Production of Hydrogen from Various Feedstock Options Using Non-thermal Plasma Catalyzed Reforming

Lyman Frost, Joseph Hartvigsen, Elango Elangovan

Ceramatec, Inc., Salt Lake City, UT 84119
lfrost@ceramatec.com jjh@ceramatec.com elango@ceramatec.com

ABSTRACT

Ceramatec has developed a method for reformation of various hydrocarbons using a non-thermal plasma system to catalyze the reformation process. The plasma provides the same type of catalytic activity as a solid catalyst but since the plasma is constantly renewed it is not sensitive to sulfur or various other contaminants that adversely affect traditional solid catalysts. The reformer can operate in a partial oxidation or steam reforming mode but these modes are usually combined in an autothermal process. Any hydrocarbon that can be vaporized can be reformed with the system. The reformer can operate with air, oxygen enriched air, or pure oxygen as an oxidant. The reformer has been deployed in the field in sizes as large as 1 MMSCF per day of natural gas.

Keywords: Reforming, plasma reforming; logistic fuel reforming, synthesis gas, hydrogen

INTRODUCTION

In an era of carbon constrained energy generation hydrogen is a very attractive fuel since its combustion generates only water. Unfortunately, hydrogen does not exist to any large extent in nature. Rather, it is found combined with other elements such as oxygen (e.g. H_2O and H_2O_2) and carbon (i.e. numerous hydrocarbon compounds like methane, petroleum gases, gasoline, diesel, solvents, etc.). At the present time, H_2 is largely generated from fossil fuels without carbon capture and storage. The US DOE reported that slightly over 50 million metric tons of H_2 were produced in 2014. Production was from natural gas (48%), refinery / chemical off-gas (30%), coal gasification (18%), and electrolysis (4%). Most of the hydrogen was produced in large steam methane reforming (SMR) plants designed for the specific purpose of H_2 production.

The economies of scale currently favor these large plants. There are a number of small scale processes such as partial oxidation, catalytic partial oxidation, and autothermal (combination of partial oxidation and steam reforming) that can be used to reform a variety of hydrocarbons. Unfortunately, reforming of these hydrocarbons with systems that contain catalysts has proven difficult due to adverse effects from the high aromatics content and deeply-bound sulfur on catalyst activity.

In partial oxidation, catalytic partial oxidation (CPOX), and autothermal reforming (ATR) processes, a sub-stoichiometric amount of air is combined with the fuel, and the mixture is burned (either with or without a catalyst) to generate synthesis gas used to fuel the fuel cell. Conventional partial oxidation processes have been plagued with soot and carbon deposition issues. The thermal mass of the catalyst in the case of CPOX or ATR operation, the hydrogen required in a hydro-desulfurization system, and the operational difficulties associated with the partial oxidation process make each of these processes difficult to use for small scale synthesis gas production.

Ceramatec has been developing a process based on non-thermal plasma catalyzed reforming that solves many of the above problems. This approach uses a low-amperage, high-voltage plasma arc to catalyze the reforming of the heavy hydrocarbons. The energy needed to complete the reformation process can be introduced by burning a portion of the fuel or by heat integration with the rest of the system. In contrast to surface energy activated reforming reactions of a solid catalyst, the non-thermal plasma creates radicals that promote the reforming process. Unlike the solid catalyst, the non-thermal plasma approach is not sensitive to sulfur since it is constantly renewed with each plasma arc generated. Likewise, without the solid catalyst bed there is no thermal mass that must be heated to temperature and thus start-up time is substantially reduced. The unit may be started in a partial oxidation mode and then switched to steam reforming as temperatures sufficient to produce steam are reached. This provides substantial flexibility in operations by going from exothermic to endothermic operations dependent only on control algorithms and the mode that makes the most sense at a point in time. The system is flexible, sulfur tolerant, and consumes a minimum of the energy value of the synthesis gas produced. The system does need some electrical energy to produce the plasma (i.e. ~ 1-3% of the energy in the input fuel). The reformer does not eliminate the sulfur from the synthesis gas but as stated it is not sensitive to sulfur and converts bound organic sulfur to hydrogen sulfide.

TECHNOLOGY

Ceramatec has developed an innovative, integrated process that retains the thermodynamic advantages of steam reforming and combines it with the robust, highly energetic reaction zone characteristic of partial oxidation. The laboratory-scale reformer in Figure 1 is compact, with an internal volume of 0.6 L and a reformation capacity of 5 kWt fuel rate. The plasma reformer generates a highly active, non-thermal plasma source of non-equilibrium electric discharges that act as an activation source for reforming reactions.

The device has at least two diverging knife-shaped electrodes along which multiple electric discharges glide. The progress of an electric discharge and plasma zone formation is shown in Figure 1 (right). Just prior to the narrowest point between the electrodes, the separate gas streams (steam – air / oxygen; steam – feedstock) are combined and enter the area between the electrodes. A high-voltage, single- or poly-phase discharge is generated at the closest point between the electrodes and is forced along the diverging electrodes by the gas flow. At some point the dielectric reaches a point where the resistance is too high and the arc extinguishes. Another discharge immediately forms at the initial spot and the process is repeated. This formation and extinguishing occurs on a millisecond basis. The geometry of the electrodes, flow conditions, and characteristics of the power supply determine the path of the arc. The electrodes do not need to be cooled since the arc is never in one location for any substantial period of time. The voltage can be as high as 20,000 volts but the current is only a few milliamps. Any gas or liquid that can be vaporized can be reformed.

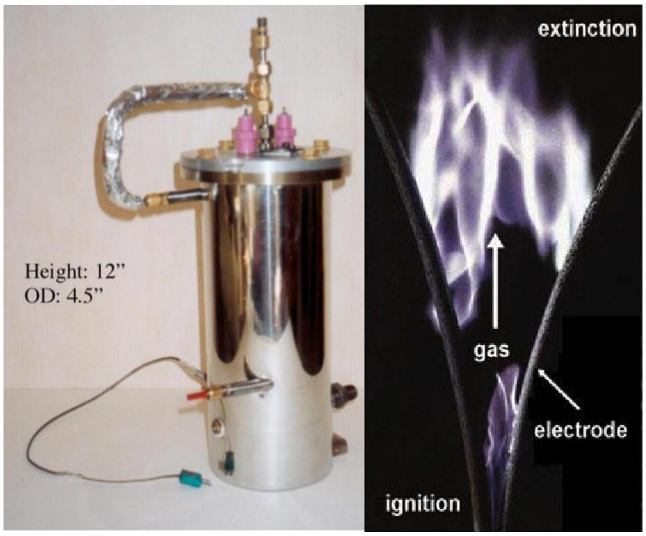

Figure 1: 5-kWt reformer (left); Plasma zone (right)

The reformer can be fabricated in a variety of orientations and sizes. Figure 2 shows a reformer that was built for TARDEC (US Army Tank Automotive Research and Development Engineering Command) that is in the shape of an "M". The plasma electrodes are in the central shaft and the outside of the "M" provides the exit for the synthesis gas. This was used to reform JP8 and provide the resultant synthesis gas to a 10 kWe solid oxide fuel cell.

Figure 2: Plasma reformer for 10 kWe SOFC

A multi-stage reformer was built to reform residual tars and oils generated by a biomass gasifier. The system was mounted at the exit of a 10 ton per day gasifier with the objective of conducting in-situ reforming of the generated tars and oils while they were still in a gaseous state. Figure 3 shows this multi-stage unit as it was being readied for installation and installed with the gasifier.

Figure 3: Reformer for biomass gasifier residuals

The reformer typically uses air and steam as the oxidants but has also successfully used pure oxygen in place of air. Under a recent testing program, a reformer was designed that used an external vaporizer to vaporize condensed paint booth hydrocarbons and successfully reform those hydrocarbons using oxygen. Figure 4 shows that unit as designed and as constructed. The unit is ~8' high and 20" in diameter including insulation.

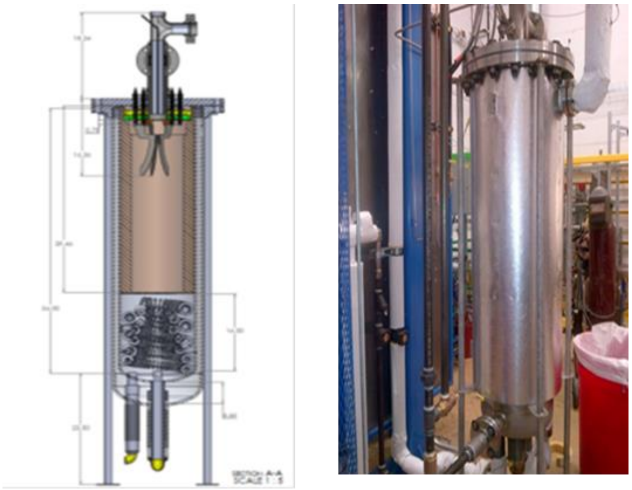

Figure 4: Reformer for mixed hydrocarbons

This same unit has been used to provide synthesis gas from natural gas for a Fischer Tropsch system. It reforms ~ 20 MSCFD of natural gas operating at atmospheric pressure. A similar unit built to operate at 50 psig would be capable of reforming ~ 100 MSCFD of natural gas.

The largest units built to date were built for an ammonia plant in Peru. These units were built to operate at 50 psig and use enriched air (41% O_2) with steam as the oxidant. After removal of the CO_2, the ratio of N_2 to H_2 is precisely the correct ratio needed for the Haber Bosch ammonia reactors. Five units were mounted on a common manifold and each unit was capable of reforming ~1 MMSCFD of wet (i.e. contains some NGL with energy content of ~1250 BTU/SCF) natural gas. Each unit is ~15' high and 5' in diameter. Figure 5 shows the 5 units mounted on the manifold. The input connections are not shown.

Figure 5: 1 MMSCFD reformers for NH_3 plant

The low electrical use is demonstrated by the fact that each of these reformers uses less than 4 kW to generate the plasma used for the reformation. The unit in Figure 4 uses slightly over 1 kW. The laboratory unit shown in Figure 1 is the smallest unit that has been built and it uses about 90 W. The rest of the energy needed for the reformation comes from the burning of part of the input hydrocarbon feed (i.e. auto-thermal reforming).

The reformer has been used to reform natural gas, gasoline, anaerobic digester gas, low sulfur diesel, JP8, NATO F76, glycerol, and mixed hydrocarbons. Figure 6 shows the results of reforming JP8 in both partial oxidation and steam reforming modes. The JP8 had a refinery analysis with a total sulfur content of 430 ppmw and an aromatic content of 15.3 % by volume. Air (POX mode) and air / steam (steam reforming) were used as the oxidants. There was only about 1.5 volume % of methane in the output from the reformer and negligible higher hydrocarbons.

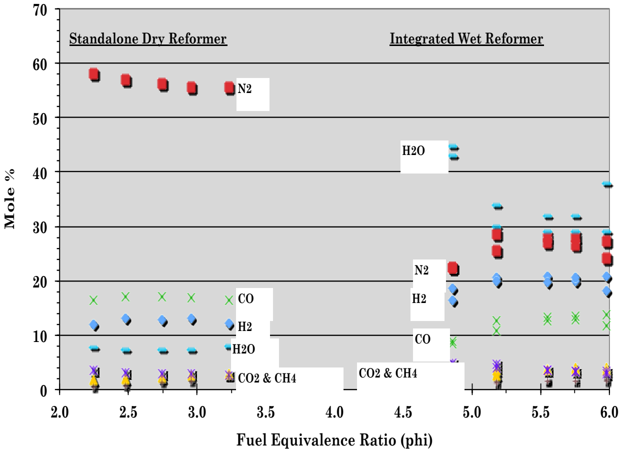

Figure 6: POX and steam reforming of JP8

The heating value of the JP-8 reformate in a partial oxidation mode is about ~73% of theoretical while the value in steam reforming mode is ~ 92% of theoretical. The higher percentage of hydrogen in steam reforming mode is from part of the oxygen for the reforming being supplied by the steam and thus hydrogen is generated.

The reforming of residual tars and oils from biomass gasification was tested using air and steam as the oxidant. The tests were done with a mixture of heavy hydrocarbons including toluene, benzene, and xylene. Residual toluene was used as the indicator of successful reformation. The reformer was operated with a variety of conditions and the results analyzed. Figure 7 shows a compilation of all the tests. The figure provides the thermal efficiency by comparing the LHV (lower heating value) of the gas coming from the gasifier to the LHV of the gas after passing through the reformer. It also shows the amount of BTX that is destroyed based on analysis. Test number 4 was selected as the best option and this was used during the field operation of the reformer with the biomass gasification unit. A gas analysis for the selected conditions is shown in Figure 8.

	LHV Gas In	LHV Gas Out	Thermal Eff	BTX
Run	kW	kW	Percent	% Destroyed
2	6.37	6.37	100	87
3	6.28	6.88	110	92
4	5.02	5.87	117	98
5	5.02	5.78	115	92
6	5.02	5.05	101	81
7	5.02	5.41	108	94
8	5.02	4.51	90	99
9	5.02	4.11	82	98
10	6.28	4.82	77	97
11	7.53	5.15	68	95
12	6.28	5.11	81	90
13	6.28	5.84	93	92
14	5.65	5.07	90	95
15	5.02	4.26	85	99

Figure 7: LHV of gas before / after BTX reforming

			Mole %	Output			
Run	H_2	N_2	CO	CO_2	BTX	CH_4	H_20
4	12	54	21	7	0	.3	6

Figure 8: Gas analysis for selected conditions (mole %)

The plasma reformer is routinely used to generate synthesis gas for a Fischer Tropsch reactor at Ceramatec. It is operated with a mixture of air and steam as the oxidant and pipeline natural gas as the input hydrocarbon. The steam is adjusted to generate a ratio of H_2 to CO of about 2.1 moles of H_2 for each CO mole. The reformer is operated at an internal operating temperature of 850 - 900° C with a steam to carbon ratio of ~1.5 – 2. An analysis of the output gas stream by gas chromatograph typically shows < .1 % CH_4 and negligible higher hydrocarbons. Figure 9 shows the rationale for the selected conditions plotting extent of reformation versus temperature and steam to carbon ratio.

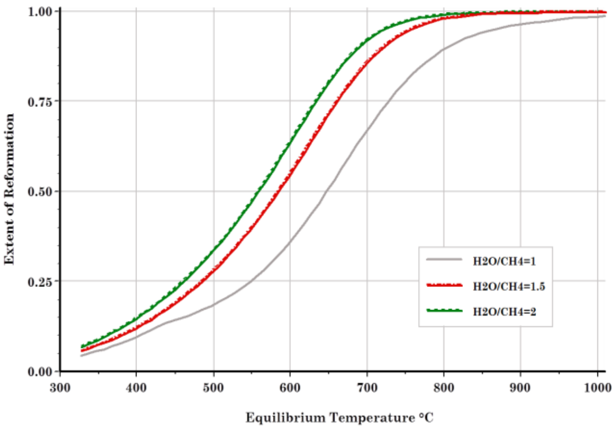

Figure 9: Extent of reformation by temperature

As can be seen, the extent of reformation approaches 100% at the selected conditions of steam to carbon of 1.5 – 2 and temperatures in excess of 850° C.

SUMMARY

Ceramatec has developed a modular reformer that can be used in a variety of formats and to reform a variety of hydrocarbon inputs. The reformer uses non-thermal plasma in place of solid catalysts and to catalyze the reforming of the hydrocarbons. The reformer can operate in either partial oxidation, steam reforming, or autothermal mode. It has been successfully demonstrated and deployed with either air, air – oxygen mixtures (enriched air), or pure oxygen as an input oxidant.

The reformer has been successfully used to reform a variety of hydrocarbons from natural gas through mixtures of complex hydrocarbons such as solvents and benzene – toluene – xylene (BTX). The reformer can be built in a variety of sizes from small laboratory sized units (~ 400 SCFD of natural gas) to commercial units (~ 1 MMSCFD of high BTU natural gas) that can be joined on a common manifold to provide large amounts of hydrogen or synthesis gas. The reformer can handle wet (i.e. contains some C_2 – C_5 content) natural gas without a pre-reformer. The reformer is reasonably simple to operate and has significant cost advantages over other reformers in the small to medium capacity range. Since there is no catalyst to heat, the reformer is able to start-up relatively quickly (i.e. ~ 30 minutes under typical environmental conditions).

This reforming approach is not applicable to very large hydrogen or synthesis gas plants since the 1 MMSCFD size seems close to the maximum that is currently practical. Very large plants that produce at ≥ 100 MMSCFD are too large for this technology at this point in its development. Likewise the technology is not applicable to solid fuels that cannot be converted to a gaseous stream.

ACKNOWLEDGEMENTS

Portions of the work described above were supported by the Office of Naval Research, the United States Army, the United States Department of Energy, and the State of Wyoming. A significant portion of the work was also supported by various private entities.