

# On the Prediction of the Ignition Delay Time of Bio-Syngas

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The growing energy demand and more stringent environmental regulations have raised concerns about the production and use of alternative fuels. Due to the potential application of the resulting gaseous streams in turbines as an energy source, slow pyrolysis of biomass including municipal waste have been extensively studied under various situations and atmospheric conditions. Nevertheless, the combustion characteristics of these complex mixtures and the chemical interactions between their constituent species are still not fully understood. Hence, the accuracy of commonly used empirical-based mixing rules for the estimation of the overall reactivity, such as laminar burning velocity and ignition delay time is inefficient. This work is addressed to the numerical prediction of the Ignition Delay Time, IDT, of bio-syngas mixtures at different fuel compositions, stoichiometries, temperature, and pressure, by means of a detailed kinetic model. A simplified tool for preliminary evaluation of the overall reactivity with respect to the above-mentioned conditions was proposed for these mixtures, as well, providing an effective feature for safety and management evaluations.

## 1. Introduction

The energy generated by the combustion of renewable sources is more than 80% of the world's "clean" energy produced worldwide (Agarwal et al., 2017). Besides, the stringent guidelines devoted to the regulation of the composition of combustion tail gas have led gas turbine manufacturers toward the utilization of renewable and environmentally friendly fuels (Lee et al., 2014). Consequently, the evaluation of alternative fuels, the development of combustion mechanisms, and technologies have been strongly incentivized and largely investigated in recent years (Knothe and Razon, 2017). So far, one of the main challenges facing the utilization of innovative, low-carbon fuels regards the flexibility of the existing infrastructures and combustion technologies, i.e., the development of fuels tailored to the existing engines may incentive the substitution of traditional fossil fuels (Kalghatgi et al., 2018). The application of gaseous fuels deriving from the gasification of biomass has been indicated as a high potential alternative solution for energy production via gas turbines (Indrawan et al., 2018). The composition of these gaseous mixtures is largely variable by the raw materials adopted, but it mainly consists of methane, carbon dioxide, carbon monoxide, and hydrogen (Robbins et al., 2012). Hence, the implementation of detailed kinetic mechanisms is required for an accurate evaluation of chemical interactions between species composing the investigated fuels due to the presence of non-hydrocarbon compounds (Salzano et al., 2018)(Gabel and Krause, 2019). Indeed, the chemistry of pure methane oxidation has been deeply investigated and analyzed under engine relevant conditions (e.g. temperature higher than 1400 K), because of its importance as a fuel and as a building block for the development of kinetic mechanism suitable for all heavier hydrocarbons (Petersen et al., 2007). Similarly, the hydrocarbons addition to methane has been largely investigated under turbine relevant conditions in terms of ignition delay time (IDT) (Huang and Bushe, 2006), whereas Fischer and Jiang (Fischer and Jiang, 2016) have recently highlighted that the full understanding of the interactions of non-hydrocarbons (i.e. CO, CO<sub>2</sub>, and H<sub>2</sub>) with methane flames still represents a big challenge for researchers, lessening the achievement of economic and environmental requirements. In this light, the development of accurate predictive tools suitable for the evaluation of ignition phenomena, based on chemical kinetics, is essential for the design of combustor (Sung and Curran, 2014).

The IDT, together with the laminar burning velocity, is a key physicochemical property of combustible-oxidant mixtures at a given temperature and pressure. Indeed, both of them can be used for the estimation of the

severity of combustion-related accidents as well as for the proper design of reactors, ancillary systems, and safety valves (Boyce, 2012). Besides, these properties are commonly adopted for the evaluation of detailed kinetic mechanisms, because of their representativeness of the overall system reactivity at elevated or low temperature, respectively. In fact, experimental apparatuses commonly adopted for the collection of IDT data operate from 600 K to 2000 K, whereas homologous systems for the evaluation of the laminar burning velocity are usually adopted for temperature lower than 600 K (Pio and Salzano, 2018a). For these reasons, bearing in mind the turbine relevant operative conditions, IDT is often selected as a stand-alone parameter to evaluate the chemistry of bio-syngas combustion. Moreover, IDT has the intrinsic advantage to allow for the correlation of characteristic reaction time with flowing time scales, thus it is vital to design ancillary and connective devices and synchronize operating cycles.

The IDT, as defined in the European Standard EN 14522:2005 (EN 14522:2005, 2005), represents the time interval between the injection of the flammable substance and the ignition itself. It represents the induction time of the system, accounting for heating, diffusion, mixing of reactants and formation of radicals involved in the flame reactions (e.g. H $\cdot$ , OH, and O) characteristic time scales. These phenomena result in rapid depletion of reactants and gain in gaseous temperature and pressure due to adiabatic and isochoric conditions. Hence, the maximum heat release rate, maximum temperature gradient, maximum concentration of OH-or CH radicals can be adopted as ignition criteria for the direct measurements of IDT, without effects on the resulting data. On the other hand, the layout and constituting materials of real apparatuses adopted for the experimental purpose can influence the collected data. Indeed, the adoption of standardized procedures and systems (e.g. ASTM D6890-13a, 2013) is strongly encouraged to limit the effect of systematic errors and obtain consistent, comparable, and significant data. In this light, a brief description of some of the most common apparatuses utilized in the last decades for the characterization of IDT, i.e. continuous flow systems (CFS), shock tube (ST), and rapid compression machine (RCM), was given. CFS is fed with the reacting mixture at the given flow rate, temperature, and pressure. The temperature profile is monitored along the reactor. If the ignition does not occur, i.e. if a negligible rise in temperature is observed, the initial conditions are changed, commonly the initial temperature is increased. This procedure is repeated until the mixture ignites.

The ignition delay times are computed as the time required to reach the flame front from the feeding point, knowing the feeding velocity. This configuration was intended to simulate the plug flow reactor to minimize non-homogeneities and disregard non-chemical phenomena, thus the feeding section should be carefully designed to reduce the risk of downstream recirculation zones and unwanted concentration gradients. However, the utilization of continuous-flow devices for ignition characterization is inherently limited at medium temperature, because of the use of electrical resistance-type air heaters. The ST is commonly adopted for kinetic evaluation because of its versatility, simplicity and high repeatability of test conditions, as already reported in the early study of Belford and Strehlow (Belford and Strehlow, 1969) and, more recently, critically analyzed by Bhaskaran and Roth (Bhaskaran and Roth, 2002). The apparatus core consists of a rectangular or circular cross-section tube equipped with a diaphragm separating low-pressure gas (even a partial vacuum), referred to as driven gas, and commonly a low molecular weight gas (e.g. helium), by high-pressure gas, referred as driver gas. Two monitoring points are conveniently located along the tube by placing likewise measuring systems, depending on the selected criteria (e.g. pressure transducer in case of pressure rise as IDT criterion). Bursting diaphragm generates a shock wave, resulting in increased driven gas temperature and pressure. The time required for the shock wave to traverse the distance between the two monitoring points is collected and related to the IDT (Bhaskaran and Roth, 2002). Recently the temperature range within ST has been adopted has been considerably broadened, since it is suitable for the evaluation of IDT from  $\mu$ s to 10 ms (Sung and Curran, 2014). Notwithstanding that, limitations for the application of ST at intermediate and the low temperature still exist. On the contrary, IDT measurable by using RCMs may variate within 2 – 150 ms (Goldsborough et al., 2017). Indeed, RCM is widely adopted for the characterization of autoignition behavior at intermediate temperature (within the range 600 K – 1400 K), i.e. for the characterization of the negative temperature coefficient region, where tailored and well-designed procedures and apparatuses are essential for the development of accurate models accounting for physical-chemical aspects, for the sake of studying combustion occurring at turbines conditions (Olm et al., 2015). This apparatus simulates a single compression stroke of an engine by rapidly compressing the premixed mixture fed in an almost adiabatic combustion chamber and evaluate the IDT by monitoring the pressure evolution along the test time. More recently, the constant volume spray combustion chamber (CVSCC) has been adopted for the measurement of spray ignition delay time for conventional and alternative fuels at intermediate temperature (i.e. ranging from 600 K to 850 K) (Goldsborough et al., 2017)(Burden et al., 2018), whereas experimental systems to collect IDT data at a lower temperature are scarcely adopted. For the sake of clarity, from now on elevated temperature will be intended as above 1400 K, low temperature as below 600 K, and intermediate temperature as the resulting interval in between of the abovementioned ranges.

## 2. Methodology

In this work, the IDT was evaluated at different fuel compositions, representative of bio-syngas mixtures, and stoichiometries, ranging from ultra-lean to stoichiometric with respect to the combustion reaction. More specifically, the effect of fuel composition was evaluated by analyzing binary fuel mixtures, at first. For the sake of clarity, the equivalence ratio ( $\varphi$ ) and content of generic  $i$ -th species in the fuel mixture ( $R_i$ ) were adopted to specify initial composition, as defined in the following:

$$\varphi = \sum \frac{m_f/m_{ox}}{(m_f/m_{ox})_{st}} \quad (1)$$

$$R_i = m_i/m_f \quad (2)$$

where  $m$  stands for mole, the subscripts  $f$ ,  $ox$ , and  $st$  are fuel, oxidant agent, and stoichiometric conditions with respect to the reaction of complete oxidation, respectively. The presence of inert agents was specified if different from the nitrogen contained in the air. Numerical simulations were carried out by means of open-source Cantera suite (Goodwin, 2003) and detailed kinetic mechanism developed at the University of Bologna (KiBo) (G. Pio et al., 2019). This mechanism represents a collection of thermodynamic and kinetic properties of about 120 species and 600 reactions, conveniently selected to represent chemical aspects of light species under an oxidative environment in a wide range of conditions. (Pio and Salzano, 2018b). Indeed, previous studies have demonstrated elevated accuracy in the description of the oxidation of  $C_4$  or lighter species (Pio and Salzano, 2019)(Pio et al., 2019). Perfectly adiabatic, the zero-dimensional stirred reactor was modeled, in accordance with the procedure detailed described in previous work (Pio et al., 2018). Temperature, OH concentration, and release heat profiles with respect to simulated time were monitored and considered as ignition criteria, being the achievement of maximum values of these quantities often adopted in the literature (Merchant et al., 2015). IDT of pure flammable species composing bio-syngas mixtures in the air was obtained at first for the sake of model validation, because of the abundances of either experimental data. Then, binary, tertiary, and more complex mixtures, included in the composition ranges reported in Table 1, were considered for further analyses. Several conditions have been tested. More specifically, the temperature from 800 K to 1400 K, equivalence ratio from 0.4 to 2 and pressure from 1 bar to 50 bar were considered.

Table 1: The range of compositions analyzed in this work as a representative for bio-syngas mixtures.

Species	Minimum, if present [%v/v]	Maximum [%v/v]
CH <sub>4</sub>	30	100
CO	20	35
CO <sub>2</sub>	50	70
H <sub>2</sub>	1	10
C <sub>2</sub> H <sub>6</sub>	1	5

In order to understand the effects of initial parameters such as initial temperature, pressure, and fuel composition, the estimated ignition delay time  $\tau$  has been correlated to the Arrhenius-like equation as in the following equation:

$$\tau = A \cdot P^{-\beta} \cdot e^{-\frac{E_a}{RT}} \cdot \prod y_i^{\alpha_i} \quad (3)$$

where  $A$  is the frequency factor,  $R$  the universal gas constant,  $E_a$  is the overall activation energy in  $J \text{ mol}^{-1}$ ,  $P$  and  $T$  are the initial pressure expressed in bar and temperature in Kelvin, and  $\alpha_i$  are the exponential coefficient (order of reaction) for the generic mole fraction of reactant  $y_i$ . In order to describe quantitatively the effects of each parameter on  $\tau$ , the rate of change (CR) is defined as:

$$CR = \left[ \frac{\tau_{max}^{-1}}{\tau_{max}} \right] \cdot 100\% \quad (4)$$

where  $\tau_{max}$  indicates the maximum value estimated for the ignition delay time of each investigated mixture, i.e., the IDT corresponding to the minimum temperature and pressure considered in this analysis.

## 3. Results and discussion

A preliminary analysis was devoted to the validation of the adopted procedure and model by comparing numerical estimation obtained in this work with experimental data of pure fuels (Figure 1, left) and mixtures

(Figure 1, right) retrieved in the literature (Petersen et al., 2007)(Huang and Bushe, 2006)(Gersen et al., 2012) under the operative conditions reported in the methodological section.

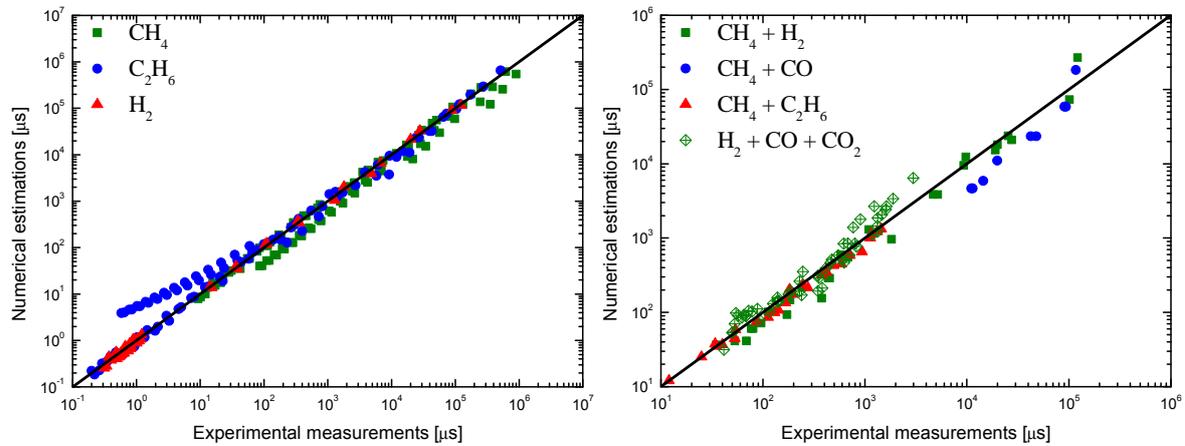


Figure 1: Comparison of ignition delay time data retrieved in the literature and estimated values for a wide range of conditions for pure methane, ethane, or hydrogen (left) and for bio-syngas representative mixtures (right).

It is worth noting that, excluding some of the ethane data at elevated temperature, i.e. low IDT, numerical estimations are fairly in agreement with the literature data presented in this work for pure species combustion in air. Confirming that the combustion core model included in KiBo is suitable to reproduce the chemistry of small radicals (i.e.,  $C_0 - C_1$ ) at the investigated conditions, as well. However, some discrepancies can be observed in the case of hydrogen and carbon monoxide additions at a temperature lower than 900 K at stoichiometric conditions, i.e., for high values of IDT. Under the studied conditions, it has been found that the addition of hydrogen and carbon monoxide to methane premixed flames at low temperatures increased ignition delay times in comparison with the pure methane case at the stoichiometric condition. On the other hand, almost negligible effects can be observed at high temperature, when more reactive compounds are added to methane. For these reasons, it is possible to conclude that hydrogen and carbon monoxide have a significant impact on the reaction pathway leading to the ignition of methane at low temperatures, exclusively. The proven accuracy of the detailed kinetic mechanism promotes the adoption of this model for further evaluation of the effect of the initial composition of bio-syngas mixtures on the overall reactivity. Starting from pure methane the empirical correlations calculated for the studied mixtures were reported in Table 2.

Table 2: The range of compositions analyzed in this work as a representative for bio-syngas mixtures.

Blends	$\beta$	$\alpha$	A [s]	Ea [J mol <sup>-1</sup> K <sup>1</sup> ]
CH <sub>4</sub>	0.15	0.31	$2.37 \times 10^{-3}$	180.70
CH <sub>4</sub> /H <sub>2</sub>	0.29	0.32	$4.64 \times 10^{-1}$	120.30
CH <sub>4</sub> /C <sub>2</sub> H <sub>6</sub>	-4.80	-0.58	$2.31 \times 10^{-3}$	139.10
CH <sub>4</sub> /CO	1.03	-0.60	$7.23 \times 10^{-2}$	143.10
CH <sub>4</sub> /CO <sub>2</sub>	-0.12	-0.02	$1.14 \times 10^{-1}$	108.60

Figure 2 shows the CR values with respect to temperature for different equivalent ratios and fuel compositions. Regardless of the equivalence ratio considered, similar trends can be observed. More specifically, either at a stoichiometric concentration ( $\varphi = 1.0$ ) or at lean fuel mixtures ( $\varphi = 0.5$ ) a very steep increase of CR with respect to the temperature up to values around 80% is first observed. In other words, the IDT is initially very sensitive to even a small variation of temperature towards lower values. This initial trend is then followed – again for both equivalence ratios – to a smoother increase, with less than a linear trend, for higher temperatures. This variation with respect to the temperature can be attributed to the migration from low temperature to high-temperature chemistry and is particularly relevant if considering the limited negative temperature coefficient behavior of methane-based mixture.

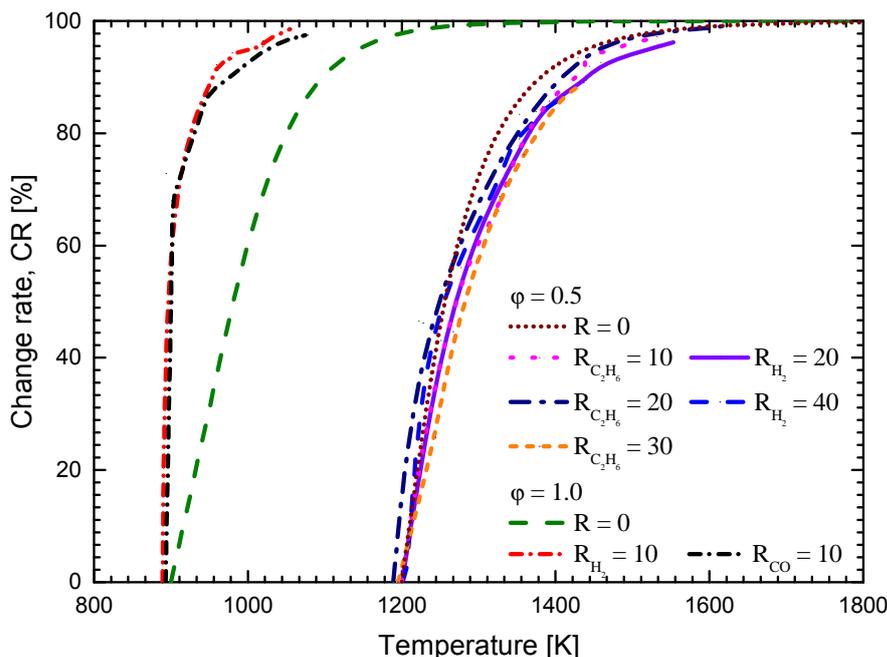


Figure 2: The effect of initial temperature on the changing rate (CR) of IDT for lean ( $\phi = 0.5$ ) and stoichiometric ( $\phi = 1.0$ ) compositions of premixed methane-air mixture added with hydrogen, ethane and carbon monoxide, as calculated by KiBo.

In this view, from Figure 2, few observations can be drawn. First, the addition of a relevant amount of ethane to methane slightly anticipates the transition from low- to high- temperature regimes for lean, premixed methane-air flames. Besides, the addition of hydrogen and carbon monoxide components at stoichiometric conditions results in considerably faster ignition at low temperatures than pure methane, and in similar values of CR when compared to each other. This phenomenon can be attributed to the similarity in composition and flame temperature for the two mixtures, which results in comparable ignition phenomena, together with the methane tendency to depreciate the addition of more reactive species up to 50% v/v when the elevated flame temperature is reached (Pio et al., 2020). Eventually, in contrast with the previous observation, the addition of hydrogen to the lean premixed methane-air mixture has a limited impact on CR. In the light of the renewed interests toward low-temperature combustion, the addition of hydrogen can be considered for engine optimization, in accordance with the suggestions proposed in the literature (Mariani et al., 2019). However, it should be carefully evaluated in turbines and combustor systems operating under lean compositions.

#### 4. Conclusions

This work evaluates the effect of initial conditions on the overall reactivity of biomass-derived gaseous fuel combustion by means of a detailed kinetic mechanism in terms of the Ignition Delay Time, which is an essential parameter for the design of combustion system. The proven accuracy with respect to experimental data from literature guarantees the correctness of the adopted approach for the bio-syngas mixtures containing elevated percentages of non-hydrocarbon species, as well. Hence, the adopted model allows for the accurate design, safety, and environmental analyses of power plants.

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