The Second Law (Exergy) Analysis of Hydrogen

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Abstract

As the carrier of the accepted future clean energy, hydrogen is endowed by many energy missions. If the hydrogen economy is realized, the hydrogen will certainly be the mina fuel, so it is very important to analyze the hydrogen explosion capacity, i.e. the fuel exergy of hydrogen. Based on the systematical analysis of fuel exergy, the fuel exergy of hydrogen is analyzed and discussed in this article, combining with the physical properties and the utilization trends. Through the comparison of the fuel exergy of hydrogen and other ideal gases, if the hydrogen is used for power generation, it will be scientific utilization only when the efficiency of the second law of thermodynamics exceeds 6.7 (the efficiency of natural gas) in the energy utilization, which will challenge the reasonable utilization of hydrogen. The result of analysis and computation indicates that the fuel exergy of hydrogen exceeded the lower heat value (LHV), and was less than the higher heat value (HHV).

Keywords: Hydrogen, Fuel exergy, Evaluation base

Because of the energy supply safety and the energy-saving and emission reduction, the new energy and new energy utilization mode develop continually. Hydrogen is the most ideal future clean energy carrier, and it only produces water vapors and heats. In recent years, the arisen fuel cell technology induced the concept of "hydrogen energy economy", which asserted using hydrogen to replace existing energy supplies. At present, hydrogen is only used in the chemical industries such as ammonia synthesis and oil refining. If hydrogen is used for fuels, hydrogen exergy should be first considered (Ni, 2003, P.1-10).

As well known, it is scientific and clear to use the second law of thermodynamics to analyze the fuel explosion, so the study of the hydrogen exergy and the comparison with other fuels are very important in theory and in practice.

1. Analysis of chemical exergy of fuels

According to thermodynamic definitions, the fuel exergy is the theoretical maximum power exportation ability of the fuel based on certain one base state. In Song Zhiping's article (Song, 1985, P.289), the chemical exergy of fuels can be denoted by

$$e_{ch,f}^{0} = h_{H,f}^{0} + T_0 \Delta s_R^0 + R_M T_0 [\sum_{pr} \alpha_j \ln \frac{p_0}{p_{0j}} + \alpha_{02} \ln \frac{p_0}{p_{0,O_2}}] \quad (1)$$

, where, the corner mark j denotes various products and reactants except for fuels in the basic reaction; pr under the summation symbol Σ denotes the products after fuels burn; p_{0j} denotes the sub-pressures of various products in the environmental atmosphere; α_j denotes the stoichiometric coefficient based on 1 molar fuel; T_0 and p_0 respectively denote the atmosphere temperature and pressure in the environmental state; $h_{H,f}^0$ denotes the HHV of fuel; and Δs_R^0 is the standard reaction entropy which is computed by the following formula.

$$\Delta s_R^0 = \sum_j \alpha_j s_j^0 \quad (2)$$

, where, s_j^0 denotes the absolute entropy of various products (Song, 1985, P.289). Table 1 lists the basic thermo-physical properties of hydrogen and methane.

The last one item of the formula (1) is the diffusion exergy, and because the relative quantity is less, and it is hard to utilized, so it is often omitted when computing the fuel exergy. Furthermore, this formula is deduced under the hypothesis condition of ideal gas, so it is hard to exactly compute the fuel exergy of the actual fuels. Zoran Rant suggested that the fuel exergy of fuels should be estimated according the LHV and HHV ($h^0_{H,f}$ / $h^0_{L,f}$) of fuels including gas, liquid, and solid fuels.

$$e^0_{ch,f} = \begin{cases} 0.950\, h^0_{H,f}, & \text{for gas fuels} \\ 0.975\, h^0_{H,f}, & \text{for liquid fuels} \\ h^0_{L,f} + r_{f,g} \cdot x, & \text{for solid fuels with } x \text{ moisture content} \end{cases} \quad (3)$$

, where, $r_{f,g}$ is the latent heat of vaporization of water inn the environmental temperature.

In addition, some scholars have studied relative theories about the evaluation of the fuel exergy analysis (Cengel Y, 2002, P.128-134 & Selçuk Bilgen, 2008, P.776-785 & V. S. Stepanov, 1995, P.235-242).

The computation of fuel exergy first needs to select the agent parameters of the environment, and the reference substance in the selected environment. Furthermore, the thermodynamic properties of the substance participating in the process in the system should be known. In fact, the environmental reference mode of the exergy function and the factor standard exergy function are very important to be perfected (Rosen MA, 2002, P.211-213).

2. Physical properties and application characteristics of hydrogen

Hydrogen is the lightest fuel gas, and comparing with other fuels such as coal, oil, and natural gas, it has its own characteristics.

First, hydrogen is not the primary energy, and there is not pure hydrogen in the nature and the preparation of hydrogen need consuming large numerous of energies, so it is very important to enhance the process efficiency of hydrogen in the end scientific and high-efficient utilization. Second, because hydrogen is the lightest substance, so it has the maximum unit volume. Under different pressures, the volume energy density of hydrogen is much more than other fuels such as methane, methanol, propane, and octane, and the storage and transportation consumption are much bigger. Third, the burning process of hydrogen is significantly different with other fuels, and it would produce water vapors in the burning, and if it is utilized by the mode of external fire, smoke would bring much latent heat of vaporization. The LHV of hydrogen is only 84.6% of its HHV, and this proportion is much lower than other fuels. Therefore, it is not neglected to return the latent heat of vaporization in the hydrogen utilization. In addition, the preparation cost of hydrogen is higher, and the energy transformation efficiency is lower, and the consumption in transportation, storage, and distribution is higher (Ni, 2003, P.1-10).

Therefore, even if hydrogen is the cleanest energy carrier, there are some problems in the utilization process to be analyzed. It is very important to discuss the scientific and high-efficient utilization of hydrogen and analyze its characteristics as the fuel. In fact, because hydrogen is different when it burns in pure oxygen and in air, its power explorations are different. In air, the latent heat of vaporization of water vapor is hard to be utilized, but as high-quality fuel, hydrogen should be burned in the pure oxygen.

3. Analysis and computation of fuel exergy of hydrogen

The computation base of the exergy value is the environmental reference state, and it is the state of the basic substance system in regulated temperature and pressure (Rosen MA, 2002, P.211-213). Generally, the temperature and the pressure of the environmental reference state respectively are 298.15K and 1bar, and the basic substance system includes the corresponding components of the basic substance in the atmosphere, and its components are seen in Table 2, i.e. the saturated moist air in above temperature and pressure.

Generally, the fuel exergy computed according to the formula (1) is higher than the HHV of the fuel except for the hydrogen, which is related with the accuracy of the concentration state parameters of water. That is because only water has phase change, so the error is much bigger than the hypothesis of ideal gas.

In some literatures, the basic substance of hydrogen was thought as the liquid water to compute the exergy of hydrogen, and the standard exergy of hydrogen is $116.648 MJ\cdot kg^{-1}$, lower than its LHV, which is almost completely different than other substances.

In fact, it is not proper to take liquid water as the basic substance to compute the exergy of hydrogen, and the gas state of water should be used. Though in the reference state, water is in the liquid state, but in the temperature and pressure of air, the balanced state of air and water certainly is the state of saturated moist air, and correspondingly, the water here is the multiple-state system, not pure water, so it is not right to take the pure liquid water as the basic substance. In addition, the burring products of common fuels (except for hydrogen + pure oxygen) are multiple-substance system with CO_2, and in the standard state, it is in the gas state, and not 100% water vapors could be condensed as water, and water vapors certainly are mixed in the burning products as the gas with certain sub-pressure. Therefore, the smokes produced in the burning of all fuels are multiple-state system, balancing with the environment and the air, so the reference substance of H should be the water in the gas state, not the liquid water.

According to the formula (1), if computing the hydrogen exergy based on the liquid water, the hydrogen exergy is 138.595 MJ·kg^{-1}, which exceeds the LHV of hydrogen 120MJ·kg^{-1}, and is lower than the HHV of hydrogen 142 MJ·kg^{-1}. As viewed from the practical utilization process of hydrogen, this result is reasonable.

At the same time, the estimation result of the formula (3) is basically consistent with the formula (1) based on the gas water, and it is 134.78MJ·kg^{-1}. About the relative process and computation result of the hydrogen fuel exergy, the result of the hydrogen exergy computed according to the estimation formula is more reasonable because of the utilization difficulty of the latent heat of vaporization and the present technical level.

4. Comparison analysis of hydrogen and natural gas

In the development of exergy analysis, the main problem is how to change the exergy analysis from the theoretical research to common technical staffs' practical tool (Wu, 2010). Therefore, after confirming the exergy value of hydrogen, the optimal utilization mode of hydrogen could be conformed by comparing with other fuels to make the best use of hydrogen.

Electricity is the power with the highest quality, and it is often regarded as 100% exergy, so it is very intuitional to convert the fuel exergy into the equivalent electric quantity to evaluate the energy utilization efficiencies of different fuels (Wu, 2011).

$$e_f^e = \frac{e_f^0}{3600} \quad [\text{kW·h·kg}^{-1}] \tag{4}$$

According to the formula (4), the fuel exergies of different fuels are different, that means the second law efficiencies to realize the energy utilization must be different for different fuels.

To obtain higher second law efficiency, high-quality fuel must have the energy utilization technology with higher technology level. Based on relative literature research, Table 3 listed the fuel exergy analysis results of hydrogen and natural gas.

The ratios in Table 3 show that if hydrogen is used for electricity generation as fuel, the second law efficiency must be higher 6.7% than the electricity generation of natural gas which efficiency is higher than pure methane, or else, it may be the unreasonable energy utilization mode.

The computation result indicates that for hydrogen, only more reasonable energy utilization mode could ensure higher second law efficiency.

5. Conclusions

As the future clean energy carrier, hydrogen may be the ideal fuel in the utilization, but because the preparation of hydrogen could consume much energy, so it is very important to reasonable utilize hydrogen energy.

Through comparison analysis, in the computation of fuel exergy of hydrogen, the reference state model should select the liquid water, and the computation result is basically consistent with the estimation formula. In the application, it is more practical to adopt the estimation formula.

By further analysis, if hydrogen is used for electricity generation as fuel, the second law efficiency must be higher 6.7% than the electricity generation of natural gas which efficiency is higher than pure methane, which could ensure the reasonable and scientific utilization of hydrogen as the fuel.

References

Cengel Y. (2002). Examining the merging and splitting processes in daily life in the light of exergy. *Energy Int.* No. 2(3). P.128-134.

Ni, Weidou, Zhang, Bin & Li, Zheng. (2003). Hydrogen Economy CO2 Mitigation IGCC. *Coal Conversion.* No. 26(7). P.1-10.

Rosen MA. (2002). Should we educate the public about energy. *Energy.* No. 2. P.211-213.

Selçuk Bilgen & Kamil Kaygusuz. (2008). The calculation of the chemical exergies of coal-based fuels by using the higher heating values. *Applied Energy*. No. 85. P.776-785.

Song, Zhiping & Wang Jiaxuan. (1985). *The Principle of Energy-Saving*. Beijing: Electric Press. P.399.

V. S. Stepanov. (1995). Chemical energies and exergies of fuels. *Energy*. No. 20(3). P.235-242.

Wu, Zhiquan, An, Liansuo & Zhou Shaoxiang, et al. (2011). Study on the Theoretical Foundation for Adjusting Energy Configuration. *Modern Applied Science*. No. 2.

Wu, Zhiquan, Zhou, Shaoxiang & An Liansuo, et al. (2010). Evaluation index system of energy saving and emission reduction based on fuel specific consumption for end products. *Journal of Power Engineering*. No. 6.

Zheng, Danxing, Wu, Xianghong & Zheng, dashan. (2002). Fundamental of Thermodynamic Consistency of Exergy Functions. *Journal of Chemical Industry and Engineering*. No. 53(7). P.673-679.

Table 1. Molar mass, LHV, HHV, and absolute entropy of pure fuels (Song, 1985, P.399)

Fuel	molecular weight/kg·kmol-1	$h^0_{H,f}$ /MJ·kg-1	$h^0_{L,f}$ /MJ·kg-1	$S^0_{m,j}$ /kJ·kg-1·K-1
H_2 (g)	2.0159	141.872	119.450	64.770
CH_4 (g)	16.043	55.476	49.841	11.603

Note: "g, l, s" respectively represent three states including gas, liquid, and solid.

Table 2. Composition of atmosphere in the reference environment

Composition	N_2	O_2	Ar	CO_2	Ne	He	H_2O
Molar fraction	0.7561	0.2028	0.0091	0.0003	1.77×10^{-5}	5.08×10^{-6}	0.03167

Table 3. Analysis results of fuel entropy based on the evaluation formula

Fuel	e^0_f	e^e_f	$e^0_f / h^0_{H,f}$	$b_e^{\min ce}$	Ratio*
Unit	$MJ\cdot kg^{-1}$	$kW\cdot h\cdot kg^{-1}$	-	$kgce\cdot kW^{-1}\cdot h^{-1}$	-
H_2 (g)	134.78	37.44	0.95	0.1089	1.067
CH_4 (g)	52.702	14.64	0.95	0.1162	1

Note: "ratio*" is the ratio with the carbon-based theoretical lowest unit consumption of fuel