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# Study of the Suitability of a Pt-Based Catalyst for the Upgrading of a Biomass Gasification Syngas Stream via the WGS Reaction

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**Abstract** In this article, the catalytic activity of a Pt-based water gas shift (WGS) catalyst is presented. The experimental study has been conducted under realistic conditions typical of pressurised oxygen gasification. The effect of temperature, space velocity, steam to carbon monoxide ratio, and gas composition on the performance of the catalyst is investigated. Despite the high CO content in the feed gas, ranging from 32% to 60% v/v, dry basis, the catalyst has shown very good performance at intermediate temperature, 300–450 °C. Carbon monoxide concentration at the reactor outlet reached values below 3% what is comparable with conventional high-temperature, first-stage WGS catalysts.

**Keywords** WGS · Pt-catalyst · Gasification · $H_2$ enrichment

## 1 Introduction

Lately, production of hydrogen or a hydrogen-rich gas from renewable sources such as biomass has attracted a lot of interest [1]. Two types of processes can be used for the conversion of biomass to hydrogen: thermo chemical or biochemical processes [2]. Among the thermo chemical processes, gasification can be considered as the most efficient and with the highest $H_2$-production capacity nowadays [3]. Gasification of biomass produces a gas which consists of $H_2$, CO, $CO_2$, $H_2O$, $CH_4$ and other hydrocarbons. One of the most advanced facilities to demonstrate biomass gasification at a relevant scale is the Vaxjo Varnamo Biomass Gasification Centre (VVBGC) in Sweden which has a biomass-fuelled pressure IGCC (integrated gasification combined-cycle) CHP (combined heat and power) demonstration facility, with a capacity of 18 MwTh., which is being rebuilt under the scope of the CHRISGAS project [4]. The aim of the project is to demonstrate, within a 5-year period, the production of a clean hydrogen-rich synthesis gas (syngas) based on steam/oxygen-blown gasification of biomass, followed by gas cleaning and upgrading.

Depending on the desired final application of the syngas obtained from the gasifier—synthesis of fuels, chemicals—the $H_2$ to CO ratio in the gas stream has to be adjusted. The most preferred method to do it is the water gas shift (WGS) reaction. In the WGS process, water reacts with carbon monoxide to yield hydrogen and carbon dioxide. This reaction is mildly exothermic and without a catalyst it requires operating temperatures higher than 650 °C. At high-temperatures (above 300 °C) the conversion is equilibrium limited, and at low-temperatures the reaction is kinetically limited. In order to lower the temperature, the reaction is aided by the use of catalysts. In industry it has traditionally carried out in two stages, one high-temperature shift (iron–chrome-based catalyst) and one low-temperature shift (copper–zinc-based). In the two-stage approach, excess steam is usually required to achieve high CO conversion and to avoid secondary reactions. Moreover, the use of a Fe–Cr and Cu–ZnO combination is not always suitable, especially in those applications where fast start-ups require a low catalyst volume and the use of non-pyrophoric catalysts, as, e.g. in fuel cells [5]. Besides its pyrophoric nature, some other reported drawbacks of the

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Cu–ZnO catalyst include its tendency to sintering and its high susceptibility to poisoning [6]. Regarding Fe–Cr catalysts the main disadvantage is the environmental and safety problems related to chromium compounds [7]. In order to overcome these limitations, strong efforts are being devoted to the development of more active, non-pyrophoric and poison resistant catalysts. Among them, platinum-based WGS catalysts have recently become very attractive. Noble metal catalysts, and especially Pt/$CeO_2$, have been reported as being good for low-temperature WGS reaction [8, 9]. Moreover, Haryanto et al. [10] found that Pt–$CeO_2$/$Al_2O_3$ catalysts in their unreduced form were active at ultrahigh temperature, and could be integrated downstream a biomass gasifier for syngas upgrading without the need of the gas stream to be cooled, i.e. in the 500–700 °C range. Very recently, Thinon et al. [11] have screened a number of WGS catalysts which consist of a metal deposited on a reducible support. In their study Pt/$CeO_2$/$Al_2O_3$, and Pt/$TiO_2$ were found to be the most active catalysts for the high temperature WGS. Pt catalysts supported on metal oxide carriers are reported to be bifunctional, i.e. both the metal and support have a significant influence on the overall catalytic performance [12].

Zirconium oxide has extensively been studied in recent years as catalyst and as support, due to its chemical and physical properties. For WGS reaction, zirconia-supported platinum catalysts emerge as an attractive catalyst, with the advantage of being non-toxic. Querino et al. [13] highlighted the beneficial effect of incorporating zirconia as a support to platinum–ceria catalysts. In their work it is claimed that Pt–ceria catalyst supported on zirconia can be a promising candidate for the WGS reaction to be carried out in just one stage at an intermediate temperature (medium temperature shift reaction). They also propose to dope the zirconium support with other metals to improve the specific surface area and the metal interaction. Among the systems studied, they found that the platinum–ceria–zirconia system resulted to be the most active for the WGS reaction. More recently, Fonseca at al. [14] have also compared Au- and Pt–ceria–zirconia catalysts finding that, though both are active for WGS reaction, the Au-based catalyst provides slightly better results. On the other hand, other authors who have investigated Pt–$CeO_2$–$ZrO_2$ catalysts claim that in spite of having high initial activity they are also susceptible to a high initial rate of deactivation [15]. CO is concluded to be the gas species with the highest impact on the rate of deactivation, but it can be counteracted by the presence of water [16].

Based on the above background, the objective of this work is to study the catalytic activity of a Pt–ceria–zirconia catalyst for bulk WGS reaction, i.e. in just one step at an intermediate temperature.

## 2 Experimental

### 2.1 Catalyst

The catalyst studied in this work was prepared and provided by CATATOR AB (Sweden). The manufacturing procedure as well as the characterisation is published in detail elsewhere [15, 16]. The catalyst consists of a support of $CeO_2$/$ZrO_2$ ($CeO_2$ to $ZrO_2$ ratio in the slurry of around 1.4) impregnated with the active phase, platinum. After calcination, the final catalyst contains 4.2% Pt. The catalyst was supplied impregnated on 240 mm × 295 mm rectangular wire mesh substrates following a procedure patented by CATATOR [17]. For testing, the catalyst was cut in circular pieces of 8 mm diameter and strung together to be fitted in the tubular reactor used in the experiments, as shown in Fig. 1.

The volume of catalyst used for the experimental trials was 1.3 and 6.21 $cm^3$, depending on the experiment to perform.

### 2.2 Experimental Unit

Catalyst testing was carried out in a Microactivity Pro Unit, whose flowsheet diagram can be seen in Fig. 2. It is an automatic and computerised laboratory rig for the study of catalytic reactions. The maximum operating gas flow rate is 4.5 NL/min. The unit can work at up to 700 °C and 30 bar.

The gas mixture was produced synthetically using mass flow controllers (Hi-Tech). Deionized water was metered by a piston pump (Gilson 307) and vaporised before entering the reactor. Dry gas and water were preheated separately, in two independent loops. To this aim the entire set-up was housed in a forced air circulation oven maintained at 190 °C. Dry gas and steam were then mixed before entering the reactor. A stainless steel tubular reactor manufactured by Autoclave Engineers was used for catalytic testing. It has an internal diameter of 9.2 mm, and it is 300 mm long. The reactor is placed in a one single zone SS304 oven, which is able to heat the reactor up to 700 °C. Gas temperature in the reactor is measured by a 1.5 mm thermocouple, directly in the catalyst bed. The reactor can be passed by and isolated—for instance to analyse the inlet gas composition—by means of a six-way valve that connects reactor inlet and outlet. For the WGS tests presented in this work, the reactor was operated in fixed-bed, downflow mode. In a typical run the reactor was pressurised to the operating pressure, and heated to the desired temperature under flow of nitrogen. When the desired temperature was attained, the nitrogen flow was stopped, and the simulated gasification gas flow was started.

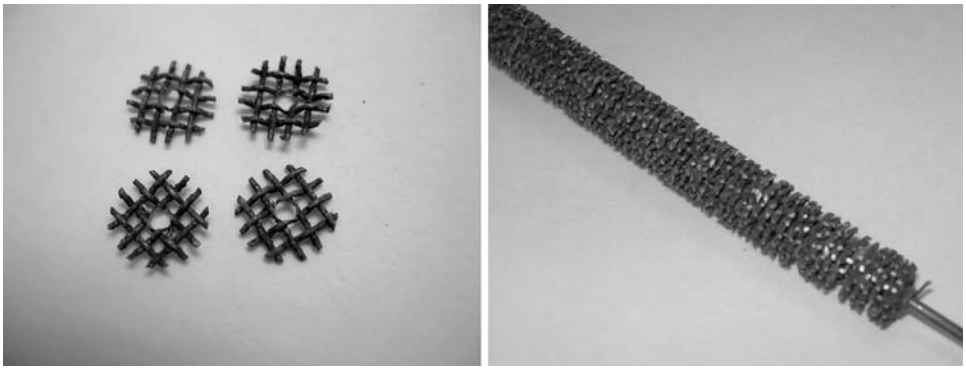

**Fig. 1** Pictures of the Pt-based catalyst used for testing (left cut to fit in the reactor and right final configuration ready to be loaded into the reactor)

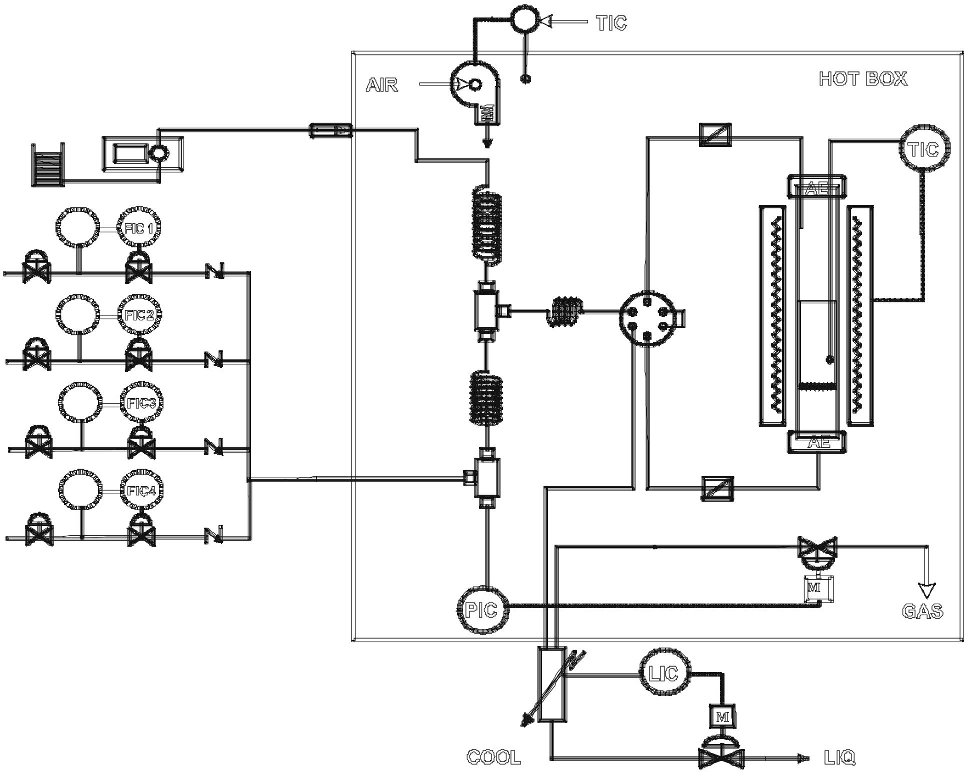

**Fig. 2** Flowsheet of the experimental unit

Inlet and outlet gas composition were analysed using a 5890 Series II Hewlett-Packard gas chromatograph equipped with a thermal conductivity detector (TCD). Two packed 530 μm columns—a 6 Ft Porapak Q, 80/100 19001A-00 and a 6 Ft Molecular Sieve 5 Å 60/80 19001A-MA2—connected in series were used to provide good gas components separation. A specific software (HP Chemstation A.6.03) was used for controlling the gas chromatograph and to analyse GC data.

## 2.3 Experimental Tests

WGS tests were performed using three different gas compositions as shown in Table 1, a binary mixture of CO in $N_2$ (B) and two gas mixtures whose composition is close to the gas composition expected at the WGS unit inlet in Värnamo GICC (M1 and M2). These latter two gas compositions were estimated based on the assumptions that the gasifier at Värnamo will operate at 900 °C (±50 °C) and with 0.4 kg oxygen/kg biomass, and 0.2 kg steam/kg syngas (M1) or 0.6 kg steam/kg syngas (M2) will be used in the steam reformer.

**Table 1** Gas composition for the experimental programme (dry basis)

| Component | B | M1 | M2 |
|---|---|---|---|
| $H_2$ | – | 40 | 45 |
| CO | 60 | 44 | 32 |
| $CO_2$ | – | 15 | 22.5 |
| $CH_4$ | – | 1 | 0.5 |
| $N_2$ | 40 | – | – |

**Table 2** Summary of tests conditions

| Test | Gas composition | $H_2O/CO$ | GHSV ($h^{-1}$) |
|---|---|---|---|
| 1 | M1 | 2 | 10,000 |
| 2 | M1 | 6.7 | 10,000 |
| 3 | M1 | 6.7 | 20,000 |
| 4 | M1 | 6.7 | 2,885 |
| 5 | B | 6.7 | 10,000 |
| 6 | M2 | 6.7 | 10,000 |

The experimental programme included the tests presented in Table 2. All the tests were performed at 10 bar which is the operating pressure in the Värnamo GICC plant. Catalytic performance has been investigated in the temperature range of 200–450 °C using simplified mixtures as well as under more realistic conditions, using the feed streams summarised in Table 1. The study has included the evaluation of the effect of space velocity, ranging from 2,885 to 20,000 $h^{-1}$, steam to CO ratio (2 and 6.7) and gas composition on the performance of the catalyst. Space velocity was estimated as the ratio of gas flow rate (wet basis) at standard conditions to catalyst volume. The space velocity range chosen for the experiments was dictated by the characteristics of the test rig, gas flow rate, and water flow rate that could be fed into the test rig based on the MFCs span and water pump capacity, and the amount of catalyst which could physically be loaded in the reactor.

In a typical experiment, the required volume of catalyst was placed in the reactor and heated until reaching the reaction temperature under flow of $N_2$. Then gas flow was switched to the dry gas reaction mixture, and steam was added. Gas compositions at the reactor inlet and outlet were measured by GC and the results compared and analysed. For each temperature, usually five to seven measurements of gas composition at the reactor outlet were taken under steady state conditions which means that the catalytic performance of the catalyst at every temperature was evaluated for 60–90 min. Given the fact that five to six temperatures were investigated for every single test, the total duration of each catalytic test was 240–540 min.

The catalytic activity of the WGS catalyst was expressed as the percentage of CO converted (mol%) $X_{CO}$ calculated according to (1),

$$x_{CO}(\%) = \frac{(F_{CO})_{in} - (F_{CO})_{out}}{(F_{CO})_{in}} \times 100 \tag{1}$$

where $(F_{CO})_{in}$, and $(F_{CO})_{out}$ are the molar flow rate of carbon monoxide at the reactor inlet and outlet, respectively. This way of expressing the catalytic activity of a catalyst is widely used.

To see how effective the catalyst is, it is important to look not only at the conversion of carbon monoxide but also at the amount of $H_2$ and $CO_2$ formed, which is known as the yield to hydrogen and carbon dioxide, i.e. at how selective the catalyst is to promote the WGS reaction. The yield to hydrogen and carbon dioxide $y_{H_2}$, $y_{CO_2}$, were calculated according to (2) and (3), similar to the expressions found in the work of Thinon et al. [11],

$$y_{H_2}(\%) = \frac{(F_{H_2})_{out} - (F_{H_2})_{in}}{(F_{CO})_{in}} \times 100 \tag{2}$$

$$y_{CO_2}(\%) = \frac{(F_{CO_2})_{out} - (F_{CO_2})_{in}}{(F_{CO})_{in}} \times 100 \tag{3}$$

being $(F_{H_2})_{out}$ and $(F_{H_2})_{in}$, the molar flow rate of hydrogen at the reactor outlet and inlet, and similarly $(F_{CO_2})_{out}$ and $(F_{CO_2})_{in}$ the carbon dioxide flow rate at the reactor outlet and reactor inlet.

## 3 Results and Discussion

### 3.1 Catalyst Performance Evaluation

The catalytic activity has been studied in terms of CO conversion and $H_2$ and $CO_2$ formation, i.e. selectivity of the catalyst to promote exclusively the WGS reaction. The study has included the evaluation of the effect of gas space velocity, steam to carbon monoxide ratio, and feed gas composition on the performance of the catalyst.

It is well known that in addition to the WGS reaction, in a gas system containing CO, $CO_2$, $H_2O$, and $H_2$, a number of side reactions may occur, which would consume CO, $H_2$, and $CO_2$ and which would therefore alter the selectivity. Among them, the following side reactions might take place:

$$CO + H_2O \leftrightarrow H_2 + CO_2, \text{WGS desired reaction} \tag{i}$$

$$2CO \leftrightarrow C + CO_2 \tag{ii}$$

$$CO + H_2 \leftrightarrow C + H_2O \tag{iii}$$

$$CO_2 + 2H_2 \leftrightarrow C + 2H_2O \tag{iv}$$

$$2CO + 2H_2 \leftrightarrow CO_2 + CH_4 \tag{v}$$

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \tag{vi}$$

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O \tag{vii}$$

$$C + 2H_2 \leftrightarrow CH_4 \tag{viii}$$

It is commonly acknowledged that some of the above side reactions may become important, especially the Bouduoard reaction [reaction (ii)] and the formation of methane through reactions (v) and (vi) if hydrogen is present, when the $H_2O/CO$ ratio ($R$) is low, usually $R \leq 2$, producing undesired products such as carbon and/or methane. In these reactions, carbon and methane can be formed either as final products or they can take part in further reactions. The extent to which these reactions proceed depends greatly on the catalyst system used, the reaction conditions and the kinetics of each reaction. According to thermodynamic calculations of the equilibrium composition with various ratios of $H_2O/CO/H_2$ in the feed gas [18], the formation of carbon would be favoured at low-temperature, particularly at low $H_2O$ to CO ratio. When this ratio, $R > 2$ carbon will not exist in the equilibrium mixtures when the reaction temperature is higher than 230 °C. When $R = 1$, the formation of carbon becomes thermodynamically favoured over the entire temperature range of interest for WGS, 200–500 °C. The effect of the feed gas composition on the formation of methane is more complicated. In general, whenever $R < 3$, methane can exist in the equilibrium composition over the whole practical temperature range in which the WGS is conducted. Nevertheless the examination based on the thermodynamic calculation is only an indication of the possibility of the formation of C and $CH_4$ in such a system if the thermodynamic equilibrium is reached. The extent to which these side reactions actually proceed will depend on the kinetics of each reaction for the catalyst used.

Tables 3–5 show the gas composition at the reactor outlet for the different operating conditions investigated. It is important to point out that the catalyst started to show activity around 220–280 °C, depending on the particular experimental conditions and that the catalyst did not require any activation. This is in perfect agreement with the observations made by others authors working with Pt catalysts supported on zirconia [14] or with different supports, e.g. alumina [19, 20], and contrary to the results of Haryanto et al. [10] who reported that the system $Pt/CeO_2/Al_2O_3$ did not show any activity for the WGS reaction at 300 °C. Maximum temperature at which the activity of the catalyst towards WGS reaction begins to decline also depends on the operating conditions. For instance, looking at Table 3, WGS activity started to decline at 380 °C when GHSV = 2,885 $h^{-1}$ and $T = 470$ °C for GHSV = 20,000 $h^{-1}$. Tests were performed until WGS started to decline and therefore temperature range shown in Tables 3–5 is different depending on the value of the other parameters. Furthermore, for the study presented here, the catalyst did not suffer any sign of initial deactivation due to carbon monoxide as reported elsewhere [15, 16], probably because our tests were carried out in presence of steam in excess. For all tests, equilibrium conversion was almost reached.

**Table 3** Gas composition at the reactor outlet for different gas hourly space velocities ($H_2O/CO = 6.7$, $P = 10$ bar, gas composition M1)

| GHSV ($h^{-1}$) | $T$ (°C) | $H_2$ | $CO_2$ | CO | $CH_4$ |
|---|---|---|---|---|---|
| 2,885 | 200 | 40.54 | 16.46 | 41.96 | 1.04 |
| | 250 | 42.92 | 19.64 | 36.41 | 1.00 |
| | 300 | 54.33 | 34.39 | 10.44 | 0.83 |
| | 350 | 58.49 | 40.39 | 0.34 | 0.78 |
| | 380 | 58.36 | 40.17 | 0.67 | 0.80 |
| 10,000 | 200 | 41.49 | 15.30 | 42.25 | 0.95 |
| | 270 | 42.54 | 16.56 | 39.97 | 0.92 |
| | 350 | 56.58 | 34.56 | 8.13 | 0.72 |
| | 380 | 59.47 | 38.30 | 1.52 | 0.70 |
| | 410 | 58.64 | 38.77 | 1.91 | 0.67 |
| 20,000 | 300 | 42.32 | 15.56 | 40.62 | 0.94 |
| | 350 | 50.73 | 26.83 | 21.63 | 0.81 |
| | 380 | 56.33 | 33.69 | 9.24 | 0.73 |
| | 410 | 58.52 | 36.80 | 3.96 | 0.71 |
| | 440 | 59.18 | 37.83 | 2.27 | 0.71 |
| | 470 | 59.00 | 37.72 | 2.58 | 0.69 |

**Table 4** Gas composition at the reactor outlet for different $H_2O/CO$ ratios (GHSV = 10,000 $h^{-1}$, $P = 10$ bar, gas composition M1)

| $R$ ($H_2O/CO$) | $T$ (°C) | $H_2$ | $CO_2$ | CO | $CH_4$ |
|---|---|---|---|---|---|
| 2 | 300 | 43.92 | 17.81 | 37.20 | 1.02 |
| | 350 | 48.41 | 25.50 | 25.22 | 0.87 |
| | 380 | 54.49 | 33.89 | 10.85 | 0.77 |
| | 410 | 56.02 | 36.55 | 6.70 | 0.74 |
| | 440 | 55.01 | 35.61 | 8.59 | 0.80 |
| 6.7 | 200 | 41.49 | 15.30 | 42.25 | 0.95 |
| | 270 | 42.54 | 16.56 | 39.97 | 0.92 |
| | 350 | 56.58 | 34.56 | 8.13 | 0.72 |
| | 380 | 59.47 | 38.30 | 1.52 | 0.70 |
| | 410 | 58.64 | 38.77 | 1.91 | 0.67 |

**Table 5** Gas composition at the reactor outlet for different feed gases (GHSV = 10,000 $h^{-1}$, $H_2O/CO = 6.7$, $P = 10$ bar)

| Gas mixture | $T$ (°C) | $H_2$ | $CO_2$ | CO | $CH_4$ | $N_2$ |
|---|---|---|---|---|---|---|
| B | 250 | 4.11 | 2.18 | 55.29 | – | 38.40 |
| | 300 | 11.03 | 10.04 | 40.62 | – | 38.29 |
| | 350 | 29.98 | 29.41 | 11.34 | – | 29.26 |
| | 380 | 36.91 | 35.74 | 1.25 | – | 26.09 |
| | 410 | 37.17 | 36.13 | 0.98 | – | 25.71 |
| M1 | 200 | 41.49 | 15.30 | 42.25 | 0.95 | – |
| | 270 | 42.54 | 16.56 | 39.97 | 0.92 | – |
| | 350 | 56.58 | 34.56 | 8.13 | 0.72 | – |
| | 380 | 59.47 | 38.30 | 1.52 | 0.70 | – |
| | 410 | 58.64 | 38.77 | 1.91 | 0.67 | – |
| M2 | 300 | 48.72 | 26.02 | 23.86 | 0.62 | – |
| | 350 | 55.70 | 35.19 | 8.60 | 0.51 | – |
| | 380 | 58.12 | 38.62 | 3.01 | 0.26 | – |
| | 410 | 58.23 | 39.08 | 2.61 | 0.15 | – |

Regarding the presence of side reactions it has to be highlighted that no secondary reactions were detected,

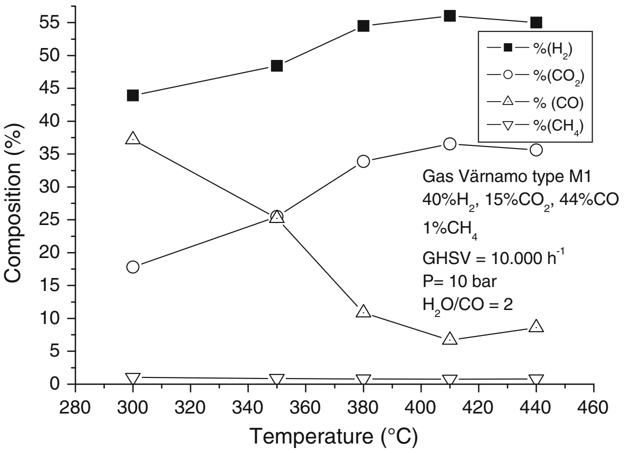

**Fig. 3** Gas composition evolution due to WGS as a function of temperature (Feed gas: 40% $H_2$, 15% $CO_2$, 44% CO, 1% $CH_4$, $P = 10$ bar, GHSV = 10,000 $h^{-1}$, $H_2O/CO = 2$)

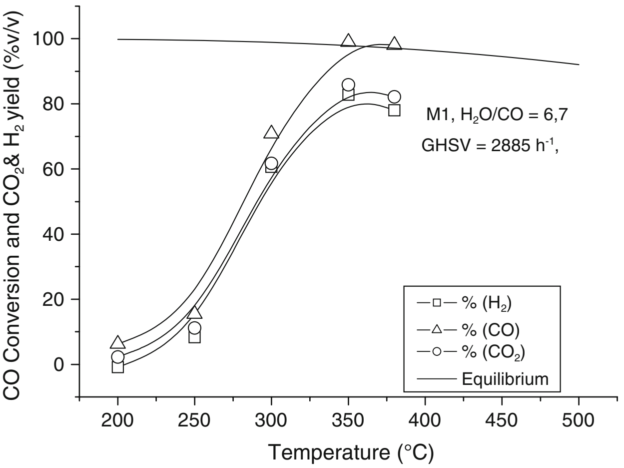

**Fig. 4** CO conversion and yield to $H_2$ and $CO_2$ (Feed gas, dry basis: 40% $H_2$, 15% $CO_2$, 44% CO, 1% $CH_4$, 10 bar, GHSV = 2,885 $h^{-1}$, $H_2O/CO = 6.7$)

except for some experiments which are further discussed below. Apart from the feed gas components no other species were quantitatively detected and measured by the gas chromatograph. Similarly, the catalyst did not show any signs of carbon deposition, nor did the lines downstream the reactor. As can be seen in Fig. 3, where the gas composition profile at the reactor outlet for a selected run is plotted against temperature, as expected, there is a decrease in CO concentration, and an increase in $CO_2$ concentration and $H_2$ concentration as the WGS reaction proceeds. As for $CH_4$, its concentration decreases due to the overall increase in the gas mole number.

Looking at Fig. 3, one can also see how at the highest temperature evaluated, CO concentration begins to increase again, while $H_2$ and $CO_2$ concentration drop. This change in composition as WGS equilibrium was approached was found for all the tests as can be checked looking at the concentration of each species at the last temperature of each experiment in Tables 3–5. These results are in agreement with equilibrium predictions plotted for comparison later in the text, e.g. Fig. 4 and also with results published elsewhere [21] for which it is stated that the reverse water gas shift reaction (RWGS) can only be neglected when CO conversion is less than 95%. As in the studies reported in our work CO conversion reached values higher than 95%, the RWGS reaction might be one possible reason for the final drop in activity at the highest temperature tested in every catalytic run.

### 3.1.1 *Effect of Gas Space Velocity*

Gas space velocity was varied between 2,885 and 20,000 $h^{-1}$. This range of space velocities was set according to information provided by CATATOR AB, and to the gas flow rate and water flow rate which were attainable in the laboratory rig and also to the amount of catalyst that could be loaded in the reactor. As explained above, gas space velocity means the ratio of gas flow rate to the volume of catalyst used in a given test. In order to see how this parameter affected the performance of the catalyst, the other variables were kept at a constant value. That is, the catalytic performance was evaluated for a feed gas mixture representing the mixture denoted as M1—40% $H_2$, 15% $CO_2$, 44% CO, 1% $CH_4$% v/v, dry basis—with a steam to CO ratio $R = 6.7$ and the pressure of the system was controlled at 10 bar.

In Fig. 4 the conversion of CO and the yield to hydrogen and carbon dioxide is presented for the test carried out at 2,885 $h^{-1}$. The equilibrium curve is also depicted for comparison. As can be seen maximum carbon monoxide conversion (98.9%) was achieved at 350 °C. However, yield to hydrogen and carbon dioxide, especially as temperature increased was lower than CO conversion. This might indicate that side reactions could have been occurred, although to an extension below the analysis system sensitivity level, since no other gas species were detected by the GC.

Figure 5 presents CO conversion and yield to $H_2$ and $CO_2$, respectively, in the test conducted at 10,000 $h^{-1}$. The catalyst showed its best performance at 380 °C yielding a conversion of CO around 95.3%. In this test, as can be seen in Fig. 5, the catalytic activity was very selective to $H_2$ and CO, with yields close to the predicted values and in accordance with carbon monoxide consumption.

The conversion of CO, and the corresponding yields to $H_2$ and $CO_2$ for the test carried out at 20,000 $h^{-1}$ are presented in Fig. 6. The catalyst performed slightly worse at this space velocity since the maximum CO conversion was only 92.9% and it was reached when the temperature

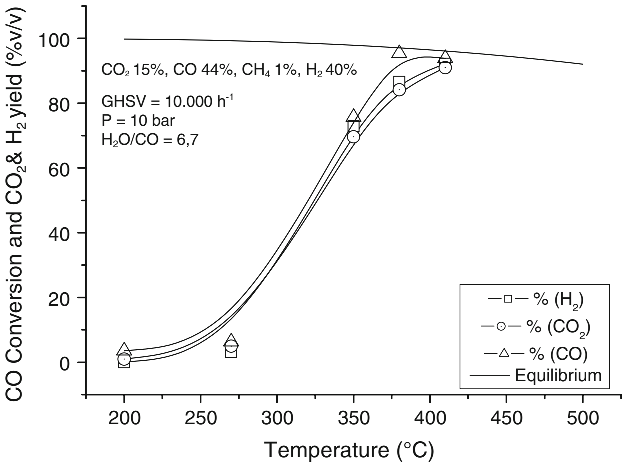

**Fig. 5** CO conversion and yield to $H_2$ and $CO_2$ (Feed gas, dry basis: 40% $H_2$, 15% $CO_2$, 44% CO, 1% $CH_4$, 10 bar, GHSV = 10,000 $h^{-1}$, $H_2O/CO = 6.7$)

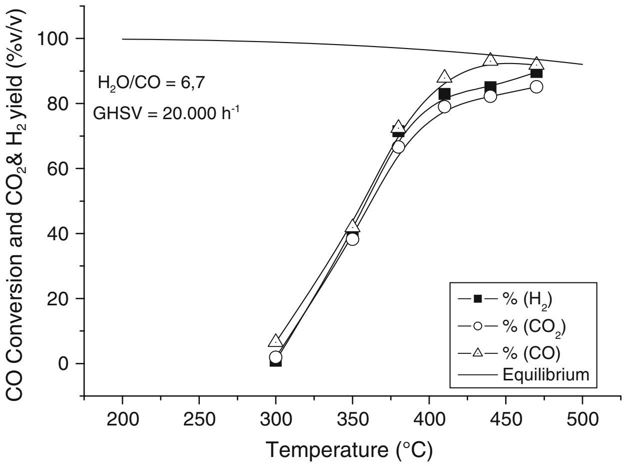

**Fig. 6** CO conversion and yield to $H_2$ and $CO_2$ (Feed gas dry basis: 40% $H_2$, 15% $CO_2$, 44% CO, 1% $CH_4$, 10 bar, GHSV = 20,000 $h^{-1}$, $H_2O/CO = 6.7$)

was set at 440 °C. Selectivity, however, was very good as can be seen in Fig. 6, and the yield to hydrogen and carbon dioxide matched up with the conversion of CO.

The overall effect of gas space velocity on the performance of the catalyst can be seen in Fig. 7, where the conversion of CO has been depicted for the three values of GHSV tested. Equilibrium curve is included for comparison. As was expected, the CO conversion increased as the contact time, i.e. space time, increased, i.e. as gas space velocity decreased. Furthermore it has been found that an increase of gas space velocity leads to a displacement in the CO conversion curve. In order for the catalyst to achieve a given conversion of CO it is necessary to shift to higher temperatures as gas space velocity increases. Moreover, higher values of gas space velocity result in worse performance of the catalyst. At low gas space

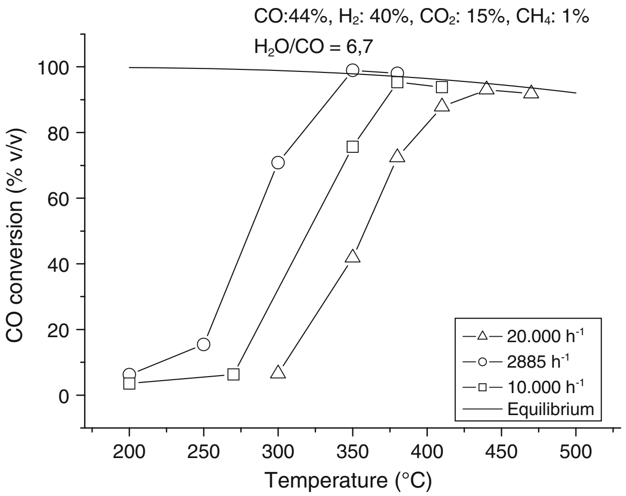

**Fig. 7** Effect of GHSV on CO conversion (Feed gas: 40% $H_2$, 15% $CO_2$, 44% CO, 1% $CH_4$, $P = 10$ bar, $H_2O/CO = 6.7$)

velocity, however, side reactions might also be fostered by the presence of the catalyst or by the gas mixture itself. Therefore, in order to implement this catalytic system, the intermediate gas space velocity tested in this work seems to be more appropriate in order to combine good performance at moderate temperatures and in the absence of secondary reactions. In spite of the good catalyst performance to promote in a selective way the WGS reaction, the study of the effect of GHSV on the catalytic activity of the Pt–$CeO_2$–$ZrO_2$ system also shows that in all cases maximum CO conversion is limited by equilibrium predictions.

### 3.1.2 *Effect of Steam to Carbon Monoxide Ratio*

It is known that the WGS reaction is thermodynamically unfavourable at elevated temperatures. In order to achieve high conversion, excess steam can be used to drive the reaction thermodynamically. The steam to carbon monoxide ratio in the feed, $R$, is therefore usually higher than that actually required by the reaction stoichiometry ($R = 1$) though the energy efficiency of the process is consequently lower.

To study the dependence of the activity of the catalyst on the concentration of water vapour, two $H_2O$ to CO ratios ($R$) were studied. The effect of the $H_2O$ to CO ratio on the catalytic performance of the Pt–$CeO_2$–$ZrO_2$ system was evaluated at 10 bar of pressure for the gas mixture designated as M1. For this study, gas hourly space velocity was set at 10,000 $h^{-1}$ taking into account that it had provided the best results during the study of the effect of gas hourly space velocity on the performance of the platinum catalyst.

Figure 8 shows the CO conversion curve as a function of temperature for the test conducted at a $H_2O/CO = 2$ ratio. The catalyst hardly showed any WGS catalytic activity at low-temperature, 300 °C as can be seen looking at Table 4, and Fig. 3. Maximum activity was achieved at 410 °C rendering approximately 78.7% CO conversion. Moreover, when the temperature was further raised, although the CO conversion levelled off, the selectivity towards hydrogen and carbon dioxide fell as the yield to $H_2$ and $CO_2$ in Fig. 8 shows. This drop in selectivity was accompanied by methane formation, which is a suggestion that side reactions begun to occur for that $H_2O$/CO ratio.

CO conversion and $H_2$ and $CO_2$ yield curves for the high $H_2O$/CO test ($R = 6.7$) are presented in Fig. 6 and experimental composition data are shown in Table 4. In the temperature range studied, the WGS reaction was produced selectively and close to thermodynamic conversion data were obtained.

When comparing the performance of the Pt–$CeO_2$–$ZrO_2$ catalytic system at low and high water to carbon monoxide ratio it is clearly seen in Fig. 9 that the catalyst was substantially more active when more steam was added to the feed gas. Besides this enhanced performance, the rise in the $H_2O$/CO ratio shifts the conversion curves to lower temperatures, what in turn makes possible to achieve, at a given temperature, higher CO conversion to $H_2$ and $CO_2$, and more selectively. Comparing the conversion curves in Fig. 9, it is readily seen that for a $H_2O/CO = 2$ ratio, the maximum CO conversion resulted to be 78.7% and it was achieved at 440 °C, and when the ratio of $H_2O$ to CO was increased to 6.7, the conversion of carbon monoxide reached 95.3% and it was attained at a lower temperature, 380 °C.

The activity of the Pt/$CeO_2$/$ZrO_2$ catalyst studied in our work thus depends strongly on the amount of steam available during the reaction, and it has been found that the excess of steam drives the reaction to the production of hydrogen. The high dependence of the activity of the ceria–zirconia supported platinum on the steam to carbon monoxide ratio is in agreement with the results reported in other works [8, 13, 22]. The positive effect of excess steam is consistent with the general acknowledged reaction path in which the promoting effect of water vapour on $CeO_2$ is explained as the oxidation of the $CeO_2$ support by water [23]. According to this mechanism, the CO molecules adsorbed on the metal would be oxidised by oxygen originating from the support which in turn would be oxidised by water. An excess $H_2O$/CO ratio would clearly allow the re-oxidation of the support more easily. Moreover, for the other prevailing explanation found in literature to describe the WGS reaction mechanism, which is based on the formation of intermediate surface formates [24, 25], a high $H_2O$ to CO ratio has similarly been reported to be beneficial for the WGS reaction, since it accelerates the forward decomposition of surface formates [26]. The experimental data gathered in this study prove that the excess of steam is advantageous to shift the forward WGS reaction independently of the reaction mechanism, whose discussion is beyond the scope of our work.

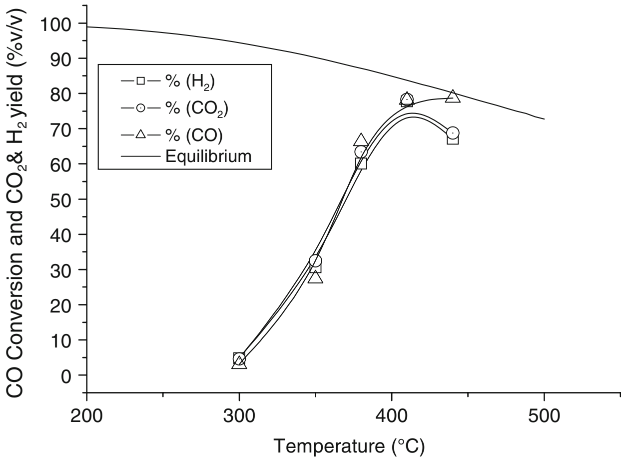

**Fig. 8** CO conversion and yield to $H_2$ and $CO_2$ (Feed gas, dry basis: 40% $H_2$, 15% $CO_2$, 44% CO, 1% $CH_4$, 10 bar, GHSV = 10,000 $h^{-1}$, $H_2O/CO = 2$)

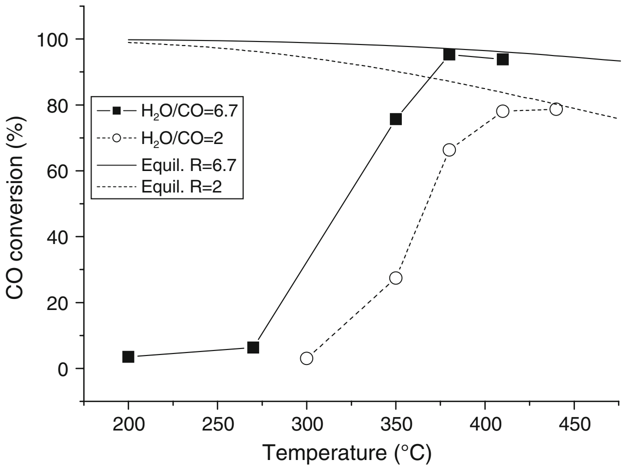

**Fig. 9** Effect of $H_2O$/CO ratio on CO conversion (Feed gas dry basis: 40% $H_2$, 15% $CO_2$, 44% CO, 1% $CH_4$, $P = 10$ bar, GHSV = 10,000 $h^{-1}$)

### 3.1.3 *Effect of Gas Composition*

To study the effect of the gas composition on the performance of the Pt-based catalyst, results using a simplified feed gas consisting of 60% CO in $N_2$—gas B in Table 1—have been compared with the catalytic performance of the catalyst under more realistic feed compositions, i.e. for a gas mixture consisting of 40% $H_2$, 44% CO, 15% $CO_2$, and 1% $CH_4$—mixture M1, dry basis—and for a gas mixture made of 45% $H_2$, 32% CO, 22.5% $CO_2$, and 0.5% $CH_4$—mixture M2, dry basis—which represent the expected gas composition downstream the steam reformer in the oxygen pressurised gasification plant in Värnamo (Sweden).

It is worth noting that, according to research works found in literature, Pt-based catalysts have been used almost exclusively for the second WGS stage at low-temperature, i.e. for gases with low CO content, typically less than 3% v/v. Based on the reaction mechanism proposed by Holmgren for $Pt/CeO_2$ catalysts [23], CO reacts with OH groups released by the oxidation of the ceria support by water. For $Pt/CeO_2$ catalysts supported on alumina, a decrease of WGS activity has been reported due to the poisoning effect of CO on Pt sites [8]. In our work, despite the high CO content in the feed gas, ranging from 32% to 60% v/v, dry basis, the catalyst showed very good performance. In other research works using the same $Pt/CeO_2/ZrO_2$ catalytic system to which we present results in this investigation, some initial deactivation due to CO was observed by Häggblad et al. [16], but as they propose in their steam treatment regeneration studies, it can be minimised increasing the water/CO ratio, as we have observed in our study. Working with a high $H_2O$ to CO ratio, $R > 2$, the measured WGS activity in every single test was fairly stable over the whole run, which can be considered as an indication that the catalyst is not suffering deactivation.

Figure 10 compares CO concentration profile at the reactor outlet as a function of temperature for the different feed gases studied. Despite the fact that the CO content in the feed gas varies considerably—CO (mixture B) = 60% v/v, CO (mixture M1) = 44% v/v, and CO (mixture M2) = 23% v/v—the final concentration of CO attained at the reactor outlet is approximately the same. For the three gas mixtures studied, when temperature reaches 350 °C, the gas leaving the WGS reactor gets to similar CO content.

The catalytic CO conversion curve obtained when the WGS reaction was conducted at 10,000 $h^{-1}$ for the simplified binary feed gas (60% CO, 40% $N_2$) using a $H_2O/CO$ ratio $R = 6.7$ is illustrated in Fig. 11. The yield to $H_2$ and $CO_2$ are also included. Maximum CO conversion was 97.4% at 410 °C. The figure shows that the reaction occurred very selectively and consequently the values of $H_2$ and $CO_2$ yields are very close to the conversion of CO.

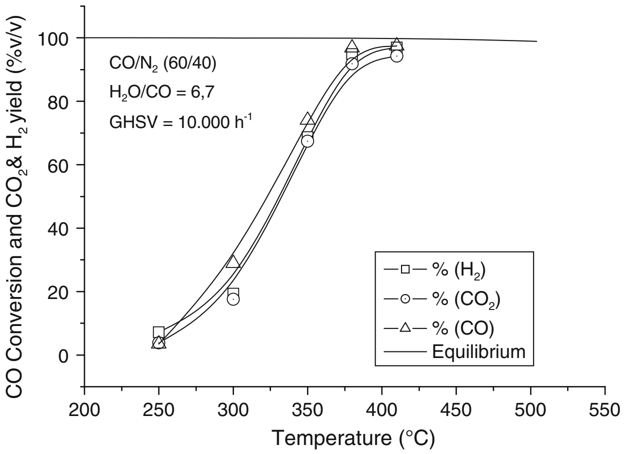

**Fig. 11** CO conversion and yield to $H_2$ and $CO_2$ (Feed gas dry basis CO 60% v/v, $N_2$ 40% v/v, 10 bar, GHSV = 10,000 $h^{-1}$, $H_2O/CO$ = 6.7)

In Fig. 12 the same curves have been plotted for the mixture M2. Compared to the feed gas designated as M1, whose results are displayed in Fig. 5, the M2 mixture has higher $CO_2$ and $H_2$ content. For the mixture M2 the presence of reaction products apparently limited a little bit the extent to which the WGS reaction progressed, as the results drawn in Fig. 12 suggest. The performance of the Pt catalyst was worse for this M2 mixture, with a maximum CO conversion of 89% at 410 °C. The reaction, however, progressed very selectively.

The overall effect of gas composition on the performance of the catalyst is illustrated in Fig. 13. Comparison of results obtained in the absence and in the presence of $H_2$ and $CO_2$ in the feed leads to the observation that the WGS

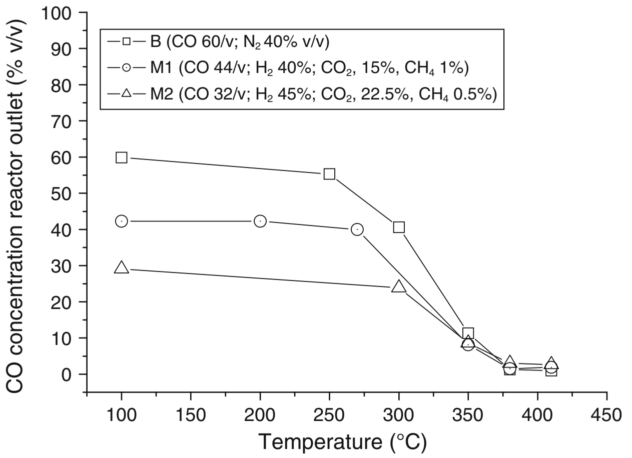

**Fig. 10** CO concentration profile at the reactor outlet due to WGS reaction over the Pt catalyst for different gas compositions. ($P$ = 10 bar, GHSV = 10,000 $h^{-1}$, $H_2O/CO$ = 6.7)

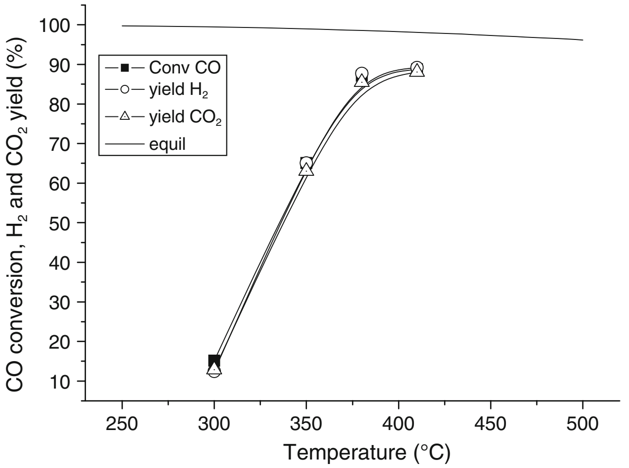

**Fig. 12** CO conversion and yield to $H_2$ and $CO_2$ (Feed gas M2, dry basis: 45% $H_2$, 22.5% $CO_2$, 32% CO, 0.5% $CH_4$, 10 bar, GHSV = 10,000 $h^{-1}$, $H_2O/CO$ = 6.7)

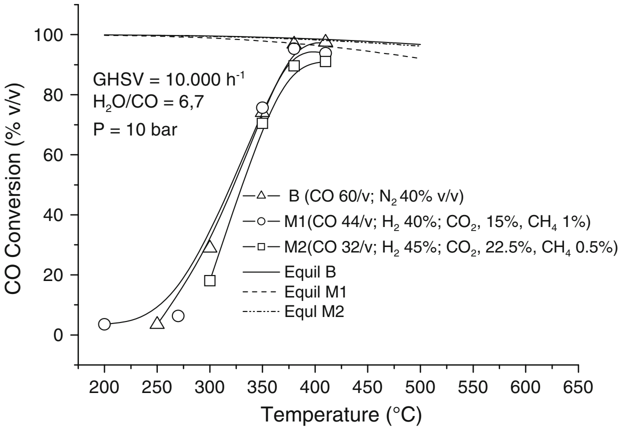

**Fig. 13** Effect of gas composition on CO conversion

activity is not significantly affected by the presence of reaction products in the feed. This finding is contrary to the results obtained by Panagiotopoulos et al. [12]. In their work, they found that the specific WGS reaction rate—expressed per gram of catalyst—of Pt/MO$_x$(CeO$_2$)/Al$_2$O$_3$ and Pt/MO$_x$(CeO$_2$)/TiO$_2$ catalysts, rCO (μmol$^{-1}$ g$^{-1}$), under realistic conditions (3% CO, 10% $H_2O$, 6% $CO_2$, 20% $H_2$, balance He) was largely affected by the presence of hydrogen and, to a lesser extent, carbon dioxide in the feed. Consequently the WGS activity of platinum catalysts was considerably lower that the activity when using a simplified gas composition conditions (3% CO, 10% $H_2O$, balance He). As in our work the presence of $H_2$ and $CO_2$ do not suppress the activity of the catalyst, this difference in behaviour might be attributed to a positive role of zirconia, since in the work of Panagiotopoulos et al. titania and alumina were used as support for the catalyst. We have also found that a higher content of CO in the feed apparently leads to a slightly higher CO conversion since CO content in the feed gas follows the order B > M1 > M2 and CO conversion increases accordingly. This fact makes the use of the Pt/CeO$_2$/ZrO$_2$ very promising as intermediate temperature WGS catalyst since in other research works where the effect of CO concentration on the catalytic activity of Pt/CeO$_2$ was studied [8], it had been claimed that in the 150–200 °C temperature range, CO conversion decreased with increasing CO concentration even at very low concentration of CO (0.5–2% v/v). On the other hand, as shown in Fig. 13, the presence of reaction products ($H_2$, $CO_2$) in the feed shifts the conversion curves of CO to slightly higher temperatures.

## 4 Conclusions

The catalytic activity of a Pt/CeO$_2$/ZrO$_2$ catalyst has been investigated using simulated gas under realistic conditions for intermediate temperature WGS reaction. Catalytic performance has been evaluated from 200 to 500 °C. Gas composition was chosen to mimic the expected gas composition at the reformer outlet in the 18 MWth biomass-fuelled, steam–oxygen pressurised IGCC demonstration plant located in Vaxjo Värnamo Biomass Gasification Centre (VVBGC) in Sweden. The pressure was kept at 10 bar, which is the process pressure in the demonstration plant.

Despite the high CO content in the feed gas, ranging from 32% to 60% v/v, dry basis, the catalyst has shown very good performance at intermediate temperature, 300–450 °C, showing potential for a first WGS stage. CO concentration at the reactor outlet reached values below 3%, what is comparable with conventional high-temperature, first-stage WGS catalysts. Equilibrium conversion was almost reached in all the tests carried out.

Higher values of space velocity lead to lower CO conversion and a higher temperature is required to achieve a given CO conversion. On the other hand, lower space velocities result in higher CO conversion at lower temperatures, though the yield to hydrogen and carbon dioxide is slightly worse.

The activity of the catalyst depends strongly on the amount of steam available during the reaction. In order for the reaction to proceed significantly an excess of steam is needed. A higher $H_2O$/CO ratio gives higher carbon monoxide conversion, and with better selectivity to the production of hydrogen. Besides this enhanced performance, the rise in the $H_2O$/CO ratio shifts the conversion curves to lower temperatures, what in turn makes possible to achieve, at a given temperature, higher CO conversion to $H_2$ and $CO_2$.

No significant differences have been found in the catalyst performance when using different feed gas compositions. A higher content of CO in the feed leads to a slightly higher CO conversion The WGS activity of the catalyst is not significantly affected by the presence of reaction products—$H_2$ and $CO_2$—in the feed, although their presence shifts the CO conversion curves to slightly higher temperatures.

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