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Publication date:
2021-10

Permanent link:
https://doi.org/https://doi.org/10.3929/ethz-b-000493492

Originally published in:
Renewable and Sustainable Energy Reviews 149, https://doi.org/10.1016/j.rser.2021.111403

Renewable and Sustainable Energy Reviews 149 (2021) 111403

Contents lists available at ScienceDirect

Renewable and Sustainable Energy Reviews

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

Experimental data supported techno-economic assessment of the oxidative dehydrogenation of ethane through chemical looping with oxygen uncoupling

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ARTICLE INFO

Keywords:
Ethylene production
Oxidative dehydrogenation
Chemical looping
Techno-economic assessment
ASPEN Plus®

ABSTRACT

Ethylene is an essential building block in the petrochemical industry and it is almost exclusively produced via ethane steam cracking, a well-established albeit highly energy and carbon dioxide intensive process. The oxidative dehydrogenation of ethane is a promising alternative to steam cracking reactions due to its exothermic nature, which decreases the overall energy requirements and carbon footprint. The need of a capital intensive air separation unit for producing oxygen limits its potential for industrial application. The current study investigates an alternative route, i.e. the production of oxygen via chemical looping, where oxygen is released in-situ by suitable oxygen carriers. The chemical looping oxidative dehydrogenation, supported by original experimental data, and the steam cracking processes are simulated with ASPEN Plus®. A comprehensive analysis of the energy requirements and an economic assessment are carried out for both processes. Compared with state-of-the-art ethane steam cracking, the proposed process provides ~28% energy savings per tonnes of ethylene produced and ~21% reduction in the resulting ethylene price. Sensitivity analysis show that the economy of the chemical looping oxidative dehydrogenation process is strongly sensitive to the feedstock price.

1. Introduction

Ethylene is one of the most important organic chemicals manufactured in the world [1]. It is the building block for the production of a wide range of chemicals, from fibers to plastics and solvents [2]. In 2019, the global ethylene production capacity was 207.6 million tonnes per annum (Mtpa) and it is forecasted to grow considerably to 264 Mtpa in 2023, mostly due to increasing demand in Asia and North America [3]. The industry standard for the production of ethylene is steam cracking [4,5]. Feedstock for the steam cracking process can be gaseous, like ethane or propane, or liquid such as naphtha, gas oil, and gas condensates [4]. Gaseous feeds are preferably used in the USA and the Middle East, while a liquid feedstock is normally used in Europe [5]. When using ethane as the feedstock, a complex network of gas phase radical reactions takes place at high temperatures (i.e. $T > 750$ °C) [5], producing ethylene and other light olefins such as propylene. Steam dilution lowers the partial pressure of the cracked compounds, favouring the desired reaction products (i.e. ethylene) over side reaction products (e.g. coke) [5]. The desired overall Reaction (1) involves the decomposition of ethane into ethylene and hydrogen:

$$C_2H_{6(g)} \Leftrightarrow C_2H_{4(g)} + H_{2(g)} \; \Delta H_{298K} = +136 \text{ kJ mol}^{-1} \quad (1)$$

Although steam dilution reduces the formation of coke in the cracking process, coke build-up is not eliminated entirely and periodic shut down and regeneration of the cracking furnaces are required [5]. The need for periodic regenerations increases the operating costs, whereas the use of steam increases the overall energy consumption [6]. The specific energy demand of ethane cracking ranges between 16 and 25 GJ/t ethylene, which is mainly supplied by the combustion of fuels (e.g. natural gas). This results in the generation of 1–1.2 t CO_2/t ethylene and considerable amounts of NO_x [5], rendering the process highly energy and carbon dioxide intensive. Neal et al. [7] showed that conventional steam cracking has over 90% thermal efficiency from a

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https://doi.org/10.1016/j.rser.2021.111403
Received 30 September 2020; Received in revised form 20 April 2021; Accepted 21 June 2021
Available online 6 July 2021

thermodynamic first law point of view, indicating limited room for further reduction in energy consumption and CO_2 emissions.

The catalytic oxidative dehydrogenation (ODH) of ethane to ethylene (Reaction (2)) is an attractive alternative to the steam cracking process [6–8]. In the presence of oxygen, the simultaneous combustion of the hydrogen produced from the cracking of the alkanes (Reaction (3)) effectively removes the thermodynamic barriers for achieving a high ethane conversion and renders the overall Reaction (2) exothermic [9,10].

$$C_2H_{6(g)} + ½\ O_{2(g)} \rightarrow C_2H_{4(g)} + H_2O_{(g)}\ \Delta H_{298\ K} = -\ 150\ kJ\ mol^{-1} \quad (2)$$

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O\ \Delta H_{298\ K} = -\ 286\ kJ\ mol^{-1} \quad (3)$$

The lower operating temperature (300–700 °C, at atmospheric pressure) and exothermic nature of Reaction (2) can lead to up to 30% energy savings compared to the conventional steam cracking process [11]. Over the past 20 years, a wide range of catalysts has been investigated for ODH, such as V-based catalysts, Sn-doped Pt, Mo/V/-Te/Nb/O, carbon nanotubes, or modified boron nitride [8–14]. The generally high selectivity (i.e. > 90%) towards ethylene reduces the number of unit operations needed for downstream ethylene purification, leading to reduced capital costs [15]. Additionally, the presence of oxygen eliminates coke deposition, such that no regeneration of the catalyst is needed [15]. Catalytic systems such as that of Mo/V/Nb mixed oxides yield ethylene productivities higher than 1 kg $kg_{cat}^{-1}\ h^{-1}$, i.e. the limit value below which the productivity is too low to be interesting for industrial application [16].

The potential advantages of the ODH process are currently not sufficient for companies to replace the well-established steam cracking processes [16]. Challenges for the industrial implementation of the ODH process include high operating and capital costs that are associated with the need of pure oxygen or oxygen-enriched air, which requires an air separation unit (ASU). The flammability of a gas mixture containing oxygen and a fuel in the single step ODH imposes additional safety concerns. Over-oxidation of the alkanes and olefins to CO and CO_2 can cause hot spots in the reactor and reduce product selectivity [17].

A cost-effective approach for producing oxygen – typically referred to as chemical looping – employs the so-called oxygen carriers (OCs), which are metal oxides capable of releasing gas-phase oxygen at elevated temperatures (500–900 °C). In such process, oxygen is produced via two reaction steps in cyclic fashion: In the first step (Reaction (4)), oxygen is released from the OC, the rate and amount of oxygen is controlled by its thermodynamic properties. In the second step (Reaction (5)), the reduced OC is regenerated in air.

$$Me_xO_{y(s)} \rightarrow Me_xO_{y-2(s)} + O_{2(g)} \quad (4)$$

$$Me_xO_{y-2(s)} + O_{2(g)} \rightarrow Me_xO_{y(s)} \quad (5)$$

The chemical looping concept has been extensively investigated over the last two decades for a wide range of fuel, electricity and chemicals production technologies [18]. Moghtaderi et al. [19] first introduced the concept of a chemical looping-based technology for air separation (CLAS), by using steam as a reducing agent. The literature shows that the oxygen production process via CLAS could produce oxygen at 40–70% lower costs than via ASU, in the context of oxy-fuel combustion [19–22]. The identification of OCs with suitable thermodynamic properties is one of the key challenges of CLAS. The OC should also transfer lattice oxygen rapidly and possess a relatively high (i.e. > 1 wt%) oxygen storage capacity (OSC) to enable long reduction and oxidation stages. In a continuously operating reactor system (e.g. one that is comprised of two fluidised bed reactors with OC circulating from one reactor to another), a high OSC may not be critical because the reducing and oxidising environments are separated from each other. However, in a semi-continuously scheme, such as the packed bed reactor employed in this work, both the reduction and oxidation reaction of the OC take place in the same reaction vessel. A low OSC would therefore imply that the transition stage between the reduction and oxidation reactions becomes significant, which would lower the gas product yields of the redox reactions owing to gas mixing effects.

Oxygen carriers with a high OSC that have been used for CLAS include those based on the monometallic oxides CuO, Co_3O_4 or Mn_2O_3 [23–25]. Their decomposition to a lower oxidation state in atmospheres of low oxygen partial pressure (pO_2) occurs typically at high temperatures (>700 °C), making them unsuitable in combination with a catalytic reaction such as the oxidative dehydrogenation of ethane that requires temperatures < 500 °C for the catalyst to give high ethylene yields. In comparison, mixed metal oxides, such as perovskites, have shown to be able to release gaseous oxygen at temperatures <500 °C in atmospheres of low pO_2 and have been investigated extensively in the last two decades for various chemical looping-based reaction schemes [26,27]. In particular, the perovskite $SrFeO_{3-\delta}$ has been identified as a suitable OC with favourable thermodynamic properties for low temperature redox cycles with spontaneous release of oxygen [28–30]. Inexpensive and readily available oxides needed for its production make $SrFeO_{3-\delta}$ a relatively cost-effective material [31]. The partial substitution of the Sr (A-site) and/or Fe cation (B-site) with other elements has been studied extensively recently and was observed to alter the oxygen sorption/desorption performance of the OC for a given set of reaction conditions [32,33]. Substitution of the Fe B-site with Co has been identified by Ikaeda et al. [34] as an effective measure to ensure faster redox kinetics compared to the unsubstituted sample ($SrFeO_{3-\delta}$). More recently, Dou et al. [33] have investigated A- and B-site co-substitution by Ca and Co, respectively, and found an excellent OSC at temperatures as low as 400 °C (1.2 wt%) when operating cyclically between 5% O_2 and air. Among other investigated systems [32], calcium substituted $Sr_{1-x}Ca_xFeO_{3-\delta}$ has received particular attention. Miura et al. [35] have found that the inclusion of Ca into $SrFeO_{3-\delta}$ results in an increase of the OSC from 0.6 wt% to 1.1 wt% and they have identified $Sr_{0.76}Ca_{0.24}FeO_{3-\delta}$ as a low-cost oxygen carrier with excellent redox properties in the context of a high-temperature (600 °C) pressure swing adsorption process. Popczun et al. [36] have carried out a computational and experimental study on $Sr_{1-x}Ca_xFeO_{3-\delta}$ and found that a low degree of Sr substitution by Ca (x = 0.05) yields the highest OSC (2.41 wt%), although a higher degree of substitution (x = 0.25) is desired for faster oxygen release. In our previous work, we have identified the perovskite with the composition $Sr_{0.8}Ca_{0.2}FeO_{3-\delta}$ as the most suitable OC candidate for CLAS applications due to its high OSC (2.15 wt%) at 600 °C and stable performance over 100 redox cycles [37].

In the current work, we investigate the possibility of implementing such a chemical looping approach into the oxidative dehydrogenation process (CL-ODH) as a potentially cost-efficient way to produce the oxygen required for the oxidative dehydrogenation (Reaction (2)) (Fig. 1).

In such a CL-ODH process, the in-situ production of gas phase oxygen

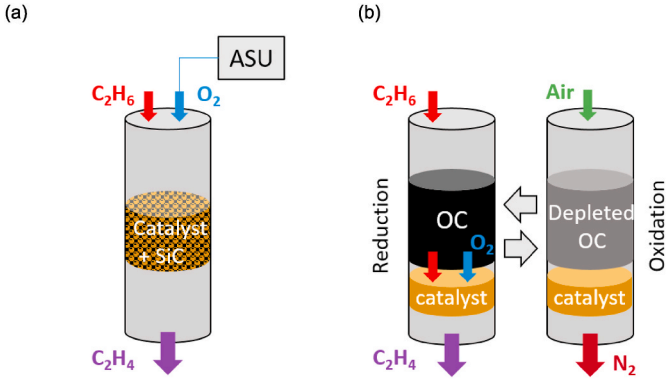

Fig. 1. Schematics of (a) a conventional ODH process and (b) the proposed CL-ODH process, with the in-situ production of oxygen by an OC.

would decrease the energy costs by eliminating the capital- and energy-intensive ASU and eliminate the explosion hazards [15]. The overall process would also provide a significant drop in NO_x and CO_x emissions compared to the ethane steam cracking process in light of a reduced energy demand [17]. The process would employ parallel packed bed reactors and periodically alter the gas atmosphere to regenerate the OC in air.

The CL-ODH process described in this work is thus different from previous works that have used the chemical looping approach for the ODH of ethane, as summarised by Zhu et al. [27]. Neal et al. [38] have investigated a CL-ODH process where the hydrogen produced by the cracking of ethane was selectively oxidised at high temperature (i.e. T = 850 °C) by the lattice oxygen of the redox catalyst. They showed that with a Na–W/Mn/MgO redox catalyst a 12% increase in the single pass yield of ethylene (from 49% to 55%) could be obtained compared to when no redox catalyst was used. In another variant of CL-ODH, $(LaSr)_2FeO_{4-\delta}$ redox catalysts promoted with alkali metals (i.e. Li, Na, or K) were shown to achieve up to 86% ethylene selectivity and 60% ethane conversion at 700 °C [39,40]. Haribal et al. [6] have reported that such process can provide an up to 82% reduction in the overall energy demand, as well as an 82% reduction in CO_2 emissions. It is noted that in the mentioned CL-ODH processes, the OCs do not release oxygen that is combined with the catalytic reaction, but rather have the hydrocarbon or the H_2 (Reaction (1) and (3)) react with lattice oxygen directly, which requires high reaction temperatures (typically > 650 °C) for the lattice oxygen transfer to proceed rapidly.

In the current work, we use a $Sr_{0.8}Ca_{0.2}FeO_3$ OC to release oxygen at temperatures at which conventional ODH catalysts can work efficiently (≤600 °C); therefore, oxygen production (i.e. oxygen release from the OC, Reaction (4)) and the catalytic conversion of ethane and oxygen (Reaction (2)) occur in the same reactor simultaneously.

Chemical looping processes often employ fluidised bed reactors, where the lifetime of the OC particles can be compromised by mechanical wear, resulting in the production of fines that are entrained from the bed. In a packed bed configuration, attrition does not occur and so material loss is negligible. The stability of the OC particles is still crucial, as the formation of fines may increase the pressure drop in the reactor [41].

In light of the above mentioned issues related to the ethane steam cracking and the potential advantages of the proposed CL-ODH process, a detailed techno-economic analysis of the two processes has been carried out to effectively evaluate the economic feasibility and superiority of the latter one. The CL-ODH process and the state-of-the-art ethane steam cracking for ethylene production are simulated using ASPEN Plus®. Note that the analysis is carried out at an elementary level and evaluates the relative potential advantages of the proposed CL-ODH process compared to the state-of-the-art ethylene production process. Consequently, the outlined economic assessment neglects important aspects such as raw resources extraction, transportation and storage, local availability of the feedstock, sales or utilization opportunities of intermediate products, etc., which may result in additional cost benefits for one or the other process. Reference variable operating costs (e.g. electricity, make up water, catalyst, etc.) in Europe are used to perform the economic analysis. However, the current study should not be interpreted for the European ethylene market only, but rather in a global perspective. Sensitivity analyses are carried out to evaluate how the estimated price of the ethylene product depends on various key process parameters. Importantly, we present, supported by original experimental results, the very first assessment of this novel chemical looping reaction scheme where the generation of gas-phase oxygen and the catalytic, oxidative dehydrogenation of ethane occur within the same reactor. Our analyses show that there are several advantages over the existing benchmark process that is steam cracking from energetic, economic and GHG emissions point of views.

2. Process descriptions

2.1. Steam cracking process

Fig. 2 shows a process flow diagram of a conventional ethane steam cracking process [7]. The upstream and downstream sections have been highlighted. It is assumed that pure ethane is used as the feed (note that ~ 2.5 vol% of contaminants, e.g. propane and methane, are normally found in industrial practice [42]). The upstream section includes the pre-heating of the feed ("HEAT1" and "HEAT2") to T = 650 °C and the cracking reactor ("CRACKER"). Pre-heated ethane is cracked at high temperature (T = 850 °C) and ~2 bar in the cracking reactor in the presence of steam (steam-to-ethane mass ratio ~ 0.4). The cracking furnaces are heated by the combustion of the fuel (e.g. natural gas) to provide the heat input at $T \approx$ 1000 °C. The actual cracking reaction typically occurs very rapidly, with ethane residence times of the order of milliseconds [5]. The downstream section consists of units for quenching, compression, refrigeration, as well as units for product separation. The hot stream leaving the cracking reactor is quenched ("COOL1") to near ambient temperature (~40 °C) to avoid further cracking. The quenched stream is separated from water ("SEP1") and then is compressed to 40 bar using a multi-stage compressor ("MULTICOMP"). The compression stages are followed by a series of distillation columns to yield high-purity ethylene by sequentially separating the light components from the heavy fraction. Firstly, hydrogen is separated in a flash separator ("SEP2") from the compressed stream and then partially recycled ("SEP3") to feed the deacetylenizer reactor. Methane is separated in the demethanizer ("DEMETH") from the components with a higher molecular mass (i.e. C2+ components). Acetylene, ethane and ethylene of the bottom product are separated from the C3+ components in the deethanizer ("DEETHAN") and then treated further with hydrogen to separate ethane and ethylene from acetylene ("DEACETY"). The streams of ethane and ethylene are then separated in the C2 splitter ("C2SPLT"). The bottom product (i.e. C3+ components) from the deethanizer is routed to the depropanizer ("DEPROP"), where C4+ components are separated from propylene and propane. In the debutanizer ("DEBUT"), C4 components are separated from C5 and aromatic species. Propane and propylene are separated in the C3 splitter ("C2SPLT"). The unreacted ethane is typically recycled and mixed with fresh feed, while methane is used as fuel gas for the heating of the cracking furnace [5].

2.2. Chemical looping oxidative dehydrogenation of ethane

The CL-ODH process is simulated by means of ASPEN Plus® (Fig. 3) using original experimental data. For the purpose of modelling, the CL-ODH process is separated into three steps: First, the OC is reduced in the reducer reactor ("REDUCER") upon flowing ethane and steam. The fresh ethane feed ("FEED") is mixed ("MIXREC") with unconverted ethane ("REC1") and then pre-heated ("PREHEAT1") to 600 °C. The steam and pre-heated ethane feeds are mixed ("MIXSTEAM") and sent to the reducer reactor. Steam is needed as diluent to achieve a stoichiometric ratio of ethane:oxygen = 2:1 required for the catalytic ODH reaction. The stream leaving the reducer is first separated ("EXOC") from the oxygen-depleted OC particles ("OC") and then from the steam ("EXSTEAM"). In the second step, the stream of ethane and oxygen ("E + O") at 600 °C is fed in the ODH reactor ("ODH REACTOR"), where oxygen reacts with ethane in the presence of a catalyst. The oxygen-depleted OC particles are regenerated in air in the oxidiser reactor ("OXIDISER") in a third step. The air feed of the oxidiser reactor is pre-heated ("HEAT5") to 600 °C and is then separated ("EXAIR") from the regenerated OC particles after leaving the reactor. The re-oxidised OC particles are recirculated to the reducer reactor to complete the redox loop. Note that the real process does not use circulating fluidised bed reactors because the OC particles stay in the same vessel, where the gas atmosphere is periodically altered for the regeneration of the depleted OC in air. The ODH reactor is operated at 600 °C and 1 bar for the

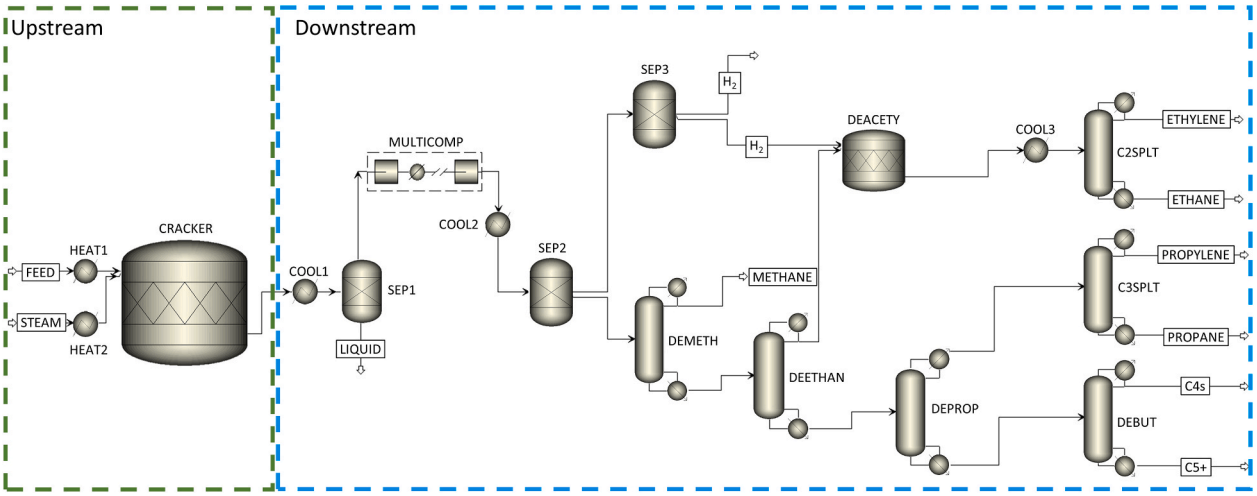

Fig. 2. ASPEN Plus® flowsheet for the conventional ethane cracking process.

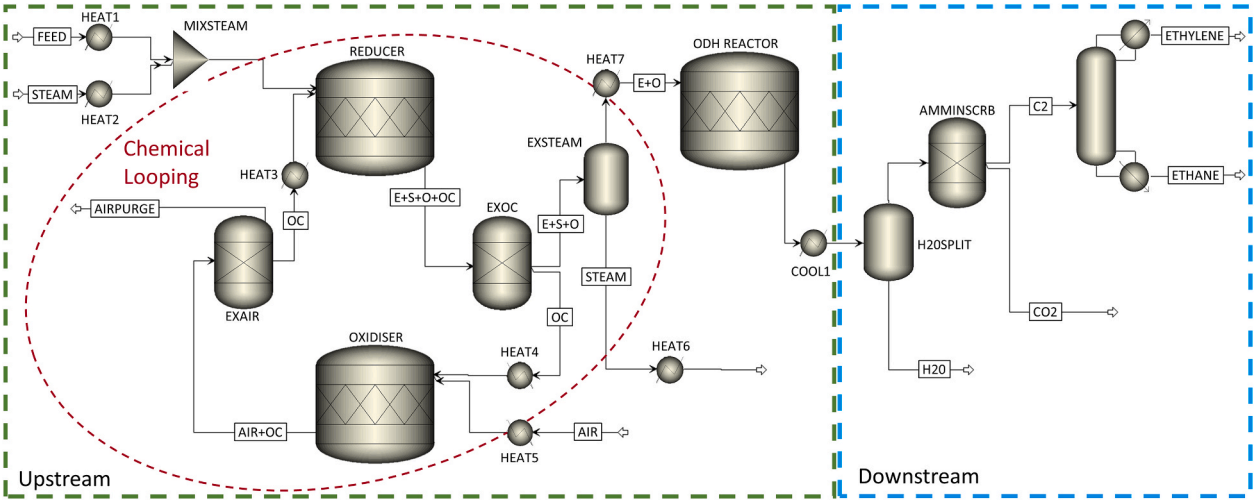

Fig. 3. ASPEN Plus® flowsheet for the chemical looping oxidative dehydrogenation of ethane. Note that for the purpose of modelling, the highlighted chemical looping part differs from the actual proposed process, where the gas atmosphere is periodically alternated for the regeneration of the depleted OC particles.

reduction and oxidation reactions. The investigated process involves $Sr_{0.8}Ca_{0.2}FeO_{3-\delta}$ as the OC, which was identified as a promising OC owing to its high oxygen storage capacity (2.15 wt%) and structural and redox stability [37]. Thermodynamic data (i.e. specific heat capacity and heat of Reaction (4)) of $Sr_{0.8}Ca_{0.2}FeO_{3-\delta}$ is not available in the ASPEN Plus® database, and was therefore measured in our laboratory and implemented in the process simulation. A specific heat capacity of 180 J K^{-1} mol^{-1} and a heat of reaction (Reaction (4)) of −181.9 kJ mol O_2^{-1} is used. Thus, the oxygen release is exothermic, which is different from conventional monometallic redox pairs, such as CuO/Cu_2O. The amount of OC needed to enable the process is calculated from the mass balances in the process simulation, by knowing the required flow of oxygen and the effective oxygen storage capacity of the OC ($Sr_{0.8}Ca_{0.2}FeO_{3-\delta}$) at the given operating temperature (i.e. 600 °C).

The hot product gas stream leaving the ODH reactor is quenched ("COOL1") and treated through a chain of downstream separation units that are similar to the steam cracking process. First, water is separated ("H2OSPLIT") from the quenched stream leaving the ODH reactor. An amine scrubbing ("AMINSCRB") unit is needed in the CL-ODH case, due to the relatively high amount of CO_2 in the product gas stream leaving the ODH reactor (i.e. ~ 8 vol%). Unconverted ethane from the downstream separation block is recirculated to the inlet of the reactor to achieve a higher overall conversion. The major difference of the CL-ODH process from the steam cracking process is the absence of the energy-intensive cracking furnaces. Additionally, the higher selectivity (~82%) of the ODH reaction compared to the ethane steam cracking process (~70%) limits the amount of by-products formed and thus reduces the number of separation units needed.

2.3. Model assumptions

The processes are simulated for a typical industrial scale capacity of ethylene production of ~625 kt/year (note that plant capacities can be as high as 1.5 million t/year [5]). The efficiency is assumed to be 85% for all heat exchangers [6]. Table 1 summarises the main process conditions used for the process simulations. The physical property databanks, property methods and ASPEN Plus® models used are summarised in Table S1 in the SI. Tables S2 and S3 in the SI show the reactions that were used in the process modelling of both processes (i.e. steam cracking and CL-ODH), and the distribution of the carbon-containing gaseous products, respectively. The conditions used in the separation columns are listed in Table S4, while the details of the deacetylenizer reactor in Table S5.

Table 1
Process conditions.

Ethane Steam Cracking	
Cracker operating pressure and temperature	1 bar, 850 °C
Ethane pressure and temperature	1 bar, 850 °C
Steam pressure and temperature	1 bar, 850 °C
Ethane conversion	60%
Compressor specifications	3 stage, intercooler at 30 °C
Chemical Looping Oxidative Dehydrogenation of Ethane	
Reduction reactor operating pressure and temperature	1 bar, 600 °C
Regenerator reactor operating pressure and temperature	1 bar, 600 °C
Ethane conversion	34%

3. Experimental section

In this section, experimental results of the CL-ODH of ethane are discussed, which form the basis for the techno-economic modelling.

3.1. Experimental setup

The performance of the CL-ODH process was assessed using a packed bed quartz tube reactor (I.D. 10 mm, 30 cm long), at a temperature of 600 °C and a total flowrate of 40 mL min^{-1} (ethane flowrate 5.5 mL min^{-1}, balance N_2) corresponding to a gas hourly space velocity, GHSV, of ~6000 h^{-1}. A schematic of the reactor and the temperature profile observed in the tube are reported in Fig. 4.

3.2. Experimental methods

The experiments were performed using 10 g of the phase-pure perovskite $Sr_{0.8}Ca_{0.2}FeO_{3-\delta}$ (sieved to 180–250 μm) as the OC (corresponding to a bed length of 5 cm) and a ~0.4 cm long catalytic bed obtained by mixing V_2O_5/SiO_2 with SiC (sieved to 200–250 μm) at a mass ratio of 1:2 [12]. Vanadium-based oxides have been studied as catalysts for the oxidative dehydrogenation of low-weight alkanes and they are already well-established catalysts for the partial oxidation of hydrocarbons to oxygenated products [16]. The bed was held in the centre of the reactor tube by using a plug of quartz wool. Mass flow meters were used to control the flow rates of the gases into the reactor, while the determination of the composition of the gas stream leaving the reactor was done by using a paramagnetic analyser for oxygen (ABB EL3020, Magnos 206) and an MKS FTIR hydrocarbon analyser (Precisive 5).

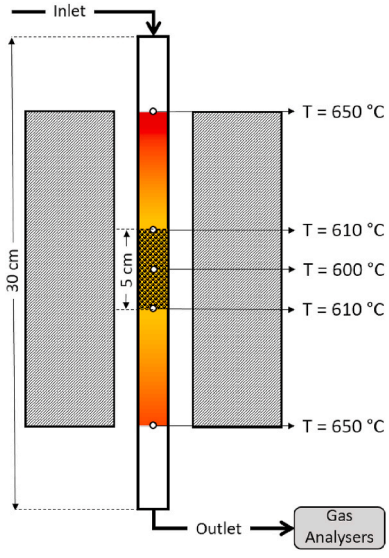

Fig. 4. Schematic of the reactor setup and temperature profile in the reactor tube. The area with black dots represent the isothermal zone where the materials are placed.

Initially, the oxygen partial pressure (pO_2) that could be provided by the OC was assessed, as reported also in Ref. [37]. Figure S1 in the SI shows the measured pO_2 profile at the outlet of a fixed bed reactor filled with 3 g of $Sr_{0.8}Ca_{0.2}FeO_{3-\delta}$ at 600 °C in a nitrogen atmosphere (40 mL min^{-1}). The result of the blank experiment (reactor filled with SiC of the same volume as in the experiment with OC) is represented by a dashed line. A rapid release of oxygen was observed initially, followed by a slow release due to the reducing available lattice oxygen. *In-situ* XRD experiments revealed that the oxygen release occurs with a phase transition from perovskite to its defect-ordered variant brownmillerite [37]. The perovskite structure is then recovered upon flowing air at the same temperature. Thus, the equilibrium partial pressure of oxygen ($pO_{2,eq}$) decreases with the removal of lattice oxygen, which inevitably complicates the design of a chemical looping process using such materials as OCs because a constant stream of oxygen cannot be obtained in a conventional fixed bed reactor.

3.3. Experimental results used for the process modelling

Fig. 5 shows the outlet gas composition of the performed coupling experiment (oxygen release combined with the oxidative dehydrogenation; reduction step in Fig. 1b). An initial high production of CO_2 (over-oxidation) was observed due to the rapid release of a large amount of oxygen by the OC and the mismatch of the desired ethane:oxygen ratio. The over-oxidation phase was followed by a stable production of ethylene with a high ethylene selectivity (~82%) for ~ 50 min. Importantly, in this period, the ethane conversion was ~34%, i.e. higher than when oxygen was co-fed. After ~80 min, the measured concentration of ethylene in the off-gas decreased, which was because the oxygen carrier became depleted in lattice oxygen (after 80, ~89% of the total redox-active lattice was converted). In the ASPEN Plus® model, the initial over-oxidation period was ignored in both the heat and mass balances and only the performance parameters of the period when the ethylene production was stable were used, as has been done in similar works [6].

4. Costs estimation

In this section, capital and operating costs are estimated for the ethane steam cracking and CL-ODH processes. Europe is selected as possible plant location; therefore, relevant economic assumptions are related to this geographic area. For an estimation of the capital cost of various plant equipment (so-called battery limits investment), the cost correlations are used as presented below based on literature methodology and reference data. The cost of a specific equipment is estimated as:

$$C_E = C_B \cdot \left(\frac{Q}{Q_B}\right)^M \cdot f_M \cdot f_P \cdot f_T \quad (6)$$

where C_E (€) is the cost of an equipment with a capacity Q (MW), C_B (€) is the base cost of an equipment with a capacity Q_B (MW), M is a dimensionless constant that depends on the equipment cost and f_M, f_P and f_T are dimensionless factors for taking into account materials of construction, design pressure and design temperature [4,43].

The overall costs of the installation of an equipment are estimated by considering the costs of installation of the equipment themselves and the related auxiliary costs (grid connection, foundations, insulation, financial charges, etc.). Additionally, the costs of the utilities are estimated by considering the costs for steam generation, refrigeration, cooling water, electricity, etc. Battery limit investment and utility investment forms the on-site investment. All the off-site costs consist of auxiliary buildings (offices, warehouses), utility systems (fire protection, communication, waste disposal), vehicles (loading and plant service vehicles) and so on. The costs estimate of the heat exchangers is based on the required

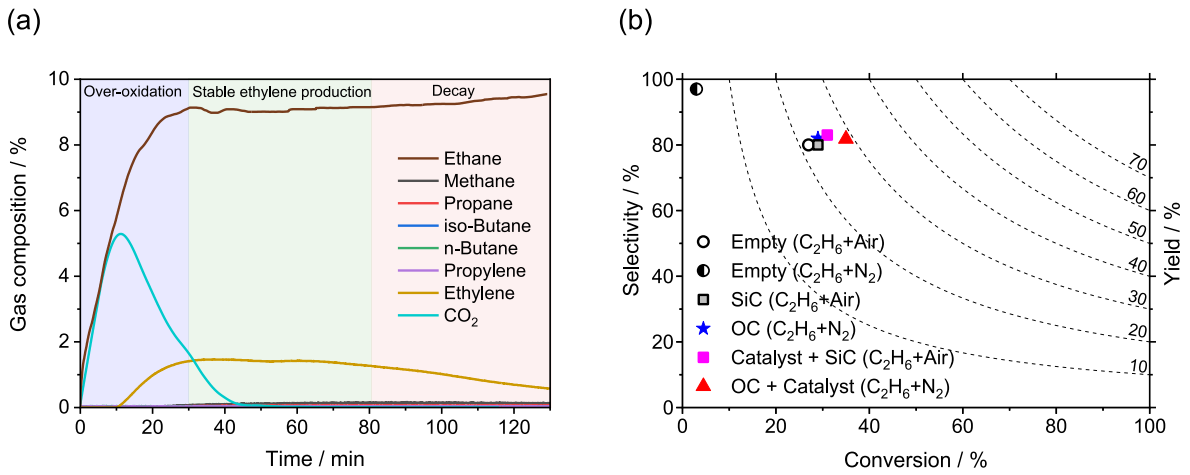

Fig. 5. (a) Outlet gas composition in the case of the coupling process at T = 600 °C (OC + catalyst, not co-feeding oxygen). (b) Summary of all of the experimental results in terms of ethane conversion, ethylene selectivity and overall yield (represented by dashed lines).

surface area which was obtained by performing a Pinch analysis (Figure S2) and using correlations in literature [43]. The estimate of the utilities and off-site costs is generally done by considering 25% of the costs of all on-site process units (reactors, separation columns, heat exchangers, etc.). Owner's cost (land, financial cost, etc.) and contingencies are estimated as 15% of the total costs of installation.

The estimation of the total investment costs considers all on-site, off-site, contingency and cost elements above. The specific investment costs (SIC, €/$kg_{ethylene}$) are calculated using Eq. (7).

$$SIC = \frac{Total\ investment\ costs\ (TIC)}{Gross\ ethylene\ production} \quad (7)$$

Operational and maintenance (O&M) costs are estimated by considering fixed costs (not proportional to the energy produced, e.g. annual charges on the capital costs, taxes, insurances, etc.) and variable costs (dependent on the produced energy, e.g. fuel costs, chemicals, catalysts, etc). Variable operating costs (VOCs, €/year) are calculated using Eq. (9)

$$VOC = \Sigma\ (cost_{raw\ material} \cdot quantity_{raw\ material}) \quad (8)$$

The direct labour costs (wages, unemployment tax, employment insurance, etc.) are calculated using Eq. (9):

$$DLC = (direct\ labour \cdot annual\ average\ salary) \quad (9)$$

Operating costs can vary significantly between different geographic areas and production sites. The data for estimating the operating costs are retrieved from literature [44–50]. The main assumptions and calculation methods that are used for the economical assessment of ethylene production by ethane steam cracking and CL-ODH are summarised in Table 2. Raw material price, cost of utilities and labour hourly rate are given in Table 3. The cost estimates are per annum assuming 8000 working hours. The lifetimes of the catalyst and the OC are considered as 2 and 5 years, respectively. The make-up of the materials after the respective lifetime period is included in the operational costs.

The price difference of gaseous ethane feedstock is significant depending on the geographic area, as it has been shown by Boulamanti et al. [51]. The proposed CL-ODH process uses gaseous ethane feedstock and would hardly be economically attractive in Western Europe, where liquid feedstock is normally employed. Hence, the average ethane price in the USA in 2019, i.e. 218.4 €/t, is used for the economic assessment [52].

Table 2
Main assumption for the economical estimate.

Cost estimate	Assumption/Calculation method
Sub-systems equipment costs ($C_{E(i)}$)	$\Sigma\ C_{E(i)}$ – calculated using eq. (5)
Utilities and offsite units (U&OU)	25% of $\Sigma\ C_{E(i)}$
Total installed cost (T_{ISC})	$\Sigma\ C_{E(i)}$ + U&OU
Owner's cost and contingency (C&C)	15% of T_{ISC}
Land purchase, permitting, surveying, etc.(LP)	5% of T_{ISC}
Total investment costs (TIC)	T_{ISC} + C&C + LP
Annual maintenance cost (AMC)	2.5% of TIC
Direct labour cost (DLC)	Calculated using eq. (7)
Administrative, support and overhead cost (A)	30% of DLC
Fixed operating costs (FOC)	AMC + DLC + A
Variable operating costs (VOC)	Calculated using eq. (8)
Operational life	25 years
Interest rate	8%
Construction period	3 years

5. Results and discussion

5.1. Energy requirements

Table 4 summarises the feed and product streams of the ethane steam cracking and CL-ODH processes. The major energy requirements of each operational unit for the ethane steam cracking and CL-ODH processes are reported in Table 5. For the cracking process, ~61% of the total upstream energy demand is used for the heat requirement of the furnaces. The CL-ODH reactions are net exothermic, which allows for the recovery of a significant amount of heat, and results in overall reduced upstream energy requirements. The main downstream energy savings of the CL-ODH process compared to the ethane steam cracking process (for which the downstream energy requirements are typically ~ 20% larger than for the upstream energy requirements [6]) are due to the reduced number of separation units because the selectivity towards ethylene is higher and the amount of by-products lower. The energy requirements of the ethane steam cracking and CL-ODH processes were determined manually via Pinch analysis, by using the resulting energy requirements from the ASPEN Plus® model and assuming a minimum pinch point

Table 3
Raw material cost.

Feedstock	Ethane	218 €/t
Materials	$Sr_{0.8}Ca_{0.2}FeO_{3-\delta}$	30 €/kg
	VO_x/SiO_2	20 €/kg
Utilities	Electricity	0.085 €/kWh
	Cooling water	0.025 €/t
	Process water	0.030 €/t
Labour	Hourly rate	18 €/h

Table 4
Major streams of the ethane steam cracking and CL-ODH process.

	T (°C)	p (bar)	Flowrate (kt/year)	Normalised Flowrate (t/$t_{ethylene}$)
Ethane Steam Cracking				
Ethane	25	1	960	1.54
Steam	110	1	290	0.46
Ethane recycle	850	1	510	0.81
Propane recycle	850	1	82	0.13
Ethylene	−84.8	1	625	1
Propylene	16	1	15.5	0.02
C4s	37	1	16	0.03
C5+	25	1	35	0.06
Chemical Looping Oxidative Dehydrogenation of Ethane				
Ethane	25	1	850	1.36
Ethane recycle	25	1	1075	1.71
Air (regeneration)	25	1	4660	7.44
Steam	100	1	990	1.58
Ethylene	−104	1	630	1
Carbon dioxide	25	1	470	0.74
Water	25	1	700	1.11
Purge	25	1	20	0.04

Table 5
Process simulation outputs of the major power contributions of the ethane steam cracking and CL-ODH processes for an ethylene plant capacity of 625 kt/year.

Apparatus	Type	Power (MW)
Ethane Steam Cracking		
Heat exchangers	Heat required	103
Reactor: Steam Cracker	Heat required	107
Multistage compressor	Heat required	35
Separation columns reboilers	Heat required	86
Deacetylenizer	Heat required	20
Heat exchangers	Cooling required	−227
Multistage compressor	Cooling required	−38
Condensers	Cooling required	−77
Total		**9**
Chemical Looping Oxidative Dehydrogenation of Ethane		
Heat exchanger	Heat required	425
Reactor: metal oxide oxidation	Heat required	280
Amine scrubber	Heat required	74
Separation columns reboilers	Heat required	15
Reactor: metal oxide reduction	Cooling required	−295
Heat exchangers	Cooling required	−414
Reactor: ODH	Cooling required	−310
Total		**−225**

temperature of 20 °C for heat transfer processes. The composite curves used for the heat integration analysis are reported in Figure S2. The resulting specific energy required for the CL-ODH process is 13 GJ/$t_{ethylene}$, whereas for the ethane steam cracking process it is 18 GJ/$t_{ethylene}$.

5.2. Estimation of greenhouse gases emissions

In this section, we discuss an elementary analysis of the pollutant emissions of both processes to quantify the potential decrease in the carbon footprint of the proposed CL-ODH compared to the ethane steam cracking process. We note that this is a simplified comparative assessment of the greenhouse emissions and a detailed life cycle assessment is beyond the scope of the current work. The outlined analysis neglects the greenhouse gases emissions from the stages of extraction and transportation of the raw resources, as well as the preparation of the feedstock. The results of the ASPEN Plus® simulations suggest that for both processes ~60% of the energy requirement comes from the fuel (i.e. natural gas) that is used to provide heat, ~35% from the steam or circulating water and the remaining energy from the power grid. The greenhouse gases emissions are assessed through CO_2 equivalents, in line with their global warming potential value for a 100-year time period. The CO_2 equivalents of the different sources of energy (i.e. fuel, steam, electricity) have been retrieved from literature [53,54]. The resulting equivalent amounts of CO_2 produced per ton of ethylene are estimated as the sum of the emitted CO_2 from each operational unit, based on their energy demands (Table 5), and are ~ 0.7 t_{CO2eq} for the ethane steam cracking process and ~0.53 t_{CO2eq} for the CL-ODH process. A typical value of the total CO_2 emissions per ton of ethylene produced via ethane steam cracking is ~1–1.2 t_{CO2eq} [54], when including also feed extraction, preparation and transportation. However, the items that are neglected in our analysis are identical for both processes and, thus, should not affect the conclusions of our CO_2 emission results. Hence, the emissions of greenhouse gases, expressed in terms of equivalent amount of CO_2 per ton of ethylene produced, are ~24% lower for CL-ODH compared to the conventional steam cracking process.

5.3. Estimation of capital, operational and maintenance costs

The estimates of capital and operating costs of the ethane steam cracking and CL-ODH processes are reported in the following section. Table 6 reports the capital costs estimate for the ethane steam cracking and CL-ODH processes. The total investment cost (556 M€) are highest for the ethane steam cracking process. Tables 7 and 8 present the fixed operating cost and the variable cost estimate, respectively. Details of the capital costs of the equipment are reported in Tables S8 and S9 in the SI. We note that the estimation of the capital costs is made by using cost correlations reported in relevant literature [43] and it is based on economic assumptions (i.e. feedstock costs, geographic location, neglect transportation and storage costs, etc.). As a consequence, the accuracy of the capital cost estimates is ±15–25% for a preliminary economic assessment, such as the one reported here [43,55].

The ethylene production price is calculated by the net present value (NPV) method assuming a zero value for the cumulative discounted cash at the end of the lifetime of the plant. This method is commonly used to compare projects with different economic data.

The economic advantage of the CL-ODH process over the conventional ethane steam cracking process is due to the lower specific capital investment costs by about 2%, and significantly lower operating costs by about 38% which lead to a lower ethylene production price, that is by about 21% (361 vs. 460 €/t). These economic elements underline the promising potential of the CL-ODH process for ethylene production compared to the ethane steam cracking process. As a comparison, the analysis is carried out also by using the price of gaseous ethane feedstock in Europe (i.e. 610 €/t) by keeping unchanged all the other variable operating costs (Table S10). The resulting ethylene production price is 1065 €/t, which highlights that the economic advantage of the process is strongly influenced by the cost and flexibility of the feedstock, as

Table 6
Capital cost estimate.

Units	Scaling parameter	Costs (M€)	
		Ethane Steam Cracking	*CL-ODH*
Total installation cost		331	283
Engineering procurement and construction costs (EPCC)	14%	45.5	11
Project contingency	18%	58.5	16.5
Total plant costs (TPC)		435	108
Owners cost	12% of TPC	52.5	13
Total overnight costs (TOC)	TPC + Owners costs	488	120
Cost of initial OC loading		–	203
Total capital requirement (TCR)		556	340
Ethylene production	kg/h	71 390	71 522
Total investment cost per $kg_{Ethylene}$	**€/kg**	**7790**	**7605**

Table 7
Fixed operating cost estimation.

Fixed O&M costs	M€/year
Annual Maintenance Cost	9
Direct Labour Cost	14
Administrative, Support & Overhead Cost	4
Total	**27**

Table 8
Variable operating cost estimation.

	Consumption (kt/year)		*Unit cost*	*Consumption (M€/year)*	
	Ethane Steam Cracking	*CL-ODH*		*Ethane Steam Cracking*	*CL-ODH*
Input					
Ethane	879	778	218 €/t	192	170
Electricity	397	−534	85 €/MWh	34	−45
Fuel	111	–	443 €/t	50	–
Make up water					
Cooling water (CW)	1820	220 485	0.025 €/t	0.05	5.5
Boiler feed water (BFW)	1960	–	0.031 €/t	0.06	–
Diluted water	263 250	–	0.031 €/t	0.01	–
Catalyst					
Oxygen carrier	–	1.250	30 000 €/t	–	37
Catalyst	–	0.120	20 000 €/t	–	2
Monoethanolamine	–	1.100	1932€/t	–	2
Chemical					
CW chemical treatment	1815	220 485	0.0025 €/m^3	0.005	0.55
BFW treatment	–	–	45 000 €/month	0.5	–
Total				**275**	**172**

discussed in the following paragraph on the sensitivity analysis results.

Cumulative cash flow analysis is an important tool for economic evaluation. In the design and construction phase, cash is needed to cover the costs of engineering, equipment procurement and plant construction. In the operation phase, the net cash flow is the difference between sales and expenditures. In our analysis, 29 years are considered as the total lifetime of the plant, which includes 3 years for the construction of the plant, 1 year for recovering the working capital and 25 years of actual operation. For both processes (i.e. ethane steam cracking and CL-ODH) the same interest rate (8%) is assumed and that the discounted cash flow at the end of the project is zero. As a result, the initial investment is recovered in ~10 years for both the steam cracking and CL-ODH process (Fig. 6).

The cost components related to the construction phase are included as 40% in the first two years and 20% in the third year. The cumulative cash flow at the end of the project life is found higher for the ethane steam cracking process, because of its higher overall capital and operational costs, which result in a higher ethylene price. In contrast, the CL-ODH process shows promising potential for the reduction of capital and operational costs, resulting in a significantly lower ethylene price.

5.4. Sensitivity analysis

In order to evaluate the dependence of the ethylene price on various parameters (i.e. ethane conversion, catalyst cost, electricity cost, interest rate O&M, feedstock and capital costs), a sensitivity analysis is performed. Accordingly, the influence of the ethane conversion (decreased to 15% or increased to 60%, from the reference value of 34%), catalyst cost (5200 €/h ± 15%), electricity cost (85 €/MWh ± 15%), interest rate (8% ± 2 abs. %), O&M (1050 €/h ± 15%), feedstock (218 €/t ± 15%)

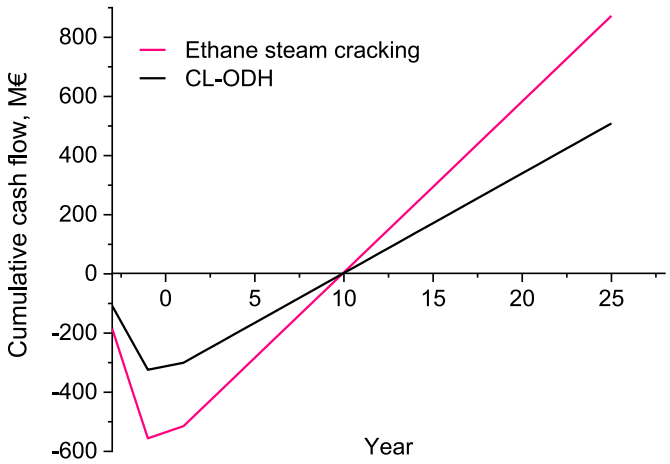

Fig. 6. Cumulative cash flow analysis of the ethane steam cracking and CL-ODH processes.

and capital costs (110 M€/year ± 25%) are investigated for the CL-ODH process. Tables 9 and 10 report the capital cost and variable operating costs for ethane conversions lower (15%) and higher (60%) than the experimentally observed one (34%). Fig. 7 illustrates the effect on various components of the ethylene price in response to changing the ethane conversion. The analysis is performed by fixing the amount of ethane fed to the system. A decrease of the ethane conversion results in an increase of the TCR by ~16%, while increasing the ethane conversion to 60% results in a decrease of the TCR by ~7% compared to the reference case. A decrease of the ethane conversion to 15% (compared to 34% of the reference case) results in a decrease in the specific total investment cost by ~ 7%. The main effect of a conversion lower than the reference case is an increase in the electricity requirements for the downstream separation processes (i.e. the separation columns). The resulting ethylene price in the case of a decreased conversion is significantly higher than in the reference case (i.e. 495 €/t against 361 €/t).

Overall, the analysis shows that the ethylene price increases by ~ 37% for an ethane conversion of 15% and decreases by ~ 6% for an ethane conversion of 60% in the catalytic ODH reaction.

Fig. 8 summarises the results of the sensitivity analysis evaluating the influence of various technical and economic parameters on the ethylene price. The variation of the feedstock price (±15%) results in the most significant change of the ethylene price. In fact, an increase of the feedstock price by 15% corresponds to an increase of the ethylene price by ~12%. This result is consistent with the calculated ethylene production price when considering the cost of gaseous feedstock in Europe,

Table 9
Influence of ethane conversion on capital costs.

Units	Scaling parameter	Cost (M€)		
		CL-ODH low	*CL-ODH*	*CL-ODH high*
Total installation cos		283	283	279
Engineering procurement and construction costs (EPCC)	14%	13	11	10
Project contingency	18%	19	16	15
Total plant costs (TPC)		125	108	100
Owners cost	12% of TPC	15	13	12
Total overnight costs (TOC)	TPC + Owners costs	140	120	111.5
Total capital requirement (TCR)	TOC * 1.14	160	138	128
Initial OC loading		190	203	205
Ethylene production	kg/h	71 522	71 522	71 522
Total investment cost per $kg_{Ethylene}$	**€/kg**	**7553**	**7606**	**7516**

Table 10
nfluence of ethane conversion of variable operating costs.

	Unit cost	Consumption (M€/year)		
		CL-ODH low	*CL-ODH*	*CL-ODH high*
Input				
Ethane	218.4 €/t	170	170	186
Electricity	85 €/MWh	13	−45	−59
Make up water				
CW consumption	0.025 €/t	2.7	5.5	4.7
Catalyst				
Oxygen carrier	30 000 €/t	35	37	41
Catalyst cost	20 000 €/t	3	2.4	2.6
MEA cost	1932.5 €/t	2.1	2.1	2.3
Chemical				
CW chemical treatment	0.0025 €/m^3	0.3	0.6	0.5
Total		**225.5**	**172.3**	**178.4**

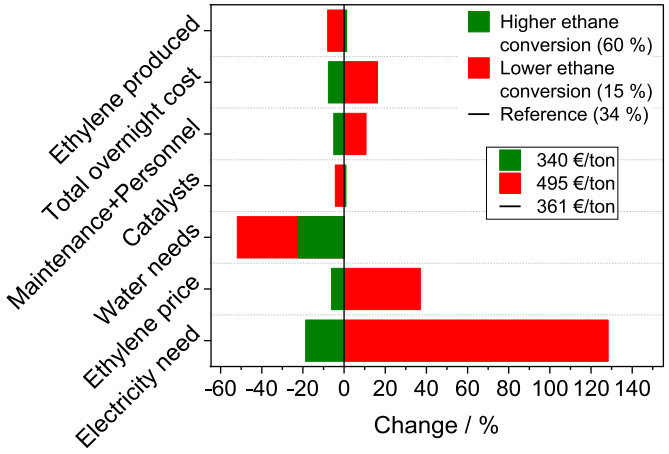

Fig. 7. Sensitivity analysis on the ethane conversion (60%, 34% and 15%) for the CL-ODH process.

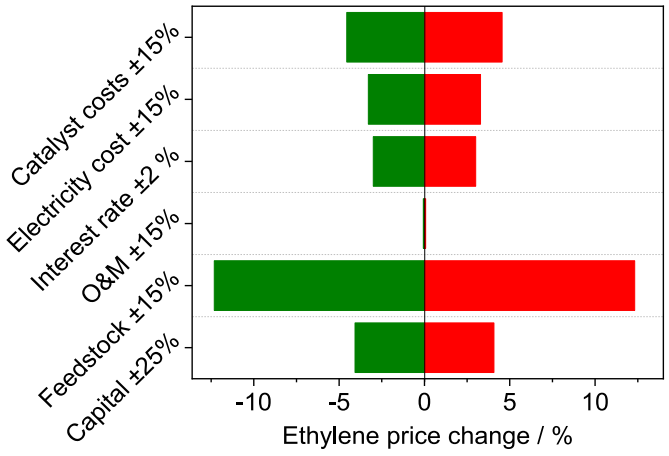

Fig. 8. Ethylene price change as a function of the investigated factors. Catalyst costs include the costs of the OC.

that is significantly higher than the cost in the USA. The ethylene price is also sensitive to the cost of the catalyst and the OC, resulting in a change of ±5%, when the costs of the catalyst and OC changes by ± 15%. A variation of the costs associated to O&M has a negligible impact on the final ethylene price.

6. Conclusions

A process simulation of the CL-ODH process is performed using ASPEN Plus®, implementing data obtained in an experimental campaign (conversion of ethane, yield of ethylene). For comparison, the industry standard for the production of ethylene, i.e. ethane steam cracking, is simulated. The analysis of the two processes shows that the energy requirements for the CL-ODH process are ~28% lower compared to the ethane steam cracking process. The major energy savings of the CL-ODH over the ethane steam cracking process are related to the exothermic ODH reaction, which allows for the recovery of a large amount of heat, resulting in overall energy savings. The main downstream energy savings in the CL-ODH process are due to the high selectivity of the ODH reaction towards ethylene, which limits the amount of by-products formed and therefore reduces the number of separation units needed.

A detailed economic analysis is performed aiming to investigate the economic potential of the CL-ODH process over the state-of-the-art ethane steam cracking process. While our study demonstrates the feasibility of this novel CL-ODH process for the conversion of ethane to ethylene, the principal reaction concept can be applied also to the ODH of other alkanes, e.g. propane or butane. Here, the resulting ethylene price for the CL-ODH process is found ~21% lower compared to the steam cracking process, with 361.5 €/t and 460 €/t, respectively. The CL-ODH process is characterised by reduced capital costs compared to the ethane steam cracking, due to a reduced amount of separation units needed in the ethylene purification part. As expected from the analysis of the energy requirements, a significant economic advantage of the CL-ODH results from a decreased electricity requirement due to the exothermicity of the ODH reaction. The cost of the catalyst and the OC in the CL-ODH process is not a negligible component of the variable operating costs, but does not hinder the overall economic advantage of the process. A simplified assessment of the greenhouse emissions, expressed in terms of equivalent amount of emitted CO_2 per ton of ethylene produced, reveals that the proposed CL-ODH is characterised by ~24% less emissions compared to the ethane steam cracking process. Finally, sensitivity analyses are performed to investigate the influence of key process parameters on the ethylene price. The ethylene price in the case of a decreased ethane conversions (from 34% to 15%) increases from 361 €/ton to 495 €/t, owing to the larger demand of electricity for the downstream separation processes (i.e. the separation columns).

Overall, this study highlights that the implementation of a chemical looping approach for oxygen production overcomes some limitations of the ODH process such as the high operating and capital costs due to the need of an ASU and safety concerns associated with the flammability of a gas mixture containing oxygen and fuel. Substantial energy savings are achieved owing to the heat recovery of the exothermic ODH reaction, while lower capital costs compared to the ethane steam cracking process are obtained owing to an overall higher ethylene selectivity, which reduces the requirements on the downstream separation units. Furthermore, the efficiency of the proposed CL-ODH process translates into a reduced equivalent amount of CO_2 produced per ton of ethylene compared to the ethane steam cracking process. The economic analysis in this study does not include aspects related to regional particularities (e.g. local supply chains, transportation and storage of feedstock, etc.), which may result in cost benefits of different magnitude for the two processes. The economic viability of the processes is strongly dictated by the feedstock costs, as it is highlighted by the sensitivity analysis, which impels further investigation to assess the economic advantages of the proposed process based on different geographic locations.

Author contribution

Giancarlo Luongo: Data curation, Formal analysis, Validation, Writing – original draft, Felix Donat: Conceptualization, Writing – review & editing, Funding acquisition, Calin-Cristian Cormos: Formal

analysis, Writing – review & editing, Maximilian Krödel: Formal analysis, Christoph Müller: Conceptualization, Supervision, Writing – review & editing, Funding acquisition.

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.

Acknowledgement

The authors acknowledge the Swiss Office of Energy (BFE, SI/501590-01) for financial support. This publication was created as part of NCCR Catalysis, a National Centre of Competence in Research funded by the Swiss National Science Foundation.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.rser.2021.111403.

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