

# Development of an Efficient, Compact, and Environmentally Friendly Hydrocarbon Reformer for the Production of Pure Hydrogen

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## ABSTRACT

Hydrogen is one of the promising clean fuels for the future. Reforming hydrocarbons (e.g. natural gas, gasoline, diesel, etc.) represents the most promising route for the production of hydrogen because it yields the hydrogen from the hydrocarbon as well as from steam. The steam reforming of natural gas to produce hydrogen and/or synthesis gas (syngas) has been extensively used in the last few decades in a number of petrochemical and petroleum refining processes, such as ammonia production, methanol production, hydrogen production for hydro-treating, and hydro-cracking.

The classical process for steam reforming of natural gas uses very large multi-tube (few hundreds) fixed bed catalytic reformers with top or side-fired furnaces burning natural gas around the catalyst tubes to supply the heat necessary for the highly endothermic steam reforming reactions. The industrial steam reforming process, although the most economical and efficient process used in industry for the production of hydrogen and/or syngas, is quite inefficient and heavily polluting.

The process suffers from a number of intrinsic limitations, which suggests extensive, well-directed, multidisciplinary research in order to “break” these process limitations and develop a new generation of hydrocarbon reformers, which are more efficient, compact, and environmentally friendly compared with the present generation of steam reformers.

This paper presents a novel auto-thermal membrane Circulating Fluidized Bed (CFB) reformer, which is highly efficient and suitable for a wide range of raw materials including renewable materials such as bio-oil from biomass. This novel reformer does not need external heat and produces pure hydrogen directly from its hydrogen-selective membrane side of the reformer, and its hydrogen yield approaches the stoichiometric yield from any hydrocarbon used.

**Keywords:** circulating fluidized bed, hydrocarbon, hydrogen, steam reforming

## 1 HYDROGEN PRODUCTION

Hydrogen as a fuel is considered clean, but production of hydrogen, which is typically done by steam reforming of hydrocarbons is not clean [1]. When steam reforming a waste hydrocarbon, such as methane, both carbon monoxide and carbon dioxide are produced as byproducts. Therefore, when considering its life cycle, hydrogen is not a zero emission fuel. Producers also use electrolysis as an alternate process, but collecting hydrogen in this manner uses electric power, which has its limitations. US electricity comes primarily from coal or natural gas, which then produces carbon monoxide and carbon dioxide emissions. US electric power companies do utilize energy sources that do not have the carbon emissions, such as nuclear, hydropower, and solar. The life cycles of these and other alternative energy sources contain other problems and challenges, which are beyond the scope of this discussion. Also beyond the scope are associated difficulties with storage and transportation of the hydrogen and its byproducts.

## 2 REFORMER EVOLUTION

Steam reformers have been the most efficient means of capturing hydrogen and syngas from a methane feedstock. The primary system configuration used in industrial reforming features a fixed bed. This system, called a first-generation reformer (FGR) [1], requires highly endothermic reactions, and therefore, consists of large furnace that surrounds hundreds of catalyst tubes in parallel. An unwanted pressure drop along the reformer tubes is possible, so large nickel-based particles are used in the catalyst. However, the large catalyst pellet size causes intra-particle diffusion decreasing the process effectiveness factor to as low as  $10^{-2}$ - $10^{-3}$  [1]. This first-generation reformer design has other limitations that also decrease system efficiency and lead to over-sized equipment compensate. As the reform reactions are reversible, achieving thermodynamic equilibrium is severely limited so

that artificially elevated temperatures are needed to keep the conversion process viable. Also, as temperature increases so does carbon formation, which deactivates the catalyst. This deactivation, in turn, requires a higher steam-to-hydrocarbon ratio in order for the process to continue [2].

A second-generation steam reformer (SGR) uses a bubbling fluidized bed with a powdered catalyst, which helps overcome the limitation of diffusion with the larger catalyst pellets used in FGR design. The change in catalyst particle size yielded an improvement of the effectiveness factor between 100 and 1000 times [3]. Researchers added composite hydrogen permselective membranes to the SGR in order to overcome the barrier of thermodynamic equilibrium, thereby achieving higher conversion rates from the reform reactions even at relatively low temperatures [4]. Additional study including the building of a pilot plant followed by experimental analysis led to a fluidized-bed membrane reformer, which is efficient but is limited. The flow rate in the bubbling fluidized bed is restricted, and therefore, limits the full range of the catalyst effectiveness factor [5-7]. In addition, either SGR system design is less than optimal for higher hydrocarbons since it does not provide for handling the excessive carbon formation nor does it operate with a low steam-to-hydrocarbon ratio [2].

In order to include higher hydrocarbons, such as gasoline, diesel, and bio-oils, as feedstocks for hydrogen production, a third generation reformer (TGR) has been planned. The new system consists of a circulating fluidized bed with a catalyst regenerator. Permselective membranes are used for two purposes: palladium-based, hydrogen membranes are used to remove hydrogen, and perovskite, oxygen membranes are used to add oxygen for the riser portion of the reforming process. An exit separator in the riser reformer further removes hydrogen from solids and gases. The system achieves catalyst regeneration as excess carbon is burned and the catalyst is separated from gases in an external cyclone. Heat from the catalyst regeneration preheats the recycled catalyst and cold water to generate steam. The catalyst recovery/recycling subsystem supplies the needed heat for the endothermic steam reforming part of the process. When the heat generated by the catalyst recovery reaches the level of the heat consumed in the steam reforming, the system achieves auto-thermal reforming [8-0].

### 3 FUTURE CFB RESEARCH

Future research into an auto-thermal circulating fluidized bed steam reformer includes modeling, functional analysis, pilot plant construction, experimentation, and system analysis. The modeling and functional analysis include a series of objectives [11] as follows to assist in identifying the construction requirements for a pilot plant.

**Objective 1:** Develop a hydrodynamic model for this novel TGR describing the flow conditions (pressure, velocity and porosity distribution) in all parts of the system (reformer, generator, cyclone, circulation connections, etc). Understanding the gas-solid particle flow is critical to the development of the design and operating process parameters. Detailed hydrodynamic flow leads directly to the scale-up design of the system.

**Objective 2:** Use and compare various CFD (Computational Fluid Dynamics) software packages for simulating the hydrodynamics of the system and its subsystems. Controls of system conditions, including materials, velocities, and physical dimensions, and boundary conditions, including inlet velocities and volumes, vary with the program.

**Objective 3:** Use the model and the CFD software packages to obtain typical hydrodynamic results for the elements within each subsystem as well the synergy among its different subsystems and elements. Necessary measurements for final system functions include flow rates, circulation rates, pressure drops, and velocity gradients. Overall system efficiency depends greatly on the performances of the reformer and the regenerator.

**Objective 4:** Conduct a parametric study on the effect of different operating and design parameters on the hydrodynamic characteristics of the subsystems as well as the integrated system. Software analyses will be used to identify starting parameters based on expected performance measures.

**Objective 5:** Investigate the gas solid flow, separation, circulation and the most suitable control strategies. Various input parameters, including inlet gas velocity, inlet geometry, and particle size, have been tested with high efficiency performances for horizontal separators [12].

**Objective 6:** Investigate the hydrodynamic effect of the weight percent of solid material for CO<sub>2</sub> sequestration from a hydrodynamic point of view in order to couple it to the reaction engineering point of view. One means of achieving CO<sub>2</sub>-free combustion while using fossil fuels as the energy source has been experimented and analyzed. Capture of the carbon dioxide was achieved through separation and disposal [13].

**Objective 7:** Investigate the effect of the hydrogen selective membranes on the hydrodynamic characteristics of the riser reformer. The eventual design of the CFB system includes hydrogen selective membranes.

**Objective 8:** Investigate the influence of the hydrodynamic characteristics on the behavior of the CFB auto-thermal membrane reformer (TGR). Compile the CFD results into useable parameters for the planned pilot plant.

**Objective 9:** The primary goal of this research is to provide the computational analysis results for the planned pilot plant project. Additionally, the results will be disseminated to various audiences.

## 4 SUMMARY

This planned research will lead to significant progress in the areas of alternative fuels, hybrid reaction-separation systems, fluid dynamics of gas/solid catalytic systems in complex configurations, pollution prevention, and sustainability. The CFB is highly flexible and may be used to process a wide range of feedstocks including: natural gas, gasoline, diesel, and renewable feeds such as bio-oils. This fundamental approach integrates system components.

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