

Compact Multi-Fuel Autothermal Reforming Catalytic Reactor for H₂ Production

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Distributed hydrogen production to feed fuel cells needs compact and versatile reforming system: ATR reaction assures compactness and process self-sustainability. The aim of this work is to realize and test a thermally integrated catalytic reactor able to realize the ATR of gaseous and liquid hydrocarbons. Heat recovery from reaction products for pre-heating of reactants allows to feed reactants at room temperature. Preliminary experimental results performed with the integrated multi-fuel reactor showed that the system is very fast to reach the steady conditions, with a very high thermal exchange efficiency, and a good approach to the equilibrium gas phase composition at the reactor outlet in terms of adiabatic temperature, hydrocarbon conversion and hydrogen production.

1. Introduction

Hydrogen fed fuel cells seem to be the most viable way to simultaneously produce energy and reduce the environmental pollution. Due to the difficulty of hydrogen transport and storage, distributed generation becomes the ideal solution, and consequentially small size production systems are required. From this point of view, autothermal reforming is the most appropriate technique for hydrogen production, due to its self-sustainable nature, as well as high reaction rate and system compactness (Ciambelli et al., 2009). In addition, the use of a liquid fuel may assure a further plant compactness, due to its higher energy density. In the literature several liquid hydrocarbons are used as fuel for autothermal reforming, among the others dodecane was considered a good substitute of commercial diesel (Gould et al., 2007).

Due to different characteristics of liquid and gaseous fuels it's very difficult to realize a multi-fuel processor. In particular, great effort was devoted to the design of the delivery system for liquid hydrocarbons, in order to obtain a quick vaporization, an uniform reactants mixture, avoiding hydrocarbon cracking reactions (Kang et al., 2007). Inlet reactants temperature is also an important parameter for ATR reaction: higher inlet temperature assures higher conversion (Roychoudhury et al., 2006).

2. Reaction system sizing

Reaction system is realized by integrating two stages: a reaction stage, in which the ATR reaction take place, and a heat exchange module, in which reactants are pre-heated by the sensible heat of the gas stream exiting the reactor. System was feed with liquid

water, air and fuel (methane or dodecane) at room temperature. Water, air and methane are pre-heated before entering the reaction module; dodecane is delivered at room temperature in liquid state, through a specifically designed high pressure injection system. In order to size reaction system for produce 4 Nm³/h of H₂, it's assumed to feed methane, water and air to the system with feed ratio H₂O/O₂/C = 0.49/0.56/1 and space velocity GHSV of 70000 h⁻¹ (Ciambelli et al., 2010). Assuming that feed temperature is 300 °C, by software GasEq, the equilibrium products concentration and the adiabatic temperature are calculated (Table 1).

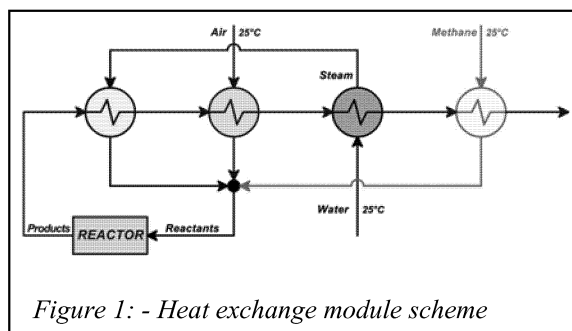
Table 1 – Calculated molar and volumetric rate at the reactor inlet and outlet.

	CH ₄	H ₂ O	O ₂	N ₂	H ₂	CO	CO ₂	C(s)	Total T (°C)
IN (mol)	1.00	1.20	0.60	2.11	-	-	-	-	300
IN (Nm ³ /h)	1.98	0.97	1.11	4.17	-	-	-	-	8.24
OUT (mol)	0.03	0.41	-	2.11	2.02	0.74	0.23	-	704
OUT (Nm ³ /h)	0.06	0.81	-	4.17	4.00	1.46	0.46	-	10.97

Since is GHSV = 70000 h⁻¹, catalyst volume was calculated by the formula (1):

$$V_{Cat} = \frac{Q_{IN}}{GHSV} = \frac{8.24 \text{ Nm}^3/\text{h}}{70000 \text{ h}^{-1}} = 1.18 \cdot 10^{-4} \text{ m}^3 = 119 \text{ cm}^3 \quad (1)$$

Heat recovery from product gas is achieved through a series of heat exchangers, formed by rectangular coils, realized by stainless tubes (o.d. 1/8", thickness 0.74 mm), and mounted in parallel way. Special manifolds, with rectangular section, allow to distribute current flux in all coils, assuring pressure drops lower than series-way installation. All heat exchangers inside module are placed transversely to the reactor stream: in this way we have a kind of tube-shell heat exchanger, where products flow through shell-side, and reactants flow through tube-side. In order to obtain an optimal heat transfer, water vaporization is realized in 2 stages: in the first one liquid water is vaporized, in the second one steam is overheated. The exchangers were disposed according to the diagram in Figure 1: such disposition assures a more uniform ΔT along heat exchange module, and prevents coke formation due to overheating of methane.



In order to obtain a regular inside geometry of heat exchange module, exchangers are realized according to dimensions in Table 2. Since air flow is very higher than water and methane ones, a different exchanger configuration assures lower pressure drops, maintaining the same geometry.

Table 2: Heat exchange module dimensions

	Steam	Air	Liquid water	Methane
Coils	5	9	10	5
Tube per coils	9	5	9	9
Surface (m ²)	0.032	0.032	0.065	0.032

3. Experimental setup

A scheme of the multi-fuel autothermal catalytic reformer is presented in Figure 2. Since the system was performed for a multifuel use, were provided two fuel feed lines, one for liquid hydrocarbons and one for gas.

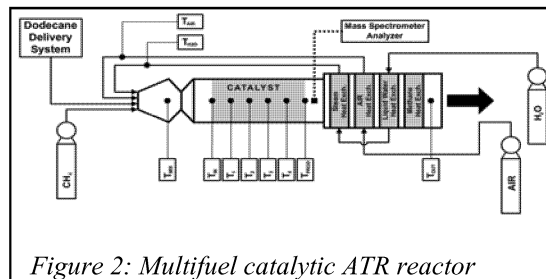


Figure 2: Multifuel catalytic ATR reactor

Ultra-pure air and methane was fed through Brooks mass flow controllers, while bi-distilled water was stocked in a 10 atm pressurized vessel, and fed by a Quantim (Brooks) mass flow controller for liquid. Particular attention was focused on dodecane

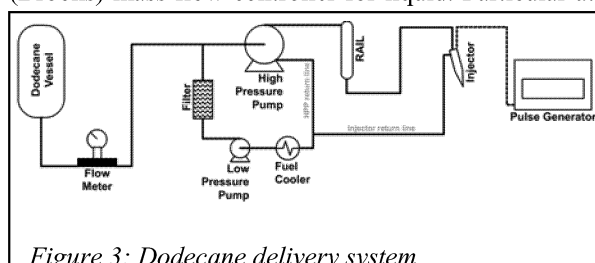


Figure 3: Dodecane delivery system

feed system. In order to obtain a very quick vaporization, good mixing with other reactants avoiding cracking reactions, it was adopted an high pressure alternate spray feed system, based on the concept of the “common rail injection system”. In Figure 3 a schematic diagram of liquid fuel delivery system is reported. A radialjet high-pressure pump (BOSCH mod. CR/CP1S3/R55/10-1S) maintains the fuel at about 1000 atm inside a rail to quench pressure fluctuations. The rail supplies fuel to an electro-injector which provides the dodecane into mixing chamber. The amount of supplied fuel is controlled by width and frequency of valve openings, driven by a specifically designed PWM circuit (GISA elettronica). The high-pressure injection of dodecane assures the atomization in very small droplets of about 20 microns, which vaporize instantly.

Dodecane is stocked in a vessel at 4 atm to provide fuel in high pressure circuit. In vessel line, a Coriolis-based mass flow controller (Brooks) is placed for measuring dodecane consumption during system operation. A rotary low pressure pump was placed for assure an appropriate flow in high pressure pump circuit.

Reaction system may be divided in three main components: mixing module, catalytic reaction module and heat exchange module. Each module is secured to the next one through a special flange, to allow quick reactor disassembly for maintenance.

The mixing module was designed with a special shape to improve the reactants mixing. Gaseous reactants were delivered in a cylindrical pre-mixing zone. After an initial mixing, the reagents are sent to the mixing chamber, in which electro-injector nozzle

was placed. Due to its double-cone shape, the mixing chamber produces an expansion followed by a sudden constriction, creating turbulences that ensure a perfect mixing of reagents. A subsequent expansion has the dual purpose of improving the mixing of reagents and to standardize the current along the whole section.

After mixing, the reactant mixture enters in the reaction module, that is made of AISI 310 stainless steel, rectangular shaped of 6 x 8 cm. Inside module the honeycomb catalyst (provided by BASF) is placed as 5 bricks sized up to 6 x 8 x 1 and at 5 mm of distance between them. Such module configuration promises great system versatility, allowing a quick catalyst replacement, continuous reaction stream mixing, and assures an easier process control along catalytic bed, as explained below.

The reaction is triggered by a pair of plugs, electrically heated up to a temperature close to 300°C. Immediately downstream the reaction module is directly attached an heat exchange module, designed as previously explained. After the heat exchange, preheated reagents are sent to the mixing module by external pipes.

Before and after each catalytic block, there is a sampling probe and a “K” thermocouple for the gas analysis and temperature monitoring to determine the product distribution and the temperature profile along the catalytic bed. In addition, by means of a series of thermocouples, the temperature of stream incoming in mixing module, in mixing chamber and after heat exchange module was monitored. Concentration analysis is achieved by a mass spectrometer (Hiden HPR20).

4. Results and discussion

In order to evaluate the effectiveness of the integrated system, we employed the thermal efficiency of reaction η , Equation (2), where n_{H_2} is moles of hydrogen produced per 1 mole of feed (methane or dodecane) and LHV is lower heating value of H_2 or fuel.

$$\eta = \frac{n_{H_2} \cdot LHV_{H_2}}{LHV_{feed}} \quad (2)$$

Experiments were conducted varying H_2O/C molar feed ratio between 0.49 and 1.09, and space velocity GHSV between 7000 and 80000 h^{-1} . Initially methane was used as hydrocarbons; after about 3 h fed hydrocarbon is switched to dodecane, without shut-down an start-up procedure. Experiments results are reported below:

Table 3 - Test results

Time (min)	GHSV	O ₂ /C	H ₂ O/C	H ₂	CO ₂	CH ₄	X-CH ₄	η	T_IN	T1	T2	T3	T4	T_PROD	T_AIR	T_H ₂ O	T_MIX	T_OUT
	25000	0.56	0.49	32.7	6.8	5.1	0.77	0.46	236	692	657	663	643	592	222	135	122	83
40	50000	0.56	0.49	36.5	5.3	2.6	0.87	0.54	400	790	732	718	712	674	397	417	297	283
110	70000	0.56	0.49	36.8	5.0	2.2	0.89	0.54	406	809	747	733	730	693	426	468	325	316
146	75000	0.56	0.79	37.7	6.4	2.2	0.89	0.57	407	807	744	730	726	688	420	496	338	268
159	80000	0.56	1.08	38.2	7.5	2.2	0.89	0.58	403	802	743	727	721	658	405	505	345	203
187	65000	0.56	1.09	32.3	7.2	0.5		0.57	670	861	805	791	787	744	429	542	360	198

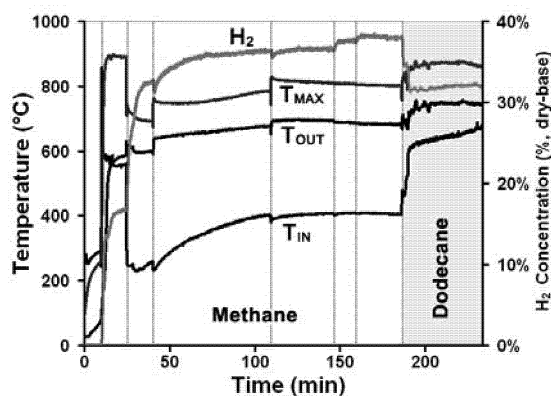


Figure 4 - Catalyst temperature and hydrogen production during catalytic test

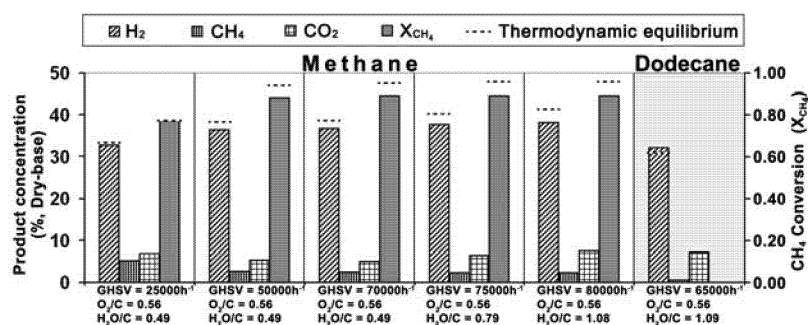


Figure 5: Product concentrations, methane conversion and comparison with thermodynamic equilibrium values at different operation conditions

As shown in Figure 4, system is easy to start-up: in less than 10 min, reactor reaches its thermal regime; in start-up phase there is an hydrogen production up to 16.6%. By switching in ATR condition ($H_2O/O_2/C = 0.49/0.56/1$), H_2 production is very higher, with a lower temperature in the catalytic bed. At every operating condition the reactor quickly reaches the steady state, particularly at higher space velocity.

By increasing the GHSV a rise of temperature along bed reactor is observed: this may be due to higher heat transfer efficiency in heat exchanger, and a reduction of heat dispersion along the system. Temperature increase leads to higher CH_4 conversion and H_2 production; however along whole test H_2 production and CH_4 conversion are very close to the equilibrium values.

At higher H_2O/C ratio, we have a slight increase of H_2 production: on the one hand, increase of CO_2 denotes the progress of WGS reaction, on the other, temperature decrease leads to a lower CH_4 conversion.

Figure 4 and Figure 5 show that by switching fuel feed from CH_4 to $C_{12}H_{26}$, we have a slight decrease of H_2 concentration, and sensible decrease of CH_4 , in agreement with the

thermodynamic equilibrium. Due to the fuel change there is a temperature raise of about 100 °C along the catalytic bed. It's very interesting to note (Table 3) that switching from CH₄ to C₁₂H₂₆, thermal efficiency was almost unchanged, and reaches a value of 0.57%, practically in full agreement with the thermodynamic calculation.

Catalyst temperature profile is contained in a range of about 150 °C during the whole test, indicating that also in terms of temperature profile the reactor work very well, limiting the typical effect of large temperature gradient along the catalytic bed.

5. Conclusions

A multi-fuel and thermally integrated autothermal catalytic reformer was designed to produce up to 4 Nm³/h of H₂ from gaseous (methane) and liquid (dodecane) hydrocarbons. An high pressure liquid delivery system was designed to obtain the optimal mixing of dodecane with other reactants. Preliminary test results show a quick start-up of catalytic system, and a fast response to feed variation. Heat exchange system coupled to reaction module allows to feed reactants at room temperature, avoiding any other external heat source, and assures product stream cooling to a WGS temperature. For both fuel a conversion degree and hydrogen production close to the thermodynamic equilibrium value is obtained. Steam-to-carbon variation produces slight effects, otherwise space velocity reduce thermal dispersions along system.

6. Acknowledgements

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