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Perspectives in the Study of Renewable Gaseous Fuels Autoignition at Low and Moderate Temperatures

Perspectivas en el estudio de la autoignición de combustibles renovables gaseosos en temperaturas moderadas y bajas: una revisión

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ABSTRACT

The increased energy demand and restrictions regarding pollutant emissions have sparked the search for different renewable energy sources, as well as for the improvement of thermal processes, with a focus on reducing the consumption of fossil fuels. Renewable gaseous fuels seem to be a promising alternative for solving this issue, along with the different high-efficiency, low-emissions technologies that operate at low and moderate temperatures (600-1000 K). However, the implementation of these approaches is limited by the autoignition phenomenon and the different difficulties in predicting its occurrence in the aforementioned operation range. To identify the reasons for this fact, we carried out a review of the different research works conducted in the field. It was evidenced that most studies focus on performing adjustment processes that require prior experimentation. This allowed identifying the need to conduct a research work focused on the autoignition phenomenon in the low and moderate temperature range while using renewable gaseous fuels, as well as on improving the predictive models for calculating ignition delay times.

Keywords: autoignition, gaseous renewable fuels, detailed reaction mechanism, ignition delay time

RESUMEN

El aumento en la demanda energética y las restricciones respecto a la emisión de contaminantes han suscitado la búsqueda de diferentes fuentes de energía renovables, así como del mejoramiento de los procesos térmicos enfocados en reducir el consumo de combustibles fósiles. Los combustibles renovables gaseosos se muestran como una alternativa útil para resolver este problema, al igual que diferentes tecnologías de alta eficiencia y bajas emisiones que operan a temperaturas bajas y medias (600-1000 K). Sin embargo, la implementación de estos enfoques se ve limitada por el fenómeno de autoignición y las diferentes dificultades para predecir su aparición en el mencionado rango de operación. Para identificar las razones de este último hecho, se llevó a cabo una revisión de los diferentes trabajos de investigación realizados en el área. Se evidenció que la mayoría de los estudios se centran en realizar procesos de ajuste que requieren una experimentación previa. Lo anterior permitió identificar la necesidad de llevar a cabo una investigación enfocada en el fenómeno de autoignición en el rango de bajas y medias temperaturas usando combustibles renovables gaseosos y en el mejoramiento de los modelos predictivos para el cálculo del tiempo de retraso de la ignición.

Palabras clave: autoignición, combustibles renovables gaseosos, mecanismo detallado de reacción, tiempo de retraso de la ignición

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Introduction

The different climate challenges and increased pollutant emissions have caused the use of renewable energies in the global energy market to become more relevant. Prior to the COVID-19 pandemic, an increase in the utilization of this kind of energy was observed over a period of five years, reaching 12.4 and 29% of the global energy demand in 2023 and 2040, respectively (Chen *et al*., 2020; US Energy Information Administration, 2016).

During the first phase of the pandemic, a significant decrease in greenhouse gas emissions was recorded. CO_2 levels decreased by 17% in April 2020 compared to the same month in 2019 (Kuzemko *et al*., 2020), and a general 12.2% reduction in CO_2 emissions of was recorded in 2020 (Q. Wang and Wang, 2020). These reductions are related to the decrease in energy consumption by the industry and business sectors due to the restrictions imposed by the sanitary authorities. In contrast, an increase in domestic energy consumption was recorded (B. Wang *et al*., 2020). However, after the end of the lockdown, and due to the economic reactivation, a significant increase in energy consumption and pollutant

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Nomenclature

β	Weight factor in the Sankaran expression	NTC	Negative temperature coefficient
ϕ'	Equivalence ratio fluctuations	RCM	Rapid compression machine
τ	Ignition delay time	R_{ef}	Reynolds flame number
τ_f	Characteristic flame time	RGF	Renewable gaseous fuels
T'	Temperature fluctuations	S	Factor considering the correlation of T and ϕ
D_{al}	Damköhler number	S_{ap}	Sankaran number
DRM	Detailed reaction mechanisms	SG	Syngas
ICE	Internal combustion engines	ST	Shock tube
MN	Methane number		

emissions was to be expected. This represented a challenge, especially for developing countries (Q. Wang and Wang, 2020). Other factors contributed to this issue, as is the case of the increase in private transport, since many people chose this alternative during the pandemic to avoid agglomeration in public transport (Cheshmehzangi, 2020). Considering that industry and transport are the highest energy consumers in many Latin American countries, whose requirements are provided for by oil-derived fuels sources, *e.g.*, natural gas for electricity production, these sectors are potential targets for the implementation of renewable energies and the reduction of greenhouse gas emissions (Burdack *et al*., 2023; Grangeia *et al*., 2023; Simsek *et al*., 2019; Wolde-Rufael and Mulat-Weldemeskel, 2022).

Renewable gaseous fuels (RGFs) are promising alternatives for achieving the aforementioned objective, especially those containing hydrogen (H_2). This component has many benefits during the combustion process in terms of emissions and efficiency, given its high reactivity and burning velocity (Elsemary *et al*., 2016). However, the addition of RGF in thermal devices cannot be arbitrary, as it may entail undesired phenomena due to changes in combustion properties. Mixture reactivity increases when RGF is added, especially in the presence of H_2, and early autoignition may occur before reaching the combustion chamber, implying significant damage to the system. In internal combustion engines (ICEs), the addition of great large amounts of RGF can produce knocking phenomena. If the compression ratio is increased to achieve higher efficiency, this issue could take place (Arunachalam and Olsen, 2012; Szwaja *et al*., 2013; Z. Wang *et al*., 2017).

In recent years, the relevance of RGFs as an energy source has grown, with an annual rate of 10.8% until 2016, but technical issues have limited their contributions to the energy supply (International Energy Agency, 2016, 2018). In this sense, understanding the phenomenon of RGF autoignition becomes relevant with regard to broadening their use in thermal devices. The most common parameter used to study autoignition in fuels is the *ignition delay time* (τ), defined as the time required by a reactive mixture under specific thermodynamic conditions to begin the reaction by itself without any external energy source. Since the 90s, interest in measuring τ for RGFs has increased, and several studies have been conducted. The experimental values of τ have been used to develop detailed reaction mechanisms (DRM) in order to predict and analyze autoignition. τ prediction is a crucial aspect in improving the design of thermal devices, as it allows controlling this phenomenon during operation and preventing its occurrence in zones that can produce damage.

For several years, most of the τ data used to adjust and validate DRMs corresponded to high temperature conditions (>1000 K), since many combustion devices operated in this range. However, due to environmental regulations, international agreements, improvements to industrial processes, and the development of new technologies and techniques operating at moderate (800-1000 K) and low (600-900 K) temperatures, *e.g.*, lean and diluted mixtures, recirculation gases, flameless combustion, HCCI engines, among others, this trend has changed in recent years. Thus, there was an increase in the number of studies on autoignition and experimental measurements of τ in these ranges. Nevertheless, τ prediction under these conditions via the zero-dimensional approach still exhibits significant disagreements, mainly when testing RGFs. The main issue is that the zero-dimensional model, which uses the DRM, overpredicts the value of τ by more than one order of magnitude, which can clearly generate oversizing or failures in a combustion device. In order to solve this issue, different adjustment approaches have been developed, which are presented in the following sections, although many of them have several limitations, since they focus on corrective actions and do not address the phenomenon in order to fix prediction issues. Most of these approaches require prior experimental measurements, which limits their application in the field of RGFs, whose chemical composition is highly variable. This hinders progress in the use of this kind of fuel.

Although some reviews on autoignition can be found in the literature, most of them focus on the behavior of engines (Chintala and Subramanian, 2017; Dimitriou and Javaid, 2020; Rönn *et al*., 2023). Some of them also encompass advances in kinetics and experimental setups to perform measurements (Goldsborough *et al*., 2017; Sung and Curran, 2014; Zádor *et al*., 2011). However, the literature review

carried out in this study could not find a work focused on the issues of autoignition prediction at low temperatures while using RGF, on the connection with the autoignition regime, or on modeling perspectives. In this vein, it is necessary to adequately understand the autoignition phenomenon under moderate and low temperature conditions, as well as its effect on RGFs compared to conventional fuels. The first step to achieving this objective is to understand the actual state of the studies related to this phenomenon and their considerations for further research. The main objectives of this work are to determine the current landscape of autoignition studies in relation to RGFs and to identify the remaining gaps. Furthermore, this review can be used as a starting point to propose and conduct additional studies focused on improving models and DRMs related to RGFs. The *General features* section presents some fundamental concepts related to τ and a brief description of the experimental setups used to measure it. In *Disagreement at low temperatures*, we outline the existing disagreement between experimental and numerical results for τ at moderate and low temperatures. Different approaches for τ prediction are discussed in the *Methodologies to improve τ prediction*. Finally, the section titled *Inhomogeneity effects* addresses the relationship with the ignition regime.

Methodology

The scope of this work encompasses the autoignition phenomenon. Therefore, our literature review focused on scientific articles in specialized combustion journals from major publishers such as ScienceDirect, Taylor and Francis, and ACS, among others. All selected works belong to journals indexed in the Web of Science database. Experimental and numerical τ results, along with the disagreement reported between them when using RGFs, were the main topics of the selected studies. The reported results were classified into three global aspects, as presented in the next sections. A critical analysis was performed to identify the current gaps in autoignition modeling at low and moderate temperatures while using RGFs. Additionally, the effect of H_2 on the disagreement between zero-dimensional model predictions was analyzed, as well as the relationship between the autoignition regime and abnormal combustion in ICEs. All calculations were carried out in the Cantera software, modeling a closed, constant-volume, adiabatic, and completely mixed reactor while only considering time as an independent variable. Surface reactions were not considered. Five DRMs were used in the calculations in order to test the effects of different kinetic models on τ prediction capabilities at low and moderate temperatures.

General features

Autoignition

Under specific pressure and temperature conditions, *autoignition* can be described as the phenomenon resulting from the start of the reaction process in a fuel-oxidant mixture without the assistance of an external energy source. Thereupon, the autoignition process is not immediate and is considered a transient phenomenon. The best way to describe this phenomenon is to take time into account. As previously mentioned, ignition delay is the most frequently used parameter with regard to the autoignition process. *Ignition delay time* is defined as the time needed by the reactive mixture to start and maintain the reaction process under fixed thermodynamic conditions. Temperature increments are regarded as minimal during this time. Only when the radical concentration in the mixture reaches a certain level does ignition take place; these radicals release the necessary energy through fuel consumption, leading to the combustion of the mixture (Warnatz *et al.*, 1996).

Furthermore, several research groups have developed different numerical and experimental approaches to determine the value of τ. Generally, the most common method consists of determining the highest concentration point of the intermediate species OH, or determining the interval until the inflection point is reached in the pressure profile (Man *et al.*, 2013; Tang *et al.*, 2013; B. L. Wang *et al.*, 2003). Since τ is a function of the elementary reactions associated with the type of fuel, and the reaction rates are highly dependent on temperature, it is accurate to deduce that τ is intrinsically temperature-dependent. The relationship between these parameters can be described using the Arrhenius form as follows:

$$\tau = A exp\left(\frac{B}{T}\right) \quad (1)$$

where A is a factor related to the reactive concentration and the preexponential coefficient, and B is linked to the activation energy, assuming a one-step global reaction. Nevertheless, this document demonstrates that this approach is more accurate under high temperature conditions.

Experimental measurement of τ

Calculating τ is crucial for developing models that address complex combustion processes in different thermal devices, as well as for building DRMs that contribute to the aforementioned objective. Therefore, various thermal reactors have been used to control pressure and temperature conditions, thereby facilitating the calculation of this parameter. However, not all reactors are suitable for measuring τ across varying pressure ranges and temperatures. Figure 1 shows the operating range of devices used to determine τ experimentally. According to the literature, shock tubes (STs) and the rapid compression machines (RCMs) are the two most popular thermal reactors, as a large portion of thermal equipment operates under similar conditions.

An ST consists of a long-closed tube, divided into the *driver section* (high pressure) and the *driven section* (low pressure). These sections are separated by a diaphragm. The experiment fills the driven section with the test

mixture while an inert gas is introduced into the second section to increase the pressure until the diaphragm ruptures. A shock wave travels rapidly to the driven section, where the pressure and temperature of the test mixture increase. Subsequently, the wave is reflected at the end of this section, generating additional compression and allowing the necessary reactions for ignition to begin. The value of τ is determined by measuring the time elapsed from the initial heating until the rapid release of energy or the formation of radicals. Therefore, in many cases, chemiluminescence measurements via some radical such as OH and induced excitation (S. Wang *et al.*, 2019) are employed.

RCMs can have different versions, but, in general, all have a test or driven section inside a cylinder where the test mixture is located, which is rapidly compressed by the movement of a piston toward the test section. The test section consists of a small chamber, like a combustion chamber in an engine. A sensor is used throughout the procedure to continuously record the pressure-time profile. In general, this refers to the time between the end of compression and the location where the temporal pressure reaches its maximum variation (Liu *et al.*, 2018).

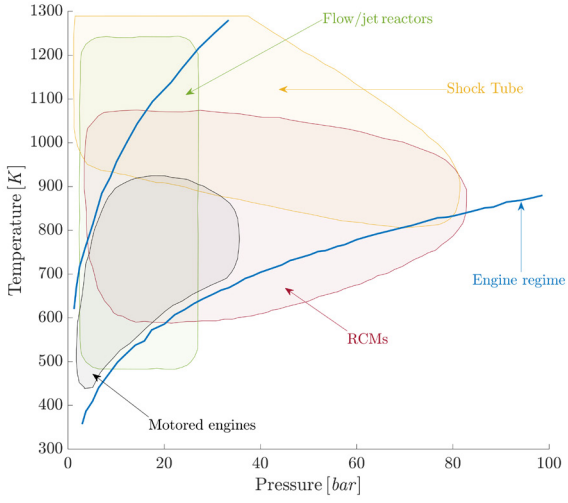

Figure 1. Operating ranges of the devices used for τ measurements
Source: Adapted from Goldsborough *et al.* (2017)

Disagreement at low temperatures

Several studies have focused on autoignition measurement and modeling by means of τ calculation. The most common model to determine τ is the adiabatic, homogeneous, close, constant-volume reactor, where the reactive mixture is considered to be an ideal gas. In general, for gaseous fuels, and especially for RGFs, the calculated values of τ at high pressures and low temperatures (600-950 K) shows significant disagreement with experimental values. Figure 2 presents a comparison between the experimental and numerical ignition delay values of $CH_4/C_2H_6/C_3H_8/H_2$, as obtained by Kuppa *et al.* (2018) using two different detailed reaction mechanisms. A better agreement can be seen in the low ignition delay values in comparison with the high ones (>200 μs). The former data group is associated with high temperatures, where the DRM and autoignition models have been more extensively studied, leading to improved performance and precision. On the other hand, for the high ignition delay values related to low and moderate temperatures, the scatter increases and becomes more extensive as ignition delay increases.

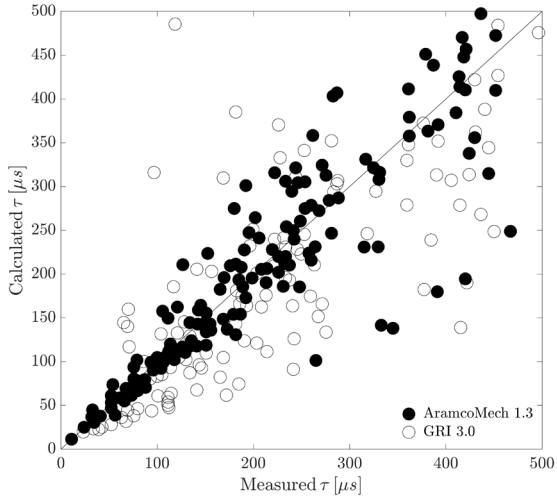

Figure 2. Ignition delay comparison for $CH_4/C_2H_6/C_3H_8/H_2$ mixtures
Source: Adapted from Kuppa *et al.* (2018)

Figure 3 shows the experimental data collected by Zhang *et al.* (2012) for CH_4 ignition delay times, along with the predictions obtained using different DRMs. The thermodynamic conditions correspond to high temperature and pressure. The excellent agreement between experimental and numerical data is evident, regardless of which DRM was used. This behavior suggests an adequate chemical kinetic description by both the DRM-evaluated and the model approximations. However, the trend changes as the temperature decreases. Figure 4 compares the predicted and experimentally measured ignition delay times for a natural gas mixture composed of 78.8% CH_4, 14% C_2H_6, 3.4% C_3H_8, and higher hydrocarbons (% in vol.) (Vallabhuni *et al.*, 2018). It is evident that a good agreement between experimental and numerical results can only be achieved for temperatures higher than 1000 K. The opposite behavior is observed at lower temperatures.

The model cannot capture the observed behavior at these temperatures. In this case, the predicted values are lower than the experimental ones. This can be considered safe from a practical standpoint, as autoignition will occur later experimentally than is expected numerically., but it is evident that the model cannot capture the actual process. According Vallabhuni *et al.* (2018), the deviations are due to the high concentration of hydrocarbons heavier than C_2. However, a detailed explanation is missing in the manuscript.

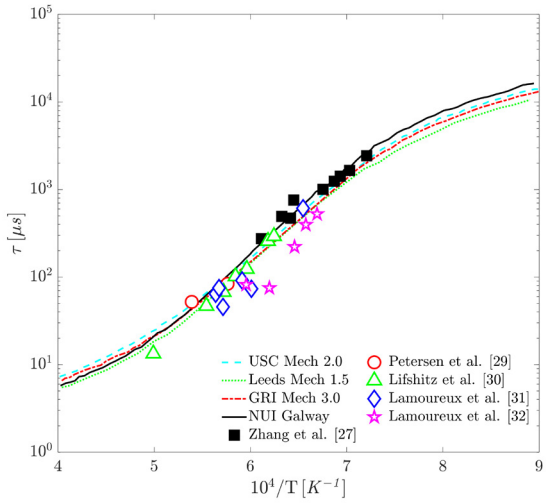

Figure 3. Ignition delay time comparison for CH_4
Source: Data from Lamoureux *et al*. (2002), Lamoureux and Paillard (2003), Lifshitz *et al*. (1971), Petersen, Hall, *et al*. (2007), and Zhang *et al*. (2012)

In the case of RGFs, the behavior is similar, but the disagreement increases at low temperatures. A comparison between the experimental and numerical values of τ, carried out by McDonell and Dunn-Rankin (2008), is shown in Figure 5. It is evident that the models cannot reproduce the observed behavior of τ at lower temperatures with any of the DRMs used. According to the authors, the low accuracy of the models may be related to the fact that H_2 autoignition does not occur in a homogenous manner. However, this is also observed in fuel mixtures without H_2, so the disagreement cannot be attributed to this factor. Moreover, the work by Davidson *et al*. (2019), for τ values of gasoline surrogates, reported disagreements in the 700-900 K temperature range, thereby supporting that the presence of H_2 in the fuel mixture is not the only reason for this behavior.

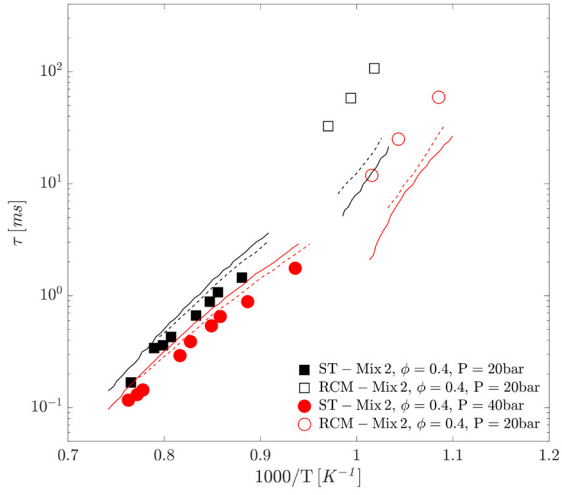

Figure 4. Ignition delay for natural gas mixture. Experimental data (symbols). Numerical data (lines) using the LLNL (straight) and NUIG mechanisms (dashed).
Source: Adapted from Vallabhuni *et al*. (2018)

Syngas (SG) also exhibits a similar behavior. Figure 6 shows ignition delay values for an SG/air mixture (7.33% H_2, 9.71% CO, 1.98% CO_2, 17.01% O_2, and 63.97% N_2 in vol.) (Yu *et al*., 2018). Significant disagreements between the experimental and numerical results appear at low temperatures. The same trend was reported by Barak et al. (2017) for an equimolar H_2/CO fuel mixture. In addition, Lee et al. (2014) collected ignition delay data for different SG compositions and highlighted the need to obtain more experimental data on these fuels at low temperatures, along with their pressure curves, in order to improve the model predictions.

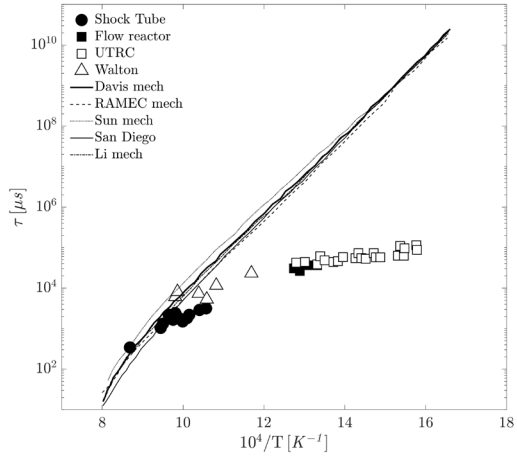

Figure 5. Experimental and numerical ignition delay values for H_2
Source: Adapted from McDonell and Dunn-Rankin (2008)McDonell and Dunn-Rankin (2008)

Hu *et al*. (2016) evaluated ten different DRMs in τ calculations for H_2/O_2 mixtures for the 850-1500 K temperature range. Only four of them allowed obtaining adequate τ predictions, exhibiting increased disagreement at low temperatures. Mansfield and Wooldridge (2014) reported the poor performance of the DRM in J. Li *et al*. (2007) regarding τ calculations for an SG, especially at temperatures lower than 1000 K. A similar behavior was observed by Donohoe *et al*. (2014) in CH_4/H_2 mixtures with the GRI-Mech 3.0 and the Aramco 1.3 reaction mechanisms.

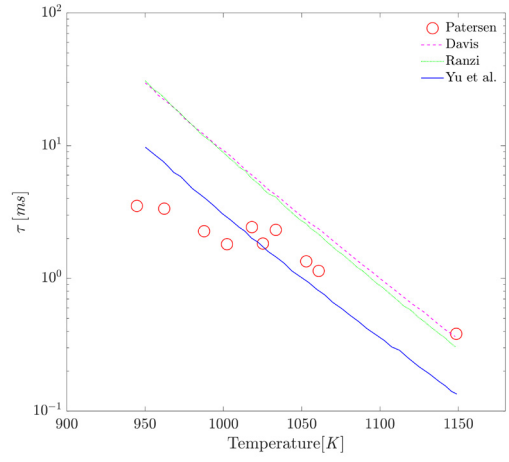

Figure 6. Ignition delay for a syngas mixture
Source: Adapted from Yu *et al*. (2018)

In order to improve the prediction capability of the models and DRMs regarding τ under low temperature conditions, different approaches have been implemented, which can be summarized in three principles: preexponential factor modifications, inclusion of the pressure rate in the model, and the consideration of catalytic effects. In the next section, some works about these principles are outlined while analyzing advantages and limitations.

Methodologies to improve τ prediction

Different methodologies have been proposed to improve the prediction capability of τ at moderate and low temperatures using zero-dimensional reactors. The main characteristic of these strategies is their corrective approach, as they use experimental results in a direct or partial manner to correct the numerical values, bringing them closer to the experimental ones. This is due to the fact that, in many cases, the objective is to use numerical results to perform a kinetic analysis, and the objective, in principle, is not to obtain an adequate prediction. In order to analyze the scope of these strategies, as well as their limitations, this work categorized them into two global groups according to the principle implemented: thermodynamics and chemical kinetics.

Thermodynamic approaches

One of the most common thermodynamic approaches is including the experimental pressure rate in the model, generally expressed as a percent per time units. This methodology is focused on considering non-ideal effects by means of the pressure increase before ignition occurs inside the reactor. Thus, the temperature rises, and the ignition acceleration is captured. As a recommendation, this approach must be applied when the experimental value of τ is greater than 1.5 ms, which implies the first and most important limitation: the need for a previously known τ before performing any calculations to improve the numerical result. On the other hand, the value of the pressure rate is not constant, and some studies report a range from 2 to 50%/ms (Lieuwen *et al*., 2009; Zhang *et al*., 2012). These values have been obtained from experimental measurements according to the pressure curve (Figure 7). It is evident that this approach can be applied when the objective is to determine ignition delay times without performing experimental tests.

Figure 8 shows some experimental τ data for a 70% H_2/30% CO (in vol.) mixture obtained in an ST, along with the numerical data generated using the SENKIN subroutine of the CHEMKIN-PRO software. The red line corresponds to the results generated with the model without any modification. As can be seen, when the temperature decreases, the disagreement between experimental and numerical data increases. The black line represents the numerical prediction using a pressure rate of 4.22%/ms in zero-dimensional model. The use of the pressure rate considerably improves the τ predictions at moderate and low temperatures. In an analogous study, albeit using only H_2 as fuel, Pang *et al*. (2009) used a value of 2%/ms. Although the prediction capability also improved, it is noticeable that the dp/dt value depends on the fuel mixture and requires previous experimental measurements.

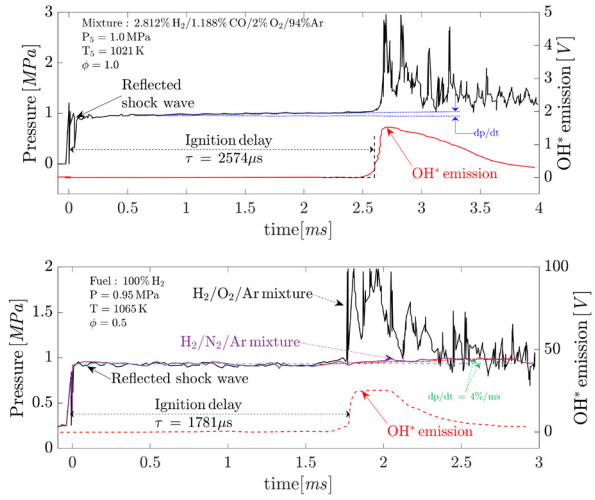

Figure 7. Pressure trace rate determination
Source: Adapted from Thi *et al*. (2014) and Zhang *et al*. (2012)

For the RCM results, the pressure and temperature at the end of compression are used to obtain τ predictions. However, in order to improve the numerical results, the pressure history curves are employed to determine the thermodynamic conditions, which must be used in the zero-dimensional model to calculate τ. The pressure equivalent is calculated as the integral average from the end of the compression to the maximum dp/dt before ignition (Walton *et al*., 2007).

The thermodynamic approaches also include dynamic predictor-corrector methodologies to improve τ predictions at moderate and low temperatures. These approaches focus on temperature correction at each time step while solving the energy equation. An example of this is the CHEMSHOCK model, which begins the solution by calculating the temperature as a conventional zero-dimensional reactor model at an instant t. Afterwards, the model assumes that the reactive mixture is isentropically compressed and recalculates the temperature for the time $t+\Delta t$. The main limitation of this approach is related to the calculation of $T_{t+\Delta t}$, wherein a measured pressure is needed, implying the need for a prior experimental test (H. Li *et al*., 2008). Figure 9 shows a comparison between experimental and numerical τ results for H_2, as obtained using the conventional constant volume reactor and CHEMSHOCK. As can be seen, the agreement improves when this approach is applied at low temperature conditions.

The approaches outlined above allow for remarkable improvements to the τ predictions, in comparison with the conventional zero-dimensional model. However, all of them require experimental measurements under the desired thermodynamic conditions. Their application is not viable for fuel mixtures with a variable chemical composition, as

is the case of RGFs and their mixtures with oil-derived fuels, where it is highly likely that experimental measurements are unavailable.

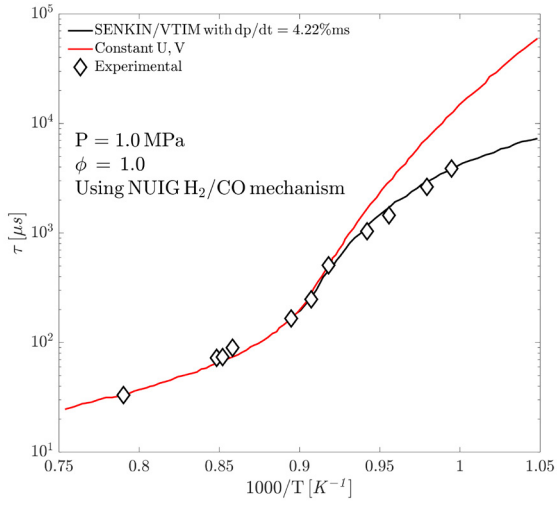

Figure 8. Ignition delay predictions, as improved by including dp/dt inclusion
Source: Adapted from Thi *et al*. (2014)

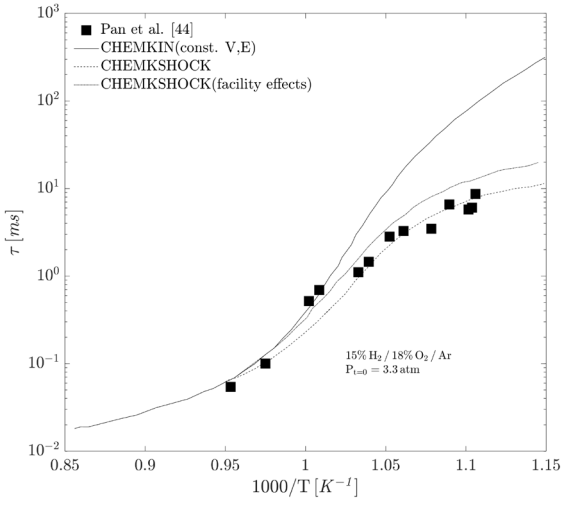

Figure 9. Ignition delay predictions for H_2, as improved using CHEMSHOCK
Source: Adapted from Pang *et al*. (2009)

Chemical-kinetic approaches

Modifying preexponential factor and kinetic parameters is another common approach to improving τ predictions (Cavaliere *et al*., 2010; Vallabhuni *et al*., 2018; Walton *et al*., 2007; Zhang *et al*., 2012). However, in this case, the main issue is that the changes are unrelated to specific reactions. Although they are commonly focused on chemical reactions in the presence of the HO_2 and H_2O_2 radicals (which is relevant in kinetics at moderate and low temperatures), there are no general rules to determine which reactions must be modified. This is dependent on the chemical composition of the fuel mixture.

Figure 10 shows a comparison between the experimental and predicted τ values reported by Amador Díaz (2017) using a DRM without any modifications and with changes in the preexponential factor of the following reactions:

$$2(OH)+M \leftrightarrow H_2O_2+M \quad (2)$$

$$H+H_2O_2 \leftrightarrow HO_2+H_2 \quad (3)$$

According to the results, only modification III significantly improves the τ predictions. Although the other alternatives do not work for this case, the studies where they were proposed exhibited good results. This suggests that the modifications cannot be universally applied, and that an adequate performance necessitates adjustments for each case – which, similarly to the thermodynamic approaches, requires experimental results.

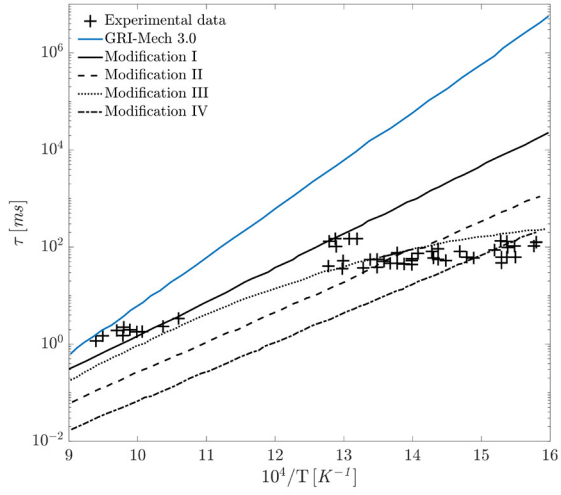

Figure 10. Ignition delay predictions improved using different modified reactions in the DRM
Source: Amador Díaz (2017)

Lee *et al*. (2017) used a genetic algorithm to obtain a reduced mechanism based on Aramco 1.3, wherein the kinetic parameters of the following reactions were modified:

$$H+O_2+CO_2=HO_2+CO_2 \quad (4)$$

$$CH_4+OH=CH_3+H_2O \quad (5)$$

The methodology was applied for H_2/CO/CH_4/CO_2 fuel mixtures. According to the authors, the reduced mechanics, along with the modified values, are suitable for calculating the ignition delays of syngas, biogas, and natural gas with the addition of H_2O, N_2, C_2H_6, and C_3H_8. However, for mixtures with C_4H_{10} or C_5H_{12}, the disagreement is significant and therefore not recommended. Another limitation of the approach becomes evident when the chemical composition is variable.

Another, different, and less common approach consists of adding new elementary reactions to the DRM, but, of course, this alternative requires important kinetic knowledge. Prince and Williams (2012) studied τ in the 500-1000 K temperature range for C_3H_8 and C_2H_6 using the San Diego DRM. When the unmodified version was used, the disagreement between experimental and numerical τ data was much greater. Although the prediction capability improved significantly with the modifications, differences remained at low temperatures. Besides, this approach also needs a fitting process that requires experimental results. In a study with a more phenomenological focus, Medvedev *et al*. (2016) used H_2 as fuel. They performed a quantum correction in the reaction rates of some initiation reactions, thereby improving the τ predictions at low temperatures and high pressures.

Zhang *et al*. (2012) conducted a numerical and experimental study using H_2, CH_4, O_2, and AR mixtures using a temperature range of 1000-2000 K and pressures from 0.5 to 2.0 MPa. In order to improve the τ predictions, the authors changed the preexponential factor of two reactions containing HO_2. Additionally, when the τ value was higher than 1.5 ms, a pressure increase rate of 4%/ms was included in the model. The differences between the experimental and numerical τ results were attributed to the uncertainties of the $H+O_2+M=HO_2+M$ reaction. However, as will be explained later, the parameters of this reaction are still being studied in light of relevant variations in τ predictions.

A review of DRMs and the subsequent proposal for a new one was performed by Jiang *et al*. (2019). The authors gathered experimental τ data for H_2/CH_4 mixtures at temperatures of 900-2000 K and pressures from 1.4 to 70 atm. The DRM obtained has 18 species and 39 reversible reactions. However, there is still disagreement for temperatures under 1000 K.

Another kinetic approach consists of compiling the seemingly most elementary reactions under moderate and low temperature conditions. Pan and Wallace (2019) applied this approach to develop the low-temperature natural gas (LTNG) reaction mechanism, focused on the combustion of natural gas mixtures. Their work included reactions considering CH_3O_2, CH_3O_2H, C_2H_5O, $C_2H_5O_2H$, and $C_2H_5O_2$ radicals in a previous DRM. Their results show an improvement in τ predictions for temperatures from 1100 and 1200 K. However, performance decreases as the temperature approaches 1000 K, with disagreements of up to four times the experimental value.

Recently, W. Li *et al*. (2023) evaluated the collision efficiency of CO_2 in $H+O_2+M=HO_2+M$, using a syngas mixture with a high CO content (>50% in vol.) under stoichiometric conditions in a ST setup. As a result, they recommended new CO_2 collision efficiency values and presented an uncertainty analysis. The new model led to a substantially improved prediction of τ at 5 atm and was validated with other syngas data reported in the literature. However, the issue under study still remains, as this approach involves fitting a specific type of fuel, and performance with other fuel mixtures needs to be tested.

The main issue with these approaches is that kinetic parameter modifications cannot be generalized for different fuel mixture compositions, thereby limiting their application (Amador Díaz, 2017). Regarding the development of DRMs focused on moderate and low temperatures, two of the most recent (Baigmohammadi *et al*., 2020; Pan and Wallace, 2019) still exhibit significant disagreements when the temperature is 1100 K or lower and the mixture contains H_2. This suggests that the differences between experimental and numerical results are not only due to kinetic effects, but also to physical effects that zero-dimensional models are not able to capture.

Inhomogeneity effects

A wide range of numerical and experimental studies have been conducted to analyze the autoignition phenomenon at moderate and low temperatures in comparison with high temperature conditions. Some characteristics and behaviors related to autoignition inhomogeneity have been identified and categorized as weak or mixed autoignition regimes. In the mixed case, a stratified ignition first occurs, and then a homogeneous behavior appears. In this section, some of the most relevant works are presented along with their findings and methodologies. Additionally, some approaches to the prediction of this phenomenon are analyzed.

In a numerical study, Basal and Im (2011) evaluated the effects of temperature and composition inhomogeneity using three possible scenarios: homogeneous concentration with inhomogeneous temperature, uncorrelated inhomogeneities in both fields, and correlated inhomogeneities. They performed DNS simulations in one and three dimensions, using heat release rate as an indicator for the autoignition regime. They found that, when inhomogeneities are present, the τ value is lower than in the homogeneous case, indicating an acceleration effect in the autoignition process. This reveals the relationship between inhomogeneities and the disagreements obtained with the zero-dimensional models.

In further work, Im *et al*. (2015) established criteria to predict the autoignition regime using the Sankaran number while only considering temperature inhomogeneities. Additionally, they defined the mixing Damköhler number from τ and the mixing time scale associated with the Taylor microscale for the temperature field as a complementary criterion, with the purpose of identifying weak and mixed regimes. The criteria were evaluated using the experimental values reported by Mansfield and Wooldridge (2014). When performing the measurements, image capture was used to identify the autoignition regimes. H_2/CO under lean conditions was used as the reactive mixture. For all analyzed cases, according to the experimental values, the criterion to predict homogeneous and inhomogeneous autoignition

exhibited an adequate performance. However, the criterion to categorize inhomogeneous autoignition as weak or mixed showed some disagreements. These may be associated with the turbulence quantities, as they were arbitrarily assumed. Although the criteria are important and valuable in predicting the autoignition regime, they do not allow establishing and direct relationship between τ predictions and the way to use ignition regime data to improve the process, especially when using zero-dimensional reactors.

Due to the evident differences and the gap in the τ prediction capabilities of the models under moderate and low temperature conditions, some researchers have recently focused on the use of molecular dynamics to more profoundly understand the autoignition phenomenon, aiming to clarify the origin of the studied disagreements.

Sirmas and Radulescu (2017) carried out a 2D simulation with the objective of analyzing the thermal fluctuations during ignition through the molecular dynamics approach. For the simulation, only one generic reaction was considered, with two reactants A and B and one product C, all of them with the same weight and size. The triggering of the reaction was determined using a limit velocity value during the collisions of A and B. This study defined τ as the time during which the limiting reactant was consumed. The effects of activation energy and heat release were analyzed. According to the results, differences of up to 40% may appear in τ estimations when the activation energy and the heat release are high. The τ obtained via molecular dynamics is lower than that calculated through the equilibrium approach. Subsequently, the authors performed a new study considering 3D simulations (Murugesan *et al*., 2019). As in the 2D case, they found that it is possible to obtain different temperature profiles for the same simulation conditions when considering random particle paths. This behavior allows stating that the ignition phenomenon has a stochastic effect. Similarly to the 2D results, when the activation energy was high, the τ values obtained via molecular dynamics were lower than those calculated using conventional kinetic gases theory. Finally, the authors made an analogy between some H_2 oxidation reactions and their molecular dynamic results, suggesting that the observed behaviors correspond to this type of reaction. However, the comparison was only qualitatively made. These works' results can help explain the disagreement observed in other approaches, as the calculations were performed with a generic reactant and therefore are not focused on a specific fuel. Nevertheless, as stated by the authors, additional studies are required to confirm and broaden the observed trends.

On the other hand, in a recent study, Luong *et al*. (2020) extended the criterion proposed by Im *et al*. (2015) for defining the ignition regime, considering fuels with a negative temperature coefficient (NTC). Additionally, for the criterion, they considered concentration inhomogeneity and its negative correlation with temperature due to fuel vaporization. Thus, a new way to calculate the Sankaran number was defined via the following equations:

$$S_{ap} = KD_{al}^{-\frac{1}{2}} \tag{6}$$

$$K = \beta \frac{1}{\left(\tau_f \tau\right)^{0.5}} \left(\left| \frac{\partial \tau}{\partial T} T' \right| + s \left| \frac{\partial \tau_{ig}}{\partial \phi} \phi' \right| \right) \tag{7}$$

For a S_{ap} greater than one, the autoignition is classified as mixed/weak, and the regime is strong for lower values. The results reveal that the modified criterion performs adequately for fuels with a NTC and allows establishing the ignition regime. However, the behavior in the NTC region is different because the temperature sensibility of τ changes considerably, *i.e.*, in the NTC region, an inhomogeneous ignition can be observed at 900 K, but, at 770 and 1045 K (outside said region), a homogeneous ignition takes place. In the NTC region, τ increases when the temperature grows, which reduces the ignition wave in the mixture, whereas the flame velocity increases, entailing a faster growth of the deflagrative flame fronts, which have more time to develop due to the higher τ.

Finally, the compilation of 1398 τ experimental data reported in the literature (Beerer and McDonell, 2008; de Vries and Petersen, 2007; Huang *et al*., 2006; Kalitan *et al*., 2007; Kéromnès *et al*., 2013; Petersen, Hall, *et al*., 2007; Petersen, Kalitan, *et al*., 2007; Shao *et al*., 2019; Vallabhuni *et al*., 2018; Walton *et al*., 2007; Zhang *et al*., 2012) and comparisons with zero-dimensional prediction models using five DRMs, *i.e.*, NUI Galway–C5_2008 (Bourque *et al*., 2009), GRI-Mech 3.0 (Smith *et al*., 2000), Aramco 1.3 (Metcalfe *et al*., 2013), 56.54 Mech (Burke *et al*., 2015), and NUI Galway–C5_2010 (Donato *et al*., 2010; Healy, Donato, *et al*., 2010a, 2010b; Healy, Kalitan, *et al*., 2010; Healy, M. Kopp, *et al*., 2010) were performed in this work in order to evaluate the effect of H_2 on prediction capabilities under moderate and low temperature conditions, wherein the effect of inhomogeneity is relevant. The data were classified into two groups: fuels with H_2 (WH) and without it (WOH). We found relative differences greater than 50% between the experimental and the numerical results. The actual overestimation actual was around 52% of the WH data group. In contrast, this disagreement level only appeared in 15% of the WOH data group. The deviations for both groups are shown in Figure 11. Disagreements higher than one order of magnitude were found for both groups. This behavior suggests that the physical and kinetic-chemical properties of H_2 have a remarkable effect on τ prediction capabilities at moderate and low temperatures (<1000 K). The greater disagreements are probably related to the high burning velocity of H_2, which promotes the reaction fronts that appear in weak/mixed ignition regimes, accelerating the phenomenon and decreasing the experimental value of τ, given that zero-dimensional models cannot capture this phenomenon.

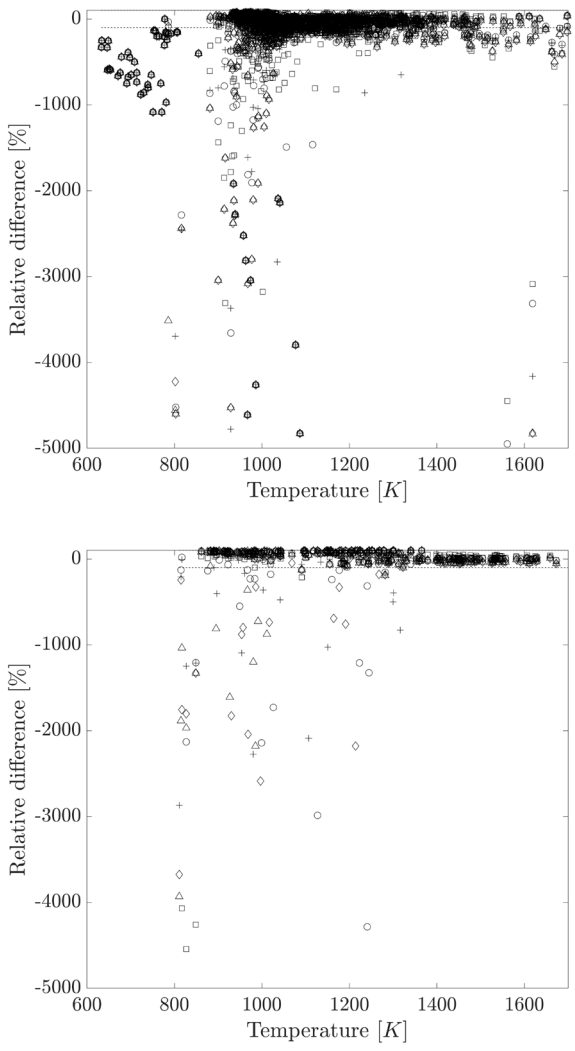

Figure 11. Relative differences between experimental and numerical τ values. WH group (up). WHO group (down). NUI Galway–C5_2008 (circles). GRI-Mech 3.0 (squares). Aramco 1.3 (diamonds). 56.54 Mech (triangles). NUI Galway–C5_2010. (cross).
Source: Authors

Autoignition regime and knocking

Abnormal combustion or knocking is one of the most relevant issues that can take place in ICEs, and it is a limitation in the use of some RGFs, especially those with high H_2 concentrations. The fundamental phenomenon related to knocking is the autoignition of the unburned mixture before it is consumed by the flame front coming from the spark plug. Therefore, a strong correlation between τ and the occurrence of knocking is expected. As presented in the previous sections, the value if τ can be affected by the autoignition regime, and, therefore, it can also influence knocking behavior. This section presents a brief analysis of the relationship between knocking and autoignition regimes, using characteristic numbers for the phenomena.

The methane number (MN) is a characteristic parameter to estimate the knocking tendency of gaseous fuel; a lower MN means a higher tendency towards detonation (Malenshek and Olsen, 2009). The MNs of different fuels, as measured by Gómez *et al*. (2016), were used for the analysis. The fuel compositions cover mixtures of CH_4, C_3H_8, H_2, and CO_2. The specific values and the designation for each mixture are shown in Table 1.

Table 1. Chemical composition of the analyzed gaseous fuel mixtures

Mixture designation	MN	Chemical composition			
		%CH4	%CO2	%C3H8	%H2
100P	36.5	0	0	100	0
50B50M	120	80	20	0	0
54B36M10H	96.5	68	22	0	10
100B	140	60	40	0	0
100M	100	100	0	0	0
83B17P	65.8	50	33	17	0
79B16P5H	65.2	47	32	16	5
75B15P10H	63.8	45	30	15	10
57B38M5H	105.3	72	23	0	5
54.5B36.5M9H	100	69.2	21.8	0	9
90B10P	100	54	36	10	0
88B12H	100	53	35	0	12

Source: Gómez Montoya *et al*. (2016)

The corresponding S_{ap} and Reynolds flame numbers (R_{ef}) were calculated for each mixture. Typical ICE thermodynamic conditions were selected, namely a pressure of 3000 kPa and temperatures of 800, 900, and 1000 K. Figure 12 shows the S_{ap} for the different MN values at the different temperatures. An increase in the S_{ap} as the MN grows is the general trend. However, this behavior depends on the temperature. For the highest temperature, all S_{ap} values are lower than one, which means that, if autoignition occurs, it will be strong (homogenous). In addition, the data are less dispersed in comparison with the other temperature values.

For 800 and 900 K, almost all the S_{ap} are higher than one, suggesting mixed or weak autoignition. As previously mentioned, τ prediction is less accurate in this autoignition regime. Therefore, the time available for the unburned mixture to be consumed by the flame front coming from the spark plug can be overestimated if it is calculated with conventional zero-dimensional models. This means that the occurrence of knocking can probably be omitted in ICE modeling.

On the other hand, it is evident that, for the same MN value, the S_{ap} can vary under the same thermodynamic conditions. For example, four different S_{ap} values were obtained with an MN of 100 at 900 K (0.83, 1.5, 1.7, and 2.1). According to that, it is possible for the same knocking tendency to entail different autoignition behaviors, which can be associated with differences in the combustion properties of the fuel

mixtures. An example of this corresponds to the variations in the R_{ef}, which are related to the laminar burning velocity of the fuel mixture (Figure 13). Nevertheless, a deeper dive is necessary to relate autoignition regimes and the knocking tendency of RGFs.

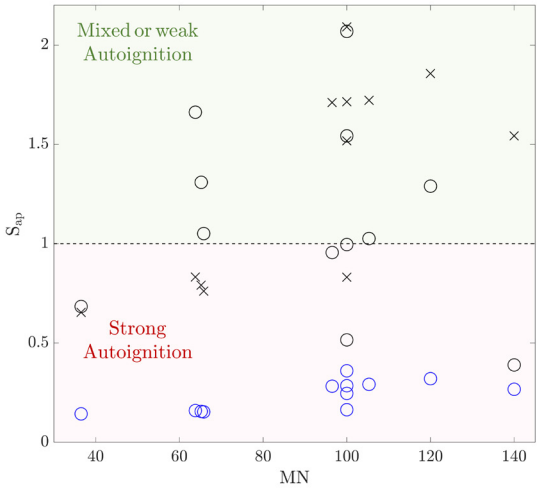

Figure 12. S_{ap} for different MN at 3000 kPa. Black circles: 800 K. Cross: 900 K. Blue circles: 1000 K.
Source: Authors

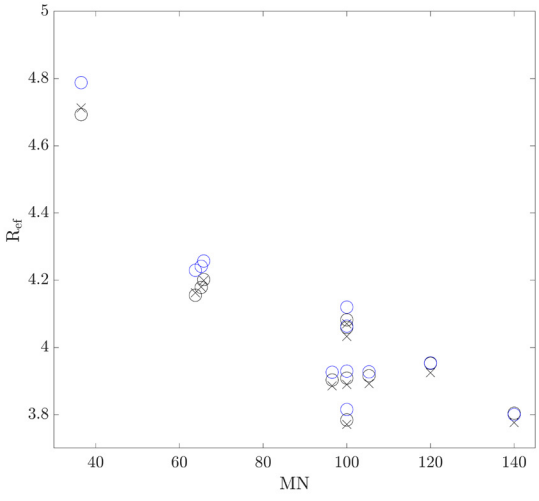

Figure 13. R_{ef} for different MN at 3000 kPa. Black circles: 800 K. Cross: 900 K. Blue circles: 1000 K.
Source: Authors

Conclusions

RGFs are a relevant alternative energy source that contributes to decreasing pollutant emissions. However, due to the high variability of their chemical composition, their fundamental combustion properties (*e.g.*, τ) have not been entirely characterized. Thus, preventing undesired autoignition phenomena becomes a complex issue, limiting the use of this kind of fuel in practical systems (engines, furnaces, and turbines). In order to broaden the use of RGFs in current thermal devices, as well as the development of new ones, it is necessary to adequately predict τ values, particularly at moderate and low temperatures, since many of the low-emissions technologies operate in this range. In order to contribute to this perspective, a literature review encompassing the main approaches and issues in τ prediction when using RGFs was performed. From said review, the following conclusions can be drawn.

Current DRMs and zero-dimensional models exhibit issues in adequately predicting τ for RGFs under moderate and low temperature conditions. The disagreement between experimental and numerical values increases when H_2 is present in the fuel mixture. This, in comparison with the exclusive use of hydrocarbon fuels. The development of specific DRMs for RGFs can improve τ prediction, taking into account the changes in kinetic pathways that the DRMs for conventional fuels cannot capture.

There is no general way to improve τ predictions using a zero-dimensional model. Furthermore, many improvement approaches require previous experimental measurements, which is not possible during the design and evaluation process. Additional studies on the autoignition phenomenon at low and intermediate temperatures, combining thermodynamic and kinetic approaches, are required to establish a more general method that allows improving τ predictions.

Thermal and composition inhomogeneities contribute to weak/mixed autoignition regimes and may be one of the reasons for the disagreement in τ predictions. There is a significant gap in the phenomenological approach to modeling inhomogeneous autoignition regimes. It is necessary to consider the flame fronts prior to volumetric autoignition in order to improve τ predictions. It is necessary to conduct research focused on autoignition under inhomogeneous temperature and concentration conditions while using RGFs in moderate and low temperature ranges, in order to identify differences with high-temperature autoignition and develop new models to improve τ prediction.

There is a relationship between the MN and the autoignition regime, although the behavior can vary according to thermodynamic conditions and combustion properties. More detailed studies on autoignition during knocking are required in order to explain the effect of mixed/weak regimes on abnormal combustion in ICEs. Furthermore, it is necessary to establish a better connection between the S_{ap} and the MN for ICE modeling using RGFs.

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CRedit author statement

Hernando A. Yepes: conceptualization, formal analysis, funds acquisition, investigation, methodology, writing (original draft), visualization and supervision. *Adalberto Salazar:* writing (original draft) and visualization. *José D. Yepes:* visualization.

Conflicts of interest

The authors declare no conflict of interest.

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