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Analysis of Engine Performance Parameters with Hydrogen Enrichment in Premixed Spark Ignition Engine Using Fuel Blend

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Abstract

Hydrogen enrichment in internal combustion engines has been a topic of research interest to improve engine efficiencies and reduce carbon emissions. Hydrogen enrichment has garnered more interest than the pure hydrogen powered engines due to less complexity involved with the modifications of the engine and fuel system as well as the infrastructure required for it. Similarly, accurate chemical kinetics has proved to provide accurate results in terms of engine performance parameters, such as, in-cylinder pressure. The present study is an extension of study performed earlier with hydrogen enrichment in gasoline direct injection engine while using C_8H_{17} as a surrogate fuel for gasoline and assumes that an on-board electrolysis system installed on the vehicle produces hydrogen for the enrichment purposes. A mesh independent study is performed using 90% iso-octane (iC_8H_{18}) and 10% n-heptane (nC_7H_{16}) blend as a gasoline surrogate with hydrogen enrichment of 0%, 1%, 2% and 3% at equivalence ratios of 0.98 and 1.3, in a premixed spark ignition engine. Numerical simulations are performed to calculate and compare the thermal and combustion efficiencies of the engine using hydrogen-enriched fuel versus iso-octane and n-heptane blend. The study also predicts and measures the engine performance parameter of in-cylinder pressure, while comparing the iso-octane and n-heptane blend against the blend enriched with hydrogen. Based on the results obtained from smaller hydrogen enrichment concentrations, the study increases the hydrogen-enrichment of the fuel to 5%, 10% and 15% to analyse the effects of enrichment on the thermal and combustion efficiencies, as well as the in-cylinder pressure.

Keywords: Spark Ignition, Hydrogen Enrichment, Pent Roof, KIVA, In-Cylinder Pressure, Combustion Efficiency, Thermal Efficiency

Introduction

Computational affordability of mathematical models has been achieved in Computational Fluid Dynamics (CFD) by assumptions that lead to simplifications in the computational problems. The thermo-chemical phenomena inside a spark-ignition combustion requires deep understanding and is quite challenging. This insight can be achieved through validation of computational simulation by performing the experiments or using the published experimental data [1]. This was achieved in the previous study when experimental comparison was performed to validate a novel reduced mechanism that predicted the engine performance parameters with good agreement for two different engine geometries. Most traditional studies utilize simplified global reactions for simulation of combustion and engine performance parameters due to computational limitations [2]. The combustion efficiency of the engine highly depends on the in-cylinder fuel distribution and equivalence ratio. Hydrogen enrichment has garnered more interest than the pure hydrogen powered engines due to less complexity involved with the modifications of the engine and fuel system as well as the infrastructure required for it. The present study is an extension of study performed earlier with hydrogen enrichment in gasoline direct injection engine while using C_8H_{17}, which KIVA fuel library uses as a surrogate fuel for gasoline, and assumed that an on-board electrolysis system installed on the vehicle produces hydrogen for the enrichment purposes. Numerical simulations were performed in a premixed spark ignition engine with pentroof geometry. A mesh independent study was performed using a blend of 90% *iso-octane* and 10% *n-heptane* as a gasoline surrogate

employing multi-step global reaction mechanism with hydrogen enrichment of 0%, 1%, 2%, 3%, 5%, 10% and 15%, at equivalence ratios of 0.98 and 1.3. The reason to use a global mechanism in the present study is to understand the effect of combustion chemistry on the engine performance parameters and benchmark the data. This will pave the way to use the gasoline reduced mechanism obtained while using the hydrogen enrichment.

Ji et al. performed an experimental investigation on a spark-ignited gasoline engine with hydrogen addition to study the engine performance parameters of emissions at idle conditions [3]. This engine was modified for hydrogen to be injected into the intake ports simultaneously with gasoline. Ji et al. named it a hybrid hydrogen-gasoline engine (HHGE), which essentially is a premixed spark ignition engine. Hydrogen was injected at volumetric fractions of 0, 3, and 6% at idle conditions to measure the effects on thermal efficiency, combustion duration and emissions using a fixed spark advance, while the hydrogen and gasoline flow rates were measured by a hybrid electronic control unit (HECU). The engine's indicated thermal efficiency improved with the increase in hydrogen addition. The CO and NOx emissions were reduced while, HC emissions were found to have reduced as well.

Karagoz et al. performed a study using a conventional electrolyser to simultaneously produce hydrogen and oxygen [4]. Like previous study modification was made to the engine for it to operate using gasoline and hydrogen-oxygen mixture. The investigation was performed for idle conditions where hydrogen energy fractions of 0, 5, 8, 10 and 15% were tested. The testing investigated the effect of hydrogen enrichment on various engine performance parameters, such as peak in-cylinder temperature, thermal efficiency, specific fuel consumption, and emissions. All engine performance parameters tested showed an improvement with increase of hydrogen energy fraction while, an increase in NOx emissions was observed.

Similar research for hydrogen enrichment has also been performed by Yang et al [5]. for a spark-ignition rotary engine. The study performed a numerical investigation of the engine performance parameters of combustion and emissions formation in a spark-ignition rotary engine. The engine was fuelled with hydrogen-gasoline blends. A skeletal mechanism of primary reference fuel was used along with the k-ε turbulence, with volumetric fractions of 0%, 2% and 4% of hydrogen. Results showed that OH, H and O radicals concentrations were increased due to hydrogen enrichment as well as accelerated combustion caused improvement and advancement of in-cylinder pressure and temperature. Peak in-cylinder pressure increased by 9.1% for 2% hydrogen enrichment while it increased 13.7% with 4% hydrogen enrichment, as compared with the peak in-cylinder pressure obtained with combustion of gasoline. The same trend was observed with an increase in-cylinder temperature that favoured the formation of nitric oxide emission, while the formation of carbon monoxide decreased.

Dieguez et alinvestigated the combustion phenomena in a 4-cylinder, 1.4 L naturally aspirated port-fuel injection spark ignition Volkswagen engine with the hydrogen enrichment and mentioned abnormal combustion as a major concern factor for the transportation sector [6]. The study investigated in-cylinder pressure, block engine vibration and acoustic measurements to investigate abnormal combustion with addition of hydrogen within the engine speed range of 1000–5000 rpm. The study proved that abnormal combustion events can be detected through acoustic measurements. This is helpful in designing various engine components, such as cylinder valves, if the engine is modified for using hydrogen as a secondary fuel.

Shi et al. performed numerical simulations to investigate a gasoline Winkle engine with hydrogen direct-injection enrichment to enhance the combustion efficiency [7]. The study utilized chemical kinetic mechanisms by constructing a three-dimensional simulation model and validated against the measured results. Average flow velocities were determined for the spark timings (ST) of 45, 35, 25, and 15°CA BTDC. With an increase in spark timing (ST), the combustion rate increased with increase in chamber temperature. Also, the reactants (C_8H_{18}, C_7H_{16}, and H_2) were burned faster with accelerated formation of intermediates (H_2O_2, OH, and CH_2O) causing an increase in the formation of nitrogen oxides (NOx) and carbon monoxide (CO). The combustion phenomenon was also affected by the rotating direction of the rotor.

Ji et al. performed a numerical investigation of the combustion process in a spark-ignited (SI) engine fuelled with hydrogen-gasoline blends and validated against the experimental results, that resulted in validating that hydrogen enrichment by volume fractions of 3% and 6% caused an increase in the peak flame propagation speed of 37.18% and 60.47% respectively, and caused an enhanced degree of flame wrinkling [8].

Apart from gasoline, hydrogen is being investigated as a secondary fuel with other primary fuels as well due to shortening of oil reserves as well as to reduce the impact of fossil fuels on the climate change [9-12]. Among the fuels is natural gas, which is mainly composed of methane and is being investigated due to its effect on the improvement in thermal efficiency of spark ignition engines as well as its low carbon content which drastically reduces CO_2 emissions. These studies have shown that the hydrogen enrichment improved combustion lead to improvement in the combustion stability due to accelerated chemical kinetics with minimum modifications in the existing engine hardware [12].

Methods

The present study is performed by using the KIVA-3V code [13]. KIVA-3V is used for numerical calculations of transient, two- and three-dimensional chemically reactive fluid flows with sprays and is developed by Los Alamos National Laboratory. The present study investigates the variation between the effect of hydrogen enrichment on the in-cylinder pressure, combustion efficiency and thermal efficiency using multi-step global reaction mechanism for a premixed case at equivalence ratio of 0.98 and 1.3. The engine geometry used 85.96 mm bore, 94.6 mm stroke, compression ratio of 11.97 and running at 2100 rpm. To perform the studies, a blend of 90% *iso-octane* (iC_8H_{18}) and 10% *n-heptane* (nC_7H_{16}) is used as a gasoline surrogate [2].

There are no moving valves in the geometry. The red colour of the mesh and geometry is chosen for greater visibility and detail. A mesh independent study is performed for the reduced mechanisms. Table 1 shows three meshes constructed for this study; Mesh # 1: 100,000 cells, Mesh # 2: 178,000 cells and, Mesh # 3: 230,000 cells. Studies are performed to verify the general trend of the engine performance parameters for in-cylinder pressure, combustion efficiency, and thermal efficiency. With all the above three meshes, the general trend of the both of the engine performance parameters remains same. Figure 1 shows the isometric view of mesh # 3.

Table 1: Mesh Independent Study

	Mesh # 1	Mesh #2	Mesh # 3
Number of cells	100,000	178,000	230,000

Table 2: Engine Geometry [2, 14, 15]

Dimension	Unit	Value
Compression Ratio	[-]	11.97
Bore	[mm]	85.96
Stroke	[mm]	94.6
Connecting Rod Length	[mm]	152.4
Clearance Volume	[cm^3]	50.0
Displacement	[cm^3]	549.0
Engine Speed	[rpm]	2100

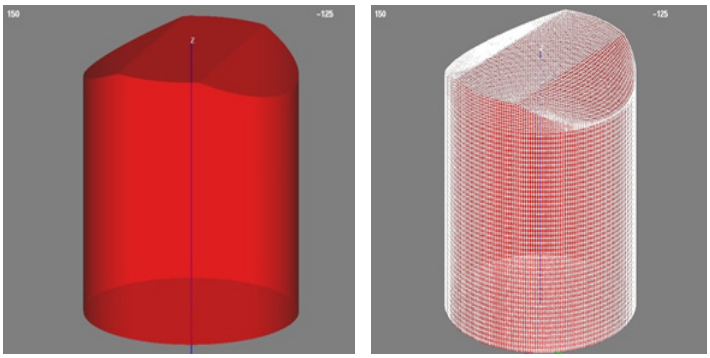

Figure 1: Pentroof Engine Geometry and Mesh – Isometric View [2]

The analysis was performed by varying the hydrogen inlet concentrations, i.e. 0%, 1%, 2%, 3%, 5%, 10%, and 15% in the *iso-octane*/*n-heptane* blend at equivalence ratios of 0.98 and 1.3, and using the global mechanism [1, 14] that used the one-step fuel reaction mechanism. For the prediction of NOx formation, three reactions from the Zeldovich mechanism were utilized. The global chemical reaction equations for the fuel are:

$$iC_8H_{18} + 12.5O_2 \rightarrow 8CO_2 + 16H_2O \quad (1)$$
$$nC_7H_{16} + 11O_2 \rightarrow 7CO_2 + 8H_2O \quad (2)$$

The global chemical reaction for the hydrogen is:

$$2H_2 + O_2 \rightarrow 2H_2O \quad (3)$$

For the prediction of NOx formation, the Zeldovich mechanism is:

$$2N_2 + O_2 \rightarrow 2N + 2NO \quad (4)$$
$$N_2 + 2O_2 \rightarrow 2O + 2NO \quad (5)$$
$$N_2 + 2OH \rightarrow 2H + 2NO \quad (6)$$

The analysis helped in determining the impact of multicomponent multi-step global reaction mechanism to understand the impact of chemical kinetics on the engine performance parameters. Comparison analysis was performed between multi-step global gasoline (90% iC_8H_{18}, 10% nC_7H_{16}) and gasoline/hydrogen mechanism for engine performance parameters: in-cylinder pressure, combustion efficiency, and thermal efficiency.

Table 3: Rate Data for Elementary Reactions Employed in The Asymptotic Analysis

Number	Reaction	B_n	α_n	E_n
1f	$iC_8H_{18} + 12.5O_2 \rightarrow 8CO_2 + 9H_2O$	4.600E+11	1.50	29.96
2f	$nC_7H_{16} + 11O_2 \rightarrow 7CO_2 + 8H_2O$	5.100E+11	1.50	29.96
3f	$2H_2 + O_2 \rightarrow 2H_2O$	1.800E+13	0.50	34.80
4f	$N_2 + O \rightarrow NO + N$	7.600E+13	1.00	75.50
4b	$NO + N \rightarrow N_2 + O$	1.600E+13	0.00	0.0
5f	$N + O_2 \rightarrow NO + O$	6.400E+09	1.00	6.26
5b	$NO + O \rightarrow N + O_2$	1.500E+09	1.00	38.75
6f	$N + OH \rightarrow NO + H$	4.100E+13	0.00	0.0
6b	$NO + H \rightarrow N + OH$	2.000E+14	0.00	46.99

Results and Discussion

Numerical input data was matched with the experimental nomenclature and data [15, 16]. Ignition energy was found to be the only toggle to replicate the experimental in-cylinder pressure. With the fuel blend at 0% hydrogen concentration, various numerical simulations were performed to optimize and replicate the in-cylinder pressure. The first step was to find the ignition energy for blow out. Once determined, various simulations were performed to replicate and match the experimental in-cylinder pressure. It was observed that a low ignition energy causes a delay in combustion which results in the lag in phase between the numerical prediction and the experimental data pressure curves even though the peak values were very close. If the ignition energy is increased, it causes sudden jump in the in-cylinder pressure which again causes a lag in the pressure curves. This is due to the absence of detailed combustion chemistry due to the simplistic nature of global reaction mechanism. The combustion efficiency remained at 100% for all equivalence ratios and hydrogen enrichments. Thermal efficiency was found to be decreasing with increasing the hydrogen enrichment which is resulted by the decrease in the pressure with increasing hydrogen concentrations.

In-cylinder Pressure, Φ = 0.98 and Φ = 1.3

Numerical simulations and comparison are performed for a mixture of 90% *iso-octane* (iC_8H1_8) and 10% *n-heptane* (nC_7H_{16}) at φ = 0.98 and φ = 1.3, with hydrogen enrichment of 1, 2, 3, 5, 10 and 15% using the global reaction mechanism. The ignition timing is 20° BTDC. Since it is a spark-ignition engine, the parameter XIGNIT is used to ignite mixture in the KIVA code. Figure 2 shows the comparison of in-cylinder pressure at φ = 0.98 and φ = 1.3, with hydrogen enrichment of 1, 2, 3, 5, 10 and 15% against the experimental data. The results obtained by all the meshes show the same general trend for the curves of in-cylinder pressure at φ = 0.98. The results show that as the hydrogen enrichment increases, the peak in-cylinder pressure starts decreasing, which points towards the fact that the engine geometry does not require major modifications to sustain any higher in-cylinder pressures.

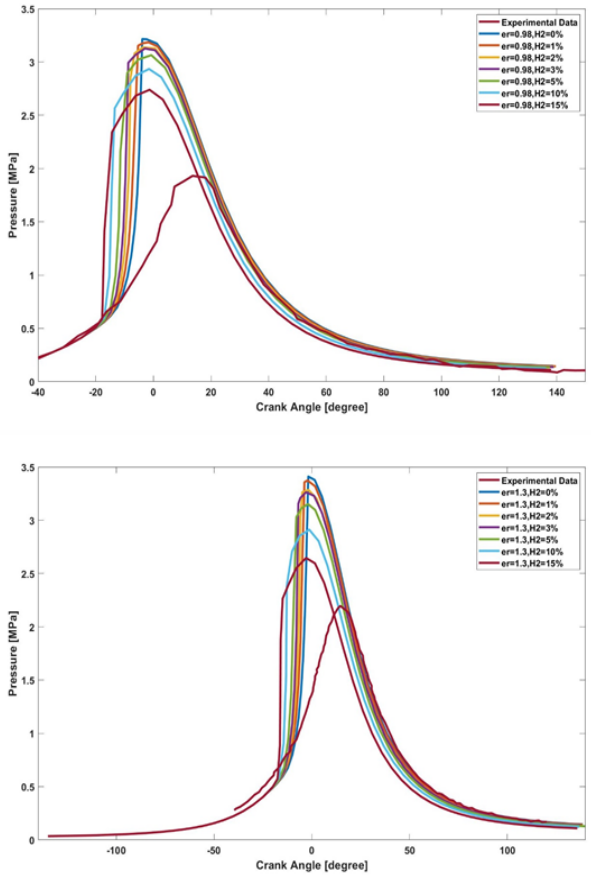

Figure 2: In-cylinder Pressure at ϕ = 0.98 (Top) and ϕ = 1.3 (Bottom)

Detailed in-cylinder flow parameter plots: Φ = 0.98

Utilizing GMV (General Mesh Viewer) [17] software for post processing of 3D temperature plots. The plots shown in Figure 3 to Figure 9 were constructed at ϕ = 0.98 to compare the temperature distribution using the global mechanism. The plots show aggressive burn out of fuel with hydrogen enrichment. Figure 3 to Figure 9 show the temperature progression after the ignition at 5° bTDC, 10° aTDC, and 20° aTDC.

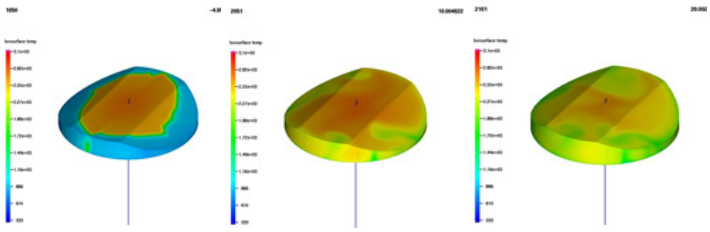

Figure 3: Temperature plots for 0% hydrogen at 5° BTDC, 10° and 20° ATDC at ϕ = 0.98

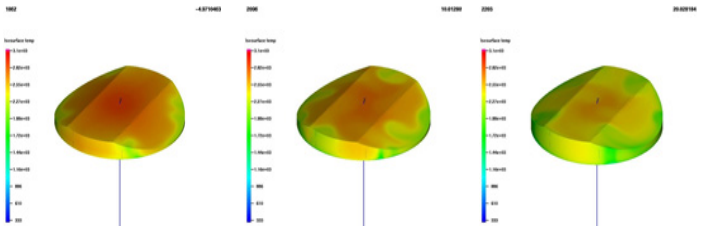

Figure 4: Temperature plots for 1% hydrogen at 5° BTDC, 10° and 20° ATDC at ϕ = 0.98

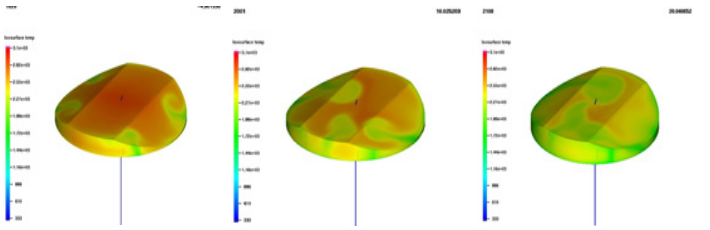

Figure 5: Temperature plots for 2% hydrogen at 5° BTDC, 10° and 20° ATDC at ϕ = 0.98

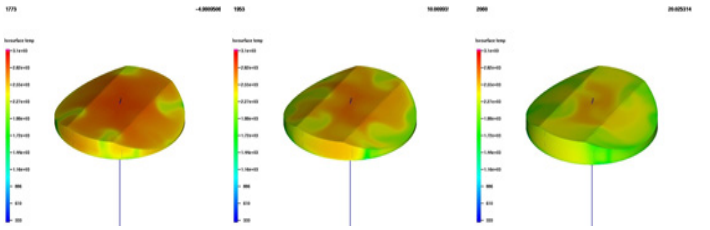

Figure 6: Temperature plots for 3% hydrogen at 5° BTDC, 10° and 20° ATDC at ϕ = 0.98

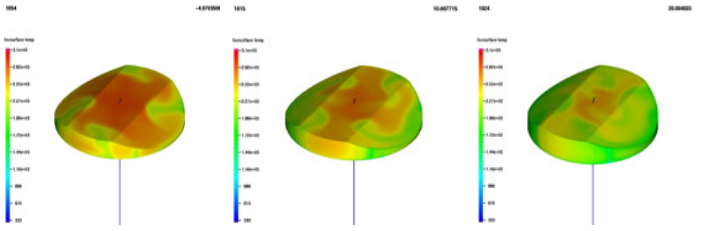

Figure 7: Temperature plots for 5% hydrogen at 5° BTDC, 10° and 20° ATDC at ϕ = 0.98

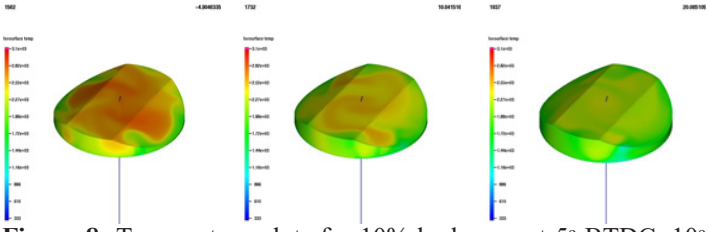

Figure 8: Temperature plots for 10% hydrogen at 5° BTDC, 10° and 20° ATDC at $\phi = 0.98$

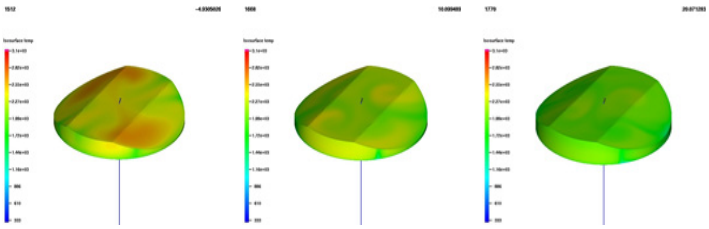

Figure 9: Temperature plots for 15% hydrogen at 5° BTDC, 10° and 20° ATDC at $\phi = 0.98$

Detailed in-cylinder flow parameter plots: Φ = 1.3

The plots shown in Figure 10 to Figure 16 were constructed for $\phi = 1.3$ to compare the temperature distribution using global reactions. The plots show an aggressive burn with hydrogen enrichment. Figure 10 to Figure 16 show the temperature progression after the ignition at 5° bTDC, 10° aTDC, and 20° aTDC.

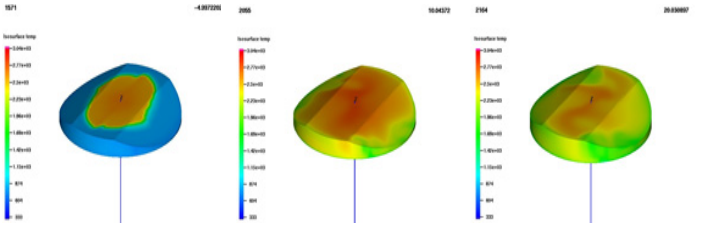

Figure 10: Temperature plots for 0% hydrogen at 5° BTDC, 10° and 20° ATDC at $\phi = 1.3$

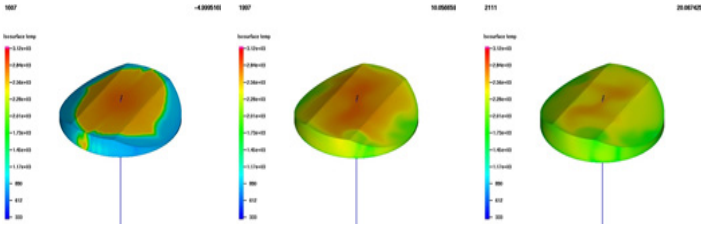

Figure 11: Temperature plots for 1% hydrogen at 5° BTDC, 10° and 20° ATDC at $\phi = 1.3$

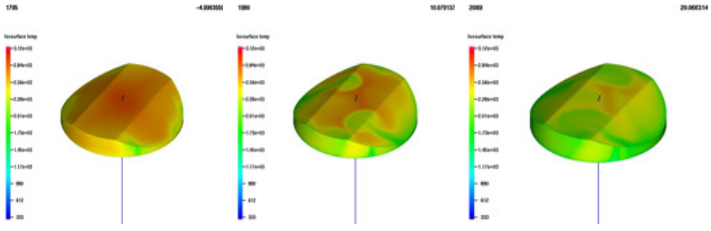

Figure 12: Temperature plots for 2% hydrogen at 5° BTDC, 10° and 20° ATDC at $\phi = 1.3$

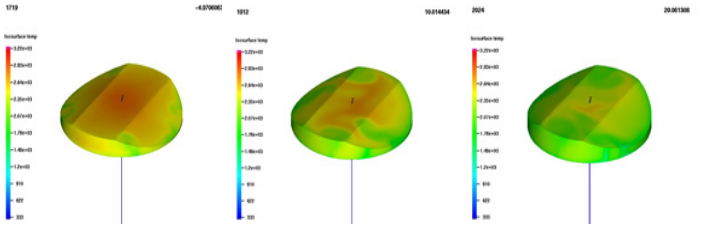

Figure 13: Temperature plots for 3% hydrogen at 5° BTDC, 10° and 20° ATDC at $\phi = 1.3$

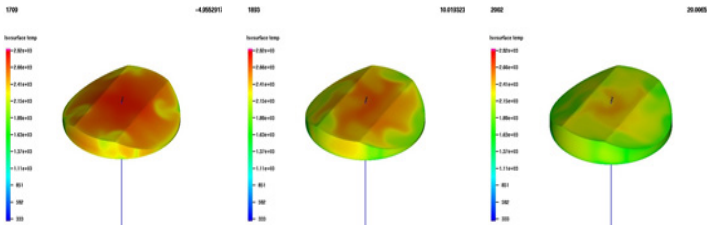

Figure 14: Temperature plots for 5% hydrogen at 5° BTDC, 10° and 20° ATDC at $\phi = 1.3$

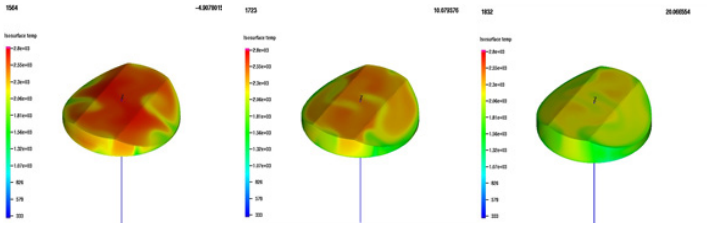

Figure 15: Temperature plots for 10% hydrogen at 5° BTDC, 10° and 20° ATDC at $\phi = 1.3$

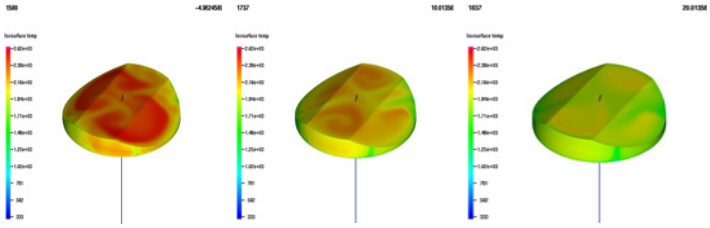

Figure 16: Temperature plots for 15% hydrogen at 5° BTDC, 10° and 20° ATDC at $\phi = 1.3$

Effect of ignition energy on ignition delay and in-cylinder pressure

Effect of ignition energy was studied on ignition delay and in-cylinder pressure. To achieve this, numerical simulations and comparison are performed for a mixture of 90% *iso-octane* (iC_8H_{18}) and 10% *n-heptane* (nC_7H_{16}) at $\varphi = 0.98$ and $\varphi = 1.3$, with hydrogen enrichment of 0% using the global reaction mechanism. For all of the cases, the ignition timing was set at 20° BTDC. The study provided valuable insight into choosing the correct ignition energy (XIGNIT) in KIVA-3V to replicate the engine performance parameter of in-cylinder pressure. Results were compared against the experimental data at 0% hydrogen enrichment. Figure 17 depicts the findings from the study which showed that with low ignition energies, there was an ignition delay using global reaction mechanism. Although the peak pressures were close to experimental peak pressures, but due to ignition delay, the phase of the plot changed. As the ignition energy was increased, there

was a sudden jump observed in the pressure. This phenomenon was observed due to the insufficient chemistry present in the global reaction mechanism.

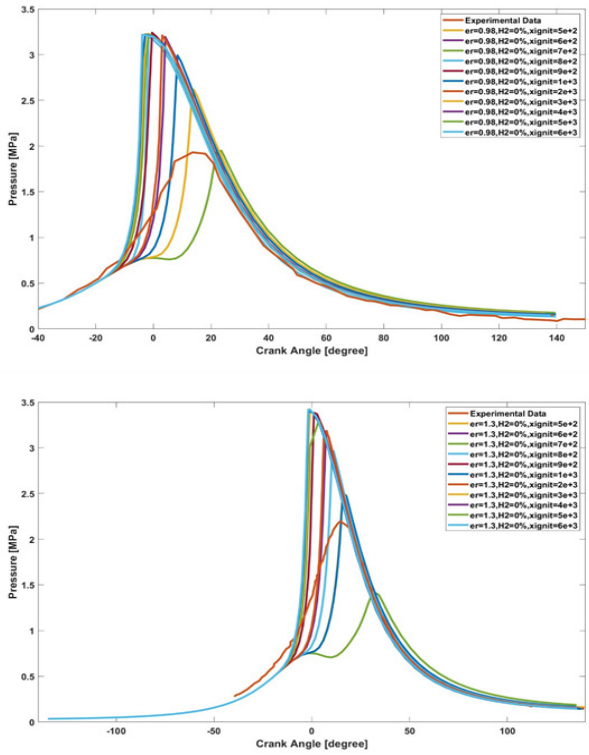

Figure 17: Effect of ignition energy on ignition delay at $\phi = 0.98$ (Top) and $\phi = 1.3$ (Bottom)

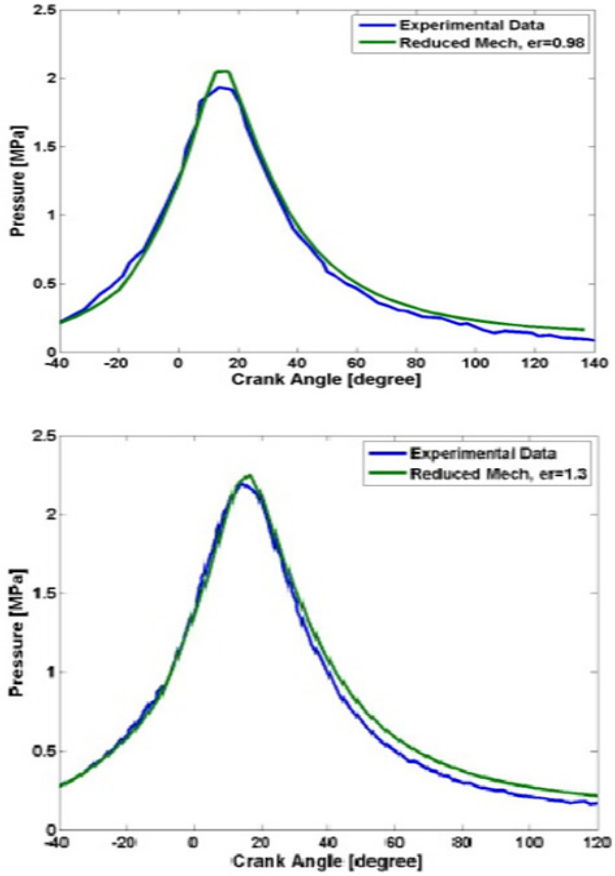

Figure 18: In-cylinder Pressure using Detailed Chemistry at $\phi = 0.98$ (Top) and $\phi = 1.3$ (Bottom)

Due to the results shown in Figure 17, it is imperative to use detailed combustion chemistry in numerical simulations to replicate the experimental results. To achieve this feat, a novel reduced reaction mechanism was constructed using SENKIN by performing sensitivity analysis for the compression and power stroke, using computational singular perturbation (CSP) method. Figure 18 shows the validation of in-cylinder pressure through using detailed combustion chemistry against the experimental data [17, 18]. The results show a good agreement and prediction of the numerical simulations against the experimental data [2].

Conclusions

A global mechanism was used with hydrogen enrichment in a SI engine geometry. The present study intended to observe the engine performance and combustion parameters of in-cylinder pressure, combustion efficiency, and thermal efficiency for equivalence ratio of 0.98 and 1.3. Since, gasoline is a complex mixture of hydrocarbons and other compounds, iso-octane *and n-heptane* were used as a gasoline surrogate. This study has provided the necessary understanding of the trend of in-cylinder pressure with hydrogen addition in a *spark-ignition engine*. It proved that the engine cylinder geometry does not need any major modification for hydrogen enrichment since the peak in-cylinder pressure decreases with increase in hydrogen enrichment percentage. The study has also shown the in-cylinder pressure trends and the need for expanding the study to use detailed chemistry which helped in predicting the combustion and engine performance parameters more accurately. The results depicted in the GMV plots also show the aggressive burn with addition of hydrogen. Future investigation into the research would be to include detailed chemistry by using detailed mechanism developed in order to understand the effect of hydrogen enrichment on the in-cylinder pressure and efficiencies.

Acknowledgements

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References

1. Arshad M, Wicklow GJ (2017) Analysis of hydrogen enrichment in gasoline fuelled premixed spark-ignition engine. Journal of Multidisciplinary Engineering Science and Technology 4: 8256-8264.
2. M Arshad (2020) Numerical simulations and validation of engine performance parameter in direct injection spark ignition (DISI) engines using chemical kinetics. International Mechanical Engineering Congress and Exposition IMECE2020-24683.
3. C Ji, S Wang (2009) Effect of hydrogen addition on idle performance of a spark-ignited gasoline engine at lean conditions with a fixed spark advance. Energy Fuels 23: 4385-4394.
4. Y Karagoz, T Sandalci, AS Dalkilic (2015) Effects of hydrogen and oxygen enrichment on performance and emissions of an SI engine under idle operating condition. International Journal of Hydrogen Energy 40: 8607-8619.
5. J Yang, C Ji, S Wang, Z Zhang, D. Wang, Z Ma (2017) Numerical investigation of the effects of hydrogen enrichment on combustion and emissions formation processes in a gasoline rotary engine. Energy Conversion and Management 151: 136-146.
6. PM Dieguez, JC Urroz, D Sainz, J Machin, M Arana, et al. (2018) Characterization of combustion anomalies in a hydrogen-fuelled 1.4 L commercial spark-ignition engine by means of in-cylinder pressure, block engine vibration, and acoustic measurements. Energy Conversion and Management 172: 67-80.
7. C Shi, C Ji, S Wang, J Yang, X Li, et al. (2019) Numerical simulation on combustion process of a hydrogen direct-injection stratified gasoline Winkle engine by synchronous and asynchronous ignition modes. Energy Conversion and Management 183: 14-25.
8. C Ji, X Liu, B Gao, S Wang, J Yang (2013) Numerical investigation on the combustion process in a spark-ignited engine fuelled with hydrogen-gasoline blends. International Journal of Hydrogen Energy 38: 11149-11155.
9. O Laget, S Richard, D Serrano, D Soleri (2012) Combining experimental and numerical investigations to explore the potential of downsized engines operating with methane/hydrogen blends. International Journal of Hydrogen Energy 37: 11514-11530.
10. F Moreno, J Arroyo, M Munoz, C Monne (2012) Combustion analysis of a spark ignition engine fuelled with gaseous blends containing hydrogen. International Journal of Hydrogen Energy 37: 13564-13573.
11. H Biffiger, P Soltic (2015) Effects of split port/direct injection of methane and hydrogen in a spark ignition engine. International Journal of Hydrogen Energy 40: 1994-2003.
12. SMV Sagar, AK Agarwal (2016) Experimental validation of accuracy of dynamic hydrogen-compressed natural gas mixing system using a single cylinder spark ignition engine. International Journal of Hydrogen Energy 41: 14272-14282.
13. AA Amsden (1997) KIVA-3V: A block-structured KIVA program for engines with vertical or canted valves, Los Alamos National Laboratory.
14. SR Turns (2000) An introduction to combustion concepts and applications, 2nd edition, McGraw Hill.
15. MD Hageman, SS Sakai, DA (2015) Rothamer Determination of soot onset and background particulate levels in a spark-ignition engine. Proc Combust Inst 35: 2949–2956.
16. MD Hageman (2014) Isolation of fundamental parameters contributing to particulate formation in a spark ignition direct injection (SIDI) engine. PhD Dissertation 3645354.
17. FA Ortega General mesh viewer user's manual, Los Alamos National Laboratory, LA-UR-95-2986.
18. AE Lutz, RJ Kee, JA Miller (1988) SENKIN: A FORTRAN program for predicting homogeneous gas phase chemical kinetics in a closed-system with sensitivity analysis, Sandia National Laboratories.