HYDROGEN PRODUCTION FROM ETHANOL PARTIAL OXIDATION IN A POROUS MEDIA REACTOR: STATE OF THE ART AND DEVELOPMENT OF AN EXPERIMENTAL APPARATUS

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Abstract. *Here, we present a review of the state of the art of the ethanol partial oxidation to produce hydrogen in catalytic and inert porous media reactors and describe the development of an experimental set up capable of testing porous media reactors fed with ethanol. Most studies in partial oxidation of ethanol over catalytic surfaces have been performed using catalytic diferential reactors, foccusing on the understanding of reaction paths and activity of catalysts. Noble metals such as Pd, Pt and Rh over metal oxide supports have been mostly used due to their higher activity and selectivity to hydrogen. Such reactors are free of any heat and mass difusion limitations. However, reactors designed to small scale applications are frequently limited by the heat and mass transfer to the catalytic sites and such applications require the use of strategies that intensify heat and mass transfer. In order to be able to reduce transport resistance, decrease response time and reactor production/mass ratio, we have designed and built an experimental apparatus to test porous media reactors in laboratory scale with accurate measurements of temperatures and concentration of gas phase chemical species. Such results will be used to validate numerical models, allowing the optimization of transport properties and chemical kinetic parameters in small scale fast response time reactors.*

Keywords*: Hydrogen, ethanol, partial oxidation, porous media.*

1. INTRODUCTION

The use of renewable primary energy sources, such as ethanol from biomass, allows the development of sustainable energy chains in countries, like Brazil, that have soil, climate, technology and tradition linked to large scale agriculture (Gosselink, 2002; Norberg-Bohn, 2000). Ethanol can be used as fuel in conventional combustion processes, such as internal combustion engines and liquid burners, or used as a source for chemical processes and hydrogen for fuel cells. Fuel cells represent an efficient use of renewable energy sources for the production of electrical power in decentralized and isolated systems as well as for the mobility sector. These are electrochemical devices that convert internal energy of chemical bond in electric power in an efficient, noiseless and with low emissions to the environment. We note that the mobility sector contributes with over 1/3 of the total amount of CO_2 produced worldly (Cacciola et al., 2001). The use of fuel cell and hybrid engines may be decisive in the reduction of pollution from vehicles in urban areas. The increase in the use of environmentally friendly fuels, besides policy driven measures (Clark II et al., 2002), must rely on the continuous development of efficient energy conversion devices. These devices most of the time must be scalable from portable to residence (or vehicle) sizes. The scalability relies on the development and application of strategies that allow for intensification of heat and mass transfer as well as chemical reaction rates (Holladay et al., 2002; TeGrotenhuis et al., 2002; Whyatt et al., 2002). As an example of such systems are the compact fuel cell modules for automotive and compact generation systems. Research has focused on the development of low weight systems with power ranging from 100 mW, as in the direct methanol fuel cells to replace lithium-ion batteries, to 50 kW for automotive applications. Recently a 1.6 W fuel cell was developed for mobile phones, working with a methanol consumption of 0.21 ml for 2 hours of conversation. The user that recharges his phone at each 2 days would take 50 days to recharge his methanol fueled phone with a 50 ml cartridge reservoir (Cacciola et al., 2001). In automotive applications, both directly fueled fuel cells and indirectly fueled fuel cells are being developed. Among the former are the direct methanol fuel cells (DMFC). The later, are the fuel cells that work with hydrogen that has been obtained from a primary fuel reforming system, such as the proton exchange membrane fuel cells (PEMFC). A comparative analysis has shown that, with the current technology, the indirectly fueled fuel cells are a 25% more efficient energy conversion device than an internal combustion engine developing the same power and are still more efficient than the directly fueled fuel cells (Klouz et al., 2002).

Here, the production of hydrogen rich gas from ethanol in inert and catalytic reactors is reviewed. Catalytic reactors have been used for a long time in automotive gas pollutant converters and as burners in combustion chambers (Arai e Fukuzawa, 1995; Barresi et al., 1992; Yoshizawa et al., 1988; Pfefferle e Pfefferle, 1986; Markatou et al., 1993; Maruko et al., 1995; Masel, 1996; Mohamad et al, 1994; Neyestanaki e Lindfors, 1994; Kaplan e Hall, 1995; Howell et al., 1996; Oliveira e Kaviany, 1997; Oliveira e Kaviany, 2001; Acevedo e Oliveira, 2006a, 2006b). The main difficulties in the design of such systems has been to achieve the necessary surface area for complete fuel catalytic conversion, minimum heat and mass transfer resistances, the needed residence time for the load of the reactor, higher selectivity and low production of poisonous or pollutant chemical species, high stability, high durability, low weight, low volume/mass ratio, low cost and potential for recycling. From these requirements, this work focuses on selectivity towards hydrogen production, combustion stability and reduction of transport resistances. This article reports an ongoing work.

2. HYDROGEN PRODUTION FROM ETHANOL PARTIAL OXIDATION

Hydrogen is produced industrially mostly by steam reforming and partial oxidation of hydrocarbon rich fuels, by coal gasification or from water electrolysis. Its worldwide production is around 500 billion Nm^3 per year (Momirlan and Veziroglu, 2005). A large number of chemical plants use hydrogen combined with carbon monoxide as a primary feedstock, which includes ammonia and methanol manufacturing, oil refining and production of gas-to-liquid fuels in Fisher-Tropsh synthesis. In general, the production of hydrogen from oxygenated hydrocarbons occurs by some combination of steam reforming and partial oxidation reactions. These reactions, for a one mol of ethanol basis, can be represented globally as

$$C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 6H_2 \text{ , } \Delta H^{\circ}_{298} = 347.4\, kJ/mol \tag{1}$$

$$C_2H_5OH + 1.8H_2O + 0.6O_2 \rightarrow 2CO_2 + 4.8H_2 \text{ , } \Delta H_{298} = 4.4\, kJ/mol \tag{2}$$

$$C_2H_5OH + 1.5O_2 \rightarrow 2CO_2 + 3H_2 \text{ , } \Delta H^{\circ}_{298} = -554.0\, kJ/mol \tag{3}$$

Reaction (1) is a simple steam reforming reaction, reaction (3) is a partial oxidation reaction and reaction (2) is a combination of both, named an auto-thermal reaction. These reactions occur simultaneously with the water-gas shift reaction, which combines CO and H_2O to produce H_2 and CO_2. The water-gas shift reaction is also used to tailor the required ratio of H_2 and CO for Fisher-Tropsh synthesis of gas-to-liquid.

Steam reforming presents the higher production of hydrogen - six moles of hydrogen per each mole of ethanol, although chemical equilibrium may reduce this figure appreciably (Fishtik et al., 2000; Ioannides, 2001; Pina e Oliveira, 2006). However, the steam reforming reaction is strongly endothermic, requiring an external energy source to take place, which represents a disadvantage on the total cost of the process (Pulgar et al., 2002). The auto-thermal is the second reaction in production of hydrogen - about five moles of hydrogen per each mole of ethanol. The stoichiometric coefficients in this reaction are chosen to render it thermally neutral, i.e., the energy required by the steam reforming reaction is supplied by the simultaneous oxidation reaction. On the other hand, it has a slow response to load variations, making it difficult for use in automotive on-board applications. Ni *et al.* (2007) present a review of the literature published before 2006 on steam and auto-thermal reforming of ethanol for hydrogen production, with emphasis in catalysts development. They observed that Rh and Ni on supports with basic sites are the most tested metals for ethanol steam and auto-thermal reforming. As Rh and Ni are inactive for water gas shift reaction, they suggested the use of bimetallic catalysts, alloy catalysts or double-layered reactor to decrease the CO emission.

Although partial oxidation presents the lower hydrogen production, its response to load variation and startup is the fast when compared to the other two routes, becoming very useful for on-board applications. In addition, it does not need an external supply of energy since it is a globally exothermic reaction, which results in a more compact reactor.

The studies about partial oxidation have been focused on experimental approaches, with emphasis on the development of noble metal catalysts. The most important experimental reactors used for investigations in partial oxidation are the microflow reactor and the porous media reactor. In the next sections, the main results with these two reactors are reviewed.

2.1. Catalytic microflow reactors

The most widely model of reactor used for experiments in partial oxidation is the microflow reactor. It consists basically in some tens of milligrams of catalyst placed inside a quartz tube. An ethanol and oxygen mixture highly diluted flows in the tube at high flow speed. Such geometry combined with high flow speed results in approximately isothermal conditions, controlled by surface chemical kinetics. These reactors allow determination of ethanol conversion, selectivity to chemical species and activity of catalysts from the measurements of inlet and exit gas phase compositions. Additionally, a series of laboratory techniques (based on infra-red absorption) can provide non intrusive in-situ measurements of population of adsorbed species as a function of temperature and gas phase composition.

Different noble metal over metal oxide as supports have been used in the partial oxidation of ethanol to produce hydrogen. Silva *et al.* (2007) evaluated Ru and Pd as catalysts supported on Y_2O_3 for partial oxidation of ethanol in a large range of temperatures, between 473 K and 1073 K. Ru/Y_2O_3 catalyst systems achieved 59 % of hydrogen selectivity and 35 % of CO selectivity at 1073 K. Pd/Y_2O_3 systems achieved higher selectivity to CO at temperatures lower than 773 K. The results show that the reaction path depends strongly on the kind of the catalyst metal. Pd promoted the decomposition of ethoxy species to CH_4, CO and H_2 while Ru promoted the acetaldehyde desorption at low temperature.

Different composites have been used as support for catalysts and their nature influences the performance of the system and the chemical reaction route. The effect of the support on the performance of Pt catalysts has been recently investigated (Mattos and Noronha, 2005a and Bi *et al.*, 2007). Mattos and Noronha have shown that acetic acid was the major product on Pt/Al_2O_3 and this is attributed to acidic properties of the support. On the other hand, methane and acetaldehyde were detected on Pt/ZrO_2, Pt/CeO_2 and $Pt/Ce_{0.5}Zr_{0.5}O_2$ catalysts and this is related to their redox properties. Bi *et al.* (2007) have investigated the low temperature partial oxidation of ethanol over Pt/Al_2O_3 and Pt/ZrO_2 catalysts. The results indicated an ethanol conversion of about 50 % and a H_2 selectivity of 95 % for Pt/ZrO_2 catalysts. This selectivity decreases with the increase in O_2/C_2H_5OH ratio or temperature.

Mattos and Noronha (2005b) investigated the effect of the metal on the performance of CeO_2 support in the partial oxidation of ethanol. The main results showed that acetaldehyde was the only product formed on Co/CeO_2 catalysts whereas methane was also produced on Pt/CeO_2 and Pd/CeO_2. Mattos and Noronha (2005c) proposed a reaction mechanism for ethanol partial oxidation to produce hydrogen over Pt/CeO_2 catalysts. Adsorption of ethanol on the support gives rise to ethoxy species. A fraction of these species can be dehydrogenated. These then react with oxygen from the support, producing acetate species and C_3^{3+}. Acetate species can be decomposed to CH_4 and CO or oxidized to CO_2. In higher temperatures, another fraction of the ethoxy species migrates to the metal particle and is decomposed in CH_4, H_2 and CO.

The use of bimetallic catalysts is suggested as an approach to enhance the hydrogen selectivity (Ni *et al.*, 2007). Sheng *et al.*, (2002) studied the reactions of ethanol over $Rh\text{-}Pt/CeO_2$ by temperature-programmed desorption and infrared spectroscopy. Their results show that ethanol decomposition, and therefore hydrogen production, requires the presence of a secondary metal such as Pt in addition to Rh. They proposed a general scheme to ethanol partial oxidation at low temperatures. Ethoxides are the main species observed upon ethanol adsorption. On the unreduced surfaces, ethoxide species are directly dehydrogenated to adsorbed acetaldehyde. Conversely, ethoxide species are directly decomposed to CO on reduced surfaces, via an oxametallacycle intermediate on Rh. The presence of Pt site increases the association reaction of the two H atoms.

Silva *et al.* (2008) investigated a double-layered system, which includes ethanol partial oxidation and water gas shift reaction to produce hydrogen from ethanol in a wide range of temperatures. The partial oxidation reactor was made from Rh/CeO_2 catalysts and the water-gas shift reactor from two types of catalysts: vanadium-modified Pt/CeO_2 and Rh/CeO_2. The partial oxidation of ethanol over Rh/CeO_2 is favored at high temperatures, achieving a hydrogen selectivity of 35 % at 873 K. The vanadium-modified Pt/CeO_2 was more active to water-gas shift reaction, probably due to its redox properties.

The use of non-noble metals in partial oxidation is not common due to their lower activity. However, this is a promising area of research due to low cost of such metals. Wang *et al.* (2002) have studied alloy catalysts of Ni-Fe at temperatures between 473 K and 573 K. They found a conversion of ethanol of 86 %, hydrogen selectivity of 46 % and CO selectivity of 5 % for $Ni_{50}Fe_{50}$ at 573 K and O_2/C_2H_5OH ratio of 1.5.

Although some of the main reaction paths have been discussed and the main findings have been supported by measurements, there is a lack of predictive detailed heterogeneous reaction mechanisms that could be used in the design and optimization of reactors. There is a need to put effort in developing these mechanisms and comparing the predictions to the available measurements.

1.3. Porous media reactors

This configuration has typical characteristics and limitations comparable to industrial scale reactors. However, there are only a few studies that develop detailed measurements and modeling. The most commonly porous media used are pellets and monoliths such as honeycomb structures and layers of ceramic foams. Due to the large dimensions of these media, intrusive measurements of temperature profiles are possible. The gas phase composition can be monitored by gas chromatography techniques.

This kind of reactor has been widely used in studies of porous radiant burners (Howell *et al.*, 1996). Recently, the production of hydrogen has been investigated in porous media reactor fed with rich methane plus air mixture (Dhamrat and Ellzey, 2006) and with methanol, methane, octane and automotive-grade petrol plus air mixtures (Pedersen-Mjaanes et al., 2005). A few works have focused on partial oxidation of ethanol to produce hydrogen in porous media reactors (Salge *et al.*, 2005 and Wanat *et al.*, 2005). Salge *et al.* (2005) investigated the catalytic partial oxidation of ethanol and ethanol-water over noble metals. They conducted experiments with bimetallic and simple catalysts such as Rh-Ce, Rh, Pt, Pd and Rh-Ru over Al_2O_3 and SiO_2 ceramic foams. The main results show that Rh-Ce catalysts presented the higher activity and stability, with conversion higher than 95 % and selectivity to H_2 of 80 %. Rh, Pt and Pd produced more CH_4 and C_2H_4 than Rh-Ce. The addition of γAl_2O_3 washcoat to Rh catalyst increased the syngas (H_2

+ CO) selectivity in 10 % due to higher surface area. Wanat *et al*. (2005) have compared the partial oxidation of some alcohols to produce hydrogen and other chemicals in millisecond contact-time reactors. They have found that ethanol and methanol produce mainly H_2 and CO while other higher alcohols can produce larger products, such as acetone from 2-propanol.

From this limited data available, a reaction path is being constructed. From this detailed reaction path, a comprehensive chemical reaction mechanism will be developed and applied to the ethanol partial oxidation. The results will be compared to an experiment, as described next.

2. DEVELOPMENT OF AN EXPERIMENTAL APPARATUS

Before presenting the experimental set-up, preliminary thermodynamic calculations are shown. The equilibrium calculations considered a mixture of ethanol and air (standard, simplified composition) at 373 K and different pressures and fuel to air ratios entering an adiabatic constant pressure reactor. Here, the fuel equivalence ratio follows the usual definition, i.e.,

$$\Phi = \frac{\left(\dot{m}_F \big/ \dot{m}_a \right)_a}{\left(\dot{m}_F \big/ \dot{m}_a \right)_S} \tag{4}$$

where $\dot{m}_F$ is the fuel mass flow rate, $\dot{m}_a$ is the air mass flow rate, the subscript s stands for stoichiometric conditions and the subscript a stands for actual conditions.

Figure 1 presents the adiabatic flame temperature and the mole fraction of the equilibrium product species. The results were obtained with the software Stanjan (Reynolds, 1996), using the same species as products as those from the Marinov mechanism for high temperature ethanol oxidation (Marinov, 1988). It turned out that under the conditions tested only the species presented in Figure 1 (H_2, H_2O, CO, CO_2, CH_4, O_2 and N_2) presented mole concentrations above 10^{-6}.

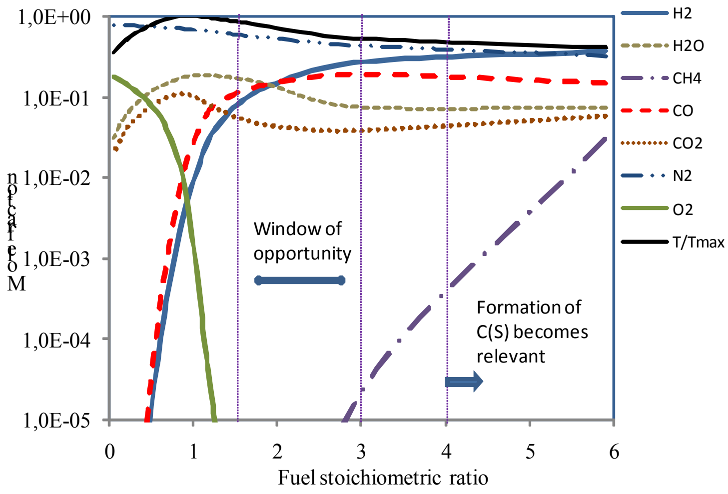

Figure 1: Equilibrium temperature and product mole fractions for an adiabatic, constant pressure reactor (p = 1 bar, T_n = 373 K, T_{max} = 2289 K).

From Fig. 1, we note that the H_2 mole fraction increases with the CO mole fraction when the mixture becomes fuel rich. Initially, there is a sharp increase around stoichiometry, then followed by a flat plateau. At $\phi < 1.5$, the H_2 production is low and at $\phi > 3$, CH_4 mole fraction increases sharply. Therefore, there is a window for equilibrium H_2 production of about 10 % to 27 % mole fraction for ϕ between 1.5 and 3. For $\phi > 4$, there is appreciable formation of solid carbon (not shown), turning it not advisable to operate a reactor at these fuel concentrations due to coke formation.

Taking the H2 mixture obtained with $\phi = 2$, an analysis of the effect of further cooling of this mixture on the equilibrium composition can be performed. Table 1 presents the equilibrium thermodynamic properties for partial oxidation at this condition. Only a few representative species are shown. Figure 2 presents the variation of the mole fraction of representative chemical species in the mixture listed in Table 1 while this is cooled. We observe an increase in mole fraction of H_2 reaching a maximum at about T = 900 K. This reveals the potential for further increase in H_2 production when we are able to probe non equilibrium mixture compositions, as it occurs in fast contact time reactors (Salge *et al*., 2005 and Wanat *et al*., 2005).

Table 1: Reactants and products equilibrium thermodynamic properties for partial oxidation of ethanol in an adiabatic, constant pressure reactor (only a few representative species are shown). Results from Stanjan.

Inlet:			**Outlet:**						
T_n	K	373	M	kg/kmol	23.69	Species mole fractions X_i:			
p	bar	101330	p	bar	101330	CH_3OH	5.1183E-13	H_2	1.3828E-01
n_{C2H5OH}	kmol	1	T	K	1695.15	CH_4	1.4059E-09	H_2O	1.4368E-01
n_{O2}	kmol	1.5	U	J/kg	-1443300	CO	1.4368E-01	NO	1.0810E-07
n_{N2}	kmol	5.64	H	J/kg	-848330	CO_2	4.4292E-02	NO_2	1.3999E-14
f	kg_F/kg_a	0.224	S	J/kg-K	10677	C_2H_5OH	2.4820E-22	N_2	5.3008E-01
ϕ	adm	2.00	v	m^3/kg	5.87	C_2H_6	1.2260E-19	O_2	3.9044E-10

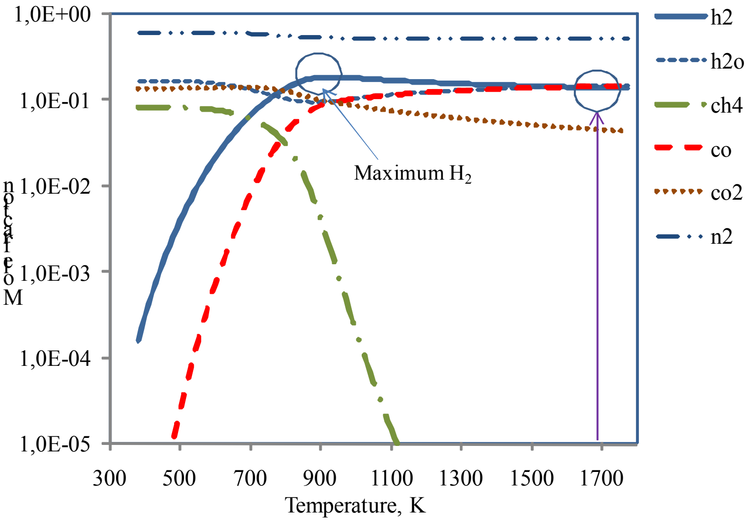

Figure 2: Equilibrium temperature and product mole fractions for an adiabatic, constant pressure reactor (p = 1 bar, T_n = 373 K, T_{max} = 2289 K).

The effect of pressure on the equilibrium mole fractions is presented in Figure 3 for an inlet mixture (atomic population) containing 1 mol of C_2H_5OH, 1.5 moles of O_2 and 5.64 moles of N_2. We note that an increase of mixture pressure displaces the equilibrium towards higher methane and smaller hydrogen productions. Operation at 1 bar provides the higher productions.

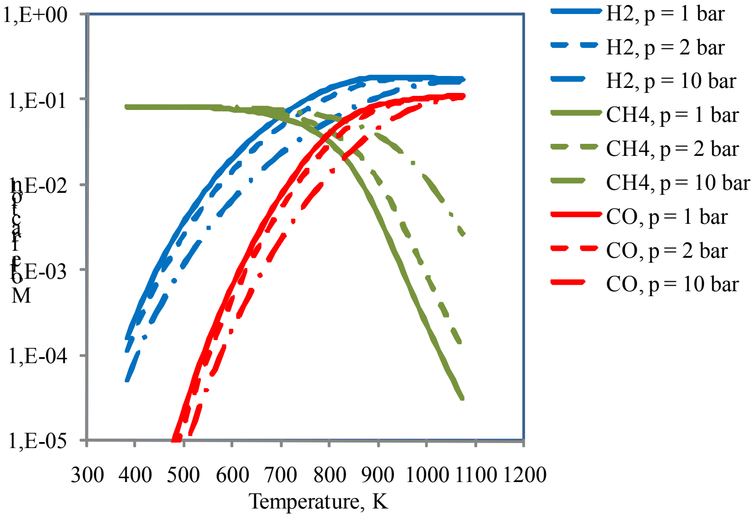

Figure 3: Equilibrium product mole fractions at different equilibrium temperatures for different pressures for an inlet mixture (atomic population) containing 1 mol of C_2H_5OH, 1.5 moles of O_2 and 5.64 moles of N_2.

A rendering of the experimental set-up being proposed is presented in Figure 4. It is divided in five subsystems: the ethanol supply system, the air supply system, the mixture chamber, the porous media reactor and systems to measure temperatures and major chemical species. The ethanol supply system is composed by a pressurized tank, a reducing and control valve, a shut-off valve, an electronic controller and an automotive fuel injector. The tank is pressurized by bottled nitrogen (95 % pure). The ethanol is sprayed in the mixture chamber by an automotive fuel injector. A reducing and control valve regulates the pressure of the tank at 300 kPa. An electronic controller, based on the component 555 timer IC, was built for this application. It controls the frequency and the opening time of the injector, allowing an accurate control of the ethanol mass flow rate between 2 and 100 cm^3/min. The ethanol used in the preliminary tests was industrial grade 92.8 % pure (contaminated with water).

The air supply system is composed of an air compressor, a tank, a reducing valve, a shut-off valve, a flow control valve and an electronic flowmeter, with measurement range between 0 to 200 liters per minute. The air is heated by an electric resistance. The temperature of the air is regulated by a controller, which includes a thermocouple type K. The air is injected in the mixture chamber in a swirl, increasing the ethanol vaporization rate. At the end of the mixture chamber, a bed of glass spheres is used as a laminarization section.

A drawing of the porous media reactor built in this work is presented in Figure 5. The reactor is made with layers of ceramic foams with diameter of 70 mm, thickness of 20 mm and 80 % of volumetric porosity. The total length of the reactor is 80 mm, however, this length can be changed by including other ceramic foams. As a first approach, the porous media reactor was made with ceramic foams (manufactured by Foseco) composed of alumina (Al_2O_3) and zirconia (ZrO_2). An injection plate with a single central orifice is placed upstream from the ceramic foams. The purpose of this injection plate is to stabilize the flame inside the ceramic foams, preventing flashback and blow-out of the flame (Catapan et al., 2007).

Type R (platinum and platinum + 13 % rhodium, from Omega Engineering) thermocouples placed inside the alumina double-holed tubes are used to measure the temperature within the porous matrix. The thermocouple measurements are processed by a data acquisition system (34970A - Agilent) interfaced with a computer. For the first measurement propose, a gas sample is collected by a cooled probe placed on the porous media reactor and is sent to the gas analyzers (Tempest 100 - Telegan), which includes CO (range of 0-10 %), O_2 (range of 0-25 %) and NO_x (range of 0-1000 ppm) sensors.

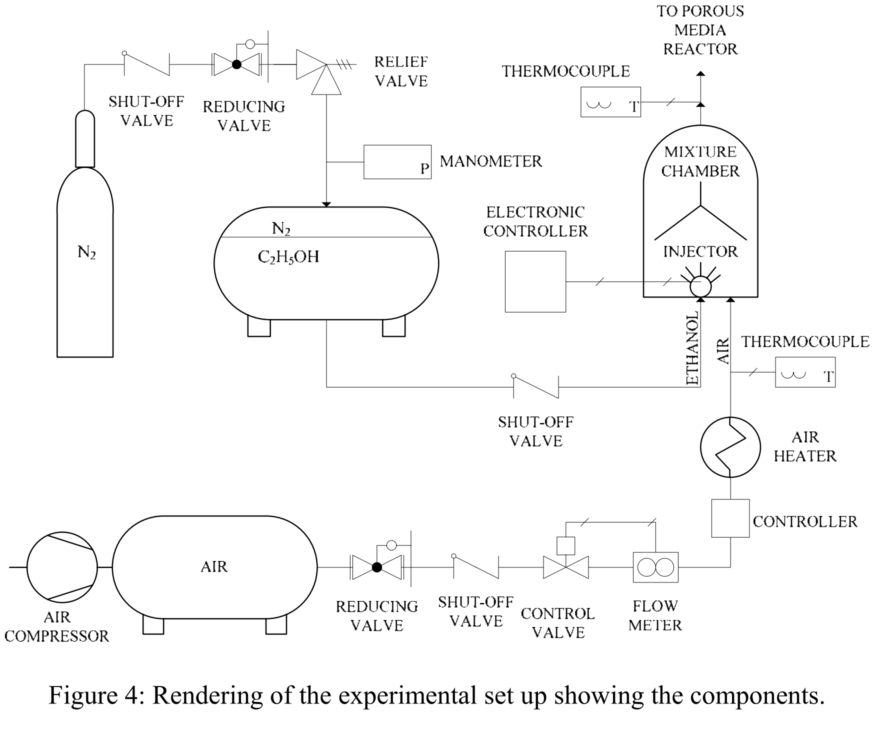

Figure 4: Rendering of the experimental set up showing the components.

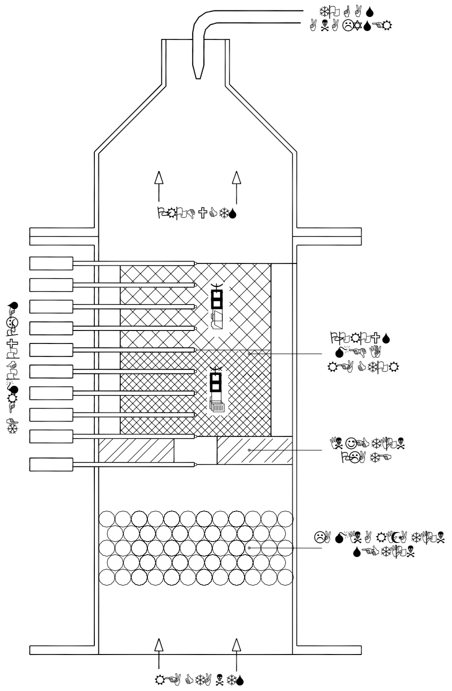

Figure 6: Rendering of the porous media reactor.

3. EXPERIMENTAL PLANNING AND CONCLUSION

The experiments are planned in two main steps. First, the stability limits of the lean ethanol-air flame inside the Al_2O_3/ZrO_2 ceramic foams, including measurements of pollutant emissions and temperatures inside the porous matrix, will be investigated. After, tests with rich ethanol-air flames on catalytic material impregnated on Al_2O_3/ZrO_2 ceramic foams, which will include stability limits and temperature measurements and minor species detection and quantifying, will be performed. For comparison purposes, tests Al_2O_3/ZrO_2 ceramic foams will be also performed.

The experimental procedure to find the stability limits is based on the procedure of Hsu et al. (1993) (Catapan et al., 2007). First, the fuel equivalence ratio and a volumetric flow rate that allows for stable flame propagation within the porous burner are set. The equivalence ratio is then slowly adjusted to the test value and the volumetric flow rate is increased until the upper limit of flame stability (the blow-out limit) is reached. Then, the burner is reinitialized and the volumetric flow rate is decreased until the lower limit of flame stability (the flashback limit) is reached. The blow-out and flashback limits are detected with the aid of the temperature measurements. The larger fuel equivalence ratio tested is limited by the degradation temperature of the porous matrix. For Al_2O_3/ZrO_2 ceramic foams this temperature is around 1600 ºC. When a stable flame is achieved, the temperature profile inside the reactor is recorded by the data acquisition system and a gas sample is collected by the cooled probe and sent to the gas analyzer.

The first measurements already performed focused on stability limits of lean premixed combustion of ethanol and air. The results showed that, for this set up, the flame can be stabilized in a very narrow range of flame speed, much narrower than the equivalent for methane. The flame speed is defined as the ratio between the unburnt reactants volumetric flow rate and the burner area. For an equivalence ratio of 0.60 the maximum temperature of the porous matrix was achieved (1773 K). For an equivalence ratio of 0.50, the flame could be stabilized for flame speeds between 35 cm/s and 45 cm/s. It is not conclusive of why this narrowing of the stability range was observed.

More measurements will be performed for lean mixtures with the objective of determining the burner stability diagram. Special care will be devoted to check for complete evaporation of the ethanol before entering the porous media reactor. Then, following these initial results, experiments will be performed with a catalytic material, such as Ni and Pt, impregnated on the surface of the ceramic foams by washcoating. Gas analyzes by gas chromatography techniques will include the detection of minor species, such as aldehydes, as an attempt to detect non-equilibrium operation.

4. ACKNOWLEDGEMENTS

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