



Steam Reforming of Methanol for Fuel Cell Grade Hydrogen Production

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Abstract: Methanol steam reforming has been characterized using different catalyst formulas and reformers, in order to provide fuel cell grade hydrogen. A bench station has been developed in order to accommodate all the inherent steam reforming equipment. Several catalyst formulations with copper and zinc oxide developed by IST have been tested and compared to a commercial catalyst from Sud-Chemie, Shiftmax 230. An automated injection system has been developed for chromatographic analysis that controls the peristaltic pump that carries the reactant and the vacuum pump that cleans the sampling loop, using data acquisition devices from National Instruments and Labview 8,5 Software. Temperature measurements have been taken along the reformer axis in order to calculate the amount of heat transfer to the reaction mechanism. The catalyst from Sud-Chemie has proven to be the most active and selective with methanol conversion rates of 100 % and selectivities of 100 %, able to produce a hydrogen flow with an equivalent power of 400W.

1 – Introduction

The vehicles with fuel cell systems present numerous challenging tasks. Handling hydrogen is a complex task. The hydrogen has to be produced, stored and delivered in several places where the users can refill. Storing hydrogen on-board is not at present a realistic option due to limitations in storage capacity [1]. Hydrogen can be produced on-board from several liquid fuels, such as ethanol or methanol. From a technical point of view methanol is the ideal fuel, as it can easily be converted into hydrogen at reasonable temperatures (<300°C).

The hydrogen production from methanol is possible through several processes: decomposition (D), steam reforming (SR), partial oxidation (PO) and oxidative steam reforming or auto thermal reforming (ATR) [2,3].

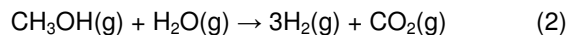
The most simple conversion method, as only methanol is used in the feeding, is thermal or catalytic decomposition (Eq. (1) [2]. The decomposition of methanol leads to a product gas containing up to 67% hydrogen and 33% carbon monoxide.



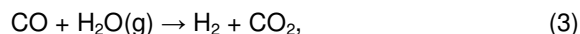


The CO formation makes the process inappropriate as this gas has harmful effects on the fuel cell performance. The reaction is highly endothermic which can affect negatively the mobile applications where energy supply is limited.

The capability to produce a gas with high hydrogen concentration, up to 75%, while maintaining a elevated selectivity towards carbon dioxide through the steam reforming (SR) process (Eq. (2)) has received considerable interest. The main disadvantage of steam reforming is that the reaction is endothermic and slow.



Steam and combined reforming are commonly operated with an excess of steam 30%-50%, in order to reduce the carbon monoxide content in the reformat products. This is done by inducing the water-gas shift (WGS) reaction in the reformer (Eq. (3)) that is exothermic [4].



The carbon monoxide content is reduced in the WGS reaction at the same time as the hydrogen content is increased in the product stream and low temperatures favor the forward reaction at equilibrium conditions [2].

In the present work steam reforming (SR) and water-gas shift (WGS) reactions are considered. The commercial methanol reforming catalysts are based in non-precious metals as Cu/Zn. Its activity is generally proportional to the available area of copper that is affected by the dispersion and the size of grain. The reaction is considered to occur at the border between the copper and the support [3]. There are several important aspects that influence the activity of the catalyst, such as the diverse elements of the catalyst (promoters / doping) as well as the method of preparation [4-10]

Several catalyst formulations have been prepared using the Neto-Azevedo catalyst preparation method, 100% Cu supported by 3 mm and 1,5 mm Al_2O_3 spheres and Cu/ZnO with 50% Cu supported by 1 mm SiO_2 spheres.

Huang et al [11] studied the effect of CeO_2 and ZrO_2 doping on Al_2O_3 supported Cu/ZnO catalysts, they prepared several Cu/ZnO/ Al_2O_3 catalysts in different species proportion. They concluded that an excessive copper percentage does not favor the reaction, in fact the most active catalyst was 50/40/10 of Cu/ZnO/ Al_2O_3 with 88,7% conversion and 0,5 % selectivity towards the formation of CO.

The CO hydrogenation rate is about 100 times lower than the hydrogenation of CO_2 . Zinc oxide is known to improve the copper dispersion and to promote the copper reduction on the surface, which improves the catalytic activity of Cu / ZnO [12].



The purpose of this work is to determine the parameters associated with the catalysts developed by the Neto-Azevedo method of catalyst preparation, namely, conversion and selectivity towards CO_2 with temperature, space velocity and time. It is also intended to obtain the thermal profiles along the longitudinal axis internal inside the reformer to allow the temperature correlation with the catalyst reactivity.

2 – Experimental

2.1 – Reformer

The conversion study of the methanol/water mixture was made using the system shown in Figure 1, which is composed by a reservoir of 200 ml containing a methanol/water mixture, a peristaltic pump, an evaporator and the reformer both inside an electrical heated furnace. Parts of the reforming products are directly fed to a gas chromatograph for analysis. The peristaltic pump used is a CTX, 6-1 SANT model and it presents a maximum flow rate of 4.8 ml/min and a minimum of 0.9 ml/min. The mixture is pumped through a stainless steel tube with a coil section with nine turns that acts as evaporator around the reformer and it is fully inserted inside the furnace tube. This allows a complete evaporation of the methanol/water mixture before it is introduced in the catalytic region. The reformer comprise a stainless steel tube 316L with 15.0 mm of internal diameter, 18.0 mm of external diameter and 215 mm of length, whit a total internal volume of 33 cm^3 and with a catalyst volume of 17 cm^3 and an interstitial catalyst volume of 7 cm^3 . Inside and outside the methanol reformer there are two guide channels to move a thermocouple type K probe at its axis allowing temperature measurements for the reactor temperature profile. The thermocouples were connected to a DBK203A of Omega and the signal was monitored and recorded using LabVIEW 8.5 from National Instruments.

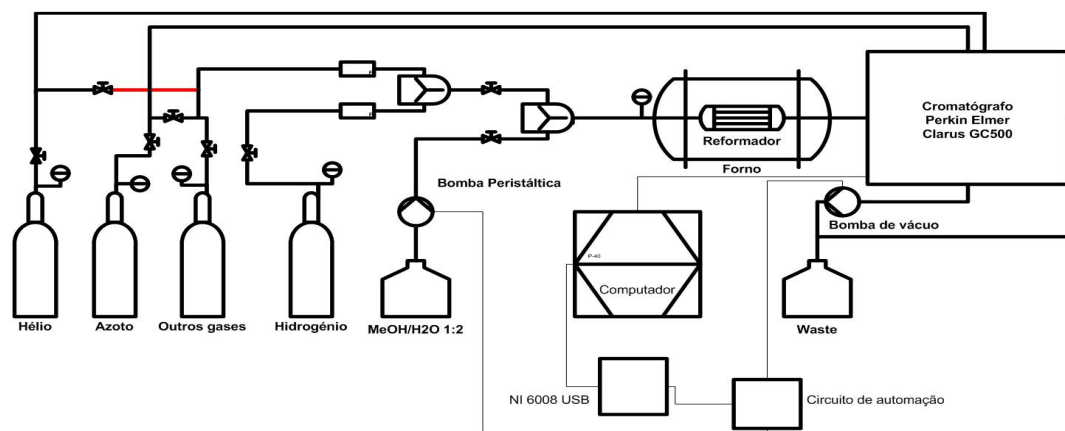


Figure 1 – Reforming setup schematics.

The pressure inside the reactor was monitored by a pressure gauge placed between the peristaltic pump and evaporator. The outlet from the reformer is connected through a heated tube to the input of



the automatic valve of the gas chromatograph. The inlet pressure of the chromatograph was regulated using a small diameter (0.5 mm) tube for the reformat gas exhaust after the heated tube. The heated tube is kept at an internal temperature of 140°C thus avoiding any kind of mixture (methanol/water) condensation. This type of connection between the reactor and the gas chromatograph and the use of the automatic valve on the gas chromatograph, introduced high accuracy, precision and simultaneity in all reaction products determination as well as methanol and water excess that did not react.

The gas samples were taken through an automatic 10 way valve on the gas chromatograph, Perkin Elmer, Clarus 500 model. Quantitative analysis was made of different gas species, particularly, hydrogen, carbon dioxide and carbon monoxide as well as unreacted methanol and water excess. The injector and the detector temperature was 140°C, the column temperature was set at 120°C. This avoids the water and methanol condensation inside the gas chromatograph. Helium was used as a carrier gas with a flow rate of 30 mL/min. An Alltech packed column was chosen model Hayesep DB 100/120, 30 "x1 / 8" x0.85 "SS, which allowed separate all gaseous constituents that were detected by a thermal conductivity detector (TCD). The signal from the chromatograph was calibrated based on seven injections of each pure gas species. The average area from these tests was associated to 100% of the gas composition.

2.2 – Catalyst characterization

In this work, all catalysts were checked for coating detachment, before insertion on the reformer as well as after reforming. In both times the catalysts were weighted, the difference in mass is coating detachment.

2.3 – Thermal profiles

Temperature readings using a K series thermocouple were taken along the longitudinal axis of the reformer by moving the thermocouple 2 cm at a time and storing the readings in a log file. The values stored in the log file were only the ones where the temperature oscillation amplitude is below 1°C. The thermocouple swept all 22 cm of the reformer.

After all temperatures were taken the thermal profile was plotted. The amount of heat transferred to the fluid was also calculated using:

$$\dot{Q}_{fluido} = \dot{m}(h_{produtos}(T_{produtos}) - h_{reagentes}(T_{reagentes})) \quad (4)$$

Knowing the relevant temperatures, the enthalpies, $h(T)$ are easily obtained from enthalpy tables and the mass flow rate, \dot{m} is also known, so the heat transfer to the fluid, \dot{Q}_{fluido} is calculated.



3 – Results and Discussion

3.1 – Reforming results

In terms of methanol conversion and selectivity towards CO_2 , the following expressions were used

$$C_{\text{CH}_3\text{OH}} = \frac{\text{CA}(\text{H}_2 + \text{CO}_2 + \text{CO})}{\text{CA}(\text{H}_2 + \text{CO}_2 + \text{CO}) + \text{CA}(\text{CH}_3\text{OH})} \times 100 \quad (4)$$

Where $C_{\text{CH}_3\text{OH}}$ is the methanol conversion, CA is the corrected area related with the different gases.

S_{CO_2} is the selectivity associated with formation of CO_2 was calculated based on the next equation:

$$S_{\text{CO}_2} = \frac{\text{CA}(\text{CO}_2)}{\text{CA}(\text{CO}_2 + \text{CO})} \times 100 \quad (5)$$

The catalysts used in the reforming process were those prepared by the Neto-Azevedo method, 100% Cu with Al_2O_3 spheres of 1,5 mm and 3 mm, codename 100%Cu Al_2O_3 1,5mm and 100%Cu Al_2O_3 3mm, a 50% Cu/ZnO with 1mm diameter SiO_2 support spheres and the commercial Shiftmax 230 from Sud-Chemie. The reformer was loaded each time with 9 g of catalyst.

Figure 2 shows the results for methanol conversion as a function of temperature, the temperature starts at 500°C and decreases at a rate of 1°C.min⁻¹. 100% conversion is achieved only for 100%Cu Al_2O_3 1,5mm and Shiftmax 230, the commercial catalyst attains full conversion from the beginning and start losing activity around 230°C where it still maintains 83% conversion, the 100%Cu Al_2O_3 1,5mm shows 100% methanol conversion from 500°C to 440°C, below that temperature the catalyst has a drastic reduction in activity and at 410°C only shows 11% methanol conversion.

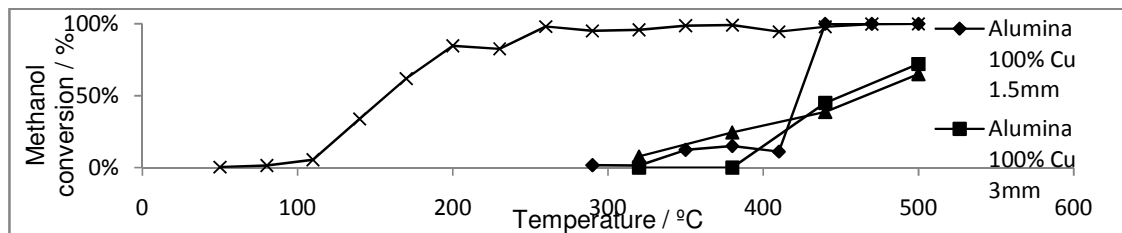


Figure 2 – Methanol conversion as a function of temperature for all four catalysts in study when subjected to a solution of water/methanol with a steam to carbon ratio (SCR) of 2 and a space velocity of 675 h⁻¹.

The 100%Cu Al_2O_3 and the SiO_2 50% Cu/ZnO 1mm displayed low methanol conversions peaking each at 72% and 65% respectively. The higher methanol conversion of the 100%Cu Al_2O_3 1,5mm compared to the 100%Cu Al_2O_3 3mm can be explained by the larger superficial area which favors activity. The best catalyst was without a doubt the Sud-Chemie Shiftmax 230 showing activity in a wide range of temperatures.

The figure 3 displays the selectivity towards CO₂ formation. The 50% Cu/ZnO with SiO₂ support remained with 99% selectivity towards CO₂ while reforming although operating in a very narrow temperature range, the 100%CuAl₂O₃3mm displayed the worst selectivity towards CO₂, the 100%CuAl₂O₃3mm showed relatively high selectivity values from 440°C to 500°C.

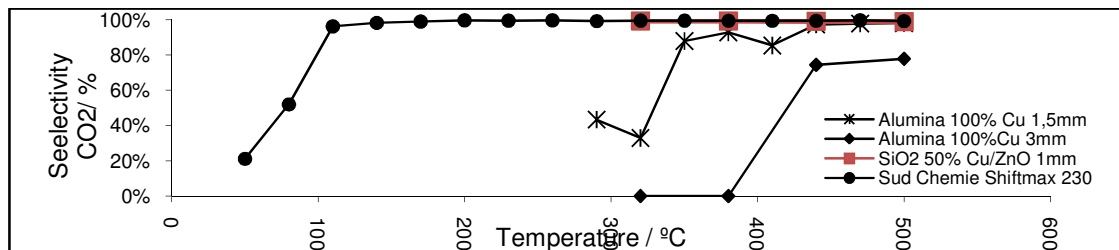


Figure 3 – Selectivity towards CO₂ formation as a function of temperature for all four catalysts while reacting with a methanol/water solution with a SCR ratio of 2. The temperature starts at 500°C and decreases at a rate of 1°C.min⁻¹

Once again Shiftmax 230 showed outstanding performance displaying 100% selectivity from 500°C to 170°C and 96% at 110°C.

When compared with the Shiftmax 230, the formulations developed in the lab fall short for activity and selectivity values, this might have to do with the active material percentage, the Shiftmax 230 is 100%(wt) made of active material, while the lab formulations only have 10%(wt).

The results for methanol conversion as a function of space velocity are shown in figure 4, the lab formulations start to lose activity right after 675 h⁻¹, being the maximum conversion rate of 68% for 100%CuAl₂O₃1,5mm by 1380 h⁻¹, the Shiftmax 230 appears to lose activity at first but at the maximum speed it returns to 100% conversion, the lower values of conversion are suspected of being sampling errors.

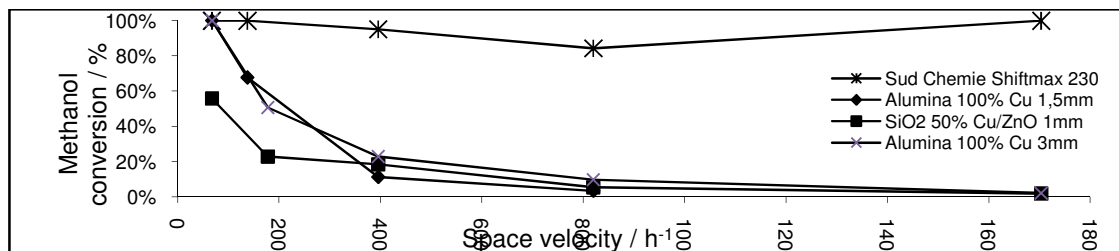


Figure 4 – Methanol conversion as a function of space velocity for all four catalysts while reacting with a solution of methanol/water in a SCR ratio of 2 at 500°C.



This figure clearly shows that the lab formulations do not reform at speeds above 675 h^{-1} , there formulations need to be thought over and reformulated in order to convert methanol at greater speeds.

The results for selectivity of the catalyst for CO_2 formation are shown in figure 5. $100\% \text{CuAl}_2\text{O}_3$ shows the worst selectivity, it starts at 90% for 675 h^{-1} and decreases over the space velocity, ending in 70% for 17036 h^{-1} , the $\text{Cu}100\% \text{Al}_2\text{O}_3 1,5 \text{mm}$ has also a tendency to decrease, but once again the larger surface area seems to favor selectivity starting at 99% for 675 h^{-1} and decreasing to 88% at 8203 h^{-1} .

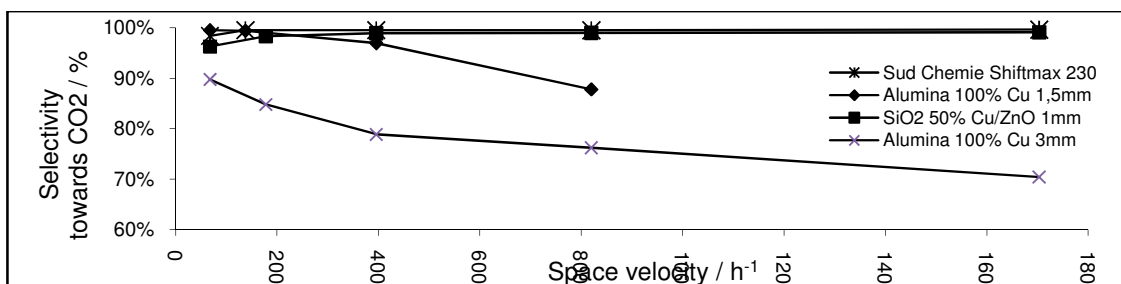


Figure 5 – Selectivity for the CO_2 formation in function of space velocity for all four catalysts while reacting with a methanol/water solution with a SCR of 2 at 500°C .

Both Shiftmax and 50% Cu supported by SiO_2 catalysts increase selectivity with space velocity. The decrease in selectivity for those two catalysts indicates that the active surface is recrystallizing or sintering which makes the catalyst more prone to methanol decomposition and not steam reforming, making these two catalysts unsuitable for methanol steam reforming.

Figure 6 illustrates methanol conversion over an 8 hour long test, this test indicates the stability and activity of the catalysts over time. All catalysts with the exception of SiO_2 50% Cu/ZnO 1mm showed conversion rates above 75% at all time, being Shiftmax the most active maintaining 100% conversion all along the test with two exceptions assumed to be sampling errors, the SiO_2 50% Cu/ZnO 1mm starts to deactivate soon after 380°C .

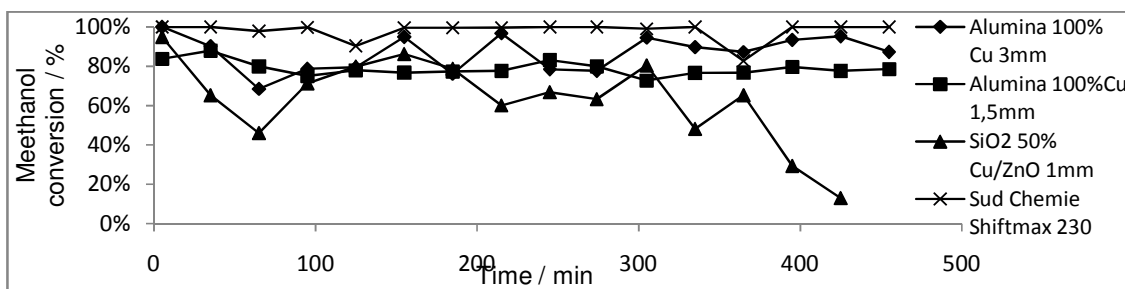


Figure 6 – Methanol conversion as a function of an 8 hour long trial for all four catalysts subjected to a methanol/water solution with a SCR of 2 at 500°C with a space velocity of 675 h^{-1} .



Once again Shiftmax 230 proves to be the best in this study, an interesting future work would be the characterization of this catalyst, see at what special velocities it deactivates, at what temperature it begins to lose selectivity and so on.

Figure 7 shows the results for selectivity towards CO₂ formation over an 8 hour long trial. Sud Chemies Shiftmax 230 maintains 100% selectivity throughout the test SiO₂ 50% Cu/ZnO 1 mm displays the second best selectivity at 98% practically without change, the 100%CuAl₂O₃1,5mm attains 95% of selectivity for the entire duration of the test.

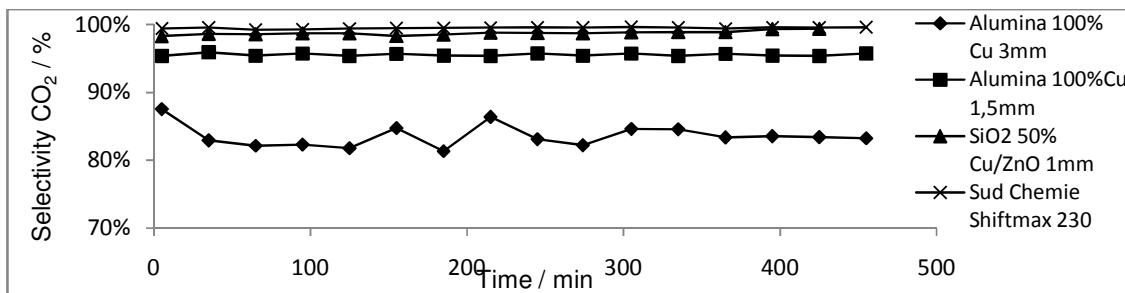


Figure 7 – Selectivity towards CO₂ production with time for all four catalysts when reacting with a methanol/water solution with a SCR of 2 at 500°C and a space velocity of 675 h⁻¹.

The 100%CuAl₂O₃3mm shows the worst selectivity towards CO₂ formation with an average value of 85%.

Once again the 100%CuAl₂O₃3mm shows to be unfit for methanol steam reforming with high CO formation which is highly prejudicial to the catalyst itself and does not produce in any way a hydrogen flow fit to be used in fuel cell applications.

3.2 – Temperature profiles

For the temperature profile, temperature measurements were made with the aid of a k series thermocouple for the SiO₂ 50% Cu/ZnO 1mm and for the Sud Chemie Shiftmax 230. Figure 8 the temperature profiles for Sud-Chemie Shiftmax 230.

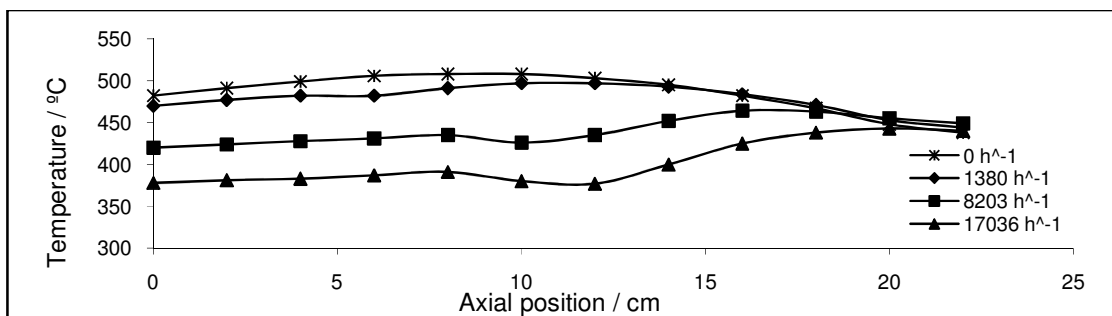




Figure 8 – Temperature profiles for the Sud Chemie catalyst while reforming a methanol/water solution with a SCR of 2 at 500°C at different space velocities, axial point 0 cm coincides with one end of the reformer.

With the increase in special velocity the entry temperature is decreasing, mainly because more solution is entering the reformer and requires energy to vaporize, additionally, even if the methanol conversion is not 100%, a hydrogen rich flow might still be producible which also diminishes the reactor temperature.

Figure 9 shows reactor temperature profiles for 100%CuAl₂O₃1,5mm while reforming at different space speeds and in absence of reforming.

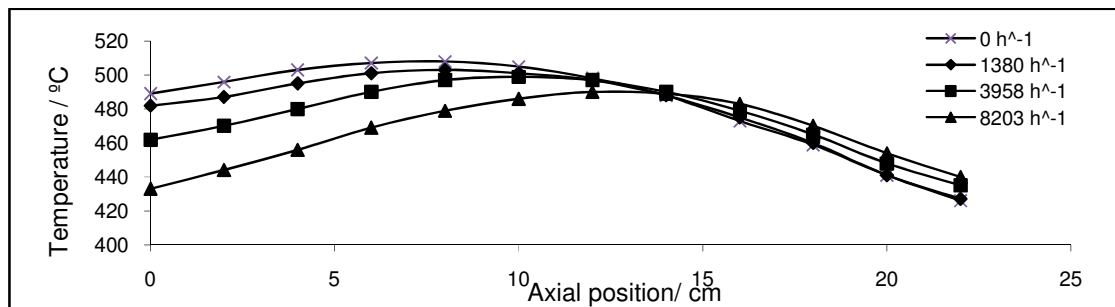


Figure 9 – Temperature profiles for 100%CuAl₂O₃ catalyst for various space velocities.

Figure 9 shows that only for 1380 h⁻¹ there is some heat transferred to the fluid while reforming at 2 cm, for the other velocities, the reaction does not occur and the heat transfer is solely for fluid vaporization.

3.3 – Heat transfer to fluid and hydrogen equivalent power

Table 3.1 shows the heat transferred to the fluid and the equivalent hydrogen power if it were to power a fuel cell.

Table 3.1 – Heat transferred to fluid (PTF) and hydrogen equivalent power (PE H₂).

Velocidade espace [h ⁻¹]	Shiftmax 230		Cu/ZnO 1:1 SiO ₂		100%CuAl ₂ O ₃ 3 mm		100%CuAl ₂ O ₃ 1,5 mm	
	PTF [W]	PE H ₂ [W]	PTF [W]	PE H ₂ [W]	PTF [W]	PE [W]	PTF [W]	PE [W]
675	1,40	6,39	1,40	2,60	3,00	8,80	2,20	8,47
1781	9,30	33,32	7,10	5,70	4,00	14,06	6,00	16,64
3958	22,50	81,39	19,00	14,10	10,00	18,84	NA	NA
8203	49,30	148,40	38,70	8,70	21,00	17,17	NA	NA
17037	115,60	406,76	80,60	3,44	25,60	5,75	NA	NA



Table 3.1 shows Shiftmax as leading in hydrogen equivalent power production and also heat transferred to the fluid, since the mechanism is an endothermic one, the more hydrogen produced, the more heat the reaction needs. Even if methanol conversion is under 100% the hydrogen production can be high if the methanol/water flow is high enough, that is the case of SiO₂ 50% Cu/ZnO 1mm where at 3958 h⁻¹ there is less conversion than at 1781 h⁻¹.

4 – Conclusions

The catalytic formulations developed at the lab revealed to fall short in terms of activity and selectivity towards the formation of CO₂ when compared to the commercial Sud Chemie Shiftmax 230, even though the latter contains approximately 6 to 7 times the amount of active material.

New formulations have to be developed in future work to compare with Shiftmax 230.

The thermal profiles were as expected, showing higher heat transferred to the fluid in the case of Shiftmax 230, meaning the more hydrogen is generated, the more heat the mechanism needs.

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