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THE OCTANE NUMBERS OF ETHANOL-CONTAINING MULTI-COMPONENT GASOLINE SURROGATES

Joinville, 2016

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Diploma thesis presented as a partial requirement to obtain a Diploma degree in Automotive Engineering in the Automotive Engineering Program of the Federal University of Santa Catarina, Joinville Campus.

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Este trabalho de conclusão de curso foi julgado adequado para obtenção do Título de Engenheiro Automotivo e aprovado em sua forma final pelo Programa de Graduação em Engenharia Automotiva da Universidade Federal de Santa Catarina.

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DEDICATION

This work is dedicated to:

- My parents, Amauri da Silva and Rosalia Forbici da Silva, who taught me that there are not obstacles that can not be overcome.
- My brother, Diego Gean da Silva.
- My grandfather, Albino Forbici (in memoriam).

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RESUMO

Motores de ignição por centelha são amplamente utilizados em veículos ligeiros. No passado, a maioria destes foram concebidos para serem movidos apenas com gasolina. Atualmente há uma tendência global para uso de etanol misturado à gasolina devido a necessidade de fontes renováveis de energia e também por conta das questões relacionadas a poluição ambiental. Em países como EUA, Brasil e também na União Europeia, existem leis que regulam o percentual de etanol na gasolina. Assim, as principais intenções dos fabricantes de motores são aumentar a eficiência e reduzir os poluentes emitidos. O objetivo deste trabalho foi estudar a influência da quantidade de etanol na gasolina em relação ao desempenho do motor através da avaliação do índice de octanagem (RON) da mistura etanol – substituto de gasolina. Neste estudo, um substituto de gasolina composto por isooctano, n-heptano, tolueno e diisobutileno foi utilizado para simular a gasolina real. Sete diferentes amostras (E0, E10, E20, E30, E50, E85 e E100) compostas pela mistura de etanol e substituto de gasolina foram utilizados para avaliar a influência da quantidade de etanol no valor de RON. Testes experimentais para determinar o índice de octanagem destas amostras foram realizadas utilizando um motor padronizado, *Cooperative Fuel Research Engine (CFR),* no laboratório do motores da Universidade de Ciências Aplicadas de Ingolstadt, na Alemanha. Para as amostras com valor de RON abaixo de 100, os procedimentos de medição foram baseados no método de ensaio ASTM D2699, enquanto para aqueles com maior valor de RON o procedimento utilizado foi baseado em metodologia usada em alguns laboratórios na União Européia, devido para o fato da não utilização de Tetraetilchumbo. Os resultados do estudo mostram que os valores de RON aumentam com a adição de etanol á gasolina. Com tais resultados foi possivel validar o substituto de gasolina utilizado, proposto por Cancino et al. (2011), já que este substituto mostra valores e o comportamento semelhantes ás gasolinas reais estudadas por Anderson et al. (2012).O aumento da percentagem de etanol na gasolina permite aumentar a taxa de compressão do motor e assim aumentar sua eficiência. Uma percentagem mais elevada de etanol também permite uma maior potência de saída do motor. Assim, quanto maior é o conteúdo de etanol misturada á gasolina, maior é o valor de RON, e maior pode ser a taxa de compressão do motor, o qual permite a melhoria da eficiência e aumento da potência. Assim, o uso de etanol permite que o motor opere dentro dos intervalos de emissões determinados por leis governamentais, e também permitem que os fabricantes de motores atinjam seus objetivos.

Palavras - chave: Número de octano, Mistura etanol - gasolina, Motor de ignição por centelha, Substituto de gasolina.

ABSTRACT

Spark ignition engines are widely used in light duty vehicles, in the past the majority was designed to run just with gasoline. Nowadays there is a global tendency to use gasoline-ethanol blends, due to the fact that there is a need for renewable energy sources and also because of the environmental concerns. In some countries, like USA, Brazil and also in European Union, there are laws which regulate the percentage of ethanol in gasoline. Thus, the main intentions of the engine manufacturers are increase the efficiency as well as the reduction of emissions. The objective of this research was study the influence of the quantity of ethanol in gasoline on the engine's performance by evaluating its research octane number (RON). In this study, a gasoline surrogate composed by isooctane, n-heptane, toluene and diisobutylene was used to simulate a real gasoline. Seven different samples of gasoline-ethanol blends (E0, E10, E20, E30, E50, E85 and E100) were used to evaluate the influence of ethanol on the RON value. Experimental tests to determine the octane number of these samples were performed using a Cooperative Fuel Research (CFR) engine in the engine laboratory at the Ingolstadt University of Applied Sciences, in Germany. For those samples with a RON value below 100, the measurement procedures were based in the standard test method ASTM D2699, while for those with higher RON, the procedure utilized was based in a methodology used in some laboratories in the European Union, due to the fact that Tetraethyl lead is not used there. The results of the study show that the research octane number for the gasoline surrogate increases with the addition of ethanol. With these results it was possible to validate the gasoline surrogate used, proposed by Cancino et al. (2011), since this surrogate shows similar values and behavior when compared to real gasolines studied by Anderson et al. (2012).Increasing the percentage of ethanol in gasoline allows increasing the compression ratio of the engine, thus there is an increase in engine's efficiency. A higher ethanol percentage also enables a greater output power from the engine. Thus, the higher the content of ethanol blended with gasoline, the greater is the octane number, consequently higher can be the compression ratio of a designed engine, which allows the improvement of efficiency and power. Therefore, the use of ethanol allows the engine operate within the emission ranges determined by governmental laws, and also allow the engine manufacturers reach its goal. Also, as the output power can be higher, ethanol in gasoline also favors for the development of downsized engines, which is also a global market tendency.

Keywords: Research octane number, gasoline-blended ethanol, spark ignition engine, gasoline surrogate.

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LIST OF ACRONYMS

ASTM	American Society for Testing and Materials
ATDC	After Top Dead Center
BDC	Bottom Dead Center
BTDC	Before Top Dead Center
CDF	Cumulative Density Function
CFR	Cooperative Fuel Research
CI	Compression Ignition Engine
CO	Carbon Monoxide
CO_2	Carbon Dioxide
DIN	German Institute for Standardization
DCR	Digital Counter Reading
ECU	Eletronic Control Unit
EPA	Environmental Protection Agency
EVC	Exhaust Valve Close
EVO	Exhaust Valve Open
FFV	Flexible Fuel Vehicles
HC	Hydrocarbons
HCCI	Homogeneous Charge Compression Ignition
IC	Internal Combustion Engine
IDT	Ignition Delay Time
IVC	Intake Valve Closes
IVO	Intake Valve Open
MBT	Maximum Brake Torque
MON	Motor Octane Number
NO_x	Nitrogen Oxides
ON	Octane Number
PFI	Port Fuel Injector
PRF	Primary Reference Fuels
PRR	Pressure Rise Rate
PXI	PCI Extension for Instrumentation
RON	Research Octane Number
RPM	Rovolution per Minute

RF	Reference fuels
SFC	Specific Fuel Consumption
SI	Spark Ignition Engine
SOC	Start of Combustion
TC	Top Center Position
TDC	Top Dead Center
TEL	Tetraethyllead
THI	Ingolstadt University of Applied Sciences
TRF	Toluene Reference Fuels
TSF	Toluene Standardization Fuels
UFSC	Federal University of Santa Catarina
UHC	Unburned Hydrocarbons
USA	United States of America

LIST OF SYMBOLS

CR	[-]	Compression ratio
°CA	[deg]	Crank angle
L_s	[mm]	Piston stroke
B	[mm]	Cylinder bore
l	[mm]	Connecting road length
V_d	[dm^3]	Displaced cylinder volume
V_c	[dm^3]	Clearance volume
$W_{c,i}$	[J]	Indicated work per cycle
P_{max}	[bar]	Maximum pressure
P_{amb}	[bar]	Ambient pressure
IMEP	[Pa]	Indicated Mean Effective Pressure
P	[kW]	Power produced per each cylinder
n_r	[-]	Number of crank revolutions per power stroke
N	[rev/s]	Crankshaft rotation
η_f	[-]	Indicated fuel conversion efficiency
η_c	[-]	Combustion efficiency
η_t	[-]	Thermal conversion efficiency
m_f	[kg]	Mass of fuel inducted per cycle
Q_{LHV}	[MJ/kg]	Fuel lower heating value
Q_{HV}	[MJ/kg]	Fuel heating value
γ	[-]	Specific heat ratio
c_p	[J/(kg K)]	Specific heat at constant pressure
c_v	[J/(kg K)]	Specific heat at constant volume
φ	[-]	Relative fuel/air ratio
λ	[-]	Relative air/fuel ratio
IDT	[μs]	Ignition delay time
Q_{ch}	[J]	Fuel chemical energy release
MAPO	[bar]	Maximum amplitude of pressure oscillation
$\hat{p}$	[bar]	Filtered in-cylinder pressure
AKI	[-]	Antiknock Index
ξ	[-]	Percentage of each substance in sample E0 (remaining fuel)

Ω	[-]	Percentage of each substance in sample E10
$\Lambda_{sample,i}$	[-]	Percentage of each substance in sample *i*
$\psi_{sample,i}$	[-]	Percentage of ethanol in sample *i*
K.I	[-]	Knock Intensity
KL_{ASP}	[-]	Percentage of engine working cyces with occurence of knock
ON_s	[-]	Octane number of the sample under study
ON_{LRF}	[-]	Octane number of the low RF
ON_{HRF}	[-]	Octane number of the high RF
$K.I_{LRF}$	[-]	Knock intensity of the low RF
$K.I_{HRF}$	[-]	Knock intensity of the high RF
$K.I_S$	[-]	Knock intesity of the sample fuel;

SUMMARY

1. INTRODUCTION

The first pratical four-stroke-cycle internal combustion engine was built in 1876 by Nicolaus Otto, which has a characteristic to be powered by liquid fuel. At that time, the engine was projected to run using a fuel that became known as gasoline. This engine is known as spark igniton engine, due to the fact that is needed a spark plug to start the combustion process. With the development of the automobile industry at the beginning of the 20th century, especially with the start of production line of the light-duty vehicle Ford T in 1908, the usage of spark ignition engines started to gradually grow up. (GIBBS et. al, 2015).

In the first decades of the 20th century, the petroleum industry turned its focus from kerosene to gasoline, due to the increase on demand. However, the vehicle's engine were also capable to run using ethanol or a blend formed by gasoline and ethanol. According to Board (2016), in the United States of America the ethanol production increased rapidly during the World War I, however at the end of the war there was a prohibition regarding to ethanol production. Until 1933 just some companies could produce it under strict government regulations. Thus, until the oil crisis in 1970s, spark ignition engines were powered mostly with pure gasoline. Therefore, the use of ethanol as a fuel has been growning since this crisis. According to Eia (2012), United States of America has been blending ethanol into gasoline since the late 1970s. However, as mentioned by Anderson et. al (2012), the usage of ethanol as a transportation fuel has increased greatly in the last two decades and is projected to increase in the future.

According to Board (2016) the ethanol use and production has increased during recent years mainly because of the environmental concerns. Gasoline-blended ethanol reduces the quantity of pollutants emitted by the combustion process, as the carbon monoxide and hydrocarbons, the concentration of carcinogens also are decreased. A global tendency is restrict the engine's emissions through different kinds of regulations, in Europe for example, the European Commission defines emission standard for light-duty vehicles through the emission standard regulation 715/2007/EC.

Also, other important reasons are related to this increase of ethanol usage, as the reduction of country’s dependence on imported oil, for those countries which are not able to produce gasoline to supply its own demand. Thus, ethanol favors to reduce the dependence on fossil fuels, once it is a renewable fuel.

Furthermore, to impulse the use of ethanol, nowadays there are legislations and regulations regarding to the percentage of ethanol which should be blended with gasoline. In

Brazil, which is the world’s largest producer of sugarcane-based ethanol, since 2015 there is a new regulation which has established that common gasoline must have 27.5% (v/v) ethanol. In USA and European Union the maximum quantity is equal to 10%.

Thus, the main reasons to use ethanol-gasoline blend are reduce the pollutants emission, as well as increase engine efficiency, which are the aims, among others, of the automobile industry. The efficiency can be increased due to the fact that ethanol leads to a higher octane number. Furthermore, its usage reduces the occurrence of engine knock.

In the quest for efficient vehicles, which are capable to reduce fuel consumption, as well as to fit in the emissions regulations, it is a fundamental importance understand how the content of ethanol influences the engines performance when it is powered by a blend composed by ethanol and gasoline. Parameters as the output power, combustion efficiency and compression ratio in which the engine can be designed, are strongly related to the ethanol percentage in gasoline.

The aim of this study is evaluate the effect of the ethanol addition on multicomponent gasoline surrogates for use in spark ignition engines, in terms of Octane Number by using a Cooperative Fuel Research engine.

1.1. Objectives

1.1.1. Main objective

To measure the Octane Number of a set of gasoline surrogate / ethanol blends, spanning a wide range of ethanol content (E0, E10, E20, E30, E50, E85 and E100) using a Cooperative Fuel Research (CRF) engine.

1.1.2. Specific objectives

In order to reach the main objective, some specific objectives are proposed:

- Evaluate the octane number values of the gasoline surrogate comparing it with common gasolines, as well as understand the influence of each substance present in this surrogate on the octane number.

- Determine for each sample of ethanol / gasoline surrogate blend the compression ratio for knocking, keeping the level of knock intensity constant for all the blends.
- Calculate the engine efficiency which can be achieved increasing the content of ethanol;
- Build up a curve which shows the sequence of events in the CFR engine operating cycle;
- Evaluate how the ethanol percentage influence in the combustion process;
- Build-up the in-cylinder pressure curve for the samples of the gasoline surrogate tested.
- Evaluate the influence of ethanol content in the maximum in-cylinder pressure, as well as in the indicated mean effective pressure.

2. ENGINE CHARACTERISTICS AND PARAMETERS

In this topic some basic geometrical relationships and parameters commonly used to characterize engine operation are discussed. These parameters are used to compare different engine operation conditions, as this thesis proposes, varying the content of ethanol is expected that some important characteristics, as power output and maximum pressure in the engine cycles, may differ for each sample of gasoline surrogate.

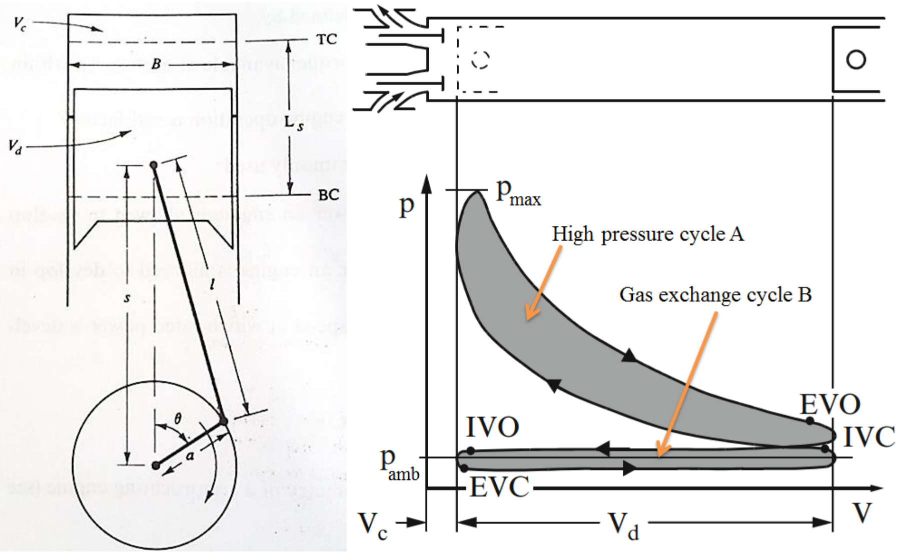
2.1. Compression ratio

This parameter is defined as:

$$CR = \frac{maximum\ cylinder\ volume}{minimum\ cylinder\ volume} = \frac{V_d + V_c}{V_c} \qquad (1)$$

In which, V_d is the engine displaced volume and V_c is the clearance volume. These volumes are shown in figure 1(a).

Figure 1 - (a) The engine cylinder geometry; (b) p - V diagram for a four-stroke engine



Font: (a) Heywood (1988); (b) Modified from Merker, Schwarz and Teichmann (2012)

Top-dead center crank position (TDC), or just top-center (TC), is the maximum upper position of the piston. Bottom dead centercenter crank position (BDC) is the piston lowest position. θ is the crank angle degree, also defined as °CA, and L_s is the stroke. In figure 1-a, ”*B*” is the cylinder bore, ”*l*” is the connecting rod lenght and ”*a*” is the crank radius.

2.2. Indicated work per cycle

The indicated work per cycle $W_{c,i}$ is obtained by integrating the curve in the p-V diagram to obtain the closed area, as shown in figure 1-b. Basically, $W_{c,i}$ is the area indicated as ”High pressure cycle A” minus the area ”Gas exchange cycle B” (HEYWOOD, 1988). P_{max} is the maximum pressure in the cycle and P_{amb} is the ambient pressure.

2.3. Indicated mean effective pressue (IMEP)

Heywood (1988) point out that the indicated mean effective pressure is an important parameter that describes engine performance. It has units of force per area, and is obtained by dividing the work per cycle by the engine displacement volume (V_d).

$$IMEP = \frac{W_{c,i}}{V_d} = \frac{P\,n_r}{V_d N} \tag{2}$$

In which, N is the crankshaft rotation, n_r is the number of crank revolutions for each power stroke per cylinder (2, for four stroke engines), P is the power produced per each cylinder.

2.4. Indicated fuel conversion efficiency (η_f), combustion efficiency (η_c) and thermal conversion efficiency (η_t)

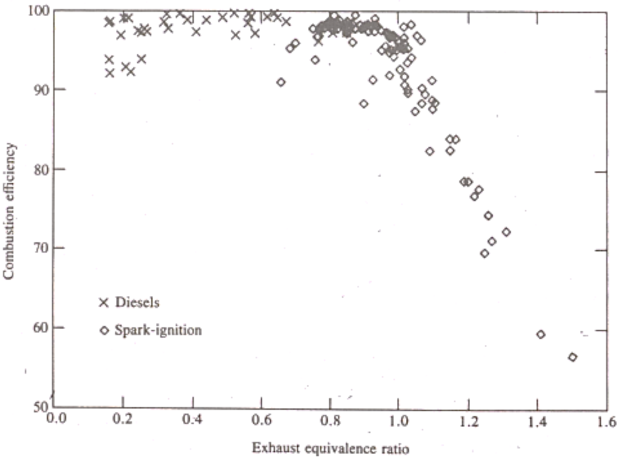
The indicated fuel conversion efficiency, according to Heywood (1988) is described mathematically as:

$$\eta_f = \frac{W_c}{m_f Q_{LHV}} = 1 - \frac{1}{CR^{\gamma-1}} \tag{3}$$

In which Q_{LHV} is the lower heating value of the fuel, and m_f is the mass of fuel inducted per cycle. Heywood (1988) also describes that, if the combustion efficiency is equal to the unity, the indicated fuel conversion efficiency is equal to the thermal conversion efficiency. Also according to this author, this efficiency express the ratio of the work produced per cycle to the amount of fuel energy supplied per cycle that can be released in the combustion process. It is a measure of the engine's efficiency. CR is the compression ratio and γ is the specific heat ratio c_p/c_v.

According to Heywood (1988), the exhaust gas of an internal combustion engine contains incomplete combustion products (e.g, CO, H_2, unburned hydrocarbons, NO_x, soot) as well as complete combustion products (H_2O, CO_2). Due this fact, during the engine combustion proces, part of the fuel's chemical energy is not fully released. Thus, the combustion efficiency (η_c) defines the fraction of fuel energy supplied which is released in the combustion process. Figure 2 shows the combustion efficiency according to the fuel/air equivalence ratio (φ). In practice the combustion efficiency is less than unity. The fuel/air equivalence ratio (φ) is the mass ratio of fuel to air which is present in a combustion process. The equivalence ratio also can be defined as the mass ratio of air to fuel, in this case, the air/fuel rario and the symbol used is (λ). Both definitions are used in this thesis, since different papers were used during descriptions of some important topics in this study, and some authors have used different terminologies.

Figure 2 - Variation of engine combustion efficiency with fuel/air equivalence ratio.



Font: Heywood (1988)

The thermal efficiency (η_t) relates the actual work per cycle to the amount of fuel chemical energy released in the combustion process (HEYWOOD, 1988), defined as:

$$\eta_t = \frac{W_c}{\eta_c m_f Q_{HV}} \tag{4}$$

These three efficiencies defined above can be related as follow:

$$\eta_f = \eta_c \eta_t \tag{5}$$

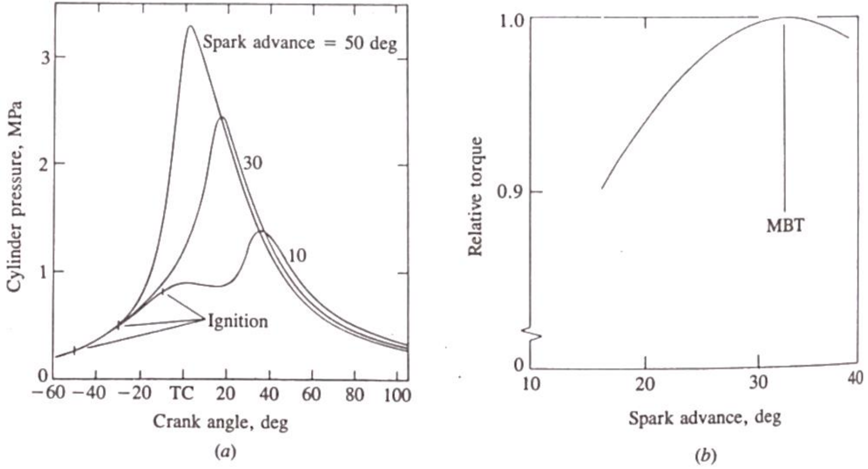
3. COMBUSTION IN SPARK IGNIGION ENGINES

According to Heywood (1988), in a convetional spark-igniton engine operating under normal conditions, combustion is initiated towards the end of the compression stroke at the spark plug by an electric discharge. Following this electric discharge, there is a period in which the energy release from the developing flame is to small to generate a pressure increase. The in cylinder pressure reaches a maximum near to the TDC.

To improve the engine's performance, the combustion process have to be properly located relative to the TDC, thus is possible to obtain the maximum power or torque.

Normally, the combustion process starts before the end of the compression stroke. Figure 3 shows how the engine torque varies with spark timing (HEYWOOD, 1988).

Figure 3 - Cylinder pressure versus cranck angle



Font: Heywood (1988)

The electric discharge determines the start of the combustion process. If the spark timing is advanced before top dead center (BTDC), there is an increase in the maximum pressure and also the area of the curve (figure 3-a) is greater, which means that the work transfer increases, and thus, the engine’s torque. In the other hand, if the spark timing is delayed BTDC, there is a decrease in the peak pressure, as can be seen comparing the spark timing in 50° and in 10°. It means that there is an optimum point (crank angle) for spark timing, point that will give the best conditions for heat and work transfer in function of the thermodynamic “equilibruim” of forces between fresh gasses, burned gasses, piston head and combustion chamber walls. There is a spark timing which gives the the maximum brake torque (MBT), it is shown in figure 3-b. In this curve, the maximum torque is reached in case of spark timing equal to 32° BTDC.

3.1. Knock phenomenon

The knock phenomena occurs commonly in spark ignition engines, also known as SI engine. In the beginning of the last century, this phenomena were so common, that was belived to be part of a normal combustion (GANESTAM, 2010). It is a phenomenon of easily detection when it occurs intensely, because it generates strong engine noise, similar to the sound of crashing metal parts, give the pin beat name (knock).

According to Heywood (1988), knock is the name given to noise that is transmitted by the engine structure due to the occurrence of autoignition.

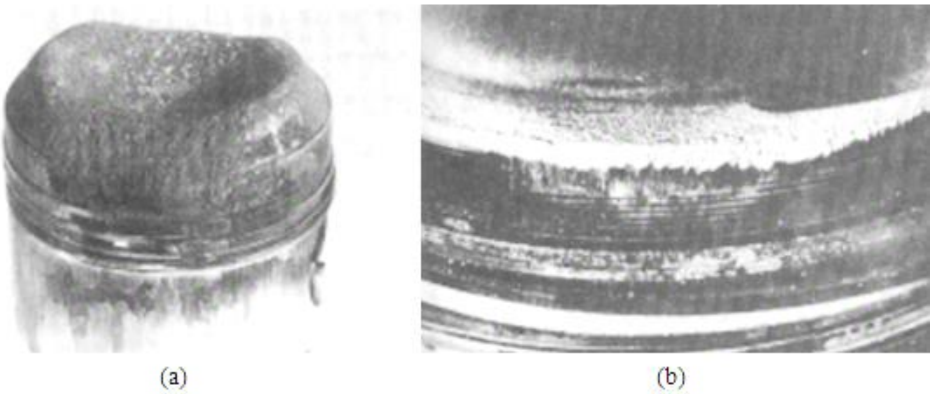
As mentioned by Johansson (2006), this phenomenon is one of the responsible for the deterioration of some engine components, such as the combustion chamber. Engines operating under severe knock conditions are more willing to erosions in the piston than those engines operating under normal conditions, ie, without the occurrence of this phenomenon. The metal particles that become detached from the piston wall, as well as from the combustion chamber, may remain in contact with these two components, and ends up damaging them further. It is also possible that these particles are absorbed by the oil from the lubrication system, and if it happens, there is a increase in the friction between engine components.

Other mechanical problem related to this knock phenomena, as described by Piernikarski, Hunicz and Komsta (2013), is the considerable reduction in engine life. When exposed to a severe knock, cracks and fractures can occur in the piston crown and also the piston-rings, resulting from the shock waves created by the detonation process. Heywood (1988) affirms that the knock process can still lead to melting the piston edges.

Other problems related to this phenomena are the increased air pollution, as well as the decreases of engine’s efficiency and the increment of fuel consumption (ZHEN et al., 2012).

Besides the mechanical problems in which the engine is exposed during the occurrence of this phenomenon, the noise generated by the engine is an aspect of paramount importance to the comfort of the vehicle passengers (SAUVAGE et al., 2012).

Figure 4 - Damage caused by self-ignition



Font: Heyhood (1988)

The previous figure shows an engine that was operated under severe knock condition for ten hours. In figure 4- a, can be seen that the piston crow is severely damaged, in figure 4-b is shown a melted piston edge.

To ensure that the engine operates on condition of maximum efficiency, maximizing the power delivered to the crankshaft as well as minimizing fuel consumption, it is necessary that the ECU (Electronic Control Unit) keep the ignition timing such that no occurrence of knock phenomenon happens (HORNER, 1995).

Knock occurs when the unburned gases suffer the process of autoignition, hence the importance of the ECU to control the engine combustion process (Horner, 1995).

Also according to Piernikarski, Hunicz e Komsta (2013), in this research field there are so much development to be done, due the trends of vehicle manufacturers to reduce the size of the engine, number of cylinders and also, simultaneously, in an attempt to increase the engine efficiency. This engine development process is called down-sizing, which usually are developed with supercharging systems. Basically there are two types of these engines: turbocharging and supercharging.

In addition, in the downsizing process, there is a tendency to increase the engine's compression ratio. However, higher compression ratios favor the occurrence of knock phenomenon, or the increasing of severity if the motor is already working with presence of low knock intensity. Therefore, downsizing technique is strongly limited by knock phenomenon and calls for highly knock resistance fuels. Supercharging systems increase the pressure of the intake air, increasing the quantity of air in the intake stroke, by this way, more air and fuel can be supplied during the first engine's stroke, as a result, more power can be developed by the engine with the same geometric properties (compression ratio).

According to Merker, Schwarz and Teichmann (2012) the conditions in which can increase the knock severity can be listed as: higher compression ratio; low speed engine; high load; fuel with low octane number; insufficient charge air colling; insuficient cooling in the chamber walls. If the conditions listed above happens while the engine operation, the knock intensity will increase.

3.2. Autoignition of gasoline

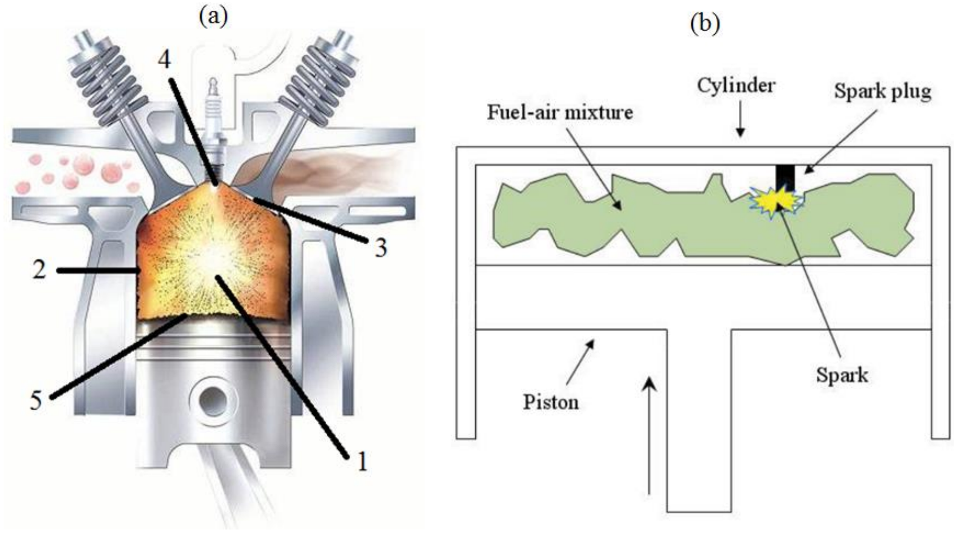
In short, self-ignition (autoignition) is the process by which occurs spontaneous combustion in the unburned gas (end-gas) in the combustion chamber. When this end-gas is exposed to favorable thermodynamic conditions in terms of temperature and pressure, a self-ignition can take place in one or more points simultaneously inside the combustion chamber. Normally the self-ignition process happens in a location distant from the spark-plug. This process can occur both before or/and after the occurrence of spark, from the spark plug (PIERNIKARSKI; HUNICZ; KOMSTA, 2013).

According to Heywood (1988) the spontaneous combustion processes can be originated from two different ways, beyond the autoignition there is a process called surface ignition. In this case, the combustion also occurs in unburned gases, but which differs from autoignition is that the ignition starts due to regions of hot spots, usually at the walls of the combustion chamber (i.e, exhaust valves or carbon deposits over the piston head).

Thus, the knocking process can be initialized by two ignition mechanisms (process) of the mixture outside of the spark plug; Autoignition: in which the spontaneous combustion occurs at any point of the unburned gases, when this mixture is under reach autoignition conditions (favorable temperature and pressure); and surface ignition: combustion begins in flow regions, in the hot spots points in the combustion chamber surface. These regions where autoignition and surface ignition can takes place are shown in the figure 5-a, in which:

- Region 1: inside the combustion chamber;
- Regions 2, 3, 4 and 5: wall of the combustion chamber, surface of the exhaust valve, spark plug or piston head surface, respectively.

Figure 5 - (a) Spontaneous combustion; (b) Normal combustion ignited from the spark plug.



Font: (a) Modified from EccoSaver (2015); (b) Ganestam (2010)

According to Nakagawa et al. (1984), the location of autoignition site varies with engine operating conditions and also with the engine characteristcs, as the location of the spark plug, manifolds and so on. The authors describe an experimentation realised in a SI engine, in their work, was found that the majority of occurrences of autoignition were in the vinicity of the cylinder wall. The normal combustion process can be illustratively seen in figure 5-b.

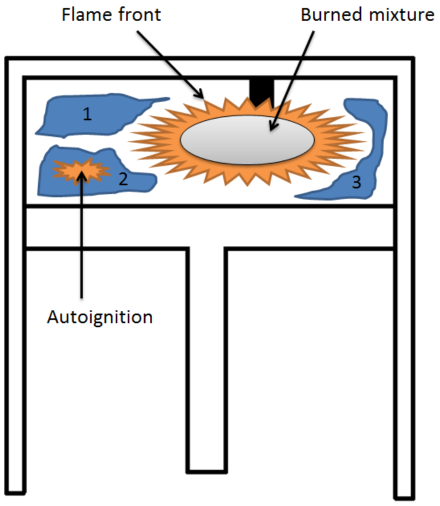
As mentioned by Ganestam (2010), after the spark begin, a turbulent flame is generated, and propagates through all over region of the cylinder chamber, moving away from the spark plug. From the moment that this flame starts, it begins to consume the fuel/air mixture, the portions of this mixture after the combustion process became a burned gas, and presents a higher temperature and higher pressure than the remnant fresh (unburned) mixture in the combustion chamber. The portion of burned gas thus passes to contribute to the total compression process of the fresh mixture (unburned gases), in other words, unburned mixture is compressed by the normal compression process in the engine cycle and also compressed by the burned mixture. This extra high pressure favors the occurrence of the phenomenon of autoignition.

Figure 6 shows schematically the burned and unburned gas areas. It is possible to observe in the figure the flame front, which is the region that separates the burned mixture from the unburned mixture.

The regions 1, 2 and 3 represents unburned mixture. In this situation, the gas in region 2 remained for a “long time” till reach the favorable conditions for autoignition (temperature and pressure), since the flame front took long time to reach and burn this part of the mixture, there was the occurrence of autoignition.

Once the self-ignition occurred in the region 2, the unburned gas in region 1 is now being compressed by both, the flame front coming from the spark plug, as well as the new flame front generated by autoignition in region 2. Then, the pressure in region 1 rises, facilitating the occurrence of autoignition also in that region.

Figure 6 - Occurrence of autoignition



Font : Author.

In short, if unburned mixture is exposed in a favorable conditions of temperature and pressure, and also the flame front take some time to burn this portion of the mixture, may occur autoignition.

Thus, according to Heywood (1988) the spontaneous ignition is accompanied by a rapid release of chemical / thermal energy, causing an increase of pressure in the portion of unburned mixture. This instantaneous pressure increase originates pressure waves, which propagating throughout the combustion chamber.

According to Ren, Randall and Milton (1999), the spread of these high-pressure waves occur at frequencies that are governed by the resonance of the combustion chamber.

The auto ignition generates high pressure waves, which travels through the combustion chamber with sonic speeds, these waves generate the typical pin beat sound (knock) (GANESTAM, 2010).

According to Merker, Schwarz and Teichmann (2012) an autoignition process that takes place before the spark ignition timing can be called as pre-ignition. The knowledge how this kind of autoignition can occurs is not yet clear. As the researches about it shows, pre-ignition is more easy to occur in supercharged engines with upper load. The autoignition time, also known as ignition delay time (IDT) is a critical parameter that influences the performance of both spark-ignition (SI) and compression-ignition (CI) engines (CANCINO et al., 2009). In short, the knock phenomenon originates from the process of autoignition.

3.3. Heat release

During combustion, the cylinder pressure increases due to the release of the fuel's chemical energy. Also according to Heywood (1988), by using the heat release approach, based in the first law of thermodynamics, is possible to relate the pressure changes directly to the amount of fuel chemical energy released by combustion. In figure 7(a) is shown the appropriate open - system boundary for the combustion chamber. The first law for this open system is:

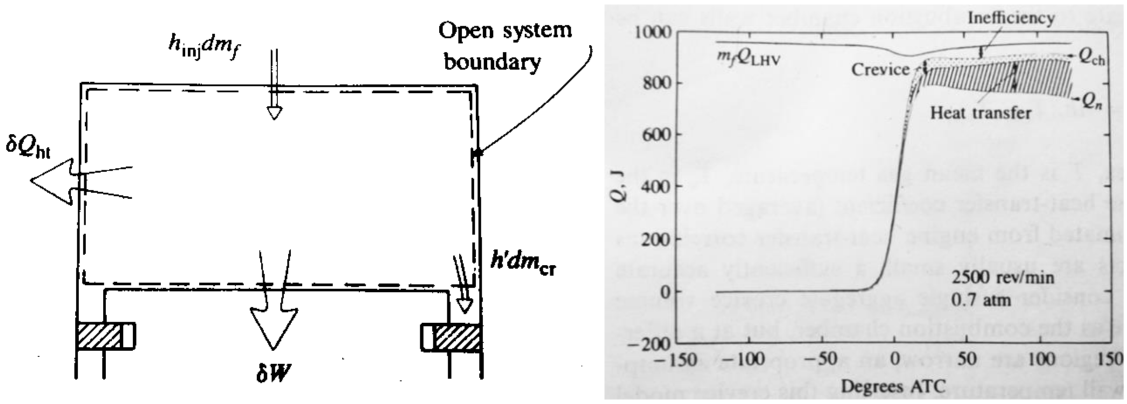
$$\delta Q_{ch} = dU_s + \delta Q_{ht} + \delta W + \sum h_i dm_i \tag{6}$$

In which these parameters can be defined as, dU_s: change in sensible energy of the charge; δQ_{ch}:represents the chemical energy released by combustion; δW: piston work; δQ_{ht}: heat transfer to the piston walls; $h_i dm_i$: mass flux which represents the flow across the system boundary; dm_{cr}: mass flux in the crevice region; dm_f: fuel mass flux in the boundary system.

Through the above equation is possible to analyse the heat release of a combustion process versus the crank angle for a conventional spark-ignition engine. It is shown in the figure 7-b. The lowest curve, Q_n, is the neat heat release (designated as δW in the above equation) . The chemical heat release, Q_{ch} is the sum of Q_n, the heat transfer (which is the term δQ_{ht} in the figure 7-a), and heat flow into the crevice region (which is the term dm_{cr} in figure 7-a).

The combustion inefficiency, which is deffined as: $(1 - \eta_c)$, can also be seen in figure 7-b, it is the difference in percentage between the chemical heat release (Q_{ch}) and the curve at the top of the figure, which is the mass of fuel within the combustion chamber times the its lower heating value of the fuel (Q_{LHV}).

Figure 7 - (a) Open system boundary for combustion for heat-release analysis; (b) Heat release analysis.



(a) **(b)**

Font: Heywood (1988)

3.4. Combustion process characterization

According to Heywood (1988), the energy-release curve, shown in figure 7-b, can be used to characterize different stages of the spark ignition engine combustion process. Basically there are three stages of the combustion process that can be defined as following:

- Flame development angle $\Delta\theta_d$: The crank angle interval between the spark discharge and the time when a small but significant fraction of the fuel chemical energy has been released. As described by Heywood (1988), usually this fraction corresponds to 10% of of the energy-release fraction, but also 1% and 5% have been used to describe it.
- Rapid burning angle $\Delta\theta_b$: The crank angle interval required to burn the bulk of the charge. This interval is defined between the end of the first stage (flame development) and the end of the flame propagation process (ussually energy release fraction of 90%).
- Overall burning angle $\Delta\theta_0$: The duration of the overall burning process. It is the sum of $\Delta\theta_b$ and $\Delta\theta_d$.

4. KNOCK DETECTION OVERVIEW

In many studies about internal combustion engines, vibration sensors are utilized to detect the occurrence of knock. These sensors can be both accelerometers as weel as knock sensors. (BRECQ; BELLETTRE; TAZEROUT, 2002). Also according to these authors, the knock detection is based on the representation of time or frequency of the collected vibration signals.

According to Ker and Duval (2007), the knock detection can be realized by using pressure sensors installed in the combustion chamber, also it is possible to use accelerometers to measure knock, these are located on the engine’s surface.Usually series production SI engines are equipped with them.

Accelerometers are commonly used in industry, due to its simplicity, but when utilized to measure acceleration in an engine, some problems can accour in data collection, due the parasitic noise related to de engine operation. (BRECQ; BELLETTRE; TAZEROUT, 2002).

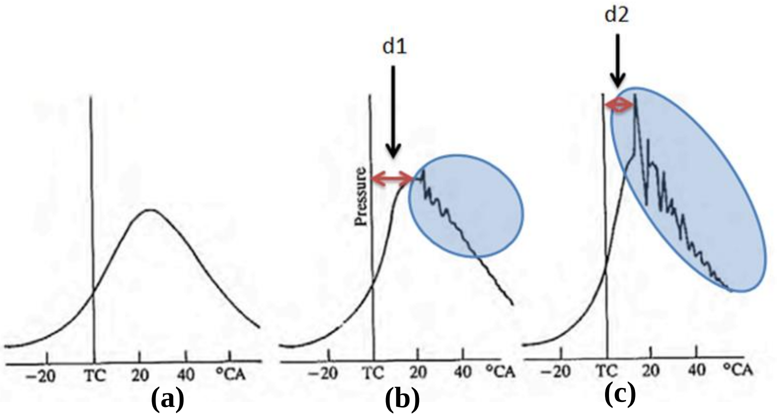
Brecq and Le Corre (2005) affirm that the pressure sensors are often used to detect engine’s knock phenomenon, due to the direct relation between pressure oscillation and this phenomenon. It is commonly used for engine research and development.

Heywood (1988) affirms that the knock phenomena not necessarily happens at every engine cycle, therefore, when operating the engine and measuring the knock, it is possible to detect that in some cycles there is no occurrence of knock, but in the other cycles it is detected. In the same engine, the knock phenomena can also vary cylinder-by-cylinder. Spark-knock is controlled by the spark advance, basically, advance the spark increases the knock severity, and retarding the spark decreases the knock severity. It occurs basically, because as mentioned in section 3, if the spark timing is advanced BTDC, there is an increase in the maximum pressure. Thus, the maximum pressure in the cylinder (P_{max}) is related to the knock intensity. The knock phenomena originates a high frequency oscilation in the pressure inner the combustion chamber, due to the high pressure waves which are originated through the detonation phenomena. Through the pressure sensors, this oscillation can be recorded. (Heywood, 1988).

The knock phenomena can be observed at the pressure history in figure 8, it shows the pressure in the combustion chamber versus the crank angle. The figure 8-a shows a normal combustion process, (b) a light knock and (c) a heavy knock.

According to Heywood (1988) the knock occurs when appears a high frequency pressure fluctuation, in figure 8-b and 8-c the blue regions are showing the occurrence of these fluctuations. In 8-a there is no trace of oscilations in the pressure curve, resulting in a uniform shape. It can be also seen that the first peak oscillation pressure, when a heavy knock occurs, happens closer to the TDC (Top Dead Center) than when a light knock happens, this difference can be observed through distance d1 and d2 in the figure (these distances are measured °CA). The higher the pressure oscillation, the higher is the knock intensity.

Figure 8 - Cylinder pressure versus crank angle



Font: Modified from Heywood (1988).

In short, knock originates in the extremely release of energy of the end-gas ahead of the propagating turbulent flame. The pressure distribution when knock occurs, shown in figure 8-b and 8-c, causes pressure waves or chock waves which propagates across the chamber (Heywood, 1988).

In figure 8, in (a) and (b) the spark accours at 28° BTDC (Before Top Dead Center), in case (c) it occours at 32°BTDC, which shows the a slight difference in spark ignition timing, results in different knock behavior.

There are basically two theories that help to explain the origin of knock. The auto-ignition theory and the detonation theory. As was explained in section 3, when the mixture in the end-gas is compressed, a critical pressure and temperature can be reached and a combustion in the end-gas can occur spontaneously, characterizing a self-combustion. The detonation theory affirms that under knock conditions, the flame front propagates under sonic velocity and the end-gas is consumed much faster than in normal flames (Heywood, 1988). This author affirms that the auto-ignition theory is most widely accepted.

According to Morgan et al. (2010), engine knock can be defined as limiting factor of a SI engine’s themodynamic efficiency caused by the autoignition of the fuel/air mixture ahead of the turbulent flame.

The tendency to knock depends on the engine design and operating variables which influence end-gas temperature, pressure and the time that the flame takes to arrive and burn this end-gas. Knock is a phenomenon that is governed by both engine and fuel factors. (Heywood, 1988).

4.1. Knock Detection Methods

According to Zhen et al. (2012), there are basically five different methods of knock detection, in which the method based on in-cylinder pressure analysis is the most widely used. It was used in this study.

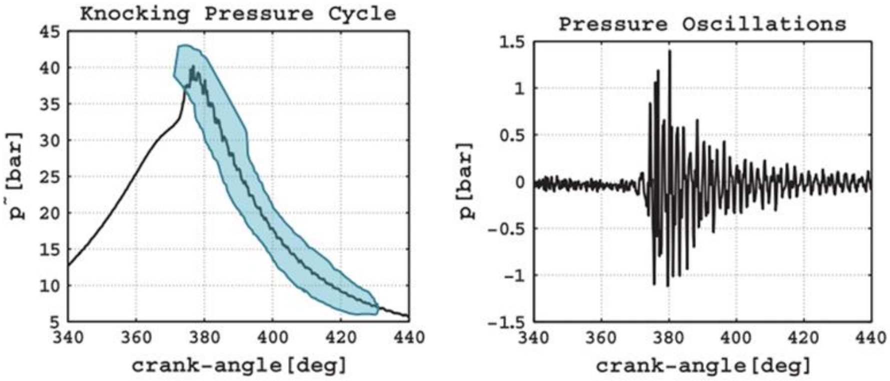
4.1.1. Method based on in-cylinder pressure analysis

Shu, Pan and Wei (2013) affirms that this is the most direct method to determine knock intensity, once the pressuse generated by the autoignition can be detected with very high signal-to-noise ratio.

This method uses pressure sensors to analyse the pressure oscillation in the combustion chamber. As already mentioned, the high knock frequency is directly related to the resonance frequencies of the combustion chamber. It is important to mention, that this method needs a pressure signal processing (ZHEN et al., 2012).

Blunsdon and Dent (1994) affirms that this phenomena excites the acoustic ressonance modes of the combustion chamber, as a result, there is an occurence of a damped pressure oscillation around the mean cylinder pressure.

Figure 9 - (a) Pressure curve; (b) Filtered pressure oscillation



Font: Modified from Gaeta et al. (2013).

As can be seen in figure 9-a, through the pressure sensor it is possible to plot the in-cylinder pressure. The blue region in this picture shows the part of the curve where knock phenomenon is occurring. The figure 9-b shows the filtered pressure oscillation, which is taken from the cylinder pressure curve, the blue part. The peak pressure in the cylinder in that case is about 40 bar, while the maximum pressure oscillation reaches 1.5 bar.

Basically, there are two ways to determine the knock intensity through the method based on in-cylinder pressure analysis. The cylinder pressure signals can be used to calculate an average pressure rise rate (PRR), through that, an average over many cycles determines the knock intensity. However, the most precise measure of knock severity is the maximum amplitude in the pressure oscillation that occur with knock combustion (Heywood, 1988).

Zhen et al. (2012) supports Heywood (1988) affirmation, is usual to use the maximum amplitude of the filtered cylinder pressure to determine knock intensity.

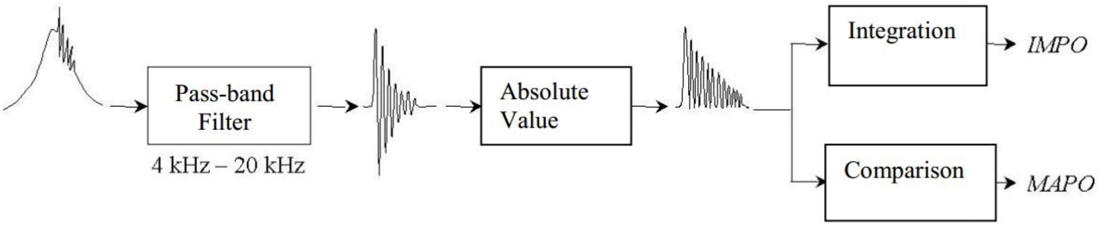
Brecq and Le Corre (2005) indicates that the signal from the cylinder pressure have to be filtered, then this signal can be used to calculate the knock intensity. Heywood (1988) affirms that this filters have to be used to remove the low frequency components from the pressure curve, the reason is that in a normal engine state operation the normal combustion generates these low frequency components and these kind of frequencies does not appears from the knock phenomena. To determine when knock is accuring, is necessary to use a band-pass filter to exclude these low frequencies, through that, just the components of the pressure signal that corresponds to the knock fluctuation remains.

Figure 9-b shows how a filtered pressure oscillation curve looks like. According to Zhen et al. (2012) the low cut-off frequency should be around 4 kHz, and the higher cut-off frequency have to be higher than the frequencies of the in-cylinder oscillations. Despite this, previous author describes this range of frequency, for Gaeta et al. (2013), the useful pressure oscillation frequencies to study knock is the range from 6 kHz to 25 kHz. Also Hudson, Gao and Stone (2001) supports this range of frequencies. Brunt, Pond and Biundo (1998) assums that for automotive engines, the range of vibration mode frequencies is tipically from 6 kHz to 20 kHz. Heywood (1988) affirms that these differences in the interval of frequencies happens because this range depends on the engine’s chamber geometry.

According to Brecq and Le Corre (2005), a scheme of the knock intensity determination can be drawn as shown in figure 10.

Basically, the pressure sensor pick-up the cylinder pressure, this signal is filtered with a pass-band filter, resulting in the filtered pressure oscillation signal, as was shown in figure 9-b. In this case the pressure signal is filtered in the range 4 kHz to 20 kHz, remembering that it depends from the engine’s characteristics. The pressure oscillation signal is processed and then is plotted only its absolute values, then is necessary to use knock indexes to determine the final value of knock intensity. In that case, the author suggests Integral of Modules of Pressure Oscillations (IMPO) or Maximum Amplitude of Pressure Oscillation (MAPO) as a technique to obtain the final value.

Figure 10 - Procedure to determine knock intensity



Font: Brecq and Le Corre (2005).

It can be found in the literature different kinds of knock indexes that can be used to determine knock intensity. Knock indexes involves mathematical equations and some of them statistical analysis. In addition to MAPO and IMPO, Zhen et al. (2012) describe a third knock indexes, which according to him, is also common used in this research area, which is called Integral of Modules of Pressure Gradient (IMPG).

MAPO is direct related to the peak of the pressure oscillation due the engine knock. IMPO is a technique which represents the energy contained in the high frequency oscillation. The last one, IMPG relates the modules of the pressure gradient (ZHEN et al., 2012). In this thesis, the frequency range is set as 4kHz to 15kHz (HAUBER; HUBER; NELL, 2015).

4.1.1.1. Maximum Amplitude of Pressure Oscillation (MAPO)

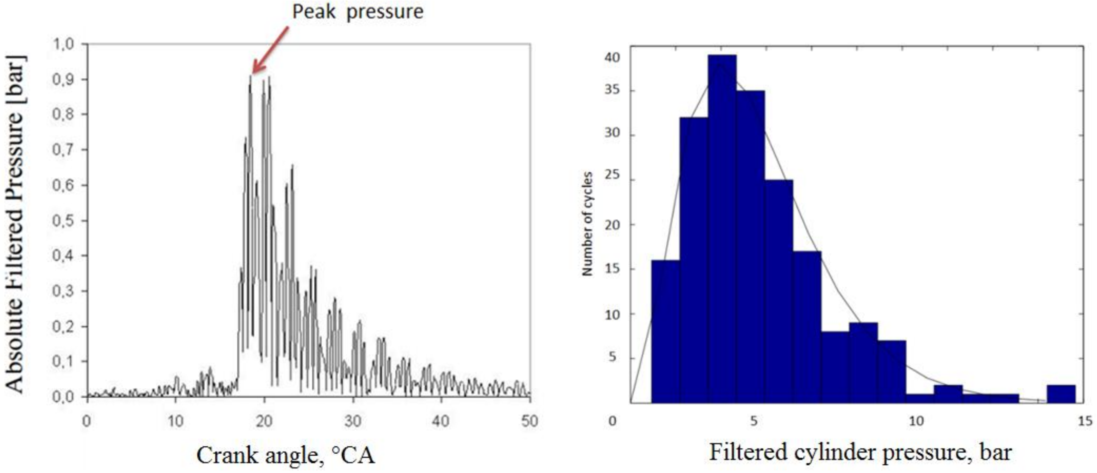
This knock indexes method will be explained in more details, the reason is that in the University of Applied Sciences of Ingolstadt - THI, the CFR engine, which is been used in this thesis, have already implemented this method in the CFR experimental set-up.

According to Zhen et al. (2012), MAPO can be mathematically described as following.

$$MAPO = \max\left(|\hat{p}|_{\theta_0}^{\theta_0+\delta}\right) \tag{7}$$

In this equation, θ_0 is the crank angle corresponding to the beginning of the collection of knock intensity (starting of the in-cylinder pressure curve, as shown in figure 9-a). δ is the increment in the window of calculation, $\hat{p}$ is the filtered in-cylinder pressure (as shown in figure 9-b). The filtered in-cylinder pressure is shown in more details in figure 11-a.

Figure 11 - (a) Filtered in-cylinder pressure; (b) Histogram of the peak pressure for each engine cycle



Font: (a) Modified from Brecq and Le Corre (2005); (b) Modified from Sinnerstad (2003)

Basically, in every engine cycle the filtered pressure values are collected and can be plotted, as can be seen in this figure. For this cycle, as the equation (7) determines, is collected the maximum pressure value, which is the peak of the filtered in-cylinder pressure, figure 11-a. For this engine cycle, the peak pressure value of the filtered curve is stored. In the next cycles the same procedure is made. After at least 300 cycles, these measured and stored values are taking into a statistical procedure to determine the knock intensity value of an engine operating point.

The peak pressure from the filtered pressure curve is plotted in an histogram, as shown in figure 11-b. Sinnerstad (2003) affirms that the statistical distribution which better fits to determine knock intensy are either Chi-square, Weibull or Gama distribution. In the previous figure is also shown the Gama distribution. Using one of these equations, is possible to plot the cumulative density function (CDF), through that, the knock intensity value (MAPO) can be determined. It is recommended to used a cumulative frequency of 95%.

5. SPARK IGNITION ENGINES, COMPRESSION IGNITION ENGINES AND HCCI.

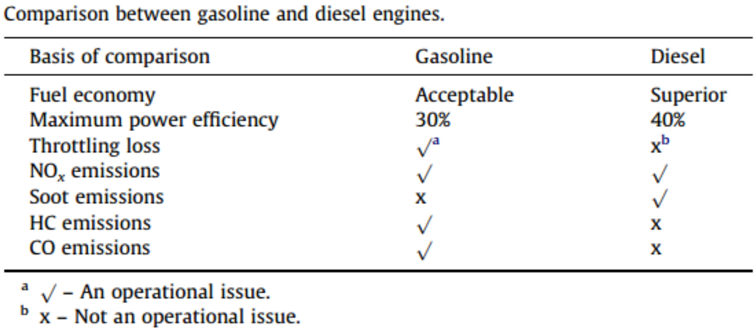
A global tendency is restrict the engine's emissions through different kinds of regulations, as an example, in Europe, the European Commission defines emission standard for light-duty vehicles as well as for heavy-duty vehicles, through the emission standard Directive 715/2007/EC and Directive 582/2011/EC , respectively.

As the aims of the automotive industries are both fuel economy and reduced emissions, HCCI engines are considered the best combustion technology to be widely used in the coming years, but for that, studies in this area of research have to be developed to make HCCI buildable (BENDU; MURUGAN, 2014). HCCI in research shows big advantages in improvement in port load efficiency (no throttling, fast combustion).

Among the types of widely used in the world in the automotive industry, there is the Spark Ignition engines (SI) and Compression Ignition (CI) (HAIRUDDIN; YUSAF; WANDEL, 2014). The SI engines have a precise control of air- fuel ratio, as well as catalytic converters, that makes this engine to be considered a source of clean power due the low emissions. However the SI engines has a limited efficiency, due the loss that are originated in the knock phenomena, also due the throttling and the flammability limits. Compression ignition engines (CI) have higher efficiency than SI engines, although engines have a higher emission rate (MAURYA; AGARWAL, 2014). A simple and useful way of comparing both engines is shown in table 1.

Although similar, through the table 1, the differences are evident, as the higher efficiency in CI (Diesel) engines, as well as a better fuel consumption, in comparison with SI engine. Some of the factors that contribute to higher efficiency of the CI engine are a higher compression ratio, the absence throttling valves and fuel lean operation. Throttling valves are necessary in the SI engines to provide the right air quantity for the combustion process. In these kind of engine, the compression ratio have to be restricted to approximate 10:1, to avoid the knock phenomena. (GAN; NG; PANG, 2011).

Table 1 - Comparison between SI and CI engines.



Comparison between gasoline and diesel engines.

Basis of comparison	Gasoline	Diesel
Fuel economy	Acceptable	Superior
Maximum power efficiency	30%	40%
Throttling loss	√[a]	x[b]
NO_x emissions	√	√
Soot emissions	x	√
HC emissions	√	x
CO emissions	√	x

[a] √ – An operational issue.
[b] x – Not an operational issue.

Font: Gan, Ng and Pang (2011).

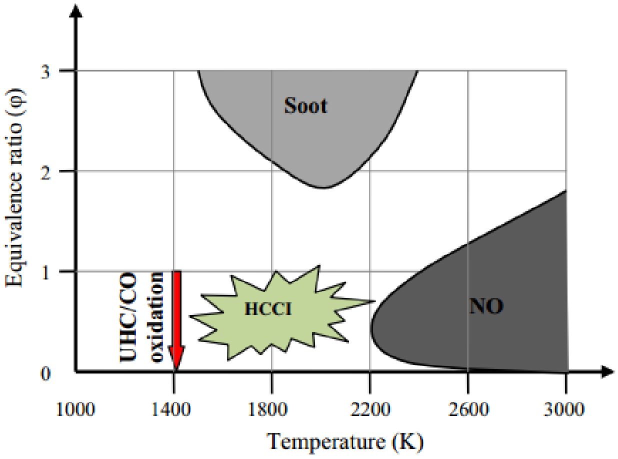
The main issues related to engines are the emission levels. Engines produce power by burning fuel and emit harmful exhaust gases, such as unburned hydrocarbons (UHC) or partially unburned hydrocarbons (HC), carbon monoxide (CO) and nitrogen oxides (NO_x) (BENDU; MURUGAN, 2014).

Yao, Zheng and Liu (2009) explain that in SI engines, as the mixture is premixed and typacally schiometric ($Lambda, \lambda = 1$), the emissions of soot are in orders of magnitude lower then CI engines. This relation can be seen in table 1. According to Gan, Ng and Pang (2011), CI engines produces lower CO and HC compared to SI engines.

The researches related that HCCI engines have the purpose of reconciling the engine efficiency of CI engine and the quality of the gases emitted by the SI engine, such as low NO_x emission. There is a fuel flexibility that can be used in this type of engine configuration (BENDU; MURUGAN, 2014).

The next figure identifies the working region of HCCI engines, regarding to emissions. The HCCI works in a region which is outside that region of generation of NO_x and soot, and also is above the unburned hydrocarbons region, the red line. Figure 12 shows the location of the HCCI engines in fuction of (φ), which is the fuel-air equivalence ratio, and temperature. As can be seen, NO_x occurs at low equivalence ratios and high flame temperature. Soot formation occurs at high equivalence ratio and temperature in the range 1500K to 2400K (GAN; NG; PANG, 2011).

Figure 12 - HCCI: Soot and NO formation.

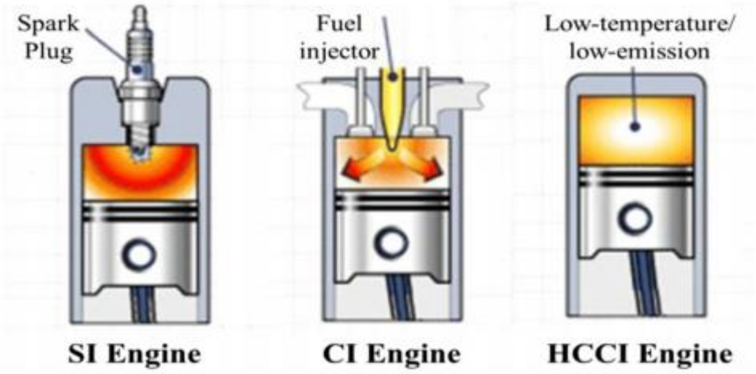


Font: Bendu and Murugan (2014).

Figure 13 shows the basic configuration of the three kind of engines, the gasoline engine (SI) has a spark plug which generates a spark to burn the air-fuel mixture in the combustion chamber. Diesel engine (CI) has a diesel injection nozzle, the ignition is started spontaneously due to high pressure inside the chamber when the injection nozzle injects diesel. The operation of HCCI engine takes its first step as the SI engine, air and fuel are admitted to the combustion chamber. The ignition process is similar to the diesel engine, the fuel and air present in the chamber, due to the high pressure, reach the autoignition point of initiating the firing process thereof. In resume, according to Yao, Zheng and Liu (2009), the HCCI principle comes from the fact that fuel and air are homogeneously mixed before combustion starts, and the fuel auto-ignites as a result of pressure and temperature increase in the compression stroke (the knock principle).

Rattanapaibule and Aung (2005) defines the HCCI engine as a machine which an homogeneous mixture of air and fuel is injected in the combustion chamber, then is compressed. This compression stroke is followed by a combustion precess that is significantly faster than SI or CI combustion. Stanglmaier and Roberts (1999) defines the HCCI combustion as autoignition combustion which is governed by chemical kinetics of the air-fuel mixture.

Figure 13 - Comparison between IC, SI and HCCI engine



Font: Bendu and Murugan (2014).

6. WAUKESHA COOPERATIVE FUEL RESEARCH (CFR) ENGINE

Cooperative Fuel Research (CFR) is a standardized engine used for research, testing and instruction in the performance of fuels and lubricants for the internal combustion engine (ASME, 2015). Waukesha is the name of the company which built this kind of engine.

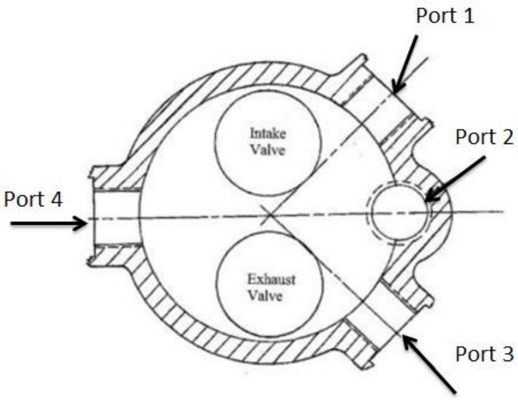
This engine was first designed to determine new methods for determination of gasoline knock. To be able to determine knock intensity, this engine has to be robust enough, and also, to determine different setups, this engine was designed with a variable compression ratio, as well as suitable for different kinds of fuels (RUIJSSCHER; EELBODE, 2014).

CFR engine is a single cylinder, four stroke spark ignition engine. The compression ratio varies through one-piece cylinder/head assembly relative to the piston (MEMME, 2012). Varying the compression ratio by manipulating the cylinder height during engine operation produces various levels of knock intensity (WAUKESHA, 2015). The variable compression ratio cylinder can be seen in figure 15-a.

The air flow is regulated using a manually operated butterfly valve, the the fuel is injected by a Port Fuel Injector (PFI). The combustion process starts through the spark plug. There is an eletrical synchronus motor which is connected to the CFR engine through belts. There are two different pulleys, which allows to change the belt position, the engine can operate in two different speed, 600 RPM or 900 RPM (RUIJSSCHER; EELBODE, 2014).

In annex A some important engine parameters are summarized. Cylinder head is shown in the figure 14. As can be seen, there is one intake valve and one exhaust valve. The cylinder head have four 18 mm threaded access ports, which makes possible to assembly spark plug and also some sensors in the combustion chamber, as for example, the pressure sensor. This allows for example, study the influence of the spark plug location in the flame propagation, as well as the quality of combustion (MEMME, 2012).

Figure 14 - CFR cylinder layout



Font: Modified from Imming (1994)

6.1. CFR Engine

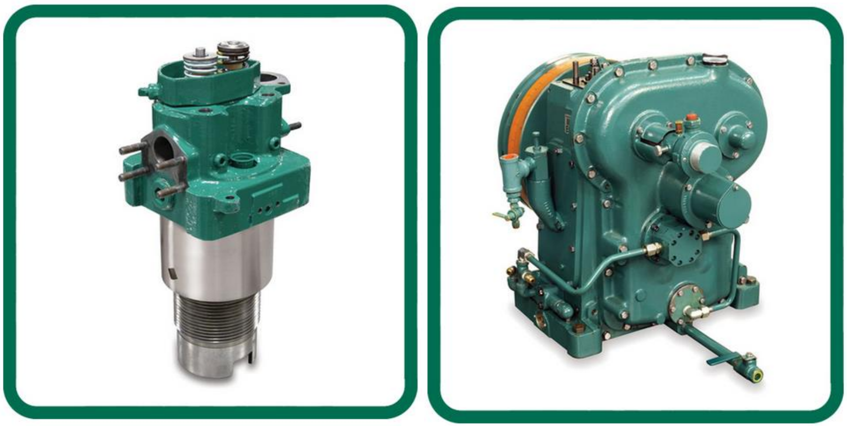
Although the CFR engine be produced by Waukesha Motor Company and also be a standardized engine, configurations regarding with location of measurement devices, like sensors, may differentiate from engine-to-engine. Also the brand and types of these measurement devices in some cases are different. Thus, motors used in different laboratories, may have different settings. There are four different CFR engines used for research, testing and instruction that are produced by Waukesha company. According to Waukesha (2015), these engine types are divided in three categories described below.

- Model F1/F2 : it is the globally accepted standard for determining and certifying the anti-knock characteristics of motor fuels. This model can run both the Research Octane Method (RON) and Motor Octane Method (MON) test, with testing capabilities in the 40-120 octane number range. It is described in ASTM methods: D2699 (RON) and D2700 (MON), and conforms to IP237 and IP236;
- Model F4: globally accepted standard for determining the octane quality of aviation gasoline and aviation gasoline blending components;
- Model F5: globally accepted standard for determining and certifying the ignition quality of diesel fuels.

6.2. Engine Characteristcs

As mentioned before, the key for testing different fuels and different leves of knocking is varying the cylinder compression ratio. The CFR motor constructive characteristics is vary the clearance volume and keep constant the displaced volume, it means that, the stroke value (L_s) remains constant. Thus, the engine head moves upward and downward to vary the clearance volume and then, change the compression ratio, figure 15-(a). The integral head design provides for improved reliability as well as accuracy of results.

Figure 15 - (a) Variable compression ratio cylinder; (b) Cast box



Font: Waukesha (2015)

Due the different conditions that the engine may operate, the engine parts have to be strong enough to resist the efforts that may suffer. Therefore the CFR crankcase, which is shown in figure 15-(b), is an heavy-duty cast box-type design to provide both strengh and rigidity.

7. THE OCTANE NUMBER (ON)

According to Chow (2013), the octane number also known as: octane rating of a fuel, represents how resistant the fuel is to autoignite. Thus, the higher the value of ON, the more resistant is the fuel to knock. Badra et al. (2015) affirms that the prediction of ON is of significant importance to the optimization and development of internal combustion engines. Octane number is one the most important properties of gasoline streams and is a measure of its anti-knock properties (GROSH; HICHEY, JAFFE, 2006). Most of the time, SI engines performance is limited by the knock phenomena, as already describes in section 4, this phenomenon is linked to the fuel resistance to autoignition, which is quantified by the ON. According to Gibbs et al. (2015), ON is a measure of gasoline's anti-knock performance, that is gasoline capacity to resist knocking while the gasoline burns in the combustion chamber. Raising the ON of a fuel, engine knock constraints are reduced, which allows to increase the compression ratio, precisely because the fuel is more resistant to avoid knock (CHOW, 2013). ON is important because it determines the engine operation condition, as the ideal compression ratio that the engine should operate using a specified fuel, then leading to a significant impact on the engine efficiency and emissions (BINJUWAIR et al., 2015). Sayin et.al (2005) affirm that the octane number have a direct relationship with exhaust emissions.

The octane number is a measure of the fuel's resistance to knock. The engine has different points of operation, this property determines whether or not a fuel will "knock" in those operations points. A higher value of ON means a higher resistance to knock (HEYWOOD, 1988). Also according to this author, ON may vary with the following parameters: type of fuel used; engine design; operation conditions during test; weather conditions during test; mechanical conditions during test; type of oil used, among others.

8. RESEARCH OCTANE METHOD AND MOTOR OCTANE METHOD.

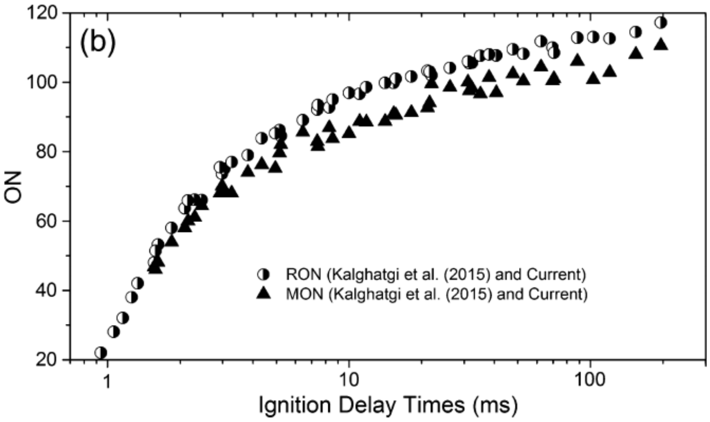
The fuel anti-knock has to be described by empirical measurements, these are known as Research Octane Number (RON) and Motor Octane Number (MON), these are measured by a Cooperative Fuels Research (CFR), which is a single cylinder engine. (BADRA et al., 2015). Using RON or MON it is possible to measure the ON of any fuel.

There are two standard methods which describes how to operate the engine to measure the octane number, these are: ASTM D2699 - for RON, and ASTM D2700 - for MON (WAUKESHA, 2015). Both methods use the same engine, but in different operation conditions. In method RON the engine speed is 600 RPM, and in MON is 900 RPM. According to Gibbs et al. (2015), RON correlates best low speed in mild knock conditions, while MON correlates better high-speed and high temperature knocking conditions and with part-throttle operation. This is the reason why MON runs at 900 RPM and RON at 600 RPM.

For any type of fuel, RON is usually greater than MON (Heywood, 1988). It can be seen in figure 16, in which is shown the ignition delay time related to RON and MON. The mainly question in this graph is see that at any point RON in greater than MON.

The difference between MON and RON indicates the sensivity of the gasoline to changes in operation conditions (GIBBS et al., 2015)

Figure 16 - Comparison RON and MON



Font: Kalghatgi, Babiker and Badra (2015).

To determine ON using RON or MON method, is necessary to use two different fuels as reference to the fuel under test. These reference fuels, RF (also called Primary Reference Fuels – PRF and /or Toluene Reference Fuels, TRF) are a blend of n-heptane (n-C_7H_{16}), isooctane (C_8H_{18}), and toluene (in case of a fuel under study which have ON more than 100), by definition n-heptane has a value of zero ON and isooctane value of 100 ON. Therefore, the ON value of a fuel under study may be in the range from 0 to 100, values of 90 can be found, for example. This number represents a blend with 10% of n-heptane and 90% of isooctane (PRF 90). In short, to determine the ON of a fuel, is measured which blend of the mixture of n-heptane and isooctane (in case of octane number equal or below 100) gives the same knock resistance to the fuel under research (HEYWOOD, 1988).

The conditions of engine operation must be chosen to ensure that the engine is operating in a range in which knock intensity is severe. The CFR engine, discussed in section 6, have its compression ratio variable during the tests to be able to generate knock (HEYWOOD, 1988).

Table 2 - Values of RON and MON for some fuels

Components	RON	MON
n-heptane	0 (defined)	0 (defined)
Iso-octane	100 (defined)	100 (defined)
Super-gasoline	95 (min)	85 (min)
Liquefied petroleum gas	103–111	–
Natural gas	120–130	–

Font: Modified from Rakowski, Eckert e Witt (2012)

As can be seen in table 2, it is possible to have some fuels with ON more than 100, this is the case for Natural Gas and Liquefied Petroleum Gas, for example.

According to Kalghatgi (2001), Primary Reference Fuels (PRFs) are the blends of the n-heptane and isooctane which define the intermediates points in the RON or MON scale. For example a PRF 95 have 95% of isooctane and 5% of n-Heptane.

The level of knock obtained with the fuel under test is bracketed by two blends of the reference fuels (RF), and these RF have to have not more than two octane number difference between them (in the case when the ON of the sample fuel is in the range between 80 to 100). The ON of this fuel under study is obtained by interpolation between the knock meter scale reading for these two reference fuels and this fuel under study (HEYWOOD, 1988).

According to Badra et al. (2015), by definiton, PRFs have zero sensivity. Heywood (1988) defines that PRFs have the same octane number by both the research and motor method, this author defines sensivity as:

$$Fuel\ sensivity = RON - MON \tag{8}$$

The primary reference fuels are paraffins, therefore, if some fuel under research is also parafinic, is expected that sensivity remains zero or near to that. In the other hand, fuels that are olefins or aromatics have a high sensivity (HEYWOOD, 1988). Also according to this author, as the determination of the fuel's octane number is realised using a CFR engine, these methods are not able to predict with certain accuracy how the fuel will behave in automotive engine under a variaty of speed, load and wheather conditions.

Heywood (1988) defines antiknock index (AKI) as the mean of the research and motor octane number. It is used to characterize the knock quality.

$$AKI = \frac{RON + MON}{2} \tag{9}$$

In resume, as higher the ON, the engine can operate with a higher compression ratio without the occurrence of knock phenomenon, and thus it gives a higher output power.

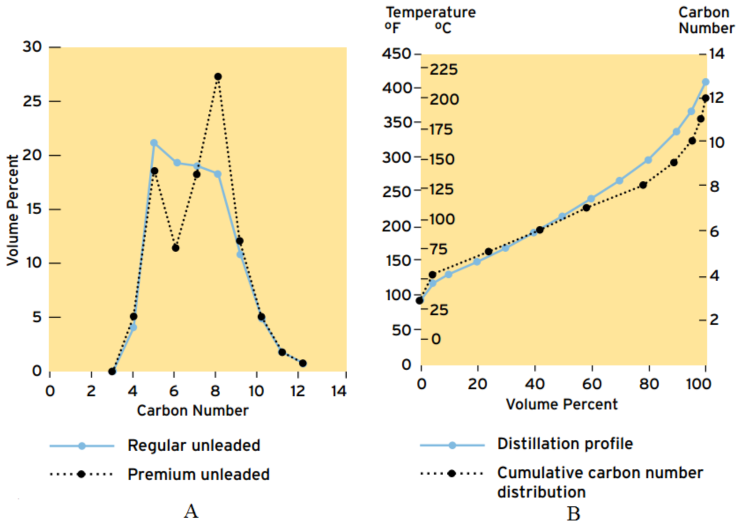
9. GASOLINE

The fuels which are used in SI and CI engines are each mixtures of hundred different hydrocarbons of various groups ($C_xH_y\{O_z\}$), these have differences in the molecular size and structure (RAKOWSKI; ECKERT; WITT, 2012).

Gasoline is a complex mixture of hydrocarbons, the constituents are those that have four to eleven carbons in their molecular structure (BAIRD; CANN, 2008). Hydrocarbons from three to twelve carbons can be found in gasoline, however, the most representative are those from four to eleven carbons in their molecular structure. There are different types of gasoline, which differ in composition, even those that presents the same octane number. Basically the diferentiation is originated from the crude oil and refinery process. The compounds that corresponds to the most part of gasoline are aromatic hydrocarbons, paraffins, iso-paraffins, naphthenes (cyclohexane for example) (SPEIGHT; ARJOON, 2012). The mixture of hydrocarbons (and oxygenates) in a gasoline determines its physical properties and engine performance characteristics (GIBBS et al., 2015).

Figure 17-a shows the carbon distribution for regular unlead and premium unleaded gasoline. For both types is possible to see that C_5, C_6, C_7 and C_8 represents each, more than 15% of the total volume of the gasoline.

Figure 17 - Gasoline carbon number distribution and carbon number distribution



A

B

Font: Gibbs et al. (2015).

Figure 17-b shows the gasoline's cumulative carbon number distribution. It is possible to conclude from the figure, that as mentioned, hydrocarbons from even three carbons can be found in gasoline, however, those between five and eight carbons in the molecular structure are the most part.

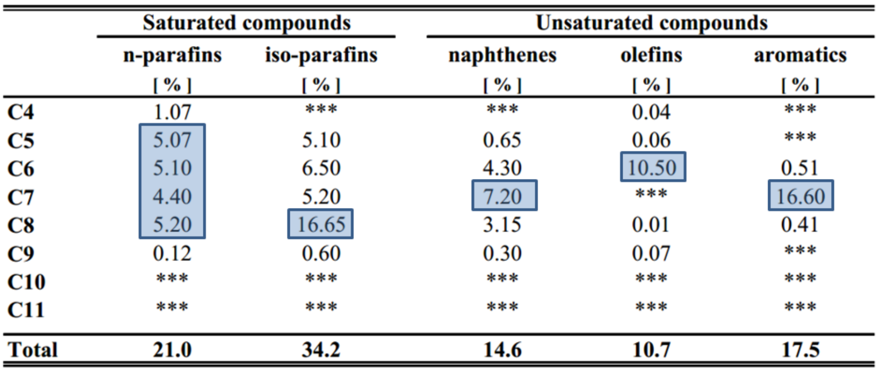
Metcalfe et al. (2007) affirms that the number of chemical species present in the real gasoline is in order to hundred, involving unsaturated and saturated hydrocarbons, and including straight or branched alkanes (n-parafins, iso-parafins), cycloalkanes (naphthenes), alkenes (olefins), cycloalkenes (cycloolefins), aromatics (Aryl compunds), ethers and esters and other componets which are often unknown.

According to Speight and Arjoon (2012), typically in gasoline, the hydrocarbon components are: Alkanes (4 to 8% v/v), Olefins (2 to 5% v/v), iso-alkanes (25 to 40% v/v), naphthenes (3 to 7% v/v), cycloalkenes (1 to 4% v/v) and aromatics (20 to 50% v/v).

Table 3 shows the composition of a typical brazilian gasoline, in this formulation there is no addition of ethanol.

From table 3, it is possible to see in the group of n-paraffins, that there are some predominant compounds, as the pentanes (C_5), hexanes (C_6), heptanes (C_7), and octanes (C_8). In the group of iso-parafins, the octane is predominant. In naphthenes group, heptane represent more than 50% of the carbons atoms. In olefins group, alkenes with six carbon atoms are majority. In the aromatics group, toluene compound represents 95% of the carbon atoms (CANCINO, 2009). The blue box in table 3 are showing the most commom element for each group.

Table 3 - Chemical composition of one kind of brasilian gasoline (mol%).



	Saturated compounds		Unsaturated compounds		
	n-parafins [%]	iso-parafins [%]	naphthenes [%]	olefins [%]	aromatics [%]
C4	1.07	***	***	0.04	***
C5	5.07	5.10	0.65	0.06	***
C6	5.10	6.50	4.30	10.50	0.51
C7	4.40	5.20	7.20	***	16.60
C8	5.20	16.65	3.15	0.01	0.41
C9	0.12	0.60	0.30	0.07	***
C10	***	***	***	***	***
C11	***	***	***	***	***
Total	**21.0**	**34.2**	**14.6**	**10.7**	**17.5**

Font: Adapted from Cataluna and Silva (2006).

Gasoline that consists primarily of straight alkanes and cycloalkanes has a poor combustion characteristics when burned in internal combustion engine. A mixture of air and gasoline of this type tends to ignite spontaneously in the engine’s cylinder before it is completely compressed and sparked, so there is the occurrence of engine knock, which results in loss of power. Gasoline is formulated to prevent the occurrence of knock (BAIRD; CANN, 2008).

9.1. Gasoline surrogates

Due the differences around world in the origin of the crude oil and refinary process, the commercial gasoline is not universally consistent. To simplify this problem, is possible to model gasoline as a simple mixture of some pure substances, it is then called: gasoline surrogate (BADRA et al., 2015). According to Wallington, Kaiser and Farrell (2006) gasoline fuels exhibit tremendous complexities due to the quasi-continuous spectrum of hydrocarbon constituents. Andrae (2008) affirms that is disarable to limit the chemical and/or physical complexity of the fuel to generate insight and understanding into the underlying fundamental processes. It is needed to use gasoline surrogates due the high number of components that composes gasoline, to a finite number of compounds and standard composition to nearly match pratical fuel.

The surrogate fuel is used both to develop a better understanding of the chemical behavior of the target fuel as well as an experimental model, it can be reproduced at differents laboratories, at different conditions and methods (CANCINO et al., 2011). Metcalfe et al. (2007) affirms that gasoline surrogates are used to represent the practical fuel and still predict characteristics of the real fuel, these disarables characteristics may include: ignition delay time, burning velocity, viscosity, vaporization and emission.

A single component fuel such as isooctane can be a good surrogate, it can be used to simulate real gasoline in some engines and in specific operation conditions, but often a more complex surrogate is used to reproduce the targets of interest, it is the PRFs fuels, a mixture of n-heptane and isooctane (Andrae, 2008). As mentioned before, there are a finite numbers of components that can perform a real gasoline. Cancino et al. (2009) describes a gasoline surrogate as a composition of ethanol, isooctane, n-heptane and toluene.

As already mentioned, PRFs are paraffins, and to have a surrogate more like a real gasoline, is needed to add a sensitive component, which is responsible to make this surrogate match the real octane number and sensivity of the real gasoline, this component is generally toluene. According to Badra et al. (2015), real gasoline fuels have sensitivities up to 11 because they contain considerable amounts of branched paraffins, olefins and aromatics.

In case in which just two components are used as gasoline surrogate, as example, ethanol and isooctane, it is called binary surrogare, in case of five components, it is called quinary surrogate (CANCINO et al., 2011). A ternary surrogate formed by n-heptane, isooctane and toluene is called as a toluene reference fuels (TRF), it is the simple mixture of toluene and PRFs. (HERZLER et al., 2007).

As mentioned, surrogates are formed by different compunds, Mehl et al. (2011) proposed a four component surrogate comprising n-heptane, isooctane, toluene, and 1-hexane (olefin). Perez and Boehman (2012) proposed a quinary surrogate adding methylcyclo-hexane to surrogare studied by Mehl et al .(2011). Cancino et al. (2011) proposed a quinary surrogate comprising by ethanol, isooctane, n-heptane, diisobutylene and toluene. As can be seen, in these groups shown in table 3, isooctane, n-heptane and toluene represents the most components of a typical gasoline, this is the reason why these compounds are often used in gasoline surrogates.

9.1.1. Fuel surrogates – some definitions

Hydrocarbons is an organic compoud consisting entirely of carbon and hydrogen. There are basically two groups, as shown bellow.

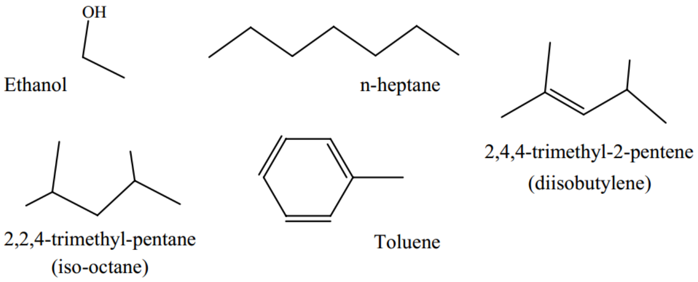
- Saturated hydrocarbons (alkanes / parafins): Acyclic branched or unbranched hydrocarbons. Organic compound that consists entirely of single bonded carbon and hydrogen. This is the most abundant hydrocarbon and can be generally designated by the formula: C_nH_{2n+2} (where *n* is the number of carbons). The simplest alkane is the methane, CH_4. Branched – chain alkanes are called iso – paraffins (BAIRD; CANN, 2008). According to Shell (2015), a linear chain is called normal chain, a branched is called “iso” and a cyclic is called ring structures. According to Heywood (1988) there are several diferent “isooctane”, depending on the relative position of the branches. Isooctane is usually referred as 2,2,4-trimethylpentane, it indicates that there are five carbons in the straight chain (pentane) with three methyl (CH_3) branches located respectively at C-atoms 2, 2 and 4.

- Unsaturated hydrocarbons: these have one or more double or triple bonds between carbon atoms;
- Petroleum contains substantial amount of cycloalkanes (naphthenes), such as mythylcyclopentane and cyclohexane (BAIRD; CANN, 2008). These are a type of saturated monocyclic hydrocarbons (with or without side chains) (MCNAUGHT; WILKINSON, 1997). The naphthenes in gasoline have rings of five to six carbon atoms, and have the same formula as the olefins, C_nH_{2n} (GIBBS et al., 2015).
- Olefins: Acyclic and cyclic hydrocarbons having one or more carbon – carbon double bounds, apart from the formal ones in aromatic compounds. The class olefins subsumes alkenes and cycloalkenes (MCNAUGHT; WILKINSON, 1997). The term Olefins is also known as Alkene, it refers to a large number of compounds that contain Hydrogen and Carbon. This group can be represented by formula: C_nH_{2n}. Gibbs et al. (2015) describes ethylene (C_2H_4) as an example of olefin, also accordding to this author, olefins rarely occur naturally in crude oil, but are formed during refining.
- Aromatics hydrocarbons: Aromatic compund is one which contains benzene ring. Common compounds other than benzene include toluene and naphthalene. (SPEIGHT; ARJOON, 2012). Like Naphthenes, some of the carbon atoms in aromatics are arranged in a ring, but they are joined by aromatic bonds, not single bonds (GIBBS et al., 2015). This ring structure accomodates additional – CH_2 groups inside chains and not by ring expansion. Toluene is an example of aromatic hydrocarbon, and this group can be represented by the formula: C_nH_{2n-6}, according to Heywood (1988).

9.1.2. Molecular structure of gasoline surrogates

In this section is shown the molecular structure of the most commom components of gasoline surrogates, these are: ethanol (oxygenated hydrocarbon), isooctane (saturated isoparafin), n-heptane (saturated n-parafin), toluene (unsaturated aromatic) and diisobitylene (unsaturated olefin) (CANCINO, 2009). The structure of these components are shown in the next figure.

Figure 18 - Molecular structure of gasoline surrogates



Font: Cancino (2009).

10. ETHANOL

As mentioned by Gibbs et al. (2015), oxygenates components have been added to gasoline for decades, nowadays the ethanol is used most exclusively. The brazilian government established in 2015 a new regulation, in which premium gasoline have to have 25% of ethanol in its content (E25). The common gasoline have to have 27.5% (BRASIL, 2015). In Brazil is also available pure ethanol in the gas stations, through that, the engine can operate with a content of ethanol in gasoline from a minimum of 25% up to 100%. According to Doe (2015), in The United States of America (USA) ethanol is blended with gasoline in various amounts for use in vehicles. Basically, there are three diferrent blends in USA:

- E10: which is a blend composed by 10% of ethanol and 90% of gasoline. According to the Environmental Protection Agency (EPA), E10 is legal for use in any gasoline powered vehicle, and it is sold in every state;
- E15: in 2011, EPA approved a new regulation, in which the ethanol content in gasoline could be increased. E15 is a blended with 10.5% to 15% ethanol. However, the gas station are not required to sell this fuel. The vehicles aproved to use E15 are: flexible fuel vehicles and conventional vehicles of model year 2011 and newer, any other vehicle can not use it;
- E85: is a high ethanol-gasoline blends containing 51% to 83% of ethanol. Eia (2012) affirms that just a small amount of this fuel is sold in USA. This fuel can be used in flexible fuel vehicles (FFV).

Also according to Eia (2012), in USA, E10 can be sold at any service station from any existing pump, while E15 and E85 requires different equipments.According to Larsen, Johansen and Schramm (2009), in Sweden the use of E85 is fairly widspread, and several other countries the usage of E5 and E10 is mandatory. In Sweden and in USA, the FFV currently on the road are compatible with blend ranging from 0 to 85 percent of ethanol content.

In April 2009 the Directive 2009/30/EC was adopted, which revises the Fuel Quality Directive (Directive 98/70/EC), through that, in Europe the content of ethanol in gasoline was incresed from 5% to 10% (E10) (COMISSION, 2015). According to Kampman et al. (2013), in 2020 is expected that around 95% of the passengers cars and vans in Europe will be compatible with E10. Rising the blend limit for ethanol is possible due the tecnology for that be already known, since E25 and also pure ethanol in Brazil. In Australia the most common blends are E5 and E10 (BIOFUELS ASSOCIATION OF AUSTRALIA, 2015). In annex B an overview of ethanol content in gasoline in some importants markets around the world are shown.

11. METHODS

This chapter will present the methodology used for the experiments adopted in this thesis, as well as the methods chosen to achieve the results.

11.1. Multi-component gasoline surrogate

As explained in section 9, the gasoline surrogate may be composed from diferrent components (hydrocarbons), in this thesis a quinary surrogate was chosen to describe gasoline's behavior.

The main objective of this thesis is analyse the influence of different quantities of ethanol in gasoline surrogate in terms of ON and others important parameters, like the influences in the indicated mean effective pressure. Based in Cancino (2009) and Cataluna and Silva (2006), one approch to gasoline surrogates is to include one or more compoments from the different groups of hydrocarnons shown in table 3, in section 9. According to Metcalfe et al. (2007), diisobutylene is intended to represent the hydrocarbon class of alkenes (olephins) in practical fuels.

The surrogate used in this thesis is based in the doctoral thesis written by Cancino (2009), and also in the paper written by Cancino et al. (2011), where it is composed by: ethanol, isooctane, n-heptane, diisobutylene and toluene. Each of these components belongs to one hydrocarbon group and its classification can be seen in section 9.1.2.

The thesis and paper written by Cancino were chosen due to the fact that it has the same focus in analyse the behavior of gasoline with different percentages of ethanol. It is also possible to complement some results from Cancino's thesis and the results of this study in terms of fuel surrogate characterization. During the results analysis, beyond these two studies, others papers and authors are used to support the results found in this thesis.

In annex C are shown the properties of these components, as the formula, molecular weight and other names.

11.1.1. Ethanol in gasoline surrogate

The analysis of the influence of ethanol in gasoline is related to the quantity of this component in gasoline, which differs from one country to another, as explained in section 10. The aim of this work is to make a study of ethanol content in the range which is used in around the world, like in Brazil, Europe, Australia and in USA, through that the results obtained are applicable for those markets.

To measure the ON of the gasoline surrogate, some samples have to be determined, each of them containing different percentage of ethanol. In these markets the minimun content of gasoline is 10% (E10), and before 2009 in Europe, a content of 5% has been used. Also, pure gasoline can be found in these markets, thus was decided that the minimum content of ethanol in the gasoline surrogate is determined as 0%. The maximun value should be 100%, due the possibility to get this value in vehicles which operates in Brazil. The value of ethanol content in the others samples were determined in the interval from 0% to 100%.

In resume, 7 different samples were determined to describe the gasoline surrogate behavior. These percentages of ethanol were chosen in accordance with those values that are used in the global markets, as explained in section 10. It is shown in table 4.

Table 4 - Content of ethanol in gasoline surrogate

Sample	N°1 (E0)	N°2 (E10)	N°3 (E20)	N°4 (E30)	N°5 (E50)	N°6 (E85)	N°7 (E100)
Ethanol (%)	0	10	20	30	50	85	100

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11.1.2. Percentage of each component in gasoline surrogate

Once determined the components of gasoline surrogates, is necessary describe the percentage of each of the substances used on it. As mentioned, the main objective is study the influence of ethanol, therefore, it must have changed its percentage for each sample (as shown in table 4), the others components in gasoline surrogate are kept unchanged.

The sample with 10% of ethanol is based in the paper written by Cancino et. al (2011), in which the same components were used. The percentage of each component for the sample with 10% o ethanol (E10) is shown in table 5.

These percentages are also based on the paper written by Cataluna and Silva (2006). As can be seen in table 3, the percentage of n-parafins (n-heptane) was 21%, iso-parafins (isooctane) was 34,2%, olefins (diisobutylene) was 10.7%,naphthenes was 14,4% and toluene 17.5%. Also according to Speight and Arjoon (2012), as mentioned in section 10, iso-alkanes and aromatics are majority. Thereby, the percentage of each component in the gasoline surrogate are similar to those found in real gasoline.

Table 5 - Percentage of each component in the sample with 10% of ethanol based in the paper written by Cancino et. al (2011).

Components	Ethanol	Isooctane	n-Heptane	Diisobutylene	Toluene
(%) (v/v)	10	30	22	13	25

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As mentioned, the objective is vary the percentage of ethanol in each sample, thus, the proportion of isooctane, diisobutylene, toluene and n-heptane have to be unchangeable in the remaining fuel of each sample.

Remaining fuel is a volume defined as: the total liters of the sample, minus the quantity in liters of ethanol. Thus, the remaining fuel of the sample is formed by isooctane, diisobutylene, toluene and n-heptane. By this methodology, the percentage of each of these four components in the remaining fuel are the same for every sample, independent of the quantity of ethanol, as well as independent of the total quantity of the sample.

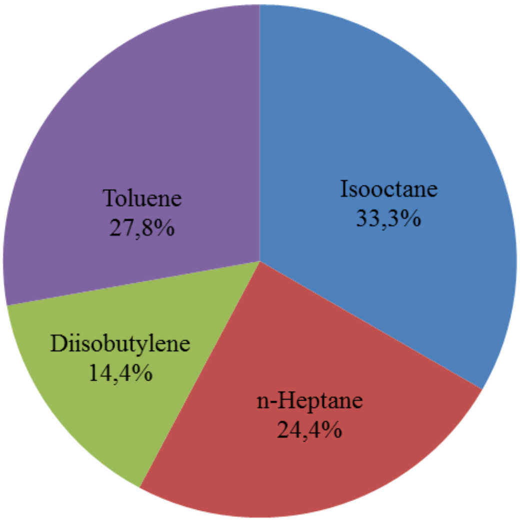
The next equation defines the percentage of isooctane, diisobutylene, toluene and n-heptane in the remaining fuel.

$$\xi_{isooctane,diisobutylene,toluene,n-heptane} = \frac{\Omega_{isooctane,diisobutylene,toluene,n-heptane}}{(1 - \%\ of\ ethanol\ in\ sample\ E10)} \tag{10}$$

Where, ξ is a value in percentage of isooctane, diisobutylene, toluene and n-heptane in the remaining fuel. Ω is the value in percentage of each of those component in the sample E10, defined and shown in table 5. Thus, this equation is a function of the percentage of ethanol in sample E10, which is the sample that has been taken as basis for this thesis.

Figure 19 shows the value in percentage of isooctane, diisobutylene, toluene and n-heptane in the remaining fuel of each sample used in this study. These values were calculated by equation 10.

Figure 19 - Proportion of the components in the remaining liters of each sample.



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11.1.3. Determining the samples

Once determined the percentage of ethanol in each sample, and also known that the proportion of isooctane, n-heptane, diisobutylene and toluene in the remaining liters of each sample have to be the same as in sample E10 (figure 19), it is possible to calculate the percentage of each component (isooctane, diisobutylene, toluene and n-heptane) in each sample. The next equation shows how to calculate this value.

$$\Lambda_{sample,i} = \xi_{isooctane,diisobutylene,toluene,n-heptane}\left(1 - \frac{\psi_{sample,i}}{100}\right) \tag{11}$$

Where, Λ is the percentage of each component (isooctane, n-heptane, diisobutylene and toluene) in each sample. The indicie i represent the number of the sample, as shown in table 4. ψ is the percentage of ethanol in each sample. As shown in table 4, for example, in sample E50, ψ is equal to 50%.

Using equation 11 and the value in percent of each component in the remaining fuel (ξ) is possible to build up a table with the percentage of each component in each sample, it is shown in the next table.

Table 6 - Quantity in percentage of each component in each sample

Sample	Ethanol (%)	Isooctane (%)	n-heptane (%)	Diisobutylene (%)	Toluene (%)
E0	0	33.3	24.4	14.4	27.8
E10	10	30.0	22.0	13.0	25.0
E20	20	26.7	19.6	11.6	22.2
E30	30	23.3	17.1	10.1	19.4
E50	50	16.7	12.2	7.2	13.9
E85	85	5.0	3.7	2.2	4.2
E100	100	0.0	0.0	0.0	0.0

Font: Author

In table 6, the blue line indicates the value of each component in percentage in the sample E10, which are fixed values. The values in colunm "Ethanol" are also fixed values, which are the percentage of ethanol in each sample. The other values were calculated through equation 11.

Was determined that the minimum volume of the sample E10 should be one liter and five hundred milliliters. This quantity was determined by observations during some ON determination made in previous experimentations realized in the laboratory where this thesis was written. This quantity is a safety value, because once started the measurement, have to be sure that the quantity is enough to do that, if not, can compromise all measurements and the results to be analyzed, because if there is not enough fuel, the measurements have to be interrupted to prepare more fuel and during this interval the engine have to be operated with a another fuel. This situation has to be avoided. Also was determined that the minimum quantity of each sample should be 1.5 liters.

As the percentage of each component in each sample is known, through table 6, and also known the quantity in liters of each sample, was possible to build up a table with the volume of each component in each sample, as shown below.

The blue line in table 7 indicates the quantity in liters. As mentioned in section 11.1.1, the content of ethanol increases sample-by-sample.

Through this methodology, the percentage of each compoment in each sample, as shown in table 6, is independent of the total volume of the sample, which means that, even changing the total volume of the sample, the percentage of each component is fixed.

Table 7 - Quantity in liters (L) of each component in each sample

	Ethanol	Isooctane	n-Heptane	Diisobutylene	Toluene	Total
E0 (L)	0.0	0.500	0.367	0.217	0.417	1.5
E10 (L)	0.150	0.450	0.330	0.195	0.375	1.5
E20 (L)	0.300	0.400	0.293	0.173	0.333	1.5
E30 (L)	0.450	0.350	0.257	0.152	0.292	1.5
E50 (L)	0.750	0.250	0.183	0.108	0.208	1.5
E85 (L)	1.275	0.075	0.055	0.033	0.063	1.5
E100 (L)	1.500	0.0	0.0	0.0	0.0	1.5
Total (L)	4.43	2.025	1.485	0.878	1.688	10.50

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In short, to prepare the samples was decided to mix n-heptane, isooctane, diisobutylene and toluene in a bottle separated from the ethanol. In a second moment, part of the volume of the blend formed by n-heptane, isooctane, diisobutylene and toluene was taken and replaced 10% of ethanol to get E10, replaced 20% to get E20 and so on. It is important to highlight that E0 is a sample formed by n-heptane, isooctane, diisobutylene and toluene. E100 is pure ethanol. From now, the volume formed by n-heptane, isooctane, diisobutylene and toluene is called “Volume of additives – sample E0”.

11.1.4. Resource to get the components of gasoline surrogate

To perform the measurements, as mentioned in previous section, a certain quantity in volume of ethanol, isooctane, diisobutylene, toluene and n-heptane were necessary to formulate the gasoline surrogate. Ethanol, isooctane, n-heptane and toluene were provided by the laboratory where this thesis was written, however was verified that diisobutylene was not available. Then, was decided to buy 2 liters of this component, even if the minimum quantity that was calculated to be used during the measurements was less than 1 liter, this decision was based on the possibility of any unplanned event occurs. Diisobutylene was purchased from the company Sigma Aldrich, under the product code: 38180.

11.1.5. Formation of the "volume of additives (E0)".

The minimum volume of 1.5 liters for each sample was determined to make a first calculation about the quantity in liters of each component that should be used in the measurements. As can be seen in table 7, using 1.5 L for each sample, the total quantity in volume of each component is: 0.878 L of diisobutylene, 1.688 L of toluene, 1.485 L of n-heptane and 2.025 L of isooctane. As mentioned, was bought 2 liters of diisobutylene, which was delivered into two bottles of 1L each, as can be seen in figure 20-a.

Figure 20 - (a) Bottles of diisobutylene; (b) Graduated cylinders - 1 L and 0.5 L

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The calculeted volume of diisobutylene, for the case in which each sample had a minimum volume of 1.5 L, was 0.878 L. As one bottle of diisobutylene had 1 L, was decided to use 1 L of diisobutylene instead 0.878 L to mix this component with isooctane, n-heptane and toluene. To measure the exactly quantity of diisobutylene in the bottle, was used two graduated cylinders glass, one with a volume of 1 L and the other with 0.5 L, both are shown in figure 20-b.

Was verified that the real volume in the bottle was 1.013 L.Through that, keeping the proportion of each of these components constant (33,3% isooctane, 14,4% diisobutylene, 27,8% toluene, 24,4% n-heptane), as shown in figure 19, was possible determine the quantity of isooctane, n-heptane and toluene that had to be used, it is shown in the next table.

Table 8 - Quantity of each component to form the volume of additives

	Isooctane	n-heptane	Diisobutylene	Toluene
Percentage (%)	33,3	24,4	14,4	27,8
Total (L)	2.338	1.714	1.013	1.948

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In the laboratory at THI there were available toluene, ethanol, n-heptane and PRF80. As there was no pure isooctane, to get the values of each component shown on table 8, a simple calculation was made to determine how much of PRF80 (80-Octane) and n-heptane should be used. In short, the next table summarises the quantity used of 80-Octane, n-heptane, diisobutylene and toluene.

Table 9 - Quantity of each component used for blend

	80-Octane	n-heptane	Diisobutylene	Toluene
Total (L)	2.922	1.130	1.013	1.948

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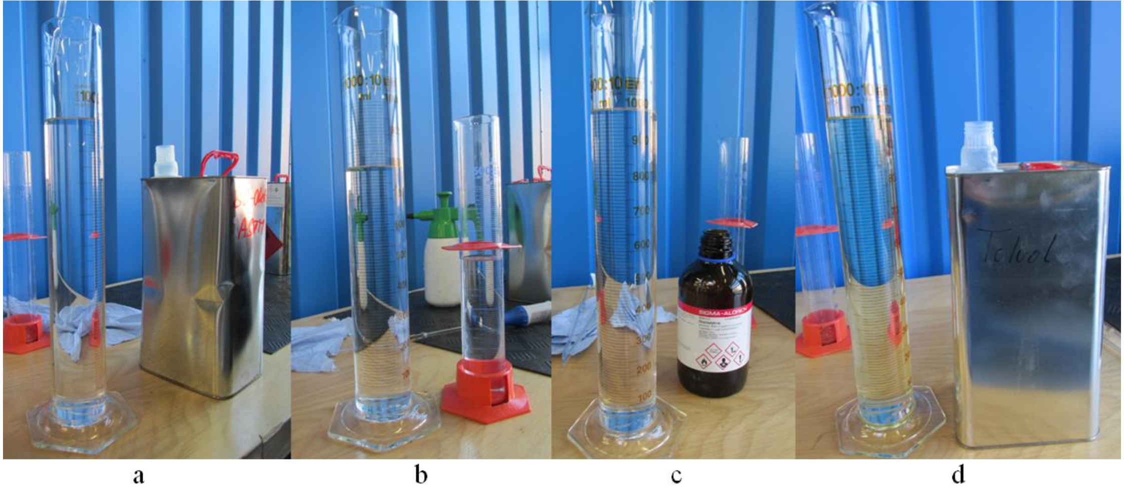
11.1.5.1. *Measuring and determining the "volume of additives"*

In this topic are shown how the blend of isooctane, n-heptane, diisobutylene and toluene were prepared. As already mentioned, were used two graduated cylinder. First was measured the quantity of diisobutylene, and after the quantity of n-heptane, 80-Octane and toluene, respectively.

During the procedure to determine the exact quantity of each component was utilised two pipettes of 8 ml each, one of them used exclusively for n-heptane and the other was used to toluene, diisobutylene and 80-Octane. Also, a pipette controller was needed to ensure the right quantity of each component, according to the manufacturer (Brand), this single macro pipette controller covers the entire range of bulb and graduated pipettes from 0.1 to 200 ml. They are shown in figure 20-c. The figure 21 shows the part of the procedure to measure the quantity of each component. The graduated cylinders were filled with 80-Octane, as shown in figure 21– (a), with n-heptane in (b), diisobutylene in (c) and toluene in (d).

Figure 21 - Determination of the quantity of each component.



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After determined the quantity of each component using the graduated cylinders, the components were added and mixed in a gallon of 20 liters, as shown in figure 22-a. Thus, in the 20 liters gallon were mixed isooctane, n-heptane, diisobutylene a toluene, resulting in E0. The total volume was 7.013 L.

Figure 22 - (a)Adding and mixing the components in a gallon of 20 L – E0; (b) 10 L bottle ethanol; (c) Mixing E0 and Ethanol

(a) **(b)** **(c)**

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11.1.6. Determination of the samples – E10, E20, E30, E50 and E85.

The ethanol which was used in this thesis was bought from the company Richter Chemie GmbH, and it has 99.9% purity. The 10 liters bottle ethanol can be seen in figure

22b. To facilitate the mixing process, a plastic bottle of 1 liter was filled with ethanol, also an aluminium bottle of 0.6 liters was filled with E0, both bottles can be seen in figure 22-c. A glass cylinder of 0.5 liters was also utilized for this process. To prepare the samples, the following quantities of E0 and E100 were mixed. It is shown in the next table.

Table 10 - Quantity of E0 and E100 in the samples

Sample	E0 (ml)	E100 (ml)
E10	50	450
E20	100	400
E30	150	350
E50	250	250
E85	75	425

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Thus, a total volume of 500 ml were mixed for each sample. They were stored also in aluminium bottles of 0.6 L, as shown in figure 23. Was written the specific content in each bottle. During the measurements, as 0.5 L was not enough to start and finalise it, the procedure of mixing E0 and E100 and store in the 0.6 L bottle, was made until the total amount was sufficient to complete the measurements, at least two times for each sample.

Figure 23 - 0.5L bottle of the samples E10 to E85

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11.2. Octane number method

As described in literature review, there are two methods that can be used to determine octane number of a fuel, in this thesis the method that was chosen is the Research Octane Number (RON).

Standard ASTM D2699 describes all of the operation conditions, engine parameters and also the fuels which can be utilized during test. For those samples with a RON value below 100, the measurement procedures were based in the standard test method ASTM D2699, while for those with higher RON, the procedure utilized was based in a methodology developed in the laboratory in which this study was realized, due to the fact that Tetraethyl lead is not used there. Some important operating conditions for RON and MON are shown in annex D.

11.3. CFR engine

The research conducted in this thesis was performed using a CFR engine from the Laboratory of Internal Combustion Engines and Automotive Technologies in the Ingolstadt University of Applied Sciences (Technische Hochschule Ingolstadt - THI), Germany.

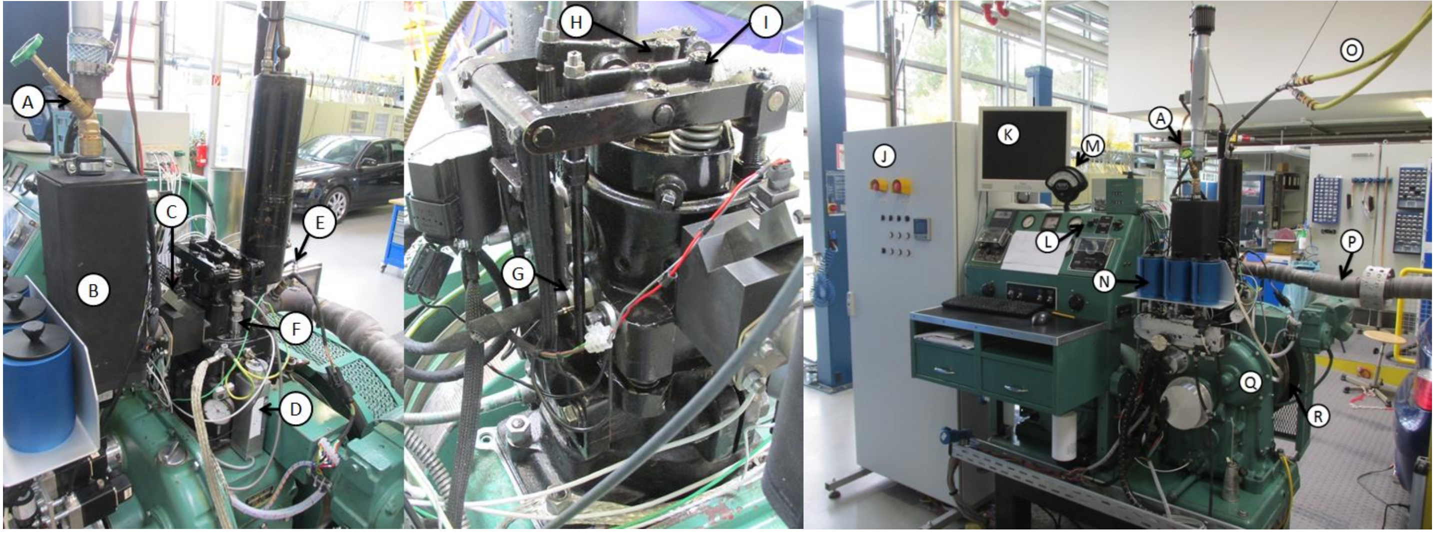
The usage of this engine was possible due to the international cooperation program "AWARE", between Brazil and Germany, involving both the institutions THI and UFSC. The engine which was utilized in this thesis is the model F1/F2 explained in section 6.1

11.3.1. Engine – Measurement devices

The engine is equipped with different measurement devices, which enable the collection of important data, as the pressure history, temperature of the exhaust gas, relation of air-fuel which is been injected in the combustion chamber.

In figure 24, shows how the measurement devices are placed in the engine. “A” is the pressure regulator, “B” is the intake manifold heater, “C” is the fuel injector, “D” is the displacement sensor of the cylinder head, “E” lambda sensor, “F” is the pickup and piezo-pressure sensor, “G” indicates the Spark Plug, “H” is the exhaust valve and “I” the intake valve, “J” is the PXI-system of the National Instruments. “K” is the computer screen, in which is possible to follow in real time the value of measurement data. L is the handle used to vary the cylinder head position. “M” is the knockmeter. “N” is the fuel bottles, used as a tank, “O” are the water pipes, used in the cooling system, “P” is the exhaust system, “Q” is the cast box, “R” is the pulley used to connect the CFR engine to the eletric motor.

Figure 24 – CFR and its measurements devices



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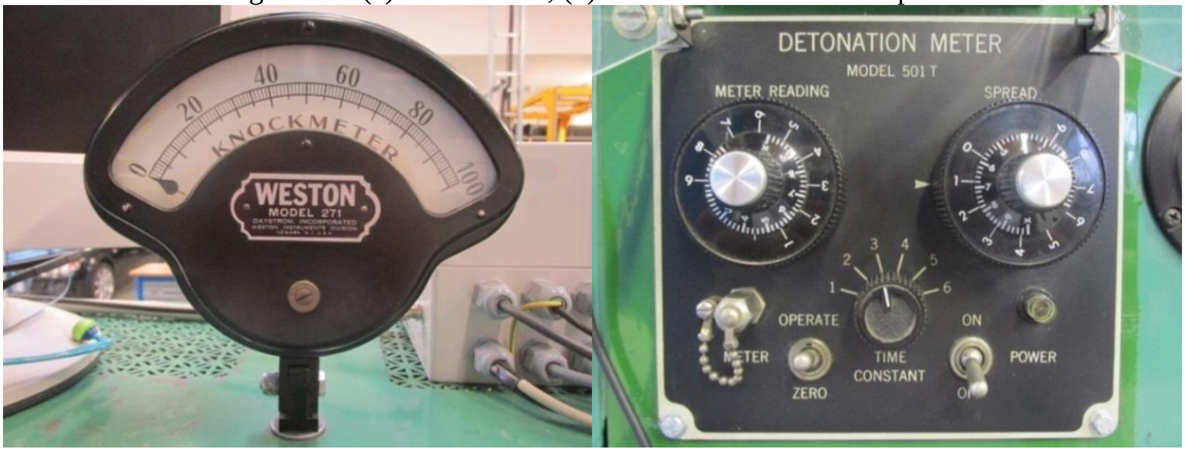
11.3.2. Knockmeter reading limits

Knockmeter is the display shown in figure 24 as letter “M”. The next figure shows in more details this equipment, which is fundamental to obtain the final results of ON of the fuel under test. Basically, as its name suggest, it measures the knock intensity (K.I) of the fuel which is feeding the engine at that moment. The scale is displayed from a value of 0 to 100, as can be seen in figure 25-a. As higher this value, higher is the knock severity in the engine.

Figure 25 - (a) Knockmeter; (b) Detonation meter - front panel



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According to ASTM (2004), index number 10.3.20.1, the knockmeter reading limits shall be from 20 to 80, even if the scale is from 0 to 100. The reason is that the knock intensity is a nonlinear characteristic below 20 and the knockmeter has the potential to be nonlinear above 80. The Knockmeter signal cames from the detonation meter.

11.3.3. Detonation meter

According to ASTM (2004), index number 3.1.4, the detonation meter (figure 25-b) is a instrumentation that accepts the electrical signal from the detonation pickup and provides an output signal for the knockmeter display (figure 25-a).

In the detonation meter there are 3 different variables that can be changed to get the value of the knockmeter reading, these are: meter reading, spread and time constant. In short, these variables don’t have a specific value to be setup, they have to be setup in the beginning of the measurement. They have influences in the response of the knockmeter, like how fast the knockmeter changes its value when the engine is been operated under knock conditions. Basically, these values depends upon the operator of the engine. Spread is defined in the ASTM (2004), index number 3.1.20, as: the sensitivity of the detonation meter expressed in knockmeter division per ON.

11.3.4. Digital counter reading (DCR) and hand crank

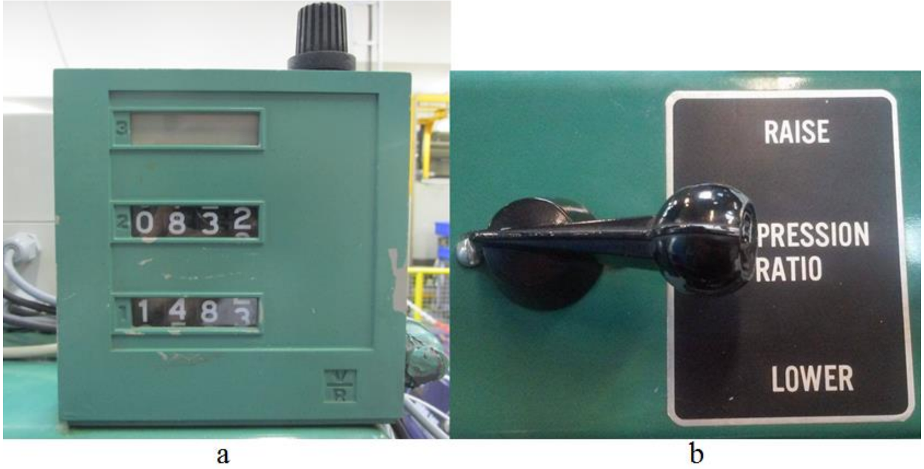
ASTM (2004), index number 3.1.3.2, defines the DCR as a numerical indicator of cylinder height. It is an important value that have to be fixed when the engine is being operated to get ON of a fuel under test, it means that, once started the measurements, to evaluate the ON of a fuel, whatever is the fuels feeding the engine (PRF, TRF or the fuel to be measured to determine the ON), the value of DCR have to be determined and kept with the same value while the measurement is realized. It is shown in the figure 26-a.

The value itself which is shown by DCR is a dimensionless value. According to ASTM (2004), DCR changes in a direct proportion to compression ratio (CR), and usually DCR is related to RON.

This dimensionless value shows if the cylinder height of the engine is being reduced or increased. If the value of DCR increases, it means that the cylinder height decreases, thus, the compression reatio increases. If the value of DCR decreases, it means that the cylinder height increases, thus, the compression reatio decreases.

To increase or decrease the compression ratio during the measurements, there is a hand crank, which the operator must use. To increase CR, is just necessary to turn the hand crank to the upper position, and to decrease CR, just turn to the lower position. It is shown in figure 26-b.

Figure 26 - (a) Digital counter reading (DCR); (b) Hand crank to compression ratio.



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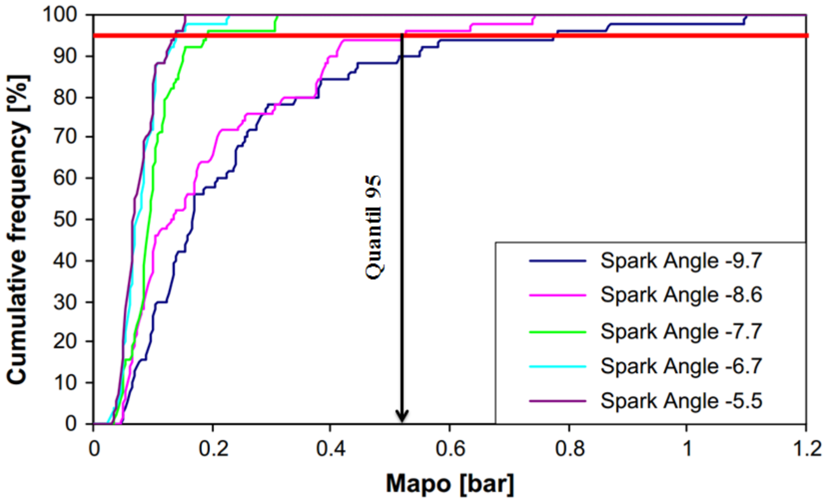
11.3.5. Measurement data diyplay in real time

The data from the measurement devices are collected by a PXI system and are shown in the in the computer screen (K- in figure 24), by this way, during the measurements is possible to monitor in real time the value given by the sensors and check if parameters, like the intake temperature, intake pressure, are according to the standard ASTM D2699. In appendix A are shown the informations that are displayed on the computer screen.There are two important parameters displayed in real time:Quantil 95 and KL_{ASP} , which are related to the knock detection, explained in section 4: Knock detection overview.

The knock intensity value is, through this method, called Quantil 95 (Maximum Amplitude of Pressure Oscillation - MAPO), is measured in bar. This value is taken from the CDF curve, it is the intersection between the value of 95% of the cumulative frequency and the cumulative pressure curve. As an example, for the operating conditions described by Galloni (2012), for a spark angle of -8.6, the intersection results in a value of MAPO equal to 0.56 bar, as can be seen in the figure 27. °CA is the value of the crank angle degree, in which the spark discharge occurs, this value is fixed as 13°CA BTDC, it was also defined in annex

D. The parameter KL_{ASP} shows in percentage, how many working cycles have the occurrence of knock phenomena, if in every cycle there is a knock detection, this value is 100%.

Figure 27 - Cumulative density frequency (CDF)



Font: Modified from Galloni (2012).

In this thesis, as a method to determine the ON, was specified that the minimum value of KL_{ASP} for every fuel used during the measurement procedure, had to be at least 82%, due the fact that to measure ON the engine have to operate under knock phenomenon occurrence.

11.4. Procedure to measure ON of a gasoline surrogate

As mentioned, for those samples of gasoline surrogate with a RON value below 100, the procedure was made following the standard ASTM D2699, for those sample with RON above 100, a procedure developed in the laboratory of THI was used, due the fact that there was no leaded fuel available.

As explained in section 8, to obtain the level of knock, and thus the ON of the fuel under test, is needed to use two reference fuels for bracketing. These reference fuels have to have not more than two octane number of difference between them (in the case when the ON of the sample fuel is in the range between 80 to 100). For those sample that presents ON above 100, is assumed that the reference fuels can differ in a maximum value of 3 ON.

Besides the reference fuels, is also needed a TSF (Toluene Standardization Fuel, which is a blend of isooctane, n-neptane and toluene, as the TRF), which is used to ensure that the engine is fit-for-use. If the engine can be classified as fit-for-use, the measurements can be performed. TRF and TSF consists of the same substances, in this thesis the designation TRF is used for those toluene fuel that are used for the bracketing process, and TSF to qualify if the engine is able to be used. The determination of the ON of the fuel under test is directly related to the value of ON and also related to the value of the K.I of these reference fuels and to the TSF.

11.4.1. Bracketing fuels and Toluene Standard Fuel (TSF)

According to ASTM (2004) the reference fuel (RF), which are utilized during the procedure to determine ON, are divided into two distiguished categories according to the ON.

- Primary reference fuel blends below 100 ON: for those fuels under test, which have ON below 100, the RF have to be a blend of isooctane (2,2,4-trimethylpentane), and n-heptane (PRF), or a blend of isooctane and PRF80;
- Primary reference fuel blends above 100 ON: blend of isooctane and tetraethyllead.

Tetraethyllead, also know as TEL, is a colorless, oily liquid with a swet, musty odor. It is probable carcinogen in humans. There are evidences that lead compounds cause lung cancer, many scientists belive that there is no safe level of exposure to a carcinogen, so all contact should be reduced to the lowest possible level (NEW JERSEY, 2007).

Due the fact that TEL is a hazardous substance, even if the standard ASTM D2699 determines that this component should be used for those fuels above 100 ON, some laboratories usually are using TRF as a substitute for TEL.

In this thesis, 7 different samples of the gasoline surrogate are used, some of them with a high content of ethanol, due this fact, was expected that these fuels may have a value of ON more than 100. Thus, is necessary to use a reference fuel able to detect ON more than 100, as the intention is not use TEL, in this thesis the reference fuels used are PRF and TRF.

11.4.1.1. PRF and TRF - Reference fuels

The knockmeter reading of the test fuel must be bracketed by two adjacent reference fuel blends selected by the two categories explained above. Is know that using PRF for the bracketing procedure, the maximum ON that this reference fuel can achieve is 100, which is pure isooctane. Pure toluene have a RON value of 120, thus TRF is used for fuels that presents ON above 100. Some of the PRF are shown in the annex E. The range of ON shown is from 87 to 100 ON. Annex F shows the ON related to TRF. Mixing toluene, n-heptane and isooctane, is possible to get different values of ON. For the range from 93.4 ON to 113.7 ON the percentage of toluene is keep constant in 74%, just the portion of isooctane and n-heptane varies. Basically, the reference fuels have to be chosen from annex E and F.

11.4.1.2. Toluene Standard Fuel (TSF)

According to the standard ASTM D2699, every determination of ON of each sample shall be performed using an engine that has been qualified as fit-for-use by rating the appropiate toluene standardization fuels (TSF). Basically during the determination of a gasoline surrogate is necesarry to use four different fuel, two fuels for bracketing (PRF for values below 100 ON, TRF for values above 100), the fuel which is to be determined the ON, and also a TSF to ensure that the engine is fit-for-use.

11.4.1.2.1. Fit-for-use procedure.

As determined by the standard ATM D2699, a TSF blend have to be selected from table 11. If the sample fuel ratings tested or to be tested during the operating period have a value of ON from 87.1 to 100, the TSF to be chosen should be above 87.1 ON and below 100 ON. If sample fuel ratings tested or to be tested during the operating period have a value of ON below 87.1 and above 100, the TSF octane number should also be in this range.

Table 11 - TSF blend ON accepted reference values – 70.1 to 110.6 ON

TSF Blend RON ARV	Untuned Rating Tolerance	TSF Blend Composition, vol %			Use for Sample Fuel RON Range
		Toluene	Isooctane	Heptane	
75.6	±0.5	58	0	42	70.1-80.5
85.2	±0.4	66	0	34	80.2-87.4
89.3	±0.3	70	0	30	87.1-91.5
93.4	±0.3	74	0	26	91.2-95.3
96.9	±0.3	74	5	21	95.0-98.5
99.8	±0.3	74	10	16	98.2-100.0
103.3	±0.9	74	15	11	100.0-105.7
107.6	±1.4	74	20	6	105.2-110.6

Author: ASTM (2012).

11.4.2. Estimation of the RF and TSF that were used for the measurements.

Before to realise the measurements for each sample, was necessary to determine the expected values of ON for each of those samples, due the fact that, was necessary to have an estimation about which reference fuel and TSF should be used for each sample.

Table 12 (column ON) shows the values of ON that were expected to be obtained from the measurements. These values were based in the papers written by Cancino (2009), Foong et. al (2014) and Anderson et. al (2012).

Table 12 - Estimation of the ON for each sample and estimation of RF and TSF for each sample

Sample	ON	RF-1	RF-2	TSF
E0	90.0 – 93.0	PRF 91	PRF 93	93.4
E10	93.0 -96.0	PRF 93	PRF 95	93.4
E20	98.0 - 102.0	PRF 98	PRF 100	99.8
E30	100.0 -103.0	PRF 100	TRF 102.5	99.8
E50	104.5 -106.5	TRF 105.9	TRF 107.6	-
E85	106.0 -108.0	TRF 107.6	TRF 109.2	-
E100	107.0 -109.0	TRF 107.6	TRF 109.2	-

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Determined the expected values, were chosen from annex E and F the reference fuels that should be used for measure RON for each sample, and the TSF was selected from table 11. Table 12 shows the RF and TSF chosen for the samples. RF-1 is the referece fuel with low ON, and RF-2 is the reference fuel with high ON.

For the samples E0, E10 and E20, the reference fuels were chosen from the annex E (for primary reference fuels). For E50, E85 and E100 the reference fuels were chosen from annex F (for toluene reference fuels). For the sample E30, was verified that the value probably should be from 100 ON to 102.5 ON, through this, one reference fuel chosen was PRF100, and the other reference fuel was defined as TRF 102.5.

As can be seen in the column “TSF”, for E0, E10 and E20, the TSF chosen are according to the range of ON which is specified in table 11. For the sample E30, as the expected value of ON was in the range from 100.0 to 102.5, through table 11 can be seen that the TSF should be chosen as having a ON of 103.3, however, was decided to use a TSF 99.8, due the fact that this value of ON was really close to that value of the reference fuel PRF100. The octane number difference between TSF 99.8 and PRF-100 is just 0.2 ON, the difference from TSF-103.3 to TRF-102.5 is 0.8 ON. As can be seen in table 11, TSF 99.8 has a rating tolerance of 0.3 ON, thus its ON value may be between 99.5 and 100.1 RON. Through that, was assumed that the engine could also be classified as “fit-for-use” using TSF 99.8.

For the samples E50, E85 and E100, the reference fuels were chosen from annex F. Thus, the TRF 107.6 should be used for these three samples, however, this fuel is the same as specified as a TSF in table 11. Through that, for these samples the engine could not be classified as fit-for-use, once there is no other TSF that could be used in the range of the ON of these samples. In resume, for each of these samples, a TSF is used as bracketing fuel.

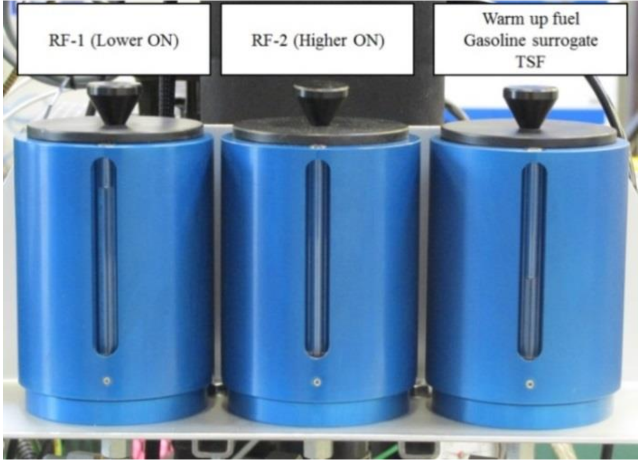
11.4.3. Procedure to measure ON

In this topic explains how the value of ON was determined for one sample, thus, all of the entire procedure was repeated for each sample.

11.4.3.1. Summary of test method (for each sample)

The measurements were performed in the following sequence: E10, E20, E30, E0, E50, E85 and E100. There are in the engine three diferrent fuel tanks, figure 28. Was defined that the reference fuel with lower value of ON (RF-1) should be placed in the left bottle, the RF-2 has a higher value of ON and was placed in the middle bottle. The warm up fuel, gasoline surrogate and TSF, were placed in the right bottle.

Figure 28 - Fuel tanks



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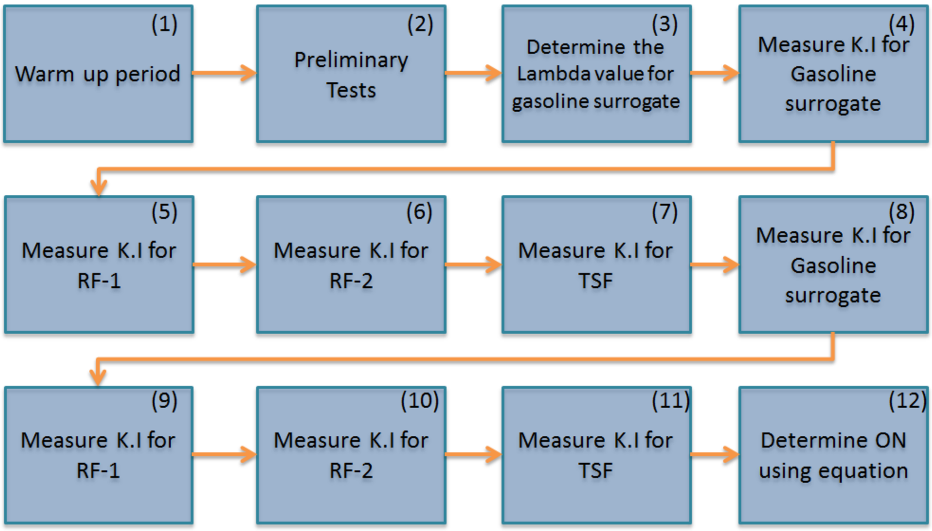
In figure 29 are summarized the basic steps to determine the ON of a gasoline surrogate. It consists essentially of 12 steps, as can be seen.

Figure 29 - The measurement procedure flowchart



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11.4.3.1.1. Warm up period

The first step in the measurement procedure was start the engine with an warm up fuel, which is a step necessary to ensure that critical variables, like the intake pressure, intake temperature, cooling water outlet temperature, and so on, are stable. Using the computer screen was possible to verify the stability of these parameters. Was decided in this thesis use a warm up fuel which had an octane number near to 95, due the fact that was expected that most of the samples should present an ON value near to that.

According to the standard, the engine had to be operated with a warm up fuel for at least one hour, and in the last 10 minutes, it must operate at typical K.I levels. Then, after 50 minutes from started the engine, the hand crank was used to increase the compression ratio until the value of KL_{ASP} was, at least 82%. Above this value a typical K.I level operation is reached. Is important to highlight that during the measurements every fuel used (RF, gasoline surrogate, TSF) had to be operated under knock conditions. Thus, the value of KL_{ASP} had to be always above 82%.

11.4.3.1.2. Preliminary tests

As mentioned , in a first moment was necessary to know about the expected values of ON for each sample, through that was possible to estimate the reference fuels and TSF that should be used. Then, before to perform next steps of the measurement procedure for each sample, was necessary to make a preliminary test to ensure that the reference fuels chosen were properly defined.

In this step, after the engine runs one hour with the warm up fuel, was started the preliminary test. To perform this test, the following steps were realised: in a first moment, using RF-1, the compression ratio was increased until the value of KL_{ASP} reached more than 82%. Then, the value of CR was kept constant, the values of the meter reading, spread and time constant in the detonation meter were setted so that the value of K.I, which is read from the Knockmeter, should be near to 80, but below this value. Then, the RF-2 was measured, its value of K.I, shown in the knockmeter, should be between 20 and 80. Finally, the gasoline surrogate was tested. If the gasoline surrogate value of K.I stayed between the values of K.I for the RF-1 and RF-2, was known that the reference fuels were chosen properly and the next steps of the measurement procedure could be followed. If the value of K.I of the sample was not in the range between the RF-1 and RF-2, would be necessary to select another reference fuel, or another pair, or just change one RF of those previous one, until the situation where the K.I for both RF was in the range from 20 to 80 K.I, and the K.I of the gasoline surrogate under test between the them.

At any gasoline surrogate under test, RF-1 should always present a higher K.I, because it has a lower value of ON. The RF-2 should always present a lower K.I, due the fact that it has a higher value of ON. This conditions were verified for every gasoline surrogate under test.

11.4.3.1.3. Determining the lambda value (λ) for gasoline surrogate

The knock intensity depends on the engine compression ratio and also is related to the lambda value. There is no direct relation between lambda and K.I, a higher value of lambda, does not means, for example, a higher value of K.I.

During the preliminary test, the compression ratio and the detonation meter parameters had to be kept unchangable, however, as that test was performed just to check if the reference fuels were properly chosen, and not to check the ON of the fuel, in this step (to determine the value of λ) was possible to change the values of CR and also the parameters of the detonation meter, if during the measurements was verified that they should be changed.

In this step, after the engine runs one hour with the warm up fuel, and also after verify if the RF of the gasoline surrogate under test were properly selected, the right bottle (figure 28) was filled with the gasoline surrogate under test. At this time, the gasoline surrogate started to be injected in the engine, and was verified if the value of KL_{ASP} stayed with its value above 82%. In the case in which this value was under 82%, the compression ratio had to be increased until reaches this value or above it (better if near to 100%). Then, after this moment, the value of CR had to be kept constant. Then, the values of the meter reading, spread and time constant in the detonation meter, were setted so that the value of K.I, which is read from the Knockmeter, was in the range of 20 to 80.

After setted these values, the lamba value was varied until get the maximum value of K.I. By this procedure, was possible to know the value of lambda which gave the maximum knock intensity.

11.4.3.1.4. Measuring K.I for gasoline surrogate, RF-1, RF-2 and TSF

In this step is written about how the knock intensity of the RF-1, RF-2, TSF and the sample of the gasoline surrogate were measured.

After determined the value of lambda for the gasoline surrogate, the values of compression ratio, meter reading, spread and time constant in the detonation meter, could not be varied any more. These values had to be chosen such that every fuel (those used for determine the ON of one gasoline surrogate) could be operated under knock conditions (with KL_{ASP} above or equal to 82%). It is imporntant to highlight, that the compression ratio had to be chosen, such that the RF-1 must show a value of K.I not more that 80, and the RF-2 must show a value of K.I above 20. The value of K.I of the gasoline surrogate had to be between them.

Once determined CR and those values of the detonation meter, and still operating the engine with the gasoline surrogate to be measured the ON, the value of K.I was read from the knockmeter, and this value was written in a specific paper, shown in appendix B.

The gasoline surrogate was refueled in the bottle twice, keeping the engine running for around 30 minutes, during this time, the K.I was read at least 5 times, and also the data from this measurement were saved. For every fuel, at least, 7 files containing 50 working cycles were saved for further analysis.

Then, after operating the engine for half hour with the gasoline surrogate, the valve from the bottle with gasoline was closed, and then, was opened the valve from the bottle with RF-1, which began to feed the engine.

After the RF-1 started to be injected, a time interval was needed to ensure that the engine was operating in stable conditions, this time was in average around 5 minutes. After this time, the same procedure as in the case with the gasoline surrogate was performed, 30 minutes operating the engine with RF-1 and in this interval, the K.I was read 5 times and also around 7 files containing the data were then saved.

Then, after measure RF-1, the RF-2 was measured following the same procedure.

Also, as the standard ASTM D2699 defines, a TSF also had to be measured to ensure that the engine was fit for use. As mentioned in section 11.4.2, for the gasoline surrogates E50, E85 and E100, one of the RF used in each of these samples was a TSF, throught that the verification if the engine was able to be used could not be made, due this fact, the step number 7 and 11 were not carried out for these three samples.

As can be seen in figure 29, after measure the TSF, the gasoline surrogate was measured again, and then the RF-1, RF-2 and finally, again the TSF. It is also defined in the standard, that is necessary to measure every fuel twice to ensure that the engine was operating under normal conditions and also to ensure that measurements were not influenced by any changes in the environmental conditons as room temperature, for example. The value of K.I for these fuels must not differ more than 1 K.I from the first measurement to the second one.

As mentioned, the K.I was read at least 5 times for each fuel for each measurement, as the measurement was made in two steps, at the end, for each fuel, there was around 10 values of K.I, then, the final value of K.I for each fuel was the average value from those 10.

After measure the K.I twice for every fuel and save the data, as well as save the values of K.I, was possible to utilise the equation 12 (explained in the next section) to finally determine the ON of the gasoline surrogate.

11.4.3.2. Equation to determine ON related to the RF

ASTM (2004) defines a mathematical equation to determine ON of a sample fuel, it is the next equation.

$$ON_S = ON_{LRF} + \left(\frac{K.I_{LRF} - K.I_S}{K.I_{LRF} - K.I_{HRF}}\right)(ON_{HRF} - ON_{LRF}) \tag{12}$$

In which, ON_S is the octane number of the sample fuel (gasoline surrogate under test); ON_{LRF} is the octane number of the low RF (RF-1); ON_{HRF} is the octane number of the high RF (RF-2); $K.I_{LRF}$ is the knock intensity of the low RF (RF-1); $K.I_{HRF}$ is the knock intensity of the high RF (RF-2); $K.I_S$ is the knock intesity of the sample fuel;

The measurement of K.I was explained in the previous topic. The ON of the RF are already known, as explained in section number 8, the number related to the RF says its ON, as an example, PRF 95 have a ON of 95.

11.4.3.3. Fit-for-use engine

As explained, the ON of the fuels used for bracketing is already known, also the ON number of this TSF is known. For example, if a TSF 89.3 is been used, is know that the ON of it is 89.3. Therefore, using the value of K.I for both reference fuels determined during the operation of the engine, also using the ON of them, and the K.I of the TSF, the equation number 12 is used to determine the ON of this TSF. If the value calculated through the equation is the same as the real value (in this example 89.3) with certain tolerance, the engine could be qualilified as: fit-for-use.

If the ON, calculated with equation 12, of the TSF blend is within the untuned rating tolerances shown in table 11 for that TSF blend, the engine is fit for use to rate sample fuels within the applicable ON range.

11.5. Graphs and curves

After measure every sample of gasoline surrogate and save the data from the measurements, some graphs were drawn up and some curves were elaborated to help to explain the results.

MatLAB ® was utilized to prepare the curves related to the in-cylinder pressure and also to build up the heat release curve. Excel 2010 was used to analyse the maximum pressure, indicated mean effective pressure, untuned TSF blend rating, and also to compare the pressure oscillation in the engine for each sample, regarding to the K.I. The ON of the gasoline surrogate related to the ethanol content was described in a graph also made using Excel.

12. RESULTS

The determination of the RON, for the samples of the gasoline surrogates used in this study, was conducted following the methodology described in section 11.4.3.

12.1. ON for the gasoline surrogate E0

Was estimated that the ON of the sample E0 could be in the range from 90 ON to 93 ON, by this way, as mentioned the following reference fuels should be used: PRF 91 and PRF 93.

Once estimated these values and fuels, the measurement could be performed. After the warm up period the preliminary test was realized, was verifyed that the K.I for this surrogate had its value above the RF-1, this means that the K.I of the E0 sample, which should be between the RF-1 and the RF-2 was out of this range.

As the value of K.I of E0 was higher than the PRF 91, was known that it has a worse quality, which means that its ON must be lower than 91. Due this situation a new set of reference fuels was chosen, in which: the RF-1 was chosen as PRF 88, the RF-2 was a PRF 90 and the toluene standard fuel chosen was TSF 89.3. They are shown in table 13.

Once defined the new bracketing fuels and the TSF that should be used, the preliminary test was remade. At this time, was verified that the K.I of the E0 sample was in the range between PRF 88 and PRF 90, then, the next step was performed.

The compression ratio was defined so that the KL_{ASP} (percentage of how many engine cycles have the occurrence of knock phenomena) should be above 82%. The compression ratio was defined as 6.39, with this value the KL_{ASP} was equal to 98.15%. The value of lambda (λ) was set as 0.97, which gave the highest value of K.I. The K.I for the gasoline surrogate E0, RF-1, RF-2 and TSF was determined. They are listed in table 13, the column ‘K.I’ shows the average value of K.I for each fuel tested for the determination of ON for the E0 sample. As can be seen, the K.I for E0 has its value between K.I for PRF-88 and PRF-90. The column ‘ON’ shows the ON value for those fuels, the yellow box are calculated values.

The column ‘K.I’ shows the average value of K.I for each fuel tested for the determination of ON for the E0 sample. As can be seen, the K.I for E0 has its value between K.I for PRF-88 and PRF-90. The column ‘ON’ shows the ON value for those fuels, the yellow box are calculated values. Once determined the K.I for those fuels and also known the

ON for PRF-88 and PRF-90, the equation (13) was used to calculate the ON for TSF-89.3 and for E0. In this case: $ON_{LRF} = 88.0$, $ON_{HRF} = 90.0$, $K.I_{LRF} = 64.0$, $K.I_{HRF} = 44.0$.

Table 13 - Values from measurement – E0

	Name	ON	K.I
RF-1	PRF-88	88.00	64.00
RF-2	PRF-90	90.00	44.00
TSF	TSF-89.3	89.20	52.00
Gasoline Surrogate	E0	89.35	50.50

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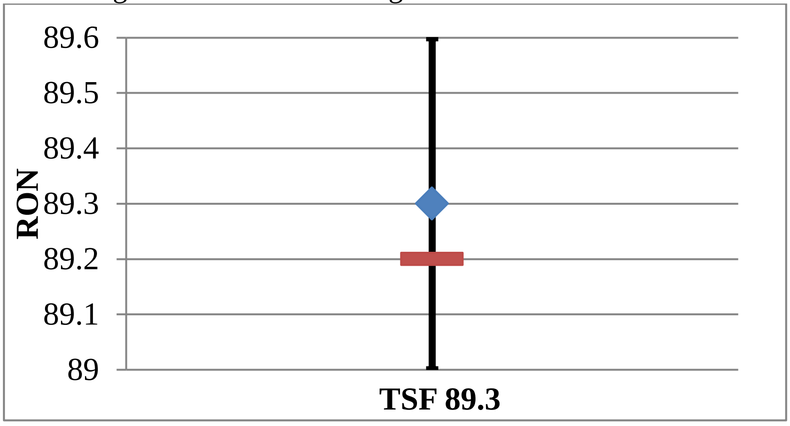
Having those values, the ON of the fuel TSF-89.3 was determined to know if the engine could be categorized as fit-for-use. In table 13, the yellow box in the line 'TSF' shows the calculated value of ON for this fuel, which is 89.20. This value is lower than 89.3, which is the real ON for that combustible. However, in the standard is written that there is a tolerance of ±0.3 ON.

Figure 30 shows the ON tolerance for the fuel TSF-89.3. The blue point is the exact value for the ON of this TSF, which is 89.3 ON. The black line defines the limit values, the red line is the calculated value. As the calculated ON was within the tolerance, the engine could be classified as fit-for-use.

Figure 30 - Untuned rating tolerance for TSF – 89.3



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The ON value for the gasoline surrogate was then determined, also using the equation (12), resulting in a value of 89.35. This value is not in the range that was expected, 90 to 93, but it is really close to that.

12.2. ON for the gasoline surrogates E10 / E20 / E50 / E85 / E100

The measurement of octane number for the samples E10 to E100 were performed in the same way as done for E0, following the steps determined and shown in figure 29.

In short, for these samples were verified that the reference fuels defined in table 12 were properly chosen. Thus, the next table summarises the RF fuels used during the measurements. For the samples E85 and E100 were used the same reference fuel.

As mentioned in 11.4.3.1.4, for the samples E50, E85 and E100 the steps 7 and 11 could not be performed, since one of the reference fuels used for them was a TSF.

Table 14 - Reference fuels used for E10 / E20 / E30 / E50 / E85 / E100

Sample	RF-1	RF-2	TSF
E10	PRF 93	PRF 95	93.4
E20	PRF 98	PRF 100	99.8
E30	PRF 100	TRF 102.5	99.8
E50	TRF 105.9	TRF 107.6 (TSF 107.6)	-
E85/E100	TRF 107.6 (TSF 107.6)	TRF 109.2	-

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In short, the compression ratio for every sample was defined so that the KL_{ASP} should be above 82%. The value of lambda (λ) was set so that the highest value of K.I could be reached. The values for K.I for which sample was determined during the measurements, and as already discussed for E0, the same procedure was performed. Using equation (12) was possible to calculate the octane number for each sample. Table 15 summarises the RON for these samples.

Table 15 - ON for the samples of the gasoline surrogate

Sample	ON
E10	94.47
E20	98.60
E30	101.97
E50	105.73
E85	108.11
E100	108.57

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For the samples E10, E20 and E30 the procedure to determine wether the engine was fit for use (steps 7 and 11 – in figure 29) was performed. Table 16 shows the octane number calculated for the TSF utilized in each sample. As in the case for E0, the calculated ON for these TSF were within the tolerance. Thus, the engine could be classified as fit-for-use for the samples E10, E20 and E30 .

Table 16 - ON for the TSF – Engine fit-for-use

	Name	ON
TSF for E10	TSF-93.4	93.34
TSF for E20	TSF-99.8	99.51
TSF for E30	TSF-99.8	99.87

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12.3. Research Octane Number - RON

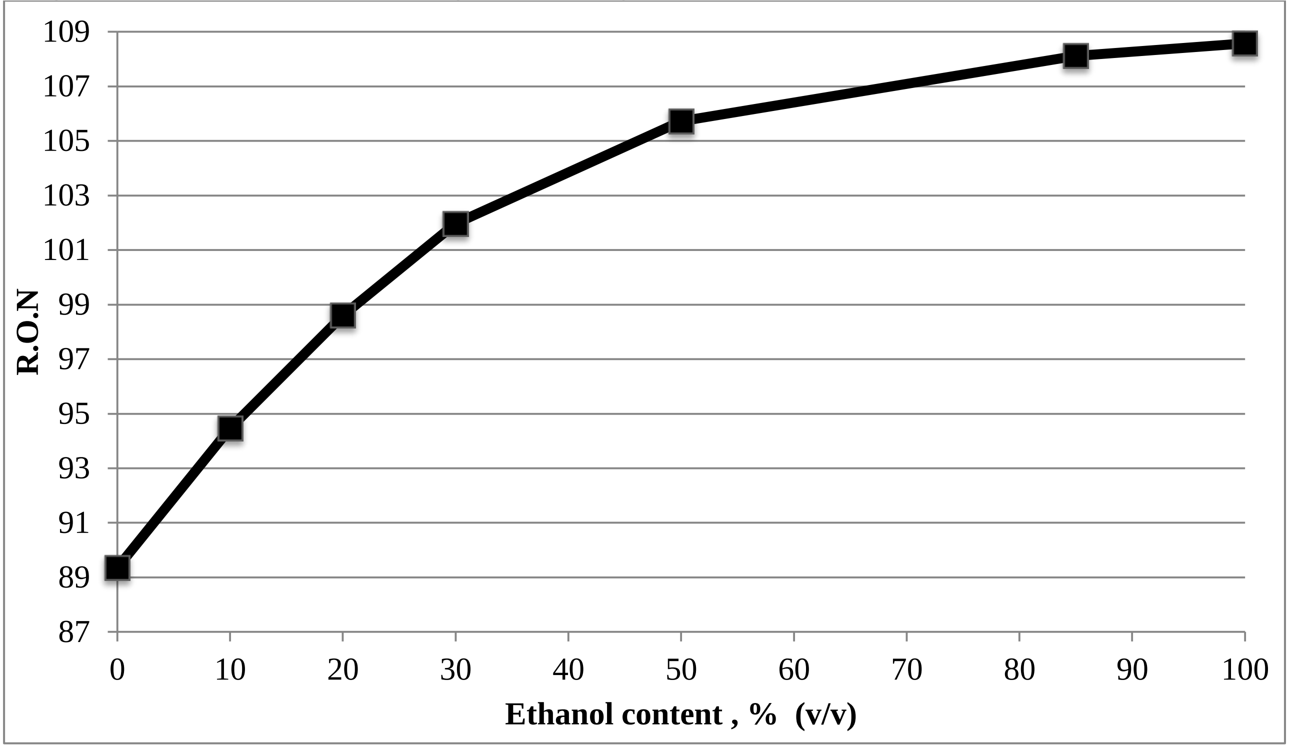
The ON of the gasoline surrogates discussed in the previous section are plotted in a graph relating the RON and the percentage of ethanol content, as shown in figure 31. The RON shows a non-linear relationship with the ethanol content.

For the interval of ethanol content under study, is possible to observe that the shape of the curve in concave down, and can be also analysed that from E0 to E30 the increase in the RON value is quite linear, as can be seen in figure 31.

There is a big step in the RON value between E0 and E30, the difference is 12.62 ON. As the curve itself is concave down, and if there is a further increase in the ethanol content the diference is reduced, as for example from E30 to E50, the RON value difference is around 3.76 ON. These results exhibits that with the increase in the ethanol percentage, the RON value also increse. There is a strong increment in RON for those gasoline surrogates located in the range with a lower percentage of ethanol (0% to 30%), as observed with the samples E0 and E30. For those gasoline surrogates in the range above 30% the growth rate starts to be significantly and gradually reduced.

Figure 32 shows a comparison between the RON determined by this study and RON for gasoline surrogates with some percentage of ethanol from literature. In the literature there are some studies that already have analised the influences of the ethanol content in the value of RON, the most believed are those studies written by Hunwartzen (1982) and Anderson et al. (2012), since they comply with the ASTM and DIN standards concerning the proper configuration of the CFR engine to handle the high fuel flow rate of ethanol. For comparison are used the datas from Anderson et al. (2012) and from Foong et al. (2014), this last authors was choosen due the fact that in his study several types of gasoline surrogates have been analysed.

Figure 31 - Measured RONs for the gasoline surrogate used in this work versus the ethanol content



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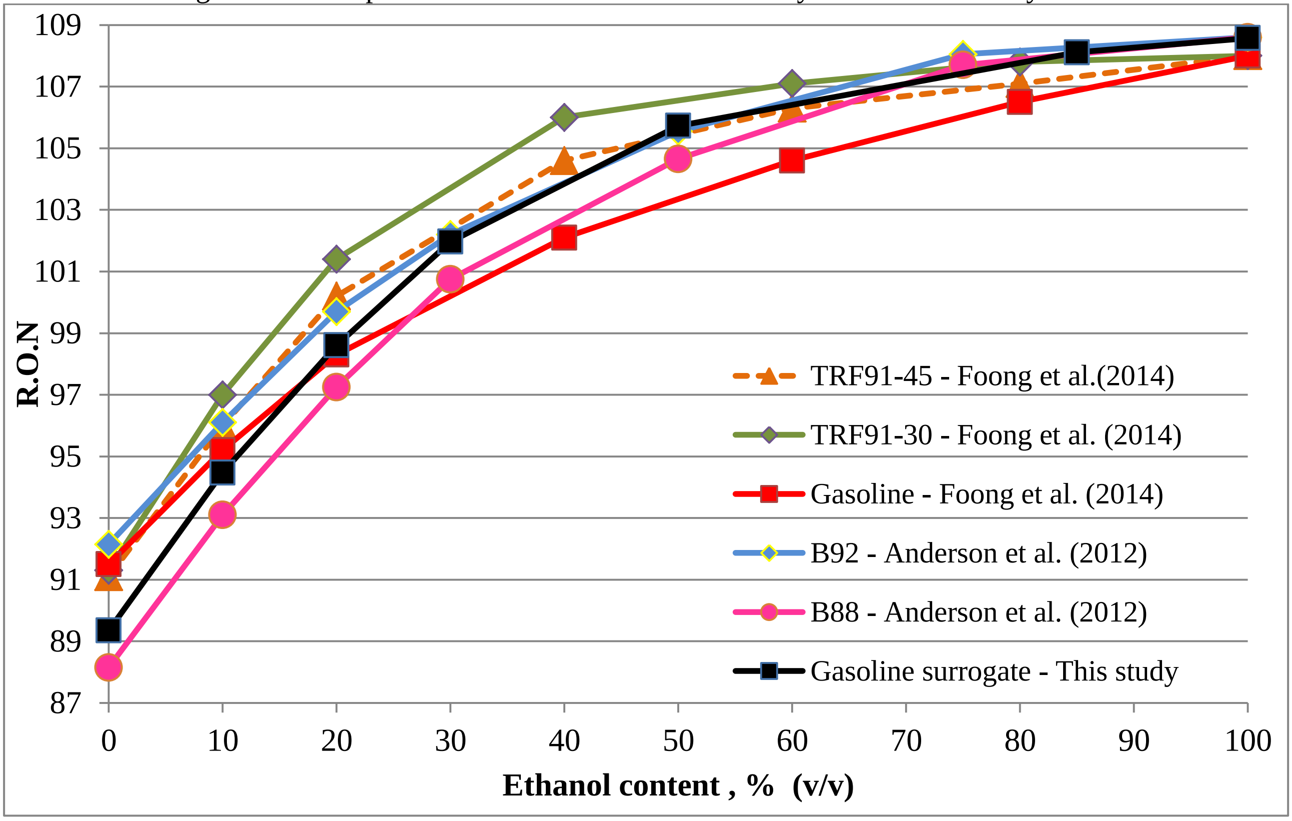
In figure 32 were plotted six different curves relating RON and the ethanol content, in which, as the legend shows, the black line is related to this study and the other curves were taken from Anderson et al. (2012) and from Foong et al. (2014).

It is important to highlight that the composition of these gasoline surrogates shown in figure 32 are different. The gasoline surrogate used in this work is a blend of ethanol, isooctane, n-heptane, toluene and diisobutylene, in which just in this study diisobutylene have been used.

Foong et al. (2014) has used a regular unleaded gasoline, which was obtained from a gas station in Melbourne, Australia, it had a density of 0.73 g/cm^3 at 25°C. The author has added ethanol in this gasoline to perform the measurements, the value of RON related with the ethanol content is shown as a red line in figure 32. It can be seen that for ethanol percentages between 10 – 20%, the RON number of real gasoline from Foong et al.(2014) and the gasoline surrogate from this study fit quite well. The orange line and green line also are showing values of RON determined by this author, in which, TRF was used as a base blend for these two gasoline surrogates. TRF91-30 means a blend with a value of RON equal to 91 (with 0% of ethanol), the index "30" means 30% (v/v) of toluene in this surrogate, the same is applied to TRF91-45.

Figure 32 - Comparison between RON from this study and from literatury



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It means that, the gasoline surrogate TRF91-30 used by Foong at al.(2014) has approximately the same quantity of toluene as in the case of the gasoline surrogate studied in this thesis with 0% of ethanol. It can be observed that the gasoline surrogate TRF91-30 shows higher values of RON for blends with ethanol between ~5% to 75%. In this thesis was used 27.8% (v/v) toluene. Table 17 shows the percentage of each subtance in the gasoline surrogate used by Foong at al. (2014), as well as the composition used in this study.

Anderson at al. (2012) has also used common gasoline, but from USA, and then mixed ethanol on it. There are two gasolines blendstocks used by this author in his studies that are used in this thesis as a mean of comparison, one gasoline with a value of 88 RON (with 0% of ethanol), identified as B88 in the figure 32 (pink line). The other gasoline has a value of 92 RON, and is identified as B92 (blue line).

Table 17 - Properties of the gasoline surrotes of this study and from literature.

Fuel	Composition (%)			
	Isooctane	n-heptane	Toluene	Diisobutylene
TRF91 - 30	53.2	17.0	29.8	-
TRF91 - 45	34.7	20.3	45.0	-
This study	33.3	24.4	27.8	14.4

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12.3.1. RON value for E0

As can be seen in the figure 32, the value of E0 for the gasoline surrogate under study by this thesis, has a value of 89.35, which is one of the lowest values in comparison with the other 5 fuels, the lowest RON is related to gasoline B88. Is important to highlight that there is not an exact value for RON of any surrogate, which means that, gasoline surrogates are utilized to be a ”substitute” of gasoline in differents studies, as there are different types of gasoline, must exist different surrogates to simulate them, in other words, can exist two or more different compositions of gasoline surrogate with the same RON value.

Then, in case of surrogate E0, can be verifyed that, using a surrogate composed by 27.8% of toluene, 33.3% of isooctane, 14.4% of diisobutylene and 24.4% of n-heptane, gives a RON value lower than those surrogates composed by TRF, also lower than a normal australian gasoline, but its value is between two common american gasolines.

The difference from E0 (this study) and TRF91-45 is 1.75 ON. Basically, as assumed, the difference in the value of RON is provenient from the different composition in those 6 fuels. Table 18 shows the composition of the gasoline studied by Anderson et al.(2012), Foong et al.(2014) and the gasoline surrogate (E0) used in this study.

To help to explain those curves in the figure 32, are used the table below and also the figures bellow, which are part of the study made by Foong et al. (2014).

Table 18 - Composition of the gasoline surrogate:this study, gasoline by Foog and Anderson.

Component	This study (% volume)	Gasoline - Foong et al. (2014) (% volume)	Gasoline B88 - Anderson et al. (2012) (% volume)	Gasoline B92 -Anderson et al. (2012) (% volume)
Total Paraffins	57.7	48.9	63.6	64.3
iso-Paraffins	33.3	35.9	42.4	48.3
n-Paraffins	24.4	13.7	21.2	15.9
Aromatics	27.8	31.7	25.7	26.0
Olefins	14.4	8.0	5.8	5.8
Naphthenes	-	11.4	4.9	3.9

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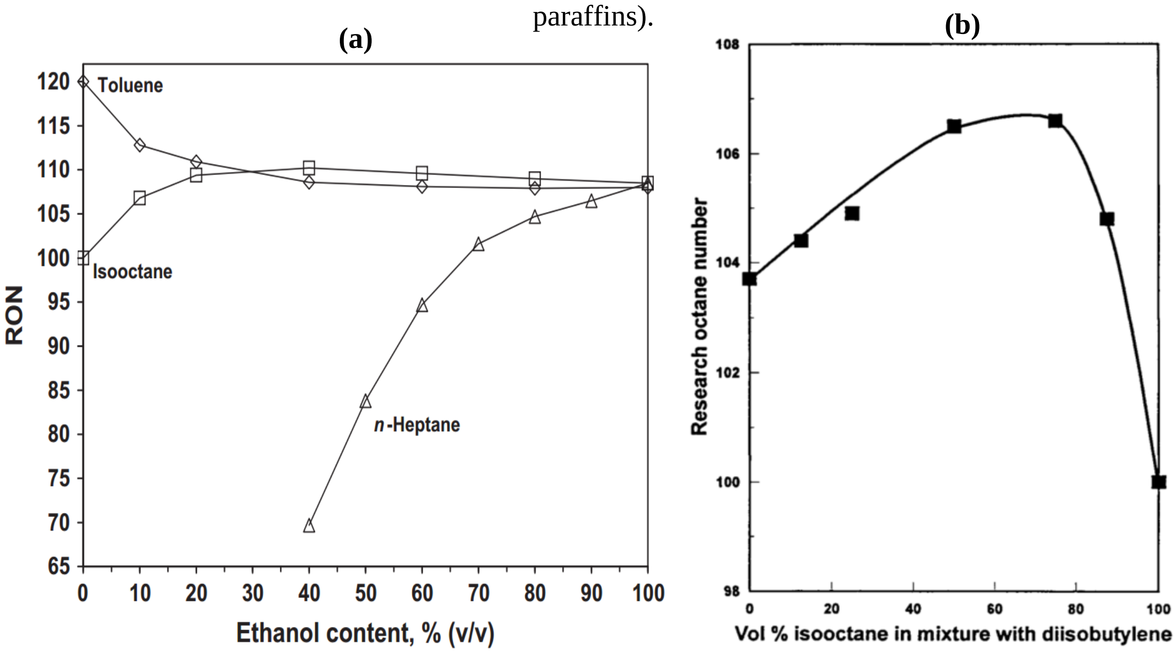
Figure 33-a show the RON values for the blends of: toluene - ethanol, isooctane - ethanol and n-neptane – ethanol.

According to Foong et al. (2014), for the blend isooctane-ethanol, the RON values with 20% to 80% of ethanol exceeds the RON value for neat ethanol. It suggests that there is a presence of some significant synergism between isooctane and ethanol.

The blend of n-heptane and ethanol also suggest a synergism between these both substances, due the fact that the RON value increase gradually with the increment of ethanol in the mixture.

Figure 33 – (a) Measured RON values for the blends: toluene-ethanol, isooctane-ethanol and n-heptane-ethanol; (b) Measured RON values for the blend: Diisobutylene (Olefin) – Isooctane (iso-paraffins).



Font: (a) Foong et al. (2014); (b) Pilling (1997).

Toluene - ethanol shows a different behavior, according to Foong et al. (2014), exist an antagonistic blending effect. Incresing the content of ethanol, results in a lower value of RON, near to 40% the RON value is approximately equal to the neat ethanol.

As in the composition of the gasoline surrogate used in this work there is diisobutylene, is important to understand the behavior of this substance. Figure 33-b shows the RON values for a mixture of diisobutylene and isooctane.

Pure diisobutylene, according to Pilling (1997) has a value of 103.7 ON. As the graph shows, adding isooctane there is an increase in RON value until near to 70%(v/v) isooctane, with a value near to 106.8. Beyond this value, there is a sharp drop in the curve, with 100% (v/v) isooctane the RON value is 100, as it should be.

Basically, this graphs help to understand what can happen with the value of RON if any change in the composition of a gasoline surrogate occurs.

The aromatic component in the gasoline surrogate used in this work has a value of 27.8% of toluene. Is known that a pure toluene gives a RON value of 120, as can be seen in figure 33-a. By this way, as the gasoline studied by Foong et al. (2014) has a higher percentage of this component, is expected that the RON value for this surrogate must be higher than the surrogate used in this work. The gasolines studied by Anderson et al. (2012) – B88 and B92 - have a close value in the percentage of aromatics in comparison with gasoline surrogate used in this work.

The percentage of n-heptane (n-paraffin) for the surrogate of this study is much higher than the gasoline studied by Anderson et al. (2012). In the curve for n-heptane in the figure 33-a suggests that, as higher is content of this component in a gasoline surrogate, lower is the value of RON. Remembering that a pure n-heptane gives a RON value equal to 0. Then, to understand why each of these fuels shown in figure 32 has its own RON for E0, is necessary to know its components and percentage of each of them.

For 0% of ethanol, the lowest value of RON is found in the gasoline B88, it has a higher content of isooctane in its composion, and lower content of n-heptane in comparison to the gasoline surrogate used in this work. Analysing just the influences of these two components in gasoline surrogate is not enough to explain why B88 has a lower value of RON than the gasoline surrogate used in this work. Is necessary to have a look in the figure 33-b, which shows the behavior of diisobutylene. As in the gasoline surrogate the content of isooctane is 2.31 times higher than diisobutylene, it suggests that this proportion helps to increase the RON value of the gasoline surrogate, due the fact that in figure 33-b, with this proportion, the RON value reaches its highest value. Then, the addition of diisobutylene in the gasoline surrogate used increases its RON value. This the reason why gasoline B88 has a lower value of RON with 0% of ethanol, when compared with the gasoline surrogate of this study, even if B88 has a higher content of isooctane.

In resume, the gasoline surrogate used in this work has a higher content of n-heptane and a close value in the content of toluene, in comparison with those gasolines studied by Anderson et al.(2012) and by Foong et al.(2014). As can be seen in figure 32, the RON value of this gasoline is 89.35 ON, while the gasoline B92 by Anderson et al.(2012) gives 92.20 ON, B88 a value of 88.15 and gasoline by Foong et al.(2014) gives 91.5 ON.

12.3.2. Tilt angle curve of the gasoline surrogate used in this work and gasolines and gasolines surrogates studied by Anderson and Foong.

Each one of the six curves shown in figure 32 shows the characteristics nonlinear dependence of RON on volumetric ethanol content. According to Anderson et al. (2012), the initial RON increase for the first 10% (v/v) ethanol, from E0 to E10, is greater than each 10% (v/v) increase.

The value of the inclination of each curve can be seen in figure 34. The y-label is the value of inclination, the x-label is the RON interval for each inclination. As one example, in the interval E0 to E10, for the surrogate TRF91-30, the curve inclination was almost 30°.

One important observation described by Anderson et al. (2012) is that, as lower is the RON for a given gasoline, greater is the RON increase with ethanol addition. It can be observed comparing the gasoline B88 and B92, in which B88 has a lower value of RON for any given value of ethanol content, but greater tilt angle for any interval of ethanol, as can be seen in figure 34.

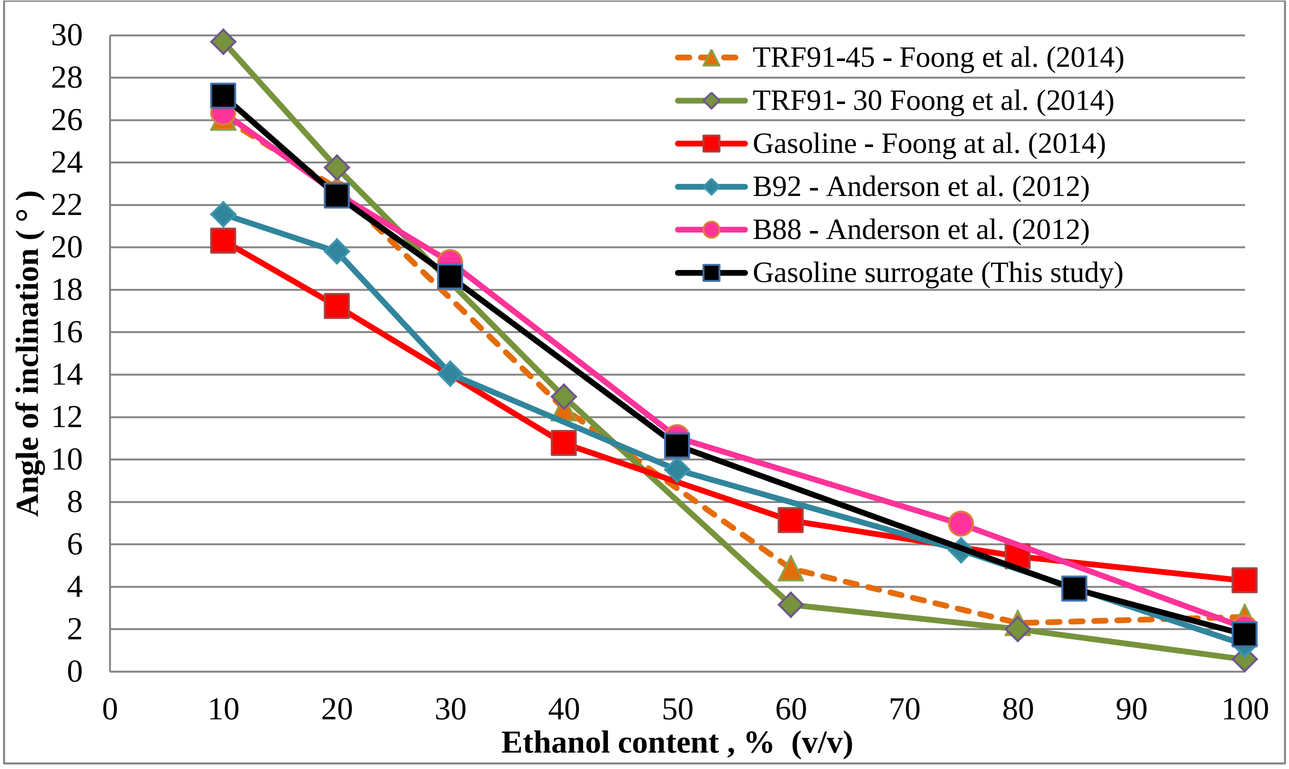
The gasoline surrogate used in this work fits in the observation done by Anderson et.al. (2012). As is known, this gasoline surrogate has a RON value (for E0) between those values for gasolines B88 and B92, therefore, to fit in the observation, the value of the tilt angle of the gasoline surrogate used here should be, for any content of ethanol, between those values for B88 and B92, and that is precisely what occurs.

As can be seen in figure 34, the black line represents the gasoline surrogate used in this work, the pink line – gasoline B88, and the blue line – gasoline B92. In the fist interval, from 0% to 10%(v/v) ethanol, the value of the tilt angle for the gasoline surrogate used is just a little bit higher than the value for B88 – 27.13° (gasoline surrogate used in this work) and 26.33° (B88) – a difference of just 0.79°. Due the fact that these gasolines have been measured in different laboratories, even using the same standard, a rating tolerance can be considered, and so, can be assumed that the tilt angle for the gasoline surrogate used and for B88 is in accordance with the observation done by Anderson et al. (2012).

In short, the tilt angle for the gasoline surrogate used in this work has a lower value for the entire range of content of ethanol compared with B88 (considering the range 0%-10% having a tolerance). At the same time, the tilt curves for both fuels are really close to each other, in the range 0% to 50%, they have almost the same value. Above 50% (v/v) the tilt angle of the gasoline surrogate used starts to be closer to the values for B92. These observations means that, the gasoline surrogate used in this work represents with good accuracy the tilt angle of gasoline B88 for the entire range of ethanol content, and have a good agreement with the values of B92 for above 50% (v/v) ethanol.

Thus, the gasoline surrogate used in this work represents the tilt angle for B88 and B92 better than the surrogates TRF91-30 and TRF91-45.

Figure 34 - RON difference between the gasoline surrogates



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In comparison with the gasoline studied by Foong et al. (2014), the gasoline surrogate used in this work has greater tilt angle in the range 0% to 80% (v/v) ethanol, which is in accordance with the Anderson’s observation. However, above 80% the tilt angle values for Foong’s gasoline are greater than the gasoline surrogate used in this work.

The gasoline surrogate used in this work fits well with the tilt angle for the gasolines B88 and B92, studied by Anderson et al. (2012), and his study comply with the ASTM and DIN standards concerning the proper configuration of the CFR engine to handle the high fuel flow rate of ethanol. Therefore this gasoline surrogate used in this work shows adequate and trustable values in accordance with ATSM and DIN.

12.3.3. RON value for the interval E0 – E100

In figure 32 can be seen that the curve for the gasoline surrogate used in this study is in the interval between the curves for B88 and B92. In the range from 0% to 50% (v/v) ethanol, it can be observed that the RON value for the surrogate used and the values for B88 are equally spaced in a value around 1.24 ON.

In the range from 0% to 30% (v/v) ethanol, as the tilt angle for the gasoline surrogate used is greater than B92 – figure 34, the difference in the RON value decreases with increment of ethanol content in percentage, as can be seen in figure 32. Above 30% (v/v) ethanol, the RON curves for the the gasoline surrogate used in this work and gasoline B92 are really closer to each other. The RON value for E30 – gasoline surrogate used – is equal to 101.97 ON, while for B92 – E30 is 102.2, a difference of just 0.23 ON. In case of 50%(v/v) ethanol, this difference is even lower, the gasoline surrogate used has a value of 0.18 ON greater. It means that, for a content of ethanol greater than 30%(v/v), the RON curve for the gasoline surrogate used in this work fits well with gasoline B92.

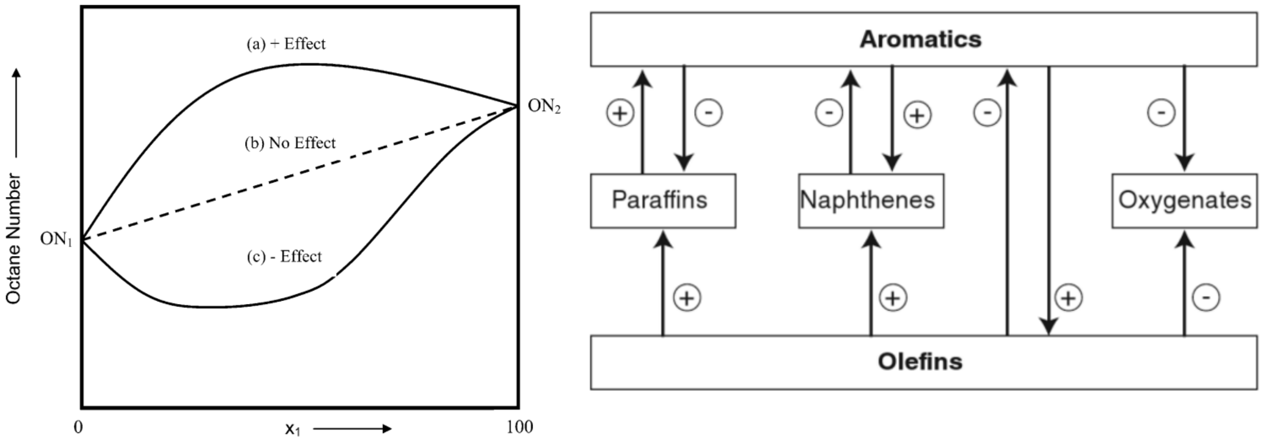
Gasoline is a complex mixture of hydrocarbons (paraffins, iso-paraffins, naphthenes, olefins, aromatics), as described by Ghosh, Hickey and Jaffe (2006), hydrocarbons of the same class interact linearly with one another regards to the RON, for blends of paraffins and olefins is common to observe non-linearity. Thus, to describe the RON values for each of the fuels shown in figure 32 is necessary to analyse the present substances and proportion of them.

Figure 35-a shows the possible relations between two species and its influences in the RON value, as an example, x_1 could be a paraffin and x_2 an olefin. A positive interaction (+) causes an octane increase, while negative interaction causes an octane loss (-). Figure 35-b shows the interactions between these hydrocarbons.

Scott (1958) has described that the interaction between aromatics and olefins result in a slight octane loss, when aromatic is added in olefins, as can be seen in figure 35-b.

Also according to Scott (1958), olefins and naphthenes mix linearly, adding naphthenes in an olefin there is an increase in RON value. Also, olefins and naphthenes provides an octane number gain in the presence of paraffins, reaching a maximum when the paraffinic concentration is in the range from 50% to 70%. It can be seen in figure 36, in which is plotted the RON values for the blend diisobutylene (olefin), and isooctane (paraffin). As can be observed, the greatest values are in the range defined by Scott (1958).

Figure 35 - (a) Typical nonliner relation between two species x_1 and x_2; (b) Interactions between different chemical families.



Font: (a) Ghosh, Hickey and Jaffe (2006); (b) Bertoncini, Courtiade-Tholance and Thiébaut (2013)

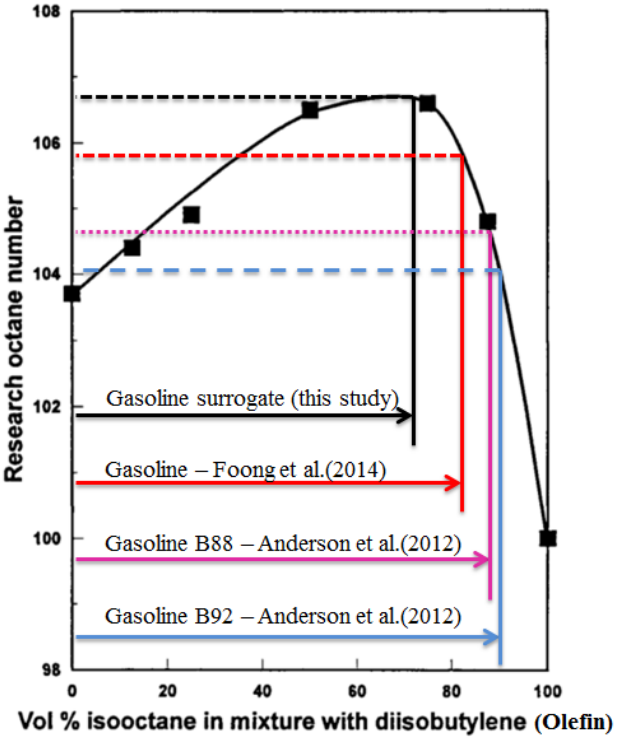
In the gasoline surrogate used in this work, diisobutylene is the olefin substance. However, for the fuels studied by Foong et al.(2014) and Anderson et al. (2012) the substance which represents the olefin chemical family is not known, just the percentage of olefin is given, as shown in table 18.

Scott (1958) has described the general behavior of the olefin chemical family regarding to the interaction with paraffins. The curve in figure 36 shows this interaction. It is known that any olefin substance resembles the behavior of diisobutylene, but each of them with different values for RON. Thus, the RON curve for diisobutylene – isooctane is used to qualitatively describe the influences of olefin into the gasoline and gasoline surrogates studied in this thesis, Foong et al. (2014) and Anderson et al. (2012).

In figure 36, the vertical axle represents the RON value, and the horizontal axle the content of isooctane in volumetric percentage in a blend with diisobutylene (olefin). Remembering that just the gasoline surrogate used in this work has diisobutylene in its content, all the other gasoline and gasoline surrogates have a different olefin in its content.

The table 19 shows in its first line the relation between isooctane and olefin in these fuels; for the gasoline surrogate used in this work, the gasoline studied by Foong et.al (2014) and the gasolines studied by Anderson et a.(2012). It means that, for example, in the gasoline B92 the content of isooctane is 8.32 times greater than the content of olefin, or in oder words, isooctane represents 89.29% of the volume of the blend isooctane- olefin. This percentage is shown in figure 36 as the blue line, is also shown the percentage for the other fuels.

Figure 36 - RON values for the blend : Diisobutylene (Olefin) – Isooctane (iso-paraffins).



Font: Modified from Pilling (1997).

Table 19 - Proportion of isooctane and olefin.

	This study	Gasoline - Foong	Gasoline B88 - Anderson	Gasoline B92 - Anderson
Isooctane – olefin relation	2.31	4.49	7.31	8.32
Vol % isooctane in olefin	69.81	81.78	87.97	89.29
aromatic – paraffin relation	0.48	0.65	0.4	0.4
Vol % aromatic in paraffin	32.51	39.33	28.78	28.79

Font: Author.

As shown in figure 36, for the gasoline surrogate used in this work, a paraffinic concentration of 69.81 % gives the maximum RON value in comparison with the other fuels, for a blend of paraffin and olefin. Thus, as greater in the RON value of the blend paraffin – olefin, greater is the influence of this interaction in the value of RON for the gasolines and gasoline surrogates which contains these chemical families (greater RON value for the mixture diisobutylene – isooctane, result in a greater RON value for the gasoline surrogate). Which means that, the interaction of isooctane and olefin in a proportion of 2.31:1, provides a octane gain in the gasoline surrogate used in this work, which is greater than for the other fuels.

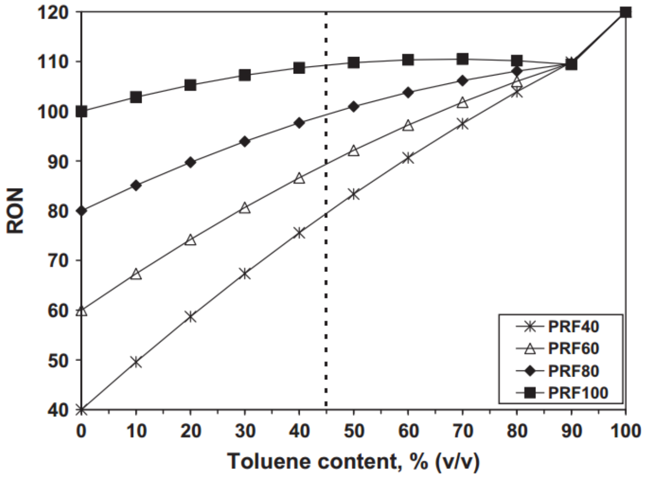
Thus, the octane gain given of the interaction of isooctane and olefin is greater for the gasoline surrogate used in this work, followed by: gasoline Foong et al. (2014), gasoline B88 Anderson et al. (2014) and gasoline B92 Anderson et al. (2014), as can be seen in figure 36. In the range of 0% to 30% (v/v) ethanol, E0 to E30, comparing the gasoline surrogate used in this work and the gasoline B92, is noted in figure 32, that the RON values for B92 are greater, but at the same time the tilt angle is lower, as seen in figure 34.

Table 18 shows the percentage for each substance. In the gasoline surrogate used the percentage of n-heptane is 24.4%, while in B92 is 15.9%, and as is known, as greater is the n-heptane quantity, lower is the RON value. At the same time, this surrogate has 33.3% of isooctane, and B92 has 48.3%. The percentage of toluene in the surrogate is 27.8% and in B92 is 26%. In figure 33-a is shown that, from E0 to E30, the blend of toluene and ethanol has a greater value of RON compared with isooctane and n-heptane, but it is decreasing with the content of ethanol in percentage (due an antagonism blending affect, according to Foog et al. (2014)). The percentage of toluene in B92 and in the gasoline surrogate used are almost the same. Thus, B92 presents a greater RON value in the range from 0% to 30% (v/v) ethanol, basically because of the difference in the isooctane percentage which is greater for B92, and also because of the and n-heptane percentage, which is lower for B92.

Comparing B92 and the gasoline surrogate used, the difference of RON decreases with content of ethanol until 50% (v/v), from 2.80 ON to -0.23 ON (which means that the RON value for the gasoline surrogate is greater than B92 for 50% (v/v) ethanol), this difference of 0.23 ON can be neglected considering a rating tolerance. Thus, for 50% (v/v) ethanol and above, the RON value for B92 and the surrogate used in this work can be assumed as having the same value. The interaction of paraffin - olefin influences the decrement of this difference. As mentioned, for this gasoline surrogate the proportion of paraffin in olefin gives the greatest RON value compared with the other fuels (figure 36). Thus, this proportion of 2.31 times more paraffin than olefin, causes an greater increment in RON value for this gasoline surrogate than for the other fuels having a different proportion. Then, the interaction of olefin – paraffin influences the decrement in the difference between the RON value of this surrogate and gasoline B92, in the range E0 to E30.

According to Scott (1958), aromatics and paraffins provide an octane gain, reaching a maximum when the percentage of aromatics is near to 67%. It can be seen in the figure 37, in which the aromatic substance is toluene and PRF represents the content of paraffin. Also according to this author, this increase is greater than the mixture olefins – paraffins. Table 19 also shows the relation of aromatics and paraffins and the percentage of aromatic in a blend with paraffin.

Figure 37 - RON value for a blend of PRF and Toluene.



Font: Morgan et al. (2010)

Thus, to analyse the RON values for the gasoline B92 and the gasoline surrogate used in this work, it is needed to evaluate the substances they contain and its percentages. B92 has a greater value of isooctane, which for above E30, as shown in figure 33-a, gives a greater RON value than toluene and n-heptane, thus a greater content of isooctane provides an increase in the RON value. However, the gasoline surrogate used in this work has a favorable reaction of olefin – paraffin, which increases the value of RON for this fuel. At the same time, the volumetric percetage of aromatics in paraffins (shown in table 19) is equal to 32.50% for the surrogate and 28.79% for B92, which means that, the octane gain with the interaction of aromatic and paraffins in the surrogate is greater than in B92, because the percentage in the gasoline surrogate used in this work is higher and closer to that value which gives the maximum octane gain for a blend of paraffin and aromatic (which is 67% - Scott (1958)).

12.3.4. RON value for E100

Table 20 shows the RON of pure ethanol from this study, also from Hunwartzen(1982), Anderson et al. (2012) and Foong et al. (2014).

As can be observed, the RON value determined in this study (108.57 ON) is in the interval proposed by Hunwartzen(1982), also is quite close to the lower value of the interval determined by Anderson et al.(2012), the difference between them is just 0.03 ON (108.6ON – 108.57ON). In comparison with the higher value found by Foong et al. (2014), this study gives a higher value for E100, the difference is 0.07 ON.

Table 20 - Reported RON for pure ethanol.

RON	Author
108.6 ± 0.4	Hunwartzen(1982)
108.6 – 108.8	Anderson et al.(2012)
108 – 108.5	Foong et al.(2014)
108.57	This study

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According to the standard ASTM (2012) there is a rating tolerance of ±1.4 ON in the 'Fit-for-use' procedure that applies for any fuel in the range from 105.6 ON to 110.6 ON. Thus, can be ensured that the value found for E100 is within the intervals proposed by Hunwartzen (1982), Anderson et al. (2012) and Foong et al. (2014)

12.4. Engine Knocking (percentage of engine cycles with knock occurrence) and Compression ratio (CR)

In this section are analysed how many engine cycles have the occurrence of knock phenomenon and also the compression ratio related with each sample of the gasoline surrogate used in this work (E0 to E100). Thus, as already mentioned, the parameter KL_{ASP} shows in percentage, how many engine cycles have the occurrence of knock.

Figure 38 shows the percentage of engine cycles with knock occurrence. Six of seven samples are above 95%, the sample E30 is a little bit lower than 85%. This difference does not affect the results, because every sample are above the value of 82%, which was the minimum target value to ensure that the engine was working under knock conditions.

The compression ratio values for each sample are shown in figure 39. Thus, as an example, for the sample E0, the engine was working with a percentage of engine cycles with knock occurrence equal to 98.15% and a compression ratio equal to 6.39.

As can be seen in figure 39, the compression ratio increases with the increment of ethanol content. It means that, to keep the percentage of engine working cycles with knock occurrence higher than 82%, is necessary to increase the compression ratio, when increasing the content of ethanol.

Thus, the engine compression ratio can be increased when using a fuel with a higher content of ethanol, because as higher is the ethanol percentage, higher is the knock resistance.

Figure 38 - Percentage of engine working cycles with knock occurrence (KL_{ASP})

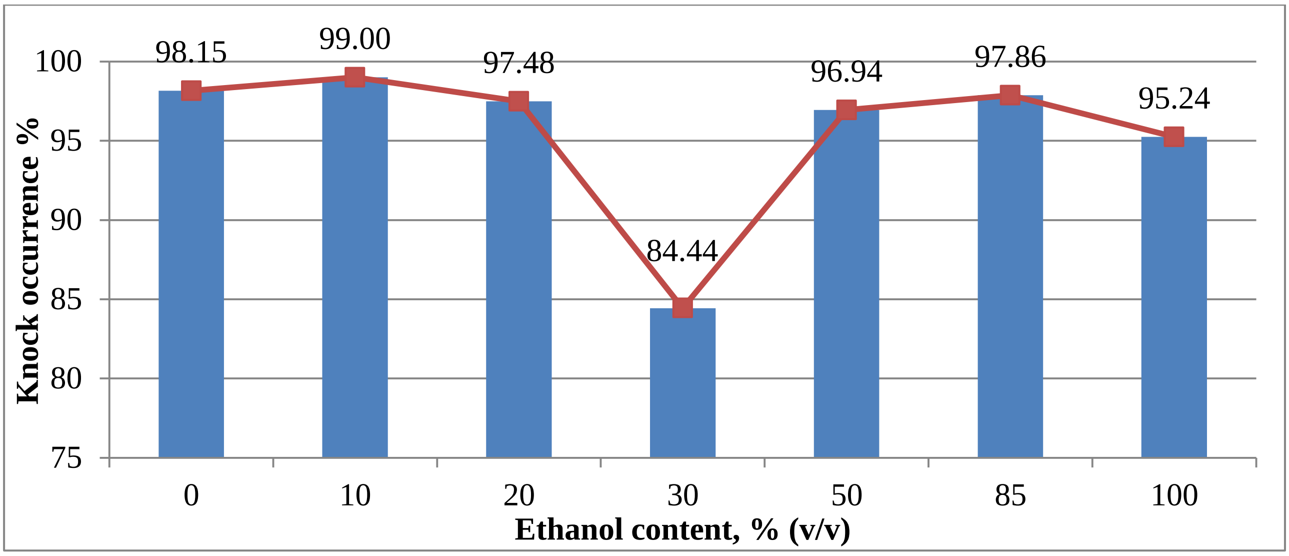

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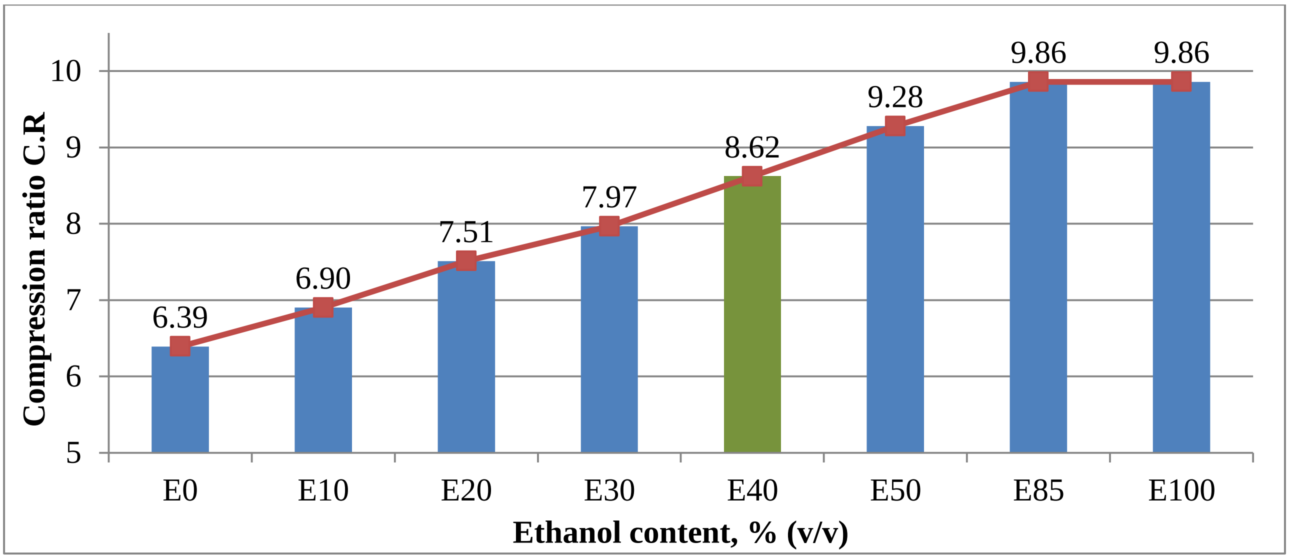
Figure 39 - Compression ratio – CR –for each sample of the gasoline surrogate used in this work under test conditions.



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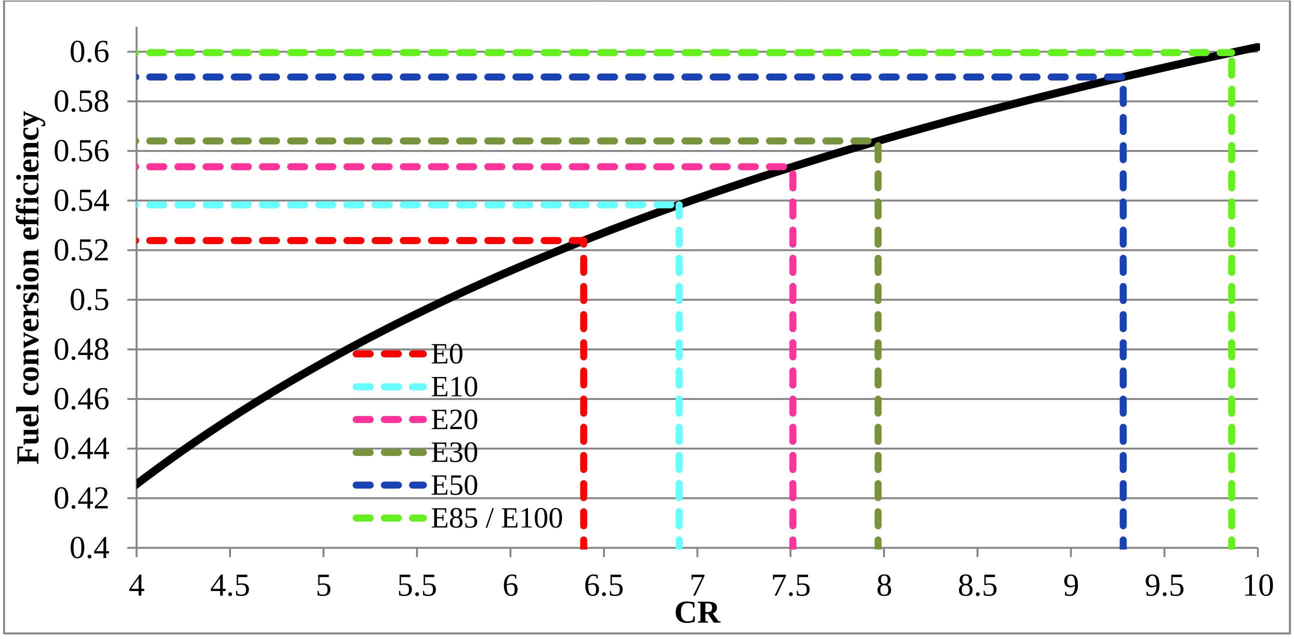
In figure 39, in addition to the samples that have been analysed in this study (E0, E10, E20, E30, E50, E85 and E100), an interpolation between the compression ratio for E30 and E50 was made to determine and plot the CR value for a sample E40 (green box). Thus, in the graph can be seen that from E0 to E50 the compression ratio increases is quasi linear, an increment value near to 0.57 per each 10% of ethanol.

From 0% to 50% (v/v) ethanol, in each 10%(v/v) the compression ratio has an increase of 0.57. From E50 to E85, there is an increase of 35%(v/v) of ethanol, for this entire interval, the compression ratio rises in 0.58. It means that, the inclination of the curve (red line in figure 39) is much lower in the interval from 50% to 85% (v/v) ethanol. The samples E85 and E100 were measured with same compression ratio.

12.5. Engine's efficiency

As mentioned by Heywood (1988), the engine's efficiency can be determined by the fuel conversion efficiency (η_f), which is given by the equation (3). According to Klein (2004), the specific heat ratio (γ) of air can be assumed as 1.4. Thus, in figure 40 are shown the engine's efficiency curve as a function of the compression ratio (black line), and the correspondent efficiency for each of the samples tested in this study. It is important to highlight that this curve shows the tendency of the engine's efficiency, since efficiency for each of the seven samples was calculated with a simplified equation which not takes into consideration the different composition of this samples.

Figure 40 - Engine's efficiency



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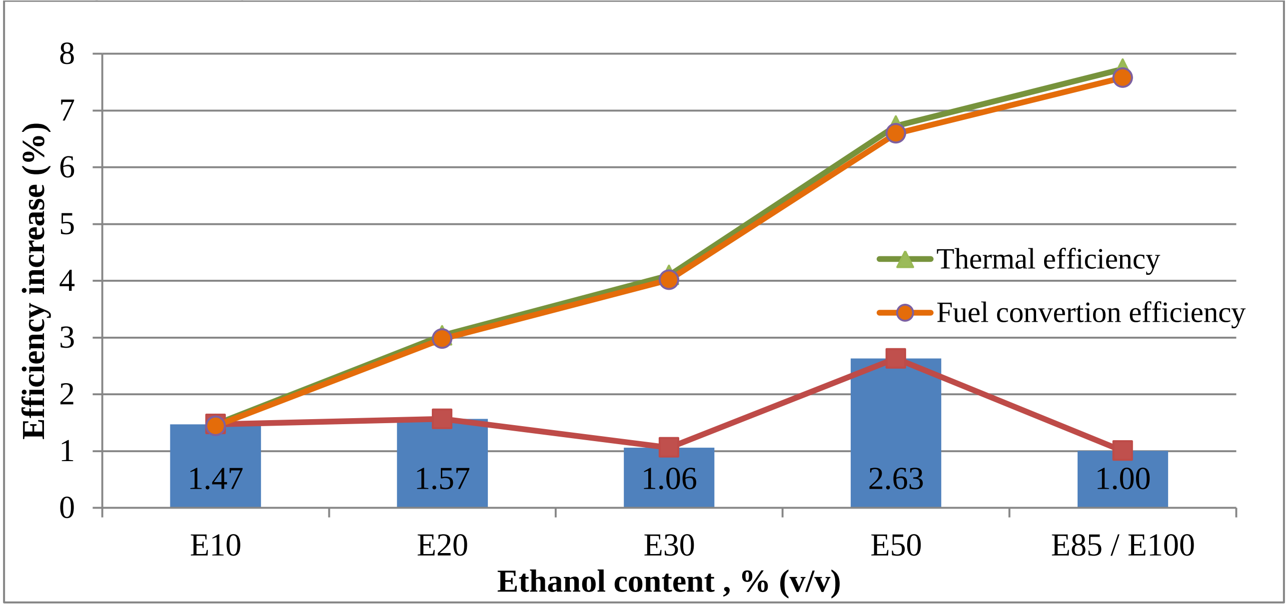
As lower is the content of ethanol, lower is the compression ratio that the engine must be operated, as already analyzed in section 12.1.4, thus lower is the engine's efficiency. E0 have efficiency equal to 52.38%, which is the lowest value for the samples studied, while the sample E85 and E100 have efficiency equal to 59.96%. Remembering that E85 and E100 have same compression ratio, thus same efficiency. Figure 41 shows a comparison chart of efficiency for the studied samples. Blue boxes show the comparison between samples. The E10 sample has increased efficiency at 1.47% compared to E0 sample, while in the sample E20 the efficiency increases by 1.57% in comparison to E10.

The orange curve is called cumulative curve, it shows how the efficiency increases with increasing the content of ethanol, being the sample E0 the reference. Thus, in the interval from E0 to E85/E100, the engine's efficiency increases 7.58%. Likewise and as shown in figure 40 and 41, increasing the volumetric percentage of ethanol in gasoline results in an increase of engine's efficiency. This happens basically because the usage of a gasoline with ethanol content allows to increasing the compression ratio.

Figure 41 - Engine's efficiency – comparison between the sample E0 and the other samples.



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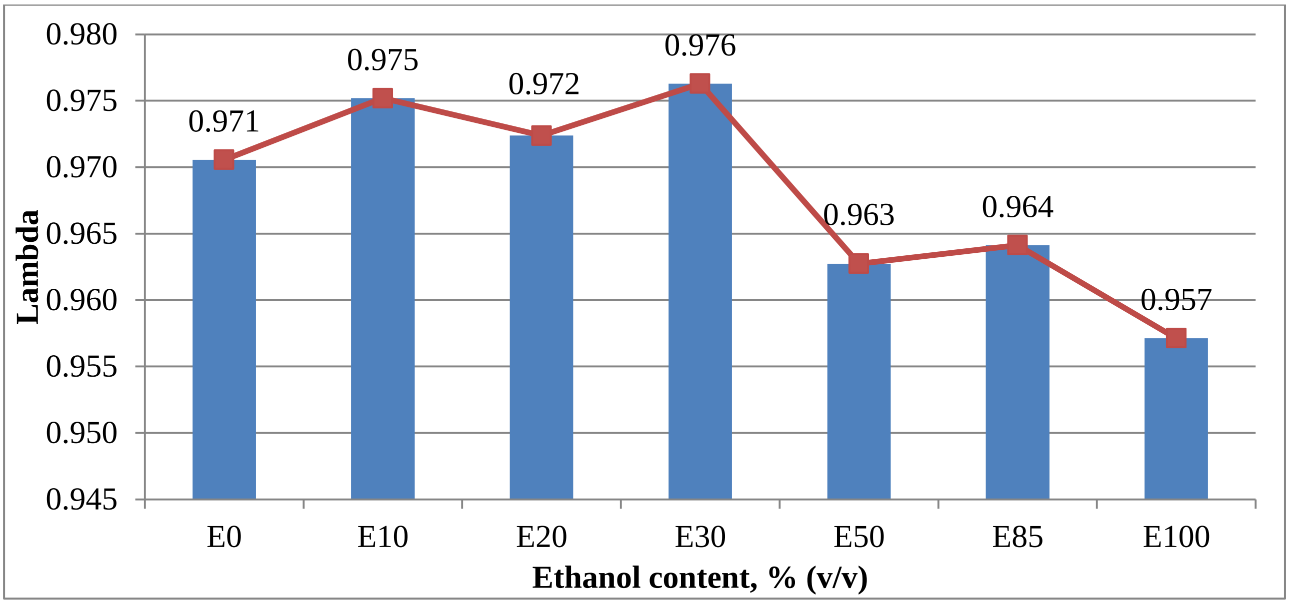
The combustion efficiency (η_c) is related to the air/fuel ratio in the combustion process. Figure 42 are shown the lambda (λ) value for each sample, which has given the maximum knock intensity value. All samples have been tested in rich mixture conditions (λ<1). The values of the equivalence ratio for the samples are next to each other, in an average value equal to 0.97. In terms of fuel/air ratio(φ), it is equal to 1.03. Thus, through figure 3, the combustion efficiency can be approximated to be the same for all samples, equal to 98%. Thus, using equation (4), the thermal efficiency can be calculated, it is shown in figure 41 as a green line, which represents a cumulative percentage, in which E0 is the reference.

In terms of efficient energy use, as higher is the percentage of ethanol in gasoline, greater can be the compression ratio, and then, higher is the fuel conversion efficiency and thermal efficiency of an engine.

Figure 42 - Air/fuel equivalence ratio (λ)



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12.6. Spark – ignition engine operating cycle

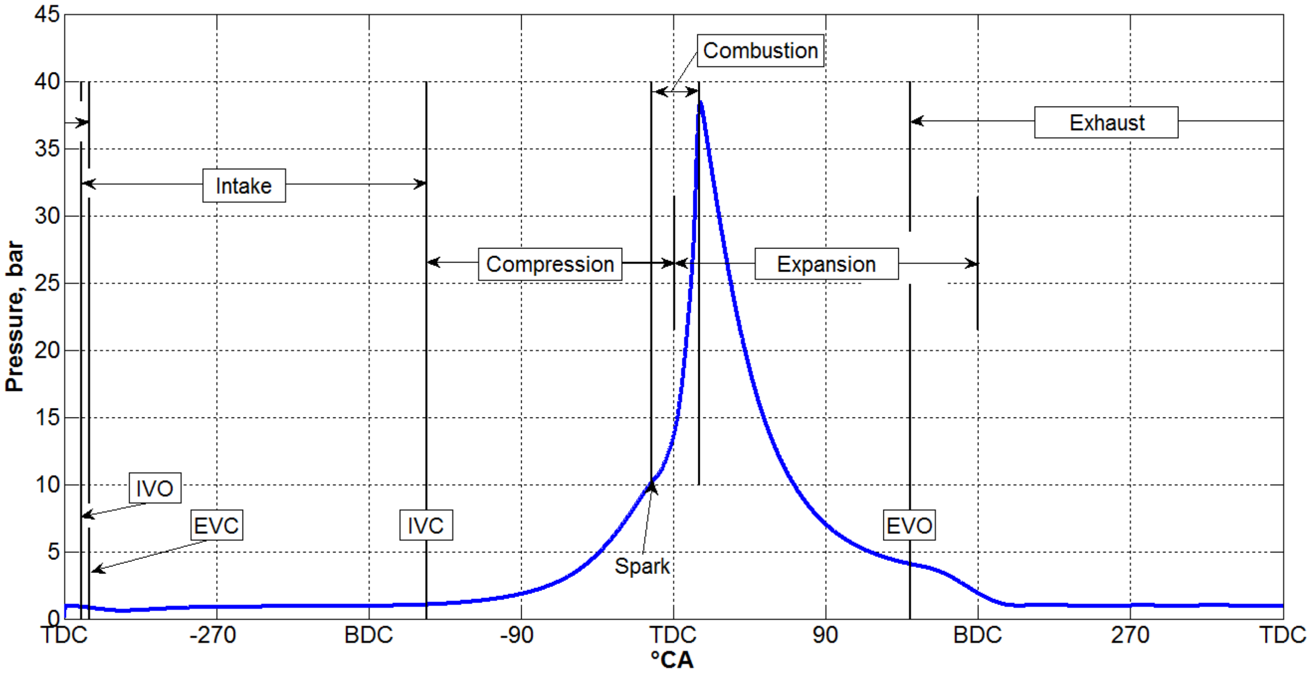
Figure 43 shows the sequence of events which takes place inside the cylinder. The sequence are equal for every sample of the gasoline surrogate used in this work (E0, E10, E20, E30, E50, E85 and E100). As a form to represent these events, is used the pressure curve for E30. The vertical axle is the pressure measured in bar and the horizontal axle is the crank angle (°CA). The zero value for the crank angle is the TDC position which is in the interval of the combustion process. After this point the value for crank angle if positive and before it, is negative.

For the CFR engine used in this study, the intake valve opens (IVO) in -350°CA, as shown in the figure. 5°CA after this event occur, the exhaust valve closes (EVC). The intake valve remains open for 204 crank angles degree, closing at -146°CA (IVC). Thus, the intake stroke is defined between the events IVO and IVC.

In -13°CA an electric discharge across the spark plug starts the combustion process, the duration of this burning process varies sample by sample. The combustion process ends when the entire amount of the fuel-air mixture have been burned.

The compression stroke begins when the intake valve closes (IVC) and ends at the top dead center TDC. While the expansion stroke start at TDC and ends at the bottom dead center (BDC) The exhaust valve opens (EVO) at 140°CA after top dead center (ATDC), in this point the exhaut stroke starts, ending just when this valve closes (EVC), at -345°CA.

Figure 43 - Sequence of events in the CFR engine operating cycle.



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12.7. Heat release in the combustion process

The duration of the combustion process is directly related to the heat release of the fuel-air mixture. Figure 44 shows the heat release curve for the samples E0 to E100. The vertical axle shows the percentage of accumulated heat release, which is in range from 5% to 95%. As described in section 3.4, the stage from the spark discharge and the small but significant fuel chemical energy that has been released, in this case equal to 5% of the heat release, is defined as: flame-development angle$(\Delta\theta_d)$. As can be seen in figure 45, as higher is the percentage of ethanol in the surrogate, and thus greater the compression ratio, shorter is the interval for the flame development. As mentioned in the previous section, the spark discharge starts for all samples at -13°CA. Thus, the flame development starts at -13°CA.

The rapid burning angle $(\Delta\theta_b)$ has almost the same value for all samples, in this study the second stage corresponds to the interval between 5% and 95% of the energy release fraction. The overall burning angle$(\Delta\theta_0)$ is the sum of $(\Delta\theta_d)$ and $(\Delta\theta_b)$. Thus, it ends when 95% of the heat release fraction has been reached. Figure 45 shows the flame-development angle, the rapid burning angle and also the overall burning angle$(\Delta\theta_0)$. The vertical axle is the crank angle interval for these stages.

Figure 44 - Heat release in the combustion process.

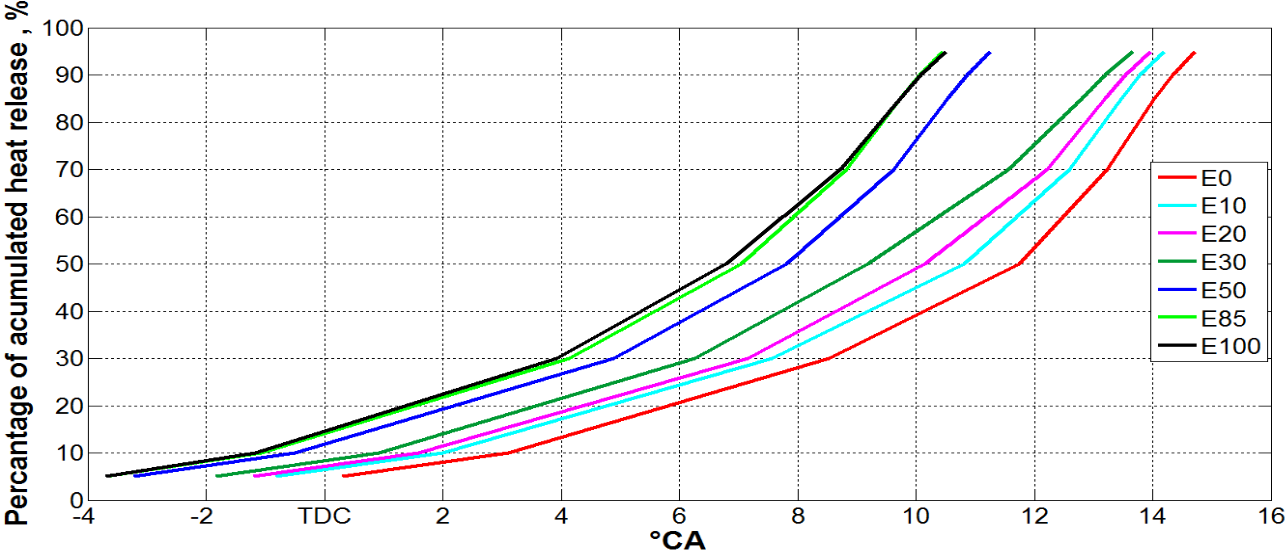

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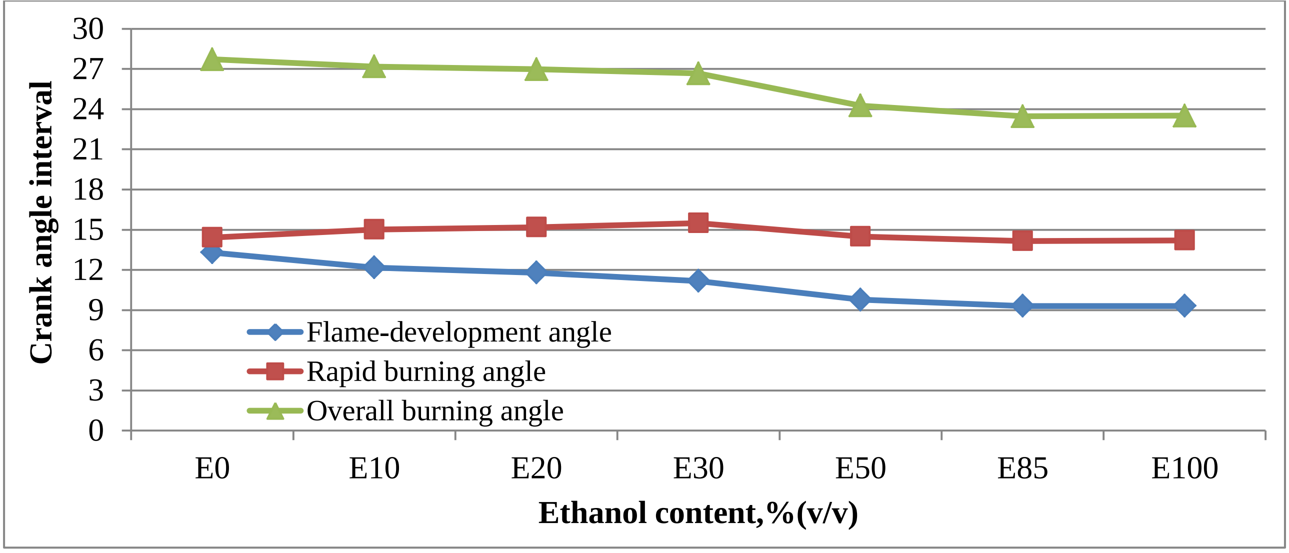
Figure 45 - Combustion process characterization



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As can be seen in figure 44 and 45, the interval for the flame development process of the sample E0 is the longest one, followed by the samples: E10, E20, E30, E50, E85 and E100 (these two last samples have the same value). According to Heywood (1988), this first stage is influenced primarily by the mixture state, composition and motion in the vicinity of the spark plug.

The increase of ethanol content allows increasing the compression ratio, in this situation, the duration of the combustion process decreases. The unique situation in which the flame development ends after the TDC occurs for the sample E0.

The interval from 5% to 95% of the heat release curve, known as rapid burning angle, has almost the same value for every sample. The sum of these two stages is the overall burning angle (green line in figure 45). It represents the duration of the burning process (combustion period), which on average lasts 25.68 crank angle degrees – starting at -13°CA and ending at 12.68°CA.

As can be seen in the figure 45, for the samples E0 to E50, as higher is the content of ethanol, the RON value and the compression ratio, shorter is the duration of the overall burning angle which means that, faster is the combustion process. However, in the interval from E85 to E100 this is not true, the overall burning angle for E85 is equal to 23.46 crank angle degrees, and for E100 equal to 23.51 crank angle degrees. The octane number of E100 is 0.46 ON higher than E85, and it has 15% more ethanol in its content than E85.

Increasing the compression ratio results in a decrement of the overall burning process. However, increasing the percentage of ethanol in the fuel increases the overall burning process.

In short, the flame development, as well as the rapid burning angle and overall burning angle depend on three factors: the octane number of the fuel, the content of ethanol in the fuel and the compression ratio of the engine.

12.8. In-cylinder pressure for the samples of the gasoline surrogates tested

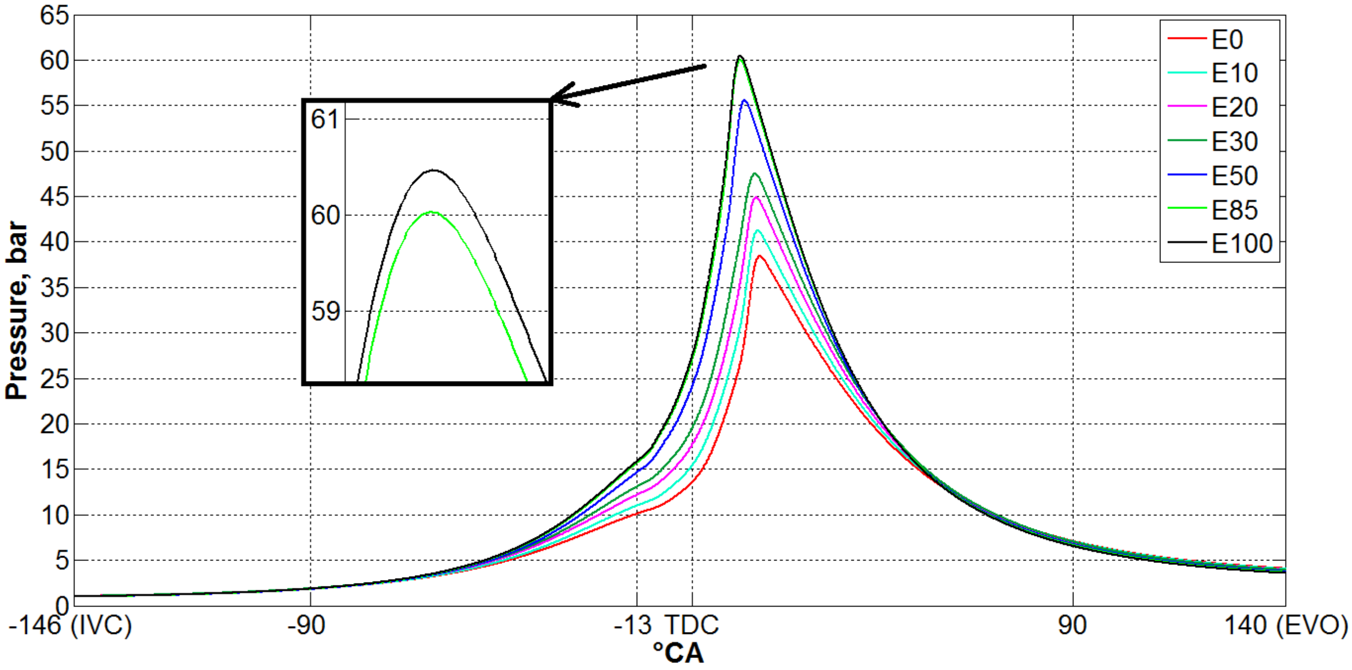
The in - cylinder pressure curves for the samples of the gasoline surrogate used in this work are plotted in figure 46. The pressure is measured in bar. The horizontal axle, which is the crank angle degree, is represented in the interval which begins at -146°CA (IVC) and ends at 140°CA (EVO). Also are identified the top dead center position and the crank angle in which the combustion starts (spark, at -13°CA).

During the measurements, an average of 350 engine operating cycles was saved for each of the samples. The data have been processed; the next figure shows the average pressure curve for these samples.

The combustion process starts at -13°CA and ends when all the mass of the mixture fuel/air have been burned. As already discussed, it is the overall burning angle, the values of this parameter can be seen in figure 45. Through figure 46 is possible to see the consequences of a longer period of combustion process.

The overall burning angle$(\Delta\theta_0)$ for the sample E0 is equal to 27.72 crank angle degrees, the longest one. The consequence is that this curve is the most shifted to the right in relation to the TDC position, as can be seen in the figure 46.

Figure 46 - Cylinder pressure for the samples of gasoline surrogate used in this work.



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In figure 46 there is a zoom region, which shows the pressure difference between E85 and E100, they are really close to each other, however at any crank angle E100 has a higher pressure than E85. The sample E100 has a higher peak pressure than E85, as these both samples were measured with same compression ratio, it means that the RON value and the fuel composition has a direct influence in the in cylinder pressure pattern.

Figure 47 shows the maximum pressure value for these samples. As can be seen, as higher is the compression ratio, the octane number (RON) and the content of ethanol, higher is the maximum pressure reached in the cylinder. Figure 48 shows, for the samples tested, in which crank angle the maximum cylinder pressure occurs. For all the samples tested, the pressure reaches a maximum after TDC.

Figure 47 - Maximum cylinder pressure in the CFR engine.

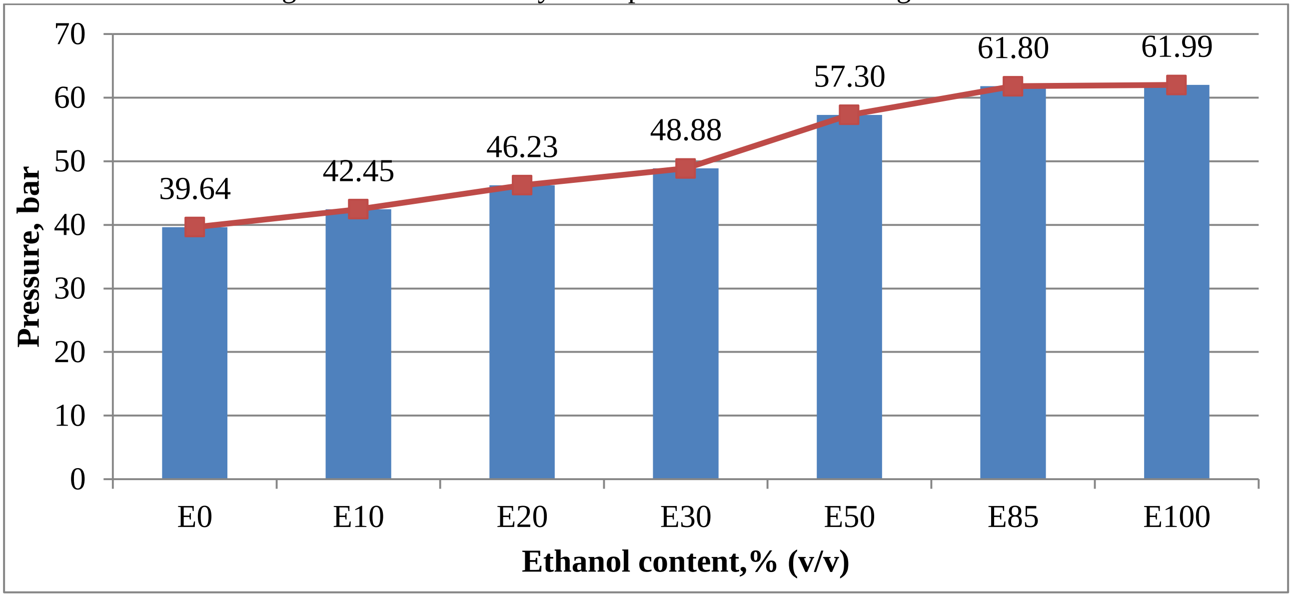

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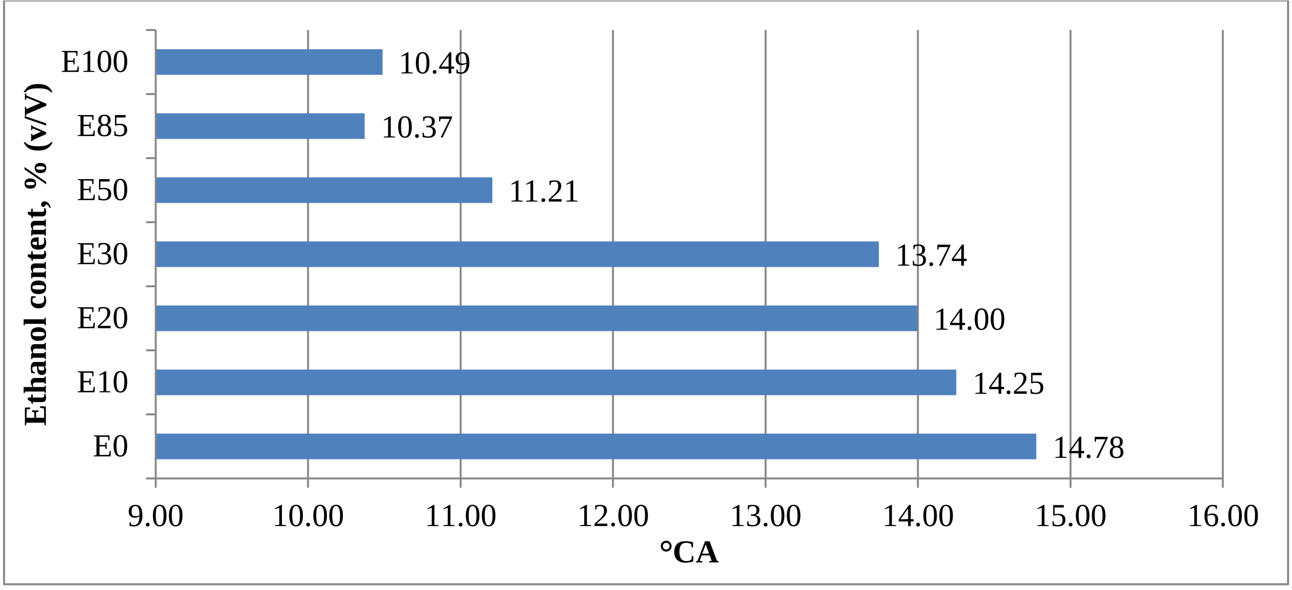
Figure 48 - Crank angle degree in which the maximum cylinder pressure occurs.



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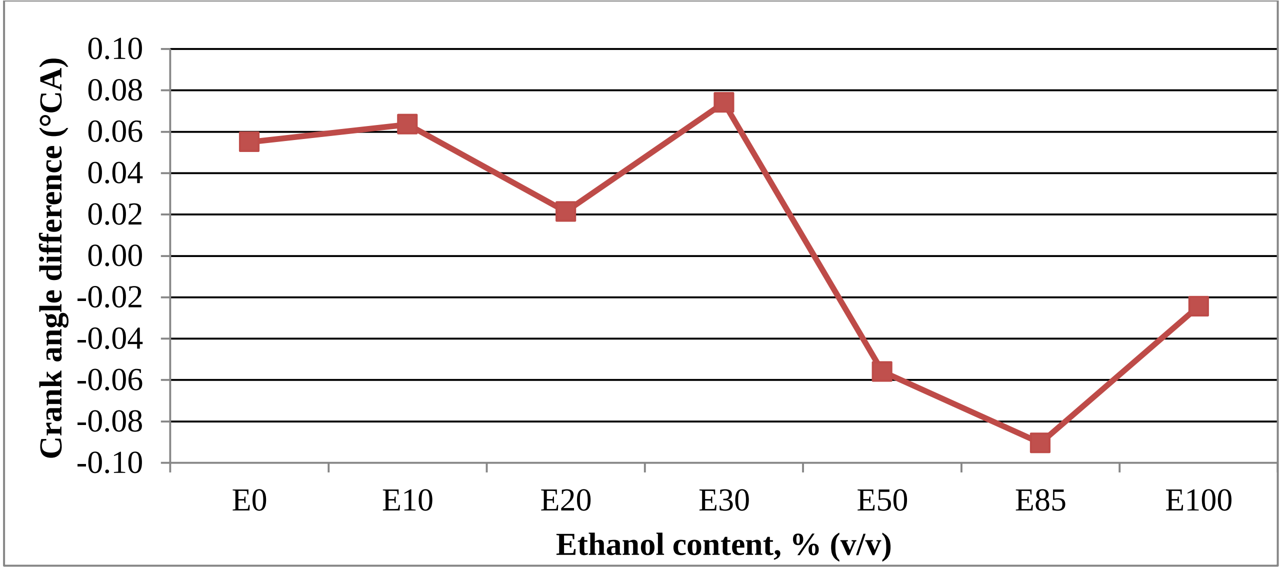
As mentioned, as longer is the overall burning angle$(\Delta\theta_0)$, more shifted to the right is the pressure curve, as shown in figure 46. Thus, the crank angle in which the peak pressure occurs is also shifted to the right in relation to the TDC position, as shown in figure 48.

In the previous figure, is notable that the peak pressure for E100 is more dislocated to the right in relation to TDC position than E85. It happens because, as mentioned in section 12.7, the overall burning angle for E100 is longer, and thus the peak pressure is also occurs later after TDC.

The end of overall burning process, which is the crank angle in which 95% of the heat release fraction is reached, and the crank angle in which the maximum pressure occurs can be compared using the figure 49. Basically, through this figure is possible to know if the maximum pressure occurs after or before the end of the combustion process (burning process).

Figure 49 - Crank angle difference between the end of the overall burning process and the angle in which the maximum pressure occurs.



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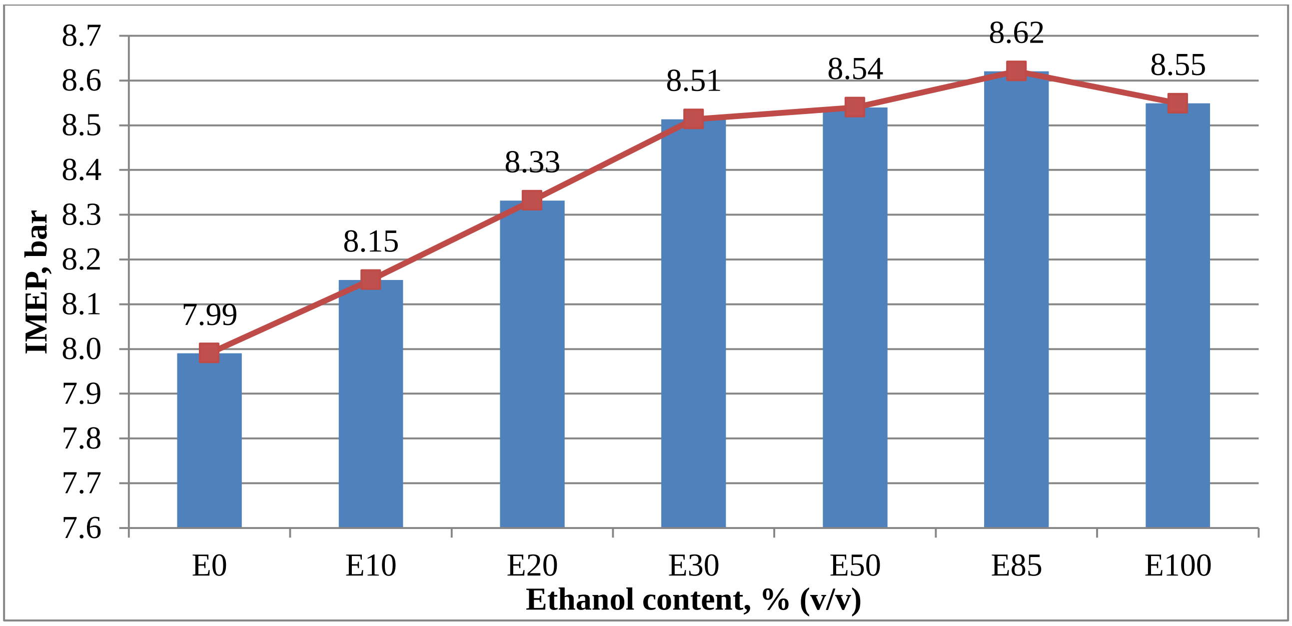
For the sample E0, for example, as the combustion process starts at -13°CA and the overall burning angle ($\Delta\theta_0$) is equal to 27.72 crank angle degree, the combustion ends at 14.72°CA (after top dead center). For the same sample, the peak pressure occurs at 14.77°CA. Thus, in the samples with positive values in figure 51, the pressure reaches a maximum value after the end of the combustion process. It is noted in the samples: E0, E10, E20 and E30. For E50, E85 and E100 the combustion process ends after the peak pressure. But basically, as can be seen in the vertical axle, the crank angle degree difference is so small that can be assumed that the end of the combustion process and the peak pressure occurs at the same crank angle degree.

12.8.1. Indicated meand effective pressure - IMEP

The indicated mean effective pressure (IMEP) is a measure of the performance of the engine, it has units of bar. As described in section 2.3, IMEP is defined as the work of the cycle divided by the engine displacement volume. In short, a higher indicated mean effective pressure means more work for the same displacement volume. Figure 50 shows the value of IMEP for the samples of gasoline surrogate tested in this study.

Figure 50 – Indicated mean effective pressure for the samples of the gasoline surrogate used in this work.



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Each sample was measured using different value of compression ratio. As shown in figure 39, just E85 and E100 were tested with same CR. However, as discussed in section 6.2, the engine displacement volume (V_d) have the same value for any of the tested samples. The power produced per each cylinder (P) of an engine (CFR has 1 cylinder) is related with IMEP by the following equation:

$$P = \frac{MEP * V_d * N}{n_r} \tag{13}$$

In which, besides V_d, the values for n_r and N are equal for any of the tested samples. The only variable parameter in equation (13) is the IMEP.

Thus, as higher is the indicated mean effective pressure, higher is the power produced by the engine. In figure 50 can be observed that, in the range 0% to 50% ethanol (v/v), increasing the content of ethanol, the RON value and the compression ratio, higher is the value of IMEP, and thus, higher is the output power.

The sample E50 and E100 have almost the same value of indicated mean effective pressure,equal to 8.54 bar. Thus, an engine operating with a fuel with an octane number equal to 105.73 (E50) and a compression ratio equal to 9.28, produces same output power if operating with a fuel which has an ON equal to 108.57 and a compression ratio equal to 9.86.

The sample E85 and E100 were tested with same compression ratio. Even with a higher value of RON, E100 resulted in a lower value of IMEP. This means that the composition of the fuel has influence in the output power.

According to Heywood (1988), if the start of the combustion process is progressively advanced before TDC, the compression stroke work transfer, which is from the pistion to the cylinder gas, increases. If the end of the compression process in progressively delayed by retarding the spark timing, the peak cylinder pressure occurs later in expansion stroke. Thus, the work produced by the engine is directly related to the spark timing, therefore the indicated mean effective pressure also varies with spark timing.

Comparing E50 and E100, the end of the combustion process for E100 occurs 0.75 °CA before the end of combustion process for E50 (as can be seen in figure 45 – green line). Thus, as the spark timing is equal to -13°CA for both samples, the duration of the combustion process is a factor that has a direct relation with the output power. As the combustion process ends early in the expansion stroke for E100, the work transferred from the piston to the cylinder in the compression stroke increases and the work transferred from the cylinder gases to the piston reduces, compared with E50. There is a decrease in the output power, and thus, decreases the indicated mean effective pressure. However, as mentioned, the IMEP for these two samples are equal, it happens because E100 has a higher content of ethanol, a higher octane number and also was measured with higher compression ratio, which compensates the loss of power when the combustion process is faster.

Thus, as higher is the value of RON, percentage of ethanol content and compression ratio, the greater the indicated mean effective pressure. However IMEP is not just dependent on this three factors, the spark timing also has an influence in this parameter, because the start of the combustion process and also its duration, affect the quantity of work transfered from the piston to the cylinder gases (during compression stroke) and also the work tranfered from the gases to the piston (expansion stroke).

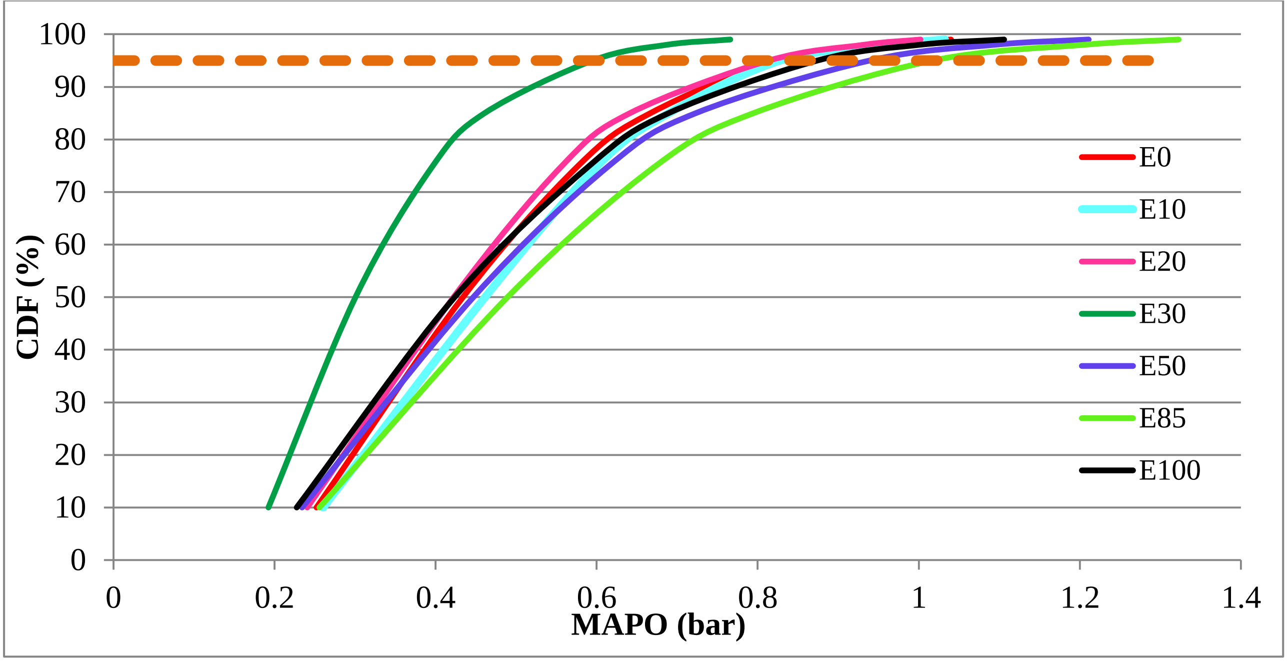
In short, the indicated mean effective pressure is dependent on four factors: spark timing, octane number (RON), compression ratio (CR) and percentage of ethanol.

12.9. Knock intensity - MAPO

As described in section 4.1.1, the maximum amplitude of pressure oscillation (MAPO), is the peak value of the filtered pressure oscillation signal. It is a value used to describe the magnitude of the knock intensity. Next figure shows the cumulative density frequency (CDF) for the samples E0, E10, E20, E30, E50, E85 and E100.

The intersection between the orange line, which represents 95% of cumulative frequency, and the cumulative frequency curves for each sample, gives the value of MAPO, which is plotted in figure 52 – red boxes.

Figure 51 - Cumulative density frequency (CDF)



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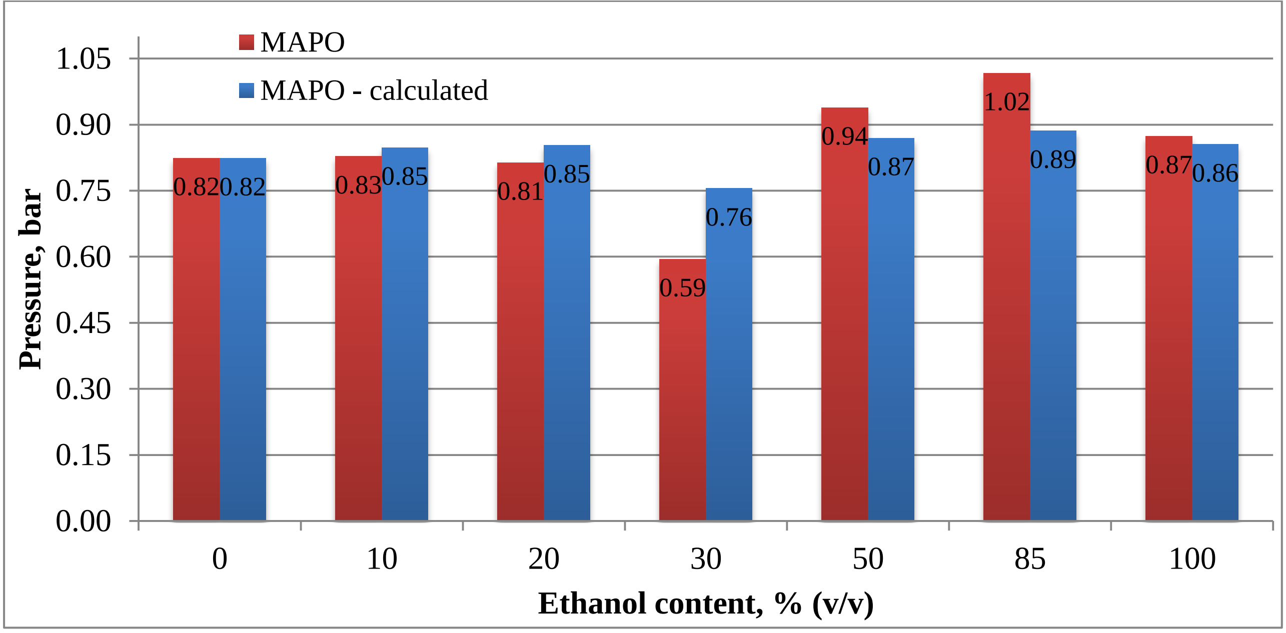
The sample E30 has the minimum value for MAPO, near to 0.6 bar. The MAPO value is directly correlated to the percentage of engine cycles with knock occurrence and also with the in-cylinder pressure curve. To prove this correlation, for each sample, the value of the percentage of engine working cycles with knock occurrence (figure 38) was multiplied by the indicated mean effective pressure (IMEP) and divided by a factor of 9.52.

Thus, for the sample E50 for example, the percentage of engine working cycles with knock, which is equal to 96.93%, was multipled by its indicated mean effective pressure, 8.54 bar. And then divided by a factor of 9.52, which gave closer values to the real ones. The following equation describes this calculation.

$$Mapo^{*} = \mathrm{KL_{ASP}}(i) * \frac{MEP(i)}{9.52} \qquad (14)$$

In which, $Mapo^{*}$ is a estimation of the real value of MAPO based in the the percentage of engine working cycles with knock occurrence $\mathrm{KL_{ASP}}$ and in the indicated mean effective pressure (MEP). The index (i) represents the sample which is been used to make the calculation.

Figure 52 - maximum amplitude of pressure oscillation (MAPO)



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The result of this calculation, for each of the samples tested, is shown in figure 52 – blue boxes. As can be seen, the equation (14) gives a good aproximation of the real values of MAPO value.

Thus, through the developed equation, can be proved that the values of the maximum amplitude of pressure oscillation (MAPO) is a direct correlation between the percentage of engine cycles with knock occurrence and the in-cylinder pressure.

13. CONCLUSIONS

This work has proposed the study of the influence of the quantity of ethanol in gasoline on the engine’s performance by evaluating its research octane number (RON). Through the methodology presented was possible to measure it using a CFR engine.

Increasing the content of ethanol in gasoline, there is also an increase in the RON value and the RON values show a non-linear relationship with the volumetric concentration of ethanol. The absolute difference of this parameter is equal to 19.22 RON from E0 to E100, i.e., the higher percentage of ethanol, the engine is more resistant to knock.

The gasoline surrogate used in this work, which was proposed by Cancino et al. (2011), showed a behavior very similar to those gasolines studied by Anderson et al. (2012). and by Foong et al. (2012). This observation allow to validate this surrogate. It means that through this study was possible to observe that this surrogate can emulate the real gasoline with good accuracy. It means that the blend of isooctane, n-heptane, diisobutyle and toluene simulates with good accuracy the real gasoline. This surrogate with 0% (v/v) ethanol was measured with a RON value equal to 89.35, while the gasolines studied by Anderson et al. (2012) have their value equal to 88.15 and the other one equal to 92.15. When plotted the curve for RON versus the ethanol content, it was observed that the curve for the surrogate used presented the RON values between those two gasolines for the entire percentage values of ethanol in gasoline.

With 100% (v/v) ethanol the RON value was measured equal to 108.57, which was in the range proposed by Anderson et al. (2012), Hunwartzen (1982) and Foong et al. (2014). These authors comply with the ASTM and DIN standards, thus is known that the RON value measured also complies with both standards.

The study of the interaction and influence of each substances on the octane number has shown that diisobutylene provided an increase in RON value for the gasoline surrogate used, due to the fact that the relation of issoctane and olefin was in a proportion equal to 2.31, which according to Pilling (1997) gives the highest octane number for this binary blend.

With the increasing of the content of ethanol is possible to increase the compression ratio keeping the same knock intensity in the engine for any blend of ethanol and gasoline. From E0 to E50, this increase is quasi-linear, from a compression ratio equal 6.39 to 9.28, which represents a growth of 45%. E85 and E100 were measured with the compression ratio, equal to 9.86.

Thus, increasing the compression ratio allows the increasing of engine’s efficiency. The engine opearing with E0 has shown a fuel combustion efficiency equal to 52.38%. The efficiency curve was plotted, and it was observed that this increase is quasi-linear with the increment of ethanol content. With E100 there was an increse to 60%, which represents a absolute gain in efficiency equal to 7.58% when compared with E0.

The higher the compression ratio and the content of ethanol, shorter is the interval for the flame development and faster is the combustion process. However, the sample E85 showed a faster combustion, even with a lower percentage of ethanol compared to E100. Thus, the flame development, as well as the rapid burning angle and overall burning angle depend on the octane number of the fuel, the content of ethanol in the fuel and the compression ratio of the engine.

The increase of the percentage of ethanol in gasoline has a direct influence in the pressure curves. The higher it is, as mentioned, faster is the combustion process, thus, the peak pressure is closer to TDC. Also, this increment leads to an increase in the maximum peak pressure. For the sample E0 this value was equal to 39.64 bar, while for E100 it was 61.99 bar, a growth equal to 56.38%. It means that the increase of ethanol percentage in the mixture, directly impact the overall flame speed of the mixture.

The value of the indicated mean effective pressure rises from 7.99 bar (E0) to 8.62 bar (E85) and afterwards there is a decrease to 8.55 bar for the sample E100. The greater the content of ethanol, greater is the output power, since it is directly related to the indicated mean effective pressure. This parameter depends on four factors: spark timing, octane number (RON), compression ratio (CR) and percentage of ethanol.

Thus, the increase of the percentage of ethanol in gasoline leads to an increase in the compression ratio of a designed engine, which enables the increase on the engine's efficiency and also an increase in the engine output power.

13.1. Recommendations

To understand the influence of each substance present in this surrogate on the octane number, in this thesis was used basically the study done by Pilling (1997), Foong et al. (2014) and Bertoncini, Courtiade-Tholance and Thiébaut (2013). In which Pilling (1997) has described the RON value for a isooctane and diisobutylene blend, neither of those authors has pictured it for a blend of diisobutylene mixed with ethanol. Thus, for a better understandment it is recommended future works about the influence of diisobutylene in the gasoline-ethanol blends, making the evaluation of the RON values for diisobutylene mixed with ethanol using a CFR engine.

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APPENDIX

APPENDIX A - Measurement data displayed in the computer screen.

Initials	Values	Unit	Description
Pos_ZK	-	mm	Cylinder height
Epsilon (CR)	-	-	Compression ratio
T_KWaus	-	°C	Cooling water outlet temperature
T_Kst	-	°C	Fuel temperature
p_Kst_P	-	bar	Pressure in the fuel pump
T_SGR	-	°C	Temperature - intake manifold
p_SGR	-	bar	Pressure – intake manifold
T_ZK	-	°C	Temperature in the cylinder head
T_KWein	-	°C	Cooling water inlet temperature
T_Oel	-	°C	Oil temperature
p_Oel	-	bar	Oil pressure
P_{amb}	-	bar	Ambient pressure
rl	-	%	Relative humidity
T_Amb	-	°C	Ambient temperature
CA	-	°CA	Spark timing
Lambda	-	-	Air-fuel equivalence ratio
Pmi (IMEP)	-	bar	Indicated mean effective pressure
P_{max}	-	bar	Maximum pressure
Quantil 95	-	bar	Quantil
KL_{ASP}	-	%	knocking working cycles

Font: Author

APPENDIX B – Measurement protocol

Measurement protocol: knock measurements on the CFR engine: RON - method								
Place, date			Meter reading			T- cooling water		
Pamb			Spread			T - oil		
Rel. Humidity			Time constant					
Measurement	Fuel	Cylinder height	Compression ratio	DCR	Lambda	Knockmeter	T - intake manifold	T - exhaust gas

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ANNEX

ANNEX A - Engine parameters

Stroke (mm)	114,3
Bore (mm)	83,06
Connecting road length (mm)	254,0
Compression ratio (-)	4:1 – 18:1
Engine Speed (RPM)	600 / 900
IVO (°ca BTDC)	350 ± 2.5
IVC (°ca BTDC)	146
EVO (°ca ATDC)	140
EVC (°ca BTDC)	345± 2.5

Font: modified from ASTM (2004).

ANNEX B - Global ethanol market

Country	Ethanol – gasoline blend	Legal use
Canada	E5	Mandatory
China	E10	Nine provinces
India	E5	Mandatory
Mexico	E6	Mandatory
Thailand	E10/E20	Mandatory
Denmark	E5	Optional
Ireland	E4	Mandatory

Font: Amarasekara (2014)

ANNEX C - Properties of the components of gasoline surrogates

Name	Ethanol	Pentane, 2,2,4-trimethyl-	Heptane	Toluene	2-Pentene, 2,4,4-trimethyl-
Other names	Ethyl alcohol; Alcohol; Alcohol anhydrous	iso-octane	n-Heptane; Dipropylmethane	Toluol; Methane, phenyl-	di-iso-butylene, DIB
Formula	C_2H_5OH	C_8H_{18}	C_7H_{16}	C_7H_8	C_8H_{16}
Molecular weight	46.06	114.228	100.2	92.13	112.21
Enthalpy of vaporization [kJ/mol]	38.56 (@ 351.5 K)	30.79 (@ 372.4 K)	31.77 (@ 371.6 K)	33.18 (@ 383.8 K)	35.2 (@ 374.6 K)
Enthalpy of fusion [kJ/mol]	3.14 (@ 111.4 K)	9.2115 (@ 165.79 K)	13.99 (@ 182.57 K)	6.636 (@ 178.15 K)	6.8 (@ 166 K)
Constant pressure heat capacity of liquid [J/mol K]	112.4 (@ 298.15 K)	242.49 (@ 298.15 K)	224.64 (@ 298.15 K)	157.09 (@ 298.15 K)	233.5 (@ 296 K)

Font: Cancino (2009).

ANNEX D - RON and MON - operating conditions

	RON	**MON**
Engine speed (RPM)	600 +/- 1%	900 +/- 1%
Timing	13° BTDC	Variable based on cylinder head
Oil pressure (PSI)	25-30	25-30
Oil temperature (°C)	57 +/- 8	57 +/- 8
Coolant temperature (°F)	100 +/- 1.5	100 +/- 1.5
Intake air temperature (°C)	52 +/- 1	52 +/- 1
Intake humidity (Kg water / Kg of dry air)	0.00356 – 0.00712	0.00356 – 0.00712
Air/Fuel ratio	Adjusted - maximum knock	Adjusted - maximum knock

Font: modified from ASTM (2004).

ANNEX E - Octane number of the blends 80 octane PRF and Isooctane

Blends of 80 PRF and n-Isooctane

Octane Number	Percent 80 PRF	Percent Isooctane
87	65	35
88	60	40
89	55	45
90	50	50
91	45	55
92	40	60
93	35	65
94	30	70
95	25	75
96	20	80
97	15	85
98	10	90
99	5	95
100	0	100

Font: ASTM (2012)

ANNEX F - Octane number for toluene blends

Octane No.	Rating Tolerance	Composition, vol %		
		Toluene	Isooctane	Heptane
89.3	±0.3	70	0	30
91.5	±0.3	72	0	28
93.4	±0.3	74	0	26
94.8	±0.3	74	2	24
96.0	±0.2	74	4	22
96.9	±0.3	74	5	21
97.2	±0.2	74	6	20
98.3	±0.3	74	8	18
99.8	±0.3	74	10	16
101.0	±0.3	74	12	14
102.5	±0.4	74	14	12
103.3	±0.9	74	15	11
104.2	±0.5	74	16	10
105.9	±1.2	74	18	8
107.6	±1.4	74	20	6
109.2	±0.8	74	22	4
111.8	±0.9	74	24	2
113.0	±1.7	74	26	0

Font: Modified from ASTM (2012).