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Development of a Two-zone Combustion Model for the
Prediction of Particulate Emissions and Engine Knock

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P151178

23/03/2021

Research Methods
ACEA 7004

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1. Introduction

Engine control has been at the forefront of the automotive industry for decades, maintaining the balance of meeting ever-increasingly stringent emissions regulations, without compromising the overall performance and characteristics demanded by the target audience. Therefore, the combustion process within the engine requires appropriate control to ensure it operates within its optimum parameters as much as possible, reducing the harmful emissions and maximise combustion efficiency.

Fundamental equations enable accurate predictions of physically unmeasurable variables based upon thermodynamic, geometric and molecular relationships. This enables a digital simulation of the combustion process to be created using pressure data acquired from a physical engine along with its geometric parameters, e.g. bore, stroke, compression ratio, con rod length. Since it is possible to determine the flame front temperatures within the combustion chamber based upon the change in enthalpy of the chemical products, the disassociation of each molecular compound can be scrutinised.

The hotter the fuel combusts, the quicker the flame propagates, but it is significantly easier for the formation of harmful Nitrous Oxide (NO_x) particulates, whereas, a flame front that is less than adequate to ignite the mixture successfully, will result in slow or incomplete combustion, leading to soot formations (Muncrief, 2016). This investigation would therefore endeavour to create a combustion model that can predict the particulate emissions back calculated from a Ford Fox 1.0 Litre three-cylinder GTDI production engine to validate the legitimacy of the model with the intent of identifying areas of improvement compared against previous studies within two-zone combustion modelling.

Expanding upon this simulation model would include the prediction of 'knock' or 'detonation', an unwanted phenomenon materialising when the air/fuel (charge) mixture within the combustion chamber has ignited before the flame front has propagated to those particular molecules (Lei Zhou, 2020). Engine designers consider knock as a main contributor to an engines performance, adjusting the ignition timing to the verge of knock occurring based upon a set test fuel's octane rating (Heywood, 1988). This method ensures that their engines are running as close to the maximum achievable combustion efficiency as possible. Afterall, if the charge mixture has the greatest amount of energy stored within its molecular structure before spontaneous combustion occurs, the less external energy is required to initiate the reaction at the appropriate time (M. W. Zemansky, 1997).

Unfortunately, it's not as simple as engineers wish. Along with numerous other chemical, mechanical or thermodynamic contributing factors, the manufacturing process undertaken within the construction of Internal Combustion Engines (ICE) guarantees that no engine operates exactly the same. The tooling used to bore out the cylinders wears throughout use within manufacturers tolerances before being replaced so these measurements can differ, causing minute variations, even within the material itself. This has a dramatic impact upon the characteristics of the combustion process, either by an external engine-to-engine or an internal cylinder-to-cylinder basis, justifying the immense necessity to account for and regulate every fluctuation that could significantly enhance or impede the overall efficiency of the engine.

1.1. Aims & Objectives

Considering the high volatility of temperatures within the combustion chamber which directly impact the level of disassociation within chemical compounds, the requirement for stringent supervision of an engine's combustion process is astronomical. Therefore, this will be the main priority for this investigation, from which, can be expanded upon to create a complete and accurate combustion simulation from fundamental principles.

If the temperature of the flame front along with both the burnt, unburnt zones within the combustion chamber could be regulated, the ability to control the charge mixture to a desired burn rate, optimising for particulate emissions and combustion efficiency to avoid wasting fuel and energy.

Analysis of the existing data supplied for the Fox engine would be required to understand its current operating parameters. This will help form an understanding to the technologies implemented within commercially manufactured engines to meet particulate regulations. Mathematical modelling will then be implemented to manipulate the existing pressure data to uncover trends within thermodynamic variables that consistently fluctuate within fractions of a second.

These trends enable the establishment of the cause and effect relationships within cyclic variation and how they influence the combustion process. From which can be incorporated into the combustion model to become a solid foundation for the accurate determination of chemical disassociation through the examination of temperatures within the cylinder. The question brought forward for this project would be is there a possibility to configure an engines combustion process with the intent of reducing or optimising the materialisation of Knock, Soot and NO_x .

2. Literature Review

Upon commencing this investigation, it was clear that research would need to be conducted into both the engine, and the fundamental principles at work during combustion. This knowledge would reinforce the mathematical equations to theoretically validate the process and enable the creation of the combustion model.

2.1. Ford Fox Engine

The Fox is a turbocharged 1.0 litre three-cylinder Ecoboost engine that is used to power several of Fords small hatchbacks vehicles, producing up to 125hp with low CO₂ emissions stated between 114 and 144 g/km (Ford Motor Company UK, 2021). The engine is a product of downsizing within the industry, where manufacturers are preferring to adopt and develop smaller capacity engines compared to their larger predecessors. By reducing the number of cylinders and introducing a turbocharger, the frictional losses endured, and fuel used will decline in proportion, while the air can be charged into the remaining three cylinders to maintain sufficient power capacity for customer acceptance (Pullen K.R, 2011).

This movement within the industry doesn't come without its downsides. Petrol cars generally produce less NO_x per kilometre than their diesel counterparts, however the independent fuel economy and emissions testing company, Emissions Analytics, uncovered that these downsized engines produce far more NO_x in real world driving than more traditional, larger engines (Emissions Analytics, 2017). The variations were significant. The Focus 1.0 EcoBoost was ranked "E", emitting between 250 and 500 mg/km of NO_x particles, immensely higher than the Euro 6 limit of 60 mg/km (Evans, 2016). This shows that realistically, as strict as the regulations are surrounding emissions of vehicles, it is significantly hard to develop an engine that can meet the emissions standard set within a laboratory in controlled conditions, when faced with a real-world environment.

2.2. Thermodynamic Principles

2.2.1. Entropy

German physicist Rudolf Clausius considered the principle that work can only be obtained from organised molecular motion, therefore, there is a tendency for thermodynamic systems to naturally become disordered, providing less energy from which to harness as work (Drake, 2021). Hence, entropy (S) is the measure of energy distribution within a system and can help define whether a thermodynamic process is either reversible or irreversible, based upon its feasibility (Lumen Learning, 2021).

A reversible process can be identified as a reaction that can return to its previous form prior to its change of state. E.g. a piston compressing gas from ambient pressure within an isolated system, can reverse to allow the gas to expand and return to ambient pressure. A process that is irreversible on the other hand, cannot return to its original state post reaction. E.g. during the exhaust stroke of a 4-stroke engine, the exhaust valve is open, allowing the combustion gases to escape down the exhaust and into the surroundings, thus they can never be retrieved and put back into the system.

The second law of thermodynamics states that the entropy of the universe is always increasing due to the dispersal of energy within the system and its surroundings (Boston University, 1999). As matter exists in one of three states, solid, liquid or gas, as the entropy of each state increases, the more disordered the configuration of the molecules are within the element (Professor Dave Explains, 2015).

This also defines the direction in which energy travels based upon its entropic influence. Heat energy will always flow from hot to cold. This is because the heat energy causes the molecules within a system to vibrate compared to its cold counterpart, increasing the overall energy within the system, thus escalating the disorder of the molecules and their dispersal into the surrounding. (Gaskell, 2017) This continues into the third law of thermodynamics, where a perfectly crystalline solid at absolute zero has an entropy of zero (Sattel, 2016). This describes a state in which an element can be at its most ordered, because the system has no internal energy at absolute zero.

2.2.2. Enthalpy

Enthalpy (H) can be described as the heat content of the system and can be used to characterise the thermodynamic process undertaken based upon the energy transference between the chemical reaction and its surroundings (Daněk, 2006).

$$H = U + PV$$

2-1 – Determination Of Enthalpy Equation

Where,

H = Enthalpy

U = Internal energy

P = Pressure

V = Volume

If the reaction absorbs energy from its surroundings, such as chlorophyll absorbing light, it is endothermic, whereas if it releases energy into the surroundings, e.g. a radiator emitting heat, it is exothermic (BBC Bitesize, 2021). This basic principle aids with the understanding of the change in enthalpy and its sign convention, whether it is positive or negative based upon the systems change of internal energy (ΔU).

Activation energy is the minimum energy required for the chemicals to initially react. Within an engine, this occurs when the temperature and pressure are high enough to either cause the charge mixture to self-combust (Diesel cycle) or requires the aid of a spark plug to ignite the mixture (Spark Ignition) depending on the compression ratio (Khan Academy, 2021).

2.3. Mass Fraction Burnt (MFB) & Ignition Parameters

2.3.1. MFB

The Mass Fraction Burnt (MFB) is the normalised quantity of fuel burned per degree of crankshaft rotation between the limits of 0 & 1. This describes the release of chemical energy as a function of crank angle and enables a burn rate analysis, a procedure developed by Rassweiler and Withrow that is still widely used today (Krzysztof Z. Mendera, 2002).

The Rassweiler and Withrow approach assumes that during combustion, the pressure rise (ΔP) at each degree of crank rotation is split into two contributing elements; the pressure increase due to combustion (ΔP_C) and the pressure change due to volume change as the piston moves (ΔP_V) (Heywood, 1988).

$$\Delta P_V = \Delta P_C + \Delta P_V$$

2-2 – Separate Elements Contributing To The Rise In Pressure Equation

By presuming that ‘ ΔP ’ is directly proportional to the heat added into the cylinder during the specified crank interval, then the MFB can be determined per degree of crank rotation (M Mittal, 2009):

$$MFB = \frac{m_{b(i)}}{m_{Total(i)}} = \frac{\sum_0^i \Delta P_C}{\sum_0^N \Delta P_C}$$

2-3 – Rassweiler & Withrow Method For Determining Mass Fraction Burnt MFB)

2.3.2. Knock

Also known as Detonation, engine “Knock” is the term given to the event that occurs when pockets of the charge mixture spontaneously ignite before the flame front propagation has reached them (L J Hamilton, 2007). Knock tends to occur at high loading operations where there is a high intake boost pressure, as opposed to part loading, where the gas exchange process to draw air into the cylinder, requires more work to overcome the lower pressure within the intake manifold (AKMA, 2017). Although similar to pre-ignition Appendix 7.1.4, these events should not be confused with one another, although the occurrence of one, can lead to the other.

Knocking is a significant factor that limits the performance and thermal efficiency of a Spark Ignition (SI) engine creating an abnormal combustion of the unburnt charge mixture releasing a sudden surge of chemical energy (Kasseris, 2011). Localised high pressure shockwaves are created within the combustion chamber, disrupting the propagation of the flame front, potentially damage internal components and reflect off the metallic components leading to a “pinging” sound (Heywood, 1988).

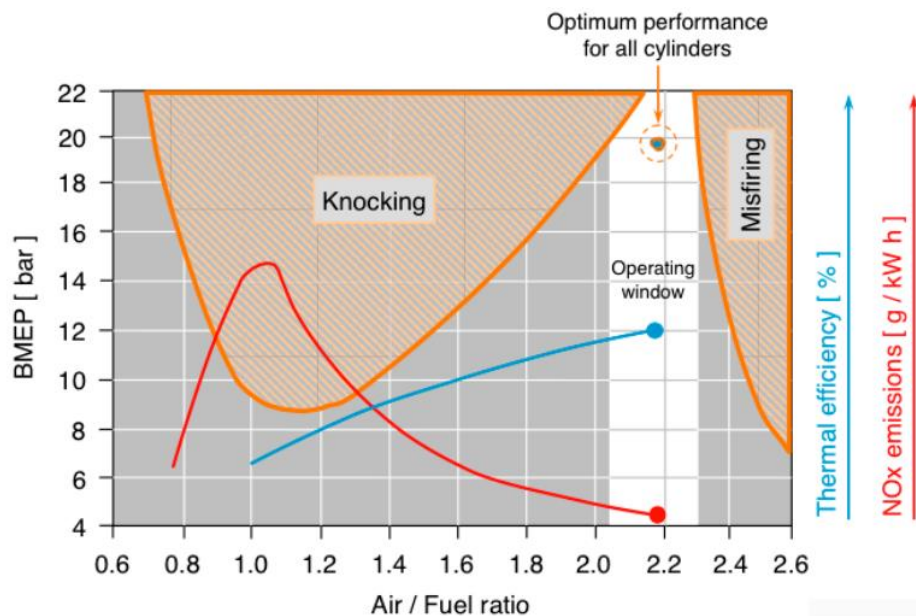


Figure 1 – Operation Window of a Wärtsilä 9L50DF Marine Engine, (La Xiang, 2018)

La Xiang et al. created a two-zone combustion model for the prediction of knock in a marine natural gas Wärtsilä 9L50DF SI engine. They determined that the optimum performance point is a compromise between the knock limitation, misfiring limit, thermal efficiency and NO_x production. This operation window is demonstrated within Figure 1 against the Air/Fuel Ratio (AFR) and Brake Mean Effective Pressure (BMEP) displaying its optimum operating point (La Xiang, 2018).

Rafal Pyszczyk investigated the prevention of knock in an attempt to increase reliability and efficiency of high-power gaseous IC engines. Discussing the possibility of 'super-knock, a large pocket of fresh gases that auto-ignites suddenly leading to pressure surge of several hundred bar when flame speeds can intensify more than double the magnitude of standard ignition (Pyszczyk, 2017).

2.4. Emissions & Disassociation

2.4.1. Particulate Emissions

There will always be a molecular disassociation caused by the combustion of chemicals due to the significant temperatures at which ICE operate at. Whether the ICE is running carbon-based fuels, alternative/organic biofuels or hydrogen, the temperature of the flame front will always cause particles to break their molecular bonds and form new chemical compounds with other molecules within the mixture (Norman D. Brinkman, 1985). These new bonds may be the result of either an electrostatic force of attraction through ionic bonding, or by means of covalent bonds in which electrons are shared between molecules (K. D. Sapate, 2008).

2.4.1.1. Soot

Even the most advanced engines in the modern era struggle to optimise the combustion process due to various inconsistencies both in construction/wear incurred or other thermodynamic principles that would lead to incomplete combustion. Almost 80% of the energy released from the combustion of fuel is wasted before it can be harnessed into mechanical energy (Skowron, 2019). These unburnt air/fuel particles are released into the atmosphere in the form of carcinogenic soot which is harmful to both the planet and its inhabitants (Empa, 2017).

2.4.1.2. NO_x

Considering the amount of Nitrogen within the Earth's atmosphere, it is physically impossible to eliminate it from being drawn into the combustion chamber of an engine during operation. Therefore, the chemical bonds between the Dinitrogen (N_2) and Dioxygen (O_2) molecules begin to break down if the temperature within the cylinder exceeds $\sim 1,300^\circ\text{C}$ (Clean Air Technology Center (MD-12), 1999). These loose particles form noncovalent bonds in various structures, such as; nitric oxide (NO), nitrogen dioxide (NO_2), nitrous acid (HONO), dinitrogen pentoxide (N_2O_5) or the nitrate radical (NO_3) (John H Seinfeld, 2016). These are harmful to humans and wildlife and have been linked to asthma and other breathing problems (Air-Quality.org.uk, 2021).

Since temperature controls the level of disassociation between nitrogen and oxygen molecules, engines that rely on self-ignition of the charge mixture to operate (compression ignition) are more susceptible to the formation of NO_x particulate matter (Günter P. Merker, 1993). Although in 2018, emissions analytics found that new diesel propelled vehicles emit

71% less particulates than their petrol equivalents (Fleet News, 2018). This proves that developments have been made to the on-board technologies aimed at reducing globally regulated emissions to the point where the 'dirty diesel' is now, on average, cleaner than its petrol counterpart.

A common application of cylinder temperature reduction attempting to control/prevent disassociation of molecules is Exhaust Gas Recirculation (EGR). As by the name, exhaust gas is recirculated from the exhaust pipe and fed back into the cylinder as dead or inert mass. This system can recuperate the inert mass from either before or after the turbocharger with either a high pressure or low pressure EGR system (X-Engineer, 2021). Both procedures depend upon the manipulation of the ideal gas law in order to achieve success.

$$PV = nRT$$

2-4 – Ideal Gas Law

Where,

P = Pressure (Pa)

V = Volume (m^3)

n = Quantity of moles (mol)

R = Universal Gas Constant ($\frac{J}{mol \cdot K}$)

T = Temperature (K)

The principle is based upon the belief that if ' P ', ' V ' & ' R ' remained constant, where ' n ' increased with the inert mass, ' T ' would have to reduce for both sides of the equation to abide by the ideal gas law (Williams, 2019). This also applies to the amount of fresh air that is drawn into the cylinder per cycle. With the added inert mass inside the cylinder, there are less fresh oxygen molecules to combust, alongside water vapour (a by-product of combustion), reducing the temperature further (Evans Halshaw, 2019).

2.4.1.3. CO₂

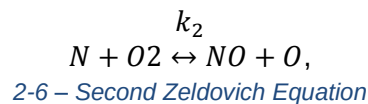
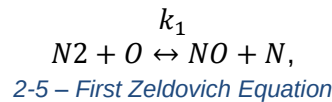
As a greenhouse gas (GHG), carbon dioxide (CO₂) is the most widely monitored by-product of combustion within road vehicles. Numerous studies have detailed the environmental damage caused by this pollutant with the global average in 2019 at 409.8 parts per million (ppm) (Lindsey, 2020). Unfortunately, due our reliance on carbon-based fuels, the carbon within the charge mixture will always react and bond with the oxygen from the air at the temperatures observed through combustion.

This is not limited to purely combustion, GHG are emitted throughout the entire lifecycle of a vehicle. Life-cycle assessment (LCA) studies have gained widespread backing by analysing the emissions of a vehicle during its operation, fuel refining process and end-of-life phases (Ryuji Kawamoto, 2019).

There are various technologies introduced with the reduction of CO₂ in mind. One proposed system utilises an on-board device that captures 90% of the emitted CO₂ using a turbo-compressor system, compressing and liquifying the encapsulated gas using waste heat from the exhaust (Shivom Sharma, 2019).

2.4.2. Zeldovich Model

Simulating the disassociation of molecules is one thing, another is the prediction of oxidation within nitrogen molecules which create the discussed NO_x particulate formations. A chemical mechanism created by Yakov Borisovich Zel'dovich in 1946 describes the governing procedure molecules obey within the reaction as a consequence of high flame temperatures (W.C. Gardiner, 2000).



Where k_1 & k_2 are reaction rate constants detailed by Arrhenius law based upon their temperature dependence which governs their forward and reverse reaction rates and the energy required for activation (Williams, 2019).

(Heywood, 1988), (McAllister, et al., 2011) and (Günter P. Merker, 2004) each have their own variant on the concentration of NO_x equation based upon their individual studies and experimentations, displaying just how incredibly hard it is to account for real world conditions within a laboratory testing environment and uncover one specific equation that provides accurate and reliable results.

2.5. Emission Regulations

With the onset of Brexit at hand, it is unclear exactly which legislation vehicle emissions will have to abide by following the separation from the European Union (EU) and their currently official Euro 6 “Regulation (EC) 2019/631” guidelines intent on reducing vehicular emissions (RAC, 2020). The regulations are updated every year, reducing the allowable limit as well as increasing the penalties incurred by the manufacturers should their average fleetwide target of 95g of CO₂ per kilometre be breached, for which in 2019, the penalty is €95 for each g/km over this target (European Commission, 2021).

Although manufacturers are struggling to meet these regulations, the European Commission expect that with the implementation of their latest legislation, adopted in 2020, would prove a reduction of 23% in GHG in 2030 when compared against 2005 (European Commission, 2021). By introducing updated regulations each year, their proposal is to ensure a smooth and gradual transition towards zero-emission mobility within the automotive industry for reskilling of workers.

In an attempt to neglect the variation previously mentioned between the realistic emission values in the real world as opposed to those conducted in a laboratory, the European Commission is hoping to implement real-time measurements of vehicle emissions throughout their lifetime (European Commission, 2020). The plan could potentially remove the existing on-board diagnostics (OBD) to facilitate the surveillance, followed by forcing hybrid vehicles to drive in electric only mode within certain locations. Furthermore, MoT checks would be affected as the vehicle would carry out a roadworthiness test automatically (Griffiths, 2021).

3. Methods

As previously discussed, mathematical modelling will be the forefront method of interpreting the engines characteristics and help to define the overall efficiency of the engine, by using the known geometry of the engine, along with the supplied cylinder pressure data. This method has been used by the author using data provided by a Ford 1.6L Sigma engine. Although not to this depth, it enabled the author to grasp the basic underlined relationships by the chemical, mechanical and thermodynamic principles and how they directly correlate to one another.

The data supplied for the Fox engine consisted of pressure in bar, provided in different formats. There is data provided for a test cycle that held the engine at 6000RPM for 500 cycles, along with two separate test cycles using averaged pressure data, held at specific RPM intervals at both full and part engine loading. A manual containing measured variables can help identify engine characteristics that are vital contributors to its operation.

The data including 500 separate cycles will enable the correlation of cyclic variation and pressure cycles that occur within each of the three cylinders when maintaining a consistent engine speed. Whereas, the data that has been averaged over 'x' amount of cycles, displays the characteristics that change via the inversely proportional relationship between the acceleration in engine speed and the reduction in time available for combustion to transpire. The data will first be manipulated within Microsoft Excel to visualise the mathematics at work, while the model will progress into MATLAB to increase the achievable complexity of the model as the project develops.

With known geometric parameters, the engine's combustion chamber and piston motion can be digitally replicated to simulate the pressure that would result from absence of combustion. This cements the polytropic relationship between pressure and volume but must consider the polytropic index value is different in compression & expansion phases (Simpson, 2017).

The MFB can be determined for each cycle by calculating the difference in pressure both with and without combustion. Without combustion, once the piston descends after Top Dead Centre (TDC), the volume would increase, hence the pressure would reduce. The point in which pressure actually increases during this time would suggest the start of combustion (M Mittal, 2009). This will identify the burn profiles within each cylinder, gaining insight into how the ignition timing is controlled, relative to the speed and loading of the engine. A common optimisation method for the reduction in emissions, fuel consumption, knock occurrence or Maximum Brake Torque (MBT) (Günter P. Merker, 2004).

By calculating the amount of air and fuel within each cylinder from the known AFR values, it is possible to determine the chemical reactions that materialise as a product of combustion. Using the known quantity of chemical compounds that constitute the air/fuel mixture, the atomic disassociation of the molecular structures can be determined based upon tabulated experimental data containing their enthalpy possessed at a specific flame temperature. The concentrations of particulates within the exhaust gas can be analysed on their potential to bond together, forming many of the various harmful known substances that are strictly regulated by governments worldwide.

This methodology would be applied to a single zone model to ensure that all calculations are correct, and trends correlate to those expected from previous studies within this subject area, such as; (Salah E. Mohammed, 2019) and (S. Mauro, 2018). The combustion model will then be expanded to incorporate a two-zone combustion model, this will include the separate temperatures of the burnt and unburnt areas of the gas within the combustion chamber. Numerous studies have been conducted into this method so they will provide a vast source of

referenceable material, such as; (L J Hamilton, 2007) and (La Xiang, 2018). With this added complexity, it is possible to measure the propagation of the flame front, along with the burnt and unburnt zones throughout each degree of crank rotation, and thus, the completion of the combustion process each cycle.

With the monitorization of the separate combustion zones, it would only seem logical to measure the potential occurrence of knock. The subsequent shockwaves from the uneven and mistimed burn can oppose the uniform propagation of the flame front and cause damage to the engine's internals, so its prevention would be advantageous. It should be noted that this would aid the justification as to the engine's current ignition, while also studying the effects of advancing/retarding the ignition has upon the knock phenomenon.

The typical way of validating a virtual combustion model is verifying the model's predictions against measured data recorded from a physical counterpart (K. Tahera, 2012). Unfortunately, due to the pandemic led on by COVID-19 and the closure of the university premises, including the workshops and dynamometer, this will not be possible. Hence, the project will be reduced to a purely theoretical basis around explaining, understanding and potentially improving the combustion process within an automotive engine.

4. Results

The data collected throughout this investigation will generally be of a quantitative nature, whereby the numerical results will define a physical or statistical parameter observed within the engine, although some variable are impossible to measure without specific, intricate and expensive devices, they can be estimated using fundamental principles adopted by the scientific community.

This numerical data will be analysed to understand how manufacturers develop engines while prioritising the prevention of known and unwanted cyclic and chemical abnormalities from arising that would threaten their reputation. The underlying characteristics throughout the combustion process will be graphed into 2D & 3D visual representations for easier analysis of common trends. Examples of the characteristics to be monitored are:

- MFB for each cylinder and RPM (%/°)
- Heat energy released from the fuel and how much can be utilised (J)
- Fuel Equivalence Ratio (FEV, ϕ)
- Ratio of specific heats (γ)
- Chemical disassociation (e.g. $CO_2 \rightarrow CO + O$)
- Particulate emissions – Soot, HC & NO_x (% or ppm)
- Knocking / Detonation prediction
- Thermal efficiency (%)
- Combustion efficiency (%)
- Cylinder and individual zone temperatures (K)
- Heat energy extracted by the turbine (J)

Although the intention is to validate this methodology and empirical evidence against experimental data, should the calculations of particulate emissions match those recorded throughout the test cycle within the manual, this would be a good indication that the data calculated can be trusted and representative simulation.

5. Evaluation

While this project is not a new area of investigation, it outlines the usefulness of replicating an engine within a virtual environment. The ability to change minute variables and simulate the engine's response proves vital on a cost-effective basis, whereby it is cheaper and more time effective to develop a new feature or design parameters digitally, rather than through the creation of a physical prototype and required testing procedure (Cunningham, 2021).

Although Excel & MATLAB can only predict results to a set degree of accuracy, this could always be improved on with the introduction of specific chemical or combustion simulation software. As equations become more complex, i.e. the transition from 1D calculations into 3D environment, requires significantly more information to become an accurate reflection of the physical counterpart. The more detailed a model becomes, the more time & processing power it will require to calculate.

This becomes a huge issue with significantly detailed simulations taking 100's of hours to achieve iterative convergence for one scenario, when conducting a study of several situations to uncover the optimum position, only to find an error rendering the gathered data useless. Therefore, balance is required between complexity and computational completion time.

Due to the timescale of the project, the fundamentals will be cemented into the combustion model, achieving as much detail and complexity within MATLAB in the pursuit of accuracy, before any further expansion is undertaken into chemical or combustion simulation software. Although, should time allow it, this is a possible avenue of exploration and validation to the numerical data generated by MATLAB.

Without the possibility of validating this combustion model in a physical scenario, the true merit achieved by this software will be in question, but the analysis conducted into the cyclic variation could be crucial in understanding potential methods of optimisation in the future.

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7. Appendix

7.1.1. Boltzmann Constant

In the late 1800's, Ludwig Boltzmann proposed that the air within a container is comprised of atoms and molecules that are continuously moving within the container, causing a pressure on the surface of the boundary (Britannica, 2021). He suggested that, should this contain steam and a person's hand be placed inside, the heat energy that would be felt is really the kinetic energy of the H₂O molecules as they collide into the hand. The more heat energy the molecules possess, the more kinetic energy they will have, so they will impact with a higher velocity and frequency, leading to a higher transference of energy into the molecules within the skin, potentially causing severe damage (Northwestern University, 2021). Therefore, temperature can be defined as the relation to the average kinetic energy that the molecules within a homogenous gas or mixture possess.

7.1.2. Gibbs Free Energy

$$\Delta G = \Delta H - T\Delta S$$

7-1 – Gibbs Free Energy Equation

The notation 'ΔG' represents the sum of the free energy that productive work can be harnessed from, accounting for the increased entropy, and hence, increased energy dispersal radiated into the surroundings (The Organic Chemistry Tutor, 2016).

A process can be identified whether it is spontaneous or not by the outcome of Gibbs free energy (ΔG). By identifying the change in both entropy and enthalpy along with the temperature of the system, the sign convention of the result defines the reaction. E.g. a negative value implies a spontaneous reaction, a result of zero indicates a system is at thermal equilibrium, whereas a positive result infers the process requires outside interference to initiate (The Organic Chemistry Tutor, 2016).

Now it should be noted that the above only applies to reactions in the forward direction, this means that they are the opposite in the reverse direction. I.e. if 'ΔG' is negative, thus implying a spontaneous reaction in the forward direction, it is hence nonspontaneous in the reverse direction. This is also highly temperature dependant, whether it is a high or low temperature may dictate whether the reaction is spontaneous or nonspontaneous at that moment in time.

This makes 'ΔG' a very interesting tool, as it can be used to estimate the boiling point of a substance with a reversible reaction. Should the corresponding values for the changes in enthalpy (ΔH) and entropy (ΔS) during the vaporisation phase change of the substance be known. Then by assuming the liquid and gas form of the substance are in thermal equilibrium at this temperature, 'ΔG' can be assumed as zero.

$$0 = \Delta H - T\Delta S$$

7-2 – Gibbs Free Energy at Thermal Equilibrium Equation

Now the equation can be rearranged to solve for the temperature (T). By adding 'TΔS' to both sides, it is possible to cancel the negative. Both sides are then divided by 'ΔS' to make 'T' the subject.

$$T\Delta S = \Delta H - T\Delta S + T\Delta S$$

↓

$$T\Delta S = \Delta H$$

↓

$$\frac{T\Delta S}{\Delta S} = \frac{\Delta H}{\Delta S}$$

$$\downarrow$$

$$T = \frac{\Delta H}{\Delta S}$$

7-3 – Gibbs Free Energy Rearranged to Find The Boiling Point of a Substance At Thermal Equilibrium

This leaves a relationship that can define the unknown variable, 'T', using known 'ΔH' and 'ΔS' values while at thermal equilibrium.

7.1.3. Partial Pressures

Each chemical consists of different molecular structures, the density and mass of these structures determine the velocity in which they collide with the boundary surface area, creating a pressure (Royal Society Of Chemistry, 2018).

As,

$$Pressure = \frac{Force}{Area}$$

7-4 – Fundamental Equation For Calculating Pressure

Should this same chemical become part of a blended mixture, there will be a total pressure exerted onto boundary surface from the mixture. But each individual chemical within the mixture exerts its own separate pressure upon the surface, known as its partial pressure (University Of Texas, 2021).

In 1801, John Dalton expanded upon the kinetic theory of gases by using the assumption that each gas within a homogenous mixture are ideal gases, therefore, do not have any intermolecular interactions with any other component molecules but abide by the respective law (Khan Academy, 2021).

Supplementing the moles of each component into the ideal gas law:

$$PV = (n_{Gas1} + n_{Gas2} + n_{Gas3} \dots)RT$$

7-5 – Ideal Gas Law Inclusive of Component Moles Equation

Divide by the volume (V) then expanding the brackets unveils the pressure of each individual component contributing to the overall pressure:

$$\frac{PV}{V} = \frac{(n_{Gas1} + n_{Gas2} + n_{Gas3} \dots)RT}{V}$$

$$\downarrow$$

$$P = \frac{n_{Gas1}}{V}RT + \frac{n_{Gas2}}{V}RT + \frac{n_{Gas3}}{V}RT \dots$$

7-6 – Ideal Gas Law Constituting the Pressure of Each Individual Component Equation

Hence, Dalton determined that the total pressure exerted from a mixture of gases, is equal to the sum of the partial pressures of the individual component gases (M. W. Zemansky, 1997).

$$P_{Total} = P_{Gas1} + P_{Gas2} + P_{Gas3} \dots$$

7-7 – Dalton's Law Of Partial Pressures Equation

Dalton's law can be rewritten to find the partial pressure of a particular gas:

$$P_{Gas1} = x_{Gas1} * P_{Total}$$

7-8 – Derivation of a Components Partial Pressure Value Equation

Since,

$$x_{Gas1} = \frac{n_{Gas1}}{V} = \frac{n_{Gas1}}{n_{Total}}$$

7-9 – Mole Fraction / Molar Concentration Equation

This can be substituted into equation 7-8 – Derivation of a Components Partial Pressure Value Equation,

$$P_{Gas1} = \frac{n_{Gas1}}{V} * P_{Total}$$

7-10 – Calculation of a Components Partial Pressure Value Using Mole Fraction Equation

7.1.4. Pre-ignition

Should the combustion chamber reach the critical temperature required to ignite the charge mixture before it's intended ignition point, known as pre-ignition. This has been prominent within compression ignition engines causing 'run-on', a phenomenon that causes the engine to continue firing even after the ignition has been switched off.

This is because the conditions within the combustion chamber are adequate enough for the combustion process to take place, given a constant fuel supply, by means of a faulty injector or carburettor float valve. In recent years, this event has declined with the introduction of electronic fuel injection systems where the injector will not be permitted to continue supplying fuel into the cylinder after the ignition has been switched off. A study has been conducted into this area within aircraft engines where they determined the spark plug as the main contributor to pre-ignition (A. HUNDERE, 1948).

This also shows just how vital the cooling system is within an IC engine and the importance of keeping the combustion chamber and its surroundings to an optimum temperature to prevent such occurrence, protecting other vital components.