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Fuel Modeling Design for Engine Virtual Development

Master Thesis of: Rodolfo Tromellini (875413)

Supervisor: Prof. Onorati Angelo

Cosupervisor: Dott. Chiodi Marco

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Abstract

In this work we describe a methodology to produce the flamelet library necessary for the 3D-CFD simulation of internal combustion engines. The first chapter is dedicated to the general situation of the energy sector with particular attention to the automotive sector and biofuels used in spark-ignition engines. Afterwards we describe the modeling of internal combustion engines by means of the 3D-CFD software *QuickSim* that has been developed at the FKFS and IVK – University of Stuttgart by Dott. Marco Chiodi. The combustion process is modeled in *QuickSim* using the flamelet regime assumption that requires the production of a database, also called flamelet library, that must be produced outside and before the simulation using a dedicated software that performs the 1D laminar flame speed simulation of the fuel of interest. The main focus of our thesis is to provide a methodology that assures the production of a realistic flamelet library. To do so we validated the reaction mechanisms that are implemented in CANTERA for the most important species against experimental data available in literature. Next, we developed a procedure to produce a surrogate with the correct composition and finally we applied this solution for two real gasolines. The whole process is finally validated by simulating an engine in *QuickSim* for which experiments were performed.

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1. Introduction

Transportation is one of the most important aspects in our daily routine and an increasing number of people that are populating the world demands for it. The transportation was based until today mostly on fossil sources; however, major problems related to these fuels are pushing a transition towards cleaner and renewable sources. This change started before in the energy system of the developed countries, especially in Europe, and is now influencing also the automotive sector.

One of the most interesting research fields for the future of the automotive is the one of biofuels. Such fuels present characteristics that are different from the standard ones and the main goal of the automotive industry is to build engines able to use it with little modifications of existing engines. To investigate their behaviour and to analyze how the engine operation changes the industry relays on two different technics: experiments and simulation.

Our thesis will focus on the simulation of biofuels at engine conditions. The work is carried out to produce a set of thermodynamic data that is used for the simulation of the engine cycle with a 3D-CFD program developed at the FKFS and IVK – University of Stuttgart.

The thesis starts from the description of how the world of energy is changing and how the automotive sector is dealing with this transformation. Afterwards there is a section devoted to a brief description of how internal combustion engines are developed using 3D-CFD tools. In the third section we will deal with the simulation of combustion and in the subsequent section two gasolines are simulated and a detailed analysis is performed. Finally the experimental validation of the procedure is briefly presented.

2. Scenario of energy demand

This thesis will try to make a small step in the direction of a more sustainable production of energy for transportation. But before we start it is important to clarify that if a clean production of energy is not coupled to an equally clean consumption of energy most of our efforts will be vain. In fact the focus of a clean production is to make available the right energy (the right quality and the right amount) at the right moment. Clean consumption, instead, means that the energy is used according to its quality and, as far as possible, to reduce the amount of energy wasted. A fundamental aspect to achieve such goals is the political support to the right initiatives that will assure the development of long term solutions that otherwise the market would discard. Luckily many countries in the world are taking measures to face these problems and a particular good job is carried out by the European Union in terms of environmental impact, energy efficiency and clean production exploiting local renewable sources. In order to better understand the today's situation in the world of energy, this section is dedicated to draw a landscape of the energy demand and production today and to foresee what could be the future of energy.

It is always difficult to make forecasts and this is even more difficult if we think of predicting how the world will deal in the future with the energy demand. Part of the confusion is due to the distance between political programs, which assure that in the turn of few years our world will be completely dominated by the diffuse generation of electricity and electric vehicles, and our daily commute where none of these revolutions seems to really take place. For these reasons someone may ask himself if there is a real change in the way of producing and consuming energy or we are just prey of marketing and political claims.

Our intention in this section is to try to delineate a scenario of how the world of energy will change in the mid-term future starting from energy statistical data [1], that tell us how the system changed in the recent period, to arrive at national [2], regional [3] and industrial policies [4], that can give an insight in the next transformations because decide the main areas of future investments.

Before going in the details, it is useful to point out which are the categories that are usually referred to and that we also will use when dealing with problematics concerning energy. First of all it is good to remember that energy sources are:

- Oil (32% of the total energy production);
- Coal (28%);
- Natural gas (21%);
- Nuclear (5%);
- Renewable energies: hydraulic, photovoltaic, biomass, biofuels, geothermal (24% overall).

Another important distinction can be done about the final consumption of the energy:

- Industry: accounts for almost the 30% of the total energy consumption and around a half of the energy demand increase;
- Transport: all the energy that is used for vehicles, airplanes and ships account for another 30% but the growth decreases sharply with respect to the past;
- Non-energy use: for example the use of oil and oil products by the chemical industry in order to produce plastics. This invoice accounts for less than 10% of the total final consumption of energy;
- Others: mainly account for residential; is the most important voice and accounts for more than 30% of the total energy consumption.

In order to have a first idea of the actual energy landscape usually one starts analyzing the three factors that, at a global level, are more strictly related to the energy demand:

- Population: is steadily growing and previsions state that it will continue like this with a 3.4% rate of increase each year up to 9 billion people in 2040 [5];
- Economic growth: principally due to the expansion of the middle class in the developing countries [4], [6] that will lift about 2.5 million people from low incomes;

- Energy intensity: is a parameter that measures the efficiency in the way of using energy. Theoretically, the increase in energy efficiency could stop, or at least coast, the increase of energy demand with respect to the economic growth. This convincement is also called as “Theory of Degrowth” [7]. Even though it has not yet been proved that an economic system based on regression or non-expansion could work, for sure the reduction of energy intensity is an interesting goal for countries in order to create a more efficient energy network. Recent investigations [4], [5] show that energy efficiency has the power to offset the overall energy increase by reducing the energy wastes but that it is not enough to stop demand’s increase.

From these data it is easy to understand why the world’s energy requirement is forecasted to grow of about 25% by 2040, trailed especially by India and the developing countries in South Asia. Demand growth for energy, however, can be satisfied using traditional energy sources such as coal and oil and, as a matter of fact, that happens in many poor countries that prefer to focus on increasing the life standards of the population by neglecting, or postponing, problematics connected to air pollution, Greenhouse Gas (GHG) production and many others that look less pressing. As we can already see from these few considerations, the role of politics is and will be fundamental in drawing the future energy system.

However, if we analyze both the production and the consumption of energy, there is no doubt that we are witnessing a change and that this change can affect deeply both our daily routine and the geopolitical equilibriums at a global level.

Starting our analysis from the production, we can see that in last period the production of energy from renewable resources grew especially in developed countries such as the European ones, in the USA and in China. What’s more, renewable energies represent more than the 40% of the new power installed worldwide and attract two thirds of the total world’s investments in new facilities for energy production [5] leading to a constantly decreasing price of the technologies because of the growing dimension of the market. Due to the fact that usually renewable energies are thought and used to exploit resources that are available locally (biomasses, sun, wind…) the whole structure of the energy system is drastically changing its own shape: the investments in new big energy plants are rapidly decreasing because the network based on renewable energies will be characterized by diffuse production of many small plants conducted not by a big company but by many small “prosumers”. The diffusion of small producers will for sure change the infrastructure of energy system that was built for one directional energy flows and that now will face multidirectional flows, instabilities of the net and fluctuating production: systems able to deal with all these problematics are the so called “smart grids”.

The most widespread renewable energies are solid biofuels and charcoal because of their non-commercial use (mostly cooking and residential heating) in developing countries [8]; the second largest source is hydro power followed by many other smaller contributions like solar, wind, geothermal, biogases and tide. Since 1990 the renewable energy share on the total of the world energy production grew at an average annual rate of 2% that is slightly more than the total growth rate. Such a growth has been trailed by solar photovoltaic and wind power with an annual growth rate of 45.5% and 24.0% respectively [8]. In OECD countries this trend is even more extreme as displayed in Fig. 1: despite of a really low overall growth (TPES: Total Primary Energy Supply) renewables witnessed an important increase in the last 26 years led by solar, liquid biofuels and waste. However, at a global level the contribution of renewable sources is still limited and represents only the 3.2% of the total primary energy supply [8] but their growing importance is a clear indication of the direction of the energy generation especially in Europe where these trends are more visible and the renewables’ share was the 14.2% in the 2016.

Others changes in the production of energy are the growing importance of Natural Gas because of its cleaner combustion and the flexibility of the gas turbines, and the fall in the number of coal production sites that are being developed and built across the world.

Nevertheless the economy is still heavily dependent on oil and will remain like this also in the mid-term but with the demand for petrol constantly decreasing [5].

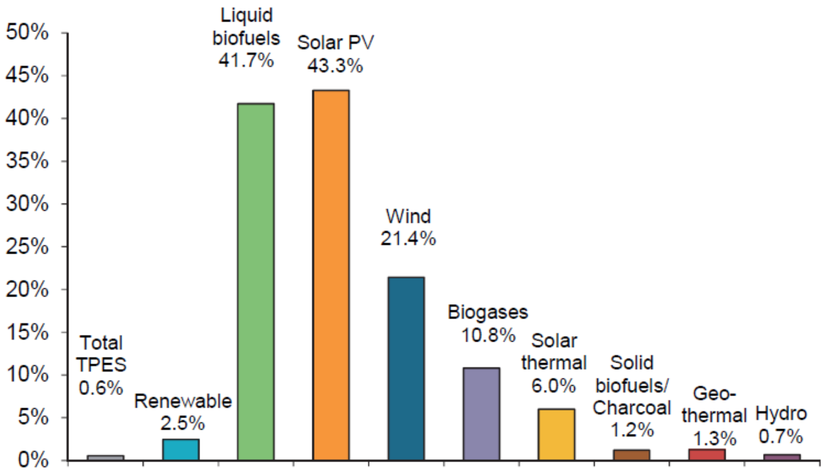


Fig. 1: Annual growth rate of renewable supply from 1990 to 2016 in OECD countries [8]

On the other hand, one of the main changes in the consumption of energy is the increasing electrification of the final consumptions that are expected to rise by a 40% by 2040. That means that electricity is substituting the traditional forms of energy in the final consumption because of its cleanliness, safety and efficiency of transportation. A potentially huge cause of the increase of the electrification in certain countries is represented by electric vehicles: prevision for 2040 state that there will be around 280 million vehicles from the actual 2 million [5]. The other great change in the energy consumption is the increase and diffusion of the energy efficiency especially for internal combustion engines vehicles and buildings that, as we already saw, represent one of the biggest invoices of the energy consumption balance. Concerning the buildings, Europe for example stated that all new buildings must be near-zero energy building (NZEB) by 2020 and all new publics buildings must be NZEB by 2018 [9]. By definition NZEBs require very little energy from the grid or nothing and, during certain periods are also able to produce more energy than the used one becoming small generation plants. Energy efficiency, however, involves also products, industrial processes and vehicles in order to finally achieve a systemic efficiency [10].
From the above description of the energy production and consumption it is clear that economy is still much dependent on oil but that there is also a strong interest in shifting to cleaner and carbon neutral systems by exploiting local renewable sources of energy that otherwise would be wasted. This will can be clearly seen in the politics that has been adopted in recent years; the most important one at European level is the 2030 Energy Strategy which sets the goals to 2030 [10]. At the Italian level instead the most important document is the SEN 2017 [11]. Both documents chose as fundamental targets the reduction of emissions of GHG, the increase of energy efficiency and of the renewable energies. The impact of these politics will be that of reducing the dependence of the European Union from the importation of oil from external countries. In fact there is a clear geopolitical design underlying these policies: reduce the dependence of the Union from the imported petrol. In order to match such a substitution of oil with local energy sources European countries are ready to invest millions in infrastructures, pilot projects, research and cooperation with private enterprises.
Maybe in our daily commute is not easy to experience these changes but, as we saw, they are actually taking place and the fact that we don't notice it means that are working well.
This thesis will from now on focus always more on transportation and fuels for internal combustion engines, but it is important to bear in mind the framework in which we are acting because it undoubtedly determines the direction of investments and research. Keeping in mind the conclusion of this first part is now time to focus on the automotive industry and its dynamics.

For this reason the next section is dedicated to a short description of the major problems that the automobile industry is facing and the answers that is giving.

1.1 Automotive sector

Transportation is one of the most important aspects of the modern way of life and the amount of energy that in the world is dedicated to the transport of things and people represents for the 30% of the total energy consumption. The automotive industry represents one of the biggest industries all around the world and is deeply connected with the changes in the energy use and in the lifestyle of people. It is doubtless that in the last decades the technological development drastically changed the shapes and the performances of cars but the energy source isn't change as most of the cars in the world still rely on oil derivatives.

As opposed to the great changes in the ways electricity is produced and used, the automotive sector in the last 50 years used oil products, such as kerosene, diesel and gasoline, for more than 95% of the total energy demand, and still today the alternative solutions, such as natural gas, biofuels and electricity, still cover only the 5% of the total [1]. However, in recent times we are witnessing something that looks like a radical change also in the automotive industry with many new technologies that try to somehow overpass the defects of the internal combustion engine (ICE). Such problems became crystal clear during the "dieselgate" scandal in September 2015, but the progress towards more efficient and cleaner motors had already started and pushed by means of many different legislations across the world with Europe, Japan and USA that play a forerunning role. Despite of having proved to be affordable and reliable, the ICE's problems are not totally solved; mayor issues are the production of GHGs, that affect the global warming, and pollutants emissions, which may cause health problems especially in the cities where their concentration is high.

The main products of the combustion of fuels are, in an ideal and complete reaction, CO2 and H2O as the following formula shows:

$$C_aH_bO_c + \left(a + \frac{b}{4} - \frac{c}{2}\right)(O_2 + 3.76N_2) \rightarrow aCO_2 + \frac{b}{4}H_2O + 3.76\left(a + \frac{b}{4} - \frac{c}{2}\right)N_2 \quad (Eq1.1)$$

Where $C_aH_bO_c$ is the formula of a generic fuel; in this simple equation we assumed that air is a perfect mixture of oxygen (21%) and nitrogen (79%).

Both CO_2 and water are not pollutants in the sense that do not cause harm to the human beings. CO_2 is the compound mostly responsible for the greenhouse effect and for the climate change. Regulations that aim to control and reduce the amount of CO_2 produced by vehicles specify the maximum amount of grams of CO_2 equivalent per kilometer that a car is allowed to produce. The most direct consequence of this constraint is that engines are becoming increasingly efficient and downsized because exploit at the maximum the energy content of the fuel. As Fig. 2 shows, CO_2 reduction and fuel economy are correlated and across the years legislations worldwide pushed towards more efficient and environmental friendly internal combustion engines. The correlation is due to the fact that the reduction of the amount of CO_2 allowed pushes the engine producers to exploit all the energy that during the combustion process is liberated from the initial chemical energy of the fuel using, for example, turbocharging. In this way the producers are not only forced to develop cleaner engines but, indirectly, to keep their technologies updated.

In a real combustion process, however, many other compounds are formed and the most important ones are: NOx, CO, unburned hydrocarbons and particulate matter. The ways pollutants are formed have much to do with physical and chemical details of the combustion process that will be not discussed here since the focus of the thesis is not the production and control of pollutants; the important concept that we want to stress here is that each of these pollutants has harmful effects on human health, especially in the high concentrations typical of cities, and that played an important role in increasing the standards of the nowadays internal combustion engines.

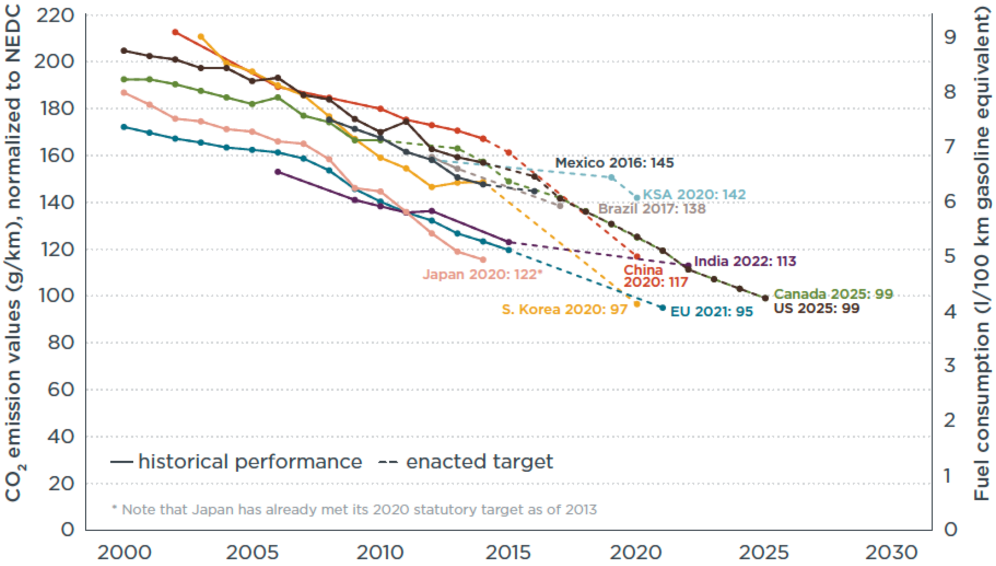


Fig. 2: Historical performances of CO2 production and fuel consumption of Internal combustion engines vehicles [12]

These pollutants are deeply, though not exclusively, connected to the energy source that for the great majority of the cases are liquid fuels.

Liquid fuels are widely spread and the reasons for this success are their great technical advantages with respect to alternative energy sources. First of all fuels present a very high energy density that is fundamental to provide long travels between refueling. A second characteristic is that fuels are easy and fast to refuel and the infrastructure is big, diffuse, easy to maintain, flexible and very stable. In fact a change in the fuel has no great impact on the distribution infrastructure both for liquid and for gaseous fuels and a sudden increase of demand, as well as an abrupt decrease of it, doesn’t cause any kind of instability. These qualities make clear that a complete abolition of liquid fuels in the mid-term future is not feasible nor realistic. The future of mobility will for sure meet new technologies able to limit the defects listed above but liquid fuels will still play an important role.

The new directions that big OEMs are testing are various but can be grossly divided in:

- Development of new combustion methods such as homogeneous charge compression ignition, premixed charge compression ignition, controlled auto ignition [13] and many others whose names change according to the OEM that propose it. All these solutions have in common to try to achieve better performances and less emissions by means of a better combustion and by approximating the ideal rapid combustion at low temperatures. In this first group of solutions both the internal combustion engines and the petrol-derived fuels are kept and just the performance are enhanced.
- Electrification or hybridizing of ICE. This second solution is more intrusive and tries to enhance the performances of the motor by coupling it with electrical devices (electrification) or electric motor and battery (hybridizing) in order to exploit the strengths of both engines. In this second solution’s type the difference with traditional ICE is more important, in particular plug-in hybrid electric vehicles reduce the relevance of the fuel because it is used just as a range enlarger for particular cases in which the battery is not enough.
- Development of biofuels and e-fuels that require changes in the motor both for the materials and for the way the engine is operated but that use the same basic technology of the ICE. The greatest advantage of such solutions will be analyzed in detail in the next section.

- Electric vehicles (EV), also called battery electric vehicles (BEV), in which the change is complete: the engine disappears and the car has completely different behaviors. The critical point of a BEV is the battery that usually is the most heavy and expansive part of the vehicle. Actually there are many concerns about batteries: are produced using Cobalt and Lithium whose price is expected to explode [14]; Cobalt is produced for more than the 60% in the Democratic Republic of Congo where Amnesty International denounced the child labor and brutal work conditions [15]. However, we shall not conclude that the situation will remain like this forever, since technological development may lead to new types of batteries that don't require such metals or political developments may lead to better conditions for people in the Democratic Republic of Congo.

Is our intention to make a short review of these technologies with the aim of showing strengths and weaknesses of each of them and the role they might play in the future of mobility.

The homogeneous charge compression ignition (HCCI) engine has been studied for a long time without many successes until now. The idea beneath the research field is to join the strengths of both homogenous charge and compression ignition engines in order to:

- Eliminate the throttling;
- Control the load using the amount of fuel injected;
- Achieve a fast combustion at low temperatures.

The basic technology remains the ICE but it is operated in a different way.

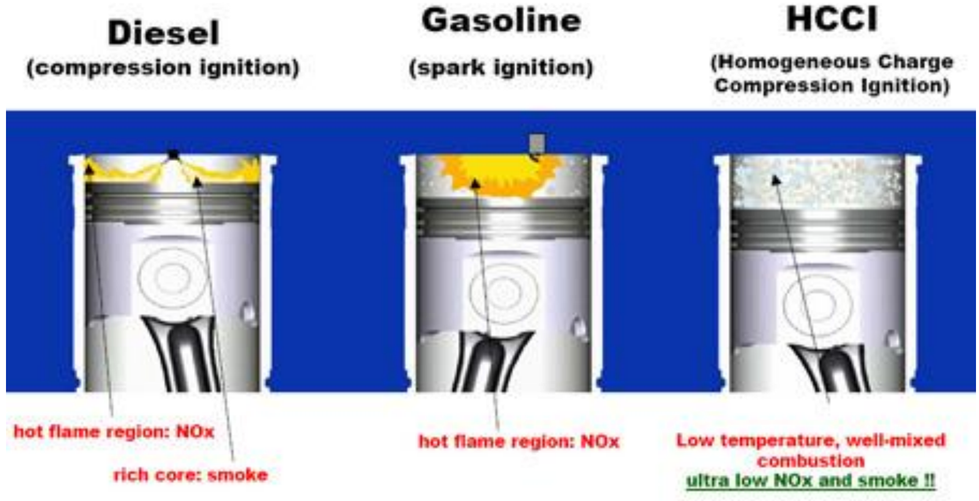


Fig. 3: Differences between Compression ignition, Spark ignition and HCCI engines

As shown in Fig. 3 the main feature of the HCCI engine is to supply the combustion chamber with a homogeneous and premixed charge diluted with exhaust gases that is forced to auto-ignite nearly at the same time without any flame front gradually propagating. In this way there is no risk of particulate formation, as shown in Fig. 4, and also NOx emissions are definitely lower. The reduction of pollutants emissions is due to the lower combustion temperature, i.e. less NOx emissions and globally leaner mixture, i.e. soot is oxidized. This technology is also predicted to reduce the fuel consumption because of the extremely fast combustion process. However, practical applications of such combustion mode are not yet ready for the market because, increasing the engine load, the required mass of auto-ignition grows and the control becomes very complicated because the pressure increase leads easily to knocking like behaviors.

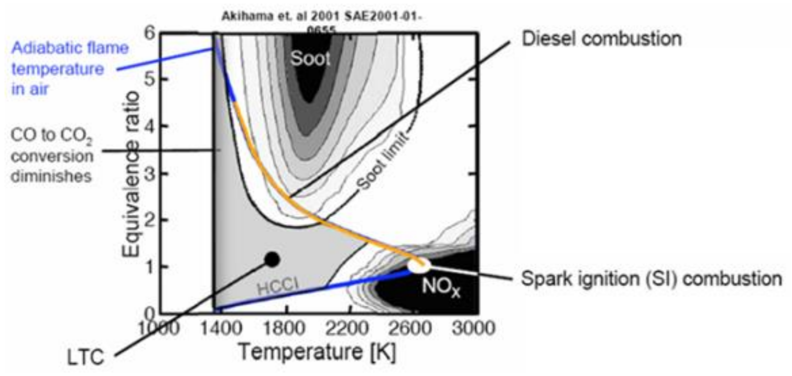


Fig. 4: Different combustion paths of Diesel, Spark ignition and HCCI combustion

The second technology that is quickly spreading is the hybrid vehicle. The main categories are: plug-in electric cars and hybrid-electric cars. Plug-in electric cars are a subcategory of EV since they are propelled by one or more electric motors using electrical energy stored on-board in battery packs that can be recharged from any external source of electricity through a plug; in case of necessity, however, they can rely on a small ICE that can produce energy on-board acting as a range enlarger. Hybrid-electric cars, instead, are vehicles that combine an ICE propulsion system with a battery-electric drive system to improve fuel consumption, emissions and performance in comparison with traditional cars. The power sources can be arranged in different way: parallel, series or both (as shown in Fig. 5).

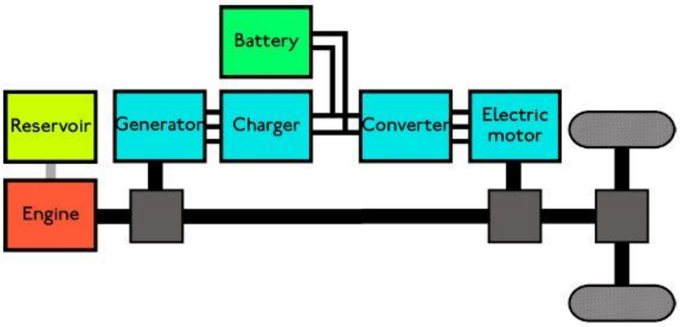


Fig. 5: Typical structure of a combined series-parallel hybrid car that allows either mechanical or electrical paths for power from the engine to wheels

The level of hybridization can widely vary from *"full hybrid"*, a vehicle that can run on just the engine, just batteries or a combination of the two, to a *"mild hybrid"*, that are typically cars with some degree of hybrid hardware. In general, the hybrid solution permits to achieve greater fuel economy (due to: downsizing of the engine that is operated at its optimum condition, regenerative breaking, start and stop system, etc.) and lower pollutants emissions because the engine is running at the minimum pollutant emission condition at nearly constant load.

The most discussed solution, however, is the electric vehicle, that received a huge attention by politics and media, causing a bit of a confusion and sometimes exaggerated reactions; for these reasons it worth to go a bit more in the detail of the technology. The greatest advantage of BEV is that, during their operation, they do not produce any GHG and pollutants apart from particulate emissions from tires and breaks. For this reason in recent years the politics of many European countries proposed to shift to a mobility completely based on BEV.

The biggest market for electric vehicles is China followed by USA and Japan, although the percentage of EVs is negligible in all these countries (less than the 1% of cars in stock is an EV). The most diffuse electric vehicles are two-wheelers and three-wheelers, diffused preeminently in China, and city buses in big cities [16]. The country with by far the highest penetration of electric vehicles is Norway [17] and for this reason it represents a "laboratory" for the EV and can be studied in order to point out which are the possible developments of this transition.

First of all is good to remind that Norway can boast a production of electric energy that is for more than 90% due to hydropower, which is not only the most efficient, clean and flexible way of producing energy but also allows a very effective storage, simply by pumping water to higher levels. This fact has a huge technical relevance because allows to use energy that has been efficiently produced and because the load's peak can be easily followed reducing in this way the possibilities of network instabilities. Coming back to EV, in 2017 in Norway have been sold more EVs and hybrid ones than the traditional models and the stock reached 2.014 million EVs [18]. This success is mainly due to the heavy policies that support the EV such as: no sales tax, no importation taxes, free parking, no eco-pass, no highway fares, preferential lanes and others [18] [19]. The total budget proposed to push the EV is about 300 million of euros that can be spent just because Norway has the biggest sovereign fund in the world thanks to the petrol and gas richness of the country [18]. However, with the growing number of cars that have to connect to grid in order to recharge, the distribution grid is showing the first problems because the increase of power that has to be delivered is huge and the electric lines are not designed for such powers. An upgrade of the grid is too expensive [20] in the near future and therefore authorities are trying to limit grid tension fluctuations using diffuse battery storage and other strategies. The bottom line of this small digression is that in order to achieve a considerable percentage of EV on the street, a vast policy of subsidy is needed and it is not affordable for many countries. Good solutions usually don't need too much help and, even though there are many forecasts that foresee a diminution in the cost of batteries making EVs a popular technology, it is more probable that the EV will gain a greater percentage in small and light cars for city use where the characteristics of the electric motor, such as regenerative breaking and no idle when the car is standing still, are more interesting.

Another interesting study can be performed on the Well-To-Wheel (WTW) basis. This analysis has much to do with the energy production system of the country where the BEV is operated: vehicles becomes part of the national energy mix and its efficiency depends on how the electricity is produced. The WTW analysis in the case of vehicle based on internal combustion engine, instead, depends only on the characteristics of the engine and is the same all around the world for a specific vehicle.

Therefore the WTW analysis for a traditional vehicle is divided in seven steps: 1) extraction, 2) transport, 3) refining, 4) distribution, 5) engine combustion, 6) power delivery system, 7) wheel; in the case of a BEV the analysis is divided in nine steps: 1) extraction, 2) transport, 3) refining, 4) distribution, 5) power generation, 6) power transmission and distribution, 7) charging, 8) motor, 9) wheel [21]. The result is that BEV usually can effectively reduce the GHG emissions even though the amount of savings is greatly dependent on the energy production system. What's more recent advances in downsizing and emission controls in ICE has greatly reduced the BEV's advantage in a WTW analysis [21] as can be seen in Fig. 6.

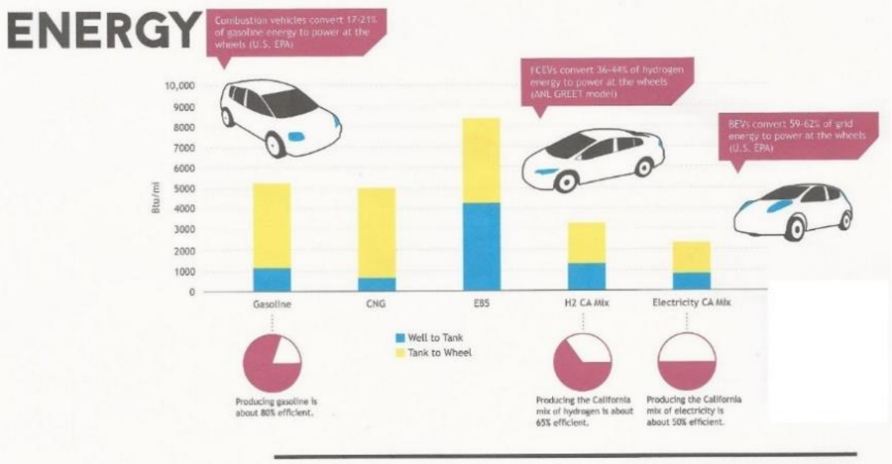


Fig. 6: Energy WTW analysis for vehicles propelled with: Gasoline, Compressed natural gas, Gasoline-Ethanol blend, Fuel cells, batteries

Other analysis that take into account real driving conditions by simulating the European driving cycle show that the greatest advantages can be achieved with vehicles with ranges below 300-400 km because for higher values the weight of the car increases too much because of the batteries and the energy consumption surpasses the one of ICE [22]. That last analysis makes clear that the future use of BEV will be mostly in cities where the low daily mileage allows for a small and light battery. In this way the advantages of BEV are correctly exploited and can effectively produce benefits for the society and the global environment; it is not by chance that one of the most interesting and fast growing sectors of the BEV are city buses [17]: such vehicles are characterized by short, standardized, urban tracks that perfectly match with the opportunity to install many small charging point along the track so that the bus can be fitted with small, light batteries.

Even though there are many projects to produce also heavy-duty transportation vehicles that rely on batteries [17], the mode in which such vehicles are used make very unlikely that electric motor will ever become competitive with ICE counterparts. The main reason is that heavy duty vehicles work most of their life at constant speed on the highways; in these conditions the advantages of the BEV exposed above cannot be exploited and the weight of batteries increases so much that the reduction of the pay load is too high.

In conclusion, BEV is an interesting technology that will have an important role in the future, especially in certain applications. Nevertheless the ICE will still play a major role in the transportation's sector even though will deeply change its shape and characteristics.

In the next paragraph we will analyze in great detail the fourth solution to the ICE's problems: the biofuels; from now on this thesis will be focused on biofuel's applications in ICEs but the reference framework has to be beard in mind in order to understand which are the ideas driving the choices.

1.2 Biofuels and e-fuels

Renewable fuels are fuels produced from natural resources, which can be restored with a rate that exceeds their consumption, through naturally recurring processes [13]. Renewable fuels are: biofuels and hydrogen produced by means of renewable energy. We will from now on deal only with biofuels neglecting the hydrogen production because its use is mostly thought for fuel cell vehicles that we will not discuss.

A biofuel is a type of fuel whose energy is derived from biological reduction of atmospheric inorganic carbon to organic compounds by living organisms. Historically, biofuels were born due to the increase of crude price during the petrol crisis in 1973 and later the Gulf War in 1991 [23] and since then continued developing thanks to the interest showed by many countries. The starting point of developing biofuels was the reduction of the dependence of rich countries, which have no fossil sources available in their territory, from poorer and instable countries, that possess huge amounts of crude oil. In this perspective biofuels can produce liquid or gaseous fuels that can be used in ICEs by exploiting locally available renewable sources, usually crops. This attention to local production of crops dedicated to biofuels has the effect to add value to the products and therefore gives possibilities to rejuvenate rural communities that often suffer for the migration of people to the cities [24]. Still, there is another characteristic of biofuels that makes them even more attractive: the possibility of achieving a CO_2 neutral, or even CO_2 negative, balance between production, refining and combustion with little changes in the whole energy system.

In fact, biofuels do not require great changes both in the distribution system and in the ICE. A generic liquid biofuel after the refining process can be distributed using the same trucks that transport gasoline; the same distribution net of other non-renewable liquid fuels can be used; the pump at fuel station is the same as well as the refueling mechanism of the car. Across this whole system only small changes should be done in order to deal with the biodegradability of the biofuel and the greater corrosion it may cause on materials, but the modifications are small if compared to the ones that are needed in order to create an electric network for EV or a hydrogen diffuse storage system for fuel cell vehicles.

More complex are the modifications to be done inside the ICE because the system has different behaviours according to level of blending of the biofuel with regular fuels. Nevertheless a general layout can be seen in Fig. 7. The most important modifications are the materials of pipes, tank, pump, injector, wires...

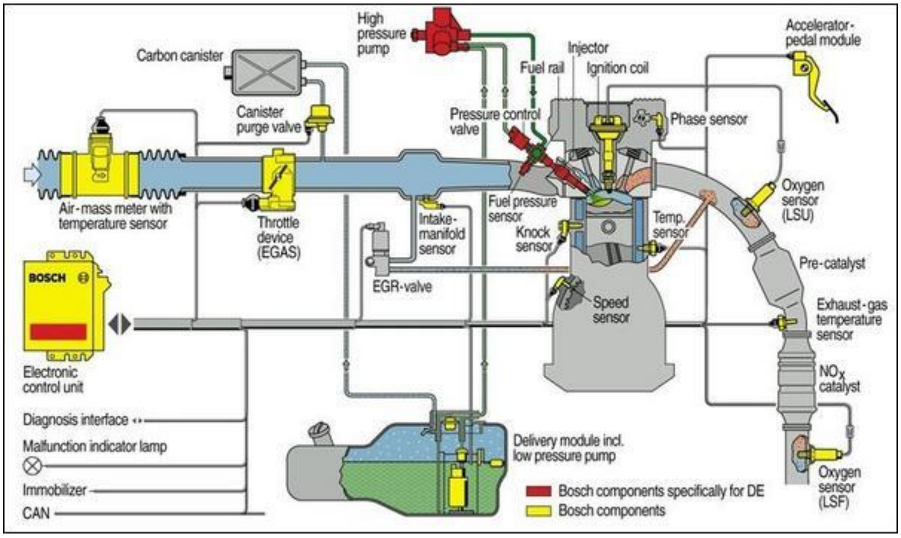


Fig. 7: General layout of a flex-fuel engine

The other fundamental modifications are the sensors that have to be added in order to tune the combustion process according to the different characteristics of the biofuel. Such sensors are the knock and the temperature in the exhaust manifold; data from those two sensors are used to precisely set the spark advance. From Fig. 7 it is also clear that the general construction of the ICE remains the same and, as a matter of fact, for gasolines with little blending of biofuels, up to 15% of ethanol in the gasoline, the effect in the combustion process is negligible and the engine can run without any modification. For the future, however, since the forecasts states that there will be an increase in the production and use of biofuels, new engines must be developed that are designed especially for biofuels.

To explain the possibility of creating a CO_2 neutral network with biofuels we consider the case of the bioethanol [13] produced via fermentation of glucose. The chemical reaction of fermentation is:

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + CO_2.$$

And the combustion of ethanol is:

$$2C_2H_5OH + 6O_2 \rightarrow 4CO_2 + 6H_2O + heat.$$

The global cycle is given by the sum of the two reactions that lead to:

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O + heat$$

That is exactly the opposite of the photosynthesis that happens in the biomass as the feedstock is growing. In reality, during the evaluation of the carbon footprint, many other factors have to be taken into account (fuel used for the machines, energy necessary for the refining process, etc...) making that calculation more complicated [25]. However, from a simplified point of view, the cycle follows these steps:

- Production of a crop that while growing absorbs CO_2 from the ambient and releases O_2;
- Harvesting of the crop;
- Processing of the crop to give the final biofuel;
- Transportation of the biofuel to the pump;
- Utilization of the biofuel in an ICE releasing CO_2.

Processes from production to transportation require energy that, in general, is provided by means of the combustion of some fuel (might be a biofuel or not) that releases in the atmosphere more CO_2. If the total sum of CO_2 absorbed during the growth of the crop is greater or equal to the total amount of CO_2 released in the atmosphere during the whole process, the cycle can be respectively CO_2 negative or CO_2 neutral. There is no absolute solution that allows to declare that biofuels are always helping to reduce the GHG emissions because each case depends a lot on the type of technology used, the efficiency of the transformation of the crop into biofuel, the characteristics of chemical reaction of refining and so on. For this reason each biofuel has to be evaluated by itself and technologies are a main factor of difference between one biofuel and another.

The most common and commercially available biofuels are: bioethanol, biodiesel and biogas. Bioethanol is the most produced biofuel worldwide and is mainly produced by USA and Brazil. The USA bioethanol is based on corn crops, while the Brazilian one is based on sugar cane.

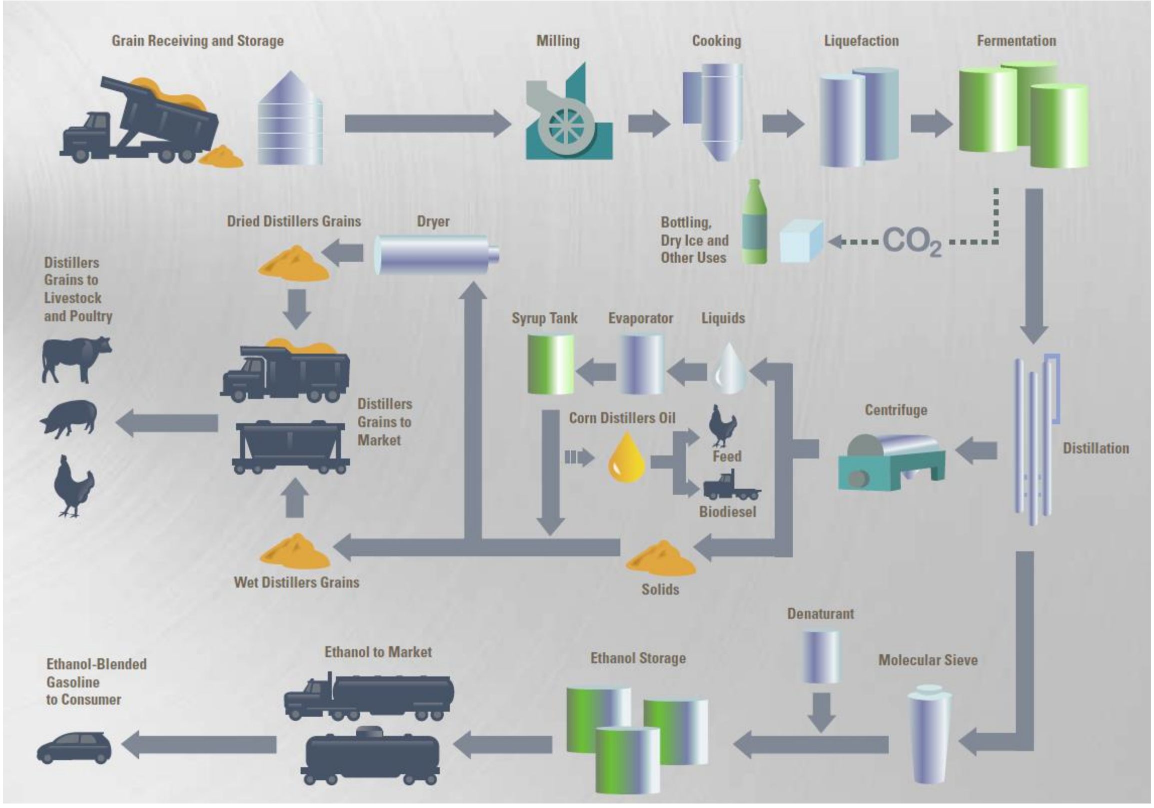


Fig. 8: Bioethanol and co-products processes

The production of bioethanol by dry milling is displayed in great detail in Fig. 8. The first step of the process consists in grounding into "meal" the entire grain kernel that afterwards is slurried with water to form a "mash". Enzymes are added to the mash to convert starch into sugar. The mash is cooked, then cooled and transferred to fermenters. Yeats is added and the conversion of sugar into alcohol begins. After fermentation the liquid part, called "beer", is separated from the solid residuals. The last steps are distillation, dehydration and blending with the denaturant to render it undrinkable [24].

It is interesting to note that there is a great effort in the valorization of co-products of the bioethanol such as CO_2, which is used to produce dry ice and for bottling, and solid co-products. Carbon dioxide, as we already saw appears during the fermentation process of glucose to ethanol and can match a number of industrial applications. The solid residuals, instead, are separated after the distillation and consist mainly in proteins, fats, and fibers that are not exploited during the processing because only the sugar fraction give as a product ethanol. The co-products are usually sold as a high-protein animal feed that is used for beef cattle (47%), dairy cattle (31%), swine (14%) and poultry (7%) [24]. As Fig. 8 shows, there is also the possibility to exploit the fat content of the co-products to produce biodiesel but nowadays is not the best choice as the animal feed encounters much higher interest on the international market.

The main use of bioethanol is blended with standard gasoline to both improve the quality of the gasoline and to reduce its price. Thanks to the ability of ethanol to mix homogeneously with gasoline, it is common in many countries, also in some European one, to find at the pump station the possibility to choose gasolines that are blended with a 5% (E5), 10% (E10) or 15% (E15) of ethanol. Those gasolines can be used also in a standard cars without any modification to the engine. If the amount of ethanol that is blended increases, the gasoline's behavior during the combustion changes so sharply that it can no longer be used in a standard engine. Nevertheless it is common in certain countries such as Brazil, USA and France to find gasolines that are blended with up to 85% of ethanol (E85) or even pure ethanol (E100). Such gasolines can run only in especially designed engines, the so-called flex-fuel. The advantages are: a reduction of the cost of gasoline at the pump, a reduction of the greenhouse emission, lower dangerous air pollutant emissions, higher octane number, higher laminar flame propagation and the reduction of the crude's import. Such advantages are deeply related with the ability of a certain engine to burn in a correct and efficient way the mixture of ethanol and gasoline or pure ethanol, which again depends on the characteristics of ethanol.

Ethanol is a biofuel that shares many points in common with gasoline and for this reason is used only in spark ignition (SI) engines. A more detailed description of such properties will be discussed in section 4, however, it worth to start with some general concepts. Higher octane number means that the mixture of gasoline and ethanol has a lower tendency to cause knocking. A higher laminar flame speed, instead, is a property of the flame front: higher the speed at which the flame front is moving, more rapid will be the combustion process and therefore completer and more efficient. The reduction of pollutants is mainly due to presence of oxygen in ethanol that helps to complete the oxidation of the partial products of combustion because of the local availability of oxygen.

Even though ethanol remains by far the most used and produced bio-alcohol, recently there is an increasing interest in other forms of alcohol that can also be blended with gasoline in order to be burned in SI engines. Examples are methanol, commonly produced starting from natural gas [13], and bio-butanol [23].

The second most important biofuel is the so-called biodiesel that is produced mostly in the European Union. Biodiesel is a liquid fuel consisting in long-chain fatty acid alkyl esters that are obtained by processing several different feedstocks such as: animal fats, oils and recycled cooking greases [23] [13]. Vegetable oils can be produced starting from a variety of different crops like soy, rapeseed, sunflower, palm oil, coconut, algae etc… The resulting fuel can be used in diesel engines without any particular modification, even though also in this case the most common use is blended together with standard diesel.

Biodiesel presents a chemical composition completely different from the petroleum-derived diesel. The two fuels are instead characterized with very similar physical properties: viscosity, density, cetane number and combustion characteristics that make the two fuels comparable. Biodiesel has many technical advantages on petrol-derived diesel such as higher cetane number, no Sulphur content, reduced pollutant emissions, low toxicity and biodegradability [13]. As for the bioethanol, also biodiesel development and utilization are pushed by the objectives of reducing GHG emissions, reducing the dependence on crude importations and creating benefit for the local population. At a global level the use and production of biodiesel is much more concentrated than ethanol: in 2015 the 73% of the total production of biodiesel was in Europe; that means that the interest in such biofuel is not as widely spread as for ethanol. One of the reasons underlying such difference is that only the European Union pushed so hard on this technology and only there the Diesel represents almost the half of the total circulating cars.

The last important biofuel that is currently produced is biogas: a result of the anaerobic digestion or fermentation of biodegradable materials. The base feedstock can be municipal waste, green waste, plant material, crops, animal excrement, sewage, etc. Raw biogas, the one resulting from the anaerobic process, is mainly composed by methane, carbon dioxide and contaminants, even though the detailed composition depends on the type of digestion process that originated the fuel. After an upgradation process and a purification biogas can be easily used in application for natural gas. A common use of such biofuel is the production of electricity by means of large ICE that are placed close to the digestion plant directly nearby the fields where the crops are grown so to minimize the energy consumption for transportation. Apart from power production applications biogas is not widespread; in the automotive industry indeed, there are no applications to our knowledge mostly because of the lack of refueling stations and the limited availability on the market of vehicles propelled by natural gas. For this reason biogas production remains very limited and localized with respect to the bioethanol and biodiesel's one.

The great advantages offered by bioethanol and biodiesel must pay the price of using an eatable crop to produce fuels. The increase in the demand of crops to produce biofuels raises also the price of such products that may lead to starving or poverty in other parts of the world. What's more, usually biofuels are available at a competitive price thanks to national programs that support the producers. This contrast is known as the *food-fuel dilemma*. The main solution to the dilemma is to change the type of feedstock. As we already saw, the most used crops for biofuels are corn and sugar cane for bioethanol and soybeans and palm oil for biodiesel, which are all eatable crops. In order to find the solution to such dilemma many alternative feedstocks have been proposed and took the name of "second generation" or "advanced biofuels". The first idea has been to exploit agricultural by-products in order to develop new liquid biofuels based on plant biomass [26]. Although plant biomass is largely underutilized and widely abundant on the earth, biofuel production from agricultural by-products could satisfy only a portion of the total demand. This pushed towards the development of dedicated biomass crops which do not compete with food in terms of land utilization and do not increase food's price. The last and more drastic step towards a full sustainability is to grow crops without using arable land; this lead to the development of biofuels based on algae as feedstock that can be grown in water [27]. An even further step is to grow biofuel crops close to an industry, to capture the CO_2 that the plant is producing as an exhaust gas and use it as a fertilizer for the algae. In these terms biofuels can become really interesting also from a CO_2 balance point of view; there aren't already data about large production of such crops, but from a theoretical point of view there is the possibility of developing CO_2 negative biofuels.

In Fig. 9 is reported a schematic overview of all the possible sources of biomass available.

The most interesting sources are probably lignocellulosic residual. Such residuals are typically composed by a 75% of polysaccharides that represent an important source of sugars; there are many possible transformations they can go through, however, the most important industrial processes are hydrolysis and fermentation to give bioethanol or gasification to give Fischer-Tropsch biodiesel.

In the recent period a number of different crops are under study to try to match with the above characteristics. Many of them are thought to be grown in desert lands in order to give a value to otherwise useless land and to avoid the competition with food. The potentially most promising crop is probably Jatropha for the production of biodiesel: a plant original of Mexico where it was mainly used for basket making but that recently attracted the interest of many researchers because of its resistance to drought and pests. However, its production process is still not enough studied and the commercialization process is on development.

Algae have undoubtedly many advantages if compared to any other possible crops grown on land: they don't require land use so avoiding all the problems connected to an intensive use of arable land, like for example the intensive use of pesticides; what's more they do not produce any *food or fuel dilemma* and, using genomic engineering, have the possibility to reach very interesting results in terms of biofuel production or minimization of the associated process costs.

Up to now algae proved to be able to produce a variety of different biofuels such as bioethanol, biogas and biodiesel [28], nevertheless, there are many issues regarding the possibility of the start a wide scale production of biofuels from algae. The biggest problems are connected to the fact that usually the production plants are modular and the reduction of cost connected to the increase of dimensions is limited.

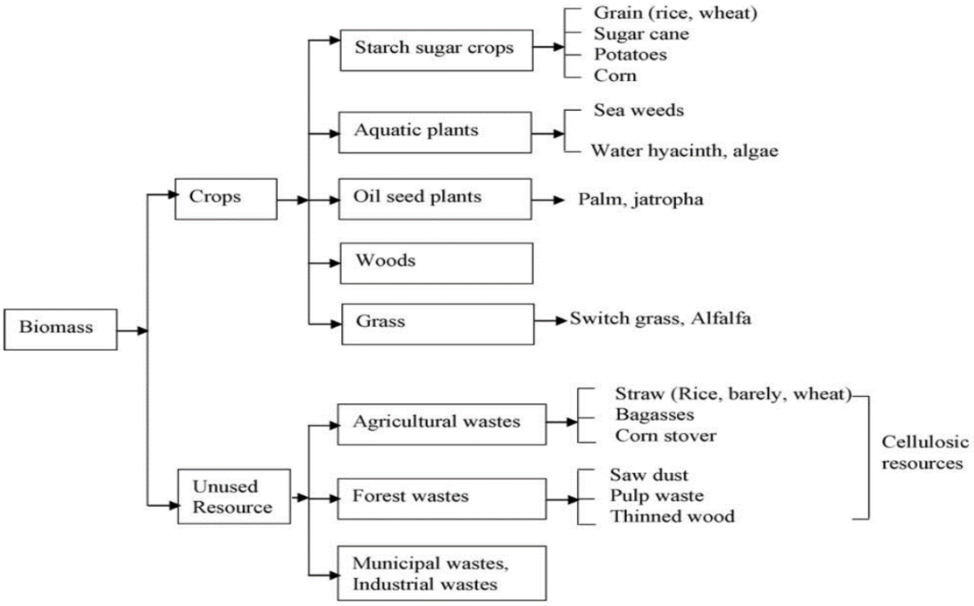


Fig. 9: Overview of the available biomass sources [26]

Another problem is that in order to maximize the production of fatty acids the crop must undergo stress conditions that may be reproduced in laboratory or in small plants but require particular equipment that is not proved to be affordable at a wider scale level. Finally, many steps of the production, including harvesting, drying and extraction, are still very expensive and represent obstacles to the commercialization.

All these biofuels, from the first or second generation, in order to prove their viability, has to show good results when their whole life cycle is analyzed. This includes: land use change, absorption of atmospheric CO_2, energy use and emissions produced during the production stages, use of fertilizers and the ability to work as a good energy vector once burned in cars. All these characteristics, however, must face a more important and stringent constrains: ethical issues. In fact, the *food or fuel dilemma* is not the only ethical problem biofuels must face, many others have been summarized by the Nuffield Council on Bioethics [29]. The answer to the question whether it is ethically approved to produce and develop biofuel is not simply based on technical characteristics but lies on a more general landscape of ethical principles that we quote as reported in [29]:

- Biofuels development should not be at the expense of people's essential rights (including access to sufficient food and water, health rights, work rights and land entitlements).
- Biofuels should be environmentally sustainable.
- Biofuels should contribute to a net reduction of total greenhouse gas emissions and not exacerbate global climate change.
- Biofuels should develop in accordance with trade principles that are fair and recognize the rights of people to just reward (including labour rights and intellectual property rights).
- Costs and benefits of biofuels should be distributed in an equitable way.
- If the first five principles are respected and if biofuels can play a crucial role in mitigating dangerous climate change then, depending on certain key considerations, *there is a duty to develop such biofuels*.

There is in our opinion the realistic possibility to achieve all these ethical principles in the near future, both because of the development of new technologies and the definition of more precise legal definition able to protect all the rings of production chain.

As we saw up to now, we are witnessing a big change both in the energy world and in the transportation one. In both these sectors what drives the change is a greater interest in green solutions that permits to preserve the Earth's natural resources. The biggest problem in the energy system is how to deal with the randomness of power production; it is common indeed that eolic turbines or solar panels have to be shut down during a period of particular high production and/or low request. To solve these problems it is fundamental to find ways to stock energy in a convenient way in order to use all the possible energy that renewable sources can produce and keep it stocked until the request increases or production drops. Many solutions have been proposed, among which there is the possibility to use excess electricity to produce hydrogen via water electrolysis. Such technology is called "Power to gas". Once hydrogen is produced it can be used in fuel cells or it can be used to produce fuels by reaction with CO_2. Such fuels are called "e-fuels" or "synthetic fuels" because are completely different from biofuels in terms of production systems even though usually they are not so different in terms of chemical composition. Synthetic fuels are fuels that are made by using electrolysis as a base process together with a source of carbon to produce liquid hydrocarbons [30]. The main technological feature is the electrolyzer cell that performs the water electrolysis. The most common types are the solid oxide electrolyzer cells (SOEC) that can work both as a fuel cells and as an electolyzer. Synthetic fuels overcome land use and have no interference in the food supply chain and for these reasons may solve some of the problems that affect biofuels. Up to now the most produced biofuel is methane but in the near future it is possible that many other kinds of fuels will be developed. The most promising are methanol and dimethyl-ester (DME) because of the well-known chemical synthesis and since they can be used directly in internal combustion engines without many modifications; in particular, methanol can be used in Otto engines and DME as an alternative to conventional diesel.

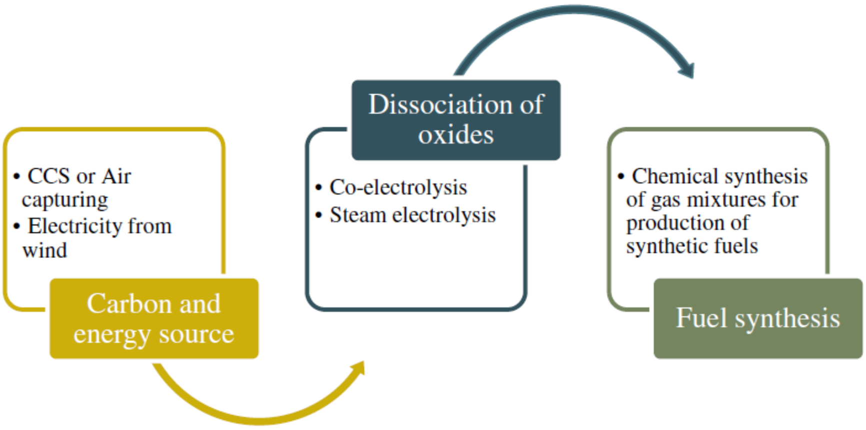


Fig. 10: Synthetic fuel production steps [30] (CCS: Carbon Capture and Storage)

In Fig. 10 is schematically reported the production steps of a synthetic fuel: carbon and energy source, dissociation of oxides, fuel synthesis. To provide the carbon source the carbon capture and storage from an industrial plant can be used in order to increase the beneficial effect in mitigating the GHG emissions. The most interesting features of e-fuels are the possibility to reduce CO_2 emissions without any *food or fuel dilemma* and their inherent flexibility in the production process that created the new idea of "fuel design". In fact, the last stage of the production process can theoretically easily adapt to create different fuels according to the needs of the costumer. This completely new possibility might have the power in the future to change the relationship between the engine and the fuel. In the midterm future ICE may be thought and designed according to a very specific fuel in order to optimize the performances and fuel efficiency. The down-side of e-fuels is that is hardly to think of a scenario dominated by renewable sources with enough energy to produce an amount of synthetic fuels that can supply the fraction of the transportation sector depending on liquid fuels.

As for biofuels, e-fuels do not require modifications in the ICE nor in the distribution system, do not cause any instability on the infrastructure and reduce the dependence on fossil fuels. It is therefore probable that also synthetic fuels will play a role in the future of mobility even though it will be probably less important than biofuels.

In conclusion, the energy's world is changing towards a cleaner and more sustainable production system based of renewable energies and electricity. The transportation sector, which until now was only marginally affected, is now preparing itself to meet a transformation that will deeply modify the way of producing fuels and the way we think of the it. Such a transformation is pushed by national or regional politics that aim to a better energy security, a reduction of the dependence on oil producer countries, a cleaner environment especially in cities and a reduction of the GHG emissions. The main actors in the midterm future will be fossil fuels, biofuels, electricity and e-fuels. The change in the types of fuels will lead inevitably in a change in the design of ICE that will have to face a variety of new different fuels.

In the next section we will go more in the detail of internal combustion engines and how they are designed using simulation tools.

2. Development of internal combustion engines using CFD

The main issue in developing the thermodynamic part of an ICE is to model the movement and the behavior of fluids in the different volumes that compose the engine. During a complete engine cycle, fluids must flow through: inlet manifold, combustion chamber, exhaust manifold and after-treatment system. In each of these different volumes the flow undergoes many physical and chemical processes such as: injection of fuel, mixing, heat transfer with the walls of the volume, compression, combustion and pressure losses in the pipes and across the valves.

In order to obtain the desired performances and to control fundamental parameters like the amount and type of pollutants emitted or the temperature in particular points and moments of the engine cycle, many different configurations have to be tested and many experiments are required in order to obtain a large enough number of parameters. Such complex work is very time and cost consuming, therefore during the last decades much research work has been spent in order to develop methodologies able to simulate the behavior of the engine and to act like "an eye in the engine". As it is easily understandable all these methodologies are based on software and numerical algorithms that can provide a very flexible representation of the engine because it doesn't require test benches nor physical construction of different parts for each alternative. The simulation methodologies can be divided in three main categories [31]:

- Real working process analysis;
- One-dimensional fluid dynamics;
- Three-dimensional computational fluid dynamics (CFD).

Real working process analysis are also called zero dimensional simulations because they don't solve the fluid motion but are just focused on the evaluation of the engine operating cycle by means of very simple models. The computational time is very short but they lack predictability and require additional information for the solution that can be obtained just by means of experimentation. Hence these models are mainly used for evaluation of parameters with the engine running.

One-dimensional simulations are a combination of both real working process analysis and simplified fluid dynamic simulations. Equations that describe the fluid movement are solved using the assumption of one-dimensionality and therefore the fluid flow field results very simplified and the mathematical problem less expensive in terms of calculation time, enabling in this way to solve very big systems, like a whole engine, in very short time. The accuracy is usually good for simple structures but requires models in the case of more complex ones.

Finally, the CFD approach is the most accurate because it solves the complete flow field of the fluid and permits to simulate in great detail every process inside the engine. However, usually the amount of time required for the simulation of the entire engine is so high that it make economically not convenient to perform such simulations because the great advantage of a fast response is lost. Nevertheless in this thesis we will deal with such approach because the software we refer to during the whole work is *QuickSim*, which was developed by Dott. Marco Chiodi and his research group at the FKFS IVK Institute in Stuttgart. As it will be discussed later, *QuickSim* is a software based on a generic CFD software (STAR-CD) that has been modified in order to deal exclusively with engine-related problems by means of several very efficient models that permits to drastically reduce the calculation time.

In this section we will shortly introduce the main concepts of CFD so that later on we can deal specifically with the simulation of combustion that was the focus of our work.

The equations that governs the motion of fluids are the so called Navier-Stokes equations and are well known since the 19th Century. Such equations are the result of the application of equilibrium principles on a control volume: mass is conserved, the rate of change of the momentum is equal to the sum of forces on a fluid particle and the rate of change of energy is equal to the rate of heat plus the rate of work done on the fluid particle. The equations can be obtained introducing the assumptions of compressible and Newtonian fluid [32]:

$$\frac{\partial \rho}{\partial t} + div(\rho \boldsymbol{u}) = 0 \qquad \text{(Eq2.1)}$$

$$\rho \frac{Du}{Dt} = -\frac{\partial p}{\partial x} + div[\mu \; grad(u)] + S_{Mx} \qquad \text{(Eq2.2)}$$

$$\rho \frac{Dv}{Dt} = -\frac{\partial p}{\partial y} + div[\mu \; grad(v)] + S_{My} \qquad \text{(Eq2.3)}$$

$$\rho \frac{Dw}{Dt} = -\frac{\partial p}{\partial z} + div[\mu \; grad(w)] + S_{Mz} \qquad \text{(Eq2.4)}$$

$$\rho \frac{Di}{Dt} = -p \; div(\boldsymbol{u}) + div[k \; grad(T)] + \Phi + S_i \qquad \text{(Eq2.5)}$$

Where:

- ρ is the density;
- $\boldsymbol{u}$ is the tensor of the velocities in the three dimensions;
- $\frac{D\phi}{Dt} = \frac{\partial(\rho\phi)}{\partial t} + div(\rho\phi\boldsymbol{u})$ are the rate of change of a certain variable in the volume; ϕ can be the velocities in the three directions or the energy;
- S_{Mi} are the source terms;
- i is the internal energy of the fluid;
- Φ is the dissipation function and represents the source of internal energy due to the deformation work on the fluid particle;
- μ is the fluid diffusivity;
- k is the thermal conductivity of the fluid.

In order to close the system, one must add the equation of state that expresses, for example, pressure as function of density and temperature. Eq2.1 is the so called “continuity equation” and represents the mass conservation in the volume; Eq2.2 - Eq2.4 are the equations of the momentum conservation in the three dimensions and Eq2.5 is the energy conservation equation. All these equations are characterized by having on the left side the variation of a certain property because of the convection and on the right side the variations due to diffusion and sources. The system is very complex because there are variables that are not separable from the fluid flow solution, such as pressure.

The exact solution may be theoretically found by making an integration in time and space of the equations on the control volume. As a matter of fact, such a solution has not yet been found and its existence is one of the Millennium’s problems chosen by the Clay Mathematics Institute. Hence, to deal with such problems different approaches has been developed. The main problem is the mathematical definition of terms that arise from the stresses on the control volume by means of momentum exchange.

Such terms are the ones that produce a chaotic and random state of motion of the fluid particles: turbulence. There are three ways to deal with turbulence: Direct Numerical Simulation (DNS), Large Eddy Simulation (LES) and the Reynolds Averaged Navier-Stokes (RANS) equations. DNS is the most precise solution of the equation because it doesn’t introduce any model for turbulence description but requires very detailed grids and very small timesteps; these characteristics make DNS a very slow method that requires big calculation capacities and whose detail level is generally pointless from an industrial point of view.

LES instead assumes that small eddies behave in an isotropic way and that are thereby prone to be modeled in order to increase the dimension of cells and of the time step, which means that smaller and simpler problems must be solved. Larger eddies instead depend much on the particular geometry of the problem and on the fluid flow field and shall therefore be solved

avoiding any model. Also in the case of LES usually the precision is higher than the required standard values for industrial application and the computational time, even though smaller than the DNS case, is still very high as well as the hardware requirements.
Finally, RANS equations perform a complete averaging of the Navier-Stokes equations both in time and in space. During this averaging process new terms arise in which the behavior of eddies must be somehow modeled. The fact that the modeling of turbulence is complete, makes RANS equations usually the fastest method with a good accuracy.
Since we are not dealing with a generic CFD problem but with an ICE modeling aimed to produce results for industrial users, we need a fast solution of the problem with good approximation but there is generally no interest in very detailed solutions; therefore, we are going to deal with RANS simulations. There is a variety of models that can be used and that has been developed for different specific applications, nevertheless, the most general and used one is the $k-\epsilon$ model. Such a model adds two more transport equations to the RANS, one for the turbulent kinetic energy and one for the turbulent eddy dissipation rate, plus an algebraic formula that is used to determine the eddy viscosity: a parameter arising from the averaging process. The $k-\epsilon$ is the most validated and used turbulence model and performs particularly well in confined flows. However, there are no devices able to reliably measure turbulence within the combustion chamber, i.e. a validation procedure of turbulence models under real engine conditions is not possible [31]. This introduces an important weakness in the process of simulation. Nonetheless, analyzing and improving the turbulence model is misleading and confusing because it is well known that it is much more influencing the mesh structure and the discretization degree [31]. For a more detailed description of the model and its applicability we suggest to refer to specific manuals like [31] and [32].
A particular attention has to be payed for reactive systems. Such systems are present in many problems where one or more reactions take place inside the control volume. The most interesting reacting system from our point of view is of course the combustion in the cylinder volume. As it will be clearer later, the combustion process is characterized by hundreds of species and many thousands of reactions and thereby the simulation of the exact process is impossible. Many different models are available in order to deal with such a complexity and in the next section the approach chosen in *QuickSim* will be discussed. Nevertheless, it is important to stress right from this moment which are the difficulties that the modeling of combustion introduces. First of all the fluid cannot be modeled as a single component gas with the properties of the mix of the different components. The easiest example is air: air is a mixture of nitrogen and oxygen, but it is usually modeled as an ideal gas with molar mass equal to the weighted average of the molar masses of the two components. However, as the air undergoes the combustion process, it reacts with the vaporized fuel to give many intermediate products and finally the exhaust gases. As the process drastically changes if the amount of oxygen slightly changes, the gas must be model during the whole process in each one of its components as a singular species. Consequently, for each specie a new equation has to be added in order to keep trace of the proportions and the quantities; such equations are the transport equations whose general form is [32]:

$$\frac{\partial}{\partial t}(\rho Y_k)+\frac{\partial}{\partial x_i}(\rho u_i Y_k)=\frac{\partial}{\partial x_i}\left(\rho D_k\frac{\partial Y_k}{\partial x_i}\right)+\dot{\omega}_k \qquad \text{(Eq2.6)}$$

Where:

- Y_k is the mass fraction of the k-specie. The sum on the mass fraction of all species must give 1 as result: $\sum_k^{all\ species} Y_k = 1$;
- D_k is the diffusion coefficient of the k-specie. Usually just one value of D_k is used for all species;
- $\dot{\omega}_k$ is the source term of the k-species in the volume.

The most difficult parameter to be evaluated is the source term because it is the point of the equations where thermo-fluid-dynamics effects and chemical effects meet each other. The value of $\dot{\omega}_k$ must take into account both information from the solution of the flow field and the chemical modeling of the system; of course, the two effects are closely related one another and the solution of the resulting mathematical system becomes even more complicated and the number of iterations required to reach convergence rises exponentially with the number of components. What's more, during the combustion some simplifying assumptions, like incompressible fluid or perfect gas assumption, may lead to completely wrong solutions; therefore, more complicated equations of state must be taken into account which increase the number of stiff equations to be solved as well as the numerical instability of the mathematical problem. The effort increase imposes to simplify the problem's formulation, for example reducing the number of species involved in the combustion but in this way some gross error is inevitably made. Hence, to add the combustion in the simulation requires deep knowledge of the process, great computational power at disposition and a considerable amount of time. All these three factors are usually unavailable.

Concerning the level of detail required, it is important to remember that during the combustion of SI engine there are two different areas separated by the flame front that are completely different one another. However, inside each area there is no real need to make distinctions between the different components as long as the whole system is characterized as the gas whose properties closely resemble the much more complicated real mixture. In this case analyzing the system starting from the single component of the mixture adds really little information to the final result but the computational time required drastically drops.

It is then clear why many alternative models have been developed to deal with combustion; it is also clear that there are possibilities to simplify the problem without losing the main information. In the next section we will deal in greater detail with the approach chosen in *QuickSim*.

We conclude describing the advantages of the use of specific models in a general process of solution for a CFD. The advantages are twofold: reduce the number of cells necessary to solve the problem and gain in accuracy because the model starts from the study and observation of many similar cases and therefore a greater detail can be reached compared to the solution that can be obtained with just the RANS equations. The drawback is that the solution is something that depends on the model we are using. In this sense there is a loss of generality of the software that in the specific case of *QuickSim* is of limited interest because it is used and designed to work only and exclusively on engines. In *QuickSim* many different phenomenological approaches, empirical correlations and *ad hoc* approximations are implemented in order to make the overall software efficient and fast. For a more detailed description of all the models we suggest to refer to [31]. In the next section we will go in deeper detail about the model used to describe the combustion, which is the most interesting one for the purpose of our thesis.

Eventually, the strength of the simulation using CFD tools is that the results can be in detail visualized in such a way that the overall effect can be thought as a virtual "eye in the engine". The solution of the complete flow field can give a more detailed insight in the engine behavior and the availability of data can be used as a way to propose modifications to the engine more precisely and without the need of experiments. Nevertheless, in order to give a good accuracy, simulations must be calibrated on the base experimental campaigns that are aimed to determine the values of parameters that better fit the data. Some parameter might be very general and require only a limited number of experiments based on general cases because the dependence on particular geometries and flow field solutions are limited. Some other parameters require instead to be calibrated on each single case. In this perspective the simulation loses much of its ability to predict fluid's behavior as well as its flexibility. Therefore, software developers are always looking for a way to make the software more predictive and less dependent on calibrated parameters.

The work of my thesis was exactly headed to the reduction of such dependence in the particular scope of the combustion. To understand better how this work is integrated in *QuickSim*, in the next section we will deal with the combustion in ICE and how it is modeled.

3. Simulation of combustion

The main event of the engine cycle is the combustion. During such process the mixture of air and fuel reacts to release the chemical energy of the combustible and transform it into heat that is then transformed into mechanical energy. Nowadays there only two possible ways to perform combustion: Spark Ignition (SI) engines and Compression Ignition (CI) engines.
Since my work concentrated on SI engines we will now shortly review the combustion process characteristic of that kind of engines.

1.1 General characteristics of the combustion

In SI engines the combustion is started by the electrical discharge of the spark plug close to the end of the compression stroke. In this kind of combustion, the fuel finds itself already at the gaseous state in the form of a homogeneous mixture together with air; thereby, this kind of combustion is called *premixed combustion* and is characterized by very high propagation velocities.
The fuel is usually characterized on the base of its chemical properties. The most important is the Lower Heating Value (LHV) defined as heat that has to be extracted to the combustion products after the stoichiometric combustion of the fuel/air mixture in order to reach the initial conditions of pressure and temperature. The LHV is a measure of the energy that enters the system and on its value all the efficiency factors are based. It is usually expressed in terms of MJ/kg and a typical value for gasolines is 42-43 MJ/kg. As the LHV increases, the energy introduced per unit mass of fuel increases, which means that for the same gross power the amount of fuel needed is lower, which is a useful feature especially in situations where the mass fluxes of fuel are limited, typically in motorsports. From a chemical point of view the LHV can be defined as the opposite of the enthalpy of combustion ΔH^0_{comb}; in formulae:

$$LHV = -\Delta H^0_{comb} = \left\{\sum_i n_i \Delta H^0_{form,i}\right\}_{REACTANTS} - \left\{\sum_j n_j \Delta H^0_{form,j}\right\}_{PRODUCTS} \qquad \text{(Eq3.1)}$$

Where $\Delta H^0_{form,i}$ are the variation of enthalpy due to the formation reaction of the i-species at standard conditions and n is the molar fraction of the species. The LHV differentiate from the Higher Heating Value because the latter considers also the condensation heat of water.
In order to describe the mixture the most important parameters are the air/fuel ratio and the other parameters that can be deduced from it. The air/fuel (α) is the ratio between the amount of air and the amount of fuel that is present in the mixture; such a ratio can be calculated both using the molar fractions or, more often, mass fractions. The most important value is the stoichiometric air/fuel ratio (α_{st}) that represents the exact amount of air that is needed in order to obtain a complete oxidation of the fuel. The value of α_{st} can be calculated simply recalling Eq1.1:

$$\alpha_{st} = \frac{MM_{O_2}\left(a + \frac{b}{4} - \frac{c}{2}\right) n_{O_2} + 3.76\, MM_{N_2}\left(a + \frac{b}{4} - \frac{c}{2}\right) n_{N_2}}{n_{fuel}\, MM_{fuel}} \qquad \text{(Eq3.2)}$$

The value of α_{st} divides the mixtures in two possible groups:

- If $\alpha < \alpha_{st}$ mixtures present an excess of fuel with respect to the amount of air introduced. In this case the mixtures are called rich (in fuel);
- If $\alpha > \alpha_{st}$ mixtures present an excess of air and are called lean.

As the value of α_{st} is variable and depends on the characteristics of the fuel but the behavior of the combustion process is generally more influenced on the distance of the mixture composition with respect to the stoichiometric one, other two parameters are defined in order to easily characterize the mixture. The first one is the air excess λ defined as:

$$\lambda = \frac{\alpha}{\alpha_{st}}. \tag{Eq3.3}$$

This parameter can be: $\lambda = 1$ for stoichiometric mixtures; $\lambda < 1$ for rich mixtures; $\lambda > 1$ for lean mixtures. The second parameter is simply the inverse of the air excess and is called equivalence ratio Φ:

$$\Phi = \frac{1}{\lambda} = \frac{\alpha_{st}}{\alpha}. \tag{Eq3.4}$$

In this second case the values of the equivalence ratio corresponding to the different mixtures are the dual of the air excess: $\Phi = 1$ for stoichiometric mixtures; $\Phi < 1$ for lean mixtures; $\Phi > 1$ for rich mixtures. These parameters play a fundamental role in the performance of the engine and the overall behavior of the vehicle, as we will see. What's more they represent an easier way to indicate the conditions at which the engine is working without the need of calculating the stoichiometric air/fuel ratio of the specific fuel.

The oxidation reactions of hydrocarbons develop across multiple steps of chain reactions dominated by active intermediate products. Generally the complete sequence of reactions that occur during an engine combustion is very complex and involves thousands of intermediate staps. However, as the combustion is a specific chemical reaction, it is always valid the general relationship from Arrhenius:

$$w_c = C\, p^n\, e^{-\frac{E_a}{RT}} \tag{Eq3.5}$$

Where:

- w_c is the combustion velocity;
- C, n and E_a (activation energy) are constants that depend on the properties of the fuel/air mixture;
- R is the universal gas constant;
- T is the temperature and p is the pressure.

Eq3.5 shows that the combustion velocity has a great dependence on the temperature but only a limited one on the pressure.

Another phenomenon that is deeply related to the combustion process is the autoignition. As the fuel and air are mixed it starts a series of preflame chain reactions that release energy and form the highly reactive intermediates products. If the energy released exceeds the energy removal the autoignition occurs and the combustion is triggered. In order to experimentally quantify such behavior, the fuel/air mixture is brought abruptly to high pressure from the starting conditions of temperature and pressure. The typical behavior of hydrocarbons is shown in Fig. 11.

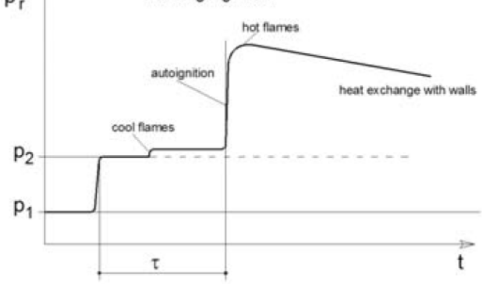


Fig. 11: Pressure vs time diagram of autoignition test.

The autoignition occurs differently from fuel to fuel. In the case of paraffins it occurs in two stages: the first one is just before the small increase of pressure due to cool flames and the second just before the real and complete ignition. The sum of these two intervals is called ignition delay time τ_{id} and can be calculated as the inverse of the combustion velocity:

$$\tau_{id} = A\, p^{-n}\, e^{\frac{E_a}{RT}} = \frac{1}{w_c} \qquad \text{(Eq3.6)}$$

Where, the various terms are the same of the Eq3.5 and A is a constant derived from empirical experiments.

Obviously, the higher is the velocity at which the reaction proceeds, the lower the time is needed to reach the ignition. For today's engine standards the value of τ_{id} is of the order of milliseconds and depends on the mixture properties as well as on the operative conditions.

The second fundamental parameter that deeply influences the combustion behavior is the laminar flame speed. To clarify the meaning of such a parameter let now imagine that we insert the fuel/air mixture in a closed vessel and that the charge is ignited right at the center of the sphere by means of a spark plug. What we would see is a flame propagating from the center of the sphere towards its boundaries dividing the volume in three different zones. The first region is the one made of the mixture through which the flame already went across and that is characterized by burned gases at high temperature and pressure. The second region is the narrow layer where the reactions occur that separates the two bigger regions; such a layer is called flame front. In the flame front there is the highest release of energy that heats the gases up to such a high temperature that visible energy is radiated. Finally there is the fresh charge that hasn't already been reached by the flame front and whose temperature remains lower even though it increases because of the compression that undergoes due to the increase of pressure in the volume. The velocity at which the flame front moves across the fresh charge is called laminar flame speed. The flame speed depends greatly on temperature, pressure and characteristics of the mixture such as composition of the fuel and λ. The typical laminar flame speed values as function of λ are displayed Fig. 12.

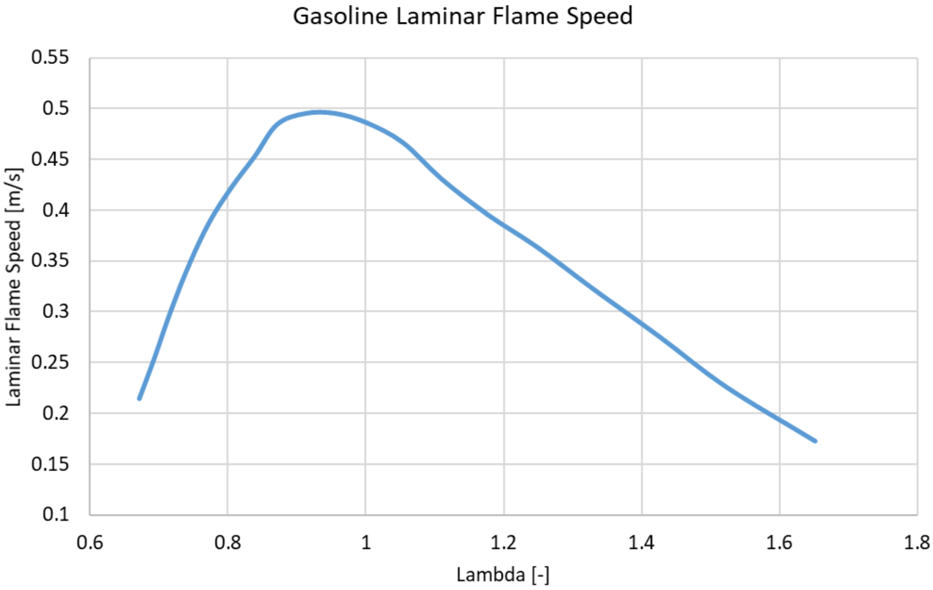


Fig. 12: Laminar flame speed of gasoline as function of the air excess at 338K and ambient pressure [33]

It is interesting to note that the laminar flame speed (LFS) has an asymmetric behavior around the stoichiometric value. In fact, the burning velocity has a maximum for slightly rich mixtures (λ~0.9) but for increasingly richer mixtures the value drops very sharply. This can be explained in terms of availability of oxygen. At λ slightly rich there is a little excess of fuel with respect to oxygen; hence, the flame front can always find the right amount of reactants to perform the combustion and therefore the velocity of propagation is the maximum one. However, if the amount of fuel is excessive, the flame front doesn't have enough oxygen available and the fuel itself acts as a diluter blocking the propagation of the flame. On the lean side, on the other hand, is the amount of air that acts as a diluter blocking the flame front propagation and some part of the energy produced during the reaction is spent to heat inert gases. Nevertheless the reduction of LFS in lean mixtures is much less steep than on the rich side, because there is always oxygen available on the contrary of rich mixtures where the higher amount of fuel chokes the flame.

The last important parameter of the combustion is the laminar flame front thickness, i.e. the dimension of the reacting layer in the direction of the propagation. This parameter is important because in this region all the reaction occur and therefore represents the limit to the LFS. During an ideally pure laminar combustion such limit is due to the speed at which reactants can diffuse inside the zone. As the LFS increases the flame thickness decreases up to a value of more or less 0.2 mm. Such a value is so small that usually the flame front can be modeled as a discontinuity between the two regions of burned gases and fresh charge.

In practical engines problems, however, the combustion is always turbulent due to the motion of gases inside the combustion chamber. Under the effect of turbulence the charge in the cylinder is moved by large vortexes whose dimension is close to that of the combustion chamber, and small eddies which are instead much smaller. The large vortexes stretch the flame front in big convolutions thereby greatly increasing the total area of the flame front. Small eddies, instead, are smaller than the flame front thickness and play an important role in intensifying the mixing in the reaction zone and in enlarging the flame front. Those two effects greatly increase the flame speed, which in this case is no longer laminar but turbulent, up to 5-20 m/s [13], which means more or less 10-40 times faster than the maximum LFS of Fig. 12. An increase in the speed of flame propagation is always an interesting feature for the behavior of the engine because combustion resemble closer the ideal instantaneous heat increase and reduces the probability of knock. Nonetheless, if turbulence is too high there might be misfire because the energy released by the spark-plug is unable to start the combustion because the first kernel is swept away and the propagation doesn't proceed.

The technical features of combustion described until now play an important role both in the modeling of the process and in the development of the engine as parameters that can be wisely adjusted in order to reach the desired performances or to solve problems that arise during the development.

In SI engines the fuel is completely vaporized and homogeneously premixed with air and residual gas (EGR), if available, before the beginning of the combustion. The starting point, also called spark advance, must be optimized in order to distribute the combustion process around the top dead center of the piston run. The value of the spark advance depends on type of vehicle, the dimensions of the combustion chamber, the engine speed at which it performs the maximum power and many other parameters; anyway, it is around the end of the compression stroke (20°-40° before top dead center [13]). At that moment an electric arch is created between the electrodes of the sparkplug that causes a great energy release and the combustion starts. The normal steps of combustion in a SI engine are:

- ignition of the mixture by means of a sparkplug;
- the flame propagates to whole volume without any sudden increase of its velocity.

The combustion can be then divided in different phases according to the major phenomena that occur. It is important to bear in mind that such division is useful to study the process and characterize it but has no real counterpart in the real combustion where, of course, the whole process smoothly proceeds without any discontinuity.

During the combustion inside the volume where the process occurs many different physical phenomena are taking place, for example the movement of the piston, the heat exchange with the coolant and the energy release, which determine the pressure history of the piston (Fig. 13). The main phases are:

- Initial flame development phase: the small volume of mixture ignited by the sparkplug is gradually transformed into a developed front of turbulent flame;
- Rapid burning phase: turbulent flame rapidly spreads over the principal part of the combustion chamber, while the volume remains theoretically constant because the piston slowly moves around the top dead center;
- Final combustion completion: the mixture completes its oxidation processes behind the flame front during the expansion stroke.

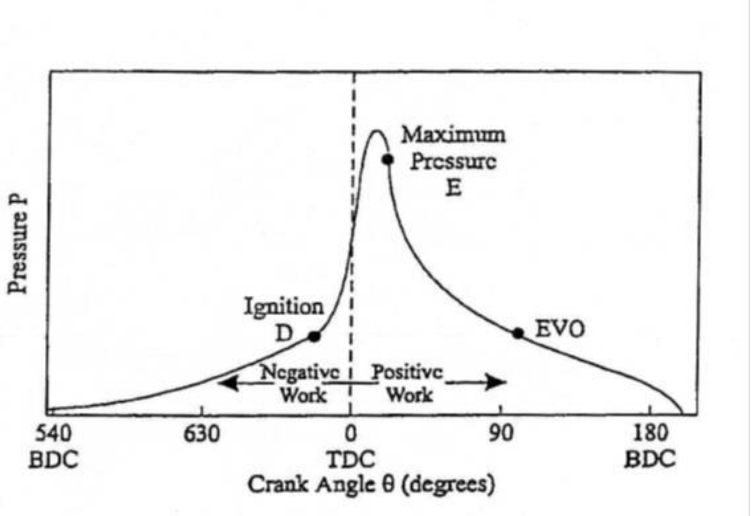


Fig. 13: Pressure history inside the cylinder during combustion

In conclusion, the laminar flame speed seems to play an important role only in the first part of the combustion as the small initial kernel is developing. Nevertheless, as we will see later, the LFS will be fundamental for the simulation of the whole process.

The two most critical combustion problems in SI engines are the surface ignition and the knock. Regarding the first problem, the ignition of the mixture is not controlled by discharge of energy between the two electrodes of the sparkplug but there is a hot point in the cylinder head that causes a second uncontrolled flame front as shown in Fig. 14. The greatest problem about this phenomenon is that it anticipates the ignition moment with comparison to the optimum one.

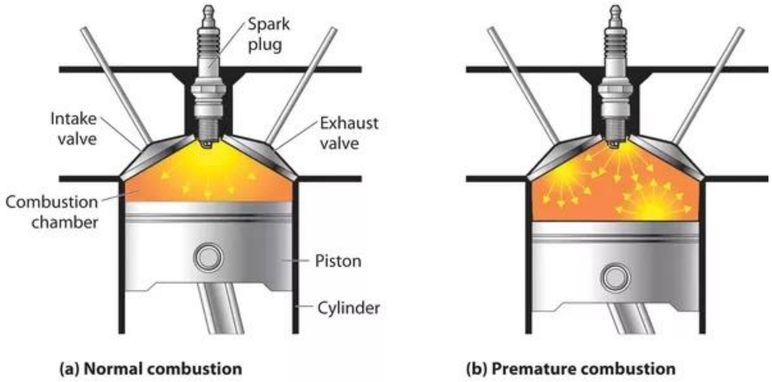
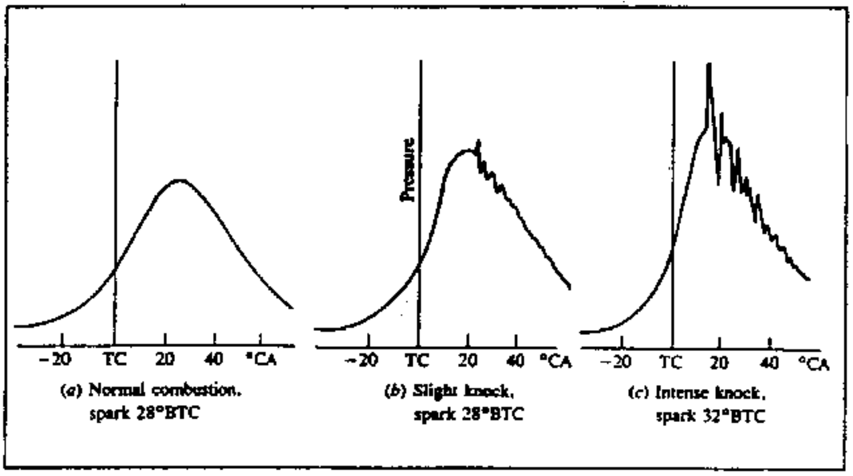


Fig. 14: Representation of surface ignition

The causes of surface ignition are mostly connected to a wrong design of a particular geometry, like sharp edges, exhaust valves, cavities in the piston and so on, or the use of a bad quality lubricant.

More problematic is the solution to the second abnormal combustion behavior. Indeed, knock is due to the auto-ignition of the remaining fresh charge (called end-gas) before the arrival of the flame front. In sever engine operating conditions it may happen that the end-gas is brought to such a high level of temperature and pressure, that one or more volumes auto-ignite ahead the arrival of the flame front. The high energy release that follows the autoignition produce a significant increase of temperature and pressure that cause shockwaves that propagate from the auto-ignition point throughout the chamber. The pressure waves are repeatedly reflected by walls and create an oscillatory pressure trend versus time, as shown in Fig. 15.



(a) Normal combustion, spark 28°BTC

(b) Slight knock, spark 28°BTC

(c) Intense knock, spark 32°BTC

Fig. 15: Pressure vs crank angle diagram of an engine where knock occurs

There are two types of knock: the light knock, which occurs only in part of the cycles (Fig. 15-b), and heavy knock (Fig. 15-c) that occurs in all the cycles and causes great damages to the engine. Solutions to the knock problems are mostly related to enhance the capacity of the end-gas to resist to knock, like using gasolines with a higher octane number, reducing the compression ratio of the engine, therefore reducing its efficiency, reducing the spark advance and others. Another type of solution is to increase the velocity of the combustion process so that the end-gas has no time to auto-ignite. The most important aspect of knock is that it poses the limits to the engine performances since it limits the compression ratio. The main problems are related to mechanical damages of the piston head as well as to the valves and to the combustion chamber.

As already stressed, abnormal combustion processes, especially knock, show the profound connection between engine and the intrinsic limits that the characteristics of the fuel may try to move towards better performances. However, performances cannot be considered the only interesting parameter that has to be matched during the development of the engine. Indeed the process and the fuel also define the quality and the quantity of the pollutants emissions that are connected to the engine operation. Due to the widespread use of ICE, especially in cities, the problem of pollutant emissions is becoming increasingly important and, therefore, controlled. In developed countries, and especially in Europe, the regulation is becoming more and more stringent about this aspect and the solutions used by the O&Ms more and more sophisticated and efficient. As we already saw, the emissions of an ICE that is working properly are CO_2, water and, in real engines, pollutants.

Carbon dioxide is regarded usually not as a pollutant, since has no poisoning effect on human health, but as an agent that increases the greenhouse effect and that is considered the major responsible of the global warming. Pollutants emissions, instead, cause problems to the human health especially in the concentrations that are typically produced during the combustion process. In our thesis we didn't deal with pollutants emissions, for this reason we won't go in deeper detail about this issue.

Now that we have described the combustion process from a theoretical point of view we can see how it is modeled.

The main pollutants species are reported in

Table *1*.

Table 1: Main pollutants species and produced impact [13]

Exhausted pollutant	Produced impact
Carbon monoxide (CO)	Poisoning, cardiovascular disease, reduce oxygen delivery to body organs
Unburned hydrocarbons (HC)	Photochemical smog, physiological harms; polycyclic aromatics hydrocarbons (PAH) have carcinogenic effects
Particulate matter (PM)	Lung damages, physiological harms, carry PAH
Nitrogen oxides (NOx)	Smog, acid rains, toxic chemicals, may cause toxic chemical compounds
Sulphur oxides (SO2 and SO3)	Smog, acid rains, lung diseases

1.2 Simulation of combustion in QuickSim

QuickSim is a simulation tool specifically designed for ICE that has been developed starting from the general CFD code STAR-CD. During the years models have been written and implemented in the software to make it more efficient and faster. The software underwent a large number of validations and applications to industrial cases that proved its ability to correctly reproduce the engine behaviour.

The main time-consuming process to compute during the simulation of the engine cycle is the combustion. The combustion of an arbitrary fuel is composed of thousands of reactions that involve hundreds of different chemical species.

Table 2: Combustion of different fuels: complexity estimation [31]

Fuel	Number of species	Number of chemical reactions
H_2/O_2 Oxidation	8	40
CH_4/O_2 Oxidation	34	400
$CH_4/O_2/N_2$ Oxidation	54	640
n-C_7H_{16}/i-C_8H_{18}/O_2 Oxidation	100	740
n-C_7H_{16}/i-C_8H_{18}/O_2 Oxidation incl. LTC	1000	7400

In Table 2 is reported an estimation of the number of species and reactions for various oxidation reactions. It becomes evident how the complexity of the reaction scheme remarkably increases with rising complexity of molecular structure of the implemented fuel. In particular combustion processes at low temperature (LTC), due to the very low reaction speed, there is a drastic increase of the number of intermediate products of combustion involved in the process.

The traditional approach is to add the reaction mechanisms for the species in the CFD software and perform the calculations required for each cell. Starting from the approach of a detailed chemical analysis of all the species present in the working fluid it is useful, in terms of CPU-time, to find a strategy that permits to substitute the original scheme with a new one described by a limited number of relevant species. This can be achieved with reduced reaction mechanism which is still a comprehensive combustion model and theoretically allows a combined calculation of both the evolution of flame propagation and the fluid properties as they are affected by the flame front. As we already saw, this type of calculation adds a huge number of transport equations and usually requires also to use more complicated and precise equations of state that take into account the different mixing behaviors of the mixture. Such a complexity makes the problem very stiff and convergence is not easily achieved. What's more the results usually heavily depend on the settings that are made on the reduced mechanism: they are reliable only at the conditions they are validated for in terms of temperature, pressure and mixture composition. Hence, such a solution is of no practical interest in CFD simulations.

In *QuickSim* the model was developed targeting a CPU-time-efficient description of the thermodynamic properties of the working fluid. The most important features that have been implemented are:

- Few scalars for the description of the mixture;
- Fast calculation of the thermodynamic properties thanks to comprehensive databases or trained neural networks.

At the flame front *QuickSim* performs calculations using two separate models for thermodynamic properties and flame propagation [31]. The description of mixture composition is based on six scalars, presented in Table 3 and in Fig. 16, which describe the reactive working fluid in an inhomogeneous mixture.

Table 3: Scalars definition as reported in [31]

Scalar No.	**Variable name**	**Description**
1	w_{Air,U_j}	Mass fraction of fresh air
2	w_{F,U_j}	Mass fraction of fresh vaporized fuel
3	$w_{EGR-Air,U_j}$	Mass fraction of air that has previously produced EGR (burned gases of the previous cycle)
4	w_{EGR-F,U_j}	Mass fraction of vaporized fuel that has previously produced EGR (burned gas of the previous cycle)
5	w_{Air,B_j}	Mass fraction of air that has previously produced burned gas
6	w_{F,B_j}	Mass fraction of vaporized fuel that has previously produced burned gas

In this approach the scalars do not refer to well defined species but are optimized in order to describe and identify the main working fluid groups of interest (fresh gas, EGR and burned gases) during all the phases of the engine operating cycle. Consequently, the modeling of all engine processes, and in particular combustion, has to be adapted and also optimized to this formulation, so that, at the end, the CFD simulation can gain in efficiency and in reliability. This approach has proved its ability to well predict the overall behavior of the working fluid in more than ten years during which underwent a big number of validations of practical industrial cases.

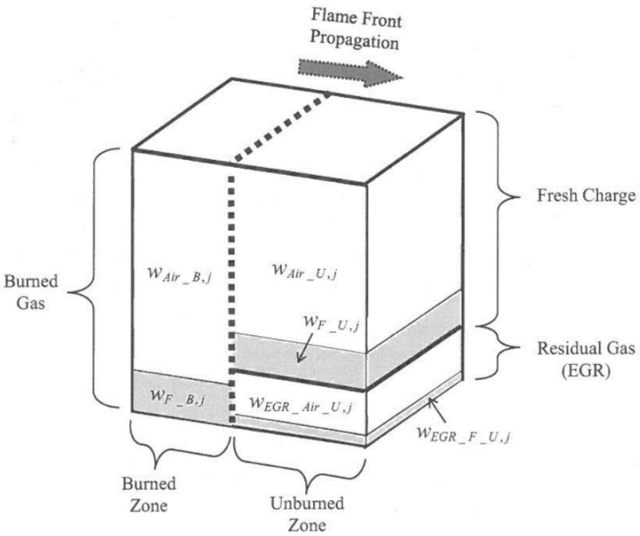


Fig. 16: Definition of the composition of the working fluid in the 3D-CFD-cell of QuickSim using six scalars [31]

The model for combustion in *QuickSim* is the so called flamelet approach. This model views the turbulent flame front as consisting of an ensemble of stretched laminar flamelets. Turbulent flames are described as wrinkled, moving laminar sheets and the major heat release happens in the vicinity of small reacting layers in regions where the air/fuel ratio is close to the stoichiometric. Such structures are called flamelets and are thought to be embedded in the turbulent flow. The main idea is that time scales of turbulence are much longer than the ones of reactions in the flame front. Hence, the flamelets are assumed to resemble the structure and characteristics of laminar flamelets that are stretched and strained by the turbulence. The great advantage of this assumption is that the properties of flamelets in terms of temperature, density and species mass fractions can be evaluated once and for all outside the flow field calculation to create a so called "laminar flamelet library" [32].

In the particular case of ICE combustion, we are interested in the velocity at which the flame front propagates. The increase in the turbulent flame speed with respect to the laminar one, according to this idea, is due to the increase of the effective surface in the wrinkled flame and, therefore, of the area where the oxidation is performed. To give a more precise idea of the effect of the turbulent stretching on the burning speed, let us now analyze the particular case of a flame propagating in a pipe.

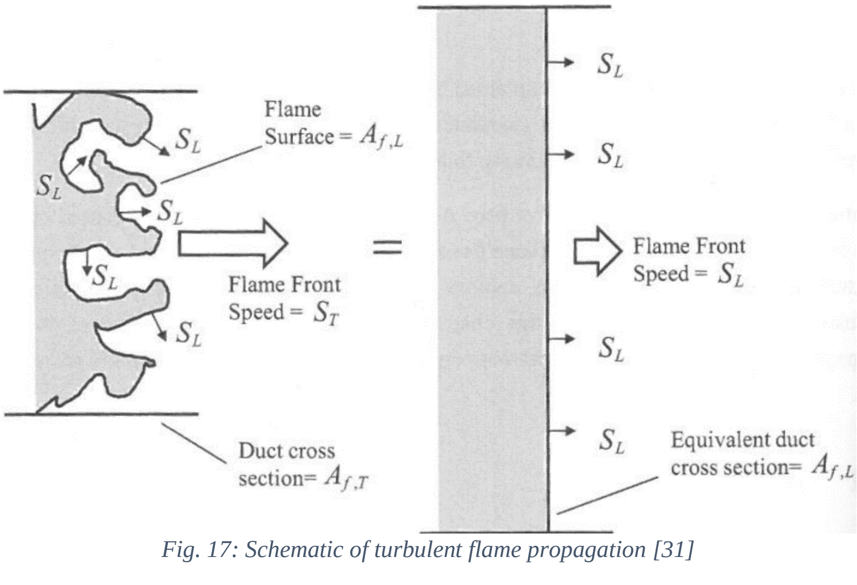


Fig. 17: Schematic of turbulent flame propagation [31]

We can define $A_{f,L}$ as the flame surface; $A_{f,T}$ as the duct cross section; S_T as the flame front speed and S_L as the laminar flame speed. Using the mass balance equation, a relationship between the laminar velocity and the turbulent one can be obtained as follow:

$$\rho_U\, S_T\, A_{f,T} = \rho_U\, S_L A_{f,L} \rightarrow S_T = S_L \frac{A_{f,L}}{A_{f,T}}. \qquad \text{(Eq3.7)}$$

Where, of course, $A_{f,L} \gg A_{f,T}$ because of the turbulent stretching. In Eq3.7 the laminar flame is the fundamental parameter that can be estimated outside the fluid flow calculation ad stored in a database as function of four variables: pressure, temperature, λ and EGR rate. During the calculation, then, in each cell of the mesh there is an evaluation of the operating conditions in order to choose from the database the corresponding value of laminar flame speed. On the other hand, the ratio of the two areas on the right hand side of Eq3.7, which is generally called K, is not a property that can be evaluated once and for all and then stored. Indeed, the factor K depends on the particular conditions of turbulence that affect one precise cell of the domain and depends on the specific geometry of the problem. Therefore it must be evaluated on the basis of some parameter that is simple to evaluate and that takes into account the wrinkling and stretching of the laminar flamelet due to turbulence. One possibility is to use the relationship of Eq3.8:

$$K = \frac{S_T}{S_L} \sim \frac{u'}{S_L} \qquad \text{(Eq3.8)}$$

Where u' is the turbulent intensity. The real behavior shows that there is no such a linear dependence but after a certain value of u' the turbulent velocity reaches the maximum value and for even greater values of turbulence intensity it declines and finally the flame extinguishes. The physical explanation of such behavior can be explained considering in detail the effect of turbulence. For low values of u' an increase in turbulence means a greater stretching, therefore an increase of the oxidation area and of the combustion speed. In this phase the turbulence acts as a combustion enhancer because, among the other things it supplies reactants towards the flame. On the other hand, the high convection rates lead to a steeper gradients of the flame surface that increase the local diffusive losses. When the finite rate of the chemical kinetics in unable to provide the reactants fast enough to the flame front to produce products which are immediately swept away together with the enthalpy, combustion slows down. Therefore the local flame temperature decreases and also the reaction rate that depends deeply on temperature. If the temperature of combustion becomes too low the reaction blocks and the flame extinguishes. This effect is more important for lean mixtures due to many different physical and chemical reasons, like the lower laminar flame speed.

The modeling of the combustion requires a tool to identify the position of the flame front. The model implemented in *QuickSim* is similar to the one proposed by Weller [34]. For more details please refer to [31].

We must now analyze gasolines in order to understand how to model the fuel.

1.3 Gasolines

Our thesis focuses on how to simulate the characteristics of a gasoline blended with ethanol in order to produce the laminar flamelet library that is then implemented in *QuickSim*.

The most widely produced biofuel is ethanol and the way it is most used is blended with gasolines in order to reduce the dependence on the fossil fuels. Since gasolines play an important role in the simulation it is fundamental to well understand their characteristics.

Gasolines are the distillation product of raw petroleum from oil wells. They consist of several hydrocarbons of different molecular weight plus some other organic fractions. Gasolines are the lightest petroleum-derived liquid product, whose density is between 0.73 and 0.76 kg/m^3 and are obtained by distillation of temperatures in the range of 25°C to 200°C. Gasolines' composition has a high variability because the mixtures usually slightly change during winter or summer, in order optimize the engine performance, and because of the great number of producers.

Gasolines' characteristics can be divided in physical and chemical ones; both of them are important because affect the engine behavior, the combustion process and other phenomena such as injection and impingement on cylinder wall.

Physical properties determine engine related important parameters and typically such values are measured during the certification process of gasolines. The most important physical properties are: volatility, viscosity, density and surface tension; however, these parameters are not usually available and are of difficult evaluation without specific experiments. The only properties of interest in our case is density that can be evaluated by means of the formula:

$$\rho_{mix} = \sum_{i=1}^{N_{species}} \frac{\rho_i}{y_i}. \qquad \text{(Eq3.9)}$$

Where y_i is the mass fraction of the different species that compose the gasoline.

Since we didn't deal with problematics connected with physical properties of gasoline there's no need here to go in further detail and for a description of how they are modeled in *QuickSim* please refer to [31].

More interesting from our point of view are the chemical properties of gasolines. Some of them are the LHV and air/fuel ratio that we already described in previews sections. The others are molecular weight, the octane rating, the chemical composition, hydrogen to carbon ratio and the oxygen to carbon ratio. The average molecular weight (MW) of gasolines is around 90 kg/kmol but it drastically drops in the case of blending of ethanol because it is a very light compound compared to the long chain hydrocarbons. The evaluation of the molecular weight can be easily done by means of the following formula once the composition in known:

$$MW_{mix} = \sum_{i=1}^{N_{species}} MW_i \, x_i \qquad \text{(Eq.3.10)}$$

Where x_i is the molar fraction.

The octane rating of gasolines is one of the most important properties of fuels and it is a measure of the resistance of fuels to knock. The knocking phenomenon is very complex and depends on many parameters such as geometries, local temperatures and load but primarily it depends on the anti-knock property of the fuel. Therefore, two different standard experimental methodologies have been developed in order to make comparable the different behaviors of various fuels. Both of these methodologies are based on the definition of a particular monocylinder engine able to change the compression ratio and to measure knock. Afterwards, two fuels are chosen as references for the two extreme knocking behaviors: isooctane is the fuel with the lower knocking tendency and n-heptane is the one with the highest tendency. The fuel that has to be tested is supplied to the engine as it is running and the compression ratio is changed until the standard knock intensity is reached. Then the compression ratio and other engine conditions are kept constant and different mixtures of the two reference fuels are supplied until the same knock intensity is reached. The molar mass of isooctane in the mixture is the octane number of the fuel. The conditions at which the engine is tested are different according to the methodologies; one of them is the so called Research Octane Number (RON) and is representative of normal operating conditions, the other one is called Motor Octane Number (MON) and is thought to model the behavior of the fuel in more severe conditions (i.e. full load, low rpm and high inlet temperature). The conditions are reported in Table 4.

Table 4: Main standardized characteristics and operating conditions for octane rating experiments [13]

Engine	Motor method	Research method
Cylinder bore [mm]	82.55	82.55
Piston stroke [mm]	114.3	114.3
Swept volume [cm^3]	612	612
Compression ratio [-]	4 - 18	4 – 18
Engine speed [rpm]	900	600
Spark advance [°CA]	14 – 26	14 - 26
Coolant temperature [°C]	100	100
Inlet temperature [°C]	149	52
Air humidity [g/kg_{air}]	3.6 – 7.2	3.6 – 7.2
Air/Fuel ratio [-]	Settled for maximum knock	

Usually RON and MON have different values for the same fuel because of the different aspects of the fuel's behavior that are testing and usually RON is greater the MON. To take into account such differences there are two more indexes that are widely used: the first one is the Anti Knock Index (AKI) that is the average value between RON and MON:

$$AKI = \frac{RON + MON}{2}; \tag{Eq3.10}$$

the second one is the Octane Sensitivity (OS), which is simply the difference between the two indexes:

$$OS = RON - MON. \tag{Eq3.11}$$

Nowadays there is the interest in developing new indexes that account for the great change in the normal engine operating conditions that happened in the last ten years or so especially due to the downsizing and boosting (turbocharging) of engines [35]. Nonetheless, for the purposes of our thesis we will always refer to RON and MON because are the most validated and because they are still a valid description of the fuel rating.

The octane rating is inextricably linked also to the composition of the fuel. Gasolines are composed by thousands of species and detailed data about the composition is unavailable unless long and expensive experiments are performed. Nevertheless, what is usually available is the so called "PIONA composition". The PIONA composition takes its name out of the most important families of chemical compounds that are present in a gasoline: paraffins, iso-paraffins, olefins, naphtenes and aromatics. In recent fuels it is common to find, together with these compounds also oxygenates that are usually a small fraction and whose molecular structure can vary widely; the most common oxygenated compounds are MTBE (methyl tert-buthyl ether), ETBE (ethyl tert-buthyl ether) and ethanol, which is the most used by far. MTBE and ETBE are compounds synthetized to increase the octane rating of the gasoline; they are not naturally present in gasolines. The different families of chemical compounds are briefly described in Table 5 together with compositional values of a typical oxygenated gasoline.

Table 5: Chemical families and main species present in a typical oxygenated gasoline

Chemical family	Main species	Indicative content of the chemical family
Linear paraffins	n-heptane n-pentane	10%
Branched (iso-) paraffins	isooctane isopentane	35%

Olefins	cyclopentene	5%
Naphtenes (cyclic paraffins)	cyclopentane cyclohexane	5%
Aromatics	toluene	30%
Oxygenated	MTBE ETBE ethanol	10%

In reality is very complicated to obtain such a detailed information about a gasoline, therefore typically more parameters are given that somehow resume the composition of the gasoline. The two ratios that usually accompany the gasoline data are the hydrogen to carbon (H/C) and the oxygen to carbon (O/C) ones. They can be calculated as:

$$\frac{H}{C} = \frac{\sum_{i=1}^{N_{species}} x_i H_i}{\sum_{i=1}^{N_{species}} x_i C_i} \qquad \text{(Eq3.12)}$$

$$\frac{O}{C} = \frac{\sum_{i=1}^{N_{species}} x_i O_i}{\sum_{i=1}^{N_{species}} x_i C_i}. \qquad \text{(Eq3.13)}$$

These two simple parameters have a relatively low relevance in describing the complex composition of the gasoline because they are too general, however, especially the O/C ratio is deeply related with other parameters like the blending of ethanol in gasoline and therefore their knowledge increases the insight on the fuel.

In conclusion gasolines are complex systems susceptible of many variations and whose properties and compositions are usually unknown or only a little information is provided. It is clear that the simulation of such systems shall not concentrate on the many small differences, but the focus shall remain the simulation of whole ICE. In this framework we must work in order to find a way of modeling gasolines that is flexible enough to cover a wide range of very similar compositions and precise enough to provide solutions that are interesting for practical applications.

1.4 Software tools

In order to perform the simulation of the combustion, *QuickSim* relies on models whose main advantages are to give a good solution in a very short CPU-time. Nonetheless, such interesting achievements require some simplification and the loss of generality of the software.

During the modeling of combustion *QuickSim* must evaluate the flame speed in each cell that is spanned by the flame front. In order to do so it uses a correlation like the one of Eq3.8 that requires both the knowledge of the turbulence intensity, which is available from the solution of the fluid flow field, and the laminar flame speed. The values of laminar flame speed, thanks to the flamelet approach, are calculated once and for all and are available in a database that is connected to *QuickSim* thus enabling the fast calculation that is one of the major advantages of the software. Similar considerations must be done to evaluate knock: in each cell *QuickSim* calculates how much time is left before the autoignition of the fresh charge according to the thermodynamic conditions. Also in this case the calculation is done before the simulation and the data regarding the ignition delay are stored in a database connected to *QuickSim*.

In both cases the database has to be designed according to the data that the simulation can provide, that means that the values of laminar flame speed and ignition delay time are both function of temperature, pressure, air excess (λ), EGR rate and the EGR composition. In particular the composition of the EGR is fundamentally an information about the λ at the previous cycle that determines the composition of the exhaust gases and how they influence the combustion if they are diluted with fresh charge. Indeed, if at the previous cycle there was an

excess of fuel (rich mixture) and some CO formed due to lack of oxygen available to complete the oxidation to CO_2, hence, when recirculated, burned gases will not act as inert diluting the fresh mixture but will burn the remaining amount of CO. Therefore, to consider the composition of the EGR is fundamental due to different behaviour of the mixture in the combustion chamber.
To produce the database of laminar flame speed and ignition delay time there are two main possibilities: to use an empirical formula like the one proposed by Gülder [36] or to perform simulations of 1D laminar flame speed using the open source software CANTERA.
The solution that has been used until recent days in *QuickSim* is the empirical formula from Gülder:

$$S_{UO}(\phi, T, P) = S_{UO}(\phi)\left[\frac{T_U}{T_O}\right]^{\alpha}\left[\frac{P}{P_O}\right]^{\beta}(1.0 - f \cdot F) \qquad \text{(Eq3.14)}$$

Where:

- $S_{UO}(\phi) = Z \cdot W \cdot \phi^{\eta} \cdot e^{[-\xi(\phi-1.075)^2]}$ is a correlation for laminar flame speed at room temperature and ambient pressure based on empirical measurements with some physics embedded;
- $Z, W, \eta, \xi, \alpha, \beta$ are constants whose value have been tabulated for many different mixtures compositions and fuels;
- F is the mole fraction of the inert diluent;
- f is a constant whose value is tabulated.

This correlation has been developed starting from a large number of experimentations done at the test bench during which the various dependencies have been analyzed (compositions, temperature, pressure and diluent) and the most general solution possible has been chosen. The great advantage of such a formula is that the calculation process of the whole database is really fast because it consists just in an algebraic correlation. The drawback, instead, is that a lot of different parameters have to be known. If the fuel that is used in the simulation is not one of the fuels analyzed in [36] and the constants aren't available somewhere else in literature, then the only solution is to perform experiments and re-calibrate the formula. In this way much of the potentials benefits of performing a simulation are lost because of the time and costs required for the experiment and the loss of predictability of the software. Such a drawback is even more critical in the case of testing new fuels which may not be available or still not even produced. Although this approach proved to be reliable and able to provide good results in a wide number of industrial applications, the lack of flexibility and the incapacity of prediction of new fuels' behavior make so that a new way of producing the database of laminar flame speed and ignition delay time are being developed.
The approach based on the simulation in CANTERA is exactly aimed to reduce the need of tuning the simulation on the kind of fuel is being used. First of all, CANTERA is a free library that can be implemented in Python; in our particular case we used Python's interface called Anaconda. CANTERA is a suite of object-oriented software tools for problems involving chemical kinetics, thermodynamics and/or transport properties. The type of objects represents phases of matter, interfaces between faces, time-dependent reactor networks and steady one-dimensional reacting flows.
The simulation of the laminar flame speed is a particular case of the more general category of the steady one-dimensional reacting flow. To perform the simulation CANTERA calculates the conservation equations of a reacting gaseous mixture with the simplifications for a 1D problem [37]:

$$\frac{d\dot{m}''}{dx} = 0 \qquad \text{(Eq3.15)}$$

$$\frac{\dot{m}''dY_i}{dx} + \frac{d}{dx}\left(\rho Y_i v_{i,diff}\right) = \dot{\omega}_i MW_i \quad for\ i = 1,2,\dots,N_{species} \tag{Eq3.16}$$

$$\dot{m}''c_p\frac{dT}{dx} + \frac{d}{dx}\left(-k\frac{dT}{dx}\right) + \sum_{i=1}^{N_{species}} \rho Y_i v_{i,diff} c_{p,i}\frac{dT}{dx} = -\sum_{i=1}^{N_{species}} h_i\dot{\omega}MW_i \tag{Eq3.17}$$

Where:

- $\dot{m}''$ is the mass flux;
- Y_i is the species mass fraction;
- $v_{i,diff}$ is the species diffusional velocity;
- $\dot{\omega}$ is the species reaction rate;
- MW_i is the species molar weight.

The set of equations includes continuity (Eq3.15), species conservation (Eq3.16) and energy conservation (Eq3.17), written as function of the generic coordinate x. A schematic of the domain is shown in Fig. 18.

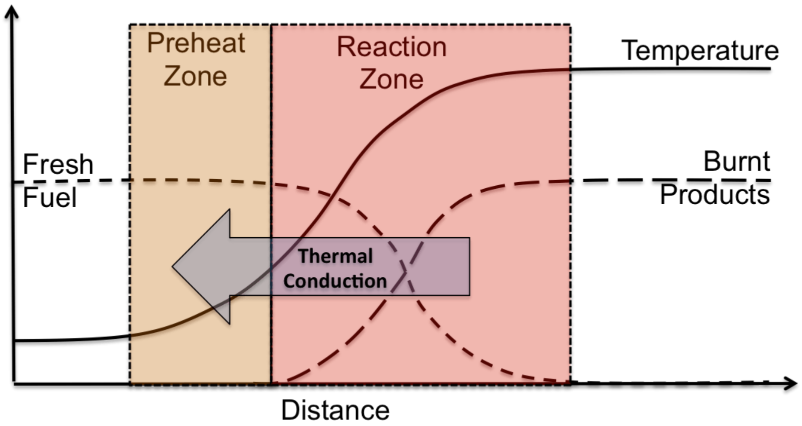


Fig. 18: Schematic of the 1D simulation's domain

The laminar flame speed can be calculated starting from the mass flux as follow:

$$S_l = \frac{\dot{m}''}{\rho}. \tag{Eq3.18}$$

In order to close the problem, CANTERA uses the ideal gas equation of state and temperature dependent polynomials for gas properties and finally a reaction mechanism is required to give an information about the species reaction rate $\dot{\omega}$. The first step is to discretize the one-dimensional domain with an initial grid. The solver will then automatically refine the mesh locally until and accurate solution of the steady state is achieved. The nth equation at the general jth point is [37]:

$$F_{j,n}(\phi) = 0 \tag{Eq3.19}$$

which depends only on the values at points j-1, j and j+1 therefore making the resulting system a banded matrix. The numerical solution is achieved using the modified Newton's method; if the solution of the steady state problem fails a pseudo-transient solution is attempted because in the case the convergence domain becomes bigger (Fig. 19).

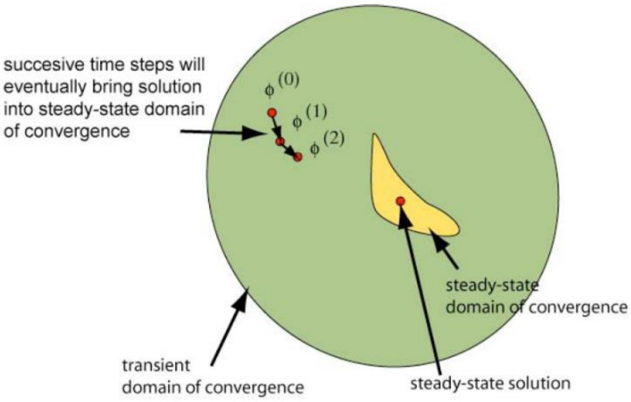


Fig. 19: Convergence domains in steady-state or pseudo-transient

Usually we checked the convergence of the system by means of the plot of the temperature. The most important check is that at the very beginning of the domain there aren't gradients because the software uses for the calculation of the laminar flame speed the value at the beginning of the domain; in the case of gradients the value is not reliable. Another important check is that the shape of the temperature's curve presents a steep gradient, i.e. the flame front is small and well localized, but without discontinuities. For the experience we did during the work, we can state that this check is fundamental when new situations are modeled because the initial grid deeply influences the convergence. Pressure and initial temperature play and important role in the system's solution and the grid has to be adapted to such parameters. Nevertheless, once that the right dimension of the initial grid is found, the convergence is generally always achieved. The temperature's shape is a parameter also to control the convergence connected to other parameters such as the reliability of the reaction mechanism, which is another fundamental part of the simulation that will be discussed in greater detail later.

CANTERA, to solve the problem, has to deal with Jacobian matrices that make the calculation procedure not very robust and greatly sensitive on the initial conditions and settings of the problem, type of reaction mechanism used and the transport model chosen. In the case of a detailed mechanism the solution might be very accurate but it can take up to several days.

Much faster, regardless the reaction mechanism used, is the simulation of the ignition delay. In this case the simulation is zero-dimensional. The software creates a net of batch reactors, i.e. perfectly stirred, in which the ideal gas is simulated as a mixture evolving towards the equilibrium state. Since the simulation is time dependent, it allows to calculate the time before the autoignition of the system occurs. The two main parameters in this case are the time step and the difference between two consecutive temperatures that is assumed to be the value at which autoignition happens. During our work we used a script where the time step is implemented as a function of the gradient of temperature and performs a refinement in the case the temperature increase is too steep until a very precise value of the autoignition time is achieved. Concerning the temperature difference, instead, we performed a sensitivity analysis by changing the value in many different situations of pressure, temperature, equivalence ratio and composition. The results are shown in Fig. 20 as representative of all the different situations tested.

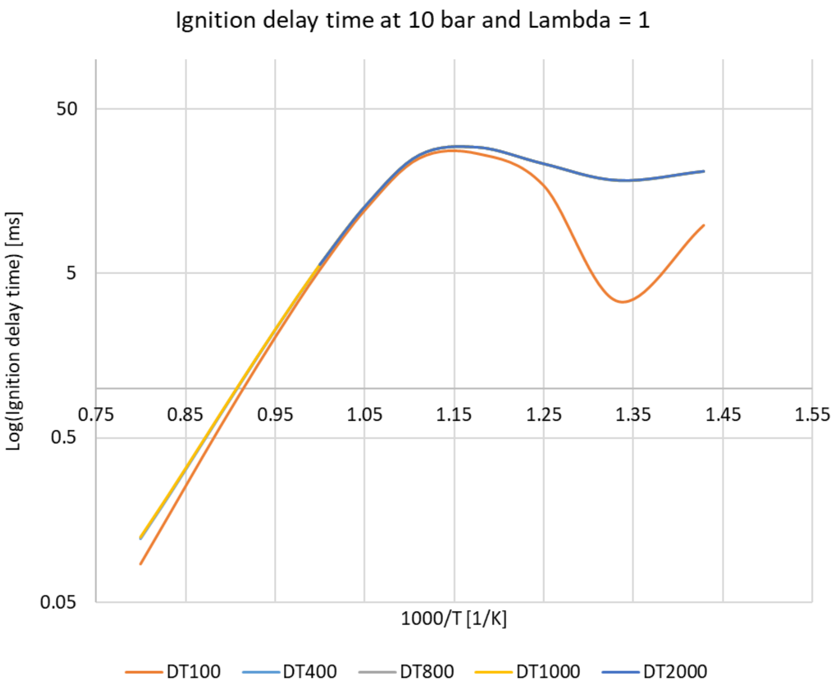


Fig. 20: Sensitivity analysis of the autoignition temperature difference of a mixture of isooctane (90%) and n-heptane (10%). In the graphic DT is the temperature difference we are analysing

The most important error appears for very low values of temperature difference when the curve shows an unrealistic decrease of the ignition delay time (IDT) at low temperatures followed by a steep increase of the same for higher values of temperature; a similar shape may actually occur in the autoignition process of paraffins, and is called the negative temperature coefficient (NTC) region. As we will see the shape of this region is, however, not so marked and the reduction in the IDT is less important and it happens at higher temperature's values. For these reasons we can exclude that this shape represents the NTC region. The only other physical phenomenon that occurs during autoignition are the cool flames that are characteristic of the paraffins' combustion and whose appearance is accompanied by a slight increase in the mixture's temperature.

It seems therefore plausible that values of temperature differences too low take into account the appearance of cool flames that, however, do not cause knock and therefore to include this information in the database is wrong. The second error appears at temperature differences too high like for example 2000°C. In this case the result is an unrealistic behaviour of autoignition at high temperature where it seems that the mixture has no autoignition. The explanation in this case is that the temperature of the mixture after the autoignition is almost constant and around the value of 2800K. If the temperature difference is set to a too high value, then, as the initial temperature increases, the temperature of autoignition should be higher and higher up to unrealistic values. For this reason, around 1000K of initial temperature the curve is interrupted. In reality, we saw that there is a wide range of temperature differences that are acceptable but the best solution that arose after many different simulations is 400K. Eventually, the simulation of IDT is much more stable and fast with respect to the 1D flame simulation. The most influencing parameter is the reaction mechanism chosen, even though convergence is almost always achieved. In conclusion, the new approach to produce the database necessary for the simulation in *QuickSim* of the combustion and the autoignition is based on the simulation of the 1D flame and the autoignition behavior in CANTERA. To perform such simulations the script need information about the composition of the mixture and a reaction mechanism. What's more all these blocks must work harmoniously together. We will now deal with reaction mechanisms.

1.5 Reaction mechanisms

The need for always more precisely designed combustion devices as well as the control of pollutants emissions from ICEs pushed in the last twenty-five years the development of many different reaction mechanisms. Such systems aim to describe accurately the chemistry of the combustion processes by means of a more or less big collection of elementary reaction steps that occur in the reacting layer. In order to do so, such systems need as input information the composition of the mixture that one wants to simulate together with the thermodynamic conditions of the system. As we will see later in greater detail, the mixture is called surrogate because tries to mimic the behavior of a gasoline, which is composed by thousands of components, by means of a limited number of species. Once that the reaction mechanism received that information the calculation can start, as we saw in the previews paragraph, until the convergence is reached. The main outputs are the chemical composition of the products and information about how the physical system has changed.

In general the first part of the reaction mechanism is a list of the species that are implemented, i.e. whose reaction path comprise all the intermediate reactions and therefore it can give a good prediction of the evolution of the system.

Reaction mechanisms are classified according to two different parameters whose effects, however, are very similar: the number of species and the number of equations. One can therefore distinguish two different kind of reaction mechanism: the detailed ones, which include a large number of species and reactions, and the reduced ones, which instead are designed for efficiently simulate a very specific problem with a smaller number of species and reactions. In literature are available many reaction mechanisms and of reviews of their performances [38].

The advantage of detailed reaction mechanism is that they can theoretically describe better the combustion because of the higher number of reactions and species; nevertheless, in many industrial applications such a precision is useless and instead the amount of time needed for the calculation grows very quickly. In order to reach a better tradeoff between accuracy and CPU-time, many reduced reaction mechanisms have been proposed. Without going into the detail of how reduced mechanisms are generated, (one can refer to the available literature on the argument like [39], [40] and [41]) the starting point is the detailed chemical reaction system which undergoes a reduction process. The most common reduction processes are the ones based on lumping of different species into one single pseudo-species. The critical points are: which species must be lumped, how to define the lumping transformation and how to estimate the kinetic parameters of the new species [40]. There are different lumping procedures and different stages of the process in order to assure the maximal efficiency of the mechanism. The final product is the reduced mechanism whose form does not depend much on the reduction process but on the dimensions of the starting detailed system. It is therefore of fundamental importance to start from a well-designed and well-validated detailed mechanism. There is also the possibility to develop a mechanism for a very specific application that is not the result of a reduction process. Also in this case, however, the developers often use as part of the mechanism the core of reactions of others well-validated mechanisms exploiting the fact that certain chemical pathways are the same for all species.

Once the reduced reaction mechanism is obtained, it is validated by means of experiments that test the ability of prediction of the mechanism in different situations. The two properties we are most interested in are the ignition delay and the laminar flame speed.

Ignition delay can be tested by means of shock tubes or rapid compression machines. Shock tubes are pipes with two different sections divided by a diaphragm that is designed to break at a very precise pressure. In one section there is the mixture of fuel and air and in the other one there is a driving gas, usually helium, whose pressure is raised until it breaks the diaphragm triggering the start of the time calculation. The pressure wave generated by the break of the diaphragm propagates through the second volume and causes the autoignition of the mixture that is detected by means of special light detectors. Rapid compression machines are instead made of a cylinder where the mixture in the initial pressure and temperature conditions remain long enough to reach the homogeneity. Afterwards a piston, that is one of the surfaces of the volume and that can move, compresses very quickly the mixture whose autoignition is detected by means of the pressure increase in the volume. The problem of rapid compression machines is that the result must take into account the heat dispersions through the cylinder walls that usually cause a delay in the autoignition because some energy is subtracted. Indeed, the values of experimental results available in literature are usually quite disperse in terms of both pressure and temperature, for this reason is quite normal to accept an error between 200% and 100% even though better solutions are usually possible.

Concerning the laminar flame speed, instead, the most common experiment is the jet stirred reactor. There are many different options on the shape and the characteristics of the reactor. An example is produced in [42]: a vessel with four windows is filled with the fuel fully vaporized and ignited. The laminar flame velocity is then determined by means of optical measurements. Usually the validation for the laminar flame speed is done at conditions close to ambient temperature and pressure and therefore a bit far from the real working conditions inside an ICE. For this reason a different validation has to be done using directly *QuickSim*.

It was in our interest to find and to test a certain number of different reaction mechanisms in order to perform validation analysis and comparisons and to finally select the best solution to be implemented. It must be clear that for the *QuickSim* library a vast number of points must be calculated (tens of thousands only considering the laminar flame speed) and therefore a good tradeoff between accuracy and CPU-time must be taken into account. Also the conditions at which to calculate the different properties have been chosen taking into account the real necessities of the simulation and the time required for the simulation.

Out of the big number of reaction mechanisms available in literature, we chose the ones that were more interesting for our purposes.

In Table 6 we reported the list of reaction mechanisms we implemented in CANTERA in order to analyze them.

The analysis started by checking if the compounds that we are interested in are actually implemented and by testing the quality of the modeling of pure compounds by means of the data available in literature. Then we tested the modeling of simple surrogates in order to verify that also the interaction between different compounds is included.

Table 6: Reaction mechanisms we investigated

Name	**Validation conditions**				**Reference paper**
	Pressure	*Temperature*	*Equivalence ratio*	*Type of validation*	
CRECK	10-80 bar	600-1250 K	0.5-1	IDT	[43]
	1-20 atm	298-470 K	0.5-2	LFS	
CAI	1-42 bar	600-1250 K	0.5-2	IDT	[44]
	1-25 bar	298-373 K	0.7-1.4	LFS	
LLNL_323	1-80 bar	900-1250 K	0.7-3	IDT	[45]
	10-25 atm	323-373 K	0.8-1.3	LFS	
LLNL_679	1-80 bar	900-1250 K	0.7-3	IDT	[45]
	10-25 atm	323-373 K	0.8-1.3	LFS	
ANDRAE	10-50 bar	700-1200 K	0.5-1	IDT	[46]
	1 atm	298-453 K	0.7-1.75	LFS	

In Fig. 21 we report the validation of reaction mechanisms for three simple surrogates and in Fig. 22 for the pure isooctane at low temperature. We used experimental data from [47], [48] and [49] for surrogates and [50] for pure isooctane.

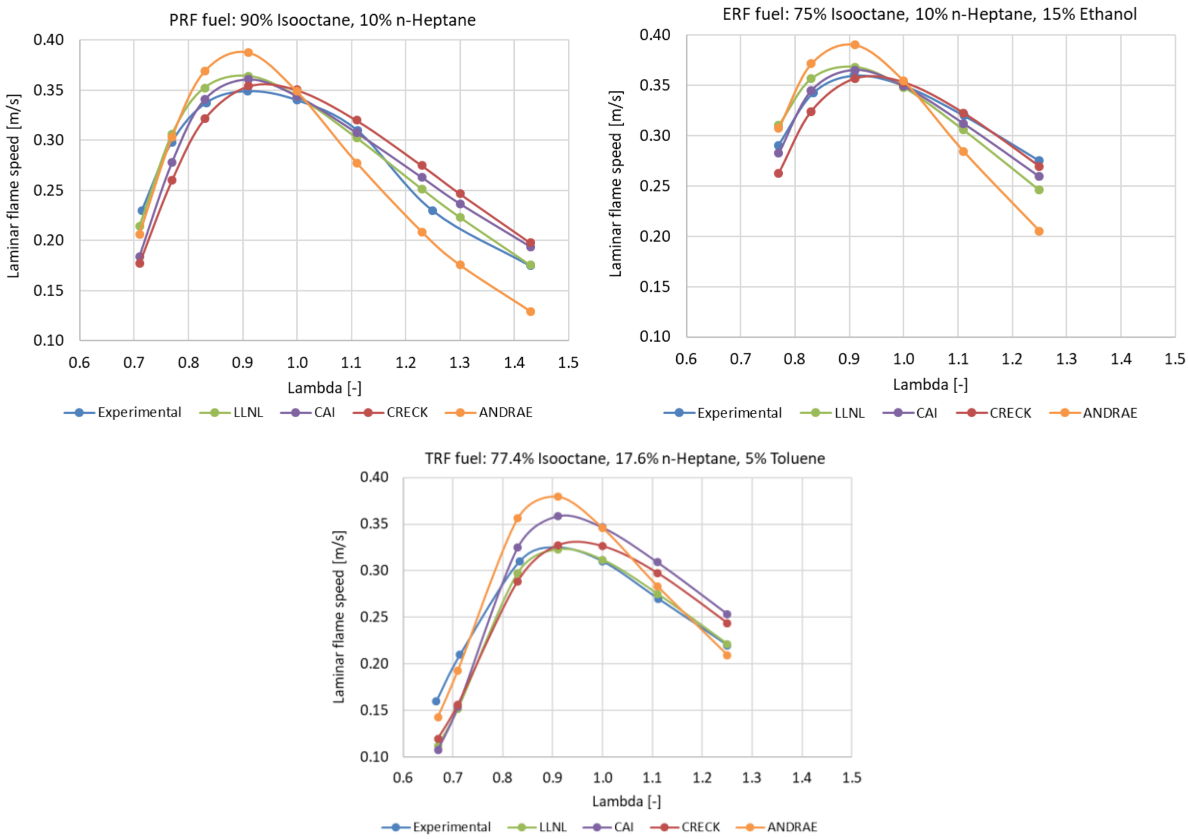


Fig. 21: Validation of reaction mechanisms by means of experimental data available in literature at: 1 bar and 298K for the PRF and ERF mixture; at 4 bar and 358K for the TRF mixture

The validation must be done, theoretically, where we will need to simulate the behavior of the gasoline. In the case of the laminar flame speed the range of temperatures and pressures is quite wide and therefore the validation has to be done both at high and low temperature. Indeed, the fact that at a certain low temperature a reaction mechanism is well validated doesn't mean that it will behave well also at high temperatures because the chemistry that is taken into account is completely different from the previous one. Therefore we performed simulations also at high temperature with data from [51] but using only the LLNL and CAI reaction mechanisms because, as we will see, are the two most accurate ones.

The trends of laminar flame speed simulations at low temperature are clear and reflects the results that we obtained simulating other pure components. For the LLNL the error between the experimental curve and the simulated one is always good, i.e. below 10%. During the simulations we used the mechanism with 323 species because of the good accuracy and the acceptable time needed for each point. The reaction mechanism is also very stable and validated. The second mechanism in order of accuracy is the CAI reaction system; the error is usually low apart from values at very rich or very lean mixtures where the value of the laminar flame speed is really low and requires more accuracy. Nevertheless, the mechanism proved to be very unstable and the computation time generally larger, or much larger, than the LLNL one. During the calculations it was quite common the one or more points have to be recalculated. For these reasons it is not very attractive for the production of the database. The CRECK reaction system is designed for a fast calculation while the results are still acceptable for mixtures not too extreme, i.e. $0.75<\lambda<1.2$. Such a characteristic makes the CRECK system very interesting for rapid evaluations and sensitivity analysis.

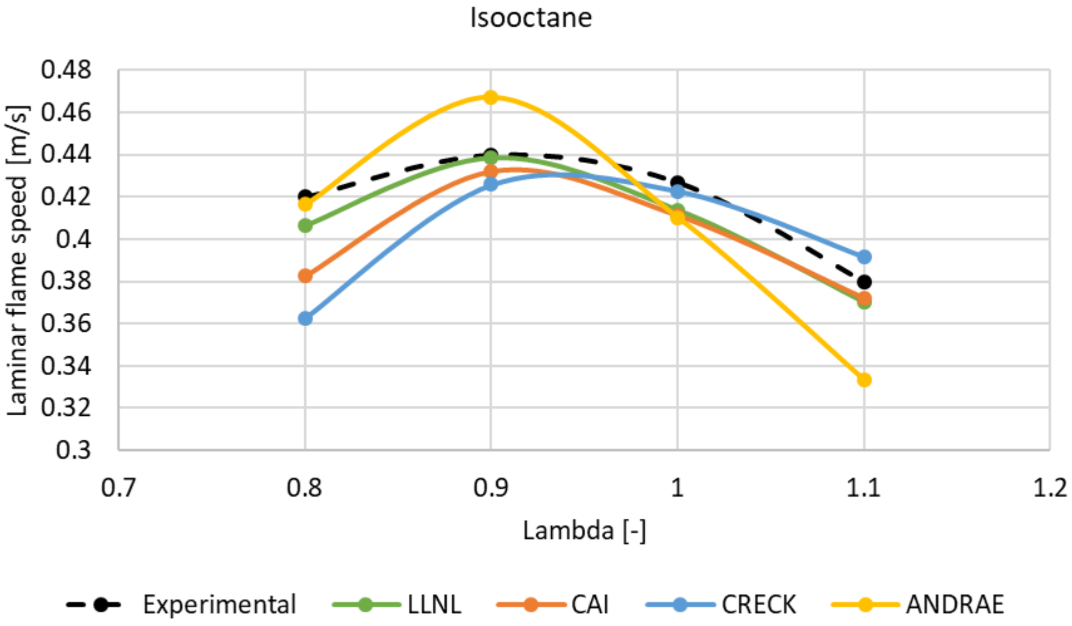


Fig. 22: Experimental validation of reaction mechanisms for pure isooctane at 1 bar and 338K

The system proved also to be generally stable and is remarkable the fact that the resulting shape of the laminar flame speed curve has always the slightly wrong behaviour: at rich mixtures there is an underestimation of the laminar burning velocity; the peak, which typically is around λ=0.9, is a bit shifted towards leaner mixtures and the whole lean side overestimate, by an almost constant value, the laminar flame speed. All these reasons make the CRECK an interesting reaction system for particular analysis with a limited interest in precise values but that need for fast response. Nevertheless, the lack of accuracy at conditions far from the peak makes the LLNL more adapt for the calculation of the laminar flamelet library.

The last reaction system in terms of accuracy is the one we called ANDRAE after one of the researchers that proposed it. The ANDRAE is also by far the fastest reaction system but the results are clearly inaccurate throughout the tested mixtures.

Another important issue with the ANDRAE is that it is very unstable and unable to calculate some points at very rich conditions. Some results show a perfect agreement with the experimental values but it must be considered as a random effect. Also in this case the system shows always the same trend with a very high peak correctly centered on λ=0.9 and the values of laminar flame speed at both rich and lean mixtures too rapidly decreasing. This very low accuracy spoils the advantages of a fast calculation time and makes this reaction system not so useful if compared with the CRECK.

In order to be complete the validation, we should assure that the reaction mechanism behaves well exactly where it is needed. In the case of the laminar flame speed the range of pressures and temperatures that may be encountered during the simulation is very wide and therefore experimental data have to be compared also at high temperatures. In order to save time, we tested only the two most precise mechanisms, as to say LLNL and CAI, which are also the ones that are more probably used for the database calculation.

The validation is reported in Fig. 23. The result is in general good agreement of the experimental data with the simulated values with very low average error. The CAI reaction mechanism results always a bit less accurate and has always at least one point where the error is greater than 10%. LLNL, instead, is much more stable and the errors more limited especially in points where the greater accuracy is required, i.e. at very lean conditions, because the value of laminar flame speed in very low and therefore a small variation causes a great error.

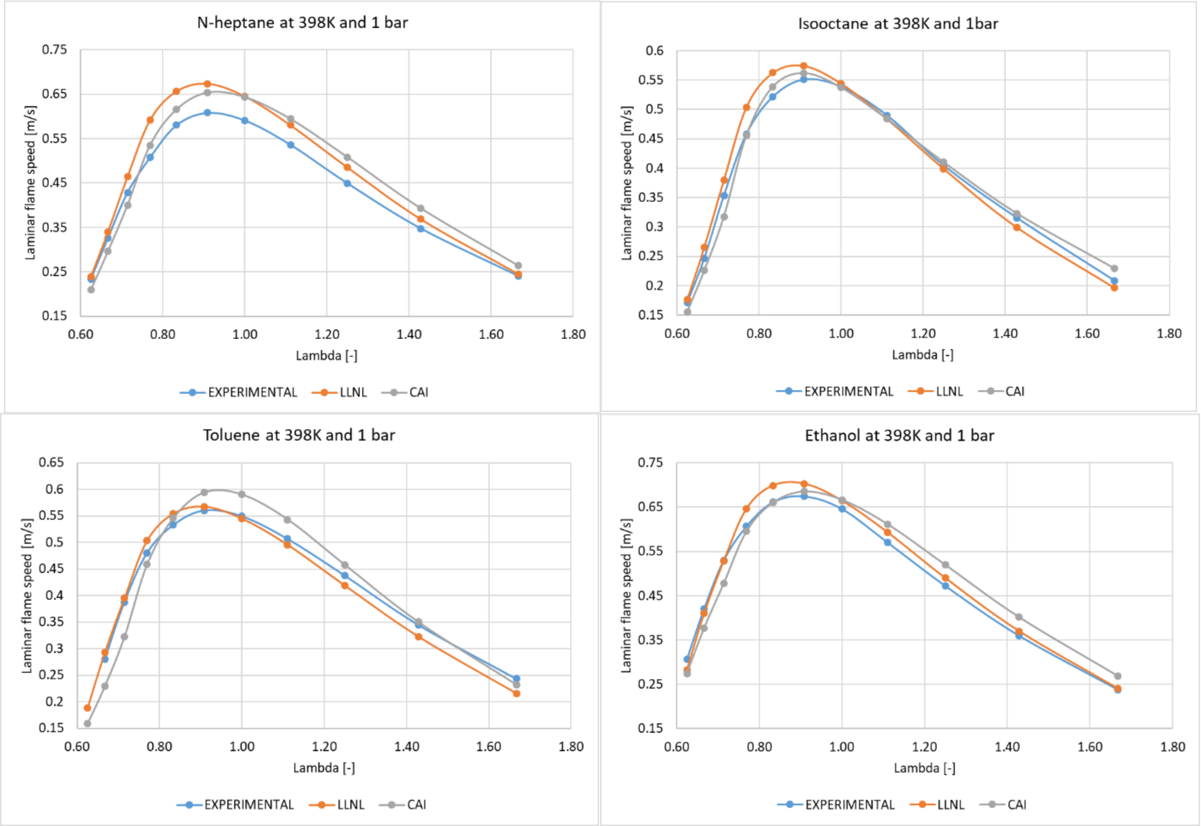


Fig. 23: Experimental validation for laminar flame speed of LLNL and CAI reactions mechanisms with data from [51]

We can therefore state that both LLNL and CAI reaction mechanisms are able to simulate well at high temperatures. Nevertheless, from other simulations that we performed at different thermodynamic conditions, we saw that after a certain temperature and with more complicated mixtures CAI shows an important offset compared to the results of the LLNL pushing the laminar flame speed towards very high values. Due to lack of experimental data at these conditions it was impossible for us to make a final validation, but it contributed to the idea that the LLNL is more reliable; such a consideration stems also from the fact that the number of reactions included in LLNL is 2649, while the CAI can count only on 1613 reactions. It is therefore legitimate to assume that some reaction at high temperature has been simplified.

Eventually, we described the behaviors of four different reaction systems we tested against experimental data and the conclusion is that the most interesting from the point of view of the precision is the LLNL with 323 species and therefore we chose it the production of the database for *QuickSim*. The other interesting reaction system is the CAI that also showed to be quite accurate even though is unstable and probably inconsistent at high temperatures.

Most of our choices were based also accounting on the time elapsed for the calculation of one point with a specific reaction mechanism whose value depends on the kind of computer one is using; it is however interesting to report the exact time in minutes in order to have an idea of the general magnitude of the work. We decided to make a comparison taking as reference the time required by the LLNL that from now on will be our benchmark. Before to go in deeper details it worth to stress the fact that the values are just indicative of the amount of time especially for the reactions systems that are not stable (CAI and ANDRAE) because in this case it may happen that for one point the calculation takes hours instead of tens of minutes.

The time required by the LLNL for one point using a normal desktop pc (i5) is around 15 minutes, the CAI takes 25 minutes (1.6 times), the CRECK 5 minutes (0.3 times) and the ANDRAE 2 minutes (0.13 times).

The problem of calculation time is much less important in the case of autoignition simulation because the system that must be solved is simpler and generally more stable. Since there was no real difference in the calculation time of the ignition delay we decided to use in any case the LLNL system that proved to be the best for the laminar flame speed. From a validation point of view the problem is more on the experimental side, due to the high dispersion of data, than on the simulation side.

The data will be presented using the typical diagram used for the ignition delay where on the x-axis is reported the value of 1000/T, where T is the temperature in Kelvin, and the y-axis is reported the logarithmic scale of the ignition delay time. This graphical representation is used because it permits to represent the ignition delay as a straight line according to:

$$\tau_{id} = A\, p^{-n}\, e^{\frac{E_a}{RT}} \rightarrow \ln(\tau_{id}) = \ln(Ap^{-n}) + \frac{E_a}{RT} = const. + \frac{E_a}{RT} \propto \frac{1}{T}.$$

The typical shape of the ignition delay time presents two straight lines with different slope and a zone that works as a connection between the two. The two straight lines have a different slope according to the fact that are working at high or low temperature. Indeed, to change the slope means that the activation energy E_a has changed, which means that the chemical reactions are different. As we will see, not all the species present two different chemistries between the high and low temperature; an example are ethanol and toluene.

The NTC region is the zone where, although the temperature is still increasing, the ignition delay time increases; this phenomenon is due to the change of chemistry between the low and the high temperatures and is typical of the paraffins. Indeed, around 800K it starts a class of chemical reactions that consume the intermediate and very reactive reaction products of the combustion process; therefore, the rate of the reaction slows down and the time needed for the autoignition increases as well as the knock tendency reduces. These reactions are related to the cool flames, which cause a small release of energy and greatly reduce the amount of highly reactive radicals available.

The curves of ignition delay simulated with different reaction mechanism may show a different behavior in the NTC region due to detail differences in the modeling of chemistry. Nonetheless the behaviors at high and low pressure is usually consistent, which means that the different chemistries are implemented correctly in all the mechanisms tested. Indeed, the both chemistries must be tested, i.e. at high and low temperatures.

It is worth noting that usually a dispersion around the NTC region is experimentally justified and during the simulation of the engine combustion process the final value at which knock happens is not a single one but the sum of the time the fresh charge spent in all the previews thermodynamic conditions. It is therefore acceptable a certain, though limited, amount of dispersion.

We made a validation of three reaction mechanism that is showed in Fig. 24, avoiding including also the ANDRAE mechanism because of the lack of precision.

The validation we did is concentrated on the final application of the simulation, i.e. the detection of knocking during the combustion process. As we know knock happens at high temperatures, around 1000K (1000/T=1) and high pressures. Therefore the experimental values used for the validation shall be considered in these thermodynamic conditions that, however, are not always easy to find. In our case, indeed, we could validate the reaction mechanisms for two different temperature conditions: high temperature or low temperature. The interest in the low temperature is limited because is the case of HCCI working of the engine, i.e. the autoignition is not spontaneous but induced. Nonetheless, as it can be seen in Fig. 24 the reaction mechanisms' result and the experimental data are in good agreement on the whole domain.

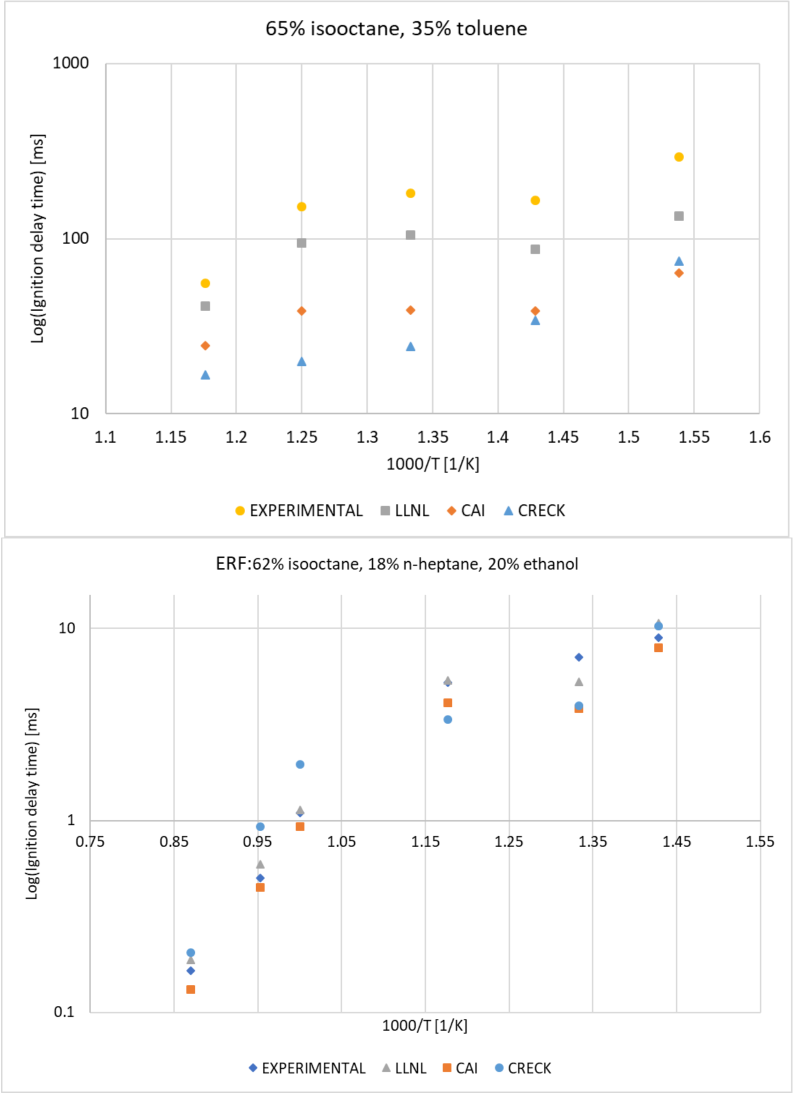


Fig. 24: Validation of reaction mechanism at high and low pressure for an isooctane-toluene mixture in stoichiometric conditions at 12 atm [52] and primary reference fuels-ethanol mixture at 30 bar and in stoichiometric conditions [53]

The biggest uncertainty is in the NTC region where the dispersion of data is greater during experimentation. The most accurate mechanism in both conditions is again the LLNL which is chosen to produce the database of the ignition delay time also in order to have a coherence with the laminar flame speed simulations.

We can therefore finally state that, among all the reaction mechanisms we tested, the ANDRAE is of little interest mostly because of its instability; the CRECK is stable and fast and therefore it is useful for sensibility analysis; the CAI is quite accurate but the simulations take long and has some problem of stability; finally the best compromise is the LLNL with 323 species because of the stability and the great accuracy at all the thermodynamic conditions.

The validation has been carried out in a limited range and for the species of interest. Such validation is far from assuring that these reaction mechanisms can simulate the behavior of fuels at engine conditions, therefore, another validation will be carried out by means of *QuickSim*. Nevertheless, the validation we performed until now is indirectly a proof that the all the software tools that we used are well implemented and able to give good simulation's results.

In conclusion, we have defined and validated the reaction mechanisms that we are going to use to perform our simulations. The second information CANTERA needs to start the calculations is the composition of the mixture. Therefore, the next paragraph will deal with surrogates.

1.6 Surrogates

Gasolines are composed by thousands of different molecules whose complete definition is usually impossible. In order to simulate a motor cycle, however, such a detailed description is useless, therefore surrogates are defined.

Surrogates are a combination of a small number of important gasoline's components whose composition is chosen with the precise goal of performing the best simulation. Indeed, there is no need to simulate all the different behaviors of the gasoline but just the ones are required for the specific calculations one wants to perform. As always, the simplification brings the advantage of fast calculations but loses in generality and information.

In order to define correctly the composition of the fuel one must deeply understand the effects of the different properties of the fuel on the engine. The other important focus is what the simulation needs for the calculations. In our specific case, since the model that we are working on concerns only the combustion and is not about the spraying of fuel and vaporization [31], we must pay attention to the chemical properties of the gasoline. Of particular interest are the octane rating, i.e. RON and MON, the α_{st}, the LHV and, when possible, a good agreement with the PIONA composition of the original fuel.

The octane rating is of course deeply linked to the autoignition behavior of the fuel. In particular, the higher the RON/MON, the lower the propensity of the fuel to knock. A good approximation of such properties is of course fundamental to produce a reliable database; it might happen that the information about RON and MON is substituted by the simple parameter AKI which is, however, still a good approximation of the fuel's behaviour.

A good match of the real α_{st} value is also fundamental for the 3D-CFD simulation of the engine. Its influence is due to the amount of air that is introduced together with the fuel during the simulation. In fact, if the α_{st} of the surrogate is, for example, too high, then the conditions at which the engine is simulated, assuming that the amount of air is kept constant, would be unrealistically rich; indeed, a high value of α_{st} means that more air must be supplied for the same amount of fuel. Such a discrepancy may lead to the selection of a wrong value of laminar flame speed that for rich mixtures it decreases sharply. The final result may therefore be that the simulated combustion of a too slow flame front. Luckily such a parameter is usually given as information of the gasoline and can be therefore be chosen directly as a property to be matched.

It has been proposed [54] to control the value of α_{st} by means of the H/C ratio because it is more probably given as a datum of the gasoline. Nevertheless, our experience proved that to use the H/C ratio as a constraint is not enough to assure a value of α_{st} close to the real one. Indeed, even though the value of α_{st} doesn't vary too much, usually a very precise match is required and the H/C ratio, because of being such a general parameter, is not able to assure it.

The LHV is not a parameter necessary during the simulations in CANTERA; its importance is again for the 3D-CFD simulation. In fact, the agreement must as good as possible since it links the amount of fuel injected and the energy released during combustion. A too big difference between the value of the real fuel and the surrogate leads to a different power output in the two cases, which reduces, if not eliminates, the advantage of the simulation. The value of LHV is usually reported on a per unit mass measurement and has a deep connection with the composition of the surrogate. Indeed the energy density is linked to the paraffinic content and therefore, if not reported, it can be estimated on the basis of the PIONA composition [55]. Based on our experience we can say that the value of LHV is not much variable and the average value for a gasoline is around 42 MJ/kg. However, for gasolines with high amount of ethanol blended in, the value drops and becomes more difficult to make an estimation.

Finally a good agreement with the PIONA composition is not a fundamental parameter but we saw that it helps to produce a surrogate whose characteristics are globally more similar to the original fuel. Since it doesn't directly affect nor the simulation in CANTERA neither the one in *QuickSim*, the complete agreement in the PIONA composition have to be seen more as a check than a fundamental property to be achieved. In fact the subdivision in classes of the families of hydrocarbons is already a simplification and, to substitute each class with only one compound that is implemented in the reaction mechanism is clearly reductive. Nevertheless it is usually helpful to specify the amount of a certain compound; indeed, this is fundamental in the case of the ethanol content and we widely used this assumption because, as we will see, this deeply influences the behavior of the surrogate. Up to a certain point the PIONA composition can be controlled by means of H/C ratio and O/C ratio. However, these two parameters are usually a "weak" boundary condition, in the sense that their ability to describe the real fuel properties is limited, and it is more interesting to match other properties.

There are many other properties, like the boiling point or the heat of vaporization, whose values are of little interest in the simulation and therefore are usually ignored or calculated once the composition is already determined. The interest in these properties regards other models, like the one for injection and vaporization of fuel, that simulate the steps before the start of combustion and that therefore were not included in this work.

Each property that is defined requires a degree of freedom, as to say, the possibility of the mixture to change in order to match more than one property. Such a possibility is given by the mixture of species that compose the surrogate. Theoretically we can include a large enough number of species in order to match all the properties of interest. Nevertheless in practice many limits are given.

It is clear that before choosing the species for the formulation of surrogates a work of validation and selection must be done. The two most important species are of course isooctane and n-heptane, also called the primary reference fuels (PRF), and whose behavior is widely validated for all the mechanisms (refer to Table 6). The importance of the reference fuels is that they are used in the RON and MON procedure. Nevertheless, once fixed one of the two properties the other one is forced to be the same, i.e. the octane sensitivity is always zero, so reducing the capability of the surrogate to simulate more complex and general behaviors. Therefore, toluene was included to form the so-called toluene reference fuels (TRF). Toluene is also a representative of the aromatics which usually are a considerable fraction of the total composition; by means of the TRF the surrogate is able to match at the same time RON and MON or one property of the octane rating and another among the ones we indicated above.

To simulate gasolines with a high blending of oxygenated compounds, also ethanol has been included as a possible compound. All these four molecules are well validated and proved to give good results in simulations at very different thermodynamic conditions. Nonetheless, following [55] and [56], we searched also for other compounds in order to mimic olefins and naphtenes. The list of possible candidates could be even longer if we take into account the possibility to include methanol as a second compound to simulate the oxygenated elements of the mixture; however, since the most used oxygenated compound is ethanol, we decided not to spend time looking for experimental values of methanol.

The compounds suggested are reported in Table 7. It is our impression that, for many practical applications, the amount of naphtenes and olefins is small enough that can be neglected. In such cases we saw that also using a simplified composition the results are good; still, for certain applications for motor-sport engines, e.g., it is fundamental to include naphtenes because of their characteristics of extremely high laminar flame speed.

We performed simulations for olefins and naphtenes that showed a general agreement with the real behaviors of such species but the little amount of such species in the gasolines we used, and generally in standard gasolines, makes it possible to neglect them therefore simplifying the problem. As it will be clearer later, at the present day, a good solution for the surrogate definition is to rely on the four more commonly used and validated compounds: isooctane, n-heptane, toluene and ethanol. Using these four species is already enough to achieve a good simulation of laminar flame speeds and ignition delay.

Table 7: Species suggested for the simulation

Real gasoline	Surrogate
Iso-paraffins	Isooctane Isopentane
N-paraffins	N-heptane
Aromatics	Toluene
Naphtenes	Cyclohexane Cyclopentane
Olefins	Cyclohexene Isooctene 2-hexene
Oxygenates	Ethanol

The values of components' properties were found in on-line chemistry databases. In particular the formation enthalpy of the species necessaries for the calculation of the LHV were taken from the NIST database. The values of RON and MON, instead, for toluene and ethanol are reported in literature. Even though there is no complete agreement about the octane rating of these components small variations around these values do not change much the final solution.
The values we used during all the calculation are reported in Table 8.

Table 8: Components' properties

Component	RON [-]	MON [-]	Density [kg/m^3]	MW [kg/kmol]	Formation enthalpy [kJ/mol]
Isooctane	100	100	690	114.2285	-224.1
N-heptane	0	0	684	100.2019	-187.8
Toluene	118	103.5	867	92.1384	50.1
Ethanol	108	92.9	789.3	46.7	-234.2

Now that all the elements for the formulation of surrogate are defined we can focus on the methodology to obtain the composition. Many of the methodologies that have been proposed in literature, like [54], [45] and [55], rely on a heavy use of computational resources because are thought for the implementation in detailed mechanism and therefore with a very large number of components. However, this is not our case since we will work with reduced mechanisms, a limited number of components and little information about the fuel. Therefore we will follow the approach proposed by [56] with some modification that we made during our work because the problems are slightly different.
First of all, one must choose which type of components are required for a good simulation of the fuel based on the information available. Since four components are enough to simulate a standard gasoline, usually the choice is limited to the inclusion of ethanol or not in the case of non-oxygenated gasolines.
The second step is the choice of the properties to be matched.
Afterwards, equations must be implemented and solved.
The equations are reported in Table 9.

Table 9: Equations used for the calculation of properties

Property	Equation
Mass balance	$\sum_{i=1}^{N_{sp}} x_i = 1$
RON	$\sum_{i=1}^{N_{sp}} f(RON_i, x_i) = RON$
MON	$\sum_{i=1}^{N_{sp}} f(MON_i, x_i) = MON$
$\boldsymbol{\alpha_{stech}}$	$\alpha_{st} = \dfrac{MM_{O_2}\left(a+\frac{b}{4}-\frac{c}{2}\right)n_{O_2} + 3.76\, MM_{N_2}\left(a+\frac{b}{4}-\frac{c}{2}\right)n_{N_2}}{n_{fuel}\, MM_{fuel}}$
	$a = \sum_{i=1}^{N_{sp}} NC_i\, x_i;\ b = \sum_{i=1}^{N_{sp}} NH_i\, x_i;\ c = \sum_{i=1}^{N_{sp}} NO_i\, x_i;$ where NC = number of carbons, NH = number of hydrogens, NO = number of oxygens of the i-specie
LHV	$LHV = \left\{\sum_i n_i \Delta H^0_{form,i}\right\}_{REACTANTS} - \left\{\sum_j n_j \Delta H^0_{form,j}\right\}_{PRODUCTS}$
Density	$\rho_{mix} = \sum_{i=1}^{N_{sp}} \frac{\rho_i}{y_i}$
H/C	$\frac{H}{C} = \frac{\sum_{i=1}^{N_{sp}} x_i H_i}{\sum_{i=1}^{N_{sp}} x_i C_i}$
O/C	$\frac{O}{C} = \frac{\sum_{i=1}^{N_{sp}} x_i O_i}{\sum_{i=1}^{N_{sp}} x_i C_i}$
AKI	$AKI = \frac{RON + MON}{2}$
Octane Sensitivity	$OS = RON - MON$
Molar weight	$MW = \sum_{i=1}^{N_{sp}} x_i\, MW_i$

As a matter of fact, the first equation to be solved is the sum of all the mass fractions of the composition equal to one; we will refer to it as the mass balance (MB) and since it is always included we will usually imply it.

The only equations that are not clearly defined are the ones of RON and MON which are generically indicated as a function of the mass fraction and the RON or MON of each mixture's components. This is due to the fact that there is no universal agreement on which should be the way of predicting RON and MON of blends of different components. There are many proposals available in literature among which the simplest one is an average value based on the mass fraction [56]. Other models involve very detailed analysis of the hydrocarbons [57] that usually are not given as part of the information about the fuel.

When we started our work we used the simple mass-weighted average; however, since in some situation we had the suspect that the predicted octane rating didn't match with the simulated behaviors of the surrogates, we adopted the method proposed by Ghosh et al. [58] that is simple to implement in an Excel sheet because is based on algebraic correlations:

$$ON = \frac{\sum_i \nu_i \beta_i ON_i}{\sum_i \nu_i ON_i} \qquad \text{(Eq3.20)}$$

where ν_i and β_i are parameters given in [58] and ON_i is the octane number (RON or MON) of the component. The results of this formula were in better agreement with the simulated behaviors even though usually the distance from the fractional mass average is not much. The mayor issue with the averaging of the octane numbers is that it doesn't take into account some non-linearities that arise from particular blends. We have also used the freely available "CloudFlame" web site that, among the many tools for fuel properties calculations, has a RON/MON calculator. Due to the fact that it is an on-line tool, however, we couldn't implement it as part of the process but we used it as a control to the predicted values. Overall, the estimations done with simpler methods were accurate.

The set of equations that we found out to be the best compromise for a four components surrogate is the following:

- Mass balance;
- Ethanol content;
- One property for the octane rating. In order of relevance: RON, MON, AKI;
- One property among, in order of relevance: α_{st}, LHV, density;
- If the system doesn't converge other properties can be tried, for example H/C ratio.

Once that the equations are written and the properties chosen, we must solve the system of equations. There are at this point two different possibilities according to the kind of system we must solve.

The simplest situation is to solve a problem in n-equations and n-unknowns. In this way the problem has only one acceptable solution and the solution is exactly the surrogate we defined by means of the properties. The solution of the system, since we are dealing with a limited number of unknowns, can be found by hand or implementing it in an Excel sheet.

It is common, though, that this simple system has no real solutions. That happens often when we set one or more boundary conditions that limit the possibility of the system to vary. Typical examples are the surrogates of gasolines with a very high blending of ethanol (E85, E50). In this case we usually fix the amount of ethanol and let vary the remaining part of the composition according to other properties. However, since the biggest fraction is by far the one of ethanol, the other properties cannot be very distant from the ones of ethanol; what's more we made simplifications due to lack of more detailed information, we are using few components instead of hundreds of species and also in our equations assumptions and simplifications are made. Therefore is not surprising that the system has no solution; we can't any longer rely on simple linear systems. The main alternative is to use a function that takes into account all the different parameters, assigns to each of them a weight and makes an optimization out of it. In our case we used the Excel's Solver as optimizer, which permits to make a multi-parameter optimization, and kept the weights equals for all the properties we matched.

The characteristic of the optimization is that we can solve the problem either using less equations than unknowns or the other way around. In both cases the solution depends theoretically also on the starting point even though we saw that in many cases the dependence is limited by the fact that the solution cannot span wide. At the end of the optimization the solution must undergo an analysis of the properties of the surrogate in order to decide whether it is an acceptable solution or not. The final result is ready for the simulation.

During our work we dealt many times with systems without solution and therefore we suggest to try to find a solution for many different sets of equations and then simulate all of them in the same thermodynamic conditions. The laminar flame speed shall not be very different from one surrogate to the other and one can easily exclude the surrogate whose value is outside the small range where the majority of the solutions stays. Next, since the behavior of all the surrogates can't be very far one another, one can choose the surrogate whose properties closer resemble the ones of the real fuel. This procedure is not much time consuming since the formulation of surrogates can be implemented in an Excel's sheet and the simulation of few points can be done in a couple of hours; on the other hand, it increases the knowledge and the sensitivity on the specific problem and makes the choice of the surrogate more conscious.

In order to validate the methodology and to verify its ability of producing surrogates of good approximation we used the data from [51] about a gasoline blended with ethanol. The information available was quite scarce while, instead, the experimental data were abundant and well reported. The experimentation in [51] is carried out by blending a 15% of ethanol in a gasoline whose composition is known, even though not in detail. Indeed, the sum of the components of the gasoline that are reported is around 83% of the total and the remaining is reported of being "cyclic unsaturated and oxygenated compounds" and therefore of little interest for our simulation. It was also reported an estimation of the RON of the blend and we were able to calculate the H/C and O/C ratios though not explicitly reported. Unfortunately the experimental data were available only for the laminar flame speed and therefore there wasn't the possibility to make a complete validation of the methodology by simulating also the ignition delay. Nonetheless we will also make a short discussion on the autoignition behavior to see the major effects of the choices that one can do during the definition of surrogates.

The data available is displayed in Table 10 where the composition's information is about the gasoline not blended and the other properties refer to the blend with ethanol.

Table 10: Gasoline's properties according to [51]

Property	Value
Iso-paraffins [mol%]	10.1
N-paraffins [mol%]	40.7
Aromatics [mol%]	32.5
RON_{BLEND} [-]	101.2
$(H/C)_{BLEND}$ [-]	1.965
$(O/C)_{BLEND}$ [-]	0.061

Following our methodology, the first thing we have to decide are the components we will use for the surrogates' definition. Due to the presence of ethanol we choose to use all the validated species: isooctane, n-heptane, toluene and ethanol. The set of surrogates we defined is reported in Table 11 together with the equations we used to define them (MB is the abbreviation of Mass Balance). Unfortunately, there was no information about important parameters like α_{stech} and LHV.

The first surrogate might look rigorous because the equations we have chosen are those of important chemical characteristics. The composition is the simplest possible in this case because toluene was left behind and only primary reference fuels and ethanol were chosen. The problems in this case are: first we assumed that the MON of the gasoline, which is unknown, was the same of that of the surrogate; second that we didn't explicitly set the amount of ethanol.

Table 11: Properties of the surrogates

Surrogate	Isooctane [mol%]	N-heptane [mol%]	Toluene [mol%]	Ethanol [mol%]	Equations
Surrogate 1	0.3885	0.0663	-	0.5452	MB, RON, MON
Surrogate 2	0.6462	0.0703	0.2835	-	MB, RON, H/C
Surrogate 3	0.4800	0.0906	0.2794	0.1500	MB, RON, H/C, $X_{ETHANOL}$
Surrogate 4	0.2695	0.1163	0.2744	0.3398	MB, RON, O/C, H/C

The latter choice was forced by the fact that the primary reference fuels can only model fuels whose RON is 100 or lower. In this case, to fix the amount of ethanol makes the system diverge and no acceptable solutions are achievable. To achieve some convergence, wrong assumptions had to be done, i.e. the MON of a surrogate, which didn't match the real gasoline's MON, was taken as an approximation of the real one.
Surrogate 2 is again made of only three components but this time ethanol is replaced by toluene. All the equations chosen refer to data of the real gasoline-ethanol blend, therefore it is the most reliable so far. As we already saw the H/C ratio is only a weak condition and no physical properties were matched but these choices are due to the lack of better information.
Surrogate 3 and 4 are both made of four species but differ one another for the equations chosen. Indeed, in number 3 the amount of ethanol was fixed while in number 4, since we wanted to match the O/C ratio, we had to let the ethanol vary and therefore we fixed also the H/C ratio. Based on our experience in defining surrogates, we can state that the choice of the O/C ratio causes almost always great difficulties for the solution of the system of equations and usually the ethanol content cannot be precisely controlled. The nature of such difficulties is that these values are really small and the only parameter that can really influence such value is ethanol because is the only oxygenated compound. The idea of including the O/C ratio is to match the stoichiometric conditions of the fuel; nevertheless, if available, is generally much more precise and more stable to choose directly the value of α_{st}. Indeed, as in this case the amount of ethanol is almost the double of the real one and this is of course unrealistic. In conclusion, Surrogate 2, 3 and 4 are done using proper equations and data available, therefore it is interesting to see which the solutions are and how they behave compare to the other surrogate that are done with excessive assumptions.
The simulation of the laminar flame speed of the five surrogates against the experimental values can be seen in Fig. 25.
The first thing one can see is that the dispersion of simulated values is limited for very lean mixtures but elsewhere it increases. The second aspect is that the gasoline-ethanol mixture has a slightly different shape from the one of simulations. Indeed, the rich mixtures side shows a less steep increase of the laminar flame speed towards the peak that is somewhat shifted to the right (i.e. lean mixtures) and after it the decrease in the lean mixture zone is smoother. The differences might be due to the experimental accuracy. Still, this set of data is a good test bench for the methodology because it permits us to show all the characteristics of the different definitions of the surrogates.
First of all, we can see that Surrogate 2 and 4 make a big overestimation of the laminar burning velocity for values of λ around 0.9. These two surrogates are exactly those who have an amount of ethanol that is much higher than the real fraction. Hence we can now see the point of giving so much importance to the amount of ethanol: if the gasoline is an oxygenated one, than the fraction of ethanol in the surrogate is fundamental to have a correct laminar flame speed. Therefore we put it as a first equation after the mass balance. Apart from the two surrogates whose ethanol content was completely wrong, the remaining two surrogates behave quite well and are all in the same ranges. This is also an aspect that has a general value: in the simulation of the laminar flame speed, apart from those surrogates which are completely wrong, all the others will behave in a very similar way and their values will have a small variance. This is the reason we said before that the "exact" surrogate doesn't exist, i.e. there are many surrogates possible whose value will not differ much and therefore could be all a good solution.

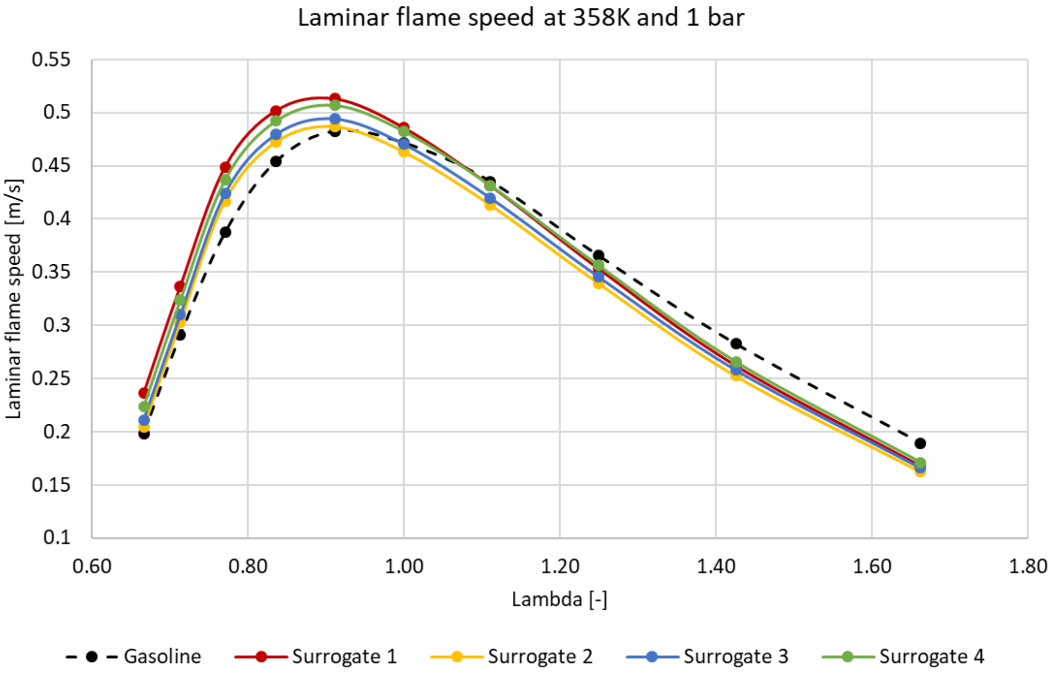


Fig. 25: Laminar flame speed simulation of the surrogates using LLNL as reaction mechanism and experimental values of the gasoline

This fact makes the solution of the problem easier, but it must still prove to be physically correct. Hence, we made a research in literature and we found an agreement, for example in [50], about the fact that the greatest influence for the laminar flame speed is the adiabatic temperature and to a less extent the composition of the blend. Of course this is true once the right amount of ethanol is chosen.

In more detail the slowest surrogate is the number 2 because of the absence of ethanol; number 3 has almost the same behavior but it is slightly faster and closer to the real gasoline.

The good agreement among surrogates, whose PIONA composition is very close to the one of real gasoline, and the experimental data must not be misunderstood as if specifying the whole PIONA composition is a good approach of formulating surrogates. Indeed, there is nothing that assures why a surrogate defined in this way shall simulate properly a real gasoline since the simplifications are too many. Such a lack of reliability is not acceptable in any case where the final simulation has some kind of industrial or scientific relevance and therefore it would resolve in a waste of time and money. Nonetheless it is evident that there is a connection between such surrogates and experimental results, but it has to be seen on the other way around: they are the proof that a surrogate may have a composition close to the one of the real gasoline and give accurate results. This, however, doesn’t mean that only surrogates with a composition close to the one of the gasoline are reliable, because of the interactions between the species. In our case indeed Surrogate 2 doesn’t have ethanol but it behaves quite well.

In fact the absence of ethanol in Surrogate 2 seems to disagree with all we said until now about the importance of setting the amount of ethanol. As we will better see later, the amount of ethanol is not much relevant on the laminar flame speed until a mass fraction of circa 5% according to our experience and literature. However, we still suggest to choose the amount of ethanol as one of the main equations in order to avoid the complications we saw in Surrogate 1 and 4 and we also suggest to use ethanol because the effects cannot be easily forecasted.

In conclusion, the average error of Surrogate 2 and 3 is below 10%, which is considered the limit of acceptability, though all of them have a bigger error at very lean mixtures mostly due to the shape of the experimental curve which might be partly due to measurement errors. This is overall a good result and means that one between Surrogate 2 and 3 can be used to produce the database for the combustion simulation. Therefore the methodology proved to be able to create surrogates capable of producing good results for the laminar flame speed.

The most important aspects that we saw are: the great influence of ethanol on the laminar flame speed and the need of accuracy in the definition of properties to be matched.

The next step is the validation of the methodology for the ignition delay whose experimental data, however, was not reported in the paper. Nonetheless, we have performed the simulation that is reported in Fig. 26.

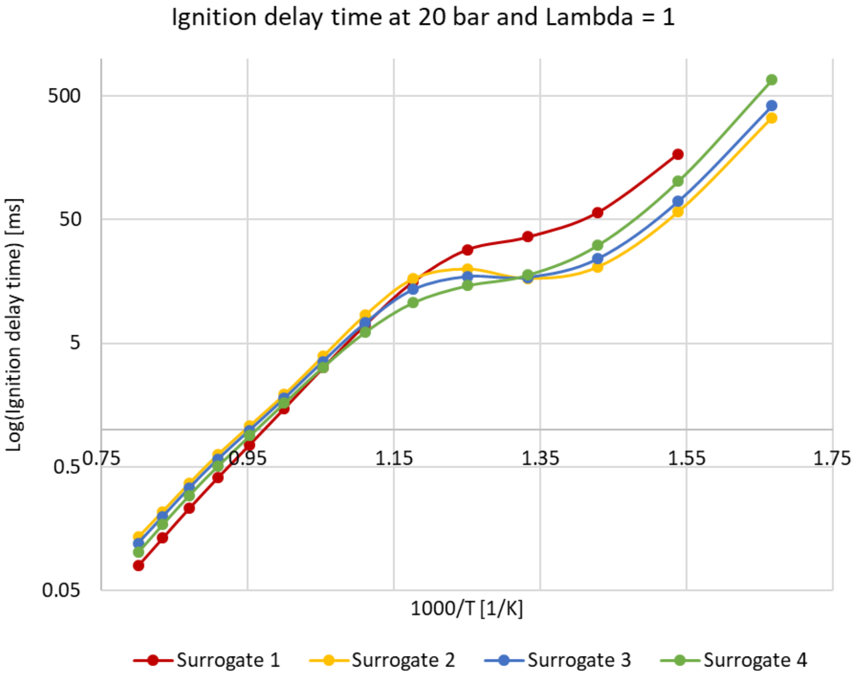


Fig. 26: Simulation of ignition delay time of the surrogates by means of the LLNL reaction system

Though this cannot be considered a full validation, we will shortly present the results in order to stress the most important aspects of the simulation of the ignition delay time.

First of all, the differences due to the compositions are more evident and the shape of the curve changes significantly. What's more one can better recognize in this case the influence of the single compound.

The variations are concentrated in the NTC region while at high temperature the behavior is very similar for all surrogates, which is the first important parameter to decide if the surrogate behaves well. Indeed, as we already saw, the slope of the curve in the high temperature region is directly linked to the chemistry of the autoignition that is itself dependent on the chemical composition of the surrogate. What's more we must always bear in mind that the final goal of this simulation is to detect knocking during the combustion process and that therefore the most important parameter is the ignition delay time at high temperature which can be predicted with good accuracy by means of the methodology we developed and that there are experimental proofs of its validity.

The NTC region is the most difficult behavior to model since it is very sensitive to the composition and therefore we will show in the next section a sensibility analysis.

The most important example is the behavior of the two surrogates whose amount of ethanol is wrong: the ignition delays at low temperatures are the double or more compared to the other surrogates. This is another good reason to pay particular attention to the ethanol mass fraction. Indeed, the ignition delay of ethanol is characterized by the absence of the NTC region and the high ignitions delay times, which explains the high value of RON. In this case we cannot state that the behaviour is wrong because of the lack of experimental values. Nonetheless, on the base that Surrogates 1 and 4 have wrong laminar flame speeds due to the too ethanol content, seems legit that also in this case the surrogate's composition is wrong.

Eventually the result of simulation at low temperature must be controlled. With respect to the high temperature solution there is a greater dispersion of data but the Surrogates 1, 3 and 4 have a very similar trend, which means that probably the simulation is accurate.

We can see that the solutions we pointed out as the best ones for the laminar flame speed, i.e. Surrogate 1,3 and 4, have a similar behavior both at high and low temperature while they differ one another in the NTC region up to a limited extent. Therefore we can be confident that the three surrogates will be able to simulate well also the ignition delay time. In our study we saw that most of the times a surrogate that behaves well for the laminar flame than it will behave well also for the ignition delay time, even though it may not be the best one.

Here the methodology may split trying to follow the best simulation by means of two different surrogates: one dedicated to the laminar flame speed and one for the ignition delay. We suggest, for the sake of simplicity to use just one surrogate for the both and to choose the one that better simulate the laminar flame speed since probably will also be one of the best for the ignition delay. In the (unrealistic) case in which experimental data regarding the ignition delay time are available, one can use it to make small modifications in the compositions of the surrogate since it is unlikely that it would influence much the laminar flame speed.

From a practical point of view, we saw that a sensitivity analysis like this or more complicate will finally resolve in the selection of a very limited number of final surrogates, i.e. two or three. Among these there is usually little difference in the simulations and therefore there is no real need for the definition of a second surrogate for ignition delay. Another aspect is that if two surrogates are produced than two different sets of properties will describe the same gasoline; though usually the differences will be small, we think that this will probably just increase the confusion.

We have made this discussion basing our considerations on the analysis of experimental data, still the methodology is thought to produce good surrogates without any data. Therefore we need to add some other step in order to be able to make a choice if we find ourselves in a situation similar to the one we are describing, i.e. we defined many different surrogates using different equations and species and we simulated them both for the laminar flame speed and for the ignition delay. The solutions we used is to eliminate the surrogates with always more stringent constraints until only the best choice remains. The constraints depend on the specific case we are working on, but an example could be the good agreement of the surrogate with the gasoline in: PIONA composition, physical properties, chemical properties…

The final result should be one single surrogate or a small group of them with very similar characteristics. As a matter of fact, in both cases we can assume that the solution is reached because if only one surrogate remains then it is the obvious choice, otherwise, as we saw, there is a little difference among the surrogates. We can finally choose one to produce the dataset.

Now that we have validated the reaction mechanisms and defined the methodology to produce the surrogates we can now simulate two gasolines of which we know only a few information about the composition and no experimental data at all. It was fundamental therefore to demonstrate that all the steps of the simulation process are validated.

As a summary the steps are:

- the software tools of CANTERA and the script in which it is implemented;
- the reaction mechanisms at high and low temperature;
- the species that will be used;
- the methodology to define the composition of the surrogates.

The whole system will be than validated by simulating the engine working point using *QuickSim* and controlling the simulation's results by means of experimental results at the test bench. Therefore the final simulation will be done using a flamelet library produced with the surrogate.

In conclusion of this section about the simulation of combustion we saw that the simulation is an interesting tool which requires a clear idea of the goal in order to choose the right description of the combustion that could be, and indeed it is, not the most precise one but the one with the best tradeoff between precision and time requirements. In the specific case of *QuickSim* the flamelet assumption requires the definition of database, the so called flamelet library, which is produced once and for all before the simulation.
We will now see an example of a real case.

4. Simulation and analysis of gasolines

The goal of all the process we presented up to here is to formulate the surrogate that can accurately simulate a gasoline of which we have little information about. This is a realistic situation that can happen during the simulation of an engine especially if the engine is being designed for an innovative fuel that maybe is not already completely developed and for which there are no experimental data.

One can think of solving the lack of data by using formulas like the one proposed by Gülder [36] and already discussed. However, such formulas have no predictive capability and must be tuned in the different parameters by means of experiments. Hence, the great advantage of the simulation is to predict the behavior of new solutions without the need of really implementing them and therefore saving time and money. Indeed, by means of the simulation of the laminar flame speed and ignition delay of a surrogate we can add to the simulation the possibility of being not only an "eye in the engine" but to predict new situations.

We will therefore now develop the process of defining surrogates for two different gasolines whose experimental values of laminar flame speed and ignition delay are unknown. Afterwards we will perform a detailed sensitivity analysis to understand the different impact on the solution of the parameters that play a role during the process of definition of surrogates. Finally, in the next section we will perform the validation of the surrogates by means of the simulation of an engine cycle with *QuickSim*.

4.1 Data

The simulation will be carried out on two different gasolines. One is an E85, i.e. a gasoline with the 85% of blending of ethanol, and the other one is an oxygenated high-octane gasoline that is called Super Plus 98.

The data were given by the FKFS IVK Institute and are reported in Table 12.

Table 12: Data available about the two gasolines

Property	Super Plus 98	E85
Aromatics content [mol %]	25.6	-
Olefins content [mol %]	7.6	-
Paraffins content [mol %]	54.2	-
Oxygenates content [mol %]	12.6	89.1
Molecular weight [g/mol]	89.9	51.3
RON [-]	98.3	-
MON [-]	87.7	-
H/C [-]	1.87	2.81
O/C [-]	0.018	0.42
LHV [MJ/kg]	42.14	32.56
α_{stech} **[-]**	14.21	9.529
Density [kg/m^3]	739.9	786.1

As it can be seen, the information about paraffinic content sums the content of iso-paraffins (branched paraffins) and n-paraffins (linear paraffins). As we saw, this information is usually enough because we suggest to use the PIONA composition as a way to control and possibly discard surrogates whose composition is unrealistically distant from the real one.

Also important is to note that the values of RON and MON of the E85 gasoline are unknown. This is due to the fact that the high amount of ethanol makes of little interest this information because it will be in any case very close the value of ethanol. About the PIONA composition of the E85 gasoline we can only report the amount of oxygenates because are private data from the FKFS IVK Institute. Still this is the most important parameter and will be enough to explain the choices we did.

Finally, in this case we have information about important physical properties that influence the simulation. We can therefore use the more complete set of equations for the definition of surrogates.

For what concerns the composition, we can in both cases neglect the amount of olefins, because below 10%, and naphtenes are not reported at all in both cases; hence our procedure can be applied without big assumptions that would have limited the validity.

4.2 Surrogates for Super Plus 98

We start now with the simulation of the oxygenated gasoline Super Plus 98.

As one can see from the composition in Table 12, the amount of oxygenates is not negligible and, as we suggested, the ethanol shall be taken into consideration. Therefore, the palette of components for the formulation of surrogates is made of: isooctane, n-heptane, toluene and ethanol.

Starting from these four components we defined five surrogates reported in Table 13.

Table 13: Super Plus 98 surrogate's compositions

Component	S98-1	S98-2	S98-3	S98-4	S98-5
Isooctane [mol%]	37.01	30.05	45.04	37.81	42.16
N-heptane [mol%]	14.82	16.46	12.92	20.45	15.92
Toluene [mol%]	35.57	40.89	29.44	29.14	29.32
Ethanol [mol%]	12.60	12.60	12.60	12.60	12.60
Equations	MB; XETHANOL; RON; H/C	MB; XETHANOL; RON; LHV	MB; XETHANOL; RON; α_{st}	MB; XETHANOL; MON; α_{st}	MB; XETHANOL; AKI; α_{st}

The compositions are all quite close one another. In general, there is a good agreement in the PIONA composition of the surrogates, which is usually a good hint that the mixture will behave well. Only the amount of toluene is always a bit higher than the amount of aromatics present in the real gasoline. Thanks to the relatively high variability, the numerical solution of the system of equation was not complicated. Indeed we were able to produce many other surrogates using other assumptions that, however, are less interesting and not presented here.

From the equations reported in Table 13 one can see that we have always specified the amount of ethanol and matched a variety of different chemical properties. The first surrogate is the only one that doesn't match any property between LHV and α_{st}; than S98-2 and S98-3 keep constant the constraint on the RON value and change the second one. Since the result of the surrogate S98-3, which matched α_{st}, is closer to the real gasoline composition, the following two surrogates are made by keeping α_{st} as a constraint and changing the octane rating parameter.

The surrogates presented are made using the more interesting properties since we want to assure that the value of such properties is right, but many other solutions are available and might give good results as well. The order in which we have chosen to formulate the surrogate starts from the idea of trying different combinations of equations but cannot be considered a full sensitivity analysis of the surrogates with respect to the equations' selection. Actually such an analysis is feasible but it require more time. In our case two different sensitivity analysis will be presented later, so there's no need to produce another one here. The logic underneath the choice of equation is to explore as many compositions as possible even when it means that clearly wrong solutions are achieved. Indeed, in absence of experimental data, a wrong solution helps in limiting the region of acceptability.

Also important is how a surrogate is able to mimic all the characteristics of the real gasoline. Since it is very hard, if not impossible at all, to reach a perfect agreement for all the properties, this test is important to check if the surrogate can predict well also other behaviors that are not explicitly matched.

Therefore, the properties of surrogates are presented together with the ones of the real gasoline in Table 14.

Table 14: Surrogate's properties compared with real gasolines properties.

Property		**Gasoline**	**S98-1**	**S98-2**	**S98-3**	**S98-4**	**S98-5**
Molecular weight [g/mol]		89.90	95.78	94.38	97.40	96.41	97.01
RON	**[-]**	98.30	98.30	98.30	98.30	92.45	95.97
MON	**[-]**	87.70	90.80	90.15	91.55	87.70	90.03
H/C	**[-]**	1.87	1.87	1.81	1.95	1.95	1.95
O/C	**[-]**	0.018	0.02	0.02	0.02	0.02	0.02
LHV	**[MJ/kg]**	42.14	42.36	42.14	42.61	42.62	42.61
α_{stech}	[-]	14.21	14.10	14.01	14.21	14.21	14.21
Density	**[kg/m^3]**	739.90	746.94	756.42	736.62	736.13	736.42

Across all the different compositions the properties are all very similar and always very close to the gasoline's value. This demonstrates that there are cases in which the combination of equations is quite free and the solution is still a good simulation. The two surrogates that approximate in a better way all the properties are S98-1 and S98-5.

Nevertheless all surrogates are precise and we expect a very similar behavior from all the solutions.

In Fig. 27 and Fig. 28 are displayed the simulations of laminar flame speed and the ignition delay time respectively.

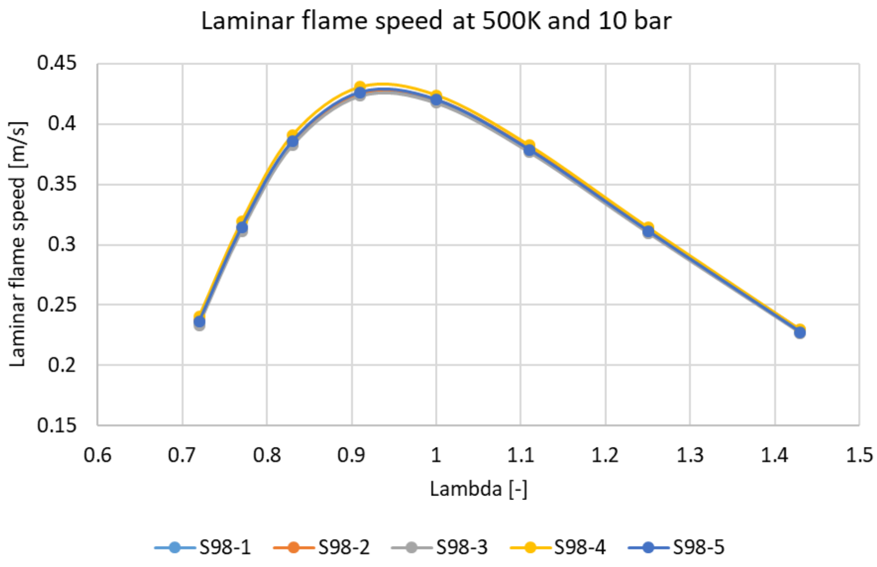


Fig. 27: Laminar flame speed of Super Plus 98 surrogates using LLNL

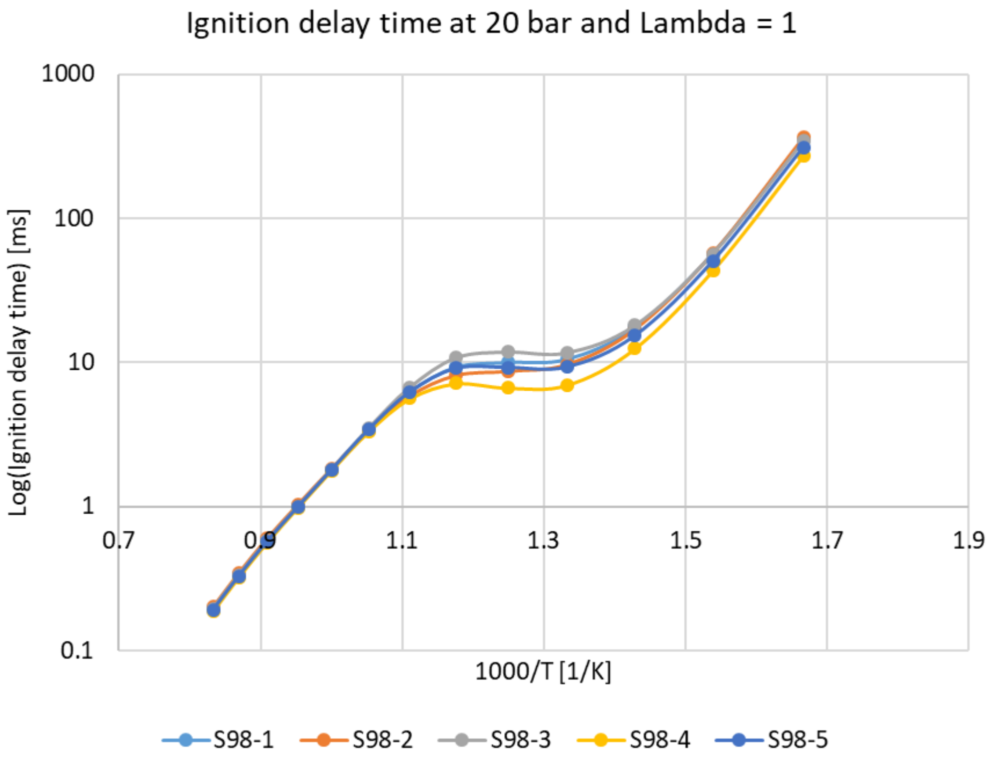


Fig. 28: Ignition delay time of Super Plus 98 surrogates using LLNL

As we expected, the laminar flame speed simulations are all very close. This is mostly due to having fixed the amount of ethanol which has a great influence on the laminar burning velocity. The fastest laminar flame speed is the one of surrogate S98-4 which has the highest amount of n-heptane; all the other surrogates have exactly the same behavior. So far, we can say that all the surrogates can be chosen for the simulation of combustion.

The ignition delay time, though it is more sensitive to the mixture's composition, also shows only small differences among the different surrogates. We can note that surrogate S98-4 has the lowest value of ignition delay, again due to the relatively high amount of n-heptane, and that surrogate S98-3 has the highest value of ignition delay which is due to the high concentration of isooctane and toluene that substitute the n-heptane. Between these two fuels lay all the others surrogates in almost a single curve. We can therefore state that the ignition delay is well simulated by any of the surrogates.

All the surrogates show a pronounced NTC region which is in good agreement with the high paraffinic content of the real gasoline. Also at high and low temperature the behavior is uniform for all the surrogates though at low temperatures the surrogate S98-4 shows a slightly lower ignition delay always due to the high amount of n-heptane. Anyway, the dispersion is limited and the simulation is always realistic; again any surrogate can well model the ignition delay of the gasoline. The only surrogate which is probably somewhat underestimating the real ignition delay time is the number 4.

After the analysis of the solutions we can state that all the surrogates are an acceptable choice for the formulation of the combustion database. From the analysis of the properties we saw that the two more precise surrogates were the number 1 and number 5; the simulation shows that these two surrogates have an almost indistinguishable behavior. Therefore both of them could be chosen. The final choice can be done according to the requirements of the problem and the equations matched: if RON is the most interesting parameter we will choose surrogate S98-1 whereas if a precise match of α_{st} is required we will use surrogate S98-5 for the simulations.

Another important conclusion concerns the equations chosen for the surrogate definition. In this case the solution of the system was really simple and we had the possibility to match a wide range of properties. Hence, the possibility to produce a wrong surrogate in this case were really low: there was no need to reduce the number of constraints, no other assumptions were needed to simplify the system, by matching one property the other ones didn't deviate much from the real value. From our experience we can say that this situation is quite common when simulating standard gasolines that are not heavily blended with ethanol. In such cases the equations used for the solution can be very flexible even though it remains fundamental to match the exact amount of ethanol.

As we will see, a much more complicated situation is the one of the E85 simulation.

4.2 Surrogates for E85

Also in the case of the E85 gasoline we will use all four components that are implemented: isooctane, n-heptane, toluene and ethanol. Actually we developed a surrogate that, for sake of simplicity and for analysis of the result is made only of ethanol and n-heptane.

The composition of E85 makes the overall behavior of the gasoline very close to the one of pure ethanol. From a numerical point of view, this makes the system's solution very difficult and equations become unstable. This might look like a great problem and a waste of time, nevertheless the problem in this case is also the solution. Indeed, the great difficulties due to the dependence of fuel from the ethanol make also the amount of the other species quite irrelevant to the final simulation's result and therefore no great accuracy is required.

Nonetheless, we have to point out that apart in the cases of very strong assumptions, like for example to model the non-ethanol content with just one specie, we had to deal with very complicated systems that forced us to reduce the number of constraints and make an optimization. This lead, of course to some non-realistic composition and, more important, the number of properties that we were able to precisely match was indeed scarce. A possible reduction of the problem, even though we are sceptics that it would solve it, might be to add new compounds. However, the composition leaves not much variability also increasing the number of species.

For these reasons we limited our investigation to four surrogates reported in Table 15.

Table 15: E85's surrogates

Component	E85-1	E85-2	E85-3	E85-4
Isooctane [mol %]	-	12.72	3.02	3.67
N-heptane [mol %]	10.9	1.01	0.96	0.88
Toluene [mol %]	-	2.04	1.89	6.35
Ethanol [mol %]	89.1	84.23	94.13	89.1
Equations	Only two species	MB; LHV	MB; α_{st}	MB; XETHANOL; Density

As it is clear, we were able to reach a solution with three equations just in the case of the density, which is, however, not a fundamental parameter. Nevertheless, choosing the density as a constrain permitted us to keep the specification on the amount of ethanol in the fuel which, instead, is fundamental. Therefore we suggest to be flexible in using the equations and to have a clear idea of the goal.

It is clear that most of these surrogates are made with important assumptions and therefore an accurate analysis is needed in order to be prepared to what we expect from the simulation's result. The first thing we can say is that the surrogate E85-3 has an amount of ethanol too high and hence we expect big deviations both in the properties of the surrogate and in the laminar flame speed. The second doubt might be about the surrogate E85-1 because of the assumption on the composition is important. However, the overall influence shall be limited. The surrogate E85-2 has a too low amount of ethanol that is counterbalanced by the amount of isooctane that has completely different characteristics and that therefore seems unrealistic as well.

In Table 16 we report the properties of the surrogates compared with that of real gasoline.

Table 16: E85 surrogate's properties compared with the gasoline's real properties

Property	Gasoline	E85-1	E85-2	E85-3	E85-4
Molecular weight [g/mol]	51.3	52.53	56.76	50.11	52.53
RON [-]	-	101.57	107.02	107.49	107.90
MON [-]	-	91.24	93.01	92.86	92.99
H/C [-]	2.81	2.79	2.63	2.80	2.58
O/C [-]	0.42	0.35	0.29	0.41	0.35
LHV [MJ/kg]	32.56	31.02	32.56	29.37	30.56
α_{st} **[-]**	9.529	10.12	10.67	9.53	9.93
Density [kg/m^3]	786.1	764.82	761.42	781.68	786.09

As we can see the properties are quite similar for all the surrogates, which proves that the composition of the non-ethanol part of the surrogate has a limited effect. Also the properties that were not explicitly reported in the gasoline's dataset are quite uniform apart from the RON and MON of E85-1 which are lower because of the strong assumption to model the remaining part just using n-heptane. The other great deviations occur for the E85-3 surrogate that we saw has an amount of ethanol too high. It is interesting that, though the big error in the composition and therefore in the behavior, surrogate E85-3 is the best approximation of the O/C ratio which, however, was not explicitly matched. Since all the other surrogates have a value of O/C lower we can deduce that in the gasoline there are compounds with a small carbon chain that with our limited palette of species we cannot imitate. This shall not be considered an error because the surrogate's goal is to mimic the laminar flame speed and ignition delay, still it is an evidence that some equations simply cannot be matched with a surrogate and is the experience of the one that is defining the surrogate that can choose which are more important than others.

If we analyze the error between the properties of the gasoline and those of the surrogates, we can see that the most accurate, i.e. the one that shows an acceptable error for all the properties, is surrogate E85-4, therefore we expect that the results of such composition to be the most accurate.

In conclusion, from the analysis of the properties the most interesting surrogate is the E85-4.

We have now to consider how the surrogate behaves in simulating the laminar flame speed and the ignition delay and, from all the information we gathered until now, we will decide which is the surrogate that will be used for the production of the database.

We start analyzing the laminar flame speed.

In Fig. 29 are reported the simulation's results of the surrogates. We can see that the simplification in the definition of the surrogate E85-1 is excessive and the laminar flame speed is too much influenced by the amount of n-heptane. The error is important throughout the domain and therefore we can discard the surrogate.

Also the surrogate E85-3 has a high laminar flame speed at λ rich and close to one while the remaining two surrogates have a laminar flame speed very close one another. The E85-2, which has a too high amount of isooctane, is the slowest.

The dispersion of data excluding the surrogate E85-1 is always lower than 10%, therefore we can, in principle, accept all the surrogates. Nevertheless, the composition of E85-3 is quite far from the real one and we can exclude also it.

Finally, we remained with two solutions that are very close one another and might be both used for the production of the database. However, we shall before check if the ignition delay time can help us in choosing one of them.

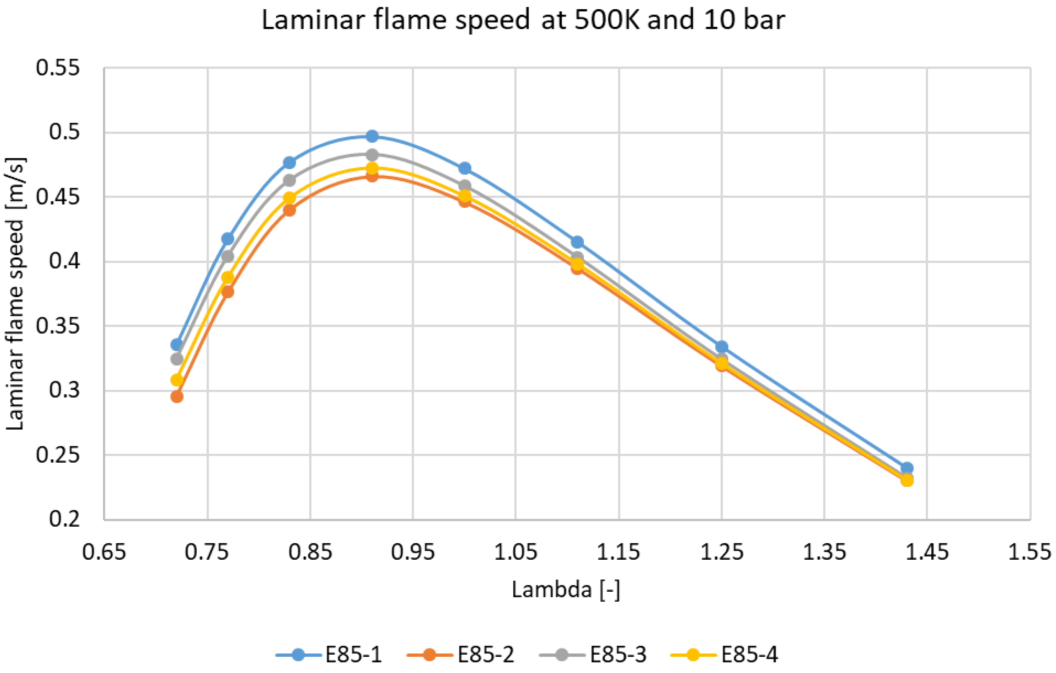


Fig. 29: Laminar flame speed of surrogates of E85 gasoline using LLNL

The simulations of ignition delay time are reported in Fig. 30. As we expected the overall behavior of the surrogates is deeply influenced by the high percentage of ethanol in the mixture. Indeed, the ignition delay of pure ethanol has no NTC region and the values are much higher than the paraffinic ones.

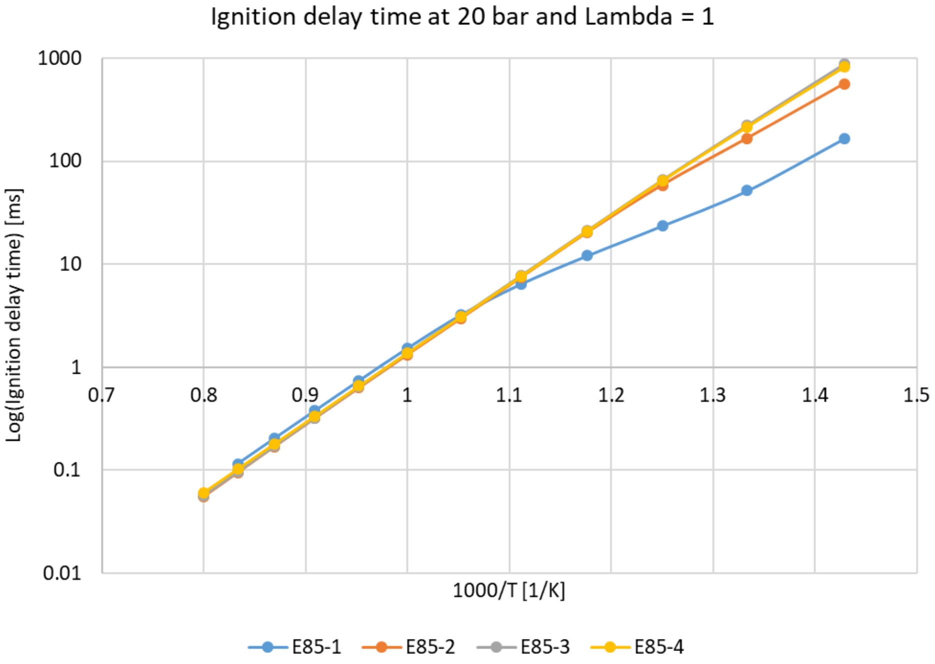


Fig. 30: Ignition delay time simulation of the E85 gasoline's surrogates using LLNL

The behavior of ignition delay at low temperature for surrogates E85-2 and especially E85-1 shows somewhat of the paraffinic behavior. In the case of E85-1 is obviously due to the too high amount of n-heptane and it represents a reason more to discard the surrogate.

In the case of surrogate E85-2 this is the result of two different effects: the too high paraffinic content, which is more than the double of the real gasoline's amount and the too low amount of ethanol. The conclusion is that this behavior is not realistic and therefore we can discard also E85-2. This was not possible to detect form the laminar flame speed because of the only small difference in the simulation. Indeed, as we will see later, the laminar flame speed depends more on the boundary conditions, i.e. temperature and pressure, than on composition.

The other two surrogates have a behavior very close to the one of pure ethanol which something that we expected. The too high amount of ethanol in E85-3 is in this case indistinguishable from the correct one of E85-4.

We can finally note that the octane rating is in general good agreement with the trend of the ignition delay that is a check of the physical accuracy of the simulation.

Eventually we can say that the surrogate which is the most indicated for the laminar flame speed simulation is also the best one for the ignition delay. Therefore we can proceed to the database production using the surrogate E85-4.

Another important conclusion that has to be draw is that a too low number of equations usually introduces too many assumptions and the control on the final properties is therefore scarce. This problem arises here and not in the simulation of the Super Plus 98 because in the latter case the system was not so determined and fixed by the amount of one single species. The stiffness of the system forces the developer of the surrogate to make some assumption in order to achieve an acceptable composition.

The detailed analysis that we performed in this work helps in finding the right assumptions to be done and therefore limiting the possible errors.

4.3 Components sensitivity analysis

Now that we have seen how the gasolines are simulated, we will perform a sensitivity analysis that permits us to better understand how component influences the overall result. Special attention will be dedicated to the amount of ethanol because of the interesting applications to model the blending of renewable fuels and gasoline.

All the surrogates are formulated using as a starting point the S98-1. The choice is due to the fact that the surrogate, as we saw, is a good approximation of the gasoline's properties and the system of equation is quite simple to solve due to the relatively equal distribution of components. Starting from this composition we produced nine different surrogates following the procedure:

- multiply the amount of one component by 1.2, 1.5 or 2;
- keeping the ratios of the other components constants, define the composition;
- the name of the compound is defined as the abbreviation of the name of the component (ISO8 for isooctane; N7 for n-heptane; TOL for toluene) plus a number which is connected to multiplication factor (1→1.2; 2→1.5; 3→2);
- example: TOL-2 means that the amount of toluene is 1.5 times the one of the base surrogate and the other components have the same ratios of the S98-1.

The compositions are reported in Table 17. A special analyses will be later carried out for the ethanol content taking into account how it is actually used in common gasolines.

The goal of this first analysis is to see if the components can change the laminar flame speed and the ignition delay and, if yes, how. The multiplication factors are chosen to achieve a trend that can be used in general applications. The second interesting point is that we start from a realistic gasoline composition and we see what happens when adding the 20%, the 50% or the 100% of a particular specie that gives a sensibility not to absolute values but on the differential behavior which is, to our opinion, a more useful knowledge when producing surrogates.

Table 17: Composition of surrogates used for the composition sensitivity analysis

Name	Isooctane [mol %]	N-heptane [mol %]	Toluene [mol %]	Ethanol [mol %]
ISO8-1	44.12	13.15	31.55	11.18
ISO8-2	55.52	10.47	25.11	8.9
ISO8-3	74.02	6.11	14.67	5.2
N7-1	35.72	17.78	34.39	12.11
N7-2	33.79	22.23	32.48	11.5
N7-3	30.57	29.64	29.38	10.41
TOL-1	32.92	13.18	42.68	11.22
TOL-2	26.79	10.73	53.36	9.12
TOL-3	16.58	6.64	71.14	5.64

In order to visualize how much each component influences the whole surrogate we performed the simulation of ignition delay and laminar flame speed for all the cases. The thermodynamic conditions are the same for all the surrogates and are 750K and 20 bar for the laminar flame speed and 20 bar and stoichiometric condition for the ignition delay, which are engine-like conditions.

We start with the isooctane sensitivity. The laminar flame speed is reported in Fig. 31 and the ignition delay time in Fig. 32.

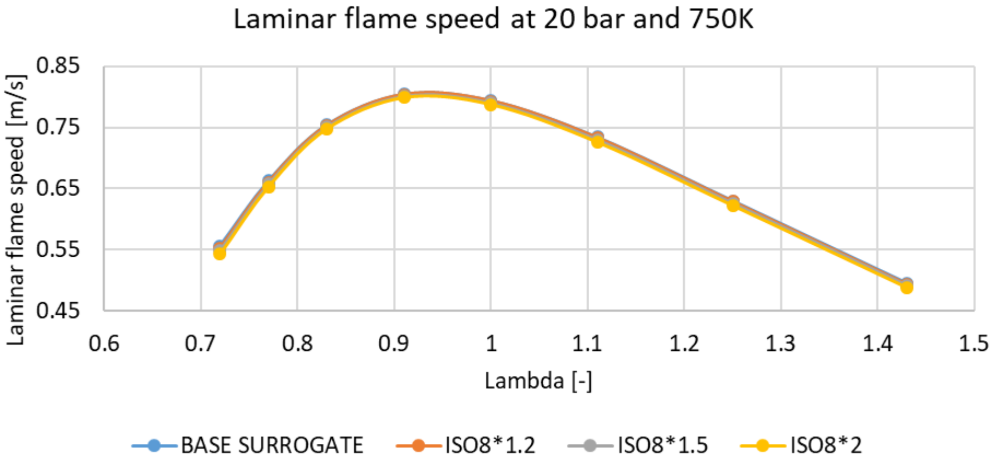


Fig. 31: Laminar flame speed of the isooctane sensitivity using LLNL

Concerning the laminar flame speed, there are no appreciable differences among the various surrogates.

In the ignition delay time, instead, a bigger difference can be noted: by increasing the amount of isooctane the NTC region becomes bigger and the difference between the high and low temperature chemistry becomes important. What's more the values of ignition delay are quite high. The great advantage of the paraffinic content in the fuel is that at intermediate temperatures, i.e. when the knock is more probable, the ignition delay increases, therefore more time is needed by the end gas to autoignite. As we can see this is in accordance with the increased RON and MON values due to the amount of isooctane.

The surrogates behave all at the same way at both high and low pressures. In conclusion isooctane has no effect on the laminar flame speed and increases the NTC region in the ignition delay time.

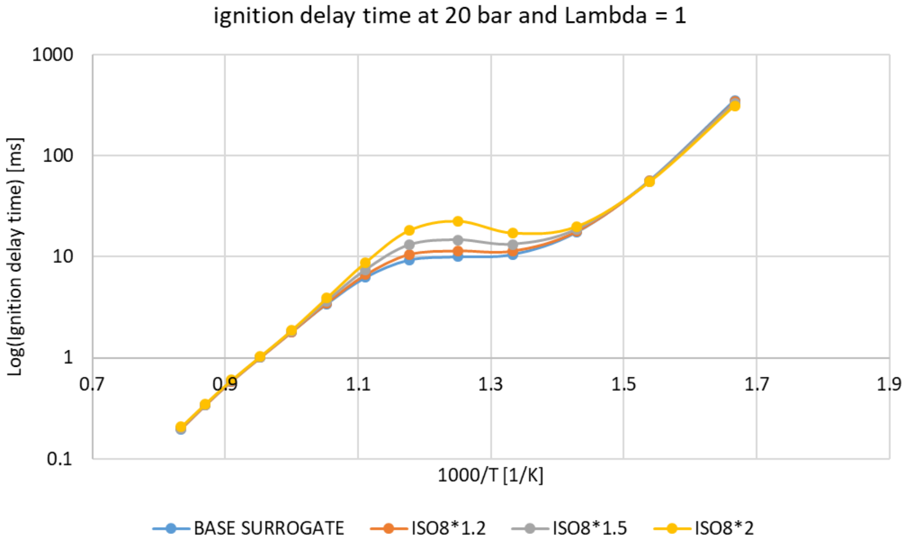


Fig. 32: Ignition delay time of the isooctane sensitivity using LLNL

The second component that we are analyzing is the n-heptane.

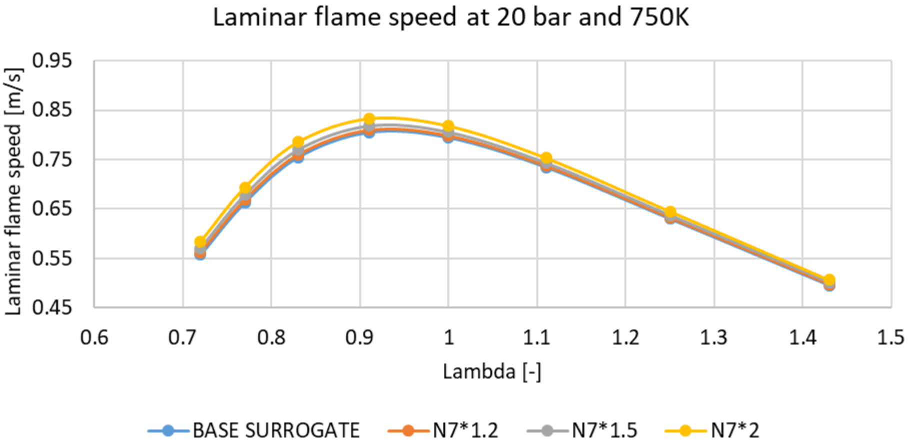


Fig. 33: Laminar flame speed of n-heptane sensitivity using LLNL

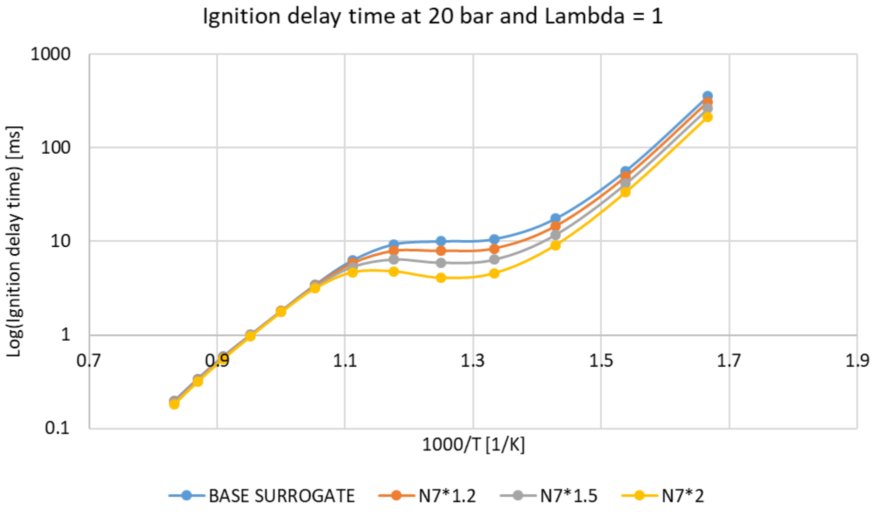


Fig. 34: Ignition delay time of n-heptane sensitivity using LLNL

In Fig. 33 and Fig. 34 are reported the results of the simulations.
There is a slight increase in the laminar flame speed, though very limited. Concerning the autoignition, instead, the ignition delay decreases but increases the NTC region. Indeed, as we will see, n-heptane is the only compound that decreases the ignition delay time. This is also the reason it has been chosen as the primary reference fuel with octane rating of zero.
The next component is toluene, which simulations are presented in Fig. 35 and Fig. 36.

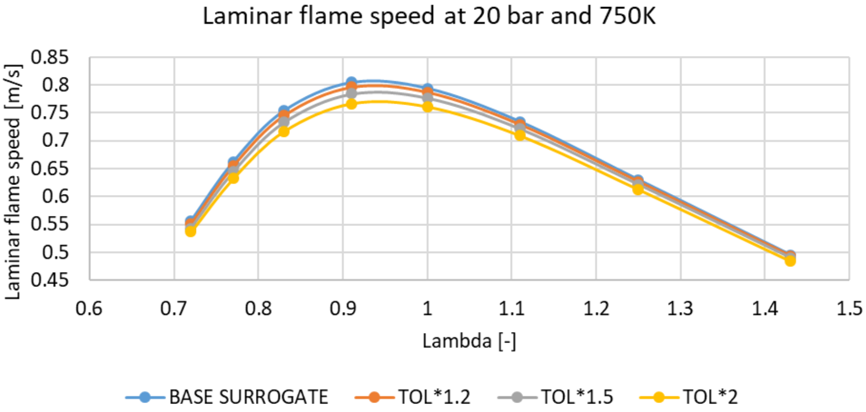


Fig. 35: Laminar flame speed of toluene sensitivity using LLNL

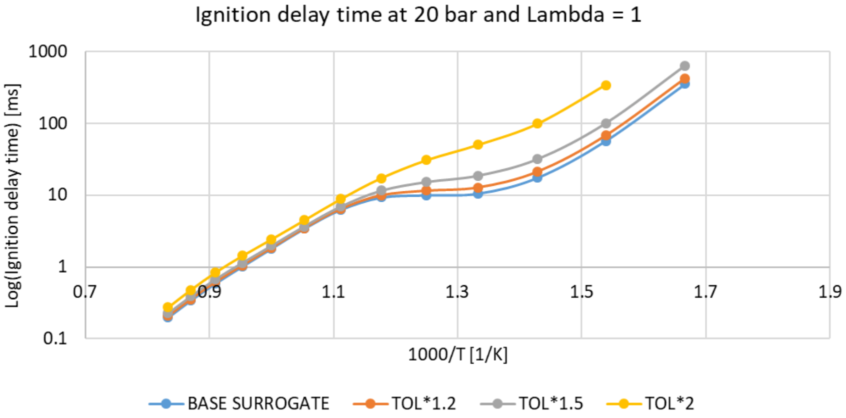


Fig. 36: Ignition delay time of toluene sensitivity using LLNL

The effect of toluene on the laminar flame is a limited decrease, while in the autoignition simulation there is a remarkable increase of the ignition delay time as well as a decrease of the NTC region.
In conclusion, we proved that the laminar flame speed is not heavily dependent on the composition of the mixture but mostly on pressure and temperature. Indeed, throughout the laminar flame speed simulations the maximum deviation was about 5% corresponding to the doubling of the toluene content with respect to the base surrogate. Nonetheless it is useful to have these characteristics clear because they help in understanding the deviations of surrogates caused by unrealistic amounts of a certain compound.
On the other hand, the ignition delay is much more sensitive to the composition of the mixture. This is due to the fact that the chemistry on which the simulation is based changes from compound to compound. Such a high sensitivity introduces a possible source of error due to the simplifications done in the surrogate formulation. However, since the information is usually limited as in our case, the ignition delay can be used to detect inappropriate or unrealistic behaviors that the laminar flame speed simulation is not able to stress like for example in the case of the E85 surrogates.
As a conclusion we report in Table 18 the numerical analysis of how all the main properties changed in the surrogates with respect to the original values of the gasoline.

Table 18: Numerical analysis of the major properties

	H/C	O/C	MW [kg/kmol]	LHV [MJ/kg]	Density [kg/m3]	Alfa [-]
Real value	1.875	0.018	89.9	42.14	739.9	14.21
Variation	34.84%	79.63%	13.16%	5.20%	13.03%	6.74%
Average error	1.00%	33.78%	8.55%	1.05%	1.18%	0.23%
Best approximation	0.77%	3.76%	3.97%	0.16%	0.11%	0.10%
Worst approximation	22.13%	83.39%	17.13%	3.91%	9.04%	3.39%

The analysis shows that, even though great variations were applied to the amount of each component, generally the variation of properties is limited especially in important parameters like LHV and α_{st}. The greatest variations are those of O/C ratio and H/C ratio which are very small numbers and therefore a small absolute variation has strong effects on the relative variation.
If we exclude the O/C ratio, whose importance is limited in the definition of surrogates, the average error, which is the arithmetic average of the errors done by each surrogate in evaluating the specific property, is always acceptable and in general very low. It is also interesting that in half of the cases also the worst approximation is below 10% even though the amount of a specific compounds was doubled.
This analysis confirms that the effect of isooctane, n-heptane and toluene on properties like molar weight, LHV, density and α_{st} is limited and therefore the possibility of reaching a good approximation, once that one or more properties are matched, is high, as the case of the Super Plus 98 surrogates further proves. Much higher variation is the one of O/C and H/C ratios which, however, in this analysis are forced to change because they are based exactly on these characteristics of the composition that has been changed.
In conclusion, if the surrogate is defined using the methodology we exposed above there are good chances of matching correctly the laminar flame speed and the most important properties. Concerning the ignition delay we saw that there is a certain degree of variability that is more difficult to avoid because of the high composition-sensitivity of the phenomenon; nevertheless, since we exposed how each specie influences the shape of the curve, one can use this information to predict the behavior of the ignition delay on the basis of the PIONA composition and control the result of the simulation.
During our work we made often use of this knowledge and we found out that can be of great help especially in the final selection of the best surrogate. Nonetheless the most important component remains ethanol; therefore in the next paragraph we will perform a more detailed analysis of ethanol blends.

4.4 Ethanol sensitivity analysis

The results of the compounds sensitivity analysis done up to now shall be taken into account when considering standard gasolines or gasolines with a limited amount of oxygenated compounds or ethanol. From now on, instead, we will analyze how the ethanol content influences the parameters of laminar flame speed and ignition delay time. We carry out this analysis by means of four surrogates that represent the typical blends of gasoline and ethanol available on the market: E10, E25, E50 and E85. The E10 is simply the surrogate S98-1 that we already used as a starting point from the previews analysis. The other surrogates were defined by fixing the amount of ethanol and keeping the same proportions between the other components as in

surrogate S98-1. In this way the final result should be close to the one of different blends of ethanol with the same gasoline.
The compositions are reported in Table 19.

Table 19: Composition of ethanol blends' surrogate

Component	E10	E25	E50	E85
Isooctane [mol %]	37.01	32.48	21.82	6.25
N-heptane [mol %]	14.82	11.98	7.92	2.39
Toluene [mol %]	35.57	30.54	20.26	6.36
Ethanol [mol %]	12.60	25.00	50.00	85.00

The compositions show well the increasing importance of ethanol. In Fig. 37 and Fig. 38 are reported the simulations of the four surrogates for the laminar flame speed and the ignition delay time.

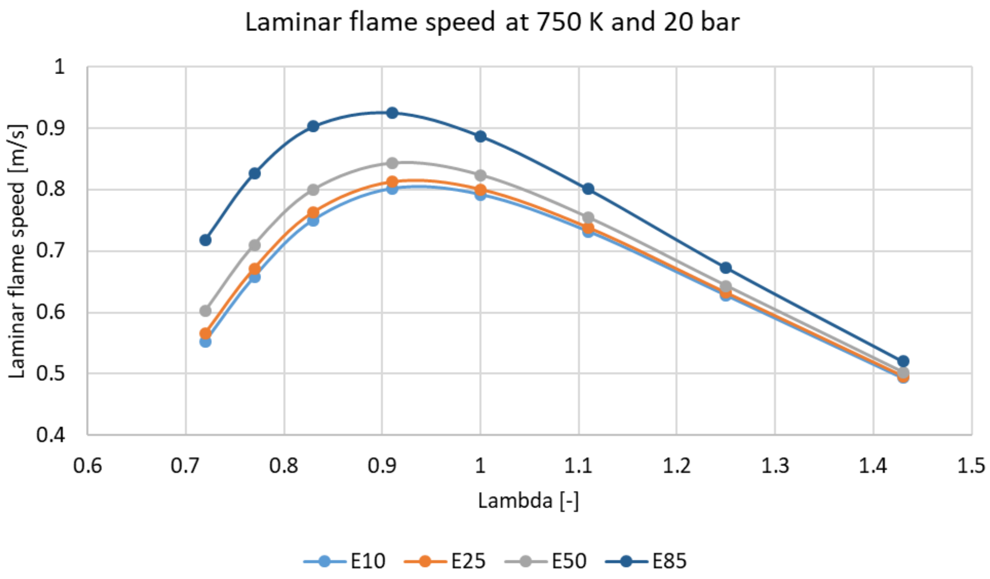


Fig. 37: Laminar flame speed simulation of ethanol blends using LLNL

Concerning the first type of simulation there is an exponential growth of the laminar flame speed with the increasing amount of ethanol. It is interesting that between E10 and E25 surrogates the difference is limited. This behavior is widely reported in literature, for example [51], though the exact amount of ethanol at which the effect of ethanol on the laminar flame speed is not negligible any longer is not universally agreed; in general a good value is around 5%.
The increase of laminar flame speed becomes very evident for the E50 and even more with the E85. Indeed, ethanol is the component that most influences the laminar flame speed; this is the reason a standard engine cannot work with gasolines that are heavily blended with ethanol: the high velocity of the laminar flame speed is so high that a different tuning of the engine has to be done by retarding the spark advance. The great differences that characterize the laminar flame speed of E50 and E85 is the reason the new generation of engines that are developed to use as fuel many different blends of ethanol and gasoline must have sensors that detect knocking and adjust the parameters needed for the engine operation. The ability of the engine to adapt to many different blends is the reason such engines are called flex-fuels.
The fast laminar flame speed can be exploited to produce an overall faster combustion process that therefore more closely approaches the ideally fast combustion and that is therefore mandatory to simulate well to be able to quantify it.

From the simulation point of view, it is fundamental to produce the surrogate with the right amount of ethanol especially for high levels of blending.

Also in the ignition delay time there is a non-linearity between the ethanol blend and the ignition delay time. In particular, growing the amount of ethanol the NTC region reduces and the ignition delay increases. For the E85, as we already saw, the behavior is almost the same of that of pure ethanol without any NTC region.

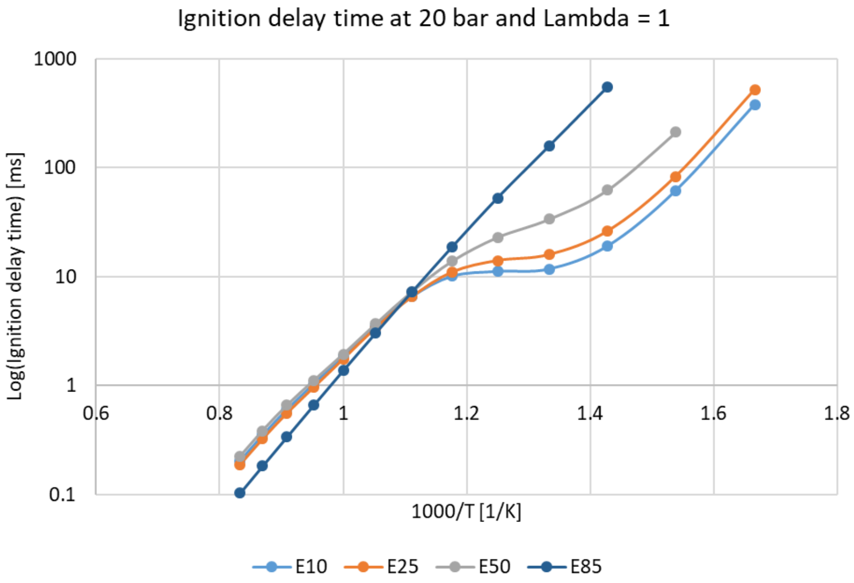


Fig. 38: Ignition delay time simulation of ethanol blends using LLNL

The analysis of the ignition delay shows how much the change in the fuel composition can influence the combustion process and therefore the characteristics of the engine. The fast laminar flame speed reduces the knock probabilities because less time is left to the end gas to autoignite. A reduction of autoignition is also helped by the higher ignition delay typical of ethanol. This can be exploited by choosing a compression ratio higher, i.e. increasing the efficiency of the overall engine, which is the second great advantage of using ethanol as a fuel.

Deeper explanation of the reasons of such behaviours lays in details of the chemistry of ethanol that will not be discussed here.

Nevertheless, the combustion of ethanol in internal combustion engines has also drawbacks. In order to analyze the complex effects of the ethanol blending on the combustion process we plotted the properties of the four surrogates we defined in this section against the ethanol content. The most interesting properties are RON, LHV, and density.

As we saw RON value is related to the ignition delay time that, in the case of ethanol blend, increases. Indeed, in Fig. 39 one can see the clear growth of RON with the ethanol blending. The trend is linear and the slope is steep, i.e. the RON value has a strong dependence on the amount ethanol. Hence, bad-quality gasolines, if blended with ethanol, can greatly increase the octane number, which is something that is usually done.

Concerning the LHV, it represents the amount of energy that is introduced in the cylinder per cycle. In Fig. 40 is reported the trend of LHV against the amount of ethanol; it is clear that the energy content of ethanol is lower and its blend with gasoline has the effect of reducing the LHV of the fuel. This is a drawback because it means that for each kg of fuel less energy enters in the cycle. In normal driving cars the most relevant difference is that more fuel has to be added during refueling in order to reach the same amount of kilometers of a standard gasoline.

Somehow this problem is solved by the increase in density as it is shown in Fig. 41. Indeed the amount of energy that enters the system is given by

$$\dot{Q}_{IN} = \dot{m}_{fuel}\, LHV = \rho \dot{V} LHV \propto \rho\, LHV \qquad \text{(Eq4.1)}$$

if we assume that the volumetric flow rate is constant, i.e. same injectors' area and same pressure difference across the injector nozzle. Therefore the energy introduced is not only linked to the LHV but also to the density of the fuel.

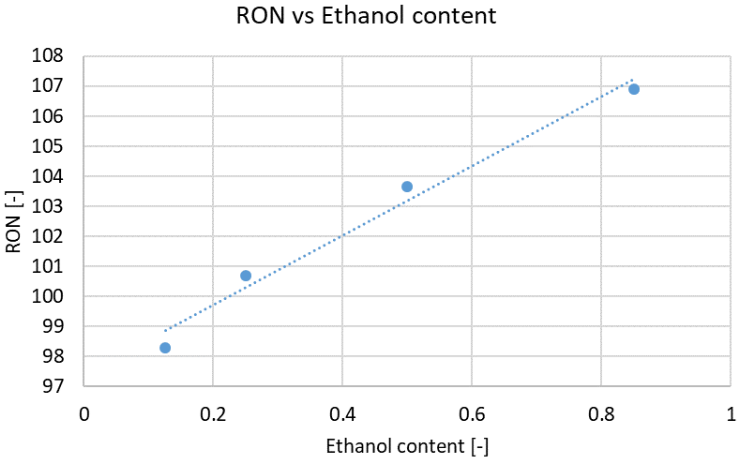


Fig. 39: Ethanol influence on RON

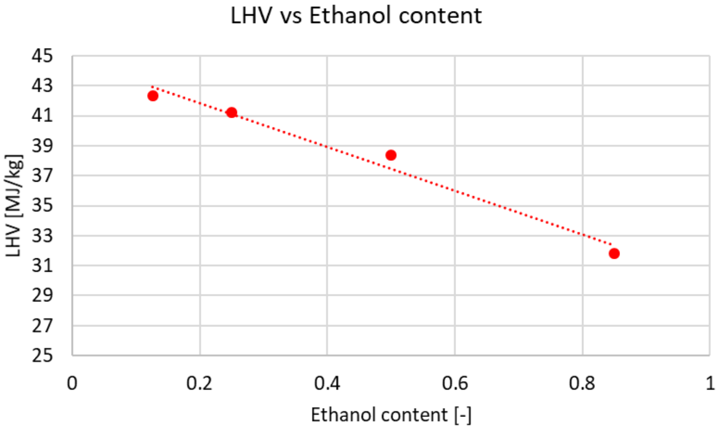


Fig. 40: Ethanol influence on LHV

The overall effect is reported in Fig. 42 where it has been calculated using the values of density and LHV of the four surrogates.

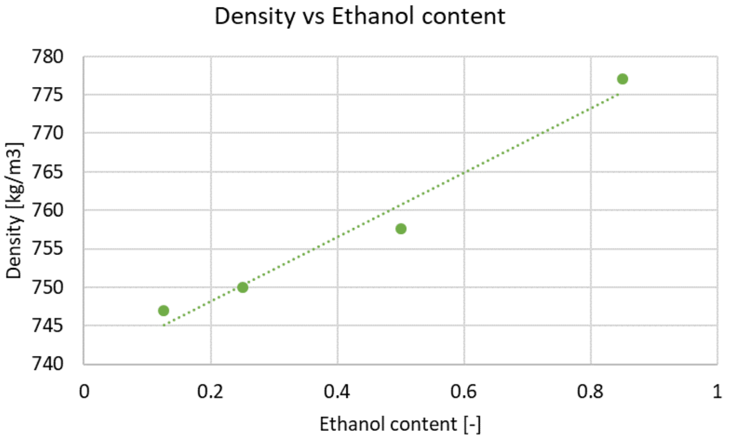


Fig. 41: Ethanol effect on density

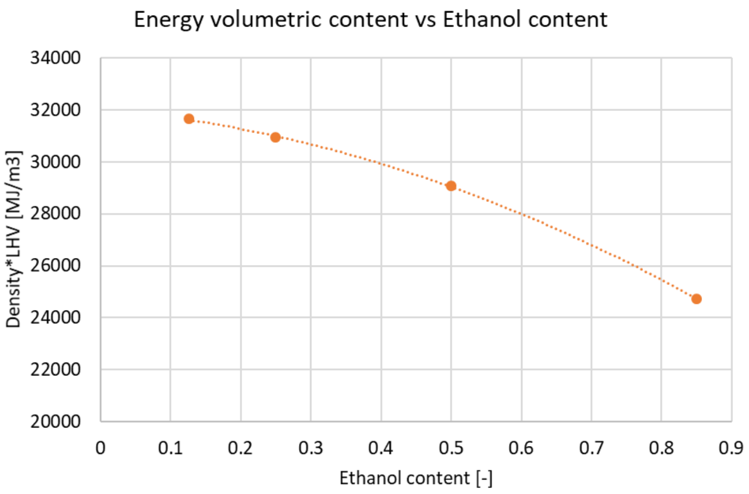


Fig. 42: Ethanol effect on the overall energy introduced in the cylinder

There is a clear decrease of the overall energy introduced in the system even though it seems to be non-linear with a small negative slope at the beginning that increases together with the ethanol content.

This parameter has also important economical applications because liquid fuels are usually sold on a per liter basis, which is a volume measurement. Hence the price of the fuel must be scaled according to the density-LHV product in order to give the actual cost per unit of energy and making it comparable with gasolines in the first approximation that the overall efficiency of the vehicle is the same.

In conclusion, the increase of density limits the disadvantages of the reduction of the LHV but there is still a decrease in the energy content of ethanol-blended fuels with respect to non-oxygenated gasolines.

Eventually we have seen how the different species can influence the behavior of a surrogate and how they modify the basic properties. It remains to be investigated the effect of the different equations that can be used to define the surrogate. In the next section, therefore a sensitivity analysis will be performed.

4.5 Equation sensitivity analysis

The remaining variable of the process that we still didn't critically analyze is the choice of equations for the definition of surrogates.

During our work we performed a kind of this analysis more on the basis of a trials and errors. Indeed, we didn't use the methodology we defined above from the very beginning, but it became clear quite soon that the amount of ethanol must be specified. Therefore, according to the species we validated and taking into account that the sum of all the mass fractions must give one as a result, only two equations more must be chosen. The choice might be not simple because of the big number of possible equations; hence one should have a sensibility on which are the most important ones and how much they affect the final solution of the simulation.

We developed the analysis using as a base reference the S98-1 surrogate of the Super Plus 98 because of the greater variability that the composition admits. The analysis was carried out in two subsequent steps: first a set of surrogates was defined using a combination of different equations in order to understand if there is any equation that is wrong to match; then for many parameters, where the system admitted a solution, a sensitivity analysis was carried out by increasing and/or decreasing the numerical value of the property that was matched and then by defining a surrogate. The second step is meant for creating a sensibility on the error that can be accepted on the gasoline's data. Indeed, who wants to define a surrogate shall know on which parameters needs a precise information and on which instead an approximation is enough.

Another important aspect of this analysis is to decide whether discard to or not a surrogate according to the difference in a predicted property and the one of the real gasoline.

For the whole process we defined around forty different surrogates whose compositions is not necessary to report since one can calculate it using the methodology exposed below. For the first step, however, compositions will be reported together with the equations used because are useful for the description of the process. Concerning the second step, instead, the compositions can be calculated in the following way:

- species: isooctane, n-heptane, toluene and ethanol;
- equations:
    - mass balance;
    - ethanol molar fraction (12.6%);
    - chemical property: RON or the chemical property whose sensitivity is investigated;
    - α_{st} or the property whose sensitivity is investigated between LHV and density;
- investigate only one property at the time keeping all the other values equals to the ones of the Super Plus 98;
- for each property investigated three surrogates are produced if the system of equations converges: for each surrogate the target property is multiplied by 0.95, 1.05 or 1.1.

During all the process the base case is surrogate S98-1.

For the first part of the sensitivity analysis five surrogates were produced using combinations of equations different from the ones used in the definition of the surrogates S98-1 to S98-5. The compositions are reported in Table 20 where with the name EQ we indicate the surrogates defined for the equation sensitivity. In the equations' section the mass balance and the specification of the ethanol content are not explicitly reported because common to all the surrogates.

Table 20: Compositions and equations of the surrogates used for the equation sensitivity analysis. OS: octane sensitivity

	S98-1	**EQ1**	**EQ2**	**EQ3**	**EQ4**	**EQ5**
Isooctane [mol %]	37.01	42.43	55.73	39.59	35.38	25.33
N-heptane [mol %]	14.82	13.54	0.20	16.39	20.61	21.27
Toluene [mol %]	35.57	31.43	31.47	31.42	31.41	40.80
Ethanol [mol %]	12.60	12.60	12.60	12.60	12.60	12.60
Equations	RON; H/C	RON; Dens.	OS; Dens.	AKI; Dens.	MON; Dens.	MON; LHV

From the composition we can only see that the surrogate EQ2 seems to have a completely wrong amount of isooctane and n-heptane. All the other values of the compositions are instead in a small range that means that probably the behaviour will be close to the one of the real gasoline.

The results of laminar flame speed and ignition delay are reported in Fig. 43 and Fig. 44.

From the laminar flame speed simulation we see a result that in general the results are very close to the ones of the Super Plus 98 surrogates. Indeed, the different mixtures behave in an almost indistinguishable manner across the domain. The only exception is surrogate EQ2 whose laminar burning velocity is much lower than the others because of the too high amount of isooctane.

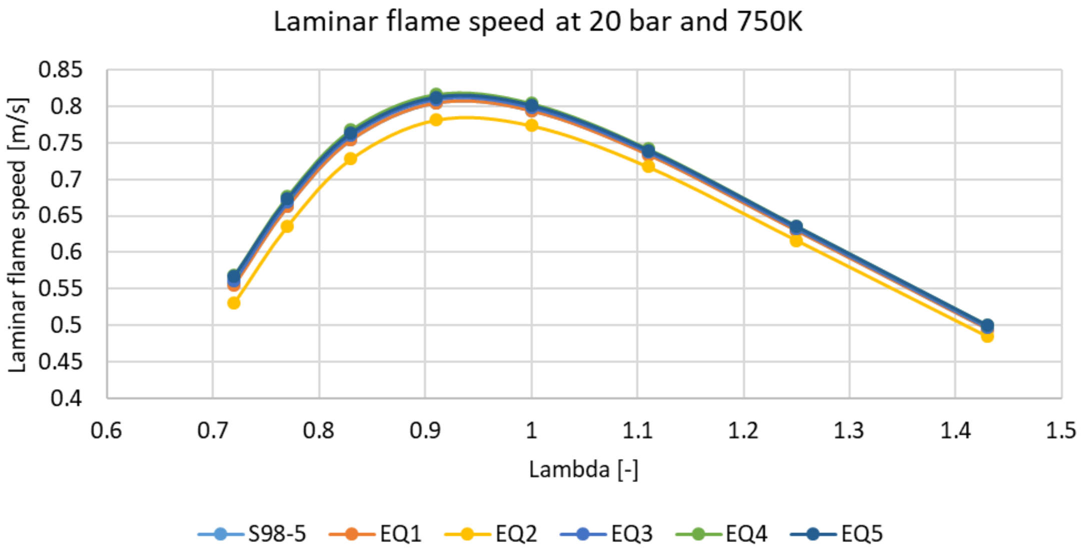


Fig. 43: Laminar flame speed of surrogates produced for equations' sensitivity using LLNL

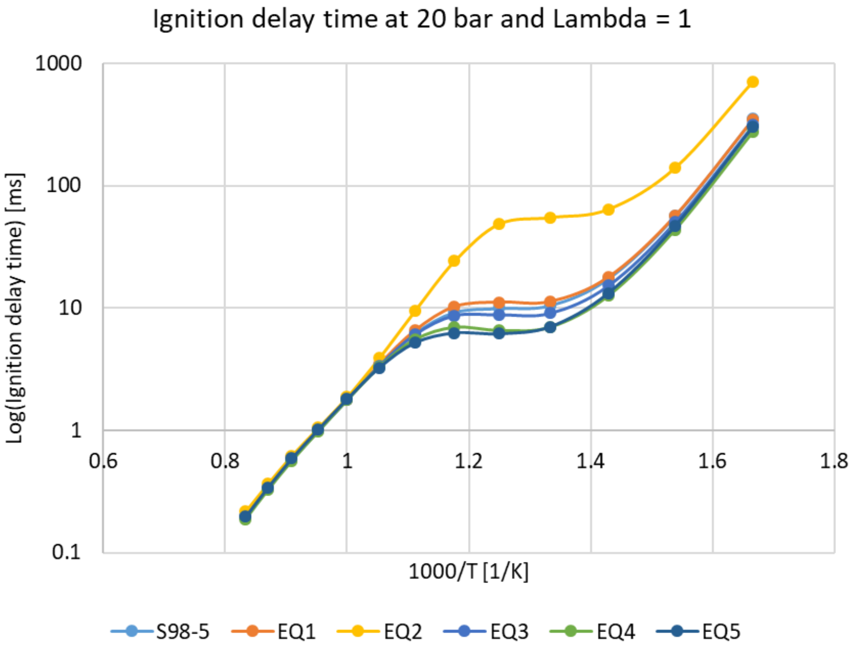


Fig. 44: Ignition delay time of surrogates produced for equations' sensitivity using LLNL

Same situation can be seen for the ignition delay time where almost all the surrogates have a very similar trend but the number 2, which have much higher values of ignition delay time.

Since the equations used for EQ2 are density and octane sensitivity but all the other surrogates that are defined using the density equation have a coherent behavior, we must conclude that to match the OS equation is wrong. This makes sense since the information about the OS, i.e. the difference between RON and MON, is a relative one and in order to reach the specified value the important information about the absolute octane rating is lost. Clearly to loose such information is unacceptable.

If we add these equations to the ones used for the definition of S98 surrogates all the equations of interest are covered. The conclusion is that only to match the octane sensitivity is completely wrong while all the other possible combinations of equations give acceptable compositions and, what's more important, coherent simulations. Therefore the possibilities to produce a good surrogate using such equations are really high.

We believe that this first step is important to define which are the real limits of the problem and to prove which are the equations able to produce good surrogates.

In the next step we are no longer looking to the accuracy of a certain mixture to simulate the combustion behavior of a real gasoline but rather how the simulation changes as effect of different assumptions in the definition. Therefore the reference is no longer the best approximation that has to be considered but the starting point for other compositions. It has been not always possible to produce three different surrogates for each condition because of the stiff equations. Nonetheless our main interest was to show the trend that the change in the constraints cause and therefore two surrogates can already give some information.

The equations we analyzed are: RON, MON, AKI, OS, H/C, O/C, molar weight, density and α_{st}. The sensitivity analysis of the α_{st} gave exactly the same compositions of the LHV one; therefore, the solution can be considered as representative of both equations. Indeed, the two properties are very close one another and both have a very strong dependence on the composition and a limited variability.

It is important to stress once again that all the compositions were obtained keeping the amount of ethanol fix, also the O/C sensibility. Therefore it doesn't represent an increase or decrease of ethanol but only the amount of carbon has been changed.

We start with the analysis of the most important chemical parameters. The first property is RON, reported in Fig. 45 and Fig. 46.

The laminar flame speed shows a clear decrease as the RON increases. This is due to the increase in the isooctane and toluene content which have high octane number and low laminar flame speed. This correlation is not trivial because there isn't an explicit relationship between RON, which measures the autoignition behavior of the fuel, and the laminar flame speed. In fact a high value of RON can be also achieved by big amounts of ethanol which, however, has a very high laminar flame speed.

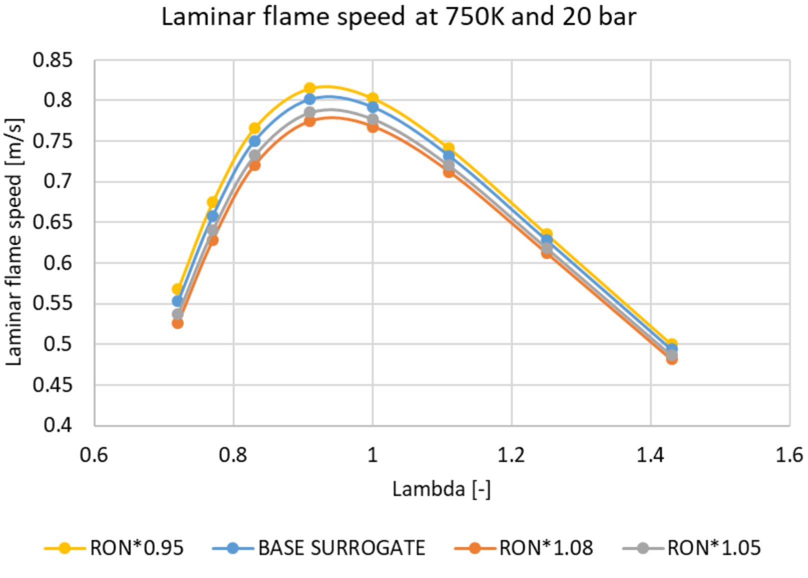


Fig. 45: Laminar flame speed varying the RON value using LLNL

Also the ignition delay time has a clear trend: as the RON increases the ignition delay increases as well and the paraffinic behaviour in the NTC region decreases. It is here clearer the effect of toluene on the mixture because is the only component that is allowed to vary that has no NTC region. Therefore the ignition delay time gives an additional information about the variation of the composition because for the laminar flame speed isooctane and toluene have the same behaviour.

The increase of RON shifts the composition towards high octane components which are isooctane and toluene; the effect of this variation is quite linear both for the laminar flame speed and for the ignition delay. On the other hand, a decrease of the RON value increases the amount of n-heptane that can be seen from the higher laminar flame speed and the lower values of ignition delay.

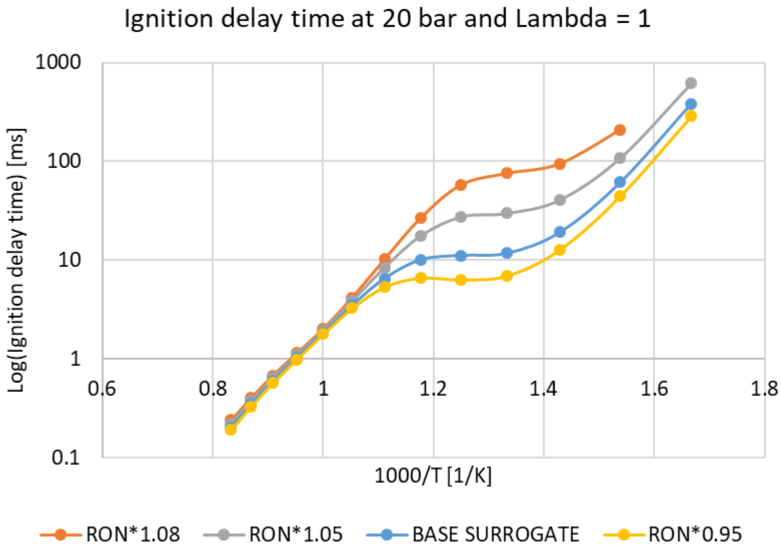


Fig. 46: Ignition delay time varying the RON value using LLNL

Same results can be achieved for MON and AKI sensitivity results are reported in Fig. 47 and in Fig. 48.

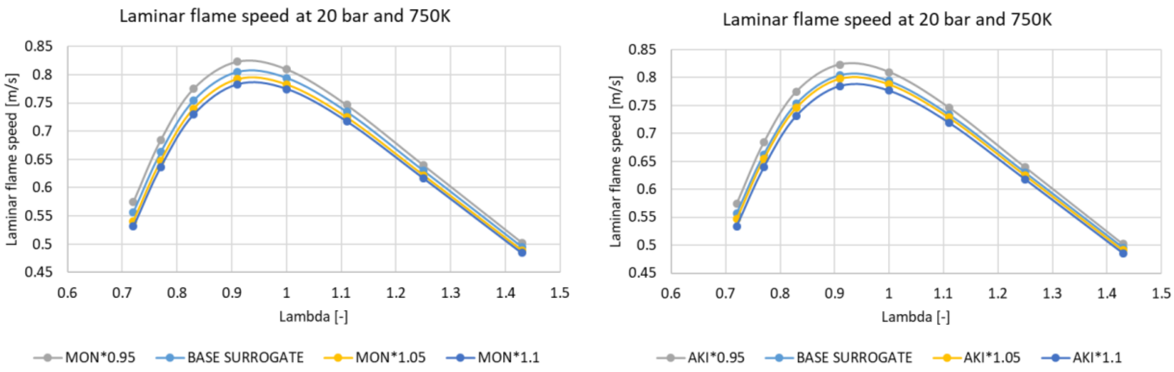


Fig. 47: Laminar flame speed of surrogates obtained by varying the values of MON and AKI using LLNL

The solutions are not the same for the different surrogates but the simulation's result is identical, i.e. increasing either MON or AKI the laminar flame speed decreases for the greater amount of toluene and isooctane, which are also responsible for the increase of the ignition delay time.

Therefore we can state that the value of any of these parameters (RON, MON and AKI) must be precise because the mixture has a great sensibility and the final simulation result is deeply influenced both for the laminar flame speed and the ignition delay time.

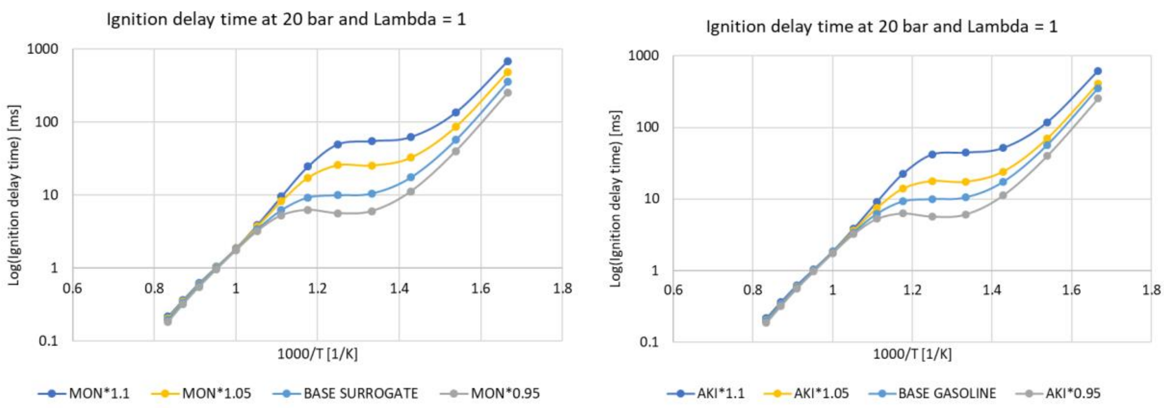


Fig. 48: Ignition delay time of surrogates obtained by varying the values of MON and AKI using LLNL

Even though we have already found out that using the octane sensibility as an equation for the surrogate's definition is wrong, we will shortly present its sensitivity analysis.

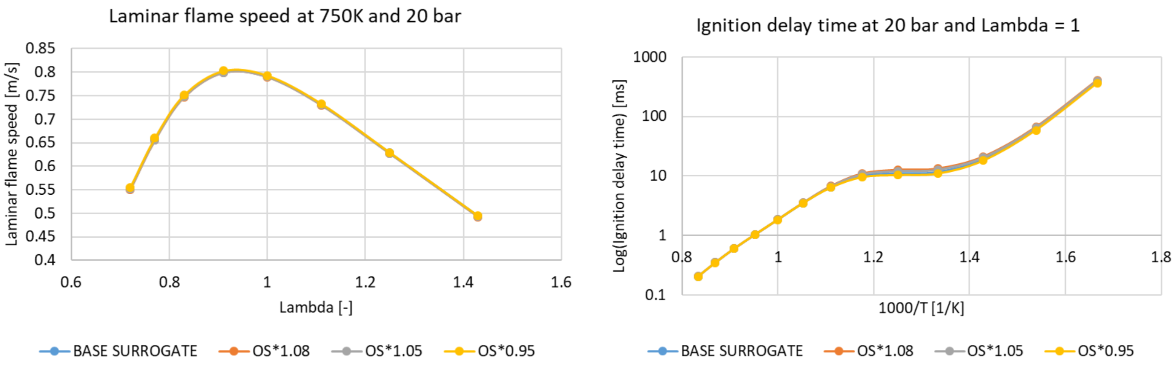


Fig. 49: Laminar flame speed and ignition delay time of surrogates defined varying the octane sensitivity using LLNL

As one can see from Fig. 49 the octane sensitivity, i.e. the difference between RON and MON, has really little interest also from the sensitivity analysis point of view since all the surrogates produced give as a result the same curve for the laminar flame speed and for the ignition delay even though we saw that the latter simulation is very composition sensitive. Such a solution can be explained with the fact that, being OS a constraint on the relation between RON and MON, its value can be matched by changing the values of both RON and MON and therefore with really small adjustments on the mixture composition.

We can conclude that the value of OS is not important for the surrogate's definition because it is a too general parameter whose influence on the laminar flame speed and ignition delay time is limited, if not absent. Therefore there is no need for great accuracy of such parameter's value. Indeed, the sensitivity analysis we conduced up to here demonstrate that once that one value between RON, MON or AKI is specified there is no need for more information about the octane rating since we saw that the surrogates defined by matching whatever of the last three parameters give results very similar. Hence we found a more rigorous justification to the choice made in the methodology to exclude the match of both RON and MON and instead using the remaining degree of freedom for other properties.

Next we analyse the chemical properties of H/C and O/C ratios. As we saw these are parameters complicated to match because really precise and small numbers based on details of the real gasoline composition which are not directly linked to any specific property but that can be used as a proof of general good agreement between surrogate and gasoline.

In particular the H/C ratio is connected to the mass fraction of paraffins. Indeed, as the H/C ratio grows, the number of hydrogens for each carbon must increase. Therefore molecules with high numbers of hydrogens are preferred and, since ethanol, which has the greatest H/C ratio, is fixed, the paraffinic content grows. Indeed the only other possibility is toluene which, however, has a brute formula of C_7H_8 that means that is more present at low H/C values.

From Fig. 50 one can see that the laminar flame speed is once again the same curve for all the surrogates, demonstrating once again that it mostly depends on the temperature and the amount of ethanol rather than on details in the mixture composition.

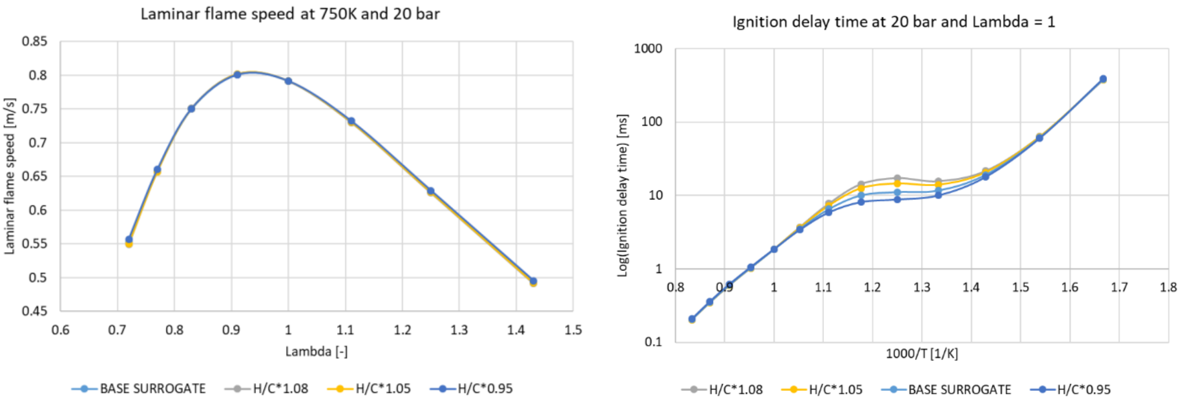


Fig. 50: Laminar flame speed and ignition delay time of surrogates produced using LLNL for the H/C ratio sensitivity

What's more, between isooctane and n-heptane, i.e. the two possible paraffins with high H/C ratios, the increase is mostly done by isooctane that replaces the toluene without changing too much the RON value; both components have a low laminar flame speed therefore the two effects are compensated.

Concerning the ignition delay one can see that the increase of isooctane increases the NTC region and slightly increases the ignition delay. The overall effect is limited to the NTC temperatures because at higher and lower temperatures the curves collapse on the two straight lines. We can conclude that the information on the H/C ratio doesn't need to be very accurate and that it is a general indication of the paraffinic content. This last conclusion is valid only for gasolines with a limited amount of ethanol because the value of H/C ratio for ethanol is two and therefore much higher than any other component implemented and therefore we can no longer state that it represents the paraffinic content of the gasoline.

The analysis of the O/C ratio was conducted keeping the amount of ethanol constant since we have already investigated the influence of ethanol blends on the gasoline. Therefore what it could be changed to reduce or enhance the O/C ratio is just the amount of carbons; as an example, if we are looking for an increase of the O/C ratio the only possibility is to reduce the number of carbons globally available in the mixture. To do so the two components whose mass fraction might be increased are n-heptane (C_7H_{16}) and toluene (C_7H_8) that are both components with seven carbon atoms instead of isooctane (C_8H_{18}) that has eight carbons; nonetheless the amount of n-heptane cannot increase indefinitely because otherwise the properties of the surrogate would change too much, therefore the only remaining solution is once again to increase the toluene.

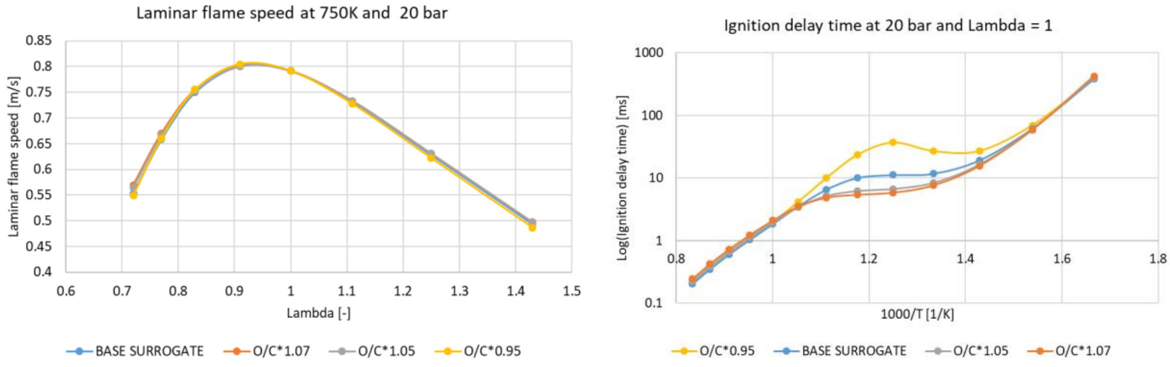


Fig. 51: Laminar flame speed and ignition delay time of surrogates produced using LLNL for the O/C ratio sensitivity

In Fig. 51 the simulations are reported for laminar flame speed and ignition delay time. As we expected the influence of the O/C ratio on the laminar flame speed is very limited. A more important variation is the one of the ignition delay time. Indeed, increasing the O/C ratio at ethanol content constant implies a reduction of the NTC and a decrease of the ignition delay because of the higher toluene content. Vice versa, for low O/C ratio values the ignition delay increases as well as the NTC region because of the higher isooctane amount.

The interest in this parameter is quite limited, as we already stressed above, because it makes the equations' system very unstable and fragile. A proof of this is exactly the case we just analysed in which to produce the surrogate with a low O/C value the amount of isooctane literally exploded and reached more than the 77%, which is of course an unrealistic value. What's more the information carried by this parameter is mostly related to the air fuel ratio, i.e. the α_{st}, which can be better matched by means of other equations that are easier and more precise. Indeed, as it can be seen in Fig. 52, where we plotted the value of α_{st} against the O/C ratio of eleven different surrogates we produced matching a variety of properties, the information of the O/C ratio is correlated with the α_{st} one. However, in order to match the precise value of α_{st} the value of O/C ratio must very precise as one can see from the very low slope of the straight line correlation, i.e. if we move down little on the y-axis (decreasing the α_{st}) we have to move a lot towards higher O/C values. This consideration gives the insight in the problem of matching the O/C ratio: very small numbers that have a great composition sensitivity.

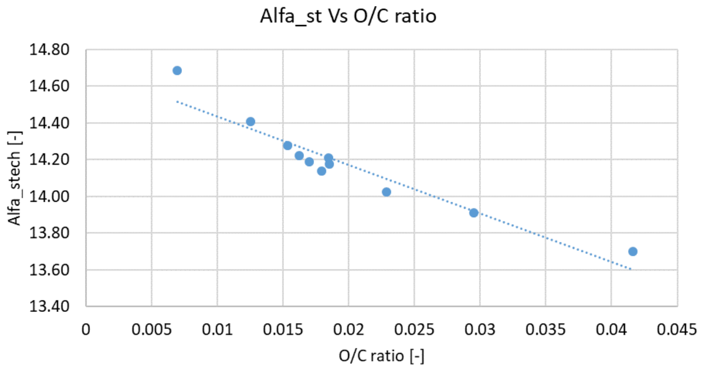


Fig. 52: Correlation between α_{st} and O/C ratio

We agree that generally is easier to find information about the O/C ratio of a gasoline rather than about the α_{st}. Nevertheless, the point we want to stress here is that there are less complicated alternatives to the O/C ratio equation. The latter is connected also to the value of LHV which, bottom line, is defined in a similar way to α_{st}.

As a conclusion, the O/C ratio shall be used just in case of lack of other information but bearing in mind the awareness that it makes the system more complicated to solve. Another solution would be to let ethanol vary which, however, is usually a too big assumption, as we saw.

The next property is the molar weight of the mixture. As we saw in Table 18 the molar weight has generally a high variability and is difficult match. What's more since its value is not fundamental for the simulation the constraint is usually omitted.

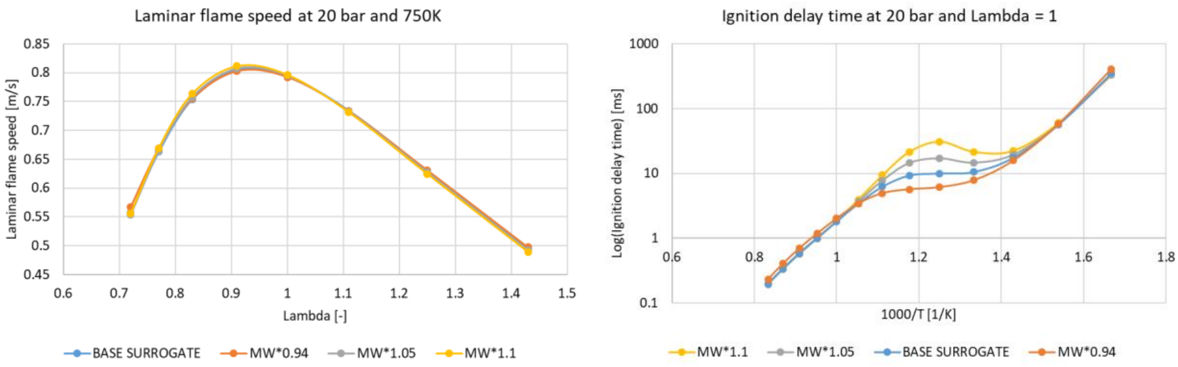


Fig. 53: Laminar flame speed and ignition delay time of surrogates produced using LLNL for the molar weight sensitivity analysis

In Fig. 53 the simulations are reported. As usual the laminar flame speed has a very limited variation for all the mixtures. In the ignition delay time the variations are concentrated in the NTC region whereas at high and low temperatures the solutions collapse on two straight lines. In the NTC region one can see that increasing the molar weight the mixture shifts towards heavier components, i.e. the paraffins which are the ones with the longer carbon chains. In the case here presented the greatest increase is the one of isooctane which is the reason of the increase of the ignition delay and of the NTC region typical of paraffins. On the other hand, for low values of molar weight the ignition delay time and the NTC region decrease because of the increase in the amount of toluene.

The interest in the molar weight is limited; however, if someone is interested in matching it, the value must be quite precise because it influences the ignition delay behaviour. Up to a certain extent this information is connected to the amount of paraffins because are the heaviest components.

The next property is density which instead is much more interesting from the simulation point of view. The densest component is toluene followed by ethanol while isooctane and n-heptane are much less dense. The density equation permits to reach a solution quite easily even though the maximum variation allowed is limited.

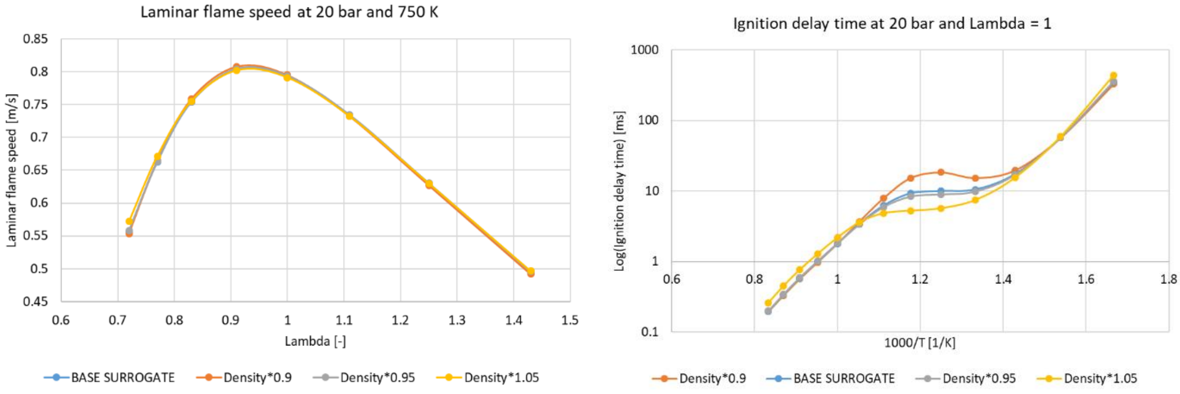


Fig. 54: Laminar flame speed and ignition delay time of surrogates produced using LLNL for the density sensitivity analysis

The simulation’s solutions are reported in Fig. 54. As usual the effect on the laminar flame speed is nothing.

In this case also the in the ignition delay time the variation is limited and for values of density close to the real one, i.e. the series _“Density*0.95”_, the two solutions are almost identical. For high values of density, the amount of toluene increases reducing the ignition delay time and the NTC region. Vice versa, at low values of density the paraffinic content increases as well as the ignition delay and NTC region.

In conclusion, to match the density of the gasoline could be a good idea, as we indeed did for the definition of the E85-4 surrogate, because it doesn't introduce too many difficulties in the system and has an important effect on the simulation. Indeed the relevance is twofold: first of all the simulation uses during the calculations the equations of state that are based on the density and therefore an error in the density may cause the wrong evaluation of a wide range of properties and their subsequent calculations; the second relevant aspect is that there is the necessity to simulate the amount of fuel injected and therefore, to make it more realistic, the volumetric flow rate at the injector as we saw for the ethanol.

The remaining properties are α_{st} and LHV. These two properties are deeply connected one another since both of them are based on the composition of the fuel in terms of carbon, hydrogen and oxygen number of atoms. While defining the surrogates for the LHV we realised that the results were the same of those of α_{st}. Therefore the analysis we report below has to be considered as valid for both properties.

The reasons of this connection can be understood starting from the mathematical formula of these properties. For a general fuel $C_aH_bO_c$ we formula of α_{st} is the following:

$$\alpha_{st} = \frac{MM_{O_2}\left(a+\frac{b}{4}-\frac{c}{2}\right)n_{O_2} + 3.76\ MM_{N_2}\left(a+\frac{b}{4}-\frac{c}{2}\right)n_{N_2}}{n_{fuel}\ MM_{fuel}}; \qquad \text{(Eq4.2)}$$

while the one of LHV, expressing the terms and eliminating the ones that are multiplied by the formation enthalpy of pure components (O_2 and N_2) that is equal to zero per definition, is:

$$LHV = \sum_{i=1}^{N_{FUEL}} x_i \Delta h_{f,i} - a\Delta h_{f,CO_2} - \frac{b}{2}\Delta h_{f,H_2O} \qquad \text{(Eq4.3)}$$

where x_i are the mass fraction of the fuel's components whose total number is N_{FUEL}. The result is the value of LHV referred to the unit of mass of fuel. In the LHV definition the only formation enthalpy that is greater than zero is the one of toluene. Therefore to increase the LHV one must reduce the overall enthalpy of the fuel and to increase the amount of CO_2 and H_2O produced.

From the equations one can see that both parameters decrease if the amount of oxygen increase. Indeed, while this is evident for α_{st}, the LHV decreases because the amount of oxygen reduces the availability of carbons that can be oxidized to CO_2. Another parameter of influence is the number of carbons: if the number of carbons increases, more CO_2 will be produced, which increases the LHV, and therefore more air is needed for the oxidation, hence the α_{st} increases. Same considerations can be done for the amount of hydrogen whose increment causes more water production. We can now better understand why the increase in the LHV or α_{st} is connected to the increase in the paraffinic content: there is great increase of carbon and hydrogen atoms.

From a chemical point of view this correlation can be explained with the fact that the energy released is the product of the redox reactions. If the amount of energy in the fuel increases also the amount of air must increase in order to provide the required oxygen.

Finally, we can state that the variables that increase the amount of one parameter have the same effect on the other.

In Fig. 55 are reported the simulation's results of the laminar flame speed and ignition delay.

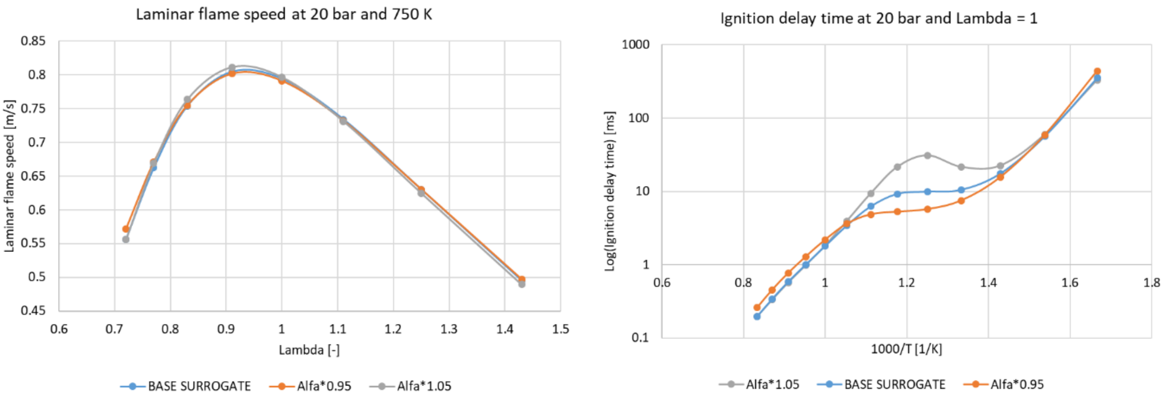


Fig. 55: Laminar flame speed and ignition delay time of surrogates produced using LLNL for the α_{st} sensitivity analysis

The first thing one can notice is that it wasn't possible to produce a surrogate whose value of α_{st} was more than 5% away from the real value. This is due to the very limited variability possible for the equations.

As usual the laminar flame speed simulation is uniform even though in this case a limited difference can be seen around stoichiometric mixtures; in particular a higher laminar flame speed is produced by the surrogate with a higher α_{st} value but it is a negligible difference.

Concerning the ignition delay, instead, there is a marked difference in the NTC region where the increase of the α_{st} coincide with the increase of paraffins and therefore the ignition delay time and the NTC curve. This is an expected result as well as the fact that a reduction of the α_{st} causes a transition towards behaviours typical of the toluene: lower ignition delay time and less marked NTC region.

Typically the value of LHV or α_{st} are reported as parameters of the gasoline and therefore it is always good to try to match them. As we saw, just one of them is enough to define both. What's more there is no need of great accuracy of the data because the variation admitted is really limited therefore ensuring a realistic value. Usually to include these equations is not complicated even though the stiffness of the system might increase.

To conclude this part dedicated to the sensitivity analysis we propose a short and simple summary (Table 21) in order to recap all the correlations. It is not fundamental to bear all of them in mind at the same time because after a relatively low number of surrogates' definitions the whole process will be more natural and fluid.

In the light of Table 21 the choices done in the definition of the methodology are clearer and what we at first defined on the basis of experience finds now a more rigorous base.

To sum up, in this chapter we used data about the gasolines to produce surrogates using a methodology above discussed. The surrogates of the gasoline Super Plus 98 give results in very good agreement between each other and therefore anyone of them can be implemented for the production of the database. The solution for the E85 gasoline was more difficult because of the complexity of the system to converge. Hence different approaches have been tried and the results show that too many simplifying assumptions produce unrealistic behaviours.

Afterwards, in order to understand how the final simulations are influenced by the many different variables that play a role in the definition of surrogates a wide sensitivity analysis has been carried out by investigating at first components. What we found is that concerning the laminar flame speed all the species but ethanol have a limited influence in the range of variability of the surrogates defined using the same gasoline's properties; on the other hand ethanol has a great influence for values above 5%. On the ignition delay there are instead two major aspect: the first one is the NTC region that is typical of paraffins; the second one is the value of ignition delay time, which is characteristic of each component.

Table 21: Summary of the sensitivity analysis (IDT = Ignition delay time)

	Constraint	Effects on Laminar flame speed	Effects on Ignition delay time
COMPONENTS	Isooctane	Limited	Increase NTC Increase IDT
	N-heptane	Limited	Increase NTC Decrease IDT
	Toluene	Limited	Decrease NTC Increase IDT
	Ethanol	<5% → Limited >5% → Increase	Decrease NTC Increase IDT
EQUATIONS	RON	Reduce	Decrease NTC Increase IDT
	MON	Reduce	Decrease NTC Increase IDT
	AKI	Reduce	Decrease NTC Increase IDT
	OS	Negligible	Negligible effect on NTC Negligible effect on IDT
	H/C ratio	Negligible	Limited increase of NTC Limited increase of IDT
	O/C ratio	Negligible	Decrease NTC Decrease IDT
	Molar weight	Negligible	Increase NTC Increase IDT
	Density	Negligible	Decrease NTC Decrease IDT
	α_{st} and LHV	Negligible	Increase NTC Increase IDT

Eventually, equations have been analysed and we found that:

- RON, MON and AKI give comparable results and that are fundamental for the definition of surrogates because of the great impact on the laminar flame speed;
- it is wrong to match the octane sensitivity because is too general relationship between RON and MON;
- among the other equations we discussed the importance of α_{st} and LHV and we found out that to match one of them is the same as matching also the other.

As a conclusion we can now state that the most important equations, apart from the mass balance that must be always satisfied, are: ethanol content, RON or equivalent (MON and AKI), α_{st} or LHV.

This is also the set of equations we suggested as a starting point. Who is interested in developing a surrogate must, however, remain flexible on the choice of equations because the solution might be difficult to achieve. Therefore the sensitivity analysis can be used as an indication to make forecasts and to choose the relevant constraints.

The only remaining step is the experimental validation of the surrogate as a good method for the simulation of combustion in internal combustion engines.

5. Experimental validation

The experimental validation was carried out by comparing data from a real engine working at a specific engine point, determined in terms of speed and load, with the simulation of the same engine in the same conditions.
The experimentation was carried out at the IVK FKFS. The gasoline available for the experimentations was the Super Plus 98 that we analysed above and the surrogate was determined in the same way we discussed above. Nevertheless the surrogates were further developed in order to produce the database that is than implement in *QuickSim*.
The engine considered in this work, whose main specifications are presented in Table 22, was analysed and tested at test bench at the FKFS in Stuttgart.

Table 22: Main engine specifications

Specification	Value
Displaced volume [cc]	846
Number of cylinders [-]	2
Stroke [mm]	68
Bore [mm]	89
Connecting rod [mm]	255
Compression ratio [-]	9.0:1
Power [kW]	92 (@7500 rpm)

The simulation domain includes the whole working flow from intake throttle to turbine inlet, as shown in Fig. 56.

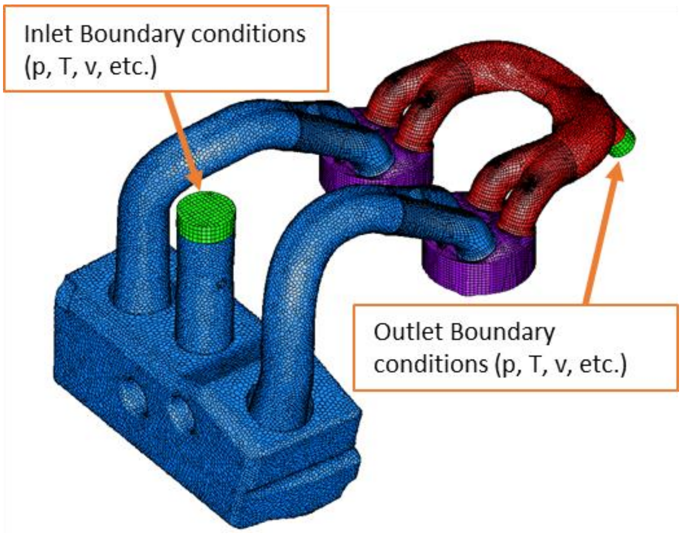


Fig. 56:Full engine model implemented in the simulation, according to test bench geometries

The implementation of dedicated models for heat transfer and combustion allows coarse meshes which in this case is composed by less than 300.000 cells for the full engine model (more information about the models used can be found in [31]). As a consequence, a fast simulation time is achieved (12 h per engine cycle). More details regarding the simulation are shown in Table 23.
The database was prepared for the whole range of thermal and chemical conditions covered by this engine during combustion:

- Lambda range: 0.5 – 2.0;
- Temperature range: 500 – 1000 K;

- Pressure range: 50 – 130 bar;
- EGR fraction range: 0 – 30%.

Table 23: Main 3D-CFD simulation details

Simulation details	
Mesh size	273400 cells
Calculation time per engine operating cycle (Single core simulation on Intel Xeon E5-2643 v4)	12 h
Operating cycles necessary to reach convergence	8-10 (depending on engine operating point)
Time step Δt	Const = 0.5/1.0 °CA (depending on stability)

The main parameters of the operating point are reported in .

Table 24: Engine operating point

	Operating point
Engine speed [rpm]	2000
Load	WOT
Intake Boost Pressure [bar]	0.97
Average Lambda @ IP [-]	1
IP [CA bTDC]	20

The results of the experimentation are reported in Fig. 57.

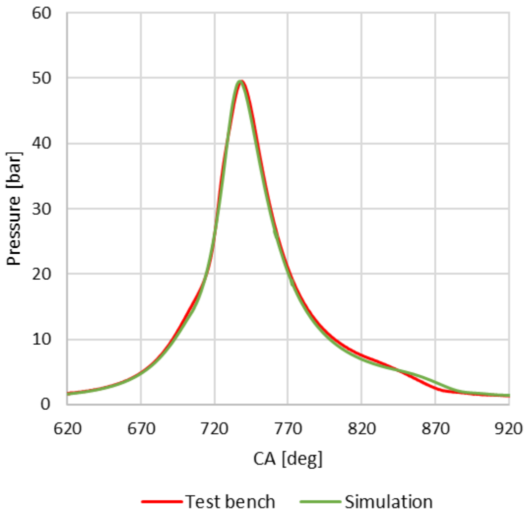


Fig. 57: Experimental validation of combustion simulation by means of fuel surrogates in internal combustion engines

The simulation and the experimental values are in very good agreement during the whole combustion process and therefore the whole methodology can be considered as validated. There was no possibility to do a more direct validation of the surrogates' capability to predict laminar flame speed and ignition delay of the real gasoline because of the lack of the experimental instrumentation and the high cost of the test. Nevertheless the simulation of the whole engine is the most interesting for our thesis because it not only proves, though indirectly, that the parameters were properly evaluated, but is a significant confirmation that the process can be properly implemented in *QuickSim*.

When thinking at the whole process and then looking at the results of the experimentation one understands that in order to achieve a good final simulation one need to take many decisions whose effects are maybe difficult to evaluate. Many assumptions are made in order to make the process time effective, others to certify the process, others to achieve a better accuracy. All these choices must be done bearing in mind the final goal as much as possible.

With the experimental validation the simulation has gained the capability of predicting the behaviour of unknown, or not yet studied, fuels that is an important feature of the simulation.

This is also the end of our discussion that circularly returns to the point it started: now there is a validated methodology to simulate the combustion of alternative fuels whose behaviour is still unknown or unreported, which was our goal.

6. Conclusions

The starting point of this work was the change in the energy strategy of many countries, especially the Europeans ones, that is triggered by the necessity of energy security and to deal with the climate change. The sector that was less affected until today by this change is transportation, which is also one of the biggest energy users. One solution to the new challenges of a clean and sustainable transportation is the production of liquid biofuels starting from natural products locally available. This causes the need for a change also in the internal combustion engines because of the different combustion mode that makes them incompatible with standard engines.
The method to develop a new engine is to use experiments and simulation. The main features of simulation are to act as an "eye in the engine" and to be able to predict new conditions without the need for building a real model and implementing it on a test bench, therefore saving money and time. However, to speed up the simulation of engine cycle some assumption must be done especially concerning the combustion process that is one of the most time-consuming processes. In *QuickSim* the combustion is simulated using the assumption of flamelet regime, which makes the process much faster because the calculation is done once and for all before and separately from the simulation itself. To do so, the simulation requires a database of the laminar flame speed and the ignition delay time of the fuel that is used.
The way to produce such a database is to define the so-called fuel surrogates and simulating them by means of a free software called CANTERA that is implemented in python. In this work we discussed and validated all the steps and the methodologies that this process requires and we achieved a final solution for it.
There is a number of aspects that need to be further developed in order to increase the capability of the system to predict the behaviour of different and not yet validated fuels.
First of all, we point out the problem of the species implemented in the reaction mechanisms. Indeed, we dealt with gasolines in which the amount of exotic components is negligible. Nevertheless, there are gasolines with high content of naphtenes or olefins. In particular the gasolines for motorsports have a great amount of naphtenes because of the extremely high laminar flame speed. Olefins, instead, are used to reduce the knocking tendency of the fuel because of their high ignition delay time. In the case of a simulation of a gasoline with non-negligible amount of such species they must be considered and included in the surrogate composition definition. To reach such a result, however, several steps are still needed.
First of all we had difficulties in identify the species because the names that are used in the reaction mechanisms differ according with the group that produced the mechanism and usually no list of the species is available.
A second step would be the validation of such species for the porpoises of the engine simulation that, as we saw, are high temperature and pressure laminar flame speed and ignition delay time.
Finally, there is probably the need to more deeply investigate the effects of naphtenes and olefins on the combustion process in order to define which compounds are the most representatives and which must be instead discarded and to implement reaction mechanisms based on this knowledge that can simulate engine combustion using a limited but interesting number of species.
This is for sure the first limitation to the definition of surrogates with more complicated compositions.
To add a compound means also to add a degree of freedom to the system of equations that solves the problem. We made a couple trials in order to see how the system behaves and, far from introducing other instabilities, the solutions were found using the same procedure as in the case with less compounds. The number of equations available is usually much bigger than the number of components and therefore it doesn't produce any limitation. It must be though stressed that a greater number of species is not always fundamental, as our work demonstrates. Indeed, the suggestion to increase the number of compounds is limited to those applications where the fuel is characterized by a non-negligible amount of naphtenes and/or olefins.

It is our opinion that these are the two more pressing limits: to find and validate the species that can represent the two remaining PIONA groups of naphtenes and olefins.
In literature there are many proposals of components that should increase the precision of the simulation which are representatives for the PIONA groups already validated, like for example methanol [59] for the oxygenated compounds or isopentane for the branched paraffins [56]. The main issue is that in order to have such a big palette of compounds the reaction mechanism must grow both in number of species and reactions, making the whole process much slower. What's more, as our work demonstrates, this level of detail seems a bit too high compared the final result. For example, we saw that the laminar flame speed has a very low dependence on most of the components. Hence, our conclusion is that there is for sure the need for more species to be implemented and validated but such species shall not further contribute to the already existing and validated PIONA groups but to fill the gaps left by olefins and naphtenes. Once these species are found, validated and implemented the sensitivity analysis shall be updated in order to understand how these new compounds influence the laminar flame speed and the ignition delay. It is our opinion that the sensitivity analysis we performed will keep its validity for all the surrogates that, for the sake of simplicity, will be developed using the four species we have implemented.
The second limit that will require further development is the validation of reaction mechanisms at engine conditions for laminar flame speed and ignition delay. Indeed, at the high temperatures and pressures typical of engine operation the chemistry is deeply different from the one at low temperature and pressure. Nevertheless, reaction mechanisms are usually validated, especially for laminar flame speed, at low temperature and pressure. In these conditions there might be a good agreement among different mechanisms that, however, is by no means a proof that the same agreement can be found also at high temperatures and pressures.
The most interesting aspect is that, during the mechanisms' validations, both LLNL and CAI had a good agreement with experimental data and between them. In this case, however, an offset is present of about 20% between the two solutions, which is of course unacceptable. We chose to use the LLNL to produce the surrogate for two reasons: is the reaction mechanism that is more validated and is also the one with the largest number of reactions and therefore the one where more high temperature reactions are included. The appearance of such offsets is not uncommon among reduced reaction mechanisms with a little number of reactions. To solve this point, it is important to produce experimental data at high pressure and temperature even though our validation is already a good proof of the reliability of the system.
Despite these limitations we proved that the whole process works well and permits to produce simulations good enough for the simulation of internal combustion engines which was our goal.
There is however a new frontier that is opening recently and in which the experience we made up to now may play an important role: the production of e-fuels specifically designed for a particular engine.
Indeed, all the analysis performed up to here have been used as a way to forecast the behaviour of an existing fuel, however, they can be as well used as a way to design a fuel whose final application is a very precise and optimized engine. This is one of the interesting development lines that are being tested right now and that could play a role in the future. The underlying idea is that to meet the always more stringent efficiency and emissions limits one of the solutions is to develop an engine precisely optimized for a specific fuel whose characteristics are known and well controlled. The production of such fuel may be integrated in an e-fuel system which is intrinsically flexible and can produce theoretically different fuels using the carbon from industrial processes and hydrogen from electrolysis performed using renewable energies. Using these two elements it could be possible to produce all the molecules necessary for the fuel.
Once that the performances that the engine must provide are defined, the development of the fuel composition is not different from producing a fuel surrogate of a real gasoline. The interaction between the chemistry and the engine, with all the thermodynamic problematics we saw, is indeed an analysis very similar to that performed in this work.

This might be the long-term future while the simulation is the present. In any case the focus is to reduce the impact of transportation on the climate. This is for sure an important goal that we feel it worth pursuit. The humankind will require always more transportation and it is rightful to give everybody the opportunity to move but we also must take care of our only planet and to preserve it, as beautiful as it is, for the generations to come.

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