

Combustion Characteristics of Hydrogen by the Thermodynamic Properties Analysis

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Abstract

Hydrogen has some remarkably high values of the key properties for transport processes, such as kinematic viscosity, thermal conductivity and diffusion coefficient. Hydrogen, as an energy medium, has some distinct benefits for its high efficiency and convenience in storage, transportation and conversion. Hydrogen has much wider limits of flammability in air than methane, propane or gasoline and the minimum ignition energy is about an order of magnitude lower than for other combustibles. Statistical thermodynamics provides the relationships that we need in order to bridge this gap between the macro and the micro. Our most important application will involve the calculation of the thermodynamic properties of the ideal gas.

Key words : Hydrogen, combustion chemistry, thermodynamic properties, burned mixture, relative air-fuel ratio, thermal conductivity

1. Introduction

The automotive engineering has undergone continuous improvements, but at the same time, various global environmental issues related to vehicle use are becoming more serious. With the increasing need to both conserve fossil fuel and minimize toxic emissions, much effort is being focused on the advancement of current combustion technology. The pollution levels recorded in large urban areas are rising concerns for public health and substantial reductions in pollutant emissions have become an important issue [1,2].

Hydrogen, as an energy medium, has some distinct benefits for its high efficiency and convenience in storage, transportation and conversion. Hydrogen has much wider limits of flammability in air than

methane, propane or gasoline and the minimum ignition energy is about an order of magnitude lower than for other combustibles [3-5].

Karim [6] described that It is the only fuel that can be produced entirely from the plentiful renewable resource water, albeit through the expenditure of relatively much energy. Its combustion in oxygen produces uniquely only water but in air it also produces some oxides of nitrogen. These features make hydrogen an excellent fuel to potentially meet the ever increasingly stringent environmental controls of exhaust emissions from combustion devices, including the reduction of green house gas emissions. Hydrogen as a renewable fuel resource can be produced through the expenditure of energy to replace increasingly the depleting sources of conventional fossil fuels. Accordingly, research into all aspects of hydrogen technology, especially in recent years has been truly massive and diversified. A concise statement and discussion of the positive features of hydrogen as a fuel and the associated limitations that

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are impeding its wide application as an engine fuel are both necessary and needed.

Saravanan and Nagarajan [7] described that One alternative method is to use hydrogen in enrichment or induction, in which diesel is used as a pilot fuel for ignition. As hydrogen is a gas, it mixes well with air, resulting in complete combustion. Hydrogen-enriched engines produce approximately the same brake power and higher thermal efficiency than diesel engines over the entire range of operation. This work involves the enrichment of air with various percentages of hydrogen in a diesel engine using diesel as an ignition source. With a lesser pilot quantity of diesel, hydrogen-enriched engines give higher brake thermal efficiency with smoother combustion than a diesel engine. Increasing hydrogen beyond a certain quantity results in knocking; at the highest diesel flow rate, thermal efficiency is found to be the same as that of diesel engines.

Statistical thermodynamics provides the relationships that we need in order to bridge this gap between the macro and the micro. Our most important application will involve the calculation of the thermodynamic properties of the ideal gas [8].

2. Thermodynamic properties

Table 1 is shown some comparative properties of hydrogen and iso-octane. These are compared to the corresponding values of hydrogen and those of iso-octane vapor representing gasoline.

It is evident that hydrogen is a remarkably light gaseous fuel that requires on volume basis the least amount of air for stoichiometric combustion; while on mass basis it requires the highest relative mass of air. Its combustion is also associated with a substantial molar contraction of around 15%. Its heating value on mass basis is the highest; but on volume basis it is the lowest. Also, since its product of combustion in air is only water, there is a significant difference between its higher and lower heating values. However, its energy release by combustion per unit mass of stoichiometric mixture is one of the

highest.

Hydrogen has some remarkably high values of the key properties for transport processes, such as kinematic viscosity, thermal conductivity and diffusion coefficient, in comparison to those of the other two fuels. Such differences together with its extremely low density and low luminosity help to give hydrogen its unique diffusive and heat transfer characteristics.

Table 2 lists some combustion properties that have much influence on the potential behavior of hydrogen as a fuel in general and for engine applications in particular. The corresponding values for the other representative fuels and commercial gasoline are also shown for comparison. It can be seen that hydrogen has a remarkably wide flammable mixture range in air to permit extremely lean or rich mixtures support combustion. It requires also a remarkably low minimum amount of energy to effect ignition with extremely fast resulting flames in comparison to those of mixtures of iso-octane with air. However, the values of its spontaneous ignition temperatures are quite similar to those of the other two fuels and the values of its maximum adiabatic combustion temperature in air are only a little higher.

The chemical kinetics of the combustion of hydrogen in air are well understood at present and its oxidation reaction rates and the associated temporal variation of the concentrations of the reactive species can be predicted well. Mainly relatively fast and nearly thermally neutral branching chain reactions are involved. Hydrocarbon fuels oxidation on the other hand, involves normally thermally significant chain reactions that contain relatively slower endothermic reaction steps that are associated with fuel breakdown. These differences together with those in the thermodynamic and transport properties of hydrogen, contribute in a big way to the substantially different combustion characteristics of hydrogen from those of other common fuels.

There is also a tendency to focus on results obtained in specific engines and over narrowly changed operating conditions.

Table 1. Some comparative properties of hydrogen and gasoline (iso-octane) [6]

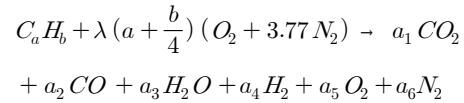
Property	Hydrogen	Gasoline (Iso-octane)
Density at 1 atm and 300 K (kg/m ³)	0.082	5.11
Stoichiometric composition in air (% by volume)	29.53	1.65
Stoichiometric fuel/air mass ratio	0.029	0.0664
No. of moles after combustion to before	0.85	1.058
Heating values		
HHV (MJ/kg)	141.7	48.29
LHV (MJ/kg)	119.7	44.79
HHV (MJ/m ³)	12.10	233.29
LHV (MJ/m ³)	10.22	216.38
Combustion energy per kg of stoichiometric mixture (MJ)	3.37	2.79
Kinematic viscosity at 300 K (mm ² /s)	110	1.18
Thermal conductivity at 300 K (mW/m K)	182.0	11.2
Diffusion coefficient into air at NTP (cm ² /s)	0.61	0.05

Table 2. Some comparative properties of hydrogen and gasoline (iso-octane) [6]

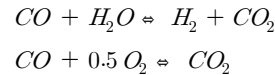
Property	Hydrogen	Gasoline (Iso-octane)
Flammability limits (% by volume)	4-75	1.2-6.0
Minimum ignition energy (mJ)	0.02	0.25
Laminar flame speed at NTP (m/s)	1.90	0.37-0.43
Adiabatic flame temperature (K)	2318	~2470
Autoignition temperature (K)	858	~500-750
Quenching gap at NTP (mm)	0.64	~2.0

3. Combustion chemistry

Assuming an arbitrary fuel C_aH_b at a local λ , the combustion chemistry can be written as [9].



This is, however, not a full description of the chemistry. It is a well-known fact that carbon monoxide is formed during combustion. The so-called water-gas shift reaction contains two reactions that can be stated as



The combustion of fuel is now sufficiently described to set up a system of equations for the equilibrium concentrations. a_1 , a_2 , a_3 , a_4 , a_5 and a_6 correspond to the equilibrium fractions of CO_2 , CO , H_2O , H_2 , O_2 and N_2 respectively. First and foremost, the atom balance gives a total of four equations that can be written in the following forms

$$a_1 + a_2 = a$$

$$2(a_3 + a_4) = b$$

$$2a_1 + a_2 + a_3 + 2a_5 = 2\lambda_{local} \left(a + \frac{b}{4} \right)$$

$$a_6 = 3.773\lambda_{local} \left(a + \frac{b}{4} \right)$$

As can be seen, there are a total of six unknown variables and only four equations. The additional two equations that are needed are given by the fact that the products are assumed to be in a state of chemical equilibrium. This gives two additional equations accounting for the water-gas shift reaction described above, where K_{p1} and K_{p2} are equilibrium coefficients [10-12],

$$K_{p1} = \frac{a_1 a_4}{a_2 a_3}$$

$$K_{p2} = \frac{a_1}{a_2 \sqrt{a_5}}$$

In the following expression for the burned specific heat at constant pressure is

$$C_{pb} = \sum_{i=1}^j f_i C_{pi}$$

where

f_i = mole fraction of component i

C_{pi} = specific heat at constant pressure of component i

The specific heat ratio is estimated using NASA interpolations of specific heats at constant pressure. The interpolating polynomials are given on a form

$$\frac{C_p}{R} = \alpha + \beta T^{-1} + \gamma T^{-2} + \delta T^{-3} + \epsilon T^{-4}$$

The specific heat ratio of burned hydrogen-air mixture can then be calculated.

$$k_b = \frac{C_{pb}}{C_{pb} - R} = \frac{C_{pb}}{C_{vb}}$$

The burned specific heat at constant volume is

$$C_{vb} = \sum_{i=1}^j f_i C_{vi}$$

where

C_{vi} = specific heat at constant volume of component i

Figure 1 shows specific heat at constant pressure of burned hydrogen-air mixtures as a function of temperature and relative air-fuel ratio. The relative air-fuel ratio range (λ) is between 0.6 to 1.8. The results show that the specific heat at constant pressure is maximum value at about 1.0 relative air-fuel ratio.

Figure 2 shows specific heat at constant volume of burned hydrogen-air mixtures as a function of temperature and relative air-fuel ratio. The relative air-fuel ratio range (λ) is between 0.6 to 1.8. The results show that the specific heat at con-

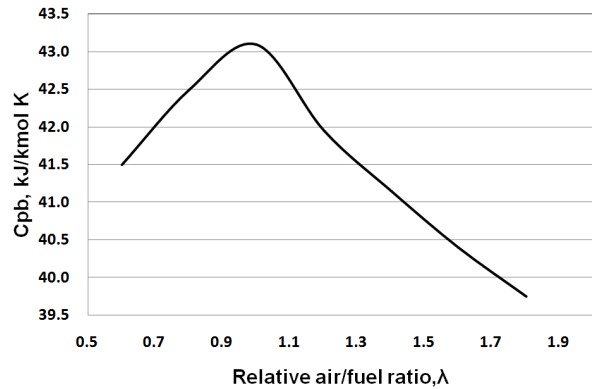


Fig. 1. Specific heat at constant pressure of equilibrium burned gases as a function of relative air/fuel ratio.

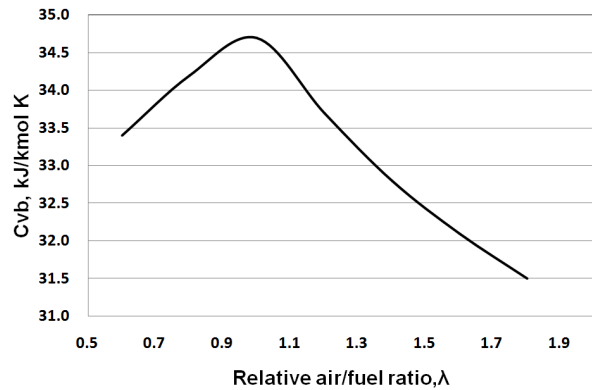


Fig. 2. Specific heat at constant volume of equilibrium burned gases as a function of relative air/fuel ratio.

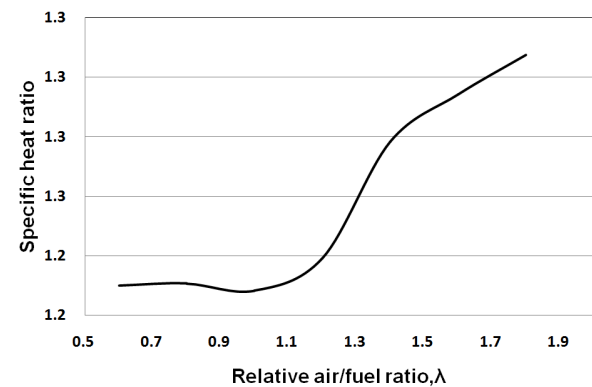


Fig. 3. Ratio of specific heat of equilibrium burned gases as a function of relative air/fuel ratio.

stant volume is maximum value at about 1.0 relative air-fuel ratio.

Figure 3 shows ratio of specific heat of equilibrium burned gases as a function of relative air/fuel

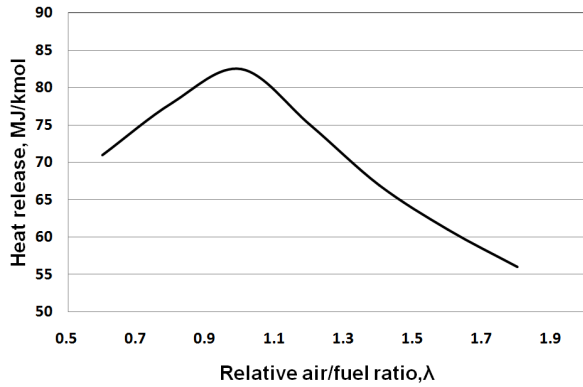


Fig. 4. Heat release of hydrogen-air mixture as a function of relative air/fuel ratio.

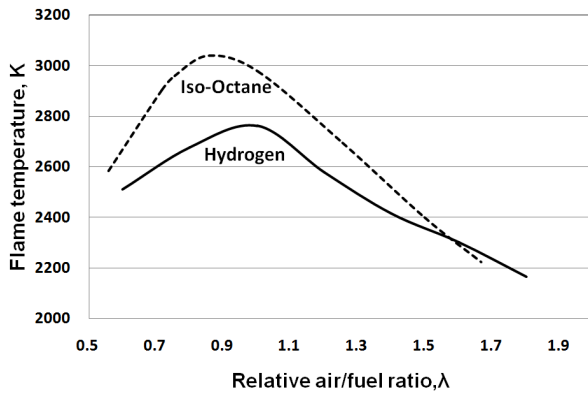


Fig. 5. Flame temperature of fuel-air mixture as a function of relative air/fuel ratio.

ratio. The relative air-fuel ratio range (λ) is between 0.6 to 1.8. The results show that the ratio of specific heat is minimum value at about 1.0 relative air-fuel ratio.

Figure 4 shows heat release of hydrogen-air mixture as a function of relative air/fuel ratio. The relative air-fuel ratio range is between 0.6 to 1.8. The results show that the heat release is maximum value at about 0.9 relative air-fuel ratio. The figure also shows that as the relative air-fuel ratio becomes leaner or richer, heat release tends to decrease due to thermal dissociation.

Figure 5 shows flame temperature of hydrogen-air and iso-octane-air mixture as a function of relative air/fuel ratio. The relative air-fuel ratio range is between 0.6 to 1.8. The results show that the flame temperature is maximum value at about 0.9 relative

air-fuel ratio. The figure also shows that as the relative air-fuel ratio becomes leaner or richer, flame temperature tends to decrease due to the thermal dissociation.

5. Thermal conductivity

Statistical thermodynamics provides the relationships that we need in order to bridge this gap between the macro and the micro. Our most important application will involve the calculation of the thermodynamic properties of the ideal gas.

The thermal conductivity of a gas is treated in the same way as its viscosity. The gas layer must be thin, and the upper plate must be at a higher temperature than the lower. The thermal conductivity is [13]

$$K_c = \frac{N V C_{vm} L_m}{3}$$

where

N : number of molecules per cubic meter

V : mean speed

C_{vm} : molecular heat capacity

L_m : mean free path

$$C_{vm} = \frac{C_v}{N_a}$$

where

C_v : specific heat at constant volume

N_a : Avogadro's number

The mean speed is given by

$$V = \sqrt{\frac{8 B T}{\pi m}} = \sqrt{\frac{8 B T}{\pi \sum_{i=1}^j Y_i m_i}}$$

where

B : Boltzmann constant

T : temperature

m : molecular weight

Y_i : mole fraction of component i

m_i : molecular weight of component i

Let us calculate the average distance traveled by a group of molecules before they make their first collision. This average distance is known as the

mean free path. If the molecules have a Maxwellian velocity distribution, the mean free path L_m is

$$L_m = \frac{0.707}{N_a \sum_{i=1}^j (Y_i \sigma_i)}$$

σ_i : collision cross section of component i

In deriving the expression for the pressure exerted by a gas, the molecules were treated as geometrical points which could fly freely from one wall of a container to the other without colliding with other molecules. Collision cross section is the area of a circle of radius d ,

$$\sigma_i = \pi d_i^2$$

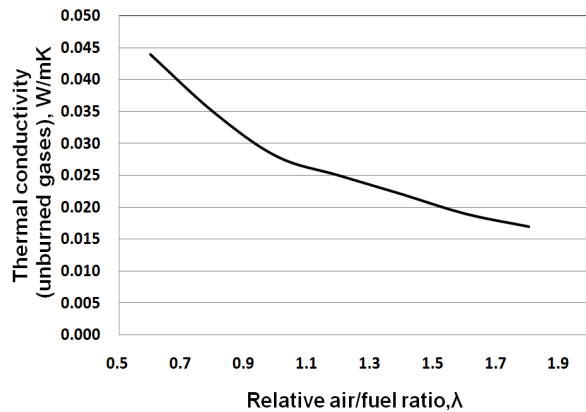


Fig. 6. Thermal conductivity of unburned fuel/air mixture as a function of relative air/fuel ratio.

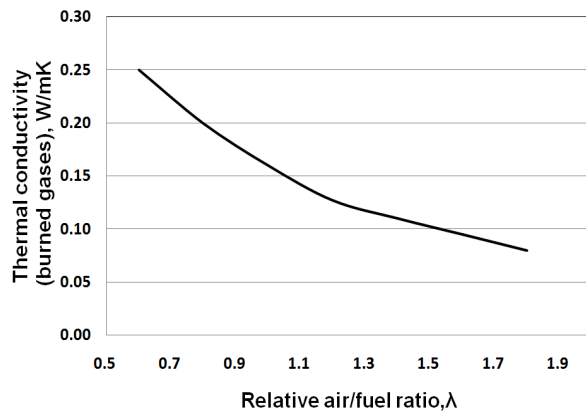


Fig. 7. Thermal conductivity of burned fuel/air mixture as a function of relative air/fuel ratio.

Finally thermal conductivity is

$$K_c = \frac{0.707 C_v \sqrt{\frac{8 B T}{\pi \sum_{i=1}^j Y_i m_i}}}{3 N_a \sum_{i=1}^j Y_i \sigma_i}$$

Figure 6 and 7 show thermal conductivity of unburned gases and burned gases of hydrogen-air mixture as a function of relative air/fuel ratio. The relative air-fuel ratio range is between 0.6 to 1.8. The results show that as the thermal conductivity of unburned gases and burned gases of hydrogen-air mixture become leaner, thermal conductivity tends to decrease due to the thermal dissociation.

6. Conclusion

The relative air-fuel ratio range (λ) is between 0.6 to 1.8. The specific heat at constant pressure represents maximum value at about 1.0 relative air-fuel ratio. The specific heat at constant volume was shown maximum value at about 1.0 relative air-fuel ratio.

The heat release and flame temperature were shown maximum value at about 0.9 relative air-fuel ratio. As the relative air-fuel ratio becomes leaner or richer, heat release and flame temperature tend to decrease due to thermal dissociation.

Statistical thermodynamics provides the relationships that we need in order to bridge this gap between the macro and the micro. As the thermal conductivity of unburned gases and burned gases of hydrogen-air mixture become leaner, thermal conductivity tends to decrease due to the thermal dissociation.

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