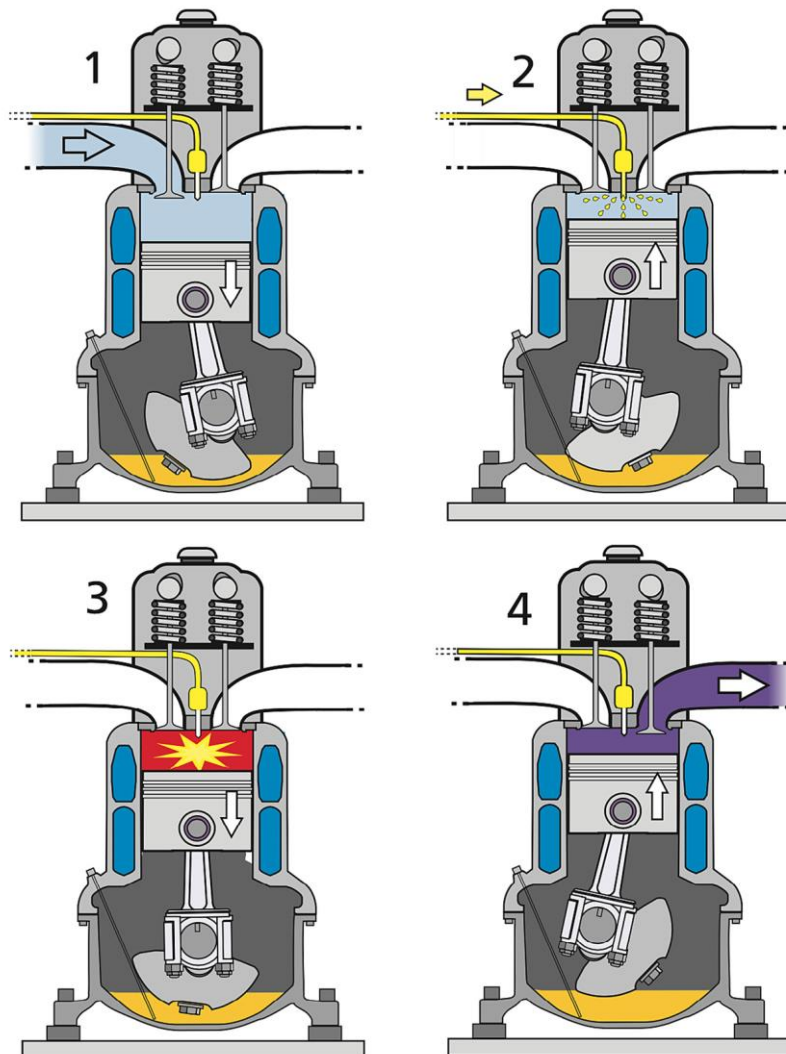


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Combustion of Fossil Fuels



An Introduction to Fossil Fuel Combustion

Fossil Oil

The production of fuel and industrial materials from fossil oil began in 1859. The year 2009, at which point the industry's output had been ever growing for a century and a half, is sometimes associated with the phrase „peak oil“, that is the point of maximum rate of oil extraction.

The better part of mankind is a consumer of oil in some respect and many communities are significantly dependent on this prevalent energy source. Modes of transport are widely run on energy from fossil oil and oil is utilized for the generation of heat and electricity and as raw material for the production of asphalt, plastic, fertilizer, paint, cosmetics and more. Fossil oil is an essential energy resource for the world today; without it life and our existence would be wholly different. The unit for the production and sale of fossil oil (crude oil) is barrels, the volumetric content of which is 159 litres (42 gallons) of crude oil, equivalent to about 145 kg.

Global oil production has been increasing steadily since the middle of the twentieth century, from a demand of 6 million barrels per day. In 2012, the demand had reached 88 million barrels per day and today, as these words are being written, it is at 90 million barrels per day, or roughly 4,700 million tonnes on an annual basis. 2,700 million tonnes thereof are consumed as fuel and 2,000 million tonnes are expended in the form of various products derived from fossil oil¹.

Fossil oil reserves can be found in the earth's crust and there is also a considerable amount in oil sands (tar sands) close to the surface of the earth, in Canada for example. The oil is recovered by means of drilling into deposits of accumulation within the earth's strata where the oil forms wells. If the deposits are located in layers at relatively shallow depth within the crust, the oil navigates its own way to the surface, making drilling rather easy. This is the conventional method of oil extraction and the easiest (also referred to as easy oil). For oil located in the depths of the earth's crust, or in instances where it is drilled for in open seas, it is more difficult to transport to the surface and the method is thus called unconventional.

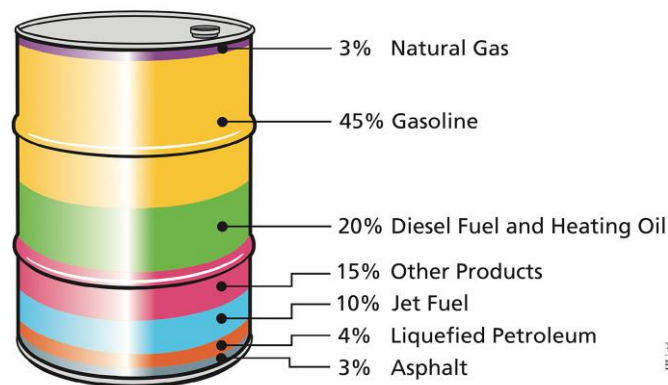
Unconventional means of oil extraction include drilling for oil below the seabed, organic oil production, fracking and tar sand processing. Fracking is practiced in the United States while tar sands are mined in Canada. The world market price must not dip below 70-80 US dollars per crude oil barrel for unconventional methods of oil extraction to remain economical. In 2010, the total fossil oil production through unconventional practices reached 17 million barrels per day.

Methods of fracking consist of vertically drilling down to a certain depth and then proceeding horizontally into the rock. Then, a large volume of water at high pressure is pumped into the borehole along with sand and proppant additive, causing the rock to fracture and allowing the hole to fill with oil from cracks and cavities in adjacent strata are forced open by the

procedure. The sand keeps the cavities open while oil flows toward the drilling core and the oil is pumped to the surface. This method is expensive but will become more prevalent as conventional oil reserves are depleted and the world market price increases.

In tar sand, the grains of sand are coated in a thin layer of petroleum. It is concentrated at the earth's surface and mined for further processing. A considerable amount of heated fresh water is used to separate the layer of oil and sand grains. Two tonnes tar sand and three to five tonnes fresh water are required to produce the equivalent of one tonne crude oil.

Fossil oils and fuels are products of crude oil straight from the depths of the earth. Fossil oil require processing in oil refineries where it is rendered useable for various machinery and vehicles. Initially, the crude oil is treated to remove sand, water and salts in order to avoid corroding refinery process units. Within the petroleum refinery, the crude oil is prepared and refined via distillation at high temperatures. This takes place in a distillation tank 50 meters high, which is filled with crude oil and heated from below. The highest temperature occurs at the bottom and decreases progressively upwards within the column. At the top, the coolest gases and gasoline collect at 20° to 150°C, further down the column there will be kerosene and aviation fuel at 200°C, followed by diesel fuel and heavy fuel oil at 300° to 370°C and at the bottom there is lubricating oil, asphalt and tar at 400°C. A preferable distillation product ratio would yield approximately one half gasoline and one fifth diesel oil².



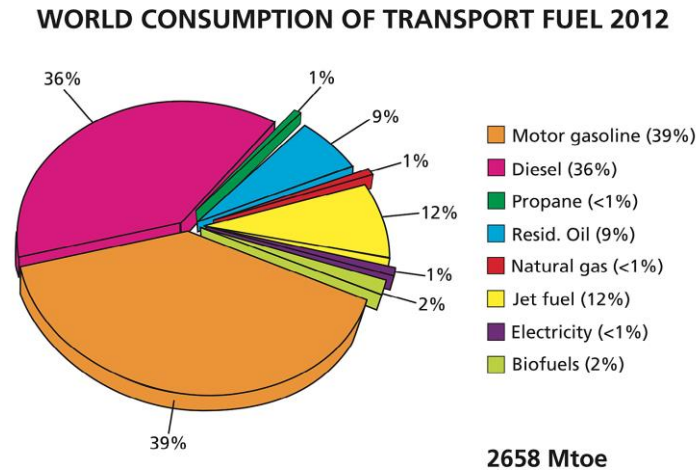
Source: U.S. Department of Energy

Today's largest fossil fuel consumers are North and Central America, using about 20 million barrels per day. Europe uses nearly 15 million barrels a day and China is up to 9 million barrels per day. Saudi Arabia and Russia are the world's principal crude oil producers, reaching 10 million barrels a day, followed by the United States.

Since the middle of the last century, crude oil world market price has varied greatly; between 1950 and 1960 the price of the barrel was 2 USD. During the first oil crisis of 1973, the price quadrupled, from 3 USD to 12 USD. In 1979, at the time of the second oil crisis, the barrel went from 13 USD to 34 USD, almost tripling the price of crude oil.

In early 1999, the price of the oil barrel was down to 10 USD but by mid 2008 it had reached 148 USD, the highest price since. In 2012, the barrel price reduced to 100 USD and today it rests at about 60 USD per barrel.

Conventional extraction is believed to have reached its maximum (peak oil) around the years 2005 to 2008. In order to maintain the supply that the nations of the world demand, oil production must be supplemented with unconventional methods and the increased production of biofuel.



The figure shows fuel used for transport in 2012³

Fossil oil is largely made up of carbon and hydrogen which form carbon dioxide (CO₂) and water following combustion in air. The combustion of fossil oil also creates sulphur oxides (SO_x) and nitrogen oxides (NO_x) and these are believed to have a detrimental effect on the environment, the atmosphere and the ozone layer. For example, running vehicles on fossil fuel in urban areas is objectionable due to engine exhaust pollutants; however, in recent years, cleaning mechanisms in diesel vehicles have greatly reduced this type of pollution.

It is a widely known fact that the world fossil fuel reserves are a finite resource. Annually, one million times more crude oil is extracted than is formed in the same time period from animal and plant biomass in the earth's crust. For this reason it is a widely held view that the supply of this energy resource will become scant in the near future. However, certain areas around the world are believed to hold undiscovered oil reserves which could be difficult to extract in the conventional manner and thus through a more expensive procedure. Consumption is rising at a greater rate than production so it is more than likely that oil prices will continue to fluctuate and that the energy source might even become unavailable before long.

Excellent combustion efficiency in diesel engines is one of fossil diesel's main advantages over environmentally friendly energy sources. Fossil fuels also currently have a truly unique position with regard to distribution and sales. However, this can be changed via the practice of effective environmental protection, focusing on health effects, sustainability and the emission reduction of compounds contributing the greenhouse effect and harming the environment by various means⁴.

Ideal Combustion of Fuel

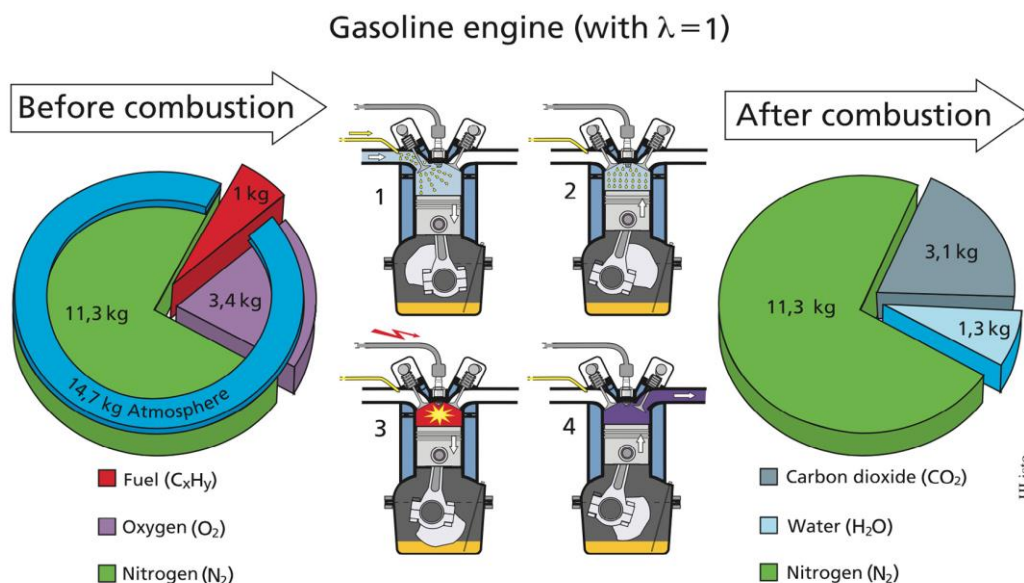
Fossil fuels are hydrocarbon compounds of 200 different combinations (C_xH_yO_z); hydrocarbon can be divided into old and new hydrocarbon compound categories. Old

hydrocarbons formed due to the effect of sunlight millions of years ago when vegetation was trapped underneath sedimentary rock prior to any natural degradation and then preserved. Petroleum oil was created in great quantities following various different chemical processes, and was concentrated in reservoirs deep within the Earth's crust. Burning this petroleum, we are consuming solar energy from eons ago and releasing old carbon into the atmosphere¹ which is added to the amount present due to natural causes. New carbon is present in organic compounds which can be utilized in the form of organic fuel such as biodiesel made from rapeseed, a means of consuming current solar energy. Organic fuel and fossil fuel have approximately the same amount of energy but the former holds 11% more oxygen mass, a benefit with regard to environmental effects of combustion⁵.

Fossil fuel is made up of remnants of biomass that grew on earth millions of years ago and has been transformed to oil in the course of time. There are several types of fossil diesel, such as heavy fuel oil, marine gas oil, automobile oil and heating oil. All of these oils are defined according to their distillation temperature in addition to the viscosity of the crude oil from which the oils originate¹.

When perfect combustion occurs in the presence of pure oxygen and at ideal conditions, such as in a gasoline engine (Otto engine), 14.7 kg of air is required for each kg of fuel (gasoline in this example) and the combustion is ignited by a spark. In this context λ (lamda) is the compression ratio and for this particular example $\lambda = 1$. The air can then be divided into 3.4 kg oxygen (O_2) and 11.3 kg nitrogen (N_2). Following combustion, exhaust gas is emitted, that is about 3.15 kg carbon dioxide (CO_2), 1.3 kg water (H_2O) and the 11.3 kg nitrogen (N_2) used in the combustion is returned to the atmosphere but no oxygen (O_2). The oxygen is consumed with the fuel because the combustion is complete.

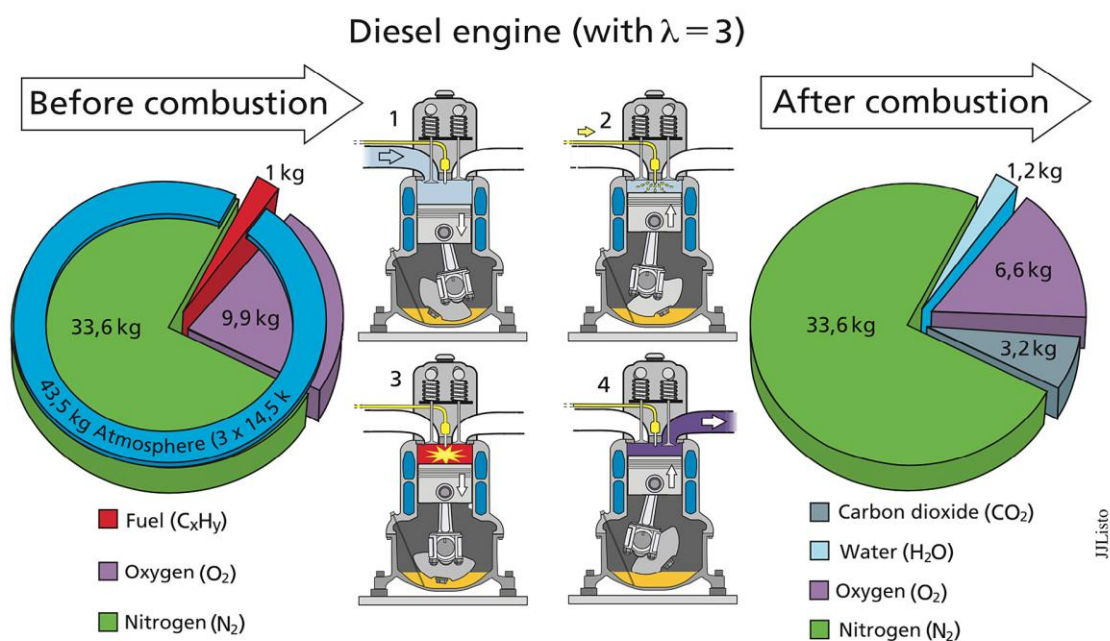
IDEAL AND COMPLETE COMBUSTION OF FOSSIL GASOLINE FUEL WITH AIR



Ideal and complete combustion of fossil gasoline fuel with air

When combustion occurs at ideal conditions in a diesel engine, three times more air is required than for gasoline, or 43.5 kg (3 times 14.5 kg) air for each kg of fuel (diesel) and the combustion is auto-ignited as a result of compression. Again λ is the compression ratio, here $\lambda = 3$. The air is divided into 9.9 kg oxygen (O_2) and 33.6 kg nitrogen (N_2). After the combustion, the exhaust gas is made up of 3.18 kg carbon dioxide (CO_2), 1.25 kg water (H_2O), 6.6 kg oxygen (O_2) and 33.6 kg nitrogen (N_2). In this case, the oxygen is not totally consumed because the combustion is complete, thus 3.3 – 3.4 kg is needed for the combustion of diesel. The amount of nitrogen required for the reaction is again fully returned after combustion.

IDEAL AND COMPLETE COMBUSTION OF FOSSIL DIESEL FUEL WITH AIR



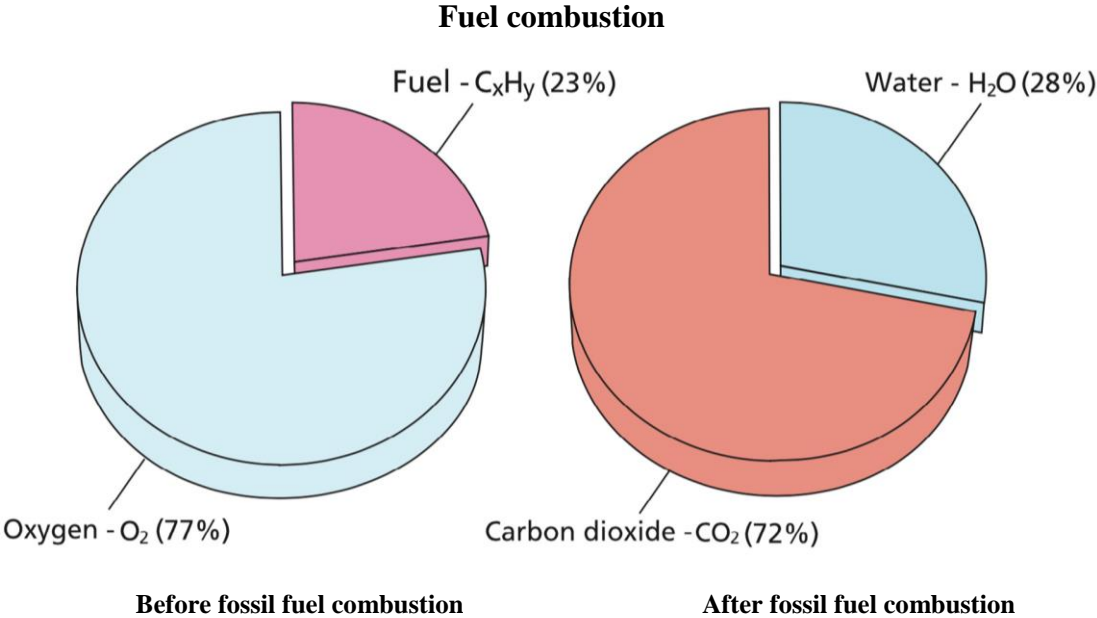
Ideal and complete combustion of diesel fuel with air

The difference between these two examples of combustion is that the gasoline is ignited via a spark (**sparkign**) while diesel oil is ignited via compression (**auto-ignition**).

Combustion and Environmental Issues

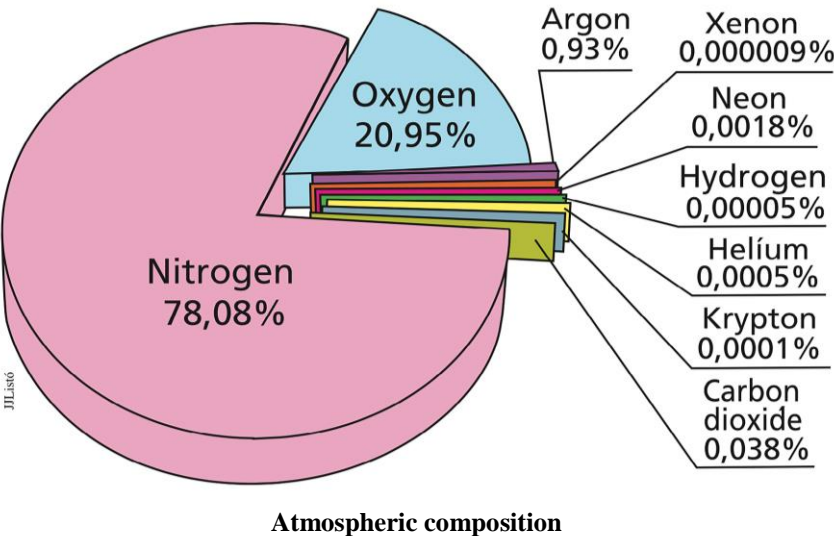
Fossil diesel is an extremely toxic substance; it does not take a large amount to cause considerable environmental pollution (for example in groundwater) which can endure for decades. Soot, which is formed during fossil diesel combustion, is also considered especially detrimental due to its fine grain and accumulation in lung tissue, before being carried to the stream and organs. Other toxins from diesel combustion are emitted to air and harmful gases (aromatic compounds) are expended from fossil diesel prior to burning. Almost all of these are harmful to the body and human health⁶. Pollution accidents involving fossil diesel are difficult to contain and even small amounts can cause coastal and open sea pollution. Unlike biodiesel, fossil diesel is degraded in nature over a long period of time and thus its transport on land and sea requires precautionary measures⁷.

The combustion of fuel involves a series of complicated chemical processes. Under ideal conditions, like those described above, 1 kg fuel is reacted with roughly 14 kg of air (approximately 12 cubic meters of air at 20°C). The air contains 3.4 kg oxygen (O₂). That is, the ratio for fuel combustion is 23% fuel and 77% oxygen.



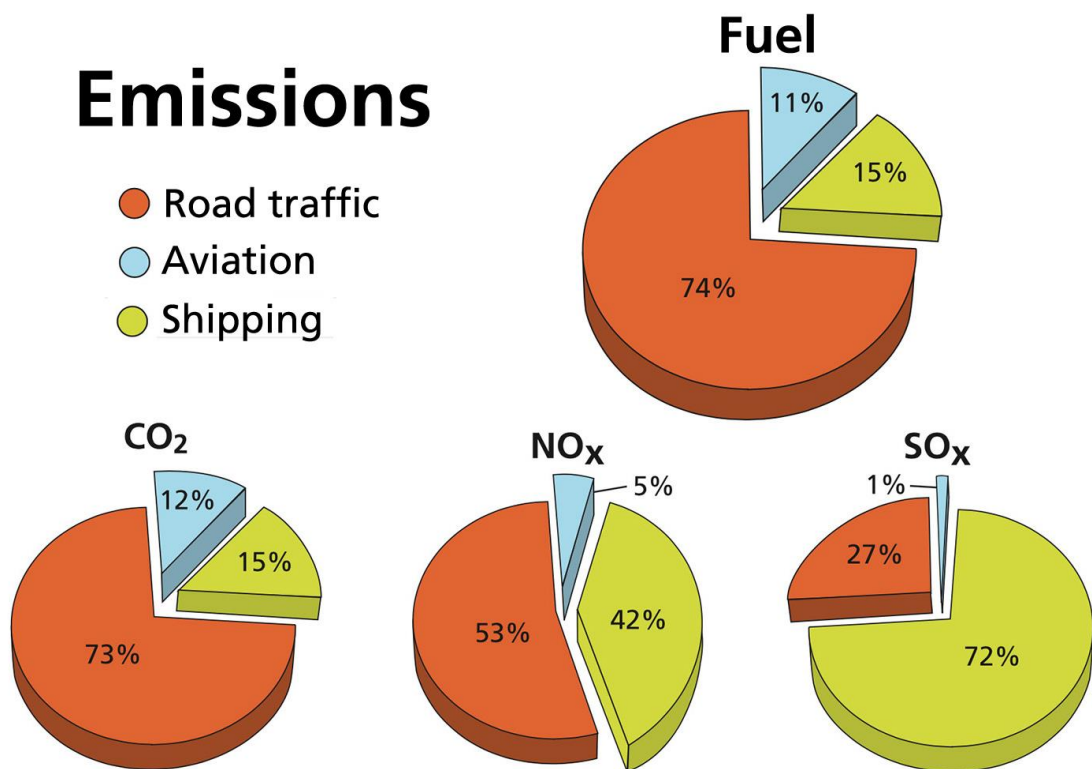
Following combustion under ideal conditions, 3.18 kg carbon dioxide are formed as well as 1.25 kg water (H₂O). The ratio after combustion is 28% water to 72% carbon dioxide (CO₂). Generally, the assumption can be made that 3.15 - 3.18 kg carbon dioxide are produced as other compounds in the fuel do not significantly affect the formation of carbon dioxide⁸.

Under normal circumstances, the atmospheric composition in the troposphere and stratosphere is highly stable. Nitrogen makes up 78% and oxygen 21% of the volume of air. The remainder, approximately 1%, consists of mostly argon in addition to several other elements and compounds.



The atmosphere also contains gases of variable concentration, such as water vapour (H₂O), carbon dioxide (CO₂), carbon monoxide (CO), sulphur dioxide (SO₂), nitrogen dioxide (NO₂), methane (CH₄) and ozone (O₃). Under normal conditions, the relative concentrations of these compounds are as described in the figure above, and this is referred to as having „fresh air“ to breathe.

Diesel engines aboard ships usually run on fossil oils with high „cetane numbers“, which refer to the fuel’s level of normal paraffin, an indicator of the ease of auto-ignition due to compression. Roughly speaking, combustion fuels for vessels can be divided into two categories: heavy fuel oil (HFO) and marine diesel oils (MDO). The former category covers heavy fuel oils while the latter includes marine diesel oil, light marine diesel oil and gas oils. Heavy fuel oils usually have a higher density than the diesel oils. This is also true for biodiesel oils, that is rapeseed oil and biodiesel produced from the rapeseed plant.



This figure demonstrates the proportions of exhaust pollutants for different fuel utilization⁹

Exhaust Gas Content

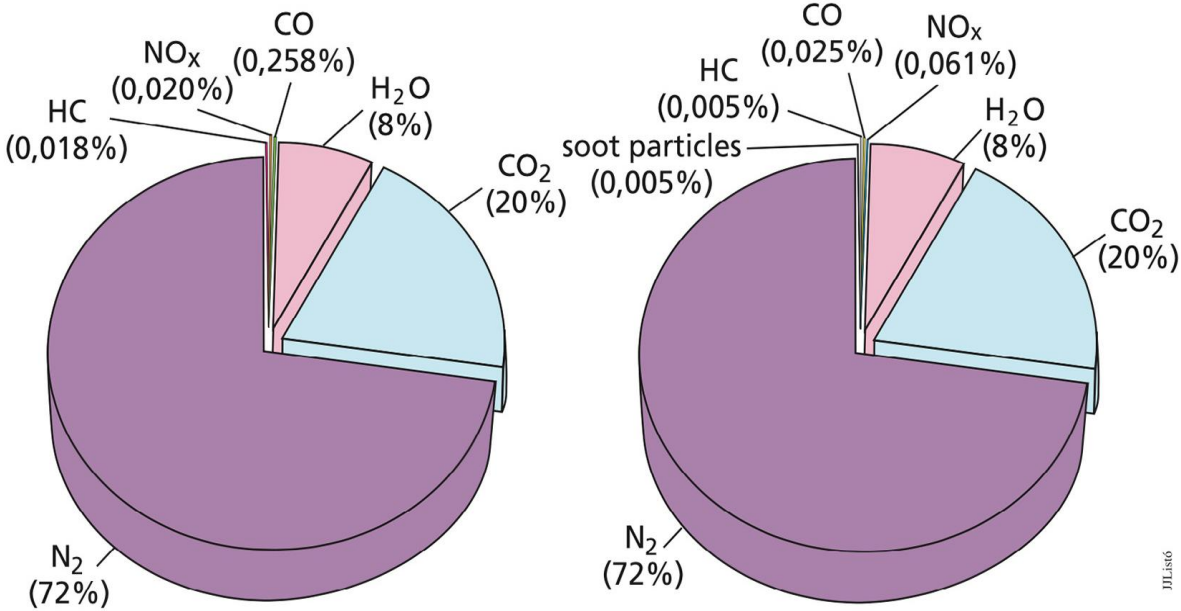
Combustion Products, a general Overview

Fossil oil’s main constituents are carbon (C) and hydrogen (H) and their combinations in the oil are represented by C_xH_y (or C_xH_{2x+2} as paraffin). The oil usually contains various other compounds to a very small extent, and this is mainly the case for heavier oils that have been processed and purified using catalysts. A few examples include aluminium, vanadium, sodium, silicium, nickel, lead and more.

Oil or fuel composition is divided into different classes, such as gaseous compounds, liquid gasoline and diesel and solid materials like tar or asphalt. Upon combustion, the fuel requires a certain amount of oxygen to generate the burn and afterwards, the exhaust is to a large extent made up of carbon dioxide and water¹⁰.

Diesel engine exhaust is dependent upon the combustion of the fuel within the engine, its structure as well as that of the machinery. Carbon dioxide (CO₂), carbon monoxide (CO), sulphur dioxide (SO₂) and water vapour (H₂O) are products of combustion in a diesel engine combustion chamber. The bulk of the products consists of carbon dioxide but the share of CO rises with increasingly incomplete combustion and also when the engine is abnormally strained. Burning heavy fuel oil, which contains a large amount of sulphur in addition to other compounds derived from the oil refining process, such as vanadium, can produce SO₃. Combined with water vapour, it may result in the formation of sulphuric acid, H₂SO₄, which causes damage to engine parts. However, the application of alkaline lubricants prevents this from occurring.

Combustion of fuel in diesel and gasoline engines is rarely complete. The exhaust materials are almost exclusively nitrogen (N₂), carbon dioxide (CO₂) and water (H₂O). However, toxic trace elements such as carbon monoxide (CO), sulphur dioxide (SO₂) and particulate matter, all harmful to the environment and human and animal health, are also formed, though only to a very small extent. Together, all of these compounds make up the bulk of emissions from fossil fuel combustion. As the engine load increases, nitrogen oxides (NO_x) and soot formation is reduced while the production of the rest of the exhaust constituents are wholly unchanged.



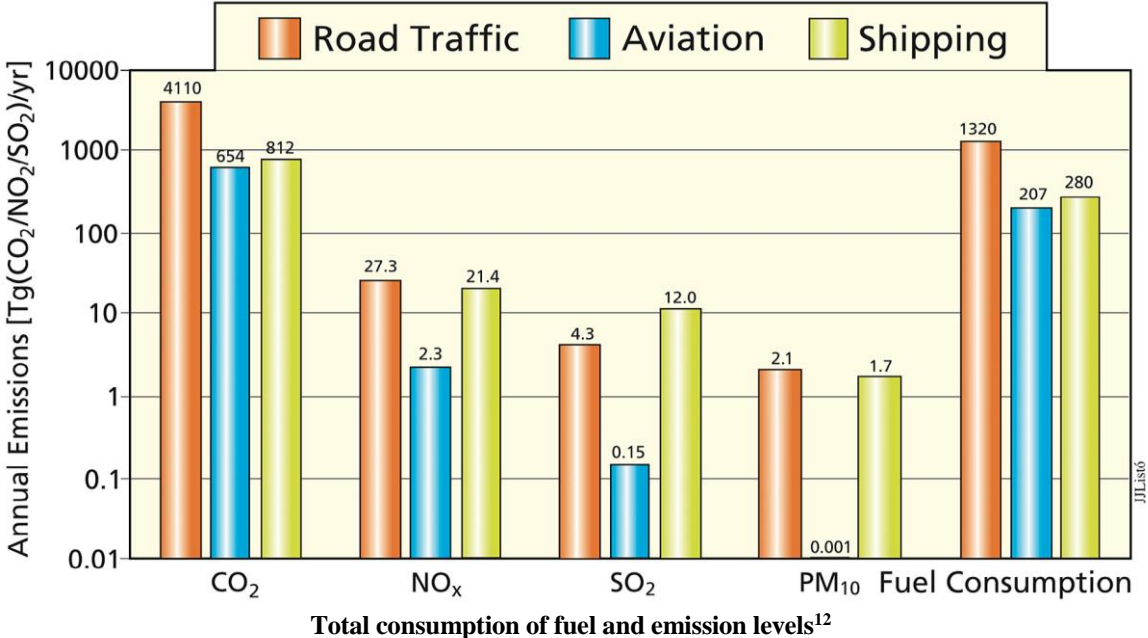
Average exhaust gas combustion in gasoline engine Average exhaust gas combustion in diesel engine

The extent of trace element emissions varies depending on type of engine, diesel or gasoline. The emission of carbon monoxide (CO), a very toxic gas, is ten times greater for gasoline engines than diesel engines while the amount of nitrogen oxides (NO_x), which are harmful for

those suffering from lung disease, is three times greater for diesel engines than for their gasoline counterparts. Soot particles have been detected as part of diesel exhaust but for gasoline engines, the particles emitted are mostly fine dust. Hydrocarbons (HC) created during incomplete combustion occur in greater quantities in gasoline engines than in those that run on diesel¹¹.

Sulphur is generally present in fossil oil, but its share is rarely over 5% volume. When fuel contains sulphurous compounds, such as sulphur dioxide (SO₂), these are, in turn, also constituents of the exhaust gas. For oil containing 1% sulphur dioxide, 0.02 kg will remain in the exhaust gas for each kg burnt oil. Therefore, the share of sulphur in marine fuels has been restricted to, for example in heavy fuel oil, a maximum allowable limit of 0.1%. Starting on January 1, 2015, a Sulphur Emission Control Area (SECA) was created where regulations are in force for fairways within these the boundaries of the SECA.

Exhaust gas is to a great extent nitrogen N₂, but also includes the greenhouse gas CO₂, and oxygen O₂ and water vapour. Moreover, it also contains other materials such as PM (Particulate Matter), thereof pure carbon, C, and the compounds CO, SO_x and NO_x which either evaporate or are condensed. The latter compounds are toxic to a varying degree and together make up less than 1% of the total exhaust gas volume, assuming normal combustion conditions. In reality, combustion is never complete and thus the amount of carbon monoxide (CO) can increase but stays within 1% for diesel engine exhaust, unlike that of gasoline engines where CO levels can reach 10%, especially during idling mode. CO is an extremely toxic gas, for which the maximum permissible exposure limit is 50 ppm or 0.005% volume in air.



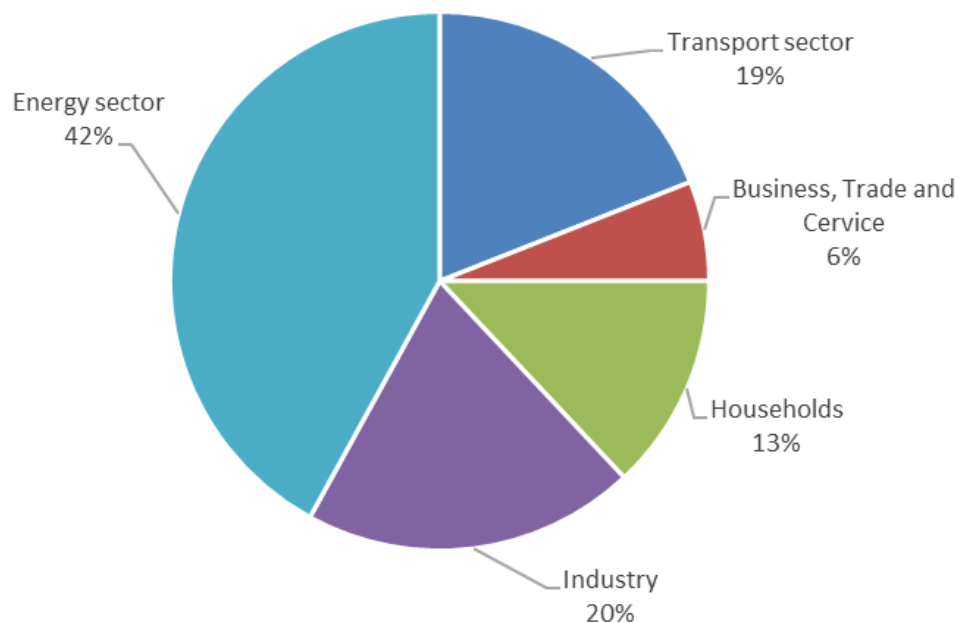
Another toxic gas associated with fossil oil consumption is hydrogen sulphide (H₂S). It is not a product of combustion and therefore not an exhaust gas constituent but according to oil product manufacturers, its formation is related to evaporation from oil containing sulphur. Its inhalation is dangerous, as it can harm the respiratory system and is highly explosive. It is

also believed to be a carcinogen, via inhalation and skin contact. The allowable limit of H₂S for occupational safety and health is, in Norway for example, 10 ppm, according to official standards.

Carbon Dioxide (CO₂)

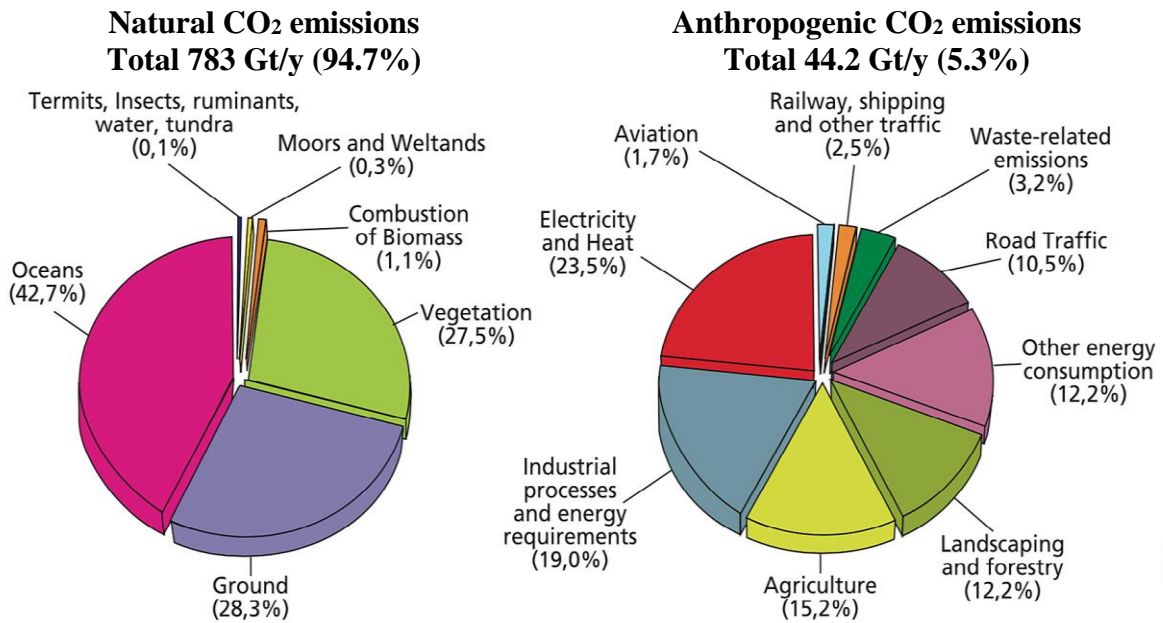
Carbon dioxide (CO₂) makes up the largest part of exhaust gas from the combustion of carbon-based fuels and is a greenhouse gas. Until now, the only means of limiting its emission has involved utilizing oil in a more efficient manner or opting for other energy sources and energy carriers that produce little or no CO₂, such as biofuel and hydrogen (H₂). One solution for limiting sulphur emissions has also been practiced for carbon dioxide emissions considering that in nature, carbon dioxide is bound in the form of limestone (CaCO₃). Due to the sheer amount of the gas, it would be difficult to use limestone for this purpose but catalytic oxidation with moist air can produce carbonic acid (H₂CO₃). In the ocean, the acid can combine with calcium to form limestone which in turn is consumed naturally¹³.

Average man-made emissions of carbon dioxide CO₂ in recent years



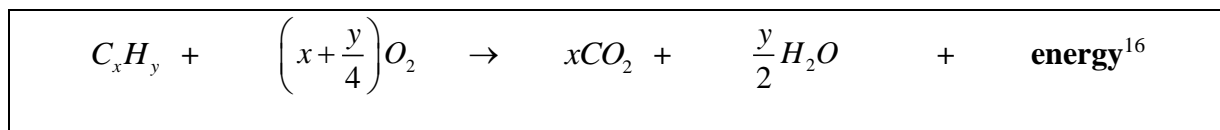
Emissions in Germany in 2005¹⁴

Carbon dioxide emissions (CO₂) mostly originate from nature itself but mankind's contribution due to energy demand is ever rising. In terms of anthropogenic emissions, the share of transport is about 19% which is equivalent to 1% of the annual global CO₂ emissions. Harbours, soil and vegetation are the greatest natural sources of emissions, approximately 98.5% of total annual emissions from natural sources of carbon dioxide.



Emissions by natural and anthropogenic causes in 2005¹⁵

Carbon dioxide is a product of fuel combustion as shown in the following chemical equation:



The fuel is in gaseous form starting at CH_4 (methane gas) through to C_4H_{10} (butane gas), in liquid form from gasoline C_5H_{12} up to and including $C_{11}H_{24}$, as liquid diesel $C_{12}H_{26}$ through $C_{17}H_{36}$ and as a solid material, such as tar, from $C_{18}H_{38}$ to $C_{22}H_{46}$ ¹⁷.

Using the chemical formula, one can calculate the amount of carbon dioxide (CO₂) in exhaust gas per kg fuel burned. However, this requires using the molecular weight of each element and compound for the calculations.

Element	Symbol	Molecular mass	Compound	Formula	Molecular mass
Carbon	C	12 kg/kmol	Carbon dioxide	CO ₂	44 kg/kmol
Hydrogen	H	1 kg/kmol	Water	H ₂ O	18 kg/kmol
Oxygen	O	16 kg/kmol	Oxygen	O ₂	32 kg/kmol
Sulphur	S	32 kg/kmol	Sulphur dioxide	SO ₂	64 kg/kmol

Carbon burnt			Carbon burnt per 1 kg C		
C	O ₂	CO ₂	C	O ₂	CO ₂
12 kg	32 kg	44 kg	1 kg	2.67 kg	3.67 kg

The amount of CO₂ present in the exhaust gas per kg carbon burnt can also be calculated using the ratio of carbon in the oil. This is demonstrated in a simple manner in the tables above and below.

Carbon dioxide amount in exhaust gas for combustion of 1 kg fuel						
Fuel	Formula	kg C	kg H	C ratio	Coefficient	CO₂/1 kg
Methane gases	CH ₄	12	4	0.75	3.67	2.75
Gasoline	C ₇ H ₁₆	84	16	0.84	3.67	3.08
Diesel	C ₁₅ H ₃₂	180	32	0.85	3.67	3.12

As an example, let us look at C₇H₁₆, normal gasoline, and its chemical equation for combustion would be the following: $C_7H_{16} + 15O_2 \rightarrow 7CO_2 + 8H_2O$. For 1 kg gasoline, 3.52 kg oxygen would be required and following combustion, the exhaust would contain 3.08 kg carbon dioxide and 1.44 kg water.

Another example is diesel oil, C₁₅H₃₂, which has low viscosity and the following chemical equation $C_{15}H_{32} + 31O_2 \rightarrow 15CO_2 + 16H_2O$. For each 1 kg diesel oil, 3.47 kg oxygen are required and the exhaust gas would consist of 3.11 kg carbon dioxide and 1.36 kg water.

Nitrogen Oxides (NOx)

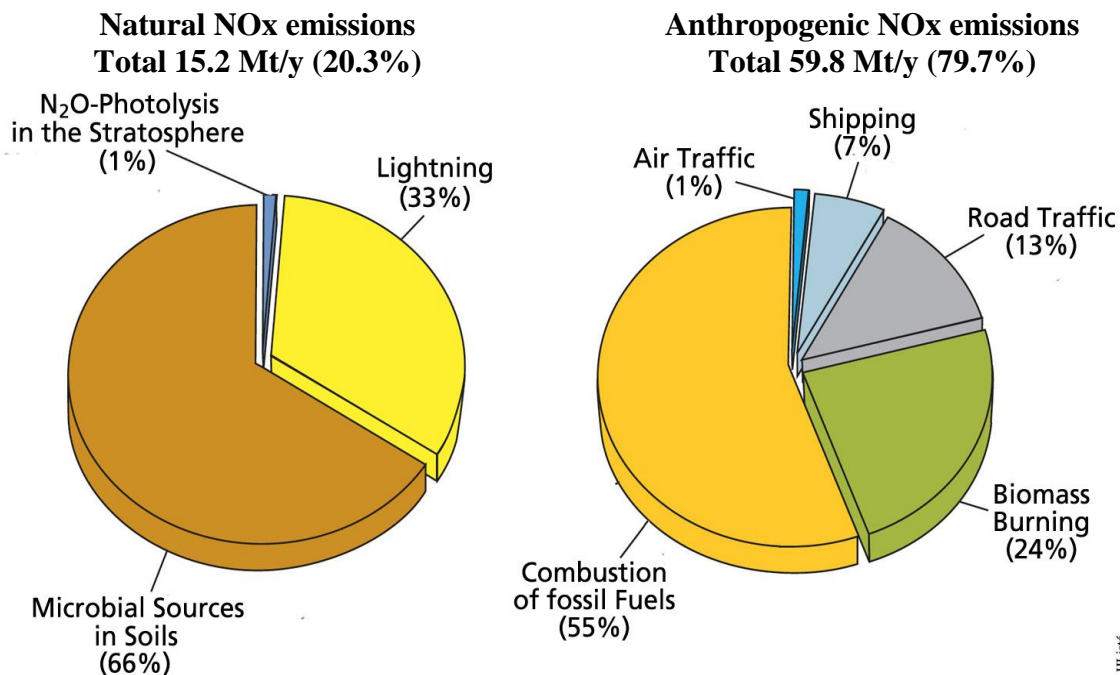
Nitrogen oxide (NOx) emissions are almost solely dependent upon combustion chamber temperature, not the type of fuel. The nitrogen present in the atmosphere is oxidized due to the heat within the combustion chamber regardless of fuel. NO₂ and N₂O are the main products. Due to the moisture in the atmosphere, nitric acid (HNO₃) is produced and can cause harmful acid rain, and this is precisely the reason for global action to reduce NOx emissions. The most effective method is catalytic oxidation with nitrogen and water. And, as a large share of nitrogen oxides originate from idling engines, this can be reduced via lower combustion temperatures or with water in fuel emulsion technology.

The amount of nitrogen oxides (NOx) created is proportional to the engine load and combustion chamber temperature:

- *Heavy fuel oil* *100% in the beginning, reduced to 60% at full load*
- *Marine oil* *100% in the beginning, reduced to 60% at full load*
- *RME (rapeseed diesel* *110% in the beginning, reduced to 70% at full load due to higher combustion temperature*

RME is non-flammable, non-toxic and is degraded in nature within 2-3 weeks. Its adoption would reduce the need for fossil fuels by 95% relative to the life cycle cost of its domestic cultivation.

The combustion emission of 1 kg diesel oil normally contains 0.04 kg NOx gas, which is mostly NO and NO₂. This applies using the assumption of an average combustion temperature within the engine combustion chamber¹⁸.



Natural and anthropogenic NO_x emissions in 2005¹⁹

NO_x emissions are largely anthropogenic and mostly due to fossil fuel combustion and transport. Shipping contributes 7% of anthropogenic emissions, which is equivalent to 5.5% of the total annual emissions of nitrogen oxides (NO_x). Natural NO_x emissions arise almost entirely as result of microorganisms and lightning.

Sulphur Dioxide (SO₂)

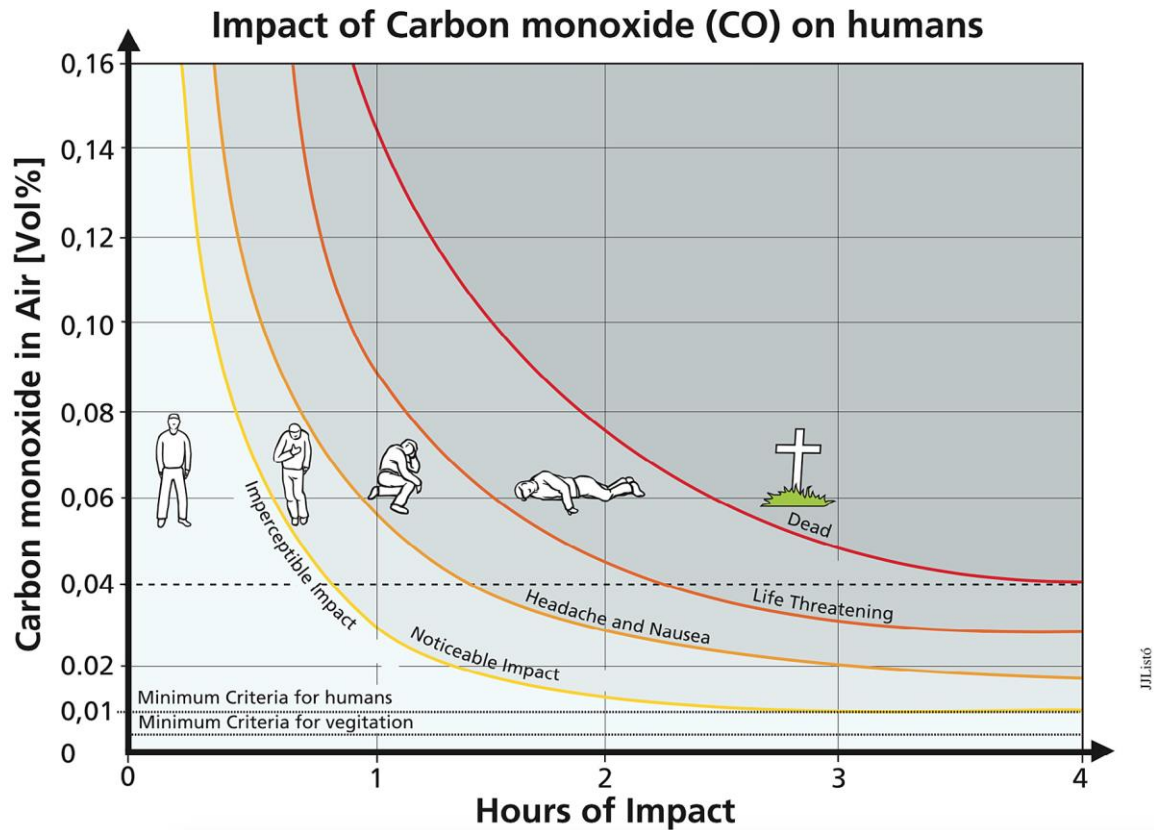
During combustion with oxygen, sulphur (S) is oxidized to form SO₂ and SO₃ gas, in amounts directly proportional to the sulphur content of the combusted fuel. The best means by which to limit SO_x emissions is to use sulphur free fuel, however, this option is more costly. Sulphur scrubbing can be carried out by cooling exhaust gases, scrubbing with calcium oxide (CaO) dissolved in fresh water or sea water, producing CaSO₄, a compound created in nature itself. The sulphate must be properly treated and stored as when sulphur oxides are emitted to air, acid rain (sulphuric acid) ensues. Due to the corrosivity of the oxides mixed with steam from combustion, basic Ca is added to the lubricant to neutralize the acid, for example 2.5% Ca for 3.0% S in the combustion fuel²⁰.

In diesel oil, the amount of sulphur dioxide (SO₂) is usually as follows:

- *Heavy fuel oil (HFO)* contains about 4.5% sulphur (S)
- *Marine diesel oil (MDO)* contains about 0.4% to 0.1% sulphur (S)
- *RME (rapeseed diesel)* contains no (0.0%) sulphur (S)

The proportional quantity of carbon monoxide in exhaust is as follows, for the purpose of comparison:

- *Heavy fuel oil* 100%
- *Marine diesel oil* 100%
- *RME (rapeseed diesel)* 70%



Hydrocarbon (HC) is unburned oil and can be found in exhaust gas following combustion where the temperature was not high enough or due to technical issues, such as a deviation in pressure. HC can be oxidized using catalysts or recycling the exhaust gas, also known as VOC for volatile organic carbon²².

The proportional quantity of hydrocarbon (HC) in exhaust depends on the engine load:

- *Heavy fuel oil* 100%
- *Marine diesel oil* 26%
- *RME (rapeseed diesel)* 15%

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