



ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

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

Technical and economic feasibility of adapting an industrial steam reforming unit for production of hydrogen from renewable ethanol

Rafael Roldán*

Centro de Tecnología Repsol, Ctra. de Extremadura A-5 Km 18, 28931 Móstoles (Madrid), Spain

ARTICLE INFO

Article history:

Received 20 August 2014

Received in revised form

16 November 2014

Accepted 1 December 2014

Available online 19 December 2014

Keywords:

Hydrogen production

Ethanol

Steam reforming

Water gas shift

Stability

Industrial scale

ABSTRACT

The steam reforming of ethanol could be a solution to reduce CO₂ emissions in industrial hydrogen plants, given its renewable character. To adapt this process into the Repsol refineries, a scheme with pre-reforming section has been considered. Ethanol steam reforming has been tested using a commercial nickel catalyst at industrial pre-reforming conditions, particularly at high pressure (25 bar). In addition, a new “Ethanol-to-shift” process using a commercial water gas shift (WGS) catalyst to convert ethanol is proposed.

The pilot plant tests show that complete ethanol conversion is reached at low space velocity (WHSV < 1 h⁻¹) or at high temperature (400 °C), with predominance of methane formation. The commercial nickel catalyst is stable for at least 530 h due to the use of high hydrogen partial pressure to inhibit coke deposition. Then, it has been proven that it is a technically feasible process for industrial scale. The WGS catalyst (Fe–Cr), however, does not achieve full conversion even at very high temperature.

An economic analysis indicates that the steam reforming process would only be viable with a low price of ethanol (around 350 €/t), which is far from the current market price.

Copyright © 2014, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

The most widely extended process for production of hydrogen in industrial plants is the steam reforming process, generally being a more economic option than partial oxidation for small and medium capacity facilities [1,2]. Particularly, this process represents the major source of hydrogen for oil refineries, where it is required in many hydrotreating processes essentially intended to produce clean fuels with a minimum content of sulphur, nitrogen and other contaminants. In terms of sustainability, the energy efficiency is one of the most relevant

drivers of the refining business. Hence, it is logical to focus on the hydrogen plants efficiency, since the steam reforming is one of the largest producers of CO₂ emissions in the refinery: it is the third contributor of the refinery (after other sources like furnaces), accounting for 10% of the emissions, and the first one among the production processes. Generally a 60–90% of such emissions are derived from the carbon contained in the hydrocarbon feed (mainly natural gas, LPG or naphtha) in units with pressure swing adsorption (PSA) purification unit [3]. This is due to the fact that the purified hydrogen is separated from a purge gas which contains impurities (H₂, CO, CO₂ and CH₄), and such purge gas is used as fuel in the furnace of

* Tel.: +34 91 7532978; fax: +34 91 7538613.

E-mail address: rroldanm2@repsol.com.

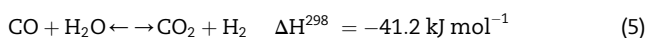
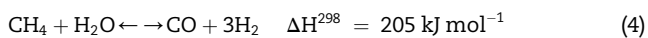
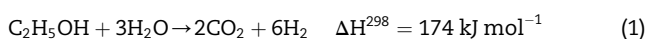
<http://dx.doi.org/10.1016/j.ijhydene.2014.12.003>

0360-3199/Copyright © 2014, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

the plant to provide the largest fraction of the high energy requirements of the reactions. Only a minor fraction of energy is supplied by make-up fuel. In this scenario, it is very valuable all the research aiming to produce hydrogen from renewable sources, like the so-called bio-ethanol (obtainable by biomass fermentation), since such process would not involve a net increase in the CO₂ emissions, but it rather would allow closing the CO₂ cycle. Moreover, such renewable hydrogen or “bio”-hydrogen could be used for hydrotreating fuels, where the product could gain such “bio” character in a certain degree, since the hydrogen molecule is incorporated in the final fuel.

In Repsol, the company I work for, there are 7 steam reforming units of different capacities (0.7–10.9 t H₂/h) in 5 different oil refineries in Spain. The reduction of the CO₂ emissions is one of the most important objectives in the company. As one of the potential ways to accomplish that goal, the purpose of the present research has been to analyze the feasibility of adapting one of such existing plants to use ethanol as feedstock, and therefore the work has focused on the steam reforming technology. Other technologies for production of hydrogen from ethanol like partial oxidation and autothermal reforming have been evaluated by others, and the comparison between them and steam reforming has determined that autothermal reforming is the most efficient process [4–6]. However, the current economic situation leads to propose efficient pathways that make use of existing assets. Therefore, this work has only considered the conversion of a steam reforming plant.

The ethanol steam reforming (ESR) has been extensively studied, considering bio-ethanol as feedstock. The endothermic reaction of ethanol with steam comprises the production of six molecules of hydrogen and also CO₂ as by-product (reaction 1). However, there is a variety of side mechanisms that can occur as it has been described in detail in recent reviews of the matter [7,8].



With insufficient steam, CO is produced instead of CO₂ (reaction 2) and just four molecules of hydrogen are obtained. Besides, ethanol can react with hydrogen to yield methane and water (reaction 3), by dehydration plus cracking. Ethanol can also dehydrogenate to acetaldehyde as intermediate, which, in turn, decomposes to CO and methane. Methane can undergo steam reforming to produce CO and hydrogen (reaction 4, being the reverse reaction, the CO methanation, also possible), whereas CO can be converted to CO₂ and more hydrogen through the exothermic water gas shift (WGS) reaction (reaction 5). An undesirable transformation is the ethanol dehydration to produce ethylene because this olefin is able to polymerize and generate coke, which can deactivate

the catalyst. Finally, more carbon may be formed by methane or CO decomposition (by the Boudouard reaction in the second case).

The catalysts studied are based on noble or non-noble metals supported on alumina or other different materials. Ethanol conversion on different noble metals has been studied, selecting Rh as the catalyst with best activity [9–11]. However, the use of cheaper non-noble metals is more attractive for commercial applications. An excellent alternative is provided by catalysts containing Ni [12–15], Co [16–18], or multimetallic combinations of both metals or even with Cu [19–21], which enhance the water gas shift activity of nickel. In spite of the activity of Al₂O₃ or MgAl₂O₄ as catalysts supports, their acidic character favours the dehydration of ethanol to ethylene and thus the coke formation. Therefore, numerous efforts have been dedicated to explore active and stable supports, like La₂O₃ [22,23], CeO₂, ZrO₂ [17,24], MgO, SiO₂, ZnO [25,26], or TiO₂ [27]. The addition of some of these materials to alumina affects not only the final acidity but also the properties of the nickel particles, and it helps to prevent carbon formation [28,29]. Moreover, the addition of alkaline metals leads to enhanced stability due to acidity decrease [30–32]. Some recent findings concern the advantages of zeolites and mesoporous materials. Chica et al. studied the high stability provided by the delaminated zeolites ITQ-2 and ITQ-18, which possess an open structure [33,34]. González-Vargas et al. introduced different proportions of Ce on the mesostructured MCM-41 looking for a high activity and stability alternative [35]. The research in this field still goes on in the search for a high activity and selectivity catalyst which at the same time is able to produce little coke and to maintain an optimum stability, so that it can guarantee a reliable operation in industrial scale.

For the use of hydrogen in the fuel cells application it is essential to reduce the CO formation in the product. This is achieved by operating at low temperature in order to favour the exothermic WGS reaction. Adversely, low temperature also increases the coke formation in the process conditions. A possible solution may be found in the process scheme depicted in Fig. 1, which can be found in some of the Repsol industrial units. The configuration includes a pre-reforming reactor operating at lower temperature than the primary steam reformer (and with different catalyst), two CO converters (high temperature shift, or HTS, and low temperature shift, or LTS) and a PSA purification unit. Although coke is inhibited at higher temperature in the conversion of ethanol [36,37], the formation of such or an upset of contaminants in the steam reformer catalyst cause local deactivation, which generates very high temperatures if the catalyst does not absorb the high heat flux available. If this happens, it may damage severely the tubular reactors, bringing about a concern for safety, plant integrity and operation reliability. To avoid this risk, it is the proposal of this research to use a pre-reforming catalyst to carry out the ethanol conversion, therefore in a lower temperature window (400–525 °C), with the advantage that the catalyst can be substituted in an easier way (it is loaded in a single adiabatic reactor) than the steam reformer catalyst (the catalyst is loaded in many tubular reactors and the loading procedure is more complicated). In this scheme, production of CO or CH₄ in the pre-reforming section

Download English Version:

<https://daneshyari.com/en/article/7716583>

Download Persian Version:

<https://daneshyari.com/article/7716583>

[Daneshyari.com](https://daneshyari.com)