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Membrane Reactor Based Hydrogen Separation from Biomass Gas – A Review of Technical Advancements and Prospects

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Abstract

The world is bound to make a gradual shift from a hydrocarbon economy towards a hydrogen economy. This shift is being facilitated by the technological development in hydrogen energy that is occurring around the world. Gasification of biomass for generating biomass synthesis gas is a promising source for the distributed power generation concept as it is based on the local raw material supply. This concept has to be augmented by hydrogen fuel cell technology for modular, efficient and environmentally benign implementation. This provides the platform for looking at the option of separating hydrogen from biomass synthesis gas which is composed of H₂, N₂, CO, CO₂, CH₄, Tar, alkali traces and particulate matter at varying compositions depending on the biomass and operating conditions. This paper makes a critical review of the attempts made to reform and separate hydrogen through a hydrogen permeable membrane reformer reactor as it provides the energy efficient route. The feasibility and various membranes from palladium to ceramic membranes used in the reactor configurations and the engineering problems of the reactor will be analyzed. The inherent problems in providing a one shot modular solution for solving the problem will be discussed in the paper.

KEYWORDS: biomass gasification, hydrogen separation reactor, hydrogen enrichment and separation, process integration

1. INTRODUCTION

The hydrogen based economy envisages energy security for all countries in the world owing to the availability of local resources for Hydrogen production which include natural gas, petroleum residues, coal, water, biomass and organic wastes etc. The technological advancements in the areas of efficient, economic and environmentally benign hydrogen production, safe storage and transportation of Hydrogen and infrastructure development for Hydrogen distribution are happening around the globe due to the alarming raise in energy demand coupled with declining fossil fuel resources. The advantage of hydrogen as an energy carrier lies in its high energy / unit mass (1 kg of H₂ has approximately the energy content of 2.7 kg gasoline) which facilitates energy portability and it is a non polluting fuel (Evenson). The developments in the fuel cell industry is opening up the possibility of hydrogen energy utilization in distributed power generation and transportation sector apart from the enormous requirement in the petrochemical industrial segment. Hence the race to develop technologies for hydrogen production from a variety of feed stocks is on.

Among the various technologies under consideration for large scale hydrogen production, reforming of Natural gas, water splitting, gasification of coal and biomass are considered more feasible. The production of Hydrogen from Natural gas is a commercial process which is in operation and not much improvement in technology is expected in this process. This process involves Steam Methane Reforming (SMR) followed by Water Gas Shift Reaction (WGSR) and energy efficiency of 89 percent can be achieved if steam byproduct is also used. Even though the cost of hydrogen production is competitive with gasoline; the environmental price is high considering the fact that it releases 11.8 kg of CO₂ per kg of Hydrogen produced which requires CO₂ sequestration (Evenson). Water splitting to generate Hydrogen has been in the research stage for a long time and still suitable low cost technology is yet to emerge. The above facets provide the space for gasification technology to be used for synthesis gas production which in turn can be converted to any specific application.

Gasification is the process that converts solid or liquid hydrocarbon feedstock's, often of lesser market value than premium gas or liquid fuels into a synthesis gas that is suitable for either electricity production or manufacture of chemicals, Hydrogen production or transportation fuels. It is the only technology that provides both product and feed stock flexibility since all carbonaceous materials can be gasified after preparation. Coal and petroleum residuals are the dominant feedstock's together accounting for over 70% of the current synthesis gas capacity followed by natural gas which accounts for another 20% (Stiegel, 2001). With the coal reserves to production ratio of over 200 years, coal gasification is seen as a more promising technology for large scale power sector (Brinkman). Coal gasification is slightly expensive than SMR, but the economy of scale coupled with the current pace of research in the catalysis, gas cleaning and CO₂ sequestration and Combined Heat Power (CHP) Cycle is bound to reduce the overall cost of the process.

But considering sustainability, in the long term hydrogen must be produced from renewable energy sources. The hydrogen production from biomass via gasification is expected to be competitive with coal gasification and has a similar efficiency. The environmental advantage will take over considering the fact that if biomass is grown sustainably in conjunction with the utilization of agricultural and forestry residues together with organic waste disposal, the life cycle carbon emission is relatively low for biomass gasification. It is estimated that less than 2 kg of carbon per GJ is released to the atmosphere during the life cycle of hydrogen production. If CO₂ sequestration is added to the system, it could lead to negative CO₂ emission of around 18 kg/GJ (Brinkman).

In the distributed small community power generation and distribution sector, biomass gasification based power generation is bound to play a major role. It is difficult for the developing countries to cater to the needs of rural and remote location electrification considering the Transmission and Distribution losses associated with the grid based power system. If small capacity modular systems that can generate power based on locally available raw materials are developed, it can go a long way in providing electricity for all people. For this to happen, the high end technologies of biomass gasification, hot gas cleaning technologies, hydrogen enrichment, hydrogen separation and fuel cell technologies should be brought together with process integration and intensification at an economical scale. The process intensification of hydrogen enrichment and separation can be carried out in a membrane reactor.

A membrane reactor is one in which both the reaction and product separation can be achieved in a same vessel. The advantage of membrane reactor in the water gas shift reaction is that, the reaction is equilibrium controlled and hence continuous removal of hydrogen will shift the reaction towards more hydrogen formation. Basically the membrane reactor consists of two parts; the space inside the reactor where the reaction occurs and the

wall of the reactor made of product selective membrane which permeates the product. The application of the membrane reactor in the hydrogen production process from biomass gasification synthesis gas can reduce the number of steps in the process. This process intensification step can reduce the capital cost of the process.

This paper takes a look at the current possibility of small scale modular power generator through the biomass gasification route. The recent developments in the area of biomass gas reforming and purification for hydrogen production to suit fuel cell application will be reviewed with specific reference to the Membrane reactor and its engineering problems.

2. BIOMASS GASIFICATION PROCESS FOR HYDROGEN GENERATION

Biomass gasification offers the combination of flexibility, efficiency and environmental acceptability for small power generation systems. The synthesis gas produced from biomass gasification is currently used to generate heat, liquid fuels synthesis by Fisher Tropsch process, chemicals and hydrogen generation. This paper will concentrate on hydrogen as an end product which is capable of feeding fuel cells for small power generating systems. The process followed depends on the end use and hence is difficult to generalize. Stevens (2001) lists the following as basic requirements for any synthesis gas for use in fuel cell/ chemicals/ hydrogen production and are reproduced below.

- The dilution of the product gas should be avoided as much as possible to avoid increase in volume due to nitrogen
- Pressurized systems are preferable to avoid the cost of compression
- Particulate loadings should be less than 0.02 mg/Nm^3
- Tar loading should be less than 0.1 mg/Nm^3
- Sulphur levels should be less than 0.1 mg/Nm^3
- Hydrocarbons must be low to prevent dilution and to reduce catalyst poisoning
- Methane should be less than 3% or reforming of methane will be required
- Olefin should be less than 4 mg/Nm^3
- Ethylene should be less than 0.1 mg/Nm^3
- The ratio of Hydrogen to Carbon mono oxide should be appropriate

The required composition of gas for the fuel cell industry is not standardized as the fuel composition limits are not available in the open literature. The low temperature Proton Exchange Membrane (PEM) Fuel cell can work with a Hydrogen purity $>99.99\%$ with the $\text{CO} < 0.2 \text{ ppm}$ (Uemiya, 2004). Hence present PEM fuel cells cannot be used with the biomass gas due to its composition. The Solid Oxide Fuel Cell seems to be a better candidate considering the fact that it can withstand the impurities of NH_3 , CH_4 , CO and CO_2 with $\text{H}_2\text{S} < 1 \text{ ppm}$ (Aravind et al., 2005). Latest literatures indicate, it can even use the carbon containing compounds as fuels. But care must be taken to reduce carbon as it may lead to carbon deposition on the anode of the fuel cell.

2.1 Process Flow Diagram

The process flow diagram for hydrogen rich gas to be produced from the biomass is as given in **Fig. 1** The biomass is prepared and fed to the gasifier from which the syngas coming out is reformed for tar removal, scrubbed with water for particulate and impurities removal and removal of sulphur. This clean gas is compressed and subjected to steam reforming followed by two stage Water Gas Shift reaction after a stage. This hydrogen enriched gas then undergoes Pressure Swing Adsorption (PSA) from which pure hydrogen is produced.

As per present literature, no commercial biomass based process for Hydrogen production is currently available. Suresh P. Babu reports based on his analysis the following gasifiers viz., BIOSYN gasification process, FERCO Silvagas process, MTCI process, RENUGAS process, Fast Internal Circulation Fluidized Bed process and CHEMREC process could be used for hydrogen production

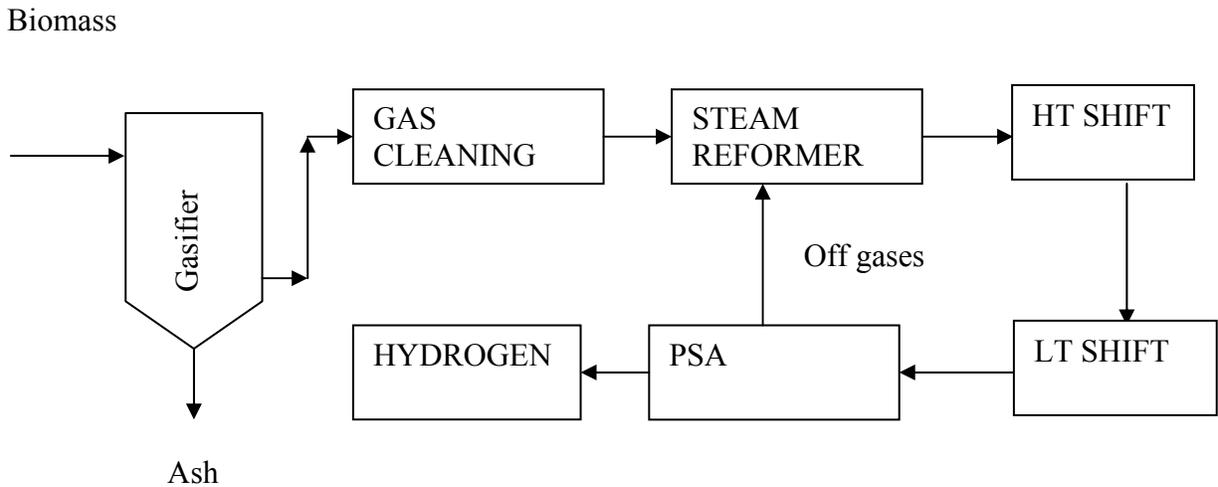


Figure 1 Schematic Process Flow Diagram for H₂ production from Biomass

2.2 Hydrogen Enrichment in the Gasifier

A variety of Biomass can be fed to the gasifier and the moisture content, ash content, volatile compounds and particle size affect the gas composition. The biomass type cannot be considered as a variable since the gasification can use only locally available raw materials. The type of gasifier also has a profound effect on the Hydrogen composition of the gas. Basically there are two types of gasifiers in commercial operation namely; Fixed Bed Gasifier and Fluidized Bed Gasifier. Among the updraft, downdraft and cross flow types of fixed bed gasifiers, the downdraft gasifier is better suited for stationary small power generation owing to low capital cost, low operating cost, low tar content, low particulate and low Nitrogen content as it is not air blown. Generally, the fixed bed gasifier generate low calorific value (4 – 6 MJ/Nm³) gas with typical gas composition of 40 – 50 % N₂ (lower for downdraft), 15 – 20 % H₂, 10 – 15 % CO, 10 – 15 % CO₂ and 3 – 5 % CH₄ with a tar and particulate loading of 0.1 – 0.2 g/Nm³ (downdraft) (Peter McKendry, 2002, Stevens D J, 2001). But the problem encountered in the downdraft gasifier is the requirement of gas cleaning and the Hydrogen enrichment for which we have to compress the gas at the hot condition to provide the pressure differential. On the other hand, Fluidized bed gasifiers are better suited for large scale operation as they operate at higher pressures and produces particulates (2 – 20 g/Nm³), Tar (1 – 15 g/Nm³), N₂, S compounds and alkali compounds [Peter McKendry (2002), Jong et al. (2003), Stevens (2001)] which needs special Hot gas cleaning techniques. They can be steam and oxygen / air blown to fluidize the biomass and provide medium calorific value (12 – 18 MJ/Nm³) or low calorific value gas. The experiment by Turn et al. (1998) on a bench scale fluidized bed has obtained a H₂ yield potential of 128 g H₂/Kg of dry ash free biomass at 850 °C with a steam to biomass ratio of 1.7 and got 78 % of the theoretical yield. The literature is replete with investigations on tar removal and this gives an impetus to the pressurized fluidized bed technology to be used in H₂ enriched gas production.

The literature reports about usage of catalysts and other additives to modify the composition of biomass gas. The catalytic activity of Dolomite, alkali carbonates and metals enrich the gas formation by reforming the tar and char. Sutton et al., (2001) made a review of the catalysts used in gasification. Calcined Dolomite addition to biomass has shown an increase of 4 – 7 % H₂ volume percentage along with increase in heating value and better tar conversion (Lv et al., 2004). The effect of Rh/CeO₂/SiO₂ catalyst was studied by Asaduallah et al. (2002) in a Fluidized Bed Reactor, and the results indicated 99 % Carbon conversion and low char and no tar formation. The

study by Caballero et al., (1997) using commercial catalysts in gasification yielded an increase of H_2 content by 4 – 14 % volume dry basis, CO by 1 – 8 % volume dry basis and gas yield by 0.1 – 0.4 m^3/Kg . It decreased the CO_2 content by 0 – 14 % and CH_4 by 87 – 99 %. Chen et al. (2003) suggests a 30 % by weight of catalyst loading of Cr_2O_3 along with rice straw and saw dust as feedstock. Devi et al., (2003) has also made a review of the primary measures on tar removal. Dayton (2002) suggests commercial Ni catalysts as having high activity for tar destruction, methane and hydrocarbon reforming and some WGSR inside the gasifier. Among these catalysts calcined dolomite is considered the economical option.

Stevens (2001) has provided a good review of the hot gas cleaning techniques. Boerrigter et al. (2004) used sintered metal candles as filters and operated at 350 – 400 $^{\circ}C$ for particulate removal which overcomes the problem of ceramic filter breakage.

3.0 PROCESS INTENSIFICATION

From the point of view of a modular system, the steam reformer, two stage WGSR and the H_2 separation units shown as separate stages in **Figure 1** needs to be integrated into a single reactor leading to application of process intensification of steam reforming and WGSR simultaneously happening inside the reactor and the produced hydrogen is continuously tapped out of reactor as shown in **Figure 2**.

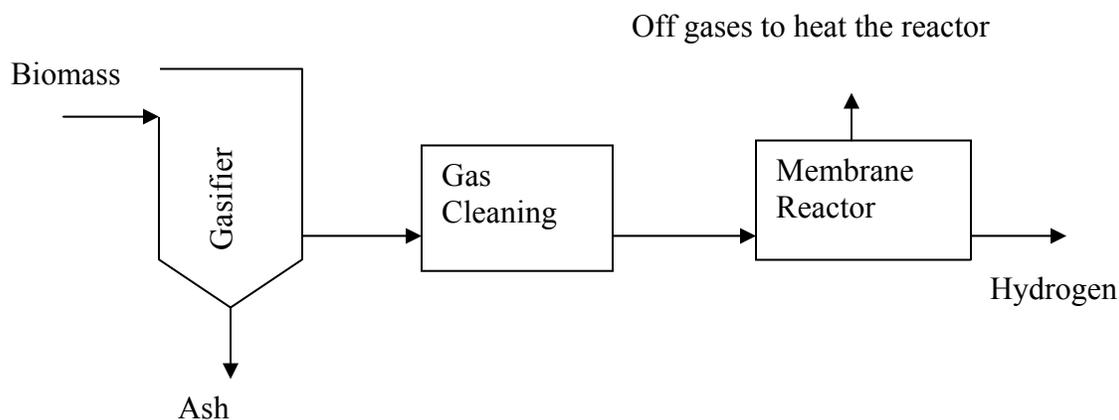


Figure 2 Schematic Flow Diagram of Hydrogen Production Process incorporating Membrane Reactor

This reactor provides two gas streams, one hydrogen rich stream that goes for the fuel cell application and another stream with CO_2 and H_2O which is either sequestered or emitted to the atmosphere after heat recovery. The continuous tapping of hydrogen from the reactor will favour continuous hydrogen production and hence higher equilibrium yield is obtained.

But no commercial reactor is available that can perform the above task. Hence a need exists to carry out research with individual components and operating conditions of biomass syngas and draw parallels with the steam reforming of methane, coal gasification and model based predictions in the following sections.

3.1 Membrane reactors

A membrane reactor is a process intensification technology in which, the wall of the reactor is replaced with a selective permeable membrane. This selective permeable membrane transports the product component from the

reactor to the exit stream and this approach is widely demonstrated to improve the conversion of equilibrium controlled reactions. Since WGS is a reversible equilibrium controlled reaction and its equilibrium constant decreases with temperature, membrane reactors can be used for this operation (Enick). The literature search will lead to considerable quantities of research on membrane reactors for steam reforming of natural gas for hydrogen production and other hydrogenation reactions. To look into the possibility of membrane reactor for our case, we start by analyzing the various hydrogen permeable membranes available.

3.2 Hydrogen Selective Membranes

High H_2 flux, robustness, low cost and high selectivity are the desired characters of these hydrogen selective membranes for hydrogen separation (Ciocco et al.). The high operating temperature and pressure of the reactors favour the use of inorganic membranes to organic membranes. *Bishoff and Judkins* compared the use of porous inorganic membranes, microporous membranes and palladium membranes for high temperature hydrogen separation and reported the following observations. The pore size of porous membrane should be less than 1 nm. The microporous membranes have hydrogen flux proportional to pressure and hence preferred from operational point of view, but produces impure H_2 . For palladium membranes, the flux is proportional to square root of Pressure.

Among the metal membranes, Palladium and Palladium alloys have been studied in detail for H_2 permeability. The high cost of Palladium, the difficulty in fabrication of defect free membrane film in micron range, long term stability at temperatures greater than 450 °C, deactivation by carbon, warping and embrittlement of pure Palladium and sulphur contamination are the problems reported to compound the commercial application of Palladium membranes. Paglieri and Way (2002) has made a good analysis on the basic theory, application, fabrication and future research areas for Palladium membranes. Morreale et al. (2003) calculated the permeability of H_2 in bulk Palladium at temperatures of 623 – 1173 K and pressure of 0.1×10^6 Pa to 2.76×10^6 Pa with the H_2 partial pressure exponent value restricted to 0.5. The permeability is given by an Arrhenius type relation where the pre exponential constant and activation energy for the correlation were 1.92×10^{-7} mol/m S Pa^{0.5} and 13.81 KJ/mol respectively. Thin films of Palladium are made by rolling, flush evaporation, sputtering, CVD, electroplating and electroless plating. The film thickness can be reduced to 50 μ m by cold rolling, 2 – 3 μ m by electroless plating and 1 μ m by CVD (Uemiya, 2004). Criscuoli et al. (2000) has predicted that a membrane thickness of 20 μ m will be commercially competitive.

Rolled Palladium over silver as tube material, have been studied by Tosti et al. (2000) and Hou and Huges (2003). Pd-Cu foils of 25 – 1000 micron thickness are commercially available and Enick subjected them to temperature range of 300 – 900 °C and pressure of 14.7 psi to 400 psi which could withstand H_2S concentration of 1000 ppm. H_2 separation of 20 μ m Pd coated on 5 μ m porous stainless steel was 17 times greater than bulk Pd membrane of 1 mm thick and 10 times greater than Pd coated Ta membrane (Ciocco et al.). Uemiya (2004) has also used Pd on stainless steel porous support and obtained good results. As it stands, the Pd coated on stainless steel can act as a good hydrogen permeable membrane. The cost of manufacture may get down with bulk manufacture.

The other materials on study for hydrogen permeation membranes are Zirconia by Kusakabe et al. (2005), Proton conducting Perovskite type oxide by Iwahara et al. (2004), Silica membrane inside macroporous alumina types by Rouessac et al. (2003), inconel 600 by Bustamante (2004), and porous stainless steel supported silica membrane by Brunetti et al (2006). Gopalakrishnan et al. (2006) has reported the fabrication of a multitube membrane module with H_2 selectivity greater than 2000.

An interesting observation by Bustamante is that inconel 600 itself catalyses the forward WGS. The advantage of such a system will eliminate the need of a separate catalyst and hence the reaction can be wall catalyzed. The studies by Brunetti, Basile have shown a CO conversion exceeding 96.8%, good permeability and higher conversions than equilibrium values using membrane reactors. The major drawback with most of the studies is that, pure individual streams are used in permeability and selectivity measurements and not as gas mixtures as required in a biomass syngas. The actual permeability and selectivity needs to be evaluated at the operating condition for the gas mixtures. Uemiya has reported that the hydrogen permeance decreases due to the coexistence of CO, unsaturated hydrocarbons or steam in the feed stream. These interactions with the membranes also need to be analyzed in detail. A look at the membranes for the process intensification step suggests that the membranes made

by Pd coated on stainless steel, Pd/Cu alloy and ceramic on stainless steel are probable candidates for the membrane reactors.

3.3 Catalysts for WGSR

Considering the gas compositions, the WGSR is more prominent than the reforming reaction due to the low hydrocarbon content in the gas and in this aspect the biomass gas varies from the synthesis gas composition from natural gas and coal gasification. It is also relatively free from sulphur. Traditionally the high temperature shift is catalyzed by the iron oxide – chromium oxide catalyst and the low temperature shift by the zinc oxide – copper oxide catalyst and these catalysts are commercially available (Hamelinck and Faaij, 2001). Giessler et al. (2003) used $\text{Cu/ZnO/Al}_2\text{O}_3$ catalyst in a molecular sieve silica membrane packed reactor and obtained 99 % CO conversion for $\text{H}_2\text{O} / \text{CO}$ molar ratio of 1 at 280 °C. Uemiya (2004) used Ni based catalyst and obtained 99.9 % purity of H_2 with Pd membrane on stainless steel support using town gas. Experiments by Enick and Bustamante (2004) have shown that in membrane reactor at high temperature and pressure, the intrinsic reaction rate may be great enough to eliminate the need for heterogeneous catalytic particles because the mass transfer of H_2 through membrane could become the rate limiting step. Hence packed catalytic bed reactors are to be used for low temperature operation and the high temperature operations can be conducted without catalysts.

3.4 Reactor Configuration and Operating Variables

Due to the non availability of biomass gas to H_2 converting membrane reactor in experimental or commercial operation, we look at the possible aspects of the reactor configurations and operating variables either modelled or experimentally available using artificial operating conditions. Traditional reactor configuration is the double tube packed bed configuration similar to the steam reforming reactor. The packing of catalyst can be either in the annular space or inside the smaller tube. If the gas outlet is at a higher pressure, the packing inside the smaller tube will be preferred. For the low pressure gas which involves a sweep gas or vacuum application, the packing in annular space is better. Barbieri^b (2006) has shown that the equilibrium of WGSR depends on the temperature, retentate and permeate pressure, molar feed ratio and the sweep factor.

Saracco et al. (1999) has made an analysis of the potential problems associated with the membrane reactors and made a review of the developments in that area. Sjardin et al., modelled four configurations of membrane reactors viz., membrane reactor with sweep gas, membrane reactor without sweep gas, membrane reactor with sweep gas and integrated CO_2 capture and membrane reactor without sweep gas with cryogenic CO_2 separation using the process simulator AspenPlus. He has reported an 84 % overall efficiency without H_2 compression and 78 % with compression up to 482 bar. Ma and Lund (2003) using a two step microkinetic model for high temperature ferrochrome catalyzed WGSR on a membrane reactor reported that finding a perfect membrane reduces the reactor size by 12 % whereas eliminating the inhibitory effect of CO_2 would reduce the size of the reactor by 76 %. Marigliano et al. (2003) used a reactor in series model to evaluate the catalytic methane steam reforming and WGSR in a Pd membrane reactor and found positive variation with pressure on the reactor. Similar model based membrane reactor analysis have been reported by Amadeo and Laborde (1995), Basile et al. (2003) and Barbieri (2005).

Criscuoli^b et al. (2000) carried out the experimental analysis of WGSR in (i) a traditional fixed bed reactor, (ii) membrane reactor with mesoporous ceramic membrane and (iii) membrane reactor with palladium membrane using gas feed mixtures similar to coal gasification gas. They used three gas mixtures for the experiments namely mix I, mix II and mix III having varying compositions of CO, CO_2 , H_2 , N_2 and CH_4 . Among these the mix II with a composition of CO – 12.27%, CO_2 – 11.49%, H_2 – 75% and CH_4 1.24% on dry basis has the representation of all the components of the biomass syngas. At a time factor of $15.45 \times 10^3 \text{ g cat min (CO mol)}^{-1}$, the CO conversion in the Pd membrane reactor, mesoporous reactor and fixed bed reactor were 51.3%, 45% and 29.17% respectively. The results were better for the membrane with palladium reactor in all the three mixtures. Further research is also needed in the analysis of the reactor flow dynamics, reaction mechanism, permeation and its effect on the reaction and reactor operating conditions of a membrane reactor for biomass gas.

With the limited quantity of experimental results available it is hard to come to a conclusion on the suitability of the reactor configuration and its operating parameters. But based on the available literature the double

tube design with or without catalysts seem to be the better option. The theoretical analysis by Ma and Lund (2003) suggests a feed composition of H₂O to CO of 3:1 as optimum. Higher time factor, higher lumen pressure and sweep gas favour better performance of the membrane reactor. The choice of sweep gas is another area of concern.

With more research being carried out, these drawbacks on the membrane reactor for hydrogen separation from the biomass syngas will vanish and a commercial membrane reactor seems to be possible. For this, active catalysts at relatively low temperature, good system design and separation membranes are needed.

4. CONCLUSION

The current trends in the use of biomass to energy projects in the world are concentrated on large scale units. Small distributed modular fuel cell coupled biomass gasification systems have a huge market considering the requirement of distributed power supply in developing countries for rural and remote location electrification. The current research on gasification and fuel cells are proceeding in a faster rate. Among the various gasifiers, Downdraft gasifier is better suited for modular power generating system considering the size, ease of operation, maintenance and capital cost. The enrichment of hydrogen in the biomass syngas is essential to improve the overall efficiency of the system and should be the primary feedstock for fuel cell. This can be achieved by modifications in the gasification system and process integration of the gas treating technology. Calcined Dolomite addition in the gasifier improves the gas yield by the catalytic destruction of tar and char. A membrane reactor after the gas cleaning stage will reduce the reforming, shift reaction and hydrogen separation equipments and offers process intensification. A tubular reactor with packing of shift catalysts can be applied for low temperature operation. The membrane wall of the reactor can be made up of either Pd on stainless steel or Pd/Cu alloy or ceramic coated stainless steel. The choice of the membrane is more economical in nature as all these options provide good hydrogen permeability. When high temperature and pressure are involved the reaction can carry forward even without a catalyst. Since much information on the effect of the gas components on permeability is not known, more data in this area is awaited. Real time data on the performance using actual biomass syngas will provide more impetus to the above ideas. The commercialization of the membrane reactor along with good process integration will reduce the size of the biomass to hydrogen plant to such a level that the combination of gasification and solid oxide fuel cell will provide a modular power generating system for remote community power generation.

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