



# Highly selective propylene production in a membrane assisted catalytic propane dehydrogenation



Antonio Ricca<sup>a,\*</sup>, Vincenzo Palma<sup>a</sup>, Gaetano Iaquaniello<sup>b,c</sup>, Emma Palo<sup>b</sup>, Annarita Salladini<sup>c</sup>

<sup>a</sup> University of Salerno, Department of Industrial Engineering, via Giovanni Paolo II 132, 84084 Fisciano, SA, Italy

<sup>b</sup> KT – Kinetics Technology S.p.A., Viale Castello della Magliana 27, 00148 Rome, Italy

<sup>c</sup> Processi Innovativi srl, Via di Vannina 88/94, 00156 Rome, Italy

## ARTICLE INFO

### Keywords:

Propane dehydrogenation  
Propylene  
Pd-based membrane

## ABSTRACT

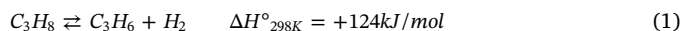
Selective propane dehydrogenation is one of the commercialised technology for the production of propylene. The main drawback of such process is closely linked to the high temperature required to reach a sustainable propane conversion that affects catalyst stability owing to coke formation on the catalyst surface. Accordingly, a periodic regeneration of catalytic bed is required. The aim of this paper is to investigate the option to perform the reaction in the presence of Pd-based membrane, that selectively removing hydrogen from reaction environment, could lead to a substantial reduction in the operating reaction temperature, decreasing the extent of reactions responsible for coke formation. The effect of operating conditions, in terms of feed composition and temperature are investigated, in order to determine the optimal operating parameters window to operate the system, and assess the overall concept performance.

## 1. Introduction

Propylene is the building block of important petrochemicals such as polypropylene and acrylonitrile. It is the second most produced derivative in the petrochemical industry, after ethylene, and is expected to have significant demand across diverse industries over the next years. Asia Pacific regions clearly dominated the global market for propylene in 2015, forecasting a continuous increasing of demand in the next future, mainly due to the increasing use of propylene (and acrylonitrile) in construction, electronic, furniture, and automotive industries. Propylene, and in general light olefins, are currently produced from light oil fractions through steam cracking (SC) and fluid catalytic cracking (FCC) processes [1,2]. Despite a large part of worldwide propylene production is achieved as co-product in steam crackers (> 55%) or as by-product in FCC units (around 35%), the high temperatures employed in such processes as well as the high instability of hydrocarbons cause the occurrence of coking and side reactions, that heavily suppress propylene yield [3]. In order to satisfy market demand increasing, being estimated in 5% per year until 2018, several on-purpose routes are emerging as propylene sources, such as propane dehydrogenation (PDH), coal-to-propylene (CTP), and olefin metathesis. It is widely accepted that, in the longer term, on-purpose propylene production technologies should be able to stabilize the supply/demand balance. In particular, PDH appeared the most suitable for satisfy the

gap between conventional processes (SC and FCC) and propylene demand.

PDH reaction (Eq. (1)) is highly endothermic, characterized by an increasing of moles number, therefore thermodynamically promoted at high operating temperatures and low pressures. At high temperature other side reactions could occur, leading to the production of lighter hydrocarbons or to coke formation, that by depositing on the catalytic surface, could cause the reaction system deactivation. In a typical catalytic behaviour, higher temperature assures higher conversion and lower selectivity; the opposite at lower temperature.



All commercially available technologies operated at temperature not higher than 650 °C, in order to reduce side reaction relevancy and catalyst deactivation. It is however worth to underline that side reactions are not limited by thermodynamic equilibrium, therefore long contact time results in lower selectivity to propylene. As a consequence, PDH industrial processes are characterized by a limited propane conversion (32–55%), with a selectivity to propylene below 90% [4].

To counter catalyst deactivation, a lot of efforts were spent in order to achieve more stable formulations. Chromium- and platinum-based catalysts are the most widely studied in this field, and are employed in the industrial processes. Among them, Pt-based catalysts arouse more interest because of their high catalytic performances and eco-friendly

\* Corresponding author.

E-mail address: [aricca@unisa.it](mailto:aricca@unisa.it) (A. Ricca).

properties: it was demonstrated that in PDH reaction Pt was capable to easier activate C-H bonds than C-C [5]. If in one hand platinum showed a marked tendency to the deactivation, Pt-Sn formulations assured higher activity, selectivity and stability, due to the promoting effect of tin. In fact it is well accepted that the addition of Sn leads Pt particle size to decrease, improving catalytic performances [6]. On the other hand, the bond strength of chemisorbed hydrocarbons may be modified by adding Sn, which may form an alloy with Pt [7,8]. Other studies pointed on the fact that Sn plays an active role in propane dehydrogenation instead of only a promoter [9].

Despite efforts in catalyst optimization, coke formation in the reaction system and consequentially catalyst deactivation, are unavoidable [10], thus requiring repeated catalyst regenerations [11]. Several techniques were proposed in order to improve catalyst stability and to enlarge the on-stream time that is the time between two regeneration cycles. The addition of steam can act as heat carrier toward the catalytic system, as well as could suppress coke deposition [12]; moreover, it results in a dilution of the system, thermodynamically promoting the propane conversion. Conversely, it was demonstrated that hydrogen addition in the catalytic system assures a very low catalyst deactivation, by preventing both carbon deposition and Pt sintering [13]; on the other hand, the addition of hydrogen, being also a product of reaction, thermodynamically disadvantages propane conversion. It was anyway widely accepted that catalyst deactivation strictly depends on reaction temperature, since lower temperature assures lower deactivation rate [14], following an Arrhenius-like law [15]. On the other hand, lower temperature depresses propane conversion, due to thermodynamic constraints. A proposed approach for increasing propane conversion was the addition of oxygen to the reaction volume in order to selectively oxidize hydrogen, thus enabling further propane conversion [16]. Such solution results in an unavoidable loss of propylene. The double target of reducing deactivation and increasing propylene conversion could be theoretically achieved by coupling a low temperature dehydrogenation stage with a H<sub>2</sub>-selective membrane [17,18], able to subtract a product to the system and thus thermodynamically promoting the production of propylene [19,20]. In a purely ideal analysis, membrane-based system allows lower operating temperature, avoiding the classical trade-off between conversion and selectivity, in addition, could severely reduce coke formation thus increasing the on-stream time. Pd-based membranes appeared the most promising solution for the employment with the PDH reaction, mainly due to their optimal selectivity/flux ratio and to the typical operating temperature (250–550 °C) that effectively matches the PDH reaction [21]. On the practical point of view, the employment of a Pd-based membrane in the PDH process results in a clear depression of permeability performances of the membrane by moving from an H<sub>2</sub>/inert mixture to a typical H<sub>2</sub>/propane/propylene system [22]. It was furthermore experienced that the performance reduction was more evident in the case of low hydrogen/propylene ratios [23]. Dedicated studies demonstrated that Pd-membrane in a PDH environment could suffer for typical coking phenomena, that by depositing on membrane surface inhibit hydrogen dissociation, resulting in a constant reduction of the membrane permeating capability [24], that in turn compromise the overall system productivity [25].

Peters et al. [26] reported a very interesting study on the deactivation phenomena of a membrane in a typical PDH environment. In their studies, authors experienced a significant reduction of hydrogen flux (up to 34% in 18.6 h of TOS) through the perm-selective layer once propane was introduced in the retentate side; a more severe deactivation was observed by introducing propylene in the system, leading to a complete membrane occlusion within 5 h. Anyway, the deactivation seems to be mitigated by reducing operating temperature, appearing non-relevant for a process temperature of 250 °C. In addition Schäfer et al. [27] also evidenced that catalytic membrane reactors for the PDH process were more prone to catalyst deactivation due to coke deposition with respect to traditional configurations. Such achievements enforced the hypothesis to operate in an as-called “open architecture”, in which

the reaction units and the separation units operate individually, so making possible to set 2 separate operating temperatures for the different stages [28,29]

The employment of a H<sub>2</sub>-selective membrane requires several constraints in terms of operating conditions, such as low propane dilution and relatively high operating pressure, aimed to maximize hydrogen partial pressure. Anyway, a lack of papers was present in the literature aimed to evaluate the catalytic performances in that unusual operating conditions. In addition, no papers were found in the literature reporting results for the membrane assisted dehydrogenation under concentrate propane mixture. In the present work, a preliminary experimental investigation on PDH reaction assisted by membrane for the propylene production is reported. The study focuses on the evaluation of operating conditions effect on catalytic unit performances, both in terms of activity and stability; furthermore, the feasibility of coupling PDH catalytic reactors to a Pd-membrane unit was investigated, in order to evaluate the influence of membrane presence in the shift of chemical equilibrium in PDH unit. To this aim a first characterization of reaction unit and membrane module separately has been performed, in order to individuate the optimal operating conditions for their integration.

## 2. Materials and methods

### 2.1. Experimental apparatus

Experimental tests were carried out in the ProCEED labs at the University of Salerno. The experimental apparatus, designed for a propylene capacity up to 0.05 kg/h, consists of 3 main units, assembled in open architecture: 2 tubular reactors (R-101 and R-102) and 1 membrane unit (M-101); the basic idea of the plant was to install in series the first reaction unit, the membrane and downstream the second reaction unit. Anyway, the plant was designed in order to assure a wide flexibility, being able to deviate process stream in order to selectively skip one, two or all the process units.

The plant scheme is depicted in Fig. 1, while in Fig. 2 is reported a picture of the experimental apparatus.

Reaction units were characterized by 2 identical tubular reactors, characterized by a nominal diameter of 1" SCH40 (o.d. 33.6 mm; wall thickness 3.78 mm), realized in stainless steel AISI 310 H. In each reactor, 31.25 g of commercial catalyst (3 mm pellets, Pt-Sn based, confidential supplier) was loaded, and locked in the central part of the unit. Reactors fitting was assured by a couple of flanges, each provided by a ¼" tube for the entrance of reactants or outlet of products; two thermocouples were placed in the reactor through 4 mm blind tubes inserted in the flanges, in order to evaluate gas temperature in the inlet and outlet sections of the catalytic bed.

The separation unit is constituted by a Pd-based commercial membrane (confidential supplier); the perm-selective layer is deposited on a stainless steel porous tube (o.d. 12.7 mm) for a length of about 254 mm, assuring a permeating surface of around 0.01 m<sup>2</sup>. The membrane tube is inserted in a shell tube (nominal diameter 1", corresponding to 33.6 mm), realized in stainless steel AISI 316 L.

All equipment units (both reactors and membrane modules) were heated through a couple of metalling heating wire, provided by Watlow, wounding the units in a solenoidal shape; two thermocouples were placed on the external surface of the modules, in order to control the wall temperature of the units. The modules were wrapped in a thick layer of insulating mat, to minimize heat loss toward the surrounding. A couple of pressure transducers were placed upstream and downstream reactor and membrane (both for retentate and permeate streams) units; pressure and temperature signals were collected by a multifunctional display and acquired by PC for overall process monitoring.

Each unit is provided with a couple of 3-way valves, one upstream and one downstream, in order to switch the process stream to pass through the process unit, or to by-pass the module. During by-pass mode, through a couple of dedicated valves, is possible to flush each

Download English Version:

<https://daneshyari.com/en/article/6581166>

Download Persian Version:

<https://daneshyari.com/article/6581166>

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