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Butadiene production in membrane reactors: A techno-economic analysis

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HIGHLIGHTS

- H₂-selective membrane reactors (MR) for the direct dehydrogenation of butane (BDH).
- Techno-economic feasibility of the MR-BDH technology compared to the benchmark.
- Lower operating temperature (−85 °C) enabled by the MR-BDH technology.
- Reduced CAPEX (−18%) and OPEX (−27%) obtained in the MR-BDH technology.
- 20% reduction in the butadiene cost of production achieved in the MR-BDH technology.

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ABSTRACT

The direct dehydrogenation of butane (BDH) is emerging as an attractive on-purpose technology for the direct production of 1,3-butadiene. However, its product yield is hindered by the high rate of carbon deposition associated to the high temperature required for the highly endothermic reaction. In this work, we evaluated the use of H₂-selective membrane reactor, to increase the yield of the dehydrogenation process at milder operating conditions. The novel proposed membrane reactor (MR)-assisted BDH technology is compared from a techno-economic point of view with the benchmark technology. The results of this analysis reveal that the MR technology enables to work at milder operating temperatures (−85 °C), reducing carbon formation (−98.5%) and reactor duty (−10%). Due to the higher reaction yields, the MR-assisted BDH technology can lower the required shale gas-based feedstock, maintaining same production capacity as in the benchmark; this will result in an overall plant efficiency of 50.92% in the MR-assisted plant, compared to 37.7% of the benchmark case. This work demonstrates that MR-assisted technology is a valuable alternative to the conventional BDH technology, reducing of almost 20% the final cost of production of 1,3-butadiene, due to the lower installation costs and the higher energy efficiency.

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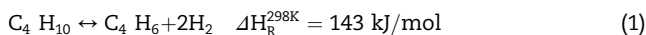
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Introduction

With a production capacity expected to increase worldwide from 16 million metric tons (MMT) in 2018 to 20 MMT in 2023, organic chemical butadiene is one of the main building blocks in the petrochemical industry [1]. The growth in 1,3-butadiene production is primarily driven by the industry demand for styrene butadiene rubber and polybutadiene rubber, which can be used in a wide variety of applications, such as automotive, electronics and construction [2].

Traditionally, 1,3-butadiene is produced as by-product of ethylene from steam crackers, using gasoil or naphtha as feedstock. These processes accounted for over 95% of the butadiene market in 2007 [3]. The recent drop in the price of ethane in the United States sparked a shift in steam cracker feeds from naphtha to ethane due to higher achievable ethylene yield, with a consequent decreasing in the production of 1,3-butadiene [4]. As a consequence, the petrochemical industry is driven towards the search for a more economic feedstock and more efficient conversion technologies to produce 1,3-butadiene [5]. In this respect, the Butane Dehydrogenation (BDH) is emerging as an attractive alternative to traditional processes. When using shale gas-derived feedstocks, this specially designed “on-purpose” butadiene technology is expected to fill the gap between demand and supply through the direct production of 1,3-butadiene [6]. In this process, 1,3-butadiene is directly produced from n-butane according to the following dehydrogenation reaction:



Nowadays, the dehydrogenation of n-butane to 1,3-butadiene is performed at industrial scale in the Houdry-CATADIENE process. However, since the dehydrogenation reaction is highly endothermic and limited by the thermodynamic equilibrium, high operating temperatures and/or low paraffin partial pressures are needed to achieve high conversions. Temperatures of 550–650 °C are required to obtain alkane conversions $\geq 50\%$ at 1 bar [5]. The elevated reaction temperatures promote side cracking reactions that lead to coke deposition and catalyst deactivation, resulting in a reduction of the overall reaction selectivity [7]. Moreover, the regeneration needed for steady operation makes the process design to be relatively complex, since it requires the cyclic operation of several reactors, alternating between dehydrogenation, purging, regeneration, reduction, and evacuation.

Most of the scientific research on BDH technology is based on the development of improved catalyst formulations to increase the reactor performance [8–12]. The effect of metals, the nature of supports, the nature of ligands and the polarity of active species is being investigated to better understand the structure-reactivity relationship and develop catalysts with higher activity at lower operating temperatures to overcome one of the main limitations for the dehydrogenation process, which is the high coking rate. However, the dehydrogenation performance of the new catalyst formulations are still unsatisfactory compared with the industrial catalysts. Research on alternative catalysts to conventional metal and metal oxide-based catalysts remains a great challenge, with a highly

demand for the development of novel efficient methods to improve their dehydrogenation performance [13].

Another interesting strategy to increase the yield of the dehydrogenation process at lower temperatures is the use of the membrane reactor technology with integrated H_2 -selective membranes [14–16]. Several authors have studied the performance of membrane-assisted dehydrogenation processes, and most of them have based their works on modeling the membrane reactor configuration. Farsi et al. [16] modeled and optimized the isobutane dehydrogenation in an industrial radial flow moving bed reactor supported by Pd–Ag membranes. An optimized configuration of the membrane reactor is identified to work at a reaction temperature 85 °C lower than in the conventional reactor. The mathematical simulation results obtained by Farsi et al. reveal that both the isobutane conversion and the isobutene productivity are enhanced about 3.1% and 3.7%, respectively, in the optimized membrane process compared to the conventional process. Shelepova et al. [17] developed a 2-dimensional non-isothermal model to simulate the dehydrogenation of propane in a catalytic membrane reactor. The results reveal that using ceramic porous membranes with an optimized thickness between 2 and 4 μm and an optimized pore size of 0.4 nm, it is possible to improve the dehydrogenation reaction performance, reaching a maximum propylene yield of 81%, against typical values of 35–42% reported for the industrial processes [18]. Wang et al. [19] investigated the use of membrane reactors for the production of benzene and hydrogen via the solar-driven non-oxidative dehydrogenation of methane. Their modeling work demonstrates that using the membrane reactor it is possible to reach methane conversions and benzene yields as high as 98.36% and 88.52% respectively, under a permeate pressure of 0.01 bar and a temperature of 700 °C. Note that without membranes, conversion rates cannot exceed 25% and benzene yields are smaller than 20% even at 800 °C due to the thermodynamic constraint. Another interesting work that investigates the potentiality of the membrane reactor technology for dehydrogenation processes is presented by He et al. [20]. In this work, the authors performed a thermodynamic analysis of a novel solar propane dehydrogenation system with a membrane reactor. The results show that compared to the performance of a traditional reactor (without membranes), an H_2 permeate pressure of 10^{-5} bar increases the conversion rate of C_3H_8 from 4.1% to 99.12% and the selectivity of C_3H_6 from 93.1% to 99.1% at 400 °C. Thus, the membrane reactor has the potential to significantly increase the reaction yield at lower temperatures via H_2 separation utilization. An interesting experimental work on the dehydrogenation of propane in a combined membrane reactor was carried out by Didenko et al. [21]. In their work, it is demonstrated at laboratory scale the potentiality of the membrane reactor technology in increasing the feedstock conversion to propylene by a factor of 1.6–2.0, respectively, under optimized operating conditions.

From the results explained above it is possible to notice that, by utilizing the membrane reactor technology, the selective removal of H_2 from the catalytic bed shifts the equilibrium beyond the thermodynamic restriction of the conventional process, leading to an increase of butadiene production. In this way, it would be possible to achieve same

conversions of butane as in the conventional process but working at milder operating conditions. The opportunity to lower the operating temperature will reduce the rate of coke formation on the catalyst increasing the catalyst deactivation timespan. Additionally, the heat duty of the reactors is expected to be drastically reduced (as the reaction temperature is lower), making the overall process more energy efficient [22]. Even though the H₂-selective membrane reactor has been extensively studied both experimentally and by modeling the reaction performance under different operating conditions, its integration in a real BDH plant has not yet investigated.

Therefore, the present work aims at assessing the techno-economic feasibility of the membrane reactor integrated process for the dehydrogenation of butane, compared to the benchmark technology. In this work, the potential application of the membrane reactor technology for BDH, widely used experimentally, is investigated for the first time at industrial level from a process performance point of view. The membrane reactor configuration will be compared with the conventional BDH, which uses packed bed reactors, highlighting the consequent changes in the overall process configuration and the influence of these modifications from a techno-economic point of view. Firstly, the methodology followed to perform the techno-economic comparison will be presented. Afterward, a detailed description of the process scheme and the design of the process equipment for both the technologies proposed will be given. The results of this study will be presented, providing a detailed discussion on the advantages and disadvantages associated to the implementation of the proposed membrane reactor integrated BDH process. Finally, the main conclusions of this work will be given, as well as recommendations to improve the BDH technology in the future work.

Methodology and assumptions

Assumptions

In this section, the main assumptions used to design the process schemes for the benchmark and the proposed MR-assisted BDH technologies, are reported.

- (1) The process schemes have been simulated using Aspen Plus as process simulator to obtain the associated mass and energy balances. Both the technologies have been designed with a fixed plant size, equal to a target production of 11.2 kg_{C₄H₆}/s, which is equivalent to 320 kiloton per year (kTA) of 1,3-butadiene. The reactors in the two processes are modeled using an in-house 1D plug flow reactor integrated in the process simulation software. More detailed specifications and assumptions made for the main process equipment are listed below.
 - Conventional Dehydrogenation Reactor: a packed-bed reactor (PBR) model is selected for the benchmark process, as the one used industrially in the conventional CATADIENE technology [23]. The reactor is modeled according to the reaction pathway proposed by Ajayi et al. [24], reported in [Appendix A0](#). The n-butane conversion is based on literature data [25]. To determine the size of the reactor, a space velocity equal to 1.8 N_{feed (l)}/h/l_{cat} is selected, in the range of the values reported in literature [26]. Afterward, the diameter and the length are calculated, assuming a l/d ratio equal to 3, together with the total number of reaction unit required.
- (2) Novel Dehydrogenation Membrane Reactor: a packed-bed membrane reactor (PBMR) model is used for the novel proposed BDH process, with the same kinetic scheme of the benchmark case. Hydrogen is removed through the membranes, which are assumed to be fully selective to hydrogen (according to the typical selectivity values reported in literature for Pd–Ag based membranes with similar thickness as the one used in this work [27–29]). To account for the removal of hydrogen from the reaction ambient, the flow rate of hydrogen permeated through the membrane, calculated from the definition of hydrogen flux (Eq. (15) on [Section BDH membrane reactor model](#)), is subtracted from the differential mass balance of hydrogen compound along the reactor length. To design the membrane reactor unit, a sensitivity analysis is carried out in order to identify the new (milder) operating conditions and the required membrane area to obtain the same conversion as in the conventional process. Knowing the membrane area, the dimension of the novel reactor and the number of reaction units are computed under the assumption of maintaining same space velocity as in the benchmark technology. This last assumption may be removed, and it can be carried out a multi-objective optimization to find the membrane reactor design that lowers the final costs, in a future work.
- (3) Distillation columns: the calculations of the distillation columns are performed using the RadFrac model of Aspen Plus. This model allows to specify the number of stages, the reflux ratio (RR) and the distillate-to-feed ratio (D:F), from which the mass and energy balances of the system are determined. In each distillation column, the single stage pressure drop is set to 10 mbar, the internals are trayed, with a tray spacing in the range of 0.6–0.7 m, a hole area/active area between 5 and 10% and an approach to flood equal to 80% [30].
- (4) Turbomachines: compressors, expanders and pumps are modeled assuming isentropic and electro-mechanical efficiencies from which the thermodynamic conditions of the outlet streams and the energy balances are derived. The isentropic efficiency is assumed to be equal to 0.85 for both compressors, pumps and expanders, while the mechanical efficiency is set equal to 0.95 in compressors and pumps, and to 0.99 in expanders [31].
- (5) Furnaces: to design furnaces to burn off undesirable by-products and generate a useable source of heat, the combustion temperature is assumed to be equal to 1100 C. The air feed is assumed to be at ambient conditions (25 C and 1 bar), while its mass flow rate is calculated, using the design spec tool of Aspen Plus, in order to have 5% of O₂ (%vol.) in the exhaust gas to guarantee a complete combustion of the gases.
- (6) Catalyst Regeneration unit (CRU): the regeneration of the deactivated catalyst is simulated by burning off the

solid coke deposited on the catalyst surface, formed during the dehydrogenation reaction. Due to lack of information concerning the coke production in the kinetic model proposed by Ajayi et al. [24], which is used in this work, coke formation is assumed to follow the deactivation reaction reported by Gascón et al. [32] for the direct dehydrogenation of propane (PDH) over a Cr-based catalyst, under the operating conditions used in the BDH processes. Knowing the amount of carbon formed per catalyst present in the reactor ($\text{kg}_{\text{coke}}/\text{kg}_{\text{catalyst}}$), an ideal separator block is used in Aspen Plus to take off the corresponding amount of unreacted n-butane from the reactor effluent. The regeneration is performed, as in a real BDH plant, by co-feeding a hot air stream (i.e. in the range of 600–800 C) with an inlet temperature fixed equal to 710 C. The burner is required to generate the heat duty needed by the dehydrogenation reaction, and the amount of air needed to perform the combustion is calculated in order to maintain the exhaust gases temperature in the range of about 621–662 °C [23,33]; the corresponding ΔT with respect to the inlet coke is considered to define the exhaust gases temperature for the MR-assisted BDH process scheme.

Technical and economic indicators

Several performance indicators already defined and used by Spallina et al. [34], are adapted to the new plant to compare the technical and environmental performance of the processes. The plant performance is calculated using two main types of indexes (Eqs. (2)–(5)): one, known as Feedstock-to-Chemical efficiency, accounts for the production of valuable products (i.e. 1,3-butadiene and hydrogen), and the other, known as Overall Energy Efficiency, evaluates the production/consumption of energy.

Feedstock-to-Chemicals efficiency ($i = 1,3\text{-butadiene, hydrogen}$):

$$\eta_{\text{FTC}}[\%] = \frac{\sum_i W_{\text{chem},i}}{W_{\text{feed}}} \quad (2)$$

Chemical Energy of component i :

$$W_i[\text{MW}] = \dot{m}_i \text{LHV}_i \quad (3)$$

Overall Energy Efficiency:

$$\eta_{\text{tot}}[\%] = \frac{W_{\text{chem}}}{W_{\text{feed}} + W_{\text{tot}}} \quad (4)$$

Overall Energy Balance:

$$W_{\text{tot}}[\text{MW}] = \sum_i \frac{\sum_i W_{\text{El}, \text{in} \leftrightarrow \text{out}}}{\eta_{\text{El}}} + \frac{\sum_i W_{\text{Th}, \text{in} \leftrightarrow \text{out}}}{\eta_{\text{Th}}} \quad (5)$$

where i represents the process equipment, $W_{\text{El}, \text{in} \leftrightarrow \text{out}}$ is the electricity consumed/produced by the process equipment, $W_{\text{Th}, \text{in} \leftrightarrow \text{out}}$ is the thermal energy usages of the process equipment, η_{El} is the efficiency of the natural gas combined cycle plant which produces the electricity, assumed to be equal to 58%, and η_{Th} is the efficiency of an industrial boiler producing the imported/exported heat, set equal to 90% [34].

Additional indicators are defined and used for the comparison of the two BDH processes in terms of their environmental performance. The feedstock-to-coke reflects the amount of coke formed in the reactors against the inlet feed of the process, as reported in Eq. (6) to be:

$$\eta_{\text{coke}}[\%] = \frac{\dot{m}_{\text{coke}}}{\dot{m}_{\text{feed}}} \quad (6)$$

where \dot{m}_{coke} is the flow rate of carbon formed in the reactors and \dot{m}_{feed} is the flow rate of feedstock of the plant, expressed in kg/s. The CO₂ Emission indicators used to evaluate the plant environmental performance are summarized in Table 1.

In Table 1, the direct CO₂ emissions refer to the fuel that is combusted in the plant, which is used for heat integration and electricity generation. Additionally, the indirect CO₂ emissions refer to the net production/consumption of energy in the plant. The carbon emissions values are taken from the work of Spallina et al., where it is assumed that the imported/exported electricity comes from a natural gas combined cycle plant emitting 96 gCO₂/MJ ($E_{\text{CO}_2, \text{CC}}$) and that the imported/exported heat is obtained from an industrial boiler, producing 63 gCO₂/MJ emissions ($E_{\text{CO}_2, \text{TH}}$) [34].

$\dot{m}_{\text{CO}_2, \text{direct}}$, $\dot{m}_{\text{CO}_2, \text{indirect}}$ are the total flow rate of the direct and indirect CO₂ emissions, respectively, and $\dot{m}_{\text{C}_4\text{H}_6}$ is the total flow rate of 1,3-butadiene produced, each of them expressed in kg/hr.

The economic analysis is performed applying the NETL (National Energy Technology Laboratory) method [35] which differentiates the expenditures of an industrial plant into capital (CAPEX) and operational (OPEX) costs, used to determine the final cost of production of butadiene (COP), according to the following Eq. (7):

$$\text{COP} \left[\frac{\text{€}}{\text{ton}_{\text{C}_4\text{H}_6}} \right] = \frac{\text{OPEX}_{\text{variable}} + \text{OPEX}_{\text{fixed}} + \text{CAPEX}}{\dot{m}_{\text{C}_4\text{H}_6, \text{year}}} \quad (7)$$

where $\dot{m}_{\text{C}_4\text{H}_6, \text{year}}$ is the total flow rate of 1,3-butadiene produced annually (ton_{C₄H₆}/year), and OPEX_{fixed} are the operational and maintenance costs.

The calculation of the CAPEX cost follows the methodology reported in Table 2.

According to this methodology, in order to calculate the TOC, the costs of the process equipment, represented by the Bare Erected Cost (BEC) need to be evaluated. For the calculation of the BEC, the capital expense of each process equipment is calculated through the approach reported by Smith et al. [37], applying the following formula (Eq. (8)):

$$C_E = \frac{\text{INDEX}_1}{\text{INDEX}_2} C_B \left(\frac{Q}{Q_B} \right)^M f_M f_P f_T \quad (8)$$

where:

INDEX₁ = Chemical Equipment index of the year 2019.

INDEX₂ = Chemical Equipment index of the year from which the base case origins.

C_E = New equipment cost with capacity Q.

C_B = Known base case cost for equipment with reference capacity Q_B.

Q = Capacity in terms of the scaling parameter of the new equipment.

Table 1 – CO₂ emission indexes.

CO ₂ Emission Indexes	
Direct CO ₂ Emissions	$E_{CO_2, \text{direct}} = \frac{m_{CO_2, \text{direct}}}{m_{C_4H_6}}$
Indirect CO ₂ Emissions	$\dot{m}_{CO_2, \text{indirect}} =$ $W_{el, \text{imp/exp}} * E_{CO_2, CC} +$ $W_{th, \text{imp/exp}} * E_{CO_2, TH}$ $E_{CO_2, \text{indirect}} = \frac{m_{CO_2, \text{indirect}}}{m_{C_4H_6}}$
Total CO ₂ Emissions	$E_{CO_2, \text{tot}} = \frac{m_{CO_2, \text{direct}} + m_{CO_2, \text{indirect}}}{m_{C_4H_6}}$

Q_B = Capacity in terms of the scaling parameter of the known base case reference.

M = Constant depending on equipment type.

f_M = Correction factor materials of construction.

f_P = Correction factor for design pressure.

f_T = Correction factor for design temperature.

The values considered in this work for the above listed parameters are reported in Table 3, with the corresponding literature source from which they have been taken (see Table 4).

The OPEX or Operating Expenditure of the plant is calculated as follow (Eq. (9)).

Table 2 – Methodology for the calculation of TOC [36].

Capital Costs (CAPEX)	
Plant component	Cost (M €)
Component A	A
Component B	B
Component C	C
Component D	D
Bare Erected Cost (BEC)	A + B + C + D
Direct costs as percentage of BEC (includes piping/valves, civil works, instrumentations etc.	
Total Installation Cost (TIC)	80% BEC
Total Direct Plant Cost (TDPC)	BEC + TIC
Indirect Costs (IC)	14% TDPC
Engineering Procurement and Construction (EPC)	TDPC + IC
Contingency and Owner's Costs (C&OC)	
Contingency	10% EPC
Owner's Cost	5% EPC
Total Contingency and Owner's Costs (C&OC)	15% EPC
Total Overnight Costs (TOC)	EPC + C&OC

Table 3 – List of parameters for the cost calculation of the process equipment.

Process equipment	INDEX 1 [38]	INDEX 2	M [37]	f_M [37]	f_P [37]	f_T [37]	Scaling parameter	Q_B	C_B [M€]	Ref.
Distillation columns	607.50	576.10	0.89	1.00	1.50	1.00	Volume m ³	92.33	3.91	[39]
Flash drum	607.50	576.10	0.82	1.00	1.50	1.00	Flow Rate kg/hr	106	1.89	[39]
Pumps	607.50	576.10	0.55	1.00	1.00	1.00	Power kW	66	0.06	[39]
Compressors	607.50	435.80	0.46	1.00	1.00	1.00	Power kW	250	0.08	[37]
Heaters (HX)	607.50	576.10	0.68	1.00	1.00	1.60	Heat duty MW	104	0.30	[39]
Counter current heat exchangers (CCHX)	607.50	576.10	0.68	1.00	1.00	2.10	Area m ²	9800	6.83	[39]
Furnace	607.50	436	0.45	1.00	1.00	2.10	Heat duty mbtu/hr	2105	0.108	[40]
Coke burner	607.50	436	0.45	1.00	1.00	3.4	Heat duty mbtu/hr	2105	0.108	[40]
Reactor	607.50	576.10	0.45	1.00	1.00	1.00	Volume m ³	100	1.73	[39]

Table 4 – Assumptions for the OPEX calculations.

OPEX O&M		
Labor [42]	M€/y	1.74
Maintenance [43]	%TOC	2.5
Insurance [43]	%TOC	2.0
OPEX Utilities		
Electricity [42,43]	€/kWh	0.035
Cooling Water [42,43]	€/ton	0.013
Steam [42,43]	€/ton	0.13
Refrigerant (from Aspen Plus database)	€/MJ	0.0029
Solvent NMP [44]	€/kg	2.4
OPEX Variables		
Shale gas (n-butane) [45]	€/Nm ³	0.18
Catalyst [46]	€/MT _{C₄H₆}	16.34
Catalyst Lifetime	Years	3
Membrane [47]	€/m ²	3000
Membrane Lifetime	Years	1

$$OPEX \left[\frac{M€}{y} \right] = (OPEX_{\text{feedstock}} + OPEX_{\text{utilities}} + OPEX_{CO_2 \text{ emissions}} + OPEX_{O\&M} + OPEX_{\text{variables}}) \quad (9)$$

All those costs are calculated under the assumption that both the benchmark and the MR-assisted technologies will be located in the USA, being the main global importer of butadiene [41]. The $OPEX_{\text{feedstock}}$ represents the cost for the shale gas to be fed to the plant, neglecting transportation costs due to the specified location of the plant. The $OPEX_{\text{utilities}}$ is the cost associated to the utilities consumption, the $OPEX_{CO_2 \text{ emissions}}$ represents the costs associated to the total CO₂ emission of the plant, the $OPEX_{O\&M}$ accounts for the labor cost and the maintenance and insurance costs, and the $OPEX_{\text{variables}}$ includes the cost for the catalyst and the membranes. Those cost voices are calculated according to the following Eq. 10–12:

$$OPEX_i \left[\frac{M€}{y} \right] = C_i * \dot{m}_i * h_{\text{year}} * 10^{-6} \quad (10)$$

with i = feedstock, utilities, CO₂ emission tax

where C_i is the specific cost/price of the i variable, \dot{m}_i is the flow rate of i variable consumed/emitted and h_{year} are the number of hours per year in which the plant is assumed to be running (7884 effective hours per year are considered).

$$OPEX_{\text{catalyst}} \left[\frac{M€}{y} \right] = C_i * \dot{m}_i * 3600 * h_{\text{year}} * N_{\text{replacements}} * 10^{-6} \quad (11)$$

where C_i is the specific cost/price of catalyst expressed per kilogram of butadiene produced (€/kg), \dot{m}_i is the flow rate of butadiene produced (kg/s).

$$\text{OPEX}_{\text{membrane}} \left[\frac{\text{M€}}{\text{y}} \right] = C_i * n_m * \pi * d_m * l_m * h_{\text{year}} * N_{\text{replacements}} * 10^{-6} \quad (12)$$

where C_i is the specific cost/price of membrane expressed per membrane area (€/m²), n_m is the total number of membranes used, d_m and l_m are the membrane diameter and length (m), respectively.

Table 4 summarizes the main values used to perform the OPEX calculations.

An additional indicator used in the economic analysis to evaluate the profitability of the plant and make a comparison of the two technologies investigated in this work, is the return of investment (ROI), defined as:

$$\text{ROI} [\%] = \frac{\text{TPI} - \text{OPEX}}{\text{CAPEX}} \quad (13)$$

where TPI represents the total product income calculated based on the amount 1,3-butadiene and hydrogen produced to be sold on the market, as:

$$\text{TPI} = \sum_i^{\text{valuable products}} \dot{m}_i * p_{\text{market},i} \quad (i = \text{C}_4\text{H}_6, \text{H}_2) \quad (14)$$

where \dot{m}_i is the annual flow rate of valuable products produced by the plant and $p_{\text{market},i}$ is the corresponding selling price; the selling price of 1,3-butadiene is taken from the market overview of North America in 2021 and it is equal to 1,05 €/kg [48], while the price of hydrogen is taken equal to 1,34 €/kg, assuming to sell it in Europe [52]. The minimum acceptable ROI for a petrochemical industry to be profitable is set to 10% [49].

Modeling of the two processes

Benchmark BDH technology

BDH conventional reactor model

The reaction zone of the BDH process consists of four parallel packed-bed reactors, designed to fulfill the requirements of an industrial scale plant. To do so, a space velocity equal to 1.8 $\text{Nl}_{\text{feed}} / (\text{h} / \text{l}_{\text{cat}})$ is selected and the main reactor parameters have been determined to satisfy the C_4H_{10} conversion target of 40 wt%. Table 5a summarizes the main assumptions considered to retrieve the design specifications of the conventional BDH reaction zone, reported in Table 5b.

Benchmark BDH process scheme

Fig. 1 shows the process scheme of the benchmark technology for the dehydrogenation of n-butane to 1,3-butadiene. The scheme reproduces the process of feedstock shale gas that undergoes the dehydrogenation reaction and a series of downstream separations to acquire a polymer grade 1,3-butadiene of at least 99.5% purity.

To develop the benchmark BDH process scheme, the CATADIENE® process is selected as reference technology. The

Table 5a – Assumptions for the conventional BDH reactor design.

BDH reaction zone assumptions		
Parameter	Units	Value
Space Velocity	$\text{Nl/h/l}_{\text{cat}}$	1.8
Bed Porosity	–	0.5
l/d ratio	–	3

Table 5b – Conventional BDH reactor unit specifics.

BDH reaction zone specifications		
Parameter	Units	Value
Diameter	m	3.3
Length	m	9.8
Volume	m ³	81.9
Amount of catalyst	kg	23,880
N of reactors	–	4

benchmark process is simulated assuming a plant capacity equal to 800 kiloton per year (KTA) of shale gas.

Feedstock shale gas (S1), with a mass composition of 97.4% n-butane and the remaining 2.6% being made of C_3 and small traces of C_{5+} , enters the plant at ambient conditions (1 bar and 25 C). The stream is firstly pre-mixed with the recycled unconverted n-butane (S15) coming from the downstream separation section, and then with recycled hydrogen stream (S9). S9 will act as a diluent to lower the cracking reactions (R2 and R3 in A0), according to which n-butane is converted into ethane and ethylene, and then into methane and propylene, respectively. After the mixer, the temperature of the outlet stream (S2) drops to –5 C. Then, the main stream (S3) is heated up to the reaction temperature of 625 C, exploiting the hot effluent gases from the reactor (S5). The resulting stream (S4) enters into the reaction zone, which consists of four parallel packed-bed reactors, working at 625 C and 0.3 bar. At the outlet of the reaction zone, it is possible to collect the solid coke that is deposited on the surface of the catalyst during the dehydrogenation reaction; this stream (S6) is being burned co-feeding a hot air stream at 710 C in the coke burner, that simulates the regeneration of the catalyst and represents the main source of heat to keep the dehydrogenation reactors in temperature under operation. The burner can fulfill the heat duty of the reaction section, which is equal to 251.3 GJ/h. The 1,3-butadiene rich stream (S5) that leaves the reaction zone is sent to a multistage compressor (MCOMP). This MCOMP, with interstage coolers, increases the S5 pressure from 0.3 bar to 17.5 bar while it lowers the temperature from 625 C to 14 C; these are the optimum operating conditions for the subsequent flash drum (FLASH) to perform the separation of hydrogen, collected as vapor phase from the top. The hydrogen rich stream (S8) is partially recycled to the inlet of the reactor, to adjust the H_2 /feedstock required for the process. The remaining amount of H_2 is ready to be sold to the market, after being additionally purified in a Pressure Swing Adsorption unit (PSA).

The 1,3-butadiene rich stream that leaves the bottom of the flash drum (S10) enters a compressor (C1) to increase its

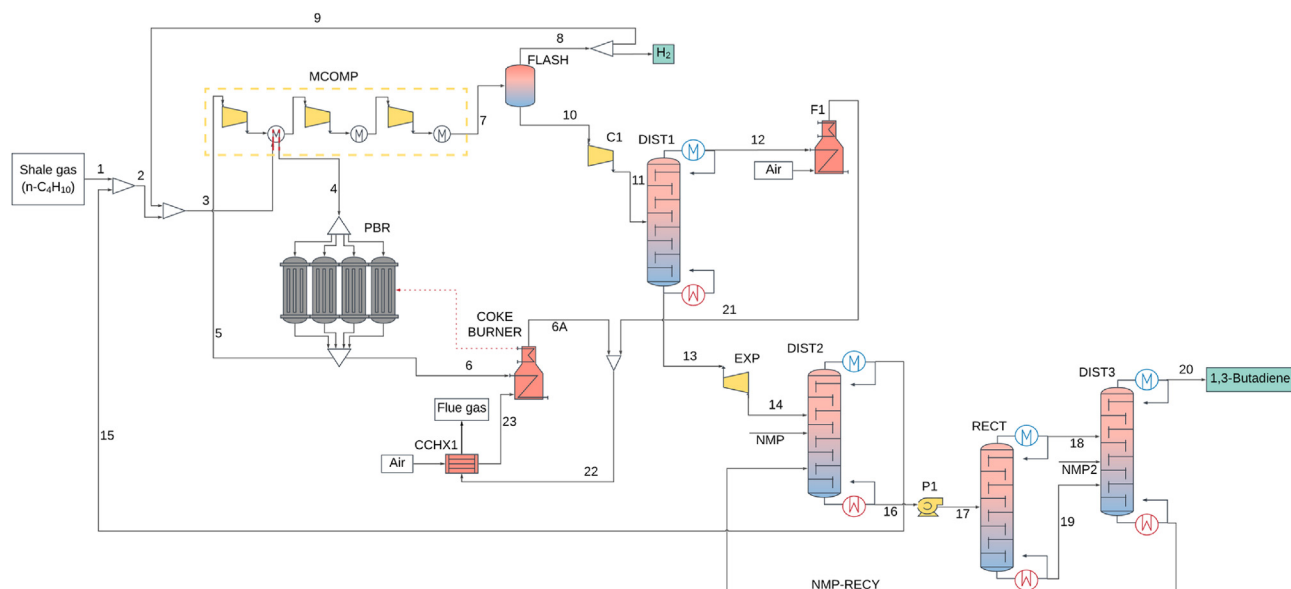


Fig. 1 – Process flow diagram of the benchmark BDH technology.

pressure to 20.2 bar, before being sent to the de-propanizer (DIST1). This distillation column, working at 20.2 bar and in a temperature range of 3 C to 104 C, is used to separate the lighter hydrocarbons (C_3 and lighter) from the C_{4+} components. This mixture of C_{4+} undesirable by-product is sent to the furnace (F1) to generate a hot source of exhaust gases at 1100 C, used to preheat the air stream entering the regeneration unit. The product stream leaving the bottom of the de-propanizer (S13) contains mostly unreacted n-butane and the desired 1,3-butadiene product, with some traces of heavier C_{5+} components. This stream is firstly sent to an expander (EXP) to reduce its pressure to 5 bar, before being sent to the downstream separation section where the final separation of 1,3-butadiene with the desired purity is performed. To do so, the use of a conventional distillation column would need extremely high number of trays as well reflux ratio, since many of the C_4 components have relative volatilities very similar to 1,3-butadiene [50]. Thus, the extractive distillation technology is employed, using N-methyl-2-pyrrolidone (NMP) as solvent.

The mixture of C_{4+} is fed into the first extractive distillation column (DIST2), together with the NMP solvent. The solvent, made of approximately 20 wt% of water, needs to have a total flow rate 9.5 times larger than C_{4+} mixtures feeding rate, in order to satisfy both purity and recovery of the final 1,3-butadiene product of at least 99.5 wt%. The overhead product (S15) mostly consists of less unsaturated hydrocarbons, containing almost 64 wt% of n-butane, and it is recycled back to the main feed entering the plant. The bottom product (S16) is sent to the rectifier (RECT), where the butadiene is separated from the NMP solvent, reaching a final purity of 92 wt%. The NMP-rich stream (S19) withdrawn from the bottom of the rectifier is recycled back to the second extractive distillation column (DIST3), where it is performed the final purification of butadiene. The 1,3-butadiene is obtained at the top of the final column with a purity of 99.7 wt%, while the heavier C_{4+} and C_5 components are removed from the bottom of the column,

together with the mixture of NMP and water, and are fed back to the first extractive distillation column. The detailed mass balance of the plant can be found in Appendix A1.

Membrane reactor-assisted BDH technology

BDH membrane reactor model

The novel reactor system has been designed integrating H_2 -selective membranes into the PBR. These membranes selectively remove hydrogen from the reaction ambient with high rates; amongst all H_2 -selective membranes, palladium-based membranes have been selected in this work, since they offer the capacity to extract high fluxes with extremely high permselectivities, due to the high permeability of Pd and its alloys (Ag, Cu, Au) for hydrogen [51–53]. These membranes are characterized by porous tubular substrates made by Al_2O_3 on top of which it is deposited the selective Pd–Ag layer. To increase the chemical and mechanical stability of these membranes, an additional thin mesoporous YSZ/ γ - Al_2O_3 protecting layer, is added on top of the selective one [54,55]. The hydrogen flux permeating through the Pd-based membranes is described by the following equation (Eq. (15)):

$$J_{H_2} = \frac{1}{\delta} Pe_0 \exp\left(-\frac{E_a}{RT}\right) \left(p_{H_2,ret}^n - p_{H_2,perm}^n\right) \quad (15)$$

where Pe_0 is the pre-exponential of the membrane permeability, E_a is the activation energy, δ is the membrane thickness, $p_{H_2,ret}$ and $p_{H_2,perm}$ are the hydrogen partial pressure at retentate and permeate side, respectively, and n is the pressure exponent (see Table 5). The values used in this work, resulting from the fitting of experimental data conducted by the same authors in another work [56], are reported in Table 6.

The novel membrane reactor system is implemented in the process scheme to achieve the same performance as of the benchmark, in terms of n-butane conversion, while lowering the operating temperature. Thus, several parametric analyses have been performed to determine the optimum operating

Table 6 – Permeability parameters for the Pg-Ag membrane selected in this work.

Permeability parameters of the Pd–Ag membranes		
Parameter	Units	Value
P_{e_0}	$\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$	4.63e^{-10}
E_a	kJ/mol	7.61
δ	μm	1.91
n	–	0.75

conditions at which the BDH can be operated with a reasonable membrane area to remove hydrogen. The maximum amount of hydrogen to be separated is set equal to 788.95 mol/s, which is the total flow rate of hydrogen produced in the reference case. Firstly, the effect of the hydrogen removal on the reaction temperature has been analyzed. Fig. 2a shows how the reaction temperature decreases as function of the hydrogen recovery, for different operating pressures. The H_2 recovery factor is defined as the ratio between the molar total flow rate of hydrogen permeated through the membrane ($m_{\text{H}_2, \text{permeated}}$ in mol/s) and the total molar flow rate of hydrogen produced during the reaction ($m_{\text{H}_2, \text{produced}}$ in mol/s), accordingly:

$$\text{H}_2 \text{ Recovery Factor} = \frac{m_{\text{H}_2, \text{permeated}}}{m_{\text{H}_2, \text{produced}}} \quad (16)$$

Working at 0.35 bar, which is the actual operating pressure of the benchmark technology, an average reduction of 3 C per each 10% of hydrogen removed can be obtained. When all the hydrogen produced during the dehydrogenation reaction is removed, a minimum temperature of 601.55 C is reached. As the membrane flux is driven by partial pressure difference across the membrane, the permeate of the membranes is kept under vacuum. Clearly, the effect of hydrogen recovery on the temperature is less pronounced compared to other endothermic reaction systems where membrane reactors are employed [57]. When increasing the operating pressure, the positive effect of the hydrogen removal on the reduction in temperature is more evident due to the bigger driving force applied across the membranes. For example, a significant reduction in the reaction temperature of almost 35 and 54C can be obtained when removing just 10% of the hydrogen produced, working at 0.5 and 1 bar respectively. Thus, the higher is the operating pressure, the higher is the ΔT achievable as function

of the hydrogen recovery factor. However, as shown in Fig. 2b, for a fixed operating pressure of 1 bar, the higher is the hydrogen recovery to lower the reaction temperature, the larger is the membrane area required. Below 540 C it would be required to install a total membrane area larger than 3940 m², which is the one needed to separate all the hydrogen produced in the benchmark process. Therefore, the optimum range of new reaction temperature is identified to be between 560 and 540 C. In this range of reaction temperatures, the required membrane area can be additionally reduced increasing the operating pressure, as shown in Fig. 3a. The membrane area can be drastically reduced increasing the operating pressure from 1 to 1,5 bar, reaching a reduction in membrane area of almost 50%, 55% and 65%, for a reduced reaction temperature of 560, 550 and 540 C respectively. However, the higher the operating pressure the lower would be the selectivity toward 1,3-butadiene and the higher the selectivity to undesired products, going below the actual performance of the benchmark case (selectivity to C_4H_6 of 64.6 wt% and selectivity to $\text{C}_1\text{--C}_2$ of 14.4 wt%), as shown in Fig. 3b. This is related to the nature of the main dehydrogenation reaction (Eq. (1)), which is prone to a volume expansion and so favored at low pressures, from a thermodynamic point of view.

Among the optimum range of temperatures and considering the effects of reducing the operating pressure identified above, it results convenient to operate the membrane reactor at the lowest temperature of 540 C, applying a pressure equal to 1.3 bar; those are the conditions at which the better trade-off between sufficient reduction in operating temperature with respect to the benchmark case, required membrane area and still high performance of the dehydrogenation reaction, in terms of butadiene selectivity, is obtained.

Once the new operating conditions have been selected and the corresponding membrane area per unit of reactor has been calculated, it was possible to re-design the novel reactor units assuming the same space velocity as in the benchmark case. The design specifications of the novel MR-assisted BDH reaction unit are reported in Table 7. For a next work, one can carry out a multi-objective optimization to find the conditions that lower the final costs, however this is out of the scope of this paper.

Membrane reactor-assisted BDH process scheme

In the proposed membrane reactor-assisted MR-BDH process, the conventional reaction system is substituted with packed-

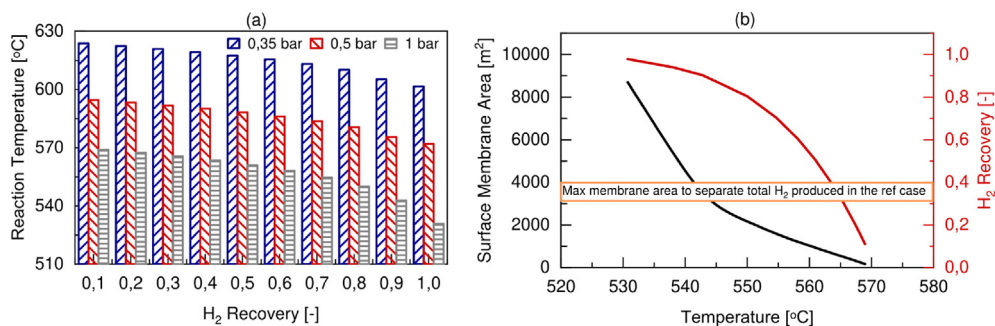


Fig. 2 – (a) Effect of the hydrogen removal on the reaction temperature, for different operating pressures. (b) Membrane area and hydrogen recovery trends as function of the reaction temperature, for a fixed operating pressure of 1 bar.

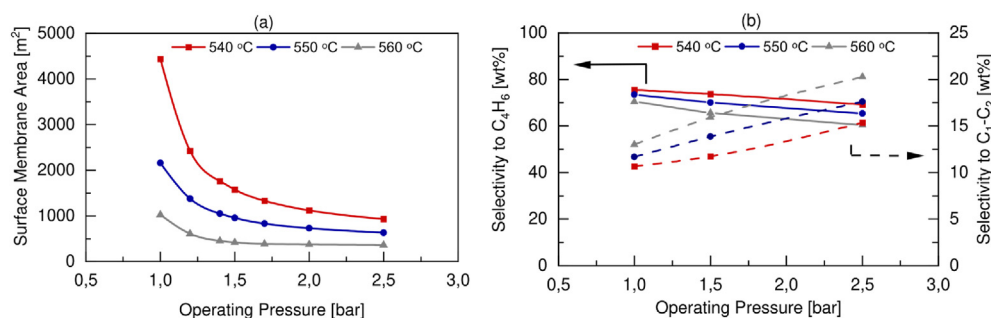


Fig. 3 – (a) Effect of the operating pressure on the membrane area for different reaction temperatures. (b) Effect of the operating pressure on the reaction performance, for different reaction temperatures.

Table 7 – Novel membrane reactor unit specifics.

MR-assisted BDH reaction zone specifications		
Parameter	Units	Value
Space Velocity	Nl/h/l _{cat}	1.8
Bed Porosity	–	0.5
Diameter	m	3.1
Length	m	9.3
Volume	m ³	70.6
Membrane Diameter	m	0.014
Membrane Length	m	9.3
Total Surface Membrane Area	m ²	1694
Amount of catalyst	kg	20146.8
N of reactors	–	4

bed membrane reactors, in which H₂ perm-selective Pd-based membranes are installed to selectively remove hydrogen from the reaction ambient. Due to the lower operating conditions of the reaction zone, the configuration of the MR-BDH plant has few modifications compared to the benchmark, represented in Fig. 1.

In this configuration, shown in Fig. 4, shale gas feedstock, with the same composition as the one of the benchmark technology, is premixed with the recycled unconverted n-butane (S19) coming from the downstream separation section, and then with part of the pure H₂ stream (S8A), removed from the reaction zone, to reach the H₂/feedstock ratio required for the process. The resulting stream (S3) needs to be pre-heated to match the operating conditions of the reaction zone. The new membrane integrated reactors operate at 540 C, which is 85 C lower than in the benchmark process. The main process stream is firstly heated up to 455 C in a first counter-current heat exchanger (CCHX1), exploiting the hot effluent gases from the reaction zone. Then, it reaches 520 C in a second counter-current heat exchanger (CCHX2) utilizing the heat contained in the flue gases at the outlet of the furnace (F1) that burns a mixture of undesirable by-products, originating at the top of both the flash drum unit (FLASH) and the first distillation column (DIST1). The final reaction temperature is obtained at the outlet of the compressor (C1), where the pressure of the process stream is increased to the reaction pressure of 1.3 bar. The reaction zone is now made of four parallel packed-bed membrane reactors, working at 540 C and 1.3 bar, at the outlet of which it is possible to distinguish three process streams: the main reactor effluent (S7), which is a mix of 1,3

butadiene, unconverted n-butane and cracking by-products, the pure hydrogen stream (S8), separated through the Pd-based membranes, and the solid carbon (S9) deposited on the catalyst surface during the dehydrogenation reaction (this stream is only for calculation purposes, as the regeneration in the real plant would occur in the packed bed). As already done in the benchmark technology, the solid carbon (S9) is sent to the coke burner together with a hot air stream (S26) at 710 C, in order to simulate the regeneration of the catalyst particles which provides the heat duty required to keep constant the reaction temperature. In this new configuration, the heat duty of the reaction zone is equal to 227.4 GJ/h, which is 10% lower than in the benchmark case, due to the lower reaction temperature achieved by the presence of the hydrogen-selective membranes.

Differently from the benchmark plant configuration, a pure hydrogen stream (100 mol%) is directly produced and separated from the reaction zone through the membranes, without the need of a flash drum unit to perform this separation. This stream of pure hydrogen is recycled back to the inlet of the reactor with a small fraction of 20 mol%, to act as a diluent to lower the cracking reactions (R2 and R3 in A0) that occur in the reaction zone. The rest is ready to be sold on the market, without the need of an additional purification in a PSA unit, as in the benchmark technology case.

The 1,3-butadiene rich stream (S7) exiting the reaction zone is firstly cooled down from 540 C to 14 C, passing through the first counter-current heat exchanger (CCHX1), and then sent to a multistage compressor (MCOMP), where it is compressed to 20.2 bar and again cooled down to –10 C. At these conditions it can enter the flash drum (FLASH) unit, in order to get rid of the 1,3-butadiene rich stream in the liquid phase (S14), before entering the downstream separation section. This section has the same configuration as the one of the benchmark technology, including the first de-propanizer distillation column (DIST1), to separate the lighter hydrocarbons (C₃ and lighter) from the C₄₊ components, and the two extractive distillation columns (DIST2 and DIST3) with an intermediate rectifier (RECT), to perform the final purification of 1,3-butadiene.

Butadiene, with a polymer grade purity equal to 99.8 wt%, is withdrawn at the top of the last extractive distillation column, while the heavier C₄₊ and C₅ components are removed from the bottom of the column, together with the mixture of NMP and water, and recycled back to the first extractive

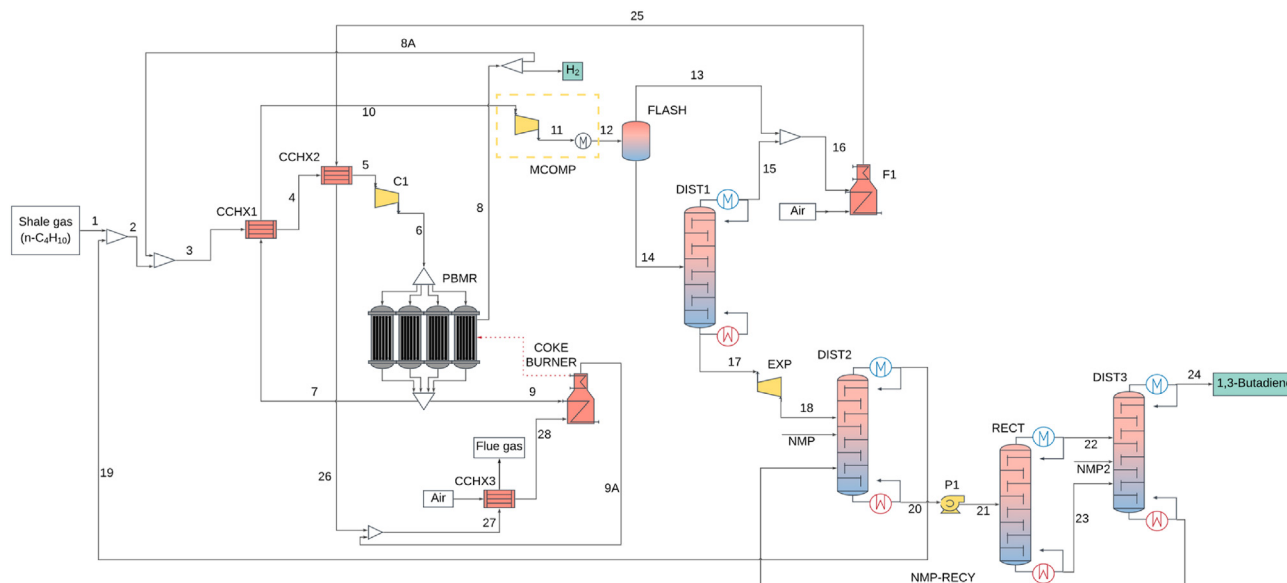


Fig. 4 – Process flow diagram of the MR-Assisted BDH Technology.

distillation column. The detailed mass balance of the plant is reported in [Appendix A1](#).

Results

Technical analysis

The main results obtained from the detailed mass and energy balances of the benchmark and MR-assisted BDH processes, and the resulting performance indicators used to perform the technical analysis are summarized and compared in [Table 8](#).

Both the benchmark and the novel MR-assisted technologies are characterized by 1,3-butadiene and hydrogen as the only sellable products. Both the plants have been designed with a fixed production capacity of 1,3-butadiene, equal to 320 kiloton per year (KTA). As a main difference with the benchmark technology, the novel MR-assisted BDH technology allows to reach the same target production by processing a lower amount of feedstock shale gas, which is reduced of almost 25%. This is mostly due to the more efficient reaction zone, characterized by a lower selectivity to the undesirable cracking products (CH_4 , C_2H_6 and C_2H_4), going from 14.4 wt% to 13.6 wt%, and most importantly a higher achievable selectivity to 1,3-butadiene, going from 64.7 wt% to 73.3 wt%. This in turn allows to have a more efficient downstream separation section, capable of producing same amount of 1,3-butadiene as in the benchmark process, but with a higher mass purity (increased from 99.7 wt% to 99.8 wt%) and a lower consumption of feedstock shale gas. As a result, the $\eta_{\text{FTC}_4\text{H}_6}$ is increased from 50.7% in the benchmark plant, to 67.5% in the MR-assisted plant.

Concerning the other sellable product, the benchmark process produces hydrogen with a lower mass purity compared to the one of the novel MR-assisted process, being equal to 11.7% in the former and 100% in the latter respectively. Nonetheless, the amount of hydrogen produced in the

novel process is slightly less than in the benchmark, which in contrast is compensated by the reduced consumption of feedstock shale gas. The η_{FTH_2} is almost comparable in the two processes, being equal to 6.9% for the novel process and to 6.6% for the benchmark case. As a result of the above considerations, the overall η_{FTC} can be increased from 57.4% in the benchmark to 74.5% in the novel MR-assisted process. In addition to that, the lower dehydrogenation temperature achievable in the MR configuration would result in a drastic reduction of carbon formation (–98.5%) with respect to the benchmark technology. This reduction makes the plant much more efficient in terms of coke produced per feedstock used with a resulting η_{coke} of only 0.2% compared to 7.8% in the benchmark case.

The energy usages reported in [Table 8](#) allow to determine the total utility usage of both plants, from which the Overall Energy Efficiency is computed. The electricity consumption is almost 71.2% higher in the benchmark process than in the MR-assisted technology. The novel MR-BDH plant has the compressor (C2) before the separation section with a much higher electricity demand with respect to the benchmark technology, due to the bigger ΔP to be reached, and it presents an additional compressor (C1) to bring the process stream to the reaction pressure. However, the presence of the multi-stage compression unit with three stages in the benchmark technology, with a high electricity demand of 44.4 MW, impacts significantly on the overall energy consumption. This will result in a net electricity equal to $1.09 \text{ MW}_{\text{el}}/\text{ton}_{\text{C}_4\text{H}_6}$ for the benchmark, compared to the one of the novel technology, equal to $0.31 \text{ MW}_{\text{el}}/\text{ton}_{\text{C}_4\text{H}_6}$.

A different situation emerges when considering the thermal duty of both plants. A detailed heat integration strategy allowed to minimize the utility consumptions needed to satisfy the thermal power requirements in both the technologies. Cooling water is being used as cooling media in the condenser of the distillation columns and, for the benchmark configuration, in the second cooler of the multistage

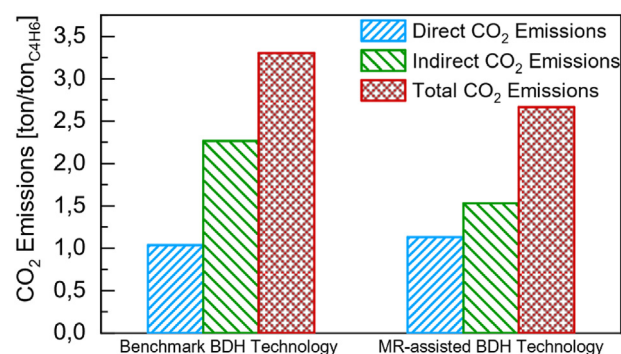
Table 8 – Technical performance comparison of the BDH plants.

	Unit	Benchmark BDH technology	MR-Assisted BDH technology
Feedstock			
Shale gas (n-C ₄ H ₁₀)	kg/hr	82,706	6224.15
Thermal Input	MW _{LHV}	1004.64	756.07
Chemical Products			
1.3-Butadiene	kg/hr	40106.83	40154.00
Purity	Wt%	99.73	99.84
Chemical Energy	MW _{LHV}	510.02	510.62
Feedstock-to-Butadiene	%	50.77	67.54
Hydrogen	kg/hr	3493.73	2764.16
Purity	Wt%	11.70	100
Chemical Energy	MW _{LHV}	66.58	52.68
Feedstock-to-Hydrogen	%	6.63	6.97
Total Chemical Energy	MW _{LHV}	576.60	563.29
Feedstock-to-Chemicals	%	57.39	74.50
Electricity			
Compressor (C1)	MW	0.03	3.87
Multistage Compressors (MCOMP)	MW	44.42	9.62
Pump (P1)	MW	0.03	0.02
Expander (EXP)	MW	-0.76	-0.92
Total Electricity	MW _{el}	43.71	12.60
Thermal Energy			
Water			
Condenser DIST2	MW	-80.07	-68.69
Condenser DIST3	MW	-123.41	-123.25
Condenser RECT	MW	-91.39	-45.34
Cooler (MCOMP.2 nd stage)	MW	-19.32	-
Total thermal water	MW/ton _{C₄H₆}	-8.09	-5.91
Steam			
Reboiler DIST1	MW	24.55	30.77
Reboiler DIST2	MW	161.38	130.15
Reboiler DIST3	MW	123.24	123.13
Reboiler RECT	MW	130.84	74.55
Total thermal steam	MW/ton _{C₄H₆}	7.29	5.10
Refrigerant			
Condenser DIST1	MW	-12.39	-15.58
Cooler (MCOMP.3rd stage)	MW	-29.41	-31.46
Total thermal refrigerant	MW/ton _{C₄H₆}	-0.0010	-0.0012
Total Thermal energy	MW _{th}	84.02	74.28
Overall Energy Efficiency	%	49.14	65.47
Olefins production			
Reactor Temperature	°C	625	540
Reactor pressure	bar	0.5	1.3
n-Butane conversion	Wt%	43.31	42.04
Butadiene selectivity	Wt%	64.65	73.31
Coke selectivity	Wt%	3.90	0.07

compressor unit; its consumption is almost 30% higher in the benchmark technology, mostly due to the bigger power requirements of the rectifier (RECT) which processes a higher

flow rate with respect to the MR-assisted configuration, resulting in a total thermal water usage per unit of product of $-8.09 \text{ MW}_{\text{th}}/\text{ton}_{\text{C}_4\text{H}_6}$ in the former compared to $-5.91 \text{ MW}_{\text{th}}/\text{ton}_{\text{C}_4\text{H}_6}$ in the latter, respectively. Part of this cooling water at the outlet of the condenser of some of the distillation columns present in each plant configuration can be recirculated back and it is used as heating media in the reboilers. In the benchmark process scheme, the reboiler of the de-propanizer (DIST1) uses the cooling water coming out from the condenser of the 1st extractive distillation column (DIST2). Moreover, the thermal power requirement of the reboiler of the 2nd extractive distillation column (DIST3) can be fully compensated by the cooling water heated up at the outlet of the condenser of the same column. Similarly, in the membrane reactor configuration, the duty of the reboiler in the 2nd extractive distillation column (DIST3) can be fully compensated by the cooling water heated up at the outlet of the condenser of the same column. The reboiler of the de-propanizer can exploit the exhaust gases (flue gas) as a hot source, leaving the plant at 252 C. In this way, the overall thermal consumption of steam per unit of product is minimized, which results to be equal to $7.29 \text{ MW}_{\text{th}}/\text{ton}_{\text{C}_4\text{H}_6}$ in the base case and to $5.10 \text{ MW}_{\text{th}}/\text{ton}_{\text{C}_4\text{H}_6}$ in the MR-assisted BDH technology. To fulfill the thermal duty of both the condenser in the de-propanizer and the last cooler in the multistage compressor (MCOMP) of both the technologies, it is necessary to use the refrigerant due to the very low operating temperatures used in these process equipment. The resulting total thermal duty per unit of product in the MR-assisted plant is 62% lower than in the benchmark, mostly due to the more energy efficient downstream separation section. This, together with the lower consumption of electricity and most importantly of feedstock shale gas, makes the MR-assisted technology to have a higher overall plant efficiency (Eq. (4)), being equal to 66.82%, with respect to the benchmark case, which can reach a total efficiency of 50.92%.

From an environmental point of view, the major contribution to the total CO₂ emissions is represented by the indirect CO₂ emissions, as shown in Fig. 5. Those emissions, which result from the import/export of electricity and/or heat, are much larger in the benchmark case than in the MR-assisted configuration, being equal to $2.27 \text{ ton}_{\text{CO}_2}/\text{ton}_{\text{C}_4\text{H}_6}$ in the former and to $1.53 \text{ ton}_{\text{CO}_2}/\text{ton}_{\text{C}_4\text{H}_6}$ in the latter respectively. This difference is related to the higher electricity import required due to the presence of the multistage compressor

**Fig. 5 – CO₂ Emissions of the BDH plants.**

unit, and to the higher thermal power associated to the more energy intensive downstream separation train in the benchmark process. The direct CO₂ emissions, originating from the combustion of purge gases and the regeneration of the catalyst, are respectively 1.04 ton_{CO2}/ton_{C4H6} in the benchmark plant and 1.13 ton_{CO2}/ton_{C4H6} in the MR plant. The increased direct emissions of the MR-assisted plant are due to the bigger amount of purge gas burned off in the furnace (F1), while the emissions associated with the regeneration of the catalyst are only 0.008 ton_{CO2}/ton_{C4H6} compared to the 0.60 ton_{CO2}/ton_{C4H6} of the benchmark case. Overall, the MR-assisted plant has a total CO₂ emission of 2.6 ton_{CO2}/ton_{C4H6} with respect to the one of the benchmark case, which results to be equal to 3.3 ton_{CO2}/ton_{C4H6}.

Therefore, it can be concluded that the main advantage of using a membrane reactor for the dehydrogenation of n-butane is a significant reduction of the carbon footprint with respect to the benchmark technology (–20% of the overall CO₂ emissions), making the MR-BDH technology more efficient from an environmental point of view.

Economic analysis

The results of the economic analysis are reported in Table 9, showing the installation costs for the main group of process equipment, the operating costs, and the final resulting COP of butadiene.

For both the technologies, the largest installation cost is associated with the downstream separation section, as shown in Fig. 6. The distillation columns represent more than 95% of the total BEC (92.6% and 96.7% respectively), due to the difficult separation of 1,3-butadiene from C₄ mixtures [50]. More specifically, the cost of the distillation columns is 14.3% lower in the MR-assisted technology due to the higher yield of 1,3-butadiene reached in the reaction zone, which makes the downstream separation section more efficient.

Table 9 – Economic comparison of the BDH plants.

	Unit	Benchmark BDH technology	MR-Assisted BDH technology
Installation Costs			
Distillation columns	%BEC	92.58%	96.75%
Turbomachines		5.64%	0.20%
Heat Exchangers		0.79%	1.92%
Reactors		0.83%	0.95%
Reg. Unit		0.12%	0.15%
Furnace		0.03%	0.02%
BEC	M€	773.42	634.03
TOC	M€	2598.54	2130.21
Specific cost	M€/ (ton _{C4H6} /hr)	64.79	53.05
Operating Costs			
Feedstock	€/ton _{C4H6}	148.40	111.55
Utilities		48.36	21.76
Catalyst		16.34	16.34
Membranes		–	4.01
CO ₂ emission tax		14.21	11.45
O&M		20.27	17.59
COP	€/ton _{C2H6}	576.28	451.86

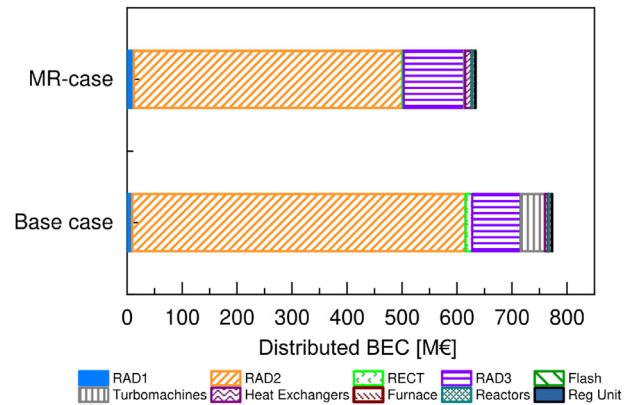


Fig. 6 – Distributed BEC of the two BDH plants.

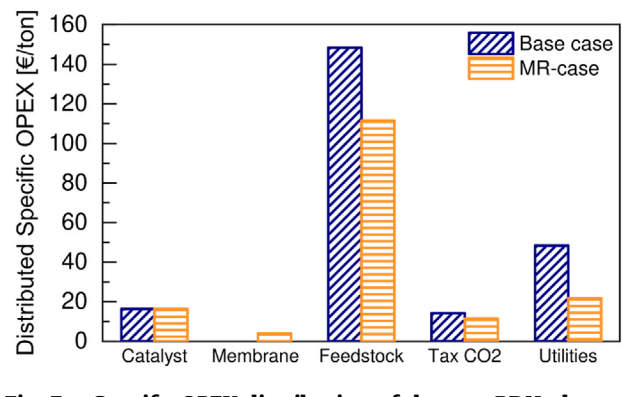


Fig. 7 – Specific OPEX distribution of the two BDH plants.

The additional advantages of using a MR-assisted technology for BDH are represented by the savings in the installation costs for the turbomachines and the reaction unit, –97.04% and –6.52% respectively. In fact, in the MR-assisted technology it is possible to eliminate the three-stage compressor unit, and to operate with a lower amount of catalyst per unit of reactor, resulting also in a reduced sizing for the reaction zone. The cost of the BDH reactors just accounts for less than 1% of the total BEC for both the technologies. The overall specific investment cost per unit of product of the MR plant results to be 53.05 M€/ (ton_{C4H6}/hr), which is almost 20% lower in comparison with the one of the benchmark BDH plant, equivalent to 64.79 M€/ (ton_{C4H6}/hr).

Fig. 7 shows the specific costs distribution associated with the OPEX and compares them for both the technologies analyzed in this work.

The major impact on the variable costs is represented by the feedstock, which accounts for the 67.6% and the 65.3% of the overall OPEX, in the benchmark and the MR-assisted technologies, respectively. However, the cost associated with the feedstock can be significantly reduced (–25%) in the MR-assisted BDH technology with respect to the benchmark case, for a fixed production capacity. The cost for utilities is higher in the benchmark technology, representing the 21.3% of the total OPEX, against the 9.6% in the MR-assisted case. This is mostly related to the higher intensive downstream separation section, requiring higher amounts of utilities in the distillation columns, and to the larger electricity demand for

the turbomachines. Since the catalyst cost is defined per unit of product, the specific catalyst cost is comparable in both the technologies, which have been designed with an equal production capacity of 1,3-butadiene. On the contrary, the worst environmental performance of the benchmark BDH plant results in a bigger impact of the costs associated with the tax (+19.3%) for the CO₂ emissions per unit of product. The costs associated with the membrane modules represent the 2.4% of the total OPEX. In conclusion, the MR-assisted technology has a specific OPEX of 165.1 €/ton_{C_{4H₆}, which is almost 30% lower than the one for the benchmark technology, being equal to 227.3 €/ton_{C_{4H₆}, mostly due to the main savings associated with the feedstock and utilities consumption.}}

Combining the investment costs, both CAPEX and fixed O&M, and the operating costs, it is possible to retrieve the final COP of 1,3-butadiene (Eq. (7)), represented in Fig. 8 for both the benchmark and the MR-assisted BDH technologies.

The use of the membrane reactor technology allows to reach a higher 1,3-butadiene yield lowering the consumption of feedstock shale gas, for a fixed production capacity. This results in a more efficient downstream separation train, with reduced associated installation and operational costs. Therefore, the final COP of 1,3-butadiene can be reduced of almost 22%, from 576.3 €/ton_{C_{4H₆} in the benchmark process to 451.9 €/ton_{C_{4H₆} in the MR-assisted process.}}

Due to the lower CAPEX and OPEX, the MR-assisted technology is more profitable resulting in a ROI of 14% compared to the one of the benchmark technology equal to 11%. Although the ROI of both options is higher than the minimum acceptable ROI of 10%, the MR-assisted BDH technology is more profitable, showing a ROI which is 27,5% higher than the one of the benchmark technology [58].

Sensitivity analysis

After the economic evaluation, a sensitivity analysis leads to investigate the effects of uncertainties of some important factors on the profitability of the BDH technologies, expressed in terms of ROI. As shown during the economic analysis, the CAPEX is the most predominant cost voice. The CAPEX is strongly influenced by the scale of the plant. Thus, linking the

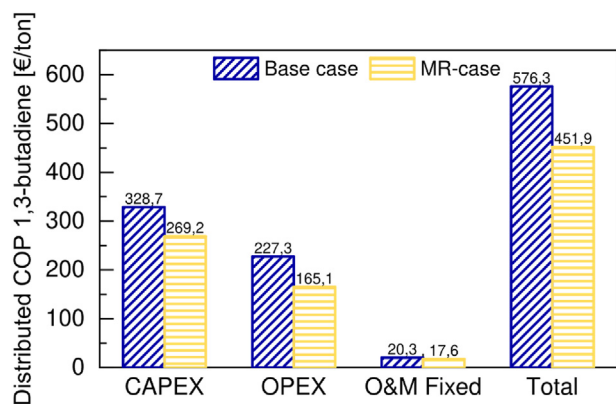


Fig. 8 – Distributed 1,3-butadiene COP of the two BDH plants.

variation of cost with the plant capacity, it is possible to investigate the effects of the variation in plant scale on the ROI of both BDH technologies [59]. As shown in Fig. 9, an increase in the annual plant production capacity would result in an exponential reduction of the ROI due to the exponential increasing trend of the installation costs for both the technologies. The benchmark BDH technology would result not to be economically feasible for a production capacity 2 times higher than the one used in this work for the techno-economic analysis. The MR-assisted BDH technology can withstand the minimum acceptable ROI for plant capacities up to 5 times bigger than the reference one.

Another important factor that can influence the ROI is the selling price of the main 1,3-butadiene product. The price of 1,3-butadiene is varied between 1505 and 700 \$/ton according to the forecast for the global price of butadiene between 2017 and 2022 [60]. The price of valuable chemical products is strongly influenced by the global geopolitical situation, and it can fluctuate significantly over years, as in case of the selling price of 1,3-butadiene which dropped from 1050 \$/ton to 700 \$/ton between 2019 and 2020. These fluctuations influence a lot the profitability of the BDH technologies, as illustrated in Fig. 10.

The lower is the selling price of 1,3-butadiene, the lower would be the profitability of BDH technologies. Among the two different configurations analyzed, the MR-assisted BDH technology results to be less sensitive to reductions in the 1,3-butadiene price, maintaining an acceptable ROI for a price as low as 700 \$/ton.

The sensitivity analysis is finally conducted on the carbon tax, which is strongly affected by the increasing need to shift towards an industrial decarbonization, required to limit the climate change. The carbon tax is varied between 0 and 80 \$/ton_{CO₂} [49,61] depending on the country. Fig. 11 shows the effects that the variation in carbon tax has on the ROI of the BDH technologies.

As expected, the higher the carbon tax the lower would result to be the return of investment. Among the two technologies, the MR-assisted BDH technology experiences a reduction in the ROI of 23.7% while the ROI of the benchmark will drop of almost 33% in the investigated range of carbon tax, reaching a ROI below the threshold for a carbon tax higher than 35 \$/ton_{CO₂}. Therefore, even though both the

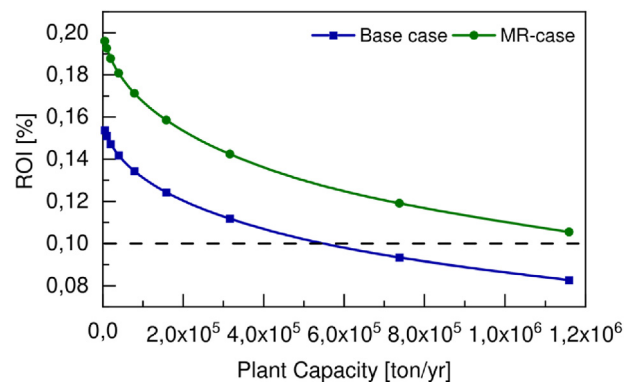


Fig. 9 – Effects of the plant scale on the ROI of both BDH plants.

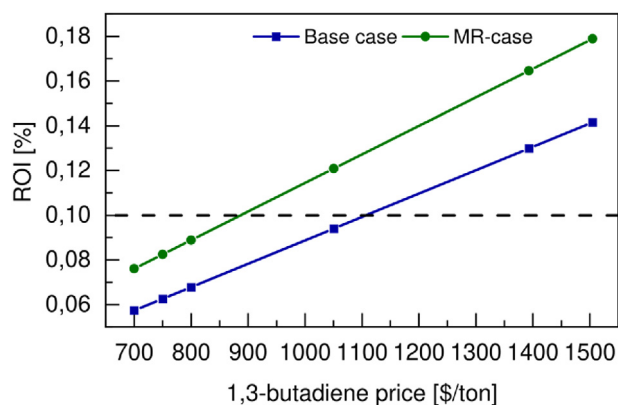


Fig. 10 – Effects of 1,3-butadiene price on ROI of both BDH plants.

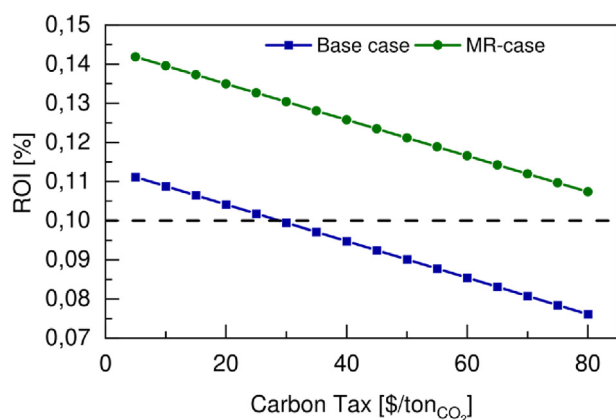


Fig. 11 – Effects of Carbon Tax on the ROI of both BDH plants.

technologies would be negatively affected by the growing stringent environmental protection policies, the MR-assisted technology would be able to maintain an acceptable ROI, mostly due to the lower CAPEX and OPEX.

Conclusions

A techno-economic analysis of a membrane reactor-assisted BDH technology has been conducted in this work to evaluate the feasibility of the implementation of membrane reactors for the direct dehydrogenation of n-butane. The novel technology has been proposed with the aim of performing the dehydrogenation reaction at milder operating conditions, to lower the energy demands and the catalyst deactivation rate, which are two of the major limitations of the current commercialized CATADIENE technology. The novel membrane reactor technology shows better performance over the CATADIENE due to the higher yield toward 1,3-butadiene and the reduced reaction temperature. The higher yields obtained in the reaction zone allow to have a more efficient downstream separation section, capable of producing same amount of 1,3-butadiene as in the benchmark process, but with a higher mass purity (increased from 99.7 wt% to 99.8 wt%) and

a lower consumption of feedstock shale gas. This in turn results in an increased feedstock-to-chemicals, including both 1,3-butadiene and hydrogen, which reaches a value of 74.5% in the novel MR-assisted process, compared to 57.4% in the benchmark. In order to lower the catalyst deactivation rate, lower operating temperatures are beneficial; this is demonstrated by the drastic reduction of carbon formation (−98.5%) reached in the MR-assisted BDH technology, making the plant much more efficient in terms of coke produced per feedstock used with a resulting η_{coke} of only 0.20% compared to 7.8% in the benchmark case.

In BDH plants the costs of heating/cooling requirements in the downstream separation section is by far the predominant energy cost due to the very challenging separation of 1,3-butadiene from the other C₄ components with close volatility. The techno-economic analysis conducted in this work shows that the higher selectivity toward 1,3-butadiene reached in the membrane reactors makes the downstream separation train much more efficient, with a drastic reduction of the thermal power import (−62%). Consequently, even the installation costs associated to the distillation columns, which represent more than 95% of the total BEC in the BDH technologies, can be reduced of almost 15% with the membrane reactor technology. From an economic point of view, the MR-assisted BDH technology is very competitive with the commercial CATADIENE technology, due to the reduced installation costs and operating costs for utilities consumption which will result in a final COP of butadiene reduced by almost 20% with respect to the one of the benchmark technology, being equal to 451.8 €/ton_{C₄H₆} in the former and 576.3 €/ton_{C₄H₆} in the latter. The techno-economic analysis conducted in this work reveal that the reduced investment costs and the increased energy efficiency obtained in the MR-assisted BDH technology, incentivize its development and commercialization in the petrochemical industry. The promising performance of the MR-assisted BDH technology bring the possibility to further study this novel technology, focusing more on the optimization of the membrane reactors and including an appropriate coke formation kinetics for the dehydrogenation of butane, to consolidate its viability at industrial scale.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ijhydene.2022.04.259>.

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