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Review

The multiple roles for catalysis in the production of H₂

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Abstract

This review describes a number of different, largely catalytic approaches for producing H₂. Since a major fraction of the world's H₂ is produced by catalytic processes, involving multiple steps with different types of catalysts, it is clear that catalysis plays a critical role in the production of H₂. This review is focused on the use of catalysis for the current and future production of H₂. Some background will be provided to give a perspective of the dramatic change in the supply and demand for H₂ in the past decade, followed by a review of how it is produced commercially, with a view to how multiple types of catalysis contribute to the total process for H₂ production. Steam methane reforming, the major approach for H₂ manufacture, will be a focal point for most of the discussion in pointing out the large number of catalytic steps that are used in this major technology. Finally, some alternative catalytic approaches for H₂ production will be described. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Hydrogen is forecast to become a major source of energy in the future. Molecular hydrogen is a clean burning fuel, can be stored as a liquid or gas, is distributed via pipelines, and has been described as a long term replacement for natural gas. Currently, steam reforming of hydrocarbons, SR, especially, steam methane reforming (SMR) is the largest and generally the most economical way to make H₂. Alternative non-catalytic, industrial chemical approaches include partial oxidation of heavy oil or coal [1]. When electricity is available and relatively inexpensive, electrolysis of water offers an alternative

commercial approach. In the last 10 years the drivers for the H₂ business have changed dramatically. Before this decade, H₂ was in plentiful supply with refineries being major sources of H₂, but that has all changed dramatically now with refineries becoming large net consumers of H₂ in an effort to reduce pollution and meet environmental regulations [2].

The National Hydrogen Program of the United States, managed by the US Department of Energy, is dedicated to encouraging and supporting the development of safe, practical, and economically competitive H₂ technologies and systems to meet our energy needs [3]. One intended outcome of this program is the ultimate, orderly phase-out of fossil fuels, with a 2005 goal of doubling the current production of H₂ and ultimately by 2025 H₂ contributing 8–10% to the total

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energy market. H_2 offers a potentially non-polluting, inexhaustible, efficient, and cost attractive fuel for energy demands. The use of H_2 as a fuel offers an important reduction in NO_x , CO, and CO_2 emissions, when non-fossil fuels are used for the production of H_2 . Within United States, a national H_2 program is dedicated to encourage and support the discovery and development of safe, practical and economically competitive H_2 technologies. This effort is based on the recognition [3] that the future world energy industry will need to use renewable sources of H_2 in order to satisfy the expected future energy demands of the consumer and industry while trying to reduce pollution from fossil fuel-based sources of H_2 .

One popular experimental approach to H_2 production is CO_2 reforming of methane, but successful implementation of this approach faces some hurdles [4,5]. Future production of H_2 may be emerging from the selective oxidation of natural gas exclusively to CO and H_2 . Research continues on photolysis, electrolysis, and thermal processes for H_2 production. Opportunities for catalysis research to contribute to the advance of some of these approaches will be described below. While there are external issues of storage, separation, and systems integration, catalysis has an important role to play in some of these chemical and engineering approaches, but it is only part of the solution.

Alternative solutions to H_2 production are an important research opportunity for the catalysis community, especially where non-fossil fuel approaches are pursued. Most scientists probably view H_2 production as a mature technology offering little incentive to further research. However, even mature technology areas are very susceptible to step out changes. As the reader will learn, there are opportunities in current, developing, and future approaches to the manufacture of H_2 . While this paper begins with the uses for and the production of H_2 , a noticeable portion of this paper will be devoted to opportunities in the current and alternative approaches for H_2 production.

This paper supplements the presentation of a plenary lecture the author gave at the 1997 Meeting of the North American Catalysis Society in recognition for receiving the Houdry Award in Catalysis. The review is not intended to be comprehensive, and focuses on large uses for H_2 . Topics such as cryogenic or membrane separation, methanol cracking, methanol

reforming, or NH_3 dissociation will not receive any attention here. The paper intends to provide an overview of the major methods for H_2 production with a focus on the dominant route to H_2 , SMR, while showing the drivers behind the H_2 production technologies and offering some thoughts and assessment of H_2 production technologies for the future. CO production and synthesis gas mixtures of H_2/CO , which are closely linked to H_2 production, will not be heavily discussed in this review. Instead, it is the author's intent to pick up from many other fine reviews [1,6–9] on this topic and move into some other perspectives and topics not often discussed. Excellent, in depth background references for topics within this review include Martin Twigg's book [10] on major processes using or producing H_2 , an encyclopedic review [11] and Hal Gunardson's new book [12] on the production of industrial gases.

2. Needs and uses for hydrogen

H_2 is a widely used feedstock in the chemical, foods, and refining industries. In refineries it is in high demand [13] and used for desulfurization, hydro-treating, and in the production of chemicals. Some project that the demand for H_2 will increase from 10% to 15% per year for the next five years (see Table 1). Both refineries and chemical companies use H_2 for the production of commodity, fine and specialty chemicals, such as toluenediamine, hydrogen peroxide, NH_3 , specialty hydrogenations, pharmaceuticals, and applications for synthesis gas (such as methanol and higher alcohols production). In 1988 methanol synthesis and other chemicals' production accounted for 6.7% of H_2 sales. Ammonia synthesis plants accounted for 40% of the world's consumption of H_2 [1] and are comprised mainly of the units to

Table 1
Non-refinery US demand for H_2 (in billions of ft^3) [13]

Market	1994	2000
Chemical processing	82	128
Electronics	9	15
Food processing	4	5
Metal manufacturing	3	4
Other markets	13	17
Total	111	169

produce the large volumes of H_2 necessary to reduce N_2 to NH_3 . Thus, NH_3 synthesis plants are really another form of H_2 production. Because of the excess capacity of NH_3 , it can be attractive to convert NH_3 synthesis plants into H_2 production units. In addition, H_2 is used by the steel industry for annealing of steels. The electronics industry uses H_2 in the production of devices. H_2 is used in large quantities in the food processing industry, especially for the hydrogenation of fats and oils. In addition, there are specialty applications for bulk quantities of H_2 as a fuel, such as in propelling the US space shuttle. (Note that Table 1 does not show the large jump in demand for H_2 by the refining industry.)

Another potential use under active consideration for H_2 is associated with the environment. Since the combustion of H_2 in air produces water without any CO_2 coproduct, it is an environmentally attractive and clean fuel. However, the use of H_2 as a fuel depends on how it is produced; producing H_2 from fossil fuels makes H_2 an indirect source of CO_2 . The real opportunities for the future with regard to concerns about the environment lie in non-fossil fuel approaches to the production of H_2 , which will be discussed below. Given that one can eventually produce H_2 from water in an efficient and cost effective manner, the combustion of H_2 back into water would offer a truly renewable fuel source. Another aspect regarding the use of H_2 as a fuel pertains to its high energy content. On a per mole basis, the combustion of H_2 offers a very intense and atom efficient means for energy production. When combusted with O_2 (such as after thermal, electrolytic, or solar decomposition of water), H_2 is the ultimate clean fuel since no CO_2 or NO_x is produced. Our Earth offers vast quantities of water, so if we could develop a technology to produce H_2 from water and then be able to combust it back to water while generating power, this would offer a very environmentally attractive technology.

H_2 has recently been described by a number of people as the “fuel of the future [14]”. If one traces back [15] to 1850, one can see that the primary sources of energy in US shifted from wood to coal in the early 1900s. Oil emerged as the major energy source after 1950, but it appears to be ebbing and natural gas is taking on an increased role; fuels are moving to richer contents of hydrogen. However, in the latter part of the next century, even our supplies of natural gas and oil

are expected to be depleted forcing a need for a new fuel. In the 1960s it appeared that this future fuel would be nuclear based, but it has proven to be unpopular. Now many are looking to H_2 to fill the gap as an increasing source of future energy needs for the world, especially given the concern about the pollution of the environment by other fossil fuel-based raw materials.

In an article by Courty and Chauvel [2], they show the dramatic shift in the supply and demand for H_2 which has evolved in the last 20 years. In the 1980s, demand for H_2 was low and less than the production of H_2 , then a by-product within most refineries. In fact, refineries often managed to supply their own H_2 needs by careful balance of reaction chemistries. With the advent of tougher emission controls for automobiles (demanding less benzene and sulfur compounds in the gasoline) and tougher nitrogen oxide emissions requirements, refineries have responded by using proven, acceptable technology which is hydrodesulfurization and hydrodenitrogenation. The past production of large volumes of benzene as a refinery product often results in by-product H_2 . The drop in the levels of aromatics in gasoline resulted in less H_2 production in the refineries coupled with a jump in the need for H_2 from dehydrogenation reactions. This has largely been the reason for the recent shift in demand for H_2 , and there is often a regionally tight relationship between supply and demand for H_2 . Refineries were once viewed as net producers of H_2 , but now they are major consumers of H_2 with the establishment of many independent H_2 production plants (using SMR or partial oxidation) on the perimeter of many of the world's major refineries. The long term forecast for supply and demand for H_2 is expected to be tight into the next century with some dramatic deficiencies forecast between supply and demand needs [2,16,17]. This conclusion is also repeated by Cromarty [18] in a recent market review on H_2 .

Demands for H_2 are often very intense within certain regions of the country. In some places around the world it is advantageous to maintain pipeline systems to satisfy multiple customers near production sites. For example, Air Products maintains H_2 pipelines in the Gulf coast and Los Angeles regions of USA (Fig. 1) and in the Rotterdam area in The Netherlands. To supply pipeline H_2 , H_2 from steam reforming operations is blended with surplus H_2 from chemicals'

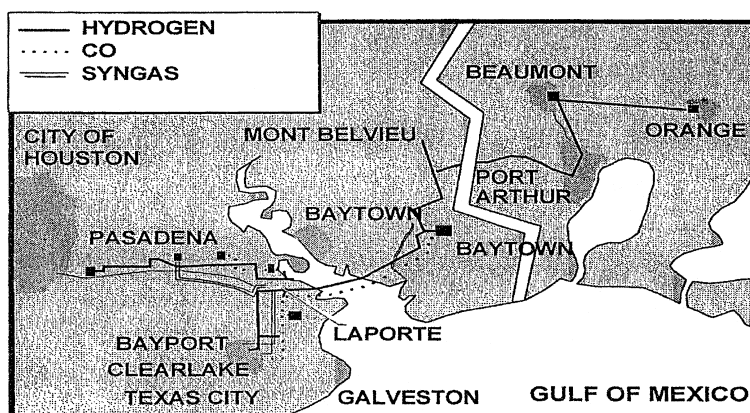


Fig. 1. Hydrogen pipeline distribution system in Texas on the Gulf coast of USA (from [12]).

production (such as ethylene production). In reviewing H_2 production, there are a number of factors which control the selection of the process. Production requirements with regard to capacity demands, purity, and pressure needs are set by the customers. Reliability of the technology and production is important to a customer, especially if the operation of a multi-billion dollar refinery depends on the continuous availability of H_2 . Feedstock availability (natural gas composition, LPG, butanes, naphtha, coke, vacuum resid, refinery off gas, etc.) and cost are controlling factors. All these factors and the by-products of the process (product purity, quality and quantity of steam produced, and cogeneration of power) play a key role in the technology chosen when building a new H_2 plant.

The price of H_2 is very dependent on the price of the feedstock. With a natural gas feed currently at ~\$2.00 million BTU, the cost of high purity H_2 is ~\$2.5/1000 SCF based upon a plant capacity of five million SCF of H_2 per day. The cost of the natural gas is \$0.89/1000 SCF of H_2 . Capital costs for such a plant amount to ~\$8.2 million [12].

3. How is H_2 produced?

3.1. Feedstocks for H_2

Table 2 summarizes some current source materials for the world's production of H_2 . It is clear that natural gas accounts for almost 50% of the world's feedstock

Table 2
Feedstocks for H_2 production [1]

Source	World capacity (1988) (%)
Natural gas	48
Petroleum	30
Coal	18
Electrolysis	4

for H_2 . Electrolysis, a seemingly environmentally attractive source for H_2 production, is a very small percentage simply because it depends on cheap power, which is regionally dependent on the presence of limited and inexpensive hydroelectric sources of power. It does not appear that the rate of and demands for dam construction can keep up with the increased demands for cheap hydroelectric power which will always be confined to niche regions around the world (see Section 4.6).

3.2. CO_2 is a coproduct

It is important to remember that since fossil fuels are used to produce most of the world's H_2 , CO_2 is a significant by-product of H_2 production, because almost all the technologies involve reactions which coproduce CO_2 . This is seen in Table 3 which indicates the level of CO_2 produced per mole of H_2 as a function of the fossil fuel-based technology that is used. It is apparent that steam reforming of methane is clearly the best approach at minimizing CO_2 coproduction with increasing levels of CO_2 being produced

Table 3
CO₂ coproduction varies with hydrocarbon feedstock [1]

CO ₂ /H ₂	Technology
0.25	Steam methane reforming
0.31	Steam pentane reforming
0.33	Partial oxidation of methane
0.59	Partial oxidation of heavy oil
1.0	Partial oxidation of coal

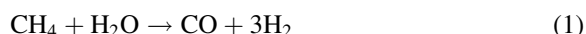
using higher hydrocarbons. Partial oxidation technologies always result in some undesirable over oxidation of the fossil fuel to CO₂. Based on CO₂ coproduction, steam reforming produces less CO₂ than partial oxidation technologies. Also, it is seen that coal is one of the least desirable sources of H₂ from the standpoint of CO₂ coproduction. Beyond feedstock selection impacting CO₂ formation, one must also consider CO₂ formation from the combustion of fuel by the burners used to provide the heat for this endothermic reaction. One should not get too engrossed with the CO₂ coproduction during H₂ production. The amount of CO₂ being produced from the world's H₂ plants is still small compared to the huge quantities of CO₂ being produced from power plants and mobile vehicles. Until we have another, cost effective means of producing H₂, the current technologies are our only approach to this important chemical feedstock.

H₂ is often suggested as a potential reducing agent to remove CO₂ or NO_x, yet such proposals need to consider the cost of this high demand reducing agent and its production; currently, it is not attractive to consider using H₂ to remove CO₂ since H₂ is often produced with CO₂ as a coproduct. From Table 3 it is clearly apparent that those that advocate H₂ as a way to remove CO₂ emission are caught in a circular argument: use of today's sources of H₂ for widespread NO_x or CO₂ control will in turn produce more CO₂. Hence, without a non-fossil, high volume fuel source for H₂, it does not make sense to use H₂ as a world scale solution to CO₂ emissions. The use of H₂ to destroy CO₂ is further complicated by the need for high pressure H₂ for the effective removal of inert CO₂. Thus, any non-fossil fuel source of H₂ will also have to be available at high pressures. The compression of gas is a very energy intensive operation, therefore, without cheap, non-fossil fuel-based, high pressure H₂, one cannot

consider H₂ as an acceptable approach to CO₂ destruction on a world scale.

3.3. Steam methane reforming

SMR typically described by reaction (1) is a widely practiced technology for H₂ production.



The reaction is highly endothermic and favored at lower pressures, but many customers of modern H₂ plants require the H₂ product at >20 atm. Since the reaction produces an increase in the net number of molecules of product, additional compression of the product would be necessary if the reaction were run at <20 atm. Although stoichiometry for Eq. (1) suggests that one only needs one mole of water per mole of methane, excess steam must be used to reduce by-product carbon formation. Addition of excess steam shifts the reaction away from carbon formation. For natural gas feeds, steam to carbon ratios of 2.5–3 are common. In addition, most modern H₂ plants use pressure swing adsorption (PSA) units for H₂ purification, and these units operate more efficiently at higher pressures.

Since reaction (1) is an endothermic reaction, the temperature of operation of most SMR units is >800°C. These extreme reaction temperatures require the use of expensive metal alloys to reduce potential issues of metal dusting often caused by CO coproduction. Thick wall tubular reactors are needed for the extreme requirements of pressure and temperature of the SMR unit, and high fuel consumption required to heat the catalyst tubes [20]. The key challenge in SMR is heat transfer for this strongly endothermic reaction: there is a critical balance between heat input through the reformer tubes and the heat of reaction [8].

SMR technology is not really just one reaction as indicated in reaction (1), but contributions from several different catalyzed reactions.

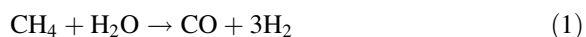
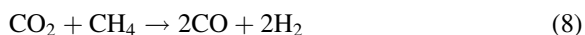
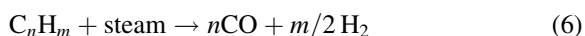


Table 4
Steps in SMR which employ catalysts

Process operation	Temperature (°C)
Sulfur conversion [HDS]	290–370
H ₂ S removal [ZnO]	340–390
Chloride removal [Al ₂ O ₃]	25–400
Pre-reforming	300–525
Steam methane reforming	850
High temperature water gas shift	340–360
Low temperature water gas shift	200
Methanation	320
NO _x removal [NH ₃ SCR]	350



It is interesting to see the number of unit operations in SMR technology which use a catalyst or an adsorbent. Table 4 summarizes the various catalysts which are used in different process approaches to SMR. While not all these are always used in one process approach, more traditional SMR without PSA technology for H₂ purification uses most of these materials. Not all function as catalysts; instead some are catalyst materials which are used for purification, such as ZnO for H₂S removal. In order to maintain the operating temperature for these steps, steam is generated or used in a complex effort of heat management.

First natural gas must be purified in a desulfurization unit; this high pressure hydrogenation reduces thiols to H₂S and olefins (usually cobalt–molybdenum catalyst at 290–370°C) as well as stripping H₂S using a ZnO unit (at 340–390°C). People often forget that

natural gas is a very regionally dependent feedstock as indicated by its composition given in Table 5. Some sources of natural gas have high levels of H₂S, CO₂, or higher hydrocarbons. The sulfur compounds must be removed because they will irreversibly poison the nickel based reforming catalysts. If there are nitrogen compounds in the feedstock, these can get oxidized to NO_x. However, much more NO_x can be generated by the burners used to heat the reformer tubes. Even low levels of NO_x have to be removed in regions which mandate NO_x emission controls. Here the technology of choice is selective catalytic reduction of NO_x with NH₃ [21]. In some cases, traces of halides also are present in natural gas feed, and these are often removed by an alumina guard bed. Under the right set of reaction conditions CO₂ can also react with the methane or H₂.

The levels of higher hydrocarbons in natural gas are an important feature that is often forgotten. Higher hydrocarbons are much more reactive than methane, and over the traditional SMR nickel catalysts, these compounds readily lead to the generation of coke which can rapidly deactivate the nickel catalysts. Thus before the SMR process unit there is often an additional process step called pre-reforming which serves to both enhance heat recovery and remove these objectionable higher hydrocarbons [22]. Pre-reforming converts all the heavier hydrocarbons in the process feed to the reformer to CH₄, carbon oxides, H₂, and steam in a lower temperature, adiabatic reactor. Thus, it is possible to reduce the SMR unit's overall steam/carbon ratio, since removal of the higher hydrocarbons dramatically reduces the tendency for carbon formation. Reducing the levels of steam decreases the pressure drop in the plant and increases the plant's efficiency [23].

Table 5
Composition of natural gas by region [19]

Region	Methane	Ethane	Propane	H ₂ S	CO ₂
USA/California	88.7	7.0	1.9	–	0.6
Canada/Alberta	91.0	2.0	0.9	–	–
Venezuela	82.0	10.0	3.7	–	0.2
New Zealand	44.2	C ₂ –C ₅ =11.6	–	–	44.2
Iraq	55.7	21.9	6.5	7.3	3.0
Libya	62.0	14.4	11.0	–	1.1
UK/Hewett	92.6	3.6	0.9	–	–
URSS-Urengoy	85.3	5.8	5.3	–	0.4

Table 6
Typical feed and product compositions of pre-reformer units [26]

	Inlet	Exit
Temperature (°C)	500	441
Pressure (atm)	33.5	33.0
CH ₄ (%)	93	71.6
C ₂ H ₆ (%)	2.1	0
C ₃ H ₈ (%)	1.0	0
H ₂ (%)	3.0	22.0
CO (%)	0	0.1
CO ₂ (%)	0	6.3

Steam/carbon=3/1; catalyst is high Ni with promoters on alumina.

Pre-reforming units allow H₂ manufacturers to operate with a variety of feed compositions by ensuring that the feed to the SMR unit is constant around the world [24]. Pre-reformers reduce the heat demands of the primary reformer unit by necessitating less fuel consumption [25]. Since pre-reformers operate at much lower temperatures (500°C) than the SMR unit, steam generated within the plant can help provide some of the heat of reaction for the operation of the pre-reformer [25]. Table 6 summarizes the conditions and output of a typical pre-reformer unit. One can see the dramatic effect that the pre-reformer has on the higher hydrocarbon levels, while producing some H₂ coproduct. There is not much work in the open literature [27] on pre-reformer catalysts. They tend to contain much higher levels of nickel (>25% as Ni) than conventional SMR catalyst [22]. British Gas developed a very high nickel catalyst for pre-reforming at 300–525°C [23,28].

The simplified process flow diagram in Fig. 2 illustrates the major unit operations within an SMR process. Fig. 3 provides a more detailed description of the

SMR process using PSA for H₂ purification and illustrating the extensive amounts of steam balance employed in these operations. SMR plants provide major sources of steam for other process operations. A large quantity of high value steam is generated; about 10–12 ton of steam/ton H₂ [29]. These plants are engineered to recover heat as steam and use that steam in other operations within the plant or the steam is sold to a nearby customer. Noting the various exit temperatures on the different unit operations one can trace the areas of steam generation and usage in a typical PSA based process which is illustrated in Fig. 4. Fig. 5 describes the process flow of a conventional SMR without PSA using CO₂ scrubbing and methanation.

In the SMR process unit, steam is used to convert methane to CO and H₂ as described in reactions (1)–(8). What actually happens inside the unit is a number of competing reactions which include reforming with both CO₂ and steam, as well as the water gas shift reaction, methanation, and carbon forming reactions. The catalyst is a high Ni catalyst (~12–20% Ni as NiO) supported on a refractory material such as alfa alumina containing a variety of promoters. Key additives are potassium and/or calcium alkali ions which mainly serve to suppress excessive carbon deposition on the catalyst [30]. These catalysts perform in excess of five years (>50 000 h) of continuous operation and are provided by a number of vendors [9], including ICI/synetix, Dycat, and United Catalysts. The catalyst is shaped into an optimal form for heat transfer, often in the shape of multi-channel wheels. A range of catalyst shapes are available which are designed on the basis of increasing the geometric surface to volume ratio while reducing the pressure drop down the long

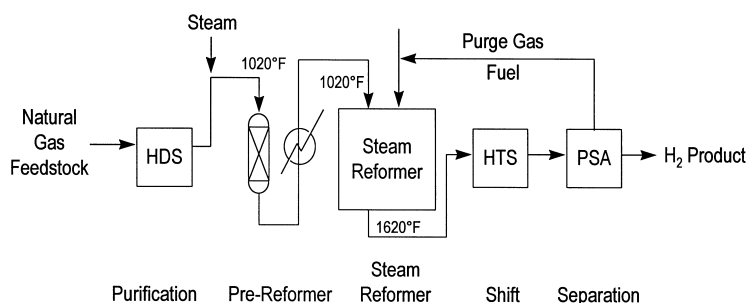


Fig. 2. Simplified process flow diagram for SMR [24].

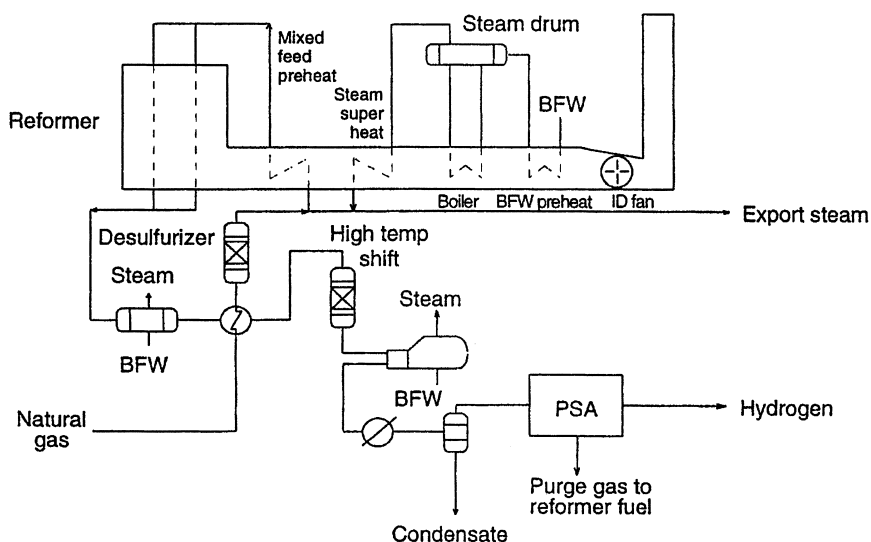


Fig. 3. SMR process flow diagram with PSA unit for H_2 purification (from [10]).

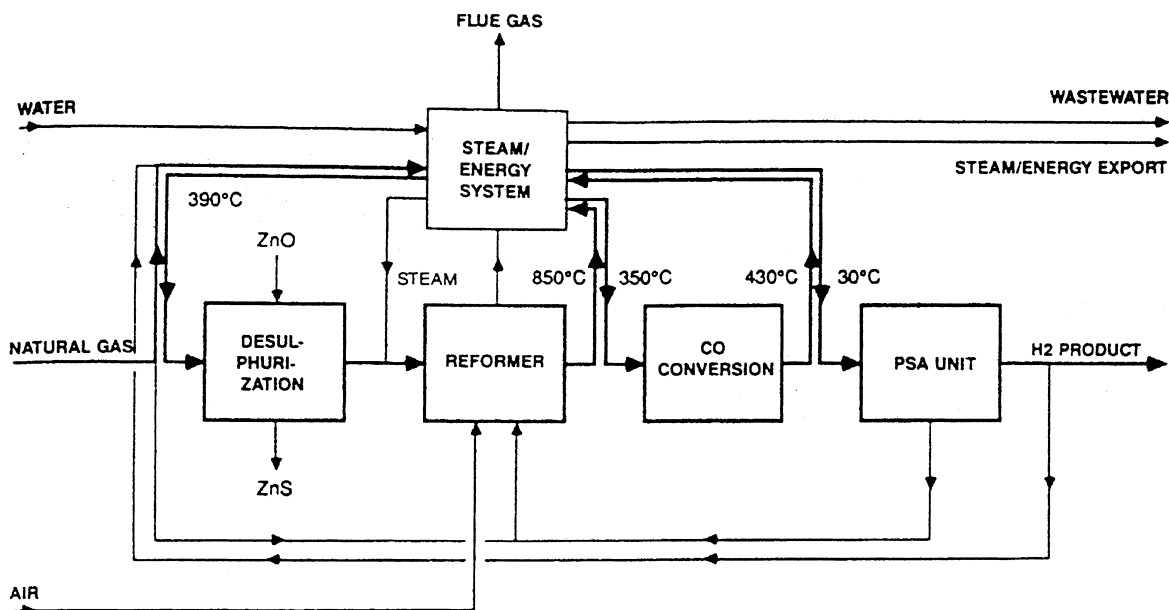


Fig. 4. SMR process flow diagram indicating steam integration and temperature regimes (from [11]).

reactor tubes. The rates of reactions in the unit are controlled not only by the kinetics of all these different reaction steps, but also by the rate of mass transfer from the bulk gas to the surface of the catalyst pellets and heat transport. The catalyst extrudates must be strong in order to avoid crushing caused by the weight

of ~40 ft of catalyst material. Effectiveness factors for the catalyst are very small and most of the catalyst loaded into conventional reactor tubes is not continually being used for the catalysis [31]. The catalyst is heated to 780–880°C and is contained within anywhere from 4 to 600 high Ni alloy thick wall tubes

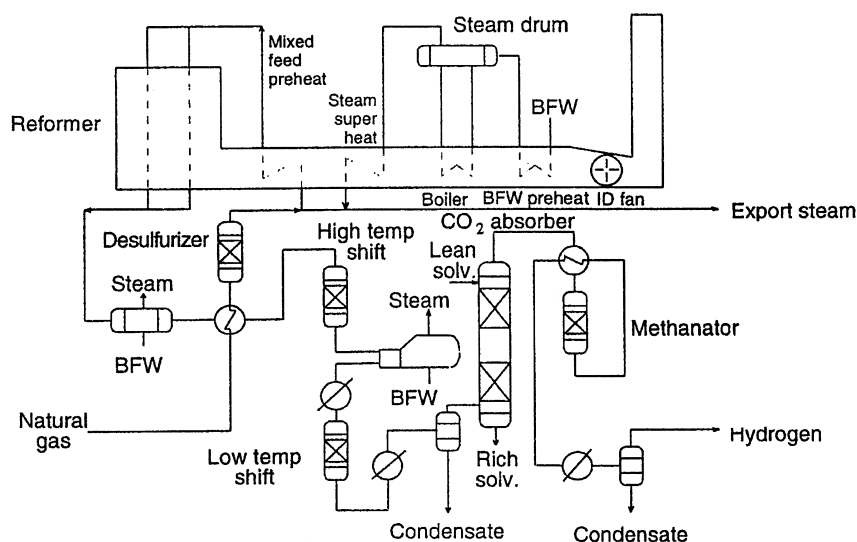


Fig. 5. SR process flow diagram with conventional CO₂ scrubbing and methanation (from [12]).

which are ~45 ft long and 5 in. inside diameter. The catalyst must be stable and tolerant of the extreme normal operating conditions of the reforming reaction. Also, it must be robust enough to cope with the stress of start-up and transients in the feed which lead to exposure of the catalyst to sulfur or excessive carbon deposition. While this is a mature catalyst, there are still areas which require further clarification. Rostrup-Nielsen [8] pointed out years ago some incompletely understood factors: heat transfer in packed tubes at the very high Reynolds number used in the process; sintering of the Ni crystallites and their impact on catalyst performance; effect of alkali promoters origin, optimization, and control; mechanism of carbon formation; and the role of sulfur with regard to carbon growth.

These tubes of catalysts are contained within a furnace box structure resembling a large rectangular barn, thus distinguishing the location of most SMR operations at a refinery. Large multiple burners are mounted along the inside walls of the firebox unit containing the vertically mounted tubes of catalyst. Because of the endothermic nature of reaction (1), the reaction often becomes heat transfer limited. 50% of the heat of combustion is used for the reaction, and a great deal of effort is spent to recover the waste heat by preheating feeds and steam generation [19]. Getting

heat into the process gas stream is critical for good reactor performance. Extra catalyst can be loaded into the tubes to increase conversion (which is equilibrium limited). Reducing the tubewall thickness allows one to reduce the operating temperature, thus providing considerable energy savings. Operating with higher heat flux to the catalyst will allow one to reduce the number of tubes to meet the production requirements of the particular unit.

Because of the multiple reactions occurring in the SMR process, CO is also a coproduct coming from the primary reformer. Unless there is a need for a mixture of CO/H₂ by the customer of the plant, most of the CO is converted back to H₂ via the water gas shift reaction (reaction (2)). This exothermic reaction does not require the high temperature of the gases as they exit the primary reformer, so the temperature of the process stream must be reduced by generating steam. Typical catalysts operate with high temperature (90–95% magnetite iron oxide, stabilized with 5–10% chromia for inlet operation temperatures of 340–360°C) or low temperature (~30% as CuO, ~33% as ZnO, and ~33% as alumina for inlet temperatures of ~200°C).

Older SMR operations (Fig. 5) used a solvent system to reduce the CO₂ levels from the process gas exiting the water gas shift operation from ~22% to

~0.01%. A common alkanolamine solvent is monoethanolamine. If there is no market for the CO₂, it is vented to the atmosphere.

Older operations of SMR plants also had a methanation reactor to destroy any trace levels of CO with H₂ since the refinery customers for H₂ cannot accept any significant levels of CO in the H₂ stream. Methanation catalysts operate at an inlet temperature of ~320°C and are comprised of nickel metal (or ruthenium) dispersed on a variety of oxide supports. Newer SMR plants which incorporate PSA operations for purifying the H₂ can also remove CO without methanation.

H₂ PSA (pressure swing adsorption) has now become a popular alternative (Figs. 2–4) to solvent based systems for CO₂ removal and the methanator unit. Prior to the product gases entering the parallel adsorbent beds at an ambient temperature, steam is removed from the gas stream and heat is recovered. Generally, with H₂ PSA, one only needs to do high pressure water gas shift [12]. With this simplification in unit operations, equipment is less expensive and H₂ purity of 99.95% is achieved [12]. Generally, an adsorbent bed of molecular sieves is used to remove all non-H₂ components in the raw H₂ process stream at 300 psig. As the concentration gradient of impurity moves upward along the adsorbent bed thus producing pure H₂, the vessel is depressurized when the gradient nears the top of the bed, and the bed regenerated. A parallel bed is then brought into service as the first bed undergoes depressurization and regeneration. By using multiple adsorption beds which are synchronized, a continuous flow of product gas is maintained. Regeneration is achieved by depressurization and purging with high purity product H₂. The purge gas at 5 psig, which contains some of the H₂ product, is burned as fuel in the primary reformer furnace. H₂ recovery from the process is 80–92% at a feed pressure of 400–500 psig and a purge gas pressure of 5 psig. For overall SMR, Scholz estimates that it offers the most energy efficient approach to H₂ production. By assessing total energy input and output, he estimates the thermal efficiency of SMR at 81% [1].

In any H₂ production operation there are concerns with regard to carbon formation [8]. Carbon formation [32] can build rapidly and shut down the process, thus it is important to keep it under control. There are two

major pathways for carbon formation:



The tendency to form carbon over the catalyst is a question of kinetics, process conditions, and reformer design [6]. These carbon forming reactions are delicately balanced by carbon consuming reactions such as reactions (10) and (11):



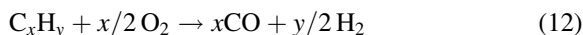
In fact it is also argued that the working SMR reduced Ni catalyst is coated with a working layer of carbon. Laboratory operations over periods of days are not sufficient to test for carbon formation; instead, new catalysts have to be tested for months under simulated process conditions and reactor configurations.

In carrying out research on improvements to SMR, one must test the catalysts at high pressures (>10 atm) because pressure can have a severe impact on carbon deposition. Catalysts can also fail because of Ni sintering or carbon deposition in cold spots within the reactor tubes. One must also remember that commercial operation uses an adiabatic reactor which results in a temperature gradient along the catalyst bed. Typical steam/carbon ratios are about 2.6 with the outlet temperature of some reformers approaching 930°C [33]. Further there are thermal reactions occurring after the products emerge from the catalyst bed. The catalyst is very sensitive to poisons. The high reaction temperature limits the life of operation of the Ni alloy reactor tubes. Finally, poorly prepared catalyst can lead to migration of the alkali in the catalyst which can then lead to downstream corrosion of the steel within the plant [10]. Any research or claims about catalyst improvement need to appreciate that many issues will control the proper selection of catalyst in the SMR reactor.

3.4. Partial oxidation of fossil fuels

The other major route to H₂ is non-catalytic partial oxidation of fossil fuels, often referred to as POX (or gasification). One key advantage of this approach is that it accepts all kinds of hydrocarbon feeds. The thermal oxidation is run at 30–100 atm with pure O₂

using a special burner inside a refractory lined vessel at $\sim 1300^\circ\text{C}$. The general reaction is described by Eq. (12):



In this case steam is not used as a feed, but with higher hydrocarbon feeds there can be a lot of coke as by-product. Since conditions are maintained net reducing, no NO_x or SO_x are produced; however, if the feed contains any sulfur compounds, H_2S and COS are by-products which must be scrubbed. A clear disadvantage is the need to have huge quantities of O_2 available continuously, thus requiring the substantial investment in an adjoining O_2 plant. Since CO is also a coproduct, one has to use high temperature water gas shift to convert CO with steam to H_2 . Additional unit operations are required for gas purification (largely to remove H_2S) and to remove soot from the waste water. In addition, the CO_2 is removed by absorption, and final traces of CO destroyed by follow-up methanation [6]. Thus POX operations can get quite complex (refer to Fig. 6), and in comparison to SMR they are less energy efficient, while eliminating more CO_2 coproduct [1]. Fig. 6 only shows part of the POX process, steam must also be generated and the product CO/ H_2 must also be purified. A strong feature of POX technology versus SMR is that the former is a very attractive process when dealing with the increasing amounts of bottom-of-the-barrel feedstocks. Scholz [1] estimated that the thermal efficiency of a POX plant feed with heavy hydrocarbons to be $\sim 70\%$ versus 81% with SMR. Secondary reforming with

added O_2 is used in some operations employing SR technologies, especially in connection for the high H_2 demands of ammonia synthesis. In the exothermic, secondary reformer, air is added to the effluent of the primary reformer. The residual methane reacts with the air providing heat for this CO producing reaction, and the unreacted N_2 is used for NH_3 synthesis.

3.5. Autothermal reforming

An alternative approach to POX and SMR is autothermal reforming [34], which is a combination of both technologies. In autothermal reforming, the energy for the production of CO and H_2 is produced by partial oxidation of the hydrocarbon feedstock. Like POX, the feeds first react in a large refractory lined vessel with O_2 for non-catalytic combustion at $1200\text{--}1250^\circ\text{C}$. (If the product H_2 is intended for NH_3 production, an air feed could be used.) One example of an autothermal reformer approach is illustrated in Fig. 7. Natural gas and steam are mixed with O_2 within the burner where partial oxidation reactions occur and provide heat for the endothermic reactions to follow. Downstream from the combustion zone (in the same reactor) is an Ni based reforming catalyst bed to carry out steam reforming (autothermal reforming does not lend itself to heavy hydrocarbon feeds). Operating pressures range from 275 to 1000 psig. Since autothermal reforming uses less O_2 than POX, the economics are less sensitive to the price of O_2 when O_2 is cheap. It requires no external fuel while offering some flexibility in feedstock.

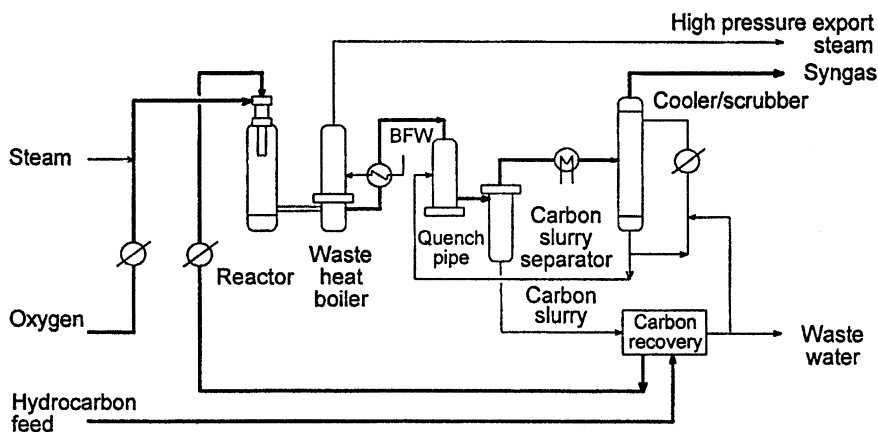


Fig. 6. Process flow diagram for POX.

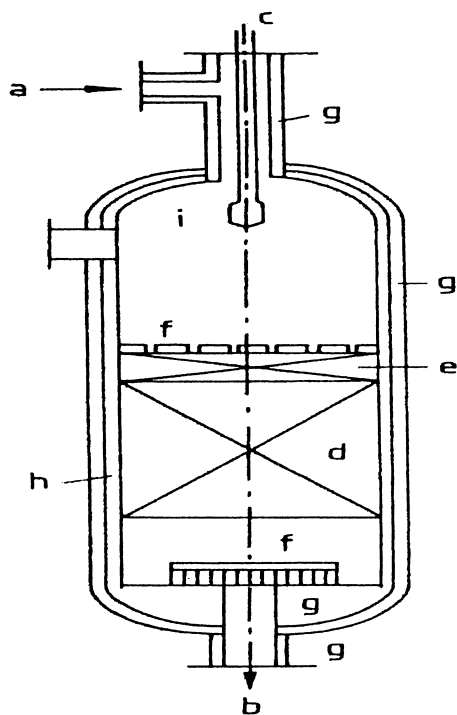


Fig. 7. An autothermal reformer with a water-cooled tip: a – gas inlet; b – reformed gas product; c – air/O₂ and steam inlet; d – catalyst; e – high temperature catalyst; f – inert material; g – internal insulation; h – additional insulation; i – burner; j – water jacket [11].

3.6. CO₂ reforming of methane

With the environmental concern about CO₂ and the increasing interest in making mixtures of CO/H₂, the reforming of methane with CO₂ is getting more attention. The large levels of CO₂ produced around the world do not provide sufficient justification for using this approach to produce only H₂; instead, the attractiveness of this approach is driven by the fact that relatively pure CO₂ is a coproduct now of H₂ production. If a customer also wants CO, this technology can be used to add more CO to the product H₂. However, CO₂/CH₄ cannot be used to produce H₂ and resolve CO₂ emission, since the carbon product still remains. Even if one uses water gas shift to convert CO to H₂, one just produces CO₂ again.

CO₂ reforming involves an even greater potential for carbon formation [35]. For reaction (7), the practical limit on H₂/CO is 1.3/1 because of the need to add

steam to the natural gas/CO₂ mixture in order to avoid excessive carbon formation. The use of CO₂ to reform methane really occurs with the assistance of steam, hence the net reaction is described in Eq. (7):



The CALCOR process from Caloric, GmbH uses a staged catalyst to get H₂/CO=0.4/1. For several years, Haldor Topsøe has operated its SPARG process which uses a partially sulfided nickel catalyst [36]. The CO₂ feedstock is available as recycle coproduct, but some import CO₂ is still required. By selectively poisoning the over active Ni sites on a conventional SMR catalyst, one can minimize coke deposition. The addition of sulfur to the catalyst does reduce its activity and thus affects overall productivity of the operation. The use of CO₂ in the feed increases the tendency of the high pressure reaction to produce excessive levels of coke due largely to the higher levels of CO in the product. Thus any catalyst must be able to control the level of carbon formation which will eventually shut the process down, if allowed to occur to any significant level. Since one makes more CO in the bed, it could readily produce more carbon over some catalysts. Avoiding carbon formation is a key problem [37]. Some improved catalysts for reaction (7) often slowly produce carbon by-product; hence, claims for new catalysts for this reaction must be based on studies over long periods of time at high pressure to establish low carbon formation or these catalyst claims must follow with time the actual level of carbon produced over the catalyst.

Another important aspect in carbon formation is the level of CO₂/CH₄ as a function of temperature. This is illustrated in Fig. 8. Anything to the left of the three curved lines results in carbon formation. A dotted line is drawn at 20 atm to indicate a preferred operating pressure. From Fig. 8, one can see the dramatic impact of pressure on CO₂ reforming. As one reduces the ratio of CO₂/CH₄, one makes more carbon, thus forcing operation to higher temperatures. By running richer in CO₂ in order to reduce the likelihood of carbon formation, one has excess CO₂ in the product which then demands more attention with regard to recycle and purification of the product.

In considering CO₂ (or any material as a feedstock) there are a number of issues that need to be appreciated but which are often forgotten. While the chem-

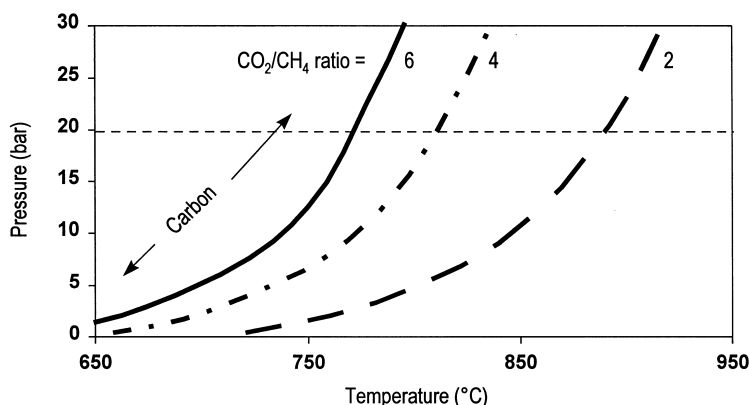


Fig. 8. Carbon formation regimes during the dry reforming of methane with CO₂ [38].

istry with CO₂ occurs as reaction (7) suggests, the use of CO₂ as a feedstock puts additional requirements on the technology if one wanted to separately react CO₂ with methane to produce H₂. Impurities will be serious catalyst poisons, hence pure CO₂ will be required; thus external sources of CO₂ coming from a powerplant will have to be purified. Since CO₂ is so inert, one must apply pressure and elevated temperatures to get it to react sufficiently. As a feedstock, CO₂ will have to be continuously available on a 24 h basis and at a constant output level. Finally, one cannot ignore the fact that most CO₂ is produced in other regions of the world, often located separately from H₂ plants; therefore, the CO₂ would have to be transported to the production site.

4. Alternative means of producing H₂

Beyond improvements to the existing approaches to making H₂, there are a number of other ways [39] that have been getting more attention. These include:

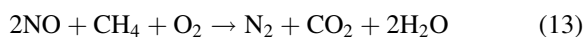
- use of methane,
- use of membrane reactors,
- solar energy for electrolysis of water,
- selective oxidation of methane,
- oxidative dehydrogenation,
- electrolysis of water using fuel cells, and
- biomass conversion.

Unfortunately only the use of solar energy for photoelectrolysis of water offers a non-fossil fuel

solution, although there are arguments that, in principle, biomass offers a CO₂ neutral approach.

4.1. Use of methane

People often forget that methane itself has a very high hydrogen atom content. While CH₄ is used via SMR as a means to make H₂, one could consider using it directly as a source of hydrogen atoms for other chemicals' processing. There are a few examples where CH₄ is decomposed to carbon and H₂. The resulting carbon is then converted in a separate step to CO or CO₂ [40]. Methane has also been used as a chemical reducing agent to convert nitrobenzene to aniline over a copper chromite catalyst [41]. In another example of using the hydrogen value of methane, we were able to reduce NO_x with methane. (Others have established that H₂ can be used to destroy NO_x [42,43], but once again it is too valuable a feedstock to use for destroying NO_x in large quantities on a worldwide scale.) Our discovery [44,45] that one can use methane (in the presence of O₂) to reduce NO_x to N₂ (Eq. (11)) is an example of using the hydrogen value of methane as an alternative way of using H₂ as a reductant for NO_x.



Perhaps, there are other reactions where one can envision using the world's vast natural gas supply to provide an alternative supply of H₂.

4.2. Use of membrane reactors

There is increasing interest to use H₂ permselective [46] metal alloy membranes to produce ultra-pure H₂ while carrying out some type of process chemistry. Some examples of Pd alloys for enhancing dehydrogenation [47] or SMR [48] reactions are given in the literature. Economic evaluations of these systems have been undertaken which suggest the promise of such operations but question the application of membrane reactors for H₂ producing reactions [49–51]. The use of membranes in enhancing H₂ production will be limited by the quality of the process feed streams available. Feeds which have CO, H₂S, or aromatics will not be acceptable due to their tendency to poison Pd surfaces. These reactors will be limited by mass transport, and they suffer from low working surface area. Membrane fouling is unacceptable with these systems. Today's Pd based alloy membranes produce very pure H₂, but almost always at low pressure. Polymer based membranes can produce up to 98% purity H₂, but they are sensitive to the presence of organic amines in the feed (often present from prior CO₂ removal operations). Earlier attempts to commercialize Pd alloy membranes for H₂ purification often exhibited unpredictable rupture of the membrane material with catastrophic failure of the alloy [52]. There is a brief description [53] of Russian technology for recovery of H₂ at high pressure from an NH₃ purge gas stream; however, this has not been verified or duplicated by others in the open literature. In a different approach, Sircar and co-workers [54,55] have demonstrated the use of carbon coated supports for recovery of H₂ from targeted refinery streams. In these selective surface flow membranes, H₂ is rejected from the membrane and it allows one to recover high pressure H₂ in an enriched retentate stream.

4.3. Solar energy for photoelectrolysis and photocatalysis of water

Water may be the ultimate feedstock for H₂ production. If one could demonstrate the use of visible light to photocatalytically decompose water into H₂ and O₂, it would have an enormous potential impact on the future production of H₂. This is not an easy problem and has been under study for decades by many groups around the world with very limited progress. Early

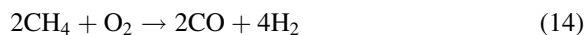
workers used ultraviolet light, which with its higher energy content was capable of energy inefficient reactions over titania and other oxides. One cannot afford to use UV sources of light; for widespread and large volume production of H₂ one would have to use the energy of the solar spectrum, which is mostly visible light. There are limited materials that can utilize the energy of the visible spectrum, and some groups are beginning to make some progress in this direction [56].

Another approach using solar energy is the use of some external power source or photovoltaic devices (which use visible light to generate power) which are then used to electrolytically decompose water. Photovoltaic devices are still rather expensive (about 10 times more expensive than the price of peak hydroelectric power [57]). Unfortunately, there are other technical and process related problems which also must be resolved.

Any solar based process must have a high energy efficiency: the quantum yield of the reaction must be high. Any device must be cost effective and avoid coproduct formation (without changes in pH). The photocatalyst must be long lived and capable of operation in hostile environments (sand storms; salt spray, etc.). Ultimately, one must also have a process for separating the H₂ from the O₂, which will entail another unit operation and more cost. Thus, only in the very long term (late 2000s or into the 22nd century) may scientists come up with a solution to these many serious hurdles. Nonetheless, this is a valuable approach to a non-fossil fuel route to H₂. Both these solar approaches only produce H₂ at 1 atm pressure; for current large volume uses of H₂, the product would have to be compressed to ~20 atm, thus necessitating the input of large amounts of electrical power.

4.4. Catalytic selective oxidation of methane to synthesis gas

The oxidative decomposition of methane into CO and H₂ is favorable, but the trick is to avoid the runaway oxidation of methane to CO₂ and water. Ideally, one wants to perform a gentle selective oxidation of methane with O₂:



and operate outside the explosive limits of CH₄/O₂.

Lanny Schmidt and Hickman [58,59] have made substantial progress in understanding this very difficult reaction using noble metal coated monoliths with very short reaction contact times. There are two recent US patents [60,61] which report interesting results suggesting that some of the hurdles can be minimized. A Shell patent [60] claims that one can perform reaction (14) using a 0.5% Rh/ZrO₂ monolith operating at 1155°C and 3 atm pressure with 97% CH₄ conversion and 92% selectivity to CO and 90% selectivity to H₂. Another recent report [62] demonstrated that the addition of Gd to cobalt oxide catalyst with a CH₄/O₂/helium ratio of 2/1/4 at 830°C gave 73% conversion with 80% selectivity to CO/H₂. Any practical extension of the latter work will require the avoidance of helium or any diluent (because of the need for separation and purification of the H₂ product), the demonstration of sustained catalyst life over months of operation, and operation in a commercially acceptable safe operating regime. A recent review by Peña et al. [6] also provides some other commentary and insight.

4.5. Solid oxide fuel cells

There are increased levels of interest [63] in using fuel cells to generate H₂. A number of fuel cell devices are under consideration. Most fuel cells generate H₂ at 1 atm or less. For bulk H₂ production this will then require higher compression to apply the technology to where most of the customers are located. Often methanol is the fuel of choice, but it must be appreciated that there will be transportation costs to move the methanol from the production site to the location of the fuel cells.

Natural gas based fuel cells are also being considered to power mobile vehicles. Fuel cells are much more efficient than the internal combustion engine [14] at generating power. Such fuel cells include a reformer to convert a fossil fuel to H₂/CO. The H₂ is then used in the fuel cell upon reaction with O₂ in air to produce chemical power for mobile engine vehicles [64]. Most of these systems employ a fossil fuel as the feedstock which means that one must first prepare the fuel. However, the US Department of Energy [13] sees H₂ fuel cells as a way to use the existing infrastructure of gasoline delivery in USA, in order to provide a fuel for mobile engines. The DOE and Arthur D. Little

recently announced new technology for converting gasoline to produce on board H₂ which will then be the source of energy to power fuel cells.

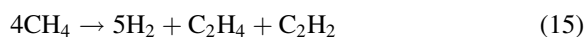
Alternatively, Parmon et al. [65] reported on the oxidation of methane to syngas over a Pt electrode catalyst in a high temperature electrochemical cell with a yttria stabilized ZrO₂ as a solid electrolyte. They claim the ability to cogenerate electricity with syngas at 100% conversion of O₂ and 50% CH₄ conversion.

4.6. Hydroelectric power

The use of hydroelectric power to electrolyze water is a non-fossil fuel alternative to the production of H₂, but its growth is very limited. Electrolytic production of H₂ is not very energy efficient and is only attractive when one has lower cost hydroelectric power nearby; for this approach, electricity costs account for 80% of the operating cost for H₂ production. Geography limits the location of dams, especially near large centers of population where the power is needed. The process water feed must be demineralized to meet purity needs (to avoid deposits on the electrodes and corrosion). Dehydration of the H₂ product may be necessary followed by compression to meet customers' needs. Scholz [1] estimates that the energy efficiency of electrolytic processes is ~64%. In addition, the construction of dams has a lot of "green" issues associated with it. The construction of huge dams can impact the river bed in the vicinity of the dam and the fish population as well. Dams alter the river temperature, pH, and the nutrient levels in the water near the dam. Construction of dams results in irreversible loss of the area behind the dam now covered by water. Finally, there are public safety issues, since dam collapse has occurred in the past. Thus, hydroelectric power does not seem to offer a viable, long term supply of cheap H₂ to satisfy the world's appetite.

4.7. Other methods for H₂ generation

Besides using methane as a source of hydrogen atoms, one can also envision pyrolysis of methane to convert it into H₂ and C₂ hydrocarbons as indicated in Eq. (15):



The difficult step in this reaction is once again to control the formation of carbon from the decomposition of methane, according to Eq. (16):



Parmon [66] discussed this concept and the use of microwave or plasma energy to carry out reaction (16). In addition, they have also considered the use of fluidized beds of nickel catalysts at 650°C at 1 atm to produce H₂. Obviously, one must also incorporate a separation step to recover the H₂ from the carbon coproducts.

Other non-catalytic approaches include the thermochemical splitting of water using a solar furnace or nuclear energy. The high quality heat which is generated with a solar furnace is used to generate electricity which is then used to electrolyze water to produce H₂ [6]. Separation of the H₂ from the O₂ must still be incorporated in these alternative approaches.

There has also been a good deal of interest in using biomass [67,68] as a means for generating H₂. While this allows one potentially to recycle the CO₂, it demands large acreage for trees which consume CO₂; power plants then would burn these trees to produce energy and CO₂.

5. External issues controlling the production of H₂

Anytime one considers new technology approaches, there are always non-technical issues which play an important role in the acceptance of any new technology. One can appear to have a great technical solution, but if it is too costly to implement or environmentally unacceptable, it will never be used. Beyond the obvious hurdles to developing new technology, one must consider some [69] of the following external issues which are related to H₂ production:

- The type of feedstock available: regional issues with regard to supply and availability (huge, local coal or natural gas reserves, etc.) can affect a decision to develop new technology.
- For partial oxidation technologies: unless one can use air, without having to separate the N₂, pure O₂ from an oxygen plant is a necessary requirement.

- The needs of the customer: some customers are unique in their requirements for product at a specific pressure, purity, and the volume.
- The cost of local power: some communities/governments provide substantial credits for power produced by a specific technology and these credits can have a big impact on the source of power one selects and where one locates the production site.
- Capital costs: scientists must not forget that exotic technologies using immense capital resources can become unattractive when matched against lower capital cost, established alternative technologies. The cost of capital, while recoverable, still can require an enormous up-front investment.
- Storage and purification of H₂: one cannot forget that if the H₂ is not pure, there will be added costs to clean it up to the customer's requirements. In addition, the construction of storage facilities for feed or product can add unacceptable costs.
- Government regulations: what local governments do by legislation or taxes can have an enormous impact on new technology. Environmental regulations can make it too expensive to operate what might seem to be a simpler process technology.
- Additional government subsidies can impact the decision on which technology to undertake. Some governments will provide development costs, cost-share new technology, or ease proprietary restrictions.

6. Summary

This review has tried to consider the entire picture in meeting the world's thirst for more H₂. The demand for H₂ is very strong and is forecast to continue well into the next century. Since H₂ is largely produced from fossil fuels with coproduct CO₂, H₂ cannot by itself offer a solution to removing the large levels of CO₂ on a worldwide basis.

SMR is one of the most attractive approaches for new H₂ plants, and it comprises many different catalytic operations, including desulfurization, pre-reforming, reforming, high and low temperature water gas shift, methanation, and deNO_x. As long as natural gas and petroleum based hydrocarbons are still relatively low cost fuels, SMR will continue to be a cheap

approach for making H_2 . Steam reforming is a mature technology, but there is fertile ground and room for technological improvement. Probably beyond 2010 future issues may eventually force adoption of alternative technology since steam reforming is an energy intensive, endoergic process, CO_2 is a coproduct, and H_2 purification is necessary. At the fundamental research level, there is a need for more catalyst studies at >20 atm where the chemistry is actually practiced. The life of the catalyst is an important criterion in benchmarking new catalysts versus commercial SMR catalysts.

There are a number of emerging and attractive approaches to H_2 production, but the greatest opportunities in the future lie with non-fossil fuel-based H_2 technologies, where major breakthroughs are needed. In considering new technologies for H_2 production, one has to consider the entire process, that is, one must have separation and purification steps, consider net energy demands and balance, the quality of the feed, etc. Ultimately, the route one chooses to produce H_2 will be a function of not only the technology advances, but also economics, the environment, and market demands.

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