



FUEL CELL CAR

Statement

In a press-release about fuel-cell cars it is said that a 3 kg hydrogen reservoir would give the same autonomy as a typical car (500 km at 100 km/h average speed, with a petrol reservoir of 40 litres). Assuming that petrol properties may be approximated by n-octane, find:

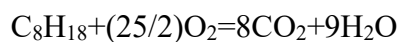
- Heating power of petrol.
- Heating power of hydrogen at 25 °C and 100 kPa, at 20 MPa and the same temperature, and at normal pressure but liquid.
- Exergy of hydrogen in the conditions above.

En un artículo sobre pilas de combustible para coches se dice que, para conseguir una misma autonomía que un coche típico (500 km a 100 km/h de velocidad media, con un depósito de gasolina de 40 litros), bastarían 3 kg de hidrógeno. Aproximando la gasolina a n-octano, se pide:

- Poder calorífico másico de la gasolina.
- Poder calorífico másico del hidrógeno a 25 °C y 100 kPa, a alta presión (20 MPa) y temperatura ambiente, y a presión ambiente y estado líquido.
- Exergía másica del hidrógeno a 25 °C y 100 kPa, a alta presión (20 MPa) y temperatura ambiente, y a presión ambiente y estado líquido.

Solution.

- The heating power of a fuel is the reaction enthalpy of combustion changed of sign. At standard conditions, the stoichiometric equation for the combustion of n-octane is:



with a molar enthalpy of reaction of $h_r^\ominus = 8(-393.5) + 9(-285.8) - (-249.9) - (25/2)0 = -5470$ kJ/mol, i.e. a higher heating value (HHV) of $5.47/0.114 = 48.0$ MJ/kg typical of hydrocarbons (LHV = $(5.47 - 9 \cdot 0.044)/0.114 = 44.5$ MJ/kg).

- Similarly for hydrogen at standard conditions: $\text{H}_2 + (1/2)\text{O}_2 = \text{H}_2\text{O}$, $h_r^\ominus = -286$ kJ/mol, i.e. a HHV = 143 MJ/kg (LHV = $242/2 = 121$ MJ/kg). That was for 100 kPa and 298 K; at that temperature but high pressure the value is the same because, for ideal substances, enthalpy does not depend on pressure, but for liquid state the temperature is $T_b = 20$ K and, to the standard enthalpy, we had to subtract the enthalpy needed to boil and heat at constant pressure the gas from 20 K to 298 K. The boiling enthalpy is 0.45 MJ/kg, and for heating the gas $c_p \Delta T = 14200(298 - 20) = 3.9$ MJ/kg (having assumed that the decrease of thermal capacity at low temperatures is not important). Thus, the higher heating power decreases to $(143 - 0.45 - 3.9) = 139$ MJ/kg when liquid hydrogen is used.
- The standard exergy of hydrogen (i.e. the minimum work needed to synthesise it from the standard atmosphere, separating H_2O , decomposing it and returning the extra O_2) is:

$$\psi_{\text{H}_2}^{\oplus} = \psi_{\text{H}_2\text{O}}^{\oplus} + g_r^{\oplus} - \frac{1}{2}\psi_{\text{O}_2}^{\oplus}$$

From Table 9.1 $\psi_{\text{H}_2\text{O}}^{\oplus}=1.3$ kJ/mol_{H₂O} and $\psi_{\text{O}_2}^{\oplus}=3.9$ kJ/mol_{O₂}, and $g_r^{\oplus}=g_{f,\text{H}_2}^{\oplus}+(1/2)g_{f,\text{O}_2}^{\oplus}-g_{f,\text{H}_2\text{O}}^{\oplus}=0+(1/2)0-(-237.2)=237.2$ kJ/mol, thus, $\psi_{\text{H}_2}^{\oplus}=236.6$ kJ/mol, i.e. 118 MJ/kg for standard conditions, meaning that the maximum work obtainable from 1 kg of H₂ at standard conditions in the reference atmosphere is 118 MJ.

It may cause surprise to see that creating H₂ from the standard environment costs 236.6 kJ/mol and one might obtain 237.2 kJ/mol just from the oxidation reaction, plus some additional exergy from the products. The explanation is that exergy of reactions are referred to standard conditions of pure separated substances, i.e. for pure H₂ and O₂ in this case, whereas the exergy for H₂ with air is lower because O₂ has to be initially separated (for accounting, not in the real process); i.e., with H₂ and air, the maximum work one might get (in an ideal fuel cell) is $\psi_r^{\oplus} - (1/2)\psi_{\text{O}_2}^{\oplus}=237.2-3.9/2=235.2$ kJ/mol, less than the 236.6 kJ/mol it costs to produce it.

For high pressure, the additional exergy (for a perfect gas) is $T^{\oplus}R\ln(p/p^{\oplus})=298\cdot 8.3\cdot\ln(20/0.1)=13$ kJ/mol, whereas for low temperature the additional exergy $c_p(T-T^{\oplus})-T^{\oplus}c_p\ln(T/T^{\oplus})=(14200\cdot 0.002)(20-298)-298\cdot(14200\cdot 0.002)\cdot\ln(20/298)=15$ kJ/mol.

In conclusion: hydrogen exergy at the standard state is 118 MJ/kg, at high pressure 124 MJ/kg, and at cryogenic temperature 125 MJ/kg. Notice that the heating power was lower at cryogenic temperature than at standard conditions, but the exergy is greater.

Comments. It is difficult to compare the performances of a typical petrol car with that of a fuel-cell car because there is not only the difference in fuel power but also on the engine efficiency. As for the heating power of fuel, a 40 litres petrol reservoir, with $\rho_{\text{petrol}}=700$ kg/m³, gives $(0.040\cdot 700)\cdot 48=1340$ MJ, whereas a 3 kg cryogenic hydrogen reservoir would give $3\cdot 125=375$ MJ, less than 30% of the former. Of course, the fuel cell engine would have double energy efficiency than the petrol engine, but even so the comparison is adverse.

It happens that in practice the volume and mass of the full reservoir is nearly the same for the three cases: petrol reservoir, high pressure hydrogen, and cryogenic hydrogen.

Modern fuel-cell cars have a hydrogen capacity of 5 kg instead of the 3 kg used in this exercise.

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