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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

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A LIQUID ORGANIC CARRIER OF HYDROGEN AS A FUEL FOR AUTOMOBILES

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* temporary co-worker

Contents

Abstract

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

$$(\text{Methylcyclohexane}_{\text{liquid}}) \xrightarrow{\text{dehydrogenation}} (\text{Toluene}_{\text{liquid}})+(\text{Hydrogen}_{\text{gas}})$$

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. Thes 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 France ≅ 0,5 U$ (1979):

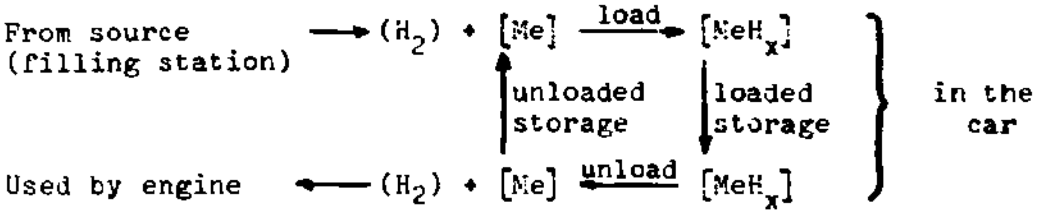
Price of electricity during low load		Price of heating oil and gasoline without taxes; SFr/litre
Year	SFr/kWh (el)	
1979	0.042	0.40
2000	0.061	0.55

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

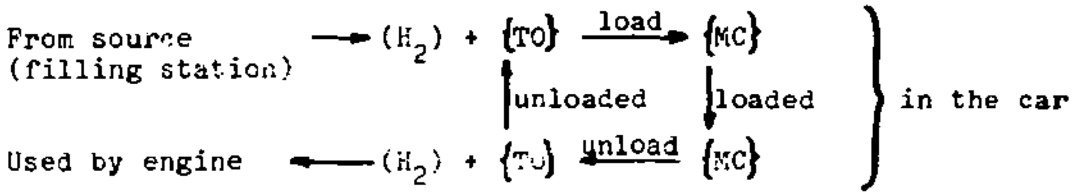
One of the important aims of future energy planners is to try and couple the nuclear power plant with the fuel system of the motor car. One possible scheme might be:

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":



The chemical reaction is:

$$(3H_2) + \{C_7H_8\} \underset{\text{unload}}{\overset{\text{load}}{\rightleftharpoons}} \{C_7H_{14}\} + \sim 210 \text{ kJ/mol MC}$$

The enthalpy Q_{de} = 210 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:

(Methylcyclohexane, Toluene, Hydrogen).

The symbols used in this paper are:

gaseous ( ) or g
liquid { } or ℓ
solid [ ] or s
x = stoichiometric coefficient
Me = metal
H_2 = gaseous hydrogen

MC = methylcyclohexane: $C_6H_{11}CH_3 = C_7H_{14}$
TO = toluene: $C_6H_5CH_3 = C_7H_8$
EG = exhaust gases
DH = district heating
HE = heat exchanger
(to) = total
(el) = electrical
(ch) = chemical
(th) = thermal
(me) = mechanical
d = day = 24 h; y = year = 360 days
h = hour
de = dehydrogenation
hy = hydrogenation
co = combustion
SFr. = Swiss Francs = 0.5 US $

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 ∿ + 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:

$$\text{Methylcyclohexane} + Q_{de} \longrightarrow \text{Toluene} + (3H_2)$$

The value of Q_{de} is: 210 kJ/mol MC
1.25 MJ/kg MC
35.2 MJ/kg H_2

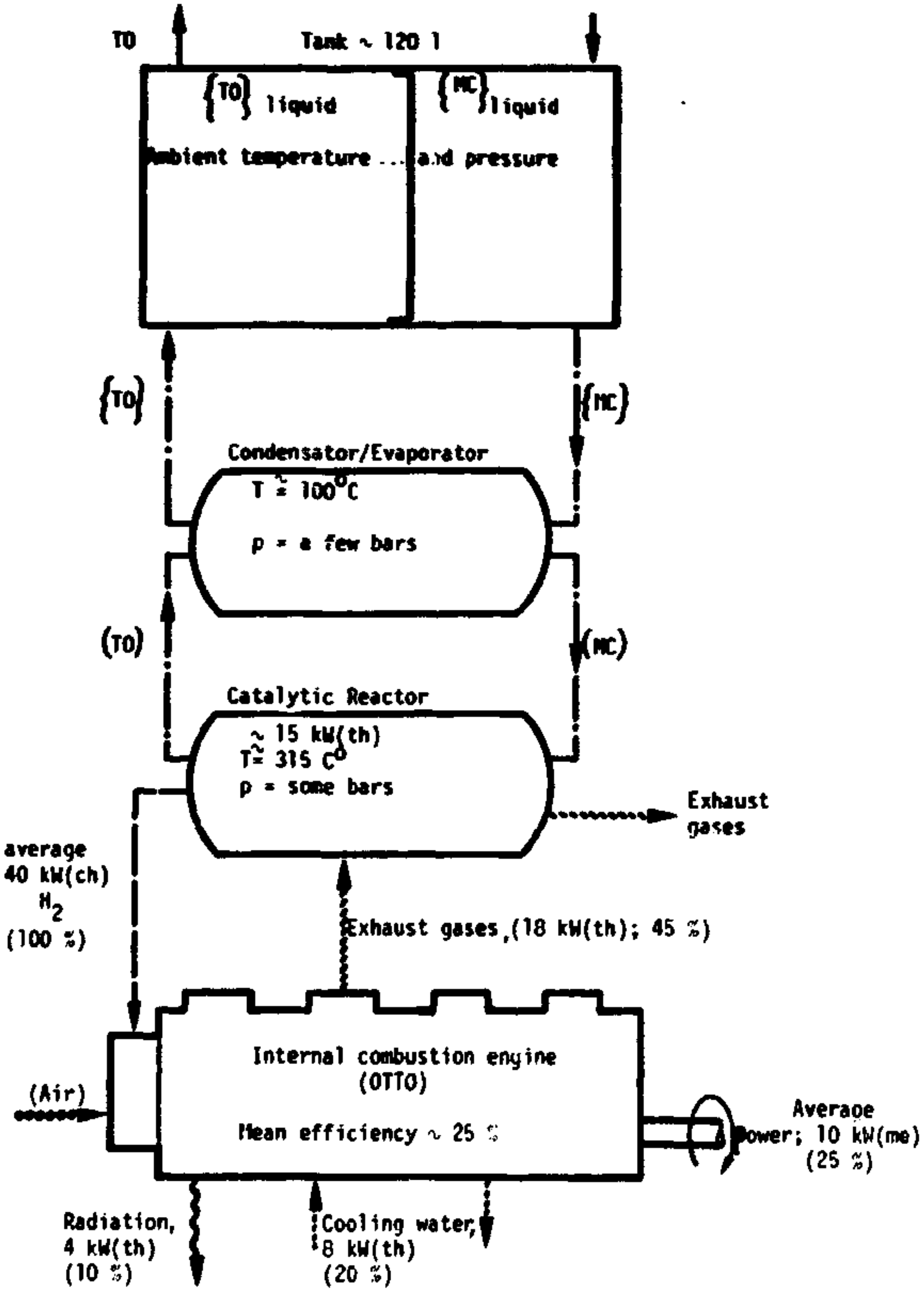
Table 1: The reference motor car.

Property	Unit	Value
Weight of car without fuel	kg	900
Peak engine power	kW(me)	20
Mean engine power	kW(me)	10
Engine volume	ℓ	1
Mechanical (thermal) efficiency	%	25 % (hydrogen) 20 % (gasoline)
Equivalence ratio for hydrogen	ϕ	0.46*
Exhaust gas temperature	°C	777**
Operation distance		
open road	km	320
city	km	170
Fuel rating		
gasoline open road	ℓ/100 km	6.45
" city	ℓ/100 km	12.8
gasoline in tank	kg	16.0[illegible]
hydrogen gas		
open road	kg/100 km	1.53
city	kg/100 km	1.90
hydrogen in tank	kg	5
Organic liquid carrier		
(6.1 weight %; 95 % efficiency)		
open road	ℓ/100 km	34.2
city	ℓ/100 km	65.0
organic carrier in tank	kg	85 (see appendix)
	ℓ	116
Organic/gasoline weight ratio		85/16=5.3

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

** see appendix 9.8

FIG 1 A SIMPLIFIED SCHEME FOR THE MTH FUELED CAR SYSTEM



Since the heat of combustion Q_{co} of hydrogen is 121 MJ/kg H_2 the relation to the heat of dehydrogenation is

$$Q_{de}/Q_{co} = 35.2/121 \cong 0.28$$

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 [illegible] 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 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 ∿ 15.2 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 MTH-System.

Property	Unit	Hydrogen fuel MTH-System		Conventional fuel
		toluene	methylcyclohexane	octane, gasoline
Formula	-	C_7H_8	C_7H_{14}	C_8H_{18}
Function		only as carrier of hydrogen		for direct burning
Molecular weight	kg/kmol	92.15	98.19	114.3
Boiling point	°C	110.6	101.2	125.6
Freezing point	°C	- 95	- 126.6	- 56.8
Heat of vaporization	kJ/g	347	321	300-350
" " "	kJ/mol	31.9	31.5	-
Vapour pressure (20°)	bar	0.03	0.07	0.03
Density (20°)	kg/l	0.867	0.769	0.72
" "	l/mol	0.106	0.127	-
Viscosity	cP	0.590		
Heat capacity	J/mol K	160.1	150.[illegible]	17[illegible]
liquid	J/g K	1.738	1.83	1.[illegible]
gas (250°)	J/g K	1.84	2.45	-
gas	J/mol K	170	243	-
Heat of dehydrogenation	kJ/mol MC	-	(20°C);204.8 (427°C);215.6	- -
Heat of burning	MJ/l	-	only hydrogen 5.64 per litre MC	total burning 32.5 per litre gasoline
Toxicity	part per Mega	100	400	300
	mg/m³ air	380	1600	1400
Price, 1979 March	US $/gallon	0.7-	?	0.7

Table 3: The calculation of the material flow for the reference motor car.

Property	Obtained by	Unit	Value
Reference car	---	---	see table 1
Average mechanical power	postulation	kW(me)	10
Efficiency	estimation	%	25 *)
Equivalence ratio	see appendix	$\phi = \lambda^{-1}$	0.46
Average thermal power	10 kW(me) x $\frac{1}{0.25}$	kW(th)	40
Average flow of heat		kJ/s	40
Heat of combustion of hydrogen	from literature	MJ/kg MJ/mol H_2	121
Hydrogen flux for power given above	(40 kJ/s)·(242kJ/mol)	mol H_2/s	0.164
Methylcyclohexane as source of hydrogen	MC $\rightarrow$ 3 H_2+TO	mol H_2 mol TO	0.333 1.0
MC flux for power given above	(0.164)x(0.333)	mol MC/s	0.0555
Efficiency of dehydrogenation process	estimation	%	95
MC flux including efficiency	(0.055)x(1,0.95)	mol MC/s	0.06

*) 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 later 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). Supplying approx 1000 hydrogen driven cars covering each 15'000 km per year.

Table 4: Simplified calculation of the catalytic dehydrogenation unit.

Property	Obtained from	Unit	Value
Methylcyclohexane flux average	see table 3	mol MC/s	0.06
Specific volume of catalyst	according Faith (1972)	$m^3 \cdot s/(mol\ MC)$	0.06
Volume of reactor	(0.06)x(0.06 mol MC/s)	m^3	0.004 calculated 0.013 for further calculation (arbitrary)
Temperature of catalyst	according Faith (1972)	K	590
Temperature of exhaust gases			
- from engine	estimation	K	1050 see table 5 and appendix
- after reactor	postulation	K	610
Logarithmic medium temperature difference	$LMTD=\frac{(1050-590)-(610-590)}{\ln\frac{1050-590}{610-590}}$	K	~ 140
Overall heat transfer coefficient	rough estimation	$W/m^2 \cdot K$	150
Heat of dehydrogenation of MC	literature	kJ/mol MC	~ 210
Heat flux to reactor	see table 3	kW(th)	~ 15.2
Heating surface needed	$\frac{15.2x10^3\ W}{(150\ W/m \cdot K)x(140\ K)}$	m^2	~ 0.73
Length of tube	arbitrary	m	0.5
Diameter of tube	$D=4x\frac{4x10^{-3}m^3}{0.73\ m}$	m	0.022 calculated for 4 litre reactor
Surface of 1 tube	(0.5)x(0.022)	m^2	0.034
Number of tubes	(0.73)/(0.034)	number	21
Volume of 1 tube	$(0.5)x(0.022^2x3.14/4)$	m^3	0.0002
Length of tubes	(0.73)/(0.034)	number	21
Number of tubes	$(4x10^{-3}m^3)/(0.002\ m^3)$	number	~ 20

Table 4: Continuation

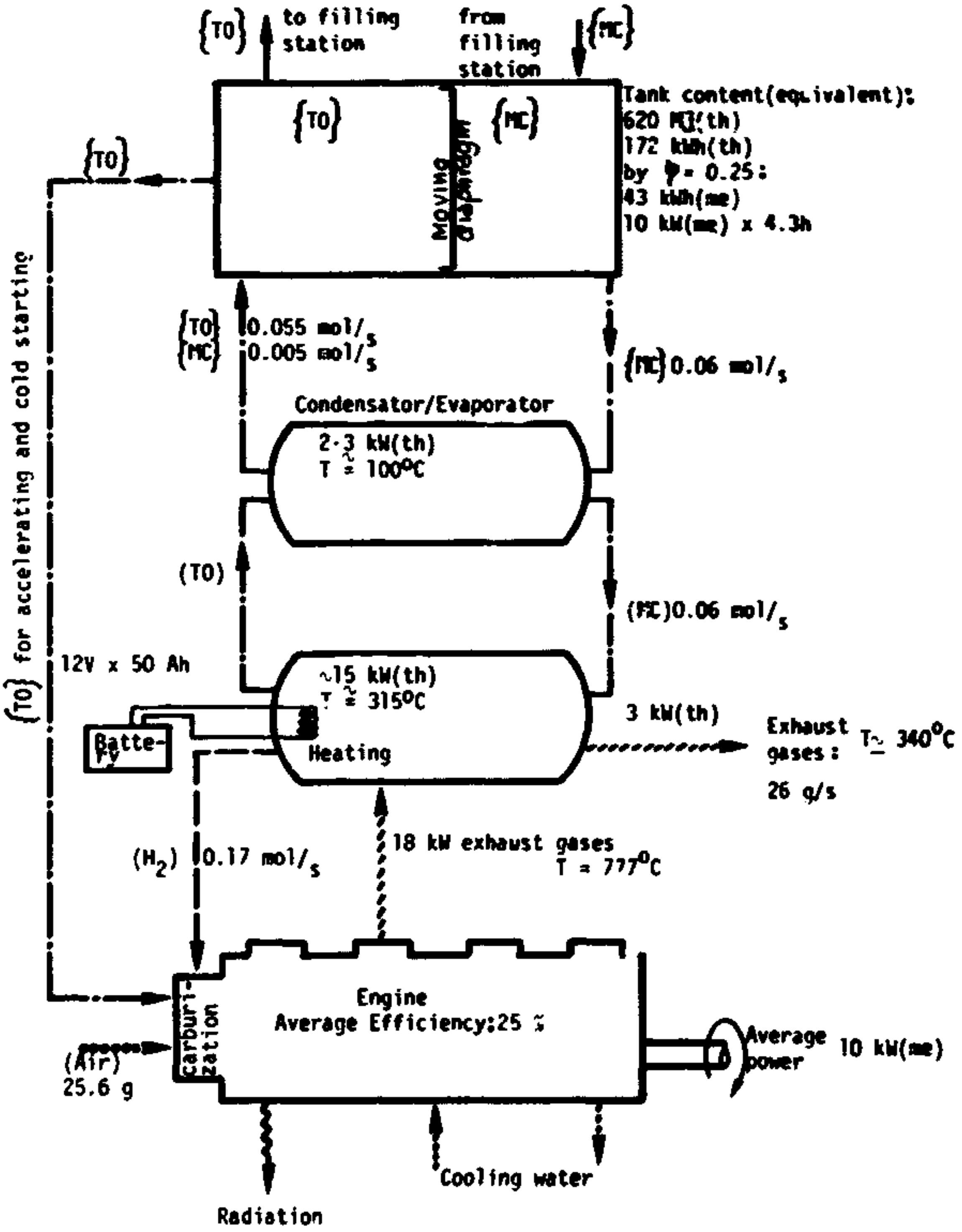
Property	Obtained from	Unit	Value
Wall thickness	arbitrary	m	$1.2 \cdot 10^{-3}$
Wall unit, surface	$(0.022)^2 x (3.14/4)$	m^2	0.042
Wall unit, volume	$(0.042) x (1.2 x 10^{-3})$	m^3	$5 x 10^{-5}$
Density of steel	literature	kg/m^3	7500
Mass of tubes	$(14) x (0.5) x (5 x 10^{-5}) x$ $x (7500)$	kg	2.6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

* 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)

Parameter	Obtained from	Unit	Value
Exhaust gases			
Hydrogen flux	from above given calculation	mol/s	0.17
Equivalence rating maximum lean	according Karim (1966)	ϕ ($\lambda = 0^{-1}$)	0.46 (λ= 2.17)
Relative mass of exhaust gases	according Finegold (1978)	$\frac{\text{g exhaust}}{\text{mol } H_2}$	151
Mass of exhaust gases	(151 g air/mol H_2)x x (0.17 mol H_2/s)	g/s	26
Specific heat of exhaust gases	estimated	J/g·K	1.2 (see appendix)
Temperature of exhaust gases: input	see appendix 9.4	°C K	777 1050
Output temperature	see appendix 9.4	°C K	337 610
Temperature difference	(T input)-(T output) = ΔT	°C	440
Heat capacity of exhaust gases	(26 g/s)x(1.2 J/g·K)x x (440 K)	J/s kW (th)	15'500 15.5
Tank volume (simplified)			
Hydrogen flux	from above	mol H_2/s	0.17
Methylcyclohexane storage, load	(0.17x1/3)x(0.127 ℓ/mol) x (4.2 hr)	ℓ	110
Toluene storage unload	(100 l) x 0.83	ℓ	92
Equivalent gasoline value	estimated	ℓ	20
Tank dimension	arbitrary	ℓ	120
	side of tank	m	(0.66)x(0.66)x x (0.25)
Tank weight (empty)	approximately	kg	20

FIG 2. THERMAL SCHEME



- 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 (∿ 130 °C) and hydgrogenation (∿ 300 °C).

FIG 3. SCHEME OF THE REGIONAL FILLING STATION

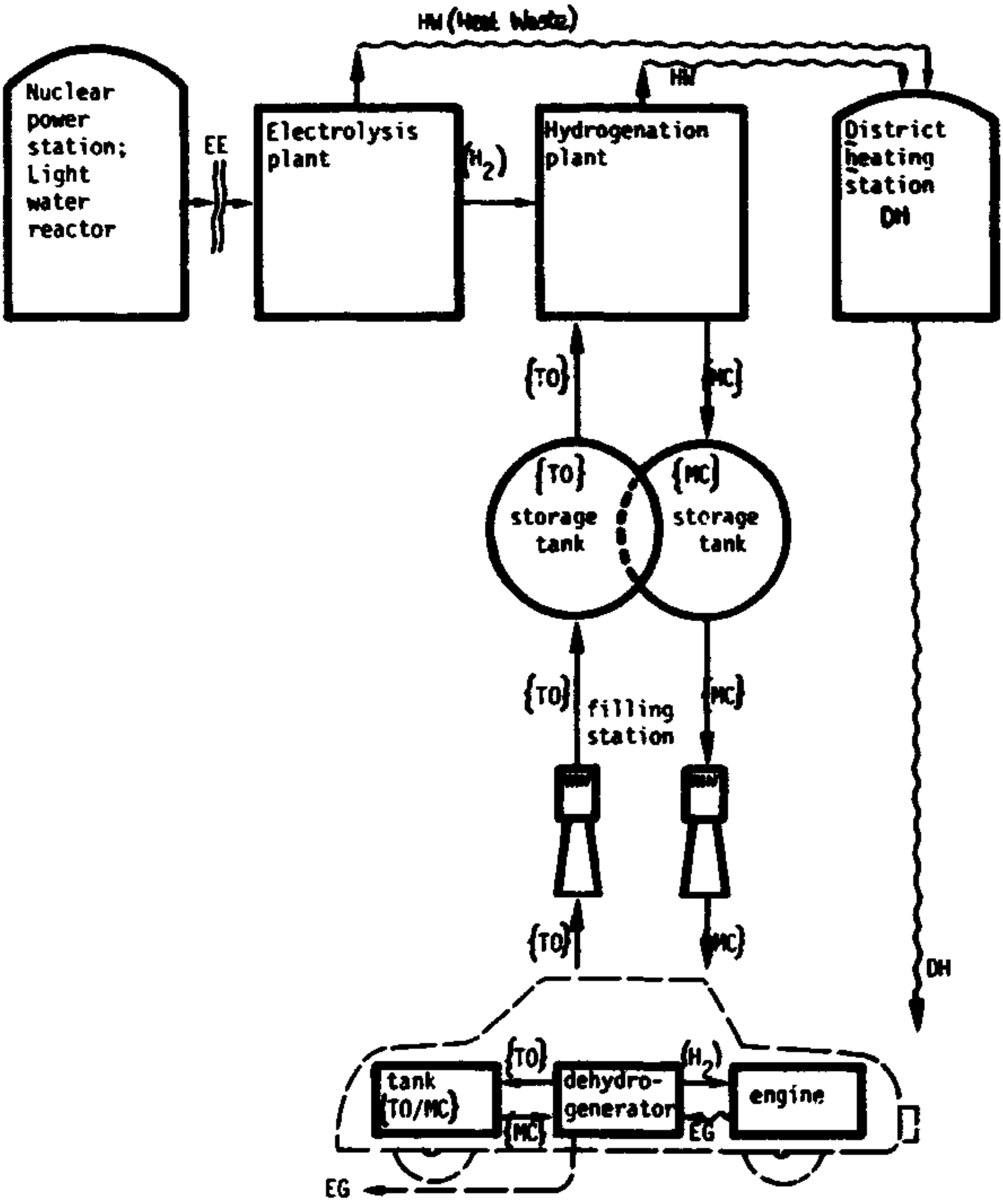


Table 6: Energy balance of the local hydrogen filling station.

Object	Operation	Unit	Value
Region	arbitrary	population	10'000
Motor cars, total	assumption	cars/region	4'000
Motor cars, hydrogen	assumption	-- " --	1'000
Electricity consumption	according GEK 2000	$\frac{\text{kW} \cdot \text{y (el)}}{\text{y} \cdot \text{capita}}$	1.1
Ration of low/high load		ratio	1.75
"Free" capacity, low load	calculated	kW (el) average	0.6
"Free" capacity in the region	0.6 x 10'000	MW (el)	6 *)
Daily "free" energy	6000 kW(el) x 8 h	GJ (el)/d	173
Electrolysis of water	efficiency, assumed	%	80
Chemical energy in H_2	173 GJ(el) x 0.80	GJ(H_2)/d	138
Amount of hydrogen	138 GJ/(0.121 GJ/kg)	kg H_2/d	1'140
Heat waste, electrolysis	173 GJ(el) x 0.20	GJ(th)/d	~ 35
Heat waste, hydrogenation	138 GJ(ch) x 0.28	GJ(th)/d	~ 38
Total heat "waste"	35 + 38	GJ(th)/d	~ 73
Ratio waste/electricity	73/173	ratio	0.42
Total amount of H_2	$1140 \frac{\text{kg}}{\text{d}} \times 360 \frac{\text{d}}{\text{y}}$	t H_2/y	410
Chem. energy in H_2	3110 t/y x 121 GJ/t	GJ(ch)/y	50'000

Table 6: Continuation

Object	Operation	Unit	Value
Energy per car	50'000/1'000	GJ(ch)/y	50
Thermal power/car	during 300 h/y	kW (th)	~ 45
Mechanical power/car	efficiency 0.25	kW (me)	~ 11
Efficiency of car with gasoline	assumption	%	20
Equivalent of gasoline	calculated	ℓ /y	$1.56 x 10^6$

*) 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

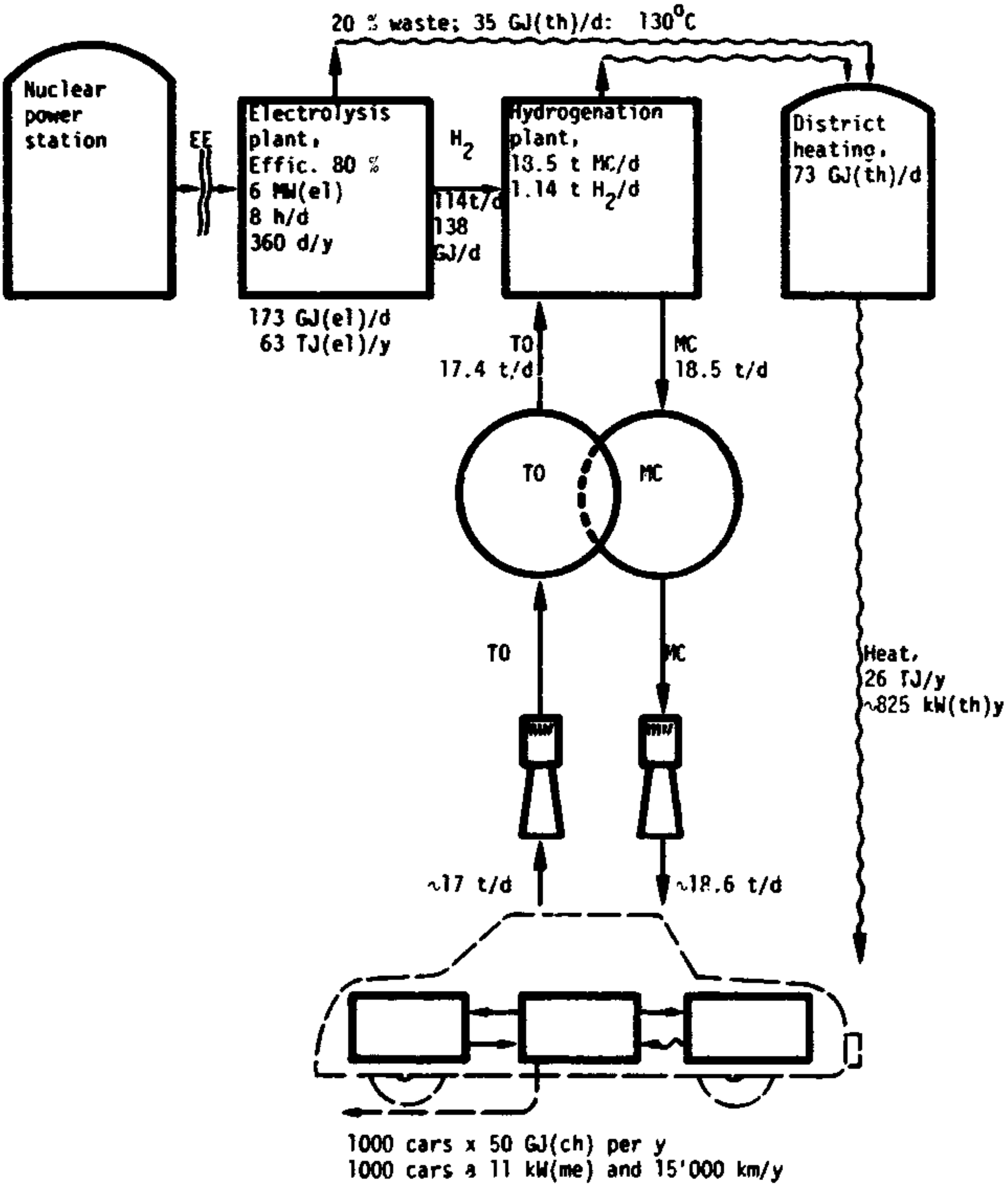


Table 7: Economic calculations

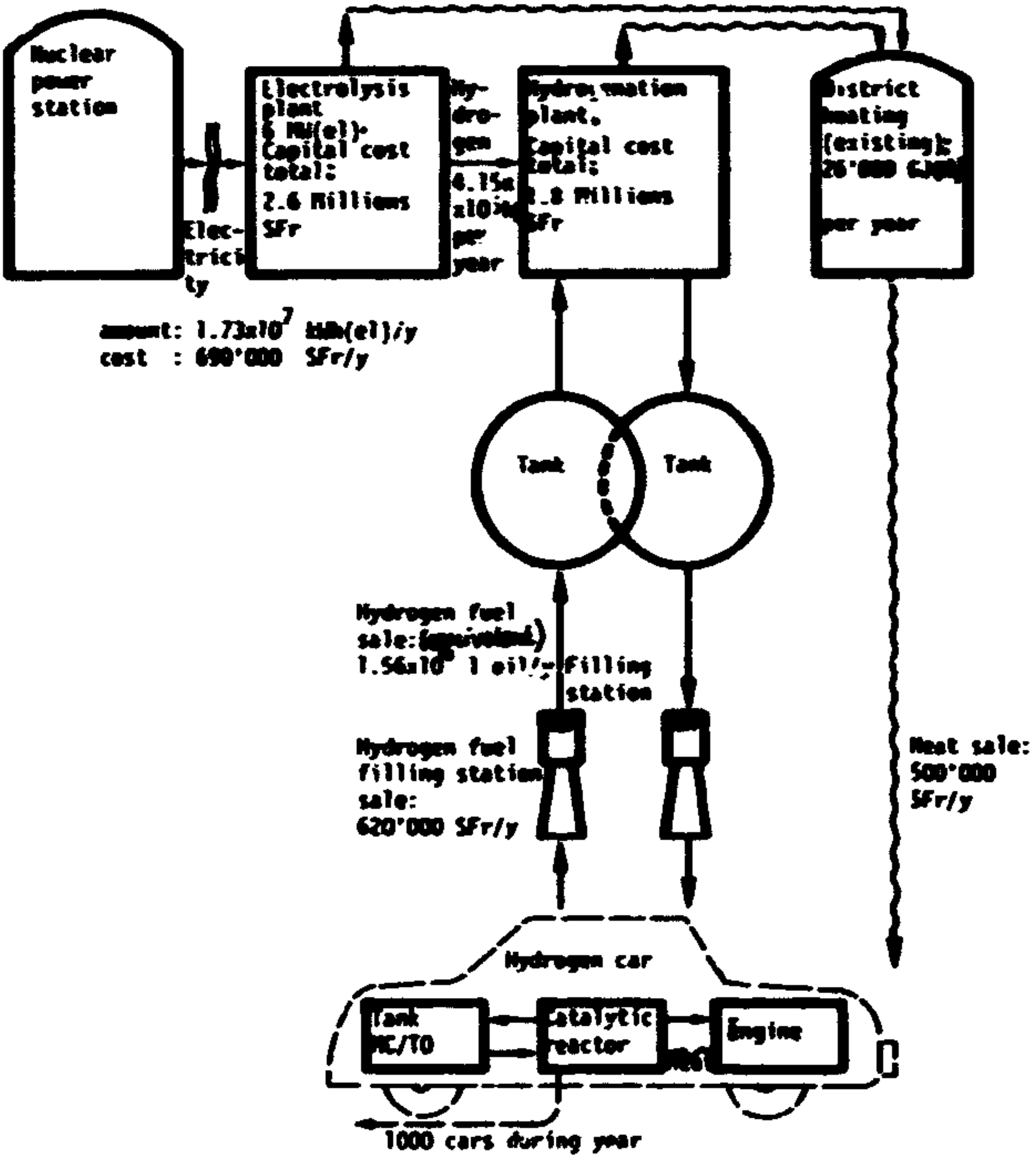
Object	Operation	Unit	Value
Price of electricity	low load period	SFr/kWh(el)	0.040
-- " --	-- --	SFr/GJ(el)	11.11
Efficiency of electrolysis	assumption	percent	80 *)
Amount of electricity	theoretical (100%) pratical: 0.121/0.8	GJ(el)/kg H_2 "	0.121 0.151
Annual hydrogen production	see table 6	GJ(ch)/y	50'000
Electricity consumption	$(50'000/0.8) \times \times (10^9/3.6x10^3)$	kWh(el)/y	1.73×10^7
Electricity cost, annualy	$1.73 \times 10^7 \times 0.04$	SFr/y	690'000
Electricity cost for hydrogen production	0.151 x 11.11	SFr/kg H_2 SFr/GJ(ch)	1.68 13.89
Capital cost of electrolysis plant	roughly calculated (see also ref 3)	SFr/y	2'600'000
Load factor	$\frac{8\text{ h} \times 360\text{ d}}{24\text{h} \times 365\text{ d}}$	factor	0.30
Life in service	according ref. 3	y	15
Annuity	arbitrary (also ref 3)	% per y	10.3
Annuity, specific	calculated	SFr/kg H_2 SFr/GJ(ch)	0.66 5.45
Operation and maintenance	roughly calculated	SFr/kg H_2 SFr/GJ(ch)	0.20 1.65
Total cost of H_2 production	calculated her	SFr/kg H_2 SFr/GJ(ch)	2.54 21.00
Capital cost of a hydrogenation plant (methylcyclohexane from toluene)	according ref. 3) roughly assumed specific cost	SFr/GJ(ch) SFr/kg H_2 SFr/GJ(ch)	6.5 .. 8.5 0.46 3.8
	capital cost, total	SFr.	1'800'000

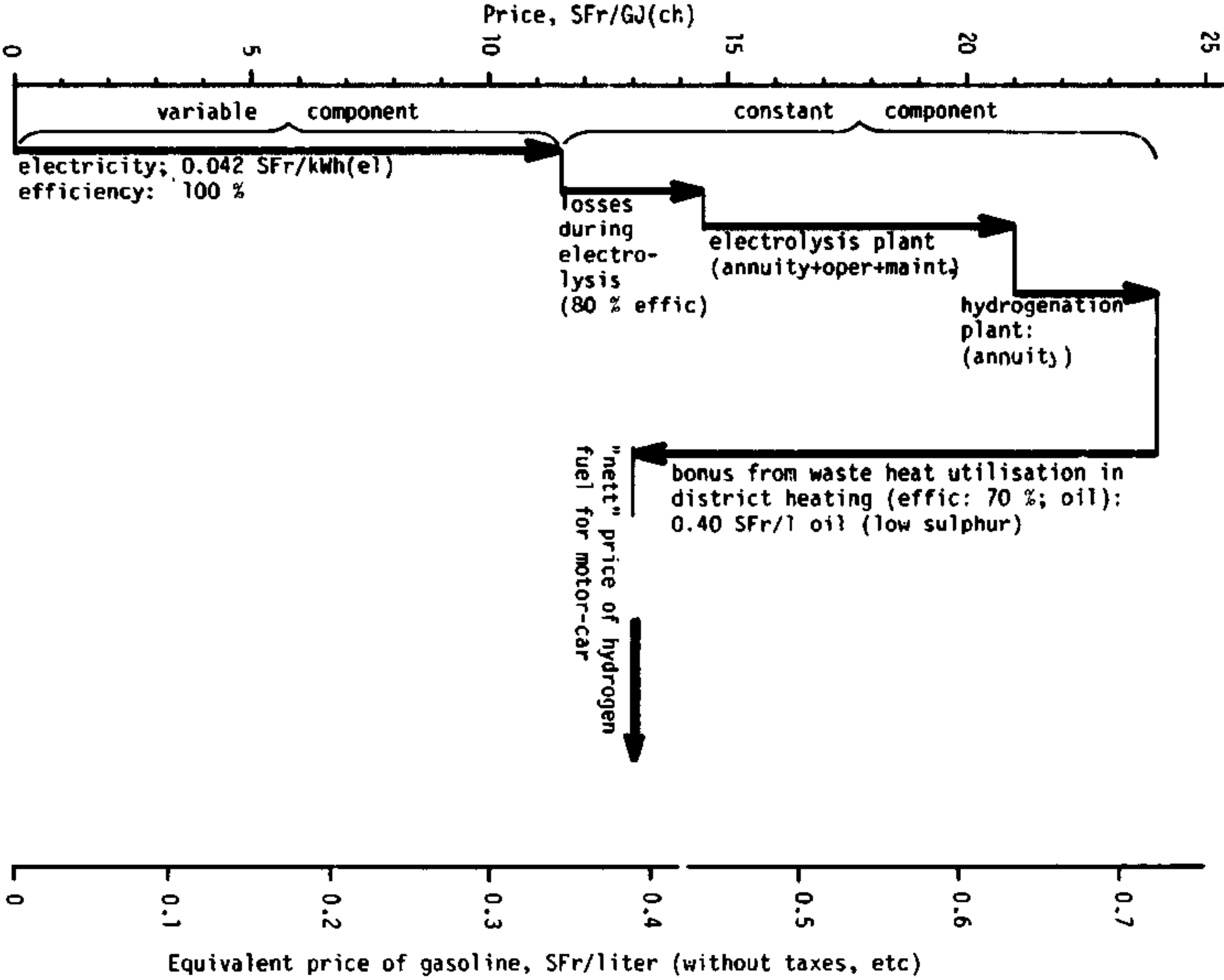
Table 7: Continuation

Object	Operation	Unit	Value
Total cost of H_2 in the methylcyclohexane	calculated	SFr/kg H_2 SFr/GJ(ch)	3.0 24.8
Heat recovery from the electrolysis and hydrogenation	from table 6 (73 GJ/d x 360)	GJ(th)/y	26'000
Heat recovered equivalent to oil	oil: 30 MJ(th)/ℓ	m^3 oil/y	870
Efficiency of burning of oil	assumption	%	70
Effective oil equivalent	870 x 1/0.7	m^3 oil/y	1'230
Price of oil (low sulphur)	arbitrary	SFr/100 ℓ	40
Value of oil equivalent	1230 x 10 x 40	SFr/y	500'000
Price of gasoline	assumption	SFr/ℓ	0.4
Value of gasoline equivalent	from table 6 ($1.56 \times 10^6 \times 0.4$)	SFr/y	620'000
Total cash	calculated	SFr/y	430'000

*) See appendix 9.9

FIG 5, CAPITAL COST





Price, SFr/GJ(ch)
0
5
10
15
20
25
variable component
constant component
electricity; 0.042 SFr/kWh(el)
efficiency: 100 %
losses during electrolysis (80 % effic)
electrolysis plant (annuity+oper+maint)
hydrogenation plant: (annuity)
bonus from waste heat utilisation in district heating (effic: 70 %; oil): 0.40 SFr/l oil (low sulphur)
"nett" price of hydrogen fuel for motor-car
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
Equivalent price of gasoline, SFr/liter (without taxes, etc)

FIG 7. PRICE OF HYDROGEN FUEL IN MTH-SYSTEM VERSUS PRICE OF ELECTRICAL ENERGY

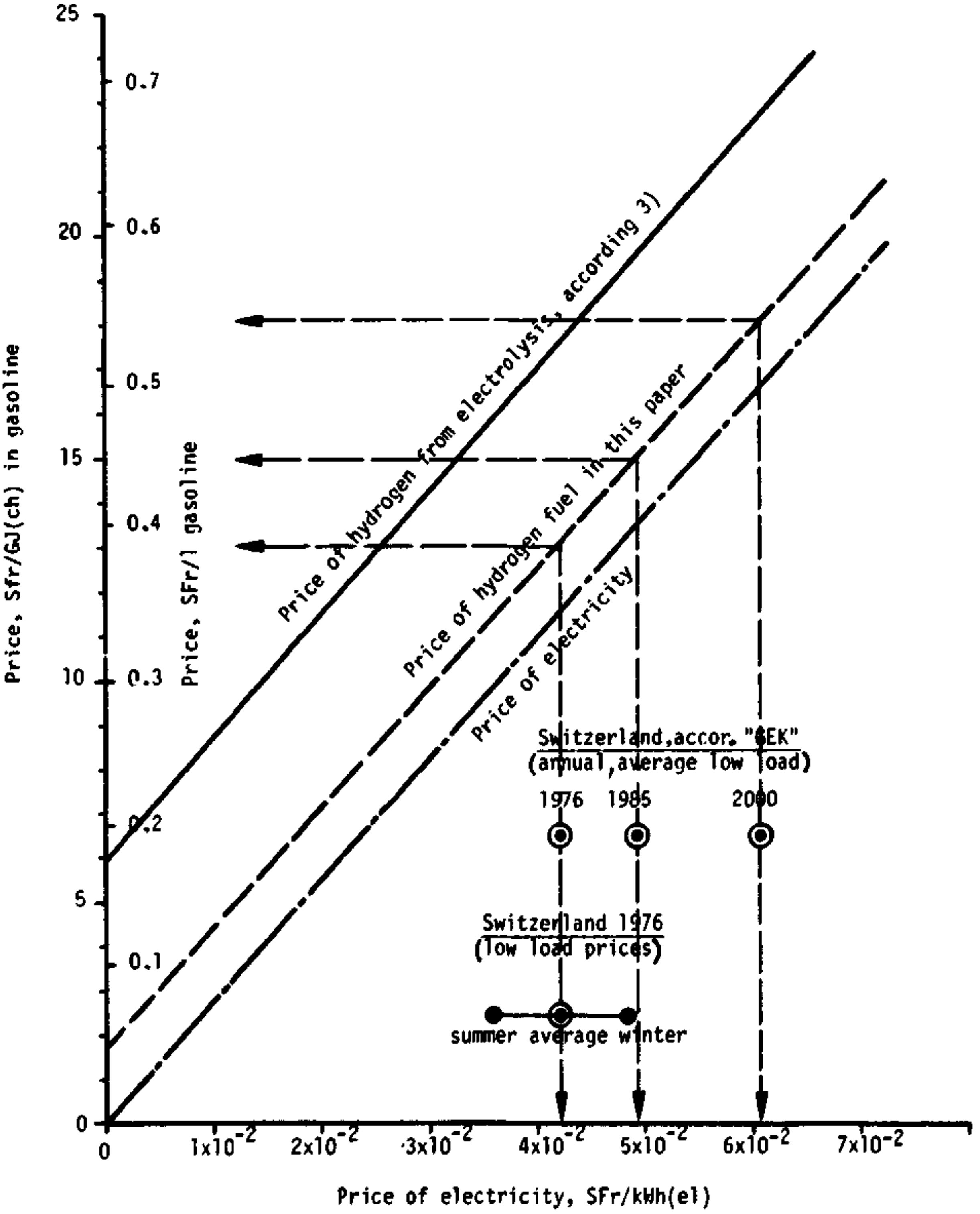
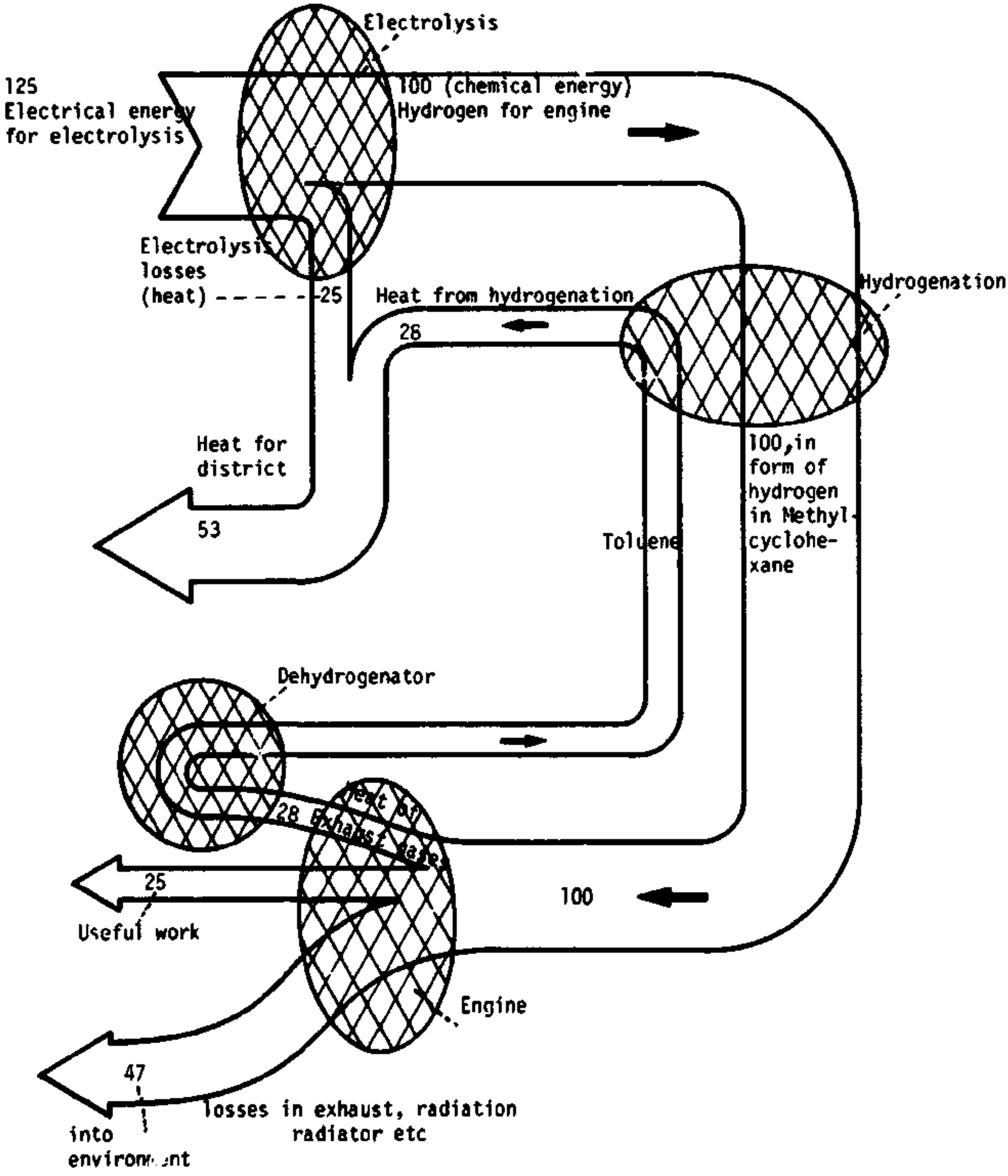


FIG 8. HEAT BALANCE IN THE HYDROGENATION-FILLING STATION



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).

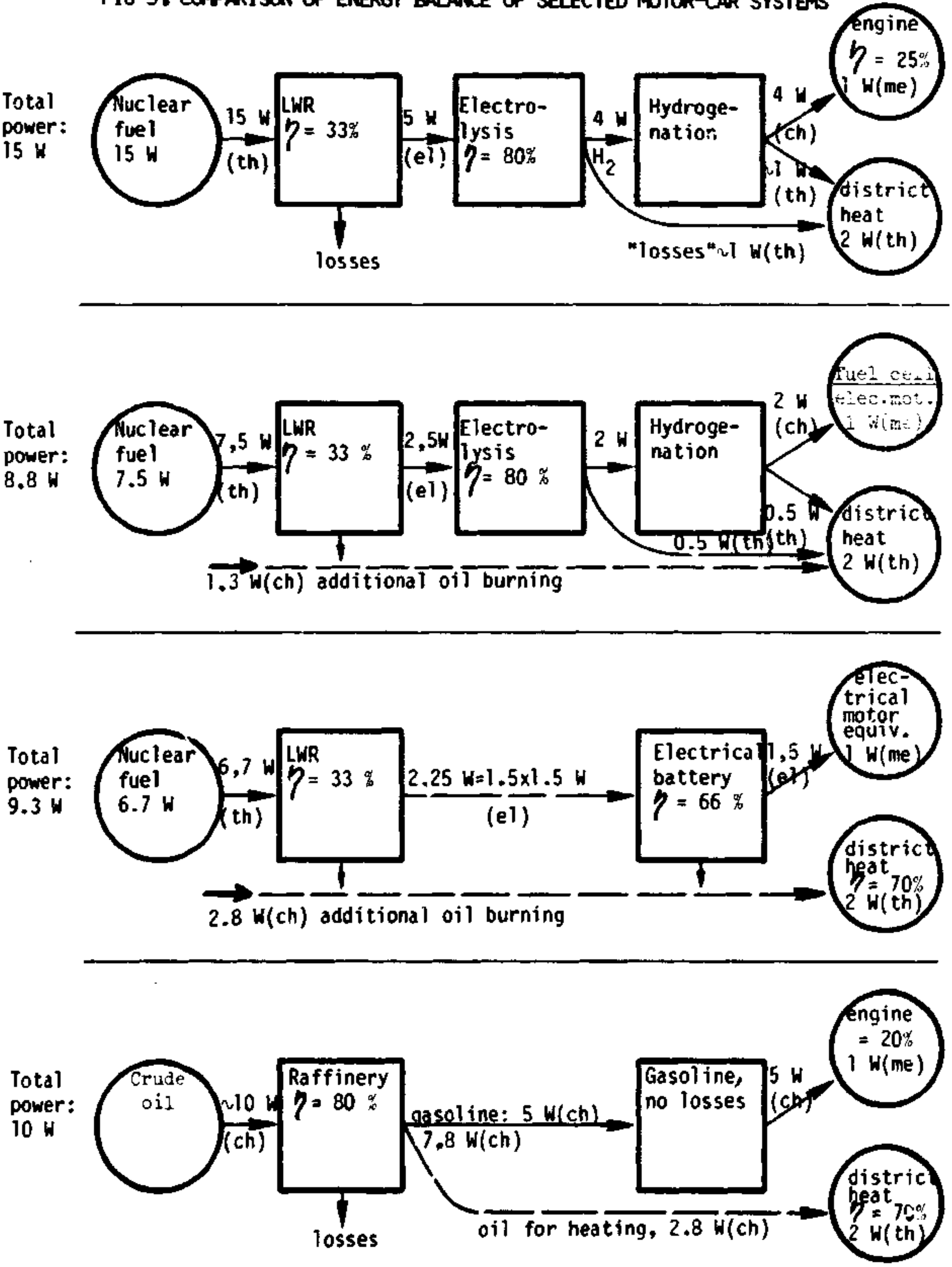
Primary Fuel	Transformation Plant	Total primary energy (Joule)*	Engine, type	Heat for district heating (Joule (th))
Nuclear fuel	Light water reactor efficiency ∿33%	15	Internal combustion engine η = 25 %	2
		8.8	Fuel cell plus electromotor	1
		9.5**	Elect battery plus motor	0
Crude oil	Refinery efficiency ∿80%	10.0	Internal-combustion engine η = 20 %	0

*) 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



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 feasable system.

The pros and contras 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 feasable 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 emmission 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 H_2/day
  - hydrogenation plant: 20 t methylcyclohexane/day
  - filling station with 2 tanks of ∿ 25 m^3
  - filling of 1000 cars each 15'000 km/y
  - a capital cost ∿ 4.4 x 10^6 SFr.

9. Appendix

9.1 Chemical reactors in the equilibrium state

a) Hydrogen production

$$(C_6H_{11}CH_3)_g \longrightarrow (C_6H_5CH_3)_g + (3H_2)g$$

Catalyser : Pt/Al_2O_3 in powder form
Temperature: 610 K
Pressure : 1 bar

Enthalpy of hydrogenation: 210 kJ/mol MC (endothermic)
Efficiency of the hydrogenation reaction: 95 %

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

$$H_2 + (\tfrac{1}{2}\ O_2 + 1.88\ N_2) \longrightarrow H_2O + (\lambda-1)\ \tfrac{1}{2}\ O_2 + 1.88\ N_2$$

Enthalpy of burning: 240 kJ/mol H_2

The value of λ is selected as 2.17 since a hydrogen/air mixture with 2 % H_2 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:

$$H_2 + 2.17\ (\tfrac{1}{2}\ O_2 + 1.88\ N_2) \longrightarrow H_2O + 0.58\ O_2 + 4.07\ N_2$$

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 ϕ.

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:

$$\Delta H'_{(to)} = \int_{298}^{T_{B(MC)}} Cp_{\{MC\}}\,dt + \Delta H_{B\{MC\}} + \int_{T_{B(MC)}}^{610} Cp_{(MC)}\,dT + \Delta H_{D(MC)}$$

From this: $\Delta H'_t = 317$ kJ/mol MC

This energy requirement ΔH_t is provided by the cooling of the dehydrogenation products ($C_6H_5CH_3 + 3H_2$) and the exhaust gases (EG).

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

$$\Delta H''_{(to)} = \int_{610}^{T_{B(TO)}} Cp\ (TO)\,dt + \Delta H_{B(TO)} + \int_{T_B}^{327} Cp_{\{TO\}}\,dT + 3\int_{610}^{327} Cp_{(H_2)}\,dT$$

$$\Delta H''_{(to)} = 101 \text{ kJ/mol } (TO + 3H_2)$$

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

$$\Delta(\Delta H) = 317 - 101 = 216 \text{ kJ/mol MC}$$

$$\Delta(\Delta H) = 5\int_{606}^{1050} Cp\ (EG)\,dT$$

Table 8: Some thermodynamic values.

Calculation of specific heat C_p

T = temperature (K)

$C_p = a + bT + CT^2$

$\Delta H = \int Cp\, dT = aT + \frac{b}{2}T^2 + \frac{c}{3}T^3$

	Coefficients			Cp at 1050 K	
	a	b	c	J/gK	J/mol K
H_2O	34.39	0.62×10^{-3}	5.61×10^{-6}	2.307	41.5
O_2	28.28	2.54×10^{-3}	0.54×10^{-6}	1.095	35.0
N_2	28.3	2.54×10^{-3}	0.54×10^{-6}	1.181	33.0
H_2	27.7	3.39×10^{-3}	-	14.655	29.3

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 (H_2) = 240 KJ/mol H_2
HD (MC) = 210 KJ/mol MC

B = Boiling
V = Combustion
D = Dehydrogenation

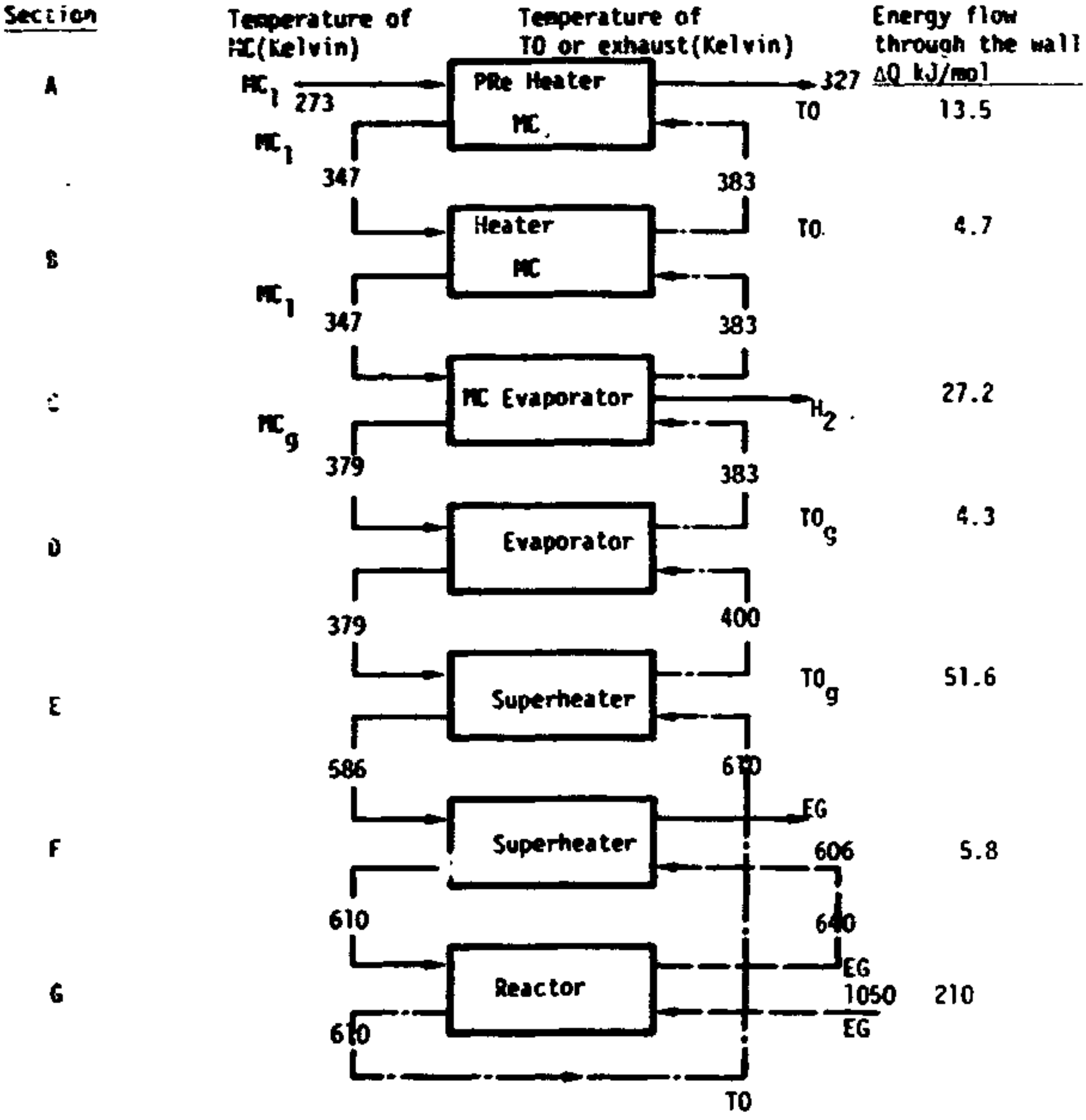
Specific heat of MC, TO

Cp {MC} = 180 J/mol {MC} · K
Cp (MC) = 240 J/mol (MC) · K
Cp {TO} = 160 J/mol {TO} · K
Cp (TO) = 170 J/mol (TO) · K
Cp [Fe] = 400 J/mol [Fe] · K

Boiling points:

T_B (MC) = 374 K
T_B (TO) = 383 K

FIG 10 SCHEME OF HEAT FLOW



Section	Function on the side: Methylcyclohexane	Toluene + H_2
A	Heat Exchange, liquid	Heat Exchange, liquid
B	Heat Exchange, liquid	Condensor
C	Evaporator	Condensor and separation H_2
D	Evaporator	Heat Exchanger, gaseous
E	Superheater	Heat Exchanger, gaseous
F	Superheater	Heat Exchanger (exhaust gases
G	Dehydrogenation Catalyser	

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

$$\Delta T = T_{in} - T_{out}$$

$$T_m = \frac{(\Delta_{TO} - T_{MC})}{\ln(\Delta T_{TO}/T_{MC})}$$

$$\dot{Q} = \Delta H \times \dot{m} \quad (\dot{m} = \text{mass flow; } \frac{\text{mol}}{\text{s}}) \quad \dot{Q} = \text{power } [W]$$

$$F = \frac{\dot{Q}}{k \cdot \Delta T_m} \; [m^2] \qquad \begin{array}{l} F = \text{surface of the heat exchanger } [m^2] \\ k = \text{heat transfer coefficient } [W/m^2\ K] \end{array}$$

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

$$\Sigma F = 2.03\ m^2$$

The Carnot efficiency for an Otto engine with hydrogen is

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

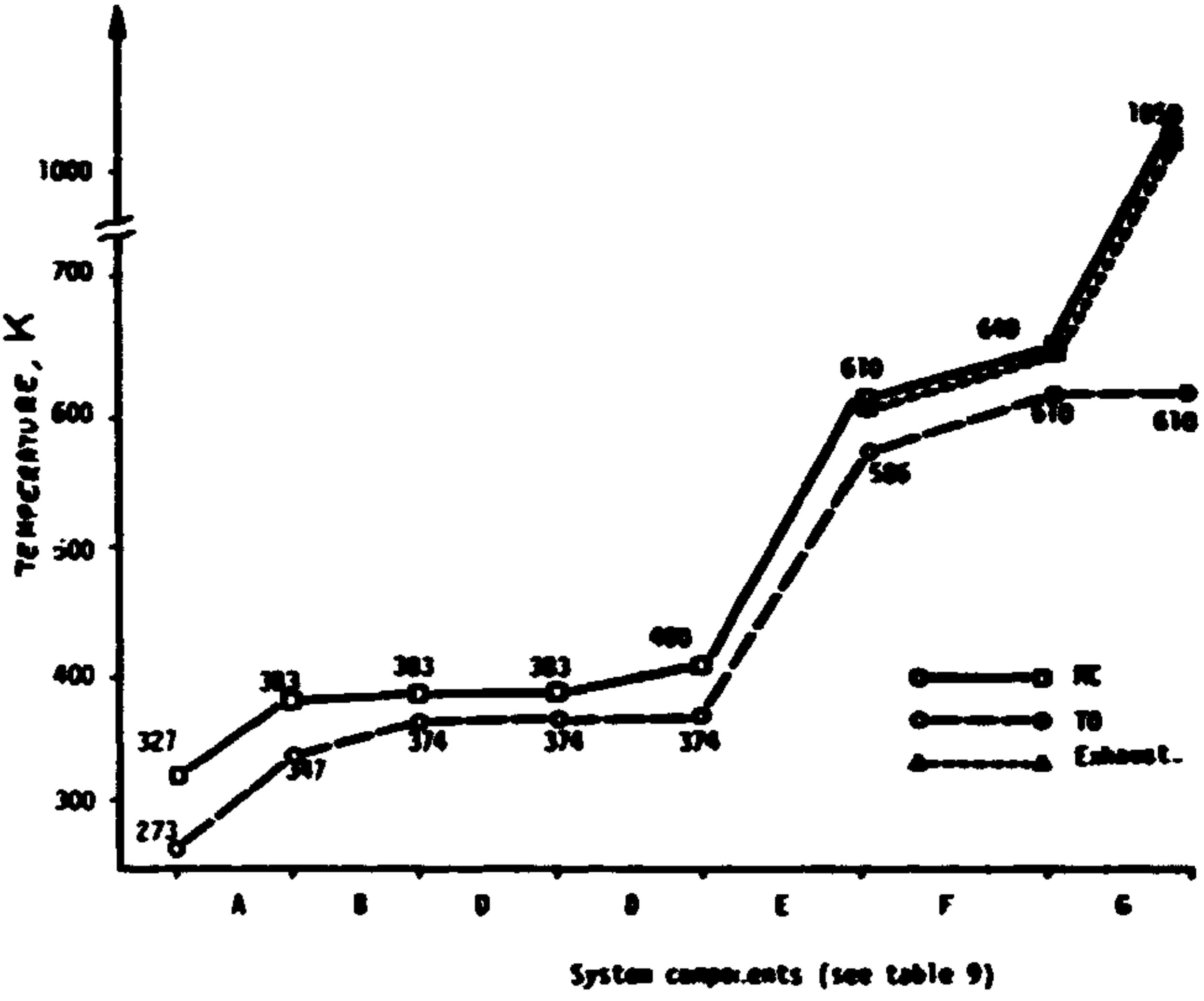
$$\eta_{carnot} = \frac{T_{max} - T_{out}}{T_{max}} = \frac{1950 - 1050}{1950}$$

<u>Table 9</u>: Calculation of the surface area

				System components				
	Unit	A liq/liq	B liq/cond	C vap/cond	D vap/gas	E gas/gas	F gas/gas	G* gas/gas
ΔT_{TO}	K	56	0	condensation	17	210	34	140
ΔT_{MC}	K	74	27	0 evaporation	0	212	24	
ΔT_m	K	64				211	28	
k	W/m^2K*	340	600	2500	600	14	14	150
T_t	K			9				
$\dot{Q}$	kW	0.75	0.26	1.5	0.24	2.84	0.32	15.2
F	m^2	0.03	0.02	0.06	0.03	1.03	0.86	0.73

* See "Wärme-Atlas" 1974.

FIG 11. THE TEMPERATURES IN THE SYSTEM



For this paper it is assumed for the hydrogen Otto engine:

$$\eta_{eff} = 0.25$$

On the relationship of η_{eff} to the Carnot efficiency is:

$$\eta_{eff}/\eta_{Carnot} = 0.25/0.462 = 0.54$$

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 (ø 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 λ = 0.1 W/m.K.

This gives a power loss of

$$\dot{Q}_{loss} = \frac{F \cdot \lambda \cdot \Delta T}{d}$$

$F = 6a^2 = 3\ m^2$ 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 $T_{TO_{out}} - T_{air}$

$\dot{Q}_{loss} = 150$ W calculated loss of heat exchanger

The catalytic reaction unit can be designed as follows

(R = Radius, (m), L = length, (m)).

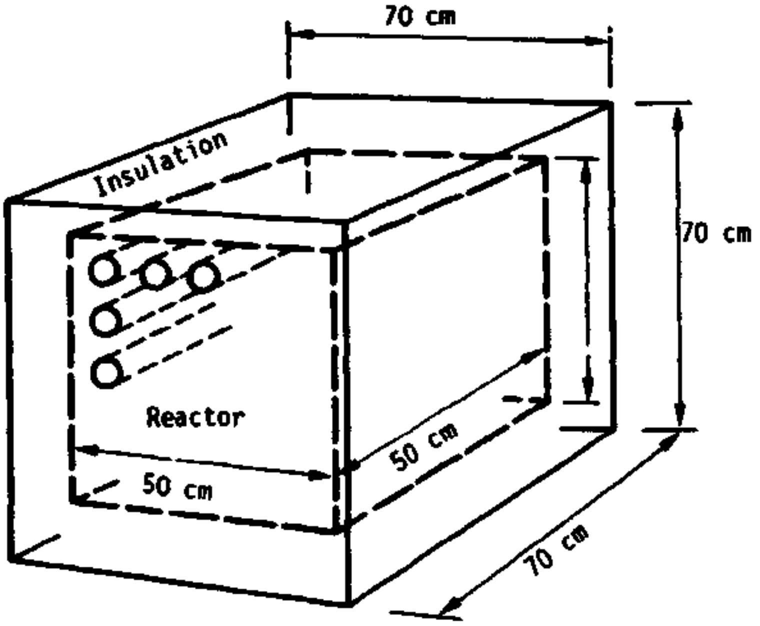
$R_i = 0.1$ m $\Delta R = R_a - R_i$ T_a = temperature at A

$R_a = 0.2$ m ΔR = wall thickness; T_i = temperature at I

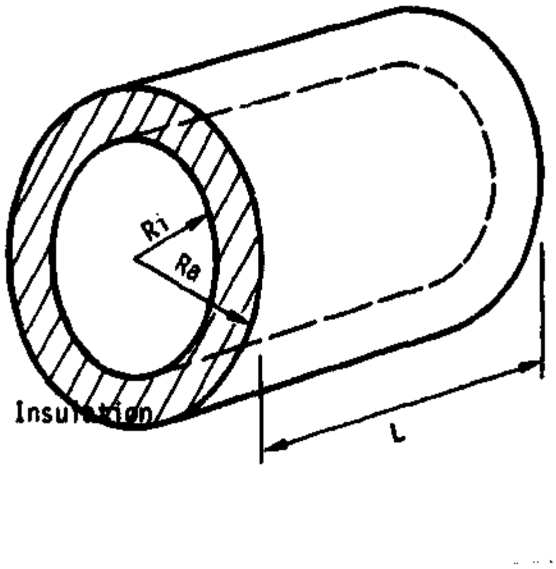
$L = 0.4$ m $\Delta T = T_i - T_a$

FIG 12. 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

$$\dot{Q}_{loss} = \frac{T_a - T_i}{\ln (R_a/R_i)} \cdot 2\pi\cdot\lambda\cdot L + 2 \left[\frac{R_a + R_i}{2}\right] \pi \frac{\lambda\cdot\Delta T}{R} \cong 30 \text{ W}$$

The total losses of the combined system is therefore ∿ 180 W.

9.6 <u>Dynamic behaviour</u> (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

  $H_2 + 2.17\ (0.5O_2 + 1.88\ N_2) \longrightarrow H_2O + 0.580\ O_2 + 4.08\ N_2 + \Delta H$

  $\Delta H = 240$ kJ

- Burning during acceleration with addition of 0.06 mol TO (e.g. 5.9 g TO)

  $$H_2 + 2.17\ (\ O_2 + 1.88\ N_2) + 0.06\ TO \longrightarrow 1.42\ H_2O + 0.42\ CO_2 + 4.08\ N_2$$

  $\Delta H = 504$ 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 CO_2 and perhaps NO_x (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 fossile 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 $Q_{HE} = \Sigma Cp \cdot \Delta T \cdot m_{HE}$ and the thermal energy necessary to start the release of hydrogen.

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

m_{tot} = $(F \cdot d \cdot p) x 2.5$; $p = 7800\ kg/m^3$; $d = 2\ mm$

F = surface (m^2)

Cp = 0.4 kJ/kg (iron)

$$\Delta T = \sqrt{T_{max} \times T_{min}} - T_u = \sqrt{1000 \times 273} - T_u = 250\ ^oC$$

T_u = temperature of the surroundings

The heat needed for a cold start is:

$Q_{HE} = 78$ kJ

This heat can be produced either by burning toluene of 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)

Gasoline - full tank	16 kg	average	8 kg
MTH system " "	85 kg	"	84 kg
Difference			76 kg
Tank for MTH system	30 kg		
Catalyser reactor	20 kg		
Other extras	20 kg		70 kg
Total additions			146 kg

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 feasability 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 °C, investment cost 250 $/kW(el)

Today's modern electrolysers 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 °C; the module system with 8-10 MW(el).

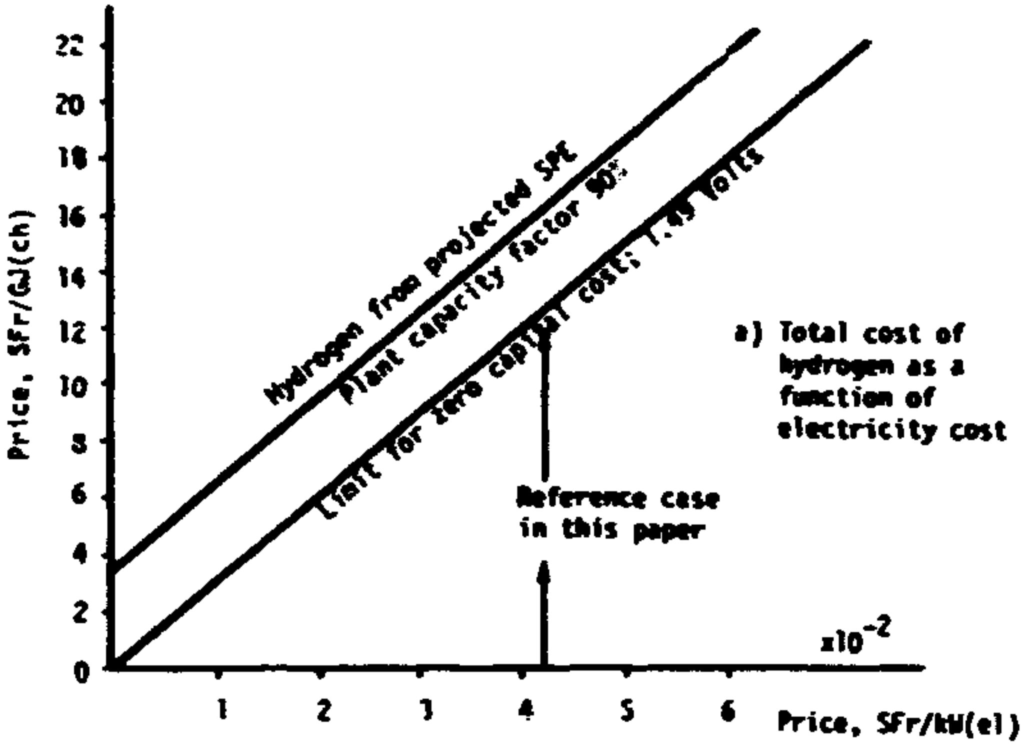
According to ref. 18 the price of hydrogen produced by electrolysis is dependent on the price of electricity and the plant capacity factor (as shown in figure 13).

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

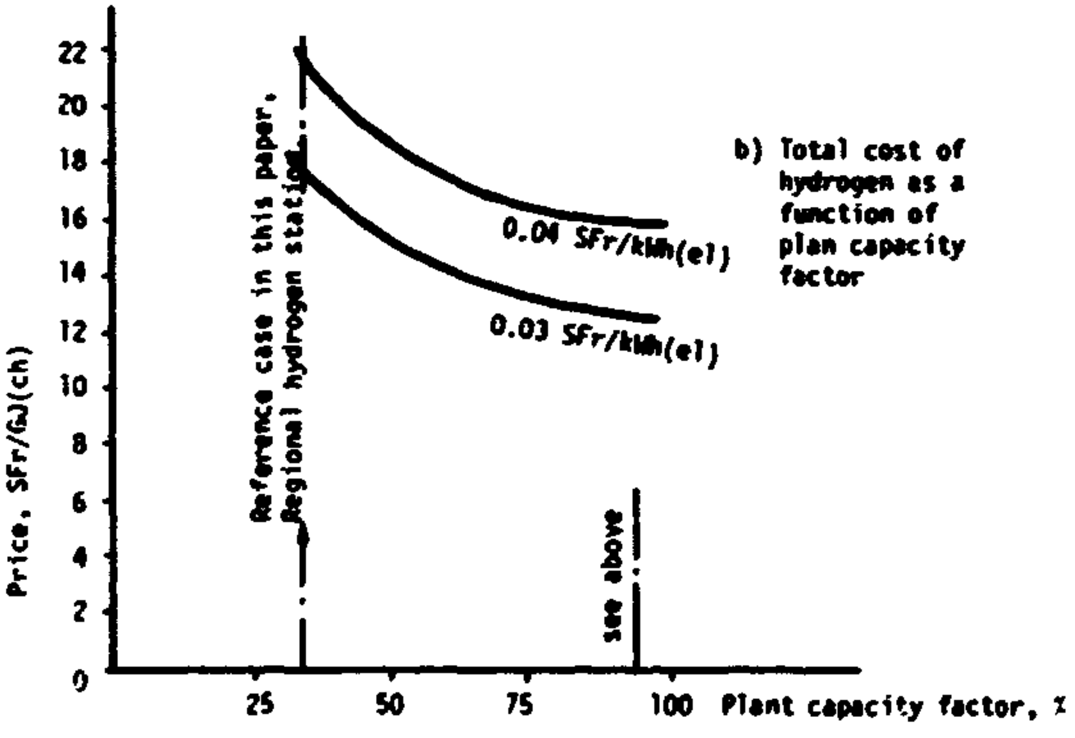
Overall system efficiency	85 - 90 %
System capital cost	50 $/kW(el)
Life	20 years
Scale up: Demo system	5 MW(el)

Temperature		150 °C
Pressure		20 bar
Estimated costs		
(1 US $ = 2 SFr.)		
1976	Electricity	9.5 SFr./GJ(el)
	Hydrogen without sale of O_2	10.7 SFr./GJ(ch) in H_2

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 plan capacity factor

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