Chapter 12
The Marketing, Distribution and Use of Petroleum Fuels

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1 Introduction

The oil industry is a very complex business, as described elsewhere in this book, comprising exploration, extraction, transport, refining, distribution and the final use of its products. Exploration and extraction are examined elsewhere; the marketing, distribution and use implications of this complex business are best examined in the logical order of:

- transport of crude oil by tankers, vessels in general and pipelines,
- refinery operations on crude oil to produce hydrocarbon products,
- distribution issues of refined hydrocarbon products,
- environmental issues of the final use of hydrocarbon products,
- trends in global fuel consumption in the next decade.

2 Transport of Crude Petroleum and Refined Products

2.1 Potential Risks in Transport and Delivery

2.1.1 Ocean Tankers and Waterway Barges

To commence at the initial production, oilfield production of crude oil is usually distant from the refineries which process it into petroleum products. Pipelines transport crude oil within continents; between continents, the economics of delivery requires very large tankers to transport crude oil to refineries. Increasingly countries

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producing crude oil construct or expand their own refinery capacity and export refined fuel products by specialist tankers.

2.1.2 Ocean and Waterway Contamination

The transport economics for large volumes of crude oil between continents requires very large vessels of the order of 250–500 k dwt capacity, or more. There are complex global flows of crude oil between source oil fields and consuming nations/continents, graphically shown in Fig. 12.1. The inherent collision hazards of moving large volumes across oceans are addressed by improvements in vessel design and construction, advanced navigation aids and increasingly sophisticated meteorological predictions.

Various incidents have occurred when these operational conditions were not fully applied. Highly publicised tanker incidents have caused massive spillages of crude oil or heavy oils; increasingly sophisticated and effective emergency containment devices recovered major amounts of the spilled oil material; but the residual, unrecovered, oils caused extensive long term damage to plant life, sea animals, birds and fish.

The previous, conventional, construction of oil tankers was single hulled, where the tank walls were very close to or formed the outer skin of the vessel. Double hulls, or double bottoms, are now required in specific marine regions to give additional protection against accidental damage from vessel collisions, collision with solid obstacles or grounding on rocks and reefs which cause leaks and spillages. Advanced navigation systems only deliver enhanced navigation standards when maintained and calibrated to high standards and then operated by competently trained and informed staff.

Crude oil spillages may occur during transfer to, or from, the tankers and jetties resulting from equipment failure, malfunction and or human error. Central to achieving and maintaining high standards of pollution risk prevention in the transport and storage of crude oils, as also for refined petroleum products, is:

- high quality training of operators,
- careful, experienced design of tanks, pipelines and further bund containment,
- well-maintained secure connection couplings,
- a regular program of hardware and procedural inspections.

Automated metering of pipe flows, tank volumes and continuous/periodic inspection devices complement the surveillance of crude oil petroleum distribution and storage. Whereas inadvertent collisions and vessel damage can cause very heavy but very localized crude oil pollution of the oceans, more widespread sea water pollution can occur when tankers discharge ‘oily water’ wastes. These wastes arise from tank washings and cleaning between cargoes, as crude oil usually throws down deposits on standing in tanks, from water used for ballast and from the bilges. The ‘Marpol Convention’, the International Convention for the Prevention of Pollution from Ships (1973) [1] has steadily developed under the auspices of the

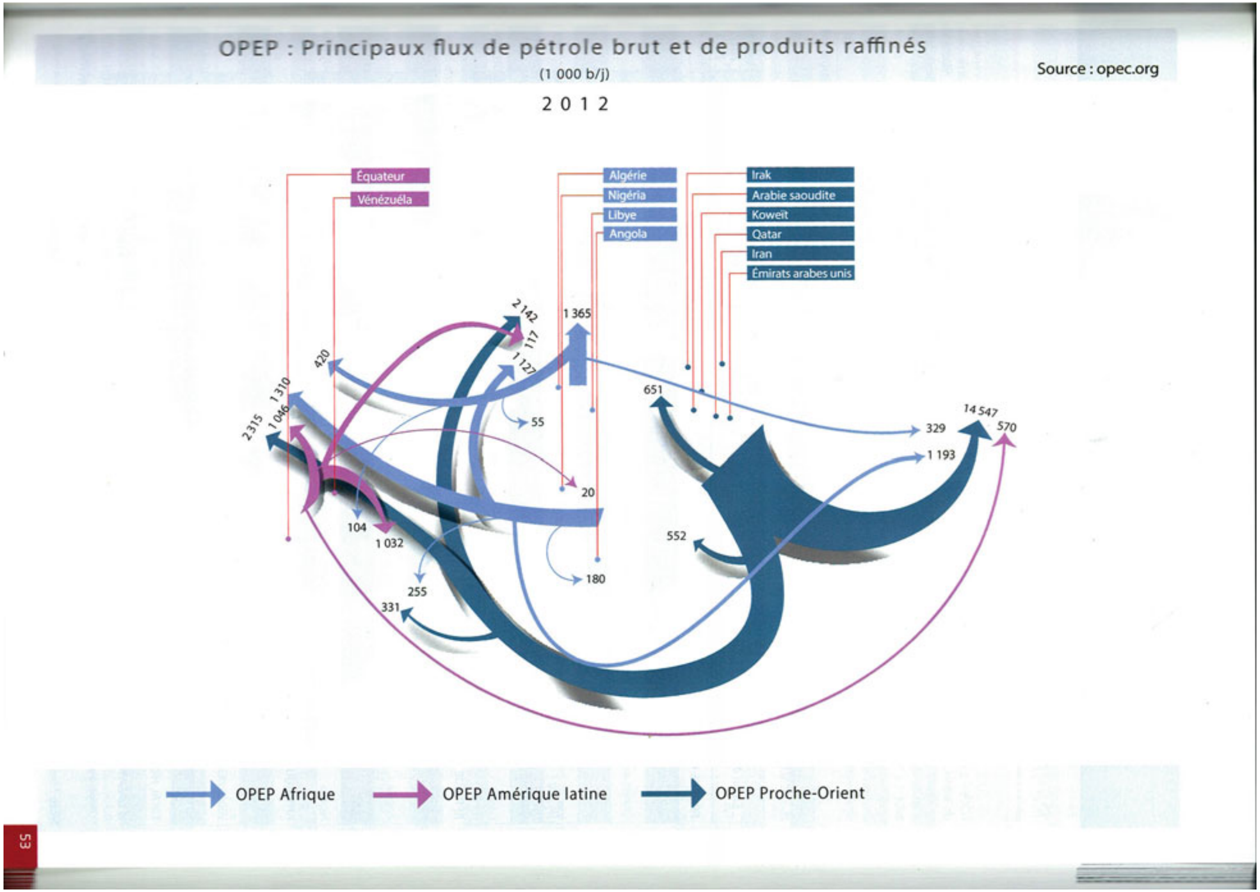


Fig. 12.1 Global crude oil distribution patterns, 2013, between continents (From Recueil des Notes D'Information Economique, Edition Janvier 2014, Comite' Professional du Petrole, ISSN 1156-2560)

International Maritime Organisation [2]. Oil-contaminated water from tank cleaning, ballasting and from the bilges must be drained to.

a ‘slop tank’ or separator tank to recover the oil and settle the aqueous phase. Contaminated water is either stored for discharge to shore tanks and subsequent appropriate treatment there, or if the oil content is below 15 ppm it may be discharged to ocean, provided the vessel is not in certain defined areas. Discharging oil-contaminated water to oceans must be fully recorded and documented; standards are closely regulated to IMO standard and subject to inspection at all times. But an increasing number of seas ***totally*** prohibit the discharge of oil-contaminated water; since 1999 contaminated water discharges from vessels are banned around the coastline of the UK and North Western Europe, the North Sea (1991), the Baltic Sea, enclosed seas such as the Mediterranean, Black and Red Seas, the Gulf of Aden (1989) the wider Caribbean (1993) and Antartica (1992). All vessels, ocean going and coastal, must store their contaminated water washings or bilge waters and discharge them to special treatment systems on shore.

2.1.3 Emission Control of Hydrocarbon and Other Vapours from Distribution

The odour of crude oil varies according to geographical source from the unpleasant to the very nauseous; the vapours above crude oil and heavy oils almost always contain hydrogen sulphide, which is extremely unpleasant but also very toxic with an OSHA TWA 8 h limit of 10 ppm, together with other similarly unpleasant compounds. Hydrogen sulphide can be treated with nitrogen heterocyclic compounds to sequester sulphur into relatively innocuous compounds with the associated emission of alkyl amines. Whilst this treatment removes the offensive smell of hydrogen sulphide, it does not reduce the sulphur content of the crude oil/heavy fuel.

The vapours of refined oils are potentially flammable, forming explosive mixtures with air within tanks or confined spaces during loading and transport. ‘Volatile Organic Compounds’ (VOC’s), must be carefully controlled to avoid fire and/or explosion hazards or asphyxiation of staff. IMO has established standards for vapour collection and control for ocean vessels, coastal and inland tankers and also at loading/unloading terminals. In addition, uncontrolled VOC emissions from oil company sites such as refineries, storage and distribution sites are increasingly required to be controlled by government environmental control policies, e.g., the EU countries [3].

When tanks are loaded with hydrocarbon fuels, equivalent volumes of fuel vapour/air mixture are expelled by discharge through high level and/or high velocity vents. The more volatile the fuel, such as petrol, the greater the potential hazard; the explosive mixture range for petrol is between 1 and 10 %. When loading petrol into tanks or barges, several studies have shown the hydrocarbon/air mixture above the liquid to be within the explosive limits for up to 80 % loading time. This potential hazard requires a very high level of operational care and technical plant for safe operation, for recalling first, that loading a volume of liquid into a tank, whether fixed on land or in a vessel will displace an equivalent volume of an air/VOC vapour mix and second, that the uncontrolled expelled vapour can vary between 5 and 35 % hydrocarbon, indicates the scale of the problem. The potential of the aggregate emission levels from volatile petrol and jet fuel on a continental basis such as Europe is high and must be controlled.

Whilst vapour control systems were initially installed for the protection of staff operating coastal tankers and barges, the emphasis has expanded to include vapour recovery as well. Vapour control and collection systems have become more important as the number of refineries has decreased to a smaller number of larger units from which distribution of hydrocarbon fuels by sea and inland waterway has necessarily increased. The principle is to contain the volatile hydrocarbon vapours within a tank which has (i) a vapour collection header with a high velocity vent to atmosphere, so that vapours are dispersed and do not ‘pool’ in the vicinity of the tank or vessel, (ii) a pressure/vacuum releasing vent, (iii) a detonation arrestor unit, and (iv) a connector to an on-shore vapour recovery unit.

Vapour recovery on loading/unloading has the form of liquid and vapour exchange using a closed, liquid/vapour piped system. Very similar systems are used for road and rail tanker loading/unloading. Several technologies are available for vapour recovery and separation/recovery when loading/unloading small tankers and barges. These include absorption into liquids of low volatility, onto activated charcoal, low temperature condensation or differential diffusion through a specific membrane. Of these, only diffusion separation is a single operation; vapour recovery following separation by the other various means requires either separate desorption or liquid separation and vapour regeneration. The initial requirements for vapour emission control and recovery were set by the German/French/Dutch authorities controlling the Rhine commercial inland waterway.

2.1.4 Road and Rail Tankers

Tanks by rail or road are used as secondary distribution where coastal and inland waterways do not reach and also where areas and depots are not supplied by pipeline. Delivery by rail has further and wider geographic penetration of areas than river transport and an economically effective distribution method which is safer than road tanker distribution and reduces heavy vehicle congestion. Rail tankers were usually top-loaded from gantries at refineries or major fuel depots and unloaded from a bottom connection into a reception tank. Bottom loading is now preferred because it reduces VOC emissions because of less liquid turbulence than top loading. Light fuels such as petrol and jet fuel are usually transported in un-insulated tanks. For fuels of much higher viscosities and waxing potential, insulated and/or heated/able tanks are used to prevent partial solidification. It is important to recall that the flow-point temperature of the heavier fuels is also time dependent – a tank car left to stand for several days in cold temperatures ***above*** the measured flow point temperature of that fuel can slowly form wax in that time.

The main commodities transported by rail tank cars in North America are crude oil and ethanol, together accounting for 68 % of the total. Other major flammable commodities transported by rail tank car are methanol, benzene and styrene. Detailed construction and use regulations apply to rail tankers and the design, operation and use of road tankers is similar. High standards of tanker design, maintenance, driver training and operation are enforced and the accident rate is low. But not low enough – recent freight tank car accidents in North America:

- Cherry Valley, Ill., one fatality, 31 tank cars involved, 885 m^3 of ethanol released and burned (2009),
- Arcadia, Ohio, 3006 m^3 of methanol released and burned (2011),
- Lac Megantic, Quebec, 47 fatalities and 6000 m^3 crude oil burned (2013),
- Heirndal, North Dakota, 684 m^3 crude oil burned (2015),

have led to increased construction standards, DoT 117 (US) and TC-117 (Canada). From October 1st. 2015, new tank cars must have thicker steel walls, more protection at each end, thermal insulation and improved protection for pressure relief and bottom-outlet valves. A program to replace or upgrade the existing tank car fleet must begin in 2017 and by 2021 tank cars must have electronically actuated pneumatic brakes which act simultaneously, rather than sequentially, to prevent 'accordion-type' pile-ups. Tank cars can form very long trains of up to 120 tank cars, between 1 and 2 km long, containing millions of gallons of the same commodity, 'unit trains', whereas finished hydrocarbon products can be delivered as smaller volumes within 'manifest' trains mixed in with other cars, both goods ('boxcars') and non-flammable, tank cars.

From the enormous volumes conveyed by single ocean tankers through to the multiple volumes delivered by many rail or road tankers, the potential risk increases from multiple transfers and transport as spills, leaks, evaporation and catastrophic releases from accidents. The petroleum industry has many years' experience of handling its products, incorporated into Regulations (of individual country's Acts as primary legislation) and 'Codes of Practice', nominally/essentially voluntary but guidance for 'good practice' which is wise and prudent to follow. The Regulations, Codes of Practice and Guidelines seek to minimise or avoid pollution of the oceans, coastal waters, rivers and canals, soil and groundwater and the atmosphere. One example is 'Guidelines for the Design, Installation and Operation of Petrol Vapour Emissions at Distribution Terminals', by the Energy Institute [4]. These controls, in their various forms, are closely and continually reviewed as a process of continuous improvement; continuing issues are the proper application of the extant legislation and good practice. New issues arise as the technology of measurement develops and more appropriate, rigorous, legislation is introduced.

2.1.5 Pipelines

Pipelines divide broadly into those which (i) carry crude oil from oil field to refinery across a continent or to a terminal for loading onto tankers for transport between continents, or (ii) those which distribute large masses/volumes of refined products to major consumption sites such as airports or major distribution terminals. Pipelines are unobtrusive, being well buried, yet economical because of their high transport throughput capacity. The maps in Figs. 12.2 and 12.3 shows the extensive

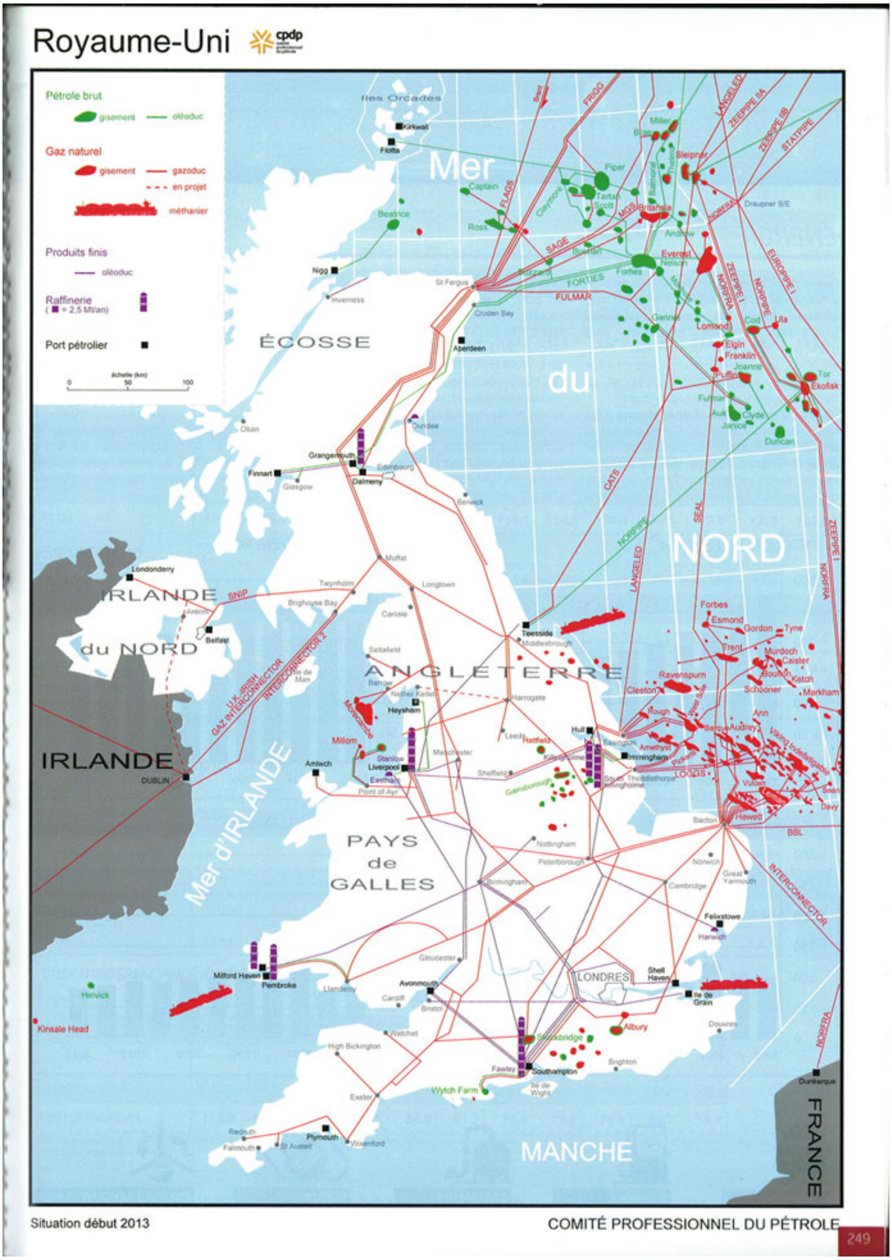


Fig. 12.2 Crude oil, refined product and natural gas pipelines in the United Kingdom 2013 (From Recueil des Notes D'Information Economique, Edition Janvier 2014, Comite' Professional du Petrole, ISSN 1156-2560)

Fig. 12.3 Oilfields and crude oil, refined product and natural gas pipelines in Northern Europe and the United Kingdom 2013 (From the International Petroleum Encyclopaedia, Penwell Corporation, Tulsa, Oklahoma, USA, www.penwellbooks.com)

network of both crude oil and product pipelines across the UK and Northern Europe, respectively, which are surprisingly comprehensive; similar complexity exists for North American pipelines. As pipelines are buried in the permeable ground they are potential sources of contamination if they physically fail or are damaged by a third party. 90 % of pipeline leakage incidents are caused by the actions of third parties.

The fore-seeable, preventive, operational/design measures of pipe weld integrity and corrosion prevention are used to preserve the integrity of pipelines. The nature of the ground in which the pipeline is buried determines further corrosion protection measures, such as cathodic protection or an impressed current to counteract corrosion processes. Performance of the pipeline integrity measures has been of a high standard when a constant program of maintenance, protection and testing/assessment has been established and followed. When these standards are not maintained, pipelines corrode, leak and burst. ‘Third party’ incidents typically occur where a construction vehicle severs a sub-surface pipeline. These incidents may be rare but nevertheless occur due to a lack of communication or due diligence by a building contractor as to what is beneath the site they are working on. In some developing countries criminal activity drills or hacks into pipelines to steal petrol, kerosene or diesel, whatever is passing through at the time. The consequences are usually dire and catastrophic, leading to severe fires when the stolen refined products ignite.

Product pipeline utility is enhanced by sending consecutive batches of refined product separated by travelling ‘plugs’, colloquially known as ‘pigs’, propelled by the hydraulic pressure within the pipelines. Complex pipework allows the introduction and removal of the ‘pigs’, which are potential sources of spills. Different designs of ‘pig’ can remove deposits from the walls of pipelines to maintain their efficiency or measure pipeline wall thickness to assess corrosion effects. Long distance pipelines from refineries to refined product distribution depots allow the final delivery of fuel to service stations as a relatively short road tanker journey.

Whilst raising the level of technological control, the introduction of electronic flow and tank level measurement control devices brings their own, new, set of issues. The Buncefield (UK) fuel storage depot catastrophic fire and explosion on 11th December 2005 was a major devastating incident for the depot and surrounding area. Occurring early on a Sunday morning, the explosion measured 2.4 on the Richter Scale; it was fortunate that the full, weekday, complement of staff was not on site and that no one was killed there nor in the surrounding housing. The Buncefield Depot had a capacity of 270 M litres of fuel. The (UK) Major Incident Investigation Board (MIIB) concluded [5] the incident was due to failure of a single liquid level alarm on a petrol storage tank. The malfunctioning single level switch alarm allowed the tank to overflow when loading through a long pipeline from a distant refinery. The excess fuel pool around the tank eventually ignited and the ensuing fire and explosion wrecked the entire site, a major regional storage and distribution centre, together with extensive damage to surrounding property. The MIIB Report also identified a range of improvements in the construction and operation of fuel storage depots. New measurement and control technologies bring their own new safety issues.

2.1.6 Soil and Groundwater Contamination

EU countries protect soil groundwater from hydrocarbon contamination from inadvertent spillage or deliberate discharge through site licensing, enforced by substantial fines for pollution incidents [3]. Hydrocarbon pollution of soil and groundwater is aesthetically unpleasant but groundwater is a major source of drinking water. The presence of trace hydrocarbons taints water and is detectable by taste at sub-ppb levels. Lighter hydrocarbons will evaporate in short time, but then present a flammability or explosion hazard in confined spaces such as drains and sewers. Heavier hydrocarbons discharged to waters as fuel or lubricating oil do not evaporate and their surface film excludes oxygen from watercourses to kill fish and aquatic life; heavier hydrocarbons also kill wildlife by coating them with oil, or a partial emulsion of oil and water, upsetting their digestive and respiratory organs and killing off their food source.

The first action to prevent contamination of soil and groundwater is ‘good site housekeeping’ to prevent leakages, seeps, weeps and spills of hydrocarbons from their transport and use. ‘Good site housekeeping’ practice, however mundane but properly practiced, is very effective in reducing hydrocarbon pollution of soil and groundwater. ‘Good site housekeeping’ commences with proven, effective design for containment of hydrocarbon spillages as hard, impermeable, surface standing for storage areas with substantial bunding (containment) structures to contain equally substantial spill volumes. Good practice in high standards of pipe connector design and maintenance, together with high standards of connection procedures, are proven to reduce hydrocarbon spillage. Equally important is good stock volume keeping such that tanks are not over-filled. Tank closure security is important to the extent of locking tank valves against criminals stealing the contents but in the process spilling large volumes of hydrocarbons; it also protects against mindless vandalism; the last two issues are increasingly important for relatively isolated or single tanks on factory premises.

The importance of preventing hydrocarbon environmental pollution is further emphasized by the high costs of cleaning soil, groundwater and watercourses together with the associated substantial fines. Water and river authorities are very competent at finding the sources of hydrocarbon emissions, quickly containing the environmental pollution, sampling and rapidly identifying the detailed nature of the contaminating material, obtaining interim legal intervention and enforcement as necessary and then prosecuting those controlling the source of the pollution.

Legislative limits are set for the maximum concentrations of hydrocarbons emitted to air or water from an industrial site, not solely for depots dealing with hydrocarbons. Maximum hydrocarbon contaminants in water are set for surface water flows, river water, effluent discharges to surface water and to sewer. The concentration limits for environmental pollution are usually set for an individual industrial site in a ‘consent to discharge’ legal document, monitored by either periodic manual or continuous automatic sampling. Effluent limits to surface water or sewer are set having regard to the manageable load upon the downstream treatment system and charged accordingly. Whilst the form of the legal controls on emissions from business premises may appear to vary from one country to another, the underlying principles of control established by European Directives ensure that they are very similar in operation [3].

The effluent discharge limits to surface water or sewer from business premises are drawn from whatever is appropriate to control the business activity conducted on the site, such as the temperature increase between input and output water flows, the pH, dissolved, suspended and precipitated solids, turbidity, colour, taste and odour in, or of, the effluents, together with dissolved organic carbon (DOC), total organic carbon (TOC), biological or chemical oxygen demand, (BOD & COD). Each of these is determined by international established and maintained standards of analysis.

2.1.7 Contamination Protection Above Ground

Solid, impermeable surfaces are used to protect ground soil from contaminating hydrocarbon spills and leaks at distribution and delivery depots. These surfaces are installed in areas used for storage tanks as containment bunds, beneath raised tanks, loading and unloading areas, from where spilled hydrocarbon fluids can be collected and retrieved. The integrity of the surfaces is crucial; the Inquiry into the Buncefield disaster [4] noted leaks in the integrity of some of the storage tank bunds.

Overfilling of tanks is a major source of hydrocarbon spills, arising from miscalculation of the volumes already in the tank and the amount to be delivered, or inattention to the completion of tank filling and the consequent overflow. Attention to detail and/or an automatic cut-off are preventative measures.

2.1.8 Hydrocarbon Recovery and Treatment

Oil recovery technology directly from spillages has improved such that high percentage efficiency can be achieved. But the recovery efficiency depends upon the nature of the soil, the water course and the nature of the hydrocarbon spilled. Complete recovery/removal of the spilled hydrocarbons is usually not achieved and further treatment of contaminated soil is necessary. Disposal of land contaminated by hydrocarbons to landfill is now more restricted as to the hydrocarbon content, from higher standards/lower allowed concentration limits, and recognition that the problem is not being addressed but moved ‘along the line’ for other people to deal with the problem at a later time. The soil volumes to be treated can be very high. Previous minor/moderate contamination of a development site might require removal of the top 0.5 m, or up to 1 m, of the site topsoil, very large volumes to be lifted, transported and disposed in a safe manner. Alternative on-site treatment methods can be used – incineration to destroy hydrocarbons present in soil can be destructive of the soil and expensive of fuel to operate;

solvent extraction is effective but care must be taken to avoid extra emissions arising from the solvent used. Biological treatment of hydrocarbon-contaminated soil can be effective for appropriate combinations of soil type and grade/type of hydrocarbon but requires time and space to be effective.

Contaminated groundwater is recovered using oil/water separators in the first instance, as in drainage sumps for water run-off from hard surfaces/hard standing, specified in the Building Regulation site consent. The efficiency of simple oil/water separators does not give sufficiently acceptable purity for the separated water and it must be treated further. Techniques for further water purification include (i) relatively gentle physical separation using tank settlement or plate impingement separators, (ii) more active physical treatment such as fine filtration, sedimentation settling, flocculation by settlement-promoting additives or air/froth flotation, or (iii) biological treatments using biofilters of various designs such as reed beds, air pumped through aerated ponds of the water being treated, or very intensive treatment by the activated sludge process. After further slow settlement, high quality water effluent from these treatments can be discharged to a water course.

2.1.9 Final Storage and Distribution

The manner that refined oil products, primarily fuels, are delivered to the final customer depends upon the volume size by final user, frequency of demand/use, nature of the oil product and the way in which the fuel will be used. ‘Use’ can vary between the limits of a fixed site, high daily consumption of a heavy fuel oil to the distribution of multiple light distillate fuel transactions in relatively small volumes of ~50 l to light road vehicles from a service station:

- **Single High Volume Users:** Building oil-fuelled electricity power stations, or utilities, close to, or contiguous to, an oil refinery was practiced in the late 1900s. Fuel oil for the power station was readily pumped ‘through the fence’ from the adjacent, or close by, refinery site, minimising large transport costs. Oil fuel is stored in above-ground tank farms on impervious hard standing within containment bunds as a reserve supply and extra capacity when the power station fuel consumption is greater than the refinery can supply, as may occur during winter.

Oil-fuelled electricity generation by steam-raising and its subsequent use in turbines has declined in Europe because of the increasing price of fuel oil (up to mid-2014!) and has lost out to gas-fired generation. Natural gas fuel allows:

- a primary gas turbine to directly drive an electrical generator,
- use the exhaust in a waste heat boiler in a second cycle to raise steam and generate electricity through a separate turbine,
- some systems use the second cycle exhaust to generate hot water as a third stage of heat and thermal transformation.

The scheme is a ‘Combined Cycle Gas Turbine’ electricity generation, CCGT, with a substantially higher thermal efficiency than coal or oil firing to raise steam for electricity generation. The ready availability of natural gas in Europe, from its own sources on land or North Sea or through pipelines from Norway, Russia or Aral/Caspian Independent States has reduced the electricity generation market for fuel oil. Some countries such as Japan are heavily dependent upon importing liquefied natural gas, LNG, in specialized, refrigerated and pressurized tankers. The development of 'fracking' in North America has led to the United States becoming one of the, if not the, major global hydrocarbon producer nations and a net exporter of natural gas and other condensible gases such as ethane.

Similar siting and supply considerations apply to petrochemical complexes adjacent, or close to, refineries. If there is no fuel oil pipeline supply to a power station or petrochemical complex, then they are supplied by rail tank car deliveries. As emphasized previously, 'good housekeeping' on site is necessary to minimize fuel oil spillage by preventive maintenance of pipelines and standard operating procedures for the filling/drawdown of tanks, to prevent over-filling and associated spillage hazards.

– **Small/Medium Industrial Users and Service Stations:** The design, construction and use regulations for oil storage tanks and pipework in small to medium factories are set to a high standard. Regulatory formats may differ between countries but they are very similar in technical design. The EU Directive 94/63/EC [6] controls Volatile Organic Compounds emissions with the aim of reducing them by 90 %. 'Stage 1' controls apply to the loading/unloading of petrol into road and rail tankers, inland waterway vessels and petrol stations. 'Stage II' controls apply more stringent controls to service stations above a certain size and to the construction of new sites. Unfortunate experience has shown that without these controls oil storage installations will contribute to soil and ground water contamination by leaks, seeps and weeps and to water course contamination by run-off.

Fixed oil product tank storage for small/medium industries divide into 'above ground' and 'buried'. The operational hazards are either over-filling in the short term or leakage by corrosion in the long term. Both eventualities lead to the requirement of the tank being sited on an impermeable surface or with a containment device of sufficient volume beneath. 'Over-filling' is prevented by 'good housekeeping' tank management and a high status level alarm; regular 'dipping' by a gauge length is recommended to check that the calculated or indicated volume of hydrocarbon fuel is actually present. The Energy Institute 'Guidance on Design and Operating Limits for Fuel Storage Tanks at Retail Filling Stations' [7], sets common standards for the definition of operating limits for retail fuel storage tanks. The Guidance also links to Approved Code of Practices (ACOPs) and the (UK) Health and Safety Executive (HSE) 'Dangerous Substances and Explosive Atmospheres Regulations Approved Code of Practice and Guidance, L133, 'Unloading Petrol from Road Tankers'. The Guidance is intended for sites fitted with overfill prevention devices and/or high level alarms. The Energy Institute has also prudently established 'Guidelines for an Emergency Action Plan for Fire and Explosion Risks at Filling Stations' [8].

The number of UK service stations as retail outlets has steadily declined from a peak of ~40,000 in 1967 down to ~8600 in 2014 [9]. The main loss has been smaller service stations, particularly for those without other viable supporting commercial activities such as garages, car sales or shops. A major effect has been the growth of the supermarket service stations now with a market share of 43 % of total UK fuel sales. Vehicle numbers in the UK increased to 35.9 M in 2014, giving 4170 vehicles/service station in 2014, compared to only 319 in 1967! The importance of the safety controls described previously is emphasised by the average total fuel throughput per service station of 3270 t/pa. The undifferentiated (petrol + diesel) average fuel consumption/vehicle in ton/year has steadily decreased by 11.5 % from 2004 to 2014, reflecting real increases in the vehicle fleet fuel efficiency.

Steel tanks/containers corrode; the issue is controlling the corrosion rate which can be minimized by applying, and maintaining, appropriate coatings and also various anti-corrosion electrochemical methods. Nevertheless, as entrained or dissolved water settles to the bottom of all tanks, corrosion and subsequent leaks occur. To anticipate these leaks in due course, a ‘double bottom’ is increasingly specified for above ground oil storage tanks on the basis that the inner tank surface will corrode and leak into the second containment, with a leak detector to notify operators. For smaller tank capacities, rotationally moulded polyethylene/polypropylene tanks, internally treated to reduce long term diffusion, are increasingly used for industrial and domestic installations.

The immediately preceding paragraphs assume that the hydrocarbon product storage is fixed. A development over the last 20 years has been the extensive use of ‘Intermediate Bulk Containers’, commonly referred to as ‘IBC’s’, to conveniently transport and store liquids and solids, including hydrocarbons. IBC’s have various forms and constructions: for liquids they are rotationally moulded thick wall polythene 1 m^3 cube tanks held within a stout wire lattice framework. Bottom drain and top filling connections are recessed to prevent damage and the base is designed for fork lift truck handling. IBC’s are ubiquitous and bridge the gap between drums of various sizes and fixed tank installations; for the same external volume they contain a significantly greater volume than an assembly of drums. IBC’s combine the advantages of a transport and storage capability and may be stacked. The intrinsic pollution problem with IBCs arises when they are damaged and leak, most frequently punctured by the mis-directed blades of a fork lift truck; the preventive, corrective, action is extensive training of fork lift truck operators.

It has been common practice for service stations to bury oil storage tanks 2–3 m below ground so that leaks are minimized by containment for the more volatile fuels, particularly for petrol. Previous practice of a minimal anti-corrosion coating on a buried steel tank has shown, over time, that corrosion in soil can be severe and the fuel gently leaks into the subsoil until the rate of loss is noticed. Best practice is to place the tank into a buried impermeable bund, combined with an impermeable lining to the steel tank. With these extra cost requirements, a GRP (glass reinforced plastic) storage tank becomes competitive because of the intrinsically corrosion resistant nature of its material. The same design considerations for the associated buried steel pipework must also be applied, such as being laid in impervious channels and regularly tested for leaks. Service station pipework systems are extensive because the filling connections for several tanks of different fuel grades are to the side of the site for operational convenience, for the delivery pipes to the filling pumps and also a pipework system to collect fuel tank vapours in an absorbent canister such that filling the tanks does not emit hydrocarbons to the atmosphere, EU Stage 1 or II controls, as described previously [6]. As the fuel is drawn down from the tank, the flow of replacement air through the absorbent canister desorbs the fuel vapours into the tank.

Delivering volatile fuels from a service station pump into a vehicle's tank displaces an equivalent volume of fuel vapour. Where hydrocarbon emissions are strictly controlled to minimize overall emissions, as in California, a large rectangular corrugated rubber shroud surrounds the petrol nozzle, connected to a vapour return pipe. The rubber shroud must be pressed firmly against the side of the vehicle to ensure a seal; a pressure microswitch ensures that sufficient pressure is applied to make the seal. When the nozzle handle is pressed to deliver the fuel, the vapour displaced from the vehicle tank is exchanged for the liquid fuel delivered from the storage tank and not emitted to atmosphere.

2.1.10 Overall Reductions in Volatile Organic Compound Emissions

VOC emission reduction is one of the environmental policy objectives of both the EU and North America because VOC's interact with pollutants and sunlight to generate photochemical smog. There are also health and resource conservation issues in containing these compounds, including Green House Gas (GHG) emissions. The European Union is committed to reducing 2030 Green House Gas emissions by 40 % relative to a baseline of 1990.

VOC emissions from industrial plant and service stations above certain sizes and throughputs are now controlled by absorption/desorption devices. The transfer loading of volatile organic compound liquids above a certain volume is now required to use vapour/liquid exchange systems.

3 Oil Product Refining

3.1 *Nature of Refining*

Oil refineries operate continuously with very high throughputs of crude oil to produce a large range of products. The composition of the input crude oil varies from one oilfield source to another; in the past European and North American refineries were configured to process crude oil from a particular, distant, oilfield source. Now, refineries are flexibly configured to process crude oil from a range of sources. In addition, refineries have been built on, or close to, the far oilfield sites. All of the crude oil input is used to produce a wide range of major and minor products for varied uses and applications. Refining crude oil is a worldwide activity and extremely competitive; only the most cost-effective survive. Every refinery seeks the maximum return from the crude oil input value by separating and upgrading products for specific markets to give maximum added value. The amount of waste from refining crude oil is extremely low and necessarily so; 0.1 % waste from a throughput of 10Mt/pa would be 10,000 tons of a highly viscous, unpleasant material which has to be stored or disposed of somewhere. The economics and waste disposal issues of crude oil refining push the operators to utilise and upgrade all materials such that maximum value is obtained and waste is absolutely minimal. Refinery products vary from:

- gases such as Liquefied Petroleum Gases, LPG,
- automotive fuels such as petrol/gasoline and diesel,
- jet fuel for aviation and paraffin/kerosine for heating,
- solvents of varying volatility,
- heating oil,
- residual fuel for marine fuel oils and heating oils,
- lubricant base oils,
- waxes,
- bitumen
- and also petrochemical feedstocks for further processes.

Increasingly refineries have to formulate each product to meet tighter performance and environmental specifications, as described later in this Chapter. A constant theme is the demand for increased product performance and quality, as in automotive petrol, diesel and marine fuels, to which refineries must respond by reconfiguring their processes. Further, new processes upgrade heavier, lower value products into lighter, high value products, e.g., by cracking or converting fuel oil grades into diesel. The demand for transport fuels as a percentage of the first distillation of an average crude oil is not sufficient for demand; therefore, the lower value, heavier fuels are cracked into lighter fractions to increase supply. Investment is needed for upgrading processes and replacement of older plant. In a very competitive business environment, the number of refineries in the UK alone has reduced from 19 in 1975 to six in 2015, albeit by concentration into larger units. An interesting trend is for the major oil companies to withdraw from refining and sell these assets to specialized refining companies.

Whilst the applications of refinery products are wide and various, almost all are fuels in one form or another and are consumed by combustion to provide motive power. The basic refinery operation itself uses between 2 and 3 % of the crude oil input for the thermal energy of the initial distillation and separation process, followed by reforming and hydrogen treatment, ‘hydrotreating’. Modern refineries use more ‘severe, i.e., higher temperature and pressure’ processing to catalytically crack heavier product grades into lighter grades such as petrol and diesel fuel. This not only increases their proportion from the original crude oil distillation value, and meet market demand for these products, but also increases their value. It also requires more energy; for a complex refinery which extensively upgrades initial distillation products into highly specified fuels and lubricants, the energy required can be 7–9 % of crude oil input.

3.2 The Main Types of Refinery Products

3.2.1 Light Fuels

The major part, around 80 %, of refinery products are light fuels classified by boiling point ranges. The lightest are petrol/gasolines, mainly used in piston-driven internal combustion engines for passenger motor vehicles, small propeller-driven light aircraft and small portable power sources for generators, mowers and chainsaws, etc.

3.2.2 Middle Distillates

The next boiling range is designated as the beginning of the ‘middle distillates’, the kerosine/paraffin where the aviation grade is very tightly specified for gas turbine jet engines, either by direct propulsion or turbine driven propellers, ‘turbo props’. Heating kerosine has roughly the same boiling point/molecular weight ranges as aviation kerosene but is much less specified. Diesel fuel is used for heavier road vehicles such as buses, lorries and agricultural tractors but has also 50 % or more of the small passenger car market in some European countries. Heavier grades in this boiling range are also used for industrial heating as ‘gas oil’ and in smaller marine engines.

3.2.3 Residual Oils

Beyond the ‘middle distillate oils’ are the ‘residual oils’ from the non-distilled residue of crude oil, used as diesel fuel in very large slow speed, 60–90 rpm, marine engines, industrial power generation and heating systems. Used in marine engines these fuels are known as Marine Fuel Oils (MFO’s), defined by ISO 8217:2010, et.seq [10].

3.3 An Example of Fuel Specification Upgrading

An example of refinery fuel upgrading is the sulphur content of ‘residual oils’, which gradually increase as the lighter fractions are removed from the crude oil. Stringent reductions in the sulphur content of Marine Fuel Oils, MFO’s, are required by various jurisdictions under the Emission Control Areas, ECA’s, defined by IMO. ECA’s are established for the European North and Baltic seas and also within 200 miles of the North American coast, including Canada and Mexico, not solely the USA. The sulphur content could previously be up to 4 %, higher for some crude oil sources but was limited, pre-2015, to 3.5 %, outside ECA’s coastal waters of the European Union and North American States. Within those ECA’s the pre-2015 MFO sulphur limit was 1.0 %; post January 2015, vessels must now use 0.1 % sulphur DMA fuel or liquefied natural gas. Future limits on MFO’s used outside of ECA’s are proposed to be 0.5 % by 2020, although this step may be delayed to 2025, in part due to the availability of refinery capacity to produce sufficient quantities of this fuel quality. These requirements complicate the operation of vessels; two qualities of fuel must be carried in two fuel tank systems. When the fuel quality is switched as a vessel approaches or leaves an ECA, the lubricant formulation should be switched as well, an additional duplication. The two fuels operate at different temperatures and ‘switchover’ between them needs careful management otherwise problems occur with engine operating continuity causing a ‘Loss Of Propulsion’, (LOP), event [13]. The United States Coast Guard recorded 93 vessel LOP incidents in Californian waters in 2014 of which 16 % were related to fuel switching on entry to an ECA. Carrying this data over to the 60,000 annual vessel transits of the Channel between England and France predicts 102 LOP incidents due to fuel switching each year, or one LOP every 3 days.

Combustion of MFO’s forms sulphur dioxide (and nitrogen oxides), which contribute to acid rain. An alternative way to reduce sulphur emissions is to apply the proven chemical engineering process of physically ‘washing out’ sulphur oxide emissions from engine exhausts by water scrubbing and, in this case, discharge of the acidified effluent into the sea. Whilst initially interesting because of the fuel cost differential of around $300/t. between the 3.5 and 1 % sulphur content fuels, the water scrubbing apparatus requires useful and expensive space on board the vessel. More fundamentally, the oceans are already shown to be acidifying due to carbon dioxide absorption; to accelerate this process by adding aqueous, acidic, sulphur and nitrogen oxides is unlikely to be accepted as a long term solution.

Addressing one problem usually leads to another; sulphur is very effectively reduced/removed from high sulphur Marine Fuel Oils by catalytic hydrogenation. The treated fuel then contains ppm-levels of silicon and aluminium oxides as very fine, extremely hard, particulates from the ceramic-based catalyst which can cause rapid wear in the engine components of high pressure fuel pumps, injectors and cylinder bores. The standard has been set by IMO in ISO 8217:2010(E), Appendix J, for Marine Fuel Oils [10] as 60 ppm for their combined aluminium and silicon content.

3.4 Other Refinery Products

Other than the fuels described above, other products from crude oil distillation and processing are the Liquefied Petroleum Gases, LPG, comprised of propane/propylene and butane/butylene in seasonally varying proportions, solvents equivalent to unreformed petrol/kerosene/diesel, paraffin wax extracted from fuels and lubricant base oils by solvent extraction, solid petroleum coke residuals used as solid fuel and heavy, viscous bitumen for road asphalt.

3.5 Trends in World Fuel Consumption

The world is a developing place, subject to the different forces of economic development requiring more power from fuels on one hand and the increasing restrictions of fuel efficiency and emission reduction on the other. Different world

Table 12.1 1993/2003/2013 fuel consumptions, in Mb/day, by global region

Product	Europe	Asia/Pacific	N.America	Total
Light distillates	4.1/4.0/3.0	3.7/6.2/9.6	9.0/10.7/10.7	16.8/20.9/23.3
Middle distillates	5.9/7.1/7.5	6.0/8.3/10.8	5.6/6.9/6.5	17.5/22.3/24.8
Fuel oil	2.4/2.0/1.0	3.6/3.4/3.3	1.6/1.3/0.6	7.6/6.7/4.9
Other products[a]	2.6/3.2/2.8	2.7/4.7/6.8	4.4/5.3/5.5	9.7/13.2/15.1
Total	15.0/16.3/14.3	16.0/22.6/30.5	20.6/24.2/23.3	51.6/63.1/68.1

Product	OECD	NonOECD	Total
Light distillates	15.1/10.7/10.7	–/7.9/12.4	
Middle distillates	14.0/16.7/16.5	–/11.2/17.0	
Fuel oil	5.3/4.3/2.9	–/5.4/6.0	
Other products	8 5/9.9/9.7	–/6.8/10.3	
Total	42.9/41.6/39.8	–/31.3/45.7	

[a] 'Other products' are petroleum coke solids, bitumen, wax, solvents, LPG, refinery gas/fuel and losses

Figures are rounded. 'Total' is the sum of Europe + Asia/Pacific + N.America. 1993 Figures for non-OECD countries are on a different geographical basis and therefore excluded

regions are subject to these in different time scales. Table 12.1 shows the different trends in the European, North America, Asia/Pacific and 'Other' world regions for the successive decades of 1993, 2003 and 2013. It is particularly useful to look at the first entry for 'gasolines' in Europe, where consumption has declined from 1994 to 2014 from the emphasis on fuel efficiency for petrol vehicles together with a market shift towards small diesel vehicles. In the three other regions, petrol consumption has markedly increased, mainly due to increased vehicle numbers but without the emphasis on fuel efficiency.

4 Environmental Issues of Using Refined Hydrocarbon

4.1 Specifications, Use and Emissions of Fuels

The initial purpose of fuel specifications was to assure the user that the product conformed to standards of suitability, purity and performance. Specifications added since include handling, safety, conformity with legal requirements, reliability and environmental issues. 'Specifications' as a wider term includes not only the specific individual fuel specifications, such as for marine fuel oils in ISO 8217:2010(E) [10] and the European automotive diesel, EN590 [11], and petrol, EN228 [12], specifications but must also have regard to the respective Material Specification Data Sheets, MSDS, and further must also conform to the various environmental legislation of various continental blocks such as the EU, individual countries, even various port authorities. Specifications vary as appropriate to each category of fuel and include dynamic performance characteristics such as cetane and octane numbers for diesel and petrol.

The sulphur content of fuels is a major environmental issue and reducing its concentration has had a dramatic effect on fuel formulation to maintain performance. Marine fuel oil is the heaviest fuel considered and with the highest potential level of sulphur content.

4.2 Marine Fuel Oil and ISO 8217:2010(E)

For economy, large vessels have very large, very efficient, single engines which operate on the turbocharged two-stroke cycle at low speeds of the order 60–80 rpm. The power output is very high, of the order of 20 MW or more and the low rotational speed enables the engine to be directly connected to the propeller without an energy-absorbing gearbox. Piston diameters can be of the order of 900 mm. The engine uses low quality, low cost residual fuel oils, termed ‘bunker fuels’, defined as the ‘Residual Marine Fuel Oils’, the RM series, in ISO 8217:2010(E). The term ‘residual’ is apt as the fuel contains the concentrated molecular debris of the crude oil from which the lighter, higher quality, fuels have been removed by distillation. However ‘residual’ the RM fuels have been in the past, standards have risen in the light of operating and environmental experience and many physical and chemical parameters are now controlled by specifications such as ISO 8217:2010(E) and its many Appendices. Generators and pumps auxiliary to the main engine use smaller, higher speed engines using distillate fuels, the DM series, as used by smaller vessels.

Residual fuel oil is a viscous, foul, material which requires on-board treatment before use. Because of its high viscosity it must be heated for pumping and the specified temperature for entry into a centrifugal solids separator/filter is 98 °C, to reduce solids, particularly catalyst fines initially at 60 ppm or less, to a level less than 15 mg/kg., as recommended by engine manufacturers, to minimise abrasive wear of engine components.

4.2.1 Ignition Quality

The Cetane Index of a fuel measures its ability for spontaneous ignition under pressure and temperature when injected as an atomised spray into the compressed air mass in an engine cylinder. The cetane number for automotive diesel is of the order of 50–55, i.e., a short delay between compression and ignition. MFOs have much lower cetane numbers, around 10–15, and the ignition delay correspondingly longer, accommodated by the very much lower cylinder speeds of large marine diesel engines.

4.2.2 Fuel Sulphur Levels and Fuel Desulphurisation

The marine fuel sulphur content reduction issue is now into its second phase of resolution. The essential issue is that fuel sulphur forms sulphur dioxide and trioxide (‘sulphur oxides’) when burned in an engine; when emitted to the environment the sulphur oxides react with water to form sulphurous/sulphuric acids and thereby acidify the environment. The sulphur content of solid and liquid land fuels was reduced from the 1960s to very low levels; use of high sulphur residual fuels by vessels on oceans, coastal waters and harbours was increasingly noticeable, environmentally incongruous and could not be justified. The successive Clean Air Acts of the UK [3], commencing in 1956, sought to restrict polluting emissions, including acid gases such as sulphur dioxide, from vessels in port. It is not now meaningful to follow the decrease in sulphur levels standards of marine fuels oils with time but to note that the starting point in the late twentieth century was up to 4.5 % sulphur content used on oceans away from continental waters: the 2015 situation is that within ECA’s, for post-January 2015 vessels must use 0.1 % sulphur DMA fuel or liquefied natural gas and a maximum of 1 % sulphur outside ECA’s on oceans. Future MFO limits outside of ECA’s are proposed as 0.5 % by 2020, but may be delayed to 2025 because of supply capacity issues.

Fuel desulphurisation is either a refinery operation or post-combustion washing. At refineries, sulphur is removed by reaction of the residual oil with hydrogen at increased pressures and high temperatures using a catalyst. The catalyst has an alumino-silicate support base and is partially physically degraded in use to give aluminium and silicon oxides as ‘fines’; these are very hard, fine, particles which could cause substantial abrasive wear in engine components unless reduced prior to use in engines. The context to the IMO limits on total aluminium and silicon are described in S.3.2 The process is effective up to 85 % reduction of the MFO sulphur content but requires considerable investment in refinery plant for a defined throughput. The sulphur is eventually recovered as elemental sulphur and used in fertiliser production, amongst other uses. Any refinery operation has substantial financial implications; the processes to remove up to 85 % sulphur from residual fuel substantially increase the price of the resulting low sulphur fuel.

Commercial shipping is intensively financially competitive; the higher cost of reduced sulphur marine fuel oil is a substantial increased operating expense and alternatives are looked for. ‘Scrubbing’, as a chemical process operation, of the engine exhaust by sea water is the major alternative which absorbs and neutralises the acidic sulphur oxides. Sea water is sprayed into engine exhaust within a chamber to cool the gases by evaporation; the cooled gases then pass into a packed chamber where a further sea water counterflow washes out the sulphur oxides. The acidified effluent from the scrubber is discharged into the vessel’s wake where it is rapidly dispersed and neutralized by the very slightly alkaline seawater. The gases are re-heated by an exhaust heat exchanger to raise their dewpoint and reduce the density of the white plume of exhaust vapour. Whilst the higher sulphur content/lower cost marine fuel oils can be used if exhaust scrubbing is used, there is an investment cost for the scrubbing equipment and also a significant space requirement on vessels where every space has commercial value. The final issue is the addition of acid effluent to open waters when the oceans are already acidifying by carbon dioxide absorption.

4.2.3 The ISO 8217:2010(E) Fuel Oil Specification [10]

The importance of definitions and standards for fuel, and marine fuel in particular, is illustrated by the current, 2015, specification for marine fuel oil, ISO 8217:2010 (E), prepared by ISO Technical Committee ISO/TC 28, *'Petroleum products and lubricants, Subcommittee SC 4, Classifications and specifications'.* The specification document consists of 48 pages and has many references to other specifications and standards. It covers all of the specification requirements gained by custom and practice over many years.

The first part comprises sections of a Foreword, Introduction, Scope, Normative References, Application, Sampling, General and New Requirements, Test Methods and the Precision and Interpretation of Test Results.

The second part consists of 'informative' Annexes for (a) Bio-derived products and Fatty Acid Methyl Esters (FAMEs), (B) Deleterious materials, (C) Sulphur content, (D) Hydrogen sulphide, (E) Specific energy, (F) Ignition Characteristics of residual marine fuels, (G) Flash Point, (H) Acidity, (I) Sodium and Vanadium, (J) Catalyst fines, (K) Used Lubricating Oil and (L) Precision and Interpretation of test results, completed by a Bibliography. Whilst the Annexes are labeled as 'informative' the stated standards and procedures within them are usually written as obligations within the contract for the supply of marine fuel oil or in the fuel clauses of a charterparty agreement between Owners and Charterers for a vessel charter. The centre of the ISO 8217 standard is two tables setting out the physical and chemical characteristics of Distillate Marine fuels, the 'DM' series and the same for Residual Marine fuels, the 'RM' series.

The *'-2010'* part of the specification title indicates that there have been previous specifications, e.g., ISO8217:2005, and that there will be subsequent, further, revisions in due course. Six revisions/amendments to the DM series were made between the 2005 and 2010 version of ISO 8217 and ten revisions/amendments to the RM series. Four new annexes were added. Whilst all changes were significant, one is chosen here to demonstrate the attention to detail of the evolving marine fuel oil market – in Annex J the 2010 permissible level of catalyst fines in Marine Fuel Oil was reduced from 80 mg/kg to 60 mg/kg. The change arose from the engine manufacturers recommendation that following on-board treatment the fuel entering the engine should contain less than 15 mg/kg Aluminium + Silicon/Fuel to ensure minimum risk of abrasive wear to engine components. The reduction recognizes an overall lower operational cleaning efficiency of the fuel than had been previously determined on-board ship. Annex J also specifies the conditions for adequate pre-treatment of fuel.

The RM series of Marine Fuel Oils (MFO), defined within ISO 8217:2010(E), is one of the few hydrocarbon fuel types that require extensive onboard purification treatment before it can be used in an engine. The RM fuels are so viscous at normal temperatures that they must be heated to dissolve any wax/hydrocarbon solids and also for pumping for delivery to a settling tank. From this tank the MFO is pumped through a centrifugal filter to remove solids and sludges into a service tank and then to the engine injectors. The efficiency of separation by this method of 'hard solids' from the marine fuel oil in the presence of soft sludges is interdependent on their concentration dependence – high sludge levels will decrease the 'hard' solid removal efficiency, and vice versa. ISO 8217:2010(E) specifies a level of 0.1 % for 'sediments'. Another separation performance parameter is the operating temperature of the centrifugal filter; ISO 8217:2010(E) specifies 98 °C as the MFO temperature for optimum efficiency. The rate of MFO passing through the centrifugal filters also affects the separation efficiency. As at least two centrifugal filters are usually installed on a vessel, they may be used in parallel, to maximise throughput with lower separation efficiency, or in series to maximize separation efficiency but with lower throughput, dependent upon the overall fuel flow rate required. The purpose of the centrifugal filters is reduce suspended solids such as sludges and the hard catalyst fines, from the maximum allowed in Marine Fuel.

Oils under ISO 8217:2010(E) of 60 mg/kg down to less than the 15 mg/kg recommended by the engine.

4.3 Fixed Large Industrial Boiler and Power Plants Fuels

The last decade has seen a substantial decline in the use of high viscosity/high sulphur oils as boiler fuel for electricity power generation, process steam raising and other industrial operations such as pumping. The cost of heavy fuel oil has increased in line with the increased price of crude oil. Gas is easier to use and fouls boilers less, for increased longer term efficiency.

A further reason for the replacement of heavy fuel oil by natural gas is the increased fuel efficiency gained by changing to Combined Cycle Gas Turbine electricity generation technology from conventional (heavy fuel) oil fired furnaces raising steam to drive steam turbine generators. CCGT technology, for the same generating capacity, is requires less footprint, less capital investment and is quicker to build than conventional oil-fired, steam raising, turbine generation.

Being land-based and fixed installations, the acid sulphur oxides emissions from plant burning high sulphur are more tightly controlled than emissions from vessel's engines on the ocean. Flue Gas Desulphurisation, FGD, has been proposed to reduce sulphur oxide emissions but requires substantial investment; large scale FGD has only been applied to coal-fired plant in Britain. The utility and availability of cleaner alternative fuels for industrial use together with restrictions on sulphur oxides emissions has considerably reduced the use of high sulphur, high viscosity fuel oil.

4.4 Small Industrial and Domestic Fuels

‘Gas oil’ is a distillate similar to automotive diesel but less tightly specified. The tendency to form smoke, the ‘smoking tendency’, arises from higher boiling point components in the fuel which take longer to burn; if the residence time of the fuel within the combustion chamber is less than the time to burn these components, then partial combustion results, forming smoke. The ISO 3405 [14] distillation procedure standard defines gas oil, amongst other hydrocarbon fuel grades, as a fuel for which 65 % (minimum) is recovered by distillation at 250 °C and 85 % (minimum) at 350 °C. A 1.5–5.5 cSt viscosity fuel is used with pressure jet burners which turbulently mix the fuel with combustion air for complete combustion.

Home heating oil/domestic kerosene has been used in the past in wick-fed convenient, low cost and portable heaters. As heating facilities and standards have increased in Europe, the US and Japan, the use of these heaters has drastically decreased although they are still used extensively for heating and cooking in Asia, particularly in rural areas. For domestic use in the EU, the fuel sulphur content must be low; for flued burners 0.2 % sulphur is the specified maximum, for unflued, wick-type, burners, the specified maximum sulphur concentration is 0.04 %. Maximum sulphur specifications vary across countries, from 0.25 % m/m in India down to 0.015 % m/m in Japan.

Further considerations, in addition to the sulphur content, are the smoke point (which should be high) and the char value (which should be low). Both are influenced by the distillation end point, reducing the overall sulphur content and by ‘sweetening’ the fuel by removing any organic sulphur compounds.

4.5 Automotive Diesel Fuel

Heavy vehicles worldwide, buses, trucks and construction vehicles, are almost entirely powered by diesel engines. The striking feature of light diesel vehicle registrations over the past decade is their rapid increase in Europe and Asia because of their superior fuel consumption relative to petrol vehicles; in some EU countries the light vehicle penetration of diesel vehicles is over 50 %; the 2014 UK market penetration was 40 %. Equally striking is their very low penetration in the North American light vehicle market.

Diesel engines operate with a substantial excess of air, i.e., a high air/fuel ratio, on the Diesel thermodynamic cycle which, together with the fuel and its method of addition/injection, allows a much higher compression ratio to be used than the Otto (petrol) cycle. The high compression ratio of diesel engines gives a better thermodynamic efficiency than the Otto (petrol) cycle which translates into lower/better fuel consumption than petrol vehicles. When compared to petrol engines, developments over the last two decades in diesel engine overall operation have been improved performance, reduced noise and vibration, reduced emissions and also reduced price differential. These improvements have been achieved through turbo-charging, intercooling, higher injection pressures from a very high pressure ‘common rail’ fuel system, electronic control of injectors and their timing, exhaust catalysts and particulate traps. Larger capacity engines may have an exhaust gas recirculation (EGR) system to reduce nitrogen oxide emissions by reduction in peak combustion temperatures. Sophisticated electronic engine management systems adjust the amount of fuel injected at the optimum time in each cycle, according to the engine operating condition of load and speed. These systems optimize overall performance of the engine and reduce fuel consumption and also emissions.

4.5.1 Diesel Fuel Composition

The composition of diesel fuel is specified within Europe by the EN590 [11] standard, introduced in concert with the European diesel emission standards, ‘Euro 1’ (1993) [15] in 1993 and has been systematically revised since to ‘Euro 6’ in 2014. The US standard for diesel fuel is ASTM D975.

The EU diesel sulphur content [11] has reduced from 0.2 % (2000 ppm) in 1993 to 10 ppm in 2009, now known as ‘ultra low sulphur diesel’. Whilst the reduction in sulphur is beneficial in performance and environmental effects, the sulphur compounds previously present had a lubricity function which is replaced by additives to prevent excessive wear of fuel pumps and injectors, as tested by EN ISO 12156-1 [16]. The physical test requirements of EN 590 is set out in Table 12.2, the Russian GOST R 52368-2005 [17] diesel regulations are similar except that the sulphur content is much higher at 350 ppm and the Fatty Acid Methyl Ester content restricted to 5 %.

Diesel fuel forms waxes when exposed to prolonged low temperatures; these clog fuel lines and the fine particulate filters used to protect the precision engineering of injectors. Up to 20 % of the gas oil components used to formulate automotive diesel can be heavier hydrocarbons of limited solubility/compatibility with the lighter hydrocarbons forming the rest of the fuel and will separate as wax at lower temperatures. The separation process depends both upon the temperature at which the fuel is held and the time for which it is held. A further sub-set of EN 590 defines ‘Winter Diesel’ which is formulated to meet certain winter weather conditions in specific countries of the European Union, e.g., the climatic differences between southern Italy and northern Finland. The primary division divides standard EN590 into ‘temperate’ and ‘arctic’ climatic zones.

The temperate climatic zones are divided into six Classes, A-F, solely on the basis of the Cold Filter Plugging Point (CFPP, ASTM D6371 [18]) value. The other properties of density at 15 °C index, viscosity at 40 °C, Cetane Index and Number are the same for Classes A-F. The CFPP test estimates the lowest temperature at which a fuel will flow through without difficulty in a fuel system, i.e., without wax crystals forming a blocking mass within the fuel pipes or filter. The Class A CFPP value is +5 °C; the subsequent CFPP values for Classes B-F progressively decrease by 5 °C increments to a CFPP of −20 °C for Class F. Many northern and eastern European countries require diesel fuel to meet a specific class in winter, thus

Table 12.2 Physical test requirements for the diesel EN590 standard

Property	Unit	Lower limit	Upper limit	ENISO Std.
Cetane index/number		46.0/51.0	–	4264/5165
Density, 15 °C	kg/m^3	820	845	3675/12185
PAH’s	%(m/m)	–	11	12916
Sulphur content	mg/kg	–	10	20846/20884
Flash point	°C	>55	–	2719
Carbon residue	%(m/m)	–	0.3	10370
Ash content	%	–	0.01	6245
Water content	mg/kg	–	200	12937
Total contamination	mg/kg	–	24	12662
Cu strip corrosion	Rating	Class 1	Class 1	2160
Oxidation stability	g/m^3	–	25	12205
Lubricity wear scar	μm	–	460	12156-1
Viscosity @ 40 °C	mm^2/s	2.00	4.50	3104
Distillation. rec’d 250/350 °C, %V/V	–	<65	85	3405
95 %(V/V) recovered at °C	–	360		
Fatty acid methyl ester %(V/V)	–	7		14078

Western and Central European governments require diesel fuel to meet Class F specification during winter, at least from the end of November to the beginning of March, known as ‘winter diesel’, ‘vinterdiesel’, ‘diesel d’hiver’.

For colder winter seasons, as in Scandinavia, a more demanding set of diesel fuel specifications are set, Table 12.3. Diesel fuel for winter in Scandinavia must meet Class 2, commonly known as ‘Polar Diesel’, ‘diesel polaires’.

‘Cloud Point’ [19] is the temperature at which a haze occurs in a cooling, clear, fuel, determined by ASTM 2500. ‘Cold Flow’ additives alter the characteristics of the wax crystals as they form to reduce the CFPP value significantly below the Cloud Point, e.g., with current additives a CFPP of −20 °C for diesel fuel can be achieved for a Cloud Point of −7 °C. Other additives used in diesel fuel are:

- polydimethysiloxanes, or ‘silicones’ of optimized molecular weight, at the low ppm level as anti-foam agents to prevent foaming spills when fuelling,
- friction modifiers which deposit in the engine upper cylinder and piston ring pack to reduce friction and improve fuel efficiency,
- detergents to remove thermally produced deposits from injectors,
- anti-wear and lubricity additive compounds to reduce fuel system and storage wear at the high pressure and shear rates used in current systems,
- corrosion inhibitors to protect metal fuel delivery and storage systems,
- cetane improvers, for easier starting,
- stabilizing compounds to prevent formation of gums and deposits,
- in some cases, a ‘pleasant odourant’ to counter the pervasive and sometimes unpleasant odour of diesel fuel, to some,

Table 12.3 Arctic climate zone diesel fuel specifications

Characteristic	Class 0	Class1	Class 2	Class 3	Class4	Unit
CFPP	−20	−26	−32	−38	−44	°C
Cloud point	−10	−16	−22	−28	−34	°C
Density @ 15 °C	←-----800–845-----→			←800–840→		kg/m^3
Viscosity @ 40 °C	←------1.5–4.0-----→			1.4–4.0	1.2–4.0	mm^2/s
Cetane index	46	46	45	43	43	
Cetane number	47	47	46	45	45	

Diesel fuel quality has substantially improved over the two decades prior to 2014 and the direction of further improvement is not clear. Diesel fuel is formulated from various difference sources of ‘gas oils’, from the ‘straight run’ gas oil distilled from crude oil, ‘hydrocracked’ gas oil, thermally cracked gas oil and synthetic gas oil from natural gas. All of these components have different densities and cetane numbers yet must be combined into a closely defined fuel between 820 and 845 kg/m^3 density and a cetane number of over 51. Premium diesel fuels are now offered with cetane values of 55 or more with decreased consumption and noticeably smoother operation.

4.5.2 ‘Bio-Diesel’

The physical properties of diesel fuel are suitable for the addition/substitution/supplementation of biofuels in the form of ‘Fatty Acid Methyl Esters, FAME’ from vegetable oils. The use of vegetable oils as diesel engine fuel has been demonstrated, e.g., tractors running on peanut oil, but their combustion tends to form internal engine deposits which limit engine between overhauls, and the oils are not stable against ‘hardening’ oxidation deposits during storage. Vegetable oils are ‘triglcerides’, with three organic acid groups esterified with the tri-hydric glycerol to form one molecule which can form solids, ‘fats’. ‘Methyl esterification’ of vegetable oils is analogous to making soap where methyl alcohol is the reactant with sodium hydroxide as the catalyst, to separate the three attached organic groups into individual esters. The methyl esters formed have much lower melting points than the triglycerides and are physically oils rather than fats; chemically they are single, separate, esters of the long chain organic acids. FAME is physically compatible/miscible with standard diesel oil and EN590 allows up to 7 % FAME content, although in 2014/5 the amount added is around 5 %.

An issue with bio-diesel is the considerably differential volatility of ‘mineral’ diesel and FAME. Under low energy operation conditions of an engine, i.e., relatively cool operation, fuel dilution of the lubricant occurs by deposited FAME. This decreases lubricant viscosity and increases the apparent volume of the lubricant. When the engine is subsequently operated at a higher energy, higher temperature level, the ‘mineral diesel’ evaporates but the FAME component evaporates more slowly and may build up in the lubricant.

4.5.3 Combustion of Diesel Fuel

Diesel combustion is initiated by a very high pressure, highly atomized and dispersed, spray of fuel injected into an adiabatically compressed, high temperature, charge of air in the engine cylinder head. The adiabatic compression process of the air drawn in is transiently thermally isolated from its surroundings. At the temperature of the compressed air charge, the injected fuel spray spontaneously ignites to generate a turbulent flame front. This accelerates across the cylinder to consume the fuel, generating heat and pressure which drives down the piston to generate mechanical power.

Improvements in diesel fuel, as described, engine design and operation have reduced diesel particulate emissions, and therefore smoke, to very low levels. There is a parabolic relationship in the diesel combustion process between particulate formation and nitrogen oxide formation, Fig. 12.4. If ignition timing is retarded then the peak combustion pressure and temperature is reduced, particulate emission increases and nitrogen oxides formation decreases. Alternatively, if ignition timing is advanced then the peak combustion pressure and temperature is increased, nitrogen oxide formation increases and particulate formation decreases. The particulates emitted have very small diameters and are characterized as PM_{10}, $PM_{2.5}$, etc., as a definition of their average diameters. These particulates are retained in human lungs following inhalation [3].

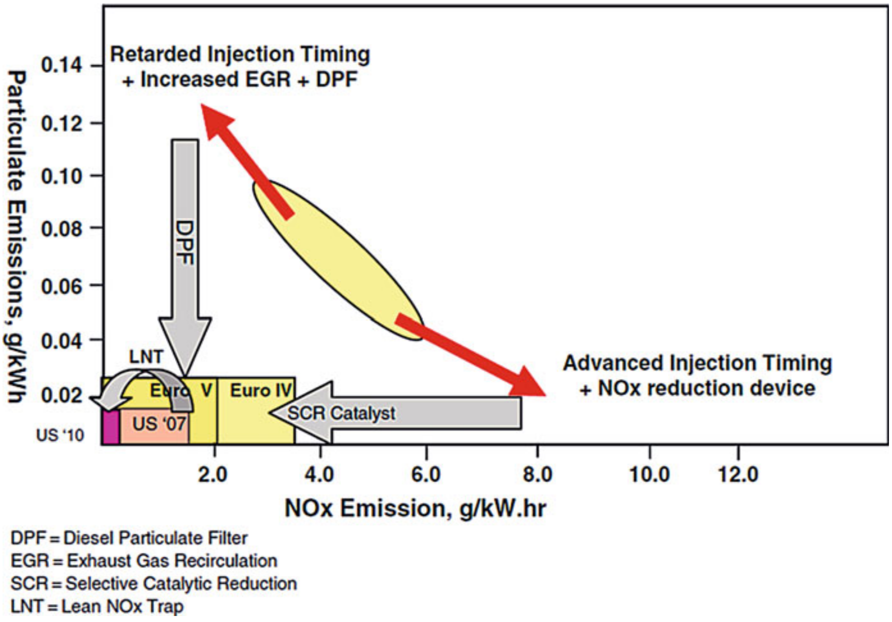


Fig. 12.4 Required decreases in diesel particulates and NO_x, showing the after treatment technologies (DPF, EGR, SCR and LNT) required to meet exhaust emission standards. Note the parabolic relationship between particulate and NO_x emissions in diesel combustion (From Atkinson D, Brown AJ, Jilbert D, Lamb G (2009) Chapter 9, 'formulation of automotive lubricants. In: Mortier RM, Orzulik S, Fox MF (eds) Chemistry and Technology of Lubricants, 3rd.Edn., Springer

Both nitrogen oxide and particulate emissions must be reduced to very low levels. A policy decision has been made to concentrate on reducing nitrogen oxides by configuring diesel engine combustion. The residual nitrogen oxides are reduced by Selective Catalytic Reduction to nitrogen and oxygen using a urea solution. North America and the EU have required substantial decreases in diesel emissions over the last two decades.

The particulates are filtered out using a coarse in-line ceramic filter. As the filtered layer of particulates builds up, the pressure drop across the filter system increases and the particulates must be removed. Almost all of the trapped particulate is carbon and is removed by increasing the filter temperature to burn it off. When sufficient pressure drop across the filter is sensed, additional fuel is programmed in the engine management system to be injected into the engine, or alternatively, into the exhaust system and ignited in the ceramic filter, to burn off the carbon.

4.6 Aviation Jet Kerosine

Aviation kerosene jet fuels are distillate fuels between petrol/gasoline and diesel, with carbon numbers between C_5 and C_{16}. Aviation fuel quality is strictly controlled to prevent engine failure in flight and such problems are extremely rare. The basic issue is to maintain that strict quality control whilst large jet fuel volumes are stored, often for long periods, transported and then transferred into the fuel tanks of aircraft. In doing so, the jet fuels contact with a range of materials and fuel-related problems can occur. Anti-oxidants and metal de-activators are added to jet fuel to improve its stability against degradation, leading to gum and sediment formation. Addition of corrosion inhibitors and lubricity additives protect the jet aircraft fuel system of tanks, pipes, filters and pumps from wear and corrosion. Anti-icing additives dissolve any free water in the fuel to prevent it freezing at high altitude temperatures, causing blockages in fuel lines and filters, and added biocides stop bacterial/fungal growth which can block pipes and filters and also corrode fuel systems metals. It was surprising to find that bacteria and fungi could grow under anaerobic conditions in jet fuel hydrocarbons within tanks; now biocides are added to prevent their growth.

Water in jet fuel has a specification limit of 30 ppm, a level at which water is absorbed, dissolved or dispersed in the jet fuel, semantic points for the presence of a polar substance, water, in a non-polar, low permittivity medium, the jet fuel. At 20 °C 30 ppm water in jet fuel gives a single phase. The presence of water in jet fuel is a constant and serious problem. It is a constant problem because movement of large volumes of jet fuel into and from storage tanks, with the associated contact with humid air which deposits water onto the cold tank walls – a problem for handling all hydrocarbons but it is particularly important that jet fuel be free from water contamination. It is a particular problem for jet fuel because upper atmosphere flights decrease fuel temperatures due to low external temperatures at which dissolved water precipitates out and falls to the bottom of the tank because of its higher density. Fine water droplets can supercool below 0 °C but on impact with surfaces, they freeze and may suddenly block fuel inlet pipes, the cause of the British Airways Flight 38 [20] accident at London Heathrow. It is impractical to remove all water from jet fuel and fuel line heaters are used on commercial aircraft to prevent water from freezing in fuel.

Stringent procedures are used to keep the water content of jet fuel below 30 ppm. Land-based vehicle jet fuel delivery tankers have a large water filter assembly in their final delivery line. Several methods are used to detect water in jet fuel, the simplest is a visual check to detect high concentrations of suspended water in fuel as a 'hazy' appearance, only meaningful as a wholly unacceptable level. More relevant is a standard chemical test to detect free water in jet fuel using a filter pad sensitive to water which indicates 'green' if the specification limit of 30 ppm 'free water' is exceeded.

4.6.1 Aviation Jet Fuel Specifications

Jet fuel specifications are stringent and rigidly enforced, subject to specifications led by the US ASTM, UK MoD DEF STANDARD and GOST for the CIS and associated states:

- Jet A-1 fuel must meet DEF STAN 91-91 (Jet A-1), ASTM specification D1655 (Jet A-1), and IATA Guidance Material (Kerosene Type) [21], NATO Code F-35 [22]. Jet A-1 is the standard specification fuel in the rest of the world,
- Jet A fuel must meet ASTM specification D1655 (Jet A) [23], and has been available within the United States since the 1950s but not usually available outside (Table 12.4).

Both Jet A and Jet A-1, with carbon numbers between 8 and 16, have flash points higher than 38 °C and a primary difference between them is the lower freezing point of Jet A-1 at −47 °C compared to Jet A at −40 °C. Another difference between Jet A and Jet A-1 is the mandatory addition of an anti-static additive to Jet A-1. DEF STAN 91-91 (UK) and ASTM D1655 (international) specifications allow for certain additives in jet fuel:

- antioxidants to prevent gum formation, usually based on alkylated phenols,
- antistatic agents, as static electricity dissipators and prevent gum formation, based on dinonylnaphthylsulfonic acid,
- corrosion inhibitors,
- fuel system icing inhibitor agents,
- biocides, to stop bacterial/fungal growth in aircraft fuel systems,
- metal deactivators, to remediate deleterious effects of trace metals on fuel autoxidation/thermal stability, such as N,N′-disalicylidene 1,2-propanediamine.

Jet B is a lighter composition, C_{5-15} naphtha/kerosene fuel, approx. 30 % kerosene and 70 % gasoline, used for enhanced cold-weather performance. Its lighter composition gives a higher volatility and a low flash point, therefore it is

Table 12.4 Typical physical properties for Jet A/Jet A-1, Jet B and TS-1

Fuel	Jet A	Jet A-1	TS-1	Jet B
Specification	ASTM D 1655	DEF STAN 91-91	GOST 10227 [24]	CGSB-3.32
Acidity, mg KOH/g	0.10	0.015	0.7 mg KOH/100 ml	0.10
Aromatic, %vol.max	25	25.0	22 (% mass)	25.0
Sulphur, mass %	0.30	0.30	0.25	0.40
Sulphur, mercaptan, mass %	0.003	0.003	0.005	0.003
Distillation, °C				
Initial boiling point		Report	150	Report
10 % recovered, max.	205	205	165	Report
50 % recovered, max	Report	Report	195	Min.125, max 190
90 % recovered, max	Report	Report	230	Report
End point	300	300	250	270
Vapour pressure, kPa, max.	–	–	–	21
Flash point, °C, min	38	38	28	–
Autoignition temperature	245	245		
Density, 15 °C, kg/m^3	775–840	775–840	min.774@20 °C	750–801
Freezing point, °C	−40	−47	−50 (Chilling Point)	−51
Viscosity, −40 °C,mm^2/s, max	8	8.0	8.0 @ −40 °C	–
Net heat of combustion, MJ/kg, min	42.8	42.8	42.9	42.8
Smoke point, min., min	18	19.0	25	20
Naphthalene, vol.%, max	3.0	3.00	–	3.0
Cu corrosion, 2 h.@ 100 °C, max rating	No.1	No.1	Pass (3 h @ 100 °C)	No.1
Thermal stability				
Filter pressure drop, mm.Hg, max.	25	25	–	25
Visual tube rating	<3	<3	–	<3
Static test 4 h@150 °C, mg/100 ml, max	–	–	18	–
Existent Gum, gm/100 ml, max	7	7	5	–

more potentially dangerous to handle and rarely used except in very cold climates. It has a very low freezing point of −60 °C and is primarily used in some military aircraft and also Canada because of its low freezing point.

As aviation transport has increased, so the demand for aviation jet fuel kerosine has increased to >5 % of all refined products from crude oil. Refineries have optimized the yield of jet fuel, a high value product, by varying process techniques. New refinery processes for jet fuel use flexible choice of crudes and coal tar sands and the production of synthetic blend stocks, sometimes requiring additives.

4.6.2 Military 'JP Fuels'

Some of JP ("Jet Propellant") military jet fuel classifications systems are almost identical to civilian classifications, differing only by the treat rates of some additives. Military fuels are highly specialized formulations and developed for very specific applications. Thus, JP-8 [25] is similar to Jet A-1 and JP-4 is similar to Jet B. JP-8 is specified and widely used by the US Military as a fuel for both jet aircraft and diesel fueled vehicles. Specifications MIL-DTL-83133, Def. Std. 91-87 and NATO code F-34 for JP-8 are projected to remain until 2025. The U.S. Navy uses a similar formula, JP-5, but with a higher flash point of >60 °C because of the greater fire risk on aircraft carriers. When JP-8 is used as a single fuel it greatly simplifies military logistics, for in addition to an aircraft fuel, JP-8 is used as a fuel for heaters and stoves and also as a fuel in the diesel engines of nearly all NATO tactical ground vehicles and electrical generators. It is used as a coolant in engines and some other aircraft components. The JP-8 formulation has icing and corrosion inhibitors, lubricants, and antistatic agents but less benzene and *n*-hexane than JP-4.

There are other JP fuel numbers for increasingly particular applications but of minor interest. There were two threads to the development of further 'JP' fuels – the first was the development of fuels for very specialized aircraft, some of which have been overtaken by other technologies, e.g., the SR-71 high altitude reconnaissance aircraft required specialised fuel development but its function is now overtaken by satellite photography. The second thread has been the development of renewable jet fuels to reduce US dependence on imported petroleum and develop secure domestic sources for military energy. However, the extensive development of 'fracking' has led the US becoming self-sufficient in hydrocarbons and then a net exporter.

Jet A-1 and Jet A is identified in trucks and storage by the UN Hazardous Material Sign with the number '1863'. Jet A trucks, storage tanks and plumbing carrying Jet A are marked with a black sticker with "Jet A" in white printed on it, adjacent to another black stripe.

4.7 Spark Ignition (Petrol/Gasoline) Fuels

Spark ignition engines operate at lower compression ratios than diesels at around 8:1. The fuel is mixed outside of the engine in the inlet manifold, now by multi-port fuel injection, previously by carburettors and drawn in by the induction stroke, then compressed and ignited close to the Top Dead Centre piston position. (GDR engines are rather different in the induction/fuel injection procedure) There have been significant improvements in engine performance over the past two decades in terms of fuel efficiency and emissions and also in the composition of petrol fuel.

Improved engine efficiency has been achieved by design changes including multiple valves per cylinder, such as three, four or even five instead of two, as one inlet and one exhaust valve. The timing of the valve opening/closing has been fixed in the past; a further development is variable valve timing of either one or both inlet and outlet valves to a pre-programmed engine speed profile, to further increase the efficiency of fluid gas transfer into and out of the engine.

Combustion modeling has contributed to improvements in efficiency and reductions in emissions. Changes in the shape of piston crowns and the corresponding combustion chamber have enhanced turbulence as the mixed air charge and petrol fuel are compressed and then ignited, improving the efficiency of combustion and reducing emissions. Overarching these development are microprocessor engine management systems, which continue to develop. The basic microprocessor inputs are engine speed, load, input air/fuel mixture, temperature and exhaust composition. The input air/fuel mixture is measured by an air flow meter and the injected fuel mass. The exhaust composition is measured by a solid state zirconia electrode. Whilst these developments reduce exhaust emissions, the levels of pollutants remaining are still too high to meet exhaust emission regulations.

The problem of controlling hydrocarbon, carbon monoxide and nitrogen oxide emissions from petrol-fuelled, spark ignition engines commences with the basic chemical equation for the combustion of petrol, taken overall as C_6H_{11} from the various types and ranges of hydrocarbons, is:

$$C_6H_{11} + 8.75O_2 = 6CO_2 + 5.5H_2O$$

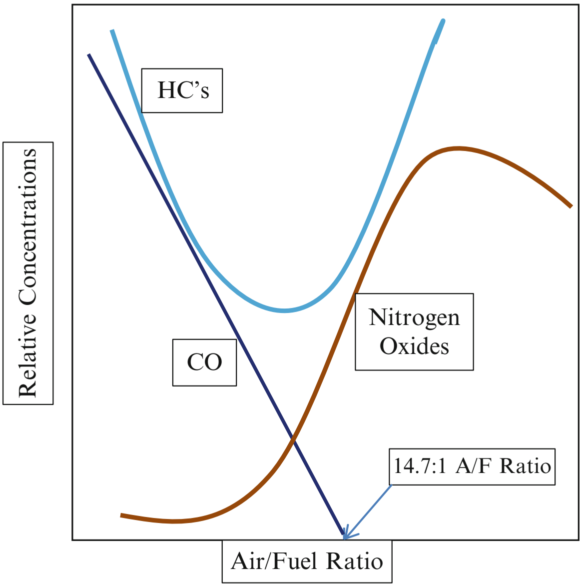
A mass balance includes the nitrogen in the combustion air at 21 % oxygen and 78 % nitrogen, as a first approximation, not including the argon, atmospheric water vapour and carbon dioxide contents, as:

$$C_6H_{11} + 8.75O_2 + 32.5N_2 = 6CO_2 + 5.5H_2O + 32.5N_2$$

Nitrogen appears on both sides of the equation because it passes through engines without reaction, other than the marginal formation of nitrogen oxides. Using simple unitary atomic weights and only considering petrol, oxygen and nitrogen, the stoichiometric, or exact chemical balance, Air/Fuel (A/F) ratio is 14.34. Allowing for trace components as described and using exact, fractional, atomic weights, the Air/Fuel Ratio is 14.7. This value is the stoichiometric value which is fundamental and pivotal to considering petrol-fuelled engine emissions:

- for above this value, ***greater*** than an Air/Fuel ratio of 14.7, the mixture is ***lean*** (of fuel), there is an excess of combustion air (oxygen) and the light blue peak

Fig. 12.5 Generalised petrol engine emissions plot against air/fuel ratio



flame front combustion temperatures are maximized, therefore nitrogen oxide formation increases,

– for below this value, ***less*** than an Air/Fuel ratio of 14.7, the mixture is ***rich*** (in fuel) and the yellow(-ish) peak flame front combustion temperatures are lower. There is insufficient air (oxygen) for complete combustion, therefore carbon monoxide is formed rather than carbon dioxide and hydrocarbons are either not burned or partially burned.

The combustion chemistry and resulting emissions of operating petrol-engined vehicles is set out in Fig. 12.5 as a general, illustrative, non-quantified scheme. It is striking that carbon monoxide emissions decrease almost linearly down to the stoichiometric value from the rich-fuel side, whereas nitrogen oxide emissions increase beyond the stoichiometric value as the combustion temperature increases until the excess air dilutes the reacting air/fuel mixture and the temperature falls.

The hydrocarbon emissions are complex with respect to changes in the Air/Fuel ratio. As the Air/Fuel ratio increases towards stoichiometric, hydrocarbon emissions decrease, as the available combustion air/oxygen increases, but then become constant. Beyond the stoichiometric point, the hydrocarbons increase, despite the excess combustion air. This non-chemical behaviour is a physical effect, that of a 'boundary layer' at the piston and bore metal surfaces, where the combustion flame front is quenched by a boundary layer of relatively cool hydrocarbon/combustion air. Increasing the turbulence of the flame front by asymetric in-piston component such as pistons and combustion chambers dramatically increases turbulence and shears the boundary layer of hydrocarbons into the main combustion process.

Overall emission reduction from petrol-fuelled engines cannot be achieved by varying the Air/Fuel ratio as a two-dimensional variation. One exhaust pollutant can be reduced by varying the Air/Fuel ratio but at the expense of increasing others. ***There is no solution to reducing overall exhaust emissions by varying the Air/Fuel ratio.*** A new, different, solution to reducing overall emissions is required, a third dimension.

That different solution to reducing overall exhaust emissions uses a catalytic convertor system. The issue is to oxidise the carbon monoxide and hydrocarbons at the same time as reducing the nitrogen oxides within the same volume. The catalyst system to do this uses platinum, palladium and rhodium variously, very finely dispersed on a fine ceramic matrix at a narrowly defined air/fuel ratio close to the stoichiometric Air/Fuel ratio condition, which can only be achieved using fuel injection systems. Hence, fuel carburetors have been replaced by fuel injection systems which are much more precise over a range of fuel mass flow. These systems are called 'three way converters' and have been mandatory for automotive emission control in Europe since 1993, in Japan and North America since 1975. They are self-heating from the destructive combustion of the polluting emissions and become fully effective at a 'light-off' temperature of around 320 °C. This means that 'three way converters' are ineffective immediately after starting the engine until that temperature is reached; equally, idling engines in congested traffic do not maintain the required temperature for the catalyst system to be effective in reducing emissions. This effect is probably a contributing factor to national environmental levels of automotive emissions not decreasing in concert with the emissions reduction achieved in the standard bench tests.

4.7.1 Petrol Composition

('gasoline' in North America), specified by EN 228 [12]in the EU has developed significantly in the last two decades to respond to substantial developments in engine technology and environmental regulation. The removal of octane improver organolead compounds on environmental and health grounds is now a historical issue; the 95/85 (Research/Motor) octane rating of petrol had to be maintained by other means to give a Euro-standard fuel. The very low level of lead allowed in EN 228, Table 12.5, reflects the low level of intrinsic/natural lead found in petroleum products but excludes added organolead compounds. Added benzene, to improve octane ratings, was replaced by up to 35 % of other aromatics with benzene limited to 1 %. Sulphur at 10 ppm is at a cost-benefit minimum, sufficient to prevent noticeable formation of reduced sulphur in the catalytic convertor system, i.e., unpleasant hydrogen sulphide emissions. The low sulphur level also protects the three way catalyst system from corrosion. Volatility is reduced due to fuel injection systems instead of evaporative, carburettor, systems. Petrol has been 'reformulated' to reduce the photochemical activity of emissions, both in the EU and North America. The oxygenates specification allows for a range of alcohols, ethers and 'others' but actuality lies with the use of ethanol up to 5–7 %, with an eventual

Table 12.5 EN 228 highway petrol fuel specification [12]

	Unit	Minimum	Maximum
Research Octane Number, RON		95	–
Motor Octane Number, MON		85	
Vapour pressure, summer,	kPa		60.0
Distillation, % evaporated at 100/150 °C	% v/v	46/75	–
Hydrocarbon composition			
Olefins	% v/v		18.0
Aromatics	"		35.0
Benzene	"		1.0
Oxygenates			
Methanol	% v/v		3.0
Ethanol	"		10.0
i-Propyl alcohol	"		12.0
t-Butyl alcohol	"		15.0
i-Butyl alcohol	"		15.0
Ethers with >5 °C-atoms/molecule	"		22.0
Other oxygenates	"		15.0
Sulphur content	mg/kg		10.0
Lead content	g/l		0.005

target of 10 %. Issues with ethanol addition to petrol are the availability of the large volumes required, the enhanced absorption of water which can lead to an aqueous ethanol phase separating from the hydrocarbon component at low temperatures and enhanced corrosion of ferrous/non-ferrous metal components of fuel systems. 98 RON value petrol formulations are available for higher performance vehicles.

4.7.2 Avgas

'Avgas' is petrol (gasoline) fuel for reciprocating piston engined aircraft spraying. Aero-piston engines operate the same as vehicle spark ignition engines but at a higher performance level. Total global Avgas volumes are low because piston aircraft are much smaller than jet-fuelled aircraft although greater in number. A range of previous grades was necessarily rationalized into two main Avgas grades, '100' and '100LL low lead', to maintain supply in an otherwise uneconomic market.

Avgas grades are defined first by their octane rating; two ratings are used, the lean mixture rating (lower) and the rich mixture rating (higher), giving a multiple numbering system, e.g. Avgas 100/130 (a lean mixture performance rating of 100 and a rich mixture rating of 130). To avoid confusion and minimise handling errors, common practice initially designates the Avgas grade by the lean mixture performance, i.e. Avgas 100/130 is designated as 'Avgas 100'.

- **Avgas 100** is standard high octane fuel for aviation piston engines with a high organolead content, dyed green for identification, specified by ASTM D 910 and UK DEF STAN 91-90 [26]. The two specifications are essentially the same but with different antioxidancy, related oxidation stability requirements and maximum lead contents.

- **Avgas 100LL** is the ‘low lead’ version of Avgas 100 (a relative term!), with a limit of 0.56 g lead/l. It has the same specifications as Avgas 100, namely ASTM D 910 and UK DEF STAN 91-90. Avgas 100LL is dyed blue.
- **Avgas 82 UL**, specified by ASTM D 6227 [27], is a specialised, relatively new grade formulated for low compression ratio engines which do not require the high octane rating of Avgas 100 and could run on unleaded fuel. Avgas 82 UL has a higher vapour pressure and can be formulated from automotive petrol; it is dyed purple.

To avoid confusion and the wrong fuels being used, all equipment using, and facilities handling the Avgas grades are colour coded for the fuel to be used; they are also prominently marked with the API designations denoting the actual fuel grade carried, stored or used.

4.7.3 The Two-Stroke Cycle and Engines

The use of two-stroke engines has been seriously restricted by environmental emission controls and are no longer used in new automotive applications other than large marine vessels. Their positive attraction is their simplicity of construction, with a minimal number of moving parts additional to the central components of crankshaft, connecting rods and pistons. In its simplest form, a two stroke engine mixes lubricant with the fuel, so no lubricant system of pump, filters, oilways and pipework is required. The lubricant is delivered as a ‘once through’ ‘system, in itself is a potential source of hydrocarbon emissions.

A two stroke petrol engine uses a conventional carburettor to generate an air/fuel mixture drawn into the crankcase. This is gently compressed into the cylinder through the inlet port uncovered when the piston is close to Bottom Dead Centre (BDC). The piston crown is shaped to deflect the incoming air/fuel charge upwards. As the piston rises from BDC it closes off the inlet port and then the exhaust port and compresses the air/fuel mixture. Close to Top Dead Centre the mixture is ignited by a spark plug and the power stroke converts the thermal energy of fuel combustion into mechanical energy, as in other engines. As the power stroke proceeds with the descending piston, the exhaust port is uncovered and the burned mixture is expelled from the system by its remaining pressure. It could be said that gas flow dynamics and sequential exhaust/inlet ports are used to replace the inlet and exhaust valves.

The advantage of the two-stroke cycle is its construction simplicity with only three major moving parts, plus the carburetor. Ignition is by a magneto-type system with a simple bob weight advance/retard timing. Power output is relatively high for the engine volumetric capacity as there is a power stroke for each complete engine rotation, hence the term ‘two stroke’ as the cycle only has induction/compression and power/exhaust strokes. The simplicity of construction of two stroke engines gives the additional advantage of being cheap to make.

The disadvantages of the two stroke cycle stem from the inevitable partial mixing of the inlet and exhaust gases, causing a high level of hydrocarbon emissions in addition to the residual, unburned, lubricant in the exhaust. Lubricant over-treatment of the fuel leads to blue smoke emission, a severe emission problem. Two stroke engine power output is limited by the inherent problem of not being able to achieve a high compression ratio. The power stroke in each rotation can lead to over-heating of the cylinder and piston, leading to pre-ignition. The torque curve of a two stroke engine is usually gentle and engine speed must be increased to a high level to generate power for acceleration. Whilst various measures can be taken to reduce emissions from two-stroke engines they are not effective enough to meet modern standards. The main problems are high hydrocarbon, HC, and carbon monoxide, CO, emissions from a number of processes:

(i) the lubricant is burned with the fuel prior to the power stroke; hydrocarbons from the lubricant and fuel can pass through the engine into the exhaust, effectively a 'short-circuited' gas flow between the inlet and exhaust ports,
(ii) high lubricant treat rates in pre-mix systems, up to 3 % lubricant treat rate,
(iii) an accumulation, 'pooling', of lubricant in the engine crankcase when idling, which causes high smoke emissions levels during subsequent acceleration.

Positive aspects of emissions from two-stroke engines are low NO_x emissions resulting from (i) exhaust gas recirculation (EGR) port scavenging where a small percentage of exhaust gas remains during each induction cycle, reducing peak combustion temperatures, and (ii) lower compression ratios, also reducing peak combustion temperatures.

Technical improvements reducing two stroke emissions include 'low smoke lubricants', graduated 'auto-lube' systems with minimal oiling rates at low engine speeds, fuel injection once the transfer ports are closed to negate 'short circuiting' in the crankcase and oxidation catalysts for two stroke applications. Despite these improvements, the four-stroke engine has become the dominant power unit for today's motorcycles; two-stroke engines are now restricted to off-road and racing applications, small, $<50\ \text{cm}^3$ motorcycles, motor scooters, snowmobiles, boating and portable equipment such as chainsaws, blowers and strimmers. Biodegradable lubricants based on ester-based technology are available for off-road use.

Two main applications remain for two stroke engines, as cheap, small, portable power sources and for very large marine engines. For the first, two issues obtrude, (i) tightening environmental legislation which may extend to, and therefore exclude, small gardening equipment and small transport vehicles, and (ii) advances of small electrical power sources. The power density of rechargeable batteries is increasing steadily and electric motors are decreasing in size with the use of rare earth magnets. It is possible within the next decade that small implements could powered by relatively powerful motors driven from rechargeable batteries, displacing small two stroke motors.

For the second, very large two-stroke engines are the norm for marine propulsion and no alternatives are currently envisaged. A measure of 'very large' engine size is the 800–900 mm piston diameter. Large marine engines are usually turbo-charged, fuel injected, cross-head designs with low speed rotation, of the order of 65 rpm. A speed reduction gearbox is not needed as this rpm value is suitable for direct connection to the vessel's propeller. The low rpm value is also advantageous for the turbocharged air introduction/exhaust gas scavenging system. Bore lubrication is by direct distribution/delivery of a high Base Number lubricant, to counter the high sulphur fuel content, through a series of quills around the circumference of the bore, with associated 'moustache' machined features to spread the lubricant. The lower end of two-stroke marine engines are conventionally pressure lubricated by a separate system using a different formulation to that used in the top end of the engine. Low speed, two-stroke, marine engines achieve very high efficiencies (for automotive systems). Their relative construction simplicity enables them to be rebuilt during a voyage, such as when a cylinder liner develops cracks.

5 Fuel Trends in the Next Decade

5.1 Predicting the Future

Predicting the future is always a hostage to fortune for any activity; predicting the future of the oil industry should be more stable because of its broad global base and ubiquity. There are many separate predictions of future Energy Demand, Gross Domestic Product and Population; a recent Outlook for Energy study by ExxonMobil Chemical Ltd. [28] brings these three trends together and shows different trends for OECD and non-OECD countries.

5.2 Trends in World Population, GDP and Energy Demand

World population will rise by more than 25 % to 2040 from 2000, Fig. 12.4, with a slight increase in OECD countries, the major increase being in non-OECD countries [25]. Whereas GDP will increase by ~200 % 2000–2040, the increase divides roughly equally between OECD and non-OECD countries. Figure 12.6 shows that OECD countries energy demand will be stable or slightly decline whereas overall, OECD plus non-OECD, energy demand could rise in line with GDP unless energy efficiency improves. The fundamental difference is that whereas OECD countries will double their GDP at constant energy consumption, non-OECD countries will treble their GDP whilst potentially increasing their energy demand by a factor of five. Energy saving measures could reduce the increase in non-OECD energy demand to a factor of between two and three. The UK reduced primary energy consumption by 3.1 % (on a temperature adjusted basis) in 2014, in a year of national economic growth, continuing the trend of the previous 9 years. The Energy

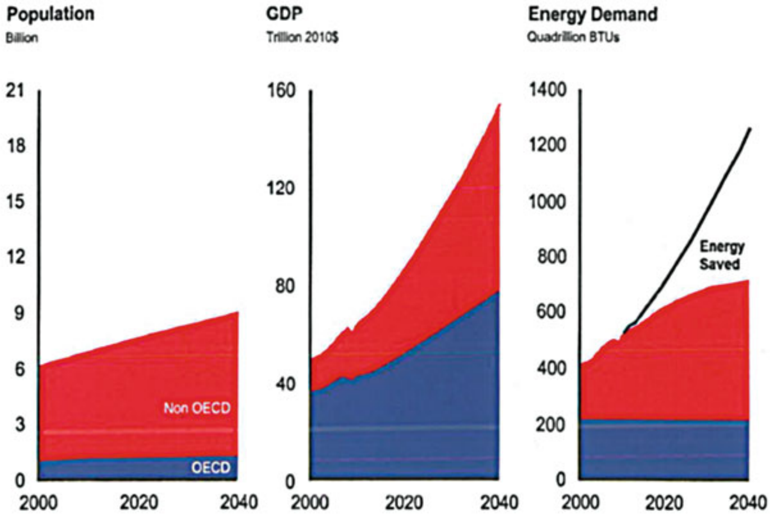


Fig. 12.6 Predicted trends in population, Gross Domestic Product (GDP) and energy demand for 2000–2040 (From Ref. [28])

Demand composition, Fig. 12.6, for 2000–2040 includes oil, gas, coal, nuclear and renewable energies.

But the energy industry, particularly the oil industry, operates in unstable economic and political times. The issue of 'Peak Oil', when the production of crude oil and natural gas will reach a natural capacity maximum and then decline, has been partially overtaken by extraction of 'tight oil' (and gas) by the technological developments of 'fracking' and also successful prospecting developments in new areas such as deep off-shore. But the factors leading to the sudden, unexpected 60 % collapse of the crude oil price from a peak of $115 per barrel in June 2014 to $46 per barrel in January 2015 has forced re-assessment of many petroleum fuel predictions, activities and investments. There have been four oil 'bear markets' between 1864 and 2008 of depressed oil prices, each taking between 11 and 20 years before previous prices were regained. Assuming that, in the relatively immediate term the crude oil price will stabilize between $57 and 82 per barrel to the end of 2016, then various future trends can be discussed and assessed.

5.3 Petrol, Jet and Diesel Fuels

On the demand side the conventional fuels of petrol, jet fuel and diesel will almost certainly maintain their predominant position as fuels for prime movers for the next decade, as part of World Energy Demand, Fig. 12.4. Whilst the 'Energy Demand' plot in Fig. 12.6 is for all energy sources, the International Energy Agency estimates that 64 % of world energy demand is for transport, mainly for petrol, contributing to

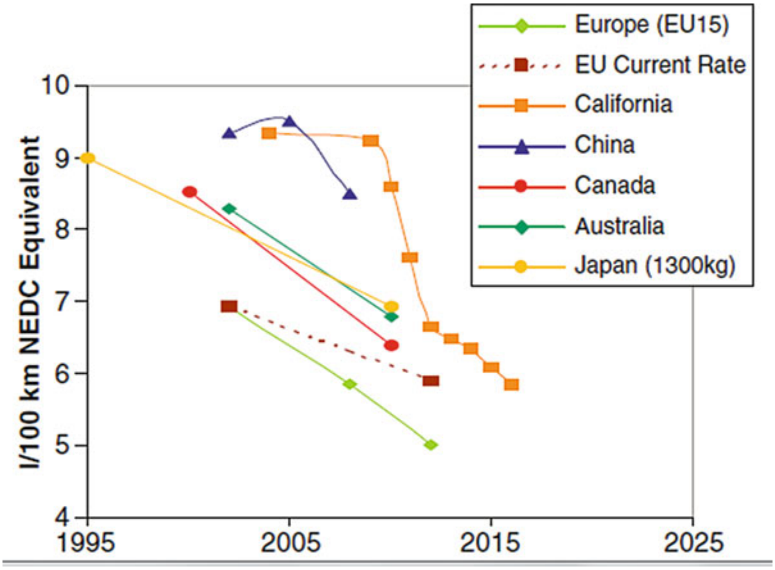


Fig. 12.7 Past and Future Fuel Consumption Standards for Light Vehicles in World Countries and Regions

the projected increase in energy demand. However, the two largest vehicle markets, China and North America, are required to reduce emissions by 30 % by 2020, in turn requiring increased fuel efficiency and thus energy saving,. The mandatory emissions of carbon dioxide, as a measure of vehicle fuel efficiency, for 100 km, in different countries are at different stages of development for different vehicle fleet compositions but the overall, inexorable, direction is to reduce carbon dioxide emissions per 1000 km and therefore improve fuel efficiency, as shown in Fig. 12.5.

For fuel specifications, after two decades of rapid change in specifications in concert with rapid changes in engine design and operation, the rate of change has now substantially decreased. Thus for petrol, lead compounds and sulphur have been severely reduced to very low levels, benzene reduced to low levels, chemical components have been reformulated, 5–10 % ethanol added and a standard octane rating of 95 established. Petrol, and now diesel, is now much more environmentally acceptable, in the older sense, with lead, benzene and sulphur drastically reduced or essentially removed. Emission regulations, such as the Euro1-6 regulations, have progressively tightened, as for passenger cars, Table 12.6.

However, the new sense of environmental definition regards petrol, and the other liquid fuels, as polluting because their combustion generates carbon dioxide. Therefore, in due, but probably longer, course they will be replaced, at least in part, by renewable sources of energy, as described in the next section. Because the changes in fuel specifications have been both extensive and thorough, it is not clear how they can be improved further. Therefore, any future changes in petrol specification are likely to be limited to small incremental change. Jet fuel specifications

Table 12.6 Euro emission standards for petrol and diesel cars, g/km

Stage	Date	Petrol cars				Diesel cars			
		CO	$\boldsymbol{HC+NO_x}$	***PM***		***CO***	$\boldsymbol{HC+NO_x}$	***NOx***	***PM***
1	07/92(1/93)	2.72	0.97	–		2.72	0.97	–	0.14
2	01/96(1/97)	2.2	0.50	–		1.0	0.7	–	0.08
		CO	***HC***	$\boldsymbol{NO_x}$	***PM***				
3	01/00(1/01)	2.3	0.20	0.15	–	0.64	0.56	0.50	0.05
4	01/05(1/06)	1.0	0.10	0.08	–	0.50	0.30	0.25	0.025
5	09/09(1/11)	1.0	0.10	0.06	0.005(di)	0.50	0.23	0.18	0.005
6	09/14(9/15)	1.0	0.10	0.06	0.005(di)	0.50	0.17	0.08	0.005

(di) – direct injection only. From 'Euro emission Standards', Automobile Association Website, 15/12/14
Implementation dates given are for vehicle type ***approvals***, dates in brackets for all new vehicle ***registrations***

are set until 2020 and diesel fuel specifications are not expected to change significantly as well. The major change in fuel compositions will be in the area of ethanol addition levels in petrol and the percentage FAME addition in diesel. Diesel fuel has drastically reduced its sulphur content level and reformulated its composition whilst establishing a cetane number of over 50. The emphasis in the next decade is on developments in diesel engine and fuel technology to concentrate on reducing Particulate Matter emissions, such as PM_{10} or $PM_{2.5}$.

All vehicles will continue to improve their fuel efficiency, continuing the progress made so far in light vehicle technologies such as advanced engine management systems, stop/start engines, lighter construction, hybrid propulsion and the effect of electric vehicles. The vehicle fleet will continue to further improve fuel economy. The total net level of vehicle emissions is a net sum, from the emissions of an increasing of number of vehicles set against their increasing efficiency and reduced emissions per vehicle, together with reduced emissions from the overall vehicle fleet as the older, more polluting, vehicles phase out.

Heavy duty vehicles will continue to be diesel driven with improved fuel efficiencies. The main issue to resolve the discrepancy between the stable level of polluting nitrogen oxides and particulates in the urban environment and the reducing trend in engine bench test emissions required by successive Euro Engine programs. The reductions in diesel engine emissions achieved on the test bed for successive Euro-emission standards are not being seen in the environment.

5.4 *The Alternative Fuels*

Alternative fuels such as hydrogen still wait to fulfill their potential and demonstration projects need considerable subsidy. Hydrogen's power density when compressed into high pressure bottles is only 5.6 MJ/l against 32.4 MJ/l for petrol at atmospheric pressure – the gas compression is an additional cost. The other alternative fuel, Liquefied Petroleum Gas, LPG, has an established market penetration, with an acceptable energy density, being readily liquefied on compression to around 10 bar with a specific density of 0.5. It is a clean burning fuel and propane, its main component, is increasingly available from natural gas sources and fracking as a very minor component.

Alternative liquid fuels arise regularly, some from biological sources such as plants or algae or from the controlled thermal degradation of refuse. The Fisher Tropsch process can take 'synthesis gas' produced from a range of sources and convert it into various hydrocarbons by varying the process conditions. The issues are:

- availability of the raw material on the very large scale required. If new syntheses of hydrocarbons from new sources are successful at the pilot plant stage, then further development into a viable real alternative source requires substantial infrastructure investment and development. As an example, the jatropha plant can supply a plant oil to 'extend' mineral hydrocarbon fuels, can grow on otherwise arid land and is inedible. It has the advantage of not posing a threat to human food supply on marginal land. But development of 'jatropha farms' on a scale to produce a meaningful supply of alternative hydrocarbons requires substantial investment over a prolonged period, as jatropha plants take several years to mature in arid, marginal desert, regions which may not have the necessary political stability to develop long term business. It is often seen that significant developments in 'alternative hydrocarbon synthesis' are not supported by the necessary raw material supply, a capacity problem.

The land use issue is of real concern, seeking to ensure that land for food production is not compromised by diversion to 'energy crops'. To address that issue, the European Union Parliament's target of 10 % renewable energy is limited to 6 % from land-based bio-fuels to 6 %, to include inedible energy crops. The remaining 4 % is intended to come from 'advanced biofuels' from algae or waste.

- the large and sustained, over years, investment required to develop alternative fuel crops; similarly, the investment required in slightly different technologies to process the new raw materials into useful hydrocarbon fuels, a financial resource issue,
- the acceptability of alternative fuels; Sect. 12.4 sets out the detailed specifications for petrol, jet and diesel fuels, part of which concern the molecular specification in terms of distillation 'bands', aromatic content, sulphur content, etc. To meet these specification requirements from alternative sources needs process developments to deliver acceptable fuels.

5.5 *Conclusion*

The demand for alternative fuels is predicated upon a constrained supply of mineral crude oil. The recent technological developments in producing crude oil from 'tight oil or gas' through what is known colloquially known as 'fracking' have changed the balance of that scenario. As one example, the United States of America has moved from a net importer/consumer of hydrocarbons to a net exporter. How long that situation applies will play out in the decade after the next.

It is clear that demand for hydrocarbon fuels will continue to increase worldwide but that within the OECD it may 'flatline' or decrease. Within the non-OECD countries, energy demand (including hydrocarbon fuels) will substantially increase, the extent of that increase is dependent upon whether energy efficiency measures can be effectively introduced and maintained.

Within established markets, the 'clean fuels' such as petrol, jet and diesel fuel specifications will only change by small increments. The 'heavier (dirty)' fuels such as Marine Fuel Oils will have their sulphur and solids contents drastically reduced in a substantial market whereas land-based heavier fuel oils are losing/has lost market share to the availability of relatively clean and convenient natural gas.

In conclusion, the quality of current fuels of diesel, jet fuel and petrol has been raised and for the foreseeable decade will continue to power prime movers. The next decade after may begin to see the expected and predicted fundamental and substantial changes in the fuel demand market.

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