Fuel Processing Technology 118 (2014) 278–286

Contents lists available at ScienceDirect

Fuel Processing Technology

journal homepage: www.elsevier.com/locate/fuproc

Energy and mass intensities in hydrogen upgrading by a membrane reactor

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ARTICLE INFO

Article history:
Received 21 June 2013
Received in revised form 22 July 2013
Accepted 23 September 2013
Available online 25 October 2013

Keywords:
Mass intensity
Energy intensity
Membrane reactor
Hydrogen
Metrics

ABSTRACT

The necessity arose in the last decennia for the redesign of industrial processes with new unit operations for addressing environmental concerns which has led to the definition of new process indexes, so-called, metrics, that together with the traditional parameters supply additional information for technology selection and identify operating conditions for making a process more profitable. Two sustainability indexes, mass and energy intensities were used in a non-conventional evaluation of the up-grading stage in hydrogen production, i.e. the water gas shift, by means of membrane reactors. Defined as the ratio between the total inlet mass and total energy involved in the reactor, with respect to the hydrogen fed and produced by the reactor, they provide useful information about material exploitation and energy efficiency. The comparative study of membrane reactor performance with respect to conventional reactors was analysed as a function of the main process variables, i.e., pressure, feed molar ratio and space velocity. The membrane reactor resulted always in being more material (20–40%) and energy (20–35%) intensive than a traditional reactor and, in most of the cases, the values of its indexes exceeded the best one of a conventional reactor, corresponding at the equilibrium.

1. Introduction

In the last decennia, many efforts are done to transform traditional industrial growth into sustainable growth. The process intensification (PI) strategy, as a new design philosophy recently introduced for bringing drastic improvements in manufacturing and processing, aims to pursue this growth in a competitive but sustainable way, reducing energy consumption, better exploiting raw materials, minimizing the wastes, increasing the plan efficiency, reducing the plant size and capital costs, increasing safety, improving remote control, etc. [1–5].

A deep understanding of the PI principles places the membrane technology and the membrane engineering in a crucial role for the implementation of this strategy [6]. Among other new unit operations involving membranes, membrane reactors (MRs) are expected to play a decisive role in the scenario of sustainable growth. They represent today a solution for several processes involving the petrochemical industry [7,8], energy conversion [9,10], and hydrogen production [11–16] and well fulfil the requirements of PI, offering better performance, lower energy consumption, and lower volume occupied with respect to the conventional operations. The synergic effects offered by MRs through combining reaction and separation in the same unit, their simplicity and the possibility of advanced levels of automation and control, offer an attractive opportunity to redesign industrial processes [17–19].

However, to make the use of a new technology more attractive, it is fundamental to define a new way of analysing its performance and highlighting its potentialities with respect to well consolidated traditional technologies. Hand in hand with the redesign of new processes comes, thus, the identification of new indexes, so-called, metrics, that together with traditional parameters usually used to analyse a process can supply additional and important information to decide on the type of operation and the identification of the operating condition windows that make a process more profitable. Up to now, many efforts are being made to define indicators of the industrial processes [20,21] and most of them are calculated in the form of appropriate ratios which can provide a measure of impact independent of the scale of the operation, or to weigh costs against benefits and, in some cases, they can allow the comparison between different operations [22]. The use of these new indexes can lead to an innovation in the analysis of the performance of the unit operations and, in the case of the membrane technology, can clearly and easily show the advantages and drawbacks that the choice of that specific technology can provide in comparison with the traditional units.

On the light of the above considerations, in this work, the upgrading of hydrogen by means of a membrane reactor is considered as a case

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http://dx.doi.org/10.1016/j.fuproc.2013.09.009

study for introducing a non-conventional analysis of the performance of an alternative unit operation. The water gas shift reaction, as the upgrading stage of the hydrogen production processes, has been considered carried out in a tubular Pd–Ag membrane reactor operating at the high temperature stage.

Traditionally, syngas mixtures containing mostly hydrogen and carbon monoxide can be generated in industrial processes at elevated temperatures by steam reforming or partial oxidation of light hydrocarbons or bio-fuels or gasification of coal and biomass and, then, fed to an upgrading stage for reducing the CO content and producing more H_2. This upgrading stage consists of the water gas shift reaction which is exothermic and characterized by no variation of the mole number:

$$CO + H_2 = CO_2 + H_2 \qquad \Delta H^0_{298} = -41 \text{ kJ mol}^{-1}.$$

Therefore, CO conversion is thermodynamically favoured by low temperatures but, on the contrary, its kinetics is promoted by a high temperature. As already widely demonstrated in the past, both experimentally [23–27] and theoretically [11,28,29], the use of a Pd-based membrane reactor provides significant improvements in terms of conversion, hydrogen recovery, and catalytic volume reduction with respect to the traditional process. The results of a quite comprehensive simulation study already published in our previous work [28] were used as the starting point for this new analysis type.

As an overall approach, the evaluation of the aforementioned metrics provides a set of tools for a comprehensive analysis of the performance of the membrane reactor and can give indications about its feasibility on a larger scale. This evaluation starts, of course, from the more "conventional" variables used to describe the performance of a reactor-like CO conversion. Figs. 1 and 2 show some of the most interesting results [28] in terms of CO conversion evaluated for a membrane reactor operating in the condition listed in Table 1. These conditions are close to the ones used at industrial level and mostly consider high GHSV, typical for the high temperature stage of the conventional reactors of water gas shift. The feed pressure was limited between 500 and 1500 kPa, assuming atmospheric pressure at the permeate side. The feed has a typical composition of a syngas stream exiting from a reforming stage, and thus already contains hydrogen and small fractions of CO_2, in addition to the carbon monoxide.

Figs. 1 and 2 describe the dependence of the conversion on the main process parameters. In particular, in Fig. 1, the MR performance is

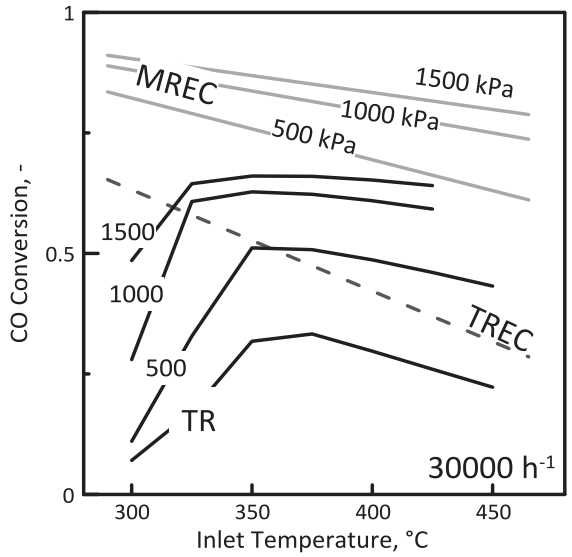

Fig. 1. Conversion as function of the temperature for different value of reaction pressure.

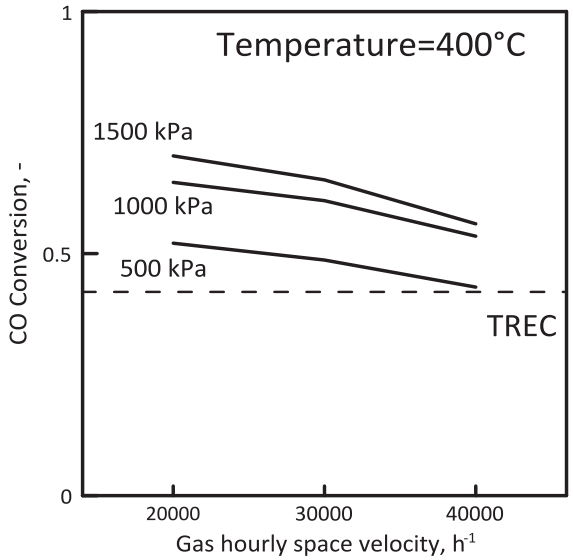

Fig. 2. Conversion as a function of the GHSV for different value of reaction pressure.

analysed as a function of the temperature and pressure and compared with that of the TR in the same operating conditions. Each point of the four curves represents the outlet conversion and temperature of the MR and TR. As general trend, CO conversion achieved in MR is greater than that of TR and also exceeds the TREC for temperatures higher than 380 °C.

All the curves, simulated for the three feed pressures, initially follow an increasing trend with the temperature reaching up to the maximum; afterwards, it slightly decreases. This trend is a compromise of various opposite effects. The reaction is in fact negatively affected by the temperature from a thermodynamic point of view, since it is exothermic, but, in the meantime, its kinetics is promoted. These effects are valid both for the TR and the MR. Indeed, CO conversion increases with temperature and then reduces once the thermodynamics constraint becomes relevant. This trend is less emphasized in the MR where, with respect to the TR, both temperature and pressure acts positively on the H_2 permeation.

Fig. 2 shows an example of how the CO conversion is affected by another important process parameter, the gas hourly space velocity (GHSV). Since in the MR, part of the H_2 fed and produced is removed through the membrane, the GHSV in a MR would be different to that in a TR at the same flow rates. For this reason the GHSV is calculated in this work at the inlet of the reactor (Eq. (1)). As a matter of fact, a high GHSV implies lower residence time between reactants and catalyst; as a consequence less hydrogen is produced and, thus, can permeate through the membrane. In fact, as also confirmed by the simulation,

Table 1
Operating conditions used in the simulations for the Pd-based MR and the Traditional reactor [28].

	Pd–Ag membrane reactor	High temperature traditional reactor
Inlet temperature	300–450 °C	
Feed pressure	500, 1000;1500 bar	
Feed mixture composition	CO: CO_2: H_2: N_2 = 20.5:19.2:51.8:8.5, % molar (dry basis)	
H_2O/CO feed molar ratio	1	
GHSV	20,000–40,000 h^{-1}	
Membrane characteristics		
Membrane permeance	$0.12\ (\pm 0.05) e^{-2.9\ (\pm 0.2)/RT}$, mol m^{-2} s^{-1} $Pa^{-0.5}$	
Membrane thickness	60 μm	
Membrane surface to catalyst amount ratio	1.5 m^2 kg_{cat}^{-1}	