A liquid organic carrier of hydrogen as a fuel for automobiles

(Nuclear power as a motive power for cars)

M. Taube, P. Taube

Würenlingen, September 1979
A LIQUID ORGANIC CARRIER OF HYDROGEN
AS A FUEL FOR AUTOMOBILES

(Nuclear power as a motive power for cars)

M. Taube, P. Taube*

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* temporary co-worker
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Abstract

A system of storing energy in a hydrogen containing fuel for the motor car is discussed. The recyclable liquid chemical carrier is:

\[(\text{Methylcyclohexane}_{\text{liquid}})_{\text{dehydrogenation}} (\text{Toluene}_{\text{liquid}}) \rightarrow (\text{Hydrogen}_{\text{gas}})\]

The reverse reaction, the hydrogenation of toluene, occurs in a regional plant connected to a source of hydrogen (electrolysis of water) with a significant by-product being heat at 200 °C for district heating. The system is able to store hydrogen in liquid form under ambient temperature and pressure even in a small motor car. The concentration of hydrogen is 6.1% by weight. The release of gaseous hydrogen from the liquid methylcyclohexane needs a chemical catalytic reactor having a temperature of 300 °C and a pressure of some bars. The reaction has been well studied. The thermal energy for the dehydrogenation is taken from the exhaust gases at 760 °C.

A layout of the most important processes of the system is given. As a reference case a "motor car of tomorrow" is taken, having a total power of 20 kW (me) and an average power of 10 kW (me). Distances travelled on the open road are 320 km, in the city 170 km. The mean efficiency of the hydrogen engine is 25%. For this car the proposed system consists of a 120 litre tank for the liquid organic carrier, and a catalytic tank of 15 litres. During a longer parking period the continuous heating of the insulated reactor requires less than 100 watts taken from a battery and can be supplied for some hours. Starting the cold engine and acceleration makes it necessary to burn small amounts of the toluene directly - less than 2% of the amount carried.
The local regional hydrogen filling station in supplying a population of approx 10,000 people having 1000 hydrogen driven vehicles, includes an electrolysis plant, hydrogenation plant for converting toluene into methylcyclohexane and the tanks for storing the two liquids.

The hydrogen is produced during periods of low electrical load (8 hours). The electrical power required is 6 MW(el): the daily production 1140 kg hydrogen which provides annually for 1000 small vehicles the power to travel 15,000 km. For the economic solution in Switzerland one has the following parameters (1 SFr = Swiss Franc ≈ 0.5 US$ (1979):

<table>
<thead>
<tr>
<th>Year</th>
<th>SFr/kWh (el)</th>
<th>Price of heating oil and gasoline without taxes; SFr/litre</th>
</tr>
</thead>
<tbody>
<tr>
<td>1979</td>
<td>0.042</td>
<td>0.80</td>
</tr>
<tr>
<td>2000</td>
<td>0.061</td>
<td>0.55</td>
</tr>
</tbody>
</table>

1. Liquid organic carrier of hydrogen as an automobile fuel.

One of the important aims of future energy planners is to try and couple the nuclear power plant with the fuel system of the motor car. One possible scheme might be:

Nuclear fuel → nuclear power station → electricity → electrolysis of water → hydrogen → fuel for the motor car.

The best known system is to use solid metal hydrides as the storage for automobile fuel:
As an alternative, Sultan and Shaw, 1975 (26) have proposed the following system using liquid "organic hydrides":

From source
(filling station)

\[
\begin{align*}
\text{Prom source} & \rightarrow (H_2) + \{\text{Me}\} \text{ load} \{\text{MeH}_x\} \\
\text{unloaded storage} & \rightarrow \text{loaded storage} \\
\text{in the car}
\end{align*}
\]

Used by engine

\[
\begin{align*}
\text{Used by engine} & \rightarrow (H_2) + \{\text{Me}\} \text{ unload} \{\text{MeH}_x\} \\
\text{in the car}
\end{align*}
\]

The chemical reaction is:

\[
(3H_2) + \{C_7H_8\} \text{ load} \{C_7H_14\} \rightarrow 210 \text{ kJ/mol MC}
\]

The enthalpy \( Q_{de} = 210 \text{ kJ/mol MC} \) comes from the hydrogenation of toluene and is not connected with the enthalpy of hydrogen burning.

The system could be used as a storage method for hydrogen fuel for the motor car as shown in figure 1. The reference car system is given in table 1.

The system proposed is called MTH:

\( \text{(Methylcyclohexane, Toluene, Hydrogen)} \).

The symbols used in this paper are:

- gaseous ( ) or g
- liquid \{ \} or l
- solid [ ] or s
- \( x \) = stoichiometric coefficient
- \( \text{Me} \) = metal
- \( H_2 \) = gaseous hydrogen
2. Physical and chemical properties of the components.

Both the components of the proposed system, that is methylcyclohexane (MC) and toluene (TO), are liquid at ambient temperatures. Their freezing points lie around -100 °C and boiling points around +100 °C. Table 2 gives their most important properties.

A rather important problem involving the storage of energy for the motor car is the fact that the dehydrogenation of methylcyclohexane requires heat \( Q_{de} \) from an external source:

\[
\text{Methylcyclohexane} + Q_{de} \rightarrow \text{Toluene} + (3H_2)
\]

The value of \( Q_{de} \) is:

- 210 kJ/mol MC
- 1.25 MJ/kg MC
- 35.2 MJ/kg \( H_2 \)
Table 1: The reference motor car.

<table>
<thead>
<tr>
<th>Property</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight of car without fuel</td>
<td>kg</td>
<td>900</td>
</tr>
<tr>
<td>Peak engine power</td>
<td>kW(me)</td>
<td>20</td>
</tr>
<tr>
<td>Mean engine power</td>
<td>kW(me)</td>
<td>1(^a)</td>
</tr>
<tr>
<td>Engine volume</td>
<td>l</td>
<td>1</td>
</tr>
<tr>
<td>Mechanical (thermal) efficiency</td>
<td>%</td>
<td>25 (%) (hydrogen)</td>
</tr>
<tr>
<td>Equivalence ratio for hydrogen</td>
<td>%</td>
<td>20 (%) (gasoline)</td>
</tr>
<tr>
<td>Exhaust gas temperature</td>
<td>°C</td>
<td>0.46*</td>
</tr>
<tr>
<td>Operation distance</td>
<td>km</td>
<td>326</td>
</tr>
<tr>
<td>open road</td>
<td></td>
<td></td>
</tr>
<tr>
<td>city</td>
<td>km</td>
<td>170</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Fuel rating</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>gasoline open road</td>
<td>f/100 km</td>
<td>6.45</td>
</tr>
<tr>
<td>city</td>
<td>f/100 km</td>
<td>12.8</td>
</tr>
<tr>
<td>gasoline in tank</td>
<td>kg</td>
<td>16.0</td>
</tr>
<tr>
<td>hydrogen gas</td>
<td></td>
<td></td>
</tr>
<tr>
<td>open road</td>
<td>kg/100 km</td>
<td>1.53</td>
</tr>
<tr>
<td>city</td>
<td>kg/100 km</td>
<td>1.90</td>
</tr>
<tr>
<td>hydrogen in tank</td>
<td>kg</td>
<td>5</td>
</tr>
</tbody>
</table>

| Organic liquid carrier                        |      |                     |
| (6.1 weight %; 95 % efficiency)              |      |                     |
| open road                                     | f/100 km | 34.2               |
| city                                          | f/100 km | 65.0               |
| organic carrier in tank                       | kg   | 85 (see appendix)  |
| Organic/gasoline weight ratio                 | l    | 116                 |

Note for Table 1: \(^a\) The operation of the hydrogen burning engine at an equivalence ratio \(\phi = 0.5 - 0.6\) improves the brake thermal efficiency by 10 \(\%\) to 20 \(\%\) compared to gasoline burning at \(\phi = 0.91\).

\(^*\) see appendix 9.3
Fig. 1A Simplified scheme for the fuelled car system.

- Tank ~ 120 l
- Condensator/Evaporator: T = 100°C, p = a few bars
- Catalytic Reactor: \( \approx 15 \text{ kW(th)} \), T = 315°C, p = some bars
- Internal combustion engine (OTTO): Mean efficiency \( \approx 25\% \)
- Exhaust gases
- Average power: 10 kW(me) (25%)
- Radiation: 4 kW(th) (10%)
- Cooling water: 8 kW(th) (20%)

Average \( H_2 \) 40 kW(ch) (100%)
Since the heat of combustion $Q_{co}$ of hydrogen is 121 MJ/kg $H_2$, the relation to the heat of dehydrogenation is

$$\frac{Q_{de}}{Q_{co}} = \frac{35.2}{121} \approx 0.28$$

Such a large amount of heat at the required temperature could be obtained from the following sources:

- exhaust gases from the engine
- additional burning of hydrogen

This paper proposes the use of the heat contained in the exhaust gases which equals 45% of the total energy balance at a temperature of 780 °C which is very high but by no means unreasonable (see appendix 9.1 and 9.4 for an exact calculation).

Additional serious problems of the system proposed are:

- the catalytic dehydrogenation of methylcyclohexane is a rather complex process
- the catalysts from this process have been extensively and intensively investigated. Not all technological details have been proven
- the best known catalysts for the dehydrogenation of methylcyclohexane are:
  - platinum on $Al_2O_3$ (ref. 24, 25)
  - vanadium oxide on $Al_2O_3$
  - copper-nickel
  - cobalt alloys
  - aluminium-cobalt-chromium-zinc
  - aluminium-chromium-molybdenum
  - nickel-phosphorus
  - aluminium-titanium-vanadium
  - chromium
  - ruthenium-silica
  - aluminium-molybdenum-nickel
- the life of the catalysts should be at least 100 h. This permits the reactivation of the catalysts every \( \frac{100}{120} \) km, that is 3 times per year. To be competitive the cost of regeneration must be below some tens of dollars.
- the dehydrogenation reaction produces some unwanted by-products. These could adversely affect the life of the catalyst but also the total recycling process, that is the hydrogenation and storage of toluene.

3. Layout of the main components in the motor car.

The most important and crucial element of the system is the catalytic dehydrogenation unit. Table 3 shows the principle calculations giving the material flows for the car. Table 4 gives the layout calculations for the appropriate hydrogenation unit.

One can conclude from the thermodynamic calculations that to achieve the hydrogenation a thermal flux of \( \approx 15.2 \text{ kW(th)} \) at more than 315 °C is needed.

The question arises whether it is possible to extract this amount of heat from the only easily available source in the car, that is the exhaust gases.

Appendix 9.3 and 9.4 give the calculation of the heat capacity of the exhaust gases.

Figure 2 shows the values obtained from the calculations referred to above.
Table 2: Physical, chemical and toxic properties of components of the
NTH-System.

<table>
<thead>
<tr>
<th>Property</th>
<th>Unit</th>
<th>Hydrogen Fuel ** System</th>
<th>Conventional Fuel octane, gasoline</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C₅H₁₂</td>
<td>C₈H₁₈</td>
</tr>
<tr>
<td>Formula</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Function</td>
<td>-</td>
<td>only as carrier of hydrogen</td>
<td>for direct burning</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>kg/mol</td>
<td>32.15</td>
<td>36.19</td>
</tr>
<tr>
<td>Boiling point</td>
<td>°C</td>
<td>118.6</td>
<td>111.2</td>
</tr>
<tr>
<td>Freezing point</td>
<td>°C</td>
<td>- 95</td>
<td>- 126.6</td>
</tr>
<tr>
<td>Heat of vaporization</td>
<td>kJ/g</td>
<td>347</td>
<td>321</td>
</tr>
<tr>
<td></td>
<td>kJ/mol</td>
<td>31.4</td>
<td>31.5</td>
</tr>
<tr>
<td>Vapour pressure (20°C)</td>
<td>bar</td>
<td>0.03</td>
<td>0.07</td>
</tr>
<tr>
<td>Density (20°C)</td>
<td>kg/l</td>
<td>0.867</td>
<td>0.789</td>
</tr>
<tr>
<td></td>
<td>l/mol</td>
<td>0.106</td>
<td>0.127</td>
</tr>
<tr>
<td>Viscosity</td>
<td>cP</td>
<td>0.590</td>
<td></td>
</tr>
<tr>
<td>Heat capacity</td>
<td>J/mol K</td>
<td>160.1</td>
<td>150.1</td>
</tr>
<tr>
<td>liquid</td>
<td>J/g K</td>
<td>1.738</td>
<td>1.53</td>
</tr>
<tr>
<td>gas (25°C)</td>
<td>J/g K</td>
<td>1.84</td>
<td>2.49</td>
</tr>
<tr>
<td>gas</td>
<td>J/mol K</td>
<td>170</td>
<td>243</td>
</tr>
<tr>
<td>Heat of dehydrogenation</td>
<td>kJ/mol</td>
<td>-</td>
<td>(290°C): 204.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(270°C): 215.5</td>
</tr>
<tr>
<td>Heat of burning</td>
<td>kJ/l</td>
<td>-</td>
<td>only hydrogen</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5.64</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>per litre neat</td>
</tr>
<tr>
<td>Toxicty</td>
<td>part per Megas</td>
<td>100</td>
<td>400</td>
</tr>
<tr>
<td></td>
<td>mg/m³ air</td>
<td>380</td>
<td>1000</td>
</tr>
<tr>
<td>Price, 19/12 March</td>
<td>US $/gallon</td>
<td>0.7-</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 3: The calculation of the material flow for the reference motor car.

<table>
<thead>
<tr>
<th>Property</th>
<th>Obtained by</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference car</td>
<td>---</td>
<td>---</td>
<td>see table 1</td>
</tr>
<tr>
<td>Average mechanical power</td>
<td>postulation</td>
<td>kW(me)</td>
<td>10</td>
</tr>
<tr>
<td>Efficiency</td>
<td>estimation</td>
<td>%</td>
<td>25 *)</td>
</tr>
<tr>
<td>Equivalence ratio</td>
<td>see appendix</td>
<td>g = \lambda ^{-1}</td>
<td>0.46</td>
</tr>
<tr>
<td>Average thermal power</td>
<td>10 kW(me) x \frac{1}{0.25}</td>
<td>kW(th)</td>
<td>40</td>
</tr>
<tr>
<td>Average flow of heat</td>
<td></td>
<td>kW/s</td>
<td>40</td>
</tr>
<tr>
<td>Heat of combustion of hydrogen</td>
<td>from literature</td>
<td>MJ/kg</td>
<td>121</td>
</tr>
<tr>
<td>Hydrogen flux for power given above</td>
<td>(40 kW/s) \cdot (24.2 kJ/mol)</td>
<td>mol H \textsubscript{2}/s</td>
<td>0.164</td>
</tr>
<tr>
<td>Methylcyclohexane as source of hydrogen</td>
<td>MC \rightarrow 3 \textsubscript{H} \textsubscript{2} + T0</td>
<td>mol H \textsubscript{2}</td>
<td>0.333</td>
</tr>
<tr>
<td>MC flux for power given above</td>
<td>(0.164) x (0.333)</td>
<td>mol T0</td>
<td>1.0</td>
</tr>
<tr>
<td>Efficiency of dehydrogenation process</td>
<td>estimation</td>
<td>%</td>
<td>95</td>
</tr>
<tr>
<td>MC flux including efficiency</td>
<td>(0.055) x (1.0, 0.95)</td>
<td>mol MC/s</td>
<td>0.96</td>
</tr>
</tbody>
</table>

*) The higher efficiency for the hydrogen engine of 25 %, rather than the 20 % efficiency of gasoline engine is based on ref. 20, 29. (see also 9.8)
4. Environmental problems

As can be seen from table 2 the toxicity of both liquid components MC and TO are the same as for gasoline.

Air pollution from the hydrogen engine compared to the gasoline engine has been extensively discussed.

The thermal pollution of the proposed motor car is essentially lower than that of the petrol driven vehicle. For the latter the heat losses are

- exhaust gases 18 kW(th)
- cooling water and radiation 12 kW(th)

Total 30 kW(th)

The car based on the MTH system has losses in the cooling water and in direct radiation of approx 15 kW(th) plus in the exhaust gases only 3 kW(th). The thermal pollution is thereby approximately halved.

These thermal differences, amounting to approx 15 kW per vehicle can be realised at the local hydrogenation station at ~ 300 °C and be used for local district heating. (see below).

5. The local filling station

This chapter considers the feasibility of the local hydrogen filling station which has the following complex functions.

- production of hydrogen by means of the electrolysis of water, during the low load period (8 h in the night). Supposing approx 1000 hydrogen driven cars covering each 15'000 km per year.
Table 4: Simplified calculation of the catalytic dehydrogenation unit.

<table>
<thead>
<tr>
<th>Property</th>
<th>Obtained from</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methylecyclohexane flux average</td>
<td>see table 3</td>
<td>mol MC/s</td>
<td>0.06</td>
</tr>
<tr>
<td>Specific volume of catalyst</td>
<td>according Faith (1972)</td>
<td>m³/s/(mol MC)</td>
<td>0.06</td>
</tr>
<tr>
<td>Volume of reactor</td>
<td>(0.06)x(0.06 mol MC/s)</td>
<td>m³</td>
<td>0.004 calculated 0.013 for further calculation (arbitrary)</td>
</tr>
<tr>
<td>Temperature of catalyst</td>
<td>according Faith (1972)</td>
<td>K</td>
<td>590</td>
</tr>
</tbody>
</table>
| Temperature of exhaust gases                          | estimation                           | K                      | 1050* see table 5 
and appendix |
| - from engine                                         | postulation                          | K                      | 610   |
| - after reactor                                       | LOGMD = \frac{(1050-590)-(610-590)}{ln \frac{1050-590}{610-590}} K | ~ 140 |
| Logarithmic medium temperature difference             | rough estimation                     | W/m².K                 | 150   |
| Overall heat transfer coefficient                      | literature                           | kW/mol MC               | ~ 210 |
| Heat of dehydrogenation of MC                         |                                     |                        |       |
| Heat flux to reactor                                   | see table 3                          | kW(th)                 | ~ 15.2 |
| Heating surface needed                                |                                      | m²                     | ~ 0.73 |
| Length of tube                                        | arbitrary                            | m                      | 0.5   |
| Diameter of tube                                      | \frac{4x10^{-3} m^2}{0.73 m}         | m                      | 0.022 |
| Surface of 1 tube                                     | (0.5)x(0.022 )                       | m²                     | 0.534 calculated |
| Number of tubes                                       | \frac{(0.73)/(0.034)}                | number                 | 21    |
| Volume of 1 tube                                      | (0.5)x(0.022² x 3.14/4)             | m³                     | 0.0002 for |
| Length of tubes                                       | \frac{(0.73)/(0.034)}                | number                 | 21    |
| Number of tubes                                       | \frac{(4x10^{-3} m^3)/(0.002 m^3)}   | number                 | ~ 20 |

Note: All calculations are approximate and subject to further refinement.
Table 4: Continuation

<table>
<thead>
<tr>
<th>Property</th>
<th>Obtained from</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wall thickness</td>
<td>arbitrary</td>
<td>m</td>
<td>$1.2 \times 10^{-3}$</td>
</tr>
<tr>
<td>Wall unit, surface</td>
<td>$(0.022)^2 x (3.14/4)$</td>
<td>m²</td>
<td>0.042</td>
</tr>
<tr>
<td>Wall unit, volume</td>
<td>$(0.042) x (1.2 \times 10^{-3})$</td>
<td>m³</td>
<td>$5 \times 10^{-5}$</td>
</tr>
<tr>
<td>Density of steel</td>
<td>literature</td>
<td>kg/m³</td>
<td>7500</td>
</tr>
<tr>
<td>Mass of tubes</td>
<td>$(14)(0.5)(5 \times 10^{-5}) x (7500)$</td>
<td>kg</td>
<td>2.6</td>
</tr>
<tr>
<td>Catalyst, volume</td>
<td>from above</td>
<td>m³</td>
<td>0.004 *)</td>
</tr>
<tr>
<td>Specific weight of catalyst</td>
<td>arbitrary</td>
<td>kg/m³</td>
<td>2000</td>
</tr>
<tr>
<td>Catalyst weight</td>
<td>$(0.004)(2000)$</td>
<td>kg</td>
<td>8</td>
</tr>
<tr>
<td>Reactor pitch</td>
<td>arbitrary (length/diameter)</td>
<td>L/D ratio</td>
<td>1</td>
</tr>
<tr>
<td>Cross section</td>
<td>$21 x (0.022 x 2)^2$</td>
<td>m²</td>
<td>0.04 see</td>
</tr>
<tr>
<td>Diameter</td>
<td>$(0.04 \times 4/3.14)^{1/2}$</td>
<td>m</td>
<td>0.22 also</td>
</tr>
<tr>
<td>Reactor volume</td>
<td>$(0.04)(0.5)$</td>
<td>m³</td>
<td>0.020 appendix</td>
</tr>
<tr>
<td>Reactor surface</td>
<td>$(0.03 x 2) + (0.5 x 0.22)$</td>
<td>m²</td>
<td>0.19 dix</td>
</tr>
<tr>
<td>Insulation, thickness</td>
<td>arbitrary</td>
<td>m</td>
<td>0.1</td>
</tr>
<tr>
<td>Heat conductivity</td>
<td>literature</td>
<td>W/m·K</td>
<td>0.05</td>
</tr>
<tr>
<td>Temperature difference</td>
<td>estimated</td>
<td>K</td>
<td>300</td>
</tr>
<tr>
<td>Heat losses</td>
<td>$(0.19)(0.05/0.1)(300)$</td>
<td>W (th)</td>
<td>$\approx 30$ arbitrary</td>
</tr>
<tr>
<td>Relative heat losses</td>
<td>$(30 W)/(40000 W)$</td>
<td>%</td>
<td>$\approx 0.2$</td>
</tr>
<tr>
<td>Electrical battery for heat losses</td>
<td>$60 W \times 10 h$ equivalent to $12 V \times 50 Ah$</td>
<td>Wh (el)</td>
<td>600</td>
</tr>
<tr>
<td>Heat capacity of reactor</td>
<td>$(0.02 m^3)(0.5 kJ/kg\cdot K) x (2000 kg/m^3)$</td>
<td>kW (th)</td>
<td>6</td>
</tr>
</tbody>
</table>

* Note: The power needed for acceleration (see appendix 9.6) is not included.
## Table 5: Exhaust gases balance and tank-volume (see appendix 9.2)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Obtained from</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Exhaust gases</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrogen flux</td>
<td>from above given calculation</td>
<td>mol/s</td>
<td>0.17</td>
</tr>
<tr>
<td>Equivalence rating maximum lean</td>
<td>according Karim (1966)</td>
<td>( \dot{V} (\lambda = 0^{-1}) )</td>
<td>0.46 (( \lambda = 2.17 ))</td>
</tr>
<tr>
<td>Relative mass of exhaust gases</td>
<td>according Finegold (1978)</td>
<td>g/exhaust</td>
<td>151</td>
</tr>
<tr>
<td>Mass of exhaust gases</td>
<td>((151 \text{ g air/mol } H_2) \times )</td>
<td>g/s</td>
<td>76</td>
</tr>
<tr>
<td></td>
<td>( (0.17 \text{ mol } H_2/s) )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Specific heat of exhaust gases</td>
<td>estimated</td>
<td>J/g*K</td>
<td>1.2 (see appendix)</td>
</tr>
<tr>
<td>Temperature of exhaust gases: input</td>
<td>see appendix 9.4</td>
<td>°C</td>
<td>777</td>
</tr>
<tr>
<td>Output temperature</td>
<td>see appendix 9.4</td>
<td>°C</td>
<td>1050</td>
</tr>
<tr>
<td>Temperature difference</td>
<td>((T \text{ input}) - (T \text{ output}) = LT)</td>
<td>°C</td>
<td>440</td>
</tr>
<tr>
<td>Heat capacity of exhaust gases</td>
<td>((26 \text{ g/s}) \times (1.2 \text{ J/g*K}) \times )</td>
<td>J/s</td>
<td>15'500</td>
</tr>
<tr>
<td></td>
<td>( (440 \text{ K}) )</td>
<td>kW (th)</td>
<td>15.5</td>
</tr>
<tr>
<td><strong>Tank volume (simplified)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrogen flux</td>
<td>from above</td>
<td>mol ( H_2/s )</td>
<td>0.17</td>
</tr>
<tr>
<td>Methylcyclohexane storage, load</td>
<td>((0.17 \times 0.3) \times (0.127 \text{ x/mol}) \times (4.2 \text{ hr}))</td>
<td>( x )</td>
<td>110</td>
</tr>
<tr>
<td>Toluene storage unload</td>
<td>((100 \text{ l}) \times 0.83)</td>
<td>( l )</td>
<td>92</td>
</tr>
<tr>
<td>Equivalent gasoline value</td>
<td>estimated</td>
<td>( l )</td>
<td>20</td>
</tr>
<tr>
<td>Tank dimension</td>
<td>arbitrary</td>
<td>( m )</td>
<td>120</td>
</tr>
<tr>
<td></td>
<td>side of tank</td>
<td>( (0.66) \times (0.66) \times )</td>
<td>( (0.25) )</td>
</tr>
<tr>
<td>Tank weight (empty)</td>
<td>approximately</td>
<td>kg</td>
<td>20</td>
</tr>
</tbody>
</table>
FIG 2. THERMAL SCHEME

Tank content (equivalent):
- 620 kJ(th)
- 172 kWh(th)

by $\varphi = 0.25$:
- 43 kWh(me)
- 10 kW(me) x 4.3h

Condensator/Evaporator
- 2.3 kW(th)
- $T = 100^\circ C$

Heating
- $\sim 15$ kW(th)
- $T = 315^\circ C$

Exhaust gases:
- $T = 340^\circ C$
- 26 g/s

Engine
- Average Efficiency: 25 %

Average power: 10 kW(me)

Cooling water

Radiation

Battery 12V x 50 Ah

(Air) 25.6 g

Condenser
- $0.06$ mol/s

Condenser
- $0.055$ mol/s
- $0.005$ mol/s

Condenser
- $0.06$ mol/s

Condenser
- $0.06$ mol/s

Condenser
- $0.06$ mol/s
- use of this hydrogen in the hydrogenation of toluene transforming it to methylcyclohexane, the hydrogen carrier in the tanks of the motor cars.

- recovery of the "thermal waste" from the electrolysis and hydrogenation plant to supply local district heating for some thousand people.

Figure 3 shows a simplified scheme of the proposed MTH system. Table 6 gives details of the calculations.

6. Some economic considerations

On the basis of established sources such as the "Schlussbericht der Eidg. Kommission für Gesamtenergiekonzeption, Bern 1978" some economic calculations have been made and are presented in Table 7. See also Figure 5.

Figure 6 also shows the partial cost of the hydrogen fuel produced in the form of liquid methylcyclohexane and the bonus in the recovery of the waste heat from electrolysis (~ 150 °C) and hydrogenation (~ 300 °C).
FIG 3. SCHEME OF THE REGIONAL FILLING STATION

Nuclear power station; Light water reactor

Electrolysis plant

Hydrogenation plant

District heating station

HN (Heat network)

H2

Electrolysis plant

Hydrogenation plant

District heating station

HN

EG

EG

Tank

Dehydrogenator

Engine
Table 5: Energy balance of the local hydrogen filling station.

<table>
<thead>
<tr>
<th>Object</th>
<th>Operation</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Region</td>
<td>arbitrary</td>
<td>population</td>
<td>10^6</td>
</tr>
<tr>
<td>Motor cars, total</td>
<td>assumption</td>
<td>cars/region</td>
<td>5000</td>
</tr>
<tr>
<td>Motor cars, hydrogen</td>
<td>assumption</td>
<td>-- &quot; &quot;</td>
<td>1000</td>
</tr>
<tr>
<td>Electricity consumption</td>
<td>according GEX ZGGO</td>
<td>kW · y (el) / y · capita</td>
<td>1.1</td>
</tr>
<tr>
<td>Ratio of low/high load</td>
<td></td>
<td>ratio</td>
<td>1.75</td>
</tr>
<tr>
<td>&quot;Free&quot; capacity, low load</td>
<td>calculated</td>
<td>kW (el) average</td>
<td>0.6</td>
</tr>
<tr>
<td>&quot;Free&quot; capacity in the region</td>
<td>0.6 x 10^6</td>
<td>MW (el)</td>
<td>6</td>
</tr>
<tr>
<td>Daily &quot;free&quot; energy</td>
<td>6000 kW(el) x 8 h</td>
<td>GJ (el)/d</td>
<td>173</td>
</tr>
<tr>
<td>Electrolysis of water</td>
<td>efficiency, assumed</td>
<td>%</td>
<td>50</td>
</tr>
<tr>
<td>Chemical energy in H₂</td>
<td>173 GJ(el) x 0.30</td>
<td>GJ(H₂)/d</td>
<td>138</td>
</tr>
<tr>
<td>Amount of hydrogen</td>
<td>138 GJ/(0.121 GJ/kg)</td>
<td>kg H₂/d</td>
<td>1140</td>
</tr>
<tr>
<td>Heat waste, electrolysis</td>
<td>173 GJ(el) x 0.20</td>
<td>GJ(th)/d</td>
<td>~ 35</td>
</tr>
<tr>
<td>Heat waste, hydrogeneration</td>
<td>138 GJ(ch) x 0.28</td>
<td>GJ(th)/d</td>
<td>~ 38</td>
</tr>
<tr>
<td>Total heat &quot;waste&quot;</td>
<td>35 + 38</td>
<td>GJ(th)/d</td>
<td>~ 73</td>
</tr>
<tr>
<td>Ratio waste/electricity</td>
<td>35/173</td>
<td>ratio</td>
<td>0.2</td>
</tr>
<tr>
<td>Total amount of H₂</td>
<td>1140 kg (\text{d}^{-1} \times 360 \text{d}^{-1} \text{y}^{-1})</td>
<td>t H₂/y</td>
<td>410</td>
</tr>
<tr>
<td>Chem. energy in H₂</td>
<td>3110 t/y x 121 GJ/(\text{ch})</td>
<td>GJ(ch)/y</td>
<td>50'000</td>
</tr>
</tbody>
</table>
Table 6: Continuation

<table>
<thead>
<tr>
<th>Object</th>
<th>Operation</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy per car</td>
<td>50'000/1'000</td>
<td>GJ(ch)/y</td>
<td>50</td>
</tr>
<tr>
<td>Thermal power/car</td>
<td>during 300 h/y</td>
<td>kW (th)</td>
<td>~ 45</td>
</tr>
<tr>
<td>Mechanical power/car</td>
<td>efficiency 0.25</td>
<td>kW (me)</td>
<td>~ 11</td>
</tr>
<tr>
<td>Efficiency of car with gasoline</td>
<td>assumption</td>
<td>%</td>
<td>20</td>
</tr>
<tr>
<td>Equivalent of gasoline</td>
<td>calculated</td>
<td>t/y</td>
<td>1.56x10^6</td>
</tr>
</tbody>
</table>

*) According to the literature the future modular unit for electrolysis will have a power of approximately 10 MW (el).
FIG 4. ENERGY FLOW IN THE REGIONAL FILLING STATION

- Nuclear power station
- Electrolysis plant:
  - Effic. 80%
  - 6 MW(el)
  - 8 h/d
  - 360 d/y
  - 173 GJ(el)/d
  - 63 TJ(el)/y
- Hydrogenation plant:
  - 11.4 t MC/d
  - 138 GJ/d
  - 1.14 t H₂/d
- District heating:
  - 73 GJ(th)/d
- TO: 17.4 t/d
- MC: 18.5 t/d
- Heat, 26 TJ/y ±825 kW(th)/y
- 1000 cars x 50 GJ(ch) per y
- 1000 cars a 11 kW(me) and 15'000 km/y
<table>
<thead>
<tr>
<th>Object</th>
<th>Operation</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Price of electricity</td>
<td>low load period</td>
<td>SFr/kWh(el)</td>
<td>0.040</td>
</tr>
<tr>
<td>-- &quot; &quot;</td>
<td>-- --</td>
<td>SFr/GJ(el)</td>
<td>11.11</td>
</tr>
<tr>
<td>Efficiency of electrolysis</td>
<td>assumption</td>
<td>percent</td>
<td>80 %</td>
</tr>
<tr>
<td>Amount of electricity</td>
<td>theoretical (100%)</td>
<td>GJ(el)/kg H₂</td>
<td>0.121</td>
</tr>
<tr>
<td></td>
<td>practical: 0.121/0.8</td>
<td></td>
<td>0.151</td>
</tr>
<tr>
<td>Annual hydrogen production</td>
<td>see table 6</td>
<td>GJ(ch)/y</td>
<td>50'000</td>
</tr>
<tr>
<td>Electricity consumption</td>
<td>(50'000/0.8) x</td>
<td>kWh(el)/y</td>
<td>1.73 x 10⁷</td>
</tr>
<tr>
<td></td>
<td>x(10⁹/3.6x10)³</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electricity cost, annually</td>
<td>1.73 x 10⁷ x 0.04</td>
<td>SFr/y</td>
<td>690'000</td>
</tr>
<tr>
<td>Electricity cost for hydrogen production</td>
<td>0.151 x 11.11</td>
<td>SFr/kg H₂</td>
<td>1.68</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SFr/GJ(ch)</td>
<td>13.89</td>
</tr>
<tr>
<td>Capital cost of electrolysis plant</td>
<td>roughly calculated</td>
<td>SFr/y</td>
<td>2'600'000</td>
</tr>
<tr>
<td></td>
<td>(see also ref 3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Load factor</td>
<td>8 h x 36C d</td>
<td>factor</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td>24 h x 365 d</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Life in service</td>
<td>according ref. 3</td>
<td>y</td>
<td>15</td>
</tr>
<tr>
<td>Annuity</td>
<td>arbitrary (also ref 3)</td>
<td>% per y</td>
<td>10.3</td>
</tr>
<tr>
<td>Annuity, specific</td>
<td>calculated</td>
<td>SFr/kg H₂</td>
<td>0.66</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SFr/GJ(ch)</td>
<td>5.45</td>
</tr>
<tr>
<td>Operation and maintenance</td>
<td>roughly calculated</td>
<td>SFr/kg H₂</td>
<td>0.20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SFr/GJ(ch)</td>
<td>1.65</td>
</tr>
<tr>
<td>Total cost of H₂ production</td>
<td>calculated her</td>
<td>SFr/kg H₂</td>
<td>2.54</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SFr/GJ(ch)</td>
<td>21.00</td>
</tr>
<tr>
<td>Capital cost of a hydrogenation plant</td>
<td>according ref. 3)</td>
<td>SFr/GJ(ch)</td>
<td>6.5 .. 8.5</td>
</tr>
<tr>
<td>(methylcyclohexane from toluene)</td>
<td>roughly assumed</td>
<td>SFr/kg H₂</td>
<td>0.46</td>
</tr>
<tr>
<td></td>
<td>specific cost</td>
<td>SFr/GJ(ch)</td>
<td>3.8</td>
</tr>
<tr>
<td></td>
<td>capital cost, total</td>
<td>SFr</td>
<td>1'800'000</td>
</tr>
</tbody>
</table>
Table 7: Continuation

<table>
<thead>
<tr>
<th>Object</th>
<th>Operation</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total cost of H&lt;sub&gt;2&lt;/sub&gt; in the methylcyclohexane</td>
<td>calculated</td>
<td>SFr/kg H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SFr/GJ(ch)</td>
<td>23.9</td>
</tr>
<tr>
<td>Heat recovery from the electrolysis and hydrogenation</td>
<td>from Table 6</td>
<td>GJ(th)/y</td>
<td>26,000</td>
</tr>
<tr>
<td></td>
<td>(73 GJ/d x 360)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heat recovered equivalent to oil</td>
<td>oil: 30 MJ(th)/t</td>
<td>m&lt;sup&gt;3&lt;/sup&gt; oil/y</td>
<td>870</td>
</tr>
<tr>
<td>Efficiency of burning of oil</td>
<td>assumption</td>
<td>%</td>
<td>70</td>
</tr>
<tr>
<td>Effective oil equivalent</td>
<td>870 x 1/0.7</td>
<td>m&lt;sup&gt;3&lt;/sup&gt; oil/y</td>
<td>1,230</td>
</tr>
<tr>
<td>Price of oil (low sulphur)</td>
<td>arbitrary</td>
<td>SFr/100 t</td>
<td>40</td>
</tr>
<tr>
<td>Value of oil equivalent</td>
<td>1230 x 10 x 40</td>
<td>SFr/y</td>
<td>500,000</td>
</tr>
<tr>
<td>Price of gasoline</td>
<td>assumption</td>
<td>SFr/L</td>
<td>0.4</td>
</tr>
<tr>
<td>Value of gasoline equivalent</td>
<td>from Table 6</td>
<td>SFr/y</td>
<td>620,000</td>
</tr>
<tr>
<td></td>
<td>(1.56 x 10&lt;sup&gt;6&lt;/sup&gt; x 0.4)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total cash</td>
<td>calculated</td>
<td>SFr/y</td>
<td>430,000</td>
</tr>
</tbody>
</table>

*) See appendix 9.9
FIG 5: CAPITAL COST

- Nuclear power station
- Electrolysis plant: 4 MW(e), Capital cost total: 2.6 Millions SFr
  Electricty
  Amount: $1.73 \times 10^7$ MWh(e1)/y
  Cost: $690,000$ SFr/y

- Hydrogenation plant: Capital cost total: 1.8 Millions SFr
  District Heating (existing): 26,000 Gcal per year

- Tank
- Tank
  Hydrogen fuel sale: $1.56 \times 10^7$ ol/y
  Filling station
  Hydrogen fuel filling station sale: $620,000$ SFr/y

- 1000 cars during year
- Engine
- Catalytic reactor
- Tank

- Heat sale: $500,000$ SFr/y
Current price of gasoline, SFr/liter (without taxes, etc):

Equivalent price of gasoline, SFr/liter (without taxes, etc):

Constant component

Variable component

efficiency: 100%

takes during electrolysis (80% effic)

Hydrogenation

Electrolysis plant

BONUS from waste heat utilisation in district heating (effic: 70%, oil):

Gross electricity (annuity+oper+maint (80% effic)

During electrolysis (80% effic)

Bonuses from waste heat utilisation in district heating (effic: 70%, oil)
FIG 7: PRICE OF HYDROGEN FUEL IN MTH-SYSTEM VERSUS PRICE OF ELECTRICAL ENERGY

Price of electricity, SFr/kWh(el)

Price, SFr/l gasoline

Price of hydrogen fuel in this paper

Price of hydrogen from electrolysis according 3)

Switzerland, accor. "SEK" (annual, average low load)
1976 1985 2000

Switzerland 1976 (low load prices)
summer average winter
FIG 8. HEAT BALANCE IN THE HYDROGENATION-FILLING STATION

125 Electrical energy for electrolysis

100 (chemical energy) Hydrogen for engine

Electrolysis losses (heat) - - - - 25

Heat from hydrogenation

26

Heat for district

53

Toluene

100, in form of hydrogen in Methylcyclohexane

Dehydrogenator

25 Useful work

28 Exhales gas

100

Engine

47 into environment

losses in exhaust, radiation, radiator etc
7. Comparison of energetics with other car propulsive systems.

The following comparison gives some interesting values for various car propulsive systems. Normalised for 1 Joule of energy in the motor-car (see figure 9).

<table>
<thead>
<tr>
<th>Primary Fuel</th>
<th>Transformation Plant</th>
<th>Total primary energy (Joule)*</th>
<th>Engine type</th>
<th>Heat for district heating (Joule (th))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nuclear fuel</td>
<td>Light water reactor</td>
<td>15</td>
<td>Internal combustion engine n = 25</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>efficiency ~33%</td>
<td></td>
<td>Fuel cell plus electromotor</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>8.8</td>
<td>Electric battery plus motor</td>
<td>1</td>
</tr>
<tr>
<td>Crude oil</td>
<td>Refinery</td>
<td>9.5**</td>
<td>Internal-combustion engine n = 20</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>efficiency ~80%</td>
<td>10.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*) Assuming additional energy for district heating (or equivalent of 2 Joules (th))

**) Corrected for the increase in weight of the 900 kg car due to the 400 kg battery (56 kWh (el)). This is an advanced battery sulphur/sodium type having 150 Wh (el)kg.

Note: The cost of the battery is assumed to be 120 SFr/kWh (el).

The optimistic cost of the battery is therefore (120 SFr/kWh (el) x 56 kWh(el)) = 5600 SFr.

For an efficient system at least one battery must be in the filling station for every 3 batteries on the road. The cost of the battery for this reference car is 9000 SFr. The cost
FIG 9. COMPARISON OF ENERGY BALANCE OF SELECTED MOTOR-CAR SYSTEMS

**Total power: 15 W**

- Nuclear fuel: 15 W (th)
- LWR: 15 W (el) 33% efficiency
- Electrolysis: 5 W (el) 80% efficiency
- Hydrogenation: 4 W (th)
- "Losses" 1 W (th)
- Engine: \( \eta = 25\% \)
- District heat: 2 W (th)

**Total power: 8.8 W**

- Nuclear fuel: 7.5 W (th)
- LWR: 7.5 W (el) 33% efficiency
- Electrolysis: 2.5 W (el) 80% efficiency
- Hydrogenation: 2 W (ch)
- "Losses" 1 W (th)
- 1.3 W (ch) additional oil burning
- Fuel cell: 1 W (me)
- District heat: 2 W (th)

**Total power: 9.3 W**

- Nuclear fuel: 6.7 W (th)
- LWR: 6.7 W (el) 33% efficiency
- Electrical motor: 2.25 W + 1.5 W (el) 1.5 x 1.5 W
- Battery: 1.5 W (el) 66% efficiency
- Electrical energy equiv.: 1 W (me)
- District heat: 2 W (th)
- 2.8 W (ch) additional oil burning

**Total power: 10 W**

- Crude oil: 10 W (ch)
- Raffinery: 10 W (el) 80% efficiency
- Gasoline: 5 W (ch) 7.8 W (ch)
- Engine: 5 W (ch) 20% efficiency
- Distillate: 70% 2 W (th)
- Losses: 7.8 W (ch) oil for heating, 2.8 W (ch)
of the car without battery 7500 SFr. Result: the battery driven car is twice as expensive as the hydrogen or gasoline driven car.

8. Conclusions

A motor car system fuelled with gaseous hydrogen stored on board by means of a liquid organic carrier of methylcyclohexane-toluene seems to be a feasible system.

The pros and cons are as follows:

Pro: - A liquid carrier of hydrogen is very attractive even for small private vehicles

- The heat of dehydrogenation could be extracted from the exhaust gases

- The fuel tank and catalytic reactors are not large: 120 l tank, 13 l dehydrogenation unit and a rather small heat exchanger for a car having a weight of 950 kg and a radius of operation of 320 km on the open road or 170 km in the city

- The start up for a cold engine at intervals shorter than 10 hours can be covered by a battery of 12 V and 50 Ah

- The start after a longer parking time can be achieved with electricity from the grid i.e. 10 kW(e) for 10 minutes, or by burning the methylcyclohexane directly

- The thermal pollution is 2.5 times lower than that of conventional engines

- The toxicity of both liquid carriers MC and TO is the same as for gasoline

- The loading of hydrogen into the toluene at the local plants
seems to be feasible at the scale of about 1000 cars. The electrical power needed for electrolytic production of hydrogen for 8 h in the night is only 6 MW(el)

- Based on an electricity price of 0.042 SFr/kWh(el) and an oil and gasoline price without taxes of 0.4 SFr/l the system can be economically self supporting. Even with an electricity price for the year 2000 (according to the GEK) of 0.061 SFr/kWh(el) the corresponding price of oil and gasoline would only be 0.55 SFr/l.

Contra: - The use of catalytic reactors is a limiting factor with their short lifetime, price and complexity of recharging
- The by-products of dehydrogenation could be harmful for the environment even though they will be only 1% of the emission on one cycle
- Much more development work remains to be done
- The proposed filling station is a complex plant and includes
- the electrolytic plant 6 MW(el); 1.14 t H₂/day
- hydrogenation plant: 20 t methylcyclohexane/day
- filling station with 2 tanks of ~ 25 m³
- filling of 1000 cars each 15'000 km/y
- a capital cost ~ 4.4 x 10⁶ SFr.

9. Appendix

9.1 Chemical reactors in the equilibrium state
a) Hydrogen production

\[ \text{(C}_6\text{H}_{11}\text{CH}_3)\text{g} \rightarrow \text{(C}_6\text{H}_5\text{CH}_3)\text{g} \text{ + (3H}_2)\text{g} \]
Catalyser : Pt/Al₂O₃ in powder form  
Temperature: 610 K  
Pressure : 1 bar  

Enthalpy of hydrogenation: 210 kJ/mol H₂ (endotheric)  
Efficiency of the hydrogenation reaction: 95%  

b) Hydrogen burning with excess air equal to λ. 
(the equivalence ration $\phi$ equals $\lambda^{-1}$)  

$$H_2 + \left(\frac{1}{\lambda} O_2 + 1.88 N_2\right) \rightarrow H_2O + (\lambda-1) \frac{1}{\lambda} O_2 + 1.88 N_2$$  

Enthalpy of burning: 240 kJ/mol H₂  

The value of $\lambda$ is selected as 2.17 since a hydrogen/air mixture with 2% H₂ lies below the explosion limit and thereby a "normal" burning of hydrogen can be achieved. At the same time the burning has a high efficiency. Thus for $\lambda = 2.17$ the following equation is obtained:  

$$H_2 + 2.17 \left(\frac{1}{\lambda} O_2 + 1.88 N_2\right) \rightarrow H_2O + 0.58 O_2 + 4.07 N_2$$  

The maximum theoretical combustion temperature for this reaction can be calculated as (specific heats see table 8).  

1'600 K (constant pressure)  
1'959 K (constant temperature)  

Note: According to (1) the engine exhaust gas temperature decreases significantly with operation at a low equivalence ratio $\phi$.  

9.2 Heat exchanger system  

The dehydrogenation of methylcyclohexane takes place in the gaseous form. To obtain a good energy extraction, a heat exchanger is used in which the enthalpy (heat) of the products (exhaust gas
and toluene) is transferred to fuel feed (methylcyclohexane).

Another heat exchanger provides the reaction heat of dehydrogenation.

9.3 Energy flow in the system

The total energy requirements of the dehydrogenation system is made up as follows:

\[
\Delta h_{\text{f}}(\text{to}) = \int_{298}^{T_B(\text{MC})} CP(\text{MC}) \, dt + \Delta h_B(\text{MC}) * \int_{T_B(\text{MC})}^{610} CP(\text{MC}) \, dT + \Delta h_T(\text{MC})
\]

From this: \( \Delta h_f = 317 \text{ kJ/mol MC} \)

This energy requirement \( \Delta h_f \) is provided by the cooling of the dehydrogenation products (C\(_5\)H\(_5\)CH\(_3\) + 3H\(_2\)) and the exhaust gases (EG).

The cooling of the gaseous toluene and hydrogen gives the following amount of heat

\[
\Delta h^\text{c}(\text{to}) = \int_{610}^{T_B(\text{TO})} CP(\text{TO}) \, dt + \Delta h_B(\text{TO}) * \int_{T_B(\text{TO})}^{327} CP(\text{TO}) \, dT + \int_{610}^{327} CP(H_2) \, dT
\]

\( \Delta h^\text{c}(\text{to}) = 101 \text{ kJ/mol (TO + 3H}_2) \)

The remaining energy is provided by the exhaust gases as follows:

\[
\Delta(\Delta h) = 317 - 101 = 216 \text{ kJ/mol MC}
\]

\[
\Delta(\Delta h) = \int_{606}^{1050} CP(\text{EG}) \, dT
\]
Table 3: Some thermodynamic values.

Calculation of specific heat \( C_p \)

\[
T = \text{temperature (K)}
\]
\[
C_p = a + bT + cT^2
\]
\[
\Delta H = \int C_p \, dT = aT + \frac{b}{2}T^2 + \frac{c}{3}T^3
\]

<table>
<thead>
<tr>
<th></th>
<th>Coefficients</th>
<th>( C_p ) at 1050 K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( a )</td>
<td>( b )</td>
</tr>
<tr>
<td>H₂O</td>
<td>34.39</td>
<td>0.62×10⁻³</td>
</tr>
<tr>
<td>O₂</td>
<td>28.28</td>
<td>2.54×10⁻³</td>
</tr>
<tr>
<td>N₂</td>
<td>28.3</td>
<td>2.54×10⁻³</td>
</tr>
<tr>
<td>H₂</td>
<td>27.7</td>
<td>3.39×10⁻³</td>
</tr>
</tbody>
</table>

Enthalpy of boiling, combustion and dehydrogenation

\( H_B \) (MC) = 31.5 KJ/mol MC
\( H_V \) (MC) = 4500 KJ/mol MC
\( H_B \) (TO) = 31.9 KJ/mol TO
\( H_V \) (H₂) = 240 KJ/mol H₂
\( H_D \) (MC) = 210 KJ/mol MC

B = Boiling
V = Combustion
D = Dehydrogenation

Specific heat of MC, TO

\( C_p \) (MC) = 180 J/mol (MC) \cdot K
\( C_p \) (MC) = 240 J/mol (MC) \cdot K
\( C_p \) (TO) = 160 J/mol (TO) \cdot K
\( C_p \) (TO) = 170 J/mol (TO) \cdot K
\( C_p \) (Fe) = 400 J/mol (Fe) \cdot K

Boiling points:
\( T_B \) (MC) = 374 K
\( T_B \) (TO) = 383 K
9.4 Energy balance and temperature distribution

To simplify the presentation and calculation the system of heat exchanger and reactor is divided into six sections A to F. (In reality only two parts - heat exchanger and reactor).

It is assumed that the heat exchangers operate in counterflow. To calculate the surface area the following formula are used

\[ \Delta T = T_{in} - T_{out} \]

\[ T_m = \frac{(\Delta T_0 - T_{MC})}{\ln(\Delta T_0/T_{MC})} \]

\[ \dot{Q} = \Delta H \times \dot{m} \] \hspace{1cm} (\dot{m} = \text{mass flow; } \text{mol/s}) \hspace{1cm} \dot{Q} = \text{power [W]}

\[ F = \frac{\dot{Q}}{k \cdot \Delta T_m} \quad [m^2] \quad F = \text{surface of the heat exchanger [m}^2\text{]} \]

\[ k = \text{heat transfer coefficient [W/m}^2\text{K]} \]

For the reference case it was assumed that

\[ \dot{m} = 0.055 \text{ mol MC/s} \]

The total surface area of the complete heat exchange system is

\[ EF = 2.03 \text{ m}^2 \]

The Carnot efficiency for an Otto engine with hydrogen is

\[ (V = \text{const}; T_{max} = 1959 \text{ K}) \]

\[ \eta_{\text{carnot}} = \frac{T_{max} - T_{out}}{T_{max}} = \frac{1950 - 1050}{1950} \]
Table 9: Calculation of the surface area

<table>
<thead>
<tr>
<th>System components</th>
<th>Unit</th>
<th>A liq/liq</th>
<th>B liq/cond</th>
<th>C vap/cond</th>
<th>D vap/gas</th>
<th>E gas/gas</th>
<th>F gas/gas</th>
<th>G* gas/gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔΤ₀</td>
<td>K</td>
<td>56</td>
<td>0</td>
<td>condensation</td>
<td>17</td>
<td>210</td>
<td>34</td>
<td>140</td>
</tr>
<tr>
<td>ΔΤ₂</td>
<td>K</td>
<td>74</td>
<td>27</td>
<td>evaporation</td>
<td>0</td>
<td>212</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>ΔΤ₃</td>
<td>K</td>
<td>64</td>
<td></td>
<td></td>
<td></td>
<td>211</td>
<td>28</td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>W/m².</td>
<td>340</td>
<td>600</td>
<td>2500</td>
<td>600</td>
<td>14</td>
<td>14</td>
<td>150</td>
</tr>
<tr>
<td>Tₜ</td>
<td>K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Q</td>
<td>kW</td>
<td>0.75</td>
<td>0.26</td>
<td>1.5</td>
<td>0.24</td>
<td>2.84</td>
<td>0.32</td>
<td>19.2</td>
</tr>
<tr>
<td>P</td>
<td>m²</td>
<td>0.03</td>
<td>0.02</td>
<td>0.06</td>
<td>0.03</td>
<td>1.03</td>
<td>0.86</td>
<td>0.73</td>
</tr>
</tbody>
</table>

FIG 11. THE TEMPERATURES IN THE SYSTEM

- 38 -

System components (see table 9)
For this paper it is assumed for the hydrogen Otto engine:

\[ \eta_{\text{eff}} = 0.25 \]

On the relationship of \( \eta_{\text{eff}} \) to the Carnot efficiency is:

\[ \eta_{\text{eff}}/\eta_{\text{Carnot}} = 0.25/0.462 = 0.54 \]

which appears reasonable.

9.5 **Possible layout of the heat exchanger and reactor.**

The surface area of the heat exchanger is about 2 \( m^2 \). With a tube cross section of 0.002 \( m^2 \) (\( \phi \) 5 cm) a total length of 12.8 \( m \) is needed. The heat exchanger could possibly be dimensioned as follows (in a cube of 0.7 \( m \)) (Figure 11 a shows a proposed layout).

The inner cube has a side 0.5 \( m \) long. To that is added 0.1 \( m \) of insulation with a thermal conductivity \( \lambda = 0.1 \) W/m.K.

This gives a power loss of

\[ Q_{\text{loss}} = \frac{F \cdot \lambda \cdot \Delta T}{d} \]

\( F = 6a^2 = 3 \) m\(^2 \) surface of the insulated cube
\( \lambda = 0.1 \) W/mK thermal conductivity of the insulation
\( d = 0.1 \) m insulation thickness
\( \Delta T = 50 \) K \( T_{\text{To out}} - T_{\text{air}} \)

\[ Q_{\text{loss}} = 150 \) W calculated loss of heat exchanger

The catalytic reaction unit can be designed as follows

\( (R = \text{Radius, (m)}, \quad L = \text{length, (m)}). \)

\( R_i = 0.1 \) m \( \Delta R = R_a - R_i \quad T_a = \text{temperature at A} \)
\( R_a = 0.2 \) m \( \Delta R = \text{wall thickness}; T_i = \text{temperature at I} \)
\( L = 0.4 \) m \( \Delta T = T_i - T_a \)
FIG 1. GEOMETRY AND ISOLATION OF DEHYDROGENATION REACTOR

a) The geometry of the dehydrogenation reactor

b) The isolation of the dehydrogenation reactor
The reactor volume without isolation is about 13 litres (see also table 4).

The power loss of the reaction unit is

\[ Q_{\text{loss}} = \frac{T_a - T_i}{\ln \left( \frac{R_a}{R_i} \right) \cdot 2\pi \cdot \lambda \cdot L + 2 \left[ \frac{R_a + R_i}{2} \right] \frac{\lambda \cdot \Delta T}{R} } \leq 30 \text{ W} \]

The total losses of the combined system is therefore \( \approx 180 \) W.

9.6 **Dynamic behaviour** (Acceleration and cold starts).

Acceleration requires a power of 20 kW(me) and could be provided by

a) direct injection of toluene into the engine (excess air!)

or

b) by additional batteries which are charged up during the journey.

a) TO Injection

- Burning during normal travel

\[ H_2 + 2.17 (0,50_2 + 1.88 N_2) \rightarrow H_2O + 0.580 \text{ O}_2 + 4.08 \text{ N}_2 \rightarrow \Delta H \]

\[ \Delta H = 240 \text{ kJ} \]

- Burning during acceleration with addition of 0.06 mol TO

(e.g. 5.9 g TO)

\[ H_2 + 2.17 (0_2 + 1.88 N_2) + 0.06 \text{ TO} \rightarrow 1.42 \text{ H}_2O + 0.42 \text{ CO}_2 + 4.08 \text{ N}_2 \]

\[ \Delta H = 504 \text{ kJ} \]

i.e. with the injection of only 5.9 g of TO the thermal power is more than doubled!
However the mechanical power does not increase by the same amount since the efficiency falls.

The advantages of this system lies in the availability of TO from the tank. (Note: With metal hydrides this advantage is not present).

The disadvantages of TO injections also for cold starts are as follows

- larger environmental impact from CO₂ and perhaps NOₓ (nevertheless still fifty times smaller than with the gasoline engine)
- lower efficiency of the engine
- increased corrosion of the heat exchanger system
- burning of the hydrogen carrier which comes from liquid fossil fuel at a rate of about 2% per fuel tank filling. That means after about 50 fillings the contents of the tank which is supposed to be recycled is completely exhausted and requires replacement.

b) Cold starts

The energy required is to supply the heat for: the heating of the heat exchange (HE) system \( Q_{HE} = \dot{E}_{CP} \cdot \Delta T \cdot m_{HE} \) and the thermal energy necessary to start the release of hydrogen.

It is arbitrarily assumed that \( m_{tot} = 1.5 m_{HE} \).

\[
m_{tot} = (F \cdot d \cdot \rho) \times 2.5; \quad \rho = 7800 \text{ kg/m}^3; \quad d = 2 \text{ mm}
\]

\( F \) = surface (m²)

\( Cp = 0.4 \text{ kJ/kg (iron)} \)

\[
\Delta T = \sqrt{T_{\text{max}}^2 - T_{\text{min}}^2} - \text{\( T_u = \sqrt{1000 \times 273} - T_u = 250 \text{ °C} \)}
\]

\( T_u = \) temperature of the surroundings
The heat needed for a cold start is:

\[ Q_{\text{HE}} = 78 \text{ kJ} \]

This heat can be produced either by burning toluene or by external electrical heating.

By burning 0.36 mol or 35 g TO the heat exchanger is brought to operating temperature and 3 mols of hydrogen produced. Thus a cold start needs about 0.04% of the fuel tank contents. After 50 starts 2% of the tank's contents are directly burnt. This amount must be replaced continuously in the MTH system.

c) Warm start

Energy required 317 kJ/mol MC thus 0.28 mol TO or 28 g TO must be burnt.

The loss of the heat transfer system of 180 W (see above) can be covered by a normal car battery. Additional equipment is necessary

- TO exhaust (as well as the hydrogen exhaust)
- process controller (microprocessor)

d) Electrically driven acceleration (using batteries)

Advantages:
- constant efficiency
- higher engine usage
- small environmental impact

Disadvantages:
- the car weighs more, requires a high fuel consumption
- additional equipment is necessary (batteries, electrical motor)
9.7 Calculation of the increased fuel required

The following assumptions have been made (see table 1):

<table>
<thead>
<tr>
<th>Fuel Type</th>
<th>Mass (kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gasoline - full tank</td>
<td>16 kg</td>
</tr>
<tr>
<td>MTH system</td>
<td>85 kg</td>
</tr>
<tr>
<td>Difference</td>
<td>76 kg</td>
</tr>
<tr>
<td>Tank for MTH system</td>
<td>30 kg</td>
</tr>
<tr>
<td>Catalyser reactor</td>
<td>20 kg</td>
</tr>
<tr>
<td>Other extras</td>
<td>20 kg</td>
</tr>
<tr>
<td><strong>Total additions</strong></td>
<td><strong>146 kg</strong></td>
</tr>
</tbody>
</table>

In relation to the weight of the car (900 kg)

\[
\frac{900 + 146}{900} = 116\%
\]

Assuming 1\% increase in weight corresponds to an increase 0.9\% in fuel, required i.e. 16\% x 0.9 = 15\%. After iterating one obtains an increase in the fuel requirements of 18\%.

9.8 Efficiency of the hydrogen engine.

Based on numerous theoretical and practical studies the hydrogen engine is much more efficient than the equivalent gasoline engine.

Van Vorst (1974) writes: "Comparison of results (for the hydrogen and gasoline engine) indicates that thermal efficiency is significantly higher. An increase in efficiency from 25\% to 100\% were noted; the greatest increase being obtained at the lower power outputs. At the highest gasoline engine efficiency the efficiency of the hydrogen engine is 25\% greater".

H. May (1976) writes: "For the higher hydrogen mixtures a higher
efficiency is obtained as is obtained from the lower hydrogen throughput, which can be expected from the theoretical calculations.”

9.9 Electrolysis of water

One of the aims of this paper is to discuss the feasibility of small scale production of hydrogen for the hydrogenation of toluene to methylcyclohexane. This hydrogen is produced from the electrolysis of water using electrical energy from a nuclear power station.

At the present time (according to ref. 20) all the large scale water electrolysis plants are built as multi-module systems with a module representing 1-2 MW (el).

\[ T = 80 \, ^\circ \text{C}, \text{investment cost 250 \$/kW(el)} \]

Today’s modern electrolyzers have an electric efficiency of 75-80 %.

A promising method of water electrolysis is based on a solid polymer electrolite membrane, unfortunately having a high price per unit cell but nevertheless a high energy efficiency (targets of 90 % are aimed at). Operating temperature is 150 \( ^\circ \text{C} \); the module system with 8-10 MW(el).

According to ref. 18 the price of hydrogen produced by electrolysis is dependent on the price of electricity and the plant capacity factor (as shown in figure 13).

According to ref. 21 the future development of electrolysis of water has the following goals:

- Overall system efficiency: 85 - 90 %
- System capital cost: 50 \$/kW(el)
- Life: 20 years
- Scale up: Demo system: 5 MW(el)
Temperature: 150 °C
Pressure: 20 bar

Estimated costs
(1 US $ = 2 SFr.)

1976
- Electricity: 9.5 SFr./GJ(el)
- Hydrogen without sale of O₂: 10.7 SFr./GJ(ch) in H₂
FIG 13. ELECTROLYSIS OF WATER

a) Total cost of hydrogen as a function of electricity cost

b) Total cost of hydrogen as a function of plant capacity factor
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