Pilot plant scale hydrogen production from bioethanol: COPROX catalyst behavior

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Abstract

Hydrogen is recognized as a promising green energy source, particularly when used to feed a PEMFC (polymer electrolyte membrane fuel cell). In this work, it was obtained by bioethanol steam reforming with CO and CO_2 as primary sub products. Since cell anode is extremely sensitive to poisoning with CO, WGS (water gas shift) and COPROX (carbon oxide preferential oxidation) reactors are employed for hydrogen purification. Catalysts prepared by our lab were tested at pilot plant scale in both the reformer and COPROX, where different active phase distributions, stoichometric excess of air and reaction temperatures were tested. The use of two different COPROX units with intermediate air injection was also considered. Catalysts prepared showed good stability and performance.

Keywords: Bioethanol steam reforming, COPROX, Hydrogen, Pilot plant scale

1. Introduction

Hydrogen is a widely used gas in different industries such as chemical, metallurgic, pharmaceutics, electronics [1]; while its application as an energy source is yet under development. It can be used for both stationary and mobile energy generation, either in internal combustion engines or in fuel cells [2]. Hydrogen advantages as a fuel are:

High energy density per unit mass (120 MJ/Kg), greater than natural gas (50 MJ/kg) and naphtha (45 MJ/kg)

Its combustion generates scarce emissions, only NO_x that may be controlled by operation temperature

Its use in fuel cells only produce small amounts of water as sub product

Efficiency attained with fuel cells is greater than that of combustion engines since they are not limited by Carnot cycle

One disadvantage is its low energy density per unit volume since, if stored as a gas, voluminous tanks or high pressures are required. At the same time, hydrogen is not found isolated in nature so energy must be employed to obtain it. Regarding hydrogen production, industries obtain H_2 from the following sources: 48 % from natural gas, 30 % from oil, 18 % from carbon and 4 % from electrolysis. Therefore, 96 % of hydrogen production involves the use of fossils resources [3].

Hydrogen may only become an alternative and environmentally friendly energy source if it is obtained from equally green resources. One of the most studied processes to produce hydrogen is steam reforming of bio fuels such as bio ethanol or glycerol, the first one obtained by biomass fermentation and the second one as biodiesel sub product.

Biomass utilization to produce hydrogen is an interesting alternative from the environmental point of view since CO_2 produced during steam reforming is employed by biomass in its growth. In conclusion, the whole process may be considered as CO_2 neutral.

2. Technological aspects

2.1. Bio ethanol steam reforming
A possible way for hydrogen production is bio ethanol steam reforming which allows to obtain H_2 and CO_2 mainly, but also other sub products such as CO and CH_4.

$$C_2H_5OH + 3H_2O \rightarrow 6H_2 + 2CO_2 \quad \Delta H° = 173 KJ/mol \quad (1)$$
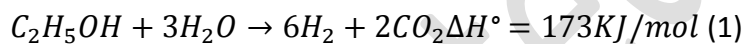
Equation 1. Bio ethanol steam reforming

This reaction is highly endothermic, so operation temperature is usually above 550 °C. Even though bio ethanol steam reforming may be simplified by Equation 1, the complete reaction scheme is far more complex, obtaining not only H_2 and CO_2, but also CO, CH_4, and, in some cases, acetaldehyde and ethylene [4]. In consequence, in addition to high activity to attain the greatest conversion possible, high hydrogen selectivity is needed to avoid the formation of non desirable sub products which may result in carbon formation [5,6].

2.1.1. Reforming catalysts
Most catalysts employed for reforming contain transition metals. Frusteri et al. [7] studied the behavior of different transition metal catalysts supported on MgO and determined the following trend in catalytic activity: Rh>Co>Ni>Pd. Haga et al. [8], in turn, evaluated hydrogen selectivity and arrived at the following trend: Co>Ni>Rh>Pt, Ru, Cu. Nickel's advantage in comparison to noble metals is its lower cost and, therefore, it has been studied extensively.

Ubogui [9] and Romero et al. [10] studied Ni-Mg-Al_2O_3 catalysts preparation and performance in bio ethanol steam reforming optimizing Mg/Ni ratio with the objective of minimizing deactivation caused by coke formation. This type of catalyst, known as hydrotalcite, is a doubled layered oxide that, upon calcination and/or reduction, posses a

high surface area, basic properties and metallic crystals both disperse and thermally stable. Furthermore, nickel based formulations have also been studied in our group for glycerol steam reforming [11] and are recently being applied in methane steam reforming [12].

2.1.2. Water-ethanol molar ratio and reforming temperature

Sarto [13] studied hydrogen yield dependence with water-ethanol feed ratio varying this parameter between 5.5 and 7 and obtained a small increase in H_2 production. It is worth mentioning that although higher water-ethanol feed ratio prevents coke formation it also implies more energy input to vaporize feed mixture.

Temperatures employed for steam reforming are between 573 K and 1200 K. García and Laborde [14] determined that, at atmospheric pressure, for temperatures higher than 650 K ethanol equilibrium conversion is always above 99 %. In addition, as seen with water-ethanol feed ratio, higher operation temperature diminishes coke formation but requires more energy input for the process.

Purification

When feeding hydrogen to a SOFC fuel cell, no purification is required since CO produced at the reformer will not poison the anode of the cell which works at 800 °C. In fact, Nissan recently announced a prototype of electric car in which the battery is powered by a fuel cell SOFC, which, in turn, will be fed by synthesis gas produced by reforming of ethanol:water mixture [15].

On the other hand, when feeding hydrogen produced to a PEM fuel cell, the purity requirement is determined by CO tolerance of the cell anode (usually below 100 ppm). Therefore, hydrogen produced in the steam reformer needs to be purified. Though several purification processes are available [16-21], catalytic purification was chosen in this work, requiring two additional reactors: LTWGS (Low Temperature Water Gas Shift) and COPROX (Carbon Monoxide Preferential Oxidation).

As mentioned for steam reforming reaction, WGS is widely used in industry to produce high purity hydrogen needed in other processes such as ammoniac production.
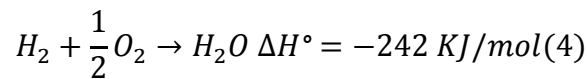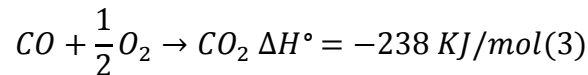
$$CO + H_2O \leftrightarrow H_2 + CO_2 \quad \Delta H° = -41\ KJ/mol \quad (2)$$

Equation 2. WGS Reaction

Water gas shift is a lightly exothermic reversible reaction. Traditional catalysts for this process contain copper, zinc and aluminum. As a consequence of low temperatures used to favor equilibrium conversion, reaction kinetics are low and alkaline promoters (Mg, Cs, Li, K, Na) are introduced [22].

At ITHES (Instituto de Tecnología del Hidrógeno y Energías Sostenibles), Ni and Cu catalysts supported on ceria based materials are being studied for their application in WGS. Poggio Fraccari [23-27] characterized these materials for their use in HTWGS and LTWGS. Recent work is committed to pilot plant scaling of this catalyst.

COPROX process consists on air injection to oxidize CO, preventing H_2 oxidation.

$$CO + \frac{1}{2}O_2 \rightarrow CO_2 \quad \Delta H° = -238 \, KJ/mol \quad (3)$$

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O \quad \Delta H° = -242 \, KJ/mol \quad (4)$$

Equations 3 and 4. COPROX reactions

Thus, COPROX catalyst must present high activity and selectivity to CO oxidation, wide temperature range operation and CO_2 and H_2O tolerance, both present in the WGS reactor exit current. Traditional COPROX catalysts contain platinum and aluminum oxide but, due to their high cost, alternative formulations using transition metals have been explored. Different ways to optimize traditional catalysts were studied, among which the introduction of additional centers for O_2 activation is remarkable since it allows diminishing temperature operation and, therefore, favor CO oxidation selectivity. Most common promoters for this purpose are reducible oxides such as FeO_x, MnO_x, SnO_x, CoO_x y CeO_2 [19]. At ITHES, studies were focused on CuO-CeO_2 catalysts: Moreno [28] developed and verified a reaction mechanism for COPROX reaction system; Semeniuk [29] used γ–alumina preformed spheres as support for pilot plant scaling and optimized both copper and cerium content: 2.5 % wt. for Cu and 30 % wt. for Ce; the use of two COPROX reactors with intermediate air injection was proposed in this work and later studied by Iglesias [30], obtaining a performance improvement. CO_2 and H_2O negative effects on activity were also studied, finding the first one is reversible while the second one, irreversible, may be due copper redistribution. Finally, impregnation study was carried modifying both cerium and copper profiles inside the catalyst particle, changing the typical uniform profile for egg-shell distribution, which resulted in better selectivities as later confirmed by Zitta [31].

Objectives

New technologies development requires experimental work and viability studies. In general, this work is first done at laboratory scale and, once this stage is overcome, scaling becomes necessary if industrial application is desired. Since laboratory conditions are very different to industrial ones, an intermediate stage is needed: pilot plant scale. At this stage, the objective is to adequate results obtained at the laboratory to industrial requirements, design scaling, etc. The purpose of the present work is the evaluation of the catalysts developed by the group at pilot plant scale, making particular emphasis on COPROX catalyst.

3. Experimental

3.1. Pilot plant description

Experiments were conducted at the hydrogen production and purification pilot plant located at the University of Buenos Aires Chemical Engineering Department. ITHES developed a hydrogen production and purification pilot plant, fed with bio ethanol which produces 1 Nm^3/h of H_2. Hydrogen obtained by bio ethanol is purified by a WGS reactor and two COPROX units (see Figure 1).

FIGURE 1 HERE

In the hydrogen production process, ethanol-water mixture is fed from a storage tank to the evaporator employing a plunger pump. Once mixture is vaporized, this current enters the steam reformer which operates at 700 °C approximately. Reformer's exit temperature is lowered by an air cooler to WGS reaction temperature, 230 °C approximately. Downstream, a condenser and flash separator allows separating liquids which are stored at a tank and gas current continues its way to COPROX units. All reactors are tubular fix bed type, heated by electric ovens, fed from the top and containing a mobile thermocouple that allows temperature measurement all along the catalyst bed. All equipment, accessories and tubing are stainless steel AISI 136.

Both the air cooler and the condenser are double tube type. Air cooler is fed by an air blower with three different entrances that allow adjusting heat removing to operation conditions. Flash separator, right downstream of the condenser, separates gases and liquids formed at the WGS exit. Separation capacity must be such that no water enters first COPROX reactor since H_2O has a negative effect on oxidation activity [28].

For composition measurement at all points, an Agilent Technologies 6820 gas chromatograph is used which has two columns: first one separates alcohols, acids, aromatic compounds while the second one separates He, H_2, O_2, N_2, CO, CH_4, CO_2 and light hydrocarbons. In addition, there are two detectors: TCD y FID.

Plant is operated from a separate control room where a Schneider Electric PLC is installed. Electric ovens are controlled by Novus PID controllers which are also used for mass control adjustment and pressure alarm setting. Control devices are connected to the PLC which, in turn, is connected to a computer where SCADA software allows modification, visualization and recording of process variables [13].

3.2. Catalysts employed

Bio ethanol steam reforming: Ni(II)-Mg(II)-Al(III) hydrotalcite type self developed catalyst was used. Ni/Mg ratio was 4 in accordance with previous work by Ubogui [9] and Romero et al. [10]. They were prepared by the urea method which consists on aging mix solutions of urea and nickel, magnesium and aluminum nitrates for 24 h at 90 °C. Then, bottles are put in ice cold bath to stop the reaction, obtaining a wet gel which is washed and centrifuged 3 times before drying overnight. At last, pellets are formed by extrusion of the gel obtained and dried at 70 °C (φ = 5 mm). Before using the catalysts it must be reduced in situ for its activation. The objective is to reduce nickel oxide to metallic nickel which is achieved by a hydrogen current at 700 °C. Since reduction process is exothermic, the current is diluted with nitrogen following a careful protocol.

LTWGS: Cu/Zn/Al Harold Topsøe catalyst was used. This solid requires a reducing pretreatment in hydrogen flow at 250 °C which is highly exothermic. In consequence, in addition to hydrogen dilution with nitrogen, temperature must be risen carefully and, eventually, following H_2 consumption by gas chromatography.

COPROX: 2.5%Cu/30%Ce/Al_2O_3 catalyst (φ = 3 mm) developed and optimized by Iglesias [30] and Zitta [31] is used. The objective is to have an active and selective catalyst since both CO and H_2 oxidation compete in these reactors. Catalyst is prepared by wet impregnation of cerium and copper nitrates on γ-alumina 3 mm spheres which are calcined at 450 °C. Cerium

is impregnated on first place with a uniform distribution and then, copper is impregnated either uniformly or eggshell by changing impregnation and drying time.

Main advantage of eggshell impregnation is that it facilitates heat and mass transfer. In addition, it also favors conversion and selectivity. Since H_2 presents a higher effective diffusivity than CO, the center of catalyst pellet acts as a hydrogen preferential sink. At the pellet center, the presence of Ce without Cu has almost no oxidation activity while at the outer shell, catalytic sites are encountered. This catalyst does not need reducing pretreatment but air flow at 250 °C is employed for surface cleaning.

3.3. Definitions
At the reforming stage, usual definitions for ethanol conversion and hydrogen yield were used (Equations 5 and 6).

$$x_{C_2H_5OH} = \frac{F_{C_2H_5OH}^{in} - F_{C_2H_5OH}^{out}}{F_{C_2H_5OH}^{in}} \quad (5)$$

$$Y_{H_2} = \frac{1}{6} \frac{F_{H_2}^{out}}{F_{C_2H_5OH}^{in}} \quad (6)$$

Equations 5 and 6. Ethanol steam reforming definitions used

For COPROX reaction system, carbon monoxide conversion, carbon dioxide selectivity and oxygen stoichometric excess (λ) were calculated as given in Equations 7, 8 and 9, respectively.

$$x_{CO} = \frac{F_{CO}^{in} - F_{CO}^{out}}{F_{CO}^{in}} \quad (7)$$

$$S_{CO_2} = \frac{1}{2} \frac{F_{CO_2}^{out} - F_{CO_2}^{in}}{F_{O_2}^{in} - F_{O_2}^{out}} \quad (8)$$

$$\lambda = 2 \frac{F_{O_2}^{in}}{F_{CO}^{in}} \quad (9)$$

Equations 7, 8 and 9. COPROX reaction system definitions used

4. Results and discussion

4.1. Steam reformer and WGSR
Both reaction temperature and water:ethanol feed ratio effects on hydrogen yield were studied previously by our group [9, 13]. It was seen that, in the range studied, hydrogen yield increases with higher temperatures and higher water:ethanol feed ratio. However, to increase either variable has a cost associated, i.e. more electric power for reactor and evaporator ovens. Therefore, conditions employed are somehow limited by economic considerations: T = 700 °C, R = 7. At these conditions, Ni/Mg/Al catalyst prepared and used

in the reformer proved to be stable with ethanol conversion being over 98 % and hydrogen yield over 90 %.

In order to test reforming catalyst stability, both the reformer and the WGS reactor were operated together. As shown in Table 1, which summarizes operative conditions for these experiments, WGS catalyst load was more than 30 times the one used at the steam reformer indicating water gas shift kinetics are slow.

TABLE 1 HERE

Figure 2 shows conversion values and hydrogen yield, which reached almost 90 %. It can be observed that ethanol conversion is complete and hydrogen molar fraction increases after WGS reactor as expected. In addition, steam reforming catalysts was stable over almost 200 h operation indicating minor coke formation in accordance with previous work [10].

FIGURE 2 HERE

Figure 3 shows CO and CO_2 molar fractions at steam reformer and WGS exits. It may be observed that CO_2 is higher and CO lower after WGS stage, as expected taking into consideration shift reaction (Equation 2).

FIGURE 3 HERE

4.2. COPROX

In first place, reactor temperature and oxygen stoichometric excess optimization was carried using a prepared mixture (75 % H_2, 3 % CO, 19 % CO_2, 3 % CH_4), taking into consideration temperature profiles along the reactor and temperature control. Two different copper distributions in the catalyst particle were used in separate experiments for their comparison.

Once these variables were chosen, the whole plant was operated together with the objective of obtaining a hydrogen current able to feed a PEM fuel cell, i.e. with CO concentrations below 100 ppm.

Figure 4 shows CO conversion and selectivity as a function of mean temperature along the COPROX reactor for both catalysts employed. These experiments were conducted with constant oven set (160 °C) and varying air flow which modified mean temperature along the reactor. It was observed that catalyst with copper egg-shell distribution had higher CO conversion in all the temperature range and higher selectivity at almost every temperature studied. As previously reported by our group [30], impregnation of the active phase at the outer surface of the catalyst pellet has two benefits: the increase of catalytic activity because of better use of catalytic sites and the increase of selectivity towards CO oxidation since hydrogen has a larger diffusivity, preventing its consumption in the inner part of the pellet.

FIGURE 4 HERE

Once copper egg-shell distribution has been identified as superior for this system, optimization of reaction conditions was conducted. Since oxidation reactions are highly exothermic, temperature control is difficult at pilot plant scale and these experiments were carried with half the mass used in the previous ones. Stoichometric air excess (λ) was varied at different reactor temperatures and, in addition to CO conversion and selectivity, temperature profile along the reactor was registered.

FIGURE 5 HERE

As it may be observed in Figure 5, for every stoichometric air excess a maximum in CO conversion is registered for an intermediate temperature, in accordance with the literature [32]. This maximum in CO conversion is explained by an increase in overall activity, i.e. both CO and H_2 oxidations, with a diminution of selectivity since H_2 oxidation has higher apparent activation energy [28]. Increasing λ allows obtaining higher CO conversion but at higher temperatures, which represent lower selectivities as previously mentioned. Therefore, representing selectivity versus CO conversion it may be noticed, for every λ, the proximity to optimum point, i.e. complete conversion and 100 % selectivity. In Figure 6, $\lambda = 1.9$ outstands as the best choice in the range studied which corresponds to a mean temperature of 195 °C.

FIGURE 6 HERE

Figure 7 shows the temperature profiles established for different stoichometric air excess employed and the same oven temperature set: 160 °C. Due to reactions high exothermicity a hot spot is observed. It is evident from the figure that temperature control is critical in this system. For instance, for $\lambda = 3.1$ temperature increase reaches 150 °C. This does not represent a risk for catalyst structure since its calcination temperature was higher, 450 °C, but it diminishes reaction selectivity.

FIGURE 7 HERE

In order to increase CO conversion, an additional COPROX unit, with intermediate air entrance, was included. This brings two new degrees of freedom: second unit temperature and λ. Both parameters were varied while the first COPROX reactor was operated at 215 °C and $\lambda = 2.5$, CO conversion 77 %. Results for the second unit are presented in Figure 8.

FIGURE 8 HERE

It is concluded that the second COPROX unit should be operated at higher stoichometric air excess and similar temperature. Using two COPROX reactors, allows obtaining final CO concentration of approximately 1200 ppm.

Finally, the whole pilot plant, i.e. reformer, WGSR and both COPROX units, were operated simultaneously to test COPROX catalyst stability in real working conditions. The conditions employed were the ones in Table 2.

TABLE 2 HERE

With this working conditions, the reformer exhibited complete ethanol conversion and 100 % hydrogen yield while at the exit of the WGSR, CO conversion was 94 % (see Table 3).

TABLE 3 HERE

Regarding this composition, some things must be noted: CO molar fraction is lower than the one used in previous tests which is desirable because it should allow a better temperature control in COPROX units. On the other hand, both CO_2 and H_2O concentration deserve consideration since these components are usual causes of deactivation [28]. While CO_2 concentration is almost the same than the one employed in previous tests, H_2O was not considered and its concentration in working conditions is elevated. However, the flash separator located between WGS and COPROX units will diminish the water content.

This current was fed to the first COPROX reactor obtaining the results in Figure 9.

FIGURE 9 HERE

These results are promising since CO conversion of 80 % represents a CO concentration of 100 ppm at the exit of the first COPROX unit, almost the desired CO concentration for feeding a PEM fuel cell. Longer stability tests are being planned for this reactor.

5. Conclusions

Automated pilot plant for hydrogen production from bioethanol steam reforming was built and successfully operated which also may be used to test other catalysts and raw materials (glycerol, methane, others). Catalysts prepared by our lab, both steam reforming and COPROX, were tested at pilot plant scale. The results showed good performance and stability at both units: 100 % ethanol conversion, 70 % hydrogen yield at the WGS exit and less than 100 ppm of CO at COPROX exit for more than 200 h.

The use of two COPROX units was proven to be necessary for reaching such low CO concentration and allowed to work at lower stoichometric excess of air, condition desirable for decreasing the mean temperature in the reactor. Optimized COPROX catalyst preparation (egg-shell type) was observed to favor oxidation activity and enhance COPROX selectivity towards CO_2 formation as expected.

6. References

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Tables

Table 1. Reformer and WGSR conditions for preliminary stability test

Reformerconditions	
Water:EthanolFeed Ratio	7
Total molar flow [mol/h]	52
Catalyst load [g]	30
Temperature [°C]	700
WGSR conditions	
Catalyst load [g]	1000
Temperature [°C]	250

Table 2. Reformer, WGSR and COPROX units operating conditions

Reformerconditions	
Water:EthanolFeed Ratio	7
Total molar flow [mol/h]	12
Catalyst load [g]	10
Temperature [°C]	700
WGSR conditions	
Catalyst load [g]	1000
Temperature [°C]	250
First COPROX	
Catalyst load [g]	15
Temperature [°C]	215
Stoichometric air excess (λ)	2.5
Second COPROX	
Catalyst load [g]	15
Temperature [°C]	200

Table 3. Gas composition at the exit of WGSR

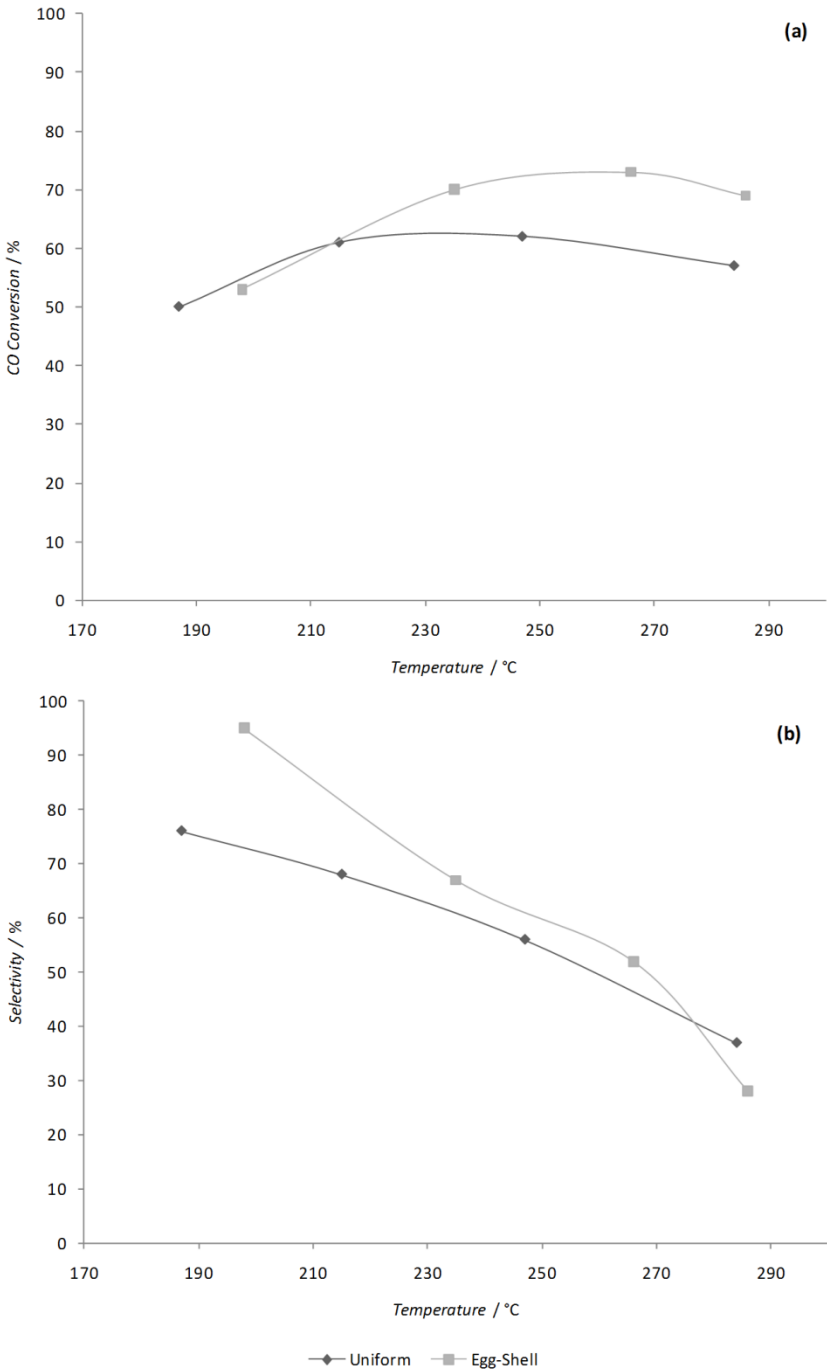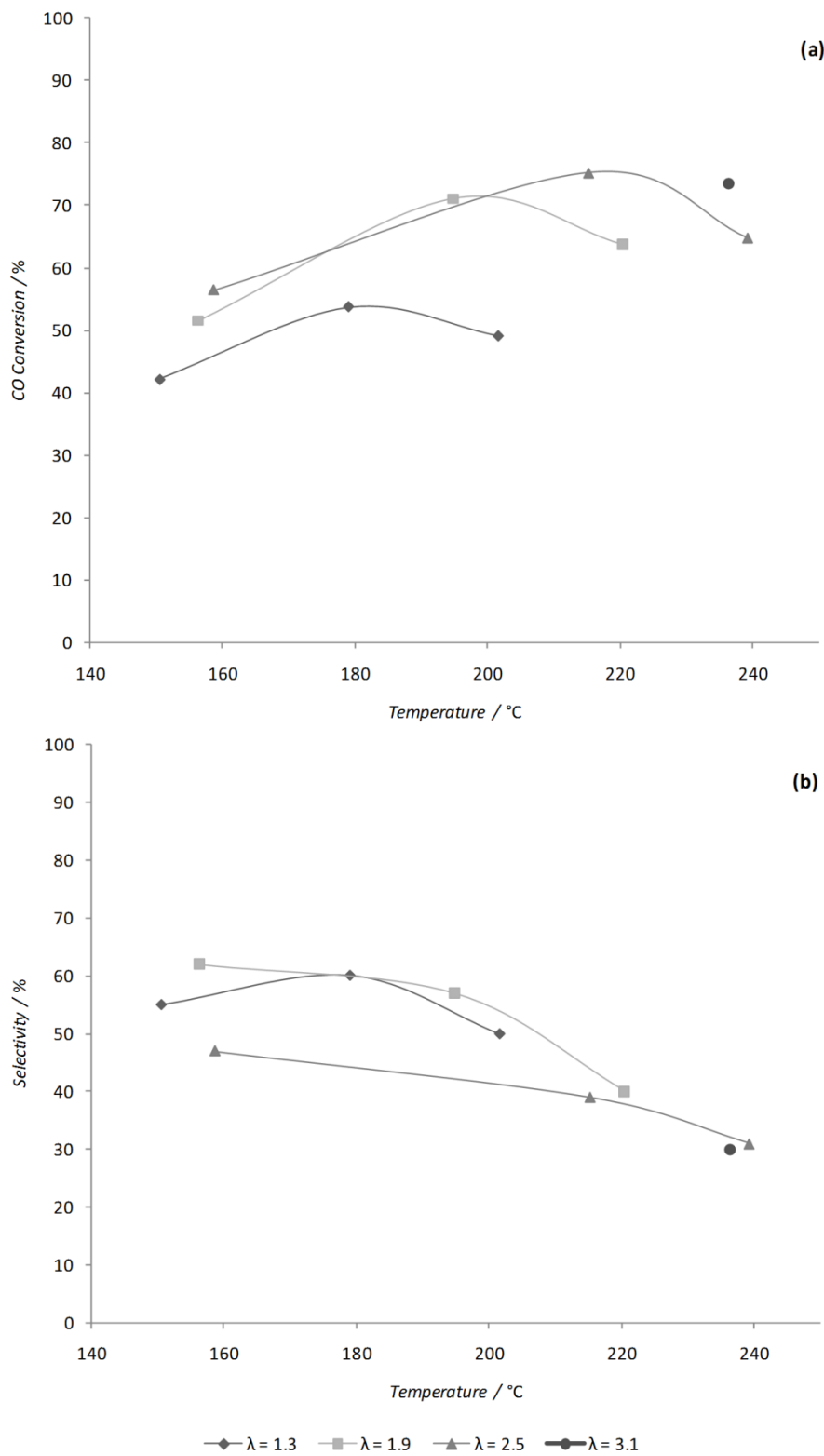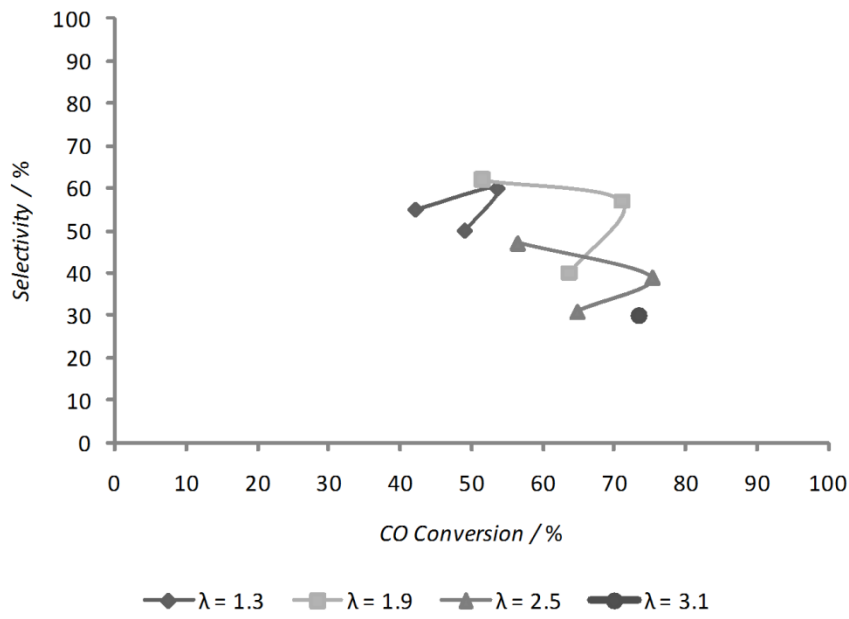| Gas	Molar fraction [%]
CO	0.4
H_2	50.5
CO_2	17.2
H_2O	22.5
N_2	8.6
CH_x	0.8

Figures
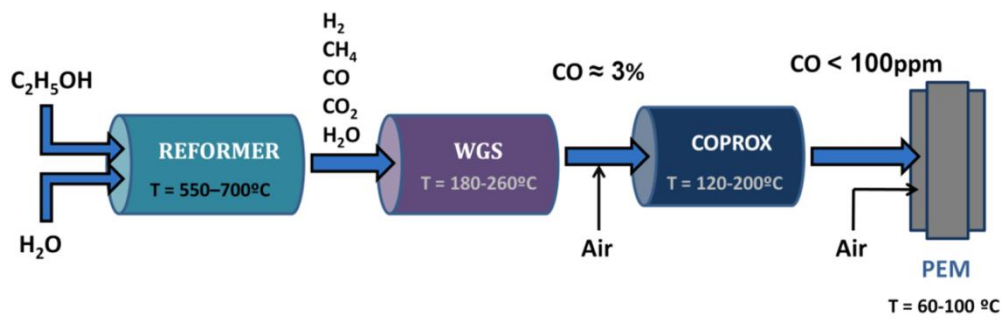
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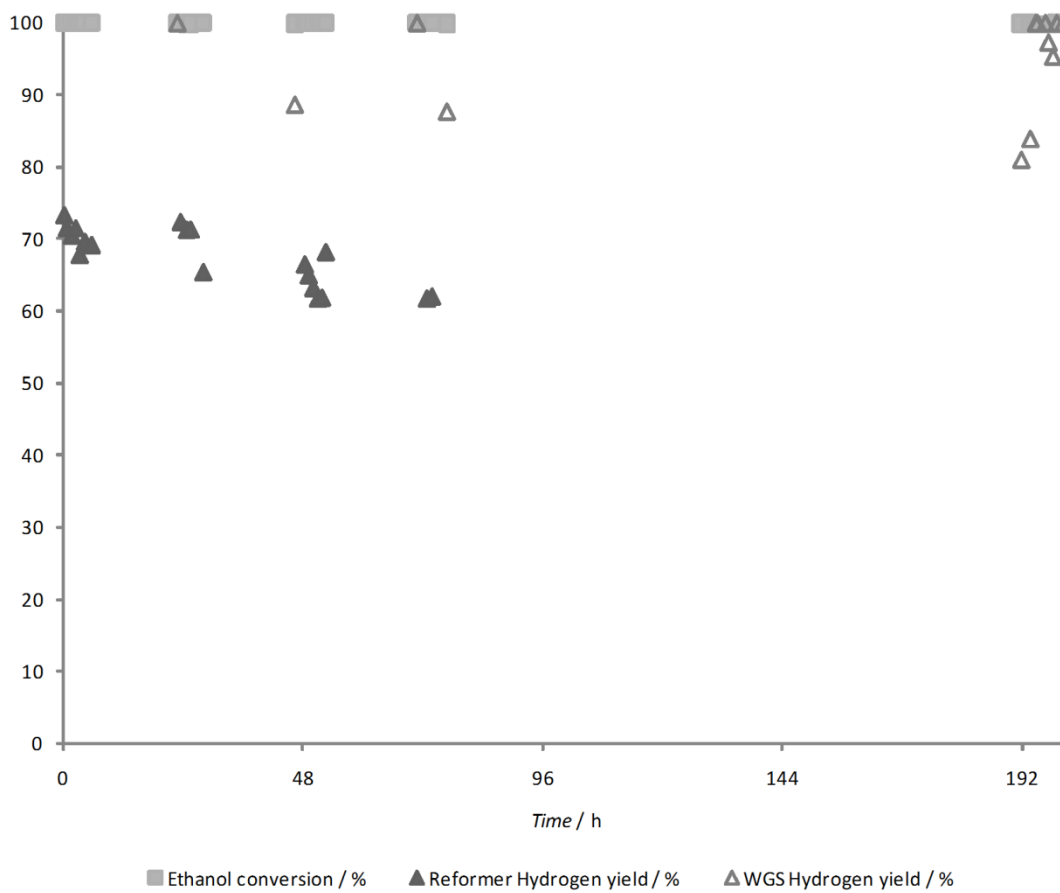
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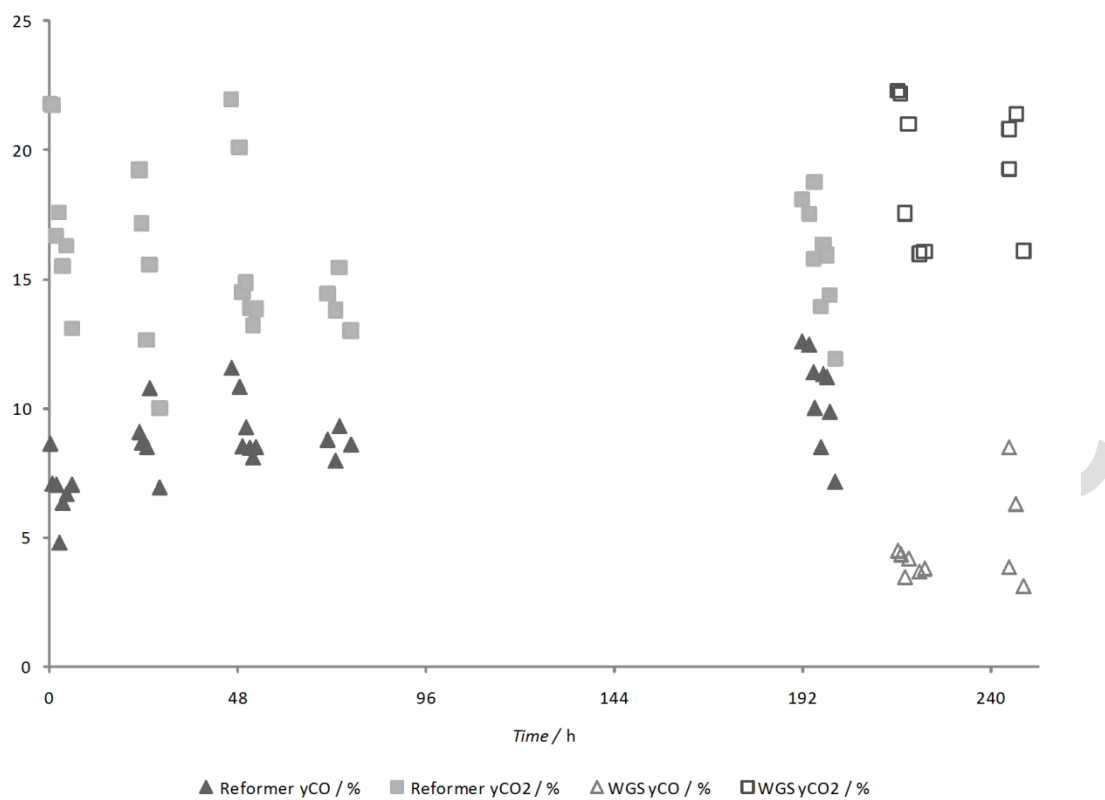
Fig. 3

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Fig. 9