REPUBLIQUE ALGERIENNE DEMOCRATIQUE ET POPULAIRE
MINISTERE DE L'ENSEIGNEMENT SUPERIEUR ET DE LA RECHERCHE SCIENTIFIQUE
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INSTITUT DES SCIENCES ET TECHNOLOGIES
DEPARTEMENT DE TECHNOLOGIE

# MEMOIRE

En vue de l'obtention du diplôme de **Master** en :
**Génie Mécanique**
*Option* : **Énergétique**

**Intitulé :**

# A STUDY OF ONE-DIMENTIONAL LAMINAR PREMIXED FLAME OF METHANE HYDROGEN MIXTURE WITH PYTHON

**Présenté par:**

- **BENAYACHE MOHAMMED HICHEM**
- **KOUDACHE FAROUK**

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| | | | |
|---|---|---|---|
| AMEUR Houari | Pr | Centre Universitaire Naâma | Président |
| NAIMA Khatir | MCA | Centre Universitaire Naâma | Encadrant |
| KAID Noureddine | MCA | Centre Universitaire Naâma | Examinateur |

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# Abstract

The laminar flame velocity is an important physical quantity to measure since it provides essential data on the fuel's reactivity, diffusivity, and exothermicity. It's also one of the parameters used to create and validate both the kinetic chemical mechanisms as well as turbulent models , despite the fact that this physical quantity has been the focus of countless experimental research for decades, there is still a gap in our understanding of multi-component fuels and effect of the premixed mixtures on the laminar flame velocity , in this study a laminar premixed flame of methane-hydrogen was studied in ambient temperature and pressure ,Cantera software with Jupyter notebook interface , and GRI-Mech 3.0 chemical reaction mechanism was used to simulate and calculate the laminar flame speed with different hydrogen fractions ( 0%,5%,10%,15% ,30%,50%), result have been discussed and compared and how increasing hydrogen fractions effect increase flame speed of the reaction , and how it effect the components production by decreasing the amount of $CO_2$ .

# Resumé

La vitesse de la flamme laminaire est une quantité physique importante à mesurer car elle fournit des données essentielles sur la réactivité, la diffusivité et l'exothermie du combustible. C'est également l'un des paramètres utilisés pour créer et valider les mécanismes chimiques cinétiques ainsi que les modèles turbulents, malgré le fait que cette quantité physique a été le centre d'innombrables recherches expérimentales depuis des décennies, il y a encore une lacune dans notre compréhension des combustibles multi-composants et l'effet des mélanges prémélangés sur la vitesse de flamme laminaire, dans cette étude une flamme prémélangée laminaire de méthane-hydrogène a été étudiée à température et pression ambiantes, le logiciel Cantera avec l'interface Jupyter notebook, et GRI-Mech 3. 0 a été utilisé pour simuler et calculer la vitesse de la flamme laminaire avec différentes fractions d'hydrogène (0%, 5%, 10%, 15%, 30%, 50%), les résultats ont été discutés et comparés et comment l'augmentation des fractions d'hydrogène a pour effet d'augmenter la vitesse de la flamme de la réaction, et comment elle affecte la production de composants en diminuant la quantité de $CO_2$.

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# List of Abbreviations

| | |
|---|---|
| A | Area |
| cp | Specific heat |
| d | Quenching distance |
| $D_{ij}$ | Multi component diffusion coefficient |
| $D_i^T$ | Thermal diffusion coefficient |
| $\mathcal{D}_{ij}$ | Binary diffusion coefficient |
| E | Total Energy |
| EA | Percentage excess air |
| $E_A$ | Activation energy |
| $E_{ign}$ | Minimum ignition Energy |
| (Fuel/Air) or FAR | Air–fuel ratio |
| H | Enthalpy |
| $\bar{h}_f^o$ | Enthalpy of formation |
| HHV | Higher heating value |
| k | Thermal conductivity |
| L | Slot width |
| LHV | Lower heating value |
| Le | Lewis numbers |
| m | Mass |
| $\dot{m}$ | Mass flowrate |
| $\dot{m}''$ | Mass flux |
| $\dot{m}'''$ | Volumetric mass production rate |
| $\dot{m}_i^m$ | Mass production rate of species i |
| MW | Molecular weight |

| | |
|---|---|
| n | Number of moles |
| u | Nusselt number |
| P | Pressure |
| Q | Heat |
| $\dot{Q}$ | Heat transfer rate |
| $\dot{Q}'''$ | Volumetric energy generation rate |
| R | Radius (m) or specific gas constant |
| $R_u$ | Universal gas constant |
| $Re_d$ | Reynolds number |
| s | Entropy |
| $S_L$ | Laminar flame speed |
| t | Time |
| T | Temperature |
| u | Internal energy |
| U | Total internal energy |
| v | Velocity of the unburned mixture |
| V | Volume |
| W | Work |
| $\dot{W}$ | Instantaneous rate of work |
| x | Distance |
| X | Mole fraction |
| Y | Mass fraction |

## Greek symbols:

| | |
|---|---|
| $\alpha$ | Thermal diffusivity |
| $\beta$ | Pressure exponent |
| $\Upsilon$ | Temperature exponent |

| | |
|---|---|
| $\delta$ | Flame thickness |
| $\Delta h_c$ | Heat of combustion |
| $\upsilon$ | Mass oxidizer-to-fuel ratio |
| $\rho$ | Density |
| $\phi$ | Equivalence ratio |
| $\dot{\omega}$ | Species production rate |

## Subscripts:

| | |
|---|---|
| ad | Adiabatic |
| b | Burned gas |
| cond | Conduction |
| crit | Critical |
| dil | Diluent |
| F | Fuel |
| i | ith species prod |
| Max | Maximum |
| Min | Minimum |
| Ox | Oxidizer |
| prod | Product |
| reac | Reactants |
| stoich | Stoichiometric |
| ref | Reference state |
| u | Unburned gas |

# Acknowledgements

Covid-19 disconnected us from our lives , Separated us and forced us to focus on our basic needs we took for granted ,food, water, medical care power, transportation and public Safety in this moment we THANK all the healthcare workers who fought with the virus to save lives , worked silently to protect us with courage and determination, to unsung heroes who helped us put food on the table , who kept clean water flowing who kept the power on at home and where it's needed , to our families , friends and lovers , Thank you very much , May you all stay forever young…

We dedicate this work to those who lost their lives to covid, we will always remember you ….

# Chapter 1: INTRODUCTION

## 1.1 BACKGROUND

When early humans discovered how to make fires, life got substantially simpler in a variety of ways, our ancestors relied on relatively simple types of energy: human muscle, animal muscle, and the combustion of biomass such as wood or crops. since than Combustion, fire, and flame are determined and speculated concerning from earliest times. each civilization has had its own rationalization for them.

Energy has evolved into a critical resource for human life. Primitive people relied on easily accessible timber to provide their heating, cooking, and other fundamental requirements

The Industrial Revolution revolutionised living in general from about 1750 to 1850. It was a critical phase in human history. During that period, factories were created to mass-produce items such as textiles, iron, and chemicals. The steam engine, which could perform more labour than humans or animals, was created, and canals and railways were created to carry commodities and materials for industry.

with technological advances in coal mining, coal, which had higher energy density as highly, The Industrial Revolution increased demand for coal which was used to power new equipment such as the steam engine.

Because of the increased demand for coal, miners were forced to go to increasingly perilous, dark, and heated depths below. The chance of tunnel collapse is one of the risks of mine operation. Another is the often-lethal trapped gas emissions that posed a danger to the miner’s life.

The miners were fully aware of fire-damp gas, which was mostly composed of methane. Because it is very combustible, even contact with a candle light would result in enormous explosions.

This hazards that inspired scientists for an early development of flame theory, in 1815, a mining explosion in the North of England motivated studies into the limits of flammability, the ignitability of various heat sources, and flame quenching at solid surfaces, all of which led to the creation of the safety lamp.

Daimler created the internal combustion engine in 1886, causing a surge in demand for oil and gas as efficient energy sources. Progress in geological theory, as well as drilling, completion, and refining technology, led a significant rise in oil and gas output. As a result, the proportion of oil and gas in the primary energy mix increased significantly, reaching more than 50% in 1965. These energy resources replaced coal as the largest energy in the world.

Since then, regardless the considerable progress of the renewable energies' development, the hydrocarbons are and will be the primary source of energy for the current time specially in transport field (airplanes, cars ...).

Biomass-derived fuels have received a lot of interest in recent years as viable replacements to petroleum-based fuels because of its renewability beside that, they shown to be sustainable and less harmful to the environment.

The combustion of this useful fuels is very complicated due to their variable and diverse chemical structure, it is critical to develop precise comprehensive kinetic models not only for these multi-component fuels, but also for diverse classes of molecules that play a vital part in their creation and consumption in flames, in order to comprehend the related combustion characteristics for such fuels.

Surrogate mixtures of pure hydrocarbon molecules may be used to simulate the physical and chemical properties of realistic fuels, which is a valuable strategy in creating precise kinetic processes for complicated fuels. its fidelity is directly dependent not only on the correctness of the pure compound models, but also on the ability to reproduce the global flame characteristics of realistic fuels. The associated kinetic schemes must then be created and verified for a wide variety of operating circumstances, represented in terms of equivalency ratio, pressure, and temperature.

In general, kinetic systems are validated using ignition delays time, species profiles, and flame speed data.

The laminar flame speed $S_L^0$ is a fundamental flame property which represent the rate where fresh gases are consumed via flame front considering a 1D unstretched propagating planar premixed flame, it depends only on the fuel/air mixture and its initial thermodynamic conditions: pressure, temperature and equivalence ratio.

Because of the importance of $S_L^0$ in kinetic model development and high-pressure combustion, there has been a surge in interest in measuring laminar flame speed in recent years. Many experimental approaches have been developed within this context: the steady burner-stabilized flames, the steady stagnation-type flames and the unsteady spherically expanding flames.

## 1.2 PRORBLEM STATEMENT

In this day's scientist been looking for a source of energy highly available and not harmful to the environment beside renewable energies, hydrogen been in the frame for past years to replace or get mixed with hydrocarbons so how this process works? How effect the performance and environment? all this question with be answered in details for a better understanding by doing a study on laminar premixed flame of methane with different fractions of hydrogen by doing a numerical approach using Cantera, and analysing the result and see the effect of different hydrogen fractions on laminar flame speed

## 1.3 THESIS STRUCTURE

This study consists of five chapters

***Chapter 2***

We have a brief theoretical approach of the thermodynamics of combustions

***Chapter 3***

A bibliographic research about hydrogen and its different properties, sources, uses and storage

***Chapter 4***

In first part we have general definitions about flame, laminar flame speed and other terms related to it

Second part we have a mathematical description of laminar flame speed

Third part we have a numerical approach of laminar premixed flame

***Chapter 5***

We gather the data simulations of multiple reactions in graphs, we discussed the result and make a conclusion about our simulation

***Chapter 6***

We will have a general conclusion and some answer for a questions

# Chapter 2: THERMODYNAMICS OF COMBUSTION

in this chapter, we talk about the thermodynamic concepts that are important in the study of combustion starting with the properties of mixtures and the 1st law of the thermodynamics passing by the combustion stoichiometry of the reactant and products mixtures. we next focus on thermodynamic topics related specifically to combustion and reacting systems as heating values as lower heating value (LHV)/ higher heating value (LHV) and the enthalpy of formation etc. The literature review chapter can be arranged in terms of the questions to be considered or objectives/purposes set out in the Introduction chapter.

## 2.1 PROPERTIES OF MIXTURES

Internal energy, u, enthalpy h, specific heat cp, and other quantities are used to characterize the thermal properties of a pure material. Because combustion systems are made up of a variety of gases, the thermodynamic characteristics of a mixture are the result of a combination of the attributes of all of the separate gas species. [1] . For gaseous mixtures, the ideal gas law is assumed, allowing the ideal gas relations to be applied to each gas component. Where ideal gas law relates pressure, volume, and absolute temperature:

$$pv = nRT \tag{2-1a}$$

$$pv = mRT \tag{2-1b}$$

$$pv = \rho RT \tag{2-1c}$$

where n is the number of moles of species and *R* is related to the universal gas constant *Ru* (= 8315 J / kmol-K) and *m* is the total masse of the system.

Where,

$$n = \sum_{i=1}^{k} n_i \tag{2-2a}$$

And

$$m = \sum_{i=1}^{k} m_i \tag{2-2b}$$

where $i = 1, 2\ldots. k$. By definition.

Two important and useful concepts used to characterize the composition of a mixture are the constituent mole fractions and mass fractions. Consider a multicomponent mixture of gases composed of n1 moles of species 1, n2 moles of species 2, etc. The mole fraction of species $i$, $x_i$, is defined as the fraction of the total number of moles in the system that are species $i$; i.e.,

$$x_i = \frac{n_i}{n} \tag{2-3a}$$

and the same with the masse

$$y_i = \frac{m_i}{m} \tag{2-3b}$$

Where

$$\sum_{i=1}^{n} x_i = 1 \quad \text{and} \quad \sum_{i=1}^{k} y_i = 1 \tag{2-3c}$$

the internal energy per unit mass of a mixture, u, is determined by summing the internal energy per unit mass for each species weighted by the mass fraction of the species.

$$u = \frac{U}{m} = \frac{\sum_i m_i\, u_i}{m} = \sum_i y_i\, u_i \tag{2-4}$$

where U is the total internal energy of the mixture and $u_i$ is the internal energy per mass of species $i$. Similarly.

enthalpy per unit mass of mixture is

$$hi = \sum_i y_i \, h_i \tag{2-5}$$

and specific heat at constant pressure per unit mass of mixture is

$$cp = \sum_i y_i \, cp \tag{2-6}$$

A molar base property, often denoted with a ^ over bar, is determined by the sum of the species property per mole for each species weighted by the species mole fraction, such as internal energy per mole of mixture

$$\hat{\mathrm{u}} = \sum_i x_i \, \hat{\mathrm{u}}_i \tag{2-7}$$

enthalpy per mole mixture

$$\hat{\mathrm{h}} = \sum_i x_i \, \hat{\mathrm{h}}_i \tag{2-8}$$

and entropy per mole of mixture

$$\hat{\mathrm{s}} = \sum_i x_i \, \hat{\mathrm{s}}_i \tag{2-9}$$

with constant specific heats during a thermodynamic process, changes of energy, enthalpy, and entropy of an individual species per unit mass are

$$\Delta u_i = c_{v,i}(T_B - T_A) \tag{2-10a}$$

$$\Delta h_i = c_{p,i}(T_B - T_A) \tag{2-10b}$$

$$\Delta \hat{\mathrm{s}}_i = c_{p,i} \ln \frac{T_B}{T_A} - R_i \ln \frac{P_{i:B}}{P_{i:A}} \tag{2-10c}$$

$P_i$,1 and $P_i$,2 are the partial pressures of species *i* at states A and B. $R_i$ is the gas constant for species $i$ (universal gas constant/molecular mass of species $i$, $Ri = {}^{\mathrm{R_u}}/_{\mathrm{M_i}}$ ).The overall change of entropy for a combustion system is

$$\Delta S = \sum_i m_i \, \Delta s_i \qquad (2\text{-}11)$$

## 2.2 THE $1^{ST}$ LAW OF THERMODYNAMIC

this principle is often referred to us as conservation of energy law, an isolated system cannot exchange energy or matter with the surrounding. this law tells us that the energy can be converted from one to and other but it cannot be created or destroyed. When a chemical system changes form a state to another the net transfer of energy to its surrounding must be balanced by a corresponding change in the internal energy of the system [2]

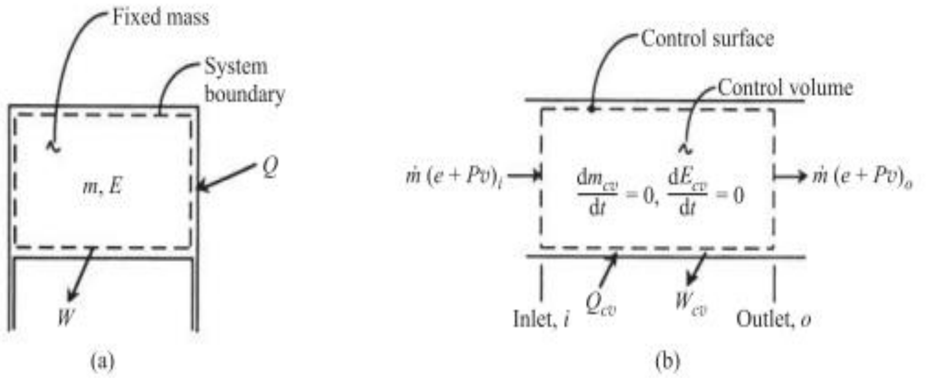


Figure 2-1.Schematic of fixed-mass system with moving boundary above piston. (b) Control volume with fixed boundaries and steady flow

if the system starts in state A to a state B, we write

$$\Delta E = E_B - E_A = Q + W \qquad (2\text{-}12)$$

Where $\Delta E$ is the change in the total energy from state A to B and Q is the heat added to the system between the 2 states and W is the work done by the system on surrounding between the 2 states [1].

The system energy is a state variable and, as such, $\Delta E$ does not depend on the path taken to execute a change in state. Equation can be converted to unit mass basis or expressed to represent an instant in time. These forms are

$$q - w = \Delta e = e_B - e_A \qquad (2\text{-}13a)$$

And

$$\dot{Q} - \dot{W} = {}^{dE}/_{dt} \tag{2-14}$$

Where $\dot{Q}$ is the Instantaneous rate of heat transferred into system and $W^{\cdot}$ is the Instantaneous rate of work done by system, or power and ${}^{dE}/_{dt}$ is the Instantaneous time rate of change of system energy.

Or we can write,

$$\dot{q} - \dot{w} = {}^{de}/_{dt} \tag{2-15}$$

where lowercase letters are used to denote mass-specific quantities [1]

## 2.3 COMBUSTION STOICHIOMETRY

The word stoichiometry is derived from the Greek "sticheron", meaning element. Most practical combustion processes occur when a fossil fuel or fossil-derived fuel burns with the oxidizer, air. The majority of these fuels contains only the elements carbon, hydrogen, oxygen, nitrogen, and sulphur. The aim of stoichiometry is to determine exactly how much air must be used to completely oxidize the fuel to the products carbon dioxide, water vapor, nitrogen, and sulphur dioxide. This does not imply that combustion is necessarily complete in any specific practical device. Nevertheless, a stoichiometrically correct mixture of fuel with air is defined as one that would yield exactly the products listed above and has no excess oxygen if combustion was complete. Figure 2-2 represents a combustion system with a complete combustion of methane with air (oxygen + nitrogen, as reactants), to form carbon dioxide, nitrogen and water (as products) [3]

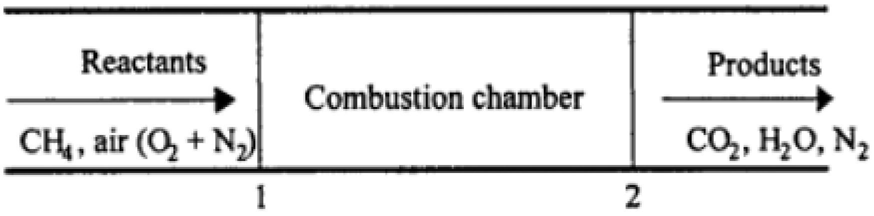


Figure 2-2.Complete combustion oh CH4 and air

a balanced stoichiometric relationship between methane (as fuel) and air (as oxidizer) With the assumption of complete combustion may be expressed by the equation:

$$CH_4 + 2\left(O_2 + \frac{79}{21}N_2\right) \rightarrow CO_2 + 2H_2O + 2 \times 3.76\ N_2$$

This equation describes the breakdown of the bonds between the atoms (or elements) forming the molecules of methane and oxygen, and their re-arrangements to construct molecules of carbon dioxide and water. The chemistry would be unchanged by the inert diluent nitrogen. The coefficients in the equation are determined from considerations of atom conservation. The coefficients in the equation are for the chemically correct, or stoichiometric, proportions of reactants with no excess fuel or oxidant. The coefficients in a chemical equation are more usually regarded as the number of kmoles of substance taking part in the reaction. Where all the substances taking part in a chemical reaction may be treated as ideal gases, the coefficients in the chemical equation may be alternatively considered as the volumetric proportions, since at a fixed temperature and pressure a kmole of any ideal gas will occupy the same volume.  The stoichiometric air-methane ratio, AFRv, by volume in the equation is [3]:

$$AFR_v = \frac{2(1 + 3.76)}{1} = 9.52$$

## 2.4 NON-STOICHIOMETRIC MIXTURE

Having considered above, the complete combustion of stoichiometric mixtures, it is necessary now to describe the lean and rich mixtures. The terms lean (or weak) and rich are used where, respectively, oxidant a fuel is available in excess of their stoichiometric proportions. It is possible to have complete combustion to C02 and H20 with a lean mixture, and the excess oxygen appearing on the product side of the chemical equation. It is however, impossible to have complete combustion of a rich mixture, and the product composition is then indeterminate without further information - this will be considered later. A departure from stoichiometric proportions may be described by a number of terms [3]:

### 2.4.1 Equivalence ratio ϕ and mixture strength. MS

The equivalence ratio, ϕ is defined as the ratio of fuel/air available to that required for the stoichiometric quantity of oxidant, i.e.:

$$\phi = \frac{(Fuel/Air)_{actual}}{(Fuel/Air)_{stoich}}$$

or

$$\frac{(FAR)_{actual}}{(FAR)_{stoich}}$$

With this definition, mixtures with ϕ< 1 called fuel-lean, while mixtures in which ϕ> 1 are called fuel-rich. Moreover, the mixture strength, MS, is in fact the equivalence ratio expressed as a percentage and is often used in reciprocating combustion engines work [3]

### 2.4.2 Relative air-fuel ratio and percent theoretical air

The relative air-fuel ratio is often called the oxidizer equivalence ratio, and is defined as the actual (AFR)actual divided by the stoichiometric (AFR)stoich i.e., 1/ϕ. Also, the percent theoretical air is defined as [3] :

Percent theoretical air = 100 / ϕ

### 2.4.3 Percentage excess air EA

This term most usually employed to describe lean or weak mixtures in engine and boiler technology and is defined as:

$$\frac{(FAR)_{actual} - (FAR)_{stoich}}{(FAR)_{stoich}} \times 100\% \tag{2-16a}$$

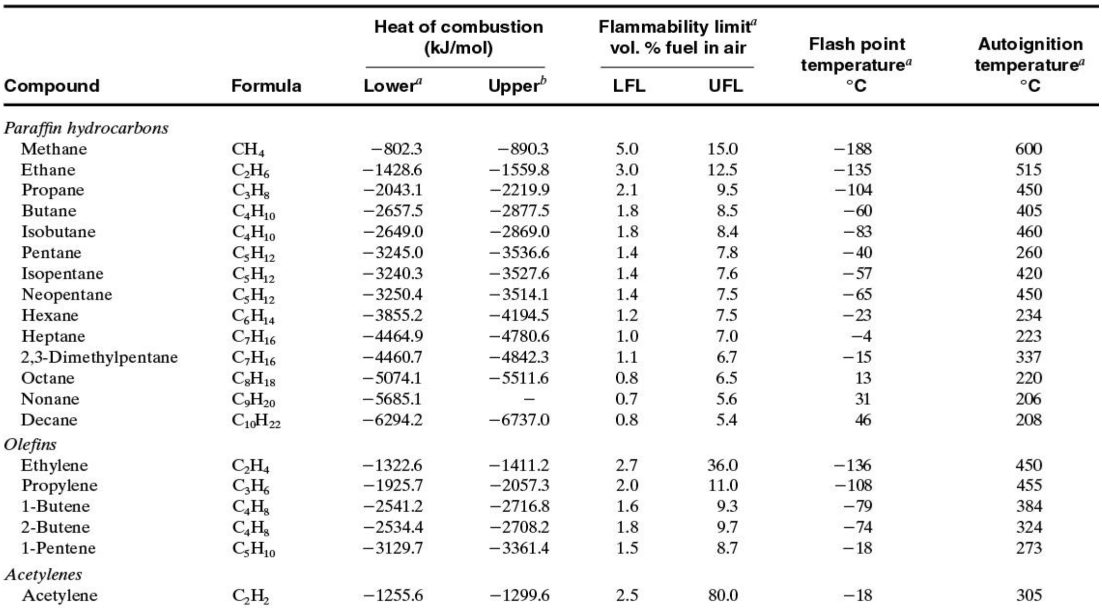
$$EA = \frac{100\%}{\phi} - 100\% = \frac{(1-\phi)}{\phi} - 100\% \tag{2-16b}$$

$$EA = \frac{100-MS}{MS} \tag{2-16c}$$

Excess air is sometimes employed to ensure complete combustion or to reduce the product temperature. Furthermore, the last equations are commonly used to specify the composition of a combustible mixture relative to the stoichiometric composition [3].

### 2.4.4 Limits of flammability

Flammability limits bracket the rich-to-lean fuel-air mixture range beyond which fuel-air cannot burn after an ignition source is removed, even if the mixture is at its ignition temperature. Some values of lean (ϕ)L and rich (ϕ)r flammability limits for some fuels are given in Table B1 (b) (Appendix B). These values are shown as equivalence ratio ϕ ((fuel/air) L, R/fuel/air) stoich where (fuel/air) L, R is the lean or rich limit of fuel to air ratio, and (fuel/air) $_{st}$ is the stoichiometric ratio [3]



| Compound | Formula | Heat of combustion (kJ/mol) Lower[a] | Heat of combustion (kJ/mol) Upper[b] | Flammability limit[a] vol. % fuel in air LFL | Flammability limit[a] vol. % fuel in air UFL | Flash point temperature[a] °C | Autoignition temperature[a] °C |
|---|---|---|---|---|---|---|---|
| *Paraffin hydrocarbons* | | | | | | | |
| Methane | $CH_4$ | −802.3 | −890.3 | 5.0 | 15.0 | −188 | 600 |
| Ethane | $C_2H_6$ | −1428.6 | −1559.8 | 3.0 | 12.5 | −135 | 515 |
| Propane | $C_3H_8$ | −2043.1 | −2219.9 | 2.1 | 9.5 | −104 | 450 |
| Butane | $C_4H_{10}$ | −2657.5 | −2877.5 | 1.8 | 8.5 | −60 | 405 |
| Isobutane | $C_4H_{10}$ | −2649.0 | −2869.0 | 1.8 | 8.4 | −83 | 460 |
| Pentane | $C_5H_{12}$ | −3245.0 | −3536.6 | 1.4 | 7.8 | −40 | 260 |
| Isopentane | $C_5H_{12}$ | −3240.3 | −3527.6 | 1.4 | 7.6 | −57 | 420 |
| Neopentane | $C_5H_{12}$ | −3250.4 | −3514.1 | 1.4 | 7.5 | −65 | 450 |
| Hexane | $C_6H_{14}$ | −3855.2 | −4194.5 | 1.2 | 7.5 | −23 | 234 |
| Heptane | $C_7H_{16}$ | −4464.9 | −4780.6 | 1.0 | 7.0 | −4 | 223 |
| 2,3-Dimethylpentane | $C_7H_{16}$ | −4460.7 | −4842.3 | 1.1 | 6.7 | −15 | 337 |
| Octane | $C_8H_{18}$ | −5074.1 | −5511.6 | 0.8 | 6.5 | 13 | 220 |
| Nonane | $C_9H_{20}$ | −5685.1 | − | 0.7 | 5.6 | 31 | 206 |
| Decane | $C_{10}H_{22}$ | −6294.2 | −6737.0 | 0.8 | 5.4 | 46 | 208 |
| *Olefins* | | | | | | | |
| Ethylene | $C_2H_4$ | −1322.6 | −1411.2 | 2.7 | 36.0 | −136 | 450 |
| Propylene | $C_3H_6$ | −1925.7 | −2057.3 | 2.0 | 11.0 | −108 | 455 |
| 1-Butene | $C_4H_8$ | −2541.2 | −2716.8 | 1.6 | 9.3 | −79 | 384 |
| 2-Butene | $C_4H_8$ | −2534.4 | −2708.2 | 1.8 | 9.7 | −74 | 324 |
| 1-Pentene | $C_5H_{10}$ | −3129.7 | −3361.4 | 1.5 | 8.7 | −18 | 273 |
| *Acetylenes* | | | | | | | |
| Acetylene | $C_2H_2$ | −1255.6 | −1299.6 | 2.5 | 80.0 | −18 | 305 |

Figure 2-3.Flammability Data for Selected Hydrocarbons. [4]

## 2.5 ENTHALPY AND ENTHALPY OF FORMATION AND HEATING VALUES

### 2.5.1 Enthalpy

In the laboratory chemical systems are not usually harnessed to do work. The only work they do is PV work arising from expansion or contraction. (An important exception in which chemical reactions are allowed to do additional work, Other than PV work, is the electrochemical cell.) If we have a chemical system at constant volume, it can do no work as $\mathrm{dw} = -\mathrm{PdV} = 0$ because

$$dU = dq + dw \tag{2-17a}$$

And

$$dU = (dq)v \tag{2-17b}$$

$$\Delta U = (q)v \tag{2-17c}$$

The increase in internal energy of the system is therefore equal to the heat absorbed at constant volume (for a system that does no work).

Most chemical experiments are carried out at constant pressure rather than at constant volume. Under such conditions the work done by the system as a result of expansion is not zero [2].

$$dw = -PdV \qquad (2\text{-}18a)$$

And

$$w = -PdV \qquad (2\text{-}19)$$

$$\Delta U = q + w = U_B - U_A = (q)_p - P(V_B - V_A) \qquad (2\text{-}20)$$

And

$$(q)_p = (U_B - PV_B) - (U_A - PV_A) \qquad (2\text{-}21)$$

$(U - PV)$, like U, is a state function, as U, P and V are all state function. We call this function the enthalpy and it is defined by

$$H = U + PV \qquad (2\text{-}22a)$$

$$\Delta H = (q)_p \qquad (2\text{-}22b)$$

And

$$\mathrm{d}H = (dq)_p \qquad (2\text{-}22c)$$

The increase of enthalpy of a system is equal to the heat absorbed at constant pressure (assuming that the system does only PV work).

Even for changes that occur at Other than constant pressure ΔH has a definite value, However, under these conditions it is not equal to the heat absorbed. Similarly, ΔU has a definite value for any change, irrespective of whether it is at constant volume, but it is only for a change at constant volume that ΔU = q [2].

The importance of this new state function, enthalpy, will become apparent when we study thermochemistry, the branch of thermodynamics concerning the heat changes associated with chemical reactions. For the moment let us note that when we see

$$CS + 3O_2 \rightarrow CO_2 + 2SO_2; \quad \Delta \mathrm{H} = -1108\mathrm{kJmol}^{-1}$$

his means that for one mole of reaction the enthalpy of the system decreases by 1108 kJ and this quantity of heat will be liberated (at constant T and P) by the reaction. One mole of reaction is when the appropriate numbers of moles of substances (as specified by the stoichiometric coefficients) on the left-hand side of the equation are fully converted to the substances on the right-hand side of the equation. When the change in a thermodynamic property is given for a particular chemical reaction or process, it always refers to a mole of reaction unless an exception to this rule is specifically indicated.

$\Delta$H and $\Delta$U are usually very similar for processes involving solids and liquids, but for gases they may be significantly different. If a gas reaction involves a change of $\Delta$n moles of in the system then as $\Delta H = \Delta U + \Delta (PV)$, and for perfect gases

$\Delta (PV) = (\Delta n)RT$.

$$\Delta \mathrm{H} = \Delta \mathrm{U} + \Delta \mathrm{nRT} \tag{2-23}$$

At 298K $RT = 2.5 kJmol^{-1}$, not a negligible quantity [2]

### 2.5.2 Enthalpy of formation

In dealing with chemically reacting systems, the concept of standardized enthalpies is extremely valuable. For any species, we can define a standardized enthalpy that is the sum of an enthalpy that takes into account the energy associated with chemical bonds (or lack thereof), the enthalpy of formation, $h_f$, and an enthalpy that is associated only with the temperature, the sensible enthalpy change,$\Delta h_s$ .

Thus, we can write the molar standardized enthalpy for species *i* as [1]:

$$\bar{h}_i(T) = \bar{h}^o_{f,i}(T)_{ref} + \bar{h}_{s,i}(T) \tag{2-24}$$

Where $\bar{h}_i(T)$ is Standardized enthalpy at temperature T and $\bar{h}^o_{f,i}(T)_{ref}$ is the enthalpy of formation at standard reference state $(T_{ref}, P^o)$ and $\bar{h}_{s,i}(T)$ is the Sensible enthalpy change in going from $T_{ref}$ to $T$ where $\bar{h}_{s,i}(T) \equiv \bar{h}_i(T) - \bar{h}^o_{f,i}(T)_{ref}$.

To make practical use of the last equation, it is necessary to define a standard reference state. We employ a standard-state temperature, $Tref = 25°C\ (298.15\ K)$, and standard-state pressure,$Pref = P\ o = 1\ atm\ (101{,}325\ Pa)$, consistent with the Chemkin [1] and NASA thermodynamic databases. Furthermore, we adopt the convention that enthalpies of formation are zero for the elements in their naturally occurring state at the reference state temperature and pressure. For example, at 25°C and 1 atm, oxygen exists as diatomic molecules; hence,

$$(\bar{h}^{o}_{f,O_2})_{298} = 0$$

where the superscript o is used to denote that the value is for the standard-state pressure.

To form oxygen atoms at the standard state requires the breaking of a rather strong chemical bond. The bond dissociation energy for $O_2$ at $298$ K is $498{,}390$ kJ/ $\mathrm{kmol}_{O_2}$. Breaking this bond creates two O atoms; thus, the enthalpy of formation for atomic oxygen is half the value of the $O_2$ bond dissociation energy, i.e.,

$$\left(\bar{h}^{o}_{f,O_2}\right) == \ 249\ 195\ \mathrm{kJ/\ kmol_O}$$

Thus, enthalpies of formation have a clear physical interpretation as the net change in enthalpy associated with breaking the chemical bonds of the standard-state elements and forming new bonds to create the compound of interest.

Representing the standardized enthalpy graphically provides a useful way to understand and use this concept. In Fig. 1.4, the standardized enthalpies of atomic oxygen (O) and diatomic oxygen ($O_2$) are plotted versus temperature starting from absolute zero. At 298.15 K, we see that $\bar{h}_{O_2}$ is zero (by definition of the standard state reference condition) and the standardized enthalpy of atomic oxygen equals its enthalpy of formation, since the sensible enthalpy at 298.15 K is zero. At the temperature indicated (4000 K), we see the additional sensible enthalpy contribution to the standardized enthalpy. In Appendix C, enthalpies of formation at the reference state are given, and sensible enthalpies are tabulated as a function of temperature for a number of species of importance in combustion. Enthalpies of formation for reference temperatures other than the standard state 298.15 K are also tabulated [1].

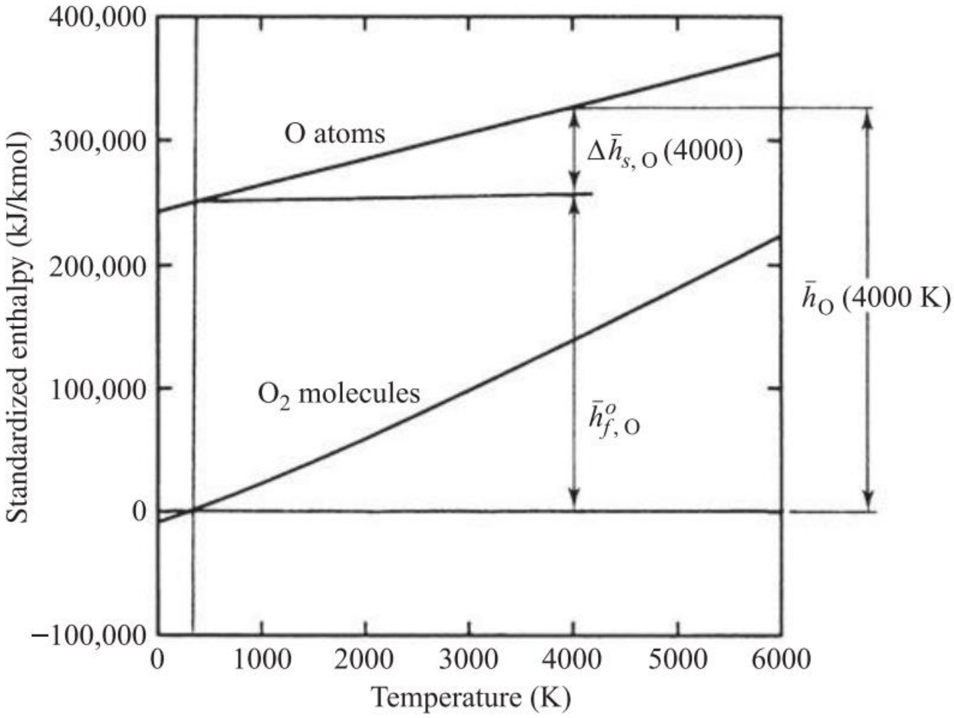


Figure 2-4.Graphical interpretation of standardized enthalpy, enthalpy of formation, and

### 2.5.3 Heating values

The heat of combustion, $\Delta h_c$ (known also as the heating value), is numerically equal to the enthalpy of reaction, but with opposite sign. The upper or higher heating value, HHV, is the heat of combustion calculated assuming that all of the water in the products has condensed to liquid. In this scenario, the reaction liberates the most amount of energy, hence leading to the designation "upper." The Lower heating value, LHV, corresponds to the case where none of the water is assumed to condense. For CH4, the upper heating value is approximately $11\%$ larger than the Lower one. Standard-state heating values for a variety of hydrocarbon fuels are given in Appendix B [5]

Knowing how to express the enthalpy for mixtures of reactants and mixtures of products allows us to define the enthalpy of reaction, or, when dealing specifically with combustion reactions, the enthalpy of combustion. Consider the steady-flow reactor, shown in Figure 2-5, in which a stoichiometric mixture of reactants enters and products exits, both at standard-state conditions (25°C, 1 atm). The combustion process is assumed to be complete, i.e., all of the fuel carbon is converted to CO2 and all of the fuel hydrogen is converted to $H_2O$ [1]. For the products to exit at the same temperature as the entering reactants, heat must be removed from the reactor. The amount of heat removed can be related to the reactant and product standardized enthalpies by applying the steady-flow form of the first law

$$q_{cv} = h_o - h_i = h_{prod} - h_{reac} \tag{2-25}$$

The definition of the enthalpy of reaction, or the enthalpy of combustion, $\Delta h_R$ (per mass of mixture), is

$$\Delta h_R = q_{cv} = h_{prod} - h_{reac} \tag{2-26a}$$

or, in terms of extensive properties,

$$\Delta H_R = H_{prod} - H_{reac} \tag{2-26b}$$

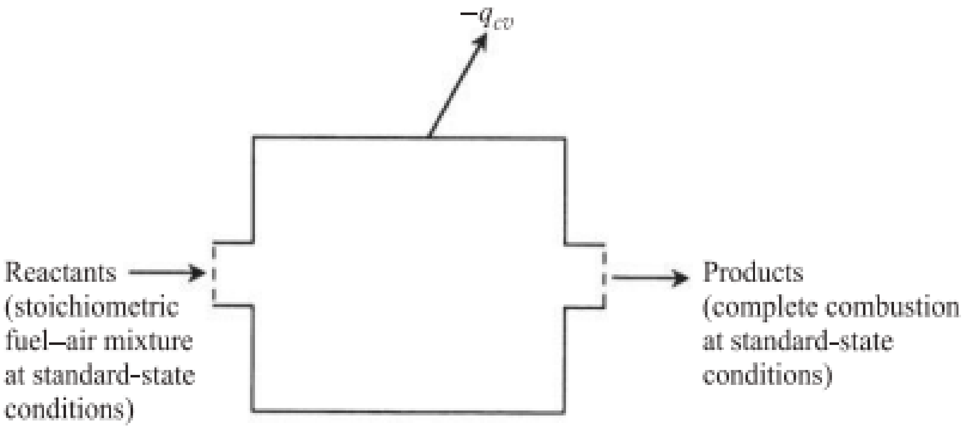


Figure 2-5.Steady-flow reactor used to determine enthalpy of combustion

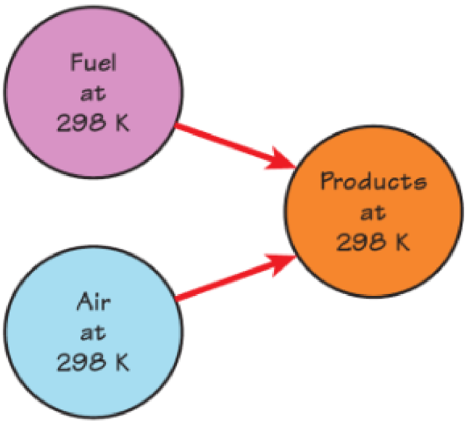
## Example:

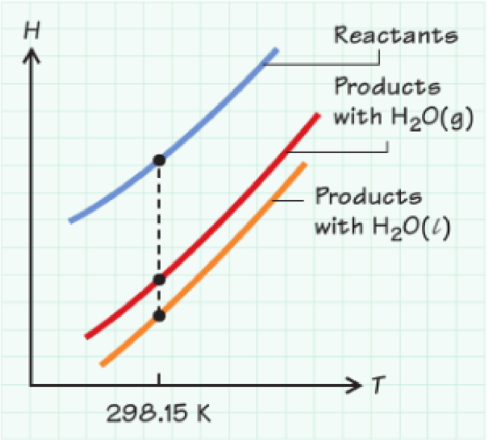
Determine the upper and lower heating values of gaseous n-decane ($C_{10}H_{22}$) for stoichiometric combustion with air at 298.15 K. For this condition, 15.5Kmol of $O_2$ reacts with each kmol of $C_{10}H_{22}$ to produce10 kmol of $CO_2$ and 11kmol of $H_2O$.Assume that air can be represented as a mixture of $O_2$ and $N_2$ in which there are 3.76 kmol of $N_2$ for each kmol of $O_2$. Express the results per unit mass of fuel. The molecular weight of n-decane is 142.284.

**Solution:**

Known: T, composition of reacts and products mixture, $m_{C_{10}H_{22}}$

Find: $\Delta h_c$ (upper and lower)





For 1Kmol of $C_{10}H_{22}$ stoichiometric combustion can be expressed for the given information as

$$C_{10}H_{22}(g) + 15.5(O_2 + 3.76N_2) \rightarrow 10CO_2 + 11H_2O(l \ or \ g) + 15.5(3.76)N_2$$

For either upper or lower heating value

$$\Delta H_c = -\Delta H_c = H_{reac} - H_{prod}$$

where the numerical value of $H_{prod}$ depends on whether the $H_2O$ in the products is liquid (defining the higher heating value) or gaseous (defining the lower heating value). The sensible enthalpy changes for all species involved are zero Since we desire $\Delta H_c$ at the reference state (298.15 K). Furthermore, the enthalpies of formation of the $O_2$ and $N_2$ are also zero at 298.15 K. Recognizing that

$$H_{reac} = \sum_{reac} N_i\bar{h}_i \quad and \quad H_{prod} = \sum_{prod} N_i\bar{h}_i$$

we obtain

$$\Delta H_{c,H_2O(l)} = HHV = (1)10\bar{h}^o_{f,C_{10}H_{22}} - [10\bar{h}^o_{f,CO_2} + 11\bar{h}^o_{f,H_2O(l)}]$$

Note that the $N_2$ contribution as a reactant cancels with the $N_2$ contribution as a product. Table D.1 (Appendix C) gives the enthalpy of formation for gaseous water; the enthalpy of vaporization, $h_{fg}$, is obtained from Table C.1 or the NIST database. We thus calculate the enthalpy of formation of the liquid water as follows:

$$\Delta H_{c,H_2O(l)} = \bar{h}^o_{f,H_2O(g)} - \bar{h}_{fg}$$

$$= -241.847\ kJ/mol - (45.87 - 1889)kJ/mol$$

$$= -285.834 kJ/mol$$

Using this value together with enthalpies of formation given in Appendices B

and H, we obtain the higher heating value:

$$\Delta H_{c,H_2O(l)} = (1)(-249.659 - [10(-393.546) + 11(-285.834)]$$

$$= 6{,}829.975 \text{ kJ}$$

$$[=] kmol \left(\frac{kJ}{Kmol}\right) = kJ$$

To express this on a per-mass-of-fuel basis, we need only divide by the number of moles of fuel in the combustion reaction and the fuel molecular weight, that is,

$$\Delta h_c = \frac{\Delta H_c}{M_{C_{10}H_{22}}} = \frac{\Delta H_c}{N_{C_{10}H_{22}} m_{C_{10}H_{22}}}$$

$$= \frac{6{,}829.975}{142.284} = 48.002\ {}^{kJ}\!\Big/_{kg_{fuel}}$$

For the lower heating value, we repeat these calculations using $\bar{h}^o_{f,H_2O(g)} = -241.847$ in place of $\bar{h}^o_{f,H_2O(l)} = -285{,}834$ kJ/kmol. The result is

$$\Delta H_c = 6{,}345.986 kJ \quad and \quad \Delta h_c = 44.601\ {}^{kJ}\!\Big/_{kg_{fuel}}$$

# Chapter 3: HYDROGEN PROPERTIES

## 3.1 INTORODUCTION

Hydrogen is the simplest element known to exist. An atom of hydrogen has one proton, one electron and a standard atomic weight of 1.008.(Figure 3-1) it has the highest energy content of any common fuel by weight, but the lowest energy content by volume. It is the lightest element and a gas at normal temperature and pressure. Hydrogen is also the most abundant chemical substance in the universe, however, doesn’t exist naturally on Earth. It is found only in compound form. Combined with oxygen as water (H2O). Combined with carbon, it forms organic compounds such as methane (CH4), coal, and petroleum. It is found in all growing things—biomass, constituting roughly 75% of all baryonic mass. [6]

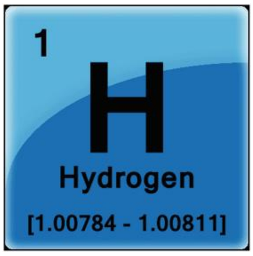


Figure 3-1,The chemical element of hydrogen

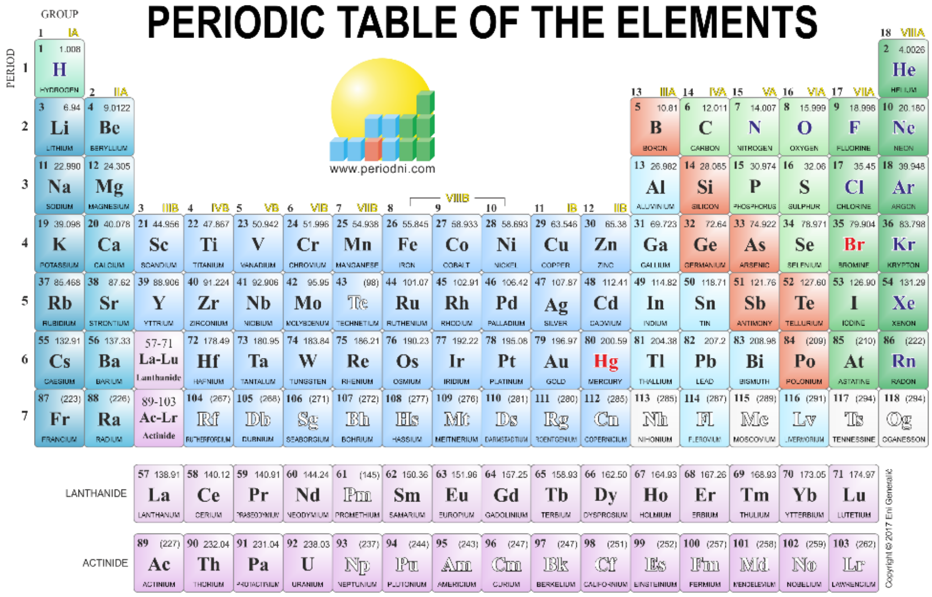


Figure 3-2.The periodic table of the elements

## 3.2 HISTORY OF HYDROGEN

The alchemist Paracelsus discovered that the bubbles produced when iron filings were introduced to sulfuric acid were combustible in the early 1500s. The identical observation was made by Robert Boyle in 1671. Because neither followed up on their discovery of hydrogen, Henry Cavendish is given credit. He collected the bubbles in 1766 and demonstrated that they were distinct from other gases. He later demonstrated that when hydrogen burns, it produces water, putting an end to the idea that water was an element. Antoine Lavoisier named the gas hydro-gen, which means "water-former."

Hydrogen is one of the most powerful gases we use—in our cars, buses, space launches from the Cape, and so on. Hydrogen has been found to be the best, oldest, and cleanest element, and is the first substance of the chemical periodic table (see. Figure 3-2).

We are currently studying future fuels. However, in order to make actual situation of hydrogen fuel and hydrogen fuel cells credible, we must examine the past. [7].

Therefore, let us look at the history of this substance that is known as hydrogen. [6]

**1776** Hydrogen was first identified as a distinct element by British scientist Henry Cavendish after he produced hydrogen gas as a result of the reaction between zinc metal and hydrochloric acid. In a demonstration to the Royal Society of London, Cavendish applied a spark to hydrogen gas, yielding water. This discovery led to his later finding that water (H2O) is made of hydrogen and oxygen.

**1788** Building on the discoveries of Cavendish, French chemist Antoine Lavoisier gave hydrogen its name, which was derived from the Greek word’s hydro and genes, meaning “water” and “born of.”

**1800** English scientists William Nicholson and Sir Anthony Carlisle discovered that applying an electric current to water produced hydrogen and oxygen gases. This process was later termed “electrolysis.”

**1838** The fuel cell effect, combining hydrogen and oxygen gases to produce water and an electric current, was discovered by Swiss chemist Christian Friedrich Schoenbein.

**1845** Sir William Grove, an English scientist and judge, demonstrated Schoenbein’s discovery on a practical scale by creating a “gas battery.” He earned the title “Father of the Fuel Cell” for his achievement.

**1874** Jules Verne, an English author, prophetically examined the potential use of hydrogen as a fuel in his popular work of fiction entitled The Mysterious Island.

**1889** Ludwig Mond and Charles Langer attempted to build the first fuel cell device using air and industrial coal gas. They named the device a fuel cell. 1920s A German engineer, Rudolf Erren, converted the internal combustion engines of trucks, buses, and submarines to use hydrogen or hydrogen mixtures. British scientist and Marxist writer J.B.S. Haldane introduced the concept of renewable hydrogen in his book Daedalus or Science and the Future by proposing that “there will be great power stations where during windy weather the surplus power will be used for the electrolytic decomposition of water into oxygen and hydrogen”.

**1937** After ten successful trans-Atlantic flights from Germany to the United States, the Hindenburg, a dirigible inflated with hydrogen gas, crashed upon landing in Lakewood, New Jersey, USA. The mystery of the crash was solved in 1997 when a 6 1 The Chemical Element Hydrogen study concluded that the explosion was not due to the hydrogen gas, but rather to a weather-related static electric discharge which ignited the airship’s silver-colored canvas exterior covering, which had been treated with the key ingredients of solid rocket fuel.

**1958** The United States formed the National Aeronautics and Space Administration (NASA). NASA’s space program currently uses the most liquid hydrogen worldwide, primarily for rocket propulsion and as a fuel for fuel cells.

**1959** Francis T. Bacon of Cambridge University in England built the first practical hydrogen–air fuel cell. The 5-kilowatt (kW) system powered a welding machine. He named his fuel cell design the “Bacon Cell.” Later that year, Harry Karl Ihrig, an engineer for the Allis–Chalmers Manufacturing Company, demonstrated the first fuel cell vehicle: a 20-horsepower tractor. Hydrogen fuel cells, based on Bacon’s design, have been used to generate onboard electricity, heat, and water for astronauts aboard the famous Apollo spacecraft and all subsequent space shuttle missions.

**1970** Electrochemist John O’Mara Bockris coined the term “hydrogen economy” during a discussion at the General Motors (GM) Technical Center in Warren, Michigan, USA. He later published Energy: The Solar-Hydrogen Alternative, describing his envisioned hydrogen economy where cities in the United States could be supplied with energy derived from the Sun.

**1972** The 1972 Gremlin, modified by the University of California at Los Angeles, was entered the 1972 Urban Vehicle Design Competition and won first prize for the lowest tailpipe emissions. Students converted the Gremlin’s internal combustion engine to run on hydrogen supplied from an onboard tank.

**1973** The OPEC (Organization of the Petroleum Exporting Countries) oil embargo and the resulting supply shock suggested that the era of cheap petroleum had ended, and that the world needed alternative fuels. The development of hydrogen fuel cells for conventional commercial applications began.

**1974** The National Science Foundation transferred the Federal Hydrogen R&D Program to the United States Department of Energy. Professor T. Nejat Veziroglu of the University of Miami, Florida, organized The Hydrogen Economy Miami Energy (THEME) conference, the first international conference held to discuss hydrogen energy. Following the conference, the scientists and engineers who had attended it formed the International Association for Hydrogen Energy (IAHE).

**1974** The International Energy Agency (IEA) was established in response to global oil market disruptions. IEA activities included the research and development of hydrogen energy technologies.

**1988** The Soviet Union Tupolev Design Bureau successfully converted a 164-passenger TU-154 commercial jet to operate one of the jet’s three engines on liquid hydrogen. The maiden flight lasted 21 min.

**1989** The National Hydrogen Association (NHA) formed in the United States with ten members. Today, the NHA has nearly 100 members, including representatives 1.2 The History of Hydrogen 7 from the automobile and aerospace industries, federal, state, and local governments, and energy providers. The International Organization for Standardization’s Technical Committee for Hydrogen Technologies was also created.

**1990** The world’s first solar-powered hydrogen production plant at SolarWasserstoff-Bayern, a research and testing facility in southern Germany, became operational. The United States Congress passed the Spark M. Matsunaga Hydrogen, Research, Development and Demonstration Act (PL 101–566), which prescribed the formulation of a 5-year management and implementation plan for hydrogen research and development in the United States. The Hydrogen Technical Advisory Panel (HTAP) was mandated by the Matsunaga Act to ensure consultation on and coordination of hydrogen research. Work on a methanol-fuelled 10-kW proton exchange membrane (PEM) fuel cell began through a partnership including GM, Los Alamos National Laboratory, the Dow Chemical Company, and Canadian fuel cell developer, Ballard Power Systems.

**1994** Daimler-Benz demonstrated its first New Electric CAR (NECAR-I) fuel cell vehicle at a press conference in Ulm, Germany.

**1997** Retired NASA engineer Addison Bain challenged the belief that hydrogen caused the Hindenburg accident. The hydrogen, Bain demonstrated, did not cause the catastrophic fire but rather the combination of static electricity and highly flammable material on the skin of the airship. German car manufacturer Daimler Benz and Ballard Power Systems announced a US$300 million research collaboration on hydrogen fuel cells for transportation.

**1998** Iceland unveiled a plan to create the first hydrogen economy by 2030 with Daimler-Benz and Ballard Power Systems.

**1999** The Royal Dutch/Shell Company committed to a hydrogen future by forming a hydrogen division. Europe’s first hydrogen fuelling stations were opened in the German cities of Hamburg and Munich. A consortium of Icelandic institutions, headed by the financial group New Business Venture Fund, partnered with Royal Dutch/Shell Group, Daimler Chrysler (a merger of Daimler-Benz and Chrysler), and Norsk Hydro to form the Icelandic Hydrogen and Fuel Cell Company, Ltd. to further the hydrogen economy in Iceland.

**2000** Ballard Power Systems presented the world’s first production-ready PEM fuel cell for automotive applications at the Detroit Auto Show. 2003 President George W. Bush announced in his 2003 State of the Union Address a US$1.2 billion hydrogen fuel initiative to develop the technology for commercially viable hydrogen-powered fuel cells, such that “the first car driven by a child born today could be powered by fuel cells”.

**2004** United States Energy Secretary Spencer Abraham announced that over US $350 million would be devoted to hydrogen research and vehicle demonstration projects. This appropriation represented nearly one-third of President Bush’s US $1.2 billion commitment to research in hydrogen and fuel cell technologies. The 8 1 The Chemical

Element Hydrogen funding encompasses over 30 lead organizations and more than 100 partners selected through a competitive review process.

**2004** The world's first fuel cell-powered submarine underwent deep-water trials (German navy).

**2005** Twenty-three states in the United States have hydrogen initiatives in place. **Today–2050**: Future Vision In the future, water will replace fossil fuels as the primary resource for hydrogen. Hydrogen will be distributed via national networks of hydrogen transport pipelines and fuelling stations. Hydrogen energy and fuel cell power will be clean, abundant, reliable, affordable, and an integral part of all sectors of the economy in all regions of the United States. [6]

## 3.3 HYDROGEN SOURCES

Despite accounting for almost 75% of the universe's elemental mass, hydrogen is a comparatively uncommon element on Earth. (see.Figure 3-3) an image taken by the Hubble Space Telescope, shows a region of ionized hydrogen in the Triangulum Galaxy. The early Earth's atmosphere was rich in hydrogen, and bacterial enzymes called hydrogenases evolved to generate energy from molecular H2 or H2O, Microorganisms proliferated under reducing conditions, and many of those have survived on hydrogen fuel to this day. [8]

Figure 3-3.Ionized hydrogen within the Triangulum Galaxy

In nature, volcanic outgassing like water vaper, carbon dioxide, sulphur dioxide, hydrogen sulphide and hydrogen halides can act as a hydrogen source like its illustrated in, shows the volcanic eruption of the Etna volcano in the cost of Sicily in Italy, which took place recently as 16 February 2021

Figure 3-4.Italy′s Etna volcano erupts on Sicily

Since hydrogen gas is not found on Earth, it can be produced from diverse, domestic resources. Currently, most hydrogen is produced from fossil fuels, specifically natural gas. Electricity—from the grid or from renewable sources such as wind, solar, geothermal, or biomass—is also currently used to produce hydrogen. In the longer term, solar energy and biomass can be used more directly to generate hydrogen. [9]

### 3.3.1 Natural gas and other fossil fuels

Fossil fuels can be reformed to release the hydrogen from their hydrocarbon molecules and are the source of most of the hydrogen currently made in the United States. Combining these processes with carbon capture, utilization, and storage will reduce the carbon dioxide emissions. Natural gas reforming is an advanced and mature hydrogen production process that builds upon the existing natural gas infrastructure. Today 95% of the hydrogen produced in the United States is made by natural gas reforming in large central plants. This is an important pathway for near-term hydrogen production. Some processes to product hydrogen using fossil fuels: [9]

- Natural gas reforming
- Coal gasification
- Carbon capture, utilization, and storage.

### 3.3.2 Solar

Sunlight can directly or indirectly provide the energy to produce hydrogen. This resource is abundant, but it is diffuse and only available for a portion of the day. Processes for hydrogen production using solar energy: [9]

- Solar thermochemical hydrogen (STCH)
- Photoelectrochemical (PEC)
- Electrolysis
- Photobiological.

### 3.3.3 Biomass

Biomass is an abundant renewable resource that can be produced domestically, and it can be converted to hydrogen and other by products through a number of methods. Because growing biomass removes carbon dioxide from the atmosphere, the net carbon emissions of these methods can be low. processes to product hydrogen using biomass: [9]

- Biomass gasification
- Biomass-derived liquid reforming
- Microbial biomass conversion.

### 3.3.4 Wind

Wind is an abundant but variable resource for generating electricity. Wind-generated electricity can power water electrolysis to produce hydrogen, which could be used to fuel vehicles, or stored and then used in fuel cells to generate electricity during times of the day when the wind resource is low. Learn more about using electrolysis to produce hydrogen from wind. [9]

### 3.3.5 Renewable and grid energy

Electricity can be used to split water into hydrogen and oxygen. This technology is well developed and available commercially, and systems that can efficiently use renewable power—for example, wind, geothermal, or solar—are being developed. using electrolysis is a way to produce hydrogen from renewable and grid electricity.

## 3.4 PHYSICAL AND CHEMICAL PROPERTIES

Hydrogen has three isotopes: deuterium (D; atomic weight 2.01410222) and tritium (T; atomic weight 3.0160497). Tritium is radioactive and emits very low energy β rays with a half-life of 12.26 years. The isotopes have different physical properties but quite similar chemical properties [10] (see. Figure 3-5)

Protium (0 Neutron, Atomic Number A = 1).

Deuterium (1 Neutron, Atomic Number A = 2).

Tritium (2 Neutron, Atomic Number A = 3).

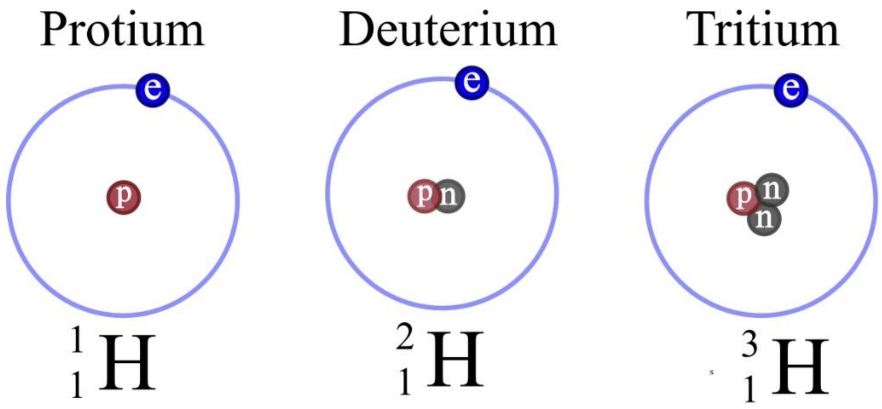


Figure 3-5..The three most stable isotopes of hydrogen

The element hydrogen's most prevalent isotope is protium. It consists of one proton and one electron but no neutrons.

### 3.4.1 Chemical properties of hydrogen

A hydrogen molecule consists of two hydrogen atoms, Hydrogen is the lightest gas being 14 times lighter than air. A colourless and odorless gas at room temperature. Liquefied hydrogen, which has very low boiling point (−252.88 °C), takes up much less space, about 1/700 times as much space as gaseous hydrogen but even in liquefied state, it is still very light. Its density is about 0.07 g cm−3 Hydrogen itself is a rather stable molecule with high bond energy (435.99 kJ mol−1) but it reacts with many different kinds of elements to form compounds with them. As is well known, hydrogen easily reacts (burns) with oxygen at a wide range of mixing ratios and forms water. This makes it possible to use hydrogen as an energy medium. The mixture of hydrogen and air can be ignited with very low energy sparks and safety precautions are required. The reactivity of hydrogen with other elements is used for various chemical industries, but this article focuses on its application as an energy medium. The reactions of hydrogen with some organic compounds can be used to store and carry hydrogen. For instance, by reacting hydrogen with benzene to make cyclohexane, hydrogen can be stored as cyclohexane, which can later be separated to benzene and hydrogen. Ammonia and metal hydrides are also applications of the reactivity of hydrogen for storage. The most important chemical properties of hydrogen as an energy medium are the ones related to combustion [10]

Table 3-1.The physical and thermodynamical properties of hydrogen.

| **Atomic** | **hydrogen** |
|---|---|
| **atomic number** | 1 |
| **atomic weight** | 1.008 |
| **ionization potential** | 13.595 electron volts |
| **electron affinity** | 0.7542 electron volts |
| **nuclear spin** | 1/2 |
| **nuclear magnetic moment** | 2.7927 |
| **nuclear quadrupole moment** | 2.1 |
| **Molecular** | **hydrogen** |
| **bond distance** | 0.7416 angstrom |
| **dissociation energy (25 degrees C)** | 104.19 kilocalories per mole |
| **ionization potential** | 15.427 electron volts |
| **density of solid** | 0.08671 gram per cubic centimeter |
| **melting point** | −259.20 degrees Celsius |
| **heat of fusion** | 28 calories per mole |
| **density of liquid** | 0.07099 (−252.78 degrees) |
| **boiling point** | −252.77 degrees Celsius |
| **heat of vaporization** | 216 calories per mole |
| **critical temperature** | −240.0 degrees Celsius |
| **critical pressure** | 13.0 atmospheres |
| **critical density** | 0.0310 gram per cubic centimeter |
| **heat of combustion to water (g)** | −57.796 kilocalories per mole |

### 3.4.2 Physical properties of hydrogen

Two types of molecular hydrogen (ortho and para) are known. These differ in the magnetic interactions of the protons due to the spinning motions of the protons. In ortho-hydrogen, the spins of both protons are aligned in the same direction—that is, they are parallel. In para-hydrogen, the spins are aligned in opposite directions and are therefore antiparallel. The relationship of spin alignments determines the magnetic properties of the atoms. Normally, transformations of one type into the other (i.e., conversions between ortho and para molecules) do not occur and ortho-hydrogen and para-hydrogen can be regarded as two distinct modifications of hydrogen. The two forms may, however, interconvert under certain conditions. Equilibrium between the two forms can be established in several ways. One of these is by the introduction of catalysts (such as activated charcoal or various paramagnetic substances); another method is to apply an electrical discharge to the gas or to heat it to a high temperature.

the concentration of para-hydrogen in a mixture that has achieved equilibrium between the two forms depends on the temperature as shown by the following : [11]

| | | | |
|---|---|---|---|
| −253.1° C | 99.82% | −153.1° C | 32.87% |
| −223.1° C | 76.89% | 0° C | 25.13 % |
| −193.1° C | 48.39% | 200° C | 25.00% |

3 of para-hydrogen and ortho-hydrogen, these forms of hydrogen can be separated by low-temperature gas chromatography, an analytical process that separates different atomic and molecular species on the basis of their differing volatilities. [11]

## 3.5 COMBUSTIVE PROPERTIES OF HYDROGEN

Beside its chemical and physical properties these following characteristics contribute to its use as a combustible fuel, [12]:

### 3.5.1 Wide range of flammability

In comparison to all other fuels, hydrogen has a wide flammability range. As a result, hydrogen can be burned in a variety of fuel-air mixtures in an internal combustion engine. One significant advantage is that hydrogen can run on a lean mixture. [13]

A lean mixture contains less fuel than the theoretical, stoichiometric, or chemically ideal amount required for combustion with a given amount of air. This is why starting an engine on hydrogen is relatively simple.

When a vehicle is run on a lean mixture, its fuel economy improves and its combustion reaction is more complete. Furthermore, the final combustion temperature is generally lower, reducing the number of pollutants emitted in the exhaust, such as nitrogen oxides. There is a limit to how lean the engine may be run, as low operation can significantly reduce power production due to a decrease in the volumetric heating value of the air/fuel mixture. [13]

### 3.5.2 Low ignition energy

The ignition energy of hydrogen is quite low. The amount of energy required to ignite hydrogen is approximately one order of magnitude less than that necessary to ignite gasoline. This allows hydrogen engines to ignite lean mixtures and ensures that they start quickly. Unfortunately, the low ignition energy implies that hot gases and hot spots on the cylinder can act as sources of ignition, causing premature ignition and flashback difficulties. One of the challenges of running a hydrogen-powered engine is preventing this. Considering hydrogen has a wide flammability range, practically any mixture can be ignited by a hot spot. [14]

### 3.5.3 Small Quenching Distance

Hydrogen has a much shorter quenching distance than gasoline. As a result, hydrogen flames move closer to the cylinder wall before extinguishing than other fuels. As a result, quenching a hydrogen flame is more difficult than quenching a gasoline flame.

The shorter quenching distance can also enhance the likelihood of backfire since the flame from a hydrogen-air combination flows more easily through a virtually closed intake valve than a hydrocarbon-air flame. The auto - ignition temperature of hydrogen is relatively high. When a hydrogen-air mixture is compressed, this has significant effects. In fact, because the temperature rise during compression is connected to the compression ratio, the autoignition temperature is an important factor in deciding what compression ratio an engine can use. The temperature rise is shown by the equation:

$$T_2 = T_1 \left(\frac{v_2}{v_1}\right)^{\gamma-1} \tag{3-1}$$

where

V1/V2 = the compression ratio

T1= absolute initial temperature

T2= absolute final temperature

γ= ratio of specific heats

The temperature cannot surpass the auto - ignition temperature of hydrogen without triggering premature ignition. As a result, the compression ratio is limited by the absolute ultimate temperature. Because of hydrogen's high auto - ignition temperature, higher compression ratios may be used in a hydrogen engine than in a hydrocarbon engine. [9]

### 3.5.4 High flame speed

At stoichiometric ratios, hydrogen has a fast flame. The hydrogen flame speed is roughly an order of magnitude higher (faster) than that of gasoline under these conditions. As a result, hydrogen engines can get closer to the thermodynamically optimal engine cycle. However, with leaner mixtures, the flame velocity reduces dramatically. [15]

### 3.5.5 High diffusivity

Hydrogen has an extremely high diffusivity. This capacity to spread in air is far larger than that of gasoline and is advantageous for two primary reasons. For starters, it makes it easier to generate a homogeneous combination of fuel and air. Second, if a hydrogen leak develops, the hydrogen disperses quickly. As a result, unsafe circumstances can be avoided or eliminated. [9]

### 3.5.6 Low density

The density of hydrogen is quite low. When utilized in an internal combustion engine, this causes two issues. To begin with, a very big volume is required to store enough hydrogen to provide a suitable driving range for a machine. Second, the energy density of a hydrogen-air combination is reduced, and hence the power output. [9]

## 3.6 HYDROGEN GAS MIXTURE

As an addition to a hydrocarbon fuel, hydrogen can be beneficial in internal combustion engines. it is frequently combined with high pressure natural gas since both gases can be stored in the same tank. When hydrogen is combined with other fuels, it is normally kept separately and combined in the gaseous form just before ignition. In general, using hydrogen in combination with other fuels that need substantial storage systems, such as propane, is impracticable. [9]

The storage of gaseous hydrogen in the same vessel as liquid fuel is not possible. Because of its low density, hydrogen will float on top of the liquid and will not mix.

Furthermore, because liquid fuels are held at very low pressures, just a little amount of hydrogen may be supplied to the vessel. [9]

Liquid hydrogen cannot be stored in the same container as other fuels. Because hydrogen has a low boiling point, it will freeze other fuels, resulting in fuel "ice"!

Hythane, for example, is a commercially accessible gas combination that includes 20% hydrogen and 80% natural gas. A natural gas engine does not need to be modified at this ratio, and experiments have shown that emissions are decreased by more than 20% (in chapter 5 we will see how hydrogen addition effect emissions). Mixtures of more than 20% hydrogen and natural gas can further cut emissions, although certain engine changes are required. [9]

Figure 3-6.Hythane Powered Bus

Because of hydrogen's low ignition energy limit and rapid burning speed, the hydrogen/hydrocarbon combination is easy to ignite, minimizing misfire and so improving emissions, performance, and fuel economy. In terms of power output, hydrogen increases the energy density of a lean mixture by raising the hydrogen-to-carbon ratio, which enhances torque. [9]

## 3.7 HYDROGEN STORAGE

Because hydrogen has the lowest gas density and the second-lowest boiling point of any known substance, it is difficult to store as a gas or a liquid. As a gas, it necessitates extremely huge storage volumes and pressures. As a liquid, it necessitates the use of a cryogenic storage system. [9]

### 3.7.1 High pressure gas

The most prevalent and advanced technique of storing hydrogen is through high-pressure gas storage systems. This kind of hydrogen storage is used in the majority of existing fuel cell cars. Storage of hydrogen as a gas typically requires high-pressure tanks (350–700 bar [5,000–10,000 psi] tank pressure). [9]

### 3.7.2 Liquid

Many of the weight and size issues associated with high-pressure gas storage systems are resolved by liquid hydrogen storage systems, although at cryogenic temperatures.

Liquid hydrogen can be stored just below its normal boiling point of –424 ºF (–253 ºC; 20 K) at or close to ambient pressure in a double-walled, super-insulating tank. [9]

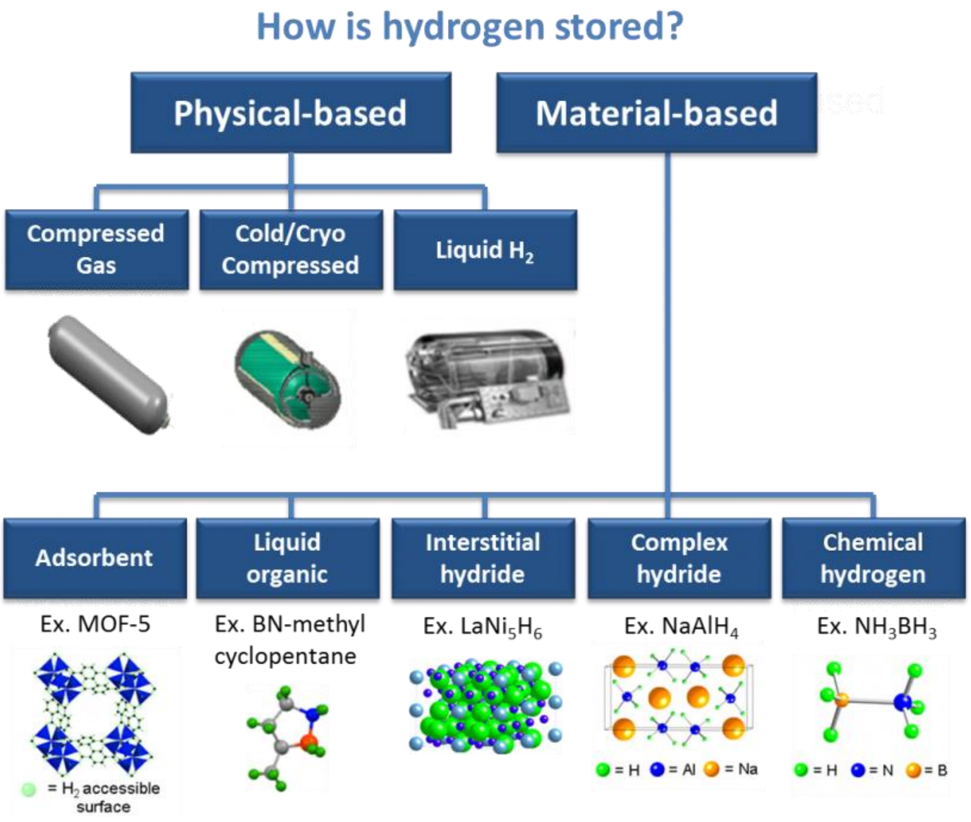


Figure 3-7.Diagram of how Hydrogen is stored

# Chapter 4: LAMINAR PREMIXED FLAME SPEED

## 4.1 INTRODUCTION

Flame is a source of energy by releasing heats, and to fully understand flames and their behaviour scientists focused one of the flame characteristics the laminar flame speed a key that helped science to understand combustible mixture and its reactivity, diffusivity, exothermicity, in the next sections we will have definitions related to the laminar flame speed and a mathematical, numerical description of the laminar flame speed and how to get it

## 4.2 DEFINITIONS

### 4.2.1 Flame

A flame is a self-sustaining propagation of a localized combustion zone at subsonic velocities It is caused by a highly exothermic chemical reaction taking place in a thin zone. the flame occupies only a small portion of the combustible mixture at any one time. [16]

A discrete combustion wave that travels subsonically is termed a deflagration. It is also possible for combustion waves to propagate at supersonic velocities. Such a wave is called a detonation. The fundamental propagation mechanisms are different in deflagrations and detonations, and, because of this, these are distinct phenomena

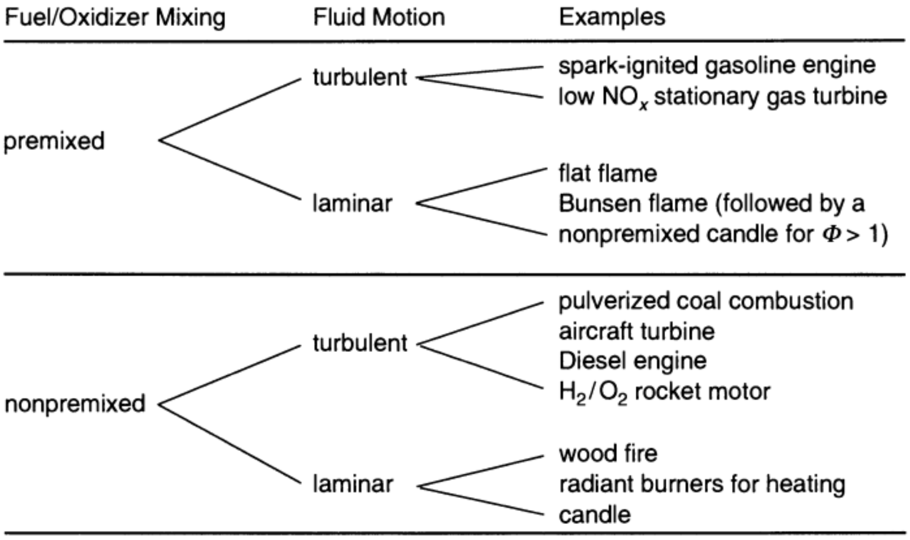
### 4.2.2 Basic flame type

In combustion processes, fuel and oxidizer (typically air) are mixed and burned. It is useful to identify several combustion categories based upon whether the fuel and oxidizer is mixed first and burned later (premixed) or whether combustion and mixing occur simultaneously (non-premixed). Each of these categories is further subdivided based on whether the fluid flow is laminar or turbulent. Table 4-1shows examples of combustion systems that belong to each of these categories. [16]

Basic flame’s categories are:

- Laminar Premixed Flames
- Turbulent premixed flames
- Laminar non-premixed flames
- Turbulent non-premixed flames
- Hybrid Premixed-Non-premixed Laminar Flames

Table 4-1.Example of combustion systems ordered with respect to premixedness and flow type



| Fuel/Oxidizer Mixing | Fluid Motion | Examples |
|---|---|---|
| premixed | turbulent | spark-ignited gasoline engine<br>low $NO_x$ stationary gas turbine |
| | laminar | flat flame<br>Bunsen flame (followed by a nonpremixed candle for $\Phi > 1$) |
| nonpremixed | turbulent | pulverized coal combustion<br>aircraft turbine<br>Diesel engine<br>$H_2/O_2$ rocket motor |
| | laminar | wood fire<br>radiant burners for heating<br>candle |

In this specific chapter we will study the laminar premixed flames

### 4.2.3 Laminar premixed flame

A premixed flame is a flame formed under certain conditions during the combustion of a premixed charge (also called pre-mixture) of fuel and oxidizer. Since the fuel and oxidizer—the key chemical reactants of combustion—are available throughout a homogeneous stoichiometric premixed charge, the combustion process once initiated sustains itself by way of its own heat release. The majority of the chemical transformation in such a combustion process occurs primarily in a thin interfacial region which separates the unburned and the burned gases. The premixed flame interface propagates through the mixture until the entire charge is depleted [17] [18].

Many studies have simplified the phenomena of the laminar flame since it's been such a complex subject; the model of 1D steady flame which is currently used is an ideal conception and representation, The flame is represented as an interface and separates the fresh gas or unburned gas (reactant side) (u) at the temperature $T = Tu$ from burned gases (product side) (b) at $T = Tb$. The species mass fraction goes from the initial state $Y = Yu$ to $Yb = 0$ in the burned gases.

Fuel and oxidizer are premixed before combustion in laminar premixed flames, and the flow is laminar. Laminar flat flames and (in fuel-lean conditions) Bunsen flames are two examples. [16]

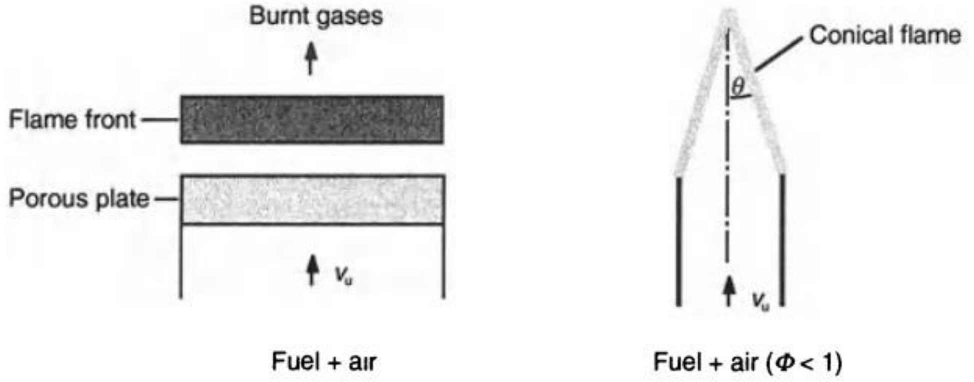


Figure 4-1.Schematic illustration of a laminar flat flame (left) and of a Bunsen flame (right).

A premixed flame is said to be stoichiometric, if fuel (e. g., a hydrocarbon) and oxidizer (e. g., oxygen O2) consume each other completely, forming only carbon dioxide (CO2) and water (H2O). If there is an excess of fuel, the system is called fuel-rich, and if there is an excess of oxygen, it is called fuel-lean, some examples: [16]

$2H_2 + O_2 \rightarrow 2H_2O$ stoichiometric

$3H_2 + O_2 \rightarrow 2H_2O + H_2$ rich ($H_2$ left over)

$CH_4 + 3O_2 \rightarrow 2H_2O + O_2 + CO_2$ rich ($O_2$ left over)

Each symbol in such a chemical reaction equation represents 1 mol. Thus, the first equation means: 2 mol H2 react with 1 mole O2 to form 2 mole H2O. If the reaction equation is written such that it describes exactly the reaction of 1 mol fuel, the mole fraction of the fuel in a stoichiometric mixture can be calculated easily to

$$x_{fuel,stoich} = \frac{1}{1+v} \quad (4\text{-}1a)$$

Here $v$ denotes the mole number of $O_2$ in the reaction equation for a complete reaction to $CO_2$ and $H_2O$. [16]

If air is used as an oxidizer, it has to be taken into account that dry air contains only about 21 %oxygen (78% nitrogen, 1% noble gases). Thus, for air xN2 = 3. 762 xO2. It follows that the mole fractions in a stoichiometric mixture with air are

$$x_{fuel,stoich} = \frac{1}{1+v\cdot 4.762}\,,\ x_{O2,stoich} = v\cdot x_{fuel,stoich}\,,\ x_{N2,stoich} = 3.762\cdot x_{O2,stoich} \qquad \text{(4-1b)}$$

v denotes, again, the mole number of $O_2$ in the reaction equation for a complete reaction of 1 mol of fuel to $CO_2$ and $H_2O$. [16]

### 4.2.4 laminar flame speed

laminar flame speed is generally considered as the velocity at which the flame front moves towards the fresh gases, or, in the case of a steady flame, as the velocity at which the inlet gases make the flame sheet steady in the laboratory flame

$$S_L{}^{\circ} = v_u \sin\alpha \qquad \text{(4-2)}$$

### 4.2.5 The Bunsen-burner flame

A Bunsen burner, named after Robert Bunsen, is a kind of gas burner used as laboratory equipment; it produces a single open gas flame, and is used for heating, sterilization, and combustion. The gas can be natural gas (which is mainly methane) or a liquefied petroleum gas, such as propane, butane, or a mixture [19] .Figure 4-2(a) demonstrate a Bunsen burner and the flame it produces. A jet of fuel at the base induces a flow of air through the variable area port, and the air and fuel mix as they flow up through the tube. The typical Bunsen-burner flame is a dual flame: a fuel-rich premixed inner flame surrounded by a diffusion flame. The secondary diffusion flame results when the carbon monoxide and hydrogen products from the rich inner flame encounter the ambient air. The shape of the flame is determined by the combined effects of the velocity profile and heat losses to the tube wall. For the flame to remain stationary, the flame speed must equal the speed of the normal component of unburned gas at each location, as illustrated in the vector diagram in Figure 4-2 (b). [1]

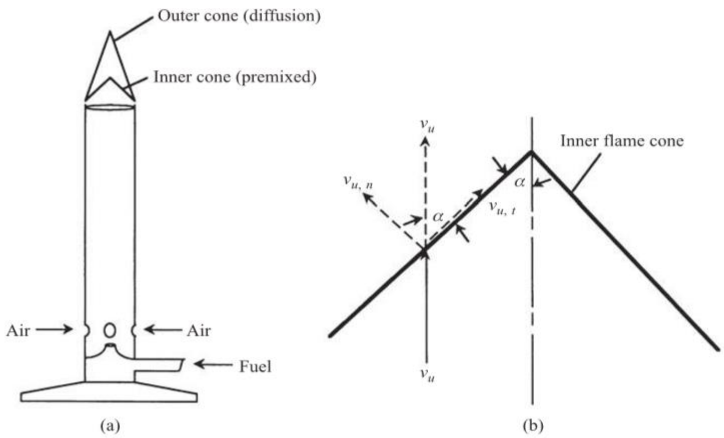


Figure 4-2.(a) Bunsen-burner schematic. (b) Laminar flame speed equals normal component of unburned gas velocity, $v_{u,\,n}$.

### 4.2.6 Flame structure

As showed in the figures ( Figure 4-3, Figure 4-4,Figure 4-5 ), which are based on law’s work [20] Three levels of complexity can be used to explain the structure and propagation of a typical premixed flame.:

- The most fundamental model corresponds to the hydrodynamic, flame-sheet level; in this instance, the flame is considered as a discontinuity (interface) between two fluid states: unburned and fresh gases, both of which are assumed to be in thermodynamic equilibrium. Transport and chemistry are not taken into account. The temperature and reactant percentages shift discontinuously at the interface, from Tu (temperature of unburned gases) to Tb (temperature of burnt gases) and from Yu (mass fraction of the fresh mixture) to Yb = 0. [21]

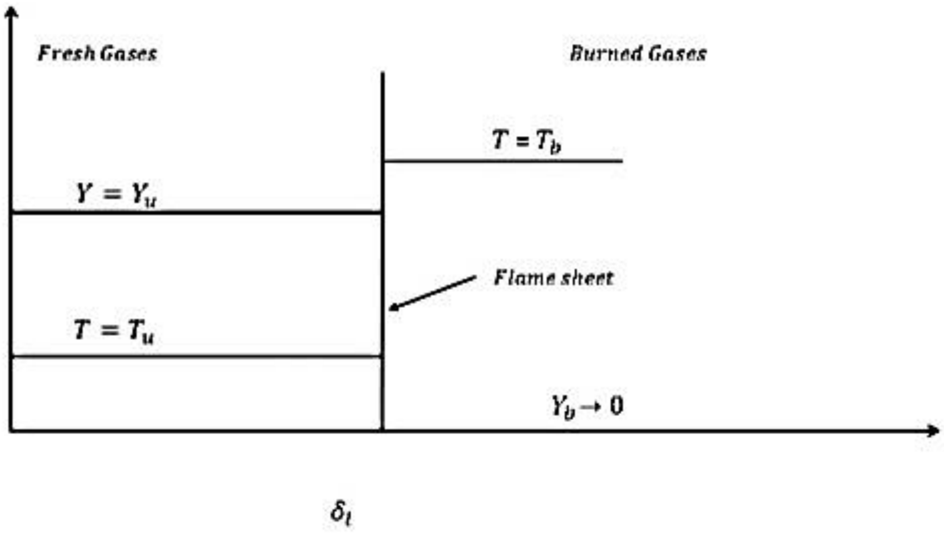


Figure 4-3.Schematic structure of a 1D, steady flame. Simplest model

- The transport properties provide a more detailed level of flame description, the flame is stretched to expose a preheat zone with a thickness $\delta_p$ that is controlled by the heat and mass diffusion processes. When the new mixture approaches the flame, heat conductivity created in the heat-release area gradually heats it. The reaction is only initiated when the temperature is near to that of the burnt gas. Once started, the reaction proceeds quickly as the deficient reactant is depleted. [21]

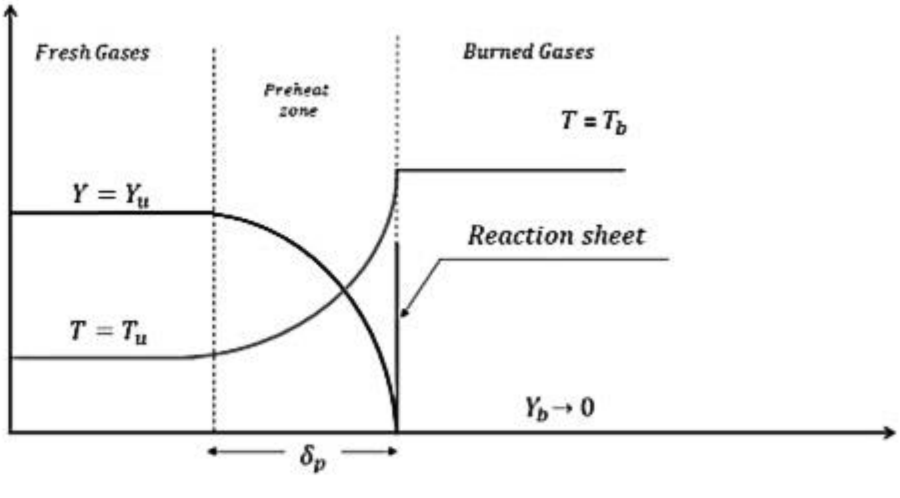


Figure 4-4.schematic structure of a 1D, steady flame. Transport dominated model.

- The final level of flame description takes into consideration thermal and molecular diffusion (theory of Zeldovich, Frank-Kamenetsky, and Semenov based on the one of Mallard and Le Chatelier [22]). As illustrated the structure of the flame is then divided into two distinct zones: a thin reaction zone (thickness $\delta r$) in which reaction and diffusion balance and a preheat zone (thickness $\delta p$) in which convection and diffusion dominate and balance. It is assumed that $\delta r << \delta p$. In the reaction zone, the reaction rate profile results from the combined effect of the activation of the reaction and the depletion of reactants. [21]

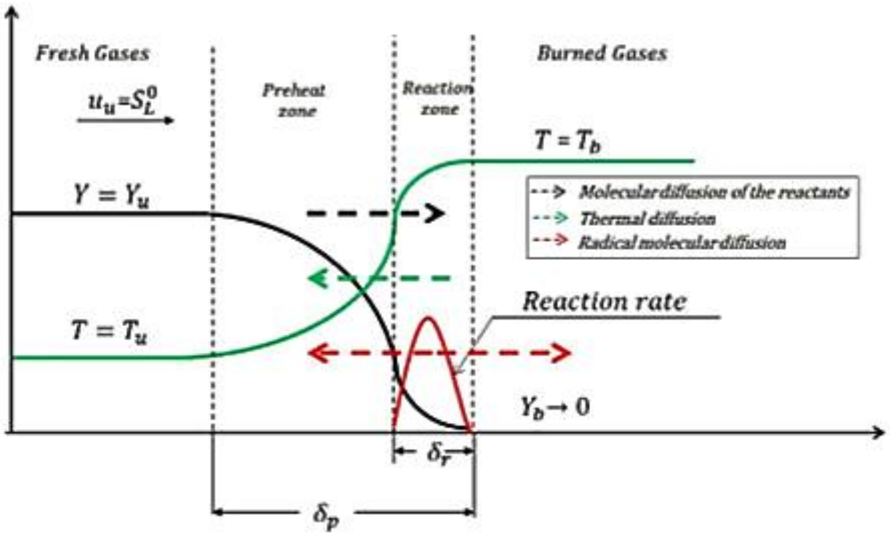


Figure 4-5.Schematic structure of a 1D steady flame. Full description model

## 4.3 MATHEMATICAL DESCRIPTION OF LAMINAR FLAME SPEED

Laminar flame theories exist and have covered many studies for decades. Kuo [23], for example, mentions more than a dozen key studies on laminar flame theory published between 1940 and 1980. The following simplified analysis is based on one-dimensional conservation relations, with extra simplifying assumptions for thermodynamics and transports parameters used. the goal is to find a simple analytic formula for laminar flame speed [1]

**Assumption:**

- One-dimensional, constant-area, steady flow.
- Kinetic and potential energies, viscous shear work, and thermal radiation are all neglected.
- The diffusion of heat and mass are governed by Fourier's and Fick's laws, respectively. Binary diffusion is assumed.
- The Lewis number, Le, which expresses the ratio of thermal diffusivity to mass diffusivity, i.e.

$$Le \equiv \frac{a}{D} = \frac{k}{\rho C_p D} \tag{4-2a}$$

  This has the result that $\frac{k}{C_p} = \rho D,$ which greatly simplifies the energy equation.

- The mixture specific heat depends neither on temperature nor on the mixture composition. This is equivalent to assuming that the individual species specific heats are all equal and constant.
- Fuel and oxidizer form products in a single-step exothermic reaction.
- The oxidizer is present in stoichiometric or excess proportions; thus, the fuel is completely consumed at the flame.

This theoretical approach was inspired by the work of Turns [1]

### 4.3.1 Conservations law

To further comprehend flame propagation, we use differential control volume presented in to apply mass, species and energy conservation.

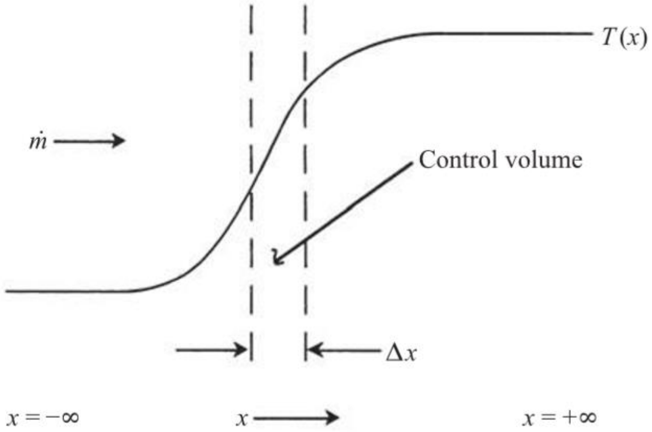


Figure 4-6.Control volume for flame analysis.

### 4.3.2 Mass conservation

$$\frac{d(\rho v_x)}{dx} \tag{4-3a}$$

Or

$$\dot{m}'' = \rho v_x = constant \tag{4-3b}$$

### 4.3.3 Species conservation

$$\frac{d\dot{m}_i''}{dx} = \dot{m}_i''' \tag{4-4}$$

Application of Flick's Law:

$$\frac{d\left[\dot{m}Y_i - \rho D\left(\frac{dY_i}{dx}\right)\right]}{dx} = \dot{m}_i''' \tag{4-5}$$

Where $\dot{m}_i'''$ is the mass production rate of species *i* per unit volume (kg / s-m$^3$).

The three species can be described with equation (4-5), where the oxidizer and products mass production rates are related the fuel production rate, since the fuel and oxidizer are being consumed, the production rate of fuel, $\dot{m}_F'''$ , and oxidizer, $\dot{m}_{Ox}'''$, are negative. The overall stoichiometry for our simple reaction is:

$$1kg\ fuel + v\ kg\ oxidizer \rightarrow (v+1)kg\ products \qquad (4\text{-}6)$$

Thus,

$$\dot{m}_F''' = \frac{1}{v}\dot{m}_{Ox}''' = -\frac{1}{v+1}\dot{m}_{Pr}''' \qquad (4\text{-}7)$$

### 4.3.4 Energy conservation

From the Shvab–Zeldovich description of energy conservation

$$\dot{m}''c_p\frac{\mathrm{d}T}{\mathrm{d}x} - \frac{\mathrm{d}}{\mathrm{d}x}\left[\left(\rho\mathcal{D}c_p\right)\frac{\mathrm{d}T}{\mathrm{d}x}\right] = -\sum h_{f,i}^{o}\dot{m}_i''' \qquad (4\text{-}8)$$

From the equations (4-7)(4-8), the right side of the above equation will be simplified as

$$-\sum h_{f,i}^{o}\dot{m}_i''' = -\left[h_{f,F}^{o}\dot{m}_F''' + h_{f,Ox}^{o}v\dot{m}_F''' - h_{f,Pr}^{o}(v+1)\dot{m}_F'''\right] \qquad (4\text{-}9a)$$

Or

$$-\sum h_{f,i}^{o}\dot{m}_i''' = -\dot{m}_F'''\Delta h_c, \qquad (4\text{-}9b)$$

where Δhc is the heat of combustion of the fuel.

$$\Delta h_c \equiv h_{f,F}^{o} + v h_{f,Ox}^{o} - (v+1)h_{f,Pr}^{o} \qquad (4\text{-}10a)$$

We may also replace $\rho Dc_p$ with $k$ due to the unity Lewis number approximation. (b)

From (4-10a) and (b), the equation (4-8) become

$$\dot{m}''\frac{\mathrm{d}T}{\mathrm{d}x} - \frac{1}{c_p}\frac{\mathrm{d}\left(k\frac{\mathrm{d}T}{\mathrm{d}x}\right)}{\mathrm{d}x} = -\frac{\dot{m}_F'''\Delta h_c}{c_p} \qquad (4\text{-}11)$$

By following Spalding's approach [24] we can find an expression for laminar flame speed related the flux mass, $\dot{m}''$,

$$\dot{m}'' = \rho_u S_L \qquad (4\text{-}12)$$

To calculate the mass burning rate, we will first assume a temperature profile that meets the boundary requirements provided below, and then integrate equation (4-11) using the given temperature distribution.

The boundary conditions far upstream of the flame are as follows:

$$T(x \to -\infty) = T_u \tag{4-13a}$$

$$\frac{\mathrm{d}T}{\mathrm{d}x}(\to -\infty) = 0 \tag{4-13b}$$

And far downstream of the flame

$$T(x \to +\infty) = T_b \tag{4-13c}$$

$$\frac{\mathrm{d}T}{\mathrm{d}x}(x \to +\infty) = 0 \tag{4-13d}$$

To simplify this analysis, we assume a simple linear temperature profile that goes from Tu to Tb over a small distance δ, as illustrated in Figure 4-7 , Where δ is the flame thickness.

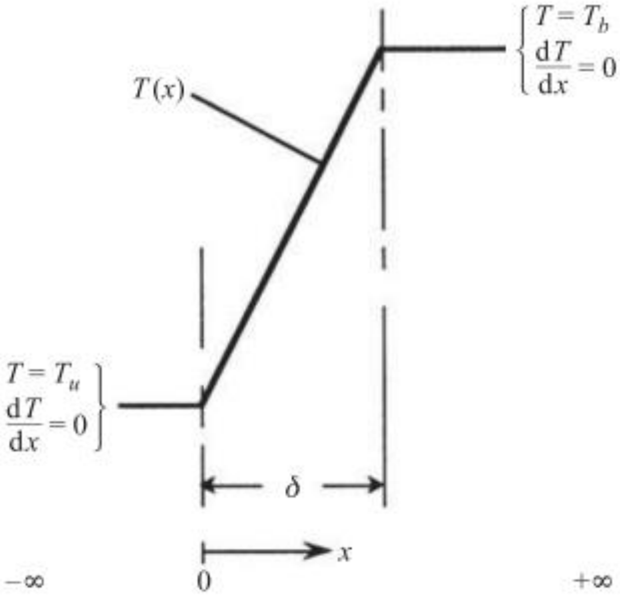


Figure 4-7.Assumed temperature profile for laminar premixed flame analysis.

By integrating the equation (4-8) over x and applying the conditions at −∞ and + ∞, yields:

$$\dot{m}''[T]_{T=T_u}^{T=T_b} - \frac{k}{c_p}\left[\frac{\mathrm{d}T}{\mathrm{d}x}\right]_{\mathrm{d}T/\mathrm{d}x=0}^{\mathrm{d}T/\mathrm{d}x=0} = \frac{-\Delta h_c}{c_p}\int_{-\infty}^{\infty} \dot{m}_F''' \mathrm{d}x \tag{4-14}$$

By evaluating the limits

$$\dot{m}''(T_b - T_u) = -\frac{\Delta h_c}{c_p}\int_{-\infty}^{\infty} \dot{m}_F''' \mathrm{d}x \tag{4-15}$$

Since $\dot{m}_F'''$ is only nonzero between $T_u$ and $T_b$ over the region δ, we can change the limits of reaction rate integral from space to temperature

$$\frac{\mathrm{d}T}{\mathrm{d}x} = \frac{T_b - T_u}{\delta} \text{ or } \mathrm{d}x = \frac{\delta}{T_b - T_u}\mathrm{d}T \tag{4-16}$$

And with changing of variables,

$$\dot{m}''(T_b - T_u) = -\frac{\Delta h_c}{c_p}\frac{\delta}{(T_b - T_u)}\int_{T_u}^{T_b} \dot{m}_F''' \mathrm{d}T \tag{4-17}$$

along with understanding the definition of the average response rate,

$$\bar{\dot{m}}_F''' \equiv \frac{1}{(T_b - T_u)}\int_{T_u}^{T_b} \dot{m}_F''' \mathrm{d}T \tag{4-18}$$

We got the simple result that

$$\dot{m}''(T_b - T_u) = -\frac{\Delta h_c}{c_p}\delta\bar{\dot{m}}_F''' \tag{4-19}$$

Since our objective is to find a simple algebraic formula for laminar flame speed, this can be done by following the same thing as before only we integrate for x = − ∞ to x = δ/2, Because a flame's reaction zone is in the high-temperature area, it is logical to suppose that m ̇_F^''' is zero in the interval − ∞ < x ≤ δ/ 2.

From Figure 4-7 we note that when $x=\delta/2$:

$$T = \frac{T_b + T_u}{2} \tag{4-20a}$$

$$\frac{\mathrm{d}T}{\mathrm{d}x} = \frac{T_b - T_u}{\delta} \tag{4-20b}$$

With the modified limits we obtain from equation (4-14),

$$\dot{m}''\delta/2 - k/c_p = 0 \tag{4-21}$$

By solving the equations (4-17)(4-19) simultaneously

$$\dot{m}'' = \left[2\frac{k}{c_p^2}\frac{(-\Delta h_c)}{(T_b - T_u)}\bar{m}_F'''\right]^{1/2} \tag{4-22}$$

And

$$\delta = 2k/\left(c_p\dot{m}''\right) \tag{4-23}$$

By applying the follow:

- The definition of laminar flame speed $S_L \equiv \dot{m}''/\rho_u$
- Thermal diffusivity $\alpha \equiv k/\rho_u c_p$.
- $\Delta h_c = (v+1)c_p(T_b - T_u)$

We obtain the final simplified theory result for the laminar flame speed,

$$S_L = \left[-2\alpha(v+1)\frac{\bar{m}_F'''}{\rho_u}\right]^{1/2} \tag{4-24}$$

And for flame thickness,

$$\delta = \left[\frac{-2\rho_u\alpha}{(v+1)\bar{m}_F'''}\right]^{1/2} \tag{4-25a}$$

Or in term of laminar flame speed,

$$\delta = 2\alpha/S_L \tag{4-25b}$$

## 4.4 NUMERICAL APPROACH OF LAMINAR PREMIXED FLAME SPEED

To complete the theoretical studies of laminar flame speed and have a better understanding, Numerical tools have been used such as solving the complete set of transport equations numerically and by using chemical simulation tools as CANTERA, CHEMKIN, for more precious data a detailed reaction mechanism such as GRI-Mech is used, as a result, the laminar flame speed may be predicted accurately.

In this study a one-dimensional premixed flame of methane-hydrogen has been simulated and analysed by and using the chemical simulation tool CANTERA, reaction mechanism GRI 3.0, to find out the role of the hydrogen on the enhancement of the hybrid fuel burning velocity. A laminar flame propagation was simulated in a wide range of equivalence ratio and hydrogen content in the fuel's mixture. (0%, 5%,10% ,15%,25%,30%, and 50%).

### 4.4.1 Software used

#### *Cantera:*

Cantera is an open-source chemical kinetics software used for solving chemically reacting laminar flows. It has been used as a third-party library in external reacting flow simulation codes, such as FUEGO and CADS, using Fortran, C++, etc. to evaluate properties and chemical source terms that appear in the application's governing equations. Cantera was originally written and developed by Prof. Dave Goodwin of California Institute of Technology. It is written in C++ and can be used from C++, Python, MATLAB and Fortran. [25]

#### *ANACONDA*

Anaconda is a distribution of the Python and R programming languages for scientific computing (data science, machine learning applications, large-scale data processing, predictive analytics, etc.), that aims to simplify package management and deployment. The distribution includes data-science packages suitable for Windows, Linux, and macOS. It is developed and maintained by Anaconda, Inc., which was founded by Peter Wang and Travis Oliphant in 2012 [26].

#### *ANACONDA NAVIGATOR*

Anaconda Navigator is a desktop graphical user interface (GUI) included in Anaconda distribution that allows users to launch applications and manage conda_packages, environments and channels without using command-line commands. Navigator can search for packages on Anaconda Cloud or in a local Anaconda Repository, install them in an environment, run the packages and update them. It is available for Windows, macOS and Linux. [27]

#### *JUPYTER NOTEBOOK*

Jupyter Notebook (formerly IPython Notebooks) is a web-based interactive computational environment for creating Jupyter notebook documents. The "notebook" term can colloquially make reference to many different entities, mainly the Jupyter web application, Jupyter Python web server, or Jupyter document format depending on context. A Jupyter Notebook document is a JSON document, following a versioned schema, containing an ordered list of input/output cells which can contain code, text (using Markdown), mathematics, plots and rich media, usually ending with the “

. ipynb" extension.

### 4.4.2 Chemical kinetics mechanism

During this study, the GRI-Mech combustion mechanism was used for including more detailed Kinetics like GRI-Mech 1.2, GRI-Mech 2.11, and GRI-Mech 3.0, for our simulation we will be using the GRI-Mech 3.0 for consisting of multiple reactions and important hydrogen-based, methane-based and carbon-based reactions. It can be used for the simulation of various multicomponent mixtures.

#### *GRI-Mech 3.0*

GRI-Mech 3.0 is an optimized mechanism designed to model natural gas combustion, including NO formation and reburn chemistry. It is the successor to version 2.11, and another step in the continuing updating evolution of the mechanism. The optimization process is designed to provide sound basic kinetics which also furnish the best combined modelling predictability of basic combustion properties. Improvements were made in the categories of updating the kinetics with recent literature results, including some new and improved target experiments to the optimization, expanding the mechanism and target selection, and examining the sensitivity to the thermodynamics. [28]

#### *Methane kinetics mechanism*

Several experimental and numerical research on methane/air combustion have been undertaken during the last few decades. Several complex chemical processes for resolving the complete chemistry of methane/air flames were established as a result of these studies. The GRI-Mech 3.0 kinetic mechanism was chosen for the current work (53 species and 325 elementary reactions). It is the most often used mechanism for simulating methane combustion, and it has been verified by several experimental results across a wide variety of temperature, pressure, and equivalency ratio working conditions.

***Hydrogen kinetics mechanism***

The GRI3.0 mechanism takes into account fuels that include hydrocarbons, while pure hydrogen does not include carbon. The stiffness of the differential equations, starting species concentrations, and solver control settings all have a substantial influence on computing time. So, in order to save time, the mechanism including the reaction necessary for hydrogen fuel is sufficient, even though the same analysis is possible with GRI3.0.

### 4.4.3 Cantera model

Since flame speed can be affected by various parameters like fuel type, fuel-oxidizer ratio (equivalence ratio), pression and initial temperature, in this study we will focus on hydrogen fractions in the stochiometric mixtures as showed in Table 2 and the effect on the laminar speed and comparison between the mixtures.

The initial temperature and pression are 300K,1atm respectively, we create a solution object “gas “using the initial conditions.

A freeflame is created with a domain length of 0.015m from the gas object, The Newton-Raphson approach is used by the Cantera solver to find a solution for a coarse grid. The solution is then monitored for slopes and curvature, and grid refinement is performed at places of interest. The solving and refining process is repeated until a converged solution fulfilling the refinement requirements is achieved.

| *Fuel* | *Mixture compositions (%)* | *Reactions* |
|---|---|---|
| $CH_4$-$H_2$ | (100/0) | $CH_4+2(O_2+3.76N_2) \rightarrow CO_2+2H_2O+7.52N_2$ |
| $CH_4$-$H_2$ | (95/5) | $0.95CH_4+0.05H_2+1.925(O_2+3.76N_2) \rightarrow CO_2+2H_2O+7.52N_2$ |
| $CH_4$-$H_2$ | (90/10) | $0.9CH_4+0.1H_2+1.85(O_2+3.76N_2) \rightarrow CO_2+2H_2O+7.52N_2$ |
| $CH_4$-$H_2$ | (85/15) | $0.85CH_4+0.15H_2+1.775(O_2+3.76N_2) \rightarrow CO_2+2H_2O+7.52N_2$ |
| $CH_4$-$H_2$ | (75/25) | $0.75CH_4+0.25H_2+1.625(O_2+3.76N_2) \rightarrow CO_2+2H_2O+7.52N_2$ |
| $CH_4$-$H_2$ | (70/30) | $0.7CH_4+0.3H_2+1.55(O_2+3.76N_2) \rightarrow CO_2+2H_2O+7.52N_2$ |
| $CH_4$-$H_2$ | (50/50) | $0.5CH_4+0.5H_2+1.25(O_2+3.76N_2) \rightarrow CO_2+2H_2O+7.52N_2$ |

Table 4-2.Reaction's stoichiometry of fuel premixed methane-hydrogen with different hydrogen fractions

The Cantera script of the simulation of the reactions is in appendix A

# Chapter 5: RESULT AND DISCUSSION

## 5.1 LAMINAR BURNING SPEED

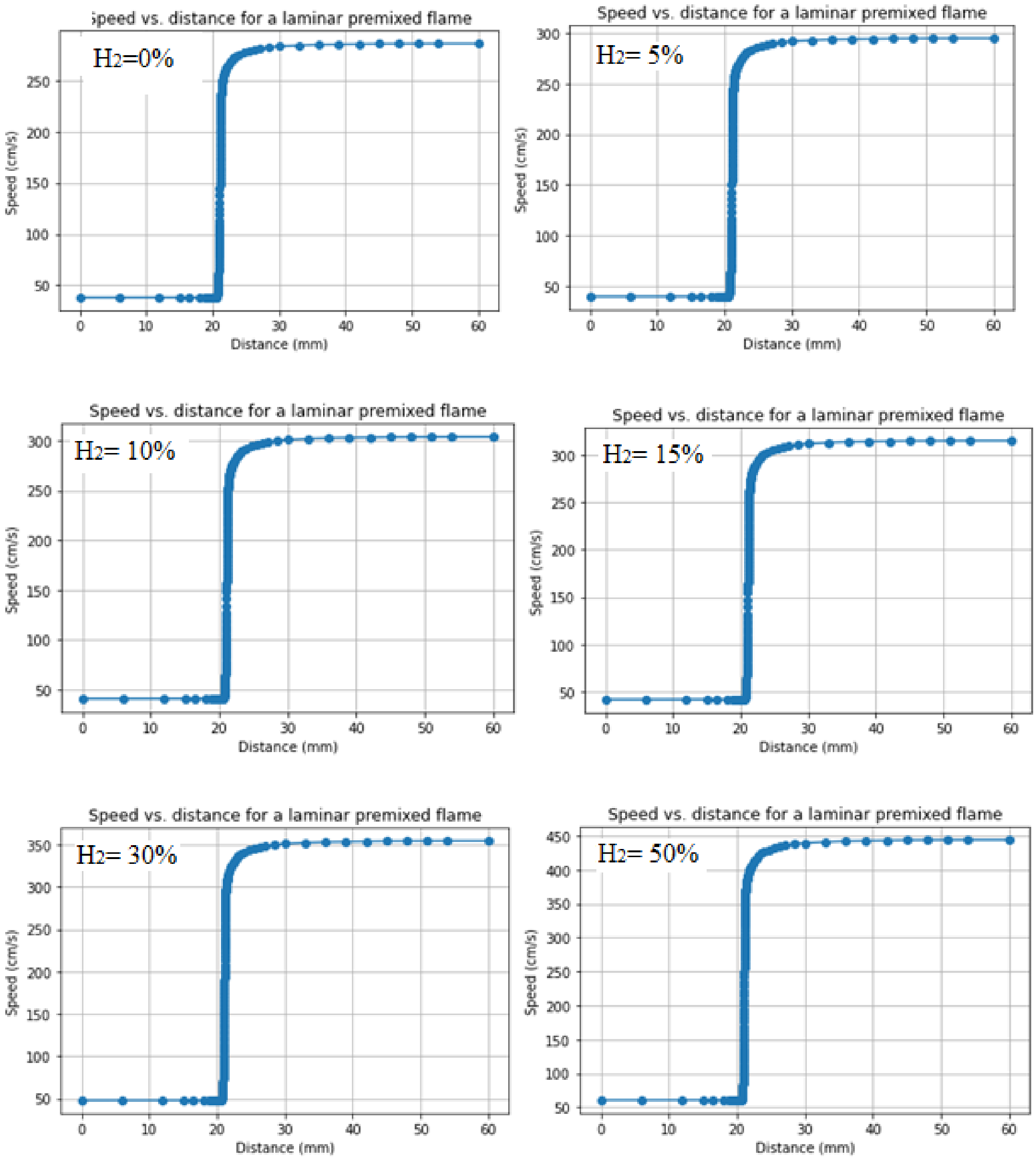


Figure 5-1.Laminar burning velocity of hydrogen–methane/air mixtures as function of the hydrogen content at 6 values of hydrogen percentages

At 300 K and 1 atm, the laminar burning velocities of hydrogen–methane/air mixes were determined by changing the fuel content from pure methane to a mixture of 50%$H_2$ and 50%$CH_4$.

In **Error! Reference source not found.** the computed values of speed are plotted versus the distance for a laminar premixed flame at six values of $\mathrm{H_2}$ percentages (= 0%; 5%; 10%; 15%; 30%; 50%). In the same plot the linear combination of the laminar burning velocity of the pure fuels is also shown.

From **Error! Reference source not found.**, at all the hydrogens percentages, it is possible to identify three regimes in the hybrid flame propagation depending on the distance in the combustion.

At low distance (0 < D < 20), a regime a linear and slight increase of the laminar burning velocity.

At intermediate distance (20 < D < 30), a regime a linear and sharp decrease of the laminar burning velocity on increasing of the distance.

At high distance (30 < D < 60) a transition regime is found.

It appears that the speed is reaching the highest values as the hydrogen percentage is getting higher as we can notice from the **Error! Reference source not found.** the speed value was about $280\,{}^{cm}/_{s}$ when the hydrogen percentage was 0% and it jumped into $450\,{}^{cm}/_{s}$ when the hydrogen percentage was 50% where this acceleration appears clearly in the 2nd regime where the laminar burning velocity calculated as follows:

$$S1_{\_linear}\left(\phi, X_{H_2}\right) = S1_{\_H_2}(\phi).X_{H_2} + S1_{\_CH_4}(\phi).(1 - X_{H_2}) \tag{5-1}$$

where $S1_{\_H_2}$ and $S1_{_CH_4}$are the laminar burning velocity of hydrogen and methane evaluated at the same equivalence ratio of the hybrid fuel ($\phi$).

## 5.2 LAMINAR BURNING TEMPERATURE AND ACTIVE RADICAL FORMATIONS

### 5.2.1 Temperature

The laminar burning temperatures of hydrogen–methane/air mixtures are in the same conditions as the velocity experiments and they were calculated by varying the fuel composition from pure methane to a mixture of $50\%$ $\mathrm{H_2}$ and $50\%$ of $\mathrm{CH_4}$.

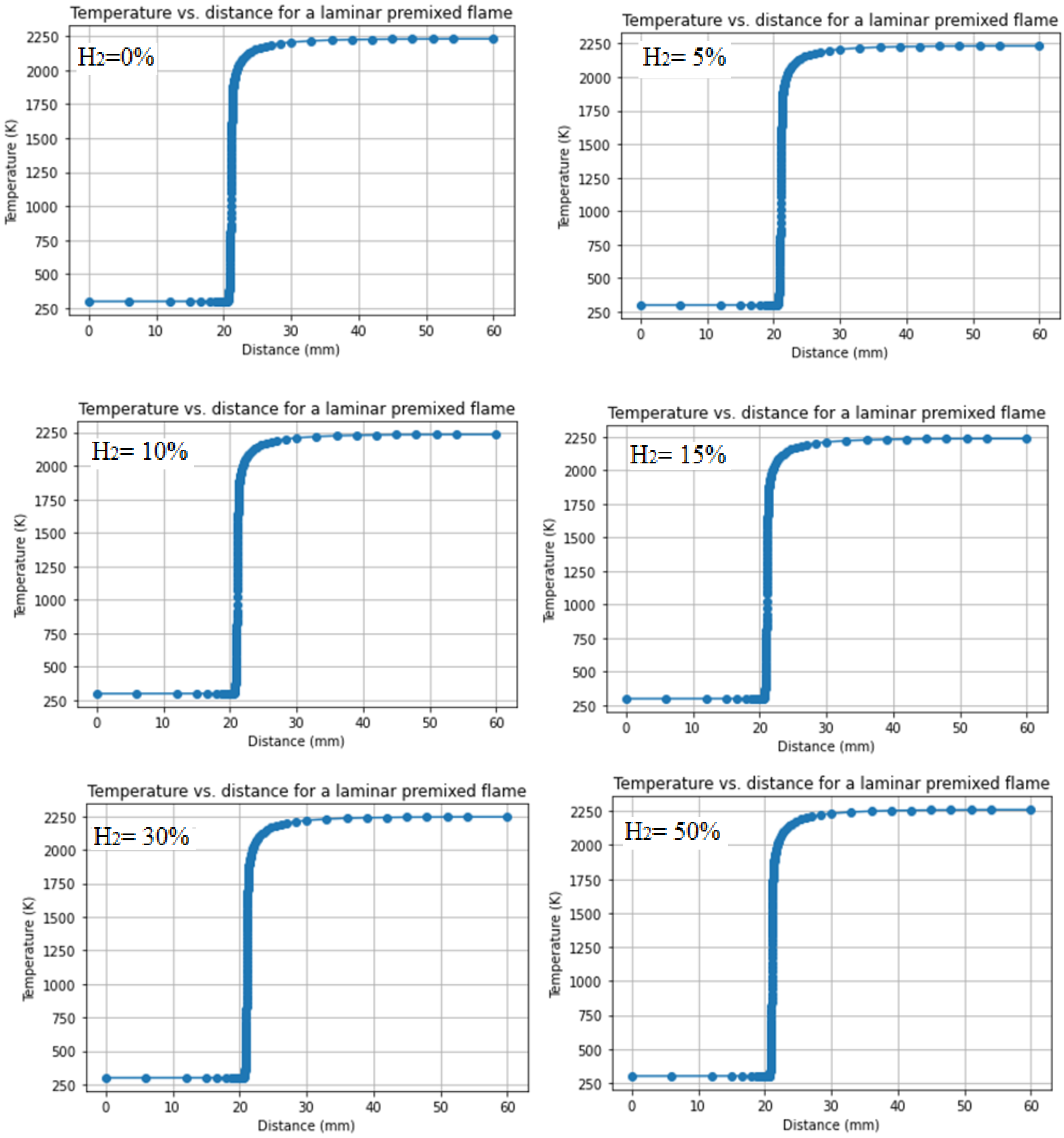


Figure 5-2.Laminar burning temperature of hydrogen–methane/air mixtures as function of the hydrogen content at 6 values of hydrogen percentages

Figure 5-2 depicts some typical spatially-varying temperature profiles of $CH_4$/air flames enhanced with various hydrogen additions. The substantial changes were typically begun early in the flame's preheat reaction zone., the earlier increase in flame temperature was observed in each experiment. There appeared to be some temperature rise competitive characteristics for the flames enriched by $H_2$. When compared to a pure $CH_4$/air flame, the $CH_4$/$H_2$/air flames with the lowest $H_2$ percentages showed a somewhat delayed temperature increase, but the $CH_4$/$H_2$/air flames with higher $H_2$ percentages showed an earlier increase.

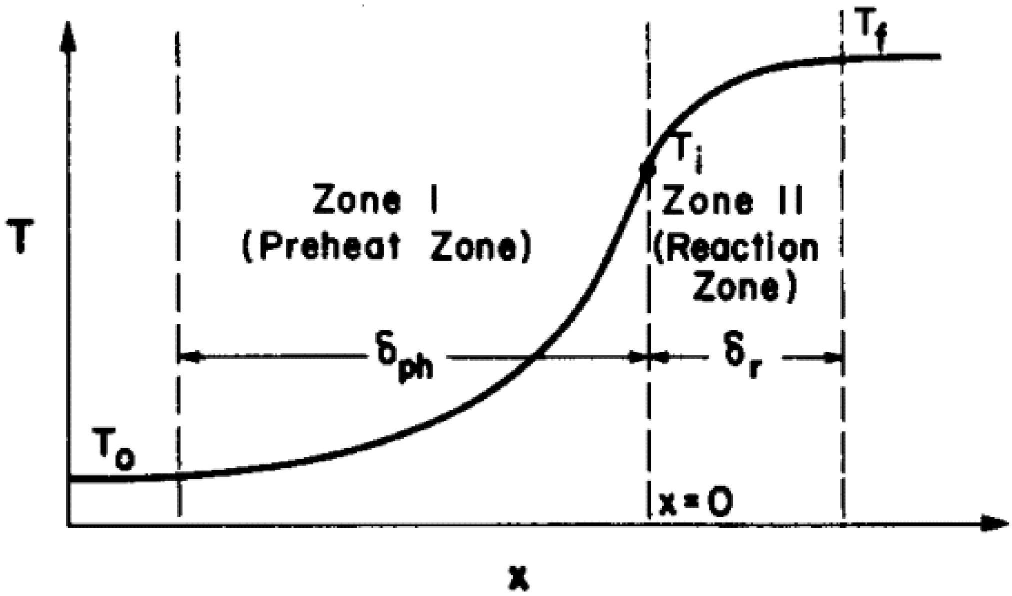


Figure 5-3.laminar burning temperatures reaction zones

### 5.2.2 Active radical formations

The controlling species in increasing the oxidation of fuel reactants are active radicals such as H, O, and OH. The geographical development of the radical pool (the sum of H, O, and OH) in the preheat reaction zone was examined to evaluate the chemical impacts of hydrogen addition on the beginning of flame kernel. Figure 5-4 depicts the results. Because these radicals were solely produced from methane, the concentrations of hydrocarbon and O2 in the mixture were the two controlling variables in the formation of O, H, and OH pools for $CH_4$/$H_2$/air flames. The amount of methane in flames reduced as the amount of fake hydrogen supplied to the flame increased. Less methane in the flame limited the production of OH, H, and even O. However, the effects of fictional hydrogen on the formation of active radicals were shown to be unpredictable.

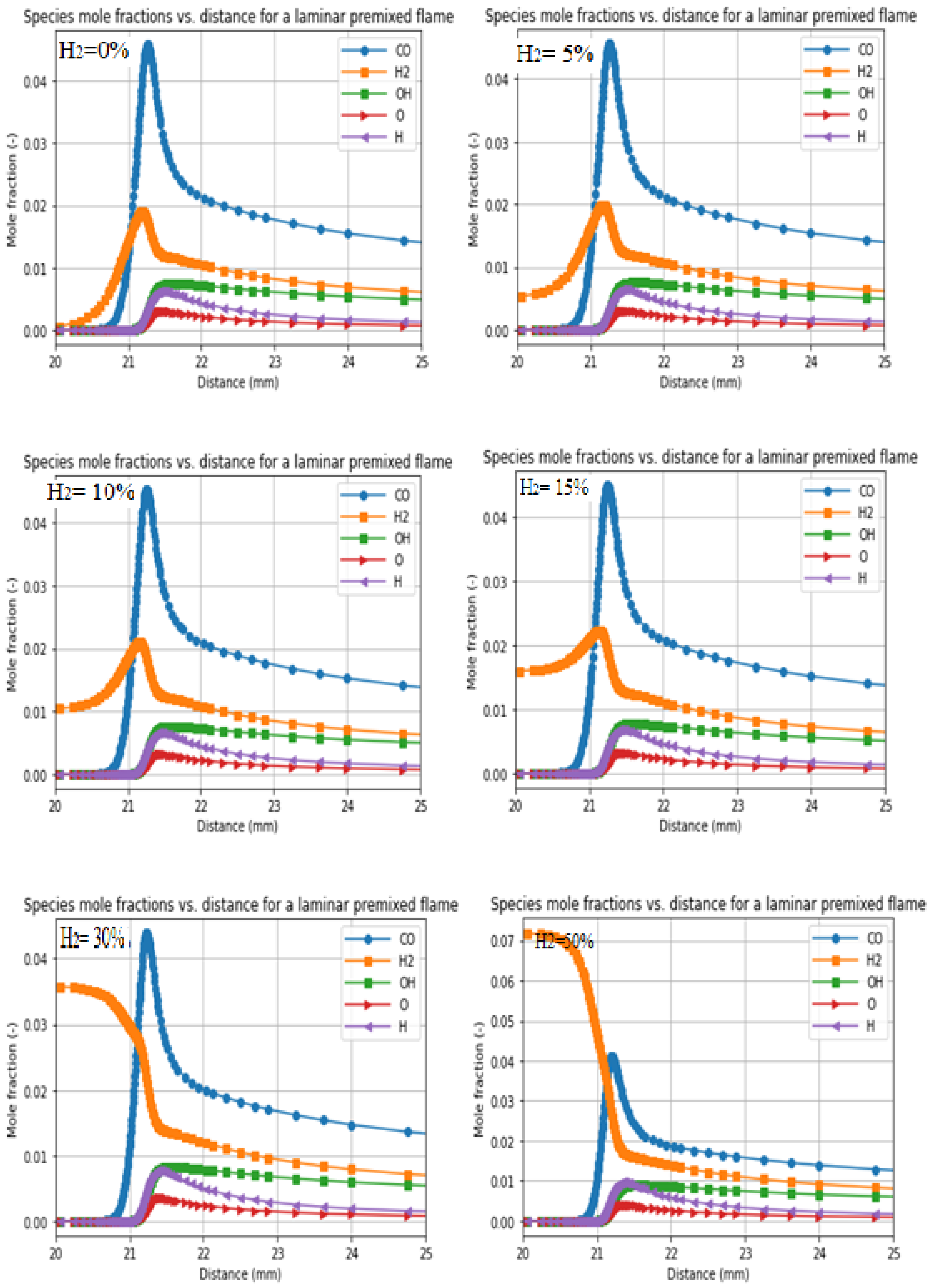


Figure 5-4.O, H, CO and OH molar concentration in the laminar burning as function of the hydrogen content at 6 values of hydrogen percentages.

When compared to the pure $CH_4$/air flame, the $CH_4$/$H_2$/air flame with the lowest $H_2$ percentages exhibited a delayed build-up of the O, H, and OH pool, whereas the $CH_4$/$H_2$/air flame with the highest $H_2$ percentages showed an accelerated profile. The trend was the same as the temperature rise of these flames. When compared to the pure $CH_4$/air flame, the $CH_4$/$H_2$/air flame with the lowest $H_2$ percentages exhibited a delayed build-up of the O, H, and OH pool, whereas the $CH_4$/$H_2$/air flame with the highest $H_2$ percentages showed an accelerated profile. The trend was the same as the temperature rise of these flames. The excessively high radical concentration in the preheat zone of the $CH_4$/$H_2$/air flame with higher $H_2$ percentages and the quickly rising flame preheat zone temperature might be cause and effect. As compared to the $CH_4$/air flame, the flames with typical hydrogen addition produced more O, H, and OH radicals in the preheat reaction zone. The enhancing impact grew more pronounced as the amount of reactive hydrogen added increased. The flames of $CH_4$/$H_2$/air. In order to compare the kinetic impacts of nonreactive and reactive hydrogen additions on the $CH_4$/air flame, a reaction path analysis was performed in terms of the reaction contribution of OH and H formation. The reaction's contribution to the creation or consumption of a particular species S is calculated as; [29]

$$C_{s,i} = {P_{s,i}} \Big/ {\textstyle\sum_{i=1}^{N} |P_{s,i}|} \tag{5-2}$$

$P_{s,i}$ indicates the reaction's transient production or consumption rate of species S, and N is the number of elementary reactions linked to the production or consumption of S species. A positive/negative value of $C_{s,i}$ indicates that the reaction produces or consumes species S.

## 5.3 REACTANTS CONSUMPTION AND PRODUCTS FORMATION

Figure 5-5 and Figure 5-6 showed a decrease of unburned hydrocarbons, carbon monoxide, carbon dioxide and, with the addition of hydrogen in the fuel. Where the $CO_2$ decrease showed clearly in the Figure 5-5 and in a smaller scaling Figure 5-6 the CO decrease and others products formation showed more clearly. And this decrease is a great result for the study of pollutant emissions due to the massive use of fossil fuels combustion, especially to the effects they can cause on the health and the environment where the focused on the use of hydrogen as a potential alternative to fossil fuels.

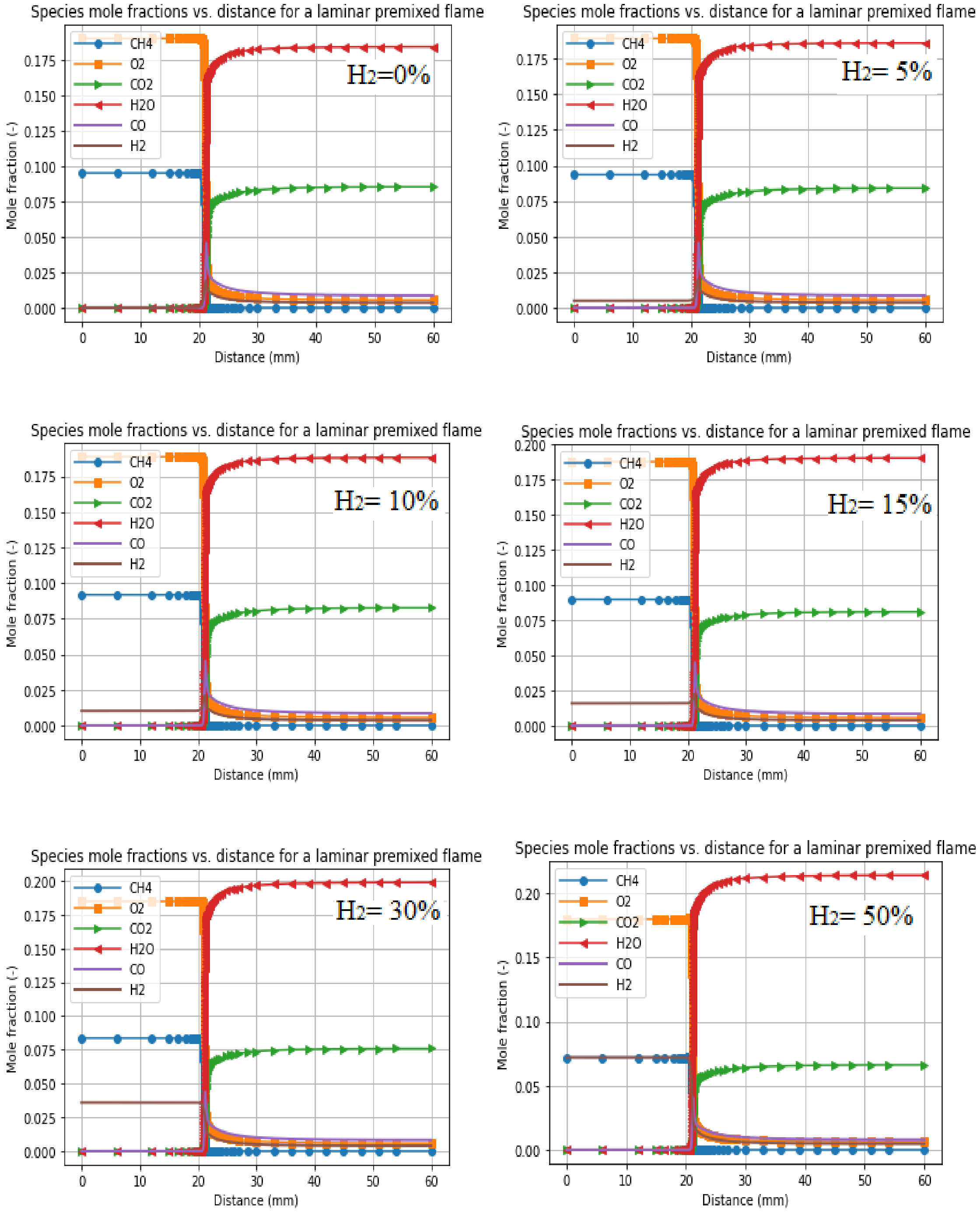


Figure 5-5.: the consumption of Reactants and the products formation in the laminar burning as function of the hydrogen content at 6 values of hydrogen percentages (from 0 to 60 distance from the burner surface)

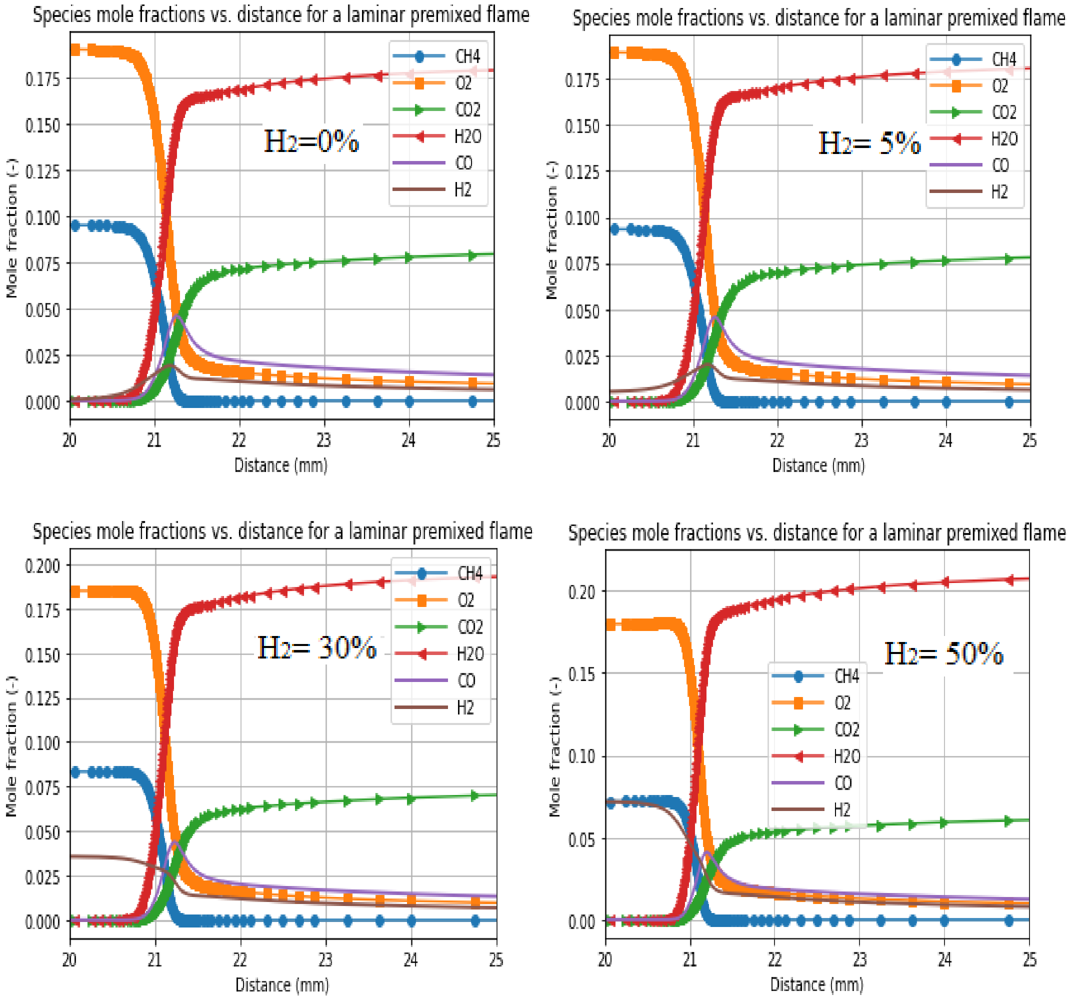


Figure 5-6.the consumption of Reactants and the products formation in the laminar burning as function of the hydrogen content at 4 values of hydrogen percentages (from 20 to 25 distance from the burner surface)

## 5.4 CONCLUSION

Not only is hydrogen a reactive fuel, but it is also an essential intermediary in hydrocarbon/air combustion. Its chemical motivation on hydrocarbon flames is the responsiveness to participate in the elementary processes, as well as the heat release by self-oxidation. An additional kinetics of hydrogen addition was proposed in the study to identify fuel-added hydrogen from flame-generated hydrogen. The hydrogen addition was treated as a fictional fuel and was included in the premixed flame modeling with one-step reaction kinetics. The following are the key conclusions:

1. With a rise in hydrogen fraction, the laminar burning velocity increases, and the peak value of the laminar burning velocity shifts to the rich mixture side. The laminar burning velocity rises linearly with the increase in hydrogen percentage in all of the experiments. In the transition regime, however, the laminar burning velocity grows exponentially as the hydrogen proportion in the fuel mixes increases.
2. In comparison to $CH_4$/air flames, hydrogen-enriched flames demonstrated earlier temperature rise and radical build-up in the preheat zone.
3. Enhancement of chemical reaction with hydrogen addition is due to the increase of H, O and OH mole fractions in the flame as hydrogen is added. A strong correlation is existed between burning velocity and maximum radical concentrations of H and OH radicals in the reaction zone of premixed flames. High burning velocity corresponds to high radical concentration in the reaction zone.
4. The hydrogen addition causes decrease of unburned hydrocarbons showed that the hydrogen will play a huge role in the future of humanity because of its effects on the health and the environment and it will be the best alternative to fossil fuels.

# Chapter 6: CONCLUSION

The premixed flame is a flame that created by the homogeneous stoichiometric combustion between a fuel (which can be a petroleum fuel or a natural gas) and an oxidizer and the process is started when it starts sustaining itself by way of its own heat release. the model of one-dimensional steady flame has been used to simplify the phenomena of the laminar flame where the flame is represented as an interface and separates the fresh gas or unburned gas to the burned gases where the species mass fraction goes from the initial state $Y = Yu$ to $Yb = 0$. The fuel and oxidizer are premixed before combustion and the flow is laminar. In our experiment we focused on the fuel used on the combustion and how can hydrogen be useful in increasing the burning efficiency and even more safe for humans lives and environment (hydrogen reacts with many different kinds of elements to form compounds with them. As is well known, hydrogen easily reacts (burns) with oxygen at a wide range of mixing ratios and forms water and its chemical incentive on hydrocarbon flames involves the reactivity to participate in the elementary reactions, and the heat release by self-oxidation) where we used a methene-hydrogen fuel with different hydrogen concentrations where we noticed different results and many changes in the burning velocity and temperature, the active radicals and reactants consumption and products formation with the changing of the hydrogen percentages in the mixture and our results are resumed by:

- an increase of the burning velocity with the increase of hydrogen fraction.
- an earlier temperature increases and earlier radical build-up in the preheat zone caused by the hydrogen addition.
- a decrease of unburned hydrocarbons in the products with the increase of hydrogen fraction.

And from the result we’ve obtained we can say that the hydrogen is not just a reactive fuel but it’s an important intermediate in hydrocarbon/air flames as well, or even farther it can be the alternative to fossil fuels and be humanity’s future while being more efficient and less harmful to health and environment.

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# Appendices

# APPENDIX A

## Cantera script of the simulation

```
# import modules
import cantera as ct
import numpy as np
import matplotlib.pyplot as plt
import time
# print Cantera version
print("Running Cantera version: {}".format(ct.__version__))
# define the gas mixture
# here we use the thermodynamic properties, reaction mechanism, and molecular transport properties from gri30.cti
gas = ct.Solution('gri30.cti')
# specify the unburned reactant mixture thermochemical state
# here we consider a stoichiometric mixture of CH4-H2 and air at ambient pressure and temperature
T_u  = 300.       # (K)
P_u  = ct.one_atm # (Pa)
fuel = {'CH4':0.5, 'H2':0.5}
air  = {'O2':1.25, 'N2':4.7}
phi  = 1.0
gas.TP = T_u, P_u
gas.set_equivalence_ratio(phi, fuel, air)
# print the state of the unburned reactants
gas()
# let's see what "FreeFlame" does
help(ct.FreeFlame)
# specify the initial size ("width") of the 1D computational domain
```

```
# the width of the domain will be extended automatically, if needed, over the course of the numerical simulation
width = 0.015 # (m)
# create the flame object by filling the computational domain with the desired gas mixture
flame = ct.FreeFlame(gas, width=width)
# specify numerical parameters used to control local grid refinement
# by default, the code will start with a coarse uniform grid
# it will then successively refine the grid, inserting more grid points locally in regions where the solution varies
#   rapidly in space
# some prior experience can be helpful to determine appropriate values
# you can experiment to see what happens if you change these values
flame.set_refine_criteria(ratio=3, slope=0.1, curve=0.1)
# specify the level of output desired
# loglevel = 1 is appropriate for current purposes
# you can decrease/increase the value of loglevel to see less/more detailed output
# valid values for loglevel are 0 (no output) to 5 (most detailed output)
loglevel = 1
# list all available attributes of "flame": that is, of a Cantera "FreeFlame" object
dir(flame)
# print the initial computational grid
flame.grid
# print the initial temperature profile
flame.T
# print the initial velocity profile
flame.velocity
# print the initial CH4 mole fraction profile
flame.X[gas.species_index('CH4')]
# for "auto=True", the code will sequentially execute the default solution stages, and will attempt to recover from any
#   errors that are encountered
ctim0 = time.time()
```

```
flame.solve(loglevel=loglevel, auto=True) # this will take a minute or so to run, depending on your computer
ctim1 = time.time()
ctime = ctim1 - ctim0
# print the final grid
flame.grid
# print the laminar flame speed in cm/s, and the computational time required
S_L = flame.velocity[0]
print("Flame Speed is: {:.2f} cm/s. Simulation took {:.2f} s".format(S_L*100.,ctime))
# plot the steady-state temperature profile
fig, ax = plt.subplots()
ax.plot(flame.grid*1000., flame.T, '-o', label='T')
ax.set(xlabel='Distance (mm)',
       ylabel='Temperature (K)',
       title ='Temperature vs. distance for a laminar premixed flame')
ax.grid(True)
#ax.legend(handlelength=4,loc='best')
fig.savefig("T_vs_x_LPF.pdf")
# plot the steady-state velocity profile
fig, ax = plt.subplots()
ax.plot(flame.grid*1000., flame.velocity*100., '-o', label='u')
ax.set(xlabel='Distance (mm)',
       ylabel='Speed (cm/s)',
       title ='Speed vs. distance for a laminar premixed flame')
ax.grid(True)
#ax.legend(handlelength=4,loc='best')
fig.savefig("u_vs_x_LPF.pdf")
# compute the profile of mass density times flow speed through the flame
rhou = flame.density*flame.velocity
# print the result
Rhou
```

```
# plot steady-state major-species mole-fraction profiles, plus CO and H2
X_CH4 = flame.X[gas.species_index('CH4')]
X_O2  = flame.X[gas.species_index('O2')]
X_N2  = flame.X[gas.species_index('N2')]
X_CO2 = flame.X[gas.species_index('CO2')]
X_H2O = flame.X[gas.species_index('H2O')]
X_CO  = flame.X[gas.species_index('CO')]
X_H2  = flame.X[gas.species_index('H2')]
fig, ax = plt.subplots()
ax.plot(flame.grid*1000., X_CH4, '-o', label='CH4')
ax.plot(flame.grid*1000., X_O2,  '-s', label='O2')
#ax.plot(flame.grid*1000., X_N2,  '-s', label='N2') # leave out N2, so that other species can be seen more clearly
ax.plot(flame.grid*1000., X_CO2, '->', label='CO2')
ax.plot(flame.grid*1000., X_H2O, '-<', label='H2O')
ax.plot(flame.grid*1000., X_CO,       label='CO', lw=2)
ax.plot(flame.grid*1000., X_H2,       label='H2', lw=2)
ax.set(xlabel='Distance (mm)',
       ylabel='Mole fraction (-)',
       title ='Species mole fractions vs. distance for a laminar premixed flame')
ax.grid(True)
ax.legend(handlelength=4,loc='best')
fig.savefig("Xmajor_vs_x_LPF.pdf")
# zoom in to see more clearly what is happening in the main reaction zone
# the x limits may need to be changed to capture the flame zone, depending on the version of Cantera that you are using
fig, ax = plt.subplots()
ax.plot(flame.grid*1000., X_CH4, '-o', label='CH4')
ax.plot(flame.grid*1000., X_O2,  '-s', label='O2')
#ax.plot(flame.grid*1000., X_N2,  '-s', label='N2')
ax.plot(flame.grid*1000., X_CO2, '->', label='CO2')
```

```
ax.plot(flame.grid*1000., X_H2O, '-<', label='H2O')
ax.plot(flame.grid*1000., X_CO,       label='CO', lw=2)
ax.plot(flame.grid*1000., X_H2,       label='H2', lw=2)
ax.set(xlim=(20.,25.),
       xlabel='Distance (mm)',
       ylabel='Mole fraction (-)',
       title='Species mole fractions vs. distance for a laminar premixed flame')
ax.grid(True)
ax.legend(handlelength=4,loc='best')
fig.savefig("Xmajor_vs_x_LPF_zoom.pdf")
# plot steady-state minor-species mole fraction profiles
X_CO  = flame.X[gas.species_index('CO')]
X_H2  = flame.X[gas.species_index('H2')]
X_OH  = flame.X[gas.species_index('OH')]
X_O   = flame.X[gas.species_index('O')]
X_H   = flame.X[gas.species_index('H')]
fig, ax = plt.subplots()
ax.plot(flame.grid*1000., X_CO, '-o', label='CO')
ax.plot(flame.grid*1000., X_H2, '-s', label='H2')
ax.plot(flame.grid*1000., X_OH, '-s', label='OH')
ax.plot(flame.grid*1000., X_O,  '->', label='O' )
ax.plot(flame.grid*1000., X_H,  '-<', label='H' )
ax.set(xlim=(20.,25.),
       xlabel='Distance (mm)',
       ylabel='Mole fraction (-)',
       title ='Species mole fractions vs. distance for a laminar premixed flame')
ax.grid(True)
ax.legend(handlelength=4,loc='best')
fig.savefig("Xminor_vs_x_LPF_zoom.pdf")
# plot the steady-state heat-release-rate profile
```

```
fig, ax = plt.subplots()
ax.plot(flame.grid*1000., flame.heat_release_rate, '-o', label='HRR')
ax.set(xlim=(20.,23.),
       xlabel='Distance (mm)',
       ylabel='Heat-release rate (W/m^3)',
       title ='HRR vs. distance for a laminar premixed flame')
ax.grid(True)
#ax.legend(handlelength=4,loc='best')
fig.savefig("HRR_vs_x_LPF_zoom.pdf")
# define a function that returns the laminar flame speed for a given reactant mixture state
# the gas mixture "gas" must be defined before calling this function
# here we suppress all output - this can be dangerous, if one is not confident that the solution will converge for all
#   cases of interest
# T_u is the unburned gas temperature (K)
# P is the constant pressure (Pa)
# fuel is the fuel desired, which must be available in "gas"
# air is the mixture of species corresponding to air, which must be defined before calling this function
# phi is the desired equivalence ratio
def gas_sl(T_u,P,fuel,air,phi):
    gas.TP = T_u, P
    gas.set_equivalence_ratio(phi,fuel,air)
    width = 0.015 # (m)
    flame = ct.FreeFlame(gas, width=width)
    flame.set_refine_criteria(ratio=3, slope=0.1, curve=0.1)
    loglevel = 0
    flame.solve(loglevel=loglevel, auto=True)
    s_l = flame.velocity[0] # (m/s)
    return s_l
# specify the values of the equivalence ratio at which to compute the laminar flame speed
```

```
phis = [0.70, 0.80, 0.90, 0.95, 1.00, 1.05, 1.10, 1.15, 1.20, 1.30, 1.40]
# compute the laminar flame speed for each equivalence ratio using the detailed reaction mechanism
# here the reactants are at ambient pressure and temperature, and are undiluted
fuel = 'CH4:0.5, H2:0.5’
air  = 'O2:1.25, N2:4.7’
T_u   = 300.
P     = ct.one_atm
# define an array to hold the computed laminar flame speed for each equivalence ratio
S_Lgas = np.zeros(np.size(phis))
# loop over the equivalence ratios, and compute the laminar flame speed for each equivalence ratio
# be patient - this may take a few minutes, depending on your computer
for i, phi in enumerate(phis):
    S_Lgas[i] = gas_sl(T_u,P,fuel,air,phi)
    print(i,phi,S_Lgas[i])
# define another function that returns the laminar flame speed from a Metghalchi-and-Keck-based correlation
# here the parameters phi_M, B_M, and B_2 have been chosen to give good agreement with gri30.cti
#   for equivalence ratios close to phi_M, and on the lean side
def MetghalchiKeckCH4(T_u,P,Y_dil,phi):
    T_uref = 298.       # (K)
    P_ref  = ct.one_atm # (Pa)
    phi_M  = 1.05       # (-) equivalence ratio at which the laminar flame speed has its maximum value
    B_M    = 38.4       # (cm/s) maximum laminar flame speed, for T_u=T_uref and P=P_ref and Y_dil=0
    B_2    = -150.      # (cm/s) rate of falloff of laminar flame speed away from phi_M
    S_Lref = B_M + B_2*( phi - phi_M )**2
    gamma  =  2.18 - 0.8 *( phi - 1. )
    beta   = -0.16 + 0.22*( phi - 1. )
    S_L    = S_Lref*(T_u/T_uref)**gamma*(P/P_ref)**beta*( 1. - 2.1*Y_dil ) / 100. # (m/s)
    return S_L
# compute the laminar flame speed for each equivalence ratio using the flame-speed correlation
# here the reactants are at ambient pressure and temperature, and are undiluted
```

```
T_u   = 300. # (k)
P     = ct.one_atm # (Pa)
Y_dil = 0. # this is included because it is needed for the flame-speed correlation
# define an array to hold the computed laminar flame speed for each equivalence ratio
S_Lmk = np.zeros(np.size(phis))
# loop over the equivalence ratios, and compute the laminar flame speed for each equivalence ratio
for i, phi in enumerate(phis):
    S_Lmk[i] = MetghalchiKeckCH4(T_u,P,Y_dil, phi)
    print(i,phi,S_Lmk[i])w
# plot laminar flame speeds versus equivalence ratio
fig, ax = plt.subplots()
ax.plot(phis , S_Lgas*100., '-o', label='gri30')
ax.plot(phis , S_Lmk*100.,  '-s', label='MK')
ax.set(xlabel='Equivalence ratio (-)',
       ylabel='Flame speed (cm/s)',
       title ='Laminar flame speed vs. equivalence ratio for CH4-air')
ax.grid(True)
ax.legend(handlelength=4,loc='best')
fig.savefig("S_L_vs_phi.pdf")
```

# APPENDIX B

## Fuel Properties

**Table B.1:** Selected properties of hydrocarbon fuels: enthalpy of formation Gibbs function of formation°, a entropy°, a and higher and lower heating values all at 298.15 K and 1 atm; boiling points[b] and latent heat of vaporization[c] at 1 atm; constant–pressure adiabatic flame temperature at 1 atm; liquid density:

| Formula | Fuel | MW (kg / kmol) | $\bar{h}_f^o$ $(kJ/kmol)$ | $\bar{g}_f^o$ $(kJ/kmol)$ | $\bar{s}^o$ $(kj/kmol)$ | HHV† (kJ/kg) | LHV† (kJ/kg) | Boiling pt (°C) | $h_{fg}$ (kJ / kg) | $T_{ad}^{\ddagger}$ (K) | $\rho_{liq}^{*}$ (kg /m3) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $CH_4$ | Methane | 16.043 | −74,831 | −50,794 | 186.188 | 55,528 | 50,016 | −164 | 509 | 2226 | 300 |
| $C_2H_2$ | Acetylene | 26.038 | 226,748 | 209,200 | 200.819 | 49,923 | 48,225 | −84 | — | 2539 | — |
| $C_2H_4$ | Ethene | 28.054 | 52,283 | 68,124 | 219.827 | 50,313 | 47,161 | −103.7 | — | 2369 | — |
| $C_2H_6$ | Ethane | 30.069 | −84,667 | −32,886 | 229.492 | 51,901 | 47,489 | −88.6 | 488 | 2259 | 370 |
| $C_3H_6$ | Propene | 42.080 | 20,414 | 62,718 | 266.939 | 48,936 | 45,784 | −47.4 | 437 | 2334 | 514 |
| $C_3H_8$ | Propane | 44.096 | 103,847 | −23,489 | 269.910 | 50,368 | 46,357 | −42.1 | 425 | 2267 | 500 |
| $C_4H_8$ | 1-Butene | 56.107 | 1,172 | 72,036 | 307.440 | 48,471 | 45,319 | −63 | 391 | 2322 | 595 |
| $C_4H_{10}$ | n-Butane | 58.123 | −124,733 | −15,707 | 310.034 | 49,546 | 45,742 | −0.5 | 386 | 2270 | 579 |
| $C_5H_{10}$ | 1-Pentene | 70.134 | −20,920 | 78,605 | 347.607 | 48,152 | 45,000 | 30 | 358 | 2314 | 641 |
| $C_5H_{12}$ | n-Pentane | 72.150 | −146,440 | −8,201 | 348.402 | 49,032 | 45,355 | 36.1 | 358 | 2272 | 626 |
| $C_6H_6$ | Benzene | 78.113 | 82,927 | 129,658 | 269.199 | 42,277 | 40,579 | 80.1 | 393 | 2342 | 879 |
| $C_6H_{12}$ | 1-Hexene | 84.161 | −41,673 | 87,027 | 385.974 | 47,955 | 44,803 | 63.4 | 335 | 2308 | 673 |
|  | n-Hexane | 86.177 | −167,193 | 209 | 386.811 | 48,696 | 45,105 | 69 | 335 | 2273 | 659 |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $C_6H_{14}$ | 1-Heptene | 98.188 | −62,132 | 95,563 | 424.383 | 47,817 | 44,665 | 93.6 | — | 2305 | — |
| $C_7H_{14}$ | n-Heptane | 100.203 | −187,820 | 8,745 | 425.262 | 48,456 | 44,926 | 98.4 | 316 | 2274 | 684 |
| $C_7H_{16}$ | 1-Octene | 112.214 | −82,927 | 104,140 | 462.792 | 47,712 | 44,560 | 121.3 | — | 2302 | — |
| $C_8H_{16}$ | n-Octane | 114.230 | −208,447 | 17,322 | 463.671 | 48,275 | 44,791 | 125.7 | 300 | 2275 | 703 |
| $C_8H_{18}$ | 1-Nonene | 126.241 | −103,512 | 112,717 | 501.243 | 47,631 | 44,478 | — | — | 2300 | — |
| $C_9H_{18}$ | n-Nonan | 128.257 | −229,032 | 25,857 | 502.080 | 48,134 | 44,686 | 150.8 | 295 | 2276 | 718 |
| $C_9H_{18}$ | 1-Decene | 140.268 | −124,139 | 121,294 | 539.652 | 47,565 | 44,413 | 170.6 | — | 2298 | — |
| $C_{10}H_{20}$ | n-Decane | 142.284 | −249,659 | 34,434 | 540.531 | 48,020 | 44,602 | 174.1 | 277 | 2277 | 730 |
| $C_{10}H_{20}$ | 1-Undecene | 154.295 | −144,766 | 129,830 | 578.061 | 47,512 | 44,360 | — | — | 2296 | — |
| $C_{11}H_{22}$ | n-Undecane | 156.311 | −270,286 | 43,012 | 578.940 | 47,926 | 44,532 | 195.9 | 265 | 2277 | 740 |
| $C_{11}H_{24}$ | 1-Dodecene | 168.322 | −165,352 | 138,407 | 616.471 | 47,468 | 44,316 | 213.4 | — | 2295 | — |
| $C_{12}H_{24}$ | n-Dodecane | 170.337 | −292,162 | — | — | 47,841 | 44,467 | 216.3 | 256 | 2277 | 749 |
| $C_{12}H_{26}$ | | | | | | | | | | | |

† Based on gaseous fuel.

‡ For stoichiometric combustion with air (79 percent N2, 21 percent O2).

* For liquids at 20°C or for gases at the boiling point of the liquefied gas.

SOURCES:

[a] Rossini, F. D., et al., Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds, Carnegie Press, Pittsburgh, PA, 1953.

[b] Weast, R. C. (ed.), Handbook of Chemistry and Physics, 56th Ed., CRC Press, Cleveland, OH, 1976.

[c] Obert, E. F., Internal Combustion Engines and Air Pollution, Harper & Row, New York, 1973.

# APPENDIX C

# Thermodynamic Properties of H2O

**Table C.1:** Saturation Properties of Water and Steam—Temperature Increments

| T (K) | P (Kpa) | V(m$^3$/kg) Sat. liquid | V(m$^3$/kg) Sat. vapor | u(KJ/kg) Sat. liquid | u(KJ/kg) Sat. liquid | h(KJ/kg) Sat. liquid | h(KJ/kg) Sat. liquid | s(KJ/kg) Sat. liquid | s(KJ/kg) Sat. liquid |
|---|---|---|---|---|---|---|---|---|---|
| 273.16 | 0.611650 | 0.0010002 | 205.99 | 0 | 2374.9 | 0.00061 | 2500.9 | 0 | 9.1555 |
| 274 | 0.650030 | 0.0010002 | 194.43 | 3.5435 | 2376.1 | 3.5442 | 25025 | 0.012952 | 9.1331 |
| 275 | 0.698460 | 0.0010001 | 181.60 | 7.7590 | 2377.5 | 7.7597 | 2504.3 | 0.028309 | 9.1066 |
| 276 | 0.750070 | 0.0010001 | 169.71 | 11.971 | 2378.8 | 11.972 | 2506. I | 0.043600 | 9.0804 |
| 277 | 0.805020 | 0.0010001 | 158.70 | 16.181 | 2380.2 | 16.182 | 25080 | 0.058825 | 9.0544 |
| 278 | 0.863500 | 0.0010001 | 148.48 | 20.388 | 2381.6 | 20.389 | 2509.8 | 0.073985 | 9.0287 |
| 279 | 0.925700 | 0.0010001 | 139.00 | 24.593 | 2383.0 | 24.594 | 2511.6 | 0.089083 | 9.0031 |
| 280 | 0.991830 | 0.0010001 | 130.19 | 28.795 | 2384.3 | 28.796 | 2513.4 | 0.10412 | 8.9779 |
| 281 | 1.062200 | 0.0010002 | 122.01 | 32.996 | 2385.7 | 32.997 | 2515.3 | 0.11909 | 8.9528 |
| 282 | 1.136800 | 0.0010003 | 114.40 | 37.194 | 2387.1 | 37.195 | 2517.1 | 0.13401 | 8.9280 |
| 283 | 1.216000 | 0.0010003 | 107.32 | 41.391 | 23884 | 41.392 | 25189 | 0.14886 | 8.9034 |
| 284 | 1.300000 | 0.0010004 | 100.74 | 45.586 | 2389.8 | 45.587 | 2520.8 | 0. 16366 | 8.8791 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 285 | 1.389100 | 0.0010005 | 94.602 | 49.779 | 2391.2 | 49.780 | 25226 | 0.17840 | 8.8549 |
| 286 | 1483600 | 0.0010006 | 88.887 | 53.971 | 2392.6 | 53.973 | 2524.4 | 0.19308 | 8.8310 |
| 287 | 1.583600 | 0.0010008 | 83.560 | 58.162 | 2393.9 | 58.163 | 2526.2 | 0.20771 | 8.8073 |
| 288 | 1.689500 | 0.0010009 | 78.592 | 62.351 | 2395.3 | 62.353 | 2528.1 | 0.22228 | 8.7838 |
| 289 | 1.801600 | 0.0010011 | 73.955 | 66.540 | 2396.7 | 66.542 | 2529.9 | 0.23680 | 8.7605 |
| 290 | 1.920100 | 0.0010012 | 69.625 | 70.727 | 2398.0 | 70.729 | 2531.7 | 0.25126 | 8.7374 |
| 291 | 2.045400 | 0.0010014 | 65.581 | 74.914 | 2399.4 | 74.916 | 2533.5 | 0.26568 | 8.7145 |
| 292 | 2177900 | 0.0010016 | 61.801 | 79.099 | 2400.8 | 79.101 | 2535.3 | 0.28003 | 8.6918 |
| 293 | 2.317800 | 0.0010018 | 58.267 | 83.284 | 2402.1 | 83.286 | 2537.2 | 0.29434 | 8.6693 |
| 294 | 2465500 | 0.0010020 | 54.960 | 87.468 | 2403.5 | 87.471 | 2539.o | 0.30860 | 8.6471 |
| 295 | 2621300 | 0.0010022 | 51.865 | 91.652 | 2404.8 | 91.654 | 2540.8 | 0.32280 | 8.6250 |
| 296 | 2.785700 | 0.0010022 | 48.966 | 95.835 | 2406.2 | 95.837 | 25426 | 0.33696 | 8.6031 |
| 297 | 2.959100 | 0.0010027 | 46.251 | 100.02 | 2407.6 | 100.02 | 2544.4 | 0.35106 | 8.5814 |
| 298 | 3.141800 | 0.0010030 | 43.705 | 104.20 | 2408.9 | 104.20 | 2546.2 | 0.36512 | 8.5599 |
| 299 | 3.334300 | 0.0010032 | 41.318 | 108.38 | 2410.3 | 108.38 | 25480 | 0.37913 | 8.5385 |
| 300 | 3.536900 | O.0010035 | 39.078 | 11256 | 2411.6 | 112.56 | 2549.9 | 0.39309 | 8.5174 |
| 301 | 3.750200 | 0.0010038 | 36.976 | 116.74 | 2413.0 | 116.75 | 2551.7 | 0.40700 | 8.4964 |
| 302 | 3.974600 | 0.0010041 | 35.002 | 120.92 | 2414.4 | 120.93 | 2553.5 | 0.42087 | 8.4756 |
| 303 | 4.210600 | 0.0010044 | 33.147 | 125.10 | 2415.7 | 125.11 | 2555.3 | 0.43469 | 8.4550 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 304 | 4458700 | 0.0010047 | 31.403 | 129.28 | 2417.1 | 129.29 | 2557. I | 0.44846 | 8.4346 |
| 305 | 4.719400 | 0.0010050 | 29.764 | 133.46 | 2418.4 | 133.47 | 25589 | 0.46219 | 8.4144 |
| 306 | 4.993299 | 0.0010053 | 28.222 | 137.64 | 2419.8 | 137.65 | 2560.7 | 0.47587 | 8.3943 |
| 307 | 5280799 | 0.0010057 | 26.770 | 141.82 | 2421.1 | 141.83 | 25625 | 0.48950 | 8.3744 |
| 308 | 5.582599 | 0.0010060 | 25.403 | 146.00 | 2422.5 | 146.01 | 2564.3 | 0.50310 | 8.3546 |
| 309 | 5.899199 | 0.0010063 | 24.116 | 150.18 | 2423.8 | 150.19 | 2566.1 | 0.51664 | 8.3351 |
| 310 | 6231199 | 0.0010067 | 22.903 | 154.36 | 2425.2 | 154.37 | 2567.9 | 0.53015 | 8.3156 |
| 311 | 6.579299 | 0.0010071 | 21.759 | 158.54 | 2426.5 | 158.55 | 2569.7 | 0.54361 | 8.2964 |
| 312 | 6.944099 | 0.0010074 | 20.680 | 16272 | 2427.8 | 162.73 | 2571.5 | 0.55702 | 8.2773 |
| 313 | 7.326199 | 0.0010078 | 19.663 | 166.90 | 2429.2 | 166.91 | 2573.2 | 0.57040 | 8.2584 |
| 314 | 7.726299 | 0.0010082 | 18.702 | 171.08 | 2430.5 | 171.09 | 2575.0 | 0.58373 | 8.2396 |
| 315 | 8.145199 | 0.0010086 | 17.795 | 175.26 | 2431.9 | 175.27 | 2576.8 | 0.59702 | 8.2210 |
| 316 | 8.583499 | 0.0010090 | 16.938 | 179.44 | 2433.2 | 179.45 | 2578.6 | 0.61027 | 8.2025 |
| 317 | 9.041899 | 0.0010094 | 16.129 | 183.62 | 2434.5 | 183.63 | 2580.4 | 0.62348 | 8.1842 |
| 318 | 9.521299 | 0.0010099 | 15.363 | 187.80 | 2435.9 | 187.81 | 2582.2 | 0.63664 | 8.1660 |
| 319 | 10.022989 | 0.0010103 | 14.639 | 191.98 | 2437.2 | 191.99 | 2582.2 | 0.64977 | 8.1480 |
| 320 | 10.546989 | 0.0010107 | 13.954 | 196.16 | 2438.5 | 196.17 | 2583.9 | 0.66285 | 8.1302 |
| 325 | 0.013532 | 0.0010130 | 11.039 | 217.07 | 2445.2 | 217.08 | 2585.7 | 0.72768 | 8.0430 |
| 330 | 0.017214 | 0.0010155 | 8.8050 | 237.98 | 2451.8 | 238.00 | 2594.6 | 0.79154 | 7.9592 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 335 | 0.021719 | 0.0010181 | 7.0788 | 258.9 | 2458.3 | 258.93 | 2603.3 | 0.85447 | 7.787 |
| 340 | 0.027189 | 0.0010209 | 5.7339 | 279.84 | 2464.8 | 279.87 | 2612.1 | 0.91650 | 7.8013 |
| 345 | 0.033784 | 0.0010239 | 4.6776 | 300.79 | 2471.2 | 300.82 | 2620.7 | 0.97766 | 7.7267 |
| 350 | 0.041683 | 0.0010270 | 3.8419 | 321.75 | 2477.6 | 321.79 | 2629.3 | 1.0380 | 7.6549 |
| 355 | 0.051081 | 0.0010303 | 3.1759 | 342.73 | 2483.9 | 342.78 | 2637.7 | 1.0975 | 75857 |
| 360 | 0.062195 | 0.0010337 | 2.6414 | 363.73 | 2490.1 | 363.79 | 2646.1 | 1.1562 | 7.5190 |
| 365 | 0.075261 | 0.0010373 | 2.2098 | 384.75 | 2496.2 | 384.82 | 2662.5 | 1.2142 | 7.4545 |
| 370 | 0.090536 | 0.0010410 | 1.8590 | 405.79 | 2502.3 | 405.88 | 2670.6 | 1.2715 | 7.3923 |
| 375 | 0.108310 | 0.0010449 | 1.5722 | 426.86 | 2508.2 | 426.97 | 2678.5 | 1.3281 | 7.3321 |
| 380 | 0.128860 | 0.0010490 | 1.3364 | 447.96 | 2514.1 | 448.09 | 2686.2 | 1.3839 | 7.2738 |
| 385 | 0.152529 | 0.0010532 | 1.1414 | 469.09 | 2519.8 | 469.25 | 2693.9 | 1.4392 | 7.2174 |
| 390 | 0.179649 | 0.0010575 | 0.97928 | 490.25 | 2525.4 | 490.44 | 2701.3 | 1.4938 | 7.1627 |
| 395 | 0.210609 | 0.0010620 | 0. 84389 | 511.45 | 2530.9 | 511.67 | 2708.6 | 1.5478 | 7.1097 |
| 400 | 0.245779 | 0.0010667 | 0.73024 | 532.69 | 2536.2 | 532.95 | 2715.7 | 1.6013 | 7.0581 |
| 405 | 0.285589 | 0.0010715 | 0.63441 | 553.98 | 2541.4 | 554.28 | 2722.6 | 1.6541 | 7.0081 |
| 410 | 0.330459 | 0.0010765 | 0.55323 | 575.31 | 2546.5 | 575.66 | 2729.3 | 1.7065 | 6.9593 |
| 415 | 0.380879 | 0.0010817 | 0.48418 | 596.69 | 2551.4 | 597.10 | 2735.8 | 1.7583 | 6.9119 |
| 420 | 0.437309 | 0.0010870 | 0.42520 | 618.13 | 2556.2 | 618.60 | 2742.1 | 1.8097 | 6.8656 |
| 425 | 0.500259 | 0.0010926 | 0.37463 | 639.62 | 2560.7 | 640.17 | 2748.1 | 1.8606 | 6.8205 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 430 | 0.570269 | 0.0010983 | 0.33110 | 661.18 | 2565.1 | 661.80 | 2753.9 | 1.9110 | 6.7764 |
| 435 | 0.647879 | 0.0011042 | 0.29350 | 682.8 | 2569.3 | 683.52 | 2759.5 | 1.9610 | 6.7333 |
| 440 | 0.733679 | 0.0011103 | 0.26090 | 704.5 | 2573.3 | 705.31 | 2764.7 | 2.0106 | 6.6911 |
| 445 | 0. 828249 | 0.0011166 | 0.23255 | 726.26 | 2577.1 | 727.19 | 2769.7 | 2.0598 | 6.6498 |
| 450 | 0.932209 | 0.0011232 | 0.20781 | 748.11 | 2580.7 | 749.16 | 2774.4 | 2.1087 | 6.6092 |
| 455 | 1.046289 | 0.0011299 | 0.18616 | 770.05 | 2584.0 | 771.23 | 2778.8 | 2.1571 | 6.5694 |
| 460 | 1.170988 | 0.0011369 | 0.16715 | 792.07 | 2587.2 | 793.41 | 2782.9 | 2.2053 | 6.5303 |
| 465 | 1.306987 | 0.0011442 | 0. 15041 | 814.2 | 2590.1 | 815.69 | 2786.6 | 2.2532 | 6.4917 |
| 470 | 1.455187 | 0.0011517 | 0. 13564 | 836.42 | 2592.7 | 838.09 | 2790.o | 2.3007 | 6.4538 |
| 475 | 1.616086 | 0.0011594 | 0. 12255 | 858.75 | 2595.o | 860.62 | 2793.1 | 2.3480 | 6.4164 |
| 480 | 1.790586 | 0.0011675 | 0. 11094 | 881.19 | 2597.1 | 883.28 | 2795.8 | 2.3950 | 6.3794 |
| 485 | 1.979285 | 0.0011758 | 0. 10061 | 903.76 | 2598.9 | 906.09 | 2798.1 | 2.4418 | 6.3428 |
| 490 | 2.183184 | 0.0011845 | 0.091390 | 926.45 | 2600.5 | 929.04 | 2800.o | 2.4884 | 6.3066 |
| 495 | 2.402884 | 0.0011935 | 0. 083149 | 949.28 | 2601.7 | 952.15 | 2801.4 | 2.5348 | 62708 |
| 500 | 2639283 | 0.0012029 | 0.075764 | 972.26 | 2602.5 | 975.43 | 2802.5 | 2.5810 | 62351 |
| 505 | 2.893182 | 0.0012127 | 0.069131 | 995.38 | 2603.0 | 998.89 | 2803.1 | 2.6271 | 6.1997 |
| 510 | 3.165582 | 0.0012228 | 0.063161 | 1018.7 | 2603.2 | 1022.5 | 2803.2 | 2.6731 | 6.1645 |
| 515 | 3.457181 | 0.0012334 | 0.057776 | 1042.1 | 2603.0 | 1046.4 | 2802.7 | 2.7189 | 6.1293 |
| 520 | 3.769080 | 0.0012445 | 0.052910 | 1065.8 | 2602.4 | 1070.5 | 2801.8 | 2.7647 | 6.0942 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 525 | 4.101980 | 0.0012561 | 0.048503 | 1089.6 | 2601.4 | 1094.8 | 2800.3 | 2.8104 | 6.0591 |
| 530 | 4.456979 | 0.0012682 | 0.044503 | 1113.7 | 2599.9 | 1119.3 | 2798.2 | 2.8561 | 6.0239 |
| 535 | 4.834978 | 0.0012809 | 0.040868 | 1138 | 2597.9 | 1144.2 | 2795.5 | 2.9019 | 5.9885 |
| 540 | 5.236977 | 0.0012942 | 0.037556 | 1162.5 | 2595.5 | 1169.3 | 2792.2 | 2.9476 | 5.9530 |
| 545 | 5.664076 | 0.0013083 | 0.034535 | 1187.3 | 2592.5 | 1194.7 | 2788.1 | 2.9935 | 5.9171 |
| 550 | 6.117276 | 0.0013231 | 0.031772 | 1212.4 | 2588.9 | 1220.5 | 2783.3 | 3.0394 | 5.8809 |
| 555 | 6.597675 | 0.0013387 | 0.029242 | 1237.8 | 2584.8 | 1246.6 | 2777.7 | 3.0855 | 5.8443 |
| 560 | 7.106274 | 0.0013553 | 0.026920 | 1263.5 | 2579.9 | 1273.1 | 2771.2 | 3.1319 | 5.8071 |
| 565 | 7.644473 | 0.0013729 | 0.024786 | 1289.6 | 2574.4 | 1300.1 | 2763.9 | 3.1785 | 5.7693 |
| 570 | 8.213272 | 0.0013917 | 0.022820 | 1316 | 2568.0 | 1327.5 | 2755.5 | 3.2254 | 5.7307 |
| 575 | 8.814071 | 0.0014118 | 0.021005 | 1343 | 2560.9 | 1355.4 | 2746.o | 3.2727 | 5.6912 |
| 580 | 9.448070 | 0.0014334 | 0.019328 | 1370.4 | 2552.7 | 1383.9 | 2735.3 | 3.3205 | 5.6506 |
| 585 | 10.117686 | 0.0014567 | 0.017773 | 1398.4 | 2543.5 | 1413.1 | 2723.3 | 3.3690 | 5.6087 |
| 590 | 10.821674 | 0.0014820 | 0.016329 | 1426.9 | 2533.2 | 1443.0 | 2709.9 | 3.4181 | 5.5654 |
| 595 | 11.563662 | 0.0015095 | 0.014984 | 1426.2 | 2521.5 | 1473.7 | 2694.8 | 3.4680 | |
| 600 | 12.345649 | 0.0015399 | 0.013728 | 1456.2 | 2508.3 | 1505.4 | 2677.8 | 3.5190 | 5.5203 |
| 605 | 13.167635 | 0.0015735 | 0.012552 | 1517.4 | 2493.4 | 1538.1 | 2658.7 | 3.5713 | 5.4731 |
| 610 | 14.033620 | 0.0016112 | 0.011446 | 1549.6 | 2476.4 | 1572.2 | 2637.0 | 3.6252 | 5.3707 |
| 615 | 14.943604 | 0.0016541 | | 1583.2 | 2456.9 | 1608.0 | 2612.3 | 3.6811 | 5.3142 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 620 | 15.901586 | 0.0017039 | 0.010400 | 1618.6 | 2434.3 | 1645.7 | 2583.9 | 3.7396 | 52528 |
| 625 | 16.908567 | 0.0017634 | 0.0094067 | 1656.5 | 2407.8 | 1686.3 | 2550.7 | 3.8019 | 5.1851 |
| 630 | 17.969544 | 0.0018374 | 0.0084538 | 1697.7 | 2375.8 | 1730.7 | 2511.1 | 3.8698 | 5.1084 |
| 635 | 19.086516 | 0.0019353 | 0.0075279 | 1744.3 | 2335.7 | 1781.2 | 2461.8 | 3.9463 | 5.0181 |
| 640 | 20.265481 | 0.0020767 | 0. 0066074 | 1799.7 | 2281.1 | 1841.8 | 2395.5 | 4.0375 | 4.9027 |
| 645 | 21.515425 | 0.0023527 | 0.0056451 | 1880.5 | 2185.2 | 1931.1 | 2281.0 | 4.1722 | 4.7147 |
| 647.096 | 22.064000 | 0.0031056 | 0. 0044553<br>0.0031056 | 2015.7 | 2015.7 | 2084.3 | 2084.3 | 4.4070 | 4.4070 |

# APPENDIX D

# Thermodynamic Properties of Ideal Gases and Carbon

**Table D.1:** H2O (Molecular Weight = 18.016, Enthalpy of Formation at 298 K = –241,845 kJ/kmol, Enthalpy of Vaporization = 44,010 kJ/kmol)

| T (K) | $\bar{c}_p$ $(kj/kmol.k)$ | $\bar{h}^o(T) - \bar{h}^o_f(298)$ $(kJ/kmol)$ | $\bar{h}^o_f$ $(kJ/kmol)$ | $\bar{s}^o(T)$ $(kj/kmol.k)$ | $\Delta\bar{g}^o_f(T)$ $(kJ/kmol)$ |
|---|---|---|---|---|---|
| 200 | 32.255 | -3227 | -240,838 | 175.602 | -232,779 |
| 298 | 33.448 | 0 | -241,847 | 188.715 | -228,608 |
| 300 | 33.468 | 62 | -241,865 | 188.922 | -228,526 |
| 400 | 34.437 | 3458 | -242,858 | 198.686 | -223,929 |
| 500 | 35.337 | 6947 | -243,822 | 206.467 | -219,085 |
| 600 | 36.288 | 10,528 | -244,753 | 212.992 | -214,049 |
| 700 | 37.364 | 14,209 | -245,638 | 218.665 | -208,861 |
| 800 | 38.587 | 18,005 | -246,461 | 223.733 | -203,550 |
| 900 | 39.930 | 21,930 | -247 ,209 | 228.354 | -198,141 |
| 1000 | 41.315 | 25,993 | -247,879 | 232.633 | -192,652 |
| 1100 | 42.638 | 30,191 | -248,475 | 236.634 | -187,100 |
| 1200 | 43.874 | 34,518 | -249,005 | 240.397 | -181,497 |
| 1300 | 45.027 | 38,963 | -249,477 | 243.955 | -175,852 |

| | | | | | |
|---|---|---|---|---|---|
| 1400 | 46.102 | 43,520 | -249,895 | 247.332 | -170,172 |
| 1500 | 47.103 | 48,181 | -250,267 | 250.547 | - 164,464 |
| 1600 | 48.035 | 52,939 | -250,597 | 253.617 | -158,733 |
| 1700 | 48.901 | 57,786 | -250,890 | 256.556 | -152,983 |
| 1800 | 49.705 | 62,717 | -251,151 | 259.374 | -147,216 |
| 1900 | 50.451 | 67,725 | -251,384 | 262.081 | -435 |
| 2000 | 51.143 | 72,805 | -251,594 | 264.687 | -135,643 |
| 2100 | 51.784 | 77,952 | -251,783 | 267.198 | -129,841 |
| 2200 | 52.378 | 83,160 | -251,955 | 269.621 | -124,030 |
| 2300 | 52.927 | 88,426 | -252,113 | 271.961 | -118,211 |
| 2400 | 53.435 | 93,744 | -252,261 | 274.225 | -112,386 |
| 2500 | 53.905 | 99,112 | -252,399 | 276.416 | -106,555 |
| 2600 | 54.340 | 104,524 | -252,532 | 278.539 | -100,719 |
| 2700 | 54.742 | 109,979 | -252,659 | 280.597 | -94,878 |
| 2800 | 55.115 | 115,472 | -252,785 | 282.595 | -89,031 |
| 2900 | 55.459 | 121,001 | -252,909 | 284.535 | -83,181 |
| 3000 | 55.779 | 126,563 | -253,034 | 286.420 | -77,326 |
| 3100 | 56.076 | 132,156 | -253,161 | 288.254 | -71,467 |
| 3200 | 56.353 | 137,777 | -253,290 | 290.039 | -65,604 |

| | | | | | |
|---|---|---|---|---|---|
| 3300 | 56.610 | 143,426 | -253,423 | 291.777 | -59,737 |
| 3400 | 56.851 | 149,099 | -253,561 | 293.471 | -53,865 |
| 3500 | 57.076 | 154,795 | -253,704 | 295.122 | -47 |
| 3600 | 57.288 | 160,514 | -253,852 | 296.733 | -42,110 |
| 3700 | 57.488 | 166,252 | -254,007 | 298.305 | - 36,226 |
| 3800 | 57.676 | 172,011 | -254,169 | 299.841 | -30,338 |
| 3900 | 57.856 | 177,787 | -254,338 | 301.341 | -24 |
| 4000 | 58.026 | 183,582 | -254,515 | 302.808 | -18,549 |
| 4100 | 58.190 | 189,392 | -254,699 | 304.243 | -12,648 |
| 4200 | 58.346 | 195,219 | -254,892 | 305.647 | -6742 |
| 4300 | 58.496 | 201,061 | -255,093 | 307.022 | -831 |
| 4400 | 58.641 | 206,918 | -255,303 | 308.368 | 5085 |
| 4500 | 58.781 | 212,790 | -255,522 | 309.688 | 11,005 |
| 4600 | 58.916 | 218,674 | -255,751 | 310.981 | 16,930 |
| 4700 | 59.047 | 224,573 | -255,990 | 312.250 | 22,861 |
| 4800 | 59.173 | 230,484 | -256,239 | 313.494 | 28,796 |
| 4900 | 59.295 | 236,407 | -256,501 | 314.716 | 34,737 |
| 5000 | 59.412 | 242,343 | -256,774 | 315.915 | 40,684 |