NTNU

The Norwegian University of Science and Technology
Norges Teknisk-Naturvitenskapelige Universitet

ADDRESS:	TELEPHONE		TELEFAX	
NTNU	Switchboard NTNU:	73 59 40 00	Department office:	73 59 83 90
DEPARTMENT OF ENERGY AND	Department office:	73 59 27 00	Hydropower section:	73 59 38 54
PROCESS Engineering	Hydropower section:	73 59 38 57		
Kolbjørn Hejes vei 1A				
N-7491 Trondheim - NTNU				

Title of report Experimental study of hydrogen as a fuel additive in internal combustion engines	Date 2008-01-15
	No. Of pages/appendixes
Author Inge Saanum	Project manager Johan E. Hustad
Division Faculty of Engineering Science and technology Department of Energy and Process Engineering	Project no.
ISBN no. ISBN 978-82-471-6583-6 ISBN 978-82-471-6597-3 (electronic)	Price group

Client/sponsor of Project The Gas Technology Center, NTNU-Sintef The Research Council of Norway	Client's ref.

Abstract

Combustion of hydrocarbons in internal combustion engines results in emissions that can be harmful both to human health and to the environment. Although the engine technology is improving, the emissions of NO_x, PM and UHC are still challenging. Besides, the overall consumption of fossil fuel and hence the emissions of CO_2 are increasing because of the increasing number of vehicles. This has lead to a focus on finding alternative fuels and alternative technologies that may result in lower emissions of harmful gases and lower CO_2 emissions. This thesis treats various topics that are relevant when using blends of fuels in different internal combustion engine technologies, with a particular focus on using hydrogen as a fuel additive. The topics addressed are especially the ones that impact the environment, such as emissions of harmful gases and thermal efficiency (fuel consumption). The thesis is based on experimental work performed at four different test rigs:

1. A dynamic combustion rig with optical access to the combustion chamber where spark ignited premixed combustion could be studied by means of a Schlieren optical setup and a high speed video camera.
2. A spark ignition natural gas engine rig with an optional exhaust gas recycling system.
3. A 1-cylinder diesel engine prepared for homogeneous charge compression ignition combustion.
4. A 6-cylinder standard diesel engine

The engine rigs were equipped with cylinder pressure sensors, engine dynamometers, exhaust gas analyzers etc. to enable analyses of the effects of different fuels. The effect of hydrogen blended with methane and natural gas in spark ignited premixed combustion was investigated in the dynamic combustion rig and in a natural gas engine. In the dynamic combustion rig, the effect of hydrogen added to methane on the flame speed and the flame structure was investigated at elevated pressure and temperature. A considerable increase in the flame speed was observed when adding 30 vol% hydrogen to the methane, but 5 vol% hydrogen also resulted in a noticeable increase. The flame structure was also influenced by the hydrogen addition as the flame front had a higher tendency to become wrinkled or cellular. The effect is believed to mainly be caused by a reduction in the effective Lewis number of the mixture. In the gas engine experiments, the effect of adding 25 vol% hydrogen to natural gas was investigated when the engine was run on lean air/fuel mixtures and on stoichiometric mixtures with exhaust gas recirculation. The hydrogen addition was found to extend the lean limit of stable combustion and hence caused lower NO_x emissions. The brake thermal efficiency increased with the hydrogen addition, both for the fuel lean and the stoichiometric mixtures with exhaust gas recirculation. This is mainly because of shorter combustion durations when the hydrogen mixture was used, leading to thermodynamically improved cycles.

Two types of experiments were performed in compression ignition engines. First, homogenous charge compression ignition (HCCI) experiments were performed in a single cylinder engine fueled with natural gas and diesel oil. As HCCI engines have high thermal efficiency and low NO_x and PM emissions it may be more favorable to use natural gas in HCCI engines than in spark ignition engines. The mixture of natural gas, diesel oil and air was partly premixed before combustion. The natural gas/diesel ratio was used to control the ignition timing as the fuels have very different ignition properties. The natural gas was also replaced by a 20 vol% hydrogen/natural gas mixture to

study the effect of hydrogen on the ignition and combustion process. Also, rape seed methyl ester (RME) was tested instead of the diesel oil. The combustion phasing was found to mainly be controlled by the amount of liquid fuel injected. The presence or absence of hydrogen resulted in only marginal changes on the combustion. Because the diesel oil and RME have much lower autoignition temperatures than both hydrogen and natural gas, the properties of the liquid fuel may overshadow the effect of the hydrogen addition. A large difference however, was found between the RME and the diesel oil with the necessity to inject much more RME than diesel oil to obtain the same combustion phasing.

The last experiments with compression ignition were performed by using a standard Scania diesel engine where the possibilities to reduce particulate matter (PM) and other emissions by introduction of combustible gas to the inlet air (named fumigation) were investigated. Hydrogen, methane and propane were introduced at different rates replacing up to 40% of the total fuel energy. Also, a biodiesel consisting of mainly RME was tested instead of the diesel oil. Because of the low density of hydrogen gas, less of the fuel energy could be replaced by hydrogen than by the two other gases. Higher rates of hydrogen would sacrifice the safety by exceeding the lower flammability limit in the inlet air. Only moderate reductions in PM were achieved at high gas rates, and because of the limitation in the practical achievable hydrogen rate it was not possible to obtain considerable reductions in PM emission by hydrogen addition. The NO_x emissions were found to be little influenced by the fumigation, but the THC emissions strongly increased with increased methane and propane rates, especially at a low engine load. Propane fumigation resulted in considerably less THC emissions than methane fumigation. The biodiesel resulted in higher PM emissions than the diesel fuel at low load, but was considerably lower at the higher loads. This is believed to be because of the low volatility of the biodiesel which may lead to emissions of un-burned fuel at low load when the temperature is low. At higher loads this is believed to be less of a problem because the temperature is higher, and the oxygen content of biodiesel is believed to increase the PM oxidation and/or reduce the formation of PM.

	Indexing Terms: English	Norwegian
Group 1	Hydrogen	Hydrogen
Gruup 2	Combustion	Forbrenning
Selected by author	Internal combustion engines	Forbrenningsmotorer
	Natural gas	Naturgass
	Biodiesel	Biodiesel

Abstract

Combustion of hydrocarbons in internal combustion engines results in emissions that can be harmful both to human health and to the environment. Although the engine technology is improving, the emissions of NO_x, PM and UHC are still challenging. Besides, the overall consumption of fossil fuel and hence the emissions of CO_2 are increasing because of the increasing number of vehicles. This has lead to a focus on finding alternative fuels and alternative technologies that may result in lower emissions of harmful gases and lower CO_2 emissions. This thesis treats various topics that are relevant when using blends of fuels in different internal combustion engine technologies, with a particular focus on using hydrogen as a fuel additive. The topics addressed are especially the ones that impact the environment, such as emissions of harmful gases and thermal efficiency (fuel consumption). The thesis is based on experimental work performed at four different test rigs:

1. A dynamic combustion rig with optical access to the combustion chamber where spark ignited premixed combustion could be studied by means of a Schlieren optical setup and a high speed video camera.
2. A spark ignition natural gas engine rig with an optional exhaust gas recycling system.
3. A 1-cylinder diesel engine prepared for homogeneous charge compression ignition combustion.
4. A 6-cylinder standard diesel engine

The engine rigs were equipped with cylinder pressure sensors, engine dynamometers, exhaust gas analyzers etc. to enable analyses of the effects of different fuels. The effect of hydrogen blended with methane and natural gas in spark ignited premixed combustion was investigated in the dynamic combustion rig and in a natural gas engine. In the dynamic combustion rig, the effect of hydrogen added to methane on the flame speed and the flame structure was investigated at elevated pressure and temperature. A considerable increase in the flame speed was observed when adding 30 vol% hydrogen to the methane, but 5 vol% hydrogen also resulted in a noticeable increase. The flame structure was also influenced by the hydrogen addition as the flame front had a higher tendency to become wrinkled or cellular. The effect is believed to mainly be caused by a reduction in the effective Lewis number of the mixture. In the gas engine experiments, the effect of adding 25 vol% hydrogen to natural gas was investigated when the engine was run on lean air/fuel mixtures and on stoichiometric mixtures with exhaust gas recirculation. The hydrogen addition was found to extend the lean limit of stable combustion and hence caused lower NO_x emissions. The brake thermal efficiency increased with the hydrogen addition, both for the fuel lean and the stoichiometric mixtures with exhaust gas recirculation. This is mainly because of shorter combustion durations when the hydrogen mixture was used, leading to thermodynamically improved cycles.

Two types of experiments were performed in compression ignition engines. First, homogenous charge compression ignition (HCCI) experiments were performed in a single cylinder engine fueled with natural gas and diesel oil. As HCCI engines have high thermal efficiency and low NO_x and PM emissions it may be more favorable to use natural gas in HCCI engines than in spark ignition engines. The mixture of natural gas, diesel oil and air was partly premixed before combustion. The natural gas/diesel

ABSTRACT

ratio was used to control the ignition timing as the fuels have very different ignition properties. The natural gas was also replaced by a 20 vol% hydrogen/natural gas mixture to study the effect of hydrogen on the ignition and combustion process. Also, rape seed methyl ester (RME) was tested instead of the diesel oil. The combustion phasing was found to mainly be controlled by the amount of liquid fuel injected. The presence or absence of hydrogen resulted in only marginal changes on the combustion. Because the diesel oil and RME have much lower autoignition temperatures than both hydrogen and natural gas, the properties of the liquid fuel may overshadow the effect of the hydrogen addition. A large difference however, was found between the RME and the diesel oil with the necessity to inject much more RME than diesel oil to obtain the same combustion phasing.

The last experiments with compression ignition were performed by using a standard Scania diesel engine where the possibilities to reduce particulate matter (PM) and other emissions by introduction of combustible gas to the inlet air (named fumigation) were investigated. Hydrogen, methane and propane were introduced at different rates replacing up to 40% of the total fuel energy. Also, a biodiesel consisting of mainly RME was tested instead of the diesel oil. Because of the low density of hydrogen gas, less of the fuel energy could be replaced by hydrogen than by the two other gases. Higher rates of hydrogen would sacrifice the safety by exceeding the lower flammability limit in the inlet air. Only moderate reductions in PM were achieved at high gas rates, and because of the limitation in the practical achievable hydrogen rate it was not possible to obtain considerable reductions in PM emission by hydrogen addition. The NO_x emissions were found to be little influenced by the fumigation, but the THC emissions strongly increased with increased methane and propane rates, especially at a low engine load. Propane fumigation resulted in considerably less THC emissions than methane fumigation. The biodiesel resulted in higher PM emissions than the diesel fuel at low load, but was considerably lower at the higher loads. This is believed to be because of the low volatility of the biodiesel which may lead to emissions of unburnt fuel at low load when the temperature is low. At higher loads this is believed to be less of a problem because the temperature is higher, and the oxygen content of biodiesel is believed to increase the PM oxidation and/or reduce the formation of PM.

Acknowledgements

1   Introduction

1.1   Background

The economic growth in the industrialized countries the last centuries has lead to an enormous increase in the use of fossil fuels. Even though the governments of most industrialized countries believe that manmade CO_2 emissions are the major cause of global warming, the emissions continue to increase. According to the International Energy Agency, (IEA [1]), 39.5% of the worlds CO_2 emissions were the result of combustion of oil in 2005. CO_2 from coal was slightly higher with 40.5% and the emissions from natural gas represent 19.7%. The main consumer of oil is the transport sector in which the road vehicles represent a large part. These facts, and the fact that combustion of petroleum products in internal combustion engines cause other environmental problems like emissions of nitrogen oxides, unburnt hydrocarbons and particulate matter has lead to an increased focus on alternatives to the fossil fuels. One such alternative is hydrogen. Hydrogen is attractive as a fuel because the products of combustion are, in principle, only water (although some emissions of NO_x, and PM and UHC emission from lubrication oil are hard to avoid when used in combustion engines). The zero emission prospect has lead to a boom in the interest in hydrogen, and planning of a future society based on hydrogen as the energy carrier. However, large challenges remain unsolved, mostly how to make the production, storing and end use economic viable and practical. The perhaps largest challenge is the extreme low density of the hydrogen gas, making it difficult to store. Another aspect is the small molecules and high reactivity and diffusivity which require extra safety considerations and choice of materials.

The most efficient energy conversion technology for vehicles that can run on hydrogen is fuel cells. Even though the energy is first converted to electricity and then to usable work in an electro motor, the energy efficiency is higher than the efficiency of an internal combustion engine. However, the production cost and durability of fuel cells are still a challenge compared to combustion engines. This has lead to a focus on using hydrogen in combustion engines. Several car manufacturers have introduced hydrogen fueled cars with internal combustion engines. However, due to low driving range and the limited availability of hydrogen, hydrogen vehicles are only used in pilot projects and research activities.

A way to overcome the main challenges and start the introduction of hydrogen as a fuel is to use hydrogen together with other fuels. Perhaps the most promising way is to use mixtures of natural gas and hydrogen in the spark ignited gas engines. Natural gas is considered to be a more environmental friendly fuel than gasoline and diesel oil because of the lower carbon/hydrogen ratio, low sulfur content and low particulate emissions from combustion. Several pilot projects have been started around the world where natural gas fueled city buses are converted to run on natural gas/hydrogen mixtures of up to 30% hydrogen by volume. By limiting the hydrogen concentration, the driving range is not sacrificed compared to pure natural gas operation. In addition, the special features of hydrogen are advantageous for the lean burn spark ignition technology, which is the most common technology for these engines. To achieve low NO_x emissions and high thermal efficiency, the air/fuel ratio is lean. There is, however, a trade-off situation between NO_x formation and emission of unburnt hydrocarbons [2]. By using a lean mixture, the NO_x emission decreases while the

unburnt hydrocarbon emission increase because of the lower combustion temperature. By introducing hydrogen, the combustion efficiency may be kept high at leaner mixtures and thus resulting in a simultaneous reduction in both NO_x and unburnt hydrocarbons. Also, in diesel engines, hydrogen addition has been reported to have a positive effect on the engines tolerance for exhaust gas recirculation with respect to particulate emissions [3]. This may mainly be attributed to the replacement of some of the diesel fuel combustion with premixed hydrogen combustion.

Due to the focus on hydrogen and the awareness and conceptions in the public, there is need for a deeper understanding of the effects when introducing hydrogen in combustion engines. This thesis focuses on different aspects of using blends of fuels and in particular of using hydrogen as a fuel additive in different engine technologies. It is focused on effects that impact our environment, like emissions of nitrogen oxides, unburnt hydrocarbons, particulate emissions, thermal efficiency and hence also CO_2 emissions. The aim is to enlighten different effects of hydrogen addition in different engine technologies by analyzing the experimental work performed as well as literature study.

1.2 Use of hydrogen in a historic perspective

The idea of using hydrogen as an engine fuel is not a new idea. In fact, the inventor of the spark ignited internal combustion engine Nicholaus Otto used gas that probably had a hydrogen content above 50 vol% [4]. This kind of city gas, mostly produced from coal, was widely used in the 1800's for street lights in cities among other things. In the 1930's the German scientists Rudolf Erren and Kurt H. Weil developed internal combustion engines solely using hydrogen as well as hydrogen together with conventional fuels. In 1938 about 100 trucks were running between Berlin and the industrial Ruhr area partly fueled by hydrogen. [5] The motivation for employing hydrogen in the Nazi regime was to be less dependent on imported petroleum fuels. It is reported that over 1000 vehicles were converted to hydrogen and hydrogen/petrol operation in England and Germany together during the 1930's [4]. The interest for hydrogen dropped after the war because of increased access to oil. However, when the British scientist Francis T. Bacon developed the first practical fuel cell in 1950, the interest of hydrogen increased again. The next real progress in hydrogen research started in the 1970's as the environmental awareness grew stronger and the oil embargo made an alternative energy carrier more attractive. A lot of governmental funded research projects took place around the world, and the idea of a "hydrogen economy" was born. As the oil prices dropped again after the oil crisis, the interest in hydrogen dropped again. In the recent years the interest in hydrogen is maybe higher than ever, especially because of the focus on CO_2's role in global warming. Several car manufacturers have made hydrogen fueled cars, both with internal combustion engines and fuel cells. However, the cars are made as demonstration models in very small volumes because the marked is not ready for hydrogen fueled cars yet, as the availability of hydrogen is very limited around the world. The highest consumption of hydrogen as a fuel is probably in city buses where the hydrogen is mixed with natural gas. In 1989, the American company Hydrogen Components Inc. started to do tests with natural gas and hydrogen. The company managed to patent different blend concentrations (Hythane) and started several projects using these blends in buses. Today, several pilot projects are in progress around the world were city buses run on a mixture of typically 20 vol% hydrogen in compressed natural gas [6].

2 Emissions from ICE

2.1 Formation of nitrogen oxides

Nitrogen oxides, or NO_x are formed in most combustion processes where nitrogen is present. NO_x is a collective term for NO, NO_2, but also nitrous oxide, N_2O, is some times added to this term. NO and NO_2 emissions cause problems for the environment because it is the major contributor to the formation of photochemical smog and ozone in urban areas. Also, it is a source of acid rain, because of the formation of nitric acid in contact with water. Nitrous oxide is considered as a greenhouse gas. The formation of NO and NO_2 can be divided into four routes, the thermal route, the prompt route, the N_2O route and the fuel-bound nitrogen route [7]. The major NO_x formation route in ICE combustion is the thermal route [8].

2.1.1 Thermal NO

The thermal NO route is the major constituent to the NO_x emission and can be described by three elementary reactions, called the extended Zeldovich mechanism:

$$O + N_2 \rightarrow NO + N \quad (1)$$
$$N + O_2 \rightarrow NO + O \quad (2)$$
$$N + OH \rightarrow NO + H \quad (3)$$

Reaction 1 has very high activation energy and is the rate limiting step. The triple-bond of the N_2 molecule is strong, thus the reaction rate is slow unless the temperature is high. When assuming quasi-steady state for N concentration, the rate of NO production may be described as:

$$\frac{d[NO]}{dt} = 2k_1[O][N_2]$$

The NO production may thus be reduced by reducing the concentration of O or N_2, or reducing the rate coefficient k_1 by reducing the temperature. The rate coefficient k_1 is considered insignificant at temperatures less than 1700 K [7].

2.1.2 Prompt NO

The prompt NO route has got its name because of the fast reactions between a CH radical and molecular nitrogen. The reaction takes place at flame fronts where the intermediate CH is produced. The product is hydrocyanic acid and atomic nitrogen.

$$CH + N_2 \rightarrow HCN + N$$
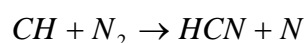
The products reacts further to NO and N_2. The activation energy of the CH + N_2 reaction is very low compared to the rate limiting step in the thermal NO reactions [7]. Prompt NO is thus produced also at relatively low temperatures and is favored by rich flames because this promotes the CH production. For most applications the prompt NO is of much less significance than the thermal NO formation.

2.1.3 NO from nitrous oxide

The nitrous oxide, N_2O is formed by attachment of an O-atom on the N_2 molecule with help from a collision with a third molecule M [7]:

$$N_2 + O + M \rightarrow N_2O + M$$
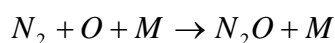
The nitrous oxide may react further with an oxygen atom and form NO:

$$N_2O + O \rightarrow NO + NO$$
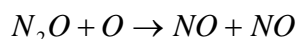
NO formation from nitrous oxide is usually small, but at lean conditions at low temperature where the formation not can be explained by the thermal or the prompt route, the remaining NO_x formation comes from nitrous oxide. That is if there is no nitrogen in the fuel.

2.1.4 NO from fuel nitrogen

Some fuels contain some chemically bounded nitrogen. Coal contains about 1 mass% nitrogen even when it is clean, and biomass may, depending on what sort, contain even more. The fuel bounded nitrogen is converted into ammonia, NH_3, and hydrocyanic acid, HCN which can react further to NO. At lean conditions about 2/3 of the fuel nitrogen is converted to NO_x, but at rich conditions, less NO_x is formed [7]. A common method of limiting the NO_x formation when combusting nitrogen containing fuels is air staging. By creating fuel rich zones and adding air downstream to oxidize the unburned compounds, less NO_x is formed. The fuel bounded nitrogen route is of minor importance for ICE, as most fuels contain very small quantities of nitrogen.

2.2 NO$_x$ from internal combustion engines

The thermal route dominates NO_x formation in combustion engines. Although fuel bounded nitrogen may be present in both gasoline and diesel oil, the concentration is low and the fuel bound route is insignificant compared to the thermal. NO is the predominant oxide of nitrogen produced. In spark ignited engines the NO_2/NO ratio is small. In diesel engines, however, NO_2 can constitute to 10-30% of the NO_x formation. NO_2 can be formed in the flame zone by reactions like [8];

$$NO + HO_2 \rightarrow NO_2 + OH$$
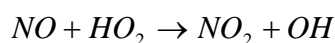
However, NO_2 can react back to NO if the flame is not rapidly quenched.

$$NO_2 + O \rightarrow NO + O_2$$
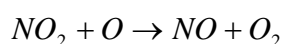
The NO_2/NO ratio in diesel engines is largest at low load because of the more extensive flame quenching due to more available cold fluid for the flame to mix with. For both compression and spark ignition engines, the ignition timing is essential to the level of NO_x formation. An early ignition will result in high peak pressure and temperature because a large part of the fuel is combusted when the piston is at the top.

The NO_x formation is thus high if the injection timing is early in a diesel engine, or spark timing is early in spark ignited engine. Near the MBT ignition timing (maximum brake torque), or the spark ignition timing that gives the highest brake thermal efficiency, the efficiency is quite insensitive to ignition timing. It is common that the ignition timing is set a bit later in order to reduce NO_x formation with a slight penalty in efficiency. For diesel engines the injection timing is also a trade off between NO_x and particulate matter emission, as later injection leads to higher formation of soot particles [8].

2.3 Formation of unburned hydrocarbons

The unburned hydrocarbon emission is a result of incomplete combustion. It is usually expressed as total hydrocarbon (THC), as ppm carbon atoms (C1) or methane. The THC may be divided into methane and non-methane emission, as complete oxidation of methane is much harder to achieve than oxidation of the heavier molecules. However, the unburned hydrocarbons consist of many compounds, some considered toxic and carcinogenic, others contribute to the formation of photochemical smog. As the hydrocarbons consist of unburned fuel, the composition is of course dependent of the fuel. However, complex molecules can be formed by reactions during the residence time in the engine. There may for example be found formaldehyde and aromatics such as benzene, toluene and xylene in the exhaust from natural gas fueled engines, although none of these compounds exists in the fuel [7]. In spark ignited engines HC emission is caused by a combination of several effects. Perhaps the most important is the flame quenching at the relative cold combustion chamber walls. The flame is not able to propagate all the way to the walls, because the low temperature in the thermal boundary layer causes radical reactions to freeze and quenching of the flame. Also, several crevice volumes cause HC to escape from the flame. The flame is then quenched at the entrance of the crevice. The largest crevice volume is above the upper piston ring, between the piston and the cylinder wall. The quenching distance, or the smallest distance between two parallel walls that a flame can propagate, depends on fuel, temperature and equivalence ratio. The dimensionless Peclet number describes the ratio of the heat release in the flame to the heat loss to the walls.

$$Pe_2 = \frac{\rho_u S_L c_{p,f} \left(T_f - T_u \right)}{k_f \left(T_f - T_u \right) / d_{q2}} = \frac{\rho_u S_L c_{p,f} d_{q2}}{k_f} \quad [-]$$

Where $\rho \, [kg/m^3], S_L \, [m/s], c_p \, [kJ/kgK], T \, [K], k \, [W/m]$ and $d_{q2} \, [m]$ refer to the density, laminar flame speed, specific heat capacity at constant pressure, temperature, thermal conductivity and quenching distance between two plates, respectively. Subscript u and f refer to the unburnt and flame conditions. The Peclet number is approximately constant at a wide range of conditions and can hence be employed to calculate the quenching distance [8].

Especially at lean conditions, flame quenching can be caused by strain. The flame may extinct locally because of high strain of the flame front caused by intense turbulence. If the mixture does not reignite, the fuel leaves the cylinder unburnt [7]. In lean burn natural gas engines this phenomenon is highly relevant because the mixture

has to be lean enough for low NO_x formation and turbulent enough for the combustion process to be sufficiently fast. HC can be emitted because of partial combustion or misfire in some of the combustion cycles. Conditions like this may occur at transients where the control system is too slow to regulate the air/fuel ratio or ignition timing correctly.

Another effect that causes HC emissions is absorption of hydrocarbons in the lubrication oil on the surface of the cylinder walls during the intake and compression stroke. The HC may then be desorbed during the exhaust stroke and follow the exhaust gas [8].

In diesel engines, some other effects also cause HC emissions. The most important is believed to be "overleaning" in the early stage of fuel injection. Part of the fuel injected during the ignition delay period mixes "too well" with air. The result is a mixture that is too lean to autoignite and can only oxidize by relatively slow thermal-oxidation reactions, which will be incomplete. Another source of HC emission is called "undermixing", or locally fuel rich air/fuel mixture. These rich zones are caused by the fuel injected at the end of the injection period, which enters the cylinder at low velocity. When the nozzle is closed, a small volume of fuel is still left in the holes and nozzle sac of the injector. This volume is heated during the combustion and expansion process and will enter the cylinder at low speed as vapor and droplets. This fuel may escape the combustion process and leave the cylinder unburnt. Also, undermixing may occur when overfueling the engine at e.g. transients if the control system regulates too slow. As for spark ignition, wall quenching of the flame is believed to be of significance in HC formation, depending on the impingement of the fuel spray on the walls [8].

2.4 Formation of CO

The formation of carbon mono-oxide in combustion engines is mainly controlled by the air/fuel ratio [8]. The CO is mainly formed under fuel rich conditions. Since diesel engines always operate at fuel lean conditions, the CO emissions from diesel engines are generally small. Spark ignited engines may operate at near stoichiometric condition and hence cause higher CO emissions. CO is one of the intermediate products in the reaction steps of hydrocarbon oxidation. The oxidation of CO to CO_2 is relatively slow compared to the other reaction steps, and CO concentration in spark ignited engines are usually well above the equilibrium concentration because the reaction is frozen before completion. However, it is believed that the carbon-oxygen-hydrogen system is close to equilibrium in the combustion products at the condition close to the peak cylinder pressure and temperature [8]. The CO oxidation is fast enough at this condition, but freezes later in the cycle when the gas is cooled by the expansion and heat losses. Also, part of the fuel does not burn at conditions close to the maximum pressure and temperature, but later in the cycle and/or close to the combustion chamber walls. Because the temperature here is lower, equilibrium is not obtained. CO is also formed in engines that operate at an overall lean air/fuel mixture, although the levels are small. This is because CO is formed in locally fuel rich regions (as in diesel engines), but also because some of the unburnt hydrocarbons partly oxidize in the exhaust system [9]. The CO emissions are however lower from diesel engines than the emissions from conventional stoichiometric operated gasoline engines with catalytic exhaust treatment [9]. The CO emissions from spark ignited

engines are very sensitive to the equivalence ratio at rich and near stoichiometric mixtures, but vary little with equivalence ratio at lean conditions. Although the CO emissions depend on the carbon content in the fuel, the emissions vary little with different fuels when compared at equal equivalence ratios [8].

2.5 Formation of particulate matter

Particulate matter formation is primary a problem in diesel engines because of the diffusion controlled combustion process in these engines. Since the particulate matter is formed in fuel rich areas, parameters that influence the fuel/air mixing rate such as droplet size and distribution govern the particulate matter formation [10]. The fuel injection technology has evolved tremendously the last decade with the introduction of electronically controlled high pressure injection. Hence, modern diesel engines emit much less particulate matter than older engines with traditionally diesel pump systems. In spark ignited engines, soot formation can result from combustion of overly rich mixtures, but in traditionally port injected engines, which are properly adjusted, it is not a significant problem [8]. However, SO_2 from sulfur in the fuel can be oxidized to SO_3 in the exhaust oxidation catalyst and form sulfuric acid aerosols in contact with water at ambient temperatures [8]. This is not commonly known to be a large environmental problem though. However, in direct injection gasoline engines, particulate emissions are known to be of concern. Because of the non homogeneous charge in these engines, considerable amounts of particles may be formed [11]. These particles are mainly in the nanometer range, which is known to be especially harmful to human health as they may penetrate the human respiratory system [12].

It is commonly accepted that soot particles are a result of further growth of poly aromatic hydrocarbons (PAH) molecules. The first step is formation of particle-like structures by conglomeration or clustering of molecules. Subsequently, the particles grow because of addition of mainly acetylene to the surface [7], and they end up as clusters of solid spherules typically a few hundred nanometers in diameter [8]. In the beginning of the formation process, the particles have a H/C ratio of about 2 (which is about the same as the diesel fuel). During the growth, dehydrogenation and oxidation processes takes place, resulting in particles consisting of mainly carbon. Most of the particles oxidize during the process. The eventual emission of soot will depend on the balance between formation and burnout [8].

3 Exhaust gas after treatment

3.1 3-way catalyst

A very efficient way of reducing HC, CO and NO_x emissions simultaneously is the three way catalyst. This technology is used in most gasoline passenger cars today. The most common design has a circular or oval cross section with a metal housing and a ceramic or metal monolith, consisting of many parallel channels to obtain large surface area. The surface of the channels is coated with a thin layer of catalytic material. Most common are coatings with platinum, palladium and rhodium deposits. The reactions at the surface can be summarized as:

$$CO + 1/2\,O_2 \rightarrow CO_2$$
$$C_x H_y + (x + y/4)\,O_2 \rightarrow x\,CO_2 + y/2\,H_2O$$
$$NO + H_2 \rightarrow 1/2\,N_2 + H_2O$$
$$NO + CO \rightarrow 1/2\,N_2 + CO_2$$
$$(2x + y/2)\,NO + C_x H_y \rightarrow (x + y/4)\,N_2 + x\,CO_2 + y/2\,H_2O$$
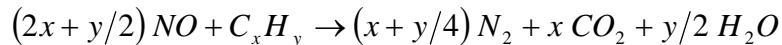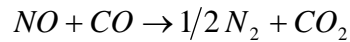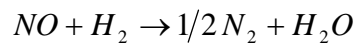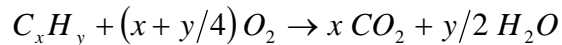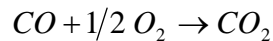
For both the oxidation and reduction reactions to take place simultaneously, the combustion has to be close to stoichiometric conditions. The oxidation will take place if the combustion is stoichiometric or lean, but the reduction of NO will take place if the combustion is stoichiometric or rich. To maintain the air/fuel ratio within the required accuracy, the fuel injection system is controlled by a closed loop lambda control system with a lambda (oxygen) sensor in the exhaust gas [9]. The control system is commonly adjusted so that the air/fuel mixture oscillates around $\lambda=1$ (stoichiometric) to ensure both oxidizing and reducing conditions in the catalyst.

3.2 Oxidation catalysts

Oxidation catalysts have the same functions as the three-way catalyst except for the ability to reduce NO_x. They have for long been used in diesel engines to oxidize CO and HC emissions, and were used in gasoline engines before the introduction of the three-way catalyst. In newer lean burn natural gas vehicles, oxidation catalysts are used to reduce the relative large emissions of HC and fine particulate matter. However, the reduction of HC is mainly non-methane HC as methane is difficult to oxidize in a catalyst [13].

3.3 Selective Catalytic Reduction (SCR)

SCR is an exhaust gas after treatment technology for NO_x reduction. The technology is well known and has been used in stationary applications for some time. SCR is now used by several manufacturers of both light and heavy duty diesel engine vehicles. Ammonia (NH_3) is the active compound in the NO_x reduction process. However, in most applications, urea ((NH_2)$_2$CO) is used. The urea is usually injected into the exhaust gas as an aqueous solution of 32.5% [14]. The urea decomposes to CO_2 and NH_3 when exposed to heat. The main reactions can be summarized in this scheme [14]:

$$4\,NO + 4\,HNO_3 + O_2 \rightarrow 4\,N_2 + 6\,H_2O \qquad (1)$$
$$6\,NO_2 + 8\,HNO_3 \rightarrow 7\,N_2 + 12\,H_2O \qquad (2)$$
$$NO_2 + NO_2 + 2\,HNO_3 \rightarrow 2\,N_2 + 3\,H_2O \qquad (3)$$
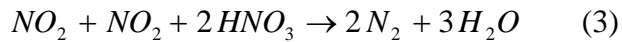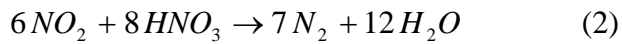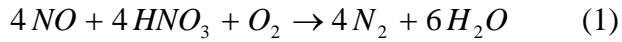
The urea is injected in front of a catalyst which reduces the required temperature for the reactions to take place. Commonly used catalyst materials are vanadium and zeolite compounds, but new materials are under constant development [15]. Reaction 3 has the fastest reaction rate, and it is hence favorable to have a 1:1 ratio of NO_2 and NO. Since the NO_x in diesel exhaust mainly consists of NO, an oxidation catalyst may be used upstream the SCR catalyst to convert some of the NO to NO_2. In addition, an oxidation catalyst for NH_3 is located after the SCR to oxidize surplus NH_3. At ideal catalyst temperature, the NO_x conversion may be over 90%. In real driving however, the average NO_x conversion efficiency may be about 70% [16], but may improve with the development of new catalyst materials and better control systems.

3.4 Lean NOx traps (LNT)

Lean NO_x traps are currently used in lean burn gasoline engines [17] and are an attractive solution for NO_x reduction in light duty diesel applications [18]. The technology is essentially the same as a three way catalyst except that the chosen materials in these catalysts have high capacity to store NO_x. During normal lean operation, NO is oxidized to NO_2 at the platinum surface and reacts further with alkaline-earth metal or alkali metal and oxygen to form nitrates, which is stored on the catalyst surface. In sequences, the catalyst is exposed to reducing agents (CO, H_2 and HC) and the stored NO_x form molecular nitrogen [17]. The reducing agents are supplied to the catalyst either by running the engine rich for a short period (spark ignited engines), or by injecting fuel into the exhaust. The fuel consumption penalty because of fuel injection into the exhaust may be about 2-3% [19]. However, by using dual leg LNT systems it may be reduced as only part of the exhaust stream may be used during the rich regenerating process. Hence, less fuel is necessary to obtain the rich mixture. Tsumagari and co-workers [20] obtained about 90% NO_x reduction with a fuel penalty of 1.4% at full load with a duel leg system. The catalyst materials are very sensitive to sulfur contamination, which reduces the NO_x conversion efficiency dramatically. Thus, the fuel must have low sulfur content. However, the sulfur may be removed from the catalyst by periodically exposing it to desulfation cycles under high temperature [18]. The lean NO_x traps may also be used in combination with SCR systems in order to increase the efficiency. One advantage of this solution is that ammonia formed in the rich cycles in the LNT may be stored and utilized in the SCR catalyst [18].

3.5 Diesel particulate filters (DPF)

Diesel particulate filters have been used for several years in passenger cars. A common design is the wall-flow filter that looks like a catalyst honeycomb except that every other passage is blocked in alternate ends forcing the flow through the cell walls. The most common filter material has been SiC but alternative materials as cordierite are becoming common [18]. Most particulate filter systems have regeneration cycles where the particulate matter is oxidized by increasing the temperature in the filter. The increased exhaust temperature is created by adding extra

fuel and hence increases the fuel consumption. Researchers are now focusing on extending the interval between the regeneration cycles and shorten the time needed for each regeneration. Also, continuous regeneration may be possible by coating the filter with catalytic materials [21]. Another way of minimizing the regeneration cycles is to have an oxidation catalyst in front of the DPF. This converts NO to NO_2 which is active in the oxidation process of the particulate matter [22]. Although DPF has been used several years, the development and understanding of the field is still increasing rapidly [18].

3.6 Emission legislations

A common European standard for emission legislations were introduced in 1992 with the EURO 1 standard. Since then, the EURO 2, 3 and 4 has been effectuated with ever more stringent requirements. Table 1, Table 2 and Table 3 sum up the maximum emission levels for the respective legislations [23].

Table 1 Emission standards for heavy duty diesel engines (motor vehicles over 3500 kg as maximum laden mass). Stationary tests (ECE and ESC) and load response test (ELR) for smoke [23]

EU Emission Standards for HD Diesel Engines, g/kWh (smoke in m^{-1})							
Tier	Date	Test	CO	HC	NO_x	PM	Smoke
Euro I	1992, < 85 kW	ECE R-49	4.5	1.1	8.0	0.612	
	1992, > 85 kW		4.5	1.1	8.0	0.36	
Euro II	1996.10		4.0	1.1	7.0	0.25	
	1998.10		4.0	1.1	7.0	0.15	
Euro III	*1999.10, EEVs only*	*ESC & ELR*	*1.5*	*0.25*	*2.0*	*0.02*	*0.15*
	2000.10	ESC & ELR	2.1	0.66	5.0	0.10	0.8
						0.13*	
Euro IV	2005.10			1.5	0.46	3.5	0.02	0.5
Euro V	2008.10			1.5	0.46	2.0	0.02	0.5
* for engines of less than 0.75 dm³ swept volume per cylinder and a rated power speed of more than 3000 min⁻¹							

Table 2 Emission standards for heavy duty diesel and gas engines (motor vehicles over 3500 kg as maximum laden mass) for the transient test cycle (ETC) [23]

Emission Standards for Diesel and Gas Engines, ETC Test, g/kWh							
Tier	Date	Test	CO	NMHC	CH_4[a]	NO_x	PM
Euro III	*1999.10, EEVs only*	*ETC*	*3.0*	*0.40*	*0.65*	*2.0*	*0.02*
	2000.10	ETC	5.45	0.78	1.6	5.0	0.16
							0.21[c]
Euro IV	2005.10		4.0	0.55	1.1	3.5	0.03
Euro V	2008.10		4.0	0.55	1.1	2.0	0.03
a - for natural gas engines only							
b - not applicable for gas fueled engines at the year 2000 and 2005 stages							
c - for engines of less than 0.75 dm³ swept volume per cylinder and a rated power speed of more than 3000 min⁻¹							

Table 3 Emission standards for passenger cars [23]

EU Emission Standards for Passenger Cars (Category M_1*), g/km

Tier	Date	CO	HC	HC+NO_x	NO_x	PM
Diesel						
Euro 1†	1992.07	2.72 (3.16)	-	0.97 (1.13)	-	0.14 (0.18)
Euro 2, IDI	1996.01	1.0	-	0.7	-	0.08
Euro 2, DI	1996.01[a]	1.0	-	0.9	-	0.10
Euro 3	2000.01	0.64	-	0.56	0.50	0.05
Euro 4	2005.01	0.50	-	0.30	0.25	0.025
Euro 5‡	2009.09[b]	0.50	-	0.23	0.18	0.005
Euro 6‡	2014.09	0.50	-	0.17	0.08	0.005
Petrol (Gasoline)						
Euro 1†	1992.07	2.72 (3.16)	-	0.97 (1.13)	-	-
Euro 2	1996.01	2.2	-	0.5	-	-
Euro 3	2000.01	2.30	0.20	-	0.15	-
Euro 4	2005.01	1.0	0.10	-	0.08	-
Euro 5‡	2009.09[b]	1.0	0.10[c]	-	0.06	0.005[d]
Euro 6‡	2014.09	1.0	0.10[c]	-	0.06	0.005[d]

* At the Euro 1..4 stages, passenger vehicles > 2,500 kg were type approved as Category N_1 vehicles

† Values in brackets are conformity of production (COP) limits

‡ Proposed

a - until 1999.09.30 (after that date DI engines must meet the IDI limits)

b - 2010.09 for vehicles > 2,500 kg

c - and NMHC = 0.068 g/km

d - applicable only to vehicles using DI engines

Separate emission legislations for gas engines were first introduced with EURO 3 in 2000. For heavy duty diesels, the emission testing was initially only a steady state engine dynamometer test. To have more representative values of the emission levels, a new stationary cycle, (European Stationary Cycle, ESC) was introduced together with a transient cycle (European Transient Cycle, ETC) and a load response cycle (European Load Response, ELR) with the EURO 3 standard. The passenger car tests are performed in chassis dynamometers, simulating road driving. The emission levels are hence given as g/km [23].

USA and Japan among others have their own legislations. The trend is however the same, emission levels are becoming harder and harder to reach for the engine manufacturers. Figure 1 shows the development of the European emission legislation for heavy duty diesels of particulate matter and nitrogen oxides. The Japanese and US targets of 2009 and 2010 are also added.
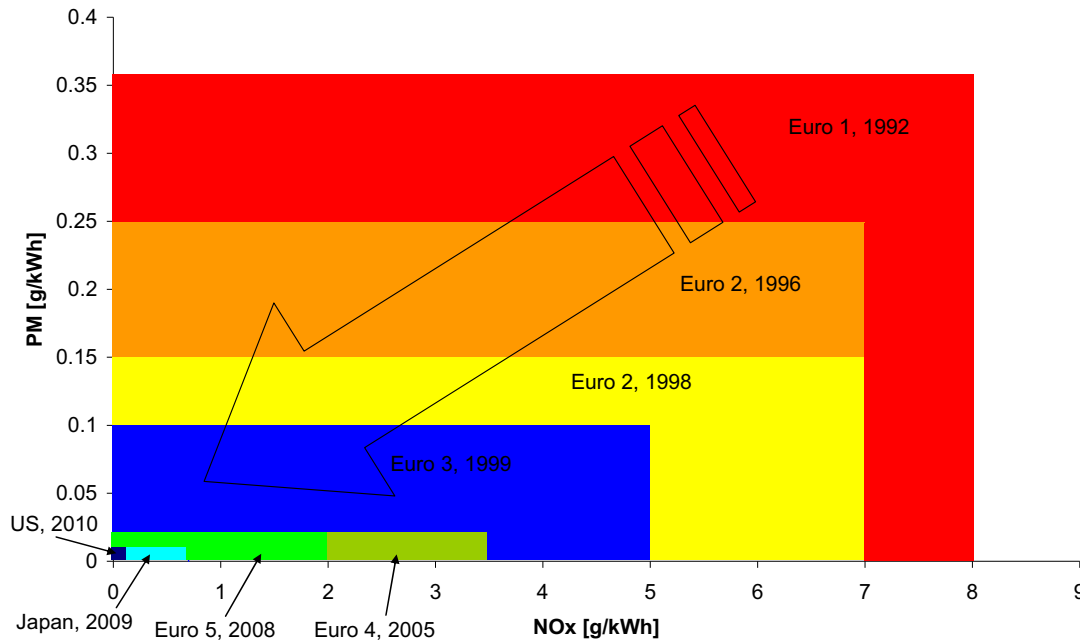
Figure 1 PM and NO$_x$ emissions legislations

The figure is a clear illustration of the challenges the engine manufacturers have coped with and are still facing. The well known trade off between soot and NO$_x$ in diesel engines does not make the situation easier.

The manufacturers of fuels are also challenged by regulations. The regulations do primarily involve the sulfur content of diesel and petrol, and minimum cetane number of diesel fuel. The maximum sulfur content of European diesel fuel was 350 ppm in year 2000, and 50 ppm in 2005. In addition, from 2005, sulfur free diesel (< 10 ppm) had to be available and will be mandatory from 2009. The maximum sulfur content of petrol has decreased from 150 ppm in 2000 to a maximum of 50 ppm in 2005 [23].

3.6.1 Greenhouse gases

In Europe today, there is no legislation on the emission of greenhouse gases. The main policy instruments are fuel taxes and awarding fuel efficient cars with lower taxes, which makes it attractive for the consumers to purchase them. However, the European Commission has proposed to set a 130 g/km CO$_2$ emission limit as an average of the car fleet by 2012. An additional reduction of 10 g/km is intended to be obtained by greater use of biofuels among other means, bringing the average CO$_2$ emission down to 120 g/km [23]. In 2004, the average CO$_2$ emission from new cars in the EU countries was163 g/km. The California Air Resources Board (CARB) developed greenhouse gas legislations for California only. The regulation became effective from 2006, and involves reduction of greenhouse gas emissions from motor vehicles starting in 2009. The emissions is going to be reduced gradually year by year to a total reduction of 30% in 2016 compared to 2004. The emissions are calculated using a CO$_2$ equivalent including the strong greenhouse gases N$_2$O and methane and fuel penalty associated with the air condition technology [23].

To meet the future emission legislations, the development of new fuels may play a key role. As new engine technologies are developing, the properties of the best suited fuel changes. It may therefore be expected that the fuel producers have to take their share of the development to meet the future legislations. The development of biofuel production in a larger scale may play a key role in reducing the CO_2 emissions.

4 Fuel requirements for different ICE technologies

4.1 Spark ignition

The air-standard Otto cycle is an ideal cycle that assumes that the heat addition occurs instantaneously while the piston is at the top dead center (TDC). The cycle is described by four internally reversible processes; isentropic compression (1-2), constant volume heat transfer (2-3), isentropic expansion (3-4) and heat rejection (4-1) [24].
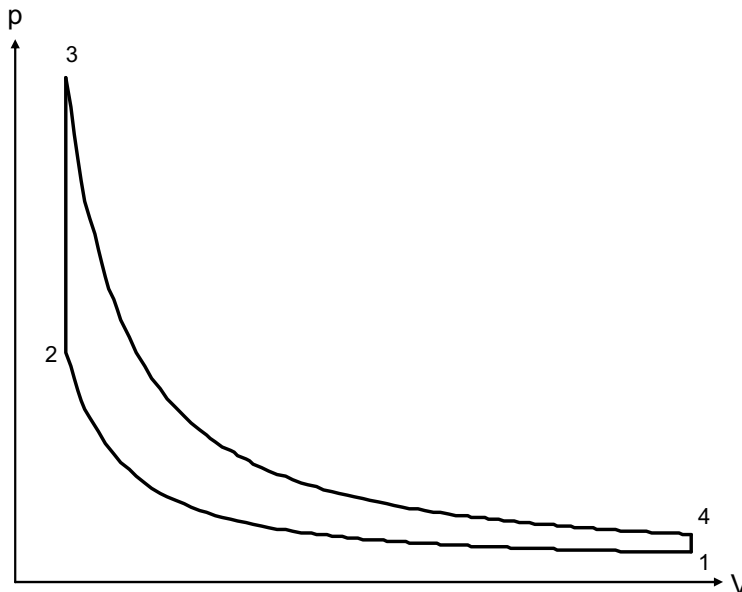
Figure 2 p-V diagram of the air standard Otto cycle

When assuming constant heat capacities, c_v and c_p, the thermal efficiency of the cycle may be written as;

$$\eta = 1 - \frac{1}{r^{\kappa-1}} \quad (1)$$

where r is the compression ratio and κ is the specific heats ratio c_p/c_v [-].

Spark ignited engines are considered to be close to the Otto cycle. However, in real processes nothing is ideal and the spark ignited engine differs from the Otto cycle in several ways. First, the heat is not added at constant volume, as this would require infinitely fast combustion or that the piston would stop at TDC until the combustion is completed. Also, the processes are not adiabatic, there are considerable heat losses through the cylinder walls, cylinder head and piston. The air and fuel are premixed or partly premixed before combustion. Most spark ignited engines operate at a constant air/fuel ratio close to stoichiometric. This makes it necessary to throttle the air when running at part load. The combustion duration is governed by the speed of the flame propagation which is very much controlled by the turbulence level in the combustion chamber. The designs of the intake ports and combustion chamber are therefore

important to achieve the desired combustion duration. In the gas exchange process work has to be added to pump out exhaust and suck air into the cylinder (pumping work). Because of the throttling of the air, the energy losses due to pumping work are high at low and part load. Especially at high engine speed, the filling and discharging of the cylinder are constrained by the inertia of the gases. Pressure waves in the inlet and exhaust are created because of the flow's discontinuity. This is compensated by increased valve opening duration (advanced opening and retarded closing). The shape and size of the inlet and outlet ports and pipes as well as the valve timing is therefore important design criteria for maximizing the cylinder filling. As most engines have constant valve opening duration, operation conditions away from the ideal point will lead to losses such as reduced effective compression ratio.

Equation 1 shows that the thermal efficiency increases with increased compression ratio. A higher compression ratio leads to higher expansion work for the same amount of heat added. However, the compression ratio is restricted by unwanted combustion phenomena. During combustion, the unburnt gas mixture (end gas) is compressed and somewhat heated by the propagating flame. If the temperature and pressure of the end gas gets too high, the mixture will autoignite. The autoignition results in very fast combustion that creates strong pressure waves that harm the parts in the combustion chamber. The phenomenon can be heard as a knocking noise and is hence called engine knock. The higher the compression ratio the higher tendency for engine knock. The mixture may also autoignite because of hot surfaces or deposits. A fuel's resistance to cause knock is characterized by its octane number (ON [-]). The octane number scale is defined by two hydrocarbons, isooctane and n-heptane. Iso-octane, which has low tendency of knock, has, by definition, an ON of one hundred, and n-heptane which has high tendency of knock has zero. The ON of a fuel is then defined as the vol% of isooctane that gives the same knock intensity at equal engine condition in a standardized test engine (CFR engine). Two different ONs are defined, the research octane number (RON) and the motor octane number (MON) [8]. In the MON test the operation conditions are more severe; i. e. the conditions are more likely to produce knock. In Europe, the octane rating at the pump is the RON.

Natural gas has much better anti-knock characteristics than petrol, which makes it possible to operate at higher compression ratios (often above 12:1). The octane number of natural gas may vary since the there are some variation in gas composition, but the main component is methane which has a RON of 120 [8]. Hydrogen however, has a higher knock tendency, limiting the operation window to leaner mixtures and/or lower compression ratio [25].

The optimal compression ratio is also affected by other factors such as heat losses and friction, as a higher compression ratio leads to higher temperatures and higher strain on engine parts. The optimal compression ratio with respect to efficiency is however much higher than commonly used in spark ignited engines, probably between 16-18:1 [8].

4.1.1 Lean burn and EGR

Most spark ignited passenger car engines run at a near stoichiometric air/fuel mixture. The advantage of this is that CO, HC and NO_x can very efficiently be reduced simultaneously in a three way catalyst (TWC). From a thermal efficiency point of

view, however, the stoichiometric combustion is not the best solution. The constraint on the compression ratio is harsher because the reaction rates are faster leading to a higher tendency of autoignition of the end gas (engine knock). Also, the flames travel closer to the walls because the quenching distance is shorter, leading to higher temperature gradients and thus, higher heat losses. Also, small charge mass to surface area ratio makes the heat losses considerable.

The thermal efficiency is also a function of the ratio of specific heats, κ, as shown in Equation 1. For mono atomic gases, i. e. noble gases, an increase in the internal energy by heat addition leads to an increased translational kinetic energy of the molecules, i.e. an increased temperature as temperature is a measure of this energy. This will also happen to a polyatomic gas, but in addition, the energy is stored as internal motion of the molecules as rotation and vibration that will not result in temperature increase [26]. This means that the molar heat capacities of constant pressure, c_p, and constant volume, c_v, is higher for diatomic than for mono-atomic gases, and even higher for more complex molecules. As the difference between the molecular c_p and c_v is the same for all gases that can be considered as ideal ($c_p - c_v = R = 8.314\ J/mol \cdot K$), κ is lower for more complex molecules. The working gas in the expansion stroke has higher concentrations of CO_2 and H_2O in a stoichiometric mixture than in a lean mixture. Hence, the effective κ is lower because the higher specific heats ratio of diatomic air. Also, κ is temperature dependent, as the part of the internal energy that is absorbed as internal molecule motion increase with temperature. This will further worsen the situation for stoichiometric combustion, because a large part of the expansion will take place at high temperature due to high flame temperature and low compression ratio. The result is high heat losses to the exhaust because of high exhaust temperature.

To increase the thermal efficiency, some car manufactures produce direct injected spark ignition engines. This makes it possible to obtain a stratified fuel charge that has a near stoichiometric fuel concentration around the spark plug, but an overall lean mixture. Higher compression ratios are possible because the knock tendency is lower when shorter time is available for pre-combustion reactions. Also, when the fuel is injected after the inlet valve is closed, the risk of losing fuel during the valve overlap period (the period were both the inlet and exhaust valves are open) is removed. This makes it possible to empty the cylinder better as the exhaust valve can close later. Smaller amounts of hot residual gases also reduce the risk of engine knock. The pumping losses are reduced because less throttling is necessary at part load compared to stoichiometric operated engines. However, NO_x formation may be high due to locally hot spots in the stratified charge and the overall excess of oxygen. NO_x reduction in three way catalyst (TWC) does not work with lean mixtures, so lean NO_x traps or lean NO_x catalysts are used.

Natural gas engines, e.g. used in city buses, are most commonly lean burn engines. The gas is usually premixed with air before combustion by port injection or gas mixer systems. The thermal efficiency at high load is not much lower than for comparable diesel engines, but at part load the efficiency is considerably lower. Natural gas consists mainly of methane which has a rather low laminar flame speed, especially at lean conditions. At low load, the temperature is low and the mixture has to be richer to maintain an acceptable burn rate and to avoid high HC emissions. The HC emissions at lean combustion may be caused by flame quenching near the walls and

too low temperature for post oxidation of the fuel flowing out of the crevices during expansion. Much research is focused on increasing the burn rate and combustion stability at lean conditions. The burn rate can be increased by increasing the turbulence. However, increased turbulence leads to higher heat losses due to higher temperature gradients near the walls. Most natural gas engines are based on diesel engines and have the same bowl in piston type combustion chamber design. In smaller spark ignited engines, the most common design is 4-valve pent roof combustion chambers with a better trade off between turbulence generation and heat losses [2]. Another method of increasing the lean burn tolerance is to use pre-chambers. The ignition takes place in a prechamber where the air/fuel ratio is much lower than the bulk mixture. The combustion is initiated in the prechamber and spreads to the main combustion chamber through an orifice. Hence much leaner mixtures may be utilized [27]. Another way to extend the lean limit for natural gas engines is direct injection [28, 29]. The same advantages as for direct injection of gasoline can be obtained. The technology is new and still under development.

Another way to obtain some of the same advantages as lean burn is to recycle the exhaust. The air/fuel mixture is hence diluted with exhaust gas instead of excess air. The knock tendency is reduced which makes higher compression ratios possible. The ratio of specific heats, however, is lower than when the mixture is diluted with air because of the high concentration of CO_2 and H_2O. As the air is displaced by the recycled exhaust, the oxygen concentration is reduced. This leads to more efficient reduction in NO_x formation than lean burn at the same degree of dilution. However, it is not possible to dilute the mixture as much as when diluting with air because the burn rate decreases more when the oxygen concentration decreases. An important advantage with EGR is that a 3-way catalyst can be utilized if the mixture is kept around stoichiometric air/fuel ratio. EGR has been used in gasoline engines at relatively low EGR rates for many years, mainly as a NO_x reduction technique. For stoichiometric operated natural gas engines with EGR as a good alternative to lean burn engines, higher rates of EGR are needed (about 20 – 25% [30]). The exhaust is then cooled and water droplet traps may be necessary to take out the condensed water.

4.2 Compression ignition engines

4.2.1 Diesel engines

The air-standard Diesel cycle is also an ideal cycle. The main difference from the Otto cycle is that the heat addition takes place under constant pressure instead of constant volume. The cycle can be described by isentropic compression (1-2), constant pressure heat transfer (2-3) and isentropic expansion (3-4).
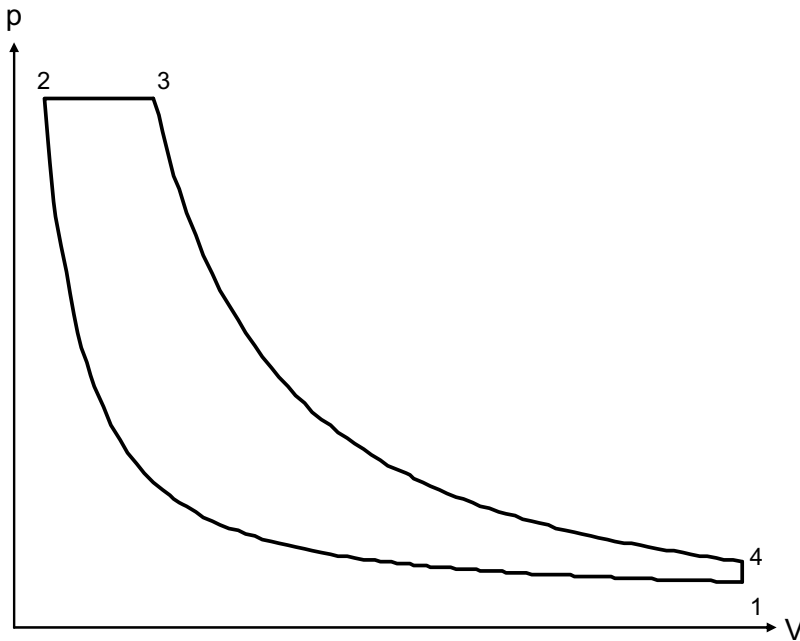
Figure 3 p-V diagram of air standard Diesel cycle

From state 2 to 3, the volume increase, and this makes up the first part of the power stroke. Because of this, the thermal efficiency of the cycle is described somewhat different;

$$\eta = 1 - \frac{1}{r^{\kappa-1}} \left[\frac{r_c^{\kappa} - 1}{\kappa(r_c - 1)} \right]$$

for constant $\kappa = c_p/c_v$. r_c is the volume ratio of state 3 (end of the heat transfer) and state 2 (the top dead center). Because of the constant pressure heat transfer, the cycle results in less specific work and, hence, lower efficiency at the same compression ratio compared to the Otto cycle. However, real diesel engines differ from the air-standard Diesel cycle in several ways. As for spark ignited engines the compression and expansion are not isentropic, heat transfer through the combustion chamber walls and piston is severe. Also, heat release is not taking place under constant pressure, but somewhere between the two extremes of constant volume and constant pressure. Since no fuel is present before the fuel injection, and the combustion starts shortly after the start of fuel injection, the diesel engine does not suffer from the engine knock problem that spark ignited engines does. The compression ratio may thus be much higher, only limited by the peak cylinder pressure and heat losses. This is the main reason why diesel engines have a higher brake thermal efficiency. Also, the diesel engine has no need for throttling the inlet air at part load as the spark ignited engine does. This result in less pumping work at low and part load compared to spark ignited engines. Because of limitations in the air/fuel mixing rate, the diesel engines have to operate under overall fuel lean condition. Although most modern diesels use EGR to control NO_x formation, an excess of air has to be present. This result in a high effective ratio of specific heats during expansion, as the concentration of CO_2 and water vapor is low. Thus, for a given expansion ratio, more work may be extracted for a given energy release in a diesel engine compared to a spark ignited engine,

especially at low load where the spark ignited engine can not run very lean. As the burn rate is controlled by the mixing rate, a proper turbulence level in the combustion chamber is important to obtain the desired burning rate. The injection rate, spray shape and droplet size are of no less importance. The design of the inlet port, combustion chamber and injection system are hence key design criteria. At least in large diesel engines, the flame may be kept away from the cylinder walls. The heat convection may hence be lower than in spark ignited engines where the flame propagates close to the walls. However, the heat convection is very much affected by the turbulence level. In small high speed diesel engines where the turbulence is high, heat convection may still be quite high. Heat losses are also caused by radiation. In diesel engines, the combustion is locally very rich which results in the formation of large amounts of soot. Most of the soot is oxidized later in the cycle, but before that the very hot soot particles emit radiation similar to a black body. The high compression ratio and the radiation heat losses make the heat losses in diesel engines generally higher than spark ignited engines of similar size [8].

The ignition quality of diesel fuel is described by the cetane number (CN). The CN is defined by the properties of two pure hydrocarbons, similar to the octane number for spark ignition fuel. Cetane (n-hexadecane) has a CN of 100 and heptamethylnonane (HMN) has a CN of 15. The CN is derived from tests in a standardized variable compression ratio engine and found from the mixture of the two hydrocarbons that give the same specified ignition delay as the fuel tested, at the same compression ratio. One could say that the CN almost represents the opposite of the ON as high CN fuels autoignite more easily than low CN fuels. More precisely, the CN represents the temperature and pressure needed to obtain a specified ignition delay time, with low temperature and pressure resulting in high CN. Straight linked hydrocarbons (n-paraffins) have generally high CN, while branched and cyclic hydrocarbons have lower CN.

4.2.2 Homogeneous Charge Compression Ignition (HCCI) engines

For more than a decade, extensive research has been focused on an engine concept that could overcome the problems of low efficiency of the spark ignited engine on one hand, and NO_x and particulate matter emissions of the diesel engine on the other hand. The HCCI engine can be described as combining an Otto and a diesel engine. The fuel is premixed with air (or air and EGR) before combustion as in an Otto engine, but the mixture is autoignited as in a diesel engine. The ignition process is related to the engine knock phenomenon in Otto engines, but by restricting the operation to lean air/fuel ratios the combustion does not become too fast and intense. The result is very low emissions of both NO_x and particulate matter because no fuel rich or hot zones are formed. The thermal efficiency may be in the range of diesel engines or higher. However, because of the complexity of both the pressure and temperature dependent autoignition process, the control of the ignition timing is not an easy task. Regulation of the inlet air temperature, dual fuel, variable valve timing with possibility to obtain negative valve overlap, variable compression ratio and variable boost pressure have been proposed as means to control the ignition timing.

The quality of a fuel, or how a fuel is suited for a HCCI engine, is not very good described by either the octane number or the cetane number. The numbers refer to experiments in the respective engine technologies, and the ignition process in HCCI is

very different from what we find in both spark ignition engines and diesel engines. In HCCI, the ignition timing is governed by the temperature and pressure history of the cycle. Since the fuel and air are premixed, the time available for reactions is very long compared to that of a diesel engine. Radical forming reaction starts well before the start of the main heat release and these radicals influence the time of ignition.

4.3 Alternative fuels

4.3.1 Ethanol

Ethanol has been used as a vehicle fuel for decades. Brazil was for a long time about the only country using ethanol as fuel, but the last years the production and use have increased rapidly. In 2006, USA was the largest ethanol producer with an annual production of 18 billion liter, closely followed by Brazil with about 17 billion liters [31]. As ethanol is mainly produced by fermentation of biomass, the interest has increased the last years because of the focus on CO_2 emissions. However, it has been discussions if ethanol is right for this purpose, as the production may be very energy consuming and require large agriculture areas that otherwise could be used for food production. However, much effort is put in developing technologies to convert cellulose into ethanol. The available feedstock is then much larger because many sorts of biomass waste may be utilized. By converting the cellulose and hemicellulose into sugars by either enzymatic hydrolysis or acid hydrolysis, ethanol may be produced through ordinary fermentation [32].

Ethanol is mainly used in spark ignited engines, either as a pure fuel or as a mixture with gasoline. Ethanol has a considerably higher research octane number (RON = 107) than gasoline (RON = 92 – 98) [8] and can hence function as an octane number improver when added to gasoline. The heating value, however, is much lower (26.9 MJ/kg) than for gasoline (about 43 MJ/kg). Ethanol may also be used as diesel fuel, both as mixtures of ethanol and diesel oil (E-diesel) and as an almost pure diesel engine fuel. However, the autoignition property of ethanol is very poor compared to ordinary diesel fuel. Some percents of ignition improving agents have to be added, and modifications to the engine have to be performed. Most of the city bus fleet of Stockholm in Sweden has successfully been fueled by ethanol for more than a decade [33].

4.3.2 Fatty Acid Methyl Esters (FAME)

FAME diesel, also often referred to as first generation biodiesel, is mainly produced from vegetable oils such as rape seed oil, palm oil and soy bean oil. The vegetable oils are refined through a transestrification process usually by the use of methanol and a catalyst, e.g. KOH. The fuel is used pure or as a mixture with ordinary diesel and can be used in most diesel engines without modifications. The engine manufacturers however, have been restrictive to guarantee for their engines when 100% biodiesel is used. Because FAME diesel contains oxygen, the energy content (about 38 MJ/kg [34]) is slightly lower than that of ordinary diesel which results in an increase of the fuel consumption. FAME diesel contains about 10 mass% oxygen, and this makes the fuel properties somewhat different from ordinary diesel. The oxygen content influences the particulate matter formation, and may result in a considerable reduction

in particulate emissions. However, some engine researchers report an increase in the PM emissions at low loads when using FAME diesel compared to ordinary diesel oil [eg.35]. The NO_x emissions tend to be higher from FAME diesel. The reasons for the increased NO_x emission are somewhat unclear. In addition to the oxygen content, FAME diesel differs from ordinary diesel by higher viscosity and density but less compressibility. This influences the fuel droplet spray formation. Zhang and co-workers [36] proposed that the increased NO_x formation is caused by less radiation heat losses from the flame zone due to lower soot formation and higher prompt NO_x formation due to the different chemical composition.

4.3.3 Second generation biodiesel

Synthetic production of diesel is a well known technology. The Fisher-Tropsch synthesis was invented in the 1920's and has been used to produce diesel from coal and natural gas through the production of synthesis gas [37]. A few factories around the world produce synthetic fuels using this or similar technologies. Best known are Sasol and PetroSA in South Africa and Shell's plant in Malaysia. The synthesis gas consists mainly of CO, H_2 and CO_2 which form hydrocarbon compounds through catalytic reactions. Very pure and high cetane number diesel fuels are possible with this technology. The same synthesis gas may be produced by gasification of biomass. No commercial production of this kind of diesel exists yet, but Choren Industries is currently building a BTL (Biomass To Liquid) plant in Germany using this technology [38] and other research activities and pilot projects are taking place around the world. Neste Oil [39] has developed a production method of upgrading vegetable and animal fat to synthetic diesel comparable to the Fisher Tropsch diesel. The technology does not include production of synthesis gas, but hydrotreatment of bio oils [39].

4.3.4 Methanol

Methanol (CH_3OH) is the simplest alcohol molecule. The properties are in many ways similar to ethanol, the research octane number is high (RON = 106) and the lower heating value is relatively low (LHV = 20 MJ/kg) [8]. The high octane rating makes methanol well suited as a spark ignition fuel. However, the heat of vaporization of methanol (1103 kJ/kg [8]) is very high compared to that of gasoline (about 305 kJ/kg [8]) which may cause some problems during cold start. Methanol has been used in the US in some extent as a mixture with gasoline (M85) in the same way as ethanol (E85) as fuel in flexifuel vehicles (FFV) [40]. However, the car manufacturers have in the last years focused on the use of ethanol in flexifuel vehicles [40]. Methanol is today mainly produced from natural gas through the production of synthesis gas and used in various industrial processes. Methanol has also been proposed as fuel in fuel cell vehicles.

4.3.5 Propane and LPG

Liquefied Petroleum Gas (LPG) is a byproduct of natural gas processing and crude oil refinement. Depending on the specification it may consist of pure propane, pure butane or a mix of propane, butane and possibly small amounts of other hydrocarbons. LPG as a vehicle fuel has been developed in a different way in each country depending on governmental motivations [9]. It can be stored as liquid at relatively low pressure and is therefore easier to store than natural gas. LPG has been used as fuel in spark ignited engines for many years and has been considered to be a clean fuel as it

results in less pollution than gasoline. Most countries designate the majority of the LPG to domestic or industrial use, but in some countries incentives from the governments have lead to extensive use of LPG as a vehicle fuel. LPG is an excellent spark ignition engine fuel because it may have a high octane number. Propane has a research octane number (RON) of 112 [8], but n-butane has only 95 [9]. Thus, the octane rating advantage compared to gasoline is dependent on the propane share in the mixture.

4.3.6 DME

Dimethylether (DME) is a gas at standard conditions but may be stored as a liquid at a relative low pressures in the same way as LPG (about 5 bar [9]). DME may be used as a diesel fuel because it has a cetane number comparable to ordinary diesel oil (55-60 [41]). The energy density is, however, lower than diesel oil (LHV = 28, 43 MJ/kg, liquid density = 668 kg/m^3 [42]). DME may be produced from synthesis gas and may hence be produced from a wide range of feedstocks (e.g. coal, natural gas or biomass). DME is an interesting fuel for diesel engines because the combustion of DME results in very low formation of particulate matter [43]. The disadvantage is of course that it has to be stored under pressure, adding complexity to the vehicles and the infrastructure. The worlds annual production of DME was in 2005 about 150 000 tons [44]. As of today, DME is mainly used as a propellant gas for hairspray etc.

4.3.7 Natural gas and hydrogen

Natural gas is a mixture of light alkanes, with methane as the main part and smaller amounts of ethane, propane and butane. There are also traces of heavier molecules. Depending on which gas field the gas is extracted from and the after treatment the composition varies, but usually the methane portion is above 80 mol% and over 90 mol% is common. Also small amounts of inert gases, mainly CO_2 and N_2 are present. Hydrogen is the lightest of all gases. The energy content of hydrogen is high on a mass basis (LHV = 119.96 MJ/kg), but because of the extremely low density it is hard to obtain high energy densities. As hydrogen gas can not be directly extracted from nature, it can not be considered as an energy source but rather an energy storage medium. Hydrogen may be produced in various ways, by electrolysis of water and reformation of natural gas among others. This thesis is focused on the use of hydrogen and natural gas. Thus, these fuels will be discussed in more detail in the following chapter.

5 Combustion characteristics of natural gas and hydrogen

The relatively stable methane molecule makes natural gas less reactive than heavier hydrocarbons like what are found in gasoline and diesel fuels. The difference in stability can clearly be seen from the difference in autoignition temperature. Also, the minimum ignition energy (MIE) is higher for methane than the heavier alkanes, which indicate that more energy has to be added before reactions are initiated. Hydrogen is the lightest of all gases, and it has very low minimum ignition energy. The H_2 molecule is however rather stable, because the H-H bond is quite strong. The bond enthalpy of H_2 is 436 kJ/mol while an average C-H bond is 412 kJ/mol [45]. Nevertheless, when the H-H bonds are broken the two H radicals are very reactive which results in very fast reactions. The strong H-H bonds are the reason why hydrogen has an autoignition temperature not much lower than methane and higher than heavier hydrocarbons. Hydrogen diffuses very rapidly into other gases and has a broad range of concentration where it is flammable in air. The lower flammability limit is not lower than most hydrocarbons, but the upper flammability limit is extremely high. The broad flammability region is often mentioned in conjunction with fire hazard, but the low minimum ignition energy is of no less importance. A small spark or a hot surface may ignite a hydrogen/air mixture much easier than a hydrocarbon/air mixture.

Table 4 Properties of some common gases and fuels [46]

	Autoignition temperature [^{o}C]	Lower Flammability Limit [vol%]	Higher Flammability Limit [vol%]	MIE [mJ]	LHV [MJ/kg]	Quench dist. [mm]
Methane	640	5.0	15.0	0.37	50.01	2.03
Ethane	515	3.0	12.4	0.285	47.51	1.5
Propane	500	2.1	9.5	0.305	46.33	1.75
n-Butane	408	1.8	8.4	0.26	45.70	2.4
i-Butane	460	1.8	8.4	0.52	45.56	2.2
Natural gas	500	4.8	13.5			
Hydrogen	520	4.0	75	0.02	119.96	0.64
Gasoline, 92 octane	390	1.5	7.6			
Diesel fuel, 55 cetane	230					

5.1 Flame speed

The laminar flame speed may be defined as the velocity of a premixed laminar flat flame into the unburnt mixture [7]. This is of course an important design criterion for many applications. Although the main part of the combustion in a spark ignited engine is highly turbulent, the laminar flame speed is an important property in the early flame developing stage. Shortly after spark discharge the reaction sheet is thin and not very wrinkled, indicating that the laminar flame speed governs the flame

propagation at this early stage. However, as the flame grows it gets more wrinkled
and the flame speed is more governed by the turbulence. A common model of the
laminar flame speed is that of Zeldovich;

$$S_L = \sqrt{\frac{\alpha}{\tau}} \ [\text{m/s}]$$

where α is the diffusivity (here the mass and thermal diffusivities are the same, or
Lewis number equal to unity) and τ is the characteristic time of reaction, expressed
as the Arrhenius expression;

$$\tau = 1/k = \left[A \cdot \exp\left(-E/RT\right)\right]^{-1} \ [\text{mol s /cm}^3]$$

High diffusivity and short reaction time promote high flame speeds. The light
molecules of hydrogen gas and the fast chemistry is the reason the flame speed of
hydrogen is much higher compared to the one of methane.
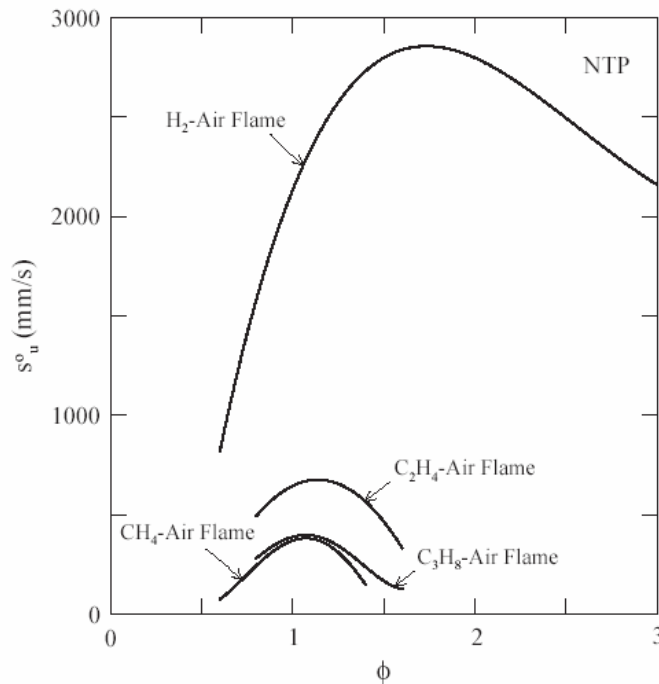
**Figure 4 Laminar flame speed of some gas/air mixtures as function of equivalence ratio at NTP
[47]**

The influence of equivalence ratio on the flame speed is quite different for
hydrocarbon gases and hydrogen. While methane, propane and butane obtain
maximum flame speed at slightly rich mixture (ϕ = 1.05 to 1.1 [48]), hydrogen has
the maximum at a very rich mixture at about ϕ = 1.7 [49, 50]. This may be explained
by the high diffusivity of hydrogen, as high concentration of hydrogen makes the
mixture more diffusive. Although a rich mixture has lower flame temperature and
hence increase the reaction time, the net effect of increasing the hydrogen
concentration from stoichiometric will be an increased laminar flame speed.

5.1.1 Pressure and temperature dependence of the laminar flame speed

In the literature the pressure and temperature dependence of the flame speed is often described as [51];

$$S_L \sim p^{(n/2)-1} e^{-E/2RT_b} \ [\text{m/s}]$$

where n is the reaction order and E is the activation energy of the reaction. This is applicable for a simplified single step reaction. However, real combustion reactions are not single step reactions, but consist of many elementary reactions, and n and E are dependent on equivalence ratio, temperature and pressure itself [49]. Several researchers have studied the pressure and temperature effects. Iijima and Takeno studied the flame speed of methane/air and hydrogen/air mixtures in a spherical combustion bomb. They found a pressure and temperature relation [49];

$$\frac{S_L}{S_{L,0}} = 1 + \beta \log\left(\frac{p}{p_0}\right)\left(\frac{T_u}{T_{u,0}}\right)^\alpha$$

where α and β are functions of the gas and equivalence ratio and the subscript u and 0 refers to unburnt and a reference condition (1 atm and 291 K), respectively. T_b is the adiabatic flame temperature. Not surprisingly they found that the flame speed increased with increasing temperature for both methane and hydrogen. The pressure dependence, however, was opposite for the two gases. The flame speed of hydrogen increased with increasing pressure while for methane it was the opposite. Other researchers have found similar trends [52]. Verhelst and co-workers [53] found that a crossover from negative to positive pressure dependence exists at an equivalence ratio of about 0.4. At leaner mixtures the flame speed decreases with increased pressure. Another common expression for the temperature and pressure dependence is the power law [54];

$$\frac{S_L}{S_{L,0}} = \left(\frac{p}{p_0}\right)^\alpha \left(\frac{T_u}{T_{u,0}}\right)^\beta$$

where α and β also here may have some dependence on the equivalence ratio. Metghalchi and Keck [54] found a good relation to this expression for experiments with propane. They used constant values of α and β. As Iijima and Takeno found for methane, they found a decrease in flame speed with increasing pressure. Experiments with liquefied petroleum gas (LPG) with hydrocarbons from C_2 to C_5 [48] show similar trends.

5.1.2 Turbulent flame speed

Dependent on engine speed and design the turbulence level in the flow varies, but in most combustion engines it is highly turbulent. The turbulence is in most applications essential to achieve high enough combustion rates for the combustion process to complete during the limited time available. The turbulence is generally generated by

shear forces from velocity gradients. In a four stroke combustion engine, these high shear forces appear in the flow several places. The inlet flow jet generates turbulence, and the flow is further modified during compression by cylinder wall interaction and squish between the piston top and cylinder head. For throttled spark ignited engines, the flow through the throttle also generates turbulence. A swirl motion of the charge may be generated by having a helical shaped inlet duct or directing the inlet duct tangentially to the cylinder wall. The flow motion is a very important design criterion in diesel engines because it controls the mixing and combustion process of the diesel spray. It is also important in spark ignited premixed combustion because it controls the burning velocity and hence the combustion duration. The turbulent burning velocity can be 20 – 30 times the laminar flame speed [8].

5.2 Flame stretch

When combustion takes place in turbulent flow fields, the flame is exposed to stretch or strain. Also in laminar spherical expanding premixed flames, the flame sheet is stretched as a result of the increasing surface area of the sphere. In application where lean combustion is favorable, like gas turbines or lean burn internal combustion engines, the flame's response to stretch is of most importance. Too high strain rates results in local extinctions of the flame and unstable combustion. In spark ignited natural gas engines it has been proposed to mix the natural gas with relatively small amounts of hydrogen to improve the lean burn capability. Hydrogen addition increases the laminar flame speed because of the high laminar flame speed of hydrogen/air mixtures. The increase in flame speed is caused by an increase in flame temperature and an increase in the pool of essential radicals, as H, O and OH [55]. However, maybe of greater importance, the hydrogen blending increases the flames tolerance against strain. Figure 5 and 6 show the flame extinction strain rate for methane flames at different hydrogen blending and equivalence ratios. The results were obtained by simulations and experiments with a jet-wall stagnation flow burner [56].
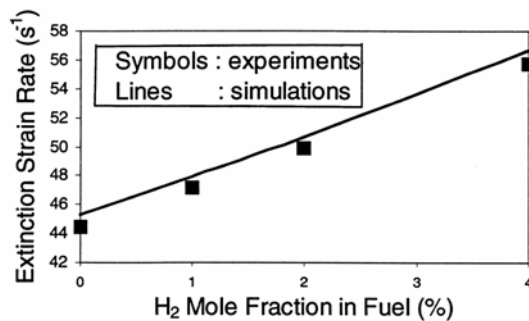
Figure 5 Extinction strain rate as function of hydrogen content in methane [56]
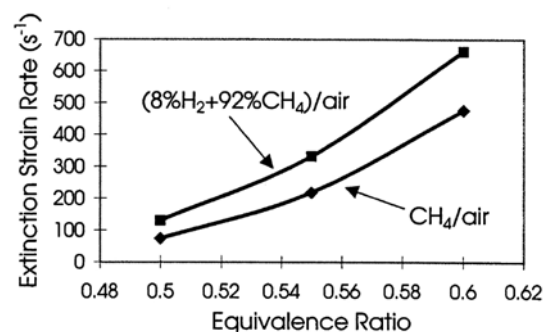
Figure 6 Extinction strain rate as function of equivalence ration for methane and hydrogen enriched methane [56]

An interesting observation from Figure 6 is that the relative difference in the extinction strain rate between the methane/air and hydrogen enriched methane/air mixture is highest at the leanest condition. This implies that hydrogen blending is especially favorable in stabilizing the flame at lean conditions.

The burning velocity may increase or decrease with an increase in stretch depending on the Lewis number of the deficient reactant [55]. In lean mixture, the deficient component is always the fuel. The Lewis number of the fuel, defined as the ratio of the thermal diffusivity of the mixture to the mass diffusivity of the fuel into the mixture, describes how the flame responds to stretch. It has also been shown that at low strain rates, the burning velocity has a linear relationship with the strain rate described by the Markstein length L, which only depends on the reactant mixture's physical and chemical properties;

$$S_b = S_b^0 - L_b \kappa_b \;\; [\text{m/s}]$$

where S_b [m/s] and S_b^0 [m/s] are the stretched and unstretched flame speed related to the burnt gas respectively, L_b [m] is the Markstein length and κ_b [1/s] is the flame stretch rate. The non dimensional Markstein number, defined as the Markstein length normalized by the nominal flame thickness is also commonly used.

$$Ma_b = \frac{L_b}{\delta} = \frac{L_b}{\alpha / S_u^0} \;\; [\text{-}]$$

where α [m^2/s] is the thermal diffusivity of the unburnt mixture and S_u^0 [m/s] is the laminar flame speed. Hydrogen and methane have very different response to strain as the Lewis numbers are dissimilar ($Le_{CH_4} \approx 0.9, Le_{H_2} \approx 0.3$, [55]). Figure 7 and 8 show the flame speed of methane/air and hydrogen/air mixtures as function of the strain rate. The hydrogen and methane flames have the opposite response to strain. The gradient describes the Markstein length.
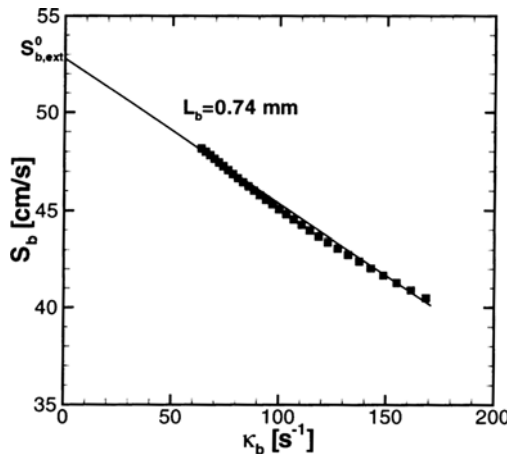

Figure 7 Effect of strain rate on the flame speed relative to the burnt gas, methane/air flame [55]
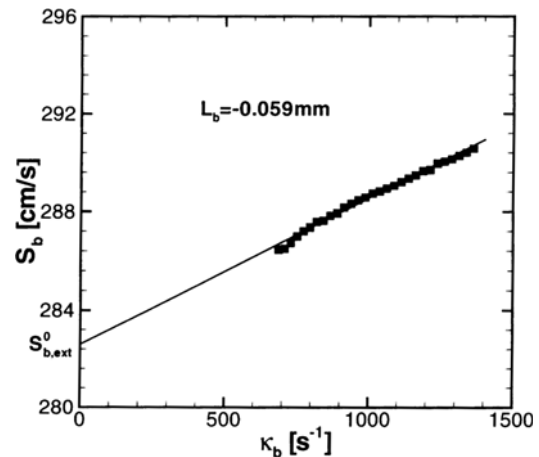
Figure 8 Effect of strain rate on the flame speed relative to the burnt gas, hydrogen/air flame [55]

5.3 Cellular flames

A premixed flame expanding from an ignition source may, in the early stage of flame development, have a smooth flame surface. However, a propagating flame sheet is unstable in nature. Because the density of the gas changes dramatically through the flame sheet, the velocity also changes. The change in velocity makes the flame sheet unstable and perturbations may grow to create a wrinkled or cellular flame structure. When this happen, the burning velocity increases markedly and the flame may eventually evolve to be turbulent [57]. However, heat diffusion provides a stabilizing effect because the heat diffusion at the tip of a bulge convex towards the unburnt gas is larger than at the tip of a bulge convex towards the burnt mixture. Because the heat can diffuse towards a larger area at the tip towards the cold unburnt gas and the temperature gradient is larger here, the flame temperature tends to decrease in this area. Correspondingly, at the tip towards the burnt mixture the heat diffusion is less which results in higher flame temperature. As the flame speed is very much dependent on the temperature, the perturbations tend to be smoothened out by thermal diffusion if the destabilizing effects are not too strong [51]. Another effect, especially relevant for lean hydrogen combustion, is illustrated in Figure 9 [51].
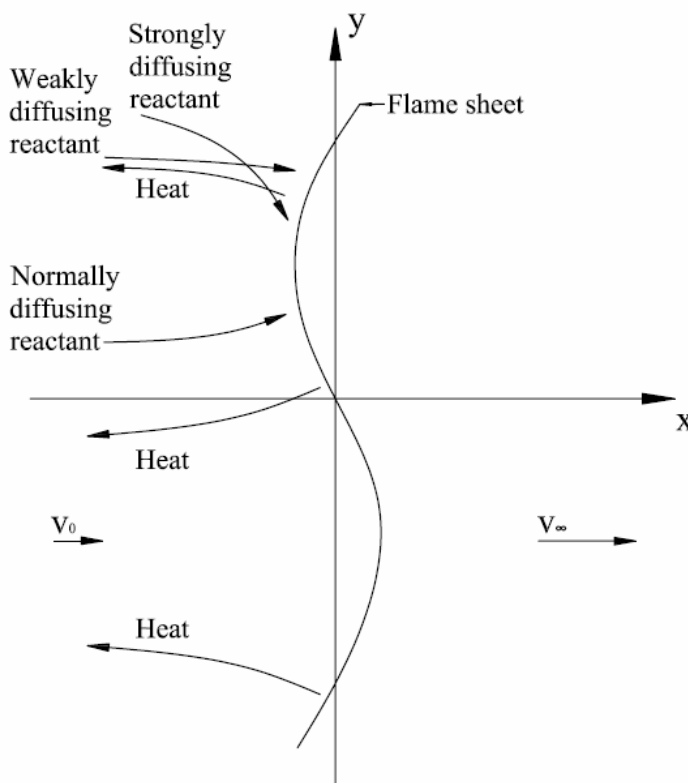
Figure 9 Schematic illustration of the diffusive-thermal instabilities

The effect is called diffusive-thermal instability, and it is of relevance when the mass diffusivity of the deficient reactant is larger than the thermal diffusivity of the mixture. In fuel lean combustion this means that the fuel Lewis numbers is less than unity. At the tip of a bulge convex towards the unburnt mixture, the gradients of temperature and species will be larger than that of a normal flat flame. This makes the fluxes of both reactants and heat increase. If the diffusivity of the limiting reactant and the thermal diffusivity of the mixture are the same (Le = 1), the effect of the increased

diffusion equals the effect of heat flux, and the flame temperature remains the same. However, if the diffusion of the limiting reactant is higher (Le < 1), the flame temperature will increase, and since the flame speed is strongly dependent on the temperature, the local flame speed will increase. The opposite will happen where the bulge is concave towards the unburnt gas [51]. This will make the bulge grow and divide into smaller bulges or cells. This effect may be viewed in relation to the effect of strain on the flame speed described above. Mixtures that have low or negative Markstein length also exhibit a strong tendency to develop cellular flame structures. The flame stretch has a stabilizing effect on the flame sheet if the flame speed decreases with stretch rate (positive Markstein length) because the stretch is higher on the front tip of the bulge. If the flame speed increases with stretch rate (negative Markstein length), the stabilizing effect vanishes and the hydrodynamic and diffusive-thermal instabilities act freely and a cellular flame structure evolves early in the flame development. Because of the higher burning velocity of a cellular flame compared to a flat flame, blending hydrogen into methane or natural gas may hence result in an increase in the burning velocity considerably higher than the increase in laminar flame speed.

5.4 Minimum ignition energy

The minimum ignition energy can be understood as the minimum amount of energy that has to be induced locally to cause ignition. A common expression for this energy is [58]:

$$E_{\min} = \frac{1}{3}\pi d^3 \rho_b c_{p,av}\left(T_b - T_u\right) \ [\text{J}]$$

where d is the quenching distance, $c_{p,av}$ is the mean specific heat capacity, T_b and T_u are the temperatures of the flame and unburnt gas respectively. This may be viewed as the energy needed to bring to the smallest volume that a flame can survive up to the flame temperature. Another way is to look at the heat loss out of the volume [58];

$$E_{\min} = \pi d^2 \frac{\lambda_{av}\left(T_b - T_u\right)}{S_{av}} \ [\text{J}]$$

Here λ_{av} [W/m K] is the heat conductivity averaged for the temperature interval. d/S_{av} [s] represent the time it takes for the gas to pass through the width of the flame to complete the combustion. These are rough estimations, but they do illustrate the physical properties that govern the minimum ignition energy. The heat loss method only takes the conductive heat transfer into account, but the radiation will also contribute to heat loss. Effects caused by non-unity Lewis numbers may influence the minimum ignition energy. It can also be questioned if the quenching distance is the correct value to represent the flame thickness.

The minimum ignition energy of hydrogen is one order of magnitude lower than that of methane. If one should explain that from the above expressions, the most obvious explanation is that the quenching distance of hydrogen is about 1/3 of that of methane. This indicates that the volume that has to be heated is much smaller and requires less energy. Also the heat capacity of a hydrogen/air mixture is slightly less in a

methane/air mixture per volume. This will be most prominent for richer mixtures as
the properties of air will dominate for lean mixtures.

The low minimum ignition energy of hydrogen may create problems when hydrogen
is used as a fuel in internal combustion engines. The problems are associated with
unwanted pre-ignition at hot spots like spark plugs or exhaust valves in the
combustion chamber [59]. Thus, engines designed for hydrogen are carefully
designed to minimize hot surfaces.

5.5 Autoignition

When heating a combustible mixture of fuel and oxidizer at constant pressure,
chemical reaction will start to run. At some point, the temperature of the mixture will
start to run away, resulting in an explosion. At which temperature this occurs depends
on the fuel, fuel concentration and vessel size, but the temperature is also strongly
pressure dependent. This may be displayed in a pressure-temperature diagram where
the explosion limits form a mirrored S [7].
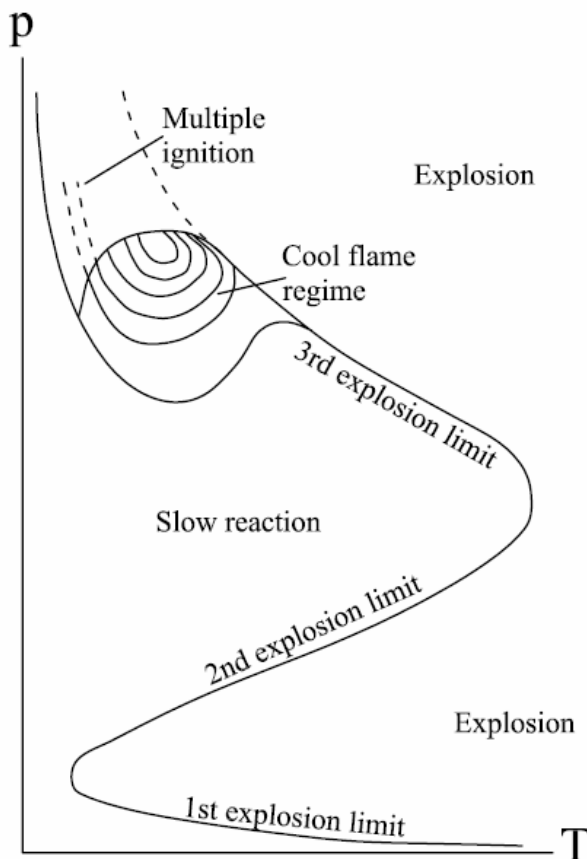
Figure 10 Principle sketch of the ignition limits

The first ignition limit may be explained by a competition between the chemical
reactions in the gas forming radicals and the surface reaction on the vessel wall
terminating the radicals. When pressure is increased above the first limit, a
spontaneous ignition occurs because the diffusion decreases with pressure and the
chain branching reactions produce radicals faster than the surface reactions terminate

them. At higher pressure, there is another area where the mixture does not ignite. The lower line forms the second ignition limit which is governed by the competition of chain branching and terminating reaction in gas phase. Low pressure promotes chain branching reactions while high pressure promotes 3-body chain terminating reactions. The third explosion limit may be explained by the balance in heat production and heat losses to the vessel walls. At pressures above the third limit, the heat production dominates over the heat losses, increasing the temperature and leads to ignition. This is also called the thermal explosion limit. The third limit of hydrogen/air mixtures will follow the dotted line to the right. For hydrocarbons, however, the third limit is more complex as the amount of elementary reactions is larger. An interesting phenomenon is the multiple ignition area and cool flame area of the third explosion limit. Here, combustion takes place at low temperature, but an explosion is inhibited by chemical reactions where a temperature increase shifts the equilibrium so that the chain branching slows down. The overall reaction may lead to a thermal explosion if the heat release in the low temperature reactions is high enough to bring the pressure above the third explosion limit. The tendency to exhibit cool flame combustion varies for different fuels. Normal paraffins give strong cool flames, branched chain paraffins are more resistant. Olefins show low luminosity flames with long induction times. For light hydrocarbons like methane, cool flames are not observed at conditions like what we find in internal combustion engines [8]. However, cool flames are also observed for methane at very rich mixtures [60].

The autoignition properties of a fuel are essential in diesel engines. When the diesel fuel is injected into the combustion chamber, the air temperature and pressure is well above the third explosion limit of a stoichiometric diesel fuel/air mixture. The cetane number (CN), which is used to describe the ignition property of diesel fuel, may approximately be described as the temperature and pressure needed to obtain a specified ignition delay time. However, in the original CN test the temperature and pressure varies during the ignition delay period because it is performed in a test engine. This ignition delay time includes time for evaporation and mixing as well as the time for chemical reactions to take place. The autoignition temperature does hence not relate directly to the CN. However, diesel fuels, that have large CN, generally have much lower autoignition temperatures than fuels for spark ignition engines that have very low (or negative) CN.

In homogeneous charge compression ignition (HCCI) engines the fuel and air are more or less premixed before compression. The mixture is hence brought through conditions of varying temperature and pressure, and the chemical reactions starts well before the main heat release which is a thermal explosion. In this kind of ignition process, the low temperature reactions can be observed as a small heat release before the main heat release if the fuel exhibit cool flame behavior. Because of the radical pool created during the low temperature reactions and the heat released, the low temperature reactions also influence the start of the main heat release [61]. The cool flame or low temperature reactions are also believed to play a role in the engine knock phenomenon in spark ignition engines [8].

6 Experimental work

In the following, an overview and the background of the experimental work is presented. Four papers were written based on the experiments. The complete papers are presented in chapter 8.

6.1 Summary of papers

6.1.1 Paper 1: "Ignition and Combustion Characterization of Hydrogen/Methane Mixtures by Visualization in a Rapid Compression Machine (RCM)"

(Presented at the SAE 7th International Conference on Engines for Automobile, Capri, Naples, Italy, September 2005)

The laminar flame speed of hydrogen is much higher than the laminar flame speed of natural gas. Mixing hydrogen into natural gas may hence speed up the combustion in lean burn natural gas engines or make it possible to burn leaner mixtures without reducing the burn rate. This is advantageous both with respect to NO_x formation and the thermal efficiency of a spark ignition engine. Flame speed data at ambient pressure and temperature for different methane/hydrogen mixtures exists in the literature. However, at elevated pressures and temperatures, flame speed data are scarce. To study the effect of hydrogen addition on the flame speed at conditions close to what is found in combustion engines experiments were performed in a hydraulically driven rapid compression machine. The flame propagation was studied by a high speed video camera taking pictures by means of a Schlieren optical setup and quarts windows in the combustion chamber. Two different methane/hydrogen mixtures were tested; 5 vol% and 30 vol% hydrogen, besides pure methane at different excess air ratios. Adding 30 vol% hydrogen to the methane was found to increase the flame speed considerably. A noticeable increase was also observed with the 5 vol% mixture compared to pure methane. The relative increase in flame speed was smallest at stoichiometric mixtures and higher at leaner mixtures.

In addition to the effect on the laminar flame speed, addition of hydrogen changes the effective Lewis number of the mixture. The mass diffusivity of hydrogen is higher than the thermal diffusivity of the mixture. This is known to have a destabilizing effect on the flame sheet which contributes to the formation of a cellular flame structure leading to a further increase in the flame propagation velocity. The introduction of hydrogen may thus influence the flame propagation speed more than the increase in laminar flame speed. The same effect also influences the flame's response to stretch which is particularly relevant in the early flame development when the flame stretch rate is high. The optical system made it possible to study the cellular structure and the typical cell sizes were quantified for the three mixtures. The 30 vol% hydrogen mixture obtained earlier development of a cellular structure and the typical cell size was much smaller than that of the pure methane and the 5 vol% hydrogen mixture. A difference in the cell size between the 5 vol% mixture and pure methane was observed at lean mixtures, but not near stoichiometric air/fuel ratios.

6.1.2 Paper 2: "Lean burn versus stoichiometric operation with EGR and 3-way catalyst of an engine fueled with natural gas and hydrogen enriched natural gas"

(Presented at the SAE Fuels and Emissions Conference, Cape Town, South Africa, January 2007)

Natural gas fueled buses are commonly used in cities because of the lower emissions of particulate matter and NO_x compared to diesel fueled buses. The gas engines are most commonly lean burn spark ignited engines where the excess air ratio is kept well at the fuel lean side to keep the NO_x formation low. However, because higher excess air ratios also leads to increased hydrocarbon emissions there is a trade off between low NO_x and low hydrocarbon emissions. It is not clear if it is possible to use the lean burn technology when new and more stringent emission legislations is applied without sophisticated exhaust gas after-treatment. In Europe, new emission legislations (Euro 5) for gas engines will take effect from 2008. The limit for NO_x emissions will then be reduced from 3.5 g/kWh to 2.0 g/kWh which may be difficult to obtain without exceeding the emission level of unburnt hydrocarbon. A well proven technology to obtain low emissions of both NO_x, HC and CO is the three-way-catalyst. The technology has been used in gasoline fueled passenger cars for many years. However, this technology requires the air/fuel ratio to be close to stoichiometric because the NO_x reducing reactions on the catalyst surface will not take place when there is a surplus of oxygen. Running an engine on a stoichiometric natural gas/air mixture is not advantageous because it leads to lower brake thermal efficiency. High heat losses, pumping losses and higher tendency for engine knock which limits the compression ratio leads to lower thermal efficiency than when the engine is run with excess air. However, some of the advantages of lean burn can be obtained by recycling exhaust (EGR) as the dilution exhaust has similar effects as the dilution with air. The air/fuel ratio can hence be kept stoichiometric and the three-way-catalyst can be utilized while the volume flow through the engine is increased. However, because of the restricted concentration of oxygen, the degree of dilution can not be as high as when the mixture is diluted with air before the combustion deteriorates. In addition, the increased concentration of CO_2 and H_2O reduces the ratio of specific heats (c_p/c_v) which leads to less work extraction during the expansion stroke for the same amount of energy released at a constant compression ratio. However, earlier work show that the thermal efficiency is not compromised severely when the EGR solution is applied. Still, the EGR solution adds complexity and costs to the system as it requires an EGR valve, EGR cooler and some sort of arrangement to prevent condensed water vapor droplets to deteriorate the combustion. In that respect it would be advantageous to still use the lean burn technology if the future emission legislations can be met.

To have a deeper understanding of and to compare the two technologies, experiments were performed for both the lean burn and the EGR technology. The engine, a Volvo TD 100 spark ignited gas engine, was fueled with pure natural gas and a mixture of 25 vol% hydrogen in natural gas to investigate the effect of hydrogen addition on both the lean burn operation and the stoichiometric operation with EGR. The most essential aspects to be investigated were if the engine's tolerance for dilution of both air and exhaust gas could be increased by the addition of hydrogen. Although the engine was not prepared to run the transient test cycle required for the Euro 5 emission legislation certification, it was of most interest to see if the engine showed signs of managing the

emission levels at stationary conditions when the engine was fueled with the hydrogen mixture for lean burn operation.

The lean limit of stable combustion was found to be higher for the hydrogen enriched natural gas than for pure natural gas. Higher excess air ratios could be obtained without deterioration of the combustion stability and high THC emissions. The NO_x-HC trade-off situation was hence improved. The assumed increase in the tolerance for EGR when hydrogen was present could not be proven because of problems with formation of water droplets in the inlet at high EGR rates which deteriorated the combustion. The hydrogen enriched natural gas resulted in higher brake thermal efficiency for both lean burn operation and stoichiometric operation with EGR. The higher brake thermal efficiency was a result of the increased burn rate when hydrogen was present, which results in a more efficient thermodynamic cycle.

6.1.3 Paper 3: "HCCI combustion of natural gas and hydrogen enriched natural gas. Combustion control by early direct injection of diesel oil and RME"

(Submitted for the 2008 SAE International Powertrains, Fuels and Lubricants Congress, Shanghai, China, June 2008)

Homogeneous charge compression ignition (HCCI) has been proposed to be the solution for a combustion engine concept that emits low levels of NO_x and PM, while simultaneously having thermal efficiency as a diesel engine. Because the charge is premixed with air and/or EGR, fuel rich and hot zones are not formed to a large degree and the NO_x and PM emissions can almost be eliminated. However, the main challenge is to control the ignition timing as this can not be controlled in a direct way as controlling the spark timing or the injection timing. The autoignition timing has to be controlled in an indirect way, by regulating the inlet temperature, varying the amount of hot residual gases in the combustion chamber by varying the valve timing, varying the compression ratio etc. Another way of controlling the ignition timing is to use two fuels of different ignition properties in such a way that the ignition properties of the air/fuel mixture can be controlled by varying the ratio between the two fuels. A higher proportion of the easily ignited fuel will advance the ignition timing while a smaller proportion will retard the ignition timing. If one disregards the inconvenience of having to fill two fuels, the dual fuel system may be considered less complex than many of the other control systems. Since a HCCI engine generally has a brake thermal efficiency comparable to diesel engines, in other words much higher than spark ignition engines at part load, using natural gas in HCCI engines is of most interest. Natural gas, which consists mainly of methane (which has a research octane number of 120) has very high resistance to autoignite. Diesel oil however, autoignite very easily. To investigate the possibility to obtain controllable HCCI combustion by a dual fuel system of diesel fuel and natural gas, experiments were performed in a single cylinder Scania D12 direct injection diesel engine with a fully controllable common rail diesel injection system. Because of the excellent autoignition properties of diesel fuel, it was expected that rather small amounts of diesel was needed to obtain autoignition and the natural gas was thus intended to be the main fuel. The natural gas was introduced to the inlet air by pulse width modulated gas injector and was thus premixed with air before combustion. The diesel oil was introduced through early direct injection to have time to mix with the natural gas/air mixture and was expected

to be partly premixed before combustion. The total fuel/air mixture was hence expected to be close to homogeneous. To investigate if hydrogen addition would influence the combustion, hydrogen enriched natural gas was also tested. The mixture consisted of 20 vol% hydrogen in natural gas. It was of particular interest to see if the hydrogen enriched gas would require less diesel oil when considering the high reactivity of hydrogen and if the combustion duration, NO_x emissions and HC emissions were influenced by the hydrogen. In addition, the diesel oil was replaced by rape seed methyl ester (RME) to investigate if this fuel, which is different from petroleum diesel in many ways, would be behave differently in the combustion process.

The main findings were that the hydrogen addition only influenced the combustion to a minor degree. A small increase in the heat release rate and a reduction in the maximum engine load were observed when the engine was fuelled with the hydrogen enriched natural gas. The required amount of diesel injection was not influenced considerable by the presence of hydrogen. A large difference was however observed between RME and diesel oil. When RME was used as the ignition improving component, the required amount of liquid injected to keep a specified combustion phasing was much higher than when diesel oil was used. This is believed to mainly be a result the low volatility of RME compared to diesel oil.

6.1.4 Paper 4 "Study of particle-, NO_x- and hydrocarbon emissions from a diesel engine fueled with diesel oil and biodiesel with fumigation of hydrogen, methane and propane"

(Submitted for the 2008 SAE International Powertrains, Fuels and Lubricants Congress, Shanghai, China, June 2008)

The more stringent emission legislations for diesel engines have lead to the necessity to introduce complex exhaust gas after-treatment systems. The trade off between particulate matter and nitrogen oxide emission is a well known problem that several engine manufacturers have chosen to solve by using selective catalytic reaction (SCR) and diesel particulate filter (DPF) systems. These systems are however rather costly and adds complexity to the system which may reduce the time of problem free operation of the engines. The high PM formation in diesel engines is caused by the inhomogeneous combustion which is a result of the injection of liquid fuel during the combustion period. This leads to the formation of fuel rich zones were particles are formed. However, most of the particles are oxidized during the combustion period. To investigate if mixing relatively small amounts of gas into the combustion air (fumigation) could reduce the PM emissions, experiments were performed in a Scania DC 1102 diesel engine. Marine gas oil (a diesel quality) and a biodiesel consisting of 80 vol% rape seed methyl ester and 20 vol% soy bean methyl ester was used as the base fuels. In theory, the PM emission should decrease when replacing some of the inhomogeneous combustion by combustion of premixed gas because the particles are mostly formed in fuel rich regions. Besides, the premixed combustion might increase the oxidation of particles already formed, especially if the gas is hydrogen which produce considerable amounts of radicals that may participate in the oxidation process. The gas was introduced upstream the turbocharger and controlled by a mass flow controller and may thus be considered close to perfectly premixed. The authors also wanted to compare the effect of hydrogen fumigation with more commercially

available gases. Methane and propane were chosen as these are similar to natural gas and liquefied petroleum gas (LPG, which also may contain butane) respectively. It was also interesting to investigate the effect of fumigation on the NO_x emission and especially the THC emission as the hydrocarbon emissions were expected to be high because of flame quenching of the lean methane/air and propane/air mixture and if the fumigation would influence the brake thermal efficiency of the engine.

The main finding was that considerable amounts of gas had to be introduced before the PM emissions were influenced significantly. A reduction in PM of about 60% was observed when 30% of the fuel energy was replaced by propane at an engine load of 10 bar BMEP. Because of the low density of hydrogen, less of the fuel energy could be replaced by hydrogen than by methane and propane. Significant reduction could therefore not be obtained by hydrogen addition. Rather large variability in the PM measurements made it difficult to determine if hydrogen could reduce the PM emission more efficiently than methane or propane at equal amounts of energy introduced by the gas. The thermal efficiency decreased with gas rate at low load for all gases, but was unaffected or slightly increased at higher loads. The NO_x emissions were not influenced considerably by the fumigation, but the emissions of THC increased with methane and propane rate. The hydrogen concentration was not measured, but the slight reduction in thermal efficiency with hydrogen rate is believed to be caused by emissions of unburnt hydrogen. The biodiesel resulted in higher PM emissions at low load but considerable less PM emissions at higher loads compared to the diesel oil. The NO_x emissions were about 15% higher when biodiesel was used compared to the diesel oil.

7 Conclusions and recommendations

The effect of using hydrogen as a fuel additive to various fuels has been investigated in both spark ignited and compression ignited combustion. Experimental work has been performed in three main categories of combustion engines technologies; Otto, Diesel and Homogeneous Charge Compression Ignition (HCCI). In addition, premixed spark ignition combustion experiments have been performed in a dynamic combustion rig (rapid compression machine) where the flow conditions were close to quiescent prior to ignition.

7.1 Conclusions

7.1.1 Effect of hydrogen addition on the combustion process

Based on the spark ignition experiments, the main conclusion that can be drawn is that hydrogen added to methane or natural gas considerably influences the flame propagation speed. The flame speed increases as a direct result of the higher laminar flame speed of hydrogen/air mixtures as compared to methane or natural gas/air mixtures at constant excess air ratio. Of equal importance however, is the extension of the lean limit of stable combustion in lean burn spark ignition engines. This effect can not only be attributed to the increase in flame propagation speed caused by the increase in laminar flame speed, but also that the flame's response to strain changes when hydrogen is added. The flame is more tolerant to strain when hydrogen is present in lean mixtures, and the tendency of local extinctions caused by strain from turbulence is hence reduced. This effect is caused by the reduction of the effective Lewis number of the mixture because of the high diffusivity of the hydrogen gas. The combustion stability is improved and the excess air ratio can be increased without increasing the emissions of unburnt hydrocarbons. The Lewis number effect could also be observed in the dynamic combustion rig experiments as the flame front exhibited a much more wrinkled or cellular structure which is believed to be caused by thermo-diffusive effects which can be attributed to a reduction of the effective Lewis number.

Adding hydrogen to compression ignition engines in the way performed in the HCCI experiments does not result in large influences on the combustion. A small increase in the rate of heat release was observed when natural gas was substituted with a mixture of 20 vol% hydrogen in natural gas. Since the combustion in this technology is less characterized by flame propagation but more by autoignition at different locations simultaneously, the effect of hydrogen does not influence the combustion rate in the same way as in spark ignited combustion. The combustion should be faster because of the faster chemical kinetics of hydrogen combustion compared to natural gas combustion, and this is observed to some degree. However, the autoignition temperature of hydrogen is high, and may, depending on the composition of the natural gas be higher than that of the natural gas. Because diesel fuel, which has much lower autoignition temperature than both hydrogen and natural gas, was used to improve the autoignition properties of the mixture, the properties of diesel may overshadow the effect of hydrogen addition. The ignition timing is hence controlled by the diesel concentration and the effect of hydrogen can first be seen later in the cycle. The oxidation of the diesel molecules may govern the rate of heat release in a

large part of the combustion process. A higher effect of hydrogen would be expected if the diesel oil was not present. The combustion timing would then have to be controlled by other means, for example control of the inlet temperature and controlling the ratio between hydrogen and natural gas. The effect of hydrogen on the combustion for the diesel engine experiments was also small. A small increase in the heat release rate could be observed in the preliminary premixed combustion phase because some of the hydrogen was ignited in this phase. During the mixing controlled combustion, the heat release rate was not considerably influenced by the hydrogen addition.

7.1.2 Effect of hydrogen addition on emissions and thermal efficiency

The emissions of NO_x, THC and CO emissions were measured for all the engine experiments. In addition, the emissions of PM and the filter smoke number (FSN) were measured during the diesel engine experiments. In the spark ignited natural gas engine, the hydrogen addition did not result in any significant change in NO_x emission at a constant excess air ratio. Because of the higher adiabatic flame temperature and flame speed of hydrogen which leads to higher maximum pressure and temperature, the NO_x emissions should increase with a hydrogen addition. However, as the ignition timing was adjusted to have a constant CAD of the maximum cylinder pressure, no consistent difference could be observed between when the engine was fueled with natural gas or hydrogen enriched natural gas. However, because of the extended lean limit of stable combustion with the hydrogen addition, the NO_x emissions were considerably reduced at the leanest mixtures. The THC and CO emissions were reduced when the hydrogen enriched gas was used, although not dramatically. When the engine was run at a stoichiometric air/fuel ratio with exhaust gas recirculation (EGR), no consistent trend could be seen on the NO_x emissions with or without the hydrogen addition. The NO_x emissions decrease almost linearly with the EGR rate and can hence be reduced by increasing the EGR rate. Because of problems with condensed water droplets from the cooled EGR that deteriorated the combustion, it was not proven that the hydrogen addition can increase the engines tolerance for EGR. It is however probable that a higher EGR rate could be achieved with the hydrogen addition if this problem was solved. However, since the stoichiometric mixture made it possible to utilize a three-way-catalyst, the emissions of both THC and NO_x were much lower with EGR than with lean burn operation. The CO emissions were in the same range for lean burn and stoichiometric operation with a three-way-catalyst. The brake thermal efficiency was higher when the engine was fueled with hydrogen enriched gas both for lean burn and stoichiometric operation with EGR. Operation with EGR resulted in a penalty in the efficiency compared to lean burn operation.

In the HCCI experiments the hydrogen addition did not influence the combustion to a large degree, and the emissions were hence not highly influenced by the hydrogen either. However, a reduction in the THC emissions was observed at late combustion phasing when the engine was fueled with the hydrogen mixture. Very low NO_x emissions (beneath 1 g/kWh) were possible as long as the combustion phasing was kept late in the cycle. However, very high NO_x emissions were observed at earlier combustion phasing (above 10 g/kWh). The diesel engine experiments also revealed that in this process the introduction of hydrogen only influenced the emissions to a

minor degree. The NO_x emissions were not influenced by the hydrogen addition at a low engine load, but increased with the hydrogen rate at higher loads. The THC emissions were not influenced by the hydrogen addition at low loads, but decreased moderately at high load. The PM was not considerably influenced by hydrogen addition. The brake thermal efficiency showed a decreasing trend with hydrogen rate at low load and a slight increase at high load. The decrease at low load is believed to be caused by incomplete combustion of the hydrogen as the hydrogen/air mixture was very lean (beneath 3 vol% hydrogen).

7.1.3 Other experimental results

During the HCCI and the diesel engine experiments other fuels were also tested. In the HCCI experiments, where the amount of diesel fuel was used to control the autoignition timing of the process, the diesel oil was replaced by rape seed methyl ester (RME). This was done to investigate if this fuel, which is very different from diesel oil in chemical composition, would be favorable in the operation of the engine. The main result was that the required amount of liquid fuel needed to obtain a specified combustion phasing increased dramatically when RME was used. This is believed to mainly be caused by the low volatility of RME compared to diesel oil which makes it vaporize later in the cycle. Also, the higher viscosity of RME results in larger droplet size and hence slower evaporation. Because of this, more liquid had to be injected to obtain a high enough concentration of the easily ignitable RME vapor in the air/gas mixture. The mixture was hence expected to be less premixed before ignition when RME was used as the ignition improving medium. After ignition the heat release rate was considerably higher when RME was used than when diesel oil was used at constant combustion phasing. A biodiesel, consisting of 80% RME and 20% soy bean methyl ester, was also tested in the diesel engine fumigation experiments. The main results were that the biodiesel resulted in higher PM emissions at low load (about 50% higher at 5 bar BMEP) but considerably lower at higher loads (about 75% lower at 10 and 15 bar BMEP) compared to the diesel oil. The filter smoke number (FSN) however, was much lower when the engine was fueled with biodiesel at all loads. This implies that the particles consisted of less soot and more organic compounds which will result in less blackening of the FSN filters because of lighter color. In these fumigation experiments, in addition to using hydrogen as the fumigation gas, methane and propane were also tested for comparison. As the energy density of these gases is much higher than that of hydrogen, higher energy rates could be supplied by the gas without exceeding the lower flammability limit or displacing considerable amounts of air. In that respect, methane and propane are better suited as fumigation gases than hydrogen, and reductions on PM emissions up to 60% was observed when 30% of the fuel energy was replaced by propane. However, the THC emissions were high especially when methane was introduced (up to 5.5 g/kWh). If this system is to be implemented in road vehicles using natural gas or LPG, an oxidation catalyst would be required.

7.2 Recommendations for further work

Hydrogen added to natural gas in lean burn spark ignition engines has been proven to be advantageous for the HC – NO_x trade off. The engine used in this experimental work was developed in the 90's and is therefore not state of the art. Although the fuel injection and ignition system was modified to have full flexibility thereby having small potential for improvements, the combustion chamber design, inlet and outlet

ducts etc. were not state of the art. Experiments should be performed in a modern natural gas engine that copes with the present emission legislations to investigate if the effect of hydrogen addition is as large as with older designs. The potential for reduced emissions and increased efficiency by hydrogen addition may be suspected to be less in better optimized engines. However, the new European emission legislations for 2008 may be hard to fulfill without stoichiometric operation with 3-way catalysts or sophisticated exhaust gas after treatment systems. A small improvement may thus be rewarding for the lean burn technology. Also, the effect of the hydrogen addition at stoichiometric operation with cooled EGR should be investigated further. The effect of hydrogen on the maximum EGR levels and the possible improvements in brake thermal efficiency should be further quantified.

Using natural gas or LPG in compression ignition engines in compression ignition engines is interesting, especially from a thermal efficiency point of view. Using natural gas together with diesel oil or other fuels in a HCCI like combustion process may be a very beneficial way of using natural gas as an engine fuel.

8 Papers

9 References

1. International Energy Agency (http://www.iea.org)
2. Tunestål, P., Christensen, M., Einewall, P., Andersson, T., Johansson, B., Jönsson, O., "Hydrogen Addition For Improved Lean Burn Capability of Slow and Fast Burning Natural Gas Combustion Chambers", SAE Paper 2002-01-2686.
3. Tsolakis, A., Megaritis, A., "Exhaust Gas Fuel Reforming for Diesel Engines – A Way to Reduce Smoke and NOx Emissions Simultaneously", SAE Paper 2004-01-1844
4. Das, L. M., "Hydrogen Engines: A View of the Past and a Look into the Future", Int. J. Hydrogen Energy, Vol. 15, No. 6, p. 425 – 443, 1990
5. Colombia Earthscape, (http://www.earthscape.org)
6. Hythane Company, LLC (http://www.hythane.com)
7. Warnatz. J., Maas, U., Dibble, R. W., 2001, "Combustion", Springer Verlag, Germany
8. Heywood, J. B., "Internal Combustion Engine Fundamentals", McGraw-Hill, 1988
9. Guibet, J. C., "Fuels and Engines, Technology Energy and Environment, Instutut Francais Du Petrole Publications, 1999
10. Bergstrand, P., Denbratt, I., "Diesel combustion with reduced nozzle orifice diameter", SAE paper 2001-01-2010
11. Graskow, B. R., Kittelson, D. B., Ahmadi, M. R., Morris, J. E., "Exhaust Particulate Emissions from a Direct Injection Spark Ignition Engine", SAE Paper 1999-01-1145
12. Chandler, M. F., Teng, Y., Koylu, U. O., "Diesel engine particulate emissions: A comparison of mobility and microscopy size measurements", Proceedings of the Combustion Institute, Vol. 31, 2007, p. 2971 – 2979
13. Ayala, A., Gebel, M. E., Okamoto, R. A., Rieger, P. L., Kado, N. Y., Cotter, C., Verma, N., "Oxidation Catalyst Effect on CNG Transit Bus Emissions", SAE Paper 2003-01-1900
14. Lambert, C., Hammerle, R., McGill, R., Khair, M., Sharp, C., "Technical Advantages of Urea SCR for Light-Cuty and Heavy-Duty Diesel Vehicle Applications", SAE Paper 2004-01-1292
15. Johnson, T. V., "Diesel Emission Control in Review", SAE Paper 2007-01-0233.
16. Hirata, K., Masaki, N., Ueno, H., Akagawa, H., "Development of Urea-SCR System for Heavy-Duty Commercial Vehicles", SAE Paper 2005-01-1860
17. Theis, J., Lupescu, J., Ura, J., McCabe, "Lean NO_x Trap System Design for Cost Reduction and Performance Improvement", SAE Paper 2001-01-1069
18. Johnson, T. V., "Diesel Emission Control in Review", SAE Paper 2007-01-0233
19. Nam, G., Park, J., Lee, J., Yeo, G., "The Effect of an External Fuel Injection on the Control of LNT System; the Diesel NO_x Reduction System", SAE Paper 2007-01-1242.
20. Tsumagari, I., Hirabayashi, H., Takenaka, Y., Hosoya, M., Shimoda, M., "Study of 2-LEG NO_x Starage-Reduction Catalyst System for HD Diesel Engine" SAE Paper 2006-01-0211

21. Ogyu, K., Oya, T., Ohno, K., Lorentzou, S., Konstandopoulos, A. G., "Study on Catalyzed-DPF for Improving the Continuous Regeneration Performance and Fuel Economy", SAE Paper 2007-01-0919

22. Ootake, M., Kondou, T., Ikeda, M., Daigo, M., Nakano, M., Yokoyama, J., Miura, M., "Development of Diesel Engine System with DPF for the European Market", SAE Paper 2007-01-1061

23. DieselNet, Online information service on clean diesel engines and emissions (http://www.dieselnet.com)

24. Moran, M. J., Shapiro, H. N., "Fundamentals of engineering and thermodynamics"

25. Karim, G. A., Wierzba, I., Al-Alousi, Y., "Methane-Hydrogen Mixtures as Fuels", Int. J. Hydrogen Energy, Vol. 21, No. 7, (1996), p. 625-631

26. Serway, R. A., "Physics For Scientists and Engineers"

27. Kubesh, J. T., "Development of a Throttleless Natural Gas Engine" NREL/SR-31141 Report, 2002

28. Taniguchi, S., Tsukasaki, Y., Yasuda, A., "Study of Compressed Natural Gas Direct Injection Engine", SAE Paper 2006-05-0214

29. Reynolds, C. C. O., Evans, R. L., Andreassi, L., Cordiner S., Mulone, V., "The Effect of Varying the Injected Charge Stoichiometry in a Partially Stratified Charge Natural Gas Engine" SAE Paper 2005-01-0247.

30. Nellen, C., Boulouchos, K., "Natural Gas Engines for Cogeneration: Highest Efficiency and Near-Zero_Emissions through Turbocharging, EGR and 3-Way Catalytic Converter", SAE Paper 2000-01-2825

31. Renewable Fuels Assosiation, RFA (http://www.ethanolrfa.org)

32. Grassi, G., "Modern Bioenergy in European Union", Renewable Energy, Vol. 16, 1999, p. 985 – 990

33. Stockholm Läns landsting, (http://sl.se/templates/Page.aspx?id=1571)

34. Horn, U., Egnell, R., Johansson, B., Andersson, Ö., "Detailed Heat Release Analysis With Regasrd To Combustion of RME and Oxygenated Fuels in a HSDI Diesel Engine", SAE Paper 2007-01-0627

35. Mayer, M., Czerwinski, J., Wyser, M., Mattrel, P., Heitzer, A., "Impact of RME/Diesel Blends on Particle Formation, Particle Filtration and PAH Emissions", SAE Paper 2005-01-1728

36. Zhang, Y., Boehman, A. L., "Impact of Biodiesel on NO_x Emissions in a Common Rail Direct Injection Diesel Engine", Energy and Fuels, Vol. 21, 2007, p. 2003 – 2012

37. U.S Department of Energy, (http://www.fe.doe.gov/aboutus/history/syntheticfuels_history.html)

38. Choren Industries, (http://www.choren.com/en/choren/)

39. Neste Oil (http://www.nesteoil.com/)

40. California Energy Commission (http://www.energy.ca.gov/afvs/vehicle_fact_sheets/methanol.html)

41. International Energy Agency (IEA), "Automotive Fuels for the Future. The Search for Alternatives" (http://www.iea.org/textbase/nppdf/free/1990/autofuel99.pdf)

42. Ying, W., Longbao, Z., Hewu, W., "Diesel emission improvements by the use of oxygenated DME/diesel blend fuels", Atmospheric Environment, Vol. 40 (2006), p. 2313 – 2320

43. Arcoumanis, C., Bae, C., Crookes, R., Kinoshita, E., "The potential of de-methyl ether (DME) as an alternative fuel for compression-ignition engines: A review", Fuel, 2007, (doi: 10.1016/j.fuel.2007.06.007)
44. Gielen, D., Unander, F., "Alternative Fuels: An Energy Technology Perspective", IEA/ETO Working Paper, ETO/2005/01
45. Atkins, P., Jones L., "Chemistry. Molecules, Matter, and Change" W. H. Freeman and Company, New York, 1997. ISBN 0-7167-2832-X
46. Babrauskas, V., "Ignition handbook : principles and applications to fire safety engineering, fire investigation, risk management and forensic science", Issaquah, WA : Fire Science Publishers/SFPE, 2003, ISBN 0-9728111-3-3
47. Law, C. K., Kwon, O. C., Effects of Hydrocarbon Substitution on Atmospheric Hydrogen-air Flame Propagation, Int. J. Hydrogen Energy, Vol. 29, (2004), p. 870
48. Liao, S. Y., Jiang, D. M., Gao, J., Huang, Z. H., Cheng, Q., "Measurements of Markstein numbers and laminar burning velocities for liquefied petroleum gas-air mixtures", Fuel, Vol 83 (2004), p. 1281-1288
49. Iijima, T., Takeno, T., "Effect of temperature and pressure on burning velocity", Combustion and Flame, Vol 65 (1986), p. 35-43
50. Qin, X., Hideaki, K., Niioka, T., "Laminar burning velocity of hydrogen-air premixed flames at elevated pressure", Experimental Thermal and Fluid Science, Vol. 21, (2000) p. 58-63
51. Willams, F. A., "Combustion Theory", The Benjamin/Cummings Publishing Company, 1985
52. Dahoe, A. E., "Laminar burning velocities of hydrogen-air mixtures from closed vessel gas explosions, Journal of Loss Prevention, 2005
53. Verhelst, S., Woolley, R., Lawes, M., Sierens, R., "Laminar and unstable burning velocities and Markstein lengths of hydrogen-air mixtures at engine-like conditions", Proceedings of the Combustion Institute, Vol. 30, (2005), p. 209-216
54. Metghalchi, M., Keck, J. C., "Laminar Burning Velocity of Propane-Air Mixtures at High Temperature and Pressure, Combustion and Flame Vol. 38, (1980), p. 143-154
55. Sankaran, R., Im, H. G., "Effects of Hydrogen Addition on the Markstein Length and Flammability Limit of Stretched Methane/Air Premixed Flames", Combustion Science and Technology, No 178, Vol 9, p. 1585 – 1611
56. Ren, J. Y., Qin, W., Egolfopoulos, F. N., Tsotsis, T. T., "Strain-Rate Effects on Hydrogen-Enhanced Lean Premixed Combustion", Combustion and Flame, Vol 124, Page 717 – 720, 2001
57. Bradley, D., Sheppard, C. G. W., Wooley, R., Greenhalgh, D. A., Lockett, R. D., "The Development and Structure of Flame Instabilities and Cellularity of Low Markstein Numbers in Explosions
58. Kondo, S., Takahashi, A., Tokuhashi, K., "Calculation of minimum ingnition energy of premixed gases", Journal of Hazardous Materials, Vol. 103, (2003), p. 11-23
59. Verhelst, S., Sierens, R., Verstraeten, S., "A Critical Review of Experimental Research on Hydrogen Fueled SI Engines", SAE Technical Paper Series, 2006-01-0430
60. Caron, M., Goethals, M., De Smedt, G., Berghmans, J., Vliegen, S., Van't Oost, E., van den Aarssen, A., "Pressure dependence of the auto-ignition

temperature of methane/air mixtures", Jornal of Hazardous Materials, Vol. 65, 1999, p. 233 – 244

61. Tanaka, S., Ayala, F., Keck, J. C., Heywood, J. B., "Two-stage ignition in HCCI combustion and HCCI control by fuels and additives", Combustion and Flame, Vol. 132, 2003, p. 219 – 239