2 FUEL PROPERTIES

2.1 General

Gasoline and diesel fuel are complicated mixtures of hydrocarbons, including aromatic, naphtenic, olefinic and parafinic components. Gasoline typically contains hydrocarbons with 5-12 carbon atoms, diesel fuel 12-18 carbon atoms /22/. As a result of incomplete combustion, complex partially oxidised compounds and soot can be formed.

Both natural gas and LPG (liquefied petroleum gas) are well suited as Otto engine fuels. Both have a relatively high knock resistance /23/. Gaseous fuels easily form a homogeneous mixture with air. This, and the simplicity of the fuel molecule, is advantageous for soot-free complete combustion (methane one carbon atom, propane three carbon atoms, Figure 2.1).

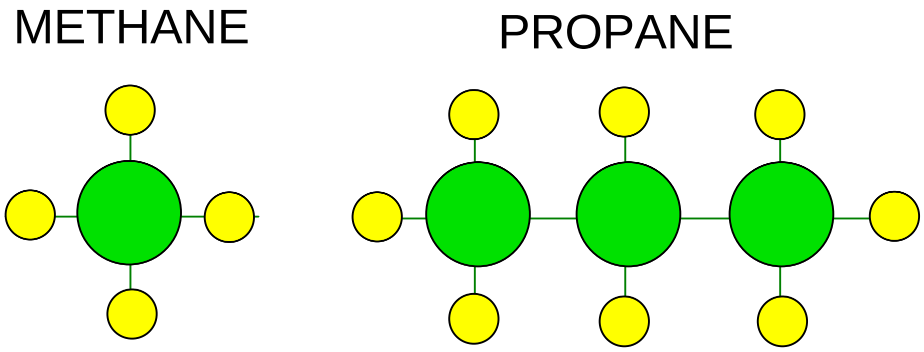


Figure 2.1. The chemical structure of methane and propane.

If, for some reason, combustion is incomplete, the hydrocarbons found in the exhaust of a natural gas fuelled vehicle is mostly methane, which is not noxious.

Both natural gas and LPG have a long history as engine fuels /24/. In general, the composition of both natural gas and LPG varies from site to site. The main constituent of natural gas is methane (CH_4). In the United States and Canada natural gas normally contains 85-95 % (by volume) methane, the remainder being carbon dioxide, nitrogen and small amounts of ethane, propane and butane /25/. Some North Sea gases can contain up to 20 % carbon dioxide, although carbon dioxide is usually reduced to below 5 % when delivered by pipeline. The natural gas supplied to Finland from Russia is very rich in methane, over 98 by volume /26/.

At normal ambient pressure the boiling point of the light hydrocarbons are: methane –62 °C, propane –43 °C, isobutane –10 °C and n-butane +1 °C /27/. Natural gas is stored on board the vehicle either under pressure at approximately 200 bar (compressed natural gas, CNG) or liquefied in an insulated pressure vessel (liquefied natural gas, LNG) /28/. LPG is always stored in liquid form under moderate pressure.

In older engine applications both natural gas and LPG are fed in gaseous form to the mechanical air and gas mixing device /29/. However, in most current designs fuel is metered by electronically controlled injectors mounted in or before the inlet manifold /23/. In the case of natural gas the fuel is in gaseous form (with the possible exception of LNG), LPG can be in either gaseous or liquid form.

In each case, the gaseous fuels easily form a homogeneous mixture with air entering the engine cylinder. This is advantageous for cold start, enrichment is not needed with gaseous fuels. With liquid fuels, the amount of fuel evaporated is decisive for forming an igniteable mixture, not the total amount of fuel supplied. In gasoline engines, over-fuelling by a factor of 5-10 is needed to secure starting. Figure 2.2 illustrates the advantages of gaseous fuel over gasoline in cold starting. However, some bi-fuel fuel systems do not utilise this advantage, if the engines are started up on gasoline.

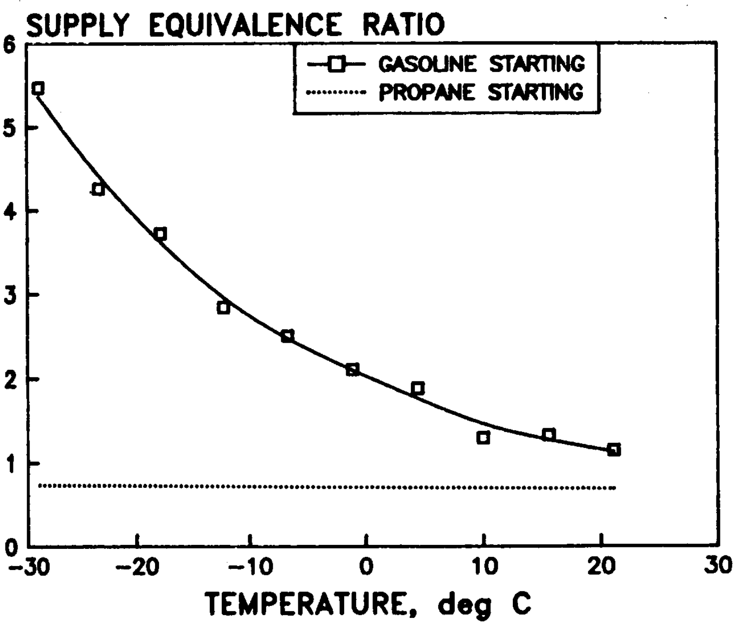


Figure 2.2. Cold start enrichment on gasoline and propane /30/.

2.2 Combustion properties

The following factors and properties, among other things, affect the performance of gases in engine and vehicle applications /23/:

- heat of combustion per unit volume
- heat of combustion per unit weight
- heat of combustion of the mixture per unit volume
- Wobbe-index
- self-ignition temperature
- knock resistance
- combustion limits

If emissions and catalyst performance are included in the list, chemical composition and sulphur content should also be added. Some sulphur compounds, which are used as odorants in natural gas, have a detrimental effect on catalyst performance.

The heat of combustion per unit volume or weight reflects the size and weight of the fuel storage on board the vehicle. The heat of combustion per unit volume of the stoichiometric air-fuel mixture, on the other hand, to some extent reflects the power density that can be achieved.

Gaseous fuels occupy a larger volume than liquid fuels, thus allowing a smaller charge of fresh air to be captured in the cylinder than is available on liquid fuels. The theoretical air and fuel ratio, density and energy density of the stoichiometric mixture and the relative energy density for some liquid and gaseous fuels are listed in Table 2.1. The values are calculated on the basis of the values listed in /27/. In the case of liquid fuels it is considered that the fuel does not reduce the amount of air captured in the cylinder.

Switching over from gasoline to methane reduces the energy density of the stoichiometric mixture by some 10 %. In a real engine, the power output of the engine is also affected by the actual air-fuel ratio, volumetric efficiency and brake thermal efficiency, among other things.

A diesel engine cannot be run on a stoichiometric mixture due to excessive smoke formation. The minimum relative air-fuel ratio value for an automotive high-speed diesel engine is in the order of 1.3 /31/. Table 1 also indicates that a naturally aspirated stoichiometric natural gas or LPG engine should have a higher power output than a naturally aspirated diesel engine.

Table 2.1. Air-*fuel ratio and energy density of the stoichiometric air-fuel mixture (l = 1).*

Fuel	Air-fuel ratio (-)	Mixture density (kg/m^3)	Energy Density (MJ/m^3)	Rel. energy density (-)
Hydrogen	34	0. 94	3.21	0.84
Methane	17.2	1.24	3.40	0.89
Propane	15.6	1.32	3 .68	096
Methanol	6.4	1.49	3.98	1.04
Ethanol	9.0	1.44	3.85	1.01
Gasoline	14.7	1.38	3.83	1.00
Diesel	14.5	1.38	3.79	0.99
Diesel (λ= 1.3)	18.9	1.36	2.92	0.76

(λ = actual air-fuel ratio/theoretical air-fuel ratio)

The Wobbe index is a measure of the interchangeability of gases. The Wobbe index relates to a comparative measure of thermal energy flow through a given size of orifice /32/. Gases which have the same Wobbe index can replace each other without a change in the relative air-fuel ratio, at the same fuel metering settings. Table 2.2 gives the Wobbe index for some gases.

Table 2.2. The Wobbe index for some gases /33/. The values for butane have been calculated using values from /27 /.

Gas	Wobbe index (MJ/m^3)
Natural gas (Groningen, Netherlands)	39.47
Methane	48.17
Ethane	62.86
Propane	74.75
LPG (60 % propane, 40 % butane)	79.2
Butane	85.2
Hydrogen	40.89
Carbon monoxide	12.84

If a mechanical fuel metering system without any kind of feedback control is used, the engine has to be tuned for a specific gas. If the gas quality changes, the engine might run either too lean or too rich, depending on the case. For example, switching from Groningen gas to pure methane would mean that the mixture becomes too rich. An engine calibrated for λ= 1 on propane would run on λ= 1.55 on methane.

If a closed-loop fuel metering system incorporating an exhaust gas oxygen sensor is used, the system can normally compensate for at least small changes in gas composition. This is one reason why the share of closed-loop fuel systems is expected to grow also for heavy-duty lean-burn gas engines.

In a diesel engine, combustion is initiated through autoignition of the fuel due to the high end-temperature and pressure of compression. The autoignition temperature of propane and especially methane are so high that these fuels are not suited for the diesel process. For autoignition with methane, a compression ratio of 38:1 and for propane 29:1 is needed /34/. Therefore, in a gas engine the gaseous fuel has to be ignited either by an electrical spark (Otto engine) or by diesel fuel (pilot injection).

On the other hand, the knock resistance of both methane and propane is high. High knock resistance is advantageous for Otto engine fuels, because continuous knocking combustion is destructive for the engine, and should be avoided. The Research Octane Number of methane is in the order of 120, and is above 100 for propane. Compression ratios close to 13:1 can be used for natural gas fuelled Otto engines /32/. Thus engine efficiency can be higher in natural gas operation compared to gasoline operation.

The knock resistance of gaseous fuels is often evaluated by the methane number. Methane, which has high knock resistance, is given the index 100. Hydrogen, which has low knock resistance, is given the index 0. If a certain gas mixture has a methane number of 70, its knock resistance is equivalent to that of a gas mixture of 70 % methane and 30 % hydrogen.

Lean-burn combustion is an interesting alternative for heavy-duty gas-fuelled engines. The engine out emission of nitrogen oxides is reduced considerably using a λ value of 1.5-1.7 instead of a stoichiometric or slightly lean mixture /35/. Compared to gasoline, methane burns somewhat more slowly, and has a higher lean limit. Propane burns faster than gasoline, and has a lean limit between gasoline and methane. Hydrogen differs considerably from the other fuels both in terms of flame velocity and lean limit, and has excellent lean-burn capabilities /36/.

The ignition energy needed is normally at a minimum close to the stoichiometric air-fuel ratio, and increases both with a leaner and a richer mixture. The ignition energy needed for lean-burn operation is considerably higher than for stoichiometric operation. The ignition energy varies also with fuel quality. The ignition energy increases in the following order: hydrogen, gasoline, propane and methane /37/. Thus a lean-burn natural gas engine sets high requirements on the performance of the ignition system.

2.3 Emission characteristics and energy efficiency

The exhaust gas composition will also vary with fuel quality. Table 2.3 gives the exhaust gas composition for an ideal engine with a stoichiometric mixture. The exhaust gases of a real engine always contain also products of incomplete combustion (carbon monoxide, hydrocarbons) and oxides of nitrogen.

Table 2.3. Exhaust gas composition for the ideal engine (stoichiometric mixture) and specific CO_2 emission of combustion /34,38/.

Fuel	Carbon dioxide CO_2 (%)	Water H_2O (%)	Nitrogen N_2 (%)	Specific CO_2 em. (g/MJ $_{fuel}$)
Hydrogen	0	35	65	n.a.
Carbon	21	0	79	93
Methane	9.5	19.0	71.5	56
Ethane	11.0	16.5	72.5	-
Propane	11.6	15.5	72.9	65
Butane	12.0	15.0	73.0	-
Octane	12.5	14.1	73.4	-
Diesel	13.4	12.6	74.0	72
Methanol	11.6	23.1	65.3	69
Ethanol	12.3	18.4	69.3	64

Burning natural gas and propane gives less carbon dioxide and more water vapour per energy unit than burning gasoline or diesel fuel. Carbon dioxide is the most important greenhouse gas. International agreements to reduce carbon dioxide have been signed /39/. The emission of greenhouse gases is dependent on both the efficiency of the whole chain and fuel chemistry. Evaluations of energy consumption and greenhouse gases should be carried out over the whole fuel chain including production, distribution and utilisation (life cycle analysis, LCA).

One argument heard in promoting natural gas as an automotive fuel is that natural gas reduces carbon dioxide emissions compared to conventional hydrocarbon fuels. This is most cases true when substituting gasoline with natural gas.

The situation is different for heavy-duty vehicles. The thermal efficiency of the Otto cycle is lower than that of the diesel cycle, and therefore the energy consumption of a heavy-duty spark-ignited natural gas or propane engine is higher compared to the diesel engine. In the case of end-use emissions, this more or less compensates for the differences in fuel chemistry. In addition, methane, which is contained in the natural gas vehicle exhaust emissions, is a very strong greenhouse gas.

Figure 2.3 shows well-to-fuel tank efficiency for different options of using natural gas /40/. It shows that up to the fuel tank compressed natural gas, including the work of compression, has the same efficiency as conventional diesel fuel from oil. To get the total efficiency, the efficiency of the vehicle also has to be taken into consideration.

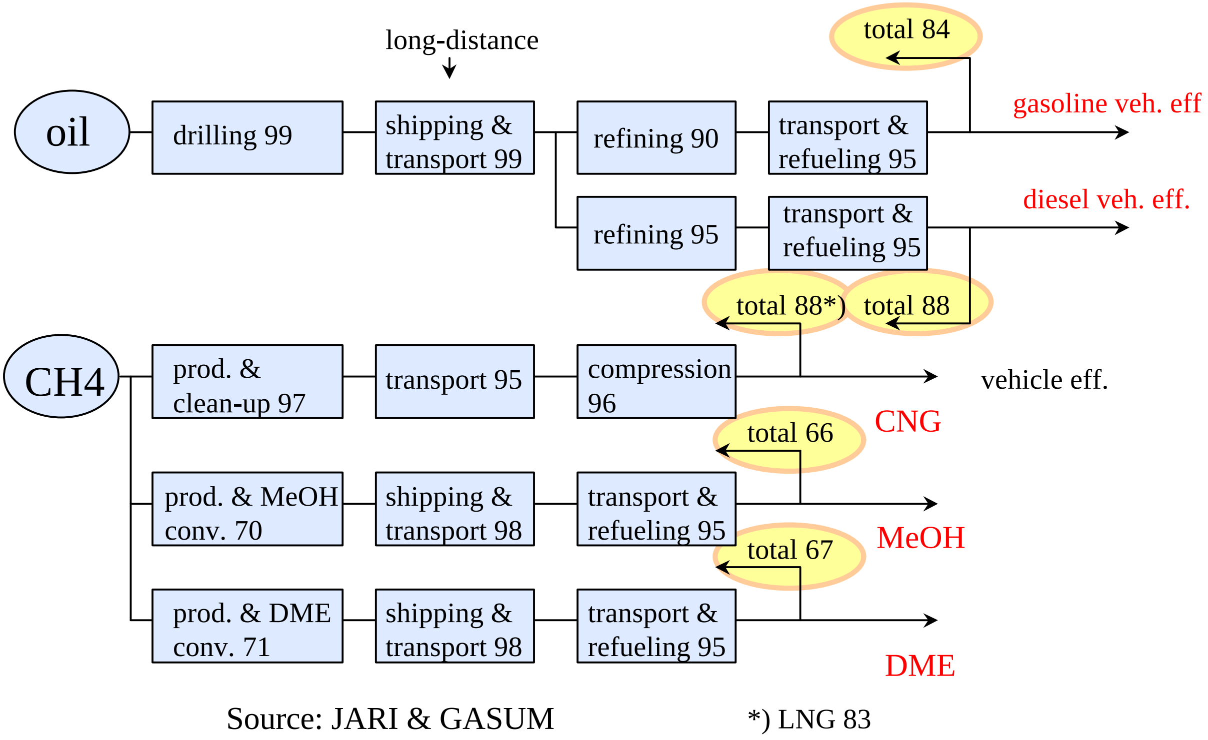


Figure 2.3. Well-to-fuel tank efficiency for oil and natural gas based fuels /40/, CNG values from Gasum Oy, Finland.

Table 2.4 gives a summary of well to wheel efficiency for different fuel and vehicle technologies /41/. The well-to-station values in this Table correlate relatively well with the values in Figure 2.3.

Table 2.5 summarises the greenhouse gas emissions (expressed as CO_2 equivalent) over the whole fuel chain for different fuel alternatives taking into consideration both energy efficiency and fuel chemistry. This particular assessment (Ecotraffic /38/) demonstrates that in the case of light-duty vehicles a switch from gasoline to natural gas reduces greenhouse gases substantially, whereas for heavy-duty vehicles small overall reductions of greenhouse gases can be achieved using either natural gas or propane instead of diesel. Some assessments are not so optimistic in the case of heavy-duty vehicles. Innas of Holland states that for heavy-duty vehicles the CO_2 with natural gas is equivalent to diesel vehicles /42/.

Table 2.4. Well to wheel efficiencies for different fuel and vehicle technologies /41/.

	Total well-station	Engine	Transm. & aux	Weight correction	Total vehicle	Total well-wheel
Bus engines		%			%	%
Diesel	0.901	35	0.84	1.00	29.4	26.5
DME	0.665	35	0.84	0.99	29.1	19.4
LPG LB	0.887	32	0.84	1.00	26.9	23.8
LPG SM	0.887	29	0.84	1.00	24.4	21.6
CNG LB *)	0.86	32	0.84	0.97	26.1	22.4
CNG SM **)	0.86	30	0.84	0.95	23.9	20.6
LNG LB	0.804	32	0.84	1.00	26.9	21.6
Methanol Diesel	0.617	35	0.84	0.99	29.1	18.0
Methanol Otto	0.617	30	0.84	0.99	24.9	15.4
Gasoline Otto	0.817	29	0.84	1.01	24.6	20.1
Bio-ethanol Die.		35	0.84	0.99	29.1	
Light-duty						
Diesel	0.901	28	0.89	1	25	22.5
DME	0.665	28	0.89	0.99	25	16.4
Gasoline	0.817	23	0.89	1.01	21	16.9
LPG	0.887	23	0.89	1	20	18.2
CNG	0.86	23	0.89	0.95	19	16.7
Methanol	0.617	23	0.89	0.99	20	12.5

*) high calorific gas **) low calorific gas

Table 2.5. Greenhouse gases over the whole fuel chain (CO_2 equivalents, grams per vehicle kilometre and relative /38/.

Fuel	Passenger car		Urban bus	
	(g/km)	relative	(g/km)	Relative
Gasoline	350	1	-	-
Diesel	-	-	1 600	1
Methanol *)	300	0.9	1 500	0.94
Natural gas	230	0.7	1 400	0.88
Propane	300	0.9	1 500	0.94

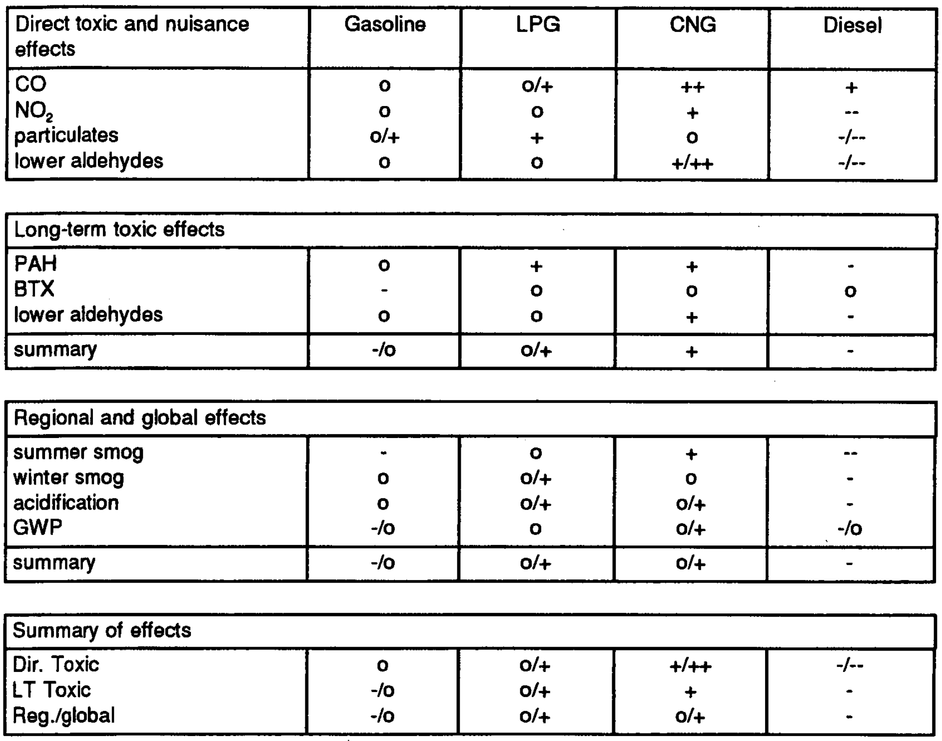
*) *from natural gas feedstock*

The possible reduction of greenhouse gases is not, however, the main reason to promote gaseous fuels for heavy-duty vehicles in urban services. More important is the possibility of reducing toxic unregulated exhaust emissions, and, to some extent, also regulated emissions.

In general, considering both light- and heavy-duty applications, the decisive factor for regulated emissions is the engine and exhaust gas aftertreatment technology used on the vehicle. Fuel chemistry, on the other hand, is clearly linked to exhaust gas toxicity, and in this respect the simple chemical structure of both methane and propane gives a clear advantage over conventional fuels. Research organisations like TNO in Holland and VTT in Finland have studied unregulated emissions from different fuel alternatives.

Table 2.6 gives a summary made by TNO of environmental and health effects of gasoline, LPG, CNG and diesel in passenger cars. In most respects natural gas is clearly better than average. The photochemical reactivity of methane and propane is low, and thus these fuels are beneficial also in reducing summer time smog formation.

Table 2.6. Evaluation of health and environmental effects of different fuel alternatives /43/.



Direct toxic and nuisance effects	Gasoline	LPG	CNG	Diesel
CO	o	o/+	++	+
NO_2	o	o	+	--
particulates	o/+	+	o	-/--
lower aldehydes	o	o	+/++	-/--

Long-term toxic effects				
PAH	o	+	+	-
BTX	-	o	o	o
lower aldehydes	o	o	+	-
summary	-/o	o/+	+	-

Regional and global effects				
summer smog	-	o	+	--
winter smog	o	o/+	o	-
acidification	o	o/+	o/+	-
GWP	-/o	o	o/+	-/o
summary	-/o	o/+	o/+	-

Summary of effects				
Dir. Toxic	o	o/+	+/++	-/--
LT Toxic	-/o	o/+	+	-
Reg./global	-/o	o/+	o/+	-

(++, + advantages, 0 average, -, -- disadvantages)

Figure 2.4 shows VTT data for unregulated emissions at low temperature (-7 ^{o}C) for a number of fuel alternatives. CNG and LPG give the lowest unregulated emissions (in this case 1,3-butadiene, benzene, formaldehyde and methanol) of all fuels.

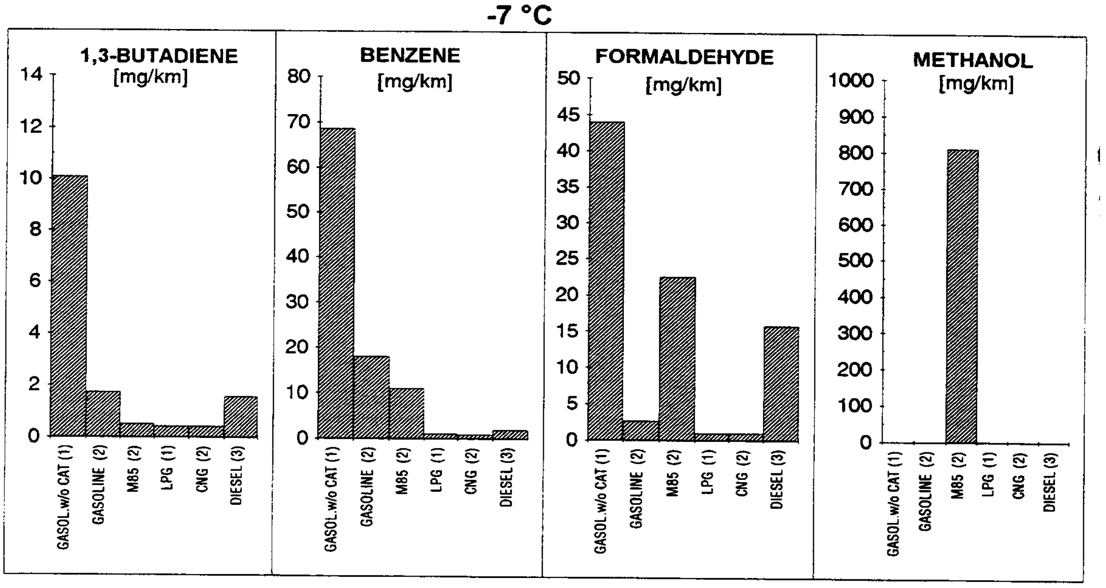


Figure 2.4. Unregulated emissions at low-temperature operation /16/.

The German Federal Environmental Agency (UBA) has made assessments on the carcinogenic potential of diesel and CNG bus exhaust. According to UBA's estimate a conventional diesel bus is roughly 100 times more harmful than a CNG bus. For Euro 3 diesel engines this ratio will drop to around 25, and only diesel engines with particulate filters will come close to gas engines, the diesel, however, still being more harmful than the CNG engine by a factor of four (Figure 2.5).

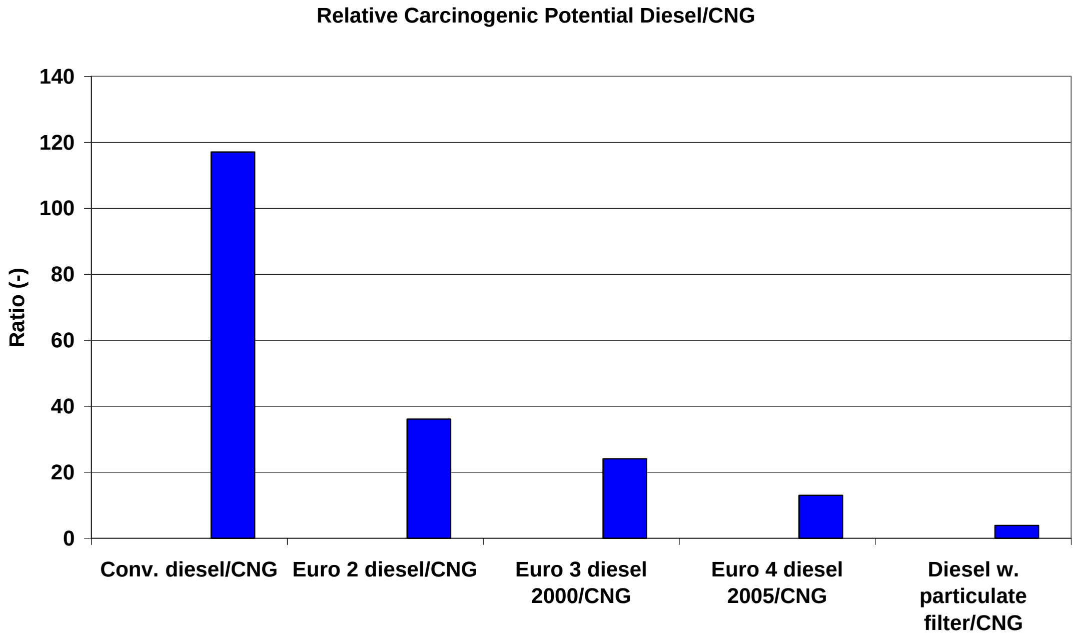


Figure 2.5. Comparison of the carcinogenic potential of diesel-/CNG bus exhaust /44/.