CONVENTIONAL ETHANOL REFORMING TECHNOLOGY DEVELOPMENTS FOR THE PRODUCTION OF HYDROGEN

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ABSTRACT

In the unsafe horizon of pollution, global warming, and energy crises, all resulted owing to the fossil fuels, hydrogen fuel obtained by steam reforming of bio-derived ethanol (bioethanol), can be a strong candidate as a clean energy carrier based on the renewable sources of energy. In this paper, the key issues related to the steam reforming of bioethanol for the production hydrogen are discussed in the view of potential application of hydrogen for polymer electrolyte membrane (PEM) fuel cell. The need for the development of catalyst for CO free production of hydrogen is emphasized to obtain a commercially viable bioethanol steam reforming system; also the commercial feasibility of hydrogen production is discussed. The proper distinguish has been done in the existing conventional reforming technologies and the new developed technologies along with catalyst developments. The commercial feasibility of reforming of ethanol or bioderived liquids (Bio-ethanol) is criticized by taking consideration of existing technologies of power production.

KEYWORDS: *Hydrogen Production, Bioethanol, Steam Reforming, Reforming Catalyst, Membrane Reactor*

I. INTRODUCTION

Modern society is profoundly tied to the fossil fuel energy and its sources which powers the society. From the commencement of the Industrial Revolution, fossil fuels have supplied this energy, enabled a modern and mobile society. But, now fossil fuel energy and its sources, evolving dangerous situations like environmental pollution, global warming and energy crises etc. To avoid this dangerous situation, it is inevitable to think on the alternative clean energy and its resources like hydrogen.

Hydrogen is the potential source of clean energy and possesses the highest energy content per unit weight (i.e. 120 KJ/g), as compare to other fuels. The benefits of hydrogen as a fuel are (1) Reduce dependence on fossil fuels (2) Environmentally benign (3) Reduce air pollution (4) Renewable in nature (5) Obtained from diverse sources (6) Carbonless Fuel (7) High energy content on weight basis (8) Higher octane rating. By keeping the view of global cycle of clean and sustainable production of energy, new eco-friendly reservoirs of hydrogen are needed and this can be fulfill by the ethanol or bio-derived ethanol (bioethanol). Hydrogen can be efficiently produced from bioethanol, represented by following simplest endothermic steam reforming stoichiometry equation.

$$CH_3CH_2OH + 3H_2O \Longleftrightarrow 6H_2 + 2CO_2 \quad \Delta H0 = +\ 174\ KJ\ mol\text{-}1 \quad (1)$$

Although, most of the used technologies to produce hydrogen are based on natural gas steam reforming, the hydrogen production from biomass (bioliquids) is a promising technology for the future, because it appears as the more attractive alternative due to its renewable characteristics (it is a part of CO_2 neutral cycle), high yield and low CO_2 emissions [1 2 3]. Ethanol is the most heavily researched renewable liquid because it is easy to store, handle, and transport due to its low toxicity and volatility. The ethanol production and transportation infrastructure already exists [4 5 6], and its forecasted worldwide production is given in the Fig.1 (Source: Market Research Analyst). Therefore reforming of ethanol (bioethanol) for the production of hydrogen appears to be the most viable midterm approach than other reforming fuels which gives hydrogen. Other renewable reforming fuel (bio-liquids) options include sorbitol, glucose, glycerol, bio-oil, methanol, propylene glycol, and less refined sugar streams (cellulose, hemicelluloses). Table 1 list the potential reforming bio-liquid feed stocks, its theoretical hydrogen yield, and advantages and disadvantages.

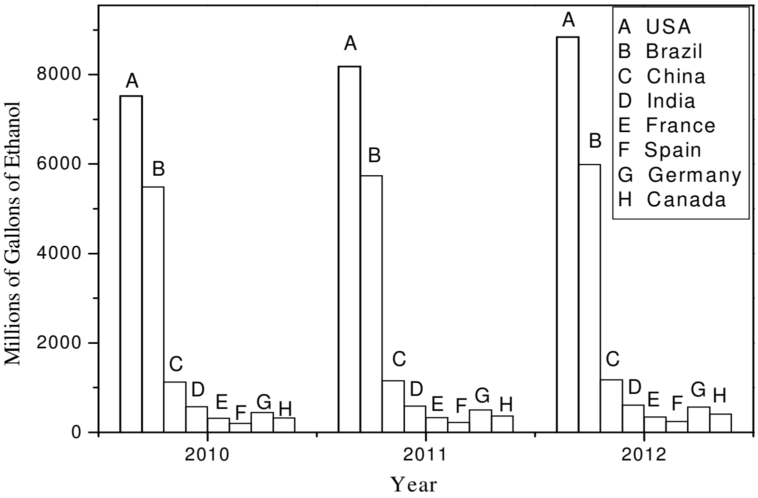

Fig.1 World Ethanol Production Forecast (Source: Market Research Analyst)

Now a day's membrane technology has created the renewed interest in the development of small-scale hydrogen production technology for the reforming of ethanol or bio-derived ethanol (bioethanol) by introduction of new conceptual catalytic membrane reactor (CMR) (see Fig. 2) and has given some extent of economical breakthrough. The conventional reforming processes for the production of 99 % pure H_2 involves the use of reforming reactor followed by CO and CO_2 separation units shown in Fig. 3, i.e. (1) Vaporizer to vaporize inlet liquid fuel and water (2) Reformer to carry out the reforming reaction in presence of catalyst (3) High Temperature Shift Reactor (HTS) to convert the dangerous CO into CO_2 and H_2 in presence of catalyst (4) Low Temperature Shift Reactor (LTS) for the complete conversion of CO to CO_2 in presence of catalyst (5) if any stresses of CO remains in the product stream, can be removed with Preferential Oxidation (PrOX) of CO into CO_2. (6) Pressure Sewing Adsorption of CO_2. These processes are usually complex, energy intensive and costly [6]. By using catalytic membrane reactor (Fig. 2), it is possible to reduce above mentioned number of unit operations in conventional reforming processes (i.e. HTS, LTS, PrOX, Pressure sewing adsorption), as shown in Fig. 3[11].

The catalysts are the center point for the research in the field of ethanol reforming technologies, over the period of last two decades, there has been a continuous improvement in the ethanol reforming catalyst and sustained a crucial role in the production of hydrogen. Since, reforming of ethanol is accompanied by many by-products (CO, CO_2, CH_4, Aldehydes); the catalyst has to optimize the hydrogen production and to discourage the by-product formation. The selection of proper support for catalyst and the methods of catalyst preparation significantly affect the overall performance of catalysts. The MgO, ZnO, CeO_2, and La_2O_3 are suitable supports for Rh and Ni due to their basic characteristics, while oxide supports plays a crucial role in the performance of catalyst. The development of bimetallic catalysts, and alloy catalysts is to be a promising answer to enhance hydrogen production and long-term catalyst stability [10]. But, still all these catalyst gives some amount of CO in the reforming reaction which is the main component responsible to increase the number of steps (HTS, LTS and PrOX) for the production of hydrogen in conventional reforming process (Fig. 3). Further research in catalyst development has been done to eliminate CO in the reforming reaction. The deployment of ZnO supported cobalt catalyst with metallic precursor was done in the view of elimination of CO in the reforming reaction and Narcis Homes and Jordi Llorca got the success to eliminate CO in the reforming reaction [62, 50, 52, 53]

Table 1: Potential Bio-Liquid Reforming Pathway (Source: U.S. Department of Energy, HFCIT Program

Bio-Liquid	Theoretical H2 Yield	Feedstock Advantages/ Disadvantages
Ethanol	0.78 kg H_2/ gallon ethanol 0.26 kg H_2/kg ethanol	Low toxicity, Low sulfur content, Use of dilute ethanol would reduce reforming feedstock costs
Methanol	0.64 kg H_2/gallon Methanol 0.22 kg H_2/kg methanol	More easily reformed to hydrogen than ethanol. High toxicity. Higher corrosively, volatility than ethanol
Glucose	0.13 kg H_2/kg Glucose	Low volatility. Non-toxic, non-flammable
Glycerol	0.15 kg H_2/kg pure glycerol	Utilizes low-value glycerol by-product from biodiesel production, Low volatility, Non-toxic, non-flammable
Bio-oil	13.8 g H_2/100 g Bio-oil, 0.06 kg H_2/ lb bio-oil	Low volatility. High reactivity; potential of forming carbonaceous deposits or converting to aromatics that are more difficult to reform to H_2
Sorbitol	0.13 kg H_2/kg Sorbitol	Low volatility. Non-toxic, non-flammable
Cellulose/ Hemicelluloses	0.13 kg H_2/kg Cellulose hemicelluloses	Low volatility. Non-toxic, non-flammable

Conventional hydrogen gas production methods are all energy intensive processes requiring high temperature (> 850 ^{0}C). The rigorous research in last decade has been given the improved technologies i.e. membrane processes, selective oxidation of methane and oxidative dehydrogenation [7, 8]. Currently methanol-water mixture reforming is the most common technology for hydrogen production on-board. However methanol as a fuel has some disadvantages connected with its high toxicity, low availability on ordinary basis and coal-natural gas based production technology, which leads to additional CO_2 emissions [9].

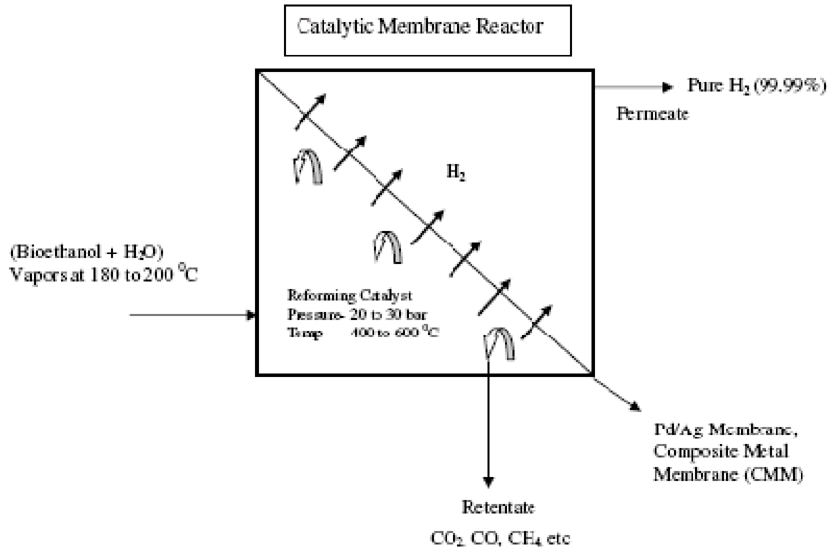

Figure 2. Catalytic Membrane Reactor Concept: Recent Development in Technology for Production of Hydrogen

The steam reforming of ethanol (bioethanol) can be carried out in different type of reactors mainly it is in fixed bed reactor, fluidized bed reactor and recently number of authors putting their efforts for studying this reaction in catalytic membrane reactor [12, 13, 14].

II. CONVENTIONAL REFORMING PROCESSES

Hydrogen market is large and growing rapidly, 95% of hydrogen is made from natural gas via steam methane reforming (SMR) [15]. The ethanol steam reforming process reactions are represented by following reactions, other reaction that can occur in the process depending on the type catalyst used [16].

$C_2H_5OH + H_2O \Longleftrightarrow CH_4 + CO_2 + 2H_2 \qquad \Delta H^0_{298} = -8.0$ KJ/mol (2)

$CH_4 + H_2O \Longleftrightarrow CO + 3H_2 \qquad \Delta H^0_{298} = 206.2$ KJ/mol (3)

$CO + H_2O \Longleftrightarrow CO_2 + H_2 \qquad \Delta H^0_{298} = -41.2$ KJ/mol (4)

Methods of hydrogen production can be broadly classified as (a) Thermo-chemical, (b) Electrolysis of water, (c) Photochemical and (d) Biological.

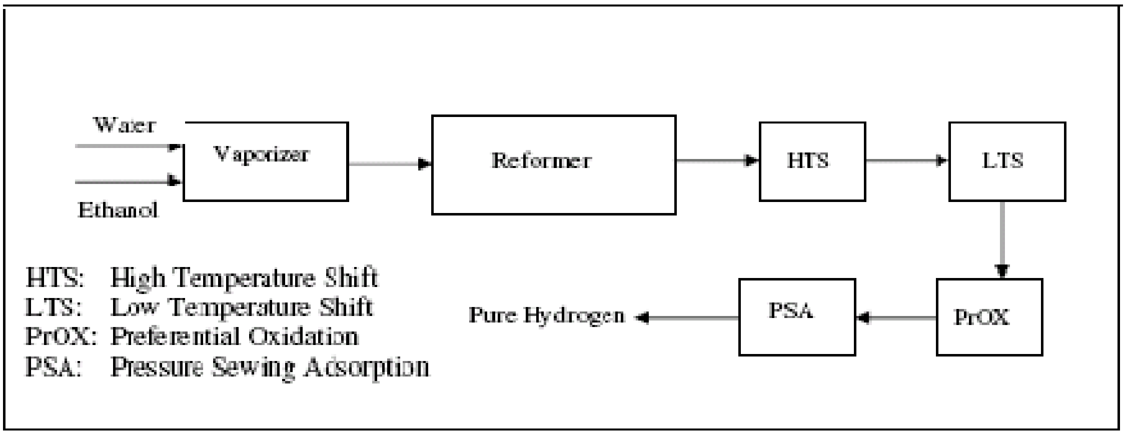

Figure 3. Conventional Reforming Process for the Production of Hydrogen

2.1 Thermo-chemical processes

2.1.1 Steam Reforming Processes (SR)

Steam reforming refers to the reaction between steam and a hydrocarbon mainly methane, ethanol and natural gas, typically producing hydrogen in the process. Use of natural gas or naphtha as a raw material is an industrial process. Typical reactions are highly endothermic in nature. Depending on the purity of hydrogen required, WGS and PrOX reactors are also appended to this process. The industrial catalyst used for this reaction is Ni/α- Al_2O_3. While the steam/carbon ratio required for this reaction is 2, generally 2.5-3.0 molar ratios are used to avoid coke formation. Since this is an endothermic and kinetically controlled reaction, temperatures in the range of 1073-1173 K are used to obtain desirable reaction rates. Main disadvantages of this process include the formation of CO_2, a global warming gas, as a byproduct, and the use of non-renewable natural gas feedstock.

2.1.2 Partial Oxidation (PO)

Partial oxidation is another industrially used process to produce H_2 or syngas from hydrocarbons, with following stoichiometry equation:

$$CxHy + 0.5x\ O_2 \rightarrow xCO + 0.5y\ H_2 \qquad (5)$$

PO compares better than SR, as it is not only non-catalytic but also does not require external thermal energy input. The process requires temperatures of 1400-1700 K and pressures ranging from 30-100 bars. Pure oxygen is used instead of air to avoid the N_2 separation step. Catalyst may be used to appreciably reduce the reaction temperature. The primary disadvantage of this process as compared to SR is low hydrogen yield.

2.1.3 Auto-Thermal Reforming (ATR)

Combining the features of SR and PO, ATR has been developed, utilizing both steam and oxygen along with the feedstock [17]. The oxygen to fuel ratio is sub-stoichiometry and can be altered to adjust the process temperature. The hydrocarbon feed stock first reacts with oxygen and the released heat is used for steam reforming reaction. This takes place on reforming catalyst placed after the burner in the reactor. The autothermal reforming of methane process was designed to save energy, because the thermal energy required is generated in the partial oxidation of methane. As this process consumes the thermal energy that it produces, it is called autothermal [18]. In this process the hydrogen yield is more than that in PO but less than that in SR. Moreover, this process does not require any external heat to be supplied.

2.1.4 Biomass Gasification and Pyrolysis

Hydrocarbons, when heated to ~1600°C, are converted to pure carbon and H_2, with no other significant side products. This, therefore, is quite a viable process for H_2 production; of course, till fossil fuel based feedstock is economically available. In biomass conversion processes, a hydrogen-containing gas is normally produced in a manner similar to the gasification of coal. However, no commercial plants exist to produce hydrogen from biomass. Currently, the pathways followed are steam gasification (direct or indirect), entrained flow gasification, and more advanced concepts such as gasification in supercritical water, application of thermo-chemical cycles, or the conversion of intermediates (*e.g.* ethanol, bio-oil or torrified wood). None of the concepts have reached a demonstration phase for hydrogen production. [19]

2.2 Electrolysis

Electrolysis of water, i.e. applying electricity to split it, is the process by which almost 100% pure hydrogen can be obtained. This is the next commonly used industrial method, after steam reforming of methane. At present, conventional alkaline electrolyte based electrolysis is economical, only if cheap electricity is available. Research is primarily focused on the feasibility of using solid oxide steam electrolyzer, PEM electrolyzer etc. [20, 21, 22, 23].

2.3 Photochemical decomposition

Photo-catalytic splitting of water, using nano-sized TiO_2 catalyst, is a potentially feasible process for production of hydrogen from water. Very low process efficiency is the main hurdle. This low efficiency is attributed to (i) rapid recombination of photo generated electron/hole pair and, (ii) backward reaction. Some sacrificial reagents such as 2- 2- 3 S /SO Ce^{4+}/Ce^{3+} [24, 5, 25] and IO_3 -/I- [26] and electron donors such as methanol [27] are under study for enhancing production. Catalyst modification techniques, such as noble metal loading [28, 29], ion doping [30], dye sensitization [31] and metal ion implantation are also being studied [32].

2.4 Bio-hydrogen

Biological hydrogen production is carried out by several methods including direct and indirect bio-photolysis, photo-fermentation and dark-fermentation, the latter being the most efficient [33]. Dark fermentation involves the use of anaerobic bacteria (Clostridium pasteurianum, C butyricum, and C. beijerinkii e) grown in the dark on carbohydrate rich substrates to produce H_2 and CO_2 and traces of CH_4, CO, and H_2S. By using Rhodospirillum rubrum, H_2 can be produced from WGS reaction when only CO is available. The main disadvantage of this method is the very slow rate of production.

III. CURRENT STATUS OF REFORMING PROCESS

The reforming process is a thermodynamically efficient way to produce high purity hydrogen from bioethanol and studies has shown that, this process is feasible for temperature higher than 230 C, being methane, carbon oxides and H_2 the main products [34, 35]. From 1996 onwards, lot of research and modifications of this environmentally benign process has been done around the World. Some of technologies to produce hydrogen, their H_2 yield, operating temperature, and production cost/Kg of H_2 and energy efficiency are given in Table 2, and it clears that ethanol steam reforming and methane steam reforming technology are the most economical hydrogen production technologies till date. Also, these technologies are compared on the basis of Feedstock and conversion efficiencies given in Table 3. The production of hydrogen from natural gas is an integral part of the strategy to introduce hydrogen into the transportation and utility energy sectors, by reducing the cost of conventional and developing innovative hydrogen production processes that rely on cheap fossil feedstocks.

Table 2: Hydrogen Production Technologies

Technologies to Produce Hydrogen	**H_2 Yield**	**Operating Temperature**	**cost ($/kg H2)*a***	**energy Efficiency (%)**
Ethanol Steam Reforming	85%	573-723	2.69-4.27	67
methane steam	5 (H_2/CO Ratio)	700–1000 °C	3.94	70

reforming				
coal gasification	39-42%	1100-1600	2.17	60
biomass gasification	62-100	100-500	7.07	45-50
water electrolysis	0.09 Kg H_2/Kg H_2O	Solid oxide electrolyzers 500-800 ^0C PEM electrolyzers 80–100°C Alkaline electrolyzers 100°C—150°C	6.82	56-73

Modification of the conventional steam methane reforming (SMR) process to incorporate an adsorbent in the reformer to remove CO_2 from the product stream may offer a number of advantages over conventional processes. Upsetting the reaction equilibrium in this way drives the reaction to produce additional hydrogen at lower temperatures than conventional SMR reactors. Although still in the research stage, the cost of hydrogen from this modified process is expected to be 25%-30% lower, primarily because of reduced capital and operating costs [36].

Table 3: Comparison for Hydrogen production technologies in terms of Feedstock and conversion Efficiencies [37]

Process	**Feedstock**	**Conversion efficiencies**	**References**
Steam reforming	Methane, glycerol, alcohols, polyols, sugars, organic acids	70–85%	[38, 39]
Aqueous reforming	Glycerol, alcohols, polyols, sugars, organic acids	35–100%	[40, 41, 42]
Electrolysis	H_2O + electricity	50–60%	[43]
Partial oxidation	Hydrocarbons (Glycerol, alcohols, polyols, sugars, organic acids)	60–75%	[38]
Biomass gasification	Biomass (Lignocellulosic biomass)	35–50%	[44]

Fuel Cells and Infrastructure Technologies Program (HFCIT), U. S. department of energy is currently supporting several distributed bio-liquid reforming research efforts [45]. These technologies target a range of bio-liquid feedstock, including ethanol, glucose, sorbitol, glycerol, and bio-oil. In the near term, distributed hydrogen production technologies may be the most viable renewable hydrogen pathway due to their lower capital investment requirements (including hydrogen transport and delivery infrastructure).

In India the production of hydrogen using reforming as energy source is in the initial stages, but is used for the other purposes like fertilizers, refineries and chlor-alkalies as shown in Fig. 4.

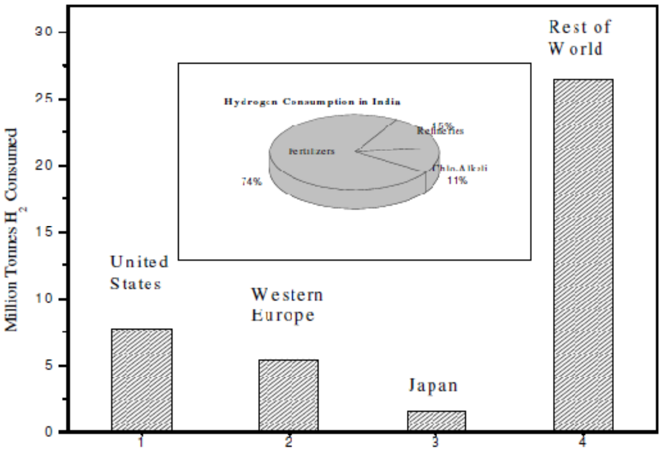

Fig. 4 H_2 Consumption worldwide and in India

Hydrogen purity is another important issue that has to be discussed, as the carbon monoxide (CO) must be less than 0.2 ppm in the hydrogen supplied to the fuel cell to avoid the degradation of catalyst in the fuel cell. Pressure swing adsorption (PSA), membrane separation, cryogenic distillation, or methanation can be used to lower the CO content of the hydrogen product [16, 46, 47] which leads to the number of unit operations (HTS, LTS, PrOX) in the production of hydrogen process except membrane separation.

The characteristics of these technologies are given in Table 4 [46]: Of the four technologies, membrane technology is the recent concept (see Fig. 3) in the production of hydrogen by steam reforming of ethanol and also, methane, having the greatest potential for hydrogen purification using membrane rather than CO purification steps (HTS, LTS, PrOX) which minimizes the capital investment. Catalysts for reforming and water-gas shift reactions could be incorporated into the membrane so that the reversible reforming/water-gas shift reactions shift to the right, favoring hydrogen production. This would enable the reforming and separation to be performed in one unit, reducing capital costs. Although the use of both inorganic (e.g., metal, ceramics) and organic (polymers) membranes has been investigated, much of current research focuses on metal and ceramic membrane technologies due to their ability to tolerate harsher conditions than organic membranes [46].

Table 4: Separation Technologies used in the production of H_2

Separation Technology	**Availability**	**Hydrogen Purity Achieved**
Pressure Suing Adsorption	Commercially available	up to 99.99%
Membrane Separation	Commercially available	up to 99.99%
Cryogenic Distillation	Commercially available	up to 95 %

Followings are some points which highlight the scope for the developments in the reforming system, 1) what are the pros and cons of fuel flexible reformers? 2) What are the impacts of bio-derived liquid feedstock impurities on pressure swing adsorption and hydrogen membranes? 3) What is the optimal Water-Gas-Shift technology for bioderived liquid reforming? 4) What are the gaps in catalyst development for bio-derived liquid reforming? 5) Are lower system efficiencies for aqueous phase reformers (compared to distributed natural gas reformers) acceptable given lower capital costs?

IV. POTENTIAL CATALYST USED FOR REFORMING OF BIOETHANOL

The use of catalysts plays a crucial role in hydrogen production through ethanol reforming. Rh and Ni are so far the best and the most commonly used catalysts for ethanol steam reforming towards hydrogen production. In terms of hydrogen production and long-term stability, MgO, ZnO, CeO_2, and La_2O_3 are suitable supports for Rh and Ni due to their basic characteristics, which favor ethanol dehydrogenation but inhibit dehydration. As Rh and Ni are inactive for water gas shift reaction (WGSR), the development of bimetallic catalysts, alloy catalysts, and double-bed reactors is promising to enhance hydrogen production and long-term catalyst stability.

The steam reforming of ethanol over Ni, Co, Ni/Cu and noble metals (Pd, Pt, Rh) has been extensively studied. The greatest concern lies in developing an active catalyst that inhibits coke formation and CO production [48]. The catalyst performance characteristics suggest strong metal-support interaction. The reaction pathway is complex and a number of undesirable side reactions occur thereby affecting the selectivity to H_2. Catalyst coking is mainly due to the formation of ethylene by ethanol dehydration. The performance of various catalyst reported in the literature is summarized in Table 5.

Table 5: Summary of different catalyst used for the steam reforming of bioethanol

Catalyst	**T (K)**	**EtOH Conv (%)**	**% Selectivity**				**Ref**
			H_2	**CO_2**	**CO**	**CH_4**	
0.06 NaCoZn	723	100	73.1	24.2	0.7	1.6	[49]
0.23 NaCoZn	723	100	73.7	24.9	0.1	1.2	[49]
0.78NaCoZn	673	100	74.2	25.0	-	0.9	[49]
0.98 NaCoZn	723	100	74.4	24.9	-	0.7	[49]
Co(N)/ZnOred	623	100	3.2	25.0	-	1.8	[50]
Co(CO)ZnO	723	100	72.6	25.0	-	2.4	[50]

Ni/Zr	973	100	75.0	18.0	5.5	1.5	[51]
Co/Zr	973	100	74.0	18.5	3.5	4.0	[51]
Cu/Zr	973	100	45.0	2.5	15.0	13.0	[51]
10Ni/ZnO	723	100	66.5	23.8	1.3	8.4	[52]
10Cu/ZnO	723	84.1	58.6	9.0	-	1.2	[52]
$Ce_2Zr_{1.5}Co_{0.5}O_8$-δ	713	100	70.0	24.0	4.0	2.0	[53]
Rh/SiO_2	873	100	70.0	15.0	5.0	5.0	[54]
Rh/CeO_2	668	100	38.8	62.3	8.2	29.5	[55]
Ni/CeO_2	668	100	29.7	56.0	4.9	39.0	[55]
$Ni-Rh/CeO_2$	668	100	34.5	55.0	8.6	33.5	[55]
$Cu/Ni/K/\gamma-Al_2O_3$	573	90					[56]

The focus of current research has shifted towards finding a transition metal alternative that can perform as well as the noble metal catalysts. Cavallaro and coworkers [57] developed a Co/MgO catalyst that showed comparable catalytic performance to Rh/Al_2O_3. It was determined that the acidic nature of the Al_2O_3 support caused an increase in coke formation on the Co/Al2O3 catalyst. Studies by Haga and coworkers [48, 58] examined cobalt catalysts on various supports. In contrast to the findings of Cavallaro, Haga determined that Co/Al_2O_3 had a greater activity and selectivity than Co/MgO in the steam reforming reaction.

Recently, Haryanto and coworkers [16] have reviewed steam reforming of ethanol, examined the various catalysts reported till date and presented a comparative analysis. They concluded that the ethanol conversion and H_2 production varies greatly with the reaction conditions, the type of catalyst and the method of catalyst preparation. The importance of process engineering related aspects is evident and these need to be discussed at length. This article is aimed at fulfilling this need. It reviews the available literature on catalytic steam reforming of ethanol. The role of the catalyst composition and the process conditions in determining product distribution is elucidated. The possible reaction pathways and the kinetic and thermodynamic considerations have also been discussed. The coupling of ethanol steam reforming with selective removal of CO_2 by chemisorptions to produce high-purity H_2 at low temperatures has been discussed. It is expected that this will provide an insight into steam reforming of ethanol.

Haga, Sahoo and coworkers [58, 59] studied the catalytic properties of Co among other metals and found that selectivity to H_2 was in the order Co > Ni > Rh > Pt, Ru, Cu. Metals alone may not assist hydrogen production significantly. So performance of metal catalysts could be improved using supports. The nature of the support also plays a key role in determining the selectivity to H_2. Choice of the support is hence crucial. Al_2O_3 is commonly used as a support in the steam reforming reaction. However, it is acidic and promotes dehydration of ethanol to ethylene, which in turn polymerizes to form coke on the catalyst surface. In contrast, MgO is basic. ZnO also has basic characteristics. CeO_2 is also basic and has redox properties [59, 60, 61].

Upon reviewing existing studies over the various reforming catalysts it is evident that the role of the support is influential in the overall performance of a reforming catalyst. Llorca and coworkers [62] investigated the performance of 1% cobalt reforming catalysts using various supports. MgO, g-Al_2O_3, SiO_2, TiO_2, V_2O_5, ZnO, La_2O_3, CeO_2, and SmO_2 prepared by impregnation. The catalysts were tested for the steam reforming of ethanol with water to ethanol ratio of 13 at a reaction temperature of 500°C and a gas hour space velocity of 5000 h^{-1}. The group determined that Co/ZnO was selective only for H_2 and CO_2 while the other oxygenated supports produced unwanted byproducts such as acetaldehyde and dimethyl ether [62, 50]. In a study by Aupretre [63] the influence of metal used as well as the role of the support was examined. The catalytic activity for the steam reforming catalysts increased with increasing hydroxyl mobility but decreased for catalysts that promoted the water gas shift reaction.

V. CHALLENGES FOR REFORMING AND SEPARATION

The ability of ethanol or bio-liquid (bioethanol) reforming to meet the demand for clean, cost-competitive renewable fuel will require advances in catalyst systems, purification technologies, and integration of these technologies into a single process. A multitude of catalyst systems have been investigated for the steam reforming of ethanol, bio-oil, sugar alcohols, and other bio-liquids. A common problem with the catalysts reviewed is deactivation due to coking which occurs when side reaction products (e.g., acetaldehyde, ethylene) deposit on the catalyst [64, 65, 66, 67]. To a certain degree, process parameters such as the steam-to-carbon (water-to-ethanol) ratio can be modified, again if it increased to limit the carbon deposits, the cost of greater process energy will require. The water-to-ethanol feed ratio and operating temperature also influences the selectivity to hydrogen. Water to ethanol molar ratios of three or greater, and temperatures above 500°C have been shown to favor the production of hydrogen over methane and other reaction intermediates [65, 67, 68]. However, higher water to ethanol ratios will require increased energy inputs.

Low-temperature (<500°C) reforming technologies are also under investigation. The advantages of low-temperature technologies are reduced energy intensity, compatibility with membrane separation, favorable conditions for water-gas shift reaction, and minimization of undesirable decomposition reactions typically encountered when carbohydrates are heated to high temperatures [2, 54]. Aqueous-phase reforming is a promising technology that has been applied to glucose, ethylene glycol, sorbitol, glycerol, and methanol. Studies have shown that the following factors promote selectivity to hydrogen rather than alkanes [65, 51] 1) Catalysts made of platinum, palladium, and nickel-tin (nickel catalysts favor alkane production). 2) More basic catalyst support materials (e.g., alumina). 3) Neutral and basic aqueous. 4) Feedstock type (in descending order of hydrogen selectivity) – polyols (selectivity decreases with increasing carbon number), glucose (selectivity decreases as weight % increases from 1 to 10).

Catalyst coking and deactivation are not significant problems as they are in steam reforming, but that may be the result of differences in feedstock reaction pathways. While hydrogen yields are highest from the aqueous phase reforming of sorbitol, glycerol, and ethylene glycol, glucose reforming which has low hydrogen yields may be more practical. Improvements in catalyst performance, reactor design, and reaction conditions may help increase hydrogen selectivity. Low-temperature gas phase reforming of ethanol is also being investigated, but there is a tradeoff between catalyst activity and resistance to deactivation (due to coking) and research is ongoing. Hydrogen purity is critical as the carbon monoxide (CO) must be less than 0.2 ppm to avoid fuel cell degradation [67]. Pressure swing adsorption (PSA), membrane separation, cryogenic distillation, or methanation can be used to lower the CO content of the hydrogen product. The characteristics of these technologies are as follows [10, 68]: PSA: commercially available, able to produce high-purity hydrogen (up to 99.99%); DOE-funded research has achieved the DOE 2005 target for hydrogen purification/separation efficiency of 82%.

VI. HYDROGEN ECONOMY

The transition of the use of hydrogen in industrial markets to a broader hydrogen economy would occur, if devices that use hydrogen (e.g., fuel cells) must compete successfully with devices that use competing fuels (e.g., hybrid propulsion systems). Equally important, hydrogen must compete successfully with electricity and secondary fuels (e.g., gasoline, diesel fuel, and methanol), at the same time to make the hydrogen commercial feasible, requires a market and a mechanically viable technology.

The world economy currently consumes about 42 million tons of hydrogen per year. About 60 percent of this becomes feedstock for ammonia production and subsequent use in fertilizer. Petroleum refining consumes another 23 percent, chiefly to remove sulfur and to upgrade the heavier fractions into more valuable products. Another 9 percent is used to manufacture methanol, and the remainder goes for chemical, metallurgical, and space purposes (Fig. 5). The United States produces about 9 million tons of hydrogen per year, 7.5 million tons of which are consumed at the place of manufacture. The remaining 1.5 million tons are considered “merchant” hydrogen. Followings are the key challenges to pave the way for commercialization of fuel cell and hydrogen infrastructure technologies:

6.1 Fuel Cell Cost and Durability

Fuel cells are efficient; they convert hydrogen and oxygen directly into electricity and water, with no combustion in the process. The resulting efficiency is between 50 and 60% about double that of an internal combustion engine [69].

Hydrogen-powered fuel cells are not only pollution free, but also can be more than two times more efficient than internal combustion technologies. A conventional combustion-based power plant typically generates electricity at efficiencies of 33 to 35 percent, while fuel cell systems can generate electricity at efficiencies of up to 60 percent (and even higher with cogeneration) [70]. The gasoline engine in a conventional car is less than 20% efficient in converting the chemical energy in gasoline into power that moves the vehicle in normal driving conditions. Hydrogen fuel cell vehicles, which use electric motors, are much more energy efficient and use 40-60 percent of the fuel's energy – corresponding to more than a 50% reduction in fuel consumption, compared to a conventional vehicle with a gasoline internal combustion engine. Long-term operation of the PEMFC has been proven, but mostly for fuel cells containing high loadings of noble metals, and under relatively ideal conditions. However, especially for automotive application, PEMFCs need to operate in a wide range of conditions, which may negatively affect durability and lifetime. The issues of cost and durability are closely related since reduction of cost is associated with the use of less or cheaper materials, e.g. reduction of Pt content or use of thinner perfluorinated, partially fluorinated or nonfluorinated membranes [71].

At present there are many uncertainties to the success of fuel cells and the development of a hydrogen economy: Fuel cells must obtain mass-market acceptance to succeed. This acceptance depends largely on price, reliability, longevity of fuel cells and the accessibility and cost of fuel. Compared to the price of present day alternatives e.g. diesel-engine generators and batteries, fuel cells are comparatively expensive. In order to be competitive, fuel cells need to be mass produced less expensive materials developed.

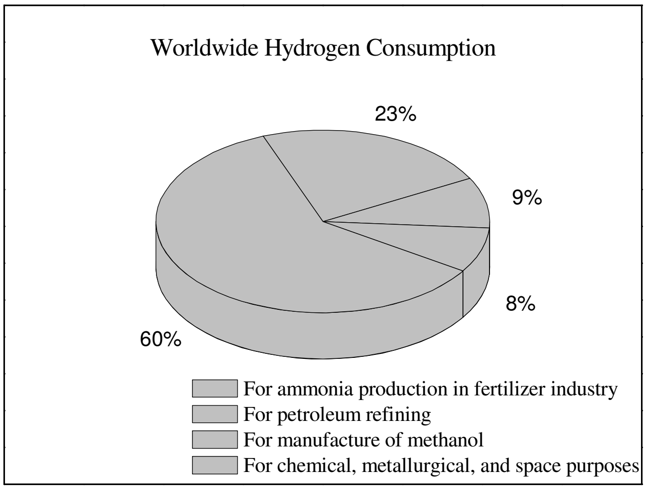

Fig. 5 Worldwide H_2 consumption in different industries

6.2 Hydrogen Storage

Today, hydrogen for transportation applications is compressed and stored in high-pressure metal and composite storage tanks. Hydrogen is also stored by cooling it to its liquid form and containing it in super-insu lated tanks. Table 6 shows the most probable (state of the art) H_2-storage methods today [72]. Hydrogen is a molecular gas. At room temperature and atmospheric pressure, 4 kg of hydrogen occupies a volume of 45 m^3. Comparative properties of hydrogen are given in Table 7.

Table 6: Physical and chemical properties of hydrogen, methane and petrol

Properties	**Hydrogen (H2)**	**Methane (CH4)**	**Petrol (–CH2–)**
Lower heating value (kWh kg–1)	33.33	13.9	12.4
Self-ignition temperature (7C)	585	540	228–501
Flame temperature (7C)	2,045	1875	2,200
Ignition limits in air (Vol %)	4–75	5.3–15	1.0–7.6
Minimal ignition energy (mW s)	0.02	0.29	0.24
Flame propagation in air (m s–1)	2.65	0.4	0.4

Diffusion coefficient in air (cm2 s–)	0.61	0.16	0.05
Toxicity	No	No	High

Table 7: State of the art technology and estimates for system volumes and weights for vehicular compressed gas, cryogenic liquid, and hydride storage of 3 kg H_2 [72]

Technology	Volume [liters]	Weight [kg]	Density [Wt. % H2]
35 MPa (350 bar) compressed H2	145	45	6.7
70 MPa (700 bar) compressed H2	100	50	6.0
Cryogenic liquid H2	90	40	7.5
Low-temperature metal hydride	55	215	1.4

High-pressure tanks can be used to store hydrogen, but present a considerable risk — the compression itself is the most dangerous and complicated part. In Japan such vessels are prohibited on the roads in ordinary cars [73]. The hydrogen storing pressure ranges for compressed tanks remain inadequate and the energy consumed to compress the hydrogen reduces the efficiency of this storage media. Current research on storage technology for hydrogen includes: Metal hydride technology, Chemical hydride slurries or solutions and Carbon nanotubes. The principal challenges to improving hydrogen storage technologies relate to increasing their efficiency, size, weight, capacity and, ultimately, their cost. The cost of on-board hydrogen storage systems is currently too high, particularly in comparison with conventional storage systems for petroleum fuels. Low-cost materials and components for hydrogen storage systems are needed, as well as low-cost, high-volume manufacturing methods.

6.3 Hydrogen Delivery

Hydrogen is currently transported by pipeline or by road via cylinders, tube trailers, and cryogenic tankers, with a small amount shipped by rail or barge. Due to the energy intensive nature and the cost associated with hydrogen distribution via high-pressure cylinders and tube trailers, this method of distribution has a range limited to approximately 200 km. For longer distances of up to 1,600 km, hydrogen is usually transported as a liquid in super-insulated, cryogenic, over-the-road tankers, railcars, or barges, and then vaporized for use at the customer site [74]. This is also an energy intensive and costly process. Therefore, breakthroughs are necessary in material science to reduce the cost of transporting hydrogen over long distances. Two fundamental questions are how much energy is required to extract hydrogen from naturally occurring, stable hydrogen-rich compounds and whether hydrogen should be produced at large-scale central locations that will require the development of a dedicated infrastructure to store and transport it to end use destinations. Both of these questions demand close evaluation of the related social, economic, and environmental costs and benefits associated with developing a hydrogen production and transportation infrastructure.

6.4 Public Acceptance

The hydrogen economy will be a revolutionary change from the world we know today. Education of the general public, training personnel in the handling and maintenance of hydrogen system components, adoption of codes and standards, and development of certified procedures and training manuals for fuel cells and safety will foster hydrogen's acceptance as a fuel.

VII. CONCLUSION

The major benefit of demonstrating the processes for H_2 production from a renewable energy source (biomass) is the high overall efficiency and zero emissions to the environment. Fundamental advances in catalysis, membranes, and gas separation could enable more efficient, lower-cost hydrogen technologies. The processes that combine hydrogen generation and separation in a single reactor (for example, membrane reactors for methane steam reforming) could improve conversion efficiency and reduce the initial cost of production of hydrogen by steam reforming of ethanol or bio-derived liquids. The overall challenge to hydrogen production is the cost reduction and storage safety. In order to succeed in the commercial marketplace hydrogen must be comparable to conventional fuels and technologies on a per-mile basis.

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