AUTOMOTIVE FOSSIL FUELS: CHARACTERISTICS, EVOLUTION AND ENVIRONMENTAL CONSTRAINTS

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Contents

Summary

This paper is aimed to present the development, characteristics and environmental impacts of the main fuels used in motor vehicles.

Basic information about several substances that were and are used to provide the energy that moves our automobiles are presented in a concise text with focus on fossil fuels - those obtained from petroleum processing. Oxygenated substances and other renewable fuels used pure or as blenders for liquid petroleum fuels are presented in a separate article.

The history of petroleum products usage as fuels, improvements in its processing and also the changes in engines design and requirements are explained as needed in order to allow the reader to have a wide knowledge on the subject.

Diesel and gasoline are the most important fuels so far, due to this most part of the text are dedicated to these fuels. Natural gas and liquefied petroleum gas are also included in the article.

The discussion around the environmental impacts of these fuels includes the well known greenhouse effect, and also other effects caused by different pollutants generated by the use of these fuels and its production.

1. Introduction to Fuels

The Automobile can be considered, without any doubt, as one of the greatest invention of the humankind. Its usage deeply modified the way that people move and transport its loads. It also created a myth without precedents that touch our vanity and gives great pleasure. It is not only the need to move, but that old passion which we have, admitting or not, by cars.

The history of automobile evolution well illustrates the humankind evolution in its period of existence. Each new discovery of science new technologies were incorporated into the cars, some of then significantly changed it, but no breakthrough in science or technology was able to replace it so far.

The source of energy needed for the automobiles to perform its function is now a major concern of humanity. The fuels have a role of great significance in many different aspects of our complex society, are reason enough to put countries at war or to take them out of poverty. Are considered national security matter for all nations and have the potential to cause huge environmental disasters if used without the necessary care.

Fuels evolved along with the cars so closely that you can not think of a breakthrough of one without the move of the other one to an equivalent level. The solution of many environmental and social problems faced today involves the evolution of these elements together.

It was in the seventies that started the concerns and actions with the objective of minimizing the negative effects over the environment of large scale use of oil. The implications of, not only the use, but physical and chemical properties of fuels and the technological level of the engines, have become better understood, and also its effects on air quality in major cities. In this context the fuel specifications underwent at the same time the requirements of the newer engines and the limits imposed by environmental laws, which at times pointed to opposite directions.

This paper objectively presents the development, characteristics and environmental impacts of the main fuels used in motor vehicles. A common feature among all of then is the fact of having more or less chemical energy stored in their organic structures, energy absorbed from the Sun that is extracted by the engines and converted into motion, so that the cars can play its role in the transportation activities and also provide us that great pleasure.

2. Introduction to Petroleum Based Fuels

Petroleum is a word with origin in Latin language that means “oil from rock”. Records of petroleum and its derivates used as fuel or as lubricants are ancient. The oldest record of the use of petroleum for illumination is from the Romans. The oil from Agrigentum, at Sicilia Island, was used as fuel for night lights at Jupiter Temple. There are also references to the petroleum from the ancient Greeks, from China 2000 years ago and from India (*Rangoon Oil*). During the North American colonization it was found that the Indians have used petroleum as medicine for many types of illness.

The first record of industrial distillation of petroleum is from Prague (Czech Republic) and date back from 1810, with the objective to obtain illumination oil.

Petroleum Industry started in Scotland with the development of industry and commerce of petroleum. In 1848 James Young of Kelly was the first to produce paraffin oil in commercial scale with his partner Meldrum. They have produced two types of paraffin oil: one thin, to be used as burning oil (fuel) for lamps, and another one, thicker and heavier, to be used as lubricant.

On August 27, 1859, in a place near to Titusville in northwestern Pennsylvania (USA), Edwin L. Drake struck oil in the first commercially successful well drilled specifically for oil and launched the modern petroleum industry. Drake was supported by William A. Smith ("Uncle Billy") and their first petroleum well was only 21 meters deep and produced 3,200 liters per day.

Nevertheless, Canadians affirm that the first successful well drilled for oil was in June 1858. It was drilled by James Miller Williams and found oil in a deep of 20 meters in a place near to Enniskillen.

The first product refined from crude oil was kerosene, which was used as fuel for lamp oil.

Since only a fraction of the crude could be refined into kerosene, the early refiners were left with quantities of petroleum by-products. These petroleum by-products attracted the attention of Rudolf Diesel, the inventor of compression ignition reciprocating engine. Diesel - whose first engine concept was designed to use coal dust as the fuel - recognized that liquid petroleum products might be better fuels than coal. The engine was re-designed for operation with liquid fuels, resulting in a successful prototype in 1895. Both the engine and the fuel still bear the name of Diesel.

Crude oil is composed almost entirely of carbon and hydrogen with some traces of other species. It varies from 83% to 87% carbon and 11% to 14% hydrogen by weight. The carbon and hydrogen can combine in many ways and form many different molecular compounds. Over 25,000 different hydrocarbon components were identified from a crude oil sample.

Crude oil can vary from thin light-colored brownish or greenish crude oils of low density, to thick and black oils resembling melted tar. The thin, low density oils are called "high-gravity" crude oils, and the thick high density ones, "low-gravity" crude oils. This convention, rather confusing to those outside the petroleum industry, is explained by the use of "API gravity".

API gravity is an arbitrary scale developed by the American Petroleum Institute. API gravity increases inversely to density, with lower density products having higher API gravities (these are the higher value products). The API gravity scale was constructed so that most values are between 10 and 70.

$$\mathrm{API} = (141.5 / \mathrm{RD}) - 131.5$$

$$RD = \rho s / \rho w$$

where:

ρs, ρw - density of the sample and of water, respectively at 15.6ºC (60ºF).

The most used classification according to API gravity is the following:

Light Petroleum: API higher than 31.1 or density inferior to 870 kg/m^3;
Median Petroleum: API between 22.3 – 31.1 or density between 920 kg/m^3 and 870 kg/m^3;
Heavy Petroleum: API between 10.0 and 22.3 or density between 1,000 kg/m^3 and 920 kg/m^3;
Extra Heavy Petroleum: API lower than 10.0 or superior to 1,000 kg/m^3.

In the refining process, the crude oil is converted into transportation fuels (gasoline, jet fuel, and diesel fuel) and other petroleum products, such as liquefied petroleum gas (LPG), heating fuel, lubricating oil, wax, and asphalt. High-gravity crude oils contain more of the lighter products needed for the production of transportation fuels, and generally have lower sulfur content. Modern refining processes can also convert low-gravity crude oils into lighter products, at an added expense of more complex processing equipment, more processing steps, and more energy.

Modern refining processes can be classified into three basic categories:

Separation Processes: The crude is separated into components based on some physical property. The most common separation process is distillation, where the components of the crude are separated into several streams based on their boiling temperature. Solvent extraction also is used to separate hydrocarbons by chemical classes. Separation processes do not change the chemical structure of feedstock components.

Conversion Processes: These processes change the molecular structure of feedstock components with the objective to produce substances with higher cost. The most common conversion processes are thermal cracking, catalytic cracking and catalytic hydrocracking, which - as suggested by the names - involve “cracking” of large molecules into smaller ones. Alkylation is a process that converts light gaseous hydrocarbons into heavier products (reverse way of cracking). Isomerization is a process to convert linear hydrocarbons into branched isomers, with higher octane number to be used in gasoline pool.

Upgrading Processes: Commonly used in *reformulated fuels* to remove compounds present in trace amounts that gives the material some undesired qualities. The most commonly used upgrading process for fuels is hydrotreating, which involves chemical reactions with hydrogen at high pressure and high temperature ambient.The fuel product line generated from crude oil developed along with the development of the internal combustion engines. In the next sections each fuel will be explored.

2.1. Environmental Constraints of Petroleum Based Fuels

Despite the enormous benefits that the mankind received from the use of petroleum, there are strong environmental impacts related to its use that must be considered.

The burnt of petroleum based fuels results in many products that can be harmful to the life in our planet, the most important to be considered are: CO_2, NO_X, CO, HCs (unburned hydrocarbons), PM (particulate matter), SO_2, N_2O and CH_4. In addition to these gases O_3 (ozone), even by not being among the tailpipe gases, could also be included in the list, since is a product of photochemical reactions of pollutants produced by the vehicles.

While some of these products are toxic and affect the life as poisons, CO_2, (carbon dioxide) N_2O (nitrous oxide) and CH_4 (methane) are chemically stable, but they act as a greenhouse gas (GHG). Greenhouse gases effectively absorb thermal infrared radiation, emitted by the Earth's surface, by the atmosphere itself due to the same gases, and by clouds. Atmospheric radiation is emitted to all sides, including downward to the Earth's surface. Thus, greenhouse gases trap heat within the surface-troposphere system. This is called the greenhouse effect ant its noticeable result the increase of surface temperature of the planet with strong negative impact to the environment.

The concentration of atmospheric CO_2 has increased from a pre-industrial value of about 280 ppm to 379 ppm in 2005. Atmospheric CO_2 concentration increased by only 20 ppm over the 8000 years prior to industrialization; multi-decadal to centennial-scale variations were less than 10 ppm and likely due mostly to natural processes. However, since 1750, the CO_2 concentration has risen by nearly 100 ppm. The annual CO_2 growth rate was larger during the last 10 years (1995–2005 average: 1.9 ppm/yr) than it has been since continuous direct atmospheric measurements began (1960–2005 average: 1.4 ppm/yr).

Transportation activity predominantly relies on a single fossil resource: petroleum, that supplies 95% of the total energy used by world transport. In 2004, transport was responsible for 23% of world energy-related GHG emissions with about three quarters coming from road vehicles. Over the past decade, transport's GHG emissions have increased at a faster rate than any other energy using sector.In 2004, the transport sector produced 6.3 $GtCO_2$ emissions (23% of world energy-related CO_2 emissions) and its growth rate is highest among the end-user sectors. Road transport currently accounts for 74% of total transport CO_2 emissions. The share of non-OECD countries is 36% now and will increase rapidly to 46% by 2030 if current trends continue. The transport sector also contributes small amounts of CH_4 and N_2O emissions from fuel combustion and F-gases (fluorinated gases) from vehicle air conditioning.

In addition to GHG contribution from petroleum, other pollutants emitted by petrol fueled vehicles also represent strong environmental concerns. Air pollution in large cities is responsible for thousands of deaths every year. In the following chapters the emission concerns of each type of fuel will be better exposed.

3. Diesel Fuel

Diesel fuel is a mixture of thousands of hydrocarbons obtained by distillation of crude oil that are blended with some additional components, from upgrading and conversion processes. Additives are used to provide specific performance requirements according to its usage. Diesel is used to feed diesel engines, which operate according to the diesel cycle. Diesel engines are also called Compressed Ignition (CI) engines, since they don't use spark plugs to start combustion; the fuel combustion is initiated only by the heat generated by the compression of air and fuel mixture. When a cold engine is cranked it has to increase the gas mixture temperature to about 400ºC to start combustion, the time required to make it happens depend on the engine design, but depend also on the diesel properties, that must be well balanced.

There are other important characteristics of diesel engines that impose specific requirements over diesel fuel: the compression ratio of diesel engines are higher than those for gasoline engines, typical values are between 15:1 to 25:1 while gasoline engines operates typically between 8:1 to 12:1. This higher CR also requires extremely high fuel injection pressures, which can reach 200 MPa (or about 2,000 atmospheres). Time of injection can be between 1 to 2 ms, injection volume can be between 1 to 2 mm^3 (that is comparable to a pin head) and the clearances of some internal components are of 1 μm (1/60 of a hair wire). This cycle can be repeated up to 10,000 times per minute. Such modern diesel engines imposed several upgrades in terms of diesel quality, these requirements add to those that come from the modern emission requirements (environmental constrains) provided a set of stringent parameters that diesel must meet.The important properties which are used to characterize diesel fuel include cetane number (or cetane index), fuel volatility, density, viscosity, composition, cold behavior, and sulfur content. Fuel properties are often improved through the use of additives. Diesel fuel specifications differ for various fuel grades and in different countries.

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Biographical Sketch

Leandro Henrique Benvenutti was born in Guaporé, from the State of Rio Grande do Sul in Brazil in November 27th, 1969. Graduated in Chemistry from the State University of Campinas (UNICAMP) São Paulo, Brazil in August, 1993; achieved Master of Science in Chemistry (Physical-Chemistry) in the same University in December, 1995 and PhD in Sciences (Chemistry) in the same University in February, 2000. Major field of study was Chemical Kinetics for Ethanol Flames.

He started his professional career at Ford Motor Company in Brazil in 2000. Working in the Powertrain Development department acquired background with Fuels and Lubricants, achieving the position of Fuels and Lubricants Technical Specialist in 2005.

His bibliographic production includes the following published articles among others: Benvenutti, L.H.; Marques, C.S. T.; Bertran, C.A. “Chemiluminescent Emission Data for Kinetic Modeling of Ethanol Combustion”. *Combustion Science And Technology*, Filadelfia, v. 177, n. 1, p. 1-26, 2005. Bertran, C.A.; Marques, C.S.T.; Benvenutti, L.H. “Temporal Evolution of Soot Particles from C_2H_2/O_2 Combustion in a Closed Chamber”. *Journal Of The Brazilian Chemical Society*, Brazil, v. 13, n. 1, p. 47-53, 2002. Benvenutti, L.H.; Miyamoto, R.N.; Lima, F.S.G.; Massa, C.V.C.; Filho, M.A.; Barreto, S.S.; Reis, E.D. “Effects of the Use of B5 Blends (5% biodiesel) over the Engine Oil of Light Pickups in Fleet Test”. *SAE Technical Paper Series E*, N. 2008-36-0294. At present time the use of Biofuels in vehicular applications is the main area of interest.

Dr. Benvenutti is member of SAE Brasil (Society of Automobile Engineers).