



# Article Chemical Modeling of Constant-Volume Combustion of the Mixture of Methane and Hydrogen Used in Spark Ignition Otto Cycles

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Abstract: This paper develops a chemical model for a closed constant-volume combustion of a gaseous mixture of methane and hydrogen. Since the combustion is strongly dependent on temperature, pressure and fuel composition, these had chosen the actual corresponding thermodynamic systems in this kind of combustion, i.e., spark ignition (SI) reciprocating engines, to assess combustion parameters and flue gas composition. The actual cycles impose extra restrictive operational conditions through the engine's-volumetric-compression ratio, the geometry of the combustion volume, the preparation method of the mixture of methane and hydrogen, (e.g., one fueling way of a homogeneous mixture obtained in a specific device or by two separate fueling ways for components), the cooling system and the delivered power. The chemical model avoided the unknown influences in order to accurately explain the influence of hydrogen upon constant-volume combustion and flue gas composition. The model adopted hypotheses allowing to generalize evaluated results, i.e., the isentropic compression and expansion processes, in closed constant-volume combustion caused by two successive steps that obey the energy and mass conservation laws, and the flue gas exhaust, which is also described by two steps, i.e., isentropic expansion through the flow section of exhaust valves followed by a constant pressure stagnation (this process, in fact, corresponds to a direct throttling process). The chemical model assumed the homogeneous mixtures of gases with variable heat capacity functions of temperatures, the Mendeleev-Clapeyron ideal gas state equation, and the variable chemical equilibrium constants for the chosen chemical reactions. It was assumed that the flue gas chemistry prevails during isentropic expansion and during throttling of exhaust flue gas. The chemical model allowed for evaluation of flue gas composition and noxious emissions. The numerical results were compared with those recently reported in other parallel studies.

**Keywords:** closed constant-volume combustion; Otto cycle; operational constraints; flue gas composition; harmful noxious

#### 1. Introduction

The combustion of mixtures of fossil fuel with hydrogen showed firstly that harmful emissions, namely carbon oxide (CO) and nitrogen oxides (NO<sub>x</sub>), are directly proportional to the hydrogen ratio in the fuel and to the flame temperature, as lower excess oxygen and/or higher preheating of the air before combustion as larger flame temperature. Therefore, the actual theoretical/experimental studies are developing means to reduce these emissions through the design of new combustion zones (e.g., moderate and intense low-oxygen dilution (MILD) combustion, and combustion inside a porous material), new methods to mix different fossil fuels with hydrogen (e.g., dual fueling in engines), new ideas regarding the pre- and postcombustion processing of working fluids (e.g., mixing blended fuel with hydrogen, and postcombustion catalytic treatment). The combustion



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**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). of a fossil fuel and hydrogen mixture in spark ignition engines has led to basic studies regarding the adaptation of actual spark ignition engines, and an increasing number are tackling specific research targets.

Ref. [1] simulated the laminar combustion rates of a mixture of hydrogen/methane/air with CHEMKIN PREMIX/GRI kinetic mechanism in NTP conditions. The authors considered large ranges for the equivalence ratio ( $\Phi$ ) and the fuel constituents, and obtained smaller laminar combustion reaction rates for mixtures than those averaged from the molecular composition. The simulation suggested that the chemical reactivity from lean to rich combustion is changing, very possibly caused by the fact that hydrogen radicals are initiating extra chemical reactions. The simulation of combustion velocities were transposed in a formula similar to Le Chatelier's Rule, with sound accuracy for lean mixtures, ranges of pressures up to 10 atm and of temperatures up to 400 K.

Ref. [2] involved distinguishing PIV (particle image velocimetry) events to study the transient reactive combustion flow of mixtures of hydrogen/methane/air through toroidal vortex structures with a fuel mixture range of 0–0.5. The results emphasized that the reactive flow had increased flow turbulence proportional to the hydrogen fraction and that the study captured the timing flame area and burning rate.

Ref. [3] used an analytical model for combustion in an Otto engine that uses hydrogenenriched fuels combustion modeling, correlated multi-zone combustion with an unique combustion model. While considering unburned fuel, the laminar flame speed was evaluated, and additionally, an improved flame shape was adopted.

Ref. [4] developed a prototype methanol–syngas engine that used dual fuel (gasoline and dissociated methanol) and found that the presence of hydrogen obtained by dissociation improved the efficiency, and increased the maximum pressure on the cycle and amplified the released heat in the recycling of exhaust heat.

Ref. [5] simulated the combustion of pure hydrogen using AVL Boost and compared it to the combustion of a water microemulsion (gasoline 90% + ethanol 8% +  $H_2O$  2%) and of pure gasoline, inside a stationary SI engine. These simulations comparatively revealed the characteristics regarding the pollutants and energy efficiency for all chosen fuels.

Ref. [6] experimentally explored the combustion of water-diluted ethanol/hydrogen in an SI engine. The injection of the water diluted ethanol during the intake process was combined with direct hydrogen injection during the compression stroke. The addition of hydrogen increases the maximum pressure and temperature of the cycle, reduces CO and hydrocarbons (HC), but increases  $NO_x$  emissions.

Ref. [7], based on AVL Boost program and some selected experiments, concluded that changing from a liquid fuel to a gaseous one assured complete combustion, the reduction in HC and CO emissions, the modification of the brake power, and improved efficiency with lean mixtures, but with an increase in NO<sub>x</sub>.

Ref. [8] aimed to find the optimal fuel blend for the combustion of ethanol/gasoline/ hydrogen mix in a SI engine. It was found that the presence of hydrogen led to a significant improvement in power and energy efficiency and combustion process, and reduced hydrocarbon emissions.

Ref. [9] studied the impact of dual fuel mixtures. They examined the combustion of mixed additional fuels (hydrogen, methane, butane, propane) with basic fuels (gasoline, iso-octane, benzene, toluene, hexane, ethanol, methanol) and evaluated the theoretical performance of an SI engine; the results emphasized that the additional fuels significantly modified the energy and exergy characteristics of the engine.

Ref. [10] defined the optimal fuel composition of a syngas/biogas/hydrogen mixture, for the control parameters of a spark-ignited engine, and thus, it was designed a flexible electronic control unit for the engine included in a solar-biomass hybrid renewable energy system, which is controlling the relation between the engine load, fuel rate, and air rate.

Ref. [11] investigated the consequences of the addition of hydrogen on gasoline-based SI engine performance with a volumetric compression ratio of 15; The best hydrogen

addition was for an equilibrium between the good burning efficiency and the increased heat loss.

Ref. [12] evaluated the use of  $CH_4$  and  $H_2/CH_4$  dual fuel in a turbocharged commonrail diesel engine at four loads and three compression ratios. The results showed that presence of  $H_2$  usually produced a larger in-cylinder pressure peak, extra noise, significant variations in ignition interval and combustion time, and earlier heat release, while dual-fuel operations produced higher total hydrocarbon (THC) and NO<sub>x</sub> but lower CO<sub>2</sub>.

Ref. [13] used a well-stirred reactor (WSR) to simulate the perfect MILD combustion under normal pressure/extended residence time. Chemkin Pro software and GRI Mech 2.11 were used for the comparison. The hydrogen addition enhanced the NNH route, decreased the prompt route and nitrous oxide intermediate route and reduced nitrogen oxide reburning, but the thermal NO<sub>x</sub> route was irrelevant due to the smaller O<sub>2</sub> mass ratio of 3% and 6%.

Ref. [14] used CFD-modeling and a chemical kinetics PDF model of turbulent combustion of the hydrogen-rich synthetic fuel for the simulations that were related to experimental data. For all synfuel mixtures, they obtained very low NO<sub>x</sub> emissions.

Ref. [15] studied the combustion (parameters, emissions) of a mixed gasoline/hydrogen fuel and its influence upon the lubricating process in a SI engine. They were considered four loads (25%, 50%, 75%, 100%) and three hydrogen concentrations (3%, 6%, and 9%). The injection of hydrogen slightly increased the combustion pressure and heat released. The hydrogen reduced CO and HC emissions, while smoke opacity worsened lubrication through oil kinematic viscosity, and increases the friction.

Ref. [16] studied the influence of hydrogen on the NO<sub>x</sub> formation during combustion in industrial furnaces. Experiments on a perfect stirred reactor (PSR) and a burner with laminar flame were compared to NO<sub>x</sub> evaluation accuracy through the known GRI and PG2018 mechanisms. The PG2018 mechanism is more accurate than the GRI 2.11 and GRI 3.0 mechanisms, especially when evaluating N<sub>2</sub>O-intermediate and NNH pathways. The experiments showed that the burner stabilized laminar flame and growth of hydrogen ratio, at a given temperature, induces a prompt NO<sub>x</sub> radical decrease and, an amplified NO<sub>x</sub> production via NNH and, a suppressed thermal NO<sub>x</sub>. Increased hydrogen ratio led suppressed N<sub>2</sub>O-intermediate pathway in the flame volume but enhanced one in the flue gas caused by the incremented H<sub>2</sub>O.

Ref. [17] is a review of the understanding of the relationship between composition/premixed fuel gas turbine combustion, stability/emissions systems, and hydrogenenriched syngas/natural gas. A comparison between syngas/conventional hydrocarbon chemicals, a survey of available technologies adaptable to syngas and hydrogen-rich fuels in large scale applications, and a review of numerical simulations for hydrogen enriched fuels combustion is also included.

Ref. [18] experimented and numerically evaluated the combustion of premixed propane/hydrogen/air ( $C_3H_8/H_2/air$ ) in porous media. The results showed that porous media based combustion of  $H_2$  assures stability and wide-ranging burning limits, while  $C_3H_8$  inhibit them, i.e., flame shape and location and temperature field. The combustion of  $H_2$  in porous media robustly improves the mean radiation temperature, but the  $C_3H_8$  fraction decreases it. The flue gas temperature in porous media combustion is lower than in free fires.

Ref. [19] includes correlated experiments on a heavy-duty single-cylinder SI engine fueled with H<sub>2</sub>, and 3D-CFD-RANS based on ECFM and sub-models simulations, to optimize the combustion process.; Direct injection and port fuel injection were selected to provide recommendations for homogeneous cylinder filling. The correlated studies emphasized the characteristics of NO<sub>x</sub> emissions and heat losses for selected experiments.

Ref. [20] used unsteady Reynolds averaged Navier–Stokes (URANS) for six simulations (various spark and injection timings) of flow through a large bore for direct hydrogen injection in an SI engine; the numerical simulations were compared to experimental data. The relationship between autoignition and spark timing and in-cylinder pressure and unburned fuel were revealed; zero-dimensional chemical simulations were used to accurately predict autoignition timing.

Ref. [21] tested gaseous fuels, including methane, carbon monoxide, hydrogen and their mixture, in a Volkswagen 1.4 L/SI engine. The engine has similar performances for constant  $\lambda = air/fuel$  ratio. The composition of the gaseous fuel significantly influence the optimum  $\lambda$  values; a simple zero-dimensional combustion model has been developed to explain qualitatively the trends induced by fuels.

Ref. [22] developed an one-dimensional combustion model of hydrogen-enriched natural gas (NG) in a SI engine. The viability of the model was proven by experiments. Combustion control strategies were verified by using various exhaust gas recirculation ratios (EGR) and hydrogen injection timings. The results revealed correlations between in-cylinder pressure peak and heat release rate, and average temperature of the hydrogen-enriched natural gas and port fuel injection and early or late direct injection. These correlations were used to find better possible volumetric efficiency, combustion efficiency, reduced NO<sub>x</sub> emissions, and identify the reciprocal influence ignition delay/EGR.

Ref. [23] utilized the response surface methodology (RSM) to find a gasohol/hydrogen mix and an engine rpm that would provide more efficient operation and reduced emissions. The analysis using a variance-assisted RSM model was used to evaluate specific fuel consumption, thermal efficiency and harmful emissions.

Ref. [24] experimentally studied the influences of spark timings, of compression ratios, of EGR values on the combustion of hydrogen and gasoline in an SI engine. Empirical correlations were found for ignition lag and combustion period as functions of compression ratio, equivalence ratio, and exhaust gas recirculation.

Ref. [25] used an in-house CFD code to produce accurate values of the indicated mean effective pressure, in a fraction of operational time, for the combustion of methane/hydrogen mixtures in an SI engine. The methodology of processing the results used numerical values from five successive cycles and transposed them in suitable relationships for main parameters as functions of a normalized distance, the distance within the computational cell, to the spark plug region. The methodology gave a smooth transition from the laminar to the fully turbulent burning regime.

Ref. [26] focused on SI dual-fuel combustion with an acetone–butanol–ethanol port injection and hydrogen direct injection, giving a stratified zone of the hydrogen-rich mixture around the spark plug. Various blends and spark timings were used to observe the effects of combustion and emissions on the test engine.

Ref. [27] used experiments and CFD simulations (developed in Converge CFD software) to observe the effect of enriching biogas with hydrogen on the combustion and on the emission for a single-cylinder, four-stroke, spark-ignition engine operated at the compression ratio of 10:1 and 1500 rpm. The results included peaks of in-cylinder pressure, COVIMEP, flame initiation, combustion durations, hydrocarbon, and NO<sub>x</sub> emissions.

Because all actual studies following the use of hydrogen in reciprocating engines were organized for limited experiments with imposed operational restrictive conditions, such as constant revolution per minute, constant power, specific cooling, accurate instrumentation, the research results are at this time somewhat poor and sometimes contradictory. This paper develops a pure chemical model for a closed constant-volume combustion of gaseous mixtures of methane and hydrogen used in Otto cycles for adopted simplifying hypotheses, actual volumetric compression ratio, isentropic compression and expansion processes, closed constant-volume combustion developed by two successive steps obeying the energy and mass conservation laws and, flue gas exhaust described also by two steps, i.e., an isentropic expansion through the flow section of exhaust valves followed by a constant pressure stagnation (this succession in fact corresponds to a throttling direct process). These simulations' restrictive conditions allowed for the generalized evaluation of all state parameters along the cycle, i.e., temperatures, pressures, and working fluid composition/pollutants. The numerical results were compared with those recently reported in other parallel studies.

# 2. The Approach of the Closed Constant-Volume Combustion in Otto Engine Cycles

#### 2.1. The Assumptions for the Otto Cycle

Let us suppose that the general basic Otto cycle, interacting with the environment by heat, mass and power transfers, see Figure 1. The engine cycle, used to realistically describe the constant-volume combustion of a homogeneous mixture of  $CH_4$  and  $H_2$  and to evaluate the flue gas composition and harmful emissions, consists of the following processes:

- 1–2: isentropic compression of homogeneous mixture CH<sub>4</sub>/H<sub>2</sub>/air prepared by a specific device;
- 2–3: closed constant-volume combustion;
- 3–4: isentropic expansion of flue gas;
- 4–5: exhaust of flue gas, assimilated via a throttling process (succession of 4–4t isentropic expansion through flow section of exhaust valves and 4t–5 constant pressure stagnation);
- 5–1: final constant-pressure exhaust of flue gas.



Figure 1. The basic Otto cycle.

#### 2.2. The Isentropic Compression of Homogeneous Mixture of CH<sub>4</sub>/H<sub>2</sub>/Air

Assumptions were made relating to the 1 kmole fuel that had a different mole composition and was mixed with air, causing different values of excess oxygen, see Figure 2:

- one kmole fuel with *x* kmole  $H_2$  and (1 x) kmole  $CH_4$  was considered;
- the air required for combustion was evaluated using the imposed hydrogen ratio in one kmole fuel, x, and excess oxygen, *exo*, respectively:  $(1 + exo) \cdot (2 1.5 \cdot x)$  kmole O<sub>2</sub> and  $3.7619 \cdot (1 + exo) \cdot (2 1.5 \cdot x)$  kmole N<sub>2</sub>;
- the imposed x and exo: x = (0, 0.25, 0.5, 0.75, 1), and exo = (0, 0.25, 0.5, 0.75, 1, 1.5, 2);
- the volumetric compression ratio:  $\pi_{12} = V_2/V_1 = 10$ .



Figure 2. The isentropic compression 1–2. O<sub>2min</sub> and N<sub>2min</sub> correspond to stoichiometric combustion.

The parameters for the state 2 were evaluated using Equations (1)–(3).

$$k_{12} = \frac{r_{CH4} \cdot (\#_{2,CH4} - \#_{1,CH4}) + r_{H2} \cdot (\#_{2,H2} - \#_{1,H2}) + r_{O2} \cdot (\#_{2,O2} - \#_{1,O2}) + r_{N2} \cdot (\#_{2,N2} - \#_{1,N2})}{r_{CH4} \cdot (\#_{2,CH4} - \#_{1,CH4}) + r_{H2} \cdot (\#_{2,H2} - \#_{1,H2}) + r_{O2} \cdot (\#_{2,O2} - \#_{1,O2}) + r_{N2} \cdot (\#_{2,N2} - \#_{1,N2})}$$
(1)

Isentropic compression with ending temperatures,  $T_2$  and  $T_1: T_2 = T_1 \cdot \pi_{12}^{k_{12}-1}$ ,  $T_1 = 298$  K (2)

Isentropic compression with ending pressures,  $p_2$  and  $p_1 : p_2 = p_1 \cdot \pi_{12}^{k_{12}}$ ,  $p_1 = 1$  bar (3)

where *r* is a mole fraction in the mixture  $CH_4/H_2/air$  (kmole/kmole); h = h(T) - h(298K) is a relative physical enthalpy in the mixture, see Table 1; and  $u = h - R \cdot (T - 298)$ , (kJ/kmole) is a relative internal energy in the mixture; R = 8.3145 kJ/kmole·K, is the universal constant of ideal gas.

# 2.3. The Closed Constant-Volume Combustion

The closed constant-volume combustion involves in two successive steps, see Figures 3 and 4.



'HHV + Physical enthalpy of intaking chemical species (state 2)

**Figure 3.** The first step of combustion giving the heat input for the second one.  $O_{2min}$  and  $N_{2min}$  are values for stoichiometric combustion. HHV, higher heating value.

The first step is conceived as a constant pressure cooling from  $T_2$  to reference temperature of 298 K followed by a combustion without dissociation, at constant pressure,  $p_2$ , and constant temperature,  $T_1$ , giving as a result the energy input for the second step, respectively the higher heating value (*HHV*), and the physical enthalpy of intaking chemical species (*ph*), see Figure 3.

	h=h(T)-h(298K); h is the Relative Physical Enthalpy of Gaseous Chemical Species; (kJ/kmole); $h=c0+c1\cdot T+c2\cdot T^2+c3\cdot T^3+c4\cdot T^4+c5\cdot T^5$ (kJ/kmole) for 298 K $\leq T \leq 5200$ K;									
	$h_{ m CH4}$ for 298 K $\leq$ $T$ $\leq$ 1500 K									
-	c0	c1	c2	c3	c4	c5				
h <sub>CO2</sub>	-10,295.73122	+29.18222805	+0.01976308361	-0.000006164587807	$+9.718495272 \times 10^{-10}$	$-5.984216612 \times 10^{-14}$				
h <sub>H2O</sub>	-7820.523838	+24.56140839	+0.006095193576	-0.000001576697822	$+2.155196747 \times 10^{-10}$	$-1.189998347  imes 10^{-14}$				
h <sub>O2</sub>	-8310.810038	+26.11440421	+0.006486554878	-0.000001879231979	$+3.125634850 \times 10^{-10}$	$-2.048055699  imes 10^{-14}$				
$h_{N2}$	-7820.523838	+24.56140839	+0.006095193576	-0.000001576607822	$+2.155196747 \times 10^{-10}$	$-1.189998347 \times 10^{-14}$				
h <sub>CO</sub>	-77,895.91761	24.23615845	+0.006957194766	-0.000002000452191	$+3.006868933 \times 10^{-10}$	$-1.79961500  imes 10^{-14}$				
h <sub>H2</sub>	-8523.602676	+28.58874847	-0.0002520099380	+0.000001072813673	$-2.405013187  imes 10^{-10}$	$+1.755178738 \times 10^{-14}$				
h <sub>OH</sub>	-8479.625232	+28.19400310	+0.0006776079283	$+7.234592056 \times 10^{-7}$	$-1.956721062  imes 10^{-10}$	$+1.522710549 \times 10^{-14}$				
h <sub>O</sub>	-6430.497036	+21.74597694	-0.0006119709133	$+1.784585133 \times 10^{-7}$	$-2.341992360  imes 10^{-11}$	$+1.452421376 \times 10^{-15}$				
$h_H$	-6191.086828	+20.77251773	+0.00001104663432	$-4.160102635  imes 10^{-9}$	$+7.310338752 \times 10^{-13}$	$+4.846517103  imes 10^{-17}$				
$h_N$	-6167.889202	+20.64973571	+0.0001887590700	$-9.970607532  imes 10^{-8}$	$+1.832411454 \times 10^{-11}$	$-2.236164634 \times 10^{-16}$				
h <sub>NO</sub>	-8047.826762	+25.12271666	+0.006900181303	-0.000002036851415	$+3.093429512 \times 10^{-10}$	$-1.856273997  imes 10^{-14}$				
h <sub>NO2</sub>	10,209.25264	+29.28985710	+0.01839187998	-0.000006044547788	$+9.772891559 \times 10^{-10}$	$-6.122580161  imes 10^{-14}$				
$h_{CH4}$	-8143.263322	+21.07695175	+0.01570851794	+0.00002221853471	$-1.604634302  imes 10^{-8}$	$+3.367601937 \times 10^{-12}$				

**Table 1.** Polynomials of physical enthalpy of chemical species participating in constant-volume combustion.



HHV + Physical enthalpy of intaking chemical species (state 2)

Figure 4. The second step of combustion consuming the heat released in the first one.

The chemical reactions pertaining to this first step are those of the direct oxidation of the fuel:

$$(1-x)CH_4 + 2\cdot(1-x)O_2 \to (1-x)CO_2 + 2\cdot(1-x)H_2O$$
(4)

$$xH_2 + 0.5 \cdot xO_2 \to xH_2O \tag{5}$$

The *HHV* was evaluated by the enthalpies of formation of involved chemical species,  $h_{f0}$ , see Table 2.

$$HHV = (1 - x) \cdot h_{f0,CH4} - (1 - x) \cdot h_{f0,CO2} - (2 - x) \cdot h_{f0,H2O} \text{ (kJ/kmole fuel)}$$
(6)

Table 2. Enthalpy formation of chemical species involved in constant-volume combustion.

	CH <sub>4</sub>	CO <sub>2</sub>	$H_2O$	H <sub>2</sub>	<b>O</b> <sub>2</sub>	$N_2$	CO	Н	0	Ν	ОН	NO	NO <sub>2</sub>
h <sub>f0</sub> (kJ/kmole)	-74,873	-393,522	-285,830	0	0	0	-110,527	+217,999	+249,170	+472,680	+38,897	+90,921	+33,100

The physical enthalpy, *ph*, of intaking chemical species was given by fictitious constant pressure cooling of the intaking gases up to reference temperature  $T_1$  = 298 K.

 $ph = x \cdot h_{2,H2} + (1 - x) \cdot h_{2,CH4} + (1 + exo) \cdot (2 - 1.5x) \cdot h_{2,O2} + 3.6719 \cdot (1 + exo) \cdot (2 - 1.5x) \cdot h_{2,N2}$ (kJ/kmole fuel) (7)

where the physical enthalpies of intaking gases correspond to  $T_2$ .

The second step of constant-volume combustion, 2i–3, consumes the energy released in the first step, *HHV* an *ph*, to finish the constant-volume combustion by a complex process of heating with dissociation of initial flue gas resulting from the first step, see Figure 4. The inlet chemical species have the temperature  $T_1$  and pressure  $p_2$ . The outlet temperature and pressure,  $T_3$  and  $p_3$ , were computed using the mass and energy conservation laws, and the Mendeleev–Clapeyron state equation.

The second step of combustion comprises the following dissociation and of recombination reactions of:

$$e \operatorname{CO}_2 \to e \operatorname{CO} + 0.5 \operatorname{e} \operatorname{O}_2 \tag{8}$$

$$0.5g H_2O \rightarrow 0.5g H_2 + g OH \tag{9}$$

$$f H_2 O \to f H_2 + 0.5 f O_2$$
 (10)

$$0.5h O_2 \to h O \tag{11}$$

$$0.5k N_2 \rightarrow k N$$
 (12)

$$0.5i H_2 \rightarrow i H \tag{13}$$

$$0.51 \text{ N}_2 + 0.5 \text{ O}_2 \rightarrow \text{i NO}$$
 (14)

$$0.5m N_2 + m O_2 \rightarrow m NO_2 \tag{15}$$

The mass balance equations include the below explained ones:

- four equations related to the balance of the kmole numbers of major chemical species, such as CO<sub>2</sub>, H<sub>2</sub>O, O<sub>2</sub>, and N<sub>2</sub>;
- eight equations interrelating all chemical species through chemical equilibrium relations;
- one mass balance for the whole process 2i 3.

The balance of the kmole numbers of major chemical species are given as:

$$a = (1 - x) - e$$
 (kmole CO<sub>2</sub>) (16)

$$b = (2 - x) - g - f$$
 (kmole H<sub>2</sub>O) (17)

$$c = exo(2 - 1.5x) + 0.5e + 0.5f - 0.5h - 0.5l - m \quad (kmole O_2)$$
(18)

$$d = 3.7619 \cdot (1 + exo) \cdot (2 - 1.5 \cdot x) - 0.5 \cdot k - 0.5 \cdot l - 0.5 \cdot m \quad (kmole N_2)$$
(19)

where e, f, g, h, i, k, l, m are the kmole involved in chemical reactions (8) to (15). For the chemical reaction  $\nu_A A + \nu_B B \rightarrow \nu_C C + \nu_D D$ , the equilibrium constant is

$$K = \frac{y_C^{\nu_C} \cdot y_D^{\nu_D}}{y_A^{\nu_A} \cdot y_B^{\nu_B}} \cdot P^{\nu_C + \nu_D - \nu_A - \nu_B}, \text{ where } P = \frac{\text{reaction pressure}}{\text{normal pressure (0.1 MPa)}}$$

The natural logarithms of chemical equilibrium constants for P = 1 were interpolated by polynomials of seventh order, see Table 3, using values from [28] (p. 773).

		-	_	_						
	$ln(K) = a0 + a1 \cdot T + a2 \cdot T^2 + a3 \cdot T^3 + a4 \cdot T^4 + a5 \cdot T^5 + a6 \cdot T^6 + a7 \cdot T^7$ for 500 K $\leq T \leq$ 3400 K, P=1									
	ln(K1)	ln(K2)	ln(K3)	ln(K4)	ln(K5)	ln(K6)	ln(K7)	ln(K8)		
a7	$+9.2326311289\times10^{-22}$	$+1.136595616\times 10^{-21}$	$+7.643759089 \times 10^{-22}$	$+8.166909930\times10^{-22}$	$+1.543529198\times10^{-21}$	$+7.070194312\times10^{-22}$	$+2.948541681\times10^{-22}$	$+1.070424351 \times 10^{-22}$		
<i>a</i> 6	$-1.469466515\times10^{-17}$	$-1.77695367  imes 10^{-17}$	$-1.219664280  imes 10^{-17}$	$-1.298258556  imes 10^{-17}$	$-2.454651317  imes 10^{-17}$	$-1.125159755  imes 10^{-17}$	$-4.688934093 \times 10^{-18}$	$-1.700672496  imes 10^{-18}$		
<i>a</i> 5	$+9.908436246 \times 10^{-14}$	$+1.173485363 \times 10^{-13}$	$+8.256023802 \times 10^{-14}$	$+8.743314794 \times 10^{-14}$	$+1.653766691 \times 10^{-13}$	$+7.586041432 \times 10^{-14}$	$+3.159040657 \times 10^{-14}$	$+1.144079969 \times 10^{-14}$		
<i>a</i> 4	$-3.683648801  imes 10^{-10}$	$-4.258599458  imes 10^{-10}$	$-3.081726001  imes 10^{-10}$	$-3.246702476  imes 10^{-10}$	$-6.143247539  imes 10^{-10}$	$-2.282012344  imes 10^{-10}$	$-1.173468673  imes 10^{-10}$	$-4.240167126  imes 10^{-11}$		
aЗ	$+8.221477783 \times 10^{-7}$	$+9.246236875\times10^{-7}$	+6.907189777 $\times ~10^{-7}$	$+7.238919496 \times 10^{-7}$	+0.000001370114593	$+6.294886934\times10^{-7}$	$+2.616956936\times10^{-7}$	$+9.424074844 \times 10^{-8}$		
a2	-0.001121518545	-0.001223384239	-0.0009467177073	-0.0009868881509	-0.001868142287	-0.0008592308402	-0.0003567351418	-0.0001278633183		
<i>a</i> 1	+0.9056894246	+0.9575982855	+0.7698066320	+0.7977691487	+1.509735517	+0.695832294	+0.2880804502	+0.1027180385		
<i>a</i> 0	-370.3187386	-385.6441663	-323.0833734	-330.5159532	-638.9027541	-289.1945752	-121.5994613	-59.57996704		

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The following are the equations interrelating all chemical species through chemical equilibrium relations:

$$\exp(\ln(K1)) = \frac{e^2 \cdot c}{a^2} \cdot P \text{ for Equation (8)}$$
(20)

$$\exp(\ln(K2)) = \frac{(f + 0.5g - 0.5i) \cdot g^2}{b^2} \cdot P \text{ for Equation (9)}$$
(21)

$$\exp(\ln(K3)) = \frac{(f + 0.5g - 0.5i)^2 \cdot c}{b^2} \cdot P \text{ for Equation (10)}$$
(22)

$$\exp(\ln(K4)) = \frac{h^2}{c} \cdot P \text{ for Equation (11)}$$
(23)

$$\exp(\ln(K5)) = \frac{k^2}{d} \cdot P \text{ for Equation (12)}$$
(24)

$$\exp(\ln(K6)) = \frac{i^2}{(f + 0.5g - 0.5i)} \cdot P \text{ for Equation (13)}$$
 (25)

$$\exp(\ln(K7)) = \frac{l^2}{d \cdot c} \text{ for Equation (14)}$$
(26)

$$\exp(\ln K8)) = \frac{m^2}{d \cdot c^2} \cdot \frac{1}{P} \text{ for Equation (15)}$$
(27)

The mass balance for the combustion step 2 full process of 2i - 3:

$$2 \cdot x + 16 \cdot (1 - x) + 32 \cdot (1 + exo) \cdot (2 - 1.5 \cdot x) + 120.3808 \cdot (1 + exo) \\ \cdot (2 - 1.5 \cdot x) = 44 \cdot a + 16 \cdot b + 32 \cdot c + 28 \cdot d + 28 \cdot e + 2 \cdot (f + 0.5 \cdot g - 0.5 \cdot i) \\ + 17 \cdot g + 14 \cdot k + h + 30 \cdot l + 46 \cdot m$$
(28)

The energy balance equation:

$$HHV + ph = \left[a \cdot \left(u_{f0,CO2} + u_{3,CO2}\right) - (1 - x) \cdot u_{f0,CO2}\right] + \left[b \cdot \left(u_{f0,H2O} + u_{3,H2O}\right) - (2 - x) \cdot u_{f0,H2O}\right] + c \cdot u_{3,O2} + d \cdot u_{3,N2} + e \cdot \left(u_{f0,CO} + u_{3,CO}\right) + (f + 0.5 \cdot g - 0.5 \cdot i) \cdot u_{3,H2} + g \cdot \left(u_{f0,OH} + u_{3,OH}\right) + h \cdot \left(u_{f0,O} + u_{3,O}\right) + i \cdot \left(u_{f0,H} + u_{3,H}\right) + k \cdot \left(u_{f0,N} + u_{3,N}\right) + l \cdot \left(u_{f0,NO} + u_{3,NO}\right) + m \cdot \left(u_{f0,NO2} + u_{3,NO2}\right)$$

$$(29)$$

The Mendeleev–Clapeyron state equation for gaseous mixtures:

$$p \cdot V = (\sum n_i) \cdot R \cdot T \xrightarrow{V=const.} \frac{p_3}{p_2}$$

$$= \frac{T_3}{T_2} \cdot \frac{(\sum n_i)_3}{(\sum n_i)_2} = \frac{T_3}{T_2} \cdot \frac{a+b+c+d+e+(f+0.5 \cdot g-0.5 \cdot i)+g+h+k+l+m}{x+(1-x)+(1+exo) \cdot (2-1.5 \cdot x)+3.8619 \cdot (1+exo) \cdot (2-1.5 \cdot x)}$$
(30)

#### 2.4. Isentropic Expansion 3–4

During isentropic expansion, see Figure 5, the chemistry of flue gas is also prevailing due to high temperatures and pressures, and therefore, the composition of flue gas is changing by variable temperature and pressure. This process was solved by defining a proper isentropic exponent quantifying the variable chemical composition of flue gas. The equations defining a reactive isentropic expansion allowed for the evaluation of the parameters of state 4. These parameters were evaluated through Equations (31)–(33) and examine the flue gas composition through two computational loops regarding the

relationship composition of temperature and pressure, which are similar to those in the case of constant-volume combustion, step 2.

$$\begin{aligned} \text{Isentropic exponent } k34 &= \frac{\Delta H34}{\Delta U34} \text{ where} \\ \Delta H34 &= \left[ a4 \cdot \left( h_{f0,C02} + h_{4,C02} \right) - a \cdot \left( h_{f0,C02} + h_{3,C02} \right) \right] + \left[ b4 \cdot \left( h_{f0,H20} + h_{4,H20} \right) - b \cdot \left( h_{f0,H20} + h_{3,H20} \right) \right] + \\ (c4 \cdot h_{4,O2} - c \cdot h_{3,O2}) + (d4 \cdot h_{4,N2} - d \cdot h_{3,N2}) + \left[ e4 \cdot \left( h_{f0,C0} + h_{4,C0} \right) - e \cdot \left( h_{f0,C0} + h_{3,C0} \right) \right] + \\ \left[ (f4 + 0.5 \cdot g4 - 0.5 \cdot i4) \cdot h_{4,H2} - (f + 0.5 \cdot g - 0.5 \cdot i) \cdot h_{3,H2} \right] + \left[ g4 \cdot \left( h_{f0,OH} + h_{4,OH} \right) - a \cdot \left( h_{f0,OH} + h_{3,OH} \right) \right] + \\ \left[ h4 \cdot \left( h_{f0,C02} + h_{4,O} \right) - h \cdot \left( h_{f0,O} + h_{3,O} \right) \right] + \left[ i4 \cdot \left( h_{f0,H} + h_{4,H} \right) - i \cdot \left( h_{f0,H} + h_{3,H} \right) \right] + \\ \left[ h4 \cdot \left( h_{f0,N0} + h_{4,N} \right) - k \cdot \left( h_{f0,N} + h_{3,N} \right) \right] + \left[ l4 \cdot \left( h_{f0,NO} + h_{4,NO} \right) - l \cdot \left( h_{f0,NO} + h_{3,NO} \right) \right] + \\ \left[ m4 \cdot \left( h_{f0,O2} + h_{4,O2} \right) - m \cdot \left( h_{f0,NO2} + h_{3,OO2} \right) \right] \\ \Delta U34 = \left[ a4 \cdot \left( u_{f0,CO2} + u_{4,CO2} \right) - a \cdot \left( u_{f0,CO2} + u_{3,CO2} \right) \right] + \\ \left[ b4 \cdot \left( u_{f0,H2O} + u_{4,H2O} \right) - b \cdot \left( u_{f0,H2O} + u_{3,H2O} \right) \right] + \left[ (f4 + 0.5 \cdot g4 - 0.5 \cdot i4) \cdot u_{4,H2} - (f + 0.5 \cdot g - 0.5 \cdot i) \cdot u_{3,H2} \right] + \\ \left[ g4 \cdot \left( u_{f0,OC} + u_{4,OO} \right) - e \cdot \left( u + u_{3,OO} \right) \right] + \left[ (f4 + 0.5 \cdot g4 - 0.5 \cdot i4) \cdot u_{4,H2} - (f + 0.5 \cdot g - 0.5 \cdot i) \cdot u_{3,H2} \right] + \\ \left[ g4 \cdot \left( u_{f0,OC} + u_{4,OO} \right) - g \cdot \left( u_{f0,OC} + u_{3,OO} \right) \right] + \left[ h4 \cdot \left( u_{f0,OC2} + u_{4,O} \right) - h \cdot \left( u_{f0,OC} + u_{3,OO} \right) \right] + \\ \left[ i4 \cdot \left( u_{f0,OH} + u_{4,OH} \right) - g \cdot \left( u_{f0,OH} + u_{3,OH} \right) \right] + \left[ h4 \cdot \left( u_{f0,OC2} + u_{4,OO} \right) - h \cdot \left( u_{f0,OC} + u_{3,OO} \right) \right] + \\ \left[ l4 \cdot \left( u_{f0,H} + u_{4,H} \right) - i \cdot \left( u_{f0,OH} + u_{3,HO} \right) \right] + \left[ m4 \cdot \left( u_{f0,NO2} + u_{4,NO2} \right) - m \left( u_{f0,NO2} + u_{3,NOO} \right) \right] + \\ \left[ l4 \cdot \left( u_{f0,NO} + h_{4,NO} \right) - l \cdot \left( u_{f0,H} + u_{3,HO} \right) \right] + \left[ m4 \cdot \left( u_{f0,NO2} + u_{4,NO2} \right) - m \left( u_{f0,NO2} + u_{3,NOO} \right) \right] \right] \end{aligned}$$

Isentropic compression ending temperatures,  $T_3$  and  $T_4$  $T_4 = T_3 \cdot \left(\frac{1}{\pi_{12}}\right)^{k_{34}-1}$ ,  $T_3$  previously computed, combustion step 2 (32)

Isentropic compression ending temperatures,  $p_3$  and  $p_4$  $p_4 = p_3 \cdot \left(\frac{1}{\pi_{12}}\right)^{k_{34}}$ ,  $p_3$  previously computed, combustion step 2 (33)



Figure 5. The isentropic reactive expansion 3–4.

#### 2.5. The Flue Exhaust Process 4-5

This process, See Figure 6, is considered as a throttling one, i.e., described by constant enthalpy. The ideal gas model was used and thus it is supposed that the temperature is almost constant because the composition variation of flue gas is not significant.



Figure 6. The flue gas exhaust process 4–5.

This simplified approach allowed for the evaluation of the final composition of state 5 only on the basis of the mass conservation law given by known values of chemical equilibrium constants for  $T_5 = T_4$  and  $p_5 = 1$  bar.

#### 3. The Numerical Solving and Results

#### 3.1. Numerical Solving

The isentropic compression can be solved through a proper mathematical procedure, the simplest of which is an iterative trial and error method and, is very easily resolved because the cylinder intaking fluid has a constant composition.

The closed constant-volume combustion, second step, must use two iterative loops, one for flue gas composition, and the other for final temperature and pressure. The first step considers the constant-volume heating of flue gas without dissociation in order to preliminarily determine the temperature and pressure of state 3 through the energy conservation law and the Mendeleev–Clapeyron state relation. These parameters allowed for the evaluation of the first computational composition of flue gas in state 3 by mass conservation law. This new flue gas composition in state 3 allowed for the re-evaluation of temperature and pressure of state 3 using the energy conservation law and Mendeleev–Clapeyron state equation. The iterative loops end when the difference between two successive steps causes an imposed error of computed parameters. The numerical results emphasized the behavior of variations in pollutants emissions (CO and NO<sub>x</sub>) and are in good qualitative agreement with other experiments that have been conducted

During expansion, the composition is changing, therefore, knowing the parameters of initial state 3, since they were previously computed, the parameters of state 4 were evaluated through Equations (31)–(33) by two computational loops regarding the relationship composition of temperature and pressure, similar procedure as in the case of constant-volume combustion, step 2.

#### 3.2. Numerical Results

The values of CO mole fractions in flue gas are included in Figure 7. The maximum mass, ppm, found in state 5 is around 170 ppm (mg CO/kg flue gas) for exo = 0 and x = 0.75. The throttling, which decreases the pressure, almost doubles CO emissions for stoichiometric combustion (exo = 0). All numerical results showed that the presence of hydrogen very slightly increases CO emissions.

The values of NO are in Figure 8. The numerical results showed two influences of hydrogen. The first influence gives NO mole fractions proportional to the mole ratio of hydrogen in fuel. The second influence highlighted a peak in these emissions for 0 < exo < 0.5.

The values of  $NO_2$  are given in Figure 9.  $NO_2$  emissions decrease as the hydrogen mole fraction in the fuel increases, even more in the case of combustion without hydrogen.

This is contrasting the emissions of NO. Similarly, NO<sub>2</sub> emissions have a peak depending

The cumulative values of  $NO_x$  are given in Figure 10. The numerical results showed similar influences of hydrogen as is in the case of NO emissions because the values of NO are much bigger than those of NO<sub>2</sub>. 0.020 CO in state 3 [mole fraction] 0.0008 CO in state 4 [mole fraction] 0.016 0.0006 0.012 x = 0.00= 0.00х x = 0.250.0004 x = 0.250.008 x = 0.50= 0.50 Х x = 0.750.0002 x = 0.750.004 0.0000 0.000 0.0 0.5 0.0 0.5 1.0 1.5 2.0 1.0 1.5 2.0**Oxygen Excess** Oxygen Excess (**b**) (a) 0.0016 CO in state 5 [mole fraction] 0.0012 = 0.00= 0.25x 0.0008 x = 0.50= 0.75x 0.0004 0.0000 0.0 0.5 1.0 1.5 2.0 Oxygen Excess (c)

on the oxygen excess.

**Figure 7.** (a) The CO mole fractions in state 3; function of excess of oxygen and x. (b) The CO mole fractions in state 4; function of excess of oxygen and x. (c) The CO mole fractions in state 5; function of excess of oxygen and x.



**Figure 8.** (a) The NO mole fractions in state 3; function of excess of oxygen and x. (b) The NO mole fractions in state 4; function of excess of oxygen and x. (c) The NO mole fractions in state 5; function of excess of oxygen and x.

The chemical modeling revealed that all interrelated parameters have variable values depending on the hydrogen mole fraction in the fuel and, on the excess of oxygen, both imposed for a certain combustion process. The numerical results included also the temperatures and pressures in states 2, 3, 4, 5, and moreover the mole composition which refers to the so-called minor chemical species, such as H<sub>2</sub>, OH, H, O, and N.

The presence of hydrogen slightly modified the temperatures and pressures of states 2, 3 and 4; however, the values of x and exo notably modified the mole composition of minor chemical species, see Figures 11–15.

State "3"



(c)

**Oxygen Excess** 

**Figure 9.** (a) The NO<sub>2</sub> mole fractions in state 3; function of excess of oxygen and x. (b) The NO<sub>2</sub> mole fractions in state 4; function of excess of oxygen and x. (c) The NO<sub>2</sub> mole fractions in state 5; function of excess of oxygen and x.

The mole fractions of  $H_2$  in state 5 are significant for x = 0 and, by comparison, are more diminished when the fuel contains hydrogen and besides very marginally changed by the excess of oxygen, see Figure 11.

The mole fractions of OH in state 5 are relatively small, and they increase when *x* increases and decrease when *exo* decreases, see Figure 12.

The mole fractions of H are directly proportional to *x* and inversely proportional to *exo*, and shows a maximum when 0 < exo < 0.5, see Figure 13.

The mole fractions of O and N are directly proportional to *x* and inversely proportional to *exo*. The O mole fractions are at the level of mass ppm, but those of N are below mass ppb (parts per billion), see Figures 14 and 15.



**Figure 10.** (a) The NO<sub>x</sub> mass ppm (mg/kg) in state 3; function of excess of oxygen and *x*. (b) The NO<sub>x</sub> mass ppm (mg/kg) in state 4; function of excess of oxygen and *x*. (c) The NO<sub>x</sub> mass ppm (mg/kg) in state 5; function of excess of oxygen and *x*.



**Figure 11.** The  $H_2$  mole fractions in state 5 (kmole/kmole).



Figure 12. The OH mole fractions in state 5 (kmole/kmole).



Figure 13. The H mole fractions in state 5 (kmole/kmole).



Figure 14. The O mole fractions in state 5 (kmole/kmole).



Figure 15. The N mole fractions in state 5 (kmole/kmole).

### 4. Critical Comparison with Results Reported Elsewhere

More reported numerically or experimentally obtained results were related to very specific restrictive conditions, e.g., power, *HHV*, imposed oxygen excess or equivalent ratio. Before any comparison, this paper's numerical results were rated using the Otto cycle parameters, i.e., the work delivered by one kmole fuel and the *HHV* of a kmole fuel, and a chosen oxygen excess corresponding to an equivalent ratio found in other studies were evaluated, see following Figures 16–22.



**Figure 16.** The useful power of Otto cycle. Wt =  $(H_3 - H_4) - (H_2 - H_1)$  (kWh/kmole fuel). H is the whole enthalpy of the working fluid related to 1 kmole fuel.



**Figure 17.** The possible power of Otto cycle supposing an energy efficiency of 0.35. Wr =  $0.35 \cdot HHV$  (kWh/kmole fuel).



Figure 18. The CO mass ppm rated to Wt (mg/kWh).



Figure 19. The CO mass ppm rated to Wr (mg/kWh).



Figure 20. The NO<sub>x</sub> mass ppm rated to Wt (mg/kWh).



Figure 21. The NO<sub>x</sub> mass ppm rated to Wr (mg/kWh).



Figure 22. The NO<sub>x</sub> mass ppm rated to *HHV* (mole/J).

The chemical modeling developed in this paper can be applied to the known thermodynamic parameters defining the chemistry of a combustion process, including: temperature of gaseous mixtures; pressure of gaseous mixtures; oxygen excess or equivalent ratio; chemical composition of reactants (i.e., chemical species fractions in the fuel and in the oxidant, i.e., air); and therefore, the initial composition of gaseous mixtures resulting from a combustion without dissociation, which is based on the known chemical composition of reactants and imposed oxygen excess. The correlated equations of mass and conservation laws and extra Mendeleev-Clapeyron ideal gas state equation, give the final temperature, pressure and composition of flue gas. The numerical results obtained were compared to other published results for similar restrictive conditions.

#### 4.1. Comparison 1

Reference [16] studied the chemistry of  $NO_x$  resulting from a constant pressure combustion of a natural gas/hydrogen mixture inside a perfect stirred reactor (PSR), various compositions and equivalence ratios. Because natural gas mainly has methane (above 95%), we adapted our model to this study's restrictive conditions, imposing identical equivalence ratio, temperature and pressure and considering methane as fuel, see Table 4.

	This paper	Ref. [16]	This Paper	<b>Ref.</b> [16]	This Paper	<b>Ref.</b> [16]	Ref. [16]
x	1	Figure 7	0.75	Figure 7	0.5	Figure 7	Figure 10
ехо	1.5	residence time 0.02 to 0.14 s	0.428571	residence time 0.02 to 0.14 s	0	residence time 0.02 to 0.14 s	residence time up to 3 s
T (K)	1700	1700	1700	1700	1700	1700	1700
p (bar)	1	1	1	1	1	1	1
Φ	0.8	0.8	0.8	0.8	0.8	0.8	0.8
NO <sub>x</sub> (mole/J)	$7.97  imes 10^{-8}$	$2  imes 10^{-10}$ to $1.35  imes 10^{-9}$	$2.77  imes 10^{-8}$	$3  imes 10^{-10}$ to $1.6  imes 10^{-9}$	$7.99  imes 10^{-10}$	$\begin{array}{c} 3.5 \times 10^{-10} \text{ to} \\ 1.7 \times 10^{-9} \end{array}$	$1 imes 10^{-7}$ to $4 imes 10^{-7}$

Table 4. Selected numerical results compared to those of Ref. [16].

The results reported by [16] are strongly influenced by the residence time, for a residence time up to 0.14 s, the numerical results of our chemical model are larger and for a residence time up to 3 s, our numerical results are smaller.

#### 4.2. Comparison 2

Reference [10] presents the results from research on the optimal fuel compositions and the control parameters of a spark ignition engine fueled with a syngas–biogas–hydrogen mix and working in a solar hybrid renewable energy system. We adapted our chemical model to the restrictive conditions identified in Tables 1 and 2, and Figure 6d from [10]. For a comparison, see Table 5.

**Table 5.** Selected numerical results compared to those of Ref. [10]. CA = 300°; blend 2; 40% syngas; 40% biogas; 20% hydrogen; and Figure 6a,b,d.

	This Model	Ref. [10]								
exo	0.952515		0.695605		0.481218		0.28866		0.171509	
(°CA)	-	300	-	300	-	300	-	300	-	300
T (K) (approx.)	1250	1250	1400	1400	1550	1550	1725	1725	1800	1800
p (bar) (approx.)	5	5	5	5	5.5	5.5	6	6	6.25	6.25
Φ	0.66	0.66	0.76	0.76	0.87	0.87	1	1	1.1	1.1
NO <sub>x</sub> (mg/kg)	299	50	622	280	1081	850	1688	1400	1676	1650

The compared results have the same magnitude and are in very good agreement for  $\Phi \ge 0.87$ .

#### 4.3. Comparison 3

Reference [14] performed CFD modeling of the combustion of hydrogen-enriched syngas fuel in a swirling flame, and a PDF combustion model with detailed chemical kinetics in a turbulent flames was used. The results of numerical simulations were compared with experimental data. This paper's chemical model adopted similar restrictive conditions regarding fuel mole composition ( $0.04 \text{ CH}_4$ ,  $0.8 \text{ H}_2$ ,  $0.02 \text{ N}_2$ , 0.04 CO,  $0.1 \text{ CO}_2$ ) from Figure 3 of ref. [14], and the approximated temperature that was based on the legend from Figure 5 of ref. [14], and on the scale of flame temperature from Figure 6 of ref. [14]. The comparison is included in Table 6.

	This	Paper	<b>Ref.</b> [14]		
Т (К)	1090	1100	~1100 K, Figures 5 and 6		
p (bar)	1	1	1		
exo	0.1	0.1	0.1		
NO <sub>x</sub> (mg/kg)	88.38	95.64	89 to 93		

Table 6. Selected numerical results compared to those of Ref. [14].

Although it is worth mentioning that Figures 5–8 from [14] are ambiguous and contain contradictory values, they do not correlate.

#### 4.4. Comparison 4

Reference [15] organized experimental investigations of a spark-ignition engine fueled by gasoline and hydrogen gas. Four engine load conditions (25%, 50%, 75%, and 100%) and three hydrogen gas mass concentration conditions (3%, 6%, and 9%) were defined for the study. On the basis of Figures 2d, 4, 7 and 9 from [15], they were approximated comparisons for similar restrictive conditions considering 100% load, i.e., in-cylinder pressure of about 4 bar at CA of 400°, combustion temperature of 1850 K to 1550 K for CA from 400° to 450°, and approximated two phase fuel composition with gasoline (0.85 C and 0.15 H<sub>2</sub> kg/kg) and with added extra 0.06 kg of H<sub>2</sub> gas. The compared results are included in Table 7. The mean specific fuel consume values, of 225.4 g/kWh, gave a specific engine power of about 3.5 kWh. The comparison is included in Table 7. Because the equivalent ratio is unknown in ref. [15], they were adopted the equivalence ratios of 0.8 and 1 and 1.2 and, evaluated the specific power on the basis of *HHV* for two phase mixture gasoline/hydrogen and supposing an energy efficiency of 0.35.

Table 7. Selected numerical results compared to those of Ref. [15].

	This Paper (Speci	<b>Ref.</b> [15]		
Φ	0.8	1	1.2	unknown
ехо	0.782094595	0.425676	0.188063	unknown
T (K)	1850	1850	1850	1850
p (bar)	4	4	4	4
NO <sub>x</sub> (mole/J)	4.91E-08	3.18E-08	7.73E-09	unknown
NO <sub>x</sub> (mg/kg)	3946.125733	2253.72	976.2172	unknown
NO <sub>x</sub> (ppmvd 15%O <sub>2</sub> )	2128.171993	4058.322	9521.072	unknown
CO (mg/kg)	28.47564843	77.82024	231.9931	unknown
NO <sub>x</sub> (g/kWh)	15.18732844	6.559401	2.385153	cca 6
CO (g/kWh)	0.109593321	0.226494	0.56682	cca 1.3

The values of NO<sub>x</sub> are very similar for  $\Phi = 1$ . The values of CO emissions in [15] are six times greater than those in the present paper's model for  $\Phi = 1$ .

#### 4.5. Comparison 5

A modern Siemens SGT5-8000H gas turbine engine was chosen to evaluate its CO and NO<sub>x</sub> emissions through flue gas. The chosen gas turbine has a compression ratio of 19.2:1, the exhaust gas temperature and pressure of 627 °C and 1 bar and respectively, it is fueled by natural gas. Values of NO<sub>x</sub>  $\leq$  25 ppm at 15% O<sub>2</sub> on fuel gas and CO  $\leq$  10 ppm at 15% O<sub>2</sub> on fuel gas were reported. For comparison we considered, as fuel, the Romanian natural gas that have 98% CH<sub>4</sub> and, it was imposed a very possible oxygen excess of x = 1.5. This paper's chemical model evaluated NO<sub>x</sub> and CO emissions at 627 °C and 1 bar:

- NO<sub>x</sub> 19.65 (mg/kg), 8.86 (ppmvd, 15% O<sub>2</sub>)
- CO  $1.4 \times 10^{-7}$  (mg/kg),  $7 \times 10^{-8}$  (ppmvd, 15% O<sub>2</sub>)

# 5. Discussions

Chemical modeling of constant-volume combustion of mixtures of methane and hydrogen used in spark-ignition Otto cycles revealed all the features regarding flue gas parameters, as temperature, pressure, composition, and extra, the magnitude of pollutants. These features are dependent on the amount of excess oxygen, which quantifies the engine load, and on the hydrogen content in the fuel.

The chemical model used the mass and energy balance equations applied to some cycles, delivering different cyclic power specified indirectly by oxygen excess, in order to find trustworthy numerical results. The gaseous chemical species were considered ideal gases with variable heat capacities depending on the temperature and with enthalpies depending also on the gaseous mixture composition, which are functions of temperature and pressure.

The different power was simulated by adjusting the oxygen excess, as it is occurs when the cyclic fuel consumption changes. The temperature ratio,  $T_3/T_2$ , on the closed constant-volume combustion was in the range of 4.65 to 2.26, corresponding to an *exo* from 0 to 2.

The inlet temperature of reactants,  $T_2$ , around 700 K  $\pm$  14 K, was slightly modified by the methane/hydrogen/air mixture composition. The energy contents of reactants, at this temperature, was quantified in the energy balance equation of combustion.

The numerical results have qualitative similarities to those of experimental studies regarding pollutants, such as CO and  $NO_x$ ; therefore, the reduction in these pollutants likely requires postcombustion devices/processes in order to decrease their levels; moreover, the chemical modeling revealed all constant-volume combustion's features related to a large domains of *x* and *exo*.

All numerical results showed that the presence of hydrogen very slightly increases CO emissions, and a noticeable variation is observed only for  $0 \le exo \le 0$ . For  $exo \ge 0.25$ , the influence of oxygen excess is insignificant. The throttling in 4–5, which decreases the pressure, almost doubles CO emissions for stoichiometric combustion (exo = 0). The maximum mass ppm found in state 5 is around 170 ppm (mg CO/kg flue gas) for exo = 0 and x = 0.75.

The numerical results showed two influences of hydrogen on the NO mole fractions. The first showed values directly proportional to the mole ratio of hydrogen in the fuel. The second influence highlighted a peak in these emissions for 0 < exo < 0.5. The influence of oxygen excess is following that of hydrogen.

NO<sub>2</sub> emissions decrease as the hydrogen mole fraction in the fuel increases. This is unlike the emissions of NO; however, similarly, NO<sub>2</sub> emissions have also a peak depending on oxygen excess.

The cumulative  $NO_x$  showed similar influences of hydrogen and oxygen excess as was in the case of NO emissions because the values of NO are higher than those of  $NO_2$ .

The presence of hydrogen very slightly modified the temperatures and pressures of states 2, 3 and 4.

The values of *x* and *exo* impressively modified the flue gas mole fractions of minor chemical species The mole fractions of  $H_2$  in state 5 are significant for x = 0 and most diminished when the fuel contains hydrogen, x > 0, and there are marginally influences by *exo* for all scrutinized domain.

The mole fractions of OH in state 5 are relatively small. They increase when *x* increases, and they decrease when *exo* increases.

The mole fractions of H are directly proportional to *x*, inversely proportional to *exo*, and have a maximum for  $0 \le exo \le 0.5$ .

The mole fractions of O and N are directly proportional to *x* and inversely proportional to *exo*. The O mole fractions are at the level of mass ppm, but those of N are below mass ppb (parts per billion).

The numerical modeling showed that the chemical reaction 10 is redundant when x > 0, i.e., it was giving values that were either complex or below zero for chemical species H<sub>2</sub> resulting from this dissociation reaction. This indicates that the main chemical reaction producing H<sub>2</sub> by dissociation is given by Equation (9).

It can be stated that as larger the hydrogen ratio in the fuel as lower the CO<sub>2</sub> dangerous emissions, not necessary any demonstration.

# 6. Conclusions

The paper presents a chemical model for the closed constant-volume combustion of gaseous mixtures of methane and hydrogen using spark-ignition reciprocating engines in order to evaluate the combustion parameters and exhaust flue gas composition. The chemical model avoided unknown influences in order to accurately explain the influence of hydrogen on constant-volume combustion and flue gas composition. The model adopted simplifying hypotheses, i.e., isentropic compression and expansion processes, in closed constant-volume combustion caused by two successive steps obeying the energy and mass conservation laws, and flue gas exhaust, which was also described by two steps, i.e., isentropic expansion through the flow section of exhaust valves followed by constant pressure stagnation (this process, in fact, corresponds to a direct throttling process).

The chemical model assumed the homogeneous mixtures of gases have variable heat capacity functions of temperatures, the Mendeleev–Clapeyron ideal gas state equation, and the variable chemical equilibrium constants for the chosen chemical reactions.

It was assumed that the flue gas chemistry prevails during isentropic expansion and flue gas exhaust.

The chemical model allowed for the evaluation of flue gas composition and for noxious chemical species magnitude after combustion, i.e., states 3, 4, and 5. The chemical modeling developed in this paper can be applied to the known thermodynamic parameters defining the chemistry of a combustion process, including: temperature of gaseous mixtures; pressure of gaseous mixtures; oxygen excess or equivalent ratio; chemical composition of reactants (i.e., chemical species fractions in the fuel and in the oxidant); initial composition of gaseous mixture resulting from a combustion without dissociation which are based on the known chemical composition of reactants and imposed oxygen excess.

This model might have one dimension (known *T*, *p*, and  $exo/\Phi$ , unknown composition) solved only on the basis of the mass conservation law, two dimensions (known either *T*, *p*, unknown  $x/\Phi$  and composition; known *T*,  $x/\Phi$  unknown *p* and composition; or known *p*,  $x/\Phi$ , unknown *T* and composition) solved by uniting the mass and energy conservation laws, and three dimensions (known  $x/\Phi$ , unknown *T*, *p* and composition, as is in this paper) solved by uniting the mass and energy conservation laws in successive computing loops.

It might be applied either for steady-state processes (e.g., constant pressure combustion) or non-steady-state processes, as it was developed in this paper, on the basis of the appropriate energy and mass conservation laws. In last case, the chemical modeling offers a "time or space based film" of the process.

Mixtures of liquid and gaseous fuels might also be involved if the first step (see Section 2.3) of combustion can be solved, i.e., if *HHV* and *ph* and chemical species resulting from a combustion without dissociation were to be evaluated.

The chemical model might be improved by taking into consideration new chemical reactions, with known chemical equilibrium constants, in NO<sub>x</sub> and CO production, and, it might be modified based on the "residence" time in a known "state" (given *T* and *p* and initial composition). If the residence time is shorter than the chemistry time, then the results of a pure chemical model might be larger or smaller than those that are experimentally found, depending on the variation speed of temperature and pressure, e.g., the quenching of chemical reactions. If the residence time is longer than the chemistry time, it is very possible that the pure chemical model might give reliable results. The influence of residence time is not well known because there are not many congruent studies. For instance, in SI engines, the revolution per minute might affect the noxious emissions even if other restrictive constant conditions are imposed. In spite of its assumed limitations, a pure chemical model is very useful in offering, at least primarily, qualitative images and/or films regarding combustion processes.

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