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Characterizing Gaseous Fuels for Their Knock Resistance based on the Chemical and Physical Properties of the Fuel

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ABSTRACT

A method is described to characterize the effects of changes in the composition of gaseous fuels on engine knock by computing the autoignition process during the compression and burn periods of the engine cycle. To account for the effects of fuel composition on the in-cylinder pressure and temperature history relevant for knocking, changes in heat capacity of the air-fuel mixture and in the phasing of the combustion process are also incorporated in the method. Comparison between pressure profiles measured in a lean-burn, high-speed medium-BMEP gas engine and the calculated pressure profiles at non-knocking conditions shows that the method accurately computes the in-cylinder pressure history when varying the fuel composition. To characterize gaseous fuels for their resistance to knock, a propane-based scale (Propane Knock Index, PKI) is reported in this study. On this scale, the knock resistance for a given gaseous fuel mixture is expressed as an equivalent fraction of propane in methane under identical engine conditions. The chemical mechanism used to compute the autoignition delay time is optimized based on RCM measurements performed at engine conditions. After optimization, the knock resistance as measured by the knock-limited spark timing (KLST) and calculated using PKI was found to agree within the uncertainty of the measurements (± 0.75 °CA) for all fuels studied, including hydrocarbon mixtures representative for liquefied natural gas (LNG) and natural gas/H₂/CO mixtures. In contrast to the method reported here, comparison of KLST for the range of gases studied with methane numbers calculated using the AVL and the MWM methods points to shortcomings in these yardsticks.

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INTRODUCTION

Increasingly stringent regulations regarding CO₂ emissions, depletion of local fuel supplies and the growing desire to enhance the sustainability of the energy supply have resulted in an increasing diversity of pipeline natural gases, a growing interest in using (bio-) LNG and CNG as a transportation fuel and the (possible) introduction of hydrogen containing gases into the natural gas infrastructure. As a result, gases with significantly different composition can be or will be traded and distributed. These variations in the gas composition influence the so-called knock resistance of the fuel. Mild engine knock increases pollutant emissions and can damage the engine in the long term, while severe knock can physically destroy the engine in seconds. Knock-protection systems safeguard against sudden physical damage, but at the expense of lower fuel efficiency and/or lower power output, or even disrupted engine service. Thus, engine knock should be avoided [1]. To ensure that the gas-fueled engines used in, for example, cars, trucks, ships and CHP units are matched with the expected variations in fuel composition, the knock resistance of the fuel must be characterized, and subsequently specified unambiguously.

The occurrence of engine knock is caused by autoignition of unburned fuel mixture, the so-called end gas, in the cylinder before the mixture is completely consumed by the propagating flame. Several empirical methods, such as the methane number approach

[2], have been developed to classify gaseous fuels for their knock sensitivity. These traditionally used methods, in which the knock resistance of a given fuel is compared with an equivalent methane/hydrogen mixture, suffer from a number of shortcomings [3, 4]. Perhaps most apparent of these is that the number is attached to the behavior of an individual engine under stoichiometric conditions, while the actual diversity of installed designs is great, and modern machines tend to operate substantially fuel lean and at higher pressures. In addition, the suitability of hydrogen as a reference gas has been disputed [3, 5] as has been the method of accounting for butane and higher hydrocarbons [6]. Furthermore, a methodology that provides insight into the origins of knock in engines by describing the microscopic details of the effects of fuel composition on cylinder processes is particularly valuable for designers and operators who wish to optimize power output while maintaining knock-free operation. As such, the necessity of having a physically correct and unambiguous method to characterize the knock resistance of the variety of fuels for the variety of engine types in the market has become urgent in recent years.

Autoignition of the unburned end gas in gas engines is initiated by rapid (exothermic) oxidation reactions, leading to heat release that exponentially increases the temperature, causing the overall reaction to auto-accelerate. Experimental studies performed in RCMs and

shock tubes show that the autoignition behavior of fuels depends strongly upon the composition, temperature (T), pressure (P) and stoichiometry [e.g., 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20]. For example, the autoignition delay time of methane-based fuels decreases substantially with increasing pressure and temperature, and with increasing fractions of hydrogen and higher hydrocarbons, such as ethane, propane and butane in the fuel. Furthermore, the autoignition promoting effect of these components can strongly depend upon the temperature. A detailed analysis of the origins of the occurrence of engine knock therefore requires knowledge of the time-dependent state (P , T) of the unburned end gas as well as any changes in this state caused by varying composition. The pressure and temperature of the end gas vary with time during the engine cycle due to the combination of mechanical compression from piston motion and compression from the progressive combustion of the charge, related to the so-called combustion phasing. Changes in the gas composition can lead to substantial variations in the thermodynamic properties of the fuel mixture [3] and in the phasing of the combustion process [21, 22, 23], which result in changes in the temperature and pressure of the end gas. For example, in [22] it has been shown that the addition of hydrogen to natural gas increases the burning velocity (combustion phasing) and reduces the heat capacity. Together, these two effects result in a substantial increase in the temperature and pressure of the end gas and is the major cause of the reduced knock resistance with increasing fractions hydrogen in natural gas. Thus, to quantify the progress of autoignition under engine conditions for different gas compositions, this composition dependence of the variation in the temperature and pressure of the end gas must also be quantified.

In this paper, we present a method to characterize the knock resistance gaseous fuels based on the combustion properties of the fuel mixtures themselves. In this method, engine knock is predicted by modeling autoignition of the compressed end gas during the engine cycle, including the changes in in-cylinder pressure and temperature experienced by the end gas upon changing gas composition [21], as described above. The model is demonstrated for a constant-speed, medium-BMEP engine for a wide range of fuel compositions typical for natural gases, containing varying fractions of methane, ethane, propane and butane. In addition, the success of the method to account correctly for the effects of CO_2 , N_2 and H_2 in natural gas is demonstrated.

EXPERIMENTAL WORK

Gas Engine

A lean-burn, high-speed, turbo-charged, intercooled 6-cylinder gas engine (MAN) for combined-heat-and-power applications (CHP) was used for the engine measurements. Table 1 lists the key specifications of the engine. We remark here that this CHP system maintains constant fuel/air ratio, engine speed and power output. The engine management systems and additional instrumentation provided precise adjustment, monitoring and registration of all relevant engine settings and process conditions. The in-cylinder pressures in all cylinders were measured with Kistler type 6052 piezoelectric pressure sensors and a Kistler type 5011 charge amplifiers connected to a Smetec Combi-Pro indication system. A crankshaft-mounted pulse generator provided 0.1 °CA resolution for the cylinder pressure data

acquisition. The Smetec Combi-Pro system was also used for knock detection through monitoring of the maximum amplitude of pressure oscillations in the high-pass-filtered cylinder pressure data in a window of consecutive cycles. Threshold settings used were 2 bar for the amplitude and 30 cycles for the window. For knock-limited spark timing (KLST) experiments ([3], see below), the knock limit was chosen to be one knock event or cluster of knock events within a 15 minute steady-state test run.

Table 1. Key specifications gas engine

Engine make & type	MAN E2876LE302
Engine configuration	- 6 cylinder in-line - turbocharged - intercooled
Combustion system & combustion stoichiometry	- mono-gas - open chamber - lean-burn
Rated power & speed (corresponding BMEP)	208 kW at 1500 rpm (13.0 bar)
Bore x Stroke	128 x 166 mm
Compression ratio	11.0:1
Engine speed	1500 rpm
Excess air ratio (λ)	1.5
Intake manifold pressure	2.2 bara
Intake manifold temperature	340 K

During the experiments, fuel for the test engine was delivered by a gas mixing unit. The fuel compositions used in the experiments are given in Appendices A and B. All mixture compositions were verified by gas chromatography. Once the composition of the fuel/air mixtures at $\lambda=1.5$ and the other relevant cylinder parameters are set, the pressure traces of the gases under non-knocking condition, needed to test the two-zone thermodynamic model discussed below, are measured at a constant spark timing of 14° CA Before Top Dead Center (BTDC). Subsequently, the spark timing was gradually advanced up to the point of the onset of borderline knock to determine the Knock Limited Spark Timing (KLST).

Rapid Compression Machine

To assess the chemical mechanisms that form the heart of the autoignition part of the model, autoignition measurements in a Rapid Compression Machine (RCM) are reported for species that specifically warranted closer examination (see below). The composition of the fuel-air mixtures for $\lambda=2$ are given in Table 2. The measurements have been performed at temperatures and pressures relevant to the unburned end gas conditions in the engine; pressures (P_c) and temperatures (T_c) after compression ranging from 30-80 bar and 940-1010 K, respectively. As will be seen below, particularly important are the measurements above ~40 bar. All measurements have been compared with numerical simulations in which the effects of heat loss and varying specific volume that occur during the RCM experiments are taken into account. The simulations are performed by using the mechanism developed in [12, 13, 14, 15]. The experimental and simulation procedures are described in detail in [10, 11].

Table 2. Fuel/air mixture compositions in RCM measurements, expressed in mole fraction for $\lambda=2$.

	CH ₄	C ₂ H ₆	C ₃ H ₈	n-C ₄ H ₁₀	i-C ₄ H ₁₀	O ₂	N ₂	Ar
A	0.0476	0	0	0	0	0.1905	0.3	0.4619
B	0.0333	0.0083	0	0	0	0.1917	0.3	0.4667
C	0.0375	0	0.0042	0	0	0.1917	0.3	0.4666
D	0.0397	0	0	0.0025	0	0.1916	0.3	0.4662
E	0.0397	0	0	0	0.0025	0.1916	0.3	0.4662

Description Two-Zone Thermodynamic Combustion Model

As discussed above, variations in gas composition can cause substantial changes in the in-cylinder conditions (P , T) affecting autoignition in the end gas [3, 22, 23]. To predict the effects of the gas composition on the in-cylinder conditions, we apply a two-zone thermodynamic model [21]. In this one dimensional model, the combustion chamber is divided into a zone consisting of unburned fuel-air mixture and a zone with the burned gases, separated by an infinitely sharp flame front. In the model we assume that during the entire engine cycle no heat exchange occurs between the two zones and that the pressure is uniform throughout the cylinder. All gases are considered as ideal gases and the composition of the individual zones is homogeneous. The enthalpy changes of the gases flowing in and flowing out of the cylinder are neglected in the model. The input data needed for the model are the engine geometry, in-cylinder conditions (P , T) at valve closure, operating conditions such as spark timing, air factor, humidity and the fuel composition. The model takes into account that the power output and the fuel/air ratio of the engine are kept constant by a control system that changes the fuel and fuel/air input accordingly.

The time-dependent state of the two zones in the combustion chamber is described using the conservation equations for mass and energy, and the ideal gas equation of state. The mixture is simulated as a single zone until the start of combustion (the spark timing); immediately after spark ignition the burned zone is created and the mixture consists of two zones; a burned zone and an unburned zone (the end gas). After the mixture is completely burned the mixture is simulated again as a single zone. The actual total volume V_T of the cylinder, which is calculated from the geometrical properties of the engine [1], is conserved at any time in the cycle:

$$\frac{dV_T}{dt} = \frac{dV_u}{dt} + \frac{dV_b}{dt}, \quad (1)$$

where the subscript u refers to the unburned mixture and b to the burned gases. By neglecting valve leakage and blowby, we may assume conservation of mass m during the combustion cycle:

$$\frac{dm_u}{dt} = -\frac{dm_b}{dt} \quad (2)$$

The conservation of energy for the unburned and burned zone are written as follows,

$$C_{p,u} m_u \frac{dT_u}{dt} + h_u \frac{dm_u}{dt} = -\frac{dQ_u}{dt} + V_u \frac{dP}{dt} + h_u \frac{dm}{dt} \quad (3)$$

$$C_{p,b} m_b \frac{dT_b}{dt} + h_b \frac{dm_b}{dt} = V_b \frac{dP}{dt} - \frac{dQ_b}{dt} - h_u \frac{dm_u}{dt} \quad (4)$$

where C_p is the heat capacity, h the specific enthalpy, P the pressure and Q the heat transferred to the surrounding surfaces (walls, and piston- and cylinder head). The heat loss Q in both zones is given by

$$\frac{dQ}{dt} = h_c A (T - T_w), \quad (5)$$

where the heat transfer coefficient h_c for both zones is determined by using the Woschni correlation formula [24, 25]. For ideal gases, assuming the pressure is uniform inside the cylinder we can write,

$$P = \frac{m_u R_u T_u}{V_u} = \frac{m_b R_b T_b}{V_b}. \quad (6)$$

The heat capacity and the specific enthalpy of the burned gas and the unburned end gas are calculated as a function of temperature during the combustion cycle using the method proposed in [26] with the thermodynamic data from [12, 13, 14, 15]. The mixture composition of the burned gases, needed as input for the thermodynamic calculations are obtained by using the PREMIX code [27] from the CHEMKIN II suite [26], using the USC Mech Version II reaction mechanism [28]. The composition of the burned gases is calculated numerically at the moment of ignition and is assumed to be constant from the start of the combustion until the exhaust valve opening.

Burning-Rate Model

To solve the governing equations given above we need to find an expression for the mass burning rate (dm_b/dt) that takes into account the operating conditions (e.g. changes in composition) and the engine parameters (e.g. turbulence intensity). The exact prediction of this burning rate is challenging, since the flame propagation is influenced by turbulence in the combustion chamber. To avoid complex CFD calculations, a one-dimensional model is chosen as proposed by Chmela [29] and applied by others [30, 31] in which the rate at which the burned mass is formed is related to the laminar burning velocity (S_L) and a fit parameter C_{model} that accounts for the impact of turbulence;

$$\frac{dm_b}{dt} = C_{\text{model}}(1 - x_B)\rho_u S_L t^2, \quad (7)$$

The laminar burning velocity S_L is calculated using the following power-law correlation [1].

$$S_L = S_{L0} \left(\frac{T}{T_0} \right)^\alpha \left(\frac{P}{P_0} \right)^\beta \quad (8)$$

Where S_{L0} is the laminar burning velocity of the fuel/air mixture at the time of spark ignition, also calculated using the PREMIX code as described above for the burned gas composition. The parameters α and β , which take into account the temperature and pressure dependence of laminar burning velocity, are dependent on the fuel composition. These parameters are taken from a database generated for this purpose from numerical laminar burning velocities for a wide range of gas compositions and at operating conditions (pressure, temperature and fuel to air ratio, $\lambda=1.5$) relevant for the gas engine used here. Using this method, only one laminar burning velocity has to be computed in detail for each phasing simulation (at the spark timing), which considerably shortens the computation time needed for the model.

It is known that differential molecular transport effects, as described by the Lewis number (ratio of thermal diffusion and mass diffusion) that is related to stretch effects in laminar flames, affect the combustion behavior of turbulent premixed flames [32, 33] at (mainly) fuel-lean conditions. In [33], it is shown experimentally that there is a strong correlation between the ratio of the turbulent- and laminar burning velocity (S_T/S_L) and the Lewis number for hydrocarbon gas compositions studied. This result emphasizes the importance of accounting for the effects of differential molecular transport of the fuel composition when scaling the laminar and turbulent flame speed. Following the suggestion of [32], we included the Lewis number in Eq. (7), yielding:

$$\frac{dm_b}{dt} = \frac{C_{\text{model}}}{Le_{\text{eff}}} (1 - x_B)\rho_u S_L t^2, \quad (9)$$

where Le_{eff} is the effective Lewis number, which corresponds to a weighted average of the Lewis numbers of the fuels present in the mixture. The effective Lewis number is calculated following the procedure described in [34, 35].

The set of differential equations (1), (2), (3), (4), (5) and (9) is solved using a fourth-order Runge-Kutta method. The changes in thermophysical properties with changing fuel composition, essential for the correct prediction of changes in the temperature history, are included in the solution of the conservation equations.

RESULTS AND DISCUSSION

Two-Zone Combustion Model

The fit parameter (C_{model}) introduced in the phasing model (Equation 9) to account for the impact of turbulence in the cylinder on the burning rate is determined via a fitting routine by using the pressure trace of the measured methane/air mixture in the engine. As was shown previously [21], a single value of C_{model} , independent of the gas composition, is sufficient to predict the pressure profiles accurately. Based on the fit parameter, engine data and gas composition, the pressure traces of the other gas mixtures (Appendices A and B) have been predicted using the two-zone combustion model. An example of the comparison between the predicted and measured cylinder pressure profiles is presented in Figure 1.

Figure 1. Comparison of measured and simulated non-knocking pressure trace.

Furthermore, Figure 2 shows the comparison of the simulation results with the measurements for a number of fuel mixtures, expanding the scale to emphasize the comparison of the peak pressure; at pressures below 40 bar the measured and simulated pressure traces are identical as shown in Figure 1. For all of the fuel mixtures studied, the maximum deviation in peak pressure is 2 bar corresponding to a deviation in peak temperature of 3 K. As illustrated in Figures 1 and 2, a small systematic shift in the peak pressure is observed in the traces along the crank angle axis in all simulations. Autoignition computations, discussed in detail below, using the experimental pressure traces show negligible differences from those using the predicted pressure trace for the gases studied, demonstrating that the predictive power of the phasing model is adequate for predicting knock.

Here we remark that computations of the pressure profiles without taking the Lewis number into account (taking $Le_{\text{eff}} = 1$), resulted in a substantial and systematic underprediction with hydrogen containing gases, up to 5 bar, while the presence of higher hydrocarbons resulted in a systematic overprediction up to 2.5 bar. The introduction of the Lewis number in equation (9) brings the predicted and measured pressure traces into the agreement shown in Figure 2. The Lewis number decreases with increasing fractions of higher hydrocarbons in the mixture, which depresses the mass burning rate and, as a consequence lowers the peak pressure, while a decrease in the Lewis

number as a result of hydrogen addition increases the mass burning rate and the resulting peak pressure. These results indicate the importance of taking into account the Lewis number when computing the mass burning rate.

Figure 2. Comparison of measured and simulated non-knocking pressure traces.

Engine Knock Model

Since knock in spark-ignited engines is an autoignition phenomenon, we simulate engine knock by modeling autoignition of the compressed end gas during the cycle by using the SENKIN code [38] in the CHEMKIN II library [26]. The autoignition process is modelled in detail using the NUI 2010 chemical mechanism developed in [10, 11, 12, 13]. The changes in pressure and temperature of the end gas during the engine cycle are captured by deriving the specific volume of the assumed adiabatic core [21, 22, 36, 39] from the pressure history computed by the two-zone thermodynamic phasing model described above. Together with the composition of the fresh cylinder charge, the input manifold temperature and pressure, the specific volume is used as input into the autoignition model. The simulated pressure histories for methane are shown in Figure 3. Clearly, when simulating non-knocking engine conditions, the results should not (and do not) predict autoignition of the end gas, as seen in Figure 3. To induce autoignition numerically, we increase the initial temperature of the end gas in the simulation [36]. Here, increasing the initial temperature by 46 K results in spontaneous ignition of the end gas at roughly 90% burn [4, 22]; the sudden spike observed in the simulated pressure history shown in Figure 3 indicates knock in the (simulated) end gas. This temperature offset is chosen such that the model predicts autoignition of the end gas near the end of the burn period for any given fuel; we use this condition to indicate ‘light knock’.

The NUI 2010 mechanism [10, 11, 12, 13] was chosen because it includes the main components in natural gas (C_1 - C_4) and shows very good predictive power for methane/oxidizer mixtures (such as mixture A in Table 2, above), while most of the of the mechanisms studied, shown in Figure 4, below, show substantial disagreement with the measurements. We note that the mechanism of Gersen et al. [11] also shows excellent agreement over the measured pressure range. However, since this mechanism only contains hydrocarbons up to ethane, it was not selected for use here.

Figure 3. Simulated autoignition of a methane mixture constrained to the complete simulated pressure and temperature history, at both the actual intake temperature T_0 (non-knocking) and at $T_0 + 46$ K (knocking).

Figure 4. Comparison between RCM measurements and simulations using several chemical mechanisms [11, 12, 13, 14, 15, 28, 40 and 41] for $\lambda=2$, $T_c=970$ K, CH_4 /oxidizer, mixture A in Table 2.

Scale for Comparing Gases

Given that different fuel mixtures will have different phasing and autoignition delay times, we note that different fuels require different initial temperatures [36] to ignite at 90% burn, which we are using as the definition of simulated light knock. To quantify the net differences between fuels in producing light knock, it is convenient to use a common scale, similar to the idea behind octane and methane numbers. Here, to compare the knock resistance of different fuel gases, we use a propane-based scale. In this scale, which we refer to as the Propane Knock Index (PKI), the knock resistance for a given gaseous fuel mixture is expressed as an equivalent fraction of propane in methane under the identical engine conditions. In this procedure, which is illustrated in Figure 5, the occurrence of engine knock at the point at which 90% of the fuel is burned (again, simulating ‘light’ knock) is calculated for a given fuel composition, in this example 3.0% i-butane or n-butane in methane (Figure 5). To find the ‘propane equivalent’, propane is added to methane under the same engine conditions as used for the gas being examined, and engine knock is calculated by the engine knock model. The model automatically changes the propane fraction in methane iteratively up to the moment that knock occurs at the same position in the cycle as the fuel under comparison.

The results for this exercise are shown in Figure 5. The calculations indicate that 3.0% i-butane (Figure 5, top) is equivalent to 4.5% propane, while 3.0% n-butane is equivalent to 7.1% propane (Figure 5, bottom), yielding PKIs of 4.5 and 7.1 for these two fuel mixtures, respectively. The observed difference in knock resistance of the butanes is mainly caused by the differences in the burning velocity: n-butane burns faster than i-butane which results in a higher end gas temperature for the n-butane/methane mixtures. The increase in end gas temperature reduces the autoignition delay time and thus lowers the knock resistance. Here we note that the observed difference between the isomers of butane is also confirmed by our knock-limited spark timing (KLST) experiments in the engine used in this study (see below); differences in knock behavior between butane isomers has also been reported in the literature [6].

Figure 5. Knock simulations for 3.0% i-butane in methane (top) and 3.0% n-butane in methane (bottom); both are shown with their “propane equivalent”, computed using the integrated model. Spark timing for both fuels is at 14 °CA BTDC.

Comparison with Experiments

As illustrated above, the PKI is a measure for the simulated knock resistance of a given fuel; mixtures with the same calculated PKI have identical simulated knock resistance. To test the veracity of the predictions we calculated the PKIs for the gas mixtures from the Appendices A and B, for which KLST measurements were also performed, according to the procedure described above. The measured KLST are plotted in Figure 6 versus the calculated PKI; mixtures with the same KLST have identical experimental knock

resistance. Also shown in Figure 6 are the measured KLST for the methane/propane mixtures used as the basis of the method (blue squares), and the best fit (solid line). As seen in Figure 6, a large spread between measured and calculated knock resistance is obtained when using the NUI 2010 mechanism [12, 13, 14, 15] for autoignition calculations. This spread in the data is much larger than the reproducibility in the KLST measurements, ± 0.75 °CA, and increases with decreasing knock resistance (increasing PKI).

Figure 6. Measured KLST vs. computed equivalent fraction of propane in a methane/propane mixture (Propane Knock Index, PKI) using the NUI2010 mechanism [12, 13, 14, 15].

The good agreement between the calculated and measured pressure profiles under non-knocking conditions (such as shown in Figure 2) suggests that the observed scatter in Figure 6 may be caused by discrepancies in the autoignition part of the engine knock model. To examine this possibility, we tested the NUI2010 chemical mechanism [12, 13, 14, 15] against measured autoignition delay times in the RCM for binary hydrocarbon mixture (C_1 - C_4) as presented in Table 2 at the conditions relevant to lean-burn gas engines. Figures 7, 8, 9 show the measured and computed autoignition delay times for mixtures B-E, presented in Table 2. The computations performed with the original NUI2010 mechanism show good agreement with the measurements up to pressures of ~ 40 bar for the mixtures studied. However, for pressures above 40 bar the measured ignition delay times are substantially shorter than those predicted, up to about 50% for mixtures C-E in Table 2. The autoignition delay times for the methane/ethane mixture (Mixture B), presented in Figures 7 show only a small overprediction, up to about 15% at pressures above 40 bar. To improve the agreement with the RCM measurements, the chemical mechanism used in this study was altered. To do so, sensitivity analyses were performed by varying the pre-exponential factor in the reactions in the mechanism¹. For important reactions (see below), a least squares fit was performed for the methane/ethane, methane/propane, methane/i-butane and methane/n-butane mixtures. Additionally, we optimized the mechanism for hydrogen containing natural gases, as reported previously [22]. The changes of the rate coefficients for individual hydrocarbons do not affect the autoignition chemistry of the other hydrocarbons.

1. We remark that the alterations to the mechanisms performed here are intended to optimize the mechanism performance for the range of pressures, temperatures and stoichiometries relevant for lean-burn gas engines, rather as a matter of convenience, than as recommendations for comprehensive mechanism improvement (see text).

Figure 7. Left: Measured and calculated autoignition delay times for a $\text{CH}_4/\text{C}_2\text{H}_6$ mixture (20% C_2H_6) at $\lambda=2.0$ and $T_c=970$ K as a function of pressure. Right: Measured and calculated autoignition delay times for a $\text{CH}_4/\text{C}_3\text{H}_8$ mixture (10% C_3H_8) at $\lambda=2.0$ and $T_c=1010$ K as a function of pressure. The measurements are shown as symbols, calculations as lines.

Figure 8. Left: Measured and calculated autoignition delay times for a $\text{CH}_4/\text{n-C}_4\text{H}_{10}$ (6% $\text{n-C}_4\text{H}_{10}$) at $\lambda=2.0$ and $T_c=995$ K as a function of pressure. Right: Measured and calculated autoignition delay times for a $\text{CH}_4/\text{n-C}_4\text{H}_{10}$ (6% $\text{n-C}_4\text{H}_{10}$) at $\lambda=2.0$ as a function of pressure at different temperatures T_c . The measurements are shown as symbols, calculations as lines.

Figure 9. Left: Measured and calculated autoignition delay times for a $\text{CH}_4/\text{i-C}_4\text{H}_{10}$ (6% $\text{i-C}_4\text{H}_{10}$) at $\lambda=2.0$ and $T_c=995$ K, as a function of pressure. Right: Measured and calculated autoignition delay times for a $\text{CH}_4/\text{i-C}_4\text{H}_{10}$ (6% $\text{i-C}_4\text{H}_{10}$) at $\lambda=2.0$ as a function of pressure at different temperatures T_c . The measurements are shown as symbols, calculations as lines.

Although a detailed analysis of the autoignition chemistry is outside the scope of this work, an example of the sensitivity analyses for methane (mixture A) and methane/propane (mixture C) mixture is shown in Figure 10. The sensitivity analysis reveals that reactions R1 and R2, below, show the largest sensitivities and only affect the autoignition chemistry of propane (blue bars in Figure 10). By increasing the pre-exponential factor for reaction R1 and R2 we obtained agreement better than 15% over the entire pressure range (Figure 7, right),

Figures 8 and 9 show that for methane/n-butane and methane/i-butane after optimization very good agreement between computations and measurements is obtained at pressures above 50 bar. Although at pressures below 40 bar the differences between measurements and computations increased somewhat, we do not expect this deviation will affect the knock predictions, since pressures below 40 bar will not affect the chemical processes causing knock in modern gas engines. We note further that a challenge to mechanism construction will be to define a mechanism that provides a consistent degree of agreement over the entire range of pressures, temperatures and compositions.

Figure 10. Sensitivity coefficients of the autoignition delay time of Mixtures A and C (Table 2) at a pressure of 80 bar and a temperature of 1010 K.

Figure 11. Measured KLST vs. computed equivalent fraction of propane in a methane/propane mixture (Propane Knock Index, PKI).

Repeating the calculations of PKI performed in Figure 5, above, using the optimized mechanism yields the results shown in Figure 11. This figure shows that modifying the autoignition mechanism to improve the agreement with the RCM measurements brings the predicted PKI and the KLST measured in the engine to within the uncertainty of the measurements (± 0.75 °CA). The consistency between the PKI and KLST measurements is as good for hydrocarbon mixtures, representative for LNG compositions, as for hydrocarbon-inert mixtures, as occur in pipeline gas, and for hydrocarbon mixtures with hydrogen and H_2/CO mixtures, relevant for coal and biomass gasification.

The results illustrate that practical demands on predicting engine knock require more stringent agreement with measured autoignition data at conditions relevant to practical engines than is often assumed. We therefore strongly recommended developing chemical mechanisms that are more accurate at such conditions.

Comparison KLST Experiments with Existing Methods for Comparing the Knock Resistance of Gaseous Fuels

The methane number(s) use a methane-hydrogen scale, with 100 having the knock equivalent of pure methane, and 0 being nominally assigned to hydrogen. The propane/methane based scale (PKI) derived here has pure methane as 0 and with an increasing value with the equivalent propane content. For the purposes of putting the current method on a scale analogous to the currently used methods, the propane based scale (PKI) is converted to a normalized knock index on a 0-100 scale, referred to as the PKI methane number.

Figure 12 shows the same excellent correlation between the PKI methane number and the measured KLST as the PKI itself in Figure 11. The largest deviation observed between the measurements and calculations is ± 3.5 MN, while the average deviation is about ± 1.2 MN. Here, the uncertainty in the predictions is determined by the uncertainty in the measured KLST used as verification, $\pm 0.75^\circ\text{CA}$ as shown in the figure.

Figure 12. Measured KLST vs. calculated PKI methane number.

In Figures 13 and 14 we compare the KLST for the gases shown in Figure 11 with the methane number (MN) computed using the AVL method [2] (version 3.2) and the MWM method [37], respectively. In Figure 13 it can be seen that for the same KLST, which for the engine means the same knock resistance, a substantial difference in the methane number of about ± 7.5 points is observed. This is much larger than the measurement uncertainty in KLST, as can be seen in the figure, and is caused by the inaccuracy in the AVL method in predicting the effects of specific compositions on knock in this engine. In contrast to our methodology, the AVL method does not discriminate between isomers of butane and as a result AVL substantially overestimates the knock-enhancing effect of i-butane by treating it as n-butane. Figure 13 also shows that the effect of hydrogen is strongly underestimated for mixtures of Dutch natural

gas (DNG²) with hydrogen, having a significantly higher MN for the same KLST as other fuel mixtures. This is particularly noteworthy since the MN number uses an experimental methane/hydrogen scale.

For engine operators, the observed large spread (roughly $\pm 2^\circ\text{CA}$) means that AVL barely allows distinction between a KLST of, for example, 20°CA BTDC and 16°CA BTDC for this engine, while using the method derived in this study allows a distinction of $\pm 0.75^\circ\text{CA}$, at the current level of verification, for example between 20 and 18.5°CA BTDC. This means that, using the AVL estimate of knock resistance, the engine is either adjusted too conservatively (late spark timing), resulting in diminished engine performance, or is at risk of knock (early spark timing) for the fuel compositions used in this study.

Figure 13. Measured KLST vs. calculated AVL methane number.

Comparison between the measured KLST and the calculated methane number using the MWM method, presented in Figure 14, also shows a large spread; the maximum deviation at constant KLST is ± 7 points for the MWM methane number. Here too, the spread in methane number is much larger than that caused by the uncertainty in KLST. As was the case for the AVL method, this spread means that for most of the gases studied it is not possible to make a clear distinction between the calculated knock resistance at a measured KLST of roughly $\pm 2^\circ\text{CA}$ when using the MWM method, as compared with the uncertainty in the current method $\pm 0.75^\circ\text{CA}$ (Figure 11). As with AVL, the large spread is partially caused by not taking into account the difference between i-butane and n-butane.

This substantial improvement over the traditionally used methods allows OEMs to guarantee higher performance engines for a wider range of gaseous fuels, whether LNG/CNG or natural gas/hydrogen mixtures. At the same time, using an accurate method to characterize knock resistance allows fuel suppliers to maximize the range of fuel compositions offered, while guaranteeing knock-free engine performance. Furthermore, in the standardization arena, such as that developing for LNG as a transportation fuel, a “correct” standard as developed using the method described here ensures that gases are not excluded from the market, or overtreated to remove knock-enhancing components without cause.

2. The detailed composition of DNG is presented in [22] and roughly consists of 82 mole% CH_4 , 2.7 mole% C_2H_6 , 0.4 mole% propane, 0.9 mole% CO_2 and 14 mole% N_2

Figure 14. Calculated MWM methane number vs KLST.

For the engine studied here, the results show that the method presented above predicts the knock behavior of a wide range of fuel compositions within the uncertainty of the measurements of knock, while the methods currently in use do not predict the behavior reliably. We are currently extending the method to engines with different regimes of end gas pressure, temperature and stoichiometry, for which we expect potentially different quantitative, and even qualitative [22], effects of fuel composition on autoignition chemistry.

CONCLUSIONS

In this paper we described a method to characterize the effects of changes in fuel composition on engine knock. Using only a single, experimental non-knocking pressure trace, the method computes the effects of changes in autoignition chemistry, combustion phasing and thermophysical properties when varying the fuel, based only on the properties of the fuel-air mixture, using fuel-specific, detailed autoignition chemistry and burning velocity calculations. The comparison of the predicted pressure histories with those measured supports the veracity of the phasing model, while the autoignition computation is assessed independently using RCM data under pressures, temperatures and stoichiometries extant in the engine studied.

A propane-based scale (PKI) has been defined to rank the knock resistance of gaseous fuels, and, when compared to knock measurements in the engine, has demonstrated excellent predictive power for the fuels studied. The large improvement in the trends predicted for engine knock upon optimizing the autoignition mechanism to improve agreement with the RCM data, particularly at pressures above 40 bar, points to the necessity of developing autoignition models with high accuracy for the conditions in real gas engines.

In contrast to the method described here, comparison of the measured knock resistance with methane numbers calculated using the AVL and the MWM methods points to shortcomings in these yardsticks in predicting knock resistance for the gas engine used in this study.

Since the method described here is based on the physical and chemical processes that govern knock, it can be adapted in a straightforward manner to new engines and fuels; extension of the method to other engine types is currently in progress.

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APPENDIX**Appendix A: Composition in mole fractions of gaseous fuels studied**

No.	CH ₄	C ₂ H ₆	C ₃ H ₈	n-C ₄ H ₁₀	i-C ₄ H ₁₀	N ₂
1	1.000	0.000	0.000	0.000	0.000	0.000
2	0.966	0.034	0.000	0.000	0.000	0.000
3	0.933	0.067	0.000	0.000	0.000	0.000
4	0.886	0.114	0.000	0.000	0.000	0.000
5	0.872	0.128	0.000	0.000	0.000	0.000
6	0.824	0.176	0.000	0.000	0.000	0.000
7	0.911	0.066	0.023	0.000	0.000	0.000
8	0.811	0.137	0.051	0.000	0.000	0.000
9	0.991	0.000	0.009	0.000	0.000	0.000
10	0.988	0.000	0.0012	0.000	0.000	0.000
11	0.982	0.000	0.0018	0.000	0.000	0.000
12	0.970	0.000	0.0300	0.000	0.000	0.000
13	0.961	0.000	0.039	0.000	0.000	0.000
14	0.944	0.000	0.056	0.000	0.000	0.000
15	0.943	0.000	0.057	0.000	0.000	0.000
16	0.926	0.000	0.074	0.000	0.000	0.000
17	0.925	0.000	0.075	0.000	0.000	0.000
18	0.900	0.000	0.100	0.000	0.000	0.000
19	0.961	0.000	0.039	0.000	0.000	0.000
20	0.901	0.000	0.037	0.000	0.000	0.062
21	0.85	0.000	0.034	0.000	0.000	0.116
22	0.775	0.000	0.032	0.000	0.000	0.193
23	0.993	0.000	0.000	0.000	0.007	0.000
24	0.985	0.000	0.000	0.000	0.015	0.000
25	0.977	0.000	0.000	0.000	0.023	0.000
26	0.966	0.000	0.000	0.000	0.034	0.000
27	0.941	0.000	0.000	0.000	0.059	0.000
28	0.931	0.000	0.000	0.000	0.069	0.000
29	0.988	0.000	0.000	0.012	0.000	0.000
30	0.979	0.000	0.000	0.021	0.000	0.000
31	0.966	0.000	0.000	0.034	0.000	0.000
32	0.949	0.000	0.000	0.051	0.000	0.000

Appendix B: Composition in mole fractions of mixtures with Dutch Natural Gas (DNG)

No.	DNG	CH ₄	C ₂ H ₆	C ₃ H ₈	H ₂
33	1.000	0.000	0.000	0.000	0.000
34	0.973	0.000	0.000	0.027	0.000
35	0.955	0.000	0.000	0.045	0.000
36	0.909	0.000	0.000	0.091	0.000
37	0.973	0.000	0.027	0.000	0.000
38	0.919	0.000	0.081	0.000	0.000
39	0.821	0.000	0.179	0.000	0.000
40	0.883	0.000	0.047	0.071	0.000
41	0.799	0.000	0.102	0.099	0.000
42	0.970	0.000	0.000	0.000	0.030
43	0.940	0.000	0.000	0.000	0.060
44	0.890	0.000	0.000	0.000	0.110
45	0.850	0.000	0.000	0.000	0.150
46	0.800	0.000	0.000	0.000	0.200
47	0.938	0.03	0.008	0.000	0.024
48	0.872	0.034	0.019	0.000	0.075
49	0.812	0.032	0.020	0.000	0.136
50	0.938	0.030	0.008	0.000	0.024

Appendix C: Notation

α - Parameter describing temperature dependence of laminar burning velocity

β - Parameter describing pressure dependence of laminar burning velocity

λ - Excess air ratio (actual air/fuel ratio divided by the stoichiometric air/fuel ratio)

ρ_u - Unburned gas density

A - Exposed combustion chamber surface area

AVL - Anstalt für Verbrennungskraftmaschinen List

BMEP - Brake mean effective pressure

BTDC - Before top dead centre

C₁-C₄ - Hydrocarbons from methane to butane including isomers

CHP - Combined heat and power

C_{model} - Fit parameter

CNG - Compressed natural gas

C_{p,b} - Heat capacity of burned gasses at constant pressure

C_{p,u} - Heat capacity of unburned gasses at constant pressure

dm_b/d_t - Mass burning rate

DNG - Dutch Natural Gas

h_b - Specific enthalpy burned gas
 h_c - Heat transfer coefficient
 h_u - Specific enthalpy unburned gas
KLST - Knock-limited spark timing
 Le_{eff} - Effective Lewis number
LNG - Liquefied natural gas
 m_b - Burned mass
MN - Methane number
 m_u - Unburned mass
MWM - Motoren Werke Mannheim
NUI2010 - Chemical mechanism from NUI Galway
OEM - Original equipment manufacturer
P - Pressure
 P_0 - Pressure at ignition conditions
PKI - Propane Knock Index
Q - Heat transferred to the surrounding surfaces (walls, and piston- and cylinder head)
 R_b - Burned gas constant
RCM - Rapid compression machine
 R_u - Unburned gas constant
 S_L - Laminar burning velocity
 S_{L0} - Laminar burning velocity of the fuel/air mixture at ignition conditions
 S_T - Turbulent burning velocity
t - Time
T - Temperature
 T_0 - Temperature at ignition conditions
 T_u - Unburned gas temperature
 T_b - Burned gas temperature
 V_b - Burned gas volume
 V_u - Unburned gas volume
 x_b - Burned gas mass fraction