Informes Técnicos Ciemat

1220
Enero, 2011

CHRISGAS Project. WP13: Ancillary and Novel Processes. Final Report: Separation of Hydrogen with Membranes Combined with Water Gas Shift Reaction

J. Mª. Sánchez-Hervás
M. Maroño
Mª. del Mar Barreiro

GOBIERNO
DE ESPAÑA

MINISTERIO
DE CIENCIA
E INNOVACIÓN

Ciemat
Centro de Investigaciones
Energéticas, Medioambientales
y Tecnológicas

Informes Técnicos Ciemat

1220
Enero, 2011

CHRISGAS Project. WP13: Ancillary and Novel Processes. Final Report: Separation of Hydrogen with Membranes combined with Water Gas Shift Reaction

J. Mª. Sánchez-Hervás
M. Maroño
Mª. del Mar Barreiro

Departamento de Energía

Toda correspondencia en relación con este trabajo debe dirigirse al Servicio de Información y Documentación, Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas, Ciudad Universitaria, 28040-MADRID, ESPAÑA.

Las solicitudes de ejemplares deben dirigirse a este mismo Servicio.

Los descriptores se han seleccionado del Thesauro del DOE para describir las materias que contiene este informe con vistas a su recuperación. La catalogación se ha hecho utilizando el documento DOE/TIC-4602 (Rev. 1) Descriptive Cataloguing On-Line, y la clasificación de acuerdo con el documento DOE/TIC.4584-R7 Subject Categories and Scope publicados por el Office of Scientific and Technical Information del Departamento de Energía de los Estados Unidos.

Catálogo general de publicaciones oficiales
http://www.060.es

Depósito Legal: M -14226-1995
ISSN: 1135 - 9420
NIPO: 471-11-002-X

Editorial CIEMAT

CLASIFICACIÓN DOE Y DESCRIPTORES

S09
BIOMASS; SEPARATION PROCESSES; HYDROGEN; MEMBRANES; CATALYSTS; GASIFICATION

CHRISGAS Project. WP13: Ancillary and Novel Processes. Final Report: Separation of Hydrogen with Membranes Combined with Water Gas Shift Reaction

Sánchez-Hervás, J. Mª.; Maroño, M.; Barreiro, Mª del Mar

55 pp. 28 fig. 20 ref. 3 tablas

Abstract:

Oxygen pressurized gasification of biomass outstands as a very promising approach to obtain energy or hydrogen from renewable sources. The technical feasibility of this technology has been investigated under the scope of the VI FP CHRISGAS project, which started in September 2004 and had a duration of five and a half years.

The Division of Combustion and Gasification of CIEMAT participated in this project in Work Package 13: Ancillary and novel processes, studying innovative gas separation and gas upgrading systems. Such systems include novel or available high temperature water gas shift catalysts and commercially available membranes not yet tried in this type of atmosphere.

This report describes the activities carried out during the project regarding the performance of high temperature water gas shift catalysts for upgrading of synthesis gas obtained from biomass gasification, the separation of H2 with selective membranes and the combination of both processes in one by means of a catalytic membrane reactor.

Proyecto CHRISGAS. WP 13: Estudio de Nuevos Procesos. Informe Final: Separación de Hidrógeno con Membranas Combinado con Estudios de la Reacción Water Gas Shift". Contribución de la División de Combustión y Gasificación del CIEMAT al Proyecto CHRISGAS

Sánchez-Hervás, J. Mª.; Maroño, M.; Barreiro, Mª del Mar

55 pp. 28 fig. 20 ref. 3 tablas

Resumen:

Una de las tecnologías más prometedoras para la obtención de energía y/o hidrógeno es la oxi-gasificación de biomasa a presión. La viabilidad técnica de esta tecnología se ha investigado en el proyecto CHRISGAS, perteneciente al 6º Programa Marco de la Unión Europea, el cual comenzó en septiembre de 2004 y ha tenido una duración de cinco años y medio.

La división de Combustión y Gasificación del Ciemat ha participado en este proyecto dentro del WP 13: Ancillary and novel processes, cuyo objetivo principal era el estudio de sistemas novedosos de separación y enriquecimiento del gas de síntesis. Dichos sistemas incluyen el estudio de catalizadores *Water Gas Shift* de alta temperatura y el estudio de membranas para la separación de hidrógeno todavía no estudiadas en las condiciones de gasificación con oxígeno y a presión.

Este documento describe las actividades realizadas por el grupo de Combustión y Gasificación del CIEMAT durante el proyecto relativas al estudio de catalizadores *Water Gas Shift* de alta temperatura para las condiciones específicas de la oxi-gasificación a presión de biomasa, los estudios de separación de H2 usando membranas selectivas y la combinación de ambos procesos mediante los estudios realizados en un reactor catalítico de membrana.

Contents

1 Introduction

The relevance of biomass as significant component in the global sustainable energy mix is increasing worldwide as fossil fuel resources begin to deplete. Electricity production (IGCC) and application in the transport sector represent promising finalist users of renewable biomass and biomass-derived fuels, especially hydrogen.

Some of the acknowledged advantages of biomass utilization include that it can expedite mitigation of greenhouse gas emissions and carbon sequestration cycles. Hydrogen or hydrogen-rich gas produced from biomass could also be used in present natural gas or petroleum derived hydrogen energy conversion devices and in fuel cells [1].

Two types of processes can be used for the conversion of biomass to hydrogen: thermo chemical or biochemical processes. Among the thermo chemical processes, gasification can be considered as the most efficient and high H_2-production capacity nowadays [2]. Although many advances have been and are being reached in biomass gasification technologies, as literature reports [1, 3-4], no commercial biomass gasification processes for hydrogen production are still available to date.

In order to go one step forward in this direction the **CHRISGAS** project (acronym for Clean Hydrogen Rich Synthesis Gas) was approved under the 6th Frame Programme. It started 1st September 2004 and ran for 5½ years. The primary aim of the CHRISGAS project at its onset was to demonstrate within a five year period an energy-efficient and cost effective method to produce hydrogen-rich gases from biomass, which could be transformed into renewable automotive fuels such as FT-diesel, DME and hydrogen. The process was planned for demonstration at Växjö Värnamo Biomass Gasification Centre (VVBGC) in Sweden, after modification to the world's first complete IGCC demonstration plant for biomass. Unfortunately these demonstration activities could not take place within the time frame of the CHRISGAS project as the rebuild and demonstration plant testing require additional funding outside CHRISGAS. Nevertheless significant basic engineering work and a number of highly successful gasification test runs have been performed at the existing IGCC plant at VVBGC during 2006 & 2007 certifying that the existing plant has maintained good operational standards over the seven years in which it was mothballed. Certain engineering and other project activities have continued during 2008 and 2009 to enable a realisation of the rebuild and testing as soon as possible after the CHRISGAS project has ended.

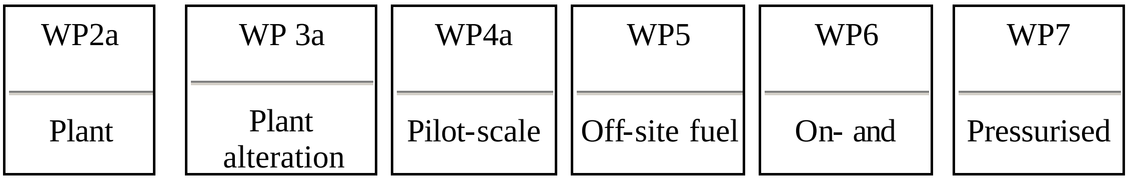
20 partners representing industry and research from 7 EU member states participated in the project. The composition of the Consortium is detailed in table 1 including all the participant countries. A maximum Community contribution to the project was set to 9,500,000 EUR.

Table 1: CHRISGAS Consortium members

CHRISGAS Partners	**Country**
Linnaeus University *(formerly Växjö University)*	Sweden
Catator	Sweden
Centro de Investigaciones Energéticas Medioambientales y Tecnológicas	Spain
Cornelissen Consulting Service	Netherlands
ENI S.p.A.	Italy
Forschungszentrum Jülich	Germany
KS Ducente	Sweden
Kungl Tekniska Högskolan	Sweden
Linde - Linde Engineering Division	Germany
Pall Filtersystems	Germany
Perstorp Oxo	Sweden
S.E.P. Scandinavian Energy Project	Sweden
Södra	Sweden
TK Energi	Denmark
TPS Termiska Processer	Sweden
TU Delft	Netherlands
Università di Bologna	Italy
Valutec	Finland
Växjö Energi AB	Sweden
Växjö Värnamo Biomass Gasification Centre	Sweden

The CHRISGAS project was based on 19 WPs [5] (Figure 1). These 19 WPs represented discreet areas of activity within the overall work programme. The development parts of the project (WP2b, WP3b and WP4b) and parts of the RTD work (WP2a, WP3a, WP4a and WP6) were conducted in the Värnamo pilot plant.

Figure 1: Research, technological development and innovation activities



modification		tests	supply and management	off-site fuel drying	fuel feeding
WP8 Gasification	WP9 Gas characterisation	WP10 HT gas filtration	WP11 Applied catalytic steam reforming	WP12 Steam reforming catalyst characterisation	WP13 Ancillary and novel processes
WP14 Process system studies	WP15 System studies	WP16 Socio-economic studies	WP17 Exploitation / dissemination		

The overall project objectives included:

- to demonstrate conversion of a solid biofuel into a medium calorific value gas by gasification at elevated pressure using a steam and oxygen mixture.
- to demonstrate purification of the generated gas at high temperature, e.g. in a high temperature filter, and by catalytic or thermal steam reforming of not only tars, but in particular of methane and other light hydrocarbons, to generate a raw synthesis gas consisting mainly of carbon monoxide (CO) and hydrogen (H_2) as energy carriers (by the end of year 5 of the project) suitable for *conditioning of the hydrogen-rich raw synthesis gas to the quality stipulated for synthesis gas.*
- to operate the Värnamo plant on different types of biomass based feedstock, including bio-residues, and to perform tests yielding operational data at 3-4 tonne biomass fuel/hr in the production of a hydrogen-rich synthesis gas.
- to operate the Värnamo plant in synthesis gas production mode for an accumulated total of 2000 hours by the end of year 5.
- to conduct desktop studies of the conditioning of the produced gas to a quality *suitable for manufacture of a variety of other potential products* (by the end of year 5 of the project). The conditioning is to be accomplished by catalytic water gas shift to adjust the CO/H_2 ratio, catalytic hydrogenation of minor

contaminants followed by removal of carbon dioxide and other acidic gases in a conventional wash system or in novel selective processes for the removal of sulphur.

- to conduct desktop studies of the production of automotive fuels from various biofuels, at the scale and cost representative of typical biomass fuel chains in various regions in Europe, thereby *giving realistic data for the future production potential on an European scale* (by the end of year 4 of the project).
- to estimate the socio-economic impact of the technology in terms of emissions, both on local air quality as well as on impact on a national and global scale, e.g. regulated emissions and greenhouse gases (considering also its' potential with respect to the EU environmental goals as expressed in response to the Kyoto Agreement, the Directive on Biofuels for Transport (2003/30/EC), etc.) and, in addition, to determine the social effects such as jobs created directly and indirectly at the plant location and in the fuel supply area, etc.

The Division of Combustion and Gasification of CIEMAT participated in **Work Package 13: Ancillary and novel processes**. The objective of this WP13 was to study innovative gas separation and gas cleaning/upgrading systems that had not yet been developed sufficiently to either motivate their testing at pilot scale within the time frame of this project or were in a development stage where the available data did not allow their evaluation, but where some attractive merits and features motivated further development.

Such systems included novel methods for the separation of certain valuable gas components, e.g. hydrogen by the use of water gas shift (WGS) membranes. These studies were performed in model gas atmospheres relevant to biomass gasification in terms of composition and main contaminants in two stages:

- Period 2005-2007: Study of novel or available catalysts for gas upgrading but not yet tried in this type of atmosphere.

- Period 2008-2009: Commercially available membranes were investigated. This has been done by permselectivity testing and separation testing.

Table 2 details the activities programmed for Work package 13. Work performed during the first two years of the project and results obtained have been already published [6].

Table 2: Chronogram of tasks for WP 13

WP13	**(Year)**	I				II				III				IV				V			
	(Quarter)	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
Task	***Title***																				
13.1	Study of gas upgrading processes	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	
13.3	Integrated System Evaluation																			▨	▨
13.4	Overall Analysis & Final Report																				▨

This document reports the contribution of the division of Combustion and Gasification of CIEMAT during the second period of the CHRISGAS project (2007 - 2009) including a detailed description of the activities carried out and the results obtained and a summary of previous work.

2 State of the Art Review

Within WP13, CIEMAT focused their R&D efforts on one of the most promising novel methods for the production of hydrogen from renewable sources: the combination of WGS reaction with selective separation of H_2 via inorganic membranes. This technology, based on the development of **catalytic membrane reactors**, arises as a sound method to generate a clean hydrogen rich stream following gasification that can be used as fuel in other processes. Prior to conducting experimental activities, and in order to gain knowledge for subsequent tasks, CIEMAT did a comprehensive review of relevant literature on the state of the art, regarding separation of hydrogen by means of membranes and water gas shift reaction. Literature review was published as deliverable D103 [7]. The following subjects were discussed:

- Catalysts for WGS reaction: Commercial and new catalysts still under study or currently being used to promote the conversion of CO under different operating conditions were reviewed.
- Membranes development for H_2 selective separation. The main types of membranes that are currently under development were described, evaluating and summarising the advantages and disadvantages of each type.
- Research activities on catalytic membrane reactors that combine WGS reaction with selective separation of hydrogen. Examples of proposed systems and configurations described on literature were analysed in order to identify those most promising according to the objectives of the project.

2.1 Catalysts for WGS reaction

The water gas shift (WGS) reaction is a mildly exothermic reaction used in many industrial processes to produce a hydrogen-rich stream from CO and H_2O.

$$\mathrm{CO} + \mathrm{H_2O} \ ? \ \mathrm{CO_2} + \mathrm{H_2} \quad (\Delta H^{o} = -41 \text{ kJ/mol})$$

Conversion of CO is limited by chemical equilibrium. The reaction is thermodynamically favoured at low temperatures, whereas it is kinetically favoured at high temperatures. In order for the reaction to proceed with a relevant conversion at intermediate temperature, a catalyst is often required.

Some traditional examples of processes involving this reaction include coal gasification processes, H_2 production for ammonia synthesis or other industrial processes such as hydro-treating of petroleum stocks. New applications of WGS reactors have recently renewed the interest in this process. Biomass-based integrated gasification combined-cycle (IGCC) is a promising technology for power and hydrogen production. To produce a hydrogen rich gas from biomass gasification requires however the development of highly active, stable and sulphur-tolerant catalysts for the high temperature WGS reaction. The application of WGS reaction to H_2 production for mobile and small-to-medium-scale fuel cells require catalysts with high activity at a wider temperature range, no need for activation prior to use, no degradation on exposure to air or temperature cycles and availability of conventional wash-coating technologies, which may result in catalysts with reduced size and weight.

The present practice in industry is to carry out the water gas shift reaction in two steps with two types of catalysts: first a high temperature WGS reaction (300-400 ºC) that is generally performed over Fe-Cr catalysts and then, a Cu-Zn catalyst, which is used in the temperature range of 200-300ºC.

According to literature, WGS catalysts can be classified in three main groups:

High temperature sweet catalysts

Iron oxide is the most often used catalyst for high temperature WGS reaction. The catalytically active phase is magnetite (Fe_3O_4) that usually comes from the partial oxidation of haematite (Fe_2O_3). However, pure magnetite catalysts suffer from sintering that reduces rapidly its activity. A stabiliser, Cr_2O_3, is commonly added and the combination of Fe_3O_4 and Cr_2O_3 gives commercially stabilised catalysts that can operate for several years before requiring replacement.

To prolong catalyst life numerous promoters have been studied and added to the catalyst formulation. Other times completely new catalysts have been proposed. A few are highlighted here and for more details see deliverable D103:

- Addition of promoters: Usually copper is added but there are other metals such as rhodium, platinum, nickel, cobalt, manganese, palladium

- Formulation of Cr-free catalysts: Replacement of chromium by aluminium, manganese, cobalt

High temperature acid catalysts

During gasification, part of the sulphur contained in the fuel is released in the product gas, mainly as H_2S. Depending on the sulphur content of the biomass, H_2S concentration in the gas can vary between 50 to several hundreds ppmv. In very extreme cases (such as coal gasification) values up to 10000 ppmv are reported. Since the current industrial catalysts are extremely sensitive to sulphur the conventional approach to solve the problem with sulphur poisoning has been to remove it before the water gas shift reaction. However, it is inevitable that trace amounts of H_2S remain in the gas stream and cause catalyst deactivation.

Some of the already explored sulphur-resistant catalysts include those based on transition metal sulphide, the use of Pt/ZrO_2 materials, or the use of carbides as promising candidates such as molybdenum carbide. All these efforts show that the development of sulphur-tolerant catalysts for the water gas shift continues to be a challenge.

Low temperature catalysts

For processes carried out at temperatures below 300 ºC commercial WGS catalysts are typically based on a $Cu/ZnO/Al_2O_3$ or $Cu/ZnO/Cr_2O_3$ structure, where zinc oxide and/or chromium oxide are generally used as structural stabilizers and promoters.

R&D efforts deal with the development of advanced low temperature catalysts for CO conversion, for instance transition metal supported-ceria (CeO_2), including platinum, rhodium, palladium or gold

2.2 Membranes for H_2 separation

Membranes are physical barriers that allow the separation of a stream into two fractions on the basis of molecular or particulate size. This technology is practised on feed streams ranging from gases to colloids and started with liquid phase separation processes. The development of gas separation membranes started later, in the mid 1940s, in the field of nuclear fuels and since then huge advances have taken place, making the application of manufactured membranes a viable option.

When describing a membrane system three general terms are used: Feed side, Permeate side and the membrane itself (see **Fig. 2**). Usually, the desired component passes through the membrane giving the permeate stream and the rest of the feed flow constitutes the retentate stream.

Gas separation by means of membranes is a concentration-driven process, which for gases is directly related to the partial pressure of gas species. In this sense, it is the differential pressure between the feed and permeate streams that influences the effective performance of a membrane

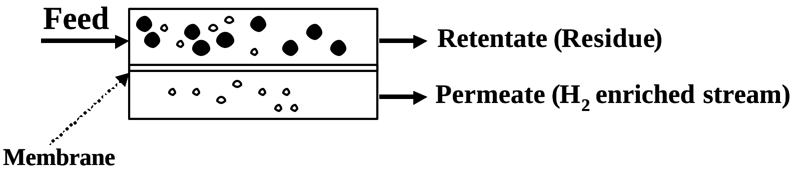


Fig. 2: Schematic representation of a membrane unit

Deliverable D103 presented a very comprehensive picture of the state of the start concerning the use of membranes for hydrogen separation from other syngas components. According to literature membranes could be classified following several criteria: membrane material (organic, inorganic), membrane structure (porous or dense), and morphology (symmetrical or asymmetrical). Permeation mechanisms were also discussed.

Taking into account the application of the membranes to be studied in this project- separation of hydrogen at intermediate temperature- two types of membranes could be applicable:

Micro-porous ceramic membranes

Porous ceramic, particularly micro-porous materials possess high permeability and moderate to high selectivity and are chemically and thermally stable. For those reasons, they are attractive for application in syngas for hydrogen production reactions. Literature survey showed that there are several types of porous membranes which have been tested for H_2 separation or production. The most frequent components of porous ceramic membranes found in literature are alumina and silica, although titania and zirconia are also valuable options. A novel family of materials, zeolites, is currently presented as very promising in the separation field.

Dense phase metallic and metallic alloy membranes

They have attracted a lot of attention, because they are claimed to be commercially available. Nevertheless, for hydrogen, there have been a limited number of metallic membranes which have proved to be effective so far. These are primarily palladium-based alloys exhibiting unique permselecivity to hydrogen and good mechanical stability. R&D has evolved from thick self-supporting membranes (50-100 µm) which showed low permeance and very high cost to current membranes which consist of a thin layer (5-20µm) of palladium or palladium alloy deposited onto a porous ceramic or metallic substrate. A number of alloying elements, and their content, are being studied -such as Ag, Cu, Ni, Fe, or Pt- in order to increase permeance and chemical and thermal stability. Literature also shows limited examples of other metallic membranes under development which are made of platinum, rhodium and iridium

2.3 WGS membrane reactor

According to the IUPAC definition, a membrane reactor is a device that combines the separation properties of membranes with the typical characteristics of catalytic reaction steps in only one unit. In particular, the membrane does not only play a role as a separator but also as a part of the reactor itself. In other words, a membrane reactor is an engineering device that selectively removes a product from the reaction system, giving the possibility of achieving higher conversion than a traditional process under the same operation conditions. For that reason, one of the main application opportunities of inorganic membrane reactors refers to the conversion enhancement of an equilibrium limited reaction by the selective permeation of a reaction product through the membrane. In our particular case, the equilibrium limited reaction to study is the water gas shift reaction and the reaction product to remove is hydrogen.

Publications found in the open literature show that both types of WGS commercial catalysts -low temperature (150-250 ºC) or high temperature (T> 300 ºC)- can be found in reported membrane reactor systems. Modifications of any of these types by doping them with different metals or new catalyst developments are attracting the attention of the researchers.

Regarding membranes, basically two types of membranes are most frequently used: ceramic, Pd and/or Pd alloys supported on alumina or stainless steel. As stated before, palladium membranes are excellent candidates for hydrogen purification, especially when incorporated with a catalytic reactor combining reaction and separation in a single unit. Their theoretically infinite selectivity to hydrogen continues to draw major research efforts. However, according to literature, the use of Pd membranes in WGS reactors imposes several limitations on the catalyst. Among them, the most restrictive one is that the catalyst must be operated above 250ºC which is typically the temperature for HT WGS catalysts to start showing activity, and whenever possible above 300ºC to minimize the risk of palladium embrittlement and phase transformation which would lead to cracks in the metal film.

Another issue frequently discussed in membrane reactor technology is membrane geometry and reactor configuration. Three different geometries are reported, coils, tubes and disks. Generally, tubular membrane assemblies are preferred to flat-plate or disk configurations because they provide a much larger surface area. Concerning reactor configuration, there are two possible configurations for tubular membrane set-ups, depending which side of the tube the catalyst is placed on: an inside-outside design or an outside-inside configuration, as **Fig. 3** shows. While the former requires larger inside diameters for a given wall thickness allowing self-supporting membranes, the second requires an adequate distribution of tubes in the reactor to guarantee a homogeneous flux of hydrogen.

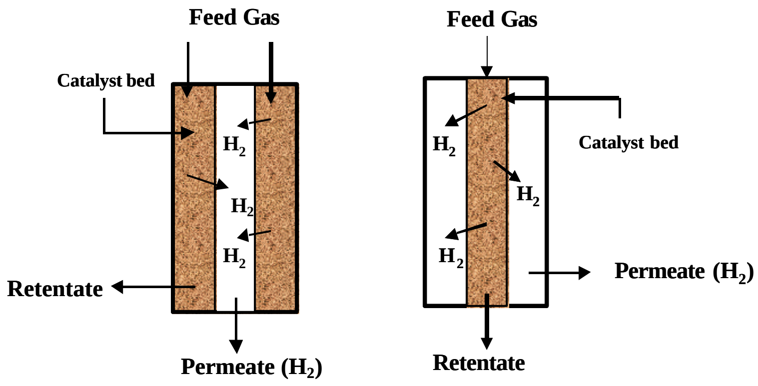


Fig. 3: Different configurations catalyst-membrane in a membrane reactor

According to the results presented in literature, the combination of the WGS reaction with a H_2 selective membrane provides better results in terms of CO conversion and/or H_2 recovery than conventional processes. However, more research is needed to scale up and integrate these systems into industrial processes such as an IGCC gasification process or to both stationary or transportation fuel cell applications.

3 Water Gas Shift Studies

CIEMAT has studied on a laboratory scale the activity of commercial WGS catalysts (Fe-Cr- and Pt-based respectively). Experiments were conducted in a fixed bed reactor using simulated gases, under the operating conditions and gas composition expected at Växjo Värnamo Biomass Gasification Centre (VVBGC) for the WGS step, i.e., under conditions typical of oxygen pressurized gasification. Catalytic activity under those conditions was determined and suitability of the catalysts to be incorporated in a palladium membrane reactor was discussed. The effect of operating parameters on CO conversion and hydrogen production was evaluated. Special attention was paid to the activity of the catalyst versus temperature due to the sensitivity of Pd membranes to temperature, below 300ºC. The effect of steam to CO ratio, feed gas composition and space velocity on the activity and selectivity of the catalysts for the WGS reaction were also studied in order to optimize CO conversion and H_2 production. Results of those studies were reported in deliverables D105[8] and D105b[9], and can also be found elsewhere[10], [11]. In this report only a brief summary will be presented..

3.1 Experimental

3.1.1 Catalysts

The Fe-Cr-based catalyst studied is a commercial high temperature WGS catalyst, industrially used in standard H_2 and ammonia production plants. It basically consists of a mixture of iron and chromium oxides. As confirmed during testing, the catalyst used in this work was supplied already in the active phase, magnetite (Fe_3O_4), so it did not require a pre-reduction step. For testing, tablets of 6x6 mm were used as shown in **Fig. 4 (left)**. Depending on the operating conditions, 5 g or 1.3 g of catalyst were placed in the reactor.

The platinum-based catalyst was prepared and provided by CATATOR AB (Sweden). The final catalyst consists of a support of CeO_2/ZrO_2 with 4.2 % Pt as the active phase. The catalyst was supplied impregnated on 240mm x 295mm rectangular wire mesh substrates following a procedure patented by CATATOR. 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. 4 (center)**. Final configuration after assembling and ready to be placed in the reactor is shown in **Fig. 4 (right).**

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

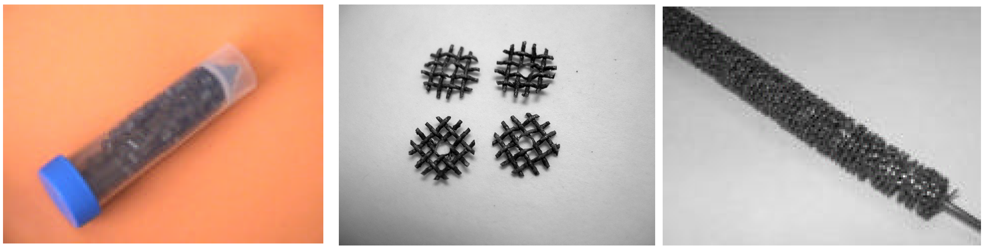


Fig. 4: Samples of catalyst used for WGS studies **(left)** Fe-Cr pellets; **(center)** Pt-based sheets; **(right)** Pt-based catalyst as mounted in the reactor

3.1.2 Experimental Unit

Catalyst testing was carried out in a Microactivity Pro Unit, whose flowsheet diagram can be seen in Fig 5. 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 700ºC and 30 bar.

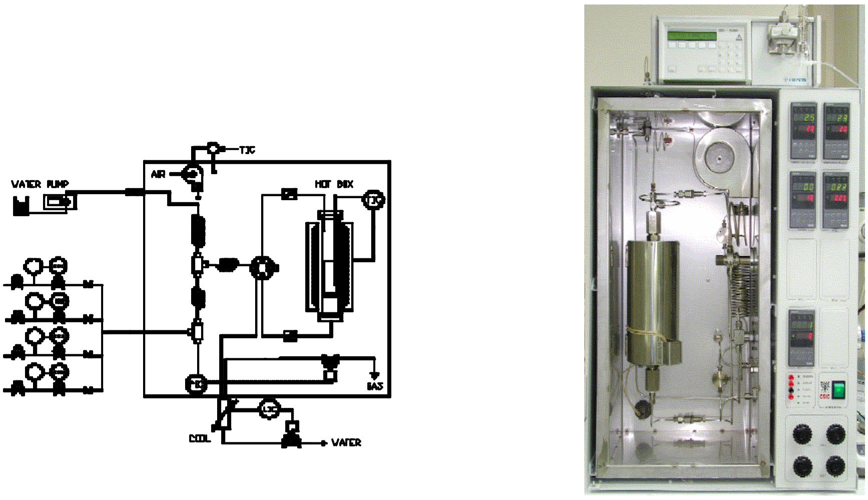


Fig. 5: Laboratory test rig for WGS studies **(left)** flow-sheet **(right)** picture

The gas mixture was produced synthetically using mass flow controllers (Hi-Tech). Deionized water was metered by a piston pump (Gilson 307) and vaporized 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 190ºC. 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 300mm long. The reactor is placed in a one single zone SS304 oven, which is able to heat the reactor up to 700ºC. Gas temperature in the reactor is measured by a 1.5 mm thermocouple, directly in the catalyst bed. The reactor can be by-passed 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, down-flow mode. In a typical run the reactor was pressurized 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 was started.

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 one 6 Ft Molecular Sieve 5Å 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.

3.1.3 Experimental tests

WGS tests were performed using three different gas compositions as shown in **Table 3**, 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 VVBGC (M1 and M2). These latter two gas compositions were estimated based on the assumptions that the gasifier at VVBGC will operate at 900 ºC (+/-50ºC) and with 0.4 kg oxygen per 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 3. *Gas composition for the experimental programme*

COMPONENT	M1	M2	B
H_2	34	32	60
CO	38	23	
CO_2	13	16	
CH_4	0,5	0,1	
H_2O	15	29	
N_2	0	0	40

3.2 Results and Discussion

Catalytic activity of the WGS catalysts studied was expressed as the percentage of CO converted (% mol) X_{CO} calculated according to equation (1),

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

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, that is, at how selective the catalyst is to promote the WGS reaction. The yield to hydrogen and carbon dioxide y_{H2}, y_{CO2}, were calculated according to expressions (2) and (3),

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

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

being $(F_{H2})_{out}$ and $(F_{H2})_{in}$, the molar flow rate of hydrogen at the reactor outlet and inlet, and similarly $(F_{CO2})_{out}$ and $(F_{CO2})_{in}$ the carbon dioxide flow rate at the reactor outlet and reactor inlet.

3.2.1 Fe-Cr-based catalyst

High temperature WGS catalysts used industrially are mostly based on iron and chromium oxides which have been reported to be very selective for the water gas shift reaction at temperatures above 300ºC maintaining stability and resistance to sintering.

Although WGS is a well studied process it cannot be assumed that the catalysts used in commercial processes will be equally suitable when used in other technologies such as gasification or membrane reactors. Very few references can be found in literature regarding the performance of high temperature WGS catalysts when used to upgrade syngas obtained from the oxygen pressurized gasification of biomass. Thus, *ad hoc* studies need to be carried out.

Hence CIEMAT conducted an experimental study under realistic conditions typical of oxygen pressurized gasification of biomass. The influence of temperature, excess steam, feed gas composition and space velocity on the activity and selectivity of the catalyst for the WGS reaction was investigated.

Deliverable D105 [2] provided detailed information about experimental results and they are also available in the open literature [10]. The effect of operating parameters on CO conversion and hydrogen production was evaluated. Special attention was paid to the activity of the catalyst versus temperature due to the limitation on operating temperature demanded by Pd membranes. The effect of steam to CO ratio, feed gas composition and space velocity on the activity and selectivity of the catalyst for the WGS reaction were studied in order to optimize H_2 production.

Catalytic activity was determined at temperatures from 250ºC to 500ºC and space velocities ranged from 2000 h^{-1} to 25000 h^{-1}. The majority of the experiments were carried out using the mixture M1 –see Table 3- which simulates the composition of an oxygen biomass gasification exit gas and particularly that expected at the WGS unit inlet on VVBGC. Some additional tests were done using a gas mixture with different concentration of CO in order to asses the influence of feed composition on the activity of the catalyst. All tests were run at 10 bar, which is the operating pressure at VVBGC.

Fig. 6 shows the influence of feed gas composition on CO conversion **(left)** and hydrogen production **(right)** respectively. As temperature increases also does conversion of CO and production of hydrogen. The temperature at which the catalyst started to show activity towards the WGS reaction was found to be around 300ºC which would be compatible with the temperature required by palladium membranes if the catalyst is going to be incorporated in a membrane reactor.

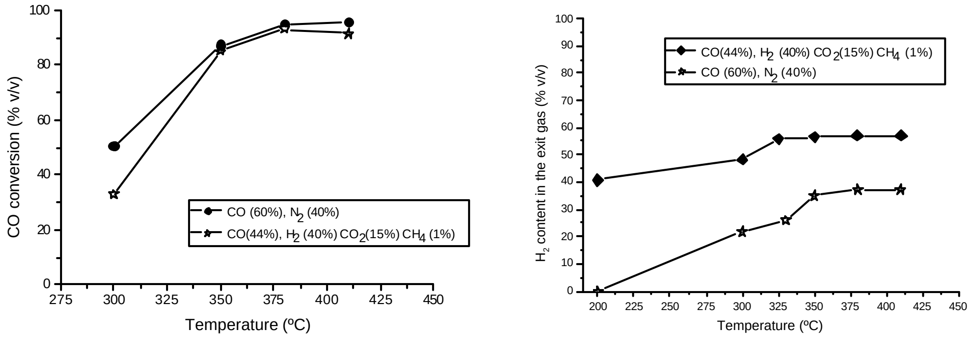


Fig. 6. Influence of feed gas composition on **(left)** Carbon monoxide conversion, and **(right)** H_2 production, at space velocity of 2,885 h^{-1} and steam to CO ratio of 6.7

Despite the high CO content in the feed gas (44%-60% dry basis) the catalyst has shown very good performance at intermediate temperatures 350ºC-450ºC, providing hydrogen content increases in the exit gas in the range of 10%-17% (dry basis) and CO concentration at the reactor outlet lower than 3% v/v.

Fig. 7 shows the influence of gas space velocity on the activity of the catalyst. Space velocity represents the contact time between gas and catalyst bed. Given the same amount of catalyst, higher space velocities result in a reduction of the contact time in the reactor. At 2885 h^{-1} and at a H_2O/CO ratio of 2, the initial content of CO in the feeding gas mixture M1 (44% v/v) was reduced to less than 10 % v/v at 380ºC. When space velocity is increased, a shift of the conversion curves to higher temperatures results in lower CO conversions at the same temperature as depicted in **Fig. 7 (left)**. In terms of CO conversion, a maximum value of 80 % v/v was reached at 2,885 h^{-1} at 380ºC while at 10,000 h^{-1} a temperature higher than 450ºC was required to reach the same CO conversion as **Fig 7 (right)** shows. Production of hydrogen followed the same trend with space velocity. Maximum H_2 content measured in the exit gas ranged between 50.1 % v/v – SV= 25000 h^{-1} and T=500ºC-, and 57.6 % v/v dry basis –SV = 10000 h^{-1} and T=440ºC-, which results in an increase of the H_2 content in the gas of 10-17 % v/v.

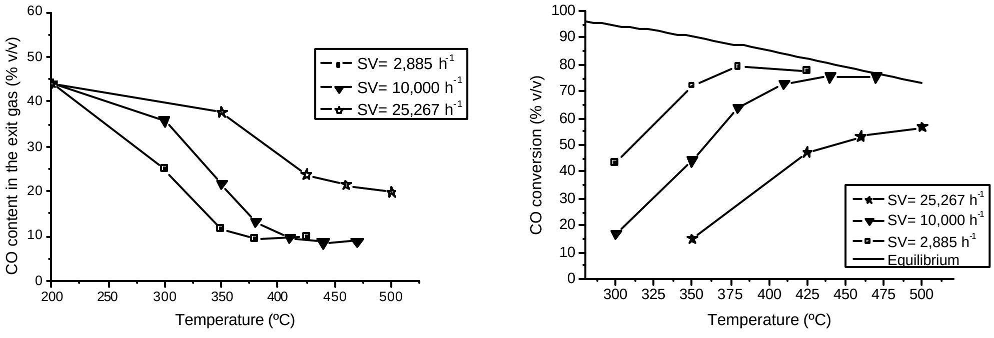


Fig. 7. Influence of space velocity on **(left)** evolution of CO content in the exit gas, and **(right)** CO conversion at a steam to CO ratio of 2, P= 10 bar, Feed gas composition 40% H_2, 44% CO, 15% CO_2, 1%CH_4

Concerning the effect of steam, experiments with steam to CO ratios ranging from 1 to 7 were carried out. According to the stoichiometry of the water gas shift reaction, at least a steam to CO ratio of 1 is required. Special interest was paid to results obtained at low H_2O/CO ratios because those conditions are the expected values to be used in a membrane reactor.

Regardless space velocity, increasing steam to CO ratio resulted in lower CO content in the exit gas, that is, higher CO conversion. CO content as low as 2.03 % v/v was achieved when using a steam to CO ratio of 6.7. The use of lower steam to CO ratio required higher operating temperatures to reach similar CO content in the exit gas.

Moreover, steam to CO ratio was found to play a key role to avoid secondary reactions, as shown in **Fig. 8**, where hydrogen and methane content evolution in the exit gas versus temperature are plotted. According to water gas shift reaction and in absence of secondary reactions, as CO is reacting with H_2O, hydrogen content in the exit gas should increase while methane content should decrease, due to the increase in overall mole number of reaction products (dry basis). **Fig. 8** shows that this is what happens at steam to CO ratio equal or higher than 2. At steam to CO ratio of 1, however, methane content in the exit gas increases with temperature, whereas production of hydrogen decreases. This happens at temperatures above 350ºC for the space velocity tested shown in **Fig. 8**, but it also happened for other values of gas space velocity not shown here. This gas composition evolution points to the possibility that at low steam to CO ratio secondary reaction are taking place, mostly likely the methanation reaction ($CO + 3H_2$? $CH_4 + H_2O$), which would be consuming CO and hydrogen to produce methane and water at temperatures below 500ºC in deficiency of steam.

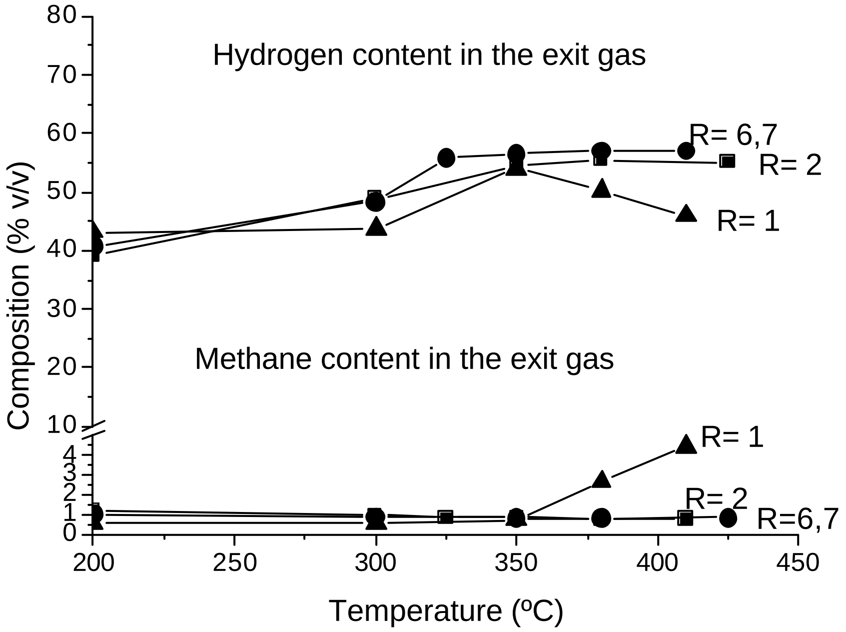


Fig. 8. Influence of steam to CO ratio (R) in the evolution of hydrogen and methane content (% v/v) in the exit gas at space velocity of 2,885 h^{-1}, P= 10 bar and feed gas composition: 40 % H_2, 44% CO, 15% CO_2, 1% CH_4

3.2.2 Pt-based catalyst

The catalytic activity of a $Pt/CeO_2/ZrO_2$ catalyst has been investigated under realistic conditions for intermediate temperature 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. The final objective has been to determine experimental conditions which provide good catalytic performance in terms of CO conversion and selectivity to H_2 and CO_2, and to see if those conditions are compatible with the operating conditions imposed by Pd membranes in order to integrate the catalyst in a catalytic WGS membrane reactor. Detailed information on the performance of the catalyst is available in deliverable D105b[9] and in the open literature[11].

Catalytic performance has been evaluated from 200ºC to 500ºC. 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). Pressure was kept at 10 bar, which is the process pressure in the demonstration plant.

In literature it is found that Pt-based catalysts have been mainly used for the second WGS stage at low temperature. In our work, 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, 300-450ºC, showing potential for the 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.

Regarding the influence of space velocity, higher GHSV values lead to lower CO conversion and a higher temperature is required to achieve a given CO conversion as shown in **Fig. 9**. 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.

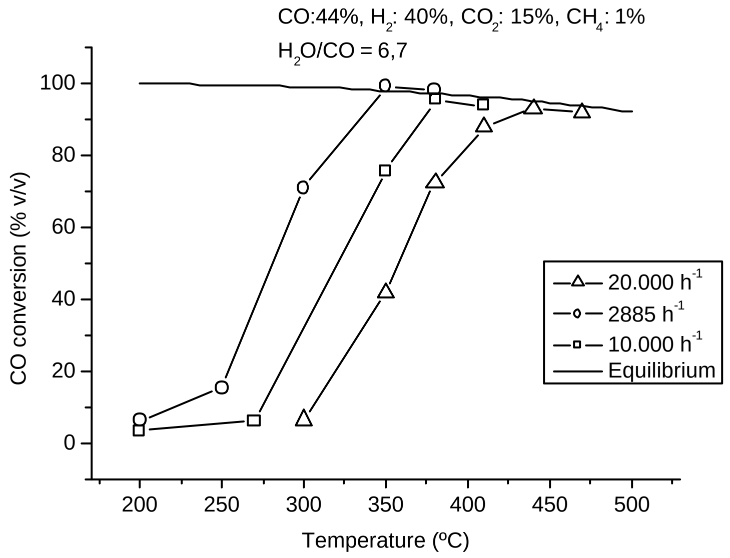


Fig. 9. Effect of GHSV on CO conversion (Feed Gas: 40% H_2, 15% CO_2, 44% CO, 1% CH_4, P=10 bar, $H_2O/CO=6.7$)

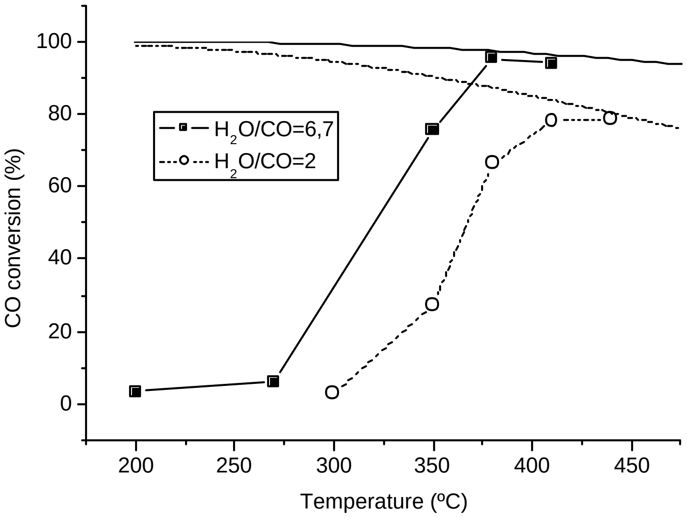


Fig. 10. Effect of H_2O/CO ratio on CO conversion (Feed Gas dry basis: 40% H_2, 15% CO_2, 44% CO, 1% CH_4, P=10 bar, GHSV=10.000 h^{-1}).

With regard to steam to carbon dioxide ratio, this parameter can be considered critical on the performance of the catalyst. The activity of the $Pt/CeO_2/ZrO_2$ catalyst studied in this work 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. 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, as can be seen looking at **Fig. 10**, and with better selectivity. 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

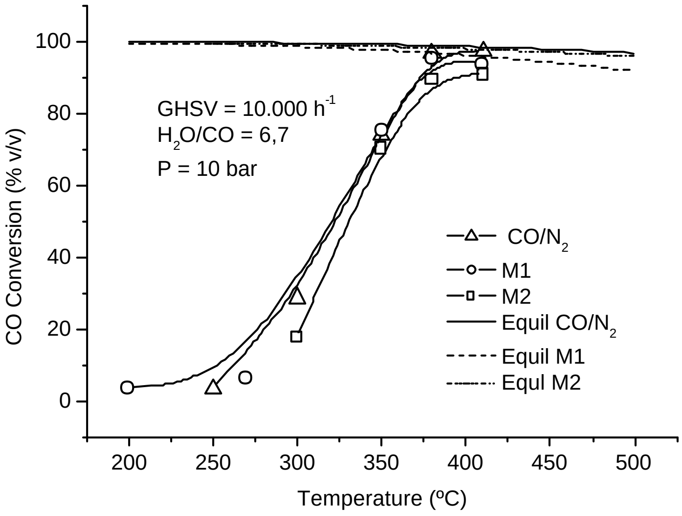


Fig. 11. Effect of gas composition on CO conversion

As for the gas composition, no significant differences have been found in the catalyst performance when using different feed gas compositions as shown in **Fig. 11**. 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.

3.2.3 Comparison of catalysts

Both catalysts studied show high CO conversion (>90%) at space velocities around 3000 h^{-1} and steam to carbon dioxide ratios of 6.7. Under such conditions, the use of the Fe-Cr based catalyst is recommended when working temperature is in the 380ºC-400ºC range. If working temperature is lower, close to 350 ºC, the Pt-based catalyst provides better results (see **Fig. 12**).

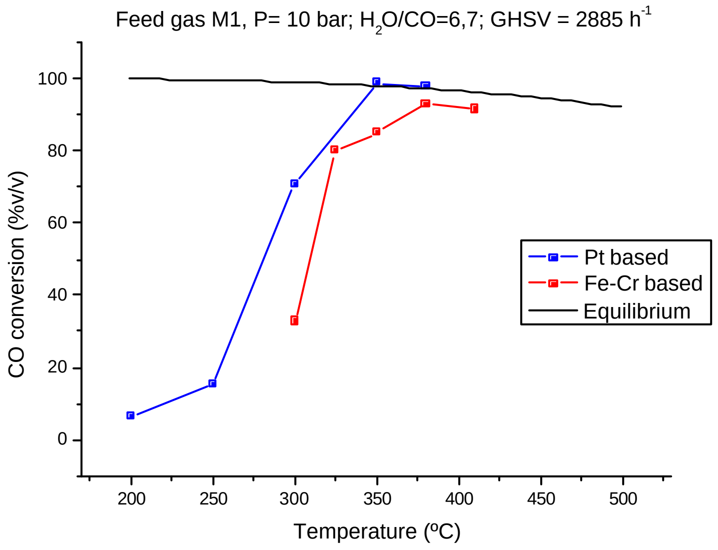


Fig. 12. Comparison of catalysts performance

3.3 Conclusions

Catalytic activity has been studied in terms of CO conversion and H_2 and CO_2 formation, that is, selectivity of the catalyst to promote exclusively the water gas shift reaction. Catalytic performance has been evaluated from 200ºC to 500ºC. The study has included the evaluation of the effect of gas space velocity GHSV in the range from 2000 to 20000 h^{-1}, steam to carbon monoxide ratio, R between 1 and 6.7, and feed gas composition on the activity of the catalyst.

Results show that different types of commercial and prepared high temperature WGS catalysts (Fe-Cr- and Pt-based) are able to convert more than 90% of the CO contained in the synthesis gas into CO_2 and H_2 under specific operating conditions (temperature, space velocity and steam to CO ratio), and therefore can be regarded as suitable to be used at VVBGC. The ferrochrome commercial catalyst studied provided good conversion of CO (less than 2-3 % v/v residual) in the temperature range of 360ºC-400ºC and at H_2O/CO ratios higher than 6. High conversion of CO was also obtained when using a Pt-based catalyst, in the temperature range of 350ºC-380 ºC and high H_2O/CO ratios. Those experiments showed very good selectivity to H_2 and CO_2.

No significant influence of gas feed composition has been found for any of the catalysts so both can be considered adequate for Växjo Värnamo Biomass Gasification Centre.

Looking at the effect of the parameters evaluated, it is seen that high 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.

Regarding the effect of steam to CO ratio, the activity of both catalysts depends strongly on the amount of steam available during the reaction. In the case of the Fe-Cr-based catalyst, in sub- or stoichiometric concentration of steam related to CO content in the gas, noticeable amounts of methane are produced. 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.

Finally from the point of view of integrating the catalysts on a membrane reactor, based on the results obtained in this work and on the discussion above, from the operating conditions viewpoint it seems feasible to integrate any of them because the temperature range in which they show good catalytic performance, 300-480ºC, is clearly compatible with the operating temperature required by Pd-membranes.

4 Studies on separation of Hydrogen by Membranes

Taking into consideration the final objective of the project- the production of a hydrogen-rich synthesis gas- the next step of our work in WP13 dealt with the study of novel hydrogen separation system. This approach would be able to provide a pure hydrogen stream from the gas mixture that leaves the WGS reactor. Among the available technological alternatives, a membrane reactor was chosen as very promising to produce firstly a hydrogen-rich gas and secondly to prove the advantages of combining the WGS reaction with a membrane selective to H_2 in one process unit.

In order to assess the suitability of such a system, the separation stage itself was studied first. In order to carry out the hydrogen separation studies a bench scale membrane reactor was designed and erected at CIEMAT. Full description of the experimental test rig is included in deliverable D106 [12].

Deliverable D108[13] reported about theoretical considerations in membrane technology worth knowing. The most relevant difficulties and challenges related to the use of palladium membranes for hydrogen separation were highlighted and the proposed strategy to undertake them was detailed.

CIEMAT studied the use of membranes for hydrogen separation on bench scale level. The performance of palladium membranes from two sources was evaluated. The first batch of Pd-membranes was prepared for CIEMAT by a partner in another project, funded by the Ministry of Education and Science of Spain. Detailes information about preparation method can be found elsewhere [14]. Permeation and selectivity studies were conducted under “simplified” operating conditions. Experiments included permeation of pure gases and mixtures (N_2 and N_2/H_2), hydrogen partial pressures ranging from 0.1 to 1 bar, moderate trans-membrane pressures -up to 2 bar- to guarantee membrane integrity, tests at room temperature using N_2, and permeation tests for mixtures N_2/H_2 at temperatures in the range of 320ºC to 400ºC. A summary of the results is presented in this report. Detailed information can be found in deliverable D104 [15] and results have been published elsewhere [16], [17].

A second batch of palladium membranes was obtained from an R&D Centre in US. In this case, according to private information made available by the supplier, the membrane can be regarded as pre-commercial since it was prepared based on membrane technology, which is at an advanced technical stage, protected by patents, and ready for industrial introduction. Permeation tests were carried out for binary mixtures, H_2/N_2 and H_2/CO_2. Hydrogen content in the mixture ranged from 30% v/v to 60% v/v. The effect of gas flow rate, temperature, gas composition, and pressure on hydrogen flux was determined. Deliverable D109[18] presents in detail information about performance for hydrogen separation of the pre-commercial membrane. Results have also been presented elsewhere [19], [20].

4.1 Experimental

4.1.1 Membranes

Two different Pd membranes have been tested. The first batch consists of membranes prepared within another project, funded by the Ministry of Education and Science of Spain, by the other partner in the project, a Spanish University (University Rey Juan Carlos). Membranes studied consist of a porous stainless steel tube (O.D. =12.7 mm; L=80 mm), **-Fig. 13 (left)-** provided by Mott Metallurgical, which has a pore size of 0.2 µm and a porosity of 20%. The porosity of the support was reduced by brushing. An intermediate silicalite layer was deposited onto the support, which was then coated with a Pd film by electroless plating. Thickness of the selective palladium layer after plating was estimated to be between 14 and 24 µm. The membrane module consists of four tubular membranes assembled on a metal distributor that forces the feed gas to flow along the membrane. The membranes are inserted in the flanges and graphite/alumina gaskets are used in each membrane-holder joint. Four spiral rods tighten the metallic structure to prevent undesirable gas leaks. The whole structure – see **Fig. 13 (right)** is located in a metal cylindrical housing of 90 mm OD x 150 mm length able to withstand pressures up to 20 bar and temperatures up to 500 ºC.

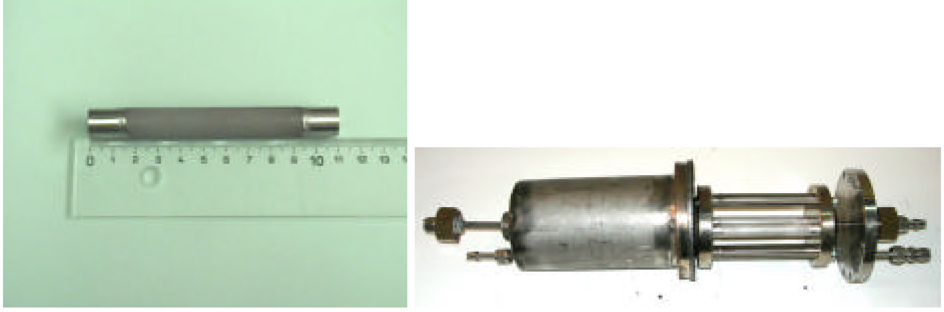


Fig. 13. **(left)** Prepared Membrane **(right)** Membrane reactor

The second membrane studied is a pre-commercial prototype supplied by a research institute in USA. The dense palladium membrane is supported on a porous tube (O.D.=2,54 cm; L= 15 cm) and it was supplied welded to a solid-wall 316SS tube **–Fig. 14 (left)-**. The final membrane-tube assembly is 70 cm long and it is housed in the tubular reactor shown in **Fig. 14 (right)**.

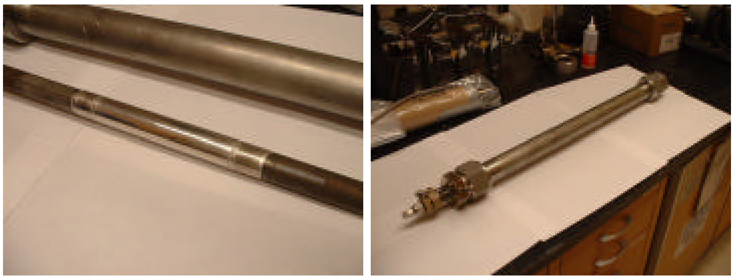


Fig. 14. **(left)** Pre-commercial membrane **(right)** Membrane reactor

4.1.2 Test rig

Experiments have been conducted on a bench-scale level, in a facility located at CIEMAT, shown schematically in **Fig. 15**, where up to 2 Nm^3/h can be treated, at a temperature of 500ºC and up to 12 bar.

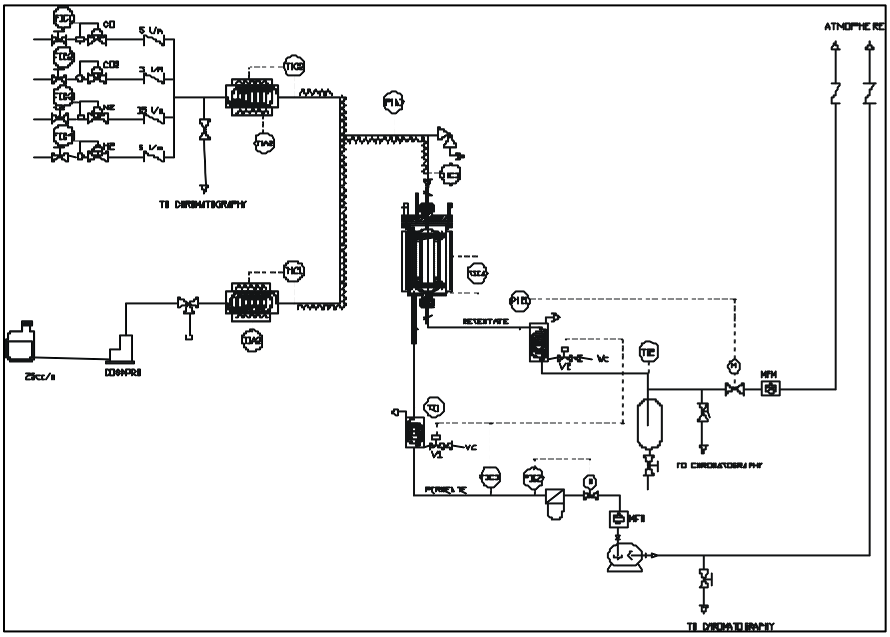


Fig. 15: Scheme of the gas separation test rig

The facility consists of a gas feeding system based on mass flow controllers (MFCs) to feed H_2, N_2, CO, and CO_2, a vaporiser for steam feeding, a gas preheating system, the membrane reactor, and the permeate and retentate conditioning system including gas cooling, the pressure control system consisting of valves (PCVs) and flow-rate measurement by means of mass flow meters (MFMs). Inlet gas, permeate gas and retentate gas compositions are measured by gas chromatography. For the full description of the facility see deliverable D106. Depending on the membrane to study it was necessary to change the membrane reactor oven. **Fig. 16 (left)** shows the test rig when the pre-commercial membrane was being studied, whereas **Fig. 16 (right)** shows in detail the membrane reactor oven for the prepared membranes case

Fig. 16. Membrane Reactor bench-scale plant **(left)** oven for pre-commercial membrane installed **(right)** oven for prepared membranes installed

4.1.3 Experimental programme

Testing programme on the prepared membranes- as proposed in deliverable D108- consisted of the study of permeation of nitrogen and hydrogen under the following conditions:

Permeation with pure N_2: The performance of the membrane was studied for the following operating conditions: Temperature: 25ºC, 320ºC y 380ºC; Feed gas flow: 500 ml/min and 750 ml/min; Trans-membrane pressure: 0.2-1.3 bar

Permeation with pure H_2: In order to determine the permeation of H_2, the performance of the membrane was studied without using sweep gas, using a stream of pure hydrogen, under the following conditions: Temperature: 320ºC; Feed gas flow: 500 ml/min and 750 ml/min; Trans-membrane pressure: 0.1-0.7 bar

In the case of the pre-commercial membrane prototype, permeation tests have been carried out for binary mixtures, H_2/N_2 and H_2/CO_2. Hydrogen content in the mixture ranged from 30% v/v to 60% v/v. The effect of gas flow rate, temperature, gas composition, and pressure on hydrogen flux has been determined. Gas flow rate (G) was set at, 0.75, 1.83 and 3.75 Nl/min. Two permeation temperatures -380ºC and

430ºC- have been studied. Retentate pressure was varied from 1 to 3.5 bar (rel). Permeate side pressure was kept atmospheric and sweep gas was not used to enhance permeation.

4.2 Results and Discussion

The performance of a membrane is usually defined in terms of permeability and selectivity.

At steady-state conditions, in our experiments since they were conducted in absence of sweeping gas, the permeate flow rate (Fp) is directly measured by the mass flow meter. If permeate flow-rate is divided by membrane surface area the permeation flux through the membrane is obtained -J (m^3/m^2 s)-. Permeability of a membrane for a specific component -P- can be defined as the ratio between permeate flow rate per unit area and driving force -or flux rate divided by driving force- as equation 4 shows:

$$P = \frac{F_p}{SDP} \qquad (4)$$

Where:

Fp is the permeate flow rate

S = surface area of the membrane

DP= driving force

In the case of porous membranes, where molecules are transported by diffusion through the pores, all gas components can permeate to some degree and the driving force is the difference of pressure between both sides of the membrane. On the other hand, for dense membranes-as Pd-based membranes- which do not have any pores, the prevailing transport mechanism is the so called solution-diffusion mechanism and only some components are able to permeate. Of all the gas components present in syngas only hydrogen is able to permeate through dense Pd membranes. If the diffusion of hydrogen through the membrane is considered the rate-limiting step, hydrogen flow will follow the Sievert´s law –equation 5- being directly proportional to the difference of the square root of the hydrogen partial pressure on both sides of the membrane:

$$J_{H_2} = \frac{Pe}{l}\left(P_{H_2 f}^{0,5} - P_{H_2 p}^{0,5}\right) \qquad (5)$$

Where:

Pe_{H2} = permeability (m^3 m/m^2 s $Pa^{0.5}$)
l = membrane thickness (m)
$P_{H2,f}$ = Partial pressure of H_2 at feed stream (Pa)
$P_{H2,p}$ = Partial pressure of H_2 at permeate stream (Pa)

Then, *permeability* through the membrane can be obtained from equation (6) as follows:

$$Pe_{H_2} = \frac{J_{H_2}}{l\left(P_{H_2 f}^{0,5} - P_{H_2 p}^{0,5}\right)} \qquad (6)$$

Besides permeability, another parameter must be considered when studying the performance of a membrane for gas separation. This parameter is called selectivity. In general, porous membranes provide high permeability but selectivity depends on the relative size ratio between molecules and pores. In this type of membranes separation of components is only possible when pore size is smaller than the mean free path of the molecules of gas. The theoretical separation factor is calculated as the square root of the ratio between molecular weights (eq. 7). In these conditions the transport mechanism follows the Knudsen diffusion.

$$\alpha = \sqrt{\frac{M_A}{M_B}} \qquad (7)$$

Conversely, the solution-diffusion mechanism provides an infinite selectivity to H_2 and this characteristic makes palladium membranes very interesting for the objectives of this work.

In summary, if the governing separation mechanism is Knudsen diffusion, permeation flux will be proportional to pressure difference between feed and permeate sides and all components will be able to permeate. On the other hand if permeation is driven by the solution-diffusion mechanism only hydrogen will permeate and permeation flux will be proportional to the difference of the square root of hydrogen partial pressure on both sides of the membrane. This approach was followed to analyse the performance of prepared and pre-commercial membranes

4.2.1 Prepared Membranes

Permeation results and discussion were published in detail in deliverable D104. A short summary is given in this report.

For prepared membranes, permeation of N_2 and H_2 was measured at different temperatures –room T (for N_2 only), 320ºC and 380ºC- at trans-membrane pressure ranging from 0.2 to 1.3 bar.

It was found that nitrogen and hydrogen were able to permeate through the membrane

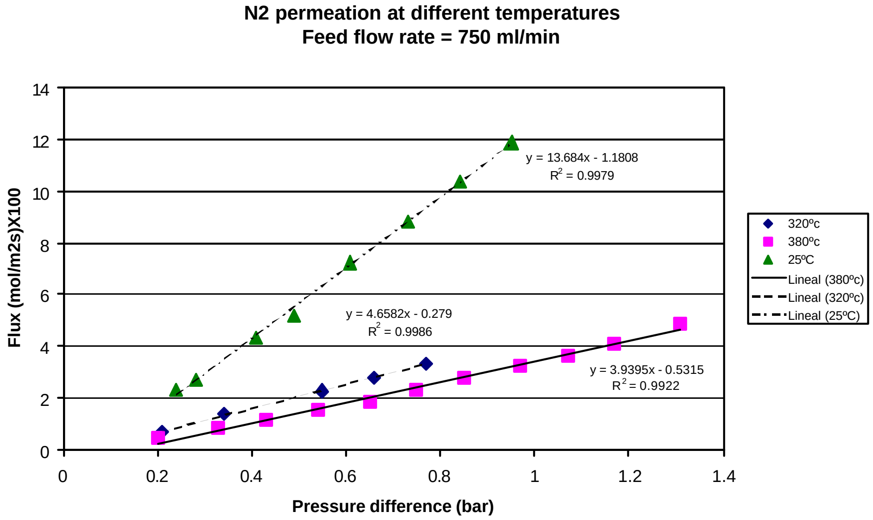


Fig. 17. N_2 permeation flux

Permeate flow-rate was found to decrease as temperature increased as is shown for nitrogen in **Fig. 17**. It can be clearly observed a linear dependence of nitrogen flux through the membrane with the difference of pressure (R^2>0.990) which suggests that Knudsen diffusion can be the prevailing transport mechanism.

Results presented in **Fig. 18** show that flux of H_2 ranges between 0.025 mol/m^{2}s and 0.08 mol/m^{2}s in the pressure range from 0.2 to 0.7 bar, while N_2 flux reached values from 0.006 to 0.025 moles /m^{2}s for the same pressure range. H_2 to N_2 separation factor achieved was around 3.75.

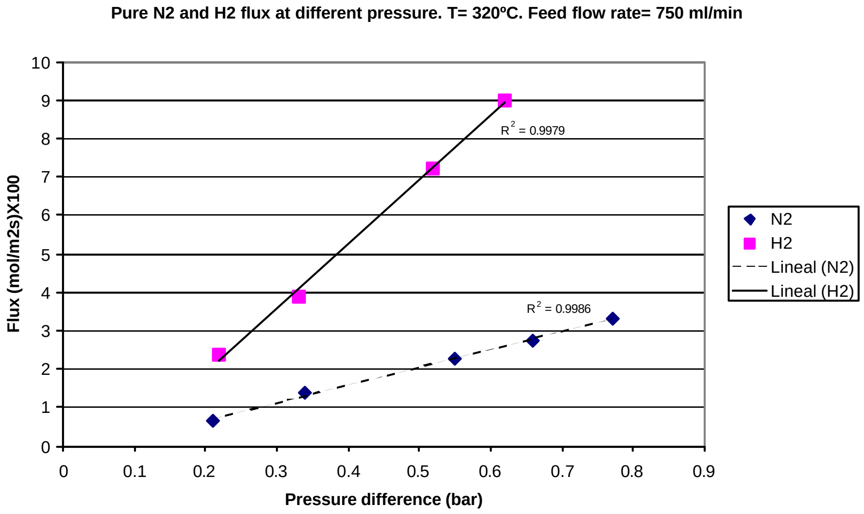


Fig. 18. Hydrogen and Nitrogen flux as a function of pressure difference

Some additional tests were conducted to check the influence of feed gas flow rate in the permeation of N_2 and H_2. Two feed flow rates have been studied: 500 ml/min and 750 ml/min. Results are shown in **Fig. 19**. Difference in performance is observed between pure N_2 and pure H_2. According to **Fig. 19 (left)**, nitrogen flux is enhanced by an increase of feed gas flow-rate whereas hydrogen flux does not depend on it. The smaller size of the molecules of H_2 seems to favour the transport of the molecules through the narrowest pores of the membrane, smoothing the effect of the increase of feed flow rate on the permeability.

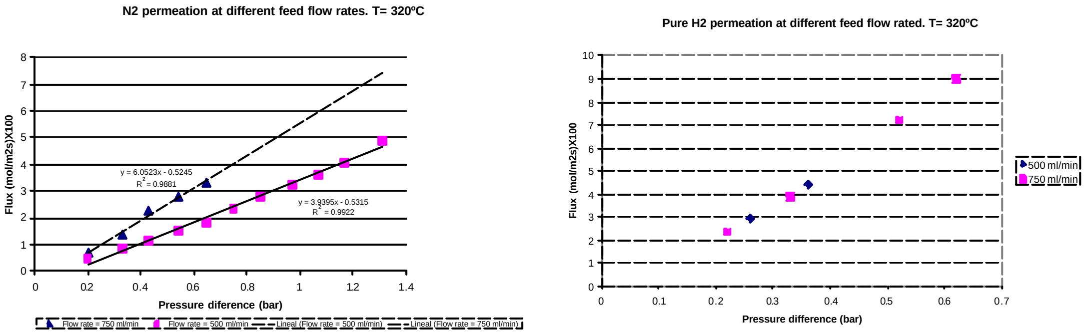


Fig. 19. Relationship between flux and feeding gas flow-rate: **(left)** Nitrogen flux; **(right)** Hydrogen flux

After testing, membranes were characterised by SEM (Scan Electron Microscopy) and by EDX (Energy Diffusion Spectroscopy). SEM images- **Fig. 20**- showed the presence of a continuous layer of palladium deposited onto the support on some parts of the membrane **(left)**, while others show discontinuities, pinholes or even small nodules **(right)**. EDX analysis showed palladium as the only species present on the deposited layer, even when analysing the interior of some pinholes. Low selectivity shown by the membranes was therefore ascribed to defects found on the palladium layer.

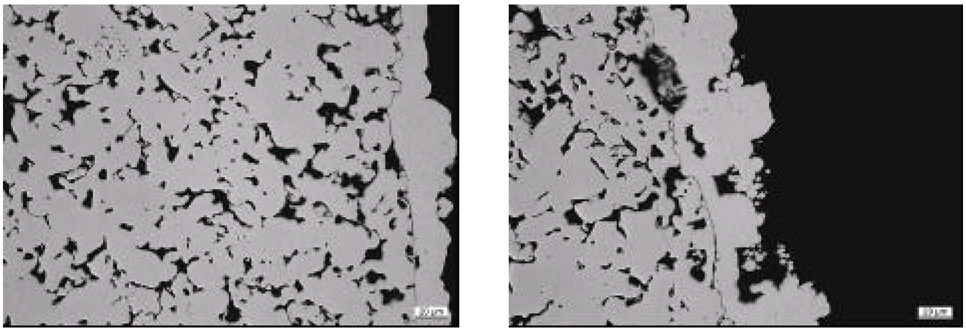


Fig. 20. SEM images of Pd-membranes after testing **(left)** continuous layer of Pd **(right)** discontinuities of Pd-layer

4.2.2 Pre-commercial Membrane

Performance of the pre-commercial membrane, in terms of permeation and selectivity to hydrogen was presented in detail in deliverable D109[16]. The main results are summarised in this report.

Permeation tests were carried out for binary mixtures, H_2/N_2 and H_2/CO_2. Hydrogen content in the mixture was set at 30% v/v and 60% v/v. Gas flow rate of the mixture was fixed at 0,75, 1,88 and 3,75 Nl/min. Two permeation temperatures, 380ºC and 430ºC were evaluated. The effect of temperature, gas composition and pressure on permeation has been studied.

Results show that the membrane has infinite selectivity to hydrogen since neither N_2 nor CO_2 permeated through it. On the other hand, hydrogen is able to permeate, as long as there is enough driving force, and is removed from the reactor as a pure permeate stream. Hydrogen flux was found to depend mainly on the difference of the square root of hydrogen partial pressure on both sides of the membrane, which corresponds to transport through a thick palladium layer following the mechanism of solution-diffusion and when diffusion of atomic hydrogen through the dense metal layer is the rate-limiting step. In the following, discussion of results is presented briefly. Results are presented in terms of hydrogen flux. At steady-state conditions, and in absence of sweeping gas as was the case for our experiments, the hydrogen flow rate measured by the mass flow meter, divided by the membrane surface, represents the hydrogen flux through the membrane, J_{H_2} (m^3/m^2s). Before starting to measure hydrogen permeation, short tests were devoted to check that nitrogen did not flow through the membrane. To this aim pure nitrogen was fed at two different gas flow-rates, 0.75 and 1 Nl/min. Reactor temperature was set at different values, room temperature, 320ºC, 380ºC, and 430ºC. Pressure was varied between 1 and 3.5 bar. Permeate flow-rate was measured by means of a volumetric gas meter, with an accuracy of 1 ml/min. In none of the tests nitrogen was detected in the permeate stream.

Looking at the effect of the different parameters studied it has been determined that an increase of gas flow-rate has a positive effect on hydrogen flux as **Fig. 21** shows.

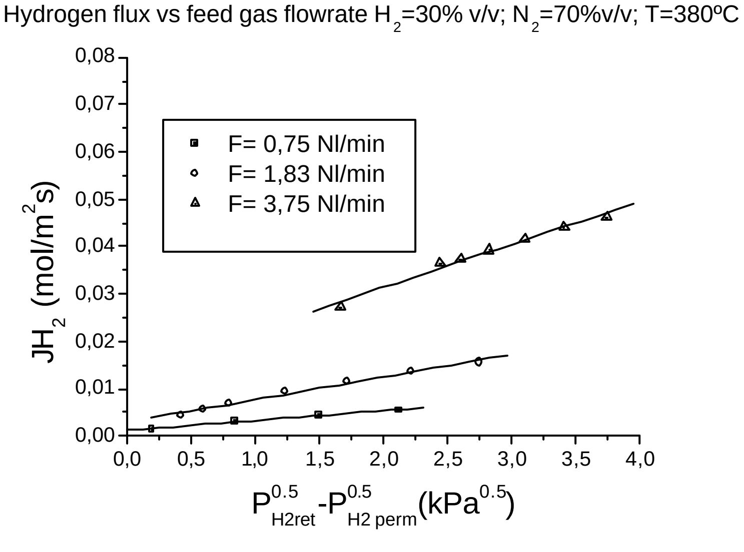


Fig. 21. Hydrogen flux as a function of feed gas flow-rate ([H_2] =30% v/v, [N_2] =70% v/v, T=380ºC

On the other hand, reduction of H_2 flux in presence of CO_2 compared to H_2 flux in H_2/N_2 mixtures is observed as depicted in **Fig. 22**.

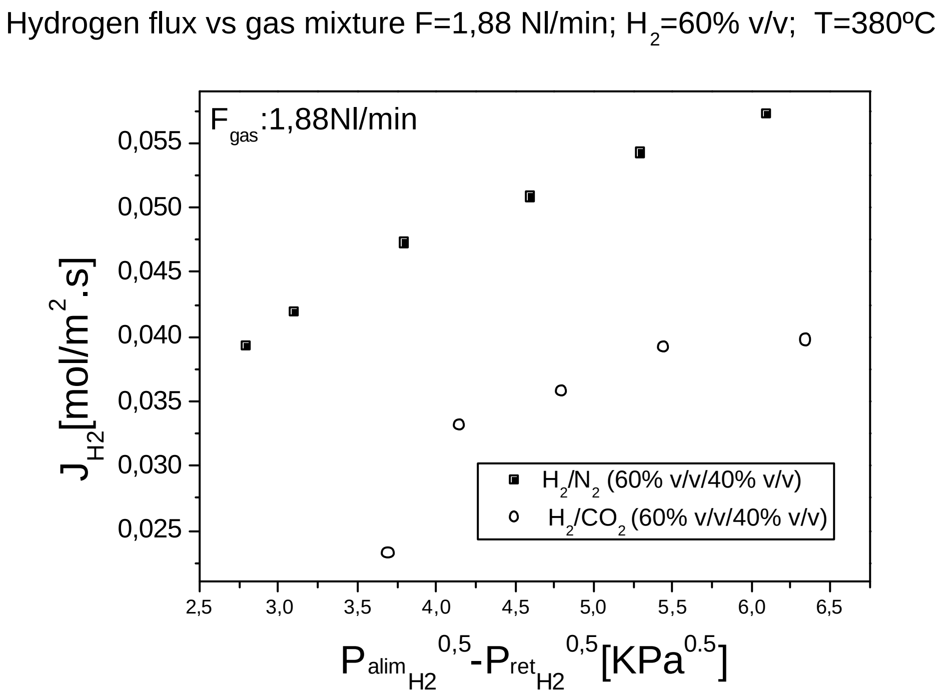


Fig. 22. Hydrogen flux as a function of feed gas (Fgas=1.88 Nl/min, $[H_2]$=60%v/v, T=380ºC)

Moreover, as **Fig. 23** shows**,** for H_2/CO_2 mixture, as temperature increases flux of hydrogen permeating through the membrane decreases. A number of effects are reported in literature to play a role on hydrogen flux, such as dilution of hydrogen by other gas components, hydrogen depletion along the membrane length, concentration polarization adjacent to the membrane surface, and effects due to surface adsorption.

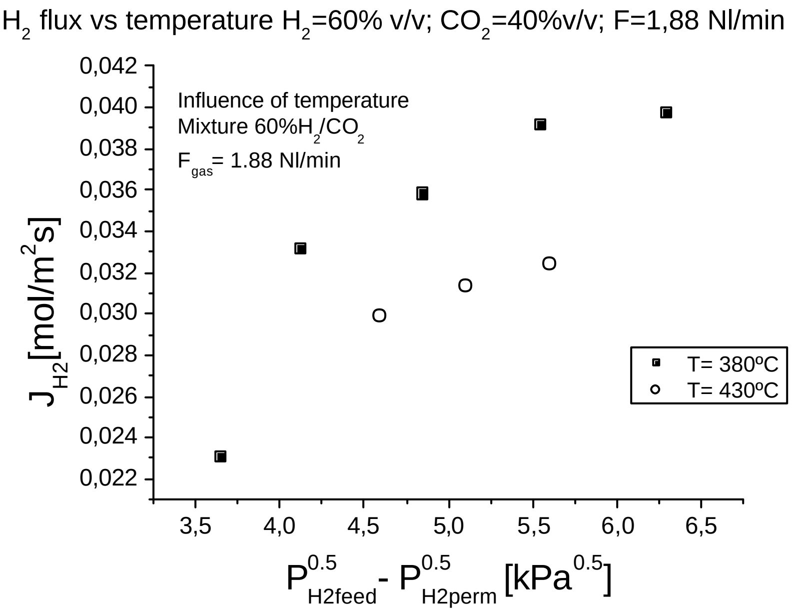


Fig. 23 Effect of temperature on hydrogen flux for H_2/CO_2 mixtures (F=1,88 Nl/min, $[H_2]$=60%v/v)

According to **Fig. 24**, hydrogen recovery depends on several parameters such as gas mixture, H_2 content in the feed, and temperature. Higher hydrogen content improves H_2 recovery due to a higher driving force. Looking at the effect of gas components, CO_2 presence in the mixture reduces hydrogen recovery. This effect is more important at 430ºC than at 380ºC.

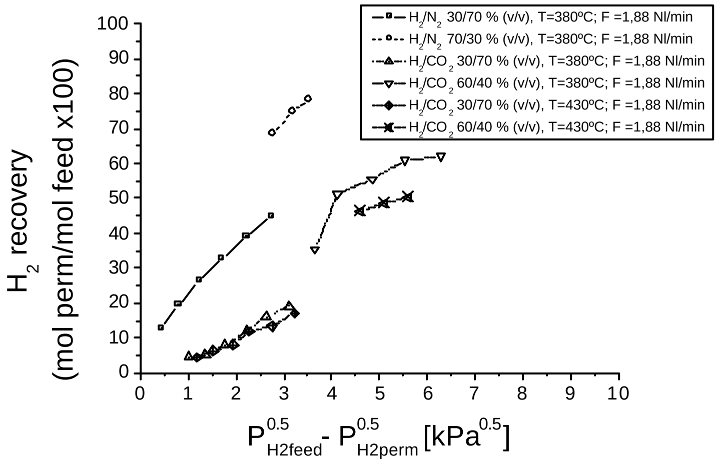


Fig. 24. Hydrogen recovery for different experimental conditions

In summary, a good correlation has been found between H_2 flux and the difference of the square root of hydrogen partial pressure on both sides of the membrane, which corresponds to the transport through a thick palladium layer following the mechanism of solution-diffusion and when diffusion of atomic hydrogen through the dense metal layer is the rate-limiting step. Furthermore the membrane shows infinite selectivity to hydrogen though permeation flux is low as expected for thick dense Pd-membranes.

4.2.3 Comparison of prepared and pre-commercial membranes

For the developed membranes the prevailing separation mechanism was Knudsen diffusion, instead of the solution-diffusion mechanism which should have been provided by a continuous dense Pd layer. The technique used to prepare the membranes was not efficient enough to guarantee the continuity of the layer of palladium deposited, hence favouring the presence of pinholes and pores which have reduced dramatically the selectivity of the membrane to H_2. The membranes showed high permeation flux but very low selectivity, close to Knudsen separation factor. These membranes did not show potential for carrying out the proposed WGS study in a membrane reactor

On the other hand, during the permeation studies with the pre-commercial membrane, neither N_2 nor CO_2 have been detected in the permeate stream, regardless operating conditions. This means that the membrane can be regarded as defect-free. The dense palladium membrane tested features exclusive selectivity to hydrogen. In this sense, results are very encouraging since they show that it would be feasible to separate H_2 from CO_2 using Pd-based membranes like the one under study, yielding a pure H_2 permeate stream and a CO_2-rich retentate stream at high pressure. Based on permeation results the membrane was considered adequate for conducting WGS experiments in membrane reactor.

4.3 Conclusions

Gas leaving a conventional water gas shift packed bed reactor will consist of clean synthesis gas with high hydrogen and carbon dioxide content, excess steam not consumed by the reaction and a low amount of CO. Separation of hydrogen from carbon dioxide after the WGS reactor is usually accomplished by means of chemical or physical solvent scrubbing, followed by a pressure swing absorption unit (PSA), and therefore close to room temperature. In this sense, the use of membrane reactors is often reported in literature as a valuable approach for hydrogen separation at high temperature. CIEMAT has explored such technology with promising results which motivate further development.

Permeation results show that by means of a palladium-based membrane reactor it is possible to completely separate hydrogen from the other synthesis gas components and produce pure hydrogen as a permeate stream, provided that the membrane is defect-free and there is enough driving force for hydrogen to permeate. In our study many parameters have been found to play a role on hydrogen permeation, as for instance, gas composition, temperature, feed gas flow-rate, pressure, etc. Nevertheless, hydrogen flux, and consequently hydrogen recovery, has been found to depend mainly on the difference of hydrogen partial pressure on both sides of the membrane. From an industrial point of view this fact poses some restrictions on the use of membranes for hydrogen separation. Hydrogen partial pressure in the feed side should always be higher than hydrogen partial pressure in the permeate side so that forward permeation takes place. In order to achieve that, a hydrogen-rich gas stream or syngas at high pressure is required as membrane reactor feed gas stream. For hydrogen-diluted or low pressure feed gases the use of sweep gas is deemed necessary.

5 Water Gas Shift Membrane Reactor Studies

Last experimental work carried out by CIEMAT in WP13 has been the study of WGS in a membrane reactor (MR) and the comparison with WGS in traditional fixed bed reactors (TR). According to the IUPAC definition, a membrane reactor is a device that combines the separation properties of membranes with the typical characteristics of catalytic reaction steps in only one unit. In particular, the membrane does not only play a role as a separator but also as a part of the reactor itself. In other words, a membrane reactor is an engineering device that selectively removes a product from the reaction system, giving the possibility of achieving higher conversion than a traditional process under the same operation conditions. For that reason, one of the main application opportunities of inorganic membrane reactors refers to the conversion enhancement of an equilibrium limited reaction by the selective permeation of a reaction product through the membrane. In our particular case, the equilibrium limited reaction to study is the water gas shift reaction and the reaction product to remove is hydrogen. Hydrogen removal from the reactor might shift the equilibrium of the WGS reaction to the right side, enhancing products formation, H_2 and CO_2, what would mean working at lower temperatures or lowering the steam to CO ratio. This last statement is somehow controversial, however, since a quasi-stoichiometric ratio of steam to carbon monoxide may enhance secondary reactions to occur, for instance Boudouard reaction or methane formation.

5.1 Experimental

5.1.1 Membrane and catalyst

The membrane reactor concept proposed in our study combines the use of a membrane selective to hydrogen permeation and a highly active catalyst for water gas shifting. Based on the results obtained in previous stages pre-commercial Pd membrane was selected to provide an efficient way for hydrogen removal. As said before, the membrane is tubular having a diameter of 1” and it is 6” long. It is housed in a 3-zone electric furnace with temperature control.

The commercial iron-chromium catalyst, suitable for high temperature WGS under the operating conditions expected for synthesis gas after the steam reforming unit in VVBGC –see deliverable D105- was selected for WGS studies in the membrane reactor. As described before, the catalyst density is 1.1 g/cc and it was supplied in pellets of 6x6 mm.

5.1.2 Test rig

Experiments were conducted on a bench-scale level, in the same facility in which hydrogen separation studies were performed.

For WGS studies in the membrane reactor, samples of the iron chromium catalyst from the same batch used for WGS studies in a conventional fixed bed reactor (see deliverable D105) were placed on the shell side of the reactor (reaction side) to make up a catalyst bed of 4.9 cm length (39 cm^3 volume), matching with the membrane zone. Inert alumina spherical pellets were also placed on the shell side of the reactor to support the catalyst. The reactor configuration chosen is depicted schematically in **Fig. 25**.

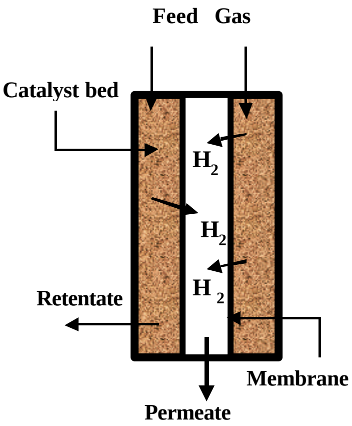


Fig. 25 Reactor configuration for Water Gas Shift Membrane Reactor (WGSMR) experiments

5.1.3 Experimental programme

Based on the results obtained in our water gas shift studies in fixed bed, for the WGS membrane reactor experiments, space velocity, temperature and steam to CO ratio were set purposely at values which were known beforehand that would not fully convert CO into CO_2 and H_2. Thus, it would be possible to see if there is any effect on CO conversion enhancement due to removing hydrogen from the reaction environment.

Gas composition used for the tests was CO, 44%v/v; H_2 40% v/v and CO_2 16%v/v, which is, except for CH_4, similar to the dry gas composition expected at VVBGC after the steam reformer.

WGS experiments in the membrane reactor were conducted at two different temperatures (320 and 380ºC). For each temperature, the reaction was carried out at several pressures on the retentate side, (1.5; 5; 8 and 10 bar), relative to atmospheric pressure. Permeate pressure was kept at atmospheric pressure and sweep gas was not used. H_2O to CO ratio was set at 3, and gas hourly space was kept at 16771 h^{-1}.

5.2 *Results and Discussion*

From the WGSMR tests two types of results are obtained: H_2 permeation for complex mixtures, under WGS reaction conditions, and CO conversion under membrane reactor conditions, which can be compared to the activity of the catalyst in absence of permeation, that is, catalytic activity in the so-called traditional WGS reactor. Results were presented in detail in deliverable D109[16]. A summary is given in this report.

5.2.1 Permeation

In addition to CO conversion, from the WGS studies in the membrane reactor the following results are obtained:

- Flux of hydrogen as a function of driving force for complex system ($H_2/CO/CO_2/H_2O$) under WGS conditions
- Effect of temperature on hydrogen flux for complex system ($H_2/CO/CO_2/H_2O$)

As obtained for binary mixtures, only hydrogen flows through the membrane even for a complex gas mixture under water gas shift conditions (CO, 19%v/v; H_2 17% v/v, CO_2 7%v/v, H_2O, 57 %v/v). Measured hydrogen permeated flux for the syngas mixture is lower than the values obtained for H_2/N_2 and H_2/CO_2 mixtures. This means that the presence of CO and H_2O influences negatively membrane efficiency due either to dilution by the presence of other gas components or to some inhibition effect. Nevertheless, it should be taken into account that driving force - the difference of the square root of hydrogen partial pressure on both sides of the membrane- under water gas shift membrane reactor conditions is very low compared to the resulting driving force for hydrogen separation studies conducted on binary mixtures.

In **Fig. 26** H_2 flux is plotted against the difference of the square root of hydrogen partial pressure on both sides of the membrane, which corresponds to the transport through the palladium layer following the mechanism of solution-diffusion. Permeation at two temperatures, 320ºC and 380ºC are shown in the graph. As can be observed, permeation increases with temperature which is often the case reported in literature for permeation of pure hydrogen. The hydrogen transport through a dense palladium film is an activated process and concerning the influence of temperature on hydrogen permeation an Arrhenius-type law is commonly used to describe the relationship between hydrogen permeation rate and temperature. Since only two temperatures were studied in this work such a relationship cannot be estimated. Concerning the effect of driving force, the term $(P_{feedH_2}^{0.5} - P_{permH_2}^{0.5})$ represents that the diffusion of atomic hydrogen through the palladium layer is the rate-controlling step, which is usually the case for thick palladium membranes. In our case, a good linear relationship between driving force and flux of hydrogen is found for 320ºC. However at 380ºC, though the number of experimental data is quite limited, relationship between driving force and flux of hydrogen is somehow poorer, which suggests that other elementary steps of the complex mechanism phenomenon of hydrogen permeation through dense palladium might be playing a role under those experimental conditions. It should be highlighted that because of the experimental operating conditions at the membrane reactor (wet feed gas composition and pressure) driving force is very small and therefore deviations from the openly agreed driving force describing hydrogen permeation can be expected.

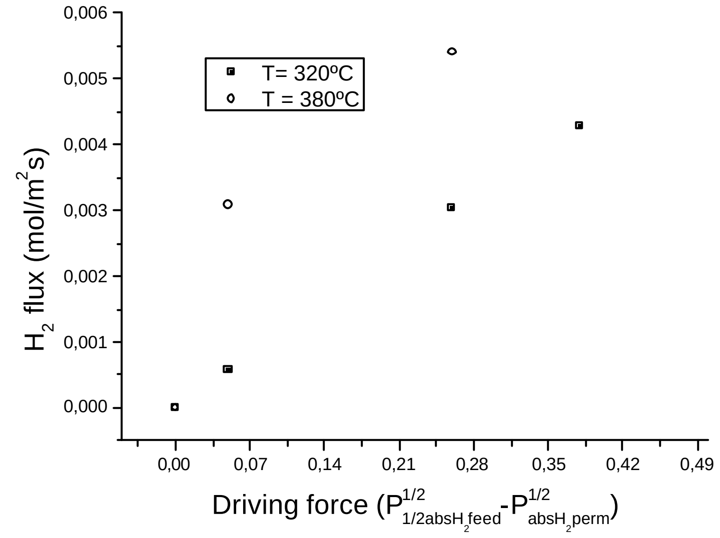


Fig. 26. Hydrogen flux under WGS conditions as a function of the difference between the square roots of the hydrogen partial pressures on the feed and permeate sides (Pperm= 0 bar. (rel); F feed gas (dry)= 4,71 Nl/min; Feed Gas composition (dry basis)=44% v/v CO, 40% v/v H_2, 16%v/v CO_2; R (H_2O/CO)= 3 mol/mol; GHSV= 16771 h^{-1})

5.2.2 CO conversion

In the following figures, CO conversion in traditional fixed bed reactor (in absence of hydrogen permeation) and in membrane reactor (in presence of permeation) are compared.

Fig. 27 shows the beneficial effect of removing hydrogen from the reaction side. WGS reaction in principle is not affected by the reaction pressure in a traditional packed bed reactor, because the overall number of moles does not change. On the other hand, as the driving force for H_2 permeation increases with the higher pressure on the reaction side- retentate side- in-situ removal of hydrogen enhances CO conversion in the case of the membrane reactor as **Fig. 27** shows. At 320ºC, CO conversion increases from 4.11 % when hydrogen is not removed, i.e. under fixed bed, traditional reactor conditions to 15.75%, when pressure at the retentate side is 10 bar rel (feed pressure 11.3 bar a), in the membrane reactor concept.

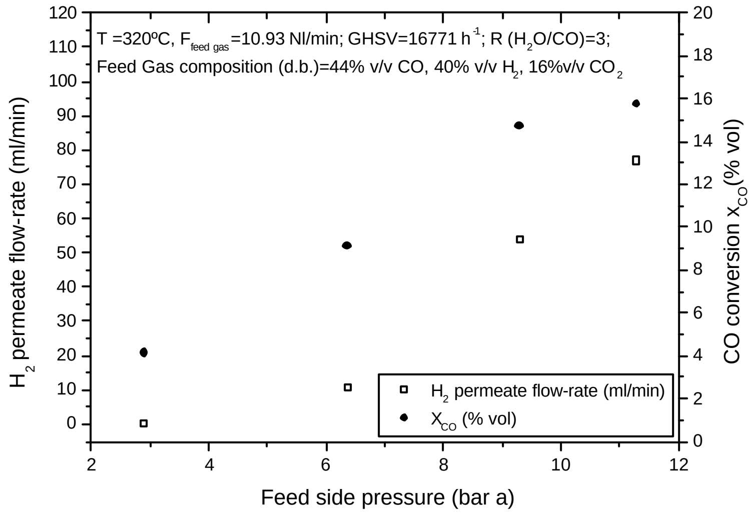


Fig. 27. CO conversion and hydrogen permeate flow at 320ºC versus retentate pressure (Pperm= 0 bar. (rel); F feed gas (dry)= 4,71 Nl/min; Feed Gas composition (dry basis)=44% v/v CO, 40% v/v H_2, 16%v/v CO_2; R (H_2O/CO)= 3 mol/mol; GHSV= 16771 h^{-1})

Removal of hydrogen through the membrane also enhances CO conversion at the second temperature studied as **Fig. 28** shows.

It can be seen that as hydrogen permeate flux increases as a result of a higher pressure and hence higher driving force, conversion of carbon monoxide also increases. At 380ºC there is an enhancement of CO conversion from 34.25% (traditional reactor, no permeation) to 60.5% when retentate pressure was set at 8 bar rel (feed pressure 9.39 bar a).

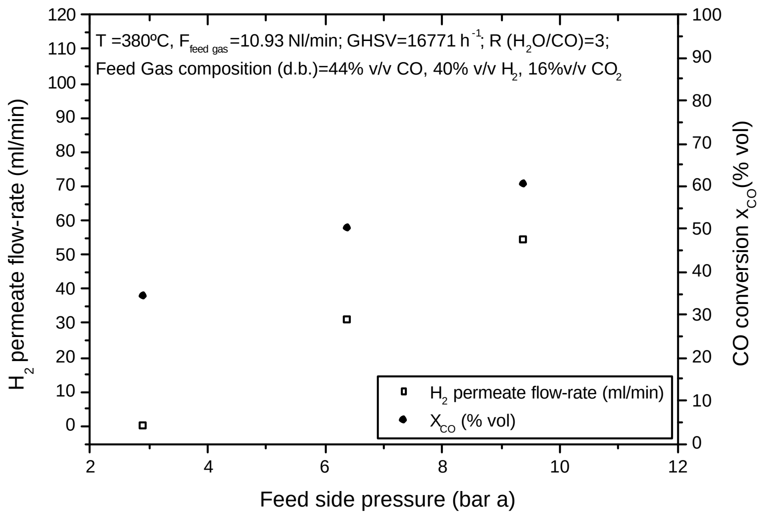


Fig. 28. CO conversion and hydrogen permeate flow at 380ºC versus retentate pressure (Pperm= 0 bar (rel).; F feed gas (dry)= 4,71 Nl/min; Feed Gas composition (dry basis)=44% v/v CO, 40% v/v H_2, 16%v/v CO_2; R (H_2O/CO)= 3 mol/mol; GHSV= 16771 h^{-1})

5.2.3 Comparison of traditional WGS reactor and membrane WGS reactor

WGS reaction in principle is not affected by the reaction pressure in a traditional packed bed reactor, because the overall number of moles does not change. On the other hand, as the driving force for H_2 permeation increases with higher pressure on the reaction side- retentate side- and thus in-situ removal of hydrogen results in an increase of CO conversion in the case of the membrane reactor. A high pressure on the reaction side facilitates permeation and therefore pushes the reaction towards further product formation, due to removal of one of the reaction products, i.e., hydrogen. At 320ºC, CO conversion increases from 4.11 % when hydrogen is not removed, i.e. under fixed bed, traditional reactor conditions to 15.75%, when pressure at the retentate side is 10 bar, in the membrane reactor concept. Similarly at 380ºC there is an increase in CO conversion from 34.25% (traditional reactor, no permeation) to 60.5% when retentate pressure was set at 8 bar rel.

5.3 Conclusions

WGSMR experiments have been conducted at two reaction temperatures, 320ºC and 380ºC. For each temperature, the reaction was carried out at several pressures on the feed side by controlling the pressure of the retentate stream, (1.5; 5; 8 and 10 bar, relative to atmospheric pressure). Permeate pressure was kept at atmospheric pressure and sweep gas was not used. H_2O flow-rate was adjusted to provide a steam to CO ratio equals to 3, and gas hourly space was kept at 16771 h^{-1}. CO, CO_2 and H_2 content of the feed gas were set according to the expected gas composition for the VVBGC facility, after the steam reformer.

The advantages of using a water gas shift membrane reactor over a traditional fixed bed reactor have been studied in terms of potential for producing a high purity hydrogen stream and for enhancing CO conversion at set operational conditions.

Concerning hydrogen enrichment, results show that by means of the membrane reactor it is possible to completely separate hydrogen from the other gas components and produce pure hydrogen as a permeate stream.

As for the potential for enhancing conversion of equilibrium limited reactions, our results show that removal of hydrogen from the reaction side by permeation to the permeate side has a positive effect on CO conversion during water gas shift experiments in the membrane reactor. Increasing pressure on the feed side allows for higher hydrogen removal. As expected, selective permeation of a reaction product through the membrane leads to conversion enhancement of the equilibrium limited WGS reaction, giving the possibility of achieving higher conversion than in a traditional reactor configuration under the same operation conditions.

6 Final Conclusions & Recommendations

In order to produce a H_2-rich gas, within the CHRISGAS project CIEMAT has accomplished the following experimental studies:

- Water Gas Shift Studies in Traditional Packed Bed Reactor
- Separation of Hydrogen using Membranes

- Water Gas Shift Studies in Membrane Reactor

Water Gas Shift studies dealt with selection of catalysts and optimisation of operating conditions to maximise CO conversion and hydrogen production. CIEMAT studied on a laboratory scale the activity of a commercial WGS catalyst (Fe-Cr-based) and a novel Pt-based catalyst provided by CATATOR AB Sweden, in a traditional fixed bed reactor using simulated gases, under the operating conditions and gas composition expected at Växjo Värnamo Biomass Gasification Centre (VVBGC). Results prove that both types of high temperature WGS catalysts (Fe-Cr- and Pt-based) are able to convert more than 90% of the CO content of the synthesis gas into CO_2 and H_2 under specific operating conditions (temperature, space velocity and steam to CO ratio), and therefore can be regarded as suitable to be used in VVBGC. The ferrochrome commercial catalyst studied provided good conversion of CO (less than 2-3 % v/v residual) in the temperature range of 360ºC-400ºC and at H_2O/CO ratios higher than 6. High conversion of CO was also obtained when using a Pt based catalyst, in the temperature range of 350ºC-380 ºC and high H_2O/CO ratios. Those experiments showed very good selectivity to H_2 and CO_2.

Although results in the traditional water gas shift packed bed reactor can be considered satisfactory, they show some limitations. In order to obtain a hydrogen rich stream, higher conversion of CO at lower temperatures and less steam excess in relation to CO content would be desired. Besides, the gas leaving the WGS reactor consists of a mixture rich in hydrogen and carbon dioxide, excess steam not consumed by the reaction and a low amount of CO. Separation of hydrogen from carbon dioxide after the WGS reactor is usually accomplished by means of chemical or physical solvent scrubbing, followed by a pressure swing absorption unit (PSA), and therefore close to room temperature. In this sense, the use of membrane reactors can be a valuable approach for hydrogen separation at high temperature. Moreover, a membrane reactor gives the possibility for combining the separation properties of the membrane with the catalytic reaction in only one unit.

Studies on separation of hydrogen by means of membranes dealt with evaluation of permeation and selectivity to hydrogen of prepared and pre-commercial membranes. CIEMAT conducted those studies on a bench scale level, in a dedicated facility built within the time frame of the CHRIGAS project. The performance of palladium membranes obtained from two sources was evaluated. The first batch of

Pd-membranes was prepared for CIEMAT by a partner in another project, funded by the Ministry of Education and Science of Spain. The second membrane studied is a pre-commercial prototype supplied by a research institute in USA. Prepared membranes showed very poor selectivity, which was basically attributed to discontinuities of the layer of palladium deposited on the surface of the porous stainless steel tube. It was concluded, therefore, that those membranes were not suitable for further studies in a WGS membrane reactor.

On the other hand permeation studies conducted with the pre-commercial membrane show that by means of a membrane reactor it is possible to completely separate hydrogen from the other gas components and produce pure hydrogen as a permeate stream. The membrane studied shows infinite selectivity to hydrogen since neither N_2 nor CO_2 nor CO permeated through it. Hydrogen is able to permeate, as long as there is enough driving force, and is removed from the reactor as a pure permeate stream. In our study many parameters have been found to play a role on hydrogen permeation, as for instance, gas composition, temperature, feed gas flow-rate, pressure, etc. Nevertheless, hydrogen flux has been found to depend mainly on the difference of hydrogen partial pressure on both sides of the membrane. From an industrial point of view this fact poses some restrictions on the use of membranes for hydrogen separation. Hydrogen partial pressure on the feed side should always be higher than hydrogen partial pressure on the permeate side so that forward permeation takes place. In order to achieve that, a hydrogen-rich gas stream or syngas at high pressure is required as membrane reactor feed gas stream. For hydrogen-diluted or low pressure feed gases the use of sweep gas is deemed necessary.

Finally, CIEMAT has studied the advantages of using a water gas shift membrane reactor over a traditional fixed bed reactor, in terms of potential for producing a high purity hydrogen stream and for enhancing CO conversion at set operational conditions. The experimental device included a Pd-based membrane and a commercial high temperature Fe-Cr-based, WGS catalyst, which was packed in the annulus between the membrane and the reactor outer shell. Results prove feasible to produce a pure hydrogen permeate stream, even in the case of complex reaction system (H_2/CO/CO_2/H_2O) under WGS conditions mixtures. Regarding comparison of CO conversion for WGS in a traditional reactor (TR) and in a membrane reactor (MR), results show that in the MR concept, removal of hydrogen from the reaction side has a positive effect on the conversion of WGS reaction at a given temperature. On increasing pressure on the reaction side, permeation is enhanced what pushes the reaction towards further product formation, due to removal of one of the reaction products, i.e., hydrogen, and hence increasing carbon monoxide conversion.

7 References

[1] Babu, S.P. (2002): "Biomass Gasification for hydrogen production-process description and research needs. Revised draft (Oct. 29, 2002)". IEA, Gas Technology Institute, IL, U.S.A.

[2] Hemmes, K.; de Groot, A. and den Uil, H. (2003): " BIO-H2. Application potential of biomass related hydrogen production technologies to the Dutch energy infrastructure of 2020-2050". ECN-C-03-028, April 2003

[3] Ciferno, J.P. and Marano, J.J. (2002): "Benchmarking Biomass Gasification Technologies for fuels, chemicals and hydrogen production". US DOE National Energy Technology Laboratory, June 2002.

[4] Yamasita, K. and Bareto, L. (2004): "Biomass gasification for the co-production of Fischer-Tropsch liquids and electricity", Interim Report IR-04-047, International Institute for Applied System Analysis, Austria

[5] CHRISGAS (Clean Hydrogen-rich Synthesis gas) proposal. Anex I: description of work. 6th Framework Programme, Proposal/Contract 502587, May 2004.

[6] Maroño, M. Sánchez-Hervás, J. Mª (2009): "Performance of HT-WGS Catalysts for Upgrading of Syngas Obtained from Biomass Gasification". Colección Informes Técnicos Ciemat, nº 1159. Editorial Ciemat, ISBN 1135-9420, NIPO 471-09-015-3.

[7] Sánchez-Hervás, J.M.; Maroño, M.; Cabanillas, A. (2005): "State of the art review on separation of hydrogen by membranes and water gas shift reaction catalysts". Deliverable D-103, CHRISGAS project, Contract SES6-CT-2004-502587.

[8] Sánchez-Hervás, J.M.; Maroño, M.; Cabanillas, A. (2006): "Report on Catalytic WGS Reaction Studies", Deliverable D-105, CHRISGAS project, Contract SES6-CT-2004-502587, 2006.

[9] Maroño, M., Sánchez-Hervás, J.M., Cabanillas, A. (2007): "Supplementary studies on Water gas Shift catalysts", Deliverable D105b, CHRISGAS project, Contract SES6-CT-2004-502587, July 2007.

[10] Maroño, M.; Sánchez-Hervás, J.M.; Ruiz, E. (2010) "Hydrogen-rich gas production from oxygen pressurized gasification of biomass using a Fe–Cr Water Gas Shift catalyst", Journal of Hydrogen Energy, Vol. 35, 1, pp. 37-45 Jan 2010

[11] Maroño, M.; Sánchez-Hervás, J.M.; Ruiz, E.; Cabanillas, A. (2008) "Study of the suitability of a Pt based catalyst for the upgrading of a biomass gasification

syngas stream via the WGS reaction" Catalysis Letters , 126, pp 369-426, Oct 2008

[12] Maroño, M.; Sánchez-Hervás, J.M.; Cabanillas, A. (2007): "Bench-scale catalytic membrane reactor", Deliverable D106, CHRISGAS project, Contract SES6-CT-2004-502587, Feb 2007.

[13] Maroño, M.; Sánchez-Hervás, J.M.; Cabanillas, A. (2008): "H_2 Permeation Tests on Prepared Membranes", Deliverable D108, CHRISGAS project, Contract SES6-CT-2004-502587, Feb 2008.

[14] Calles, J.A.; Sanz, R; Alique, D. (2009) Study of preparation of Pd-based membranes by electroless plating over PSS support. Euromembrane 2009, Montpellier, Book of Abstracts, p. 216.

[15] Maroño, M.; and Sánchez-Hervás, J.M. (2009): "Report on experimental results of hydrogen separation by membranes", Deliverable D104, CHRISGAS project, Contract SES6-CT-2004-502587 (Feb 2009)

[16] Maroño, M.; Sánchez-Hervás, J.M. and Barreiro M.M (2008) "Estudios de enriquecimiento en H_2 de gases de gasificación mediante el uso de un reactor catalítico de membranas: catalizadores WGS y membranas inorgánicas de Paladio" Informe final Proyecto HENRECA (ENE2004-07758-C02-01) Colección Informes Técnicos CIEMAT. NIPO: 471-08-049-6 Publisher CIEMAT. ISSN: 1135-9420 (Dec 2008) (In Spanish)

[17] Sanchez J.M.; Maroño, M. and Barreiro M.M. (2009) "Permeability and selectivity to H_2 of Pd membranes supported on porous stainless steel tubes"; J.M. Sánchez, M.Maroño, M.M. Barreiro, Euromembrane 2009, Montpellier, France 6 -10 September 2009

[18] Sanchez J.M.; Maroño, M. and Barreiro M.M. (2010): "Report on MCR tests and Performance of Membrane catalytic reactor versus Water gas shift reactor", Deliverable D109, CHRISGAS project, Contract SES6-CT-2004-502587 (Feb 2010)

[19] Sanchez J.M.; Maroño, M. and Barreiro M.M. "Separation of CO_2 and H_2 using palladium membranes (for integration in power generation with CO_2 capture)", Euromembrane 2009, Montpellier, France 6 -10 September 2009

[20] Sanchez J.M.; Maroño, M. and Barreiro M.M. "Preliminary Studies of Water Gas Shift catalysts and a Pd-based membrane for H_2 and CO_2 production & separation in a Catalytic Membrane Reactor", 9th International Conference on Catalysis in Membrane Reactors, ICCM9, 28 June- 2 July, 2009, Lyon, France

1135- 9420