crude: API gravity higher than 31.1 degrees.  
 Medium Crude: API gravity between 22.3 and 31.1 degrees.  
 Heavy Crude: API gravity below 22.3 degrees.

Converting to fundamental units, light crudes are below 870 kg m<sup>-3</sup>, medium crudes are between 870 and 920 kg m<sup>-3</sup> and heavy crudes are above 920 kg m<sup>-3</sup>.

### 2.2 Densities and viscosities of crudes from different sources

#### 2.2.1 Examples

The Table below, split into three parts, gives six examples each of light, medium and heavy crudes from different parts of the world.

#### Light crudes.

Crude	Density/kg m <sup>-3</sup>	Kinematic viscosity/cSt	Reference
Forties field, North Sea	810	2.12 (40°C) 1.81 (50°C)	[1]
<b>Asgard</b> Blend, North Sea	777	1.46 (20°C)	[2]
Niger Delta (‘Bonny light crude’)	860	4.99 (40°C) 4.05 (50°C)	[3]
South China Sea (‘Nanhai light’)	827	6.50 (40°C) 5.00 (50°C)	[4]
Tapis, Malaysia	805	3.0 (21°C)	[5]
Abuttifel, Lybia	809	25 (38°C)	[6]

**Medium crudes.**

Aljerf, Lybia	875	8.7 (37.8°C)	[6]
Niger Delta ('Bonny medium crude')	903	12 (38°C)	[7]
Orinoco Basin, Venezuela ('Mesa 28')	890	13.3 (38°C)	[8]
Iraq ('Basrah medium')	870	41 (10°C)	[9]
Hungo, Angola	880	23.6 (20°) 8.6 (50°C) 2.93 (100°C)	[10]
Alaska North Slope Blend	910	23.9 (10°C)	[11]

**Heavy crudes.**

Menemota, Venezuela	930	69.1 (38°C)	[8]
Boscan heavy crude, Venezuela	999	11233 (38°C)	[8]
'Sumatra heavy crude', Indonesia	929	300 (40°C) 175 (50°C)	[12]
'Omani heavy crude', Mukhaizna	957	7160 (30°C)	[13]
Frade Block, Brazil	947	129 (40°C) 75.3 (50°)	[14]
Eden Yuturi, Ecuador	937	136 (50°C)	[15]

In examining the information in the Table we first note that the temperature interval across which the kinematic viscosity of the Hungo crude is given enables the values to be examined for conformity to a functional form the same as that for pure organic compounds used in the previous chapter. This is in the boxed area below, where symbols are as used and defined in the previous chapter.

$$\begin{aligned}
 \nu(T_2)/\nu(T_1) &\approx \mu(T_2)/\mu(T_1) = \exp(\Delta E/RT_2)/\exp(\Delta E/RT_1) \\
 &\Downarrow \\
 \ln[\nu(T_2)/\nu(T_1)] &= (\Delta E/R)[(1/T_2) - (1/T_1)] \\
 \text{Putting } T_2 &= 373\text{K}, \nu(T_2) = 2.93 \text{ cSt } T_1 = 293\text{K}, \nu(T_1) = 23.6 \text{ cSt gives:} \\
 &\Downarrow \\
 \Delta E &= 23.7 \text{ kJ mol}^{-1} = 0.4\text{L} \\
 L &= 59 \text{ kJ mol}^{-1}
 \end{aligned}$$



A single value of the heat of vaporisation cannot of course apply to a crude oil, but the value obtained in the calculation can at least be compared with values for pure compounds. There is probably little value in attempting to comment on the value for  $L$  above beyond saying that it is approximately what is expected for a single hydrocarbon compound of about  $C_{15-20}$ . One should also note that there is nothing at all incorrect about using applying the mole concept to such a substance as crude oil. In the fundamental definition of a mole there is no requirement that all components be of the same molecular identity. Quite the contrary, for example the mole concept is frequently applied to mixtures of gases including air. So a mole of crude oil is simply the amount which contains an Avogadro number of molecules, diverse in structure and size though those molecules will be.

### 2.2.2 Viscosity and pumping

The steady flow equation, that is the First Law of Thermodynamics for an open system, can be applied to a pump and to a good approximation pressure energy only, to the exclusion of thermal, kinetic and potential energies, need be considered. The performance characteristics of a particular pump are then ‘capacity’ – gallons per minute – against head pressure with water as the fluid being pumped. The kinematic viscosity of water at 20°C is 1 cSt. If the liquid is more viscous than water – as all of the crude oils in the above tables are – ‘viscous effects’ apply and pump performance is affected. There are in the literature and on numerous web sites (e.g. [16,17]) charts, issued by the Hydraulic Institute, for correcting pump performance for liquids other than water. Such a graph the interested reader can very easily download for him/herself.



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As an example of application of the charts, in [17] a pump delivering water at 750 gallons per minute at a head pressure of 100 feet of water is considered. It is shown that if the pump is used for a liquid of viscosity about 200 cSt the capacity drops by about 5%. Two further points can be made. First, it is clear from the charts that effects on the capacity of viscosities of less than 10 cSt are likely to be negligible. Secondly, some of the most viscous crudes in the tables above would be off-scale, that is outside the scope of the charts. In practice such crudes would probably be diluted with a refined material before pumping, as is very common with Venezuelan crudes. That would bring the viscosities into a range where pump performance could be assessed by charts such as those in [16] and [17].

### 2.2.3 Viscosity of blended crude oils

Crude oils often are blended. This is partly because very many are ‘out of spec’ in sweetness (absence of sulphur) and in lightness (reciprocal density). Blending enables an oil as sold to be controlled in these terms, and such a blend will be priced according to how close the sweetness and lightness are to those of one of the benchmark crudes such as West Texas Intermediate, Brent or the OPEC basket.

Application of the Grunberg-Nissan equation for two blended liquids<sup>3</sup> to crude oils requires a few approximations to be made. The Grunberg-Nissan equation is:

$$\ln \mu_{12} = x_1 \ln \mu_1 + x_2 \ln \mu_2 + x_1 x_2 \gamma_{12}$$

where  $\mu$  denotes dynamic viscosity and  $x$  mole fraction, subscripts 1,2 and 12 referring respectively to the two components and to the blend. The parameter  $\gamma_{12}$  is termed the interaction parameter. In applying to the blending of crude oil we note the following. First as the two oils being blended are both composed of non-polar molecules  $\gamma_{12}$  can be set to zero.

Secondly, were an average molecular weight to be assigned to each oil and determined (perhaps by freezing point depression of a pure organic liquid) values for the two would not intuitively be expected to differ by much. Mole fractions can therefore be replaced by mass fractions. This gives the simplified form:

$$\ln \mu_{12} = \phi_1 \ln \mu_1 + \phi_2 \ln \mu_2$$

where  $\phi$  denotes mass fraction. A calculation utilising this is in the boxed area below.

Given the approximations made there is nothing to be gained from distinguishing the densities of

the crude oils from each other. This gives:

$$\ln \rho v_{12} = \phi_1 \ln \rho v_1 + \phi_2 \ln \rho v_2$$

⇓

$$\ln \rho + \ln v_{12} = \phi_1 \ln \rho + \phi_1 \ln v_1 + \phi_2 \ln \rho + \phi_2 \ln v_2$$

$$\ln v_{12} = \phi_1 \ln v_1 + \phi_2 \ln v_2 + \ln \rho (\phi_1 + \phi_2)$$

But  $(\phi_1 + \phi_2) = 1$  by definition, therefore:

$$\ln v_{12} = \phi_1 \ln v_1 + \phi_2 \ln v_2$$

Consider then a 50:50 blend of two crude oils two orders of magnitude apart in kinematic viscosity, say 10 cSt and 1000 cSt. This has kinematic viscosity:

$$\exp\{0.5(\ln 10 + \ln 1000)\} = 100 \text{ cSt}$$

which on a logarithmic scale is mid way between the kinematic viscosities of the two constituent crudes.

## 2.3 Coefficient of thermal expansion

The density of any liquid is of course a function of the temperature, there being expansion as the temperature rises therefore a reduction in the density. The quantity relevant to this is the coefficient of thermal expansion, (symbol  $\beta$ ) defined by:

$$\beta = - (1/\rho) \, d\rho/dT \quad K^{-1}$$

$\beta$  is itself a function of temperature but a fairly weak one, and for approximate calculations on an unspecified crude oil a single value of around  $0.0007 \text{ K}^{-1}$  will suffice. A calculation in which use is made of this figure is in the boxed area below.

It is widely held (e.g., [18]) that the oil in a well increases in temperature by 30°C for every 100 m well depth. Europe's largest onshore oilfield is on the south coast of England, the Wytch farm field.

The deepest wells at the field are 1600 m and the oil is typically 41.2oAPI which converts to a density of 820 kg m<sup>-3</sup> at say 20oC. The temperature at 1600 m will be  $\approx 70$ oC (343K). Returning to the equation:

$$\beta = - (1/\rho) \, d\rho/dT$$

⇓

$$\beta(343 - 293) = -\ln \{\rho(773K)/\rho(293K)\}$$

Using  $\beta = 0.0007 \text{ K}^{-1}$  gives:

$$\rho(343 \text{ K}) = 792 \text{ kg m}^{-3}$$

## 2.4 Acoustic impedance

### 2.4.1 Further background

The background material on acoustic impedance in the previous chapter will be continued before values for crude oils are discussed. The general trends between the phases for acoustic impedance (symbol  $Z$ , units rayl) is:

solids > liquids > gases

In the previous chapter some values were given for organic liquids, which were seen as simplified analogues of petroleum liquids. Values for a number of solid substances are given below.

Substance	$Z$ /Mrayl	Reference
Stainless steel	45.8	[19]
Concrete	8	[19]
Pine wood	1.5	[19]
Granite	26.8	[19]
Silica	12.6	[19]
Sandstone, water saturated	10	[20]

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Now the speed of sound in a gas ( $v$ , units  $\text{m s}^{-1}$ ) is simply:

$$v = \sqrt{(\gamma P / \rho)}$$

where  $\gamma$  is the ratio of principal specific heats,  $P$  ( $\text{N m}^{-2}$ ) the pressure and  $\rho$  ( $\text{kg m}^{-3}$ ) the density. Putting:

$$Z = \rho v$$

gives:

$$Z = \sqrt{(\gamma P \rho)} \text{ kg m}^{-2}\text{s}^{-1} \text{ (rayl)}$$

Now for air  $\gamma = 1.4$ . At 1 bar ( $10^5 \text{ N m}^{-2}$ ) pressure and  $20^\circ\text{C}$  the density is easily shown, from the ideal gas equation, to be  $1.15 \text{ kg m}^{-3}$  giving:

$$Z = 401 \text{ rayl}$$

which compares well with the value of the acoustic impedance of air at 1 bar,  $20^\circ\text{C}$  of 412 rayl given in [21]. In the boxed area below the value of  $Z$  for methane – the principal component of natural gas – is calculated.

$Z = \sqrt{(\gamma P \rho)}$ <p>Now for methane <math>\gamma = 1.3</math> and at 1 bar pressure, <math>20^\circ\text{C}</math> its density is <math>0.64 \text{ kg m}^{-3}</math></p> $\Downarrow$ $Z = 288 \text{ rayl}$
---

The above calculations give precise values to the comparison made previously of  $Z$  values of solids, liquids and gases.

#### 2.4.2 Acoustic impedance of crude oils

These have the values expected of liquids of their density range, typically around 1.3 Mrayl. It is not however the precise value of the acoustic impedance that is of importance in practical applications. It is that where there is an oil-rock interface there will be an *acoustic mismatch* because of an order of magnitude difference in the acoustic impedance at such an interface. By way of illustration:

$$Z_{\text{sandstone}} / Z_{\text{crude oil}} = 10 / 1.3 = 8 \text{ to the nearest whole number.}$$

When ultrasound is applied such mismatch is the basis of a diagnostic signal and this approach is used in exploration for oil. At the interface of crude oil and associated gas:

$$Z_{\text{methane}}/Z_{\text{crude oil}} = 288/(1.3 \times 10^6) = 2 \times 10^{-4}$$

Where non-associated gas is in contact with sandstone the ratio will be 50000 and the degree of acoustic mismatch huge.

## 2.5 Thermal conductivity

### 2.5.1 Introduction

A reader might wonder why the thermal conductivity of a crude oil is important. The answer is that crude oils are frequently heat exchanged on their way into a refinery column. Even if conditions in the heat exchanger are such that heat transfer to the oil is primarily by convection the thermal conductivity is relevant because heat transfer by conduction across the thermal boundary layer significantly influences the convection coefficient.

### 2.5.2 Values for crude oils

Thermal conductivities of crude oils vary with temperature, although not as strongly as their viscosities do. At around room temperature values in the approximate range  $0.12$  to  $0.15 \text{ W m}^{-1}\text{K}^{-1}$  are expected [22]. The variation with temperature is such that in heat transfer calculations where temperature differences are up to  $100^\circ\text{C}$  or so a single value of the thermal conductivity can be used without significant error. Denser crudes tend to have higher thermal conductivities, although the effect is not large.

## 2.6 Electrical conductivities

It was stated in the previous chapters that the electrical conductivity of a hydrocarbon material is relevant to safety in that a low conductivity prevents removal of electrical charge generated by splashing. It was also shown that one would expect a value of  $\approx 100 \text{ pS m}^{-1}$  for an organic liquid at room temperature. It is noted in [23] that when different crudes at the same temperature are compared there can be significant differences: West Texas crude is only a third as conducting as crude from the Alaskan North Slope. It is intuitively reasonable that if there is a strong temperature dependence there will also be a strong composition dependence.

## 2.7 Refractive index

The presence of asphaltenes and waxes in crude oil does not necessarily preclude refractive index measurement, and the refractive index can be correlated with other properties including the viscosity and the temperature below which solid deposition occurs ('cloud point'). However, crude oil alone is usually too opaque for a direct measurement to be made. The way round this is to dilute the oil with toluene to give a sample sufficiently transmissive for a refractive index measurement to be made.



If this is done for various proportions of toluene and oil and the refractive index plotted as a function of the composition of the mixture there can be extrapolation to obtain a value for the oil alone in the absence of toluene. Recent work [24] of this type has furnished a value of 1.4785 for the refractive index of a Russian crude of API gravity 30°. The same piece of work examines 45 crude oils, of density range  $800 \text{ kg m}^{-3}$  (45° API) to  $950 \text{ kg m}^{-3}$  (17° API), for a correlation of refractive index with density. Such a correlation holds well up to about  $880 \text{ kg m}^{-3}$ , there being a steady rise in the refractive index from 1.45 to 1.50 over that density interval. The correlation is sustained at higher densities although there is considerable scatter. Similar trends are reported in work by El Ghandoor et al [25]. They report refractive indices for seven crudes ranging from 30 to 50 °API. A monotonically dropping refractive index, from 1.50 to just under 1.45, is displayed across the API index range.

## 2.8 Concluding remarks

Crude oil is one of the most important products on world markets and the one which influences the economy most strongly. That a scientist or engineer should have a good appreciation of the properties of crude oil is therefore important. That crude oils vary widely in their physical properties is clear. An attentive reader with a little imagination will in his or her mind link that to the different benchmark prices which apply, e.g., Brent, New York Mercantile Exchange (NYMEX) and the OPEC basket.

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## 3 Physical properties of gasolines

### 3.1 Introduction

Gasoline might of course simply be a straight run distillate from crude oil. It might have been blended with reformed naphtha as an extender, and it might have had octane enhancers added. Increasingly important is FCC – fluid catalytic cracked – gasoline. This is made from higher boiling material by cracking, which is a more vigorous process than reforming. A particular gasoline might not have originated from crude oil at all. It might have been made from ‘syncrude’ from shale oil, or it might have been made from tar sands. Another route to gasoline is synthesis gas made from coal or natural gas.

It is clear then that gasoline comes from very varied sources and that provided certain specifications are met the origin will be irrelevant to the final user. It is likely that a motorist driving up the west side of the US will whilst in California, Oregon and Washington buy gasoline made from crude oil, but on crossing the border into western Canada he/she might well purchase gasoline made from tar sands. Quality control of gasoline production in each case will ensure that, so to speak, the car’s engine will totally unaware of differences in origin of fuel it receives.

The ‘gasoline substitutes’ of interest in this chapter are methanol and ethanol.

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## 3.2 Densities and viscosities

### 3.2.1 Typical values

Gasolines have densities in the range 710 to 770 kg m<sup>-3</sup> (68 to 52°API). The density of iso-octane, the benchmark hydrocarbon for performance, is 688 kg m<sup>-3</sup>. Kinematic viscosities are usually in the range 0.4 to 1 cSt. For example ‘Shell V-Power Gasoline’, currently the best selling premium gasoline in the US having a research octane number of 100, has a kinematic viscosity in the range 0.5 to 0.75 cSt at 40°C [1]. Conventional gasolines differ little in their kinematic viscosities and this quantity is not as important a factor in quality control as it is for some other petroleum products including lubricating oils. When ‘unconventional’ sources of fuel for spark ignition engines are being investigated the viscosity might well fall outside the range given above. For example [2] with ‘catalytically upgraded’ pyrolysis oil from wood otherwise suitable for substituting for gasoline the viscosities were in the range 25 to 43 cSt. The value for iso-octane is 0.74 cSt.

### 3.2.2 Viscosities of blends

Gasoline itself might in fact be a blended material if, as mentioned in the introductory part of this chapter, it has been extended with reformed naphtha (frequently called ‘blendstock’) or FCC gasoline. It is however with the blending of gasoline of whatever nature and origin with alcohol fuels that we are concerned in this section.

Methanol-gasoline fuels do exist, but there is not the same degree of use as there is with ethanol-gasoline fuels. This is not difficult to understand. The *raison d'être* of ethanol-gasoline fuels is that the ethanol component is carbon neutral. Methanol is usually made from coal or natural gas via synthesis gas, in which case it is not carbon neutral.

The ethanol-gasoline blend of lowest ethanol content is E10, which is 10% ethanol balance gasoline. Its viscosity amongst other properties is discussed in a recent paper by Kiatkittipong et al. [3]. These workers compared a commercial E10 ‘gasohol’ with FCC gasoline and with the same FCC gasoline blended with alcohol. The kinematic viscosities at room temperature were respectively 0.89 cSt, 0.67 cSt and 0.84 cSt. These are all in the range given above for ‘gasolines’ generically. There are Flexi Fuel Vehicles (FFV) which can use any fuel in the composition range from neat gasoline to E85. Clearly, the viscosity variation between the fuels across the range of gasoline-ethanol proportions is not a difficulty in operation. (The first E85 forecourt dispenser in the UK came into service at the time this chapter was being written [4].) Note that although the simplified form of the Grunberg-Nissan equation used in the previous chapter for crude oils would be suitable for application to the blending of straight-run gasoline and reformed naphtha it would **not** be suitable for gasoline-ethanol blends. This is because for gasoline and ethanol the approximation  $\gamma_{12} = 0$  would not hold. Gasoline-alcohol fuels are further discussed in Chapter 8.

### 3.2.3 The vehicle fuel pump

Typically an electric fuel pump in a modern car will operate at a pressure of 90 p.s.i. [5] This figure is examined in the boxed area below.

$$90 \text{ p.s.i.} \approx 6 \times 10^5 \text{ N m}^{-2}$$

By far the major component of the energy will be pressure energy, the kinetic and potential energy changes on pumping being relatively very small. This can be expressed:

Pressure energy =  $P/\rho$  where  $P$  is the pressure and  $\rho$  is the density. Putting our value for the pressure and a mid-range value of  $740 \text{ kg m}^{-3}$  for the density:

$$\text{Pressure energy} = 6 \times 10^5 \text{ N m}^{-2} / 740 \text{ kg m}^{-3}$$

$$= 810 \text{ m}^2 \text{s}^{-2} (\equiv \text{J kg}^{-1})$$

Now for a vehicle travelling at 40 miles per hour with a fuel consumption of 50 miles per gallon:

Fuel used in 1 hour = 0.8 gallon  $\equiv$  3 litres or 2.2 kg

Rate of supply of mechanical energy by the pump  
 $= 810 \text{ J kg}^{-1} \times 2.2 \text{ kg} / (3600 \text{ s}) = 0.5 \text{ W}.$

That the pump operates at about half a watt when the car is cruising at 40 m.p.h. is intuitively a very sensible result. The variation of viscosities between gasolines is a negligible factor in the performance of such a pump which is why, as noted previously, viscosity is not the most important factor in the quality control of gasolines. The very high values noted for pyrolysates [2] would probably not preclude their use. If the calculation is repeated for the process of transferring gasoline from refinery exit to terminal at a rate of  $1 \text{ m}^3$  per minute with the same pump head pressure, the power required is 10 kW.

### 3.3 Coefficient of thermal expansion

A generic value of  $0.00095 \text{ K}^{-1}$  for gasolines is given in [6]. A point which will be examined subsequently in this book is that although the principle of mass balance obviously applies to refining, **volume** balance does not. There is always net increase in the volume. This is the effect of 'refinery gain' and its primary origin is a positive volume change ( $\Delta V$ ) for the separation of the respective components. It is typically 6% [4]. Having regard to the fact that crude oil is sold by unit volume – the barrel – and that distillate is sold in litres or gallons 'refinery gain' is of importance when yields of distillate are evaluated.

It is also clear however that gasoline tapped off at its refining temperature will be at a significantly lower density than at room temperature. Consider a gasoline having an API density of  $60^\circ$  at  $15^\circ\text{C}$ , corresponding to a density of  $740 \text{ kg m}^{-3}$ . Using a calculation like that for Wytch farm crude in the previous chapter and the above value of  $\beta$ , it is easily shown that at a take-off temperature of  $200^\circ\text{C}$  the gasoline will have a density as low as  $565 \text{ kg m}^{-3}$ . The specific volume consequently goes up from  $0.00135$  to  $0.00180 \text{ m}^3 \text{ kg}^{-1}$ .

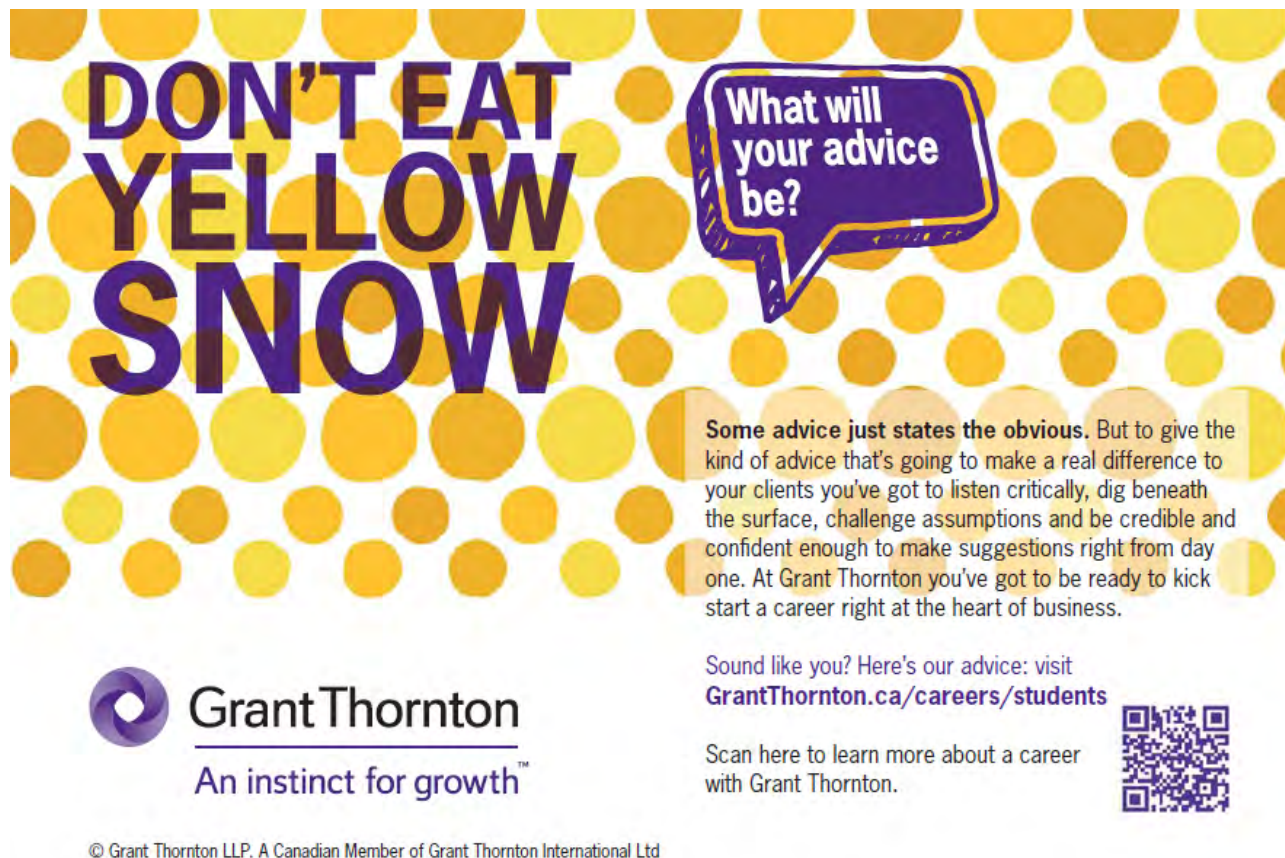
### 3.4 Acoustic impedance, thermal and electrical conductivities

The acoustic impedance of a gasoline is typically 1 Mrayl, of the same order as for crude oils but somewhat lower. Acoustic principles can be used in the detection of leaks of distillates such as gasoline. There is however another, more interesting, application to gasolines. The octane number of a gasoline can be correlated with acoustic impedance. This enables the octane number of a gasoline to be determined whilst it is flowing in a pipe at a refinery, a clear improvement over the measurement of the octane number for samples by the traditional approach. There have been a number of related patents.

The thermal conductivity of a gasoline is about the same as for a typical crude oil. A value of  $25 \text{ pS m}^{-1}$  would be typical of the electrical conductivity of gasoline.

### 3.5 Refractive index

The refractive index of iso-octane is 1.39 and intuitively we expect values for gasolines to somewhere close to that. One of the primary applications of optics to gasoline is the detection of contaminants from the higher boiling ranges. Such contaminants are usually from the kerosene boiling range. If the refractive index of a particular gasoline in its unadulterated state is measured, aberrations from that value signify contamination and this can be made quantitative. As with the discussion of viscosities of crude oils in the previous chapter, our purpose is best served by examining reported information from the research literature.



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S. Roy [8] provides a plot of the refractive index of a gasoline-kerosene mixture with percentage kerosene. It rises from just below 1.42 for gasoline alone to just over 1.43 for 50% kerosene. The graph rises most steeply at low kerosene concentrations and the resolution is such that 2% or even less of kerosene could reliably be detected. This investigator also presented the Beer-Lambert absorbance for gasoline-kerosene mixtures across the same concentration range with light at the single wavelength of 630 nm. The pure gasoline was totally transparent to this, whereas there was significant absorption at 5% kerosene rising approximately linearly over the concentration range, so here again is a powerful tool for inspecting gasoline for the presence of heavier hydrocarbons.

Numerous sources give a value of 2 for the dielectric constant of gasoline. Using the expression given in Chapter 1:

$$\text{refractive index} = (\text{dielectric constant})^{0.5}$$

this gives a value of  $\sqrt{2} = 1.414$  for the refractive index, in encouraging agreement with the experimental values quoted above.

## 3.6 Vapour pressure

### 3.6.1 Reid Vapour Pressure (RVP)

There is of course no such thing as ‘the vapour pressure’ of a gasoline. This is because the observed vapour pressure depends upon the volume into which the vapour expands. The standard industry measure is the Reid Vapour Pressure, where the volume occupied by the vapour is the same between tests, hopefully enabling at least comparative differences between gasolines to be measured. The RVP, which is measured at 38°C, is sometimes determined for crude oil and for other petroleum fractions including kerosene. A synthesis of selected recent literature appertaining to the RVP of gasolines and blends containing gasoline follows in tabular form.



Reference	Substance(s)	Findings
[9]	Two gasolines blended with ethanol at up to 8% by volume and with ethyl tertiary butyl ether (ETBE) at up to 16% by volume <sup>4</sup> .	RVP for each gasoline alone $\approx$ 55 kPa. A rise ( $\approx$ 3 to 5 kPa) in the RVP with ethanol at 8% and a drop ( $\approx$ 2 to 3 kPa) with ETBE at 16%.
[10]	Gasoline from a Brazilian refinery.	RVP of 61.7 kPa. RVP of 'white spirit' from the same source 3.9 kPa.
[11]	Gasoline-ethanol blends of across the entire concentration range.	A rise from 53.6 kPa for the gasoline alone to a maximum of 57.4 kPa with 60% ethanol.
[11]	Gasoline-ethanol blends <b>also</b> containing ETBE up to 10%. <b>Gasoline A</b> a 'winter gasoline' having a high RVP. <b>Gasoline B</b> a 'summer gasoline' having a low RVP.	Gasoline A alone: RVP 68.2 kPa. Gasoline A with 5% ethanol: RVP 74.1 kPa Gasoline A with 5% ethanol and 5% ETBE: RVP 72.8 kPa Gasoline B alone: RVP 55.3 kPa. Similar trends with ethanol and ETBE as for Gasoline A.
[12]	FCC gasoline of API gravity 61°	A RVP of 48 kPa
[3]	Commercial E10 'gasohol' FCC gasoline FCC gasoline blended with alcohol (See section 3.2.2)	RVP/kPa: $\Rightarrow$ < 62 $\Rightarrow$ 44.8 $\Rightarrow$ 51.2

Trends evident from the limited but certainly representative entries in the table are that ethanol raises the RVP and ETBE lowers it. ETBE is one of a number of oxygenated additives for gasoline. Methyl tertiary butyl ether (MTBE) is another, and it has been observed that this causes a rise in the RVP as does methanol when that is blended with gasoline.

FCC gasoline tends to have somewhat lower values of the RVP than a 'base gasoline'. The vapour pressure of iso-octane at 38°C is 14 kPa, suggesting that for vapour pressure purposes iso-octane is not the best reference hydrocarbon compound. Cyclopentane has a vapour pressure of 68 kPa at 38°C and is thus a good benchmark for 'winter gasoline'.

### 3.6.2 Refinements to the RVP

When the RVP is measured there is air in the confined space which was previously dissolved in the test sample. Corrections for this can be made by means of charts [13] and the vapour pressure so determined is called the True Vapour Pressure (TVP). Moreover, if the RVP, which is of course always determined at 38°C (100°F), is known for a particular hydrocarbon stock its TVP at other temperatures can be determined from the chart. The chart itself will not be reproduced as an interested reader can very easily download it from web sites including [13].

Hatzioannidis et al. [14] found that *for a limited number of gasolines experimentally examined* the following holds:

$$\text{RVP/kPa} = 1.0091(\text{TVP/kPa}) + 5.53$$

from which, for example, a gasoline having a RVP of 50 kPa will have a TVP of 44 kPa. This The present author has checked this against the plot in [13] and obtained a value of 46 kPa to the nearest whole number.

This is reasonable agreement, but it is emphasised that the plot in [13] is intended to be used across a wide range of distillate RVP values whereas the correlation above appertains only to those particular gasolines (some of which contained additives) examined in [14] so if it is used more widely it must be with caution.

Of course, the so-called true vapour pressure is not **the** vapour pressure any more than the RVP is. It has already been explained that no such vapour pressure exists for a distillate because of the dependence of the vapour pressure on the space which the vapour occupies. The TVP is merely the RVP corrected for air (and water vapour) in the measurement space.

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### 3.7 Thermal conductivity

In [15] the following is given as applying to any petroleum derived liquid:

$$10^6 k / \text{cal s}^{-1} \text{cm}^{-1} \text{ } ^\circ\text{C}^{-1} = 333 - 0.19t$$

where  $t$  is the temperature in  $^\circ\text{C}$ . So for  $t = 20^\circ\text{C}$  this gives:

$$k = 329 \times 10^{-6} \text{ cal s}^{-1} \text{cm}^{-1} \text{ } ^\circ\text{C}^{-1} \equiv 0.14 \text{ W m}^{-1}\text{K}^{-1}$$

and this should be compared with values given in Table 1.4. A value of  $0.15 \text{ W m}^{-1}\text{K}^{-1}$  for gasoline at room temperature is given in [16]. At  $200^\circ\text{C}$ , which might be the upper boiling limit depending on the width of cut taken in refining, the value according to the above correlation would be  $0.12 \text{ W m}^{-1}\text{K}^{-1}$ .

### 3.8 Concluding remarks

Spark ignition engines have become more and more advanced in their design and operation, to a very large extent precluding DIY maintenance. A result has been vehicles which can accept fuels of varied composition and this relates to carbon dioxide emission control. These points will be discussed more fully in the coverage of alcohol-containing fuels.

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# Appendix on natural gas condensate

## A1 Introduction

Oil and gas in a deep well are of course significantly higher in temperature than ambient. Natural gas, associated or non-associated, on cooling releases hydrocarbon up to about  $C_5$  in liquid form and this is called natural gas condensate<sup>5</sup>. Where non-associated gas is high in condensate the field from which it comes is known as a condensate field; there are several such in the southern part of the UK sector of the North Sea. Condensate from associated gas is usually combined with the liquid stream for piping to a terminal. Condensate can be blended with gasoline and this occurs in countries including New Zealand. Hence coverage of condensate in this part of the book is appropriate. The same physical properties that have been discussed for gasoline will be outlined for condensate in this appendix.

## A2 Physical properties of natural gas condensate

Natural gas condensates vary widely in the balance of the respective constituents, therefore their densities also vary widely. Reference [1] gives a range of 620 to 760 kg m<sup>-3</sup> (97 to 55 °API). The kinematic viscosity of a particular condensate [2] at 30°C was measured as 0.7 cSt, making it less viscous than water which has a value at 30°C is 0.8 cSt. Its Reid vapour pressure [3] is in excess of 2.5 bar.

## A3 Concluding remarks

In reporting statistics for oil production, 'totals' incorporate crude oil condensate, shale oil and oil from tar sands as well as gas-to-liquid fuels. The highest average for a single day in 2008 on this basis was 81.73 million barrels per day. For crude oil and condensate without the other sources the highest daily average was 72.75 million barrels per day. Crude oil and condensate are often lumped together in such accounting, although there is one notable exception. An OPEC country is assigned a production quota and must meet it for continued membership. The quota is expressly a quantity of crude oil and a crude oil/condensate aggregate figure is not acceptable for this purpose.

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3. <http://pubs.acs.org/doi/abs/10.1021/ef060074h>
4. <http://www.theoil Drum.com/tag/opec>

## 4 Physical properties of kerosenes

### 4.1 Introduction

In the distillation of crude oil there is a gap between gasoline and kerosene, the fraction known as naphtha. Unprocessed naphtha is unsuitable for blending with gasoline as it lowers the octane number. Naphtha is unsuitable for blending with kerosene as, quite apart from any performance considerations, it lowers the flash point. We saw in a previous chapter that reformed naphtha is frequently blended with gasoline. Naphtha can also be steam reformed to make fuel gas or synthesis gas. Like gasoline, kerosene can come from sources other than crude oil including shale and tar sands.

Kerosene is of course used to power jet aircraft. A jet fuel might be kerosene alone or it might be ‘wide cut’ taking in some of the heavier components of the naphtha boiling range additionally to the kerosene. In such fuels however kerosene will always be in preponderance. A jet engine is a gas turbine, and burning is continuous at a combustion chamber. This is in contrast to a petrol or diesel engine where ignition occurs at the required stage in the thermodynamic cycle. Consequently there is no analogue for kerosene of the octane number for gasoline.

### 4.2 Density

A typical density for a kerosene jet aircraft fuel would be  $780 \text{ kg m}^{-3}$  or 50°API [1]. Of course, there is a large difference between the temperature at which an aircraft on the ground receives fuel and that at which the aircraft cruises. At a cruising height of  $\approx 10000$  metres the temperature will be about  $-50^\circ\text{C}$  (223 K). The calculation performed in section 2.3 for crude oil is repeated below for kerosene. Symbols are as previously and the temperature at which the aircraft is refuelled is taken to be  $15^\circ\text{C}$  (288 K). It can be seen from the calculation that at cruising altitude the kerosene is 11 degrees lower on the API scale than on the ground, that is, its density has significantly *increased* as a result of ascent.

$$\beta = - (1/\rho) \text{ d}\rho/\text{d}T$$

$$\Downarrow$$

$$\beta(223 - 288) = -\ln \{\rho(223\text{K})/\rho(288\text{K})\}$$

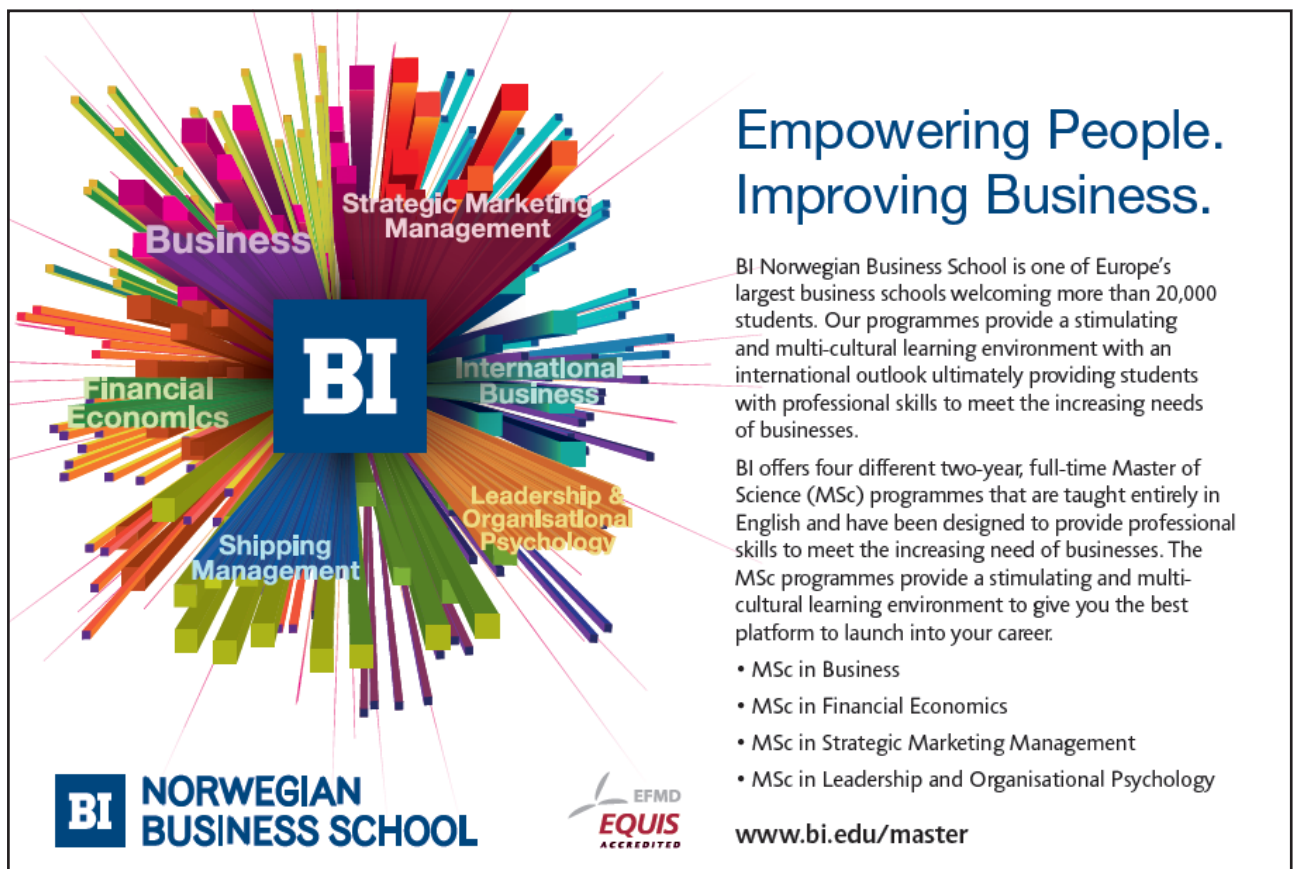
$$\text{Using } \beta = 0.00099 \text{ K}^{-1} [2] \text{ and } \rho(288\text{K}) = 780 \text{ kg m}^{-3} \text{ gives: } \rho(223 \text{ K}) = 832 \text{ kg m}^{-3} \text{ (39o API)}$$

These figures are closely matched by a graph of density against temperature for a particular jet fuel [3]. The units of density in [3] are lb per US gallon and these have had to be converted to  $\text{kg m}^{-3}$  for this discussion. The fuel under consideration has a density of  $760 \text{ kg m}^{-3}$  at  $+20^\circ\text{C}$  and a density of  $808 \text{ kg m}^{-3}$  at  $-40^\circ\text{C}$ . The interested reader can easily confirm that this corresponds to a  $\beta$  value of  $0.0010 \text{ K}^{-1}$ .

### 4.3 Solid deposition

The temperature at which wax appears is an important factor in jet fuel specification. At the cloud point wax appears<sup>6</sup>. Specification for jet fuels take note of this, and a value of  $-47^{\circ}\text{C}$  applies in some countries. In others (including Russia) jet fuels are commonly used which have a cloud point not above  $-50^{\circ}\text{C}$ . When an aircraft crashed at Heathrow early in 2008 there were suggestions, subsequently dismissed, that the fuel had experienced solid deposition a few hours earlier whilst the aircraft was flying over Siberia where the temperature at the altitude of the aircraft was about  $-75^{\circ}\text{C}$  [4].

The temperature at which a matrix structure within the fuel is formed which precludes flow is called the *pour point*. Often when a fuel initially reaches the pour point only something like 1% of the total mass is in the solid state, and the pour point is usually less than  $10^{\circ}\text{C}$  below the cloud point (see section 4.4). Below the cloud point the temperature dependence of the viscosity changes and with some fuel systems this makes for difficulties. With jet aircraft however it is the pour point which determines the lowest operating temperature [5]. In an airliner there is a temperature sensor within the fuel which, if the fuel drops to a temperature below that considered safe, sends a signal to the cockpit.



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Additives are available by means of which the pour point of a jet fuel can be lowered, known as ‘pour point depressants’. These work analogously to the solute in simple freezing point depression of a single liquid compound. They are added in amounts of less than 1%, and many consist of copolymers of ethylene and vinyl esters [6]. Urea has been shown to be an effective pour point depressant under certain conditions [7]. Ethylene glycol monomethyl ether and diethylene glycol monomethyl ether [8] have been widely used. A jet fuel might also contain a corrosion inhibitor. This can have a side-effect on viscosity and solid deposition behaviour as will be explained more fully in the next section.

## 4.4 Viscosity

### 4.4.1 Viscosities at flight altitudes

Viscosities at the temperature of flight are relevant to performance, and accordingly review of a study of the viscosities of jet fuels at such temperatures [9] will be commence this section. Assigning for the purpose of this summary the descriptors Fuel X and Fuel Y to two of the fuels which feature in [9], viscosities and supplementary data are given in the table below.

	<b>Cloud point /°C</b>	<b>Pour Point /°C</b>	<b>Kinematic viscosity at -20°C (253K)/cSt</b>	<b>Kinematic viscosity at -40°C (233K)/cSt</b>
<b>Fuel X</b>	-52.6	-58.0	3.9	8.4
<b>Fuel Y</b>	-46.5	-	4.9	11.9

Fuel X was further studied for wax deposition behaviour [9]. At the cloud point temperature of -52.6°C the bulk liquid was free of wax, but wax was becoming evident at the interface of the fuel and the container wall. On further cooling to the pour point of -58.0°C wax appeared in the bulk liquid after 37.5 minutes, and the inside container wall was coated with wax. Wax in the bulk liquid had become much more abundant after another five minutes and had consolidated in parts of the sample after another five minutes. When a proprietary corrosion inhibitor was present the cloud point of Fuel X was found to rise to as high as -40°C. This is believed to be due to the provision of nucleation sites for incipient wax by the constituents of the additive.

### 4.4.2 A correlation for variation of viscosity of kerosene with temperature

The author has discovered in a rather obscure source [10] a correlation for the temperature dependence of the kinematic viscosity of kerosene aviation fuel. It is:

$$\log\log(\nu + 0.73) = 9.3398 - 3.9899\log T$$

where  $\nu$  is the kinematic viscosity in  $\text{mm}^2\text{s}^{-1}$  ( $\equiv \text{cSt}$ ) and  $T$  is the temperature in Kelvin. The correlation was obtained by fitting experimental measurements. Letting  $T$  be 233 K gives:

$$\nu = 5.4 \text{ cSt}$$

and letting  $T$  be 253 K gives:

$$\nu = 2.9 \text{ cSt}$$

and broad consistency with the values for Fuels X and Y in the above table should be noted. As the kerosene being supplied advances within the fuel system its temperature rises because of conduction to the pipes from the combustion chamber and it is believed [10] that temperatures of up to  $120^\circ\text{C}$  (393K) are experienced by the fuel. Putting a value for  $T$  of 393 K in the correlation gives:

$$\nu = 0.52 \text{ cSt}$$

It is clear then that kerosene will drop in viscosity by about an order of magnitude between the tank temperature and the warmest part of the fuel lines. At the reference temperature for viscosity measurement, which is  $60^\circ\text{F}$  ( $15^\circ\text{C}$  288 K), the above correlation gives a value of 1.4 cSt which is only about 40% higher than the value for water at the same temperature. ‘General purpose’ values of the kinematic viscosity of kerosene at this temperature are often a little higher; as an example [11] gives 2.5 cSt.

#### 4.4.3 Kerosene as a diluent for lubricating oils

The suitability of a lubricating oil for a particular purpose depends strongly on the viscosity, and a lubricating oil can be diluted with kerosene to a required viscosity. An ASTM (American Society for Testing and Materials) source gives the following information for oils of various kinematic viscosity after blending with kerosene of kinematic viscosity 3 cSt. Blending is 50:50 at  $40^\circ\text{C}$  in each case.

Viscosity of the lubricating oil before blending with kerosene diluent/cSt.	Viscosity after 50:50 blending with kerosene of kinematic viscosity 3 cSt.
32	8
68	10
100	12
220	15
460	18
680	20

The values for the diluted oil can be compared with those from the simplified Grunberg-Nissan equation which in Chapter 2 was applied to crude oils. The working is in the boxed area below.

With symbols as in Chapter 2, and assigning subscript 1 to the oil and subscript 2 to the kerosene:

$$\ln \mu_{12} = \phi_1 \ln \mu_1 + \phi_2 \ln \mu_2$$

Noting that  $\phi_1 = \phi_2 = 0.5$  and that  $\nu = \mu \rho$

$$\ln \nu_{12} \rho_{12} = \phi_1 \ln \mu_1 \rho_1 + \phi_2 \ln \mu_2 \rho_2$$

$$\ln \nu_{12} = \phi_1 \ln \nu_1 + \phi_2 \ln \nu_2 + \ln[(\rho_2 \rho_1)^{0.5} / \rho_{12}]$$

Now the argument of the logarithm containing the densities will be very close to unity making the logarithm itself very close to zero and negligible, hence:

$$\ln \nu_{12} = 0.5 \ln \nu_1 + 0.5 \ln \nu_2$$

$$\nu_{12} = \exp\{0.5 \ln \nu_1 + 0.5 \ln \nu_2\}$$

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In the table below the kinematic viscosities for the diluted oil from the ASTM document and those from the above treatment are compared. In brackets in columns two and three are the per cent decline in viscosity, that is:

$$[(v_{12} - v_1)/v_1] \times 100$$

$v_1/\text{cSt}$	Blend viscosity ( $v_{12}$ ) from the ASTM document/cSt	Blend viscosity ( $v_{12}$ ) from the simplified Grunberg-Nissan equation/cSt
32	8 (-75)	10 (-69)
68	10 (-85)	14 (-79)
100	12 (-88)	17 (-83)
220	15 (-93)	26 (-88)
460	18 (-96)	37 (-92)
680	20 (-97)	45 (-93)

The values of the viscosity of the diluted oil diverge by up to about a factor of two for the larger values of  $v_1$ . In its estimation of the percentage drop through kerosene blending the simplified Grunberg-Nissan equation does appear to deliver the goods.

#### 4.5 Acoustic impedance

Reference [12] gives a value of 1.07 Mrayl for the acoustic impedance of kerosene. Values for gasolines and kerosenes are close to each other and both are significantly lower than that for a typical crude oil. The acoustic impedance of the fuel is the principle of ultrasonic measurement of levels in aircraft fuel tanks. For example, the new model Boeing 777 series will carry such a device [13]. Ultrasonic fuel tank gauges are beginning to replace the earlier type which used the capacitance of the fuel as a basis for determining the height of the liquid surface. This is discussed more fully below.

#### 4.6 Capacitance

The capacitance is a measure of the charge which can be held by a dielectric per unit potential difference across it. Its units are thus:

$$\text{coulomb/volt} = \text{farad}$$

In a capacitive aircraft fuel gauge a metal electrode is immersed in the fuel and the metal fuel wall forms a second electrode. As the level of liquid recedes the capacitance experienced by the electrode pair changes. Capacitances in this sort of application are of the order of picofarads (pF).



## 4.7 Electrical conductivities

Kerosene jet fuel typically has  $50 \text{ pS m}^{-1}$  conductivity [14]. Often a static dissipator additive (a.k.a. as a conductivity improver) is used to increase the electrical conductivity so as to prevent ignition from an electrical discharge during aircraft refuelling. Some specifications require a conductivity as high as  $600 \text{ pS m}^{-1}$  in which case the static dissipator additive has to raise the conductivity by up an order of magnitude. The limit on the amount of static dissipator additive is 3 milligrams per litre of fuel. This is because amounts any higher would interfere with fuel tank level measurements by capacitance. A widely used static dissipator additive is Stadis 450, manufactured by Octel, the active ingredient of which is dinonylnaphthylsulfonic acid (DINNSA). Pour point depressant additives, being non-ionic, do not affect the capacitance.

## 4.8 Refractive index

Tables of values for the refractive indices of liquids give values of typically 1.448 [15] for the refractive index of kerosene. We saw in our discussion of the refractive index of gasolines in the previous chapter that when a gasoline is contaminated with kerosene the refractive index can provide a measure of the degree of contamination. This idea was taken further [16] when gasoline-kerosene blends in the composition range pure gasoline to pure kerosene were examined for refractive index. Up to a kerosene content of 5% balance gasoline, the refractive index is indistinguishable from that for the neat gasoline which is 1.418. With greater amounts of kerosene there is a rise to 1.425 at 30% kerosene and to 1.440 at 100% kerosene. We note in passing that the kinematic viscosity of the blends studied in [16] rises from 1.0 to 2.2 cSt across the composition range.

## 4.9 Vapour pressure

RVP values for kerosenes are much lower than for gasolines as would be expected from their higher boiling range. An equation of the form:

$$P = A \exp(-B/T)$$

where  $P$  is the vapour pressure,  $T$  the temperature and  $A$  and  $B$  are constants has sometimes been applied to the vapour pressure of kerosenes. Such an equation applies rigorously only to pure hydrocarbon compounds, being an integrated form of the Clausius-Clapeyron equation. In this case  $B$  is the heat of vaporisation divided by the gas constant. That complex mixtures of hydrocarbons when examined experimentally often conform to such a functional form is well known (e.g., [17]). In reference [18] several kerosene jet fuels were examined for temperature dependence of vapour pressure and the results fitted to an equation of the form above. One of the fuels was found to fit the equation:

$$P/\text{kPa} = 6905 \exp(-2196.53/T)$$

Putting  $T = 311\text{K}$  which is the temperature of an RVP measurement:

$$P = 5.9 \text{ kPa}$$

A similar fuel was found to conform to:

$$P/\text{kPa} = 2779.43 \exp(-1773.77/T)$$

giving a RVP of 9.3 kPa. Work cited in reference [18] gives, for another kerosene jet fuel:

$$P/\text{kPa} = 653436.08 \exp(-4243.3/T)$$

giving an RVP of 0.78 kPa (6 mm Hg). That some kerosenes do have RVP values as low as this is well known.

When with results of the type outlined above  $\ln(P/\text{kPa})$  is plotted against  $10^3\text{K}/T$  the result is a line of slope  $-B$  (units K). As we have seen, for a pure compound:

$$B = \Delta H_{\text{vap}}/R$$



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so a steep slope would signify a high heat of vaporisation. We expect intuitively that the same would apply to the kerosenes. In the example equations given above the constant in the exponential varies by a factor in excess of two. That the one with the highest value of B is the one with the lowest RVP is significant.

#### 4.10 Thermal conductivity

The equation used in the previous chapter for gasoline, viz.:

$$10^6 \text{ k/cal s}^{-1} \text{ cm}^{-1} \text{ } ^\circ\text{C}^{-1} = 333 - 0.19t$$

with symbols as defined previously is believed to hold for any petroleum fraction, so the value of  $0.14 \text{ W m}^{-1}\text{K}^{-1}$  at  $20^\circ\text{C}$  obtained for gasoline is expected to hold for kerosene. Many sources including [19] give a value of  $0.15 \text{ W m}^{-1}\text{K}^{-1}$ . At  $250^\circ\text{C}$ , which is in the neighbourhood of the upper boiling limit, the value calculated from the correlation is  $0.12 \text{ W m}^{-1}\text{K}^{-1}$ .

#### 4.11 Concluding remarks

Supply of kerosenes to the huge yet very vulnerable airline industry will continue. 'Carbon footprints' of air travel are sometimes offset in financial terms by passengers. It is unlikely that the costs incurred by carbon emissions would be a major threat to the economic viability of the industry as such emissions are minor, about 2% of the total. The cost of fuel is important, and the last few years (since about the time of the 2005 Gulf Coast hurricanes) have seen unprecedentedly erratic changes in the price of crude oil. In some ways there is more flexibility for use of novel fuels with jet engines, since combustion in such a device is continuous not intermittent as stated earlier in this chapter there is no analogue of the octane number. The flexibility is however restricted by the very large temperature swings a jet fuel experiences in flight and effects of this on fuel pumping. There will be a return to this theme in the chapter on biodiesels.

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# 5 Diesel fuels

## 5.1 Introduction

Diesel fuels find application in compression ignition engines and in gas turbines. As 'light fuel oil' they are also used in heating. The diesel fraction from crude oil is the heaviest of the atmospheric distillates; material beyond that is either vacuum distillate or residue. The performance index for a diesel fuel is the cetane number, and the benchmark value is 50. Whereas the octane number for a gasoline relates to the resistance to *unintended* compression ignition in advance of the spark the cetane index relates to resistance to delay of *intended* compression ignition. The two are just about opposite conceptually, which is why the view that the cetane number is the counterpart for diesel of the octane number for gasoline is misleading and better avoided.

The current research literature on fuels for compression ignition engines is dominated by biodiesels. These are becoming increasingly important and have a chapter to themselves later in this text. Mineral diesel, that is diesel from crude oil, shale or tar sands will be the subject of this chapter. The important difference between biodiesel and mineral diesel is that the former is carbon neutral and the latter is not. A typical density for diesel is  $850 \text{ kg m}^{-3}$ , corresponding to an API gravity of 37 degrees. A coefficient of expansion of 0.00083 applies [1].

## 5.2 Solid deposition

### 5.2.1 Background

As we saw in the previous chapter, with kerosene the cloud point is relevant only at the very low temperatures experienced by aircraft at altitudes of the order of 10000 metres. With diesel solid deposition can occur at higher temperatures. The cloud point and pour point have already been defined in this book. With diesel there is a further measured temperature, the cold filter plugging point (CFPP) defined [2] as the lowest temperature of a diesel sample at which it will pass through a fine mesh, the spacings of which are specified in the ASTM and other standards for CFPP determination. The CFPP is obviously between the pour point and the cloud point and is expected to be closer to the former. The following information on cloud points and pour points of mineral diesels is from a very recent research paper [3]. For the purposes of this discussion they are called fuels A to E.

	Fuel A	Fuel B	Fuel C	Fuel D	Fuel E
Density (20°C)/ $\text{kg m}^{-3}$	831.6	831.4	831.6	833.7	835.6
Cloud point/°C	-18	-8	-8	-8	-10
CFPP/°C	-13	-4	-4	-5	-7

The cloud point and CFFP are seen to be separated by 3 to 5°C across the range of samples. The possibility of interference of the functioning of a diesel engine by solids in the fuel is clear from these figures. This necessitates pour point additives. By means of a calculation like that in the previous chapter for gasoline and using the value for the coefficient of expansion of diesel given above, it is easily shown that Fuel A would have a density of 806 kg m<sup>-3</sup> at its cloud point.

### 5.2.2 Cloud point depressants

Again, our discussion is best taken forward by examination of suitable research literature. The author has selected from the information in [4] one data point for cloud point depression by an additive. It was pointed out in a previous chapter that the action of such a depressant can be seen as a simple colligative property entirely analogous to simple freezing point depression. A related calculation is in the boxed area below.

One data pair from [4] is:

Cloud point depression of 1oC with 5% cloud point depressant. The depressant is 85% 2,6 dimethyl octane, molecular weight 142. The minor constituents of the additive are of similar structure, so a value of 142 will be used for the molecular weight of the additive. The relevant equation is:

$$\Delta(\text{CP}) = k_f c$$

where  $\Delta(\text{CP})$  is the cloud point depression (oC),  $c$  is the concentration of depressant (mol per kg solvent) and  $k_f$  is the depression constant (oC kg mol<sup>-1</sup>). Now a concentration of the additive of 5% corresponds to 0.35 mol per kg of solvent giving:

$$k_f \approx 2.8 \text{ oC kg mol}^{-1}$$

No more than order-of-magnitude correctness for this figure is being claimed. We note however that it is exactly half way between the value for water and that for benzene, respectively 1.86 and 5.12 oC kg mol<sup>-1</sup>. The view that the action of the additive is colligative is broadly supported by the result.

A further point can be made. Some cloud point depressants are not simple hydrocarbons as in the above calculation but are polymers. These would not be added in amounts as high as 5%. For an additive the dominant constituent of which is a C<sub>10</sub> hydrocarbon inclusion at 5% level might be possible without affecting the cetane number although this would of course have to be considered. In [4] it is reported that the additive at 5% level reduces the cetane index by 1.3 units.

There are additives for lowering the CFPP of a diesel including acetate copolymers [6]. The author has examined numerical results from these along the lines of the calculation in the box above, and has found that impossibly high values of  $k_f$  result. The meaning of this is of course fairly clear: the action of such additives is not colligative, but involves prevention of nucleation of wax.



### 5.3 Viscosities

A diesel fuel is likely to have a kinematic viscosity at room temperature of up to about 5 cSt. The correlation in section 4.4.2 indicates that kerosenes at room temperature have kinematic viscosities between 1 and 2 cSt and in Chapter 3 it was stated that gasolines have kinematic viscosities in the range 0.4 to 1 cSt. The increase in viscosity with refining temperature is clear. This is better understood as increase in viscosity – ‘resistance to flow’ – with increasing size of the hydrocarbon molecules.

Some of the literature discussed in relation to solid deposition in the previous paragraph also contains viscosity information and this is summarised in the table below. There is also information taken from an additional reference [7].

Reference.	Viscosity information.
3	Viscosities at 20°C in the range 4.992 to 5.408 cSt. Viscosities at 40°C in the range 3.120 to 3.353 cSt.
4	A rise in viscosity with increased amounts of the additive, up to 3.9 cSt at 10% additive.
7	Two low-sulphur diesels, densities 832 and 838 kg m <sup>-3</sup> . Respective viscosities at 40°C 2.86 and 2.78 cSt.



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## 5.4 Refractive index

The refractive indices of the low-sulphur diesels which feature in the final row of the table at the end of the previous section are 1.4595 and 1.4745. Again a mild trend of increase with density is evident, a typical value of 1.448 having been noted in Chapter 4 for kerosenes and values of around 1.42 having been noted in Chapter 3 for gasolines. The refractive index of n-cetane, the benchmark hydrocarbon against which diesels are assessed, is 1.432 [8]. The dielectric constant for diesel fuels varies across quite a wide range, from about 2 to about 6, making the correlation used for the lighter fractions for calculating the refractive index from the dielectric constant unsuitable for diesels. The meaning of the correlation, which even for a pure hydrocarbon compound is only approximate, is not altogether lost when diesels are considered. Taking the mean of the two values of the refractive index earlier in this paragraph and squaring it gives a value for the dielectric constant of 2.15, which is within the range given though certainly at the low end of it. The dielectric constant of n-cetane at 20°C is 2.08 [9], giving a value of the refractive index of:

$$\sqrt{2.08} = 1.442$$

which is 0.7 of one per cent higher than the experimental value given above. Further information on the refractive indices of diesels is given in calculation form in the boxed area below.

In the paper by Riazi and Roomi [10] which was also drawn on in Chapter 1 the following equation is given for petroleum fractions having average molecular weights below 300:

$$I = 0.328\nu - 0.003\rho^{0.915}$$

where  $I$  is the refractive index parameter as defined in Chapter 1,  $\nu$  the kinematic viscosity in cSt and  $\rho$  the density (water = 1). We saw above that diesels have kinematic viscosities of around 5 cSt and densities of around 850 kg m<sup>-3</sup> (i.e.,  $\rho = 0.85$ ). Inserting these numbers into the above equation gives:

$$I = 0.28 = (n^2 - 1)/(n^2 + 2) \text{ where } n \text{ is the refractive index}$$

⇓

$$n = 1.47$$

which is a result consistent with the values given previously in this section.

A reader utilising the correlation in the box above might well make the judgement that the term  $\nu^{-0.003}$  is so close to unity across the range of values of the kinematic viscosity of diesels that it can be omitted without any loss of precision.



## 5.5 Electrical conductivity

A value of the electrical conductivity of about  $50 \text{ pS m}^{-1}$  is required for a diesel fuel not to create a static discharge when in rapid movement and straight-run diesel might well have a value this high or higher. Ultra-low sulphur diesel (ULSD) has become the norm in many countries since about 2006, and the processes involved in removing the sulphur tends to lower the conductivity. Very interesting comparisons are made in reference [11], in which a particular 'pre 2006' diesel is compared with a ULSD in terms of electrical conductivity. The values are respectively 226 and  $10 \text{ pS m}^{-1}$  and the latter is clearly unacceptable. It is shown in [11] how use of a particular additive can raise the conductivity of ULSD to several hundreds of  $\text{pS m}^{-1}$ , ensuring the safety of the product from the electrostatic discharge point of view.

## 5.6 Lubricity

Lubricity is a measure of the extent to which abrasion caused by the movement of one metal surface against another is mitigated by a particular hydrocarbon, and lubricity values for diesel fuels (and their carbon neutral alternatives, as will be fully explained in a later chapter) are of some importance. Lubricity is determined [12] in an apparatus whereby a steel ball rotates whilst in contact with fixed steel plate, the entire assembly being immersed in the fuel of interest. The 'scar diameter' on the fixed steel plate after such a test, units microns, is termed the lubricity. A fuel with a good degree of lubricity will give rise to a **small** scar diameter. There are standard procedures for this test approved by bodies including ASTM.

Literature cited previously in this chapter contains lubricity information and this is summarised in the table below. Information from a further reference [13] is also given.

Reference	Details of lubricity
4	Lubricity for the diesel without additive $470 \mu\text{m}$
7	Lubricities for the two fuels 425 and $555 \mu\text{m}$
11	A lubricity value of $581 \mu\text{m}$ for ULSD
13	A value of $450 \mu\text{m}$ for a ULSD without a lubricity additive

The ULSD has the highest value (i.e., the poorest lubricity) of the diesels in the table, and it is known that the processes involved in making ULSD have an adverse effect on lubricity, as they do on electrical conductivity. Toluene is an example of a lubricity enhancing additive. Standards vary from place to place; in the US  $520 \mu\text{m}$  is seen as the maximum acceptable value for a diesel fuel.

Tests like that for lubricity are fraught with potential irreproducibility even if performed according to a recognised and approved procedure. Consequently the view is often taken that when a particular hydrocarbon product is examined for lubricity it should be against a standard hydrocarbon so that the basis of the test result is comparative. The standard substance and that being examined will be tested in the same apparatus without adjustment of conditions between the tests. This approach was taken in the work described in reference [14] in which the wear scars were measured in more than one direction and averaged. Such values for the 'high lube standard' and 'low lube standard' at a test temperature of 25°C were 320 and 654  $\mu\text{m}$  respectively. A regular diesel having had no desulphurisation gave a value of 413, whilst a ULSD without an additive gave 613  $\mu\text{m}$ . The same ULSD with a lubricity additive gave 303  $\mu\text{m}$ .

These results confirm what has been said in this paragraph previously about ULSD and also affirm the effectiveness of a suitable lubricity additive. Cetane (a.k.a. hexadecane) gave an averaged value of 412  $\mu\text{m}$ . It was noted in the previous section that cetane is a little aberrant in terms of refractive index but from the investigation in [14] it appears to have a lubricity comfortably below the maximum value for usage. The actual value is below the maximum figure for the US quoted above but, given that [14] was a comparative study, the important observation is that the value is much closer to that of the 'high lube standard' than that of the 'low lube standard'. The equality, to within much less than one per cent, of the values for cetane and for the regular diesel is further evidence that cetane is a suitable model compound for lubricity as well as for resistance to ignition delay. Of the pure compounds examined in [14] 1-dodecene had the poorest lubricity (746  $\mu\text{m}$ ) and 1-hexadecene the best (309  $\mu\text{m}$ ). With regard to the latter it can be deduced that introduction of a double bond into the cetane structure gives it even better lubricity. This section has of course been concerned with the lubricity of fuels. Lubricants *per se* will be discussed in a later chapter.

## 5.7 Vapour pressure

Vapour pressures of diesels at room temperature are very low; that discussed in [14] has a vapour pressure of 0.4 mm Hg ( $\equiv$  0.053 kPa). That for cetane is less than 1 mm mercury [15], yet another 'plus' for cetane.

A calculation concerning the vapour pressure of a diesel is in the boxed area below.

Imagine diesel vapour in equilibrium with liquid, the space into which the diesel vapour expands also containing air at 1 bar.

$$\text{Total pressure} = 100.053 \text{ kPa}$$

Assigning subscripts A to the air and D to the diesel vapour:

$$P_A V = n_A RT$$

$$P_D V = n_D RT$$

⇓

$$n_D / (n_A + n_D) \approx n_D / n_A = P_D / P_A$$

$$= (0.053/100) \times 10^6 \text{ parts per million (p.p.m.)}$$

$$= 530 \text{ p.p.m.}$$

We first note that a p.p.m. in the hundreds is certainly likely to exceed the odour threshold and this is consistent with common experience in the handling of diesel. No odour threshold appears to have been established for cetane. We can cautiously compare diesel with n-dodecane in these terms as this has a vapour pressure of 0.3 mm Hg, a value typical of a diesel. Its odour threshold is 5 p.p.m. [16].



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The value of 530 p.p.m. can be broadly compared with threshold limit values for pure hydrocarbon compounds. The threshold limit value (TLV) for styrene is 20 p.p.m. [17]. That for cyclohexane is 300 p.p.m. [18]. That for toluene is 50 to 100 p.p.m. [19]. Other examples can be given but enough has been said to support the view that the diesel concentration in the calculation is sufficient to be harmful.

## 5.8 Thermal conductivity

The correlation previously applied to gasoline and to kerosene:

$$10^6 k / \text{cal s}^{-1} \text{ cm}^{-1} \text{ } ^\circ\text{C}^{-1} = 333 - 0.19t$$

at 20°C and at distillation temperatures will in our coverage of diesel be applied for negative values of  $t$ , that is, temperatures below 0°C. At temperatures in the region of the cloud point, say -10°C, the prediction of the correlation is:

$$k = 335 \times 10^{-6} \text{ cal s}^{-1} \text{ cm}^{-1} \text{ K}^{-1} \equiv 0.14 \text{ W m}^{-1} \text{ K}^{-1}$$

so this property is not significantly affected by the low temperature at aircraft cruising altitudes. The thermal conductivity is of course relevant even where heat transfer is by convection, as at aircraft speeds it is likely to be. This is because in convective heat transfer there is conduction across the thermal boundary layer. That is why the thermal conductivity of the fluid appears in the denominator of the Nusselt number, the dimensionless form of the heat transfer coefficient which in forced convection depends on the degree of turbulence expressible as the Reynolds number.

## 5.9 Concluding remarks

A significant proportion of the vehicles on the highways of the world use diesel engines. A generation ago there was some suspicion as to their reliability and, to reduce the discussion to a mildly materialistic level, concern that a diesel car purchased new would not a few years later attract a good trade-in price. A measure in meeting carbon emission targets is use of biodiesel-diesel blends, or biodiesel alone. Biodiesels have a chapter to themselves later in the book.

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## 6 Products of refinery residue

### 6.1 Heavy fuel oils

#### 6.1.1 Introduction

The terms ‘heavy fuel oil’ and ‘residual fuel oil’ are approximately synonymous. By far the main application is shipping, where in addition to purely residual oils other oils comprising blends of residue with distillate are used. They are both examples of ‘bunker fuel’ and this term might also be applied to distillate oil for marine use. Such distillate will be in the diesel boiling range.

#### 6.1.2 Density and viscosity of residual oils

Examples of density-viscosity pairs for various bunker fuels are obtainable from the web pages [1] of the O.W. Bunker group, one of the world’s major suppliers of fuel oil for marine use. The information in the table below is taken from [1].

Product name	Density/kg m <sup>-3</sup>	Maximum kinematic viscosity at 50°C/cSt
RMA 30	960 (16°API)	30
RMD 80	980 (13°API)	80
RMF 180	991 (11°API)	180
RMH 380	991 (11°API)	380
RMH 700	991 (11°API)	700
RMK 700	1010 (9°API)	700

The number in the product name is the maximum kinematic viscosity at 50°C is cSt. Bunker fuels are always identified in this way. Viscosity is without doubt the most important property of a bunker fuel. This is because a modern fuel supply system on a vessel releases fuel to the combustion chamber at a particular viscosity, called the viscosity set point. The fuel supply system can adjust the viscosity of the influx fuel by temperature regulation only within a limited range, so supply of a fuel very distant from the viscosity set point will cause malfunction.

Residual fuel oils can be blended with each other to a target viscosity. A residual material can be blended with a distillate to a target viscosity. A distillate for this purpose needs to be a heavy one so that it will not cause the flash point of the final blended product to be too low. We should intuitively expect that the simplified treatment given in Chapter 2 of this text for viscosity blending would give reasonable results if applied to viscosity control of bunker fuel.

The viscosities in the table – up to approaching  $10^3$  cSt – would not apply to any single hydrocarbon compounds which are liquids at room temperature. These will rarely have kinematic viscosities exceeding a few tens of cSt. A crude oil has to be seen as a solution of wax (molecular weights 300 to 400) and asphaltenes (molecular weights  $> 1000$ ) in an organic solvent, and such a system cannot be approximated by any ‘model compound’.

### 6.1.3 Solid deposition from heavy fuel oils

It would be difficult to assign a pour point to a heavy residual fuel oil. This is because, as already noted, it is charged with wax and asphaltenes. Molar weights of the waxes in particular are not far distant from those of some of the liquids in which the wax and asphaltenes are dissolved. The distinction between dissolution and suspension, required for cloud point determination, could not reliably be made. Pour point is however important in the use of residual fuel oils. The oils in the table in section 6.2 all have a pour point of  $30^\circ\text{C}$  with the exception of RMA 30 which has a pour point of  $0^\circ\text{C}$  for winter use and  $6^\circ\text{C}$  for summer use. This is the least viscous of the oils in the table and has a pour point well below that of the others. There are pour point depressants for residual fuel oils (e.g., [2]) and these work similarly to CFPP depressants for diesel discussed in the previous chapter, that is, they work by preventing nucleation and not according to the principles of freezing point depression. Alternatively [3] residual oils with different propensities to solid deposition can be blended to a target pour point.

### 6.1.4 Vapour pressures of residual fuel oils

All of the oils in the table in section 6.2 all have a flash point of  $60^\circ\text{C}$ , signifying a vapour pressure at that temperature which is not negligible. As already stated, residual fuel oils vary widely in composition. Factors affecting the composition include the nature of the parent crude (for example, whether predominantly paraffinic or aromatic) and the temperature cut taken in the diesel range. There can also be inclusion of distillate material or even unwanted by-products of cracking and these will obviously raise the vapour pressure. Shell in specifying a purely residual oil [4] give a vapour pressure of less than  $0.1\text{ kPa}$  ( $10^{-3}\text{ bar}$ ). This particular oil has a kinematic viscosity at  $50^\circ\text{C}$  of  $700\text{ sCt}$  and a density of  $1010\text{ kg m}^{-3}$ . The pour point is not given, but otherwise the oil appears to conform closely to the one in the last entry of the table.



The Shell specifications [4] give a vapour density at 15°C of not exceeding 5, where air on the same scale is unity. This provides a means of estimating the composition of the vapour. This follows in the boxed area below.

The molecular weight is  $(5 \times 28.8) \text{ g} = 144 \text{ g}$

Using an empirical formula of  $\text{CH}_2$  this gives a molecular formula of:



Now this corresponds fairly closely to decane  $\text{C}_{10}\text{H}_{22}$ .

The vapour pressure of this compound at 15°C is  $5 \times 10^{-4} \text{ bar}$ .

Consistency with the Shell specification of less than  $10^{-3} \text{ bar}$  is therefore evident if the vapour is approximated to a single model compound.

## 6.2 Motor oil

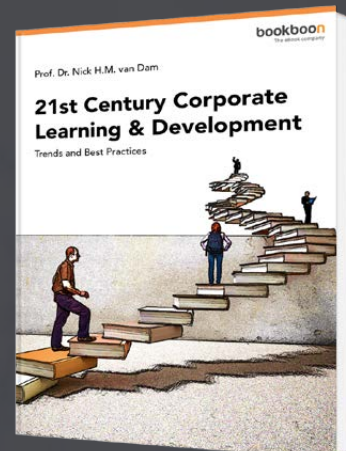
### 6.2.1 Introduction

Lubricant oil for motor vehicles can be made from residual refinery product. The most important property of a lubricant oil is its viscosity. This is explained more fully below.

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### 6.2.2 Viscosities

A single-grade motor oil has a viscosity which varies steeply with temperature, limiting its use to conditions where the temperature changes are such that the viscosity remains in the required range. The temperature dependence of viscosity can be made much weaker by inclusion of a suitable additive. Such additives are polymeric in nature.

An oil so treated is a multigrade oil. A multigrade oil remains close to its 'cold start' viscosity at the highest temperature it experiences in circulation by reason of the action of the polymer additives. Although single-grade oils might in today's world still find application to such devices as lawnmowers, lubricants for automotive use are almost always multigrade. Below is a partial coverage of the categorisation of multigrade oils by the Society of Automotive Engineers (SAE) [5].

<b>Multigrade.</b>	<b>Kinematic viscosity at 40°C/cSt.</b>	<b>Kinematic viscosity at 100°C/cSt.</b>
5W-30	64	11
10W-30	69	11
10W-40	94	14.3
20W-50	166	18.7

In Chapter 2 when discussing the temperature dependence of viscosity for crude oil an expression of the Arrhenius type was used, the coefficient in the exponential being linked to the heat of vaporisation. Sometimes a simpler exponential function:

$$\nu = \nu_0 \exp(-bT)$$

where  $\nu_0$  and  $b$  is a constants is used, and possibly that is more helpful when lubricant oils are being considered. Using the  $\nu$ ,  $T$  data pairs for 5W-30 to solve for  $b$  and  $\nu_0$  gives, for that particular oil:

$$\nu = 5.6 \times 10^5 \exp(-0.029T)$$

In Chapter 2 we considered the Arrhenius approach for a crude oil:

$$\nu(373K) = 2.93 \text{ cSt } \nu(293K) = 23.6 \text{ cSt}$$

Fitting this to the above equation gives:

$$\nu = 4.8 \times 10^4 \exp(-0.026T)$$

In the table below  $\nu_0$  and  $b$  so calculated are given for all of the oils in the above table.

Oil	$\nu_0/\text{cSt}$	$b/\text{K}^{-1}$
5W-30	$5.6 \times 10^5$	0.029
10W-30	$1.1 \times 10^6$	0.031
10W-40	$1.5 \times 10^6$	0.031
20W-50	$1.3 \times 10^7$	0.036
Crude oil (from Chapter 2)	$4.8 \times 10^4$	0.026

Certain conclusions can reasonably be drawn from these figures. The crude oil the viscosities of which are compared with those of the lubricants has a viscosity encompassed by the values for the lubricants. In fitting to the exponential function the coefficient 'b' varies little between the four lubricants and between the lubricant and the crude. The quantity  $\nu_0$  is of course the hypothetical 'kinematic viscosity at absolute zero', and it is an order of magnitude lower for the crude oil than for the least viscous of the lubricants. Across the lubricants it rises by about a factor of 20. The limited evidence then is that the effect of the polymer additive has been to affect the viscosity *per se* rather than its temperature dependence. The crude oil, of course, contains no such additive.

A property related to viscosity is lubricity. This has been discussed for fuels in previous chapters and is also a quantity in the characterisation of motor oils. It was stated in Chapter 5 that, in the US, 520  $\mu\text{m}$  is seen as the maximum acceptable value for a diesel fuel. A reader should recall that this is a scar dimension measured after metal surfaces have been in contact under specified conditions in the presence of the subject hydrocarbon. One's intuition might well be that motor fuels have lubricities lower than this, but not by an order of magnitude. Such a view is supported by 'scar' data for lubricant oils where these are available. For example [6] a proprietary lubricant having a kinematic viscosity at 40°C of 115 cSt (placing it in those terms 10W-40 and 20W-50 the table of viscosities above) has a 'scar' value of 350  $\mu\text{m}$ . This is exactly one third below the value for diesel quoted above.

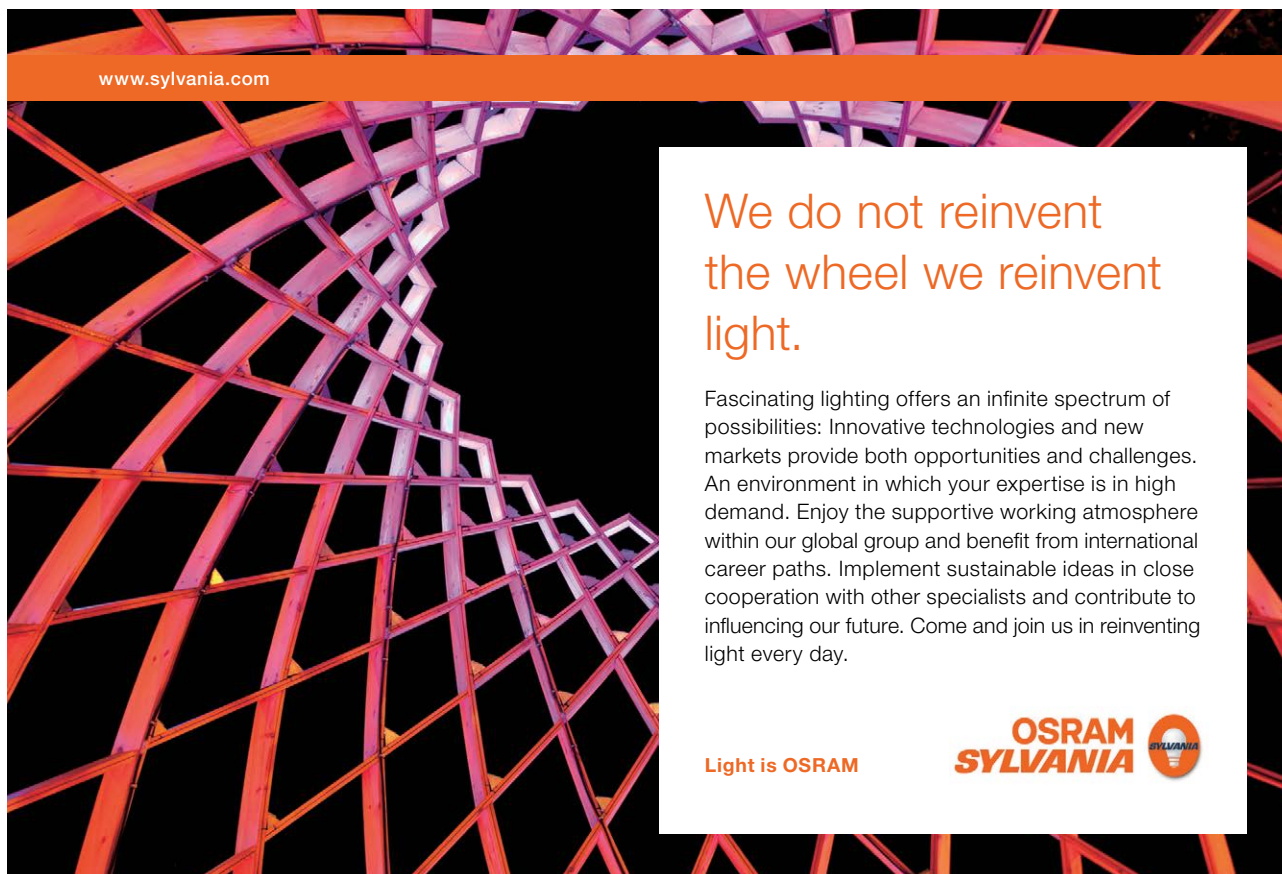
The oil specifications of which [6] are given above is in fact a 'semi-synthetic oil', that is, it is composed partly of petroleum based material and partly of synthetic oil. Synthetic motor oils are made from alpha olefins of  $\text{C}_{20+}$  and other organic compounds including diesters, so their only relevance in a chapter concerned with refinery residue is that they are blended with mineral oil as noted. Alpha olefins are made from petroleum distillate by cracking, therefore so-called synthetic oils are actually extensively processed petroleum stock. The Society of Automotive Engineers (SAE) terminology for oils [5] applies to synthetics and to semi-synthetics as well as to purely mineral oils.

### 6.2.3 Particle deposition

Pour points of lubricating oils are very low, almost always below  $-20^{\circ}\text{C}$ . Particle deposition from lubricating oil is not from any process akin to 'freezing' but from breakdown of the oil over a sustained period of usage resulting in carbon particle formation. This is of course an example of pyrolysis, which is a chemical phenomenon. The propensity of a particular lubricating oil to carbon deposition is determined as the carbon residue, which is the percentage by weight of solid remaining after the oil has been totally evaporated. Pyrolysis will occur in a small degree concurrently with evaporation in such a test. Carbon residues so measured of 1 to 2% are expected for lubricant motor oils.

### 6.2.4 Vapour pressure

This quantity is not a performance criterion in lubricant motor oil performance. That is not to say that it is of no interest: information on the variation in vapour pressure of such an oil across the temperature range it experiences is required. At  $300^{\circ}\text{C}$  it can be as high as 0.05 bar. Values (in mm Hg) for a lubricant oil of kinematic viscosity 82 cSt at  $40^{\circ}\text{C}$  are given in [7] across the temperature range 40 to  $290^{\circ}\text{C}$ . At  $40^{\circ}\text{C}$  the value is  $2.5 \times 10^{-7}$  mm Hg (0.25 torr), and this rises to 7.4 mm Hg at  $290^{\circ}\text{C}$ .




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In Chapter 4 of this text an equation of the Clausius-Clapeyron form was applied to a kerosene with the express qualification application was on an empirical basis as the Clausius-Clapeyron equation itself applies only to a pure chemical substance. In the boxed area below the vapour pressure versus temperature data for the lubricating oil under discussion are examined in this way.

The integrated form of the equation is:

$$\ln(P_2/P_1) = -(\Delta H_{\text{vap}}/R)[(1/T_2) - (1/T_1)]$$

where  $-\Delta H_{\text{vap}}$  is the heat of vaporisation. The information above provides two P,T data pairs viz.:

$$T_1 = 313 \text{ K}, P_1 = 2.5 \times 10^{-7} \text{ mm Hg}$$

$$T_2 = 563 \text{ K}, P_2 = 7.4 \text{ mm Hg}$$

Inserting these into the equation gives:

$$\Delta H_{\text{vap}} = 101 \text{ kJ mol}^{-1}$$

A rough calculation performed with reservations can sometimes score a bull's-eye, and this is true of the above. The value of the heat of vaporisation corresponds exactly [8] to that for eicosane –  $\text{C}_{20}\text{H}_{42}$  – a straight chain alkane which has itself found application as a lubricant. There is even a blog on eicosane as a lubricant [9], in which it has been suggested that its viscosity is on the low side. This point is examined below.

The dynamic viscosity of eicosane at 50°C [10] is:

$$0.00316 \text{ kg m}^{-1}\text{s}^{-1}$$

Using a density [8] of  $\approx 750 \text{ kg m}^{-3}$ :

$$\nu = (0.00316/750) \text{ m}^2 \text{ s}^{-1} = 4.2 \times 10^{-6} \text{ m}^2\text{s}^{-1} = 4 \text{ cSt approx.}$$

which is a low value but not so much so as to preclude lubricant use. A more conventional engine lubricant will have a lower viscosity than this in the hottest places where the lubricant is circulated.

### 6.2.5 Electrical conductivity

The most interesting side to electrical conductivities of lubricating oils is the huge difference between those which are simply residual petroleum stock and those which contains esters which, as noted previously in this chapter, some lubricating oils do. This effect is shown strikingly in work reported by Harvey et al. [11] in which three lubricants from the Shell Vitrea range [12] are compared with Exxon Turbo 2380<sup>7</sup> oil. The latter contains esters. The Shell oils studied in [11] have kinematic viscosities at 21°C in the range 60 to 600 cSt, and the two examples of the Exxon Turbo 2380 oil examined have values of 35 and 40 cSt at the same temperature. Electrical conductivities of the Shell oils are in the range 0.4 to 2.1 pS m<sup>-1</sup>, whereas the Turbo 2380 samples give values of 1370 and 1410 pS m<sup>-1</sup>. The effect of the esters has therefore been to raise the electrical conductivity by about three orders of magnitude, and this is due to the polar nature of the esters which have been incorporated into it. Returning to the discussion in section 1.5, water at 20°C has a value of 5.4 μS m<sup>-1</sup> or  $5.4 \times 10^6$  pS m<sup>-1</sup>. Notwithstanding the conductivity enhancement, the ester-containing oil is many orders of magnitude short of being an electrolyte.

## 6.3 Petroleum jelly

### 6.3.1 Introduction

This has an important place in the history of the oil industry, having been discovered in nineteenth century during oil production at Titusville Pa, scene of the celebrated Drake Well [13]. Although there has been some debate of the matter, the term petrolatum is usually taken to be a synonym. One also encounters the term 'soft paraffin'.

### 6.3.2 Physical properties [14]

Constituents of petroleum jelly are C<sub>25+</sub>. Being not a single organic compound but containing many such compounds, petroleum jelly does not have a melting point but a melting range. The lower limit of this range is likely to be between 40 and 60°C. By 100°C there will always be significant amounts of liquid, and this will have a kinematic viscosity in the range 5 to 25 cSt. The acoustic impedance impedance of petroleum jelly is 3 Mrayl [15].

The petroleum jelly industry is by now far advanced and any reader of this text will have had experience of Vaseline or a similar product. A heavier product still is paraffin wax, which contains compounds up to C<sub>40</sub> or higher. Its discovery in the nineteenth century, when the use of candles for illumination was still common, provided an alternative to tallow for the manufacture of candles. Like petroleum jelly, paraffin wax can be produced in food grade. The familiar red wrapping around a piece of Edam cheese is an example of food grade paraffin wax.

## 6.4 Concluding remarks

This section provides an opportunity for the discussion of ‘value adding’. Residual material not destined for fuel oil use has often been used as cheap gasification feedstock or as the basis of the production of carburetted water gas from blue water gas. This will continue in some parts of the world especially if, as is predicted, there is a swing back to gasification of coal. No value adding to the residual material is needed for these applications. However, viscosity adjustment of such materials and attention to other properties including pour point transforms them into lubricants, materials of precise specification for which there is a colossal market. Such is the potential of value adding.

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# 7 Coal tars

## 7.1 Introduction

### 7.1.1 General background

When a coal decomposes ('carbonises') there are three classes of product: solid, liquid and gaseous. The solid we refer to as coke or as char. The gases include hydrogen and carbon monoxide. The liquid product is known as coal tar. Carbonisation of coal on the industrial scale began in the late eighteenth century. At that time charcoal was being used to make iron from iron ore, in response to the huge demand for iron brought about by industrialisation. Much of the south of England had until that time been heavily forested and very conspicuous gaps were created through removal of the trees for charcoal production. Over time coke replaced charcoal as a metallurgical reductant. Steel manufacturers naturally tended to establish themselves close to coalfields. The conurbation of Sheffield, Rotherham and Barnsley is probably the best example of this in Britain. The best example in the US is Pittsburgh.



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When coke is made, gas and tar are always by-products. The gas became used in lighting, there being gas lamps in London by the 1820s. Later, gas was reticulated to homes; by the end of the nineteenth century many homes in the UK had gas 'laid on', still largely for illumination as an alternative to candles. The tar product of coal carbonisation became feedstock for the very earliest organic chemistry industry. Germany was the leading nation in this respect. Coal tar as a source of chemicals continued until the 1920s at which stage it was replaced by cracked hydrocarbon products. The author has made elsewhere [1] the comment that the development of cracking technologies and cessation of reliance on coal tar revolutionised the organic chemistry industry. From then on the US, especially in the Gulf Coast states, became the leader though not to the exclusion of Germany. Many companies including IG Farben, BASF and Hoechst were active in this respect in both countries.

### 7.1.2 Comments on coal tars

The term tar generally means the liquid decomposition product of any organic substance, for example wood or peat. It is with coal tars specifically that this chapter is concerned. Coals vary very widely in nature. The most important determinant in the 'nature' of a coal is its degree of maturity along the coalification series. The least mature coals are lignites a.k.a. brown coals. Scenes of production of these include N. Dakota USA and the Latrobe Valley in south eastern Australia. More mature coals include bituminous coals, and it is from such coals that coke for use as metallurgical is made. The more mature the coal, the smaller the yield of decomposition products including tars. In general, the fate of coal tars is simply that they are burnt along with the rest of the coal. When coal is burnt decomposition and combustion are concurrent, so tars and gases having been released simply burn alongside the residual solid. It is when coal is used for purposes other than direct combustion, that is when it is carbonised or gasified, that the tars are of importance. In discussions of liquid products of coal decomposition, a distinction is sometimes made between tars and oils, on the basis of solubility in particular solvents. The author's view is that this is pointless if not confusing and is better avoided.

Because coals vary so widely, so do coal tars. Even the tar from a particular coal will vary in composition depending on the ceiling temperature of carbonisation, the coal particle size and the heating rate. Carbonisation of coal is a 19<sup>th</sup> Century technology by no means obsolete in the 21<sup>st</sup>. The question of comparability of unprocessed coal tars with heavier petroleum fractions has been the subject of much debate for a century or more. The term 'coal tar fuels' (CTF) means fuel oil comprising not petroleum residue as with such fuels discussed in the previous chapter, but coal-derived liquid. These were once widely used in applications including steam raising, interchangeability with petroleum residual fuel oil being aimed for. The property most difficult to match is the cloud point, which is higher for CTF. This necessitates flushing out with a solvent such as kerosene when petroleum fuel oil is used in plant previously used with CTF. The debate on the feasibility of gasoline and diesel substitutes from the distillation of coal tar has been going on at least since 1923 [2].

## 7.2 Distillate products from coal tars

The processing of tars remains an important industry in countries including the US (e.g. [3]) and Japan (e.g. [4])<sup>8</sup>. Tar distillate is considerably less of a 'rag bag' of organic compounds than petroleum distillates are.

At temperatures up to about 100°C, the distillation product of coal tar is benzole, a.k.a. benzol. This consists of benzene, toluene and xylenes (BTX) in whatever proportions. The kinematic viscosities of these compounds singly are all around 1 cSt, the smallest value being that for *m*-Xylene which is 0.68 cSt at 25°C [5]. Separation of BTX from coal tar into its constituent compounds in high purity by further distillation is straightforward. The heavier distillate, when cooled to below its cloud point, yields crystals of useful compounds including phenol, *o*-cresol

## 7.3 Coal tar pitch

### 7.3.1 Introduction

The residue of distillation of coal tar is pitch. It can be the primary product in tar processing in which case the conditions of distillation including the maximum temperature can be controlled to give a pitch of desired properties. Pitches vary in nature from semi-solid at room temperature to hard and brittle. Most start to melt at temperatures in the region of 100°C and their rheology is of some importance.

### 7.3.2 Viscosities

Clearly solid and liquid will often be in co-existence and the viscosity is a factor in any application. This can be determined from the classical [6] penetrometer test. In the test the penetration of a needle into a 100 g sample of the subject pitch at 25°C is determined, contact with the needle have been of five seconds' duration. From the results the dynamic viscosity can be calculated according to:

$$\mu(\text{poise}) = 5.9 \times 10^9 / (\text{penetration depth})^{1.93}$$

where the penetration depth is in units decimillimetres:

$$1 \text{ decimillimetre} = 10^{-4} \text{ m.}$$

The penetration depth across a range of pitch samples was found in [6] to range from 1.0 to 195 decimillimetres. These figures are examined in the boxed area below.

Considering first of all the penetration depth value at the high end of the range:

$$\mu = 5.9 \times 10^9 / (195)^{1.93} \text{ poise} = 2.2 \times 10^5 \text{ poise}$$

Now 1 poise = 1 g cm<sup>-1</sup> s<sup>-1</sup> = 0.1 kg m<sup>-1</sup> s<sup>-1</sup>, hence  $\mu$

$$= 2.2 \times 10^4 \text{ kg m}^{-1} \text{ s}^{-1}.$$

Now the density of a coal pitch is roughly the same as that of water, so the kinematic viscosity can be estimated as:

$$\nu = 2.2 \times 10^4 \text{ kg m}^{-1} \text{ s}^{-1} / 1000 \text{ kg m}^{-3} = 22 \text{ m}^2 \text{ s}^{-1} \text{ or to one significant figure } 2 \times 10^7 \text{ cSt.}$$

and this exceeds any value of a kinematic viscosity previously given in this book. For the penetration depth value of 1 decimillimetre the kinematic viscosity is  $6 \times 10^{11}$  cSt.

That values of the viscosity of coal tar pitch are exceedingly high is confirmed in much more recent work than that in [6]. Li and Li [7] present results for dynamic viscosities of pitch, including one of 16000 kg m<sup>-1</sup> s<sup>-1</sup> at 200°C. Using the same density as previously, this gives for the kinematic viscosity:

$$\nu = 16000 \text{ kg m}^{-1} \text{ s}^{-1} / 1000 \text{ kg m}^{-3} = 16 \text{ m}^2 \text{ s}^{-1} \equiv 1.6 \times 10^7 \text{ cSt}$$

This corresponds quite closely to the value at a much lower temperature for the pitch in [6] having given a penetration depth of 195 decimillimetre.

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Viscosities of fluids can be determined from the rate of exit of a sample fluid under gravity through an orifice. Time of the order of *decades* is required for a value of the viscosity of a coal tar pitch to be obtained in this way. At the University of Queensland in 1930 such an experiment was commenced [8], and it is still in progress! The first drop exited in December 1938 and seven further drops between then and November 2000. Fitting of the results so far has given a value for the dynamic viscosity:

$$\begin{aligned}\mu &= 2 \times 10^8 \text{ kg m}^{-1}\text{K}^{-1} \\ \Downarrow \\ \nu &= 2 \times 10^{11} \text{ cSt}\end{aligned}$$

which is of the same order of magnitude as one of the values in [6].

### 7.3.3 Vapour pressure

When it was first proposed to construct ‘dust-free roads’ by using tar instead of the inorganic materials used previously there was concern that the vapour from the tar would harm vegetation. Such fears were later shown to be without foundation provided that tars selected for such use did not in pre-use testing start to boil below 140°C [9], and there was the obvious health advantage that persons were no longer inhaling fine dust from the roads or experiencing eye irritation from it.

Reference [10] gives a generic value for the vapour pressure of coal tar pitch of < 0.01 kPa. In the boxed area below is an estimate of what the odour threshold of the materials in the pitch vapour would have to be if the vapour were to be detectable by the sense of smell.

Considering air at room temperature and 1 bar pressure:

$$P_a V = n_a RT$$

where subscript ‘a’ denotes air. For the vapour, using subscript ‘v’:

$$P_v V = n_v RT$$

Combining the two:  $n_v/n_a = P_v/P_a = (0.01/100) = 10^{-4}$  or 100 p.p.m.

Many pure organic substances have odour thresholds much lower than this; that for benzene is 12 p.p.m. One would therefore expect that a coal tar pitch having the vapour pressure in the inequality in the previous paragraph would be detectable by the olfactory sense, and that inhalation in an unventilated area would be harmful. The vapour pressure for newly manufactured pitch will of course drop as the pitch loses its lightest constituents on standing.

## 7.4 Fine chemicals from coal tar

When, as described in a previous section, coke became the principal metallurgical reductant for iron production the coke ovens used were the 'beehive' type. These are now very few and far between, if not totally non-existent, having been replaced by the 'by-product' type. In a by-product coke oven condensibles are collected, and these become a source of organic compounds.

Such compounds include BTX and heavier aromatics, which have already been discussed. The condensibles can be processed into 'fine chemicals' and this practice was becoming prevalent in the US by the mid 20<sup>th</sup> century [11]. Six of the more common of the liquid fine chemicals obtainable from feedstock originating at coke ovens are discussed in the table below. Comments follow the table.



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Chemical.	Selected physical properties.
Pyridine, $C_5H_5N$	Normal boiling point: 115°C Liquid density: 982 kg m <sup>-3</sup> Dielectric constant [12]: 12.5 Refractive index [13]: 1.51 Kinematic viscosity (20°C): 1 cSt Acoustic impedance: 1.39 Mrayl
Benzaldehyde, $C_6H_5CHO$	Normal boiling point: 178°C Liquid density: 1042 kg m <sup>-3</sup> Dielectric constant [12]: 17.8 Refractive index [14]: 1.54 Kinematic viscosity (25°C): 1.3 cSt
Benzyl chloride, $C_6H_5CH_2Cl$	Normal boiling point: 179°C Liquid density: 1103 kg m <sup>-3</sup> Dielectric constant [12]: 6.4 Refractive index [15]: 1.54 Kinematic viscosity (30°C): 1.0 cSt
Benzoyl chloride, $C_6H_5COCl$	Normal boiling point: 197°C Liquid density: 1211 kg m <sup>-3</sup> Dielectric constant [12]: 23 Refractive index [16]: 1.49 Kinematic viscosity (30°C): 0.5 cSt
Benzyl alcohol $C_6H_5CH_2OH$	Normal boiling point: 205°C Liquid density: 1044 kg m <sup>-3</sup> Dielectric constant: 13 Refractive index: 1.54 Kinematic viscosity (25°C) [17]: 7 cSt
2,6 Xylenol $C_8H_{10}O$	Normal boiling point: 203°C Liquid density: 1010 kg m <sup>-3</sup> Refractive index [18]: 1.54 Kinematic viscosity (80°C) [19]: 1 cSt

In addition to pyridine itself methylated pyridines – picolines – are manufactured from coal tar. Benzaldehyde can be made by direct partial oxidation or, perhaps more commonly, from chlorination of toluene and hydrolysis of the product. Benzoic acid, a solid at room temperature, is also made in this way. Primary products of the chlorination include benzyl chloride and benzoyl chloride. Of the six isomers of xylene (dimethyl phenol), 2,6 xylene is commercially the most important being used in the manufacture of resins for applications including printed circuit boards.

Most of the liquids in the table above have kinematic viscosities of the same order of magnitude as that for water. The simple correlation linking refractive index with dielectric constant which, in previous parts of the book, has been shown to apply to many hydrocarbons, does not apply to any of the liquids in the table all of which contain an element other than carbon and hydrogen. Equivalently, the presence of oxygen, nitrogen or chlorine raises the dielectric constant. The contrast between the values for benzene (2.3) and pyridine (12.5) is very convincing proof of this.



## 7.5 Concluding remarks

Uncertainties in world oil supply affects not only fuel availability but also the petrochemical industry. If as some experts predict there is a swing back to coal or to coal gasification, matters can be engineered so that by-product tars for petrochemical manufacture become available. Indeed, it has long been standard practice in parts of the world including Australia for BTX produced at coke ovens to be passed along to petrochemicals manufacturers. Additionally coal provides a route to chemicals via synthesis gas as noted in a previous chapter. These are issues not to be lost sight of in the very challenging circumstances of hydrocarbon supply and demand in these times.

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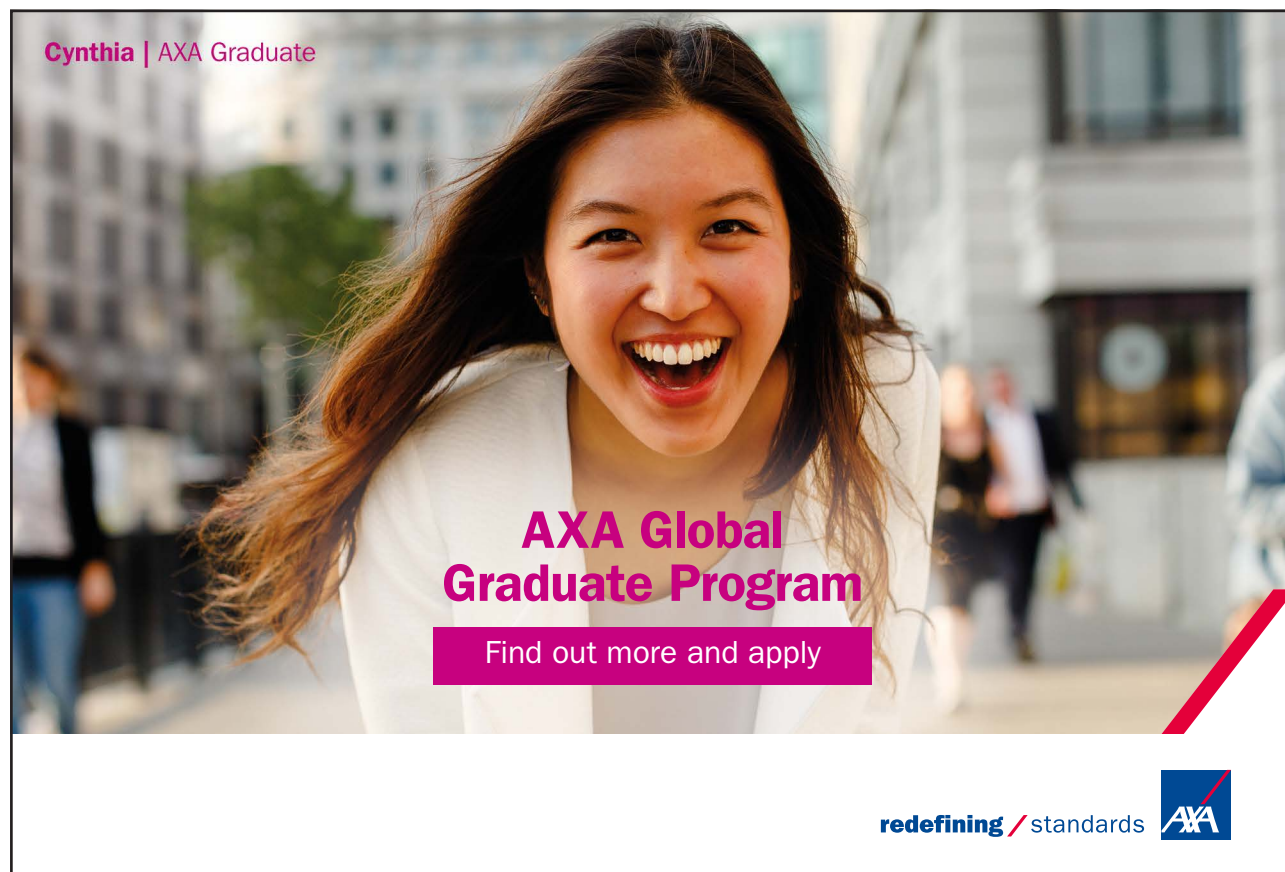
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# 8 Alcohol-containing fuels

## 8.1 Introduction

The two alcohols of most importance in fuel technology are the two most structurally simple: methanol and ethanol. Both are good fuels for spark ignition engines, having high octane ratings. Ethanol is made from fermentation processes, either from sugar directly or from sugar made by breaking down the starch in corn or sorghum. The 'selling point' of ethanol is its carbon neutrality by reason of its plant origin. With methanol matters are not so straightforward [1]. Methanol made from the decomposition of biomass, or from synthesis gas made from biomass, is carbon neutral. Methanol made from natural gas or from coal via synthesis gas is not carbon neutral. The carbon neutrality of methanol is therefore ambiguous, a point made previously in Chapter 3.

This chapter will review methanol and ethanol and then move on to gasoline-alcohol blends. These are being used on a massive scale at the present time.



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## 8.2 Methanol

As methanol is a pure chemical compound its physical properties are precise. For example, there is no need to talk of the Reid Vapour Pressure (RVP) of methanol as there is no dependence of the vapour pressure on the space into which the vapour expands as there is with gasoline. Selected physical properties of methanol liquid are given in the table below having been taken from [2] unless otherwise indicated.

Property	Value
Normal boiling point	65°C
Density (10°C)	801 kg m <sup>-3</sup>
Vapour pressure at 38°C	0.35 bar (35 kPa)
Thermal conductivity (10°C)	0.204 W m <sup>-1</sup> K <sup>-1</sup>
Kinematic viscosity (10°C)	0.9 cSt
Kinematic viscosity (50°C)	0.5 cSt
Refractive index (25°C)	1.33 [3]
Dielectric constant	33
Acoustic impedance	0.87 Mrayl [4]
Capacitance	94 pF [5]
Coefficient of expansion	0.0012 °C <sup>-1</sup>

We saw in Chapter 1 that:

$$v(T_2)/v(T_1) = \exp(\Delta E/RT_2)/\exp(\Delta E/RT_1)$$

and that  $\Delta E$  is 30 to 40% of the heat of vaporisation. Applying the values of the kinematic viscosity for methanol at two temperatures from the table above:

$$\begin{aligned} \ln[v(T_2)/v(T_1)] &= \Delta E/R\{(1/T_2) - (1/T_1)\} \\ &\Downarrow \\ \Delta E &= 11 \text{ kJ mol}^{-1} \end{aligned}$$

The heat of vaporisation in the temperature range of interest is actually 34 kJ mol<sup>-1</sup>, and  $\Delta E$  is 32% of this so there is good conformity. There is scope for enhancing the precision of the calculation by avoiding the implicit assumption that the density variation over the temperature range is negligible (that is, by using the ratio of dynamic viscosities instead of the ratio of kinematic viscosities).

### 8.3 Ethanol

Property	Value
Normal boiling point	78.5°C
Density (25°C)	789 kg m <sup>-3</sup>
Vapour pressure at 38°C	0.15 bar (15 kPa)
Thermal conductivity (20°C)	0.169 W m <sup>-1</sup> K <sup>-1</sup>
Kinematic viscosity (10°C)	1.9 cSt
Kinematic viscosity (50°C)	0.9 cSt
Refractive index (18°C)	1.36
Dielectric constant	24
Acoustic impedance	0.95 Mrayl
Capacitance	33 pF
Coefficient of expansion	0.0011°C <sup>-1</sup>

If the viscosity calculation performed above for methanol is repeated for ethanol the result is:

$$\Delta E = 14 \text{ kJ mol}^{-1}$$

which is 33% of the heat of vaporisation which of 43 kJ mol<sup>-1</sup>.

### 8.4 Comparisons of methanol and ethanol with gasolines

In the tables of properties of methanol and ethanol the vapour pressure at 38°C has been given as this is the temperature at which RVP measurements on gasolines are performed. Returning to the information in section 3.6.1 of this book, the value for methanol is lower than any value for a gasoline given there, and the value for ethanol much lower. The methanol value might conceivably correspond to the ‘summer RVP’ for a gasoline, but the ethanol value would be most unlikely to. This can be roughly correlated with boiling points. Gasoline boiling ranges do of course vary significantly, but 60°C is often given as the initial boiling point of a typical gasoline. The boiling point of methanol is close to this, whereas that of ethanol is well above it.

In section 3.2.1 the range 0.5 to 0.75 cSt at 40°C was given for the kinematic viscosities of gasolines, and those of either alcohol are comparable to this. The acoustic impedance is also about the same for the alcohols as for gasolines. The refractive indices of the alcohols are close to each other, and that of methanol is almost indistinguishable from that of water. The alcohol values are somewhat lower than those for gasolines given in section 3.5. Thermal conductivities are significantly higher (by almost a factor of two in the case of methanol) for the alcohols than for gasoline. The dielectric constants are much higher for the alcohols. Those for the alcohols are a third to a half the value for water. The coefficients of expansion of the alcohols are only very slightly higher than the generic value of 0.00095 K<sup>-1</sup> for gasolines given in section 3.3.

## 8.5 Methanol-gasoline blends

These are less common than ethanol-gasoline blends but do find application in countries including China where the composition range available is M15 to M80 (15% methanol and 80% methanol respectively, balance gasoline in each case). Vapour pressures of gasoline-methanol blends were studied by Pumphrey et al. [6], whose experimental work spanned the whole composition range from a pure sample of a particular gasoline to pure methanol. Between about 20% methanol and 60% the vapour pressure of the blend is about 20 kPa higher than that of the gasoline only. There is then a steep drop, to 20 kPa below the vapour pressure of the gasoline for pure methanol, consistently with the statement above that methanol alone would at most attain the summer RVP of a gasoline.

Viscosities of methanol-gasoline blends have been examined in a recent piece of work by Lee [7]. Blends of a gasoline of API index 53° and methanol were examined at 20°C. The gasoline alone had a kinematic viscosity of 0.51 cSt. A blend comprising 15% of this gasoline balance methanol, that is an example of an M85 fuel, had a kinematic viscosity of 0.73 cSt. In section 3.2.1 it was stated that gasolines have kinematic viscosities in the range 0.4 to 1 cSt, and the example given for an M85 fuel is comfortably within this range.

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## 8.6 Ethanol-gasoline blends

### 8.6.1 Introduction

These are of major importance as fuels for spark-ignition engines. One often encounters ‘E85’ and so on, signifying a particular percentage of alcohol, balance gasoline. Ethanol-gasoline blends across the composition range will be discussed in this section.

### 8.6.2 Vapour pressures

The specification EXY, where for E85 *X* denotes 8 and *Y* denotes 5, is a nominal one, with the numeral representing only approximately the percentage of alcohol. We have seen that the vapour pressure of a gasoline is important and that the RVP might require seasonal adjustment. The vapour pressure has to be adjusted by means of the ratio of gasoline to alcohol. This is the basis of ASTM classifications of such fuels, some examples of which taken from [8] are given below.

Volatility class	1	2	3
% ethanol	79	74	70
Vapour pressure at 38°C/kPa	38–59	48–65	66–83

Note that the vapour pressures are all in significant excess of that of ethanol alone at 38°C, indicating that the gasoline is raising the vapour pressure. Note the consistency between the vapour pressures in the table above and those given in section 3.6.1 for a range of gasolines.

When E85 fuel is manufactured, it is to target octane rating and target vapour pressure. In order fully to specify such a fuel both the nominal proportion of ethanol and the volatility class need to be known. This can be more fully understood by reference to a study in 2006 [9] of samples of E85 obtained from outlets in ten states of the US<sup>9</sup>. It is reported in [9] that the E85 samples of volatility class 1 had a median alcohol content of 81.6% and a median vapour pressure of 41.7 kPa.

The ethanol content is just below the nominal one of 85% and just above the value which corresponds to the vapour pressure according to the ASTM classification of volatilities in the above table.

For E85 of volatility class 2, [9] gives the median ethanol content as 77.1%. For ‘volatility class 3/2’ (not defined in the table above) the median ethanol content is 74.6%. Consistently with these figures, reference [9] states that E85 has an ethanol content in the range 70 to 85%. Of course, the figures from [9], though having their basis in an authoritative study, should not be seen as hard numbers for the variation in composition of E85 with vapour pressure but as suitably chosen examples of how the composition of E85 can vary.

The table below gives vapour pressure information for a range of ethanol-gasoline blends. Comments follow the table.

EXY as defined above. Reference.	Details.
E5 [10]	RVP in the range 70 to 82 kPa depending on the composition of the gasoline. Corresponding limits for the gasolines in the absence of ethanol 70 and 77 kPa
E10 [11]	E10 made by 'splash blending', that is, by the distributor and not at source. E10 so produced has an RVP of 100 kPa, very close to that of the gasoline alone.
E10 [12]	A statement that the ethanol content can raise the RVP 'disproportionately'.
E10 [13]	A BP document recording trials with E10 in Queensland Australia. Higher vapour pressure of E10 noted, consistently with the comment in the previous row.
E10 [14]	RVP of 86 kPa. RVP of the gasoline alone 62 kPa.
E15 [15]	RVP of 68 kPa RVP of the gasoline alone 62 kPa.
E15 [16]	RVP of 25 kPa. The 'gasoline' actually a blend of simple organics including hexane, toluene and <i>p</i> -xylene in known proportions.
E20 [17]	RVP of 66.2 kPa.
E40 [17]	RVP of 63.0 kPa
E50 (summer) [18]	RVP of 52.5 kPa
E50 (winter) [18]	RVP of 62.5 kPa
E60 [17]	RVP of 57.4 kPa
E60 (summer) [18]	RVP of 52.0 kPa
E75 (summer) [18]	RVP of 44 kPa
E85 (summer) [18]	RVP of 32 kPa
E85 (winter) [18]	RVP of 37 kPa
E85 [19]	RVP up to 83 kPa
E88 (summer) [18]	RVP of 29.4 kPa
E92 (summer) [18]	RVP of 24.9 kPa

To the information given in the first row of the table, taken from reference [10], can be added the observation also recorded in [10] that the higher the proportion of unsaturated hydrocarbons in the gasoline the smaller the effect of the 5% ethanol on the RVP. The difference is 1 kPa if the proportion of unsaturated hydrocarbons is 80%, rising to 5 kPa for 20% unsaturated hydrocarbons.



Clearly with blends low in ethanol such as E5 and E10 the chief determinant in the vapour pressure will be the RVP of the gasoline. The disproportionate effect of a small amount of ethanol on the vapour pressure is presumably due to the replacement of a miscellany of organic compounds with boiling points up to 200°C or higher with a single one of boiling point 78.5°C. The effect will be most marked when the gasoline with which the alcohol is being blended has a low RVP because it is rich in the higher boilers. The figures in the fifth and sixth rows of the above table reveal this effect. The figure in the sixth row is for a simulated gasoline as described, this alone having an RVP of 17 kPa. In the work described in reference [17] the gasoline alone has a RVP value of 57.6 kPa, which ascends by about 20% in going to E30 and E40, returning almost exactly to the 'E0' value for E60.

All of the ethanol-gasoline blends in reference [18] have an octane number of 95. The 'E0 blend', that is gasoline alone, has a summer value of 58.0 kPa and a winter value of 87.5 kPa. Whereas low amounts of ethanol in a blend predominantly gasoline raise the RVP more than proportionately as noted, small amounts of gasoline in a blend predominantly ethanol appear, from the results in [18], to do likewise. A rise of over 50% in RVP occurs between E100 and E92.



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### 8.6.3 Further details of E85

E85 is probably the most widely used of the ethanol-gasoline blends at the present time. Conclusion of this section with a discussion of some of its properties other than vapour pressure is therefore appropriate.

We saw in Chapter 3 that a value of  $25 \text{ pS m}^{-1}$  would be typical of the electrical conductivity of gasoline. Ethanol alone for fuel use in Brazil<sup>10</sup> has an electrical conductivity specification [20] of  $500 \text{ }\mu\text{S m}^{-1}$ , a factor of 20 million higher than the value given in the previous sentence for gasoline. The conductivity of E85 is of the order of  $\mu\text{S m}^{-1}$  the precise value depending on the amount of gasoline since, as we have seen, this can be as low as 70%. The high electrical conductivity of E85 does of course make for safety in handling, electrical charge generated by movement being readily conducted away before it can form an ignition source.

Reference [7] gives a value for the dynamic viscosity of a particular example of E85 of 1.016 cP which, using a density for ethanol only, converts to a kinematic viscosity of 1.3 cSt. This is almost twice the value given for an M85 fuel earlier in this chapter and at the high range of value for gasolines. This is not an important factor: it was argued in Section 3.2.3 that variations in the kinematic viscosity of the fuel, be it gasoline or a blend, do not measurably affect fuel pump performance.

Lubricities of gasolines or of alcohol-gasoline blends have not previously been discussed. Here it will simply be stated that E85, in common with other ethanol-gasoline blends, has a poorer lubricity than gasoline alone and that this is a factor in the manufacture of flexi-fuel vehicles (FFV).

## 8.7 Concluding remarks

Ethanol-gasoline blends are of ever increasing importance for two reasons: their ability to stretch gasoline quantities and, more importantly, their ability to reduce fossil-fuel derived carbon dioxide emissions. The second of these is perhaps the greatest challenge facing the world at this time.

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## 9 Biodiesel fuels

### 9.1 Introduction

These are of increasing importance because of their carbon neutrality. Examples include soybean oil, sunflower oil, palm oil and rapeseed oil (a.k.a canola oil). Spent cooking oil, an example of which is 'yellow grease', has also found application to fuel use. Some such oils can be used as fuels for compression ignition engines unprocessed; this is often true of soybean oil. More commonly treatment by esterification will be required to give a satisfactory cetane number. Physical properties of biodiesel fuels will be discussed in this chapter, starting with viscosity.

### 9.2 Viscosity

The table below gives values from the recent literature of kinematic viscosities of biodiesel fuels.

Nature of the biodiesel	Kinematic viscosity/cSt	Reference
Esterified soybean oil	4.2 @ 40°C	[1]
Esterified canola oil	4.5 @ 40°C	[1]
Esterified soybean oil	3.6 @ 40°C 1.4 @ 100°C	[2]
Esterified yellow grease	4.3 @ 40°C 1.5 @ 100°C	[2]
Esterified coconut oil	2.4 @ 40°C 0.9 @ 100°C	[2]
Esterified palm oil	4.2 @ 40°C 1.4 @ 100°C	[2]

Model compounds for biodiesels include methyl oleate, structural formula  $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOCH}_3$ . Its cetane number [3] is 59, higher than that of a typical diesel, biodiesel or diesel-biodiesel blend. Its kinematic viscosity at 40°C is 4.5 cSt [4]. As well as being a model compound, methyl oleate is an actual ingredient of many biodiesels as is methyl linoleate which features in the section 9.4. Its kinematic viscosity at 40°C is 3.65 cSt.

### 9.3 Thermal conductivity

Castro et al. [5] give thermal conductivity values for the following biodiesels (amongst others).

Nature of the biodiesel	Thermal conductivity/W m <sup>-1</sup> K <sup>-1</sup>
Sunflower oil esterified with ethanol	0.21
Soybean oil esterified with ethanol	0.18
Soybean oil esterified with methanol	0.18

#### 9.4 Refractive index

In the esterification of oil to make biodiesel glycerol initially present in the unprocessed plant oil, being denser than the product ester, separates and is taken off at the bottom of the reactor. In [6] refractive indices of soybean derived material of various proportions of glycerol were reported. The untreated oil had a glycerol content of about 10%, and the totally esterified oil a glycerol content of zero. The refractive index of the latter was 1.457 and that of the latter 1.473 and the rise in refractive index with glycerol content was linear. The refractive index of methyl oleate is 1.454, very close to the value for the totally esterified oil in the work under discussion.

In [7] biodiesels containing different proportions of methyl oleate and methyl linoleate were investigated for refractive index. The molecular formula of the former is  $C_{19}H_{36}O_2$  and that of the latter  $C_{19}H_{34}O_2$ , there being one double bond in the carbon structure of methyl oleate and two in the carbon structure of methyl linoleate. The biodiesels with a preponderance of the linoleate had lower refractive indices than those with a preponderance of the oleate, indicating that unsaturation raises the refractive index.

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## 9.5 Particle deposition

### 9.5.1 Single compounds

The esters methyl stearate, methyl oleate, methyl linoleate and methyl linolenate are  $C_{18}$  compounds and have respectively no double bonds and one, two and three double bonds<sup>11</sup>. They occur in biodiesels and are used as model compounds in studying the properties of biodiesels. We therefore expect intuitively that their freezing points would give an indication of the range of cloud points of biodiesels.

Accordingly the freezing points of three of these compounds are given in the table below. A value for methyl linolenate has evaded the author; it is reported as 'not available' on safety data sheets and the like. The value for methyl palmitate, which is  $C_{16}$ , is in the final row of the table.

Compound	Freezing point/°C	Reference.
methyl stearate	+38	[8]
methyl oleate	- 20	[9]
methyl linoleate	-37	[10]
methyl palmitate	+ 30	[11]

For a single compound the cloud and pour points must, by the phase rule, be the same. Manufacturers' information for 'methyl oleate' sometimes gives them as being spaced by 10°C or more. Such a figure is valid only for a product containing methyl oleate at a particular percentage composition and not for the pure compound.

### 9.5.2 Biodiesel cloud points

Examples from recent research literature are given in the table below.

Nature of the biodiesel	Cloud point/°C	Reference
Methyl stearate, methyl oleate methyl linoleate and methyl palmitate in various proportions.	Lowest value of -3° for composition (mole fraction basis) methyl oleate 0.8, methyl linoleate 0.1, methyl stearate 0.1, no methyl oleate. Highest value of +17°C for methyl oleate 0.79, methyl stearate 0.21, no methyl linoleate or methyl palmitate.	[12]
Milkweed methyl ester, two samples.	-0.8 and -1.1	[13]
Milkweed ethyl ester, two samples.	5.1 and 2.5	[13]
Soybean methyl ester, two samples.	Both +1.5	[13]
Soybean ethyl ester, two samples.	+ 8.4 and + 8.9	[13]
Seventeen samples of rapeseed oil esterified with methanol under a range of reacting conditions, e.g., amounts of alcohol per unit amount of unprocessed oil.	All in the range -3 to 0	[14]
Sunflower methyl ester.	+1	[15]
Peanut oil methyl ester.	+5	[15]
Mahua <sup>12</sup> methyl ester.	+18 Reduction by 10 degrees on blending with 20% ethanol. Reduction by 13 degrees when blended with 20% kerosene.	[15]
Babassu oil, esterified.	+4	[15]

Both of the values in the first row are encompassed by the values for the pure esters given in the previous table. Common milkweed (*Asclepias syriaca*), which features in the second and third rows, is currently harvested to make fibre materials and the work on it described in [13] is exploratory. Soybean oil was studied for comparison, and in each case the use of ethanol instead of methanol as the esterifying reagent raises the cloud point significantly. Babassu oil (final row of the table) is extracted from Babassu palm which occurs widely in South America.

There is a good deal of interest at the present time in use of biodiesel fuels for jet aircraft. We saw in section 4.3 of this text that cloud points of the order of -50°C are necessary in jet aircraft use. Cloud points of biodiesels are much higher than this. The limited data in the penultimate row of the table indicate that biodiesel blends with conventional jet fuel might with suitable development have sufficiently low cloud points. Such blends will of course engender carbon credits. There have been test flights using biodiesel, but with one engine only receiving such fuel and the remainder receiving conventional fuel.



## 9.6 Vapour pressures

As with some of the other properties considered it is helpful first to examine the vapour pressures of pure methyl esters. The normal boiling points, at which by definition the vapour pressure is 1 bar, of methyl palmitate, methyl stearate, methyl oleate and methyl linoleate are respectively 338, 352, 349 and 366°C [16]. Pure methyl esters do of course have a single boiling point: a biodiesel, which will comprise several such compounds, has a boiling range. Applications of the Clausius-Clapeyron (C-C) equation to a biodiesel is not fundamentally sound, as the equation is only for a pure chemical compound. There is however no difficulty with the suggestion that the temperature dependence of the vapour pressure of a biodiesel has the same form as the C-C equation, in which case assignment of a value to the heat of vaporisation becomes arbitrary. The C-C equation can of course be rigorously applied to the pure ester compounds in which case the heat of vaporisation will have a precise value.

Vapour pressures of biodiesels of various known compositions across a temperature range have been studied by Goodrum [17] and, certainly for a limited number of data points in each case, conformity with an equation of the C-C form confirmed. Initial boiling points, that is attainment of a vapour pressure of 100 kPa, were observed at 369°C for a particular rapeseed ester and at 348°C for a particular soybean methyl ester. These fall comfortably within the range of normal boiling points for the pure esters given in [16].

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## 9.7 Concluding remarks

The fuel technology research literature is dominated by biodiesels at present. This is a measure of their importance for the present and the future.

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# 10 Hydrocarbons existing either as cryogenics or as liquefied gases

## 10.1 Introduction

Referring to the title, the most common of the former is LNG (liquefied natural gas) and the most common of the latter is LPG (liquefied petroleum gas), which have primary constituents respectively methane and propane. The critical temperature of methane is such that it cannot be made into a liquid by pressure application at room temperature, therefore LNG is a cryogen, and liquid at the normal boiling point of methane (112K) is in equilibrium with vapour at 1 bar. By contrast propane **can** be liquefied at room temperature, and at 25°C the equilibrium vapour pressure is about 8 bar. It is therefore stored as a liquid under its own super-atmospheric vapour pressure. Falling between methane and propane in the alkanes homologous series is ethane. Its critical temperature is 32°C. The first part of this chapter will compare the physical properties of LNG and LPG. Discussions of other examples of such hydrocarbons will follow.

## 10.2 Vapour pressures

This has in some degree been anticipated in the previous section. Vapour pressures of pure methane and pure propane are of course, at a particular temperature, fixed and invariant. In practice LNG will contain a few chemical species other than methane including higher hydrocarbons and diluent nitrogen. LPG might well be a blend of propane and butane, possibly with the latter in preponderance in which case the vapour pressure will be greatly reduced. LNG and LPG are both good fuels for spark ignition engines, although the former has not yet come into such use widely. Their vapour pressures are very much higher than the Reid Vapour Pressures given for gasolines in an earlier chapter. This is relevant to utilisation and to the storage and transportation which precede it.

### 10.3.1 Comparison of properties<sup>13</sup>

The table below gives properties of liquid methane and of liquid propane. Comments, by way of comparison with other liquid fuels considered in this volume, will be made.

Property	Liquid methane	Liquid propane
Normal boiling point/K	112	231
Density at the normal boiling point /kg m <sup>-3</sup>	420	582
Coefficient of thermal expansion /K <sup>-1</sup> <i>Calculated in the boxed area following the table.</i>	0.01	0.002
Kinematic viscosity at the normal boiling point/cSt	0.25	0.36
Thermal conductivity at the normal boiling point /W m <sup>-1</sup> K <sup>-1</sup>	0.19	0.13
Dielectric constant	1.7 (at the normal boiling point) [2]	1.6 (at 273K) [2]
Refractive index <i>Calculated from the dielectric constants.</i>	1.30	1.26
Prandtl number at the normal boiling point.	1.88	3.49

In considering the density of liquid propane at the normal boiling point, we recall that LPG is at a much higher temperature under a vapour pressure of about 8 bar as noted. A related calculation is in the box below.

$$\beta = - (1/\rho) \, dp/dT \, K^{-1}$$

with symbols as defined in a previous chapter. Now from tables the density of liquid propane at 92 K (19°C) is 504 kg m<sup>-3</sup>. This provides a route to calculating  $\beta$  for liquid propane. Integrating and rearranging:

$$\beta = - \ln(\rho_{292}/\rho_{231})/(292 - 231) = 0.002 \, K^{-1}$$

The value of  $\beta$  obtained for liquid propane is just twice the generic value for gasolines given in Chapter 3, an observation of some interest. Considering methane along similar lines, at the critical temperature of 190K liquid at a density of 182 kg m<sup>-3</sup> is in phase equilibrium with vapour at 4.5 bar. The interested reader can easily confirm that this signifies a value for  $\beta$  of 0.01 K<sup>-1</sup>, half an order of magnitude higher than the value for liquid propane and a full order of magnitude higher than the value commonly used for gasolines. The calculated values for liquid methane and for liquid propane have been entered in the table.

The kinematic viscosities in the fourth row of the table conform fairly closely to those given at room temperature (that is, at temperatures much higher than the normal boiling point either of methane or of propane) in Chapter 1 for a number of pure organic compounds. The value for liquid propane at 292 K is 0.22 cSt which must be seen as the value for LPG composed primarily of propane or with propane in a very high preponderance. Values for gasolines are comparable to this as we saw in Chapter 3.



In reviewing the thermal conductivities given in the table, which were taken from [1], we return to the correlation given in Section 3.7:

$$10^6 k / \text{cal s}^{-1} \text{cm}^{-1} \text{ } ^\circ\text{C}^{-1} = 333 - 0.19t$$

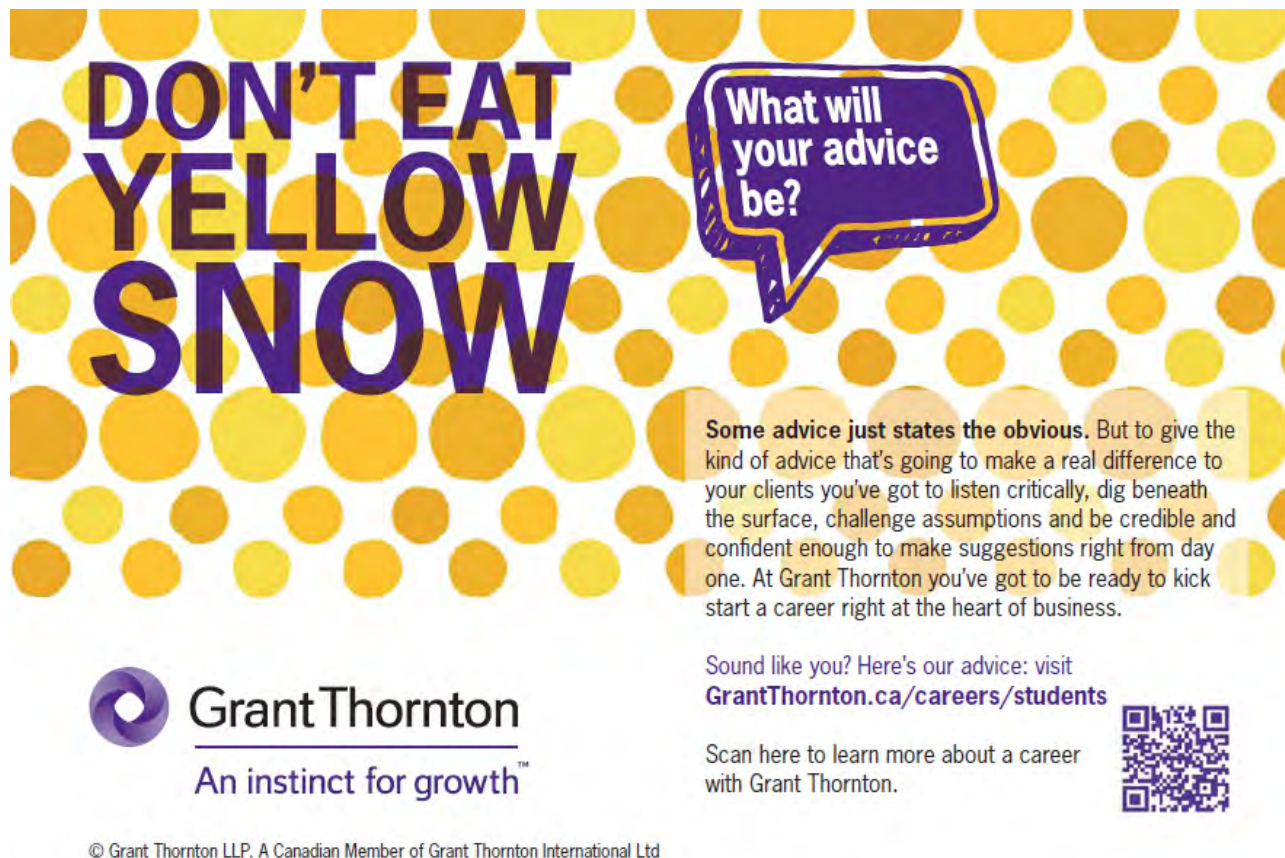
with symbols as defined previously. Inserting for methane  $t = -161^\circ\text{C}$  and converting to SI units:

$$k = 0.15 \text{ W m}^{-1}\text{K}^{-1}.$$

The corresponding calculation for propane ( $t = -42^\circ\text{C}$ ) gives a value of  $0.14 \text{ W m}^{-1}\text{K}^{-1}$ . Agreement is therefore better for propane. The dielectric constant given in row six of the table for propane is the value at  $0^\circ\text{C}$ . The equilibrium vapour pressure at this temperature would of course be several bar. In the following row are given the refractive indices calculated from:

$$\text{refractive index} = (\text{dielectric constant})^{0.5}$$

which, in an earlier chapter, was shown to hold well for gasolines. Several sources (e.g. [3]) give a value of 1.29 for liquid methane. A closely similar value to this is given in at least one literature source for liquid propane. Little variation in the refractive index is observed across the range  $\text{C}_1$  to  $\text{C}_4$ .



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### 10.3.2 Consequences of the high pressure in stored liquefied gases

Leakage of propane from an accidentally created orifice in a vessel holding it as a liquefied gas is discussed as a calculation in the boxed area below.

The equation which will be applied to leakage of propane through an accidentally created orifice in a storage container is:

$$Q = AP \sqrt{\left\{ (M\gamma / RT) [2 / (\gamma + 1)] \right\}^{(\gamma + 1) / (\gamma - 1)}}$$

where  $Q$  = mass flow rate of gas ( $\text{kg s}^{-1}$ ),  $A$  = discharge area ( $\text{m}^2$ ),  $P$  = upstream pressure ( $\text{N m}^{-2}$ ),  $M$  = molecular weight ( $\text{kg mol}^{-1}$ ),  $R$  = gas constant =  $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $T$  = gas temperature (K) and  $\gamma$  = ratio of principal specific heats.

A reader is encouraged to consult other sources (e.g. Perry's Chemical Engineers' Handbook) for background on the equation and conditions for its applicability.

Consider a container of LPG, approximating in composition to pure propane, at  $25^\circ\text{C}$ . Its pressure will be 9 bar ( $\equiv 9 \times 10^5 \text{ N m}^{-2}$ ) as noted. Imagine that a hole the size of a five pence coin

develops. Such a coin has a diameter of 18mm and an area of:

$$\pi \times 0.009^2 \text{ m}^2 = 2.5 \times 10^{-4} \text{ m}^2$$

The value of  $\gamma$  for propane is 1.136 the molar mass is  $0.044 \text{ kg mol}^{-1}$ . Putting  $P = 9 \times 10^5 \text{ N m}^{-2}$ ,  $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$  and  $T = 298\text{K}$  gives on substitution:

$$Q = 0.6 \text{ kg s}^{-1}$$

It is possible from this to calculate the mechanical power with which propane exits the orifice. The pressure energy is:

$$\Delta P / \rho_{\text{liq}} \text{ J kg}^{-1}$$

where  $\Delta P$  is the drop in pressure on orifice exit ( $= 8 \text{ bar}$ ) and  $\rho_{\text{liq}}$  the liquid density ( $= 493 \text{ kg m}^{-3}$ ). The rate of expenditure of pressure energy is then:  $(8 \times 10^5 / 493) \text{ J kg}^{-1} \times 0.6 \text{ kg s}^{-1} = 975 \text{ W} \equiv \mathbf{1.3 \text{ horse power}}$

Now this is about the power at which a fuel dispenser at a filling station operates. Such devices often incorporate either a  $\frac{3}{4}$  h.p. or a 1 h.p. pump<sup>14</sup>. Our example considers release of LPG through a very small hole, and the effect of the pressure is equivalent to there being a standard petrol dispenser to aid release. This gives a perspective on the consequences in the event of leakage of the high internal pressures associated with liquefied gases.

## 10.4 Ethylene

Ethylene ( $\text{CH}_2=\text{CH}_2$ ) is obtained by cracking petroleum distillate and is an important 'building block' in petrochemical manufacture. Large quantities of it are transported. Ethylene has a critical temperature of  $9^\circ\text{C}$ .



At that temperature its vapour pressure is approximately 50 bar. The vapour pressure can be brought down by refrigeration and this is the way in which ethylene is usually transported by sea. The vapour pressure will be above atmospheric as the temperature will be above the normal boiling point, therefore ethylene in such a state is a **refrigerated liquefied gas**, an expression not encountered previously in this volume. This is a preferable term to ‘cryogenic ethylene’ which is often encountered and which would only be accurate if the ethylene was cooled all the way down to its normal boiling point of  $-104^{\circ}\text{C}$ .

We saw previously that LPG has a vapour pressure at room temperature of about 8 bar. Ethylene has no ‘vapour pressure at room temperature’ because of its low critical temperature. If, as sometimes happens, a stationary or marine tank for LPG is to be used for ethylene the vapour pressure of the ethylene can by refrigeration be brought down to that for which the vessel was designed. Refrigeration down to  $-50$  to  $-60^{\circ}\text{C}$  will be required bring the vapour pressure down to that of an LPG payload without refrigeration.

The normal boiling point of ethylene (104K) is close to that of methane (112K). That of ethane (184K) falls between that methane and that of propane (231K). Some of the properties for methane and propane given in the previous table are given for ethylene and ethane in the table below. Comments follow.

Property	Liquid ethylene	Liquid ethane
Normal boiling point/K	104	184
Density at the normal boiling point/kg m <sup>-3</sup>	568	546
Kinematic viscosity at the normal boiling point/cSt	0.29	0.20
Thermal conductivity/W m <sup>-1</sup> K <sup>-1</sup>	0.19	0.19
Prandtl number at the normal boiling point.	1.96	1.88

The most important source of ethane is natural gas liquids (NGL) or (equivalently) ‘condensate’. When natural gas cools on removal from a reservoir via a well higher hydrocarbons present in it condense. These are up to about C<sub>4</sub>, and condensate is an important resource. Some of the non-associated gas fields of the southern North Sea contain large amounts of C<sub>2</sub> to C<sub>4</sub> hydrocarbons giving condensate in high yield when the gas is taken to a production platform. Such fields are often called ‘condensate fields’.

Methane is important as the primary constituent of natural gas. Propane and butane are important as the constituents of LPG. Ethylene is important as the simplest alkene having accordingly a major place in petrochemical synthesis. Ethane has no such niche. It can however be used as a refrigerant when it is known as R170. This takes us into the next part of the chapter.

## 10.5 Simple hydrocarbons used as refrigerants

Refrigeration cycles *per se* are outside the scope of this book, but simple hydrocarbons for use as refrigerants are comfortably inside it. There has been a move towards hydrocarbons and away from chlorofluorocarbons (CFCs) as refrigerants because of harm done by the latter to the ozone layer

Additionally to ethane the following simple hydrocarbon compounds find use as refrigerants [4]: propane (R290), n-butane (R600), isobutane (R600a) and propylene (R1270). The last three of these have normal boiling points respectively 273, 261 and 225 K. The refrigerating effect is expressed as:

$$T_c(s_g - s_f)$$

where  $T_c$  (K) is the cold enclosure temperature and  $s_g$  and  $s_f$  ( $\text{J kg}^{-1}\text{K}^{-1}$ ) are the specific entropies of respectively refrigerant vapour at liquid at the higher surrounding temperature  $T_h$ . We expect intuitively, working on a 'Trouton's constant' basis, that this could be re-written:

$$\text{Refrigerating effect} = \Delta h_{\text{vap}} T_c/T_h \text{ J kg}^{-1}$$

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where  $\Delta h_{\text{vap}}$  ( $\text{J kg}^{-1}$ ) is the heat of vaporisation at  $T_h$ . Imagine then a refrigerating device operating under conditions such that  $T_h = 300\text{K}$ . The values of  $\Delta h_{\text{vap}}$  at this temperature for a selection of refrigerants – hydrocarbons and CFC – are given in the table below.

Refrigerant	$\Delta h_{\text{vap}}(300\text{K})/\text{J kg}^{-1}$
ethane (R170)	139
isobutane (R600a)	323
propylene (R1270)	333
$\text{CHCl}_2\text{F}$ (R21)	228
$\text{CClF}_3$ (R13)	565

The ratio  $T_c/T_h$  will never differ hugely from unity and  $\Delta h_{\text{vap}}(T_h)$  is a reasonable indicator of the efficacy of a refrigerant, a point which has perhaps been given less emphasis in coverages of the subject than it might have been. It is clear from the above that simple hydrocarbons can, on this measure, ‘hold their own’ against CFCs.

## 10.6 Concluding remarks

Liquefied petroleum gas is a highly important fuel in which there is massive trade as is liquefied natural gas. Japan, vulnerable through lack of her own hydrocarbon resources, imports a great deal of both.

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4. <http://intergas.co.uk/hydroref.html>

# 11 Postscript

Can a book of 100 pages possibly have a place in an area as vast and as complex as hydrocarbon science and technology? I believe that it can. It is an ill-informed judgement of a piece of scholarship which equates brevity with superficiality. This book is very focused and is intended to bring out new perspectives rather than to reproduce information readily available elsewhere. It is to that, not to any deficiency in content, that the book owes its modest length.

I recently read in an account of the life of a 20<sup>th</sup> Century scholar in a subject area totally different from my own that he 'seems to fall in love with his material, such is the intensity of his engagement with it'. Whilst that might be seen as fanciful or even as lacking a sense of proportion, I think that most professional scholars could relate to it. To have studied a topic closely and deeply is an enriching experience. At this career stage I have a strong desire to share such insights as I have with people who have most of their professional lives in front of them. That has been my aim in writing this text and I venture to hope that others will follow.



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# 12 Endnotes

1. Joint Army, Navy and Air Force.
2. American Petroleum Institute.
3. It was originally published in 'Nature' in 1949 and is still in widespread use in applications including haematology.
4. There will be more on the RVP of gasoline-alcohol blends in Chapter 8.
5. The term natural gas liquids (NGL) is a synonym for condensate.
6. There is also a freeze point (not *freezing* point) for such fuels, defined as the temperature at which in a sample having been taken below its cloud point so that wax is present the wax melts on re-heating. It is typically 4 to 5°C above the cloud point.
7. At the time of preparing this text, Exxon Turbo 2380 is not being manufactured.
8. Though with imported coal: Japan no longer mines coal.
9. IL, IN, IA, MI, MN, MO, NE, ND, SD, SC. Note that whereas the first nine form a landmass SC is isolated from all of the others being well south east of the landmass.
10. Brazil was using ethanol-gasoline blends, in particular E10, to power motor vehicles many decades ago [21], long before such fuels became prevalent in other countries. The same is true of Cuba.
11. These names are not those based on International Union of Pure and Applied Chemistry (IUPAC) nomenclature. Whilst an organic chemist might prefer to apply such nomenclature to these substances a fuel technologist would be less likely to, and their common names are more helpful in a treatment like this. The acids from which the linoleate and the linolenate are derived, linoleic acid and linolenic acid, are present in linseed oil and that is the origin of their respective common names.
12. *Mahua Indica*, a widely occurring plant species in several regions of India.
13. The tome by Hewitt, Bott and Shires [1] has been drawn on in this section.
14. The author is grateful to P. Deller of Premier Group, Nottingham UK, manufacturers of petrol pumps, for supplying this information.