CATALYTIC REACTOR CONFIGURATIONS FOR HYDROGEN GENERATION AND INLINE FUEL CELL OPERATION

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Introduction - Processor Description. Utilization of improved reactors and reaction systems for hydrogen production and delivery in the fuel cell is of high importance for the optimized operation of the cell. Both low and high temperature fuel cells use hydrogen as fuel in anode to produce electricity via electrochemical molecular hydrogen oxidation or decomposition reactions. We have reported on improved catalytic permeators using inorganic membranes for in-situ hydrogen and hydrogen-carbon oxide mixtures separation and delivery in the cell [1-4]. We have examined methane steam reforming combined with water gas shift and paraffinic hydrocarbon dehydrogenation reactions from a kinetic, catalytic and process synthesis point of view [1-4]. Catalysis studies are underway to produce improved catalysts with minimal deactivation. Nickel based catalysts are our starting point due to their low cost and strong performance measures (constant activity on stream for variable feedstocks). The main reactions occurring in gas phase are [1-8]:

\[
\begin{align*}
\text{CH}_4 + \text{H}_2\text{O} &= \text{CO} + 3\text{H}_2 \\
\text{CO} + \text{H}_2\text{O} &= \text{CO}_2 + \text{H}_2
\end{align*}
\]

\[\Delta H^{\circ}_{298} = -206.1 \text{ kJ/mol} \text{ and } \Delta H^{\circ}_{298} = -41.15 \text{ kJ/mol},\]

Current work is on improved process and reactor configurations for hydrogen fuel delivery in the interconnected cell. Variable composition feedstocks rich in methane are considered. Current designs utilize improved permeative and catalytic materials with different properties for achieving final desired product composition, purity and throughput. The proposed systems are applied to produce hydrogen based fuel mixtures for continuous, reliable fuel-cells operation or direct hydrogen enhanced combustion. Specifically, this initial communication reports on single reactors, multifunctional reactors, and reaction-separation systems including systems of permeators and permeators -for hydrocarbon to hydrogen conversion. Exit hydrogen mixtures are used to continuously power fuel cells. Part of the product reformed gas can be used in consecutive chemical synthesis applications; as example part of a \text{H}_2, \text{CO}, \text{CO}_2 rich product is used for alternative methanol synthesis [1-4]. We present and analyze new processes for steam hydrocarbon reforming and water gas shift reactions including work in experimental design, operation, and best parameter selection and optimization of such systems for specific fuel cell applications. The proposed processes are of increased significance in the area of clean power generation with enhanced pollution minimization. This includes reduction in \text{CO}_2 emissions from hydrocarbon reforming plants via \text{CO}_2 conversion in consecutive synthesis or recycling routes; also reduction of NOx emissions due to clean power generation from the fuel cell. There are unique characteristics of the examined operational systems to perform multiple tasks; among others to utilize equilibrium shift principles in hydrocarbon conversion and hydrogen yield through the removal of selective permeative gases out of the conversion zone and utilization of byproduct gases as chemical synthesis blocks [1,2,3]. Similar multifunctional operational systems including permeators and permeators, or other operation type reactor-separator networks are suited for environmentally benign and energy efficient higher hydrocarbon reforming. Objective of similar studies is integrated process development for the fuel cell power industry, with increased processing capacity, efficacy, separation, and further utilization of primary and secondary hydrocarbon feedstocks and their produced byproducts. Reduction in carbon deposition propensity is an excess requirement for such reforming, especially in view of converting higher hydrocarbons into hydrogen rich exit mixtures. Nickel and nickel based catalysts enriched with earth type metals such as Ca, K, and La are again the starting research point for constant activity continuous operations. Advanced materials in microporous or dense phase can be used as activated structure hydrogen or hydrogen-carbon oxide receptors and transmitters in above operations to recover hydrogen and hydrogen-carbon oxide mixtures directly out of the reactor or from the post reacted exit streams. These include metals, ceramics, high temperature polymers, special types of carbon based and composite materials [1]. Dense type materials are better candidates than microporous ones. The rejected hydrocarbons and/or CO streams from the following membrane permeator or separator can be recycled into the inlet of the reformer/gas shift reactor for increasing the process efficiency via the utilization of the unreacted materials. Product mixtures of \text{H}_2 and \text{CO}_2 from the permeate stream can be used directly as anode feed gas into an adjacent molten carbonate fuel cell unit [4]. Similarly, separated product mixtures of \text{H}_2 and \text{CO} can be used directly as anode feed gas into an adjacent solid oxide fuel cell unit [1-4]. In several reactor-catalyst instances the main reactor operates at high enough conversions and produces hydrogen rich mixtures for direct use in the fuel cell, thereby eliminating the need for the downstream separator and associated costs.

Results and discussion. Related modeling of such multifunctional reactors and systems for the aforementioned applications is under way to describe their function, operational range, yield and capacity. The models used, simulate relevant acquired data and predict conditions for best multifunctional reactor and process operation by variation of key intrinsic parameters [1,3,5,7,9]. The proposed efficient reactor/processor systems configurations and their specific fuel cell-power generation applications seek to perform multiple unit operations within a single or integrated type module which makes them advanced in comparison with up to now proposed and utilized conventional and permeable type of reactors [1,2,5,9]. They project a promising advancing technology for primary and secondary hydrocarbon to hydrogen upgrading reactors for use in continuous (inline) fuel cell processes. The described positive technical aspects/effects are fortified in view of the environmental and economic benefits that these processes possess especially in connection with directly powering fuel cell stacks. In the Figures below we present some comparative modeling analysis of the described reforming processors for continuous fuel cell operation. Fig.1 shows the required methane feed rate in the reformer, for various types of fuel cells of constant 100kW output power and variable cell efficiencies for two types of reaction systems. A single reactor of 90% conversion with a single inlet and outlet, and a reactor-permeator cascade of 60% conversion with \text{CH}_4 and \text{CO} recycling in the feed are compared. Hydrogen is produced by the combined methane steam reforming and water gas shift reactions in both cases and assumed to be fed clean in the fuel cells. It is characteristic that an increase in fuel cell efficiency (such as use of a higher efficiency SOFC or MCFC

Fuel Chemistry Division Preprints 2002, 47(2), 665
cell) lowers the methane requirement in the reactor necessary for powering the consecutive fuel cell. Fig. 2 shows the total rate of hydrogen consumption by the fuel cell for various efficiency fuel cells. A double reaction scheme is considered in the feed reactor as in Fig. 1 which powers a constant 100 kW fuel cell by use of the produced hydrogen. It is characteristic that the hydrogen requirement for high temperature fuel cells is about half the one required for lower efficiency cells. Thus, use of a smaller reformer or lower methane flowrates are required for the high temperature fuel cells, which in turn results into smaller overall installation costs. Fig. 3 finally, plots the output power produced by a high temperature fuel cell (constant 60% efficiency) interconnected with the reformer for different reforming reaction and feed conditions. A jump from 500 to 700°C in reformer temperature increases by three fold the cell power output (kW) for all feed conditions.

Acknowledgements: DOE support for this project is gratefully acknowledged by the authors.