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Hydrogen and methanol: a comparison of safety, economics, efficiencies and emissions

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Abstract

Fuel cell cars will appear on the market early in the next century. A question still remains — whether these vehicles will store onboard, hydrogen or, the hydrogen-rich carrier, methanol. There are a number of key areas surrounding this question, three of which are safety, economics and efficiency and emissions. Each of these issues was examined using the available literature. It can be seen that it is only with emissions that a clear difference appears and then hydrogen shows an advantage over methanol. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

- Within the past 2 years 18 prototype fuel cell vehicles have been produced [1].
- Most of the major OEM's are gearing up for a year 2004 launch of fuel cell cars.
- Ford's P2000 and DaimlerChrysler's NECAR 5 are currently undergoing real world tests in California in the Californian Partnership Driving for the Future
- Jürgen E. Schrempp of DaimlerChrysler, at the launch of the NECAR 5 was quoted as saying "Today we declare the race to demonstrate the technical viability of fuel cell vehicles over. Now, we begin the race to make them affordable" [2].

All these points can be seen as evidence that fuel cell cars are on their way and soon. One question that still seems to be unanswered though is whether the customer will be refuelling their vehicle directly with hydrogen or via the hydrogen-rich carrier, methanol. This is a very important issue not just from a refuelling infrastructure perspective but also from the public perception and from the gearing up of production, retraining of staff and me-

chanics, developing guidelines and dealing with safety issues that will need to put in place for the new fuel. It is unlikely economically and historically that both will develop equally side by side at the same time. Historically, there were a number of vehicle technologies and fuels on the market in the late 1800's. The competition for the dominant fuel was won by petrol and these other technologies and fuels were virtually forgotten. Petrol won over its rivals initially due to the price of the vehicle and then the development of the surrounding infrastructure clusters. This has developed into a technological lock-in where possibilities for new fuels or technology are initially severally limited [3]. Fuel cells are now seen as a possibility of braking this lock-in, but it could lead to another situation where one fuel has dominance. DaimlerChrysler has said that their 2004 vehicle will be powered by methanol [2]. Will this give methanol an edge? The buying public may not be too keen once they are used to one fuel to swap to another.

Three key issues that may help to decide which might be the leader — hydrogen or methanol — are safety, economics and efficiency, and emissions. This paper will examine each of these issues but will not touch on areas such as distribution and refuelling. The issues of distribution and refuelling are very important as mentioned above in the concept of cluster technology. For a good overview

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Table 1

Physical properties of hydrogen, methanol and petrol relevant to accident safety

	Hydrogen [5]	Methanol [6]	Petrol [6]
Molecular weight	2.016	32.04	107
Liquid density	71 (LH ₂),	791	
(gm/l^{-1})	0.0013 (GH ₂)		
Vapour density	$14 \times lighter$	$1.1 \times \text{heavier}$	$2-5 \times heavier$
relative to air $(=1)$			
Volatility (RVP-psi)	-	4.6-5.3	9-15
Boiling point (K)	20.27	338	
Minimum ignition	0.14	0.02	0.024
energy (mJ)			
Diffusion coefficients	0.61	0.0042	0.05
$(cm^2 s^{-1})$			
Flammability limits	4-75	6-36.5	1-7.6
(vol.%)			
Explosive limits	18.3-59.0	6–36 [7]	1.1-3.3
(vol.%)			
Fraction of heat in	17-25	17	30-42
radiative form			
Flame temperature	2318	?	2470
in air (K)			

of the infrastructure issues, refer to Scott $(1997)^{1}$ and specifically for hydrogen to Directed Technologies (1997).

2. Safety

Of the two fuels, hydrogen has the "explosive" public image and there is concern as to how the public may react to refuelling with what some perceive as a very dangerous fuel. Methanol, by contrast, has quite a safe public image. In the USA, the IndyCar 500 has been running successfully on Methanol for a number of years [4]. Table 1 outlines a number of important properties of hydrogen and methanol relevant to the assessment of safety in case of an accident, and as a comparison the figures for petrol are included, were known.

These properties are important in assessing the risk of fire in an accident or leak, and in the case of fire, in helping to analyse the severity of the situation. The first two important points are:

- Only fuel vapour will ignite.
- There are two types of situation in which the important physical properties differ slightly. These are:
 - Well-ventilated spaces, natural ventilation or mechanical; and
 - Totally enclosed spaces with no ventilation.

A fuels' volatility is a measure of how quickly a liquid will turn into a vapour, so as hydrogen is already a gas, it

does not have a measure for volatility. Methanol has nearly half the volatility of petrol and therefore a lower risk of producing an ignitable vapour. Once a vapour is produced, it then must build up to a flammable concentration. Below the lower, "lean", limit the concentration is too low and above the upper, "rich" limit the concentration is too high. To allow a fuel vapour (or gas for hydrogen) to build up, there must be one of two conditions. It must be heavier than air and therefore accumulate around the leak or it must be in an enclosed space and therefore without a route for the escape of light gases. Both petrol and methanol are heavier than air and therefore will accumulate, though methanol at a much lower rate than petrol, which due to its weight tends to "pool" around a leak. At the other end of the scale is hydrogen, the lightest element of the periodic table. It is 14 times lighter than air and therefore in areas with any ventilation it will disperse, though in totally enclosed spaces it will accumulate like methanol and petrol. Liquid hydrogen is different from gaseous hydrogen in that it does tend to pool like petrol but reverts to it's gaseous state quickly and then disperses.

The flammability range is highest for hydrogen of all the fuels but, due to its physical nature, it is virtually impossible in areas with any ventilation to accumulate the concentration to reach its high lower limit. If a leak or rupture were to occur in an enclosed space, allowing air in to mix with hydrogen due to its high flammability range, it will stay at potentially volatile mixtures longer. This could be viewed as an important safety consideration as places such as tankers that have no natural ventilation, but without an ignition source, it still would not ignite. Methanol has a much smaller flammability range but petrol has the least. Therefore, even though petrol would be the quickest of the three to reach its lower flammability limit, it would also be the quickest of the three to exceed its upper flammability limit.

In case of fire, an important consideration is the amount of heat that is radiated from the flames. This is to allow assessment of the likelihood of surrounding objects catching fire. Returning to the data in the table, both hydrogen and methanol give off substantially less heat in a radiative form than petrol and therefore surrounding objects are less likely to catch fire.

 Table 2

 Comparative risks in case of an accident

 Summer Our concentration

Source:	Own	assessment.
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	Hydrogen	Methanol	Petrol
Ventilated area			
Producing a flammable mix	3	2	1
Fire spreading	2	2	1
Visibility of flame	1	1	3
Enclosed space			
Producing a flammable mix	1	2	3
Producing an explosive mix	1	2	3

¹ S. Scott, "Fuel distribution infrastructure study for transport applications for fuel cell powered vehicles", ETSU, 1997. Directed Technologies "Hydrogen infrastructure report", Ford Motor, 1997.

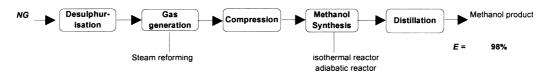


Fig. 1. SMR of natural gas to produce methanol [9].

Though not highlighted in the table, one point that should be made is that, unless there is contamination, both hydrogen and methanol will burn with an invisible flame. Due to the need for fuel cells to have a high purity of fuel, the addition of any colorants or odourants may be technically problematic. Once on fire, though, hydrogen will burn at nearly the same temperature as petrol. Table 2 summarises the information in cases of ventilated areas and enclosed spaces, where 1 — highest risk and 3 — lowest risk.

So in the case of safety, both hydrogen and methanol come out as safer fuels than petrol, though between the two new fuels, there is no clear winner. In ventilated spaces, gaseous hydrogen is safer than methanol, but the reverse is true in totally enclosed spaces.

3. Economics and efficiency

There are many production processes possible for hydrogen and methanol. The current main industrial processes include Steam Methane Reforming (SMR) of natural gas, coal gasification, and for Hydrogen, electrolysis of water [8]. These processes are well known and understood and in the short to medium term are expected to be the main producers of both hydrogen and methanol.

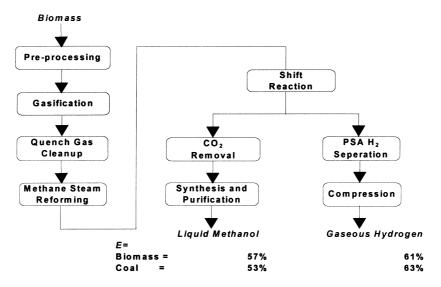


Fig. 2. Renewable energy and electrolysis to produce hydrogen and methanol.

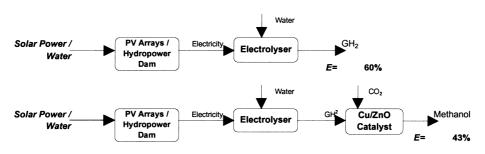


Fig. 3. Biomass gasification to produce methanol and hydrogen [10].

Table 3

Comparison of production costs of hydrogen and methanol from current processes and future techniques

SMR natural gas	Production process	Cost (\$/GJ)		Notes
		Hydrogen	Methanol	
Bailey [13] quoted in	SMR NG/Hydrogen	4.30		Natural gas cost \$1.89 per GJ, 1980 figures
Hammerli [14]				
Ogden et al. [15]	Large scale SMR NG/	5–9		No additional information provided on conditions
Various authors quoted in Basye	Hydrogen Large scale SMR NG/	4.14-7.03		Plant size 1.4 and 6.67 million Nm ³ /day, natural gas
and Swaminathan [12]	Hydrogen	4.14 7.05		cost \$2.15 and \$1.9 per GJ, includes by product
	, ,			steam credits, 1994 and 1997 figures
Basye and Swaminathan [12]	Small scale SMR NG/	10-27		Plant size 0.028 and 0.0028 Nm ³ /day, 1997 figure
de Percin and Werner [16]	Hydrogen Medium scale SMR NG/		7.8	
de Ferchi and werner [10]	Methanol		7.0	
de Percin and Werner [16]	Large scale SMR NG/		6.85	
	Methanol			
Brinkman [17]	Large scale SMR NG/		5.63	1989 Costs for US, no other data
Brinkman [17]	Methanol Large scale SMR NG/		7.25	Projected long-run costs in Canada from 1989
	Methanol		1.23	rojected long-tuli costs in Canada from 1989
<i>POX Oil</i> Steinberg and Cheng [18],	POX heavy Oil/Hydrogen	7.7, 9.13 and		Plant sizes are 36,200, 34,757 and 187×10^6 GJ
Morre and Raman [19], IKARUS	TOX heavy On/ Hydrogen	28		/day (assuming 24-h day), figures from 1995, 1989
report [20] quoted in Basye		20		and 1996, respectively
and Swaminathan [12]				
Gasification of Coal				
Bailey [13] quoted in	Coal/Hydrogen	8.50		First generation Koppers-Totzek process, 1980 figures
Hammerli [14]	com/ Hydrogon	0.00		The generation respects Totten process, 1900 ingues
Bailey [13] quoted in	Coal/Hydrogen	6.90		Second generation Koppers-Totzek process, 1980 figures
Hammerli [14]				
ChemEng News [21], and	Coal gasification/Hydrogen	4.2–19.95		Both Koppers–Totzek process, cost of coal feedstock
Liepa and Borhan [22] quoted in DeLuchi [23]				\$1.91 and \$2.27 GJ, respectively, 1979 and 1986 costs, respectively
National Research Council [24]	Coal gasification/Methanol		19.3	1988 costs, no other information
Johansson et al. [25]	Coal gasification/Methanol		9.05	1989 pretax cost, 5000 tonnes/day plant capacity
	- ,			
Gasification of biomass Ogden et al. [15]	Biomass or coal/Hydrogen	8-10		No additional information provided on conditions
Mann [26] quoted in Basye	Biomass gasification/	13-23		Plant size 907 and 27 tonnes/day, respectively,
and Swaminathan [12]	Hydrogen	10 20		figures from 1995
Johansson et al. [27]	Biomass gasification/		6.56-15.34	Plant size 9090 and 1814 dry tonnes/
	Methanol			day, respectively, 1993 costs
DeLuchi et al. [28]	Biomass gasification/		9.55-14.10	Plant size 1650 dry tonnes/day, 1991 costs
K-+-f-1[10]	Methanol		0.02 14.10	
Katofsky [10]	Biomass gasification/ Methanol		9.83-14.18	Plant size 1650 dry tonnes/day, 1993 costs
Larson and Katofsky [29]	Biomass gasification/Metha	nol	9.62-15.4	Plant size 1650 dry tonnes/day, 1992 costs
	<i>c ,</i>			
Electrolysis		17.22		Hadren factoria and a state from FOIHIPD
Sprecht et al. [30] Dutta et al. [31]	Electrolysis/LH ₂ Electrolyser/LH ₂	17.33 26.1		Hydropower feedstock, projected costs from EQHHPP Grid electricity feedstock, 1990 costs
Dutta et al. [31]	Electrolyser/LH ₂ Electrolyser/LH ₂	20.1 98.8		PV feedstock, 1990 costs
Dutta et al. [31] Dutta et al. [31]	Electrolyser/LH ₂	30.5		PV feedstock, 2000 projection of costs
Hammerli [14]	Bipolar electrolyser/	20.39		0.08 MW capacity, electricity cost 2 cents/kW h, 1978
	pressurised Hydrogen	20.37		technology and costs
Hammerli [14]	Bipolar electrolyser/	10.15		3.5 MW capacity, electricity cost 2 cents/kW h, 1978
	pressurised Hydrogen			technology and costs
Hammerli [14]	Bipolar electrolyser/	9.61		50 MW capacity, electricity cost 2 cents/kW h, 1978
	atmospheric Hydrogen			technology and costs
DeLuchi [23]	Electrolysis/LH ₂	28.3-75.6		Feedstock solar power, middle-term projected low and
Moore et al. [16] quoted in	Small scale electrolyser/	49.1		high cost estimates Plant size 3 kg/day, 1996 figures, 65% efficiency
Basye and Swaminathan [12]	Hydrogen	47.1		1 Iant Size 5 kg/ uay, 1990 figures, 65% efficiency
	11,010501			

Table 3 (continued)

SMR natural gas	Production process	Cost (\$/GJ)	Notes
		Hydrogen	Methanol	
Basye and Swaminathan [12]	Alkaline water electrolyser/ Hydrogen	20-30		No figures on size, efficiencies at 70-80%
Sprecht et al. [30]	Electrolysis/Methanol		3.13	Hydropower feedstock, projected costs from EQHHPP

Figs. 1 and 2 outline simple block diagrams of SMR and electrolysis of water and show the efficiencies of the production process (NB this efficiency figure is the conversion figure of the feedstock into methanol or hydrogen and does not include any measure of the efficiency of the extraction of natural gas and coal or the conversion of solar/hydropower into electricity). Fig. 3 shows the process of biomass gasification, a process that is generating a lot of interest due to its potential to provide a closed loop cycle in terms of renewable energy and emissions. The gasification of coal is essentially the same process after the preprocessing step.

The cost of production of hydrogen and methanol could play a key role in deciding which gets an overall advantage. Table 3 outlines a number of estimated costs for current production techniques and predicted future costs. Note that these costs are in \$/GJ and have not been normalised to any year, they are left in the year of publication of the data.

As can be seen from these data, there is a wide range of costs in the literature all using a wide variety of assumptions or base costs. What it does show is there does not appear to be a vast difference between the cost of producing hydrogen and the cost of producing methanol on a large scale using today's technology. The costs for producing from renewable feedstocks are substantially higher Some see them as prohibitively high, but these costs are predicted to fall. LBST of Germany have completed a study looking into predicted future costs of renewable produced electricity. Table 4 shows the results of the study for biomass, hydropower and direct solar photovoltaic (in the USA).

There are a number of equations that can be used to calculate the cost of production of hydrogen but not the equivalent for methanol. For hydrogen, the information includes the following.

Table 4	
Future costs of electricity pre-	oduction from renewable sources [11]

— • • • •

Production costs	Present (ECU/kW h _e)	Future (ECU/kW h _e)
Biomass	0.07-0.085	0.03-0.05
Hydropower	0.01 - 0.04	0.02-0.04
Direct solar PV	0.43	2000:0.17, 2030:0.03-0.06

• SMR cost — 60% of the production cost is attributed to feedstocks, 30% to capital and the final 10% to operation and management costs. The equation by Ogden quoted in Bayse and Swaminathan [12], gives the cost of small SMR plants at:

Installed Cost = $\$1.03 \times 10^6$

 \times (plant capacity in million Nm³/day)^{0.3}.

• For electrolysers, Bayse and Swaminathan calculate that 70-80% of the total cost is from the cost of the electricity, capital charges are 15-20% and the operation and management charges can be as little as 5% of the overall production cost. This is important if there was to be serious consideration of the use of renewables to provide the electricity for the electrolyser. As can be seen from Table 4, if PV's can obtain some of this cost reduction, it would go a long way to making the system more attractive.

• DeLuchi [23] gives an equation for the calculation of the cost of solar produced hydrogen as:

$$GH_{\rm c} = N_{\rm e} + P_{\rm co} (H_{\rm e}/P_{\rm e})^{-} 1,$$

where: GH_c — cost of gaseous hydrogen produced (\$/mm Btu H₂); N_e — the non-energy costs of electrolysis (\$/mm Btu H₂); P_{co} — cost of electricity at the site of generation (\$/mm Btu power); H_e — energy in the hydrogen produced (mm Btu/year); P_e — the amount of power used to produce H_e ; H_e/P_e — efficiency of the electrolysis unit.

• For biomass or coal as a use as feedstock, the process is more capital intensive and the cost of the feedstock is expected to be around 25–30% of the total production costs (Katofsky [10]).

The efficiency of the process from the feedstocks extraction through to the end use in the fuel cell is an issue that has not been explored often. For fuel cell use, efficiencies of the stack are often quoted as already much higher than a standard production internal combustion engine. To extrapolate this backwards to see the efficiencies of the extraction, production process right through to the engine or fuel cell stack produces some interesting results. Table 5 outlines these efficiencies.

The renewables show up as not being an efficient process. This is due to the low efficiencies involved in the

Table 5

Efficiencies from feedstock extraction through to fuel cell use Authors' own calculation.

	%	Extraction efficiency	Conversion efficiency	Storage and dispensing	Reformer efficiency	Fuel Cell stack efficiency	Calculated overall efficiency
Hydrogen	Steam reforming of natural gas	98.2	86 [10]	65 [38]	N/A	58 [39]	32
	Coal gasification	75	63 [10]	65		58	18
	Hydropower/electrolysis	90 [33]	60 [30]	65		58	20
	LH2-EQHHP	90 [29]	85 [29]			58	29
	Biomass gasification	15 [34]	61 [28]	65		58	6
	Solar electrolysis	35 [35]	85 [29]	65		58	8
Methanol	Steam reforming of natural gas	98.2	70 [36]	99.8	77 [39]	51 [39]	27
	Coal gasification	75	53 [37]	99.8	77	51	18
	Hydropower/ electrolysis	90 [29]	43 [29]	99.8	77	51	15
	Biomass gasification	15 [34]	57 [28]	99.8	77	51	3
	Solar electrolysis	35 [35]	43 [29]	99.8	77	51	6

collection of the biomass and the conversion of incoming solar radiation into electricity. An interesting point that comes out of the table is that methanol does not drop much efficiency percentages even with the reformer onboard. This implies that the litres per kilometre difference would be small. It is obvious that a lot of the efficiency is being lost in the storage and dispensing of the hydrogen. The figures are for hydrogen stored in a compressed form in tanks. If the work on metal hydrides and carbon nanotubes succeeds, then these efficiency figures could increase dramatically [40]. For comparison purposes, Table 6 outlines Shell and DaimlerChrysler calculations for the NG process.

4. Emissions

This is the area where most claims are made for the virtue of fuel cells over internal combustion engines and between proponents of both hydrogen and methanol. Many predicted emissions figures are available as until recently there have been no real world tests on these fuel cell vehicles. Table 7 shows values from the literature that are all normalised to CO_2 g/km equivalent. Where possible, this has been subsplit into upstream emissions and vehicle use emissions though it is uncertain as to where some of

Table 6

Comparison of three sets of efficiencies from Shell, DaimlerChrysler and this study

SMR-NG	Shell [31]	DaimlerChrysler [32]	This study
Hydrogen (%)	27	28-32	32
Methanol (%)	19	27	27

the authors have placed this split. For an overall impression, the percentage of emissions as compared with a standard petrol internal combustion engine have been included.

From the given data, significant differences between the estimates can be seen. The following points are also shown:

- for hydrogen, the total figures are consistently lower than for methanol;
- from coal production, hydrogen comes out nearly a factor of 10 cleaner than methanol and methanol from coal seems to emit as much pollutants as a petrol ICEV;
- the reduction in emissions become more significant when methanol and hydrogen can be produced from renewables.

5. Summary

5.1. Safety

• Both hydrogen and methanol are safer than petrol.

• In certain situations, with current engineering, hydrogen is a higher risk than methanol.

5.2. Economics and efficiencies

• There is no clear economic reason why one fuel should be favoured over the other and if the cost reductions in renewables come about, why renewables should not be favoured over fossil fuel feedstocks. Table 7

CO ₂ equivalent emissions produced from a range of production processes for hydrogen and methanol
NB for the conversions into CO ₂ equivalent the 1992 IPCC figures were used [48].

Source	Vehicle type	CO ₂ equivale	CO_2 equivalent emissions (g/km)		Percentage of gasoline ICEV (%)
		Upstream	Vehicle	Total	
Mark [41]	Gasoline ICEV	68.3	204.9	273.2	100
Adapted from Kartha and Grimes [42]	NG/Hydrogen/FC	23.9	0^{a}	23.9	8.8
Mark [41]	NG/Hydrogen/FC	100	0	100	36.6
Adapted from Lipman and DeLucchi [43]	NG/Hydrogen/FC	21.2	0^{a}	21.2	7.8
Adapted from Hart and Bauen [44]	NG/Hydrogen/FC	92.1	0	92.1	33.7
Mark [41]	NG/Methanol/FC	48.4	82.6	131	48
DeLuchi [27]	NG/Methanol/FC	96	90	186	68
Adapted from Kartha and Grimes [42]	NG/Methanol/FC	30.1			
Adapted from Hart and Hörmandinger [45]	NG/Methanol/FC	31.6	104.5	136.1	49.8
Mark [41]	Biomass/Hydrogen/FC	43.4	0	43.4	15.9
Adapted from Kartha and Grimes [42]	Biomass/Hydrogen/FC	10.3	0^{a}	10.3	0.46
Adapted from Lipman and DeLucchi [43]	Biomass/Hydrogen/FC	6.8	0^{a}	6.8	2.5
Adapted from Kartha and Grimes [42]	Biomass/Methanol/FC	4.8			
Mark [41]	Biomass/Methanol/FC	28	0	28	10.2
DeLuchi [27]	Biomass/Methanol/FC	75	0.6	75.	27.5
Adapted from Kartha and Grimes [42]	Coal/Hydrogen/FC	45.1	0^{a}	45.1	16.5
Adapted from Lipman and DeLucchi [43]	Coal/Hydrogen/FC	43	0^{a}	43	15.8
Adapted from Kartha and Grimes [42]	Coal/Methanol/FC	51.9			19
Adapted from Ogunlade [46]	Coal/Methanol/FC	275-277	0-5	275-282	100-103.2
Mark [41]	Solar/Hydrogen/FC	17.4	0	17.4	6.4
Adapted from Lipman and DeLucchi [43]	Solar electrolysis/Hydrogen /FC	4.8	0^{a}	4.8	1.7
DeLuchi [27]	Liquid Hydrogen/FC ^b	44-72	0-5	44-77	16.1-28.2
Adapted from Ogundale [46]	Gaseous Hydrogen/FC ^b	44-68	0-5	44-73	16.1-26.7
Adapted from Klaiber [47]	Hydrogen FC ^b	102.2	0^{a}	102.2	37.4
Adapted from Klaiber [47]	Methanol FC ^b	36.3	102.7	139	50.9

^aAssumption of ZEV.

^bUnknown primary energy source.

• There are no clear efficiency gains by using direct hydrogen instead of reformed hydrogen onboard the vehicle with the current technology of storing the hydrogen.

5.3. Emissions

• When using renewable feedstocks, hydrogen shows a significant advantage over methanol.

6. Conclusion

There are no overall clear benefits between the two fuels. The decision of which fuel becomes dominant may not be decided by any of these issues, but by which between the two first develops the infrastructure, public image and "buyability". Whether this leads to another technological lock-in is still uncertain.

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