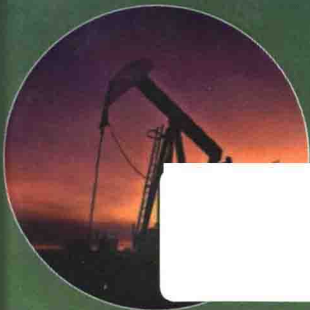


FUELS AND FUEL-ADDITIVES



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Preface

Petroleum based fuels are being used for over 100 years and the specifications of such fuels have evolved to meet the changing demands of the users. New processes have been used to convert maximum refinery streams into useful distillate fuels of acceptable quality at reasonable profits. Technically many products can be conveniently used as fuels, such as methanol, ethanol, other alcohols, gasoline, diesel, gas oil, dimethyl ether, natural gas, liquefied petroleum gas, compressed natural gas, coal derived liquid fuels, bio fuels, hydrogen and many others. However, engine technologies have developed around gasoline and diesel fuels over others. The pricing of the crude oil also favors petroleum fuels in the engines. Whenever, crude oil prices go up, alternate fuels are extensively discussed and investigated. Based on the current oil availability and prices, the use of petroleum based fuels and lubricants will continue in the current century. However, alternate fuels will find their place wherever, cost benefit analysis permits or regulations force their use. According to an IFP study, gasoline demand seems to be static and is likely to decrease in future, whereas diesel and kerosene markets will grow by 5%. It is an indication that in future, the use of hydro-conversion technologies will increase in their refineries and FCC throughput will decrease.

Environmental considerations, regulation of emission norms, energy efficiency and new engine technologies during the last twenty years have been responsible for dramatic changes in the fuels and additive quality. The dynamics of these changes and their interrelationship need to be properly understood, since the subject has now become quite complex. The present book on the "Fuel and Fuel-additives" is a unique effort to bring out these aspects. It discuss the science and technology involved in the production and application of modern conventional and alternate fuels, and fuel additives. Additives can be incorporated into fuels to improve a product's properties or to introduce new properties. Generally, they are produced synthetically and are used in low concentrations (1–500 mg/kg) in the finished product. A separate chapter on fuel additives has been incorporated, providing complete details of chemical additives used in oil industry.

This book has been jointly authored by an oil industry professional Dr. S. P. Srivastava and a chemical engineering professor Dr. Jenő Hancsók; combining both industrial and fundamental experience in their respective fields.

The book discusses the production of gasoline, diesel, aviation turbine fuel, and marine fuels, from both crude oil and alternative sources and discusses the main properties of these products in a simple language. Related environmental issues, fuel quality up gradation and application of fuel additives have been discussed in greater details.

Dr. Jenő Hancsók is grateful to Zoltán Varga, and Zoltán Eller, as well as to his postgraduate students, for their assistance in preparing the manuscript.

This book would thus be useful to all those engaged in the teaching, research, application and marketing of petroleum products.

S. P. Srivastava and Jenő Hancsók

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CHAPTER 1

Petroleum-Based Fuels – An Outlook

1.1 INTRODUCTION

Petroleum-based fuels have been used to power automotive vehicles and industrial production for well over 100 years [1–2]. Petroleum is one of the most important fuels derived fossil energy sources.

Currently, global annual energy consumption is about 12.2×10^9 tons of crude oil. Energy consumption is expected to increase to 17.5×10^9 tons of oil by 2035 [3–9]. Southeast Asia's energy demand alone will expand by about 75% by 2030 based on the strong economic growth trends in China and India [8–11]. The reserves of oil, gas, and coal that we depend on are therefore declining, and oil production is becoming ever more expensive, and causing significant environmental impact as well.

The industrial sector uses more energy than any other end-user sector, and currently it consumes about half of the world's total delivered energy [7]. Huge amounts of energy are consumed in manufacturing, mining, and construction, mainly by processing and assembly equipment but also by air conditioning and lighting. Worldwide, industrial energy consumption is expected to grow by 1.75×10^9 tons from 2010 to 2030, while transportation by about 0.6×10^9 tons and other energy consumption by about 0.8×10^9 tons during the same time period [7].

Industrial energy demand varies across countries depending on the level and mixes of economic activity and technological development. About 90% of the increase in world energy consumption is projected to occur in the non-OECD countries, where rapid economic growth is taking place. The key countries—Brazil, Russia, India, and China—will account for more than two-thirds of the growth of non-OECD industrial energy use by 2030 [7,9]. The transportation sector follows the industrial sector in world energy use, and it is of particular interest worldwide, as extensive improvements are being continually made in the quality of engine fuels.

To comply with climate change regulations, the energy sector is required to limit the long-term concentration of greenhouse gases to 450 ppm (mg/kg) of carbondioxide equivalent in the atmosphere so that the global temperature rise can be contained

Fuels and Fuel-Additives, First Edition. S. P. Srivastava and Jenő Hancsók.

to about 2 °C above the pre-industrial level [12]. In order for this target to be met, energy-related carbon dioxide emissions need to fall to 26.4 gigatonnes (ca. 26.4×10^9 tons) by year 2050 from the level at 28.9 Gt in 2009 [7,13]. Even given this outlook, fossil fuel demand will peak by year 2020.

The projected growth of energy consumption is based on the fast increase in the world population and in the standard of living. The world population was estimated to increase to about 7.03 billion (7.03×10^9) by April 2012 [14]. The fastest population growth rate (about 1.8%) were witnessed during the 1950s and then for a longer time period during the 1960s and 1970s. At this rate the world population is expected to reach about 9 billion (9×10^9) by year 2040 [4,14].

In North America and Western Europe, the automobile population has been growing roughly in parallel to the human population growth. But in the developing world, the automobile population growth is becoming almost exponential, due to effect of faster economic growth [15].

Globally, the number of vehicles on the road may reach 1 billion (10^9) by 2011 [15]. The growth is being fueled primarily by the rapidly expanding Asian market, which will see 5.7% average compound annual growth in vehicles in operation in the next three years. Asia will account for more than 23% (231 million vehicles) of global vehicles in use by 2011 [15]. Thus every seventh person in the world will have a vehicle by 2011. Europe and the Americas will account for 34% and 36% of the global share of automobiles by 2011, respectively. The Americas and Western Europe will continue to see approximately 1.3% and 2.0% compound annual growth in the next three years respectively, while Eastern Europe's vehicle population growth rate is forecasted to be 4.3% [15].

With the growth in the number of vehicles, especially passanger cars with internal combustion engines, fuels consumption has gone up significantly [9,16,17]. This has had a deleterious effect on the environment.

A large part of energy consumption is in form of engine fuels. Fuels for internal combustion engines produced from primarily sources are composed of combustion-able molecules. Heat energy is a derivative of fuel's oxidation, which is converted to kinetic energy. Different gas, liquid, and solid (heavy diesel fuel, which is solid below 20 °C) products are usable as engine fuels [8,9,18–20]. These fuels are classified as crude oil based—namely gasoline, diesel fuels, and any other gas and liquid products [18–21]—and non-crude oil based—namely natural gas based fuels—compressed natural gas (CNG) and dimethyl-ether—biofuels, like methanol, ethanol, any other alcohols and different mixtures of them; biodiesel; biogas oil (mixtures of iso- and n-paraffins from natural tryglicerides). Liquefied petroleum gases (LPG), which can be crude oil or natural gas based, and hydrogen are derivatives from different fuel sources [22–38].

Over the years fuel specifications have evolved considerably to meet the changing demands of engine manufacturers and consumers [20,39–42]. Both engines [43–45] and fuels [9,20,39,41,42] have been improved due to environmental and energy efficiency considerations. New processes have been developed to convert maximum refinery streams into useful fuels of acceptable quality at reasonable refinery margins [8,9,46,47].

Gasoline and diesel fuels have been preferred [20] in the development of engine technology. The price of crude oil is also often at a level that makes petroleum–based fuels in engines desirable for economic reasons [46,47,53–54]. Whenever crude oil prices do rise, the issue of alternative fuels comes up [9,22–27,48–51], but the discussions and investigations get dropped out soon after crude oil prices settle down [28]. The oil crises of the 1970s and 2008 reflect this tendency. However, oil is not going to last forever, and it is also not going to be exhausted in the near future [5,7,9,10]. So, while the use of petroleum-based fuels and lubricants may continue in the current century, it is likely that a significant decrease will occur after crude oil usage peaks [3,7,10,11,52].

The application of alternative fuels will find a place wherever cost–benefit analyses permit or wherever regulations force their use. (The use of compressed natural gas in all of New Delhi's city transportation vehicles is an example. This was decreed by the Supreme Court of India and is now being enforced in the other cities of India as well.)

While world gasoline demand is expected to be static and possibly to decrease in future, the consumption of diesel and kerosene, the rail and water transport fuel, will likely expand 1,3% to 15% by 2030 [9,16,17]. With the demand for heavy fuel oil expected to decrease [9,16,17], heavy fuel oil is being converted into lighter products such as LPG, gasoline, and diesel [53–55].

The world demand for middle distillate fuel, mainly diesel oil and heating fuel, will grow faster than that for any other refined oil products toward 2030 [9,56]. Globally, new car fleets are shifting to diesel from gasoline, and therefore the demand for middle distillates will grow and account for about 60% of the expected 20 million barrels per day (bpd) (2.66×10^6 t/day) rise in global oil production by 2030. In 2008, the difference in demand between gasoline and diesel was around 3 million bpd (0.4×10^6 t/day). By 2020, the projected gas oil/diesel demand is 6.5 million bpd (0.9×10^6 t/day), higher than for gasoline, and by 2030, the difference exceeds 9 million bpd (1.2×10^6 t/day). The expected global demand for diesel and gas oil (mainly used for heating) will grow to 34.2 million bpd (4.5×10^6t/day) by 2030 from 24.5 million bpd (3.3×10^6 t/day) in 2008. Gasoline demand will rise to about 25.1 million bpd (2.9×10^6 t/day) by 2030 from 21.4 million bpd (2.5×10^6 t/day) in 2008. Jet fuel/kerosene demand will rise to 8.1 million bpd (1.0×10^6 t/day) from 6.5 million bpd (0.8×10^6 t/day), while residual fuel demand, used as a refinery feedstock and as marine fuel, will fall to 9.4 million bpd from 9.7 million bpd.

The United States accounts for most of the world's gasoline demand, whereas in Europe the demand for diesel is increasing [4,9,42] due to the rising number of diesel vehicles [15]. India and several other Asian countries also consume more diesel fuel than gasoline [4,49]. With the development of more fuel-efficient diesel vehicles, the demand for diesel will increase significantly and its use might have to be restricted to meet future demand. However, gasoline-powered engines seem still to be favorable for hybrid vehicles.

Among the primary energy carriers, in absolute terms, coal demand will increase to the highest rate, followed by gas and oil over the projected time period [4]. Nevertheless, oil still remains the largest single fuel source by 2030, even if its share drops from the present 34% to about 30% (in 2010 ca. 92.3% and in 2030 ca. >85% fuels from petroleum) [4,11].

The projected worldwide crude oil demand reflects the leading role of crude oil in engine fuel production. The global total crude oil demand in 2011 was 4.05×10^9 t, and this is expected to increase to 4.4×10^9 t/year by 2015, and to 5.25×10^9 t/year by 2030 [25–27]. Non-OECD countries contribute to the increase by more than 90%; China and India account for more than 50% alone [4,49].

Among the alternative fuels, the biofuels (e.g., first-generation ethanol and biodiesel, second-generation bioethanol from lignocelluloisic materials and the biogas oil blends of iso- and n-paraffins processed from natural triglycerides) [40,51,57,58] will become an increasingly important unconventional source of the liquid fuel supply, likely reaching around 5.9 million barrels per day by 2030. Particularly strong growth in biofuel consumption is projected for the United States [58], where the production of biofuels could increase from 0.3 million barrels per day of the 2006 level to 1.9 million barrels per day by 2030 [58,59]. The Energy Independence and Security Act passed in 2007 has made the use of biofuels compulsory in the United States. Sizable increases in biofuels production are projected for other regions as well: the OECD countries with 10% biofuel energy by 2020 [60], non-OECD countries in Asia [49], and Central and South America [58]. The total biofuel production of the world was ca. 60 million tons oil equivalent. For bioethanol, in 2012, Middle and South America: ca. 12.1 Million tons oil equivalent, Europe and Eurasia: ca. 2.2 million tons oil equivalent and North America: ca. 25.7 million tons oil equivalent and production of other countries was ca. 2.0 million tons oil equivalent. For Biodiesel, Middle and South America: ca. 4.5 million tons oil equivalent, Europe and Eurasia: 7.6 million tons oil equivalent and North America: ca. 2.8 million tons oil eq. (BP Statistical review 2013), and production of other countries was ca. 3.1 million tons oil equivalent.

1.2 ENVIRONMENTAL ISSUES

Environmental pollution from fossil fuel use has long been a major government concern, and over the past 20 to 30 years, attempts have been made to control pollution by improving the quality of fuels and lubricants. The combustion of fossil fuels leads to the formation of CO_2, CO, unburned hydrocarbons, NO_x, SO_x, soot, and particulate matter. Liquid fuels, by nature, are volatile and produce volatile organic compounds (VOC), as emitted especially by gasoline. From time to time different countries have attempted to enforce regulations to minimize these harmful emissions. Their legislators have prompted major inter industry cooperation to improve fuel quality, lubricant quality, and engine/vehicle designs (Figure 1.1) [39].

Environmental issues thus drive the development of modern fuels, engines, and lubricants. The advances in these industries are interrelated, although biofuel development has the strongest linkages to environmental concerns, binding government legislation, engine development, exhaust treatment catalysts, tribology, and the fuel economy [39,60].

Greenhouse gas emission, global warming, and climate change are other important issues related to fuels and lubricants. About 10,000 years passed between the last

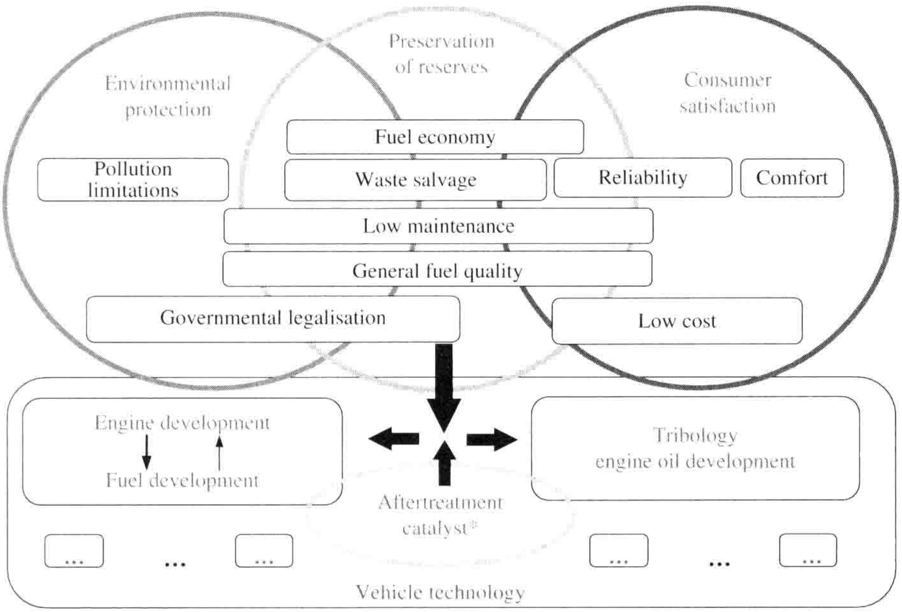

FIGURE 1.1 The mechanism of the development of vehicles and fules

Ice Age and the Industrial Revolution. During that time period the atmospheric CO_2 level varied by only about 5% [12,13]. From the start of the Industrial Revolution to 2030, in about 150 years, the amount of atmospheric CO_2 will have doubled [7,12,13]. World carbon dioxide emissions are projected to rise from 28.8 billion (28.8×10^9) metric tons in 2007 to 33.1 billion (33.1×10^9) metric tons by 2015 and 40.4 billion (40.4×10^9) metric tons by 2030—an increase of 39% over the examined period [7,12,13]. The only way to reduce carbon dioxide emissions is to reduce the consumption of hydrocarbon fuels and/or improve the energy efficiency of engines and equipment using hydrocarbons. The biggest single contributor to the rise in greenhouse gases is the burning of fossil fuels. Since in hydrocarbon fuels the CO_2 emission is proportional to the amount of energy produced, a reduction in energy consumption will reduce the CO_2 emission as well [12,13]. Improving energy efficiency is the first step in reducing carbon dioxide emission. This calls for a combined engineering effort to introduce more efficient fuels, better power systems, and new materials and processes.

Through coordinated action, it may be possible to lower the long-term concentration of greenhouse gases in the atmosphere to around 450 ppm (mg/kg) of the carbondioxide equivalent. This would correspond to the global temperature goal of environmentalists of not exceeding the 2 °C rise of the pre-industral period temperatures. To meet this target, energy-related carbon dioxide emissions must be lowered to around 26.4 gigatonnes (26.4×10^9 tons) by 2030 from the 28.8 gigatonnes (28.8×10^9 tons) of 2007 [7].

1.3 CLASSIFICATION OF FUELS

Engine fuels can be any liquid or gaseous hydrocarbons used for the generation of power in an internal combustion engine. There are several materials that can be used in the internal combustion engine either alone or blended as a component. These materials are classified as follows [19]:

- Drivetrains:
  - Otto engines (gasolines, PB, CNG, ethanol, etc.)
  - Diesel engines (diesel gas oils, CNG, dimethyl-ether, etc.)
- Origin:
  - Produced from exhaustible energy carriers,
  - Produced from renewable energy carriers (biofuels based on biomass)
- Number of feedstock resources:
  - One resource (e.g., fatty acid methyl esters from only triglyceride and fatty acid containing feedstocks)
  - Multiple resources (e.g., ethanol; from sugar crops, from crops containing starch, lignocellulose, hydration of ethylene)

Alternative fuels are those fuels that are other than gasoline or gas oil derived from petroleum. The main types of motor fuels are shown in Figure 1.2. [61].

The choice of fuel to use depends on the engine design, availability of the energy source, environmental protection issues, energy policy, safety technology, human biology, the aftertreater catalytic system, lubricants, additives, economy, traditions, and so forth [62,106]. The fuel industry categorizes the different types of fuels as follows:

Gasoline A volatile mixture of liquid hydrocarbons generally containing small amount of additives suitable for use as a fuel in a spark-ignition internal combustion engine.

Unleaded gasoline Any gasoline to which no lead have been intentionally added and which contains not more than 0.013 gram lead per liter (0.05 g lead/US gal).

E85 fuel A blend of ethanol and hydrocarbons in gasoline with 75–85% of ethanol. E85 fuel ethanol must meet the most recent standard of a region or country.

M85 fuel A blend of methanol and hydrocarbons where the methanol is nominally 70% to 85%.

Racing gasoline A special automotive gasoline that is typically of lower volatility, has a narrower boiling range, a higher antiknock index, and is free of significant amounts of oxygenates. It is designed for use in racing vehicles, which have high compression engines.

Aviation gasoline A fuel used in an aviation spark-ignition internal combustion engine.

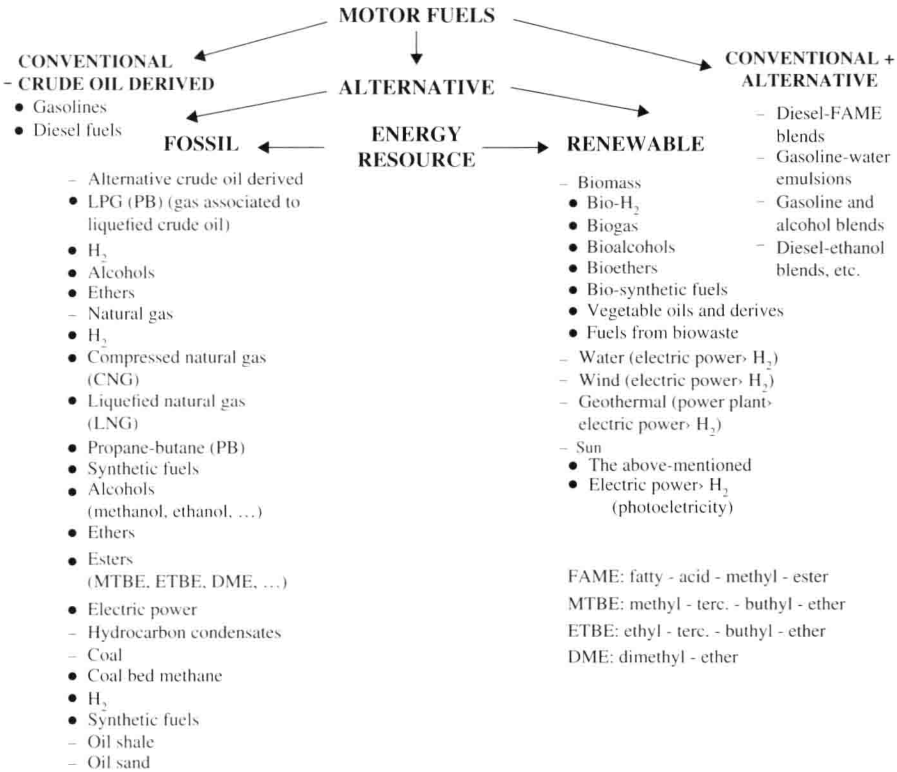

FIGURE 1.2 Classification of conventional and alternative fuels

Petroleum gases (LPG) Gas phase hydrocarbons, mainly C_3 and in low quantity C_4. Their quality is determined by the country or regional standards.

Compressed natural gas (CNG) Predominantly methane compressed at high pressures suitable as fuel in internal combustion engine.

Aviation turbine fuel A refined middle distillate suitable for use as a fuel in an aviation gas turbine engine.

Diesel fuel A middle distillate from crude oil commonly used in internal combustion engines where ignition occurs by pressure and not by electric spark.

Low or ultra-low sulfur diesel (ULSD) Diesel fuel with less than 50 and 10 mg/kg respectively.

Biodiesel A fuel based on mono-alkyl esters of long-chain fatty acids derived from vegetable oils or animal fats. Biodiesel containing diesel gas oil is a blend of mono-alkyl esters of long chain fatty acids and diesel gas oil from petroleum. A term B100 is used to describe neat biodiesel used for heating, which does not contain any mineral oil based diesel fuel.