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Feasibility of the direct generation of hydrogen for fuel-cell-powered vehicles by on-board steam reforming of naphtha

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Abstract

A process flow sheet for the production of hydrogen to run a 50 kW fuel-cell-powered-vehicle by steam reforming of naphtha is presented. The major units in the flow sheet involve a desulfurization unit, a steam reformer, a low temperature (LT) shift reactor, a methanation reactor, and a membrane separator unit. The flow sheet is simulated using HYSYS (a steady state simulator) and the material and energy flows for each stream are obtained. For the peak load of 50 kW, it is found that 14 l/h naphtha is needed, which means that a 70 l fuel tank in the vehicle is sufficient for 5 h drive. The amount of water needed is not a critical factor, since it is generated in the fuel cell and quantities of water-makeup can be kept at the minimum level.

Catalytic processes involved are briefly reviewed and commercial catalysts used are indicated. The amount of catalyst required in each reactive unit is computed by employing the design parameters (temperature, pressure, and space velocities) reported in the literature. In the desulfurization step, it is found that about 1.6 l of a bed of ZnO is capable of handling a stream of naphtha with 1500 ppm of sulfur for 45 h of continuous operation before regeneration or replacement of the bed becomes necessary. This, however, is based on operation at 10 atm. Operation at lower pressure level will increase the desulfurization catalyst requirements, maybe to a prohibitive level. Over the reformer Liquid-Hourly Space-Velocity range of $1-4 \text{ h}^{-1}$, the amount of the supported nickel catalyst varies from 14 to 4 l, respectively. For the LT shift reactor the amount of catalyst required ranges from 4 to 60 l on going from 3×10^2 to $4 \times 10^3 \text{ h}^{-1}$ typical Gas-Hourly Space-Velocity. The catalyst here is $CuO-ZnO$ supported on Al_2O_3. The last methanation step to remove traces of poisonous CO requires about 3.5 l of nickel supported by various oxides. To selectively separate hydrogen, it is suggested to use a palladium–silver membrane, which is reported to give ultra-pure hydrogen.
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Keywords: Liquid-hourly space-velocity; Gas-hourly space-velocity; Steam-to-carbon ratio

1. Introduction

Interest in fuel-cell-powered vehicles has recently been revived owing to severe environmental legislation currently being introduced all over the world. Requirements for zero emission have already been advanced in some countries (e.g. California, USA). The most practical fuel to use with fuel cells is hydrogen. The main reason for this is its high electrochemical reactivity compared with that of more common fuels from which it is derived, such as hydro-carbons, alcohols, or coal. Moreover, no side products are

involved in the electrochemical conversion of hydrogen [1]. There are many routes to generate hydrogen. The most promising are those not requiring electricity in any intermediate steps. The choice, however, is totally dictated by the economics of the application under study. Having hydrogen in pressurized vessels or in a cryogenic state has been of major concern with regard to safety. The ultimate goal would be the generation of hydrogen on-board the vehicle from a hydrocarbon feedstock. This goal would be optimum if regular gasoline or a similar liquid fuel (which can be delivered through the existing petrol station networks) is directly used in generating the required hydrogen. There have been some research attempts in this direction to investigate steam reforming and partial

oxidation of gasoline and some heavier hydrocarbon streams [2,3].

The main objective of this work is to investigate the technical feasibility (in terms of catalyst requirements) of generating hydrogen (on vehicle board) by the steam reforming of naphtha. Toward this end, a process description will be presented, followed by material, and energy balances. Some examples on sensitivity analysis will also be shown.

2. Process description

Generating hydrogen by the steam reforming of hydrocarbons is a well-known technology. Tailoring the process for fuel-cell-powered vehicles, however, introduces additional constraints. Here, the purity of hydrogen becomes essential to avoid poisoning the electrodes of the fuel-cell system. This could necessitate a selective membrane separation technology. This can be accomplished using palladium–silver membrane, which can be integrated directly to the reaction system (membrane reactor) or separately employed in later stages. The first choice (membrane reactor), however, offers attractive features regarding energy density of the whole system, which is an important criterion to judge the performance of fuel-cell-powered-vehicles. Compactness is also enhanced because conversion levels in such membrane reactors are increased. A significant amount of research work on membrane reactors is underway [4,5] and there are also signs of successful technological developments [6].

The flowsheet for the direct generation of hydrogen using steam reforming of naphtha on-board vehicle, which is suggested here, is shown in Fig. 1. The process can be described as follows: naphtha feedstock is vaporized and passed through a bed of zinc oxide to remove sulfur contamination, which is a potential poison for reforming catalysts and fuel-cell electrodes. Naphtha is then passed through the reformer, where it is catalytically reacted with steam to produce a mixture of steam, H_2, CO, CO_2, and CH_4. Heat is supplied to the reformer by the combustion of either a portion of the incoming naphtha or a portion of the generated hydrogen. The gas mixture is then cooled down by the incoming process water and directed to the low temperature (LT) shift reactor, where CO is converted catalytically to CO_2. The remaining traces of CO is further converted to CH_4 in the methanator and the gas mixture at this point contains about 53% H_2, 17% CO_2, 28% H_2O, and some traces of CH_4. Both the shift and methanation reactions are exothermic. Before directing the product gas mixture to the selective membrane, it is compressed to 3 atm. The pure hydrogen stream is then sent to the anode of fuel cell and the unused H_2 from the fuel cell is combusted to provide the required heat in the reformer. This unconverted H_2 is assumed to be 30% of the amount entering the fuel cell (corresponding to 70% conversion in the fuel cell). The other stream leaving the membrane separator, which has less H_2, undergoes a process to recover water. This water will be combined with the water recovered from the fuel cell and circulated back to the reformer after being vaporized by the reformer products and then heated to the reformer temperature.

3. Feedstock requirements

3.1. Basic assumptions

The objective here is to roughly estimate the amount (mass and/or volume) of naphtha required to produce sufficient hydrogen supply to run a 50 kW fuel cell. Toward this goal, the following assumptions are made:
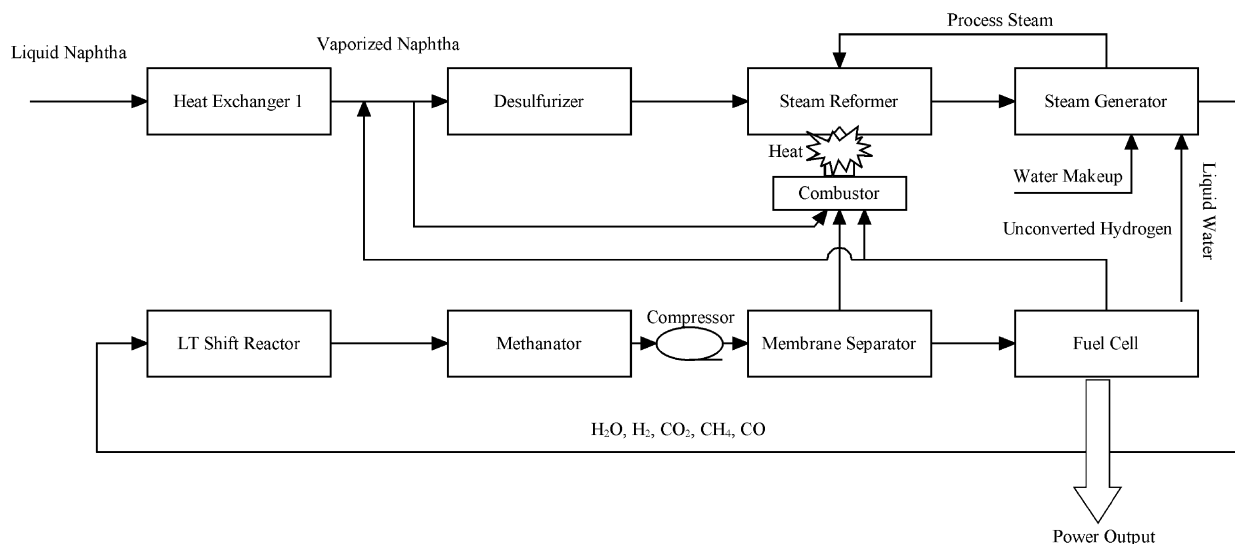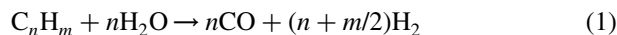

Fig. 1. Schematic diagram of the flowsheet for the production of hydrogen by steam reforming of naphtha.

- Hydrogen is generated via steam reforming and shift reactions as follows [7]:

$$C_nH_m + nH_2O \rightarrow nCO + (n + m/2)H_2 \quad (1)$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O \quad (2)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (3)$$

- The above reactions are assumed to reach equilibrium under their respective conditions. This means that reaction (1) is almost complete under the reformer conditions of temperature (500 °C) and pressure (1 atm).
- The Steam-to-Carbon Ratio (SCR) of the input to the reformer is 3.5.
- 1/8 lb of hydrogen is needed to generate 1 kW h in a fuel cell [8]. This is equivalent to assuming an overall efficiency of 52% based on ΔH of the reaction:

$$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O \quad (4)$$

- The processed naphtha has the following characteristics [9]: H% = 15, C% = 85, specific gravity = 0.7, and molecular weight = 103 g/mol. The carbon percentage, together with the molecular weight, when used to calculate n and m in C_nH_m will give $n = 7.3$ and $m = 15.5$. These assumptions are, therefore, equivalent to saying that the processed naphtha can be approximated by n-heptane, n-C_7H_{16}.
- The Liquid-Hourly Space-Velocity (LHSV) for the reformer, based on the naphtha flow rate lies in the range 1–4 h^{-1} [10].
- The membrane separator is sufficiently efficient to recover 75% of the produced H_2.
- The degree of electrochemical conversion of H_2 in the fuel cell is 70%. One-third of the remaining 30% is recycled and mixed with the vaporized naphtha stream (a necessary condition for the desulfurization unit) and the rest is combusted in the reformer to provide the required heat.
- Naphtha in the gaseous phase is desulfurized at 500 °C before it enters the reformer.
- The reformer is assumed isothermal at 500 °C and isobaric at 1 bar. The reformer is treated as an equilibrium reactor, for which the product distribution is computed by minimization of the total Gibbs energy of

Table 1
Equilibrium composition at 500 °C and 1 bar of the gas exiting the shift converter

Species	Molar flow rate (kmol/h)	Mole fraction	Mole fraction (dry)
CH$_4$	0.053	0.012	0.017
H$_2$O	1.218	0.277	–
CO$_2$	0.822	0.187	0.258
H$_2$	2.310	0.525	0.725
CO	0.000	0.000	0.000

Table 2
Hydrogen, naphtha, and steam requirements for 25 and 50 kW power output

Item	25 kW	50 kW
Hydrogen (mol/h)	1000	2000
Naphtha, mol/h (kg/h)	50 mol/h	100 mol/h
	(5 kg/h = 7.14 l/h)	(10 kg/h = 14.28 l/h)
Steam, mol/h (kg/h)	1225 mol/h (22.0 kg/h)	2450 mol/h (44 kg/h)

the reaction mixture at the respective temperature and pressure. This has been performed using the steady state simulator HYSYS.
- The shift reactor is an adiabatic equilibrium reactor with reactants entering at 200 °C. This is followed by the methanator, which is again treated as an adiabatic reactor. However, in the methanator the CO_2 conversion to CH_4 is suppressed by choosing CO_2 as inert in the simulator to correctly simulate the experimental process.

3.2. Equilibrium composition

Our immediate objective here is to compute the amount of hydrogen produced from 1 mol n-C_7H_{16} and (3.5×7) 24.5 mol of steam (remember SCR = 3.5 based on carbon atoms in the processed naphtha). The computation is done using HYSYS and (based on 1 mol of naphtha) the results are shown in Table 1.

3.3. Hydrogen, naphtha and steam requirements

Based on the assumption that 1/8 lb of hydrogen is needed to generate 1 kW h in a fuel cell [8], the molar flow rate of H_2 needed to run 1 kW fuel cell can easily be shown to be 28.3 mol/h (i.e. 1/8 lb × 1000 g/2.2046 lb × 1 mol/2 g). Assuming an efficiency of 70% for hydrogen utilization in the fuel cell, naphtha and steam requirements are calculated in a straightforward manner for two levels of power output of the fuel cell, i.e. 25 and 50 kW. The results are shown in Table 2.

Based on the amounts of naphtha and steam computed above and the assumptions advanced before, the process was simulated using HYSYS [12]. The computation converged with material and energy flow rates (in addition to other properties). It is to be noted that water can be balanced in the whole process but in our case and because of conservative assumptions, about 0.5 kmol/h of water-makeup is needed.

4. Sensitivity analysis

Sensitivity analysis addresses the question of how a certain (dependent) variable responds to changes in some other independent variable(s) in the process. Using HYSYS, the following three cases are worked out:
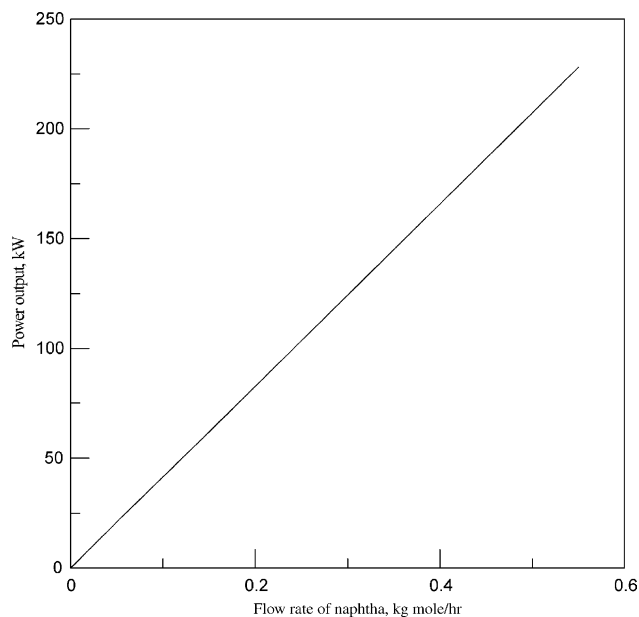
Fig. 2. The effect of naphtha flow rate on the produced output.

- The output power of the fuel cell versus naphtha flow rate.
- The output power of the fuel cell versus steam-to-naphtha-ratio (which is 7 × SCR).
- The mole fraction of hydrogen versus steam-to-naphtha-ratio.

As shown in Fig. 2, the power output of the fuel cell goes linearly with the molar flow rate of naphtha. In the light of the assumptions advanced before and the fact that naphtha is the limiting reactant, this result is expected. The effect of SCR on the power output is presented in Fig. 3. It is seen that excess steam has a significant effect on the power output (hydrogen generation) up to an SCR of 3.5, beyond
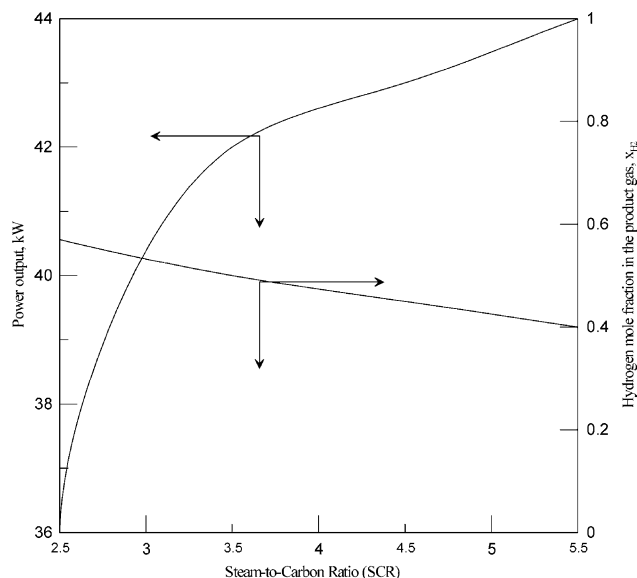

Fig. 3. Effect of SCRs on the power output and hydrogen mole fraction in the product gas.

which the power output levels off. Steam is produced in reactions (2) and (7) and consumed in reactions (1) and (3). The effect of SCR is dictated mainly by the equilibrium of these different reactions at their respective operating conditions. Fig. 3 also reveals the effect of SCR on the mole fraction of hydrogen in the gas mixture leaving the shift unit. As expected, hydrogen becomes more and more diluted with increasing steam ratio.

5. Catalysis and catalyst requirements

This paper describes briefly the different catalysts involved in the whole process of generating hydrogen for a fuel-cell-driven vehicle and computes catalyst requirements for each catalytic process. The target design parameters are taken from the literature and a conservative approach is adopted. This will, preliminarily, establish the technical feasibility of the process from the point of view of size and compactness of the proposed naphtha reformer-fuel cell system.

5.1. Steam reforming

5.1.1. Commercial catalyst
The following requirements are essential for a good reforming catalyst: (1) it should have the required activity and selectivity at the lowest possible temperature and the lowest possible pressure drop (maximum conversion with minimum side reactions). In particular, minimum carbon formation propensity is required; (2) it must have a reasonable lifetime; (3) it must withstand extraordinary conditions of transients (startup and shutdown); and (4) it should have the stability for in situ regeneration.

The active component of the steam reforming catalyst is nickel. It is dispersed throughout the support material as fine crystallites produced by reduction of nickel oxide. The metals of group VIII are all active for steam reforming but some are chemically instable under reforming conditions, which renders them industrially inappropriate [11]. Noble metals like cobalt, platinum, palladium, iridium, ruthenium, and rhodium are all active for steam reforming but too expensive for commercial use [9]. The nickel oxide content of the unreduced catalyst is a parameter that influences the catalyst activity and usually is between 15 and 25% [11,13]. Catalysts of lower nickel content have also been commercialized [14]. Many commercial catalysts specific for steam reforming of naphtha are in current use. For example:

- Catalysts and Chemicals Inc., Ref. [10]: High NiO on calcium aluminate refractory supports, C11-2 and C11-5, NiO on a refractory support for the inlet part and the exit part of a reformer C11-7 and C11-8
- Katalco Corporation, Ref. [10]: NiO on alumina, 22-6(35), NiO−alumina−silica-promoter, 46-1 and 46-2

- ICI, Ref. [7]: $NiO-CaO-SiO_2-Al_2O_3$ (57-1, 46-1, 54-2) and $NiO-CaO-SiO_2-Al_2O_3-MgO-K_2O$ (46-1)

In addition to the above-mentioned commercialized catalysts, a number of patented catalysts for reforming hydrocarbons are cited in Ref. [14]. For example, the following patented catalysts are mentioned for reforming high boiling hydrocarbons:

- $2CaO \cdot Fe_2O_3$ in fluid bed for vac. resid. oil (Mitsui, Japan)
- $2CaO \cdot SiO_2$, $3CaO \cdot SiO_2$ in fluid bed for vac. resid. oil (Mitsui, Japan)
- Ni ore (Ni, Co, Fe, SiO_2, MgO) for heavy oil (Hitachi, Japan)
- $CaSO_4/Al_2O_3$ at 1000 °C for resid. oil (Idemitsu, Japan)
- CaO at 900 °C for heavy oil (Ishikawajima, Harima, Japan)
- Na + Ca aluminates, 1000 °C for resid. oil (Mitsui, Japan)
- $CaSO_4/Al_2O_3$ at 1000 °C for resid. oil (Idemitsu, Kosan, Japan)
- $CaO \cdot Al_2O_3$ at 1000 °C fixed bed for resid. Oil (Mitsui, Japan)

The life of steam reforming catalyst can be 4 years or more under the following conditions [9,10]: temperature 550–825 °C, pressure 3–40 atm, with SCRs from 2:1 to 6:1, LHSV of $1-4\ h^{-1}$ based on naphtha. The product gas varies with the composition of the naphtha and with the operating conditions. The following gas was produced at 750 °C, 8 atm and H_2O:C of 3.3:1: CH_4 4%; H_2 69%; CO 14%; CO_2 12% [10].

5.1.2. Steam reforming catalyst support

Because of steam reforming conditions, the mechanical properties of the reforming catalyst become crucial and hence have undergone extensive research investigation [11]. Typical conditions for such a process could be a reformer temperature range of 550–825 °C and a system pressure from 3 to 140 atm [10]. An adverse effect on mechanical stability, however, is the mechanical vibration resulting from the vehicle motion. Conditions prevailing in a naphtha-fed steam reformer generating hydrogen for a fuel-cell-powered-car are expected to be of less severity regarding temperature and pressure.

Most industrial catalysts for steam reforming are supported on ceramic oxide or oxides stabilized by hydraulic cement. Typical ceramic supports are α-alumina, magnesia, magnesium aluminum spinel, zirconia, and calcium aluminate [11,13]. An added benefit regarding support in the case of processing naphtha feedstock is LT operation, which means that high area supports such as γ-alumina and chromia can be used. Unfortunately, these supports suffer from substantial sintering above 550 °C, especially in the presence of high steam partial pressure

[11]. Catalysts stabilized by cement may show shrinkage and decrease in strength by frequent exposure to high temperature. Silica is avoided as a support in this case because of its volatility (as $Si(OH)_4$). Catalysts based on magnesia, although resistant to high temperature steaming, are sensitive to steaming at LT because of the risk of hydration of MgO to produce $Mg(OH)_2$, which has a higher molar volume, thus leading to catalyst break down. This is not likely to happen at temperatures above 350 °C [11].

The trend, therefore, has been towards ceramic-based catalysts. For steam reforming of naphtha, calcium aluminate support is in widespread use because of its natural alkalinity, which helps in suppressing carbon formation. The main commercially used catalyst supports can be ranked as follows in decreasing order of carbon forming tendency: α-alumina > magnesium aluminate (spinel) > calcium aluminate > alkalized calcium aluminate [13].

5.1.3. Carbon formation on steam reforming catalyst

With steam reforming of naphtha the problem of carbon deposit on the catalyst becomes highest priority. Carbon could be formed via different routes such as [11]: (1) reaction of hydrocarbons and CO over transition metals to form filamentous carbons (Whisker carbon), which is favored above 450 °C; (2) reaction of the adsorbed species to form a film of non-reactive deposits that may encapsulate and deactivate the nickel surface. This form is favored at temperatures below 500 °C; (3) thermal cracking of hydrocarbons that may start at temperatures above 650 °C as steam cracking reactions produce olefins; and (4) the decomposition of heavy hydrocarbons into carbon (carbon formation by irreversible reactions) that could commence at 650 °C. High steam/carbon ratio is essential to minimize all these formations.

For a given catalyst and operating conditions, the risk of carbon formation strongly depends on the unsaturated character of the hydrocarbon feedstock. Therefore, the content of aromatics is a critical parameter to evaluate and control for carbon-free operation in steam reforming of naphtha. Moreover, steam reforming of aromatics proceeds relatively slowly. Interestingly, a sensitive method of monitoring the loss of catalyst activity with naphtha feedstock is by following the gradual increase in aromatics concentration in the product [7].

The influence of the reforming catalyst on carbon formation is usually expressed in terms of the catalyst ability to adsorb water. The higher the capacity for water adsorption, the less is the risk of carbon formation. Normal alumina-based catalysts for steam reforming of natural gas have low values of water adsorbability and thus are not suitable for naphtha feedstock [11]. One method of increasing water adsorption on the catalyst support is by promoting the catalyst with alkali. The exact role of the promoter is debatable but neutralizing acidic sites in the support is thought to be the key in its functional mechanism.

The use of alkali promoted nickel catalysts for the reforming of naphtha feedstock has been discussed elsewhere [15]. It has been shown that the combination alkali promoted and non-alkali promoted commercial catalysts can be utilized to effect the reforming of a wide range of hydrocarbon feedstock. Some adverse effects of promoters, such as reducing the catalytic activity, have been reported in many previous studies [11,14]. A nickel catalyst containing potassium is the basis of the ICI naphtha reforming process [14]. In the Kellogg process, the risk of carbon deposition is dealt with by having two nickel catalysts, the first being alkalized and the second a high-activity reforming catalyst: they are termed the ICI naphtha and methane reforming catalysts 46-1 and 57-1, respectively, [14].

5.1.4. Poisons of steam reforming catalyst

The most severe poison for the nickel-based steam reforming catalyst is sulfur, which is invariably present as inorganic and/or organic sulfides in most naturally occurring feedstock. Sulfur is strongly adsorbed on nickel sites with a sticking coefficient close to 1.0 for less than 70% of a full monolayer [11]. As such, sulfur deactivates the catalyst (reversibly) more seriously at lower temperatures:

$$H_2S + * \rightarrow S{-}* + H_2 \quad (\Delta H_{ads} = -155\,kJ/mol\,S_2) \quad (5)$$

therefore, the minimum concentration of sulfur that will result poisoning of the catalyst varies with temperature. For example, sulfur content must be reduced to below 0.04 ppm when working at 700 °C whereas at 750 °C the same catalyst can handle a naphtha stream with a sulfur content of 1 ppm [9]. Mathematical modeling of a fixed bed steam reformer that processes naphtha has predicted H_2S breakthrough after 6000 h of operation when the sulfur content is 0.0075 ppm and approximately 300 h when the sulfur content in the feed is 0.075 ppm [11]. Poisoning of the steam reforming catalyst by sulfur will also aggravate carbon deposition on the catalyst surface and aromatic slip in the output. Fortunately, sulfur content can be reduced to a very low level by using a bed of zinc oxide:

$$ZnO + H_2S \rightarrow ZnS + H_2O \quad (\Delta H_{298} = -75\,kJ/mol) \quad (6)$$
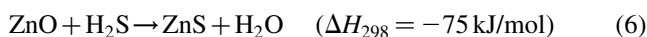
It is interesting to note that the equilibrium constant of this reaction at 300 °C is 5.9×10^6 and that with a high-quality zinc oxide sulfur content can be reduced to below 10 ppb [11]. This suggests that naphtha feedstock could be desulfurized on-board without disturbing much the compactness of the system as whole. For efficient utilization of the zinc oxide the bed needs to be operated in the temperature range 350–650 °C [9].

Arsenic in very small quantities can irreversibly destroy the catalyst activity. Concentration of As_2O_3 as little as 50 ppm on the catalyst will seriously affect its performance, and with 150 ppm there is a serious risk of carbon deposition. The presence of 1 ppm of As_2O_3 in the steam entering the reformer will impair the performance of the reformer in a matter of few days [9].

Table 3
Volume requirements of reformer catalyst in liters

25 kW fuel cell		50 kW fuel cell	
LHSV = 1 h^{-1}	LHSV = 4 h^{-1}	LHSV = 1 h^{-1}	LHSV = 4 h^{-1}
7.14	1.79	14.28	3.57

5.1.5. Steam reforming catalyst's requirements

The LHSV for the reformer, based on naphtha flow rate is in the range 1–4 h^{-1} [10].

$$LHSV\,(h^{-1}) = V_{naphtha}\,(1\,h^{-1})/V_{catalyst}\,(l)$$

$$V_{catalyst}\,(l) = V_{naphtha}\,(1\,h^{-1})/LHSV\,(h^{-1}) = 7.14/1 = 7.14\,l$$
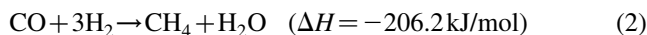
$$for\,LHSV = 1\,h^{-1} = 1.79\,l\,for\,LHSV = 4\,h^{-1}.$$

The results of such simple computations are presented in Table 3.

5.2. LT water–gas shift catalytic operation

5.2.1. Commercial catalysts

The formulation of the LT shift catalyst is important in terms of selectivity as under LT shift conditions methanation of both CO and CO_2 is thermodynamically very favorable:

$$CO + 3H_2 \rightarrow CH_4 + H_2O \quad (\Delta H = -206.2\,kJ/mol) \quad (2)$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad (\Delta H = -164.9\,kJ/mol) \quad (7)$$

If this catalyst enables these reactions to take place then appreciable amounts of hydrogen will be consumed. Moreover, in view of the high exothermic nature of these reactions, high temperatures could result in destructive effects to the catalyst.

The commercial LT shift catalyst currently in use is based on formulations containing copper oxide, zinc oxide, and alumina. The active ingredient is copper, which has good activity for both water–gas shift reaction and methanation reaction. Optimum performance regarding activity and service life was obtained from catalysts having the composition ranges: 30–40% CuO, 30–50% ZnO, 15–35% Al_2O_3. For example, the ICI commercial catalyst has the composition [9]: 33% CuO, 34% ZnO, 33% Al_2O_3.

Recently it has been reported that addition of calcium-based CO_2 acceptor to a commercial steam reforming catalyst permits the production of > 95% H_2 in a single-step process [16]. A method for the production of clean hydrogen in two steps has also been recently reported in the literature [17]. The two steps involved are the decomposition of methane to CO-free hydrogen and surface carbon in the first step followed by steam gasification of this surface carbon in the second step. Zeolite catalysts (Cu- and Cu,Zn-ZSM-5) have been recently investigated [18]. Appreciable activity and selectivity at 300–400 °C is claimed.

Table 4
Volume of the converter catalyst in liters needed

25 kW fuel cell		50 kW fuel cell	
GHSV $= 300 \text{ h}^{-1}$	GHSV $= 4000 \text{ h}^{-1}$	GHSV $= 300 \text{ h}^{-1}$	GHSV $= 4000 \text{ h}^{-1}$
29	2.2	58.14	4.36

5.2.2. LT shift catalyst requirements

The Gas-Hourly Space-Velocity (GHSV) for the shift conversion is in the range 300–4000 h^{-1} [10]. The catalyst requirement is calculated in a straightforward manner:

$$\text{GHSV (h}^{-1}) = V_{\text{dry feed gases}} \text{ (l h}^{-1})/V_{\text{catalyst}} \text{ (l)}$$

$$V_{\text{catalyst}} \text{ (l)} = V_{\text{dry feed gases}} \text{ (l h}^{-1})/\text{GHSV (h}^{-1})$$

From the equilibrium gas composition presented in Table 1, the amount of dry gases produced based on 1 mol naphtha is 27.5 mol/h, therefore,

Total dry gas $= (27.5)(50) = 1375$ mol/h $= 8720$ l/h

for the 25 kW case and $= (27.5)(100) = 2750$ mol/h

$= 17\,442$ l/h for the 50 kW case

Hence for the 25 kW case and GHSV $= 300 \text{ h}^{-1}$ we have:

$$V_{\text{catalyst}} \text{ (l)} = V_{\text{dry feed gases}} \text{ (l h}^{-1})/\text{GHSV (h}^{-1})$$
$$= 8720/300 = 29 \text{ l}$$

and for the 25 kW case and GHSV $= 4000 \text{ h}^{-1}$ we have:

$$V_{\text{catalyst}} \text{ (l)} = V_{\text{dry feed gases}} \text{ (l h}^{-1})/\text{GHSV (h}^{-1})$$
$$= 8720/4000 = 2.2 \text{ l}$$

The catalyst requirements (in liters) for the converter are shown in Table 4.

5.3. Desulfurization catalytic operation

5.3.1. Commercial catalyst

Naphtha often contains significant quantities of organic sulfur compound as thiophenes and benzothiophenes. As stated previously, sulfur is a poison for nickel steam reforming catalysts, but the poisoning is reversible and in practice there is a threshold limit for given conditions, below which the poisoning effect is not apparent. The severity of (steam reforming catalyst) poisoning with sulfur varies inversely with temperature. For example, 5 ppm of sulfur will yield practical poisoning if the reformer is operated at 500 °C, whereas the critical sulfur level at 1000 °C is 70 ppm. This critical sulfur level that will result in practical poisoning, based on data presented in Ref. [9],

can be correlated with temperature as:

Critical Sulfur Level in ppm $= 0.13 \, T \, (°C) - 60$

For many years, hydrogen sulfide was removed by absorption in beds of iron oxide. This is a low-cost material with a high absorption capacity, but unfortunately is not suitable in combination with a steam reformer. This is because of the relatively high equilibrium partial pressure of H_2S and the ease of stripping off the absorbed H_2S by hydrogen and steam under conditions of startup and shutdown [9]. Zinc oxide reacts almost completely with H_2S to yield ZnS according to the reaction:

$$ZnO + H_2S \rightarrow ZnS + H_2O \tag{8}$$

A typical composition of a current commercial desulfurization catalyst (ICI catalyst 32-4) is as follows [9]: 90% ZnO, 2% CaO, and the balance is Al_2O_3.

5.3.2. Desulfurization catalyst requirements

The objective here is to roughly estimate the mass and the replacement time of the zinc oxide bed needed to process the previously calculated amount of naphtha for the 50 kW case. The computation will be based on the following assumptions.

Catalyst (ICI catalyst 32-4) characteristics [9]:

ZnO	90.0%
CaO	2.0%
Al_2O_3	Balance
Surface area	25 m^2/g
Bulk density	1.1 kg/l
Diameter	3.0–5.0 mm

Operating conditions:

GHSV [9]	500 h^{-1} (the typical range is 500–1000 h^{-1})
Temperature	500 °C
Pressure	10 atm
Sulfur content in naphtha	1500 ppm (w/w) (a very conservative assumption)

All sulfur will be assumed as H_2S: $ZnO + H_2S \rightarrow ZnS + H_2O$

The molar flow rate of naphtha $= (10$ kg/h$)$ $(1000$ g/kg$)$ (mol/100 g) $= 100$ mol/h

Volumetric rate of gaseous naphtha at 500 °C and 10 atm (assuming ideal gas) $= 100 \times 8.314 \times (500 + 273)/(10 \times 101\,325) = 0.634$ m^3/h $= 634$ l/h

Assuming 25% recirculated hydrogen [13], the total flow rate $= 634 + 634/4 = 800$ l h^{-1}

Required catalyst volume $= 800$ l $h^{-1}/500$ $h^{-1} = 1.6$ l

Mass of the catalyst $= 1.6$ l $\times (1.1$ kg/l$) = 1.8$ kg

Total moles of ZnO $= 0.9 \times 1.8$ kg $\times (1000$ g/kg$)/(71$ g/mol$) = 25.4$ mol

At the operating conditions stated above, the total amount of sulfur absorbed before H_2S breakthrough is

Table 5
Working hours of 1.8 kg ZnO-bed for the case of 10 kg naphtha/h (50 kW fuel cell), GHSV of 500 h^{-1} for different levels of sulfur contamination in the feed

Sulfur level, ppm (wt/wt)	500	1000	1500
Working time (h)	130	65	43

conservatively assumed to be 80% of the theoretical amount [13], therefore:

Total amounts of S absorbed $= 0.8 \times (25.4 \text{ mol})(32 \text{ g/mol})$

$= 650$ g sulfur

Based on 1500 ppm (1.5 g sulfur/kg naphtha) of the feed, the mass flow rate of sulfur:

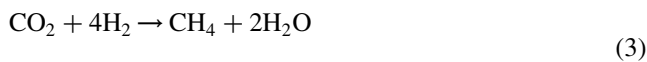(10 kg naphtha/h)(1.5 g sulfur/kg naphtha) $= 15$ g sulfur/h

Time for complete utilization of the ZnO bed $= 650/15 = 43$ h

Note that these calculations are for a pressure of 10 atm. Lower pressure would require more zinc oxide and at a pressure of 1 atm the catalyst requirements could be prohibitive. Table 5 contains catalyst requirements and replacement time for different cases of sulfur level in the naphtha feedstock.

5.4. Methanation catalytic operation

5.4.1. Commercial methanation catalyst

The objective of this catalyst is to effectively remove the traces of CO in the gas stream (exiting the shift converter) by converting it into methane. Some of CO_2 will also be methanated but fortunately this reaction proceeds only after substantial amounts of CO have been converted [9]

$$CO + 3H_2 \rightarrow CH_4 + H_2O \quad \Delta H_{298} = -206.2 \text{ kJ/mol} \quad (2)$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$
$$\Delta H_{298} = -164.9 \text{ kJ/mol} \quad (3)$$

The presence of CO in the produced gas stream gives rise to concern, firstly for environmental considerations and secondly because it is a dangerous poison for the catalytic system in the fuel cell. CO_2 and CH_4 have only mild effects [19] on the catalytic system of the fuel cell and therefore the gas stream can be sent directly to the fuel cell.

The commercial methanation catalyst is nickel metal supported by various oxide mixtures, such as alumina, silica, lime, and magnesia, together with compounds like calcium aluminate cements. Nickel content of the catalyst may reach up to 30% and the service life is in the range of 6–8 years [9]. The methanation reactions are both exothermic and therefore care must be taken for the exit temperature not to exceed a certain limit especially when dealing with a feed of high CO concentration. In this case part of the product gas is cooled and recycled to

control the temperature rise. On the other hand, care must be taken during heating up and cooling down to avoid the formation of nickel carbonyl ($Ni(CO)_4$), which is extremely toxic, almost odorless gas, favored below 150 °C. The operating temperature range in the methanator is 230–350 °C and over this temperature range the equilibrium constant of CO methanation varies from 0.13×10^{11} to 0.48×10^6 [9].

5.4.2. Methanation catalyst requirements

Commercial methanation processes are operated with an average GHSV of 5000 h^{-1} [9,10]. Based on the total dry gas flow rate computed in Section 5.2, which is 8720 l/h for the 25 kW case and 17 442 l/h for the 50 kW case, and a GHSV of 5000 h^{-1} the catalyst requirements are as follows:

$$V_{\text{catalyst}} (\text{l}) = V_{\text{dry feed gases}} (\text{l h}^{-1})/\text{GHSV} (\text{h}^{-1}) = 8720/5000$$

$$= 1.75 \text{ l} (25 \text{ kW case})$$

$$V_{\text{catalyst}} (\text{l}) = V_{\text{dry feed gases}} (\text{l h}^{-1})/\text{GHSV} (\text{h}^{-1}) = 17442/5000$$

$$= 3.5 \text{ l} (50 \text{ kW case})$$

5.5. Purification of hydrogen [20]

It is obvious that the product gas mixture exiting the (steam reforming) reaction system contains appreciable amounts of water vapor, carbon dioxide, and small amounts of methane as well as the desired hydrogen product. In view of compactness requirements and the need for a robust hydrogen generation system to be integrated with the fuel-cell system in the future proposed electric vehicle, a hydrogen purification step becomes inevitable [1].

Hydrogen purification processes can be classified into the following categories [20]:

- Chemical (catalytic purification)
- Physical (metal hydride separation, pressure swing adsorption, and cryogenic separation)
- Selective diffusion (noble metal membrane, polymer membrane, and solid polymer electrolyte cells).

The review of Grashoff et al. [20] presents an easy-to-follow tabulated comparison between these techniques. Physical techniques are best suited to large-scale applications and thus will be deemed inappropriate for inclusion in medium vehicle fuel cell applications.

Based on hydrogen selectivity of the technique and its resistance to poisoning by constituents present as impurities in the feed gas, palladium–silver alloy membrane was found to be of high potential in separating hydrogen from a wide range of feedstocks. A recovery level up to 99% with ultra-purity level of up to 99.9999% is possible using this technique. It is the inclusion of silver in this alloy that made successful the commercialization of this separation

technique in the early 1960s. Interestingly, the maximum hydrogen permeability was obtained from a 23% silver alloy membrane, which also has suitable mechanical strength. For example, at a pressure of 1 atm, the solubility of hydrogen in the 23% Pd–Ag alloy is about 140 mg per 100 g of alloy at 183 °C versus less than 20 mg per 100 g of alloy of Pd–Pt and Pd–Au at the optimum composition of Pt and Au. In an environment of hydrogen, at temperatures below 300 °C and pressures below 20 atm, pure palladium will undergo embrittlement and distortion. Unsaturated hydrocarbons, halogens, and sulfur compounds can lead to rupture of the membrane [21].

Rare-earth-palladium alloys, with hydrogen permeability significantly better than that in silver–palladium alloys have been reported [20]. A 6–10% yttrium–palladium alloy has shown hydrogen permeability twice as that shown by the optimum 23% silver–palladium alloy. Moreover, yttrium–palladium alloy has better mechanical properties, which permit improved hydrogen permeability by enabling higher differential pressures or thinner diffusional membranes.

Group V metals, such as tantalum, vanadium, and niobium show equilibrium isotherms similar to those of palladium and, moreover, they exhibit high diffusion coefficients for hydrogen and lower intrinsic cost. However, the well-documented embrittlement problem precluded their commercialization.

6. Conclusions

The different operations involved in the process of on-board generation of hydrogen from naphtha for a fuel-cell-driven vehicle have been briefly reviewed. To establish preliminarily the technical feasibility of the process (from the point of view of size and compactness of the whole process), catalyst requirements for each catalytic process have been computed using the available literature design parameters. The proposed flow sheet for the production of hydrogen to run a 50 kW fuel-cell-powered-vehicle involved a desulfurization unit, a steam reformer, a LT shift reactor, a methanation reactor, and a membrane separator unit. It was found that 14 l/h of naphtha is needed, which means that a 70 l fuel tank in the vehicle is sufficient for 5 h drive. Over a LHSV range of $1-4\,h^{-1}$ for the reformer, the amount of the supported nickel catalyst varies from 14 to 4 l. For the LT shift reactor, the amount of catalyst (CuO–ZnO supported on Al_2O_3) ranges from 4 to 60 l on going from 3×10^2 to $4 \times 10^3\,h^{-1}$ GHSV. The methanation process, which is used to convert traces of poisonous CO to methane, required about 3.5 l of catalyst (nickel supported by various oxides). To selectively separate hydrogen, it is suggested to use a palladium–silver membrane, which is reported to give ultra-pure hydrogen. From the point of view of size and compactness of the whole

process, therefore, it is seen that the process is technically feasible; the different units, in addition to the fuel cell, can be laid down and distributed on the total surface area of the vehicle, which will also impart the vehicle with an enhanced stability.

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