Aspects of ethanol: laminar, turbulent and dynamics combustion

Virginia Fratalocchi

Graduation Committee:

Chairman and Secretary

prof. dr. G.P.M.R. Dewulf

University of Twente

Supervisor

prof. dr. ir. T.H. van der Meer

University of Twente

Co-supervisor

dr. ir. J.B.W. Kok

University of Twente

Committee Members

prof. dr. ir. H.W.M. Hoeijmakers

University of Twente

prof. dr. ir. C.H. Venner

University of Twente

prof. dr. D.J.E.M. Roekaerts

Delft University of Technology

prof. dr. H.B. Levinsky

University of Groningen

prof. dr. L.P.H. de Goey

Eindhoven University of Technology

The research in this thesis was performed in the framework of the European Union Marie Curie Initial Training Network project COPA-GT (COupled PARallel simulations of Gas Turbines).

Aspects of ethanol: laminar, turbulent and dynamics combustion
Virginia Fratalocchi

PhD thesis, University of Twente, Enschede, The Netherlands
December 2017

ISBN: 978-90-365-4449-8

DOI: 10.3990/1.9789036544498

URL: <https://doi.org/10.3990/1.9789036544498>

Copyright ©2017: Virginia Fratalocchi

ASPECTS OF ETHANOL: LAMINAR, TURBULENT AND DYNAMICS COMBUSTION

DISSERTATION

to obtain
the degree of doctor at the University of Twente,
on the authority of the rector magnificus
Prof.dr. T.T.M. Palstra
on account of the decision of the graduation committee,
to be publicly defended
on Friday the 8th of December 2017 at 14:45

by

Virginia Fratalocchi

born on the 7th of August 1985
in Ascoli Piceno, Italy

This dissertation has been approved by the supervisor:
prof. dr. ir. T.H. van der Meer

and by the co-supervisor:
dr. ir. J.B.W. Kok

Copyright ©2017: Virginia Fratalocchi
ISBN: 978-90-365-4449-8
URL: <https://doi.org/10.3990/1.9789036544498>

a mamma, papa' e Laura

Contents

Summary	1
Samenvatting	5
1 Introduction	9
1.1 Low-calorific fuels applications	11
1.2 Research objectives	13
1.2.1 Aim of the thesis	13
1.3 Content of the thesis	14
Bibliography	16
2 Combustion modeling	19
2.1 URANS equations	19
2.2 Modeling of the mean reaction rate $\overline{\dot{\omega}_n}$	22
2.2.1 Tabulated chemistry	23
2.2.2 Turbulent flame closure	26
2.3 Numerical solution in Ansys CFX	26
Bibliography	27
3 The CSP/PSR approach...	29
3.1 Introduction	29
3.2 Chemical reacting system	32
3.3 CSP algorithm	34
3.3.1 The CSP pointers	36
3.3.2 Number of global steps	40
3.4 Analysis of chemical time scales	43
3.5 One-dimensional laminar database	46
3.5.1 1D freely propagating flame	48
3.5.2 Premixed laminar Bunsen flame	49
3.6 Conclusions	53
3.7 Appendix	54
Bibliography	54
4 Turbulent premixed combustion...	59
4.1 Introduction	59

4.2	Turbulent premixed combustion	62
4.2.1	The flamelet regime	64
4.3	Chemistry tabulation	65
4.3.1	Stochastic method for turbulence-chemistry interaction	67
4.4	Numerical simulations in laminar and turbulent regimes	68
4.4.1	1D premixed laminar flames	70
4.4.2	Turbulent premixed jet flame	72
4.5	Conclusions	78
4.6	Appendix 1	81
	Bibliography	81
5	Spray flames	87
5.1	Experimental setup	87
5.2	Numerical approach	88
5.2.1	Lagrangian tracking	89
5.2.2	Heat and mass transfer	90
5.2.3	Interphase source terms	91
5.3	Computational domain	92
5.3.1	Boundary conditions	92
5.4	Results and Discussion	93
5.4.1	Gas temperature	93
5.4.2	Droplets velocity	93
5.5	Conclusions	95
	Bibliography	101
6	Ethanol turbulent spray flame response...	103
6.1	Introduction	103
6.2	Characterization of unsteady spray flames	105
6.3	Numerical configuration	108
6.4	Simulation results	111
6.4.1	Spray flame forced response	112
6.4.2	Spray flame vs Prevaporised ethanol flame	115
6.4.3	Effect of initial slip velocity on the forced flame response	121
6.5	Conclusions and discussion	123
6.5.1	Conclusions	123
6.5.2	Discussion	124
	Bibliography	125
7	Conclusions and recommendations	127
7.1	Conclusions	127
7.1.1	Combustion of pre-vaporised ethanol flames	127
7.1.2	Dynamics of turbulent spray flames	129

7.2 Recommendations	130
A Chemical kinetics mechanisms	133
Bibliography	133
Acronyms	135
Nomenclature	137
Publications	139
Biography	141
Acknowledgements	143

Summary

The combustion process is currently the main heat, power and propulsion supplying system in a wide range of sectors, such as: thermal and power generation, and aero and ground transportation. In order to meet the growing energy demand from one side, and to fulfill the more restrictive emissions regulations on the other side, a more efficient and cleaner combustion system design is required.

When designing a combustor, the engineering concerns depend on the specific application, however, common key aspects are: reduction of the toxic emissions, fuel flexibility and flame stability. In this scenario, the industry has been going and is going towards the development of new complex technologies and the usage of new fuels. Since experimental measurements are often too expensive or time consuming, the numerical modeling represents an attractive tool to investigate reactive flows in industrial applications. A key aspect in capturing the physics of the combustion processes in practical designs, is the accurate representation of the interaction between the chemistry and the turbulence. This represents a great challenge, especially because of the large range of time and length scales of the phenomena involved.

In the last few decades, as a response to the need of low-cost computational tools, combustion models based on tabulated chemistry were developed. The main concept on which this approach is based is that a turbulent flame can be represented by a 1D flamelet. The interaction between turbulence and chemical reactions is then taken into account for example by means of a presumed shape Probability Density Function (PDF). In order to retain the accuracy of the detailed chemistry and limit the computational costs of the simulations, a turbu-chemical database is built prior to the simulation, and the fluid properties are retrieved during run-time. The storage of the data is a parametrized function of specific controlling variables, such that only the transport equations of these variables are solved, rather than transporting the total number of species. The flamelet assumption is generally valid in the combustion regimes which establish in gas turbines engines. The Computational Fluid Dynamics has received a growing interest not only to explore new combustor designs, but also to explore the performances of new bio-fuels. In this context, the question if the numerical models adopted to study the burning characteristic of traditional fossil fuels can also well represent new fuels, has to be addressed.

Summary

The present PhD thesis focuses on exploring a variety of combustion aspects of one of the most attractive liquid bio-fuels: ethanol. The two areas studied are the combustion characteristics of the ethanol as prevaporised gas fuel in turbulent flames, and the forced ethanol spray flame response to fluctuations of the gas velocity. The first part of the dissertation is concerned with the combustion of prevaporised ethanol and the combustion is treated with a tabulated chemistry approach based on an optimized choice of the reaction progress variable. The approach is developed for premixed combustion, in which case the single controlling scalar is the reaction progress variable. A Computational Singular Perturbation algorithm is used, along with a sensitivity analysis of the chemical time scales performed in a Perfectly Stirred Reactor, to determine the optimal combination of the species mass fractions defining the reaction progress variable. This approach is first validated against laminar flames and it is found that the choice of the reaction progress variable has a relevant effect in the solution of the reacting field.

Following, the same formulation is applied in a confined turbulent jet flame, where the turbulence-chemistry interaction is predicted by means of a presumed-shape PDF. Blends of ethanol/water/iso-octane were used to test the capability of the method and it is found that the adopted framework simulation can be successfully extended to complex fuel mixtures. In such simulation framework, the database is implemented in the commercial software Ansys CFX, where Reynolds averaged Navier-Stokes equations are solved in steady state regime.

In the second part of the thesis, numerical simulations of a piloted turbulent ethanol spray flame are presented. Both steady and transient simulations are performed in the Eulerian-Lagrangian framework. Due to an intrinsic limitation of the commercial code, the database could not be coupled with the Lagrangian solver. For this reason the available models in CFX were used to perform the spray flame simulations.

The reference test-case is the Sidney spray flame, on which a large set of measurement data is available. Simulations were validated against two flames in particular, the EtF6 and the EtF7. A study on the effect of the boundary conditions assigned to the gas phase is performed. The spray is modeled under the main assumption of the dilute spray regime such that all phenomena of atomization, break-up and collisions are neglected. The mixture entering the computational domain is a mixture of air and gaseous ethanol and liquid ethanol. The flame is stabilized by a pilot flame, modeled as hot burnt gas. The combustion model used in these simulations is the Burning Velocity Model, so-called because the closure of the chemical source term occurs by means of the burning velocity, multiplied by the gradient of the reaction progress variable. A good agreement is found between the experimental data and the droplet velocity. The solution of the temperature

indicate, however, that an investigation of other combustion models should be considered.

Finally, the forced spray flame response is studied with URANS simulations and presented in the last chapter. Two frequencies signals are chosen as upstream perturbation of the gas flow. The reference test-case, EtF6, is simplified and the liquid ethanol is injected as mono-dispersed spray. The behaviour of the droplets under gas velocity oscillations is investigated in terms of spatial distribution and evaporation rate, and compared to the acoustic-free case. The spray flame response is also compared to the response of prevaporised ethanol flames, at constant global equivalence ratio. The analysis is made both in the time and frequency domain, and a comparison of the discrete flame transfer function is performed between spray and gaseous flames.

The methodology proposed for ethanol and its blends is successful in laminar and turbulent regimes. Moreover, the features of heat loss and non-premixed combustion can easily be implemented in the proposed formulation. The response of the ethanol spray flame to gas velocity oscillations is an important investigation towards the study of flame stability.

In conclusion, the aspects of ethanol combustion presented in this dissertation provide insights in the modeling techniques used to simulate reactions of complex ethanol blends and its burning characteristics in off-design transient regimes. The tools developed will assist in the design of gas turbine combustors fired on blends of ethanol and other species.

Samenvatting

In een groot aantal sectoren is momenteel het verbrandingsproces het belangrijkste systeem dat voor warmte, kracht en voortstuwing zorgt, zoals warmte- en energieopwekking en lucht- en grondtransport. Om enerzijds de groeiende vraag naar energie aan te kunnen en anderzijds te voldoen aan de strengere emissienormen, is een efficiënter en schoner ontwerp van het verbrandingssysteem vereist.

Bij het ontwerpen van een verbrandingsinstallatie zijn de technische aandachtspunten afhankelijk van de specifieke toepassing, maar belangrijke gemeenschappelijke aspecten zijn reductie van de toxische emissies, flexibiliteit in brandstof en vlamstabiliteit. De industrie werkt al in deze richting en zij stevent af op de ontwikkeling van nieuwe, complexe technologieën en het gebruik van nieuwe brandstoffen. Omdat experimentele metingen vaak te duur of tijdrovend zijn, vormt de numerieke modellering een aantrekkelijk hulpmiddel om reactieve stromingen in industriële toepassingen te onderzoeken. Een belangrijk aspect bij het vastleggen van de fysica van verbrandingsprocessen in praktische ontwerpen, is de nauwkeurige weergave van de interactie tussen de chemie en de turbulentie. Dit vormt een grote uitdaging, vooral vanwege het grote bereik van de tijd- en lengteschalen van de betrokken verschijnselen.

Als antwoord op de behoefte aan goedkope computationele hulpmiddelen, werden in de afgelopen decennia verbrandingsmodellen op basis van getabuleerde chemie ontwikkeld. Het belangrijkste concept, waarop deze benadering is gebaseerd, is dat een turbulente vlam door een 1D flamelet kan worden voorgesteld. De interactie tussen turbulentie en chemische reacties wordt dan in aanmerking genomen bijvoorbeeld door middel van een veronderstelde vorm via de kansdichtheidsfunctie (PDF). Om de nauwkeurigheid van de gedetailleerde chemie te behouden en de computationele kosten van de simulaties te beperken, wordt vooraf aan de simulatie een turbu-chemische database gebouwd en worden de vloeistofeigenschappen in runtime vastgesteld. De opslag van de gegevens is een geparametriseerde functie van specifieke controlevariabelen, zodanig dat alleen de transportvergelijkingen van deze variabelen worden opgelost, in plaats van de vergelijkingen voor alle stoffen op te lossen. De aanname van flamelets is over het algemeen geldig in verbrandingsregimes die in gasturbines aanwezig zijn. Computational Fluid Dynamics heeft een groeiende belangstelling gekregen, niet alleen om nieuwe ontwerpen van verbrandingsmotoren te verkennen, maar ook om de prestaties van

nieuwe biobrandstoffen te onderzoeken. In dit verband moet de vraag worden onderzocht of de numerieke modellen, die zijn gebruikt om de verbrandingskenmerken van traditionele fossiele brandstoffen te bestuderen, ook die van nieuwe brandstoffen kunnen representeren.

Dit proefschrift richt zich op het verkennen van verschillende verbrandingsaspecten van een van de meest aantrekkelijke vloeibare biobrandstoffen: ethanol. De twee bestudeerde onderwerpen zijn de verbrandingseigenschappen van ethanol als voorverdampte gasbrandstof in turbulente vlammen en de geforceerde respons van de ethanol-verstuivingsvlam op fluctuaties van de gassnelheid. Het eerste deel van het proefschrift heeft betrekking op de verbranding van vooraf verdampte ethanol en de verbranding wordt behandeld met een getabuleerde chemiebenadering op basis van een geoptimaliseerde keuze van de reactievoortgangsvariabele. De benadering is ontwikkeld voor voorgemengde verbranding, waarbij slechts een scalaire grootte wordt gebruikt, namelijk de reactievoortgangsvariabele. Het Computational Singular Perturbation algoritme wordt gebruikt, samen met een gevoeligheidsanalyse van de chemische tijdschalen, uitgevoerd in een Perfectly Stirred Reactor, om de optimale combinatie te bepalen van de massafracties die de reactievoortgangsvariabele definiëren. Deze benadering wordt eerst gevalideerd tegen laminaire vlammen en het blijkt dat de keuze van de reactievoortgangsvariabele een relevant effect heeft op de oplossing van het reagerende veld.

Hierna wordt dezelfde formulering toegepast in een “confined turbulent jet-flame”, waarbij de turbulentie-chemie-interactie wordt voorspeld door middel van een veronderstelde vorm van de PDF. Mengsels van ethanol/water/isooctaan werden gebruikt om de mogelijkheden van dit model te testen en het bleek dat dit aangenomen raamwerk met succes kan worden uitgebreid tot samengestelde brandstofmengsels. In een dergelijk simulatiekader is de database geïmplementeerd in de commerciële software Ansys CFX, waarbij Reynolds Averaged Navier-Stokes-vergelijkingen zijn opgelost in een stationair regime.

In het tweede deel van het proefschrift worden numerieke simulaties van een pilot-vlam gestabiliseerde turbulente ethanol-verstuivingsvlam gepresenteerd. Zowel stationaire als transiënte simulaties worden in het Eulerian-Lagrangian-raamwerk uitgevoerd. Vanwege een intrinsieke beperking van de commerciële code, kon de database niet worden gekoppeld aan de Lagrangiaanse oplossingsmethode. Om deze reden werden de beschikbare modellen in CFX gebruikt om de verstuivingsvlamsimulaties uit te voeren.

De referentie-testcase is de Sidney-verstuivingsvlam, waarvoor een groot aantal meetgegevens beschikbaar is. Simulaties werden gevalideerd tegen twee vlammen in het bijzonder, de EtF6 en de EtF7. Een onderzoek naar het effect van de randvoorwaarden, die voor de stroming in de gasfase zijn aangenomen, is uitgevoerd. De verstuiving wordt gemodelleerd onder de be-

langrijkste veronderstelling van het verdunde verstuiwingsregime, zodat alle verschijnselen van verneveling, verbreking en botsingen worden verwaarloosd. Het mengsel dat het rekendomein binnenkomt, is een mengsel van lucht, gasvormige ethanol en vloeibare ethanol. De vlam wordt gestabiliseerd door een waakvlam, gemodelleerd als heet verbrand gas. Het verbrandingsmodel dat in deze simulaties wordt gebruikt, is het Burning Velocity Model, zo genoemd omdat de sluiting van de chemische bronterm plaatsvindt door middel van de verbrandingssnelheid, vermenigvuldigd met de gradiënt van de reactievoortgangvariabele. Een goede overeenstemming wordt gevonden tussen de experimentele gegevens en de druppelsnelheid. De oplossing van de temperatuur geeft echter aan dat een onderzoek naar andere verbrandingsmodellen moet worden overwogen.

Tenslotte wordt de geforceerde respons van de verstuiwingsvlam bestudeerd met URANS-simulaties en in het laatste hoofdstuk gepresenteerd. Twee frequentiesignalen worden gekozen als stroomopwaartse verstoring van de gasstroom. De referentie-testcase EtF6 wordt vereenvoudigd en de vloeibare ethanol is geïnjecteerd als een mono-verspreide spray. Het gedrag van de druppeltjes onder oscillaties van de gassnelheid wordt onderzocht in termen van ruimtelijke verdeling en verdampingssnelheid, en vergeleken met het geval zonder akoestische verstoring. De respons van de verstuiwingsvlam wordt ook vergeleken met de respons van vooraf verdampte ethanolvlammen, bij een constante globale equivalentieverhouding. De analyse wordt zowel in het tijd- als in het frequentiedomein gedaan en een vergelijking van de discrete vlamoverdrachtsfunctie wordt uitgevoerd tussen verstuiwings- en gasvormige vlammen.

1 Introduction

Energy plays a vital role in our life. The main challenge that the power generation and aerospace industries have to face today is the mitigation of the emissions despite the rapidly growing demand for transport and electricity. To accomplish this target, industrial and research groups have been exploring new sectors of sustainable energies. As a result, hydroelectricity, solar and wind energy, and many more more renewable energies sources, have seen their efficiency and production increased and their costs decreased through out the years. However, the statistics on the '*world total primary energy supply by fuel*' given by the International Energy Agency shows that a departure from the traditional fuels seems unrealistic in the next few decades. By reading the projected data to 2040 of primary energy supply in fig. 1.1, it appears that combustion is likely to be the dominant energy supplying system in the foreseeable future. A side effect of the combustion process is the emission of greenhouse gases such as CO_2 , pollutants as NO_x , particulates, and the environmental issues which originate, such as acid rain and global warming.

Figure 1.1: Total primary energy supply: Outlook by fuel to 2040. The data are expressed in Mtoe, ton of oil equivalent ($1 \text{ toe} = 41.87 \times 10^9 \text{ J}$).

The aviation sector is one of the most active in the engagement of tackling the global CO_2 emission. In 2012 the aviation sector accounted for 3% of

global CO_2 emission, as reported by the ENVI (Environment, Public Health and Food Safety) Committee, [3]. In 2009, the International Air Transport Association (IATA) has set a number of goals for the air transport, amongst which sustaining a CO_2 neutral annual growth [9] and an improvement of fuel efficiency of 1.5% per year from 2009 to 2020. To tackle these engineering challenges, the ICAO adopted in 2016 the first global scheme, CORSIA (Carbon Offset and Reduction Scheme for International Aviation), that a great number of aviation industries have begun to implement. Stabilizing the emissions at the 2020 levels, aiming at a further dramatic reduction by 2050, implicates, besides a bucket of specific policies, the search for innovative combustion technologies.

Even more urgent is the need to limit the carbon dioxide production and greenhouse emissions in the electrical power generation sector. Based on the global emissions of 2010, the International Panel on Climate Change (IPCC) report assessed that the burning of coal, natural gas, and oil for electricity and heat is the largest single source (35%) of global greenhouse gas emissions [12]. For the first time ever, in 1995, the Paris Agreement brought 195 nations together into a common cause to combat the climate change and limit the global temperature increase. Twenty years later, the global warming is still a threat and despite blind policies are in the process of denying it, the majority of the countries envision a low carbon future.

In this scenario, gas turbine engines represent an efficient and versatile source of power in a wide variety of sectors such as power plants, aircraft and marine transportation. Figure 1.2 shows a heavy duty gas turbine generally installed for industrial power generation, operating with a wider range of fuels, among them bioethanol. The basic engineering concerns driving a gas turbine combustor design are: high-combustion efficiency, low pollutants emission, ability to burn multiple fuels and also alternative fuels, freedom from combustion-induced instability, an uniform outlet temperature and reliability, [10]. The role played by each of these design requirements depends on the specific application, nevertheless two common principles can be identified, and they are: low fuel consumption and low emission. For the successful implementation of these objectives, conventional gas turbine power plants make an important contribution thanks to their flexibility. This is crucial to ensure an efficient integration with renewable energy production and combined cycles.

To decrease the NO_x levels, the concept of lean premixed combustion (LPM) is applied in most of the combustion systems. However, the ratio fuel/air has to be carefully calibrated in order to not promote the CO formation, which shows an opposite trend of the NO_x production. Moreover, the downside of these LPM systems is that they are prone to thermoacoustic phenomena which can lead to combustion instability [11].

Figure 1.2: SGT5-4000F gas turbine of Siemens portfolio

1.1 Low-calorific fuels applications

In addition to developing new combustion technologies, the usage of sustainable alternative fuels will also play an important role in achieving the emission reduction goal. Although the usage of alternative fuels in aviation represents still a young industry, an increasing employment is seen in power supply systems. The combustion of carbon free fuels, such as ammonia or hydrogen, and biofuels (ethanol, methanol, butanol or biodiesel), has different characteristics compared to traditional fuels and its understanding becomes crucial.

In fig. 1.3 a comparison is shown of the fuels with respect to their lower heating value and hydrogen content. The new combustion technology of gas turbine engines must ensure a full functionality over a wide range of lower heating values (LHV) of liquid and gaseous fuels. The usage of low-calorific fuels requires the injection of a larger fuel mass flow in the combustion system. In case of liquid fuels, preheating might be necessary to lower the viscosity of the fuel and achieve the desired spray atomization, which is one of the driving parameters of the mixing of the reactants inside the combustion chamber. In literature, the effect of the viscosity on the combustion performance has been experimentally investigated in a micro gas turbine operating with a viscous biofuel [13]. The development of biofuels in combustion systems is receiving increasing attention from several energy supplier sectors. Ethanol is extensively used in internal combustion engines and recently, the usage of alcohol compounds is emerging in turbine engines for power generation and aircraft propulsion [10]. In [8] is reported that methanol-based electricity

1 Introduction

Figure 1.3: Comparison of the fuels with respect to their lower heating value and hydrogen content. Reproduced from [8].

generation is almost economically competitive with natural gas and fuel oil.

From fig. 1.3, it can be seen that ethanol has a heating value lower than bio-diesel but higher than methanol. One of the requirements for ethanol to be competitive in the energy market is lowering the production costs compared to the traditional fuels. One possible way to achieve this goal is exploring the combustion performance of hydrous ethanol over anhydrous ethanol. Several studies have shown this path to be promising [2]. The design of a gas turbine combustion system is a complex process, often involving numerous conflicting requirements.

However, in the last decades, the growth of Computational Fluid Dynamics (CFD) has had a major impact in understanding both the physics and the leverage of the different techniques in the physical design of a combustor. The research is constantly prompted into developing CFD tools capable of modeling reacting flows, in an accurate and feasible way. One of the main challenges to be faced within the formulation of combustion modeling is the interaction of chemistry and turbulence, due to their different scales. Additional thermodynamic complexities arise in liquid-fueled flames, in which case the correct prediction of the reacting field depends also on the capability of capturing the evaporation and the spatial distribution of the injected spray. In the field of spray flames, despite the intrinsic complexities, the numerical analysis becomes even more significant because experimental investigations are an expensive and difficult task. This is true in particular when flame transient effects, such as thermoacoustic phenomena, need to be investigated.

1.2 Research objectives

This thesis has been realised in the framework of the Marie Skłodowska Curie project, COPA-GT (COupled Parallel simulations of Gas Turbine). As the name suggests, this project focuses on the CFD of gas turbines. The basic design of a gas turbine engine is composed of a compressor, a combustor and a turbine. The compressor pressurizes the air, through as many stages as are required to achieve the design pressure ratio. Afterwards, the air enters the combustion chamber and contributes as oxidizer to the combustion of the fuel. The hot products of combustion are directed towards the turbine, where they expand and exit into the atmosphere. During the expansion process, the kinetic energy of the hot gases is converted into mechanical work transferred to the shaft to produce electric power, or converted into propulsion force in aircraft engines. Gas turbine engines can operate on gaseous or liquid fuels, and their combustor design reflects the employed fuel. In case of liquid fueled combustion systems, the processes of atomization and evaporation represent a crucial step in the combustion system performance. Spray quality also affects stability limits and pollutant emission levels [10]. The COPA-GT project originates from the ambitious goal to develop CFD tools able to perform coupled simulations of the different components of the engine by taking into account their interactions and/or multiphysics processes. Consequently, phenomena of heat transfer, aerodynamics, combustion, vibrations and noise production must be all accounted for. This is a great challenge since each physical phenomenon is critical even when studied alone.

1.2.1 Aim of the thesis

The scope of this thesis is to explore two main areas of interest:

- the combustion characteristics of ethanol as a prevaporised gas fuel in turbulent flames;
- the forced ethanol spray flame response to fluctuations of the velocity.

All gas turbine combustion systems operate in turbulent regime. Accounting for the interaction between chemical reactions, turbulence and thermodynamics remains a difficult task in combustion modeling, especially because of the wide range of time and length scales involved. The modeling of detailed chemistry, involving hundreds of species and reactions, is a prohibitive approach in CFD of practical applications.

Thus, the importance to have kinetic mechanisms with a minimum number of species and reactions involved, and a new numerical strategy that does not solve for all the species but only for a reduced number of representative

variables. A methodology well developed in the last few decades is represented by the tabulated chemistry, which is based on the main assumption that the characteristic 3D turbulent flame can be represented by means of a set of 1D laminar flames. A well known and validated method based on this approach is the Flamelet Generated Manifold (FGM) method, formulated by [15], [14].

In the present work, tabulation of detailed chemistry of prevaporised ethanol and ethanol blends is applied in turbulent premixed flames. The proposed formulation is based on *a priori* assessment of the reaction progress variable, which accounts for all the time scales involved in the chemical reactions. This procedure is well established for methane/air oxidation, as showed by [7] and [1] and it is extended, in the present work, to ethanol oxidation. First, an investigation of the effect of the definition of the reaction progress variable is carried out in the laminar regime. Next, the turbulent-combustion interaction effects are incorporated by means of a presumed-shape Probability Density Function (PDF). RANS simulations are performed and the tabulated chemistry is embedded in the commercial software Ansys CFX. The capability of this approach was tested in case of prevaporised ethanol and ethanol blends flames.

As already mentioned, one of the main engineering concern in designing a combustor is the stability of the flame, under both steady and unsteady conditions. In the past decades, the study of the forced response of gaseous flames has been at the center of great attention. Open questions still remain to address in case of spray flames, where the good mixing of the reactants and the heat released by the flame are strongly related to the evaporation and the dispersion of the liquid fuel injected into the chamber. When the spray flame is exposed to a perturbation, such can be an upstream velocity or pressure fluctuation, the issue to address is the effect on the heat released by the flame, the evaporation and spatial distribution of the droplets, and the interaction between each other. A variation of the evaporation rate, as well as of the displacement of the droplets inside the chamber, can result in a change of the flame structure or even its position. The emissions can also be affected by a variation of the temperature field, or of the mixing of the fuel inside the chamber. Knowledge of the dominant phenomena in reactive multiphase flows is crucial for developing numerical techniques which can be used in combustor designs, to explore stationary and dynamics aspects.

1.3 Content of the thesis

An outline of this dissertation is given here.

Chapter 1: The background of this work and the motivation behind it are presented.

Chapter 2: The URANS equations governing the reacting fluid flows are here presented. This chapter focuses on the modeling aspects of the turbulence-chemistry interaction. Two approaches for the closure of the mean reaction term are discussed. First, the chemistry tabulation process applied to premixed turbulent combustion is introduced. This combustion model is adopted for the prevaporised ethanol simulations, chapters 3 and 4, and the governing equations are introduced. Lastly, the Turbulent Flame Closure (TFC) formulation, on which the Burning Velocity Model is based, is described. Due to a limitation of the CFX source code, the tabulated chemistry could not be implemented by means of user subroutines into CFX in case of spray flames. The CFX available TFC combustion model is adopted, therefore, in the simulations of ethanol spray flame, chapters 5 and 6.

Chapter 3: The methodology to project the multi-dimensional detailed chemistry onto a single-dimensional reaction progress variable is described. A chemical database is generated to represent the prevaporised ethanol combustion. Two are the techniques adopted to define an optimal expression of the reaction progress variable: the Computational Singular Perturbation (CSP) method and a sensitivity analysis of the time scales, evaluated with a Perfectly Stirred Reactor (PSR). The thermo-chemical databases computed with these methods are compared in the cases of a freely propagating flame and a Bunsen flame, in the laminar premixed regime and under stoichiometric conditions.

Chapter 4: The tabulated chemistry approach is applied to mixtures of air and pure anhydrous ethanol and ethanol blends. A freely propagating flame is used to compare the species concentration and temperature profiles predicted with detailed chemistry and with the CSP/PSR-based reaction progress variable. The chemistry-turbulence interaction is taken into account by means of a stochastic method.

Chapter 5: The major results of turbulent spray flames simulations are presented in this chapter. Two flames from the Sydney experimental database are taken as reference: EtF6 and EtF7. RANS simulations are performed, in which the gas phase is solved as a continuum medium in the Eulerian framework, and the spray evolution is predicted by enabling the Lagrangian solver. The two phases interact in a two-way coupling model. The combustion is treated with the Burning Velocity Model (BVM), available in CFX. This model is a version of the TFC model. The effect of the boundary conditions of the equivalence ratio at the jet exit plane are validated against the measured droplets mean diameters, temperature and velocity profiles.

Chapter 6: URANS simulations are carried out to investigate the effects of the gas velocity oscillations into the forced spray flame response. Two frequencies are chosen as forcing signals to the flames: 200 Hz and 2500 Hz. The response of a mono-dispersed spray flame is compared with the forced

response of a pre-vaporised ethanol flame, with the same global equivalence ratio. The main parameters of interest, which are illustrated in the results, are the evaporation of the droplets, the temperature field and the response of the flame in the frequency domain. The computational domain, the initial conditions of gas and liquid loading of the EtF6 test-case, as well as the Lagrangian model introduced in chapter 5, are used in this part of the work. However, given the high number of parameters driving thermoacoustic phenomena in spray flames, some simplifications of the boundary conditions, with respect to the original test-case, were made. The Stokes number is kept constant at the inlet, and the liquid fuel is injected as a mono-dispersed spray. The study of the flame response is made via a non-dimensional characterization of some relevant parameters.

Chapter 7: The conclusions drawn at the end of each chapter are summarized here, along with guidelines for future research.

Appendix A provides a list of the reduced chemical kinetics mechanisms used in this work.

Chapters 3 to 5 are based on manuscripts which have been published in journals or are in the reviewing process. For this reason, there might be repetitions of concepts and references.

The link between chapters and journal papers is as follows: chapter 3 corresponds to reference [4], chapter 4 corresponds to reference [5] and chapter 6 corresponds to reference [6].

Bibliography

- [1] Bogdan Alexandru Albrecht. *Reactor modeling and process analysis for partial oxidation of natural gas*. University of Twente, 2004.
- [2] Baine B Breaux and Sumanta Acharya. The effect of elevated water content on swirl-stabilized ethanol/air flames. *Fuel*, 105:90–102, 2013.
- [3] Martin Cames, Jakob Graichen, Anne Siemons, and Vanessa Cook. Emission reduction targets for international aviation and shipping. *Study for the ENVI Committee. Directorate General for Internal Policies Policy Department a: Economic and Scientific Policy. European Parliament*, 2015.
- [4] V Fratalocchi and JBW Kok. The computational singular perturbation/perfectly stirred reactor approach in reduced chemistry of premixed ethanol combustion. *Combustion Science and Technology*, 189(10):1659–1680, 2017.

- [5] V Fratalocchi and JBW Kok. Prediction of turbulent premixed combustion of ethanol/water/iso-octane blends. (*Submitted*), 2017.
- [6] Virginia Fratalocchi and Jim BW Kok. Ethanol turbulent spray flame response to gas velocity modulation. *Combustion Theory and Modelling*, pages 1–19, 2017.
- [7] S Goevert, D Mira, JBW Kok, M Vazquez, and G Houzeaux. Turbulent combustion modelling of a confined premixed methane/air jet flame using tabulated chemistry. *Energy Procedia*, 66:313–316, 2015.
- [8] T Johnke H Kliemke. Gas turbine modernization –fuel conversion and special fuel applications for the asian market. http://www.siemens.com/content/dam/internet/siemens-com/global/products-services/energy/services/performance-enhancement/modernization-upgrades/gas-turbines/pdf/gas-turbines/gt-mod__fuel-conversion_asian-market_e50001-g500-a142-x-4a00_en_lr_final.pdf, 2014. Accessed: 2017-08-15.
- [9] A IATA. Global approach to reducing aviation emissions. *First Stop: Carbon Neutral Growth from*, 2020, 2009.
- [10] Arthur H Lefebvre. *Gas turbine combustion*. CRC press, 1998.
- [11] Tim Lieuwen and Keith McManus. Introduction: Combustion dynamics in lean-premixed prevaporized (lpp) gas turbines. *Journal of Propulsion and Power*, 19(5):721–721, 2003.
- [12] Rajendra K Pachauri, Myles R Allen, Vicente R Barros, John Broome, Wolfgang Cramer, Renate Christ, John A Church, Leon Clarke, Qin Dahe, Purnamita Dasgupta, et al. *Climate change 2014: synthesis report. Contribution of Working Groups I, II and III to the fifth assessment report of the Intergovernmental Panel on Climate Change*. IPCC, 2014.
- [13] JLHP Sallevelt, JEP Gudde, Artur Krzysztof Pozarlik, and Gerrit Brem. The impact of spray quality on the combustion of a viscous biofuel in a micro gas turbine. *Applied energy*, 132:575–585, 2014.
- [14] JA van Oijen, A Donini, RJM Bastiaans, JHM ten Thijs Boonkamp, and LPH de Goey. State-of-the-art in premixed combustion modeling using flamelet generated manifolds. *Progress in Energy and Combustion Science*, 57:30–74, 2016.

BIBLIOGRAPHY

- [15] JA Van Oijen, FA Lammers, and LPH De Goey. Modeling of complex premixed burner systems by using flamelet-generated manifolds. *Combustion and Flame*, 127(3):2124–2134, 2001.

2 Combustion modeling

The evolution of fluid flows can be described by a system of partial differential equations, consisting of the conservation of mass, momentum, energy and species concentrations. In modeling combustion processes, extra terms appear in the governing equations, which account for the chemical reactions. Moreover, the need to track the consumption and the production of the species involved in the reactions arises. In this chapter, the URANS equations applied to reacting fluid flows are presented. In particular, it is discussed how to tackle the closure of terms resulting from Favre averaging procedure.

2.1 URANS equations

The Reynolds decomposition and subsequent time averaging of any quantity ϕ in a turbulent field produces a decomposition into a mean $\bar{\phi}$ and a fluctuating ϕ' component:

$$\phi(x, t) = \bar{\phi}(x) + \phi'(x, t) \quad (2.1a)$$

$$\bar{\phi}(x) = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T \phi(x, t) dt \quad (2.1b)$$

with T time interval, and x spatial coordinate. In combustion processes, where large density gradients occur, the Favre average is usually preferred [8], [4]:

$$\phi(x, t) = \tilde{\phi}(x) + \phi''(x, t) \quad (2.2a)$$

$$\tilde{\phi}(x) = \frac{\int_0^T \rho(t) \phi(x, t) dt}{\int_0^T \rho(t) dt} = \frac{\overline{\rho \phi}}{\bar{\rho}} \quad (2.2b)$$

Applying the Reynolds decomposition and the Favre average to the balance equations, and neglecting the action of external forces, one can obtain the

following system of URANS equations in Cartesian coordinates x_i :

$$\frac{\partial \bar{\rho}}{\partial t} + \frac{\partial (\bar{\rho} \tilde{u}_i)}{\partial x_i} = \bar{S}^\rho \quad (2.3a)$$

$$\frac{\partial \bar{\rho} \tilde{u}_i}{\partial t} + \frac{\partial (\bar{\rho} \tilde{u}_i \tilde{u}_j)}{\partial x_i} + \frac{\partial \bar{p}}{\partial x_j} = \frac{\partial (\bar{\tau}_{ij} - \bar{\rho} \widetilde{u_i'' u_j''})}{\partial x_i} + \bar{S}^u \quad (2.3b)$$

$$\frac{\partial \bar{\rho} \tilde{Y}_n}{\partial t} + \frac{\partial (\bar{\rho} \tilde{Y}_n \tilde{u}_i)}{\partial x_i} = - \frac{\partial (\bar{V}_{n,i} \tilde{Y}_n + \bar{\rho} \widetilde{u_i'' Y_n''})}{\partial x_i} + \bar{\dot{\omega}}_n + \bar{S}^y \quad n = 1, N \quad (2.3c)$$

$$\frac{\partial \bar{\rho} \tilde{h}}{\partial t} + \frac{\partial (\bar{\rho} \tilde{h} \tilde{u}_j)}{\partial x_j} = \frac{D\bar{p}}{DT} - \frac{\partial (\bar{q}_j - \bar{\rho} \widetilde{u_j'' h''})}{\partial x_j} + \bar{\tau}_{ij} \frac{\partial u_i}{\partial x_j} + \bar{S}^h \quad (2.3d)$$

A detailed derivation of the full set of equations can be found in [7], [8]. Only some of the aspects of the turbulent modeling in the framework of reacting flows are analysed here. The variables S^ρ , S^y , S^u , and S^h represent the source terms due to the exchange of mass (accounted in both the continuity and species equations), momentum and heat between two phases of a mixture. These terms appear only when multiphase flows are modeled, and they will be discussed in Chapter 5. The averaging procedure introduces unknown quantities which need to be modeled. These terms, along with the approximations used to perform their closure, are summarised in table 2.1.

Table 2.1: Unclosed terms in Favre averaged equations and their closure approximations

Unclosed term	Closure approximation	Assumption
$-\bar{\rho} \widetilde{u_i'' u_j''}$	$\mu_t \left(\frac{\partial \tilde{u}_i}{\partial x_j} + \frac{\partial \tilde{u}_j}{\partial x_i} - \frac{2}{3} \frac{\partial \tilde{u}_k}{\partial x_k} \delta_{ij} \right) - \frac{2}{3} \bar{\rho} k \delta_{ij}$	Boussinesq [9]
$\bar{\rho} \widetilde{u_i'' Y_n''}$	$-\frac{\mu_t}{Sc_t} \frac{\partial \tilde{Y}_n}{\partial x_i}$	gradient transport [8]
$\bar{\rho} \widetilde{u_i'' h''}$	$-\frac{\mu_t}{Sc_t} \frac{\partial \tilde{h}}{\partial x_i}$	gradient transport [8]
$\bar{V}_{n,i} \tilde{Y}_n$	$-\bar{\rho} \bar{D}_n \frac{\partial \tilde{Y}_n}{\partial x_i}$	$\approx -\bar{\rho} \bar{D}_n \frac{\partial \bar{Y}_n}{\partial x_i}$

Additional terms appear in table 2.1, which need to be evaluated: the turbulent viscosity μ_t ($\mu_t = \rho \nu_t$) and the turbulent Schmidt number Sc . In

this work, the two-equation $k - \epsilon$ model is used to evaluate μ_t , which reads as:

$$\mu_t = \bar{\rho} C_\mu \frac{k^2}{\epsilon} \quad (2.4)$$

The Schmidt number is assumed to be constant and equal to 0.9. A full description of this approach can be found in standard literature, e.g. [9]. More attention is given in the next paragraphs to the species and the energy equation.

Species conservation equation

The last term in table 2.1 represents the diffusive flux of the species Y_n , in which $\overline{V_n}$ describes the mass diffusion of species n , relative to the mass averaged flow velocity $\bar{u}$. The approximation used to close this term is based on the mass diffusion coefficient D_n , and follows the Hirschfelder and Curtis formulation [2]. A further simplification can be made by assuming that all species diffusivities are equal: $D_n = D$. Under this hypothesis, the diffusion velocity obeys Fick's law:

$$\overline{V_{n,i}} = -\frac{D}{Y_n} \frac{\partial \tilde{Y}_n}{\partial x_i} \quad (2.5)$$

The governing equation for the species conservation becomes:

$$\frac{\partial \bar{\rho} \tilde{Y}_n}{\partial t} + \frac{\partial (\bar{\rho} \tilde{Y}_n \tilde{u}_i)}{\partial x_i} = \frac{\partial}{\partial x_i} \left((\bar{\rho} D + \frac{\mu_t}{Sc_t}) \frac{\partial \tilde{Y}_n}{\partial x_i} \right) + \bar{\omega}_n + \bar{S}_{mp} \quad n = 1, N \quad (2.6)$$

Energy equation

The enthalpy h transported in the energy equation in eq. (2.3) is the sum of the sensible and chemical enthalpy:

$$\tilde{h} = \sum_{n=1}^N \Delta \widetilde{h_{f,n}} \tilde{Y}_n + \int_{T_0}^T C_p dT \quad (2.7)$$

where $h_{f,n}$ is the enthalpy of formation of the species n , and C_p is the specific heat capacity of the mixture. The enthalpy flux $\tilde{q}_j$ is written as:

$$\tilde{q}_j = -\left(\lambda \frac{\partial T}{\partial x_j} \right) + \left(\rho \sum_{n=1}^N h_n Y_n \overline{V_{n,j}} \right) \quad (2.8)$$

where the temperature gradient follows the Fourier's law, and the radiative flux is neglected. In practice, $\bar{q}_j$ is modeled as:

$$\bar{q}_j = -\frac{\overline{\lambda}}{c_p} \frac{\partial \bar{h}}{\partial x_i} \approx -\frac{\bar{\lambda}}{\bar{c}_p} \frac{\partial \bar{h}}{\partial x_i} \quad (2.9)$$

The second term of the RHS of eq. (2.8) is canceled by the term due to enthalpy transport by the species gradient. When looking at the relevant terms in the Navier-Stokes equation (before Reynolds-Favre averaging):

$$\dot{q}_j = -\frac{\lambda}{c_p} \frac{\partial h}{\partial x_i} + \left(1 - \frac{1}{Le}\right) \sum_{n=1}^N h_n \frac{\partial Y_n}{\partial x_i} \quad (2.10)$$

derived by using the eq. (2.5) and introducing the Lewis number as the ratio between the thermal and mass diffusivity:

$$Le = \frac{\lambda}{\rho c_p D} \quad (2.11)$$

Under the major assumption of unity of the Lewis number, the contribution of enthalpy transported by thermal and mass diffusivity cancel each other and the second term in the RHS of eq. (2.10) vanishes.

Throughout this thesis, the hypothesis of ideal gas is assumed to be valid and the mixtures follow the equation of state of ideal gas:

$$\bar{p} = \bar{\rho} \frac{R\bar{T}}{\bar{W}} \quad (2.12)$$

where ρ and W are the mixture density and molecular weight, and R the ideal gas constant.

Lastly, the unknown quantity that remains to be closed is the mean reaction rate $\overline{\dot{\omega}_n}$.

2.2 Modeling of the mean reaction rate $\overline{\dot{\omega}_n}$

The closure of the mean reaction rate in the species transport equation can be done in several ways and represents one of the main objectives of the turbulent combustion modeling research. The choice of the combustion model should be dictated by the specific regime in which the combustion system operates. In general, the reactions in gas turbine engines take place in the so-called flamelet regime, in which the combustion is assumed to occur without interfering with the reaction layer.

In this thesis, two combustion models based on the flamelet concept, but

with different formulations for modeling the turbulence-chemistry interaction, are adopted. The key aspects are introduced in the following sections.

2.2.1 Tabulated chemistry

The tabulated chemistry approach is based on the concept that a turbulent flame can be treated as an ensemble of laminar flamelets. The eq. (2.6) becomes computationally prohibitive when detailed kinetic mechanisms are used and the consumption/production of a great number of species N has to be tracked. The flamelet-based combustion model avoids the expense of complex chemistry calculations on run-time, by pre-calculating a turbu-chemical database from 1D premixed flamelets using detailed chemistry.

The reacting fluid properties are stored in the database, parametrized by a controlling scalar, *reaction progress variable* c , which describes the evolution of the reaction process. A full description of the methodology adopted to build the tabulation, along with its applications in laminar and turbulent combustion, is presented in Chapter 3 and 4.

The reaction progress variable variable is expressed in terms of defined composed species mass fractions (η), and defines the whole range of the combustion process, from the unburnt state ($c = 0$) to a fully burnt state ($c = 1$). This tabulation procedure is performed by mapping the solution of a set of 1D laminar flamelets into the c -space. In the new 1-dimensional c -space, the N species transport equations are replaced by the transport equation of one scalar: the reaction progress variable. Consequently, the consumption rate, $\dot{\omega}_n$, of the species involved in the reaction is determined by the source term of the reaction progress variable, S_c :

$$S_c = \frac{\sum_{n=1}^N b_n \dot{\omega}_n}{\eta^b - \eta^u} \quad (2.13)$$

In the current work, the weighting factors b_n , on which the definition of η is formulated, are chosen based on an analysis performed on the chemical time scales of the reacting species. A detailed description is given in Chapter 3.

The variable S_c in eq. (2.13) is the reaction progress variable source term calculated in the laminar solution. The question to address, is how the turbulent fluctuations can be taken into account. The interaction between the turbulence and the chemistry is done via a statistical method, in which the turbulent variable source terms are described by an assumed shape Probability Density Function (PDF) [10]. Under this approach, the Favre averaged reaction source term, $\tilde{S}_c$, is the PDF weighted scalar:

$$\tilde{S}_c = \frac{1}{\bar{\rho}} \int_0^1 \rho S_c(c) P(c) dc \quad (2.14)$$

Being $P(c)$ the PDF of the reaction progress variable.

Result of the $\tilde{c}$ -averaging process is an additional term: the variance of the reaction progress variable, $\widetilde{c''^2}$. The current work focuses on turbulent premixed combustion so the reaction progress variable is the only controlling scalar and the fluid properties are stored as a function of $\tilde{c}$ and $\widetilde{c''^2}$. In the next session, the solution strategy adopted to perform the look-up table procedure is described.

Look-up table strategy

The turbu-chemical database is implemented into a commercial software package Ansys CFX, and a brief description of its main numerical discretization features is given at the end of the chapter. The implementation follows the same approach used by [5]. At the beginning of each simulation, the database is read and stored in the memory of the program. Together with the continuum, momentum and enthalpy equations, the transport equations for $\tilde{c}$ and $\widetilde{c''^2}$ are solved by the code. During run-time, the fluid properties tabulated in table 2.2 are retrieved from the database, as a function of $\tilde{c}$ and $\widetilde{c''^2}$, via linear interpolation. It has been shown by [3] that linear interpolation leads to accurate results, if the c grid is fine enough. The only term in table 2.2 which has not been introduced yet is c_{p_j} . These are the NASA coefficients, function of temperature, which fit in the polynomial expression used to calculate the temperature, (see eq. (4.11)).

Table 2.2: Thermo-chemical fluid properties stored in the tabulation

$\tilde{c}$	$\widetilde{c''^2}$	$\tilde{y}_n$	$\tilde{S}_C$	$\bar{T}$	$\bar{\rho}$	$\bar{\mu}$	$\bar{W}$	$\bar{\lambda}$	c_{p_j}
-------------	---------------------	---------------	---------------	-----------	--------------	-------------	-----------	-----------------	-----------

The set of transport equations solved in the code are listed, under the following hypothesis:

- the flow is mono-phase;
- absence of external forces, and volumetric heat sources;
- viscous heating and pressure gradients are neglected in the enthalpy equation;
- no radiation of heat transport;
- unity of Lewis number for all the species.

$$\frac{\partial \bar{\rho}}{\partial t} + \frac{\partial(\bar{\rho}\tilde{u}_i)}{\partial x_i} = 0 \quad (2.15a)$$

$$\frac{\partial \bar{\rho}\tilde{u}_i}{\partial t} + \frac{\partial(\bar{\rho}\tilde{u}_i\tilde{u}_j)}{\partial x_i} + \frac{\partial \bar{p}}{\partial x_j} = \frac{\partial \overline{\tau_{ij}^{eff}}}{\partial x_i} \quad (2.15b)$$

$$\frac{\partial \bar{\rho}\tilde{h}}{\partial t} + \frac{\partial(\bar{\rho}\tilde{h}\tilde{u}_j)}{\partial x_j} = \frac{\partial}{\partial x_j} \left(D^{eff} \frac{\partial \tilde{h}}{\partial x_j} \right) \quad (2.15c)$$

$$\frac{\partial \bar{\rho}\tilde{c}}{\partial t} + \frac{\partial(\bar{\rho}\tilde{c}\tilde{u}_j)}{\partial x_j} = \frac{\partial}{\partial x_j} \left(D^{eff} \frac{\partial \tilde{c}}{\partial x_j} \right) + \tilde{S}_c \quad (2.15d)$$

$$\frac{\partial \bar{\rho}\tilde{c}''^2}{\partial t} + \frac{\partial(\bar{\rho}\tilde{c}''^2\tilde{u}_j)}{\partial x_j} = \frac{\partial}{\partial x_j} \left(D^{eff} \frac{\partial \tilde{c}''^2}{\partial x_j} \right) + \widetilde{S_{c''^2}} - \overline{P_{c''^2}} - \overline{D_{c''^2}} \quad (2.15e)$$

The term τ_{ij}^{eff} is the sum of the laminar stress tensor and the Reynolds stress.

The molecular diffusion term D^{eff} results from the sum of the laminar, D , and the turbulent, D_t , contributions:

$$D^{eff} = \bar{\rho}\bar{D} + \bar{D}_t = \bar{\rho}\bar{D} + \frac{\mu_t}{Sc_t} \quad (2.16)$$

In the transport equation of the variance of reaction progress variable, few terms need a further clarification and they are respectively the source term $\widetilde{S_{c''^2}}$, the production $\overline{P_{c''^2}}$, and the dissipation $\overline{D_{c''^2}}$:

$$\widetilde{S_{c''^2}} = 2(\widetilde{S_c c} - \tilde{S}_c \tilde{c}) \quad (2.17a)$$

$$\overline{P_{c''^2}} = -2\overline{\rho u_i''} \frac{\partial \tilde{c}}{\partial x_i} = -2\frac{\mu_t}{Sc_t} \frac{\partial \tilde{c}}{\partial x_i} \frac{\partial \tilde{c}}{\partial x_i} \quad (2.17b)$$

$$\overline{D_{c''^2}} = 2C_c \bar{\rho} \frac{\epsilon}{k} \tilde{c}''^2 \quad (C_c \approx 1) \quad (2.17c)$$

The production term is closed using the gradient assumption, and the scalar dissipation rate of the c fluctuations is linked to a turbulent mixing time, using a linear relaxation assumption [8].

The transported enthalpy, along with the tabulated c_{p_i} coefficients, is used to calculate the temperature following a Newton methodology. Such iterative procedure, uses the tabulated temperature as initial guess.

Due to a limitation of the external code, it was not possible to link the user-defined database with the Lagrangian solver. Thus, to perform the simulations of the ethanol spray flame, a combustion model available in CFX was used: the Burning Velocity Model (BVM).

2.2.2 Turbulent flame closure

In the BVM model, the closure of the mean reaction rate is performed by means of the turbulent flame speed and assuming proportionality of the source term with the progress gradient [1]. A reaction progress variable describes the transition from a non-reacted state to a reacted state and its source term is written in this approach as:

$$\bar{S}_c = \rho_u s_t |\nabla \tilde{c}| \quad (2.18)$$

The expression of the turbulent burning velocity s_t , adopted in this work, was developed by Zimont [11]:

$$s_t = AGu'^{3/4} s_L^{1/2} \lambda_u^{-1/4} l_t^{1/4} \quad (2.19)$$

where A is a modelling coefficient, G is a stretching factor which takes into account the reduction of the flame velocity due to large strain rate, u' is the velocity fluctuation component, and λ and $l_t = k^{3/2}/\epsilon$ are respectively the thermal conductivity and the turbulent length scale. The subscript u indicates the unburnt mixture. The laminar flame speed s_L is implemented by following the polynomial law, function of the equivalence ratio, proposed by [6] for ethanol. In case of partially premixed flames, an additional controlling variable is needed to describe the local mixing between the streams of oxidiser and reactants. This variable is called mixture fraction, f and is defined in CFX as the mass fraction composition of the fuel [1]. Assuming equal diffusivity for the chemical components, the transport equation of the mean mixture fraction is written as:

$$\frac{\partial \bar{\rho} \tilde{f}}{\partial t} + \frac{\partial (\bar{\rho} \tilde{f} \tilde{u}_j)}{\partial x_j} = \frac{\partial}{\partial x_j} \left(D^{eff} \frac{\partial \tilde{f}}{\partial x_j} \right) + \tilde{S}^f \quad (2.20)$$

where $\tilde{S}^f$ represents the source term due to the exchange of mass in case of multiphase mixtures.

2.3 Numerical solution in Ansys CFX

CFX uses an element-based finite volume method to discretise the Reynolds Averaged Navier-Stokes equations [1]. The solution variables and fluid properties are stored at the mesh nodes, which differ from the integration points. Shape functions are used to approximate the solution fields (and their gradients) at the integration points. This is, for example, the case when, in the Eulerian-Lagrangian framework, the properties of the continuum flow have to be evaluated at a specific particle location. The shape functions adopted in

CFX are tri-linear. The set of equations solved by Ansys is given in eq. (2.3). The spatial derivatives for the diffusive terms are calculated with shape functions, and the advection terms are evaluated throughout this work with a high resolution scheme.

The time discretization is carried out with an implicit scheme, the Backward Euler scheme. An algebraic multigrid technique is used to improve the convergence rate during the iterative process of solving the system of discretized equations.

Bibliography

- [1] CFX ANSYS. Ansys cfx realease 14.5 user guide. *Canonsburg (PA): ANSYS Inc*, 2012.
- [2] Charles F Curtiss and Joseph O Hirschfelder. Transport properties of multicomponent gas mixtures. *The Journal of Chemical Physics*, 17(6):550–555, 1949.
- [3] A Andrea Donini. *Advanced turbulent combustion modeling for gas turbine application*. PhD thesis, Technische Universiteit Eindhoven, 2014.
- [4] A Favre. Statistical equations of turbulent gases. *Problems of hydrodynamics and continuum mechanics*, pages 231–266, 1969.
- [5] S Goevert, D Mira, JBW Kok, M Vazquez, and G Houzeaux. Turbulent combustion modelling of a confined premixed methane/air jet flame using tabulated chemistry. *Energy Procedia*, 66:313–316, 2015.
- [6] Ömer L Gülder. Laminar burning velocities of methanol, ethanol and isooctane-air mixtures. In *Symposium (international) on combustion*, volume 19, pages 275–281. Elsevier, 1982.
- [7] Kenneth K Kuo. *Principles of combustion*. Wiley New York et al., 1986.
- [8] Thierry Poinso and Denis Veynante. *Theoretical and numerical combustion*. RT Edwards, Inc., 2005.
- [9] Stephen B Pope. *Turbulent flows*, 2001.
- [10] FA Williams. *Combustion theory* 2nd, 1985.
- [11] Vladimir L Zimont. Gas premixed combustion at high turbulence. turbulent flame closure combustion model. *Experimental Thermal and Fluid Science*, 21(1):179–186, 2000.

3 The CSP/PSR approach in reduced chemistry of premixed ethanol combustion

Abstract

Ethanol is a bio-fuel widely used in engines as a fuel or fuel-additive. It is in particular attractive because it can be easily produced in high quality from renewable resources. Its properties are of interest in many fields, such as gas turbines applications as well as fuel cells. In the past decades, the research in Chemistry and Engineering has put a lot of effort into a better understanding of its gas phase chemical kinetic properties during combustion processes. This work describes a methodology to define an optimal expression of the reaction progress variable in the context of tabulated chemistry in laminar premixed combustion. The choice of the reaction progress model is based on the investigation of the wide range of consumption rates of the species involved in the reaction. Two methods are used: the Computational Singular Perturbation (CSP) method and a sensitivity analysis of the time scales evaluated with a Perfectly Stirred Reactor (PSR). The thermochemical databases computed with these techniques are compared in the cases of a freely propagating flame and a Bunsen flame, in the laminar premixed regime and under stoichiometric conditions. The influence of the chemical kinetics on the laminar flame speed is estimated from the results of the freely propagating flame. The case where the differences in the performances between the databases become more pronounced is the Bunsen flame, where some databases lead to a premature ignition prediction of the flame.

3.1 Introduction

In the past few decades, industry and research in the combustion field have faced the challenge to improve the combustion systems in order to address the necessity to decrease emissions of pollutants. An essential strategy to respond to the environment issues was to include non-fossil fuels in the primary energy source; this action opened the way to the investigation of the performance of several alternative fuels, for example the bioalcohols (ethanol,

methanol and butanol). The interest for these cleaner fuels has directed the aim of the research to a better understanding of the fundamentals of their chemical kinetics. [31] proposed a chemical kinetic mechanism to predict and investigate the combustion process of methanol; work from [2] and [4], gave an insight on the oxidation of butanol. Only a few complex kinetic mechanisms have been proposed for ethanol combustion, for example [21] and [18]. One of the advantages of using such fuels is their blending properties, as studied by [3]. Both experimental ([6]) and numerical studies play a major role in this process, but numerical analysis is especially attractive for the relatively low cost. However, when detailed chemistry is used, the larger the size of the kinetic mechanism, the higher the computational cost. Numerical simulations of flames might even be prohibitive if mechanisms with hundreds of species and reactions are taken into account. This applies specifically for turbulent combustion. To address the problem of the computational cost, the necessity of reduced kinetic mechanisms arises, as well as the need to decrease the number of degrees of freedom of the reaction phenomena. Thus the importance of kinetic mechanisms with a minimum number of species and reactions involved, and a new numerical strategy that does not solve for all the species but only for a reduced number of representative variables.

In this paper, in particular, the attention is towards the usage of ethanol in combustion, due to its properties as fuel blender, its potential in hydrogen production for fuel cell application ([20]) and in new gas turbine applications ([26]).

Proving good agreement with the detailed mechanisms of ethanol oxidation, [28], and [22], built a mechanism with 46 species; [25], reduced it to 38. In CFD (Computational Fluid Dynamics), encouraging results, especially from the computational cost point of view, were achieved when the tabulated chemistry approach was introduced. In this context, a thermochemical database is built and parametrized in terms of a number of controlling variables; this number of controlling variables usually depends on the complexity of the phenomena to be studied. Transport equations of these variables are solved during the combustion simulations and the thermal-transport properties, as well as the source terms, are retrieved from the pre-computed database. The variable describing the state of the reaction is called *reaction progress variable*, " c ", which in premixed flames, in case heat losses are not modeled, is the only control variable. A well known and validated method based on this approach is the Flamelet Generated Manifold (FGM) method, formulated by [29] and [1]. A wide set of flames has been explored by several authors, and with different techniques. The importance of reduced global mechanisms has been highlighted by [5], and ethanol flames were also deeply investigated by [17]. However, despite the look-up table technique has proven to give accurate results, the procedure to choose the most effective reaction progress variable

is not well established, and, at contrary, it is often based on the intuition of the investigator; this is especially true for fuels not as extensively studied as the common fossil-fuels. In this work, a methodology to find a definition of c is shown for methane and further optimized for ethanol, with the potential to be extended to other fuels. A rigorous definition of the reaction progress variable is not an easy task, due to the sensibility of the controlling variables to the operating conditions, to the characteristics of the flame (premixed, or diffusional), and in particular to the wide range of time scales involved in the chemical reaction process. A crucial part of modeling the combustion process is the ability to resolve in an efficient way the meaningful time scales. An algorithm designed to select the slow and the fast time scales is the Computational Singular Perturbation (CSP) method, proposed by [14] and [8], and further elaborated by [16] for methane oxidation. This method was used by [22], to build a 20-step reduced mechanism for ethanol, in the context of an In Situ Adaptive Tabulation (ISAT), a technique first developed by [24].

The CSP algorithm, which normally is used to project the space of species created by a detailed mechanism on a low-dimensional manifold, is adopted in this paper to optimize the expression of the reaction progress variable.

It is shown that this procedure is well established for methane/air oxidation, as also proven by [7]. However, the present work shows some limitations of this methodology when applied to ethanol oxidation.

Therefore, following the criterion proposed by [16], the CSP method is combined with an analysis of the characteristic chemical time scales: this investigation is performed in a Perfectly Stirred Reactor, with the PSR package from Chemkin-II ([12]). In a PSR environment, the reference time is given by the extinction time and the chemical time scale is chosen to be the consumption of molar concentration of the species. In this context, as made clear by [16], it is possible to define a threshold value to separate the space of the species between slow and steady state species. To assess the influence of the definition of c , the tabulations are validated against freely propagating laminar premixed flames. Predictions of the laminar burning flame, as well as species mass fractions and temperature profiles, are compared with those obtained with Chemkin-II ([12]). When looking at the ethanol flame, the PSR simulations give insight in why the CSP method fails in some situations to find an optimal expression of the reaction progress variable. The existence of a critical time scale is found, above which the species can be classified as dormant. When validating the tabulated chemistry, it is concluded that the influence of the dormant species in the construction of a slow sub-domain not only can be neglected, but has to be. Thus, the database is parametrized with the reaction progress variable defined through the CSP method filtered by the PSR time scale analysis. Its performance is verified against a freely propagating and a Bunsen flame. The simulations, all in steady state and

based on tabulated chemistry, are carried out with the commercial software CFX Ansys. For each simulated test-case, the thermochemical database is implemented in CFX and looked up at each iteration through an user-defined Fortran routine. The structure of the paper is as follows: the equations describing the species evolution in a reacting flow, along with a brief overview of the chemical reaction rate formulation, are given in section 3.2. Next a summary of the CSP theory, and its application to methane/air and ethanol/air flames, is given in section 3.3. The sensitivity analysis of the chemical time scales is reported in section 3.4. Finally, the laminar thermochemical database is presented for ethanol oxidation, and validated against a 1D freely propagating flame solution obtained with the Premix package from Chemkin-II and a Bunsen flame, in section 3.5.

3.2 Chemical reacting system

The temporal evolution of species mass fractions, velocity, density and enthalpy, of an arbitrary compressible mono-phase reacting flow is determined by transport phenomena such as convection or diffusion, action of surface or body forces and variation of internal and kinetic energy. The system of equations is closed when, to the conservation equations, an equation of state is added to establish the relationship between the state variables, in conjunction with additional terms describing the thermodynamics and molecular parameters of the single species, and their production or depletion rate. The energy and the mass balance account for the chemical reaction rate $\dot{\omega}_n$ [$kg/m^3/s$] of the species n . The full set of equations is described in detail and also derived for multicomponent flows in [13] and [30]. Our focus is on projection of the transport of all species on one or several progress variables. The transport of the species is described by the species transport equation, as given by:

$$\frac{\partial \rho Y_n}{\partial t} + \frac{\partial (\rho u_i Y_n)}{\partial x_i} = \frac{\partial}{\partial x_i} \left(\rho D \frac{\partial Y_n}{\partial x_i} \right) + \dot{\omega}_n \quad n = 1, \dots, N \quad (3.1)$$

where $Y_n = \rho_n/\rho$ is the mass fraction of the n -th species. The Fick's law has been used on the diffusional velocity and the mass diffusion coefficients of the species are approximated to the bulk diffusivity and so $D_{n,l} = D$. The hypothesis of unity Lewis number is assumed to be valid, and the mass diffusivity can be calculated as thermal diffusivity $\rho D = \lambda/c_p$, with the mean value of the thermal conductivity, λ , and the specific heat at constant pressure, c_p . To derive an expression for the reaction rate of each n -th species, all the elementary reactions involved in its formation, or destruction, are taken into account. The general form describing an elementary reaction r that can

proceed forward and backward is:

$$\sum_{n=1}^N \nu'_{nr} M_n \xrightleftharpoons[k_f]{k_b} \sum_{n=1}^N \nu''_{nr} M_n \quad r = 1, \dots, R \quad (3.2)$$

where M_n indicates the n -th species and ν represents the stoichiometric coefficients of reactants ($'$) and products ($''$), defined through the total number R of reactions. The symbols k_f and k_b refer respectively to the forward and backward rate constants; for a given chemical reaction, the rate constants depend only on temperature, through the empirical Arrhenius formulation ([13]). The law of mass action ([9]) describes the proportionality between the reaction rate q of an elementary reaction and the concentrations of the reactants. This proposition can also be extended to opposing reactions, and the net reaction rate of the reaction r is given by:

$$q_r = k_{fr} \prod_{n=1}^N [X_n]^{\nu'_{nr}} - k_{br} \prod_{n=1}^N [X_n]^{\nu''_{nr}} \quad (3.3)$$

where $[X_n]$ is equal to the molar concentration of the n -th species. Finally the net source term due to all reactions $\dot{\omega}_n$ [$kg/m^3/s$] of eq. (3.1) can be expressed as:

$$\dot{\omega}_n = W_n \sum_{r=1}^R (\nu'_{nr} - \nu''_{nr}) \left[k_{fr} \prod_{n=1}^N [X_n]^{\nu'_{nr}} - k_{br} \prod_{n=1}^N [X_n]^{\nu''_{nr}} \right] \quad (3.4)$$

where the molar concentration can be converted into mass fractions by: $[X_n] = \rho Y_n / W_n$, with W_n molecular weight of the n -th species. To ensure an accurate evaluation of the rate constants, eq. (3.3) can be recast in terms of the equilibrium constant $K_C = k_f/k_b$, where the ratio of $k_{f,b}$ is easily derived by satisfying the thermodynamic equilibrium condition $[X]_{n_{equil}} = 0$. All the variables needed for the calculation of the kinetic parameters are stored in the chemical reaction mechanism, built for that specific fuel oxidation, under specific initial conditions. The closure of the source term, eq. (3.4), for each species creates a system of ordinary differential equations (ODEs) characterized by a wide range of time scales. Those time scales are determined by the kinetic reaction rates of the reactions involved in the consumption/formation of the species. Each species evolves with its own rate, and the global reaction involves both slow and fast processes.

$$\tau_{chem_n} = \frac{[X_n]}{\frac{d[X_n]}{dt}} \quad n = 1, \dots, N \quad (3.5)$$

Equation (3.5) describes the time scale of the decay, or formation, of the concentration of a species. A fast reaction corresponds to a small chemical time scale, and 'viceversa' a slow reaction leads to a large value of chemical time scale. Generally in a chemical kinetic system, the range of rates is spread over several orders of magnitude. This physical feature translates into a mathematically stiff system to solve ([13]). In the following section 3.3, a method aimed to reduce the stiffness of this system is described and applied to a laminar premixed flame. The analysis is farther investigated in the case of a homogeneous reactor, where a characteristic time is chosen to divide the space of the species into fast and slow domains.

3.3 CSP algorithm

The Computational Singular Perturbation algorithm is used to reduce large detailed kinetic mechanisms. The derivation of reduced mechanisms is based on the concept that the evolution in time of a reacting system is driven by a small number of reaction rates. This is because after an initial transient time, some of the species reach an invariant state, called steady-state. The CSP algorithm identifies the steady-state species and the fastest elementary rates associated with them; the reduced mechanism is then created by removing those species from the original detailed scheme.

An extensive description of the CSP method can be found elsewhere ([19]). In this section, a description is given to the key definitions of some variables. The evolution in time of a chemical reaction results from diffusion-convection transport phenomena and chemical kinetics. Being y the N -component vector of species mass fractions, if L is a spatial operator and $\dot{\omega}$ represents the non-linear chemical source term, eq. (3.1) can be written in a compact way as:

$$\frac{\partial y}{\partial t} = L(y) + \dot{\omega}(y) \quad (3.6)$$

where the chemical source term assumes the form:

$$\dot{\omega}(y) = W(y) \sum_{r=1}^R (S_r(y) R_r(y)) \quad (3.7)$$

with W the species molecular weight, S_r the r -th component of the stoichiometric vector S_R and R_r the r -th element of the R -dimensional reaction rate's vector. Depending on the detailed kinetic mechanism, this system of equations usually involves a large number of species and elementary reactions. The CSP algorithm aims at simplifying this system, by reducing the

N-dimensional space of species into a S dimensional manifold:

$$S = N - M - E \quad (3.8)$$

where E is the constant vector of E elements, and M is the number of the steady state species associated to the fastest time scales.

The slow time scales are rate determining for the chemical process, and any perturbation caused by the M species production or destruction rate can be neglected. The fast species are exactly the ones identified by the so-called CSP pointers. For the construction of the global reduced mechanism, the species space is divided in a set of three linearly independent N-dimensional column basis vectors a_i :

$$a_r = [a_1, \dots, a_M] \quad (3.9a)$$

$$a_s = [a_{M+1}, \dots, a_{N-E}] \quad (3.9b)$$

$$a_c = [a_{N-E+1}, \dots, a_N] \quad (3.9c)$$

and in their dual N-dimensional row vectors $b^i = a_i^{-1}$, ($i = r, s, c$). Equation (3.6) can be rewritten as:

$$\frac{dy}{dt} = L(y) + a_r b^r \omega + a_s b^s \omega + a_c b^c \omega \quad (3.10)$$

and further simplified under the constraint of conservation of E elements which leads to $(b^i W S_r) R^r \equiv 0$, for $i = 1, \dots, E$ and $r = 1, \dots, R$:

$$f^c = b^c \omega \equiv 0 \quad (3.11)$$

The products in the summation $\sum a_i f^i$ are called *modes*, and the terms a_i , f^i are referred to as the *direction* and the *amplitude* of the i -th mode, respectively ([15]). Let two sets of orthonormal a_0, b^0 be initial guesses and J the Jacobian of the source term:

$$J_{ij} = \frac{\partial \omega_i}{\partial Y_j} \quad (3.12)$$

The CSP N-dimensional vectors a^i and b^i are expressed as follows:

$$a_r = J a_{0r} \tau_0^0 \quad (3.13a)$$

$$b^s = b^{0s} [I - a_r b^{0r}] \quad (3.13b)$$

$$b^r = \tau^0 b^{0r} J \quad (3.13c)$$

$$a_s = b^{0s} [I - a_r b^r] a_{0s} \quad (3.13d)$$

3 The CSP/PSR approach...

with $\tau_0^0 = (b^{0r} J a_{0r})^{-1}$ and $\tau^0 = (b^{0r} J a_r)^{-1}$. The CSP pointers introduce M algebraic equations that satisfy:

$$f^r = (b^i W S_r) R^r \approx 0 \quad i = 1, \dots, M \quad r = 1, \dots, R \quad (3.14)$$

The next step is the evaluation of the fastest rates of the elementary reactions involved in the depletion of those M species. Afterwards, the constant matrices b^i can be calculated:

$$\hat{b}^r = [I_{M \times M}, O_{M \times N-M}] \quad (3.15a)$$

$$\hat{b}^s = \hat{b}^{s0} [I_{N \times N} - \hat{a}_r \hat{b}^r] \quad (3.15b)$$

where the $M \times N$ -dimensional column vectors in a_r are expressed as:

$$a_r = W S_r (b^r W S_r)^{-1} \quad (3.16)$$

S_r is a $N \times M$ matrix where the stoichiometric vectors of the selected M fastest reactions are stored. b^c represents the $E \times N$ matrix of the molar species element composition. Finally, the matrix a_i is obtained from:

$$\hat{a} = \begin{bmatrix} \hat{b}^r \\ \hat{b}^c \\ \hat{b}^s \end{bmatrix}^{-1} = [\hat{a}_r \quad \hat{a}_c \quad \hat{a}_s] \quad (3.17)$$

Finally the species domain can be separated into the slow (s) and the fast (r) subspaces.

3.3.1 The CSP pointers

It becomes clear now that a representative numerical solution of a reacting system is needed to collect the necessary information on the reaction rates and on the species mass fractions. A 1D freely propagating premixed laminar flame is solved with the software Chemkin Premix. The initial composition is a stoichiometric mixture of air and prevaporised ethanol burning at constant atmospheric pressure. The thermochemical and transport properties required for the flame computation are taken from the San Diego kinetic mechanism, which counts 50 species and 43 reactions ([27]). The governing equations are discretized on a grid, initially coarse, refined during the calculation where the highest gradients occur. When a final solution is found, profiles of species mass fractions and temperature are available as functions of a spatial axial coordinate, $x[cm]$, which goes from 0 at the cold boundary condition, to the user-defined computational end x_{end} . In the species domain, the CSP vectors are used to select those which can be classified as steady-state species. Thus,

the flame solution is integrated in the CSP algorithm and the local pointers are calculated for each point of the flame grid, as the diagonal components of $b^r a_r$:

$$D^i = \frac{Diag(a_i b^i)}{\sum_i b_k^i a_i^k} \quad (3.18)$$

with $i = 1, \dots, N$ and $k = 1, \dots, M$. The trace elements are normalized to sum to 1, and the pointers closest to unity identify the steady-state species. A generic flow field solved by Chemkin is shown in fig. 3.1; the profile of the reactants and an intermediate species concentrations are plotted along with the temperature, against the spatial grid. Subsequently, the local pointers obtained by eq. (3.18) are plotted for three selected species of interest.

Figure 3.1: General form of the chemkin laminar flame solution

Figure 3.2a gives a clear example of a species participating only in a fast subspace. The local pointer assumes a constant unity value on the entire flame evolution and so C_2H_2 represents a good candidate as a steady-state species. When looking at fig. 3.2b, one can conclude that also C_2H_5OH is a steady-state species; that is the case only when the mechanism is reduced to 1 – *step*, but it cannot be generalized. The reaction zone is limited to a small part of the domain, where the local pointer is in fact null. There the C_2H_5OH is intuitively a major species. Downstream the flame front, the fuel is consumed at high rate, and the pointer assumes unity value. In fig. 3.2c it can be seen that the CO pointer (D_{CO}) is equal to one only in a restricted portion of the domain, corresponding to the "pre-reaction" zone; this behaviour is characteristic of a non-steady state species. As highlighted by [19] looking only at the CSP local pointers does not always give complete information on the behaviour of the species. As shown in fig. 3.2, at each point more than one species can be marked as steady or, in other words, the eq. (3.18) assumes several values when pointing at one species along the grid. Moreover, when defining a 'locally' steady state set of species, the number

(a)

(b)

(c)

Figure 3.2: Local pointers for C_2H_2 (a), C_2H_5OH (b), CO (c) for $S = 6$, $\phi = 1.0$

Table 3.1: Major species as function of ϕ obtained by integration expressed by eq. (3.20)

$\phi = 0.4$	O ₂	CO ₂	CH ₄	S-CH ₂	CH	C ₂ H ₄ OOH	C ₂ H ₄ O	N-C ₃ H ₇	C ₃ H ₆ OOH
$\phi = 1.0$	CO ₂	CH ₃ O	C ₂ H ₄ OOH	C ₂ H ₄ O	CH ₃ CO	CH ₃ CH ₂ O	I-C ₃ H ₇	N-C ₃ H ₇	C ₃ H ₆ OOH
$\phi = 1.8$	CO ₂	T-CH ₂	S-CH ₂	CH	C ₂ H ₄ OOH	C ₂ H ₄ O	HCCO	C ₂ H	C ₃ H ₆ OOH

of steady state relations and the CSP vectors a_i and b^i are y -dependent. Characteristic of a *global* reduced mechanism, instead, is that a unique global pointer is associated to each species, and the vectors a_i and b^i have constant components. The local pointers, weighted with the mole fraction, X , and the net production rate of each species q^i , are integrated over the spatial length, L , of the 1D flame:

$$I^i = \frac{1}{L} \int_0^L D^i \frac{1}{X_i + \epsilon_1} \frac{|q^i|}{|q_{max}^i| + \epsilon_2} dx \quad (3.19)$$

The ratio q^i/q_{max}^i ensures that the reaction rate is accounted for where it is meaningful; ϵ_1, ϵ_2 are small numbers preventing floating points. Based on eq. (3.19), the species with the largest values of I^i are selected as steady-state species. The importance of the terms that form the integral eq. (3.19) is extensively analyzed by [19], for a stoichiometric CH_4 /air flame. In their work it is argued that the set of major species becomes unrealistic when terms X and q^i are discarded from eq. (3.19). That argumentation is extended here to the case of a C_2H_5OH /air flame. The importance of the correct form of integration of the local pointers is shown in the following table 3.1 for a lean, stoichiometric and rich mixture. For sake of clarity, $[I]$ stands for inert species and $[S - CH_2]$ and $[T - CH_2]$ for singlet and triplet methylene, respectively ([28]). As will be discussed in detail in section 3.3.2, besides the inert species, the major reactive species involved in the oxidation are always CO₂, H₂O, O₂ or CO. However, when only the local pointer is integrated along the domain, and the global pointer I^i is written as follows:

$$I^i = \frac{1}{L} \int_0^L D^i dx \quad (3.20)$$

the resulting reduced mechanism is formed by species evolving with very small chemical timescales. As an example, one of the reactions assumed to be rate determining is:

which however involves species whose concentration in the burnt mixture is negligible. In table 3.1 the major species are listed, besides the inert species

which are included but not shown in the table. It is clear that some of these species, such as $\text{C}_3\text{H}_6\text{OOH}$ or S-CH_2 , are not suitable choices to represent the subspace of slow species. In fact, these species are relevant only close to the reaction zone and their time scales is negligible when compared to other species. Applying eq. (3.20) leads to a misunderstanding of the SS species. When the steady-state species have been selected, the rates of the elementary reactions involved in the consumption of those species are integrated along the numerical grid; the highest the integral, the fastest the elementary reaction. Finally, having obtained the set of steady state species and fastest reactions, the original mechanism can be reduced to a S-step mechanism.

3.3.2 Number of global steps

Aim of the CSP algorithm is to select a set of S global steps which can accurately represent the original scheme of reactions. Chosen the kinetic mechanism, inputs for the CSP algorithm are: a numerical solution of a laminar flame and the number (M) of steady state species. When the last is fixed, recalling eq. (3.8), the number of global steps S is consequently determined and viceversa.

In the San Diego mechanism: $E = 6$ and $N = 50$; when varying the number of global steps for example between 6 and 1, we can obtain a reduced mechanism with $M = 38$ and $M = 43$, respectively. When the degrees of freedom of the system decrease, the numerical calculations become faster, especially when the turbulence chemistry interaction is also treated, at the cost of a reduced accuracy. The choice of the number of global steps is a crucial step, but there is not a general criterion to follow.

In fig. 3.3, an example is given of the values of the global pointers obtained for a 6-step reduced mechanism, via the eq. (3.19). For sake of clarity, the names of the species are not included in the figure, but the region corresponding to the slow species is highlighted.

As previously explained, the higher values of the pointers correspond to those pointing at the steady state species.

To assess the influence of the equivalence ratio on the chemistry involved in the reduced mechanism, the global pointers of the species are plotted in fig. 3.3 for lean, stoichiometric and rich condition. It can be seen that it is always possible to determine a threshold value based on which the species can be classified as slow or fast. The majority of the species is concentrated where the points agglomerate into a quasi-flat curve, which corresponds to the species in steady state. The area of the graph where $I^i \leq 1$ corresponds to the group of the slow species.

When the mixture becomes very rich, as shown in table 3.2, the C-2 chain becomes dominant over OH. Also, the initial fuel ethanol is not in the list

Figure 3.3: Global pointers for a lean, rich and stoichiometric ethanol/air oxidation, for $S = 6$.

Table 3.2: Major species as function of ϕ , for $S = 6$

$\phi = 0.4$	N ₂	AR	HE	O ₂	OH	H ₂	H ₂ O	CO	CO ₂	CH ₄	C ₂ H ₄ O	C ₂ H ₅ OH
$\phi = 1.0$	N ₂	AR	HE	O ₂	OH	H ₂	H ₂ O	CO	CO ₂	CH ₄	C ₂ H ₄ O	C ₂ H ₅ OH
$\phi = 1.8$	N ₂	AR	HE	O ₂		H ₂	H ₂ O	CO	CO ₂	CH ₄	C ₂ H ₄	C ₂ H ₂ C ₂ H ₄ O

of the major species, meaning that its depletion rate is not rate determining. This can be explained by the excess of fuel in rich conditions. It is also interesting to notice that the 12 non steady species for $\phi = 1.0$ and $\phi = 0.4$ are the same. The following table 3.3 reports the major species identified when the number of global steps is equal to four. To the knowledge of the authors there is not a systematic analysis of the optimum number of global steps for an ethanol flame. Of course the necessary number of global steps to describe the combustion chemistry depends on the targeted system description: is this about ignition, flame burnout or pollutant emission. In this paper, the construction of a single-step global mechanism is aimed at mapping the chemical

Table 3.3: Major species as function of ϕ , for $S = 4$

$\phi = 0.4$	N ₂	AR	HE	O ₂	H ₂	H ₂ O	CO	CO ₂	C ₂ H ₄ O	C ₂ H ₅ OH
$\phi = 1.0$	N ₂	AR	HE	O ₂	H ₂	H ₂ O	CO	CO ₂	C ₂ H ₄ O	C ₂ H ₅ OH
$\phi = 1.8$	N ₂	AR	HE		H ₂	H ₂ O	CO	CO ₂	CH ₄	C ₂ H ₄ C ₂ H ₄ O

Table 3.4: Major species for $\phi = 0.4, 1.0, 1.8$, $\times$ ($S = 1$), $\circ$ ($S = 2$), $\otimes$ ($S = 1$ and 2)

	$\phi = 0.4$	$\phi = 1.0$	$\phi = 1.8$
N ₂	$\otimes$	$\otimes$	$\otimes$
AR	$\otimes$	$\otimes$	$\otimes$
HE	$\otimes$	$\otimes$	$\otimes$
O ₂	$\otimes$	$\otimes$	$\otimes$
H ₂ O	$\otimes$	$\otimes$	$\otimes$
CO ₂	$\otimes$	$\otimes$	$\otimes$
CO	$\circ$	$\circ$	$\otimes$
H ₂			$\circ$
C ₂ H ₄ O	$\otimes$	$\otimes$	$\otimes$

evolution of the reacting system into a 1 – *reaction progress variable* space, while the detailed chemistry is handled by the pre-computed database.

The table 3.4 is the list of the $(N - M)$ non steady state species, when the number of global steps S is 1, 2 or both. The two sets of species differ from each other especially at rich condition, while towards the lean mixtures they have in common most of the species, with the exception of CO. However, the chemistry of the C-chain is present by means of CO₂, and it can be assumed that fixing $S = 1$ might lead to the same grade of accuracy when $S = 2$. As observed, the reduced mechanism is related to the specified initial conditions, and so it represents a safe choice when treating premixed flames. When liquid fuels are used, however, the regimes of combustion are only partially premixed-like. Thus, the applicability of the same global mechanism to a broader range of mixtures fractions represents a main assumption. This hypothesis is based on the observation that the reaction will mainly occur within the stoichiometric flamelet; also, looking at the above tabulated list of fast species, the species O₂, H₂O and CO₂ are always identified as the major ones at the lean/stoichiometric side.

One of the advantages of the CSP method is that the derivation of the global mechanism is a mathematical process, which does not require a particular expertise of the user on the kinetic schemes. However, as found by De Jager in [11], a correct mathematical solution for the b^i (eq. (3.13)) does not always ensure a correct physical behaviour. The physical meaning of the CSP b^i vectors cannot be investigated a-priori, and only the performance of the reduced global mechanism can be tested. When the species listed in table 3.4 are used to map the flame domain from the spatial x coordinate of the 1D laminar flame, to a parametric c space, there is not a 1 to 1 relation between the temperature and the species composition with the reaction progress

Figure 3.4: Temperature and source term profiles stored in the database obtained with CSP algorithm

variable. Instead, the combination of species mass fractions composing the c should ensure a 1 to 1 relation of all the variables to c . An example of a non-physical feature shown by the database is given in fig. 3.4.

This is in contrast with CH_4 combustion and is a sign of an inaccurate selection of the steady state species. A further investigation is therefore carried out with the Perfectly Stirred Reactor (PSR) method. Section 3.4 shows that only by using the PSR method it is possible to obtain a unique behaviour of the reacting flow's properties.

3.4 Analysis of chemical time scales

The characteristic chemical time scale describing the consumption rate of the species involved in a reaction is expressed by eq. (3.5). When τ_{chem_n} is small compared to a reference time in the reactor or across a laminar flame, the corresponding reaction is in equilibrium and the species can be seen in steady state. Referring to previous work from [16] and [22], a homogeneous reacting system, where the diffusion time does not play a role, is chosen to identify the characteristic chemical time scales of the species. In such environment, the conservation of the species can be written as eq. (3.6) where the transport effects described by the first RHS term go to 0:

$$\frac{\partial y_n}{\partial t} = (\dot{\omega}_n)_{slow} + (\dot{\omega}_n)_{fast} \quad (3.21)$$

Equation (3.21) represents a stiff system, where the division of $\dot{\omega}_n$ between slow and fast subspaces is only related to the change of species concentrations, given the residence time and the initial conditions of pressure and temperature. This implies that only the chemical properties of the mixture are taken into account. Another advantage of using a homogeneous reactor is the ab-

3 The CSP/PSR approach...

Figure 3.5: Normalized characteristic time versus residence time of stoichiometric CH_4 /Air flame, evaluated with PSR

sence of gradients which usually develop across the flame front, and therefore the possibility to describe the life time of the species with a single time scale.

A set of simulations is run in the Perfectly Stirred Reactor (*PSR*) with the objective of selecting the fast and slow species. A series of simulations of the ethanol/air reaction are performed; at each simulation, the residence time is manually decreased to identify the extinction time: the minimum residence time below which the reaction does not occur. The maximum residence time is imposed as representative of the equilibrium conditions. In a laminar flame the species concentrations evolve along a spatial coordinate. But in the case of a homogeneous system, like the PSR, where the reactants/products are uniformly distributed inside the reactor, the species concentrations are just a function of the residence time.

Based on the discussion argued by [16], the variables evaluated in the present approach are: the chemical time scales of the species and a reference characteristic time index of the evolution of the reaction, that is subsequently used to normalize the calculated specie's chemical time scales. As reference time is chosen a well defined time scale in the PSR: the extinction time. The extinction time is defined as the minimum residence time, τ_{res} , for which the reactions can take place under specific initial conditions. It only depends on the composition and temperature of the input flows. First, the results reported in [16] on a CH_4 /air flow into a PSR are reproduced and shown in fig. 3.5, where the non-dimensional time is plotted against a range of residence time. There is good agreement with the data of this paper, fig. 3.5a, and what is found in [16], fig. 3.5b. The reaction reaches equilibrium condi-

Figure 3.6: Normalized characteristic time versus residence time of stoichiometric C_2H_5OH/Air flame, evaluated with PSR

tions at residence time of $10s$ as can be concluded from the flat tail of the curves. The best candidates for steady state species are those associated with the smaller chemical time scales, for example C_2H , C_2H_5 and C_2H_6 . It can be observed that the magnitude of the normalized time scales for species in fig. 3.5a deviates from fig. 3.5b. The reason might be found in the fact that the PSR analysis by Lu is carried out with the Gri 3.0 mech. The same approach is used to identify the steady state species for ethanol/air oxidation. Also, it is assumed that the combustion will take place, especially in case of liquid fuel, near the stoichiometric conditions, and so steady state species found under a certain condition are kept for the whole range of flammability. Normalized time scales of fast and slow species are shown in fig. 3.6. It is clear that the time scales of the radicals, or intermediate species are shorter than the products or major species. In fig. 3.6 it can be seen that, for short residence time, the time scales increase with the extinction time, and they do not change anymore after τ_{res} reaches value of $10s$. Eventually, at large residence time, ($\tau_{res} \gg 100s$), all species can be assumed to be in chemical equilibrium and the distinction between fast and steady species becomes meaningless. Thus, the area of the graph of major interest is the one limited by the extinction time and ($\tau_{res} < 100s$). The species characterized by a small time scale, ($t_{norm}[-] \ll 1$) in fig. 3.6a, are good candidates for being steady state species. This criterion matches the results obtained by the CSP pointers. Some of the species suitable to represent the global reaction are depicted in fig. 3.6b, as slow species. What is also found here is that one of the species (C_2H_4O) pointed as slow by CSP has a normalized chemical time scale much bigger than the others ($(t_{norm})_{C_2H_4O}[-] \gg 1$). The reaction rate

of such species is not in the period of interest, and even if its mode is not exhausted, it is negligible. The information obtained by the PSR analysis is used to manually exclude the species C_2H_4O from the set of the slow species. This is done by assigning a value of global pointer much higher than 1 in the CSP algorithm. The final set of slow species used to construct the global mechanism is now given by: the inert AR , N_2 , HE and the major species: CO , CO_2 , O_2 and H_2O . This scheme is mathematically correct and also physically valid, as will be demonstrated in section 3.5.

3.5 One-dimensional laminar database

The reduced manifold moves in a new sub-space where the chemical rates are determined by timescales associated to the $N - M$ species. Recalling that the only term of eq. (3.10) which plays a role in the chemical source term is $f^s = a_s b^s \omega$, let η be a composed species defined by:

$$\eta^i = \sum_{k=1}^N \left(b_k^i \frac{W}{W_k} \right) Y_k \quad (3.22)$$

where the CSP $\hat{b}^i$ vectors are weighted in terms of mass with W being the mean molecular weight of the mixture, and W_k the molecular weight of the k -th species. As stated above, b^r is associated with the fast timescales, so in the space of the composed species, eq. (3.10) can be cast as:

$$\frac{d\eta^s}{dt} \simeq L(\eta^s) + f^s \quad (3.23a)$$

$$\frac{d\eta^c}{dt} = L(\eta^c) \quad (3.23b)$$

$$b^r \omega \simeq 0 \quad (3.23c)$$

and the M components y_n of vector Y corresponding to the fastest timescales are identified as steady-state species. As previously mentioned, a definition of the reaction progress variable, c , is needed to represent the evolution of the combustion from the flame coordinate or PSR time coordinate solved by Chemkin to the rpv-space. A definition of c can be based on:

$$\eta = \sum_{k=1}^N b_k Y_k \quad (3.24)$$

In eq. (3.24), η is the composed species mass fraction and it is defined according to a weighting factor b_k , which is optimised using CSP. Finally, the

reaction progress variable can be written as follows:

$$c = \frac{\eta - \eta_u}{\eta_b - \eta_u} \quad (3.25)$$

with eq. (3.25) the reacting domain is covered from the unburnt side ($c = 0$), u, towards the burnt region ($c = 1$), b. A comparison is made between the b-vector obtained with the CSP method, b_{csp} , and a set of user defined combinations of species mass fractions. Results are shown in the following section.

Choice of the reaction progress variable

A parametric combination of the mass fractions of some species is often used to define a reaction progress variable. The question is how to choose this set of weight factors for the species, and an answer is given here by observing fig. 3.6b. The species which are in the range close to unity of the normalized time scale are the most suitable to represent the evolution of the reaction. A few combinations of weights for CO_2 , CO , H_2 , H_2O and O_2 have been tested, leading to the following final sets of the b-vectors:

- $b_1 = \{b_{CO_2} = 2, b_{CO} = 1, b_{H_2O} = 0.05, b_{O_2} = 0.05\}$
- $b_2 = \{b_{CO_2} = 2, b_{H_2} = 0.05, b_{H_2O} = 0.05\}$
- $b_3 = \{b_{CO_2} = 2, b_{CO} = 1, b_{H_2} = 0.05\}$
- $b_4 = \{b_{CO_2} = 2, b_{CO} = 1\}$

The weight for the species not mentioned in the list above are null. In fig. 3.7 the source term of the reaction progress variable obtained with the four definitions of b-vector and b_{csp} is plotted. All five definitions of b give a very similar profile of the temperature, which is almost linearly increasing with the reaction progress variable. For sake of clarity only the csp-based temperature curve is shown in fig. 3.7. Referring to the first and second definition of b , some inaccuracy can be observed in fig. 3.7, at $c = 0$, where the source term is not vanishing. A very small negative value of the source term, at $c = 0$, is also noticed in the database built with $b_2(CO_2, H_2, H_2O)$. As stated in [7] for a CH_4 /air flame, a less steep curvature of the source term is beneficial when turbulence is treated, and assumed shape PDF-integration is used. The vectors b_1 and b_{csp} show the source term with a maximum value lower than the one built with $b_3(CO, CO_2, H_2)$ and $b_4(CO, CO_2)$ especially towards higher values of c . It is interesting to see how the contribution of H_2 makes the profile of the source term smoother and spread over a large range of c . On the other hand, when more weight is given to CO and CO_2 the source term appears

Figure 3.7: Source term of all b vector databases and temperature profile obtained by b_{csp}

sharper and narrower. A b vector gives a good result for the projection of the detailed chemistry when it satisfies the condition of a 1 to 1 projection and leads to a source term which has a Gaussian shape as a function of progress variable, as opposed to δ shape. Both b vectors b_2 and b_{csp} satisfy these two conditions. But, b vector b_2 was obtained by intuition combined with trial and error, while the b vector b_{csp} was obtained systematically without any further tuning. The listed definitions of b , and so of the reaction progress variables, are used to simulate the chemical reactions of a premixed 1D laminar flame, and a Bunsen flame. The look-up database is built and retrieved at each iteration by the solver, prior to solving the transport equation of the reaction progress variable. The tabulation is made by mapping all the flow properties over an equidistant grid of c , made of 100 points.

3.5.1 1D freely propagating flame

The calculated one-dimensional database is tested imbedded in CFX against the solution of a 1D freely propagating flame obtained with Chemkin Premix.

A stoichiometric mixture of air and ethanol burns at $p = 1 \text{ atm}$ and $T_{inlet} = 300 \text{ K}$. The 1D laminar database described in section 3.5 is implemented in the commercial CFD code, Ansys CFX. The CFD code solves for the momentum, continuity, enthalpy equations and for the additional transport equation of the

reaction progress variable:

$$\frac{\partial \rho c}{\partial t} + \frac{\partial (\rho u_i c)}{\partial x_i} = \frac{\partial}{\partial x_i} \left(\rho D \frac{\partial c}{\partial x_i} \right) + \dot{\omega}_n \quad n = 1, \dots, N \quad (3.26)$$

At each iteration, the value of c is calculated from eq. (3.26), and the properties of the fluid and the chemical source term are retrieved from the database, via linear interpolation. The calculated c will fall in an interval of two known points in the database, c_0 and c_1 . The interpolated value of the variable of interest is calculated as a weighted average between the values given by c_0 and c_1 . The weights are given by the distance from those points, such that the closer point has a bigger weight. The thermochemical mechanism used for the simulations carried out with Chemkin and CFX is the San Diego mechanism, which includes 50 species and 43 elementary reactions. The Chemkin final solution is found on a non-uniform grid of 516 points, and the Lewis number is taken equal to one. The grid domain discretized in CFX is a uniform 70000 nodes mesh, and also in this case the differential diffusion is not modeled. The laminar flame speed, S_L calculated with Chemkin Premix is assigned as boundary condition; its value is 35cm/s , lower than the velocity measured by [10] ($\approx 40\text{cm/s}$). The discrepancy is caused by the unity of Lewis number, as also noticed in [23] for the case of a methane flame. The flame modeled with the csp-based b vector and with $b_2(\text{CO}_2, \text{H}_2, \text{H}_2\text{O})$ and $b_4(\text{CO}, \text{CO}_2)$, is stable when $S_L = 35\text{cm/s}$ is prescribed to the cold flow at the inlet. The databases built with $b_1(\text{CO}_2, \text{CO}, \text{O}_2\text{H}_2\text{O})$ and $b_3(\text{CO}_2, \text{H}_2, \text{CO})$ predict the same results only when increasing the velocity at the inlet by 8%. When $S_L = 35\text{cm/s}$, a flash back phenomenon is observed. In fig. 3.8 the profiles of the temperature and some species are plotted, to compare the performance of the thermochemical databases in combination with CFX against the solution obtained with Chemkin Premix. Only the results from b_4 are compared with b_{csp} and Chemkin Premix, since the vectors b_1 , b_2 and b_3 show a similar behaviour of b_4 .

The source term being not equal to zero at $c = 0$ is not affecting the behaviour of the major species, or the temperature. Despite species such as CO and OH are well modeled, the effects on the calculation of intermediate species would have to be further investigated. The csp, b_2 and b_4 -based databases perform well in the $1D$ premixed flame. The b_1 and b_3 vectors lead to similar results, but different ignition behavior can be expected.

3.5.2 Premixed laminar Bunsen flame

A second test of the performance of the databases is made by studying a premixed pre-vaporised ethanol-air Bunsen flame. The results are compared with a numerical analysis made by [22], carried out with a 20-step ethanol

Figure 3.8: Profiles of Temperature, $Y_{C_2H_5OH}$ and intermediate species

reduced kinetic mechanism and a detailed mechanism consisting of 46 species and 235 reactions [27]. The inlet of the burner is 0.2cm wide and the length between the inlet and side-wall is 0.1cm wide. The length of the domain from the horizontal wall to the outlet plane is 0.4cm ; the walls are treated as adiabatic. The mixture of ethanol/air is injected at 1.0m/s with a laminar plug flow profile, as in the reference simulations [22]. In fig. 3.9, fig. 3.10 and fig. 3.11 the temperature, CO mole fractions and chemical source term respectively are plotted.

Figure 3.9: Temperature [K] contours

In fig. 3.9a the temperature profile predicted by the csp-based database is shown; the b_2 - and b_4 -databases, not reported for sake of brevity, predict a very similar field. The peak of temperature is reached at around 0.3cm from the ignition plane. A qualitative comparison can be done with the results found in [22], where the tip of the flame is located between 0.18cm and 0.25cm from the ignition plane. On the other hand, it can be seen in fig. 3.9b that the b_3 database, as well as the b_1 not shown here, lead to different results. The flame does not settle itself at the end of the duct but it stabilizes upstream in the inlet duct. Of course a similar prediction of the CO mole fraction and the RPV source term can be observed respectively in fig. 3.10c and fig. 3.11c. The faster ignition suggests an over-prediction of the laminar flame speed when using the b_1 and b_3 databases in the calculation. However, the shape of the cone in fig. 3.9b appears to be less steep when compared to fig. 3.9a. This is probably due to the fact that where the flame (fig. 3.9b) attaches, the flow crossing the flame front is blocked by the wall of the duct. In fig. 3.10 and fig. 3.11 the flow field predicted using the b_2 database is also shown. In

Figure 3.10: CO mole fractions [-]

Figure 3.11: Source term [$kg\,m^{-3}\,s^{-1}$] contours

fig. 3.10b it can be seen that CO is gradually increasing across the flame. Instead, fig. 3.10a, which has the same behavior of the b_4 case, shows a higher gradient of CO. This is confirmed also by looking at fig. 3.11, where the csp-database (fig. 3.11a) produces a sharper increase of the source term across the reaction zone, than the b_2 case. This flow prediction matches the results obtained on the 1D laminar flame, explained in section 3.5.1. Referring to fig. 3.7, it can be seen that the $b_2(\text{CO}_2, \text{H}_2, \text{H}_2\text{O})$ source term spreads over a wider range of the reaction progress variable, and reaches a lower maximum value.

3.6 Conclusions

An optimization of the reaction progress, c , under the tabulated chemistry approach has been performed, and its effects on laminar flame calculations investigated. In this work, the reaction progress variable describing the evolution of the reacting system is defined as a combination of the species mass fractions involved in the kinetic mechanism. In such expression, the weight of each species is calculated with the CSP method; in particular, this algorithm is applied for an ethanol/air mixture. Besides the thermochemical properties characterizing the kinetic mechanism, the main input of the CSP algorithm is a numerical solution of the reacting system. A 1D freely propagating premixed laminar flame is solved with Chemkin Premix and the solution is passed into the CSP algorithm. This methodology has proven to give good results in the case of methane oxidation. However, it leads to unsatisfactory results when applied to a more complex fuel such as ethanol. As suggested by the work of [16], an adequate choice for the CSP input data is represented by the time scale analysis performed with the PSR. Within the PSR, the transport processes are not taken into account and the steady-state species can be selected only based on the chemical time scales. A stoichiometric mixture of methane/air is first used to compare the results shown by [16]; subsequently, the efficiency of this approach has been tested with the ethanol/air mixture. A sensitivity analysis of the consumption rate has been performed with the PSR method and the species have been divided in three groups: fast (steady), slow and dormant. This information has been used to manually correct the set of major species indicated by CSP, in particular by neglecting the species (dormant) whose time scale was out of the range of interest. The so obtained laminar chemical database, was then validated against freely propagating premixed laminar flames and premixed Bunsen flame. An additional set of databases built without the usage of CSP method has been also used for comparison. In total five databases have been assessed and the CSP/PSR based reaction progress variable leads to satisfactory results, with

the main advantage that the chemical database can be created following a clear, systematic and established procedure.

Aknowledgment

The authors thankfully acknowledge the People Programme (Marie Curie Actions) of the European Union's Seventh Framework Programme (FP7, 2007 – 2013) under the grant agreement No. FP7-290042 for the project COPA-GT. Also the authors would like to thank C.K. Law for his helpful support and T. Lu for his inspiring technical advises.

3.7 Appendix

In fig. 3.12 part of the output given by the CSP algorithm is shown. In particular, the species listed in the kinetic mechanism, the steady state species selected by CSP/PSR analysis and the weight coefficients composing the b_{csp} vector.

Bibliography

- [1] Bogdan Alexandru Albrecht. *Reactor modeling and process analysis for partial oxidation of natural gas*. University of Twente, 2004.
- [2] G Black, HJ Curran, S Pichon, JM Simmie, and V Zhukov. Bio-butanol: Combustion properties and detailed chemical kinetic model. *Combustion and Flame*, 157(2):363–373, 2010.
- [3] P Dagaut and C Togbé. Oxidation kinetics of mixtures of iso-octane with ethanol or butanol in a jet-stirred reactor: Experimental and modeling study. *Combustion Science and Technology*, 184(7-8):1025–1038, 2012.
- [4] P Dagaut, SM Sarathy, and MJ Thomson. A chemical kinetic study of n-butanol oxidation at elevated pressure in a jet stirred reactor. *Proceedings of the combustion Institute*, 32(1):229–237, 2009.
- [5] Rishi Dubey, Karnam Bhadraiah, and Vasudevan Raghavan. On the estimation and validation of global single-step kinetics parameters of ethanol-air oxidation using diffusion flame extinction data. *Combustion Science and Technology*, 183(1):43–50, 2010.
- [6] FN Egolfopoulos, DX Du, and CK Law. A study on ethanol oxidation kinetics in laminar premixed flames, flow reactors, and shock tubes. In


```

SPECIFIED VALUES FOR NUMBER OF
- STEADY STATE RELATIONS      :          43
- ELEMENT CONSERVATION RELATIONS :          6
-----
= NUMBER OF SPECIES           :          50
-----

SPECIES LIST OF CHEMICAL MECHANISM:
N2      AR      HE      H      O2
OH      O       H2      H2O     H02
H2O2    CO      CO2     HCO    CH3
CH4     CH2O    T-CH2   S-CH2  C2H4
CH3O    C2H5    C2H6    CH     C2H2
C2H400H OC2H300H C2H3     CH2CHO C2H4O
HCCO    CH2CO   C2H      CH2OH  CH3OH
CH3CHO  CH3CO   C2H5OH   CH2CH2OH CH3CHOH
CH3CH2O C3H4      C3H3     C3H5    C3H6
C3H8    I-C3H7 N-C3H7   C3H600H OC3H500H

STEADY STATE SPECIES SELECTED :
HCO     S-CH2   CH3O     C2H5     CH
CH2CHO  C2H4O   C2H      CH2OH   CH3CO
CH2CH2OH CH3CHOH  CH3CH2O C3H4     C3H5
C3H8    I-C3H7 N-C3H7   OC3H500H C3H600H
C2H400H C3H3   OC2H300H HCCO     T-CH2
C3H6    H2O2   C2H3     CH3OH   C2H6
C2H2    H02    CH2O     CH2CO   CH3
CH4      O      H       CH3CHO  C2H4
OH       C2H5OH H2

COMPOSED COMPOSITION OF RPV RELATIONS :

0.50 H      1.00 O2      0.50 OH     1.00 O      0.50 H02
0.50 HCO    -0.50 CH3    -1.00 C2H4  -0.50 CH3O  -0.50 C2H5
-1.00 C2H6   0.50 CH     0.50 C2H400H 1.00 OC2H300H -0.50 C2H3
-0.50 CH2CHO -1.00 C2H4O   0.50 HCCO   -1.00 CH2CO  0.50 C2H
-0.50 CH2OH  -1.00 CH3CHO  -0.50 CH3CO -1.00 C2H5OH -0.50 CH2CH2OH
-1.50 CH3CHOH -0.50 CH3CH2O -1.00 C3H4  -0.50 C3H3  -1.50 C3H5
-1.00 C3H6   -1.00 C3H8  -0.50 I-C3H7 -1.50 N-C3H7 -0.50 C3H600H

```

Figure 3.12: Output of CSP/PSR calculation for the definition of the b_{csp} vector.

BIBLIOGRAPHY

- Symposium (international) on combustion*, volume 24, pages 833–841. Elsevier, 1992.
- [7] S Goevert, D Mira, JBW Kok, M Vazquez, and G Houzeaux. Turbulent combustion modelling of a confined premixed methane/air jet flame using tabulated chemistry. *Energy Procedia*, 66:313–316, 2015.
- [8] DA Goussis, SH Lam, and PA Gnoffo. Reduced and simplified chemical kinetics for air dissociation using computational singular perturbation. 1990.
- [9] Cato Maxilian Guldberg and Peter Waage. Concerning chemical affinity. *Erdmann’s Journal fr Practische Chemie*, 127:69–114, 1879.
- [10] Ömer L Gülder. Laminar burning velocities of methanol, ethanol and isooctane-air mixtures. In *Symposium (international) on combustion*, volume 19, pages 275–281. Elsevier, 1982.
- [11] Bram Jager. *Combustion and noise phenomena in turbulent alkane flames*. University of Twente, 2007.
- [12] Robert J Kee, Fran M Rupley, and James A Miller. Chemkin-ii: A fortran chemical kinetics package for the analysis of gas-phase chemical kinetics. Technical report, Sandia National Labs., Livermore, CA (USA), 1989.
- [13] Kenneth K Kuo. *Principles of combustion*. Wiley New York et al., 1986.
- [14] SH Lam and DA Goussis. Conventional asymptotics and computational singular perturbation for simplified kinetics modelling. pages 227–242, 1991.
- [15] SH Lam and DA Goussis. The csp method for simplifying kinetics. *International Journal of Chemical Kinetics*, 26(4):461–486, 1994.
- [16] Tianfeng Lu, Yiguang Ju, and Chung K Law. Complex csp for chemistry reduction and analysis. *Combustion and Flame*, 126(1):1445–1455, 2001.
- [17] Likun Ma, Bertrand Naud, and Dirk Roekaerts. Transported pdf modeling of ethanol spray in hot-diluted coflow flame. *Flow, Turbulence and Combustion*, 96(2):469–502, 2016.
- [18] Nick M Marinov. A detailed chemical kinetic model for high temperature ethanol oxidation. *International Journal of Chemical Kinetics*, 31(3): 183–220, 1999.

- [19] A Massias, D Diamantis, E Mastorakos, and DA Goussis. An algorithm for the construction of global reduced mechanisms with csp data. *Combustion and Flame*, 117(4):685–708, 1999.
- [20] LV Mattos and FB Noronha. Hydrogen production for fuel cell applications by ethanol partial oxidation on pt/ceo 2 catalysts: the effect of the reaction conditions and reaction mechanism. *Journal of Catalysis*, 233(2):453–463, 2005.
- [21] TS Norton and FL Dryer. An experimental and modeling study of ethanol oxidation kinetics in an atmospheric pressure flow reactor. *International Journal of Chemical Kinetics*, 24(4):319–344, 1992.
- [22] Masaki Okuyama, Shinichiro Hirano, Yasuhiro Ogami, Hisashi Nakamura, Yiguang Ju, and Hideaki Kobayashi. Development of an ethanol reduced kinetic mechanism based on the quasi-steady state assumption and feasibility evaluation for multi-dimensional flame analysis. *Journal of Thermal Science and Technology*, 5(2):189–199, 2010.
- [23] Thierry Poinot and Denis Veynante. *Theoretical and numerical combustion*. RT Edwards, Inc., 2005.
- [24] Stephen B Pope. *Turbulent flows*, 2001.
- [25] Olaf Röhl and Norbert Peters. A reduced mechanism for ethanol oxidation. In *4th European Combustion Meeting (ECM 2009)*, Vienna, Austria, April, pages 14–17, 2009.
- [26] JLHP Sallevet, JEP Gudde, AK Pozarlik, and G Brem. The impact of spray quality on the combustion of a viscous biofuel in a micro gas turbine. *Applied energy*, 132:575–585, 2014.
- [27] Mechanical San Diego Mechanism web page and University of California at San Diego Aerospace Engineering (Combustion Research). Chemical-kinetic mechanisms for combustion applications, 2015. URL <http://combustion.ucsd.edu>.
- [28] Priyank Saxena. Numerical and experimental studies of ethanol flames and autoignition theory for higher alkanes. 2007.
- [29] JA Van Oijen, FA Lammers, and LPH De Goey. Modeling of complex premixed burner systems by using flamelet-generated manifolds. *Combustion and Flame*, 127(3):2124–2134, 2001.
- [30] FA Williams. Turbulent combustion. *The mathematics of combustion*, 2:267–294, 1985.

BIBLIOGRAPHY

- [31] S Yalamanchili, WA Sirignano, R Seiser, and K Seshadri. Reduced methanol kinetic mechanisms for combustion applications. *Combustion and flame*, 142(3):258–265, 2005.

4 Prediction of turbulent premixed combustion of ethanol/water/iso-octane blends

Abstract

Numerical simulations of laminar and turbulent reacting flows in premixed combustion regime were performed for fuel blends composed of ethanol, water and iso-octane. A combustion model based on tabulated chemistry, in the flamelet regime, was adopted. A systematic definition of the reaction progress variable is made with the Computational Singular Perturbation algorithm (CSP) and a sensitivity analysis of the chemical time scales. Four blends of fuels are chosen to test the suitability of the combustion model, with air as the oxidiser. The chemistry tabulation of each mixture is validated against the solution of a laminar flame obtained via detailed chemistry. The laminar flame speed and the species concentration in flames of pure ethanol, wet ethanol (*E70W30*), iso-octane and ethanol blended with iso-octane (*E85*) are discussed. To investigate the performance of the combustion model in the framework of an industrial application, a lab-scale premixed jet flame is used as test case. A look-up table is created and embedded in the commercial software CFX Ansys, in which RANS simulations are performed. It is found that the anhydrous and wet ethanol have the highest laminar burning velocity, however their reaction rates in the turbulent regime are slower than the iso-octane flames. A qualitative comparison is made with experimental data of a methane/air jet flame and satisfactory results were found, based on an analytical RPV (reaction progress variable) definition.

4.1 Introduction

Ethanol represents an attractive alternative fuel to reduce both the global heating issue and the fossil fuel depletion. The bio-fuels production and applications in internal combustion engines is reviewed in [1], where it is claimed that the transportation and agricultural sectors, as major consumers of fossil fuels, can benefit from the usage of bio-diesel and bio-ethanol. In Europe wheat and sugar beet are the main crops grown for bio-ethanol production

[7]. The chemical and physical properties of ethanol are well defined and an extensive literature exists on its production, atomization characteristics and combustion performance. Each application has to be evaluated case to case because several factors play an important role in determining whether or not the bio-fuels application is economically viable and efficiently performing. One of these factors is certainly the environmental impact of the bio-fuel's feedstock, however the global assessment of the bio-fuels life cycle is out of the purpose of this work. Thus, besides the analysis of the fuel sources, the areas of major concern of interest for a wide range of research are: the fuel production and distribution, its combustion performance and a fundamental study of its burning characteristics. By investigating different aspects, the experimental and numerical works share the common goal to achieve a positive energy balance of ethanol production and consumption.

An intermediate step of the ethanol production through fermentation is an ethanol-water mixture. The process of water removal, called distillation, is carried out with an energetic cost which scales linearly with the quantity of removed water up to 20%, [14] and [18]. After that point, the energetic expenses increase exponentially. When the azeotrope mixture is reached, corresponding to a concentration of ethanol-in-water equal to 96%, a dehydration process is used to obtain anhydrous ethanol. The usage of wet ethanol, so called when the amount of water is greater than 5% by volume, has the advantage to contain the production price of the fuel and its cost. However, it causes an inhibition of the heat release rate per kg fuel and, for the same amount of output power, the addition of water causes an increase of volume and chimney loss.

A great effort has been put on understanding to what extent the content of water can be increased without lowering the combustion efficiency. [19] shows that a HCCI engine can run on a mixture of 35% ethanol and 65% water by volume, while keeping high thermal efficiency and low levels of NO_x emissions. An optimum usage of wet ethanol was also found by [28] in a HCCI engine using exhaust heat gas recovery. The efficiency and emissions of hydrous ethanol have been explored experimentally by [21] in a small SI engine for a generator. An analysis of both energy performance and cost of a direct injection SI engine fueled with anhydrous and hydrous (10% water content) ethanol has been carried out by [16]. Different fuel blends were tested and numerically simulated by [2] in SI engines. Several percentages of water by volume of ethanol were used and they concluded that the mixture *E70W30* showed the best operational performance. The use of ethanol is not only attractive as fuel, but also as fuel additive, in particular blended with gasoline. Ethanol and gasoline present opposite characteristics: the ethanol's latent heat of vaporization is higher than gasoline. This has a cooling effect on the combustion temperature and might result into lower NO_x emissions. From the other side,

the heat of combustion of gasoline is greater than ethanol's, implying a bigger fuel consumption when ethanol is used under the same operational conditions. [30] explored the efficiency of a direct injection engine, operating at various blends of ethanol and gasoline. They studied the emissions of CO and NO_x, and the combustion stability and efficiency. Also, they highlighted how the higher ethanol's laminar flame speed, in respect to gasoline, plays a role in the combustion initiation. [34] reported a wheel-to-wheel analysis of a range of ethanol-gasoline mixtures in turbocharged engines, focusing on CO₂ emissions. A comparison between emissions, thermal efficiency and specific fuel consumption of hydrous ethanol and a blend of ethanol-gasoline was carried out by [4].

For fuel design, the optimal gasoline-ethanol blend depends also on the state of the art of the technology and technical factors. [8] expressed the importance of fundamental studies on the octane numbers of ethanol blended with gasoline and its surrogates. Another fundamental experimental investigation was made by [22] to explore the burning rate of pure ethanol and ethanol blended fuels. An important fundamental parameter involved in flame propagation is the laminar flame speed. [17] performed an experimental and numerical investigation on laminar flames of ethanol-water mixtures oxidation. In particular they studied the effect of water on intermediate species formation, laminar burning speeds and reaction rates of elementary reactions. If several detailed kinetic models are available to model the oxidation of ethanol, the physico-chemical properties of gasoline cannot be studied with a specific chemical model. To represent the chemistry of such fuel, simpler surrogates have to be used, as [29] did to study the laminar burning velocity of gasoline and components such as iso-octane, toluene and n-heptane. With regard to numerical investigations, a solid methodology to explore the combustion phenomena, in several regimes, is the so called tabulated chemistry. The complex system of detailed chemical reactions is represented by reduced numbers of grades of freedom, while keeping the accuracy of detailed chemistry.

Common fuels have been extensively studied with this approach, but a research gap is found in the fundamental definition of the reaction progress variable involved in the reactions of complex fuels and fuel blends. In previous work, [9] an optimization of the reaction progress variable based on a rigorous methodology was performed for stoichiometric mixtures of ethanol-air mixtures in the laminar regime. In this paper, that research is extended to numerical simulations of turbulent premixed flames of air and ethanol, wet ethanol, iso-octane and ethanol/iso-octane mixtures. A discussion about the main combustion regimes and the most suitable numerical model to represent them is reported in the first two paragraphs. Following, the numerical procedure is explained in section 4.3. The simulations, all in steady state and based on tabulated chemistry, are carried out with the commercial software

CFX Ansys. For the simulated test-case, the thermochemical database with tabulated chemistry is implemented in CFX and looked up at each iteration through an user-defined Fortran routine. To assess the influence of the definition of the reaction progress variable, the tabulations are validated against a freely propagating laminar premixed flame. The results are shown in section 4.4. Finally, the behaviour of the different mixtures of fuels and air are evaluated in a well known test case and its geometrical details along with results of experimental analysis can be found in [15].

Previous numerical work has proved the capability of the flamelet model to capture the physics of the present combustor [31], [10]. In this paper, there is a new investigation of ethanol and ethanol blends, by means of a systematic definition of the reaction progress variable in lean premixed combustion. The main advantage of this methodology is the opportunity to study a wide range of complex blends of fuel, under different operational conditions, following a clear and analytical procedure.

4.2 Turbulent premixed combustion

Combustion of premixed reactants is investigated. A detailed understanding of laminar premixed flames is important because it often represents the starting point to investigate turbulent reacting flows. The structure of a laminar flame can be divided into three main regions: a preheat zone, where fuel and oxidizer enters the reaction zone through convection-diffusion process; a reaction zone, identified in the so called inner layer (of thickness l_δ), and the products zone [26]. The flame propagates into a mixture of fresh premixed reactants at a characteristic velocity, the laminar flame speed s_L . Such flame speed is an important parameter also for analysis of turbulent flame propagation.

A systematic study of premixed turbulent flames began with Damkohler (1940), who formulated an expression of proportionality between the laminar and the turbulent burning velocity. Subsequently, Karlovitz et al. developed a new theory, introducing the concept of 'flame-generated turbulence' [11]. He suggested an expression for the turbulent burning velocity based on the laminar flame speed and the root mean square of the fluctuation velocity (turbulent intensity). It becomes clear that the interaction vortex/flame is a relevant phenomenon. In order to estimate the effects of the turbulence on the flame and to choose the appropriate combustion model, it is useful to define the time, length and velocity scales involved. A non-dimensional analysis based on the chemical and turbulent time scales has lead to the construction of the well known turbulent combustion regime diagrams [3], [23].

The classification of the combustion regimes applied in this work follows

the theory of Peters [24] and the spectral diagram of Poinso et Al. [25], and it is supported by a more recent analysis of [5]. The combustion diagram, shown in fig. 4.1 a, is based on the Reynolds number and the ratio between the chemical time scale and the Kolmogorov time scale, expressed by the Karlovitz number. The characteristic parameters adopted for its construction are now introduced. Recalling that the laminar flame propagates at constant laminar burning velocity s_L , the laminar flame thickness l_F can be defined through the mass diffusivity D as:

$$l_F = \frac{D}{s_L} \quad (4.1)$$

In practical applications the laminar flame thickness can be estimated based on the maximum temperature gradient [26]:

$$l_F = \frac{(T_b - T_u)}{\max|\frac{\partial T}{\partial x}|} \quad (4.2)$$

The thickness of the inner reaction zone l_δ is in general one order of magnitude smaller than l_F , and its measure is provided by species such as CH and HCO [35]. Assuming the Schmidt number $Sc = \nu/D$ equal to one, and using eq. (4.1), the turbulent Re_t number can be defined as:

$$Re_t = \frac{u'/s_L}{l_F/l_t} \quad (4.3)$$

where l_t is the integral turbulent length scale and u' the velocity fluctuation. Several equivalent forms of the Ka number can be derived and Peters proposed the following expression based on the integral scales:

$$Ka = \left(\frac{u'}{s_L}\right)^{3/2} \left(\frac{l_t}{l_F}\right)^{-1/2} \quad (4.4)$$

If the Kolmogorov length scale, η , is taken as reference of the turbulent length scale, and so Re_t equals 1, one obtains: $Ka = (l_F)^2/(\eta)^2$. Another relevant expression for the Karlovitz number is based on the Kolmogorov length scale and the thickness of the inner reaction layer:

$$Ka_\delta = l_\delta^2/\eta^2 \quad (4.5)$$

where the Kolmogorov length scale is defined as $\eta = (\nu^3/\epsilon)^{1/4}$, with ϵ the average rate of dissipation of turbulence kinetic energy, and ν kinematic viscosity.

Figure 4.1: (a) Turbulent combustion diagram constructed by Peters, 1999, [24] (b) Spectral diagram by Poinso et Al. [25] (Both in log-log scale).

4.2.1 The flamelet regime

Most of the combustion devices work in the so called flamelet region, and its definition in the combustion diagrams has been at the center of considerable research in the past. The main assumption behind the flamelet model is that the turbulent flame can be represented by an ensemble of one-dimensional flames. Especially in turbulent regimes, such a model allows to reduce the computational cost while keeping the accuracy of detailed chemistry. The diagram in fig. 4.1 allows to identify the combustion regimes and the transition lines. Despite the fact that actual limits are not as rigorous as shown in the combustion diagram, they can certainly give a general idea of the existing regimes. The regions of interest are delimited by the iso-line of $Re_t = 1$ and below that the reactions take place in the laminar regime. The flamelets region was originally associated to the wrinkled and corrugated flamelets areas, separated in fig. 4.1 by the line $u'/s_L = 1$, and delimited by the iso-line $Ka = 1$ and $Re_t > 1$, [3], [23]. The corrugated flamelet area is of practical interest because it is characterized by $u'/s_L > 1$; in this area the turbulence can have an effect only on the flame front of the flame but not on its structure. The area above $Ka = 1$ is characterized by scales of turbulence smaller than the flame thickness: the eddies interact with the structure of the flame, by increasing the scalar mixing in the preheat zone. However, as pointed out in 1999 by Peters [24], if the Kolmogorov scale is too small, its interaction with the flame thickness can be ineffective. Based on that, he already suggested to move the region of the broken reaction zone up in the diagram, in respect to the traditional Borghi diagram.

Moreover, the viscous dissipation can also cause the decay of such small eddies before they interact with the flame [25]. Supported by these observa-

tions, Poinso et Al. [25] used the concept of quenching in order to establish the upper limit of the flamelet regime. DNS simulations performed by [25] resulted into the construction of the spectral diagram in fig. 4.1 b. They proposed a practical definition of the 'extended flamelet' regime: *a premixed turbulent reacting flow is an extended flamelet regime if any line connecting one point in the fresh gases to another point in the burnt products crosses (at least) one active flame front*. As a result, the thin reaction zone (TRZ) was associated to the region between $Ka > 1$ and $Ka_\delta < 1$. In fact, for the flame stretching to occur, the condition $Ka(r) > 1$ (with r characteristic length scale of the flow) is necessary, but it doesn't imply a local or global quenching of the flame. The state B, in fig. 4.1 b, represents a turbulent field characterized by length scales unable to quench the flame. It can be concluded that this point, belonging to the TRZ of fig. 4.1 a, is also covered by the flamelet regime.

In conclusion: if the eddies are smaller than the laminar flame thickness ($\eta < l_F$) but greater than the inner reaction zone ($\eta > l_\delta$), the flamelet model is assumed to be valid. These observations allow the extension of the flamelet regime into the thin reaction zone as well. For sake of completeness, the regime at the top of the diagram, characterized by $Ka_\delta > 1$ is called broken reaction zone (BRZ). Since $\eta < l_\delta$ the small eddies can enter the inner reaction zone and disrupt the structure of the flame. A consideration about the scales involved in the simulations targeted of this work is important to ensure that the flamelet model is suitable for the presented cases. Turbulent flames of four premixed blends of air and fuels are investigated, where the fuels are:

- ethanol (C_2H_5OH);
- a mixture of 70% of ethanol and 30% of water ($E70W30$);
- iso-octane (IC_8H_{18});
- a blend of 85% ethanol and 15% of iso-octane ($E85$).

Table 4.1 lists the ratios (u'/s_L) , (η/l_F) and (η/l_δ) , based on the results obtained in this work. For the four cases also $Ka_\delta \ll 1$, and it can be confirmed that the present simulations are in the region of the flamelet regime.

4.3 Chemistry tabulation

In the present work, a tabulated chemistry approach is used to study a set of reacting flows, in the laminar and turbulent regime. This combustion model is based on the definition of a variable describing the spatial/temporal evolution of the reaction, from unburnt to burnt mixture. In case of premixed flames, when heat losses are not taken into account, the control variable is one, and

Table 4.1: Ratio of (u'/s_L) and (η/l_δ) for mixtures of air and: ethanol (fuel1), E70W30 (fuel2), iso-octane (fuel3), E85 (fuel4).

	u'/s_L	η/l_F	η/l_δ
fuel(1)	11.5	0.18	3.9
fuel(2)	13.1	0.14	4.0
fuel(3)	15.0	0.11	5.4
fuel(4)	23.4	0.08	5.6

called *reaction progress variable (RPV)*, " c ". From now on, " c " is the only variable considered in the numerical model description and its formulation. The tabulation procedure has the following steps:

1. a one-dimensional laminar flame is computed, using detailed chemistry, in PREMIX [12];
2. a reaction progress variable is defined based on the CSP algorithm and a sensitivity analysis of time scales performed with PSR [12];
3. the solution of the flame in 1) is mapped into the c -space in order to build a thermo-chemical laminar database;
4. the turbulence-chemistry interaction is taken into account and the final turbulent database is built.

The details of the actions summarized in 1), 2) and 3) are fully described in [9]. For sake of clarity, the main aspects of this procedure are here described. As previously mentioned, a definition of the reaction progress variable, c , is needed to represent the evolution of the combustion from the flame coordinate or PSR time coordinate solved by Chemkin to the rpv -space. A definition of c can be based on:

$$\eta = \sum_{k=1}^N b_k Y_k \quad (4.6)$$

In eq. (4.6), η is the composed species mass fraction and it is defined according to a weighting factor b_k . The question is how to choose this set of weight factors b_k . The authors developed an analytical method that identifies the most relevant species in the reacting process and assesses systematically their weighting factor in the c formulation. This was achieved with the use of the CSP algorithm, corrected with the sensitivity analysis of the time scales performed in PSR. Finally, the reaction progress variable can be written as follows:

$$c = \frac{\eta - \eta_u}{\eta_b - \eta_u} \quad (4.7)$$

with eq. (4.7) the reacting domain is covered from the unburnt side ($c = 0$), u, towards the burnt region ($c = 1$), b. These steps lead to the construction of a laminar database, where species mass fractions, source term, T , μ (viscosity), ρ (density), k (thermal conductivity) and cp coefficients are stored as function of c . Finally, a stochastic approach is used to build the turbulent database, and the procedure is presented in the next paragraph section 4.3.1.

4.3.1 Stochastic method for turbulence-chemistry interaction

The variables describing a turbulent field can be represented through their mean and variance parts. If turbulence is seen as a stochastic phenomenon, so is the interaction between turbulence and chemical kinetics. In RANS simulations of reacting flows, the Favre-averaging is adopted to level the density fluctuations and, as a result, unknown chemical terms need additional closure treatment. In this work, the closure is performed by means of a Probability Density Function, characterized by a presumed- β shape. Each scalar ϕ is then assumed to be described by its probability of falling in a certain state:

$$\tilde{\phi} = \frac{1}{\bar{\rho}} \int_0^1 \rho \phi(c) P(c) dc \quad (4.8)$$

The $P(c)$ assumes the β shape and it is expressed by means of two positive parameters, α and β as:

$$P(c; \alpha, \beta) = \frac{\Gamma(\alpha + \beta)}{\Gamma(\alpha)\Gamma(\beta)} \quad (4.9a)$$

$$\alpha = \tilde{c} \left(\frac{(1 - \tilde{c})\tilde{c}}{\tilde{c}''^2} \right) \quad (4.9b)$$

$$\beta = \alpha \frac{(1 - \tilde{c})}{\tilde{c}''^2} \quad (4.9c)$$

Outside the range of validity of the β shape, a δ -PDF is used instead. In fig. 4.2a the PDF weighted source term of the reaction progress variable is plotted for each reacting mixture, with the variance of c as a parameter. The pure ethanol/air flame shows the highest value of the source term $\tilde{S}_c$, and the iso-octane/air flame the lowest. The dilution of gaseous ethanol with vapour water results in a lower value of $\tilde{S}_c$, compared to pure ethanol, indicating a reduction of the chemical reaction rates. Also, the peak of $\tilde{S}_c$ of the three ethanol-blended mixtures moves towards lower values of c compared to the pure iso-octane curve. These curves correspond to the laminar conditions, in which the reaction progress variable variance is zero ($\tilde{c}''^2 = 0$). In fig. 4.2b the source term of the ethanol/air flame is represented for different levels of $\tilde{c}''^2$. The highest curve corresponds to $\tilde{c}''^2 = 0$ and for increasing levels

Figure 4.2: PDF source term of reaction progress variable: (a) four mixtures at null c variance, (b) ethanol/air flame at different levels of c variances (0, 0.027, 0.055, 0.136, 0.205).

of turbulence, there is a reduction of the peak reached by the source term. Therefore, increasing values of reaction progress variable variance correspond to lower reaction rates.

4.4 Numerical simulations in laminar and turbulent regimes

The calculated one-dimensional database is tested imbedded in CFX against the solution of a 1D freely propagating flame solved in Chemkin Premix, and a turbulent jet flame. The 1D database described in section 4.3 is coupled with the commercial CFD code, Ansys CFX, [9]. The CFD code solves for the momentum, continuity, enthalpy equations and for the additional transport equation of the reaction progress variable:

$$\frac{\partial \rho c}{\partial t} + \frac{\partial (\rho u_i c)}{\partial x_i} = \frac{\partial}{\partial x_i} \left(\rho D \frac{\partial c}{\partial x_i} \right) + \dot{\omega}_n \quad n = 1, \dots, N \quad (4.10)$$

and additionally the equation of state of ideal gas. At each iteration, the value of c is calculated from eq. (4.10), and the properties of the fluid, as well as the chemical source term, are retrieved from the database, via linear interpolation. The calculated c will fall in an interval of two known points in the database, c_0 and c_1 . The interpolated value of the variable of interest is calculated as a weighted average between the values given by c_0 and c_1 . The weights are given by the distance from those points, such that the closer point has a bigger weight. The temperature is calculated from the enthalpy

by using a set of NASA coefficients stored in the database [20], [10]. An iterative Newton method is used to calculate the temperature implicitly, by solving the following expression:

$$h = \sum_{n=1}^5 \frac{a_n}{n} T^n + a_6 \quad (4.11)$$

The thermochemical mechanism used for the simulations of mixtures of anhydrous and wet ethanol is the San Diego mechanism, which includes 50 species and 43 elementary reactions [27]. The reduced chemical mechanisms used in the calculation of the $I-C_8H_{18}$ and $E85$ flames are respectively formed by: 73 species, 296 reactions [33] and 80 species, 349 reactions [32]. The grid domain discretized in CFX is a uniform 70000 nodes mesh, and the Lewis number is taken equal to one, as for in the Chemkin calculations. The laminar flame speed, S_L calculated with Chemkin Premix is assigned as boundary condition. The presented cases are listed in section 4.2.1; four simulations are carried out with mixtures of air and ethanol, iso-octane, ethanol diluted with water ($E70W30$) and ethanol blended with octane ($E85$).

The value of temperature at the inlet, and pressure, are taken from the turbulent jet flame operating conditions. The premixed mixtures are pre-heated at 573 K, and the fuel/air equivalence ratio is such that the adiabatic equilibrium temperature in all simulations equals 2080 K. This results in a difference of ratio $fuel/air$, as summarized in table 4.2. The values of laminar flame speeds obtained with PREMIX are listed in table 4.2, along with the equivalence ratios calculated with the analysis at equilibrium. Due to the oxygen content, the pure ethanol flame has the highest laminar burning velocity, when compared with the other mixtures containing hydrocarbons. Compared to the pure ethanol flame, the $E70W30$ has a higher content of fuel to compensate the effect of water on the flame temperature. The variation of the laminar flame speed with fuel-oxidant ratio is governed predominantly by the variation of the temperature with the mixture fraction [13]. Figure 4.10a and fig. 4.10b in section 4.6 display that the formation of C_2H_4 , H_2CO and

Table 4.2: Boundary conditions of laminar flames

	s_L [$cm\ s^{-1}$]	ϕ [-]
ethanol/air	79.0	0.71
iso-octane/air	47.0	0.65
$E70W30$ /air	75.0	0.78
$E85$ /air	65.0	1.0

CH_3 are not affected by the water addition. However, the water content of 30% in ethanol flame, causes a decrease of the flame speed of 5%. An explanation of this phenomenon can be found in the strong suppression of O , noticeable in fig. 4.4a. A sensitivity analysis carried out by [17] shows that the reaction $H + O_2 = O + OH$ has the most relevant influence on the laminar flame speed. Thus, a suppression of the radical production O results in a decrease of the burning velocity. The same phenomenon can be seen by comparing the E85 and pure iso-octane flame speeds. The burning velocity of E85 increases almost 50% respect to the pure iso-octane case. The increase of the mole fractions peak of C_2H_4 , H_2CO and CH_3 , due to the ethanol addition, is shown in fig. 4.10c and fig. 4.10d. Also in this case, the O radical increased in the iso-octane/ethanol flame compared to the pure iso-octane flame, fig. 4.4a. To the knowledge of the author, there are not experimental measurements of the burning velocity of such mixtures, preheated at 573 K at the inlet. However, the feature of the iso-octane/ethanol's burning velocity being smaller than the ethanol's is proved in [6].

4.4.1 1D premixed laminar flames

The profiles of the major species and intermediates, along with the temperature, are plotted for the four flames, and always a good agreement is found between the PREMIX and the CFX solution. In fig. 4.3 the laminar field of the mayor species and temperature solved with Premix and CFX are shown. An excellent agreement between the two computations can be observed in all the presented cases. The overlapping of the Premix and CFX profiles means that the transfer of the laminar flame solution to the c -space (section 4.3) has been performed successfully. Looking, in particular, at the temperature profile, the pure and the wet ethanol flames have a similar behaviour, while the E85 and iso-octane flame present a different profile. However the difference is not remarkable, the addition of ethanol causes a sharper increase of temperature, and so a decrease of the flame thickness. This is in agreement with the values of the ration η/l_F listed in table 4.1.

An analysis of the effect of ethanol dilution in water and ethanol blending in octane, can be carried out looking at fig. 4.4. The mole fraction peak of the O radical is greater in E85, (red lines), than in *iso - octane* flame, (gray lines), and is smaller in E70W30, (blue lines), than in *ethanol* flame, (gray lines). The addition of ethanol in the iso-octane/air mixture promotes the production of O , due to the presence of O in ethanol. According to fig. 4.4b the greatest formation of OH occurs in the E70W30 flame. With the OH profile being very similar in the case of E85 and pure ethanol flames, one can conclude that the main effect of water is the promotion of OH . It is interesting to notice that the CO formation is driven by the content of

Figure 4.3: Laminar field profiles of ethanol/air flame (a), E70W30/air flame (b), iso-octane/air flame (c), E85/air flame (d). Bold lines: CFX with optimum c , dashed line: Chemkin.

ethanol. In fact, fig. 4.5a shows that the addition of water plays a minor role, while the addition of ethanol in *E85* increases the peak and the final mole fraction of *CO*. Based on the elementary reaction $CO + OH = CO_2 + H$, the peaks of *CO* and *OH* explain why in fig. 4.5b, the wet ethanol is the bigger producer of CO_2 . Comparing the production of CO_2 in the *E85* and pure iso-octane flames, the difference is less remarkable than when comparing the *CO* mole fraction peak in those flames. This is due to the fact that the oxygen content in ethanol enhances the equilibrium of *CO* to drift to CO_2 .

4.4.2 Turbulent premixed jet flame

To explore the performance of the databases in the turbulent regime, a lab scale burner is used as test-case [15]. The turbu-chemical properties are stored in a two dimensional tabulation, function of progress variable and variance of the progress variable. The methane/air and hydrogen/air mixtures of the original combustor are replaced with the four mixtures of air and pure ethanol, pure iso-octane, ethanol/iso-octane and ethanol/water. In order to reproduce the initial aerodynamic field of the original burner test case, the velocity prescribed at the inlet in the simulations corresponds to the inlet velocity of the experimental setup $v_{in} = 90\text{ m s}^{-1}$. The adiabatic temperature, of the methane/air flame case, is also retained. As a result, the mixtures of air and pure ethanol, pure iso-octane, ethanol/iso-octane and ethanol/water are injected at different equivalence ratios, as for the presented laminar flames. A no-slip velocity condition is imposed at the walls, and the turbulence is treated with the $k - \epsilon$ model. The mesh, composed by 2×10^6 nodes, is refined at the flame location. A key aspect of the burner is a pronounced recirculation zone that develops at the side of the flame. Thus, the hot burnt gases are transported back towards the nozzle and that is the mechanism that stabilizes the flame.

In the proposed numerical analysis the heat losses are not taken into account, and the walls are modeled as adiabatic. Results of RANS simulations are displayed, in which the turbulent field is monitored along the traversal direction, at specific axial coordinates. In the figures, each plot corresponds to one of the following locations: $x/d = 1$, $x/d = 4$, $x/d = 10$ and $x/d = 15$, with x the axial coordinate indicating the distance from the nozzle, and d the nozzle's diameter. Also points representative of the experimental measurements of a few variables of the CH_4 flame are addressed in the plots. The profiles of temperature, fig. 4.6, are affected by the simplification of adiabatic walls. The cooling of the burnt gas, due to the recirculation zone and the induced long residence time, is appreciable in the experiment profiles. Compared to the methane flame, the high hydrocarbon mixtures seem to have a longer flame: at $x/d = 10$, the core zone of the methane flame reaches already 1000K, in

 (a) $O[-]$

 (b) $OH[-]$

Figure 4.4: Mole fraction profiles computed by CFX (solid) and Premix (dashed): C_2H_5OH flame (—), $E70W30$ flame (—), IC_8H_{18} flame (—), $E85$ flame (—)

(a) $CO[-]$

(b) $CO_2[-]$

Figure 4.5: Mole fraction profiles computed by CFX (solid) and Premix (dashed): C_2H_5OH flame (—), $E70W30$ flame (—), IC_8H_{18} flame (—), $E85$ flame (—)

Figure 4.6: Temperature profiles: experiments CH_4 flame (circle), ethanol flame (—), E70W30 flame (---), iso-octane flame (—), E85 flame (---)

contrast to the cold zone of the other flames. However, the inclusion of the heat loss towards the walls is not expected to have a significant effect in the prediction of the flame length [10].

The ethanol flame has not reached the adiabatic temperature at $x/d = 15$, as is noticeable from the plot of the C_2H_5OH mole fraction as well. From fig. 4.7a, one can observe that at $x/d = 15$ there is a residual amount of ethanol (blue line), while the fuel in the other flames is fully consumed. That is also in agreement with the plots of water mole fractions of the ethanol flame, fig. 4.7b, that does not reach the equilibrium composition at $x/d = 15$. This seems to be in contrast with what observed in the laminar regime, where the burning velocity of the pure ethanol flame is the highest among the others. The iso-octane flame sees a delay in the flame front propagation in the laminar regime. At contrary, in the turbulent jet, it is the fuel more rapidly consumed. To understand the reasons behind these trends, two aspects can be pointed out: the lean composition of the laminar iso-octane flame, $\phi = 0.65$, (table 4.2), and the relatively high ratio of u'/s_L . In fig. 4.8a and fig. 4.8b the profiles of O_2 and OH are displayed. The profiles of the oxidiser are in agreement with the other major species behaviour. The turbulent profiles of OH resemble the laminar behaviour. This feature addresses the assumption on which the tabulated chemistry is based. The turbulent flame can be represented as an ensemble of laminar flames since their internal structure is not significantly altered by the turbulence. The OH production increases in the reacting zone as can be expected. However, a quantitative evaluation of this species should also take into account the heat loss in the chemistry tabulation. The axial velocity

Figure 4.7: (a) Mole fraction profiles of C_2H_5OH (—, ethanol flame), C_2H_5OH (---, E70W30 flame), IC_8H_{18} (—, iso-octane flame), IC_8H_{18} (---, E85 flame), C_2H_5OH (—, E85 flame). (b) Mole fraction profiles of H_2O in: ethanol flame (—), E70W30 flame (---), iso-octane flame (—), E85 flame (---)

Figure 4.8: Mole fraction profiles of O_2 (a), OH (b) in: ethanol flame (—), E70W30 flame (---), iso-octane flame (—), E85 flame (---)

field, fig. 4.9a, shows the same profile for all the mixtures. The aerodynamics of the methane jet is well reproduced, especially at the locations where also the temperature fields match. A deviation from the original experimental data is observed in the transverse velocity behaviour, fig. 4.9b, especially in the recirculation zone. The deviation is less significant in the zone close to the nozzle ($y/d = 4$, $y/d = 5$) but it still indicates an inaccuracy of the model.

Reasons of these dissimilarities are related to the adopted non-adiabatic tabulation, which does not well predict the temperature gradients, to the RANS model, and to the different fuel chemistry. As already stated, the ethanol and wet ethanol flames length is longer than the iso-octane and *E85* flames, and this is visible also in fig. 4.9c. At $x/d = 15$ the RMS velocity of ethanol and *E70W30* has a lower magnitude, in the core zone of the flame, compared to the other mixtures. This is due to the slower chemical reaction rate. The overall prediction of the RMS of the transverse velocity compares well, especially at the reacting layers.

4.5 Conclusions

A numerical investigation has been performed in the premixed combustion regime of laminar and turbulent flames. Four different mixtures have been used to assess the suitability of the method adopted for the chemistry tabulation. That also allowed a comparison between the performances of the different fuel blends: pure ethanol, wet ethanol (*E70W30*), pure iso-octane and a blend of 85% ethanol and 15% of iso-octane (*E85*). An initial consideration regarding the relevant time scales of the presented reacting flows revealed:

- the smallest turbulent time scales are smaller than the flame thickness ($\eta < l_F$)
- the inner reaction layer is smaller than the smallest turbulent length scale ($\eta > l_\delta$)

Thus, a flamelet model was assumed to be valid and the tabulated chemistry approach was used to perform the simulations. The turbu-chemical databases were built based on an optimized choice of the reaction progress variable, carried out with the CSP algorithm and a PSR sensitivity analysis of the time scales. Excellent agreement was found between the laminar flame field computed with detailed chemistry and the solution obtained with the CSP based databases. The four blends of fuels were simulated by fixing the adiabatic temperature. In particular, the adiabatic temperature of the methane/air flame from [15] was taken as a reference. As a result, due to the different heating values of ethanol and iso-octane, four different equivalence ratios, ϕ ,

Figure 4.9: Velocity profiles: experiments CH_4 flame (circle), ethanol flame (—), E70W30 flame (---), iso-octane flame (—), E85 flame (---)

were obtained: 0.71 for ethanol/air, 0.78 for *E70W30*, 1.0 for *E85* and 0.65 for iso-octane.

The addition of water into the ethanol mixture caused a decrease of the burning velocity, because of changes in the radical formation. The blend of ethanol and iso-octane, as expected, showed a laminar velocity higher than the pure iso-octane flame. Following, turbulent premixed flames were modeled in a combustor, for which experimental measurements are available for methane/air flames [15]. This is because of the absence of data for the investigated blends.

In order to reproduce the same aerodynamic field of the lab-scale burner, the inlet velocity in the simulations was imposed equal to the experimental setup. The turbulent intensity at the nozzle inlet, u'/u is the same for all mixtures but, contrary to the laminar regime, the burning rate is favored by the lean mixture of iso-octane over the high flame speed of ethanol. Also the ratio u'/s_L might have played a role in the slow spreading of the ethanol flame, but the effect of different chemical mechanisms employed in the database definition should be investigated. The profiles of *OH* in the turbulent regime resemble the behaviour in the laminar flames. This represents a key aspect in the main assumption that turbulent 3D flame can be represented by 1D laminar flamelets. Only a qualitative comparison with experimental data can be made, however RANS simulations gave good comparisons of temperature and velocity field. Apparently the velocity field is mainly driven by the combustion-induced temperature gradient. This was mildly affected by the different fuel chemistries, while the equilibrium temperature was held constant. A more accurate prediction is expected by including enthalpy levels effects in the chemistry tabulation.

A priori assessment of the chemical time scales was performed in this work to find an optimum RPV definition. A systematic methodology was followed to predict the combustion of alternative fuels characterized by complex chemical structures. The results of a confined turbulent jet flame has shown the capability of the model to represent industrial framework applications.

Acknowledgment

The authors thankfully acknowledge the People Programme (Marie Curie Actions) of the European Union's Seventh Framework Programme (FP7, 2007 – 2013) under the grant agreement No. FP7-290042 for the project COPA-GT.

4.6 Appendix 1

Intermediate species computed in the 1D laminar freely propagating flame:

Figure 4.10: Mole fraction profiles of radicals: (a) ethanol, (b) E70W30, (c) iso-octane, (d) E85.

Bibliography

- [1] Avinash Kumar Agarwal. Biofuels (alcohols and biodiesel) applications as fuels for internal combustion engines. *Progress in energy and combustion science*, 33(3):233–271, 2007.
- [2] WM Ambrós, TDM Lanzasova, JLS Fagundez, RL Sari, DK Pinheiro, MES Martins, and NPG Salau. Experimental analysis and modeling of internal combustion engine operating with wet ethanol. *Fuel*, 158:270–278, 2015.
- [3] R Borghi. On the structure and morphology of turbulent premixed flames. In *Recent advances in the Aerospace Sciences*, pages 117–138. Springer, 1985.

BIBLIOGRAPHY

- [4] Rodrigo C Costa and José R Sodré. Hydrous ethanol vs. gasoline-ethanol blend: Engine performance and emissions. *Fuel*, 89(2):287–293, 2010.
- [5] LPH De Goey, T Plessing, RTE Hermanns, and N Peters. Analysis of the flame thickness of turbulent flamelets in the thin reaction zones regime. *Proceedings of the Combustion Institute*, 30(1):859–866, 2005.
- [6] Patricia Dirrenberger, Pierre-Alexandre Glaude, Roda Bounaceur, Hervé Le Gall, A Pires da Cruz, AA Konnov, and F Battin-Leclerc. Laminar burning velocity of gasolines with addition of ethanol. *Fuel*, 115:162–169, 2014.
- [7] Robert Edwards, Vincent Mahieu, Jean-Claude Griesemann, Jean-François Larivé, and David J Rikeard. Well-to-wheels analysis of future automotive fuels and powertrains in the european context. Technical report, SAE Technical Paper, 2004.
- [8] Tien Mun Foong, Kai J Morganti, Michael J Brear, Gabriel da Silva, Yi Yang, and Frederick L Dryer. The octane numbers of ethanol blended with gasoline and its surrogates. *Fuel*, 115:727–739, 2014.
- [9] V Fratalocchi and JBW Kok. The computational singular perturbation/perfectly stirred reactor approach in reduced chemistry of premixed ethanol combustion. *Combustion Science and Technology*, 189(10):1659–1680, 2017.
- [10] Simon Gövert, Daniel Mira, Jim BW Kok, Mariano Vázquez, and Guillaume Houzeaux. Turbulent combustion modelling of a confined premixed jet flame including heat loss effects using tabulated chemistry. *Applied Energy*, 156:804–815, 2015.
- [11] Béla Karlovitz, DONALD W Denniston Jr, and FREDERIC E Wells. Investigation of turbulent flames. *The Journal of Chemical Physics*, 19(5):541–547, 1951.
- [12] Robert J Kee, Fran M Rupley, and James A Miller. Chemkin-ii: A fortran chemical kinetics package for the analysis of gas-phase chemical kinetics. Technical report, Sandia National Labs., Livermore, CA (USA), 1989.
- [13] Kenneth K Kuo. *Principles of combustion*. Wiley New York et al., 1986.
- [14] Michael R Ladisch and Karen Dyck. Dehydration of ethanol- new approach gives positive energy balance. *Science*, 205(4409):898–900, 1979.

- [15] Oliver Lammel, Michael Stöhr, Peter Kutne, Claudiu Dem, Wolfgang Meier, and Manfred Aigner. Experimental analysis of confined jet flames by laser measurement techniques. *Journal of Engineering for Gas Turbines and Power*, 134(4):041506, 2012.
- [16] Thompson Diórdinis Metzka Lanzasova, Macklini Dalla Nora, and Hua Zhao. Performance and economic analysis of a direct injection spark ignition engine fueled with wet ethanol. *Applied Energy*, 169:230–239, 2016.
- [17] Junjie Liang, Gesheng Li, Zunhua Zhang, Zhuang Xiong, Fan Dong, and Rui Yang. Experimental and numerical studies on laminar premixed flames of ethanol–water–air mixtures. *Energy & Fuels*, 28(7):4754–4761, 2014.
- [18] Emilio Luis López-Plaza, Salvador Hernández, Fabricio Omar Barroso-Muñoz, Juan Gabriel Segovia-Hernández, Salvador M Aceves, Joel Martínez-Frías, Samveg Saxena, and Robert Dibble. Experimental and theoretical study of the energy savings from wet ethanol production and utilization. *Energy Technology*, 2(5):440–445, 2014.
- [19] Joel Martinez-Frias, Salvador M Aceves, and Daniel L Flowers. Improving ethanol life cycle energy efficiency by direct utilization of wet ethanol in hcci engines. *Journal of Energy Resources Technology*, 129(4):332–337, 2007.
- [20] Bonnie J McBride, Sanford Gordon, and Martin A Reno. Coefficients for calculating thermodynamic and transport properties of individual species. 1993.
- [21] R Munsin, Y Laoonual, S Jugjai, and Y Imai. An experimental study on performance and emissions of a small si engine generator set fuelled by hydrous ethanol with high water contents up to 40%. *Fuel*, 106:586–592, 2013.
- [22] Shintre Parag and Vasudevan Raghavan. Experimental investigation of burning rates of pure ethanol and ethanol blended fuels. *Combustion and Flame*, 156(5):997–1005, 2009.
- [23] N Peters. Laminar flamelet concept in turbulent combustion twenty-first symposium (international) on combustion-the combustion institute 1231. 1986.
- [24] N Peters. The turbulent burning velocity for large-scale and small-scale turbulence. *Journal of Fluid mechanics*, 384:107–132, 1999.

BIBLIOGRAPHY

- [25] T Poinso, D Veynante, and S Candel. Quenching processes and premixed turbulent combustion diagrams. *Journal of Fluid Mechanics*, 228:561–606, 1991.
- [26] Thierry Poinso and Denis Veynante. *Theoretical and numerical combustion*. RT Edwards, Inc., 2005.
- [27] Mechanical San Diego Mechanism web page and University of California at San Diego Aerospace Engineering (Combustion Research). Chemical-kinetic mechanisms for combustion applications, 2015.
- [28] Samveg Saxena, David Vuilleumier, Darko Kozarac, Martin Kriek, Robert Dibble, and Salvador Aceves. Optimal operating conditions for wet ethanol in a hcci engine using exhaust gas heat recovery. *Applied energy*, 116:269–277, 2014.
- [29] Louis Sileghem, VA Alekseev, Jeroen Vancoillie, KM Van Geem, EJK Nilsson, Sebastian Verhelst, and AA Konnov. Laminar burning velocity of gasoline and the gasoline surrogate components iso-octane, n-heptane and toluene. *Fuel*, 112:355–365, 2013.
- [30] Dale Turner, Hongming Xu, Roger F Cracknell, Vinod Natarajan, and Xiangdong Chen. Combustion performance of bio-ethanol at various blend ratios in a gasoline direct injection engine. *Fuel*, 90(5):1999–2006, 2011.
- [31] JA van Oijen, A Donini, RJM Bastiaans, JHM ten Thijs Boonkamp, and LPH de Goey. State-of-the-art in premixed combustion modeling using flamelet generated manifolds. *Progress in Energy and Combustion Science*, 57:30–74, 2016.
- [32] Hu Wang, Adam B Dempsey, Mingfa Yao, Ming Jia, and Rolf D Reitz. Kinetic and numerical study on the effects of di-tert-butyl peroxide additive on the reactivity of methanol and ethanol. *Energy & Fuels*, 28(8):5480–5488, 2014.
- [33] Hu Wang, Mingfa Yao, and Rolf D Reitz. Development of a reduced primary reference fuel mechanism for internal combustion engine combustion simulations. *Energy & Fuels*, 27(12):7843–7853, 2013.
- [34] Bo Zhang and S Mani Sarathy. Lifecycle optimized ethanol-gasoline blends for turbocharged engines. *Applied Energy*, 181:38–53, 2016.
- [35] Bo Zhou, Christian Brackmann, Zhenkan Wang, Zhongshan Li, Mattias Richter, Marcus Aldén, and Xue-Song Bai. Thin reaction zone and distributed reaction zone regimes in turbulent premixed methane/air flames:

Scalar distributions and correlations. *Combustion and Flame*, 175:220–236, 2017.

5 Simulations of turbulent piloted ethanol spray flames

RANS simulations of ethanol turbulent spray flames are performed and compared to experimental measurements. The results shown in this chapter have been presented to the spray flame workshop TCS-5, held in 2015. Focus of these workshops is to collect the progress on experimental and numerical techniques in spray combustion [9], [10]. In particular, emphasis was given to the effect that the inflow conditions of the gas and liquid phases can have on the flame structure. The results are compared to the available experimental data and other contributor's results.

5.1 Experimental setup

The reference test-case is the well known Sydney spray flame. The experimental setup was built and studied at the University of Sydney by Masri et al. [2], [6], [8]. A schematic of the burner is shown in fig. 5.1: a nebulizer located 250 mm upstream the jet exit plane injects ethanol liquid. The fuel mixes with the carrier stream of air and exits the nozzle. The main flame burns at atmospheric pressure and is stabilised by a pilot flame, which is a stoichiometric premixed mixture of C_2H_2 and H_2 . This condition is such that both flames have the same C/H ratio. A stream of ambient air co-flow surrounds the hot flows.

One of the main advantages of this configuration is that no atomization or dense-spray related phenomena have to be taken into account when modeling the spray behaviour. The reason is that the droplet at the exit plane are in the dilute regime and phenomena of break-up and collisions are not relevant. However an amount of liquid fuel evaporates in the upstream pipe, before reaching the nozzle exit plane. This aspect represents a drawback due the uncertainty associated to the the measurement of the vaporised fraction (or liquid loading) of the fuel at the exit plane.

In fig. 5.1 it can be seen that the inlet of the control volume is fixed at the nozzle exit plane. The characteristics of the injector, such as droplet velocity and diameter distribution, are taken into account by means of the boundary conditions imposed at the inlet of the grid domain.

Figure 5.1: Left: schematic of the piloted spray burner, taken from [8]. Right: sketch of the simulated domain in dashed line.

5.2 Numerical approach

RANS simulations were performed using the software Ansys CFX. The combustion model adopted is the Burning Velocity Model, and a description of it can be found in Chapter 2. The multiphase flow is modeled within the Eulerian-Lagrangian approach, in which the gas phase is the continuum medium and the liquid phase is tracked into the domain as dispersed phase.

Let consider a liquid ethanol mass flow rate of 0.1 kg/s, and suppose that the liquid can be represented by spherical droplets of diameter of $40\mu\text{m}$ or $100\mu\text{m}$. The particles per second would be of the order of $10e+9$ and $10e+8$ respectively.

In both cases, keeping track of all the physical particles would be impracticable, so the Lagrangian solver's equations are solved for representative particle trajectories called *parcels*. Each parcel is assigned a different size, mass or velocity, which has the same value for particles belonging to the same parcel. The Euler-Lagrange formulation solves two sets of coupled equations for the gas and liquid phases. The inter-phase coupling is performed through the source terms, taking into account the momentum exchange, the mass and the heat transfer.

The RANS equations are solved in the gas phase domain, while the particles are treated as moving mass points. The main assumptions in the liquid phase modeling are:

- the spray is in a dilute regime;
- the particles are spherical, incompressible and single-component;
- details of the flow around the particles (boundary layers, vortex shedding and so on) are neglected.

In the following sections, the governing equations of the liquid phase are described. The subscript P denotes the properties of the liquid particles; when the subscript is omitted, the terms are referred to the gas phase.

5.2.1 Lagrangian tracking

The Lagrangian tracking model is a standard model implemented in CFX within the separated flow analysis formulation [1]. The local properties of the dispersed phase are calculated from spatial averaging over particle trajectories which are crossing a certain control volume. The particle motion is calculated analytically by integrating the force balance on the droplet, following Newton's law:

$$\frac{dx_P}{dt} = U_P \quad (5.1a)$$

$$m_P \frac{dU_P}{dt} = \sum F_{tot} \quad (5.1b)$$

where x_P and U_P are the displacement and velocity vectors of the particle P . The drag and the buoyancy forces are taken into account in the right-hand side of eq. (5.1). The buoyancy force represents the action of the density gradient between the two phases. The drag law follows the well known Schiller-Naumann formulation [12], and is defined as:

$$F_D = \frac{1}{2} C_D \rho A U_{slip} |U_{slip}| \quad (5.2)$$

where A is the projected particle surface area ($\pi d^2/4$), U_{slip} is the difference between the gas phase velocity and the liquid phase velocity and ρ the gas density. C_D is the drag coefficient and depends on the particle Reynolds number Re_P :

$$C_D = 0.424 \quad Re_P > 1000 \quad (5.3a)$$

$$C_D = \frac{24}{Re_P} (1 + 0.15 Re_P^{0.687}) \quad Re_P < 1000 \quad (5.3b)$$

where the particle Re number is defined based on the slip velocity, the particle diameter d_P and the gas kinematic viscosity ν :

$$Re_P = \frac{d_P |U_{slip}|}{\nu} \quad (5.4)$$

In the presented work, the influence of the flow on the particle trajectories is as relevant as the counteracting influence of the particles on the flow, and the two-way coupling is enabled. To account for the turbulent interaction

between the gas and liquid phase, turbulent particle tracking is enabled.

As formulated by Gosman and Ioannides [5], the instantaneous fluid velocity is decomposed, at the droplet location, in a mean and a fluctuating velocity components. The fluctuating component causes the dispersion of the droplets such that the trajectory is determined by its interaction with the turbulent eddies.

5.2.2 Heat and mass transfer

The transport equation for the particle temperature results from the contributions of the radiative (Q_r) and convective (Q_c) heat transfer, and the term associated to the mass transfer (Q_m):

$$m_P c_P \frac{dT_P}{dt} = Q_r + Q_c + Q_m \quad (5.5)$$

The heat transfer model is based on the *infinite conductivity model*, in which the droplet temperature T_P is assumed to be spatially uniform throughout the droplet but can vary in time [13]. The radiative heat transfer is assumed to be negligible in the present work.

The rate of change of temperature of the droplet, eq. (5.5), becomes:

$$m_P c_P \frac{dT_P}{dt} = \pi d_P \lambda Nu (T - T_P) \zeta \frac{1}{e^\zeta - 1} + \dot{m}_P \Delta h_{vap} \quad (5.6a)$$

$$\zeta = \frac{c_P |\dot{m}_P|}{\pi d_P \lambda Nu} \quad (5.6b)$$

The first term of the RHS, in which λ is the thermal conductivity [$J/(smK)$] and Nu is the Nusselt number, corresponds to Q_c . The correlation adopted for the Nusselt number, Nu , is that of Ranz and Marshall [11]:

$$Nu = 2 + 0.6 Re^{0.5} Pr^{1/3} \quad (5.7)$$

with the Prandtl number, Pr , equal to $(\mu C_p / \lambda)$. In eq. (5.6), a so called blowing factor, ζ , is included to account for the simultaneous mass and heat transfer. An analogy was found between the parameter ζ and the formulation adopted by [4]. In his work, El Wakil multiplies the convective heat transfer term by a factor, $z/(e^z - 1)$, to correct the standard heat transfer coefficient without mass transfer. The variable z is defined in the same way of ζ .

The last term of the RHS of eq. (5.6) represents the amount of latent heat of vaporization. The liquid evaporation rate $\dot{m}_P$ is determined, when the particle temperature is below the boiling temperature, by the formulation of

[13]:

$$\frac{dm_P}{dt} = \pi d_P \rho D \frac{W_{vap}}{W_{mix}} \ln \left(\frac{1 - x_s^v}{1 - x_{vap}^v} \right) Sh \quad (5.8)$$

where x_s^v is the equilibrium vapour mole fraction of the evaporating component at the droplet surface, x_{vap}^v is the mole fraction of the evaporating component in the gas phase, ρD is the dynamic diffusivity of the component in the continuum and W are the molecular weights of the vapour and the mixture, in the continuous phase. The Sherwood number is modeled, in analogy with eq. (5.7):

$$Sh = 2 + 0.6 Re^{0.5} Sc^{1/3} \quad (5.9)$$

where the Schmidt number, Sc , is equal to $(\mu/(\rho D))$. The variables x_s^v , x_{vap}^v are calculated assuming the vapour phase surrounding the droplet, at saturated conditions such that the vapour partial pressure equals the fuel saturation pressure at the droplet surface. The vapour pressure is calculated by using the Antoine equation [14], in which the A, B and C coefficients were properly tuned for ethanol [15]:

$$p_{vap} = p_{scale} \exp \left(A - \frac{B}{T_P + C} \right) \quad (5.10a)$$

$$x_s^v = \frac{p_{vap}}{p_{ambient}} \quad (5.10b)$$

The gas phase mole fraction is calculated on the basis of the transport equations specific to the combustion model.

5.2.3 Interphase source terms

In Chapter 2, the Favre-averaged equations governing the reacting flows were introduced. The source terms specifically related to the multiphase mixtures are here reported. The source terms to be added in the continuous phase is multiplied by the number flow rate, which is the mass flow rate divided by the mass of the particle [1]. The particle momentum, heat and mass sources transferred to the continuous phase, calculated based on eq. (5.2), eq. (5.6) and eq. (5.8), are:

$$\frac{dS^u}{dt} = -F_D \quad (5.11a)$$

$$\frac{dS^h}{dt} = -Q_c \quad (5.11b)$$

$$\frac{dS^\rho}{dt} = -\dot{m}_P \quad (5.11c)$$

Table 5.1: Inflow conditions of EtF6, EtF7.

	EtF6				EtF7			
	U	f_{exit}	ϕ_{global}	c	U	f_{exit}	ϕ_{global}	c
main flame	36	0.05	1.8	0	60	0.067	1.8	0
pilot flame	12	0.1	1.0	1	12	0.1	1.0	1
co-flow air	4.5	0.0	-	0	4.5	0.0	-	0

5.3 Computational domain

The EtF6 and EtF7 are the test-cases chosen to perform the simulations. The control volume of the flame is reduced to a half cylinder, which is discretised with a 2.7 million cells multi-block structured mesh. The inlet plane of the computational domain is taken at the jet nozzle exit plane, as represented in fig. 5.1. The central nozzle diameter is $d = 10.5$ mm and the cell size of the smallest cell in the core zone of the flame is 0.2 mm. The grid extends 20 diameters in the radial direction and 95 diameters in the axial direction. The same grid is used for all the test-cases.

5.3.1 Boundary conditions

The boundary conditions are inflow and outflow (inlet/outlet) and open boundaries in the radial direction to model an open environment. The experimental data are available at specific axial, y/d , and radial, x/d , locations, normalized with the diameter. For the EtF6 flame, the equivalence ratio at the jet exit is varied to study the effect of the boundary conditions on the flame. In table 5.1 the values imposed at the inlet, to the velocity U , fuel mole fraction f_{exit} and reaction progress variable c are shown: The global equivalence ratio is given by ϕ_{global} and it is the ratio of liquid fuel injected upstream carrier air. The pilot is modeled as a mixture of burnt hot gases ($c = 1$), with an inlet temperature equal to 2500 K, calculated at chemical equilibrium. Given that adiabatic temperature, the burnt velocity of the pilot is calculated as 12m/s.

Liquid phase

The nozzle has been divided in seven annuli, representative of the seven radial locations at which the measurements data are available. Five discrete droplet size groups are defined by the value of the mean diameter. The 25 μm drop diameter is representative of the 10-20 μm size class, and so on, with the bigger tracked particle of 45 μm . From each annulus all the groups are injected

with their own mass flow rate and velocity. An uniform distribution of the equivalence ratio is assumed at the jet exit plane. The mass flow of the gaseous mixture is fixed at the jet exit and the liquid loading is adjusted in order to keep the overall equivalence ratio of the test case. The mass flow rate for each droplet group size, at each annulus, is calculated based on the volume flux measured at the first axial station. Also, the droplets velocities are specified for each group size, at each annulus, as reported by the experimental data at $x/d = 0$. The gas phase velocity, and so the turbulence intensity at the inlet, are assumed to be equal to those of the smallest droplets. To investigate the influence of the inflow boundary conditions, two simulations of the EtF6 flame were performed, by changing the equivalence ratio at the jet exit plane: 0.5 and 0.065.

5.4 Results and Discussion

5.4.1 Gas temperature

In fig. 5.2, the gas phase radial temperature profile, expressed in terms of difference with the inlet temperature T_0 , is plotted at two axial locations. The equivalence ratio at the jet exit plane does not play a relevant role in the temperature profile calculation. In the EtF6, the temperature near the centerline, at $x/D = 10$, is underpredicted, fig. 5.2a. This might be related to the combustion model used. The source term of the reaction progress variable is dependent on both the gradient of the reaction progress variable and the turbulent burning velocity. In the core zone of the flame, there is no source of ignition ($|\nabla \tilde{c}| = 0.0$), and the burning velocity is too small to sustain the reactions, being the mixture very lean. A delayed ignition can also be caused by an incorrect prediction of the evaporation rate. Also the flame spread and the maximum temperature, in fig. 5.2b, seem to be over predicted. The same behaviour can be observed in fig. 5.2c and fig. 5.2d. These inaccuracies might be related to the intrinsic limitation of the RANS modeling to capture the large scale mixing. The centerline temperature in the EtF7 calculation is well captured, fig. 5.2c. Compared to the EtF6, the liquid loading of the EtF7 is much higher and a longer core cold flow is expected. At $x/D = 30$, however, the temperature is under predicted, fig. 5.2d. This can be the result of an incorrect prediction of the evaporation rate.

5.4.2 Droplets velocity

The droplets velocity profiles of the axial and radial components are presented here. For case EtF6, the axial velocity close to the nozzle ($y/d = 5$) is well captured (fig. 5.3). A slight discrepancy can be seen for the $(0 - 10)\mu\text{m}$ group

Figure 5.2: Mean value of gas phase radial temperature at axial locations $y/D = 10$, (a), (c), and $y/D = 30$, (b), (d). Top: EtF6, bottom: EtF7. ($\bullet$) Experiments, ($---$) present study $\phi_{exit} = 0.65$, ($---$) present study $\phi_{exit} = 0.5$, ($---$) UM $\phi_{exit} = 0.2$, ($---$) UM $\phi_{exit} = 0.5$.

of droplets, at $y/d = 5$ towards the edge of the nozzle ($x/d = 0.5$). For the EtF6, the under prediction of the velocity is higher for the case $\phi = 0.65$ so the lower liquid loading, compared to the $\phi = 0.5$, might play a role in the velocity prediction. As the droplets progress downstream, there is an over prediction of the evaporation rate, such that no droplets are detected at $y/d = 20$. The decay of the bigger droplets $(30 - 40)\mu\text{m}$ seems to be better predicted, especially corresponding to the case of ($\phi = 0.5$).

For the EtF7, a good agreement is found on the axial velocity of the $(30 - 40)\mu\text{m}$ group of drops, (fig. 5.5). Once again, the evaporation is not correctly predicted for the small drops $(0 - 10)\mu\text{m}$.

The evolution of the radial profile of the velocity shows a better trend for EtF7 (fig. 5.6) compared to the EtF6 (fig. 5.4), in particular for the big droplets compared to the small ones. It is worth mentioning that as an inlet condition the radial velocity was set to zero. The slow evolution of U_{mean} for the $(30 - 40)\mu\text{m}$ droplets and the absent evolution for the $(0 - 10)\mu\text{m}$ suggests a deficiency of RANS simulations. It can be observed, generally for all the cases, an under prediction of the radial component of the velocity.

5.5 Conclusions

RANS simulations were carried out for two Sydney ethanol flames EtF6 and EtF7, using the BVM combustion model. The interaction between the gas and liquid flows is modeled in a two-way coupling, in the Eulerian-Lagrangian framework. The results are compared with the experimental data.

The temperature is not affected by the equivalence ratio at the jet exit plane, which suggests that these flames have a non-premixed like behaviour. A better match with the measured temperature, especially near the center-line of the flame for the EtF6 and at the tip of the flame for EtF7, can be obtained by switching to LES. The mean axial velocity of the droplets is well captured both for the EtF6 and EtF7. However, especially when observing small droplets, $(0 - 10)\mu\text{m}$ class size, an over prediction of the evaporation rate is observed, especially for the cases with higher equivalence ratio at the exit (and so lower liquid loading). The radial component of the velocity, however, shows discrepancies, especially when conditioned to small droplets. This is an indication that the droplets do not acquire a radial velocity, U_{mean} from the gas flow. An improvement of the results can be achieved by prescribing a U_{mean} at the injection and, once again, by favoring an LES approach. In general, a good agreement is found with the experimental data, however, the employment of a combustion model, whose chemical source term is based on kinetic rate, is recommended [3]. Also, a new spray flamelet/progress variable approach, where the manifold is built by taking into account the evaporation,

5 Spray flames

Figure 5.3: EtF6: axial profile of the droplets mean velocity: droplet class $(0-10)\mu m$ (left), droplet class $(30-40)\mu m$ (right); top to bottom: ($y/d = 5$), ($y/d = 10$), ($y/d = 20$) and ($y/d = 30$). (●) Experiments, (---) present study $\phi_{exit} = 0.65$, (---) present study $\phi_{exit} = 0.5$, (---) UM $\phi_{exit} = 0.2$, (---) UM $\phi_{exit} = 0.5$.

Figure 5.4: EtF6: radial profile of the droplets mean velocity: droplet class $(0-10)\mu\text{m}$ (left), droplet class $(30-40)\mu\text{m}$ (right); top to bottom: $(y/d = 5)$, $(y/d = 10)$, $(y/d = 20)$ and $(y/d = 30)$. (●) Experiments, (---) present study $\phi_{exit} = 0.65$, (---) present study $\phi_{exit} = 0.5$, (---) UM $\phi_{exit} = 0.2$, (---) UM $\phi_{exit} = 0.5$.

5 Spray flames

Figure 5.5: EtF7: axial profile of the droplets mean velocity: droplet class $(0-10)\mu m$ (left), droplet class $(30-40)\mu m$ (right); top to bottom: ($y/d = 5$), ($y/d = 10$), ($y/d = 20$) and ($y/d = 30$). (●) Experiments, (---) present study $\phi_{exit} = 0.65$, (---) present study $\phi_{exit} = 0.5$, (---) UM $\phi_{exit} = 0.2$, (---) UM $\phi_{exit} = 0.5$.

Figure 5.6: EtF7: radial profile of the droplets mean velocity: droplet class $(0-10)\mu\text{m}$ (left), droplet class $(30-40)\mu\text{m}$ (right); top to bottom: $(y/d = 5)$, $(y/d = 10)$, $(y/d = 20)$ and $(y/d = 30)$. (●) Experiments, (---) present study $\phi_{exit} = 0.65$, (---) present study $\phi_{exit} = 0.5$, (---) UM $\phi_{exit} = 0.2$, (---) UM $\phi_{exit} = 0.5$.

5 *Spray flames*

represents an interesting possibility [7].

Bibliography

- [1] CFX ANSYS. Ansys cfx realease 14.5 user guide. *Canonsburg (PA): ANSYS Inc*, 2012.
- [2] Yung-Cheng Chen, Sten H Stårner, and Assaad R Masri. A detailed experimental investigation of well-defined, turbulent evaporating spray jets of acetone. *International journal of multiphase flow*, 32(4):389–412, 2006.
- [3] Hossam A El-Asrag, Markus Braun, and Assaad R Masri. Large eddy simulations of partially premixed ethanol dilute spray flames using the flamelet generated manifold model. *Combustion Theory and Modelling*, 20(4):567–591, 2016.
- [4] Mc M El Wakil, OA Uyehara, and PS Myers. A theoretical investigation of the heating-up period of injected fuel droplets vaporizing in air. 1954.
- [5] AD Gosman and E Loannides. Aspects of computer simulation of liquid-fueled combustors. *Journal of Energy*, 7(6):482–490, 1983.
- [6] James Dakshina Gounder, Agisilaos Kourmatzis, and Assaad Rachid Masri. Turbulent piloted dilute spray flames: Flow fields and droplet dynamics. *Combustion and flame*, 159(11):3372–3397, 2012.
- [7] Yong Hu, Hernan Olguin, and Eva Gutheil. A spray flamelet/progress variable approach combined with a transported joint pdf model for turbulent spray flames. *Combustion Theory and Modelling*, pages 1–28, 2017.
- [8] AR Masri and JD Gounder. Turbulent spray flames of acetone and ethanol approaching extinction. *Combustion Science and Technology*, 182(4-6):702–715, 2010.
- [9] Bart Merci and Eva Gutheil. *Experiments and Numerical Simulations of Turbulent Combustion of Diluted Sprays: TCS 3: Third International Workshop on Turbulent Spray Combustion*, volume 19. Springer Science & Business Media, 2014.
- [10] Bart Merci, Dirk Roekaerts, and Amsini Sadiki. *Experiments and Numerical Simulations of Diluted Spray Turbulent Combustion: Proceedings of the 1st International Workshop on Turbulent Spray Combustion*, volume 17. Springer Science & Business Media, 2011.
- [11] WE Ranz. Evaporation from drops 1. *Chem. Eng. Prog.*, 48:141, 1952.

BIBLIOGRAPHY

- [12] L Schiller. ber die grundlegenden berechnungen bei der schwerkraftaufbereitung. *Ver. Deut. Ing.*, 77:318–321, 1933.
- [13] William A Sirignano. *Fluid dynamics and transport of droplets and sprays*. Cambridge University Press, 1999.
- [14] George Wm Thomson. The antoine equation for vapor-pressure data. *Chemical reviews*, 38(1):1–39, 1946.
- [15] Wikipedia. Antoine equation — wikipedia, the free encyclopedia, 2017. [Online; accessed 26-August-2017].

6 Ethanol turbulent spray flame response to gas velocity modulation

Abstract

A numerical investigation of the interaction between a spray flame and an acoustic forcing of the velocity field is presented in this paper. In combustion systems, a thermoacoustic instability is the result of a process of coupling between oscillations in heat released and acoustic waves. When liquid fuels are used, the atomization and the evaporation process also undergo the effects of such instabilities, and the CFD of these complex phenomena becomes a challenging task. In this paper, an acoustic perturbation is applied to the mass flow of the gas phase at the inlet and its effect on the evaporating fuel spray and on the flame front is investigated with URANS numerical simulations. Two flames are simulated: a partially premixed ethanol/air spray flame and a premixed prevaporised ethanol/air flame, with and without acoustic forcing. The frequencies used to perturb the flames are 200 Hz and 2500 Hz, which are representative for two different regimes. Those regimes are classified based on the Strouhal number $St = \frac{D}{U} f_f$: at 200 Hz, $St = 0.07$ and at 2500 Hz, $St = 0.8$. The exposure of the flame to a 200 Hz signal results into a stretching of the flame which causes gas field fluctuations, a delay of the evaporation and an increase of the reaction rate. The coupling between the flame and the flow excitation is such that the flame breaks-up periodically. At 2500 Hz, the evaporation rate increases but the response of the gas field is weak and the flame is more stable. The presence of the droplets does not play a crucial role at 2500 Hz, as shown by a comparison of the discrete flame function in case of spray and prevaporised flame. At low Strouhal number, the forced response of the prevaporised flame is much higher compared to the spray flame.

6.1 Introduction

Combustion instability is a major issue in combustion systems, especially when the reactions occur in the lean-combustion regime. When close to the lower flammability limit, the reacting mixture is more sensitive to any upstream perturbations, and the interaction combustion/acoustic is more likely

to happen. In liquid-fueled combustion systems, the unsteady burning rate caused by the acoustic waves can also affect the spray structure through temperature fluctuations. Conversely, the gas velocity oscillations can cause an enhancement of the evaporation and, subsequently, a modification of the mixture fraction. This will cause a secondary effect on the heat released by the flame. Modeling of spray flames is a difficult task due to the interaction of several phenomena that occur over a wide range of temporal and spatial time scales, such as atomization, droplet collisions, heating and evaporating droplets, gas-liquid turbulence interaction and chemical reactions. Several numerical investigations are described in the literature, aimed at gaining insight into the physical phenomena that characterize the effect of a pulsating gas flow field on a single burning droplet. Only a few experimental investigations have achieved a good understanding of the influence of the sound waves on droplets' injection, dispersion, and turbulence.

A summary of earlier work on this topic will be provided below. A commonly used tool to determine the correlation between the unsteady heat released by the flame and the acoustic perturbation upstream the flame is the (FTF) Flame Transfer Function [13], [4]. Yi et al. [18] measured a FTF in a turbulent liquid fuel combustion rig submitted to fuel modulation. They found the flame spectra to be similar to those in the gaseous combustion and this can be attributed to the small inertia of the droplets and to the consequently fast mixing. On the other hand, a stronger impact of the spray on the reaction rate, and so on the gain of the FTF, is observed in the case of laminar spray flames ([14]). The important role played by the turbulence is shown by [17], who presented an experimental investigation of the impact of acoustic waves on an air-atomized evaporating ethanol spray. They observed a change of the spray velocity and penetration under high-amplitude velocity oscillations. As they reported, this is in agreement with numerical studies showing an increase of the evaporation rate due to acoustic velocity. A numerical analysis was performed by [12] to investigate the interaction between spray flames and acoustic waves, in particular when the acoustic frequency is close to the natural frequency of the spray flame. Self-excited oscillations were also experimentally investigated by [3] in a kerosene spray flame. They concluded that the mixing of the droplets, and so the evaporation, has an impact on the burning rate and this is related to combustion instabilities.

An extensive numerical analysis has been performed by [2] on the effects of slip velocity fluctuations on a single droplet burning. The NO formation was predicted to vary with the forcing frequency, depending on the droplet-to-flame distance changes. Because of the small temperature gradient between the droplet flame and the surroundings, no significant increase of the evaporation rate was observed. Naturally, there are a few uncertainties about whether the single burning droplet model is fully able to describe the more

complex physics of a spray.

[8], performed experiments to study the vortex structures in a reacting spray exposed to pressure waves. They described a clear interaction with the turbulence field, through the use of non-dimensional characteristic parameters, such as the Strouhal number and the Stokes number. Representative of the evolution of the reacting flow are the time scales associated with the forcing acoustic cycle and the time scales describing the evaporation and the fluid mechanical response of the flow. An important contribution to the study of forced flames response is the work done by [15]. They computed and analyzed the effects of several regimes of Strouhal number on chemistry and temperature of methane-air diffusion flames.

In this paper, effort has been made to numerically investigate a turbulent piloted spray flame exposed to low amplitude gas velocity oscillations. The CFD is performed using a commercially available numerical code, CFX Ansys, by solving the URANS set of equations. The flow field is solved in the Eulerian-Lagrangian framework and gas and liquid phases are coupled in a two-way manner. The studied test-case is a non-confined turbulent flame burning at atmospheric pressure and stabilized by a pilot flame. The boundary conditions of the main flame and the burner's configuration are taken from the well known ethanol flame of the University of Sidney ([11], [5]). The main advantage of this flame is that the spray can be modeled in the dilute regime and hence phenomena of break-up and droplet interactions can be neglected.

This paper is based on previous work done by [6]. The results shown in [6] are here integrated with new simulations aimed at comparing the spray flame response with a purely gaseous reacting flow. The response of a mono-dispersed spray flame is compared with the forced response of a pre-vaporised ethanol flame, with the same global equivalence ratio. A preliminary study on dimensionless parameters is carried out in section 6.2, as an attempt to characterize the dynamics of the spray flame. The numerical procedure followed in the simulations is explained in section 6.3. The results of the simulations performed are discussed in detail in section 6.4. Final conclusions are formulated in the final section 6.5.

6.2 Characterization of unsteady spray flames

The characterization of the spray flame response to acoustic forcing covers a wide range of phenomena involving a variety of temporal scales. An important contribution to describe the forced flame response by means of dimensionless variables was made by [8]. They analyze the reacting gas field and the spray structure, submitted to the acoustic forcing, by determining three main parameters: the mechanical time of the flow, the relaxation time of the droplets

and the evaporation time. These physical variables are linked to the acoustic modulation through the forcing acoustic time, which is the inverse of the forcing frequency ($t_{ac} = 1/f_f$). Despite a strongly non-linear response of the flame, they could observe a major trend of the flame fluctuations, based on the value of the Strouhal number. The largest combustion/vortex interaction occurs for $St \leq 1$, while towards higher frequencies, $f_f \geq 240$ Hz, the fluctuations tend to decrease. At the maximum frequency imposed, 700Hz, they measured a phase speed equal to the value of the inlet fresh gas velocity. In eq. (6.1) the Strouhal number is written as:

$$St = \frac{D}{U} f_f \quad (6.1)$$

where D is the diameter of the main flame nozzle, U is the gas bulk velocity at the inlet and f_f the forcing frequency. Equation (6.1) is valid when the flame is submitted to a mono-harmonic signal and a unique value can be given to f_f . This is the case for the flames (a) and (b) investigated in this paper and listed in section 6.3: $St = 0.07$ at 200 Hz and $St = 0.8$ at 2500 Hz. These values are in agreement with the field observed in the simulations: at 200 Hz the flame shows a strong entrainment of the pilot into the core zone, while at 2500Hz the flame front appears wrinkled but not disrupted. The behaviour of the spray flame, (a), is very similar to the correspondent gaseous flame (b). In addition to the eq. (6.1), another formulation of the Strouhal number can be given based on the turbulent length scale:

$$St_t = \frac{D}{\sqrt{k^3 \epsilon^{-2}}} \quad (6.2)$$

where k is the turbulence kinetic energy and ϵ the turbulence eddy dissipation. To distinguish the two definitions of Strouhal number in eq. (6.1) and eq. (6.2), a subscript t (for turbulent) is written in eq. (6.2). The second relevant parameter represents a measure of the mechanical response of the droplets: the Stokes number. If the effects of the relative convective motion are not taken into account, then the particle relaxation time is written as [8]:

$$t_{rel} = \frac{\rho_l d_d^2}{18\mu_g} \quad (6.3)$$

The liquid density ρ_l and the droplet diameter d_d are calculated at the inlet conditions and the gas dynamic viscosity μ_g at high temperature. The Stokes number describes how closely the particles follow the fluid streamlines: when $\sigma \ll 1$ the inertia of the particles is negligible, and when $\sigma \gg 1$ the particles are likely to detach from the flow streamlines. There are several definitions

of the Stokes number, and the formula used here is:

$$\sigma = \frac{t_{rel}}{t_e} \quad (6.4)$$

where t_{rel} is the relaxation time and t_e is the characteristic eddy lifetime, simply defined as k/ϵ . In the case of a stationary flame, at a distance of 10 cm from the nozzle, eq. (6.4) is observed to give a value of 0.8. This value is slightly higher than the one estimated in [7]; this discrepancy is probably due to the different definitions of eq. (6.4). Based on the Stokes number calculation, the dispersed phase is expected to follow the fluid. A parameter proposed by [8] relates the liquid relaxation time to the forcing frequency by the following definition:

$$\sigma_l = \frac{t_{rel}}{t_{ac}} \quad (6.5)$$

where l indicates the liquid phase. Equation (6.5) is defined as acoustic Stokes number (σ_{ac}), by [14]. At 200Hz, $\sigma_l = 0.2$ and the liquid is responsive to the acoustic perturbation and its dispersion is affected by the forcing frequency. At 2500Hz, $\sigma_l = 2.6$ and the influence of the velocity fluctuations on the dispersed phase is weaker than in the low frequency case. However, since the Stokes number calculated with eq. (6.4) is less than unity, if the gas field is susceptible to the perturbation, also the spray is. This statement is true in this case because droplets of only one size band are injected into the domain, and the Stokes number is calculated based on a specific droplet size diameter. In the general case of a polydisperse spray, as the original validation test-case, the Stokes number assumes different values, depending on the size band [9]. An important time scale to take into account when studying the behaviour of spray flames is the evaporation rate. In a piloted flame, the lifetime of the droplet is affected not only by its reacting vapour phase, but also by the heat transferred by the hot pilot. The liquid mass injected from the center of the nozzle travels a longer distance, before evaporating, than the liquid located at the periphery of the jet. From the steady state calculation, the range of the evaporation time is calculated to be: $0.003 < t_{evap} < 0.012$. If the droplet evaporates before undergoing an entire acoustic cycle, the dispersion will not be affected by the forcing. The condition $t_{evap} > t_{ac}$ is satisfied at $f_f = 2500$ Hz, but not completely fulfilled at $f_f = 200$ Hz. The droplets traveling from the periphery of the nozzle, close to the pilot, only survive half of the acoustic cycle before evaporating.

Figure 6.1 represents a sketch of the regimes of response of the spray. The acoustic Stokes number (eq. (6.5)) on the x-axis is plotted versus the forcing frequency, y-axis. The iso-line of Stokes number (eq. (6.4)) equal to 1, divides the diagram in three main areas:

Figure 6.1: Regimes of response of the ethanol spray to reacting gas modulations. Area I: droplets following gas region. Area II: spray detaching from the flow region. Area III: spray uncoupled with gas and acoustics.

- area I ($\sigma < 1$, $\forall \sigma_l$): droplets following gas region. Regardless the value of the acoustic Stokes number, the liquid phase is likely to follow the gas and the acoustic waves;
- area II ($\sigma > 1$, $\sigma_l < 1$): spray detaching from the flow region. The spray is responsive to the acoustic wave but is likely to detach from the flow.
- area III ($\sigma > 1$, $\sigma_l > 1$): spray uncoupled with gas and acoustics. The inertia of the liquid is such that it is not responsive to external perturbation and is not attached to the gas.

For $\sigma \geq 1$, it is possible to determine the frequency f^* above which the liquid becomes less responsive to the acoustic forcing. The frequency f^* becomes lower with increasing Stokes number. The lower limit, f_m , is given by the condition $f_m > 1/t_{evap}$, below which the droplet will evaporate before the end of the acoustic cycle. The gray area indicates the droplets which will not survive the acoustic cycle. The frequency f_m moves towards higher values for increasing Stokes number. This is because the evaporation time becomes higher for bigger droplet, which corresponds to higher Stokes number.

6.3 Numerical configuration

The burner object of the presented work was designed and studied experimentally at the University of Sydney. The turbulent ethanol-air spray flame is burning at atmospheric pressure. The nebulizer is located 250 mm from the

Figure 6.2: (a) Sketch of the simulated domain, dashed line [6], (b) Imposed velocity at the main flame inlet, $f = 200$ Hz (-) and $f = 2500$ Hz (-)

nozzle exit plane, and an amount of ethanol vaporizes already along the tube upstream the jet exit plane. At the inlet of the numerical grid, a partially premixed mixture of prevaporised ethanol and air is injected, along with the liquid loading. The liquid fuel is assumed to be in the dilute regime and the droplets in spherical shape. The main flame is stabilized by a pilot flame, which is a stoichiometric mixture of acetylene, hydrogen and air. The hot flow is surrounded by a stream of co-flowing air, at ambient conditions. A detailed description of the geometry and a wide set of initial conditions adopted in an experimental set-up of non-reacting jets and flames can be found elsewhere ([11], [7]). Figure 6.2a shows the numerical domain, limited by the dashed line, and the streams of flow entering the domain. The control volume of the flame is reduced to a half cylinder and is discretized in a structured mesh of 1×10^6 nodes. Symmetry boundary conditions are used to represent the symmetric reacting flow field; an opening boundary condition is applied to the external surface of the half cylinder to simulate the surrounding air. In total seven simulations were performed:

- (a) Open spray flame submitted to two mono-frequency forcing: one of 200 Hz, and one of 2500 Hz ([6]);
- (b) Open prevaporised ethanol/air flame submitted to two mono-frequency forcing: one of 200 Hz, and one of 2500 Hz;

The purely gas-fueled flame has the same global equivalence ratio of the spray flame ($\phi = 2.4$). However, in the spray flame configurations the ethanol/air

gas mixture, injected at the inlet along with the liquid, is a lean mixture. The simulations are performed following the Eulerian-Lagrangian approach. The interphase coupling takes place with a 2-way coupling, through source terms in the solved equations. The particle motion is solved for representative trajectories (parcels), by integrating the Newton's law. The particle temperature is assumed to be spatially uniform within the droplets and the evaporation model is the Spalding-like formulation as implemented in CFX. The mass flow of the liquid fuel at inlet is based on the Sydney spray flame database and the injection of the parcels takes place uniformly over the nozzle plane. The combustion is treated with the available Burning Velocity Model [1]. The mixing is modeled by means of the mixture fraction and the spatial/temporal evolution of the reacting flow is described by the reaction progress variable 'c'. The kinetic mechanism used in the simulations is the 235-step reaction mechanism, composing of 46 species, by Marinov [10]. Other details of the numerical setup can be found in [6].

The main flame is perturbed, at the inlet, with an harmonic wave, represented by a sinusoidal signal that includes the forcing frequencies. The transient mass flow rate of the air/ethanol gas mixture is implemented as follows:

$$m(t) = m[1 + A_f \sin(2\pi f_f t_{step})] \quad (6.6)$$

The time-dependent component has a constant amplitude, A_f , equal to 0.12 of the mean gas mixture mass flow. In this paper, two cases are investigated concerning the slip velocity at the inlet. One simulation is performed in which a velocity equal to 15 m/s is imposed to the droplets, at the inlet. In this way, when the mean velocity of the gas phase undergoes the prescribed time (frequency)-dependent oscillations, also the slip velocity follows the same fluctuations. A representation of the time dependent profile of the slip velocity is given in fig. 6.2b; this case is presented in section 6.4.3. A second set of simulations is carried out with the assumption of zero slip velocity at the inlet and the results are shown in the next paragraph section 6.4. The total simulation time is 0.9s, with a time step of $2\mu s$. Due to the high computational time required by the Lagrangian tracking, the fuel droplets are injected only every 0.2 ms. One complete acoustic cycle of the 2500 Hz perturbation covers a time lap of 0.4 ms and the acoustic cycle of 200 Hz has a period of 5^{-3} s. The injection of the droplets takes place in a time interval such that at least two injections are made per acoustic cycle at high frequency (and 10 at low frequency). This should ensure that the liquid loading is present at each acoustic cycle.

Figure 6.3: Decay of liquid diameters along representative clusters of droplets, at five radial locations r/d , and acoustic period $T_{2500Hz} = 0.4$ ms and $T_{200Hz} = 5$ ms

6.4 Simulation results

Two cases of forced flame response to inlet flow modulation are shown in this paragraph. The frequencies used to perturb the two phases fluid mass flow rate at the inlet are 200 Hz and 2500 Hz. First, a brief discussion on the flow time scales is made. In the case of a mono-dispersed spray, the Stokes number can be assumed constant. However, in this specific test-case, the evaporation time varies along the radial coordinate, moving from the core zone of the flame towards the pilot. Figure 6.3 shows the decay of the droplets diameter in the non-forced spray flame. The radial location, r , is normalized by the nozzle diameter d . Each line represents a cluster of droplets injected at a specific location, from the centerline ($r/d = 0$) towards the edge of the flame ($r/d = 0.5$). The droplets injected close to the pilot are exposed to a much higher temperature and they heat up faster than the liquid in the cold core zone. This leads to a higher evaporation rate going from the pilot to the centerline. On the x-axis the acoustic periods at 200 Hz ($T_{ac} = 5$ ms), and at 2500 Hz ($T_{ac} = 0.4$ ms) are also indicated. The mass of liquid with an evaporation time lower than the acoustic periods will evaporate before the completion of the acoustic cycle. The interaction between liquid and gas phase is modeled in a two-way coupling, meaning that a change in the liquid field will affect the gas field and vice-versa. The effect of the droplets on the turbulence field of the gas becomes even larger in the case of acoustic-forced

flow. The evolution of the Lagrangian tracks and the Eulerian gas field are described in the next paragraphs section 6.4.1. A comparison of the spray flame with a prevaporised ethanol flame is made in section 6.4.2.

6.4.1 Spray flame forced response

Several can be the responses of a flame exposed to acoustic forcing. In this paragraph it is shown that, in case of liquid-fueled flames, one of the parameters which can be used as a well defined measure of the change of the flame structure is the spray penetration. In table 6.1 the maximum axial penetration of the spray is compared in the case of perturbed and non-forced flames. From table 6.1 it can be observed that the higher the frequency, the shorter the distance traveled by the droplets before evaporating. As stated in section 6.4, the boundary conditions of the liquid's velocity slightly differ between the forced and the non-forced case. The slip velocity is null in the forced cases and equal to 5 m/s in the stationary flame. However, due to the small size of the droplets, the initial slip velocity decays quickly and the $f_f - free$ case is taken as a reference. This assumption is validated in section 6.4.3, where the spray response of two flames, with $u_s = 0$ m/s and $u_s = 5$ m/s, are compared, both in case of 2500 Hz forcing. The traveling distance of the spray exposed to the highest frequency is shorter than the distance of the non-forced flame. This is the result of a shorter evaporation time, as can also be observed in fig. 6.4. Figure 6.4a and fig. 6.4b show the diameter lifetime of the tracks injected at the same location of the acoustic-free case, fig. 6.3. The gas modulations at 200 Hz and 2500 Hz have an opposed effect on the spray response. In particular, at low frequency the acoustic wave interacts with transport phenomena of the liquid phase. At specific Δt , pockets of cold fuel detach from the flame causing a perturbation of the spray dispersion. In fig. 6.5 the forcing signal, which is the velocity at the inlet, is plotted versus the time. The evolution of the spray dispersion is shown for one acoustic period (T_{ac}), and each ball in the figure is a graphical representation of the so-called parcels of droplets (where each parcel represents a fixed number of physical droplets). The entrainment into the spray occurs every T_{ac} and the droplets travel downstream and evaporates when entering the hot region of the post-flame. This leads to a delay of the evaporation time for the droplets

Table 6.1: Axial spray penetration [m] under acoustic forcing and in stagnation flame.

$f_f - free$	$f_f = 200$ Hz	$f_f = 2500$ Hz
0.248	0.314	0.206

Figure 6.4: Decay of liquid diameters along representative clusters of droplets, at five radial locations r/d , under $f_f = 200$ Hz, (a), and $f_f = 2500$ Hz, (b).

clustered at the center-line, as can be observed by comparing the diameter decay at $r/d=0$ in fig. 6.3 and fig. 6.4a. When the flame is exposed to 2500 Hz, the forcing signal does not cause a disruption of the liquid jet but plays an effective role in the evaporation rate. In fig. 6.6 an histogram of the total number of droplets across the full cross-section of the spray versus the axial locations is shown. One can see that the number of droplets is decreasing faster at high frequency than at 200 Hz, and this can only be explained by a faster evaporation rate. Recalling fig. 6.1, the inertia of the droplets is such that the liquid jet most likely follows the gas flow, under both the exciting signals. In order to understand the phenomena behind the response of the dispersed phase, the gas field has to be observed. The 200 Hz forcing frequency results into a deformation of the flame front which undergoes a periodic action of stretching and contraction. At the end of each acoustic period, there is a disruption of the flame, that causes a detachment of pockets of cold gas from the core zone of the flame. This series of phenomena leads to an entrainment of the hot gases coming from the pilot into the flame zone. When the flame is exposed to 2500 Hz, the effects of the acoustic waves occur at small scales, on the flame front. Local deformations take place in the shear layer between the cold core zone of the flame and the pilot. The flame front appears wrinkled, causing an increase of the flame surface area. Figure 6.7 shows the instantaneous contour of the ratio $(S_c)_{\text{forced}}/(\bar{S}_c)_{\text{stationary}}$ at the maximum and the minimum amplitude ((c) and (e) of fig. 6.5) of the acoustic cycle. $S_{c_{\text{forced}}}$ is the chemical source term and $\bar{S}_{c_{\text{stationary}}}$ is the source term, averaged over the simulation time, of the non-forced flame. At 200 Hz the length of the flame front changes periodically with the acoustic wave. It can be observed that

Figure 6.5: Sketch of the spray dispersion at every T_{ac} , in correspondence of the lowest peaks of forcing signal.

Figure 6.6: Counts of physical droplets [-], versus axial distance [m].

the magnitude of the source term changes in the course of the acoustic cycle, in particular it increases at $3\pi/2$, when the stretching of the flame reaches its maximum value, (e). As shown in fig. 6.5, after that point, the spray breaks-up and cold pockets of gas are released downstream. The phenomena of decreasing in radius and increasing in length are simultaneous, but locally the flame front maintains its smooth profile. In the same figure, it can be observed that at 2500 Hz the flame length does not vary, but the flame front is highly corrugated.

6.4.2 Spray flame vs Prevaporised ethanol flame

The heat released by the flame represents an important indicator of the effects of the forcing signal on the flame. Based on the combustion model used in the simulations, the heat released is calculated as follows:

$$\dot{Q} = \eta \int_v \omega_c dV \quad (6.7)$$

where η [kJ/kg] is the heating value of the fuel and ω_c [kg/m³/s] is the reaction progress variable source term. Figure 6.8 shows the fluctuating component of the heat released in case of non-forced flame. The peaks will also affect the fluctuations of $\dot{Q}$ of the forced cases. As can be seen in fig. 6.9, under acoustic forcing, the induced fluctuations have a periodic oscillation, which is not linearly related to the forcing. In fig. 6.9 the fluctuations of the heat

Figure 6.7: Instantaneous contour of the ratio $(S_c)_{forced}/(\bar{S}_c)_{stationary}$ at $\pi/2$ and $3\pi/2$.

Figure 6.8: Time series of the fluctuations of heat released of acoustic non-forced spray flame.

released are plotted for the spray and prevaporised flames configurations. Three main observations can be made:

- The amplitude of the fluctuations is much higher at 200 Hz than at 2500 Hz.
- At 200 Hz the fluctuations of the spray flame (dashed line) are smaller than the prevaporised case (solid line), and vice-versa at 2500 Hz.
- At 200 Hz the period of the fluctuations of the spray flame shows two frequencies, in the other cases the oscillations are characterized by one frequency.

Figure 6.9: Time series of the fluctuations of heat released (200 Hz left, 2500 Hz right). Solid line gaseous configuration, dashed line spray.

As shown in fig. 6.6 and fig. 6.4a, at 200 Hz the evaporation of the liquid fuel is delayed because clouds of droplets are transported into the burnt gases. The rate of fuel burning is lower in the spray flame than in the pre-vaporised case, and this explains why the fluctuations of $\dot{Q}$ are larger in the gaseous flame than in the liquid-fueled flame, fig. 6.9 (left). Moreover, the oscillations of the dashed lines in fig. 6.9 (left) show a series of a sharp peak followed by a flat profile. The flat portion of the curve, which is not present in the prevaporised flame, can be related to the delayed evaporation of the liquid. The stretching of the flame leads to a contraction of the jet; the spray penetration increases and the energy released by the fuel is lower than in the pre-vaporised case. This leads to a strong non-linear response. An opposite behaviour is observed at 2500 Hz, in fig. 6.9 (right): the heat released by the spray flame is locally larger than the energy emanated by the pre-vaporised case. This is due to the enhancement of the evaporation rate, as was shown also in fig. 6.6 and fig. 6.4b. It can also be observed that the heat released oscillates at the same frequency in the case of liquid and gas-fueled flame, fig. 6.9 (right). The magnitude of the heat released fluctuations is lower at 2500 Hz than at

Figure 6.10: Time series of the gas temperature monitored at $y = 20$ cm. (spray flame (solid line), pre-vaporised ethanol/air flame (-o-), stationary spray flame (dashed line), stationary prevaporised flame (-+ line)).

200 Hz. In fact, as also observed in fig. 6.7, the flame appears to be more stable when exposed to high frequency forcing. This is confirmed by observing the time series of the gas temperature. Figure 6.10 shows the instantaneous gas temperature, monitored at a distance y of 20 cm from the nozzle along the centerline, in the case of forced and non-forced flames. The solid black line corresponds to the forced spray flame, the line-with-circles to the forced prevaporised configuration, the dashed line to the non-forced spray flame and the line with "+" symbols to the steady non-forced prevaporised flame. On the left column (a) there are the fluctuations resulting from the 200 Hz forcing, on the right column (b) the field exposed to 2500 Hz.

At 2500 Hz, fig. 6.10b, the temperature in the spray flame increases from a mean value of 1000 K to 2200 K. This is in agreement with the faster evaporation rate observed at high frequency, and suggests a shortening of the flame. The change of evaporation rate plays a major role in the characterization of the gas field. In fact, looking at the prevaporised flame in fig. 6.10b, only small fluctuations can be observed, and an increase of the temperature mean value of 100 K. Moreover, when the evaporation is completed downstream, the acoustic wave does not effect the gas temperature, fig. 6.11b. The ΔT between the acoustic-free spray and prevaporised flame at $y=30$ cm can be explained by the different boundary conditions assigned to the flames. The global equivalence ratio is maintained constant in the simulated test-cases. Thus, the gaseous mixture is injected at rich conditions in case of prevaporised flame, and at quasi-stoichiometric conditions in the spray flame configuration. At 200 Hz, the gas field appears perturbed, both in liquid and gas fueled-flames. In the spray flame, the evaporation is completed and the

Figure 6.11: Time series of the gas temperature monitored at $y = 30$ cm. (spray flame (solid line), pre-vaporised ethanol/air flame (-o), stationary spray flame (dashed line), stationary prevaporised flame (-+ line)).

oscillations are a few Kelvin. In the prevaporised case, the chemical reactions are not completed yet and the amplitude of the fluctuations is of 1000 K.

Frequency domain analysis

The response of the flame to acoustic fluctuations can be quantified by means of the flame transfer function (FTF). In this case, a flame transfer function is calculated at two discrete frequencies: 200 Hz and 2500 Hz. It describes the variation of the heat released by the flame due to an acoustic perturbation which takes place upstream of the flame. As explained in section 6.3, the acoustic perturbation is caused by the mass flow fluctuations, eq. (6.6). This translates into a fluctuation of the velocity at the inlet, and the formula used to calculate the discrete flame function is defined as:

$$FTF(\omega) = \frac{(\dot{Q}'(\omega)/\bar{\dot{Q}})}{(u'(\omega)/\bar{u})} \quad (6.8)$$

The time series of heat released and velocity are monitored during the simulations and subsequently split into the fluctuating and the mean components. The obtained variables are then mapped into the frequency domain by using a fast Fourier transformation. The magnitude and the phase of the FTF are calculated by assuming a sinusoidal waveform and they are shown in fig. 6.13 and fig. 6.12. At high frequency the corrugation of the flame front causes an increase of the reaction rate, but the stretching and contraction of the flame exposed to 200 Hz amplifies this phenomenon even more. This explains why the transfer function gain is higher at 200 Hz than at 2500 Hz, both in case of

Figure 6.12: Discrete FTF magnitude of spray flame ($\diamond$) and pre-vaporised (+) flame, at 200 Hz (black) and at 2500 Hz (red).

prevaporised and spray flame. Moreover, the response of the flame at 2500 Hz has a small amplitude (< 0.1), as it was proved by the relatively small oscillations of the time series of heat released, fig. 6.9 (right). The acoustic forcing has a direct effect on the evaporation rate; however, the enhancement of the evaporation rate has a small impact on the reaction rate. In fact, the gain of the FFT in the spray and prevaporised flames has a similar amplitude. At 200 Hz, the delay of the evaporation of the droplets is such that the response of the spray flame is much smaller than the forced response of the prevaporised flame. The effects of the acoustic wave on the phase are similar in the gas and liquid-fueled flames. In fig. 6.13 the point marked with a represents the phase at 200 Hz. Assuming a linear behaviour of the phase, the point b corresponds to the phase at 2500 Hz. The magnified area in the graphs shows how far the point b is from the points c and d that represent the phase at 2500 Hz adjusted by multiples of π . In the prevaporised flame, fig. 6.13b, the point d is close to the linear response of the phase, while it is shifted in case of spray flame. The combustion time delay, t_{delay} , can be calculated from the slope of the lines plotted in fig. 6.13. Following the formula of eq. (6.9):

$$\tau = \frac{|\angle FTF|}{2\pi f_f} \quad (6.9)$$

a time characterization is found for the spray flame, fig. 6.13a, and for the prevaporised case, fig. 6.13b. A comparison is made in table 6.2: In case of the prevaporised flame, the time delay is slightly higher than in the spray, with a difference of 0.5×10^{-3} s. However, as observed by [14] it can be concluded that the droplet dispersion is affected by the acoustic wave, but with the same phase characterizing the gas field.

Figure 6.13: Discrete FTF phase, spray (a) and Prevaporised flame (b).

Table 6.2: Combustion time delay τ [ms]

	τ
Spray	3.1
Prevaporised	3.6

6.4.3 Effect of initial slip velocity on the forced flame response

In section 6.2 a set of dimensionless parameters was calculated to determine the regimes of behaviour of a spray flame exposed to acoustic forcing. The test-case studied in this paper is characterized by a Stokes number lower than unity, so the droplets tend to follow the gas streamlines and not to maintain their velocity due to inertia. Therefore, one can assume that if a slip velocity between the liquid and the gas phase is imposed at the inlet, it will decay fast. The effect of the gas velocity modulation on the initial velocity of the droplets is investigated here. Two unsteady simulations are performed: in one case, the initial slip velocity, u_s , is imposed to be zero. In the other case, the droplets are injected with a constant initial velocity, such that the perturbation imposed at the gas flow rate translates into slip velocity fluctuations (fig. 6.2b). In fig. 6.14 it can be observed that the evaporation rate and the heat released by the flame do not vary when a slip velocity is imposed or not. Figure 6.14a shows the time series of the heat released by the flame in the two cases, and the graphs overlap. The spray penetration is the same at each axial location, fig. 6.14b, and it can be assumed that also the spray dispersion does not change. In fig. 6.15b the time series of the gas velocity at two monitoring points along the centerline is illustrated. The black line corresponds to the axial coordinate closer to the nozzle exit plane,

$y=10$ cm, and the blue line represents the velocity at $y=20$ cm. At both axial locations the circle symbols overlies on the line, at each time. The same behaviour is shown by the temperature monitored at a distance $y=20$ cm from the nozzle plane, fig. 6.15a. To conclude the slip velocity imposed at the inlet decays fast and does not have impact on the combustion or evaporation dynamics.

Figure 6.14: (a) Time series of heat released by the flame submitted to 2500 Hz, with $(u_g - u_l) = 0$ m/s (black) and $(u_g - u_l) = 5$ m/s (blue). (b) Counts of droplets along the axial direction.

Figure 6.15: (a) Time series of the gas temperature at $y = 20$ cm from the nozzle. (b) Time series of the gas velocity at two monitoring points: $y = 10$ cm ($u_s = 0$ m/s (black) and $u_s = 5$ m/s (blue)) and $y = 30$ cm ($u_s = 0$ m/s (line) and $u_s = 5$ m/s (circle))

6.5 Conclusions and discussion

URANS simulations have been performed in the Eulerian-Lagrangian framework. Two regimes of Strohmahl numbers, St , have been investigated, under the same Stokes number equal to $\sigma = 0.8$. The response of a turbulent piloted spray flame exposed to a 200 Hz ($St = 0.07$) and 2500 Hz ($St = 0.8$) has been computed and compared to the non-forced spray flame and to the prevaporised ethanol/air flame.

6.5.1 Conclusions

The main effects of the acoustic on the spray flame can be summarized in five key points:

- for $St = 0.8$ the acoustic wave induces a corrugation of the flame front, (fig. 6.7) and the evaporation rate of the droplets increases (fig. 6.4); the effect of the modulation is confined in the region of the steady flame.
- for $St = 0.07$ the combustion/acoustic coupling causes a periodic stretching and contraction of the flame (fig. 6.7) which causes a delay of the evaporation rate and an increase of the combustion rate; the oscillations cause pocket of cold gas to detach from the flame and travel far downstream.
- the forced response of the spray and prevaporised flames at 2500 Hz has a similar amplitude and small compared to the 200 Hz response, fig. 6.12; thus the droplets do not play a major role in case of 2500 Hz signal.
- at 200 Hz the gain of the flame transfer is higher in case of prevaporised flame, due to the delay of evaporation rate in the spray flame case; at both low and high gas modulation, the phase of the flame transfer function is not significantly affected by the liquid phase.
- the spray penetration in the flame exposed to 2500 Hz is about 5 cm shorter than the spray penetration in the non-forced spray flame. The 200 Hz forcing results, instead, into an increase of the spray penetration of about 5 cm compared to the non-forced case.

An interpretation of the main findings can be done by analysing the results separately in the temporal and in the frequency domains.

6.5.2 Discussion

Temporal domain

The acoustic forcing of the turbulent spray flame results into a faster evaporation rate at 2500 Hz and, compared to the non-forced case, the mean value of the temperature at the centerline increases (fig. 6.10b). The shape of the flame remains almost unaltered, however the flame front appears wrinkled. Thus, the enhancement of the evaporation rate can be related to the interaction of the acoustic field with the flame front. The Stokes number is small enough to ensure that the droplets follow the gas streamlines under both the forcing modulations. At a Strouhal number $St = 0.8$ this results into a stable flame, where the dispersion of the droplet is not altered by the forced perturbation. [15] found that, for growing Strouhal number, the methane flame object of their CFD seemed to have characteristics similar to the non-forced case. A so called weakly coupled state established, as described by [16]. The same phenomenon is observed in this work. However the turbulence seems to play a crucial role in this case, compared to the laminar regime studied by [15], in the oscillations of the flame front. Under 200 Hz perturbation, pockets of cold gas detach from the tip of the flame and travel into the gas burnt downstream the flame. The droplets follow the gas and the evaporation undergoes a delay. So, the effects of the modulation for $St = 0.8$ are confined in the region of the corresponding steady flame. Instead, the oscillations induced at $St = 0.07$, propagates far downstream the flame. In both cases, the dispersion of the spray follows the gas behaviour: it remains almost unchanged for $St = 0.8$, and is entrained by the gas for $St = 0.07$.

Frequency domain

The changes of the combustion rate as a response of the perturbations imposed at the inlet velocity of the gas phase can be studied into the frequency domain, by calculating the flame transfer function in the two forcing points: 200 Hz and 2500 Hz. The amplitude of the flame transfer is higher at 200 Hz than at 2500 Hz and, in particular, the response of the prevaporised flame has a gain equal to four times the gain of the corresponding spray (fig. 6.12). At 2500 Hz the response of the spray and the prevaporised flame is very similar. This suggests that at high oscillations, the presence of the droplets does not play a crucial role. The combustion delay calculated through the phase of the flame transfer function shows a similar behaviour for the gas and the liquid-fueled flames, (fig. 6.13). The presence of the liquid droplets do not affect the gas phase.

Aknowledgment

The authors thankfully acknowledge the People Programme (Marie Curie Actions) of the European Union's Seventh Framework Programme (FP7, 2007 – 2013) under the grant agreement No. FP7-290042 for the project COPA-GT.

Bibliography

- [1] CFX ANSYS. User manual, release 14.5. *ANSYS Inc*, 2012.
- [2] CH Beck, R Koch, and H-J Bauer. Numerical investigation of the time scales of single droplet burning. *Flow, turbulence and combustion*, 82(4): 571–598, 2009.
- [3] Mastorakos de la Cruz García, E Mastorakos, and AP Dowling. Investigations on the self-excited oscillations in a kerosene spray flame. *Combustion and Flame*, 156(2):374–384, 2009.
- [4] F Duchaine, F Boudy, Daniel Durox, and Thierry Poinsot. Sensitivity analysis of transfer functions of laminar flames. *Combustion and Flame*, 158(12):2384–2394, 2011.
- [5] Hossam A El-Asrag, Markus Braun, and Assaad R Masri. Large eddy simulations of partially premixed ethanol dilute spray flames using the flamelet generated manifold model. *Combustion Theory and Modelling*, 20(4):567–591, 2016.
- [6] Virginia Fratalocchi and Jim BW Kok. Numerical investigation of a non-confined spray flame exposed to acoustic forcing. In *ASME Turbo Expo 2015: Turbine Technical Conference and Exposition*, pages V04AT04A032–V04AT04A032. American Society of Mechanical Engineers, 2015.
- [7] James Dakshina Gounder, Agisilaos Kourmatzis, and Assaad Rachid Masri. Turbulent piloted dilute spray flames: Flow fields and droplet dynamics. *Combustion and flame*, 159(11):3372–3397, 2012.
- [8] E Halle, O Delabroy, F Lacas, D Veynante, and S Candel. Structure of an acoustically forced turbulent spray flame. In *Symposium (International) on Combustion*, volume 26, pages 1663–1670. Elsevier, 1996.
- [9] A Kourmatzis, W O’Loughlin, and AR Masri. Effects of turbulence, evaporation and heat release on the dispersion of droplets in dilute spray jets and flames. *Flow, turbulence and combustion*, 91(2):405–427, 2013.

BIBLIOGRAPHY

- [10] Nick M Marinov. A detailed chemical kinetic model for high temperature ethanol oxidation. *International Journal of Chemical Kinetics*, 31(3): 183–220, 1999.
- [11] Assaad R Masri and James D Gounder. Details and complexities of boundary conditions in turbulent piloted dilute spray jets and flames. In *Experiments and Numerical Simulations of Diluted Spray Turbulent Combustion*, pages 41–68. Springer, 2011.
- [12] Colette Nicoli and Pierre Haldenwang. A resonant response of self-pulsating spray-flame submitted to acoustic wave. *Combustion Science and Technology*, 182(4-6):559–573, 2010.
- [13] P Palies, T Schuller, D Durox, and S Candel. Modeling of premixed swirling flames transfer functions. *Proceedings of the combustion institute*, 33(2):2967–2974, 2011.
- [14] C Pera and J Reveillon. Direct numerical simulation of spray flame/acoustic interactions. *Proceedings of the Combustion Institute*, 31(2):2283–2290, 2007.
- [15] Mario Sánchez-Sanz, BAV Bennett, MD Smooke, and A Liñán. Influence of strouhal number on pulsating methane–air coflow jet diffusion flames. *Combustion Theory and Modelling*, 14(3):453–478, 2010.
- [16] Anthony W Strawa and Brian J Cantwell. Investigation of an excited jet diffusion flame at elevated pressure. *Journal of Fluid Mechanics*, 200: 309–336, 1989.
- [17] RI Sujith. An experimental investigation of interaction of sprays with acoustic fields. *Experiments in Fluids*, 38(5):576–587, 2005.
- [18] Tongxun Yi and Domenic A Santavicca. Forced flame response of turbulent liquid-fueled lean-direct-injection combustion to fuel modulations. *Journal of Propulsion and Power*, 25(6):1259–1271, 2009.

7 Conclusions and recommendations

The presented research originates from the need to refine numerical and modeling tools which can be used to describe the complex phenomena of turbulent reacting flows of fuel sprays, in a feasible and accurate way. Turbulent liquid spray flames can be found in several industrial applications, and ethanol plays an important role as a biofuel, in a low-pollutant emission combustion systems scenario. To ensure the stability of the flame and a low production of pollutants over a wide range of initial operating conditions, the investigation of the unsteady behaviour of the flames is of crucial importance when designing a combustion system.

The main issues addressed in this dissertation were the modeling of pre-vaporised ethanol flames, and the study of forced spray flame response to upstream perturbations. The main findings of the research presented in this dissertation were shown in the core chapters 3 to 6, and are summarized in this conclusive chapter 7.

Lastly, some recommendations for future work are proposed.

7.1 Conclusions

In this work, insight was gained on diverse aspects of ethanol combustion. Numerical simulations were performed with the commercial software Ansys CFX, by using the available combustion models, and implementing external user-defined routines. The first part of this session presents conclusive remarks on the simulations performed on laminar and turbulent prevaporised ethanol flames. The second part is dedicated to the results obtained in the study of an ethanol spray flame and its response to acoustic modulations.

7.1.1 Combustion of pre-vaporised ethanol flames

In chapters 3 and 4 the modeling of premixed pre-vaporised ethanol flames was addressed. The combustion was treated with the tabulated chemistry approach, and a methodology to *a priori* assess the reaction progress variable was refined. The main concept on which this methodology is based, is the projection of the detailed chemistry space into a low-dimensional chemical

manifold. Laminar flamelets are therefore tabulated based on controlling scalar parameters.

Several researchers have proven the suitability of this combustion modeling, in gas turbine engines. However, a research gap emerges in the definition of such controlling scalar parameters, also in the flamelet-based combustion models available in Ansys. In chapter 4, it was shown that such investigation becomes important especially when dealing with complex mixtures of fuels, which can not always be treated with the same tools adopted for the traditional fuels. Two methods were combined to determine the optimum combination of species defining the reaction progress variable: the CSP analysis and a sensitivity analysis of the times scales carried out with a PSR. When this approach was applied to ethanol combustion, as a result of the sensitivity analysis of the species consumption rate, the species were divided in three groups: fast (steady), slow and dormant. This information was used to correct the set of major species indicated by CSP, in particular by neglecting the species (dormant) whose time scale was out of the range of interest. The CSP/PSR method to define the reaction progress variable leads to the most accurate choice of species weight factors.

The obtained chemical database was then implemented in Ansys CFX, and a set of laminar flat and Bunsen flame was simulated. An excellent match was found with the 1D freely propagating laminar flames solved with detailed chemistry. The chemical manifolds obtained with other definitions of RPV shown a different distribution of the chemical source term over the reaction progress variable space, compared to the CSP/PSR based RPV. The latter results into a RPV's source terms spread more uniformly. This feature leads to less steep gradients in the manifold space, therefore to the best feasible tabulation. The way the RPV is defined has an even bigger impact on the prediction of the Bunsen flame. In particular, for some expressions of the RPV, the ignition of the flame takes place close to the inlet, upstream the wall where the stabilization of the flame is expected to occur.

The so assessed procedure was then extended to the prediction of a turbulent premixed flame. The interaction of chemistry and turbulence was accounted for by means of a PDF integration. Tabulations of lean mixtures of air and ethanol and blends of ethanol/water and ethanol/iso-octane were performed and verified against freely propagating laminar flames predicted with detailed chemistry. Excellent agreement was achieved, for temperature and species mole fractions of all the mixtures. It was found that the ethanol/air mixture has the highest laminar flame speed among the other mixtures. While, the addition of water into the ethanol mixture results in a decrease of the laminar flame speed. The addition of ethanol into the iso-octane/air mixture causes an increase of the laminar flame speed compared to pure iso-octane.

The turbulent simulations were carried out on an existing methane burner, and the composition of the ethanol blends mixture was determined by the adiabatic temperature being equal to the methane burning inside the burner. It is found that the iso-octane flame reaches completed combustion when the ethanol is still not fully burnt. The results were compared to experimental data measured in methane/air combustion. The aerodynamic field was well reproduced, nonetheless the observed discrepancies can be addressed by using a more accurate turbulent modeling approach, and increasing the dimension of the manifolds to account for the heat loss.

7.1.2 Dynamics of turbulent spray flames

Simulations of ethanol turbulent piloted spray flames were presented in chapters 5 and 6. The Sydney ethanol flame was taken as reference case, and the experimental database was given by professor A. Masri. First, RANS simulations were performed in the Eulerian-Lagrangian framework, in which the interaction between the gas and liquid phases was solved in a two-way coupling. The combustion was treated with the Burning Velocity Model, in combination with an empirical laminar flame speed polynomial law, specific for ethanol oxidation. The spray evolution was predicted under the main assumption of dilute regime, such that phenomena of atomization and droplet collisions were negligible and not modeled.

Two flames configurations were used as comparison with the experimental measurements: the EtF6 and EtF7. In general, good agreement was found with the axial droplet velocities and the gas field temperature. Some discrepancies were observed in the droplets radial velocities and the gas temperature close to the nozzle. This can be read as a RANS turbulence modeling deficiency. Moreover, the definition of the initial velocities of the droplets, close to the measured data plays a crucial role in the prediction of the mixing of the flow, as well as a combustion model which is capable of capturing the partially premixed-like behaviour of the flame.

There are numerous lines of research focused on improving the state of the art of the modeling of dilute spray flames. An important field, in which a more in-depth insight urges into the physics of the phenomena involved, is the response of spray flame to acoustic perturbations. The final chapter 6 of this thesis presented results of URANS simulations performed to explore the forced response of the spray and the heat released by the flame to gas velocity fluctuations. The models used to predict the combustion field and the spray evolution reflected the ones used in chapter 5. The EtF6 flame was perturbed with two frequency signals imposed at the gas inlet velocity, and the initial conditions of the droplets were simplified such that a monodispersed spray was injected.

An increase of the evaporation rate was appreciated when the flame was exposed to a high frequency signal, while the medium frequency excitation caused a disruption of the flame front, and of the spray displacement. These results have shown that the study of the thermoacoustic, as well as stability phenomena, in spray flames must account for the interaction between the convective flow, the heat released by the flame and the spray evolution.

7.2 Recommendations

Based on the insight gained in this work, the following recommendations are proposed for future work:

- An extension of the CSP/PSR approach to define the optimum weights of the species mole fractions in the reaction progress variable definition is proposed. More validations are needed to verify if the chemical time scales selected for a specific mixture composition can be representative of the reactions over the entire range of flammability limits of the fuel. With the goal to model non-premixed flames one should verify if the counterflow diffusion flames would represent a better choice to build the flamelet tabulation.
- More detailed comparisons with experimental data would allow a refinement of the tools presented in chapter 4. The prediction of the combustion of complex fuels blends was successful, however better results are expected if heat loss is included in the chemical tabulation.
- The current grid spacing of the reaction progress variable space in the tabulation is uniform. A dynamic refinement of the tabulation might lead to more accurate results, especially where high gradients occur.
- The spray flame simulations shown a good capability of the software to represent the flame behaviour. A refinement of the initial conditions of the droplet and gas velocity might lead to more accurate predictions.
- The use of the tabulated chemistry is expected to perform better in capturing the flame behaviour, especially the prediction of the temperature at the centerline of the flame.
- The exploration of the forced flame response should be extended to low frequencies signals. To gain an insight into the effect of the Stokes number on the spray response to velocity fluctuations, a polydisperse spray should be considered.

- A comparison of the URANS simulations with experimental data, currently not available, would be beneficial.
- Last, one common discrepancy observed both in the prevaporised and spray ethanol flames with measured data, was the velocity of the gas and droplets. A more accurate prediction of the RMS velocity, as well as the large scale mixing of the flow is expected by performing LES simulations.

A Chemical kinetics mechanisms

The chemical kinetics mechanisms used in this work are:

- San Diego mechanism which includes 50 species and 43 elementary reactions [2]. (Chapters 3 and 4);
- Marinov mechanism for ethanol oxidation [1] (Chapters 5 and 6);
- Wang mechanism for $I - C_8H_{18}$ and $E85$ flames are respectively formed by: 73 species, 296 reactions [4] and 80 species, 349 reactions [3] (Chapter 4).

Bibliography

- [1] Nick M Marinov. A detailed chemical kinetic model for high temperature ethanol oxidation. *International Journal of Chemical Kinetics*, 31(3):183–220, 1999.
- [2] Mechanical San Diego Mechanism web page and University of California at San Diego Aerospace Engineering (Combustion Research). Chemical-kinetic mechanisms for combustion applications, 2015.
- [3] Hu Wang, Adam B Dempsey, Mingfa Yao, Ming Jia, and Rolf D Reitz. Kinetic and numerical study on the effects of di-tert-butyl peroxide additive on the reactivity of methanol and ethanol. *Energy & Fuels*, 28(8):5480–5488, 2014.
- [4] Hu Wang, Mingfa Yao, and Rolf D Reitz. Development of a reduced primary reference fuel mechanism for internal combustion engine combustion simulations. *Energy & Fuels*, 27(12):7843–7853, 2013.

Acronyms

BVM	Burning Velocity Model
CFD	Computational Fluid Dynamics
CSP	Computational Singular Perturbation
FGM	Flamelet Generated Manifold
HCCI	Homogeneous charge compression ignition
FTF	Flame Transfer Function
ISAT	In Situ Adaptive Tabulation
LES	Large Eddy Simulation
LHS	Left Hand Side
LHV	Lower Heating Value
LPM	Lean Premixed Combustion
PDF	Probability Density Function
PSR	Perfectly Stirred Reactor
RANS	Reynolds Averaged Navier Stokes
RMS	Root Mean Square
RHS	Right Hand Side
RPV	Reaction Progress Variable
TFC	Turbulent Flame Closure
URANS	Unsteady Reynolds Averaged Navier Stokes

Nomenclature

The most recurring symbols are here listed. Unlisted symbols are defined when used in the text.

Roman letters

b	Reaction progress variable's weighting factors $[-]$
c	Reaction progress variable $[-]$
C_p	Specific heat capacity at constant pressure $[J/kg/K]$
D	Diffusion coefficient $[m^2/s]$
f	Mixture fraction $[-]$
h	Specific enthalpy $[J/kg]$
x	vector spatial coordinate $[m]$
k	Turbulent kinetic energy $[m^2/s^2]$
l	length scale $[m]$
p	Pressure $[Pa]$
$\dot{q}$	Heat flux $[W/m^2]$
R	Ideal gas constant $[J/mol/K]$
t	time $[s]$
s	Flame speed $[m/s]$
S_c	Reaction progress variable source term $[kg/m^3/s]$
T	Temperature $[K]$
X	Mole fraction $[-]$
Y	Mass fraction $[-]$
W	Molecular weight $[kg/mol]$

Greek letters

ϵ	Kinetic energy dissipation rate [m^2/s^3]
η	Composed species mass fraction $[-]$
ϕ	Equivalence ratio $[-]$
λ	Thermal conductivity [$W/m/K$]
μ	Dynamic viscosity [$kg/m/s$]
μ_t	Turbulent dynamic viscosity [$kg/m/s$]
ν	Kinematic viscosity [m^2/s]
ρ	Density [kg/m^3]
τ	Viscous stress tensor [$kg/m/s^2$]
$\dot{\omega}$	Chemical source term [$kg/m^3/s$]

Subscripts

b	Burnt
u	Unburnt
t	Turbulent
L	Laminar
n	Species
P	Particle

Publications

Publications in refereed journals

- Fratalocchi, V., and Jim B. W. Kok. "The Computational Singular Perturbation/Perfectly Stirred Reactor Approach in Reduced Chemistry of Premixed Ethanol Combustion." *Combustion Science and Technology* 189.10(2017) : 1659 – 1680
- Fratalocchi, V., and Jim B. W. Kok. "Ethanol turbulent spray flame response to gas velocity modulation." *Combustion Theory and Modelling*, pages 1 – 19, (2017)
- Fratalocchi, V., and Jim B. W. Kok. "Prediction of turbulent premixed combustion of ethanol/water/iso-octane blends". (Submitted).

Publications in refereed conference proceedings

- Fratalocchi, V., and Jim B. W. Kok. "The CSP/PSR approach in reduced chemistry of premixed ammonia combustion." *Proceedings of Energy Procedia* 2017, *ICAE2017*, Cardiff, UK, August 21 – 24, 2017.
- Fratalocchi, V., and Jim B. W. Kok. "Numerical Investigation of a Non-Confined Spray Flame Exposed to Acoustic Forcing." *Proceedings of ASME Turbo Expo* 2015, GT2015–42375, Montreal, Quebec, Canada, June 15 – 19, 2015.
- Gövert S., Fratalocchi V., and Jim B. W. Kok. "Characterization of low frequency combustion dynamics of hot blast stoves by means of a flame transfer function based on cfd forced response simulations: comparison of different hot blast stove designs." *Proceedings of ASME Turbo Expo* 2015, GT2015 – 42198, Montreal, Quebec, Canada, June 15 – 19, 2015.
- Fratalocchi V., and Jim BW Kok. "Modelling of the dynamic interaction between a reacting spray and an acoustic field in a turbulent combustor." *Proceedings of the 21st International Congress on Sound and Vibration, ICSV 21*, ISBN 9781634392389, Beijing, China, July 13 – 17, 2014.

Workshops

- Contribution to 6th *Workshop on Measurement and Computation of Turbulent Spray Combustion* (TCS6), Rhodes, Greece, June 2015.

Publications in non-refereed conference proceedings

- Fratalocchi V., and Jim BW Kok. "Dynamics of a premixed turbulent piloted PP ethanol/air flame." *Proceedings of the 21st International Congress on Sound and Vibration, ICSV 21*, Bangkok, Thailand (2013).

Biography

Virginia Fratalocchi was born on August 7th 1985 in Ascoli Piceno. This small beautiful town lies in a valley of central Italy, and is well known for the *olive all'ascolana* (ascoli's olives). People from Ascoli are proud to be born in a city which was founded several centuries before Rome, as it is celebrated by this famous sentence: '*Quando Ascoli era Ascoli, Roma era pascoli*' (when Ascoli was Ascoli, Rome was a field). After attending the humanistic high school, she moved to Rome and she was pleased to find out that it wasn't a field anymore.

She studied Mechanical Engineering at University La Sapienza, Rome, where she earned her Master of Science Degree in January 2011 and appreciated for the first time the world of the CFD. That was also the year she moved abroad, to a lovely place in the seaside coast of the UK, Brighton. She spent few months there, learning the language and taking a break from CFD.

In *October* 2011 she started working at Unatrac Ltd, as support in the sales department of construction machines. That was a positive experience, which however lasted only one year.

October 2012 was the moment the most incredible and intense adventure of her life began: a PhD project, at Twente University, Enschede, The Netherlands, whose result is this dissertation.

In *January* 2017 she started working as CFD engineer for a dutch company, Innecs Power Systems, until she moved back to the UK.

In *May* 2017 she began a new challenge in a challenging city, London, where she currently works as application engineer in the pre-sales team of Siemens PL, luckily still focused on CFD.

When she is not in front of her computer, working or writing this thesis, she travels, and does her favourite sports, bouldering and running, or tries new ones. She also spends time drawing, convincing herself she is able to paint. Last but not least, some healthy laziness on the couch watching series.

Acknowledgements

Not even a month until my PhD defense, and here I am writing the chapter of my thesis that I have awaited the most, the acknowledgments. This is the time when I look back and I can finally smile, I look forward and I feel the adrenalin flowing for those 45 minutes still to come. After that, I stop looking because my superstition (yes I am Italian, partially from the south) kicks in.

A PhD is like an incredibly long ultra-run. Pace is never always steady, sometimes you go fast and strong, other times you need to slow down, and lots of times you just find yourself stuck. I believe two are the moments that you actually enjoy the most, the start and when you make it back home. And now, I find myself smiling also at all the moments in between, the good and the bad ones, and more importantly at all the people that I can picture in my head, cheering me along the way. Some of those people have never left my side, of others I lost track of where they were going, but to all of them I want to dedicate a thank-you.

First things first, I would like to express my gratitude to those who gave me the opportunity to join the COPA-GT project: Prof. Theo van der Meer, my promoter, and Dr. Jim Kok, co-promotor of this thesis. Thank you Theo for your support and motivating talks. During my interview you asked me if I have had ever visited the city of Twente, and when I answered no (blaming between me and me my poor geography knowledge), you just said of course you haven't, there is not such a city! After 5 years I still remember that ice-breaker joke, and my geography knowledge is still at the same level too. Thank you Jim, for trusting my work even when I was doubting it. The Netherlands is a flat land, they say, but these past years I felt like going up and down quite often, and you have supported me while giving me the freedom in my research and pushing me to always improve it. I had the best experiences presenting my work in conferences all around the world, and I am grateful for that. Your passion for your Volvo was inspiring, even if I am still stuck with a Fiat. I also would like to thank the members of my graduation committee, for the time and effort you spent reviewing my thesis.

A sincere thank you goes also to Artur. I always enjoyed our conversations and appreciated your suggestions on how to best deal with my work, I wish you a brilliant career. Thank you Genie and Henk-Jan, your stories about your trips to Italy always made me proud of my country. Thank you Sally, your help was always important, especially at the end of my journey. Last

Acknowledgements

but not least, I can't forget Wouter, thank you for helping me with my IT issues, and always in a kind way. I should also thank the IT guys who saw me in tears when I lost the only back-up disk of some data, which turned to be the only copy I had of those data (not a relaxing time that was).

The COPA-GT project involved several partners whom I am grateful to, especially the Siemens combustion department at Mulheim where I spent a month of my PhD. I would like to thank Dr. Phil Stopford from Ansys. His support and suggestions during my work were always helpful.

Finally thank to you my dear colleagues, who today I am happy to call friends. Mina, thank you for giving me the boost to go ahead when things seemed overwhelming, and thank you Amir for being such a kind person. You make a lovely family. Thank you Dani, for our talks about any kind of topic, I am really glad you ended up in our office and I am even more glad you began this journey too. Thank you Alex, for being always nice and ready to offer your help, except once when I managed to make you furious, I am still sorry for it. Thank you Riza, you are a great dancer and say no more. Thank you Umair, especially for tolerating my daily attempts to smash the desk. Thank you Ilias, for being friendly even without smiling, that's a skill. Thank you Rafa for your humour and your incredible stories on your crazy house. Thank you Citra because I can still hear you laughing from my office in London, and that makes me laugh too. And thank you Lucia, you made a great gluten-free tiramisu. The biggest thank-you goes to Simon, my colleague, friend and paranymph. You made that room N215 home, and we had such a great time traveling together.

There are also many people who I met outside the corridor of the department, and I am glad they were there. Davide, a milanese doc, Riccardo, Mattia, the Spanish/catalan crew Cristina, Marina and Gerard. Alex with his terrific jokes, and Miriam who I share many nice memories with. I will never forget my home, Mooienhof, which was a place of parties, dinners and authentic moments; a place that I shared with Marco first and with a kind couple after, Andrea and Effie. Thank you Giuseppe, because I lived an erasmus-like experience when you arrived in Enschede, and while we were having fun we became good friends. Thank you Aga and Matteo, for the house-building party that I remember as one of our best event together, until your wedding. Your polish wedding is now definitely the best event I have shared with you, so far. Thank you Tommaso, I miss our lunches and bouldering sessions together, and thank you Lore for all your candour and your skin products, I miss both! I cannot thank enough one polentone, Alberto il professo', it was hard to say goodbye to our coffee breaks. To you three thanks, one for becoming a true friend, one for running the Bata with me, and the third one for having introduced me to your half, Ludovica. Our best memory together Ludo? The 12 hours driving back together to Italy in my

500. And now I just look forward for what is next on our journey amica! p.s. Of the three, Olga is still my favourite dog! They say a happy intestine makes a happy person, then I am thankful for the pure joy that you gave me Cati. I look back at 5 years ago when we met, and all the colourful moments we lived together in Enschede give me a heartwarming feeling. Of course, thank-you to your men as well, Federico and Ettore, both for the good time and entertainment.

Enschede was an intense experience, and now a new one has begun and once again I was lucky to find awesome colleagues that I would like to thank for the great time we had already and the time which is still to come. During these almost seven years abroad I also realised how much I miss the people who have been part of my life since I remember. There is one person I will always be grateful to, Professor Enrico Sciubba, from my beloved University of Rome, La Sapienza. Your knowledge and your free spirit have always been inspiring, your students are lucky ones.

Thank you to those with whom the distance doesn't count: the Salvatorelli with the new entry Filippo who I can't wait to meet, Franci and Claudia. How I miss our time in Rome! Thank you to my friends from Ascoli, who have been there before the Nokia 3210 was out: Laura M. for your affection, my ciccia Laura V. (I esteem your path as a surgeon only as much as I hope to never find myself along it) and Aleandro who is my secret Santa this year (yes now you know it)! Thank you my dear Paolo, for being my authentic friend for 20 years now, no matter the kilometers between us, we will always be the closest.

To conclude I want to thank those who are not only part of my life but are my life: my family. I have a big one, so I can't name all of of them but I wish the best to all my cousins, and I want to say hello to my uncle Piero. My biggest and warmest thank you is dedicated to my parents, and my little sister Laura. Thank you mamma e papy, for your love, support and strength, for ever. You are always there for me, even when I make it complicated, and I want you to know that I will always be here for you. Everything I am and I do is only possible because of you My little sister Laura, who is not that little anymore. You are the first doctor of the family, I am so proud of who you are and I admire the commitment you put in what you do. You are the best gift our parents ever gave me. I would like to thank Lorenzo as well, who is a nice addition to the family. Finally, I'd like to thank Giorgio and his family, who also gave me their support during this challenging experience.

Giorgio I am grateful for your unconditional love, in every gesture, every day of our lives. A special thank-you for having always believed in me and my work, without you I wouldn't be writing the final words of this thesis. And these final words are for you, my friend, my love, my soul.

Acknowledgements

Virginia, November 2017.