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Process economics and safety considerations for the oxidative dehydrogenation of ethane using the M1 catalyst

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ABSTRACT

Olefins or unsaturated hydrocarbons play a vital role as feedstock for many industrially significant processes. Ethylene is the simplest olefin and a key raw material for consumer products. Oxidative Dehydrogenation (ODH) is one of the most promising new routes for ethylene production that can offer a significant advantage in energy efficiency over the conventional steam pyrolysis process. This study is focused on the ODH chemistry using the mixed metal oxide $MoVTeNbO_x$ catalysts, generally referred to as M1 for the key phase known to be active for dehydrogenation. Using performance results from the patent literature a series of process simulations were conducted to evaluate the effect of feed composition on operating costs, profitability and process safety. The key results of this study indicate that the ODH reaction can be made safer and more profitable without use of an inert diluent and furthermore by replacing O_2 with CO_2 as an oxidant. Modifications of the M1 catalyst composition in order to adopt these changes are discussed.

1. Introduction

The US is presently the largest producer of the shale gas and by 2040, production is expected to nearly double [1]. This abundant supply of the shale gas not only reduces price, but also increases the supply of ethane by 25%. One of the most valuable products that can be produced from ethane is ethylene and ethylene is a key building block in the chemical industry, providing and provides the starting point for many essential consumer products; e.g. cosmetics, electronics, plastics, pharmaceuticals.

The conventional method of olefin production is steam cracking of naptha or alkanes and this accounts for 70% of total olefin production [2]. However, in USA most of the technology is based on shale gas cracking. This gas phase reaction carried out at temperature in excess of 800 °C where paraffinic naphtha is decomposed in the presence of steam and the absence of air. The reaction is highly endothermic and requires substantial energy to activate the reactant molecules. In steam cracking, paraffinic naphtha decomposes in the presence of steam to form a variety of products including olefins, paraffins and hydrogen. The endothermic nature of the reaction coupled with the high temperature leads to substantial fuel consumption and costs. Energy costs typically account for 70% of total production costs in the steam cracking process [2]. Additionally, coke deposition is a major problem. While the presence of steam does offer some ability to oxidize coke deposits, it is unable to prevent gradual coke accumulation. Consequently, commercial reactors must be periodically de-coked resulting in increased downtime [3].

Another route of olefin production is direct dehydrogenation of alkanes to olefin. Alkane catalytic dehydrogenation is an endothermic equilibrium reaction that is generally carried out using a catalyst. Typical catalysts are Cr_2O_3/Al_2O_3 and $Pt/Sn/Al_2O_3$. In the dehydrogenation reaction, alkanes decompose into an olefin and an H_2 molecule [4,5]. Catalytic dehydrogenation technologies for light olefin production have been mainly considered for propane and butane dehydrogenation. In fact, there is no commercial technology for ethane catalytic dehydrogenation and the key challenge in dehydrogenation reactions arise from their equilibrium-limited thermodynamics. Furthermore, in order to yield economically attractive selectivities and conversions for ethane dehydrogenation, high temperatures such as 800 °C and above are required [5,6].

Oxidative dehydrogenation, unlike steam cracking and direct dehydrogenation, is a thermodynamically favorable, exothermic reaction forming water. Additionally, ODH can operate at lower temperatures (300–550 °C) than any of the aforementioned processes when using an appropriate catalyst. The exothermic nature of the reaction together with the lower temperature requirement leads to more than 30% energy savings as compared to the steam cracking process [7]. Additionally, the deposition of coke is largely eliminated due to the

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Table 1
Summary of the processes.

Process	Temp.	Pressure (bar)	C_2H_6/ O_2/ Steam/ N_2	GHSV (h^{-1})	g cat./ mol/h ethane	Conv.%	Selec.%	Ref.
A	380	1	10/10/ 10/70	1200	–	74	89	[20]
B	400	1	10/10/ 10/70	1200	–	67	62	[20]
C	375	1	10/10/ 10/70	1200	–	57	91	[20]
D	360	1	15/10/ 10/65	1200	–	67	93	[20]
E	430	1	9/7/0/ 84	–	160	65	92	[21]

presence of oxygen, which can oxidize coke to form carbon dioxide preventing the routine de-coking procedures necessary in current commercial reactors.

There are, however, a number of current challenges preventing oxidative dehydrogenation from being widely implemented. The difficulties inherent in oxidative dehydrogenation reactions revolve around selectivity control. Bulk mixed metal oxides such as $MoVTeNbO_x$ based catalysts are the most promising catalysts due to their ease of preparation, long lifetimes and favorable reaction conditions (temperature, pressure) [8,9]. These catalysts generally consist of M1 and M2 crystalline phases and lesser amounts of other phases such as MoO_3, Mo_4O_{11}, Mo_5O_{14} [10–13]. The orthorhombic M1 phase consists of pentagonal rings connected by corner sharing MO_6 octahedrons (M = Mo, V) in the (001) crystal plane to form hexagonal and heptagonal rings with Te-O units. The M2 phase has pseudo-hexagonal rings hosting Te-O units without any pentagonal or heptagonal rings in the (001) crystal plane [13,14]. It is hypothesized that the introduction of Nb causes the evolution of M2 to M1 phase [15,16]. The M1 phase does not form without V, Nb or Te in the synthesis mixture although a high concentration of Te replaces M1 phase by less active/inactive M2 phase [17]. M1 phase is mainly active for oxidative dehydrogenation of light alkanes [18,19]. The M1 catalyst shows excellent selectivity, making it an attractive catalyst for further consideration into a commercialization option.

This research work developed conceptual processes based on results from key patents and presents a safety analysis of the processes. Based on the learning outcomes, profitable and safe processes are proposed and key targets for catalyst design are presented.

2. Experimental

2.1. Summary of the processes

The ODH reaction conditions and performance characteristics are collected from two key patents and are summarized in Table 1. Each process is identified by a letter used for reference throughout this work.

2.2. Overall generalized process description

The overall generalized process is described in Fig. 1. All processes are simulated using Aspen HYSYS 8.4 software. For comparison purposes, all the process were modeled with no heat loss. The basis of the process calculation is 1000 kmole of ethane/h obtained from a refinery at 25 °C and 20 bar. Steam and nitrogen are obtained from a utility plant and air is compressed before being sent to the reactor. Fresh ethane is preheated by heat exchange from the reactor effluent. Later, the mixture of ethane, nitrogen, and steam are further preheated before being sent to the reactor. The “conversion reactor” model is used to represent the reactors and a pressure drop of 200 kPa is used to represent the overall pressure drop throughout the reactor. After reaction, steam is condensed, separated out and further used as process coolant before being sent for steam generation. The steam free process stream is compressed to 60 bar (compression ratio of 3 was used per stage with an efficiency of 75% and three intercoolers were used) to feed to the membrane systems (MEDAL™ and NITROSEP™), where residual O_2, CO_2 and N_2 are assumed to be separated out from ethane and ethylene for all processes [22,23]. For all these processes, the membrane separation units are assumed to be a black box separation unit with a very high separation efficiency (99.995%) and selectivity ($\approx$1), and the estimated life time of these units are assumed to be 1 year. Then ethane and ethylene are separated out using cryogenic distillation, from where polymer grade ethylene (99.95%) is obtained. The product ethylene is taken out and the residual ethane is recycled back to the reactor. According to the patent description, the by-products from the ODH are mainly CO_2 and water and other impurities are N_2 [20,21].

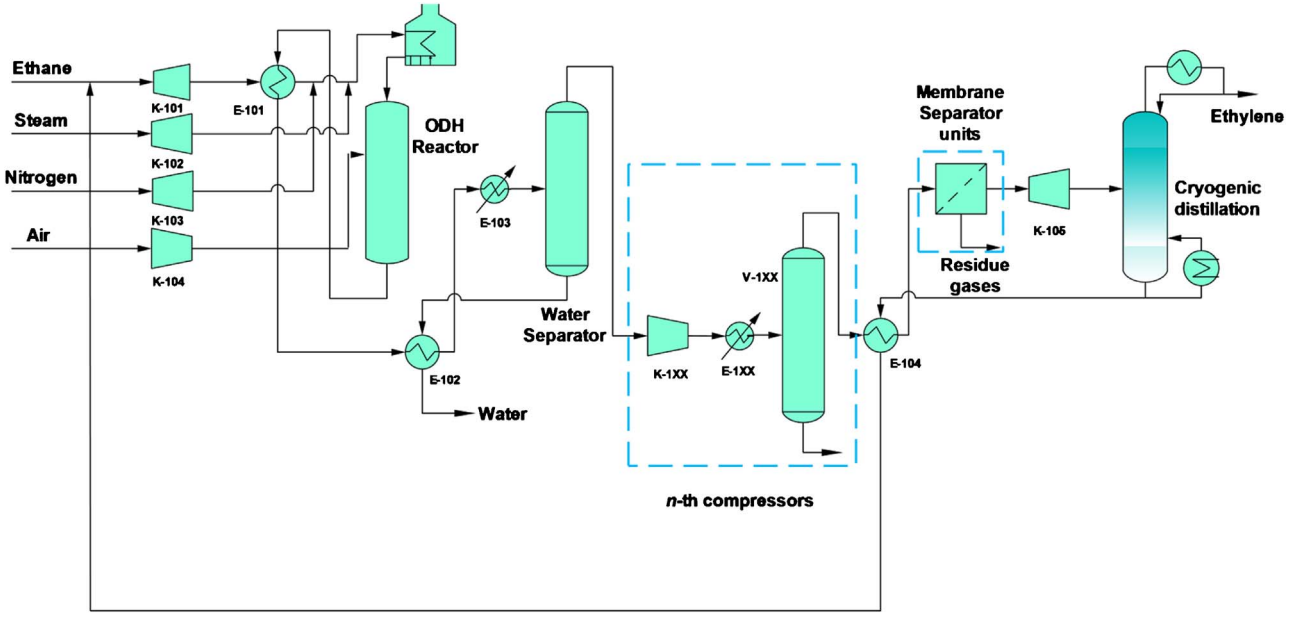

Fig. 1. Overall generalized process flow diagram of the ODH process.

Table 2
Cost of raw materials and products.

Parameters	Price
Ethane[a]	0.15 $/kg
Ethylene[b]	0.978 $/kg
Catalyst[c]	44.1$/kg
Nitrogen	0.02$/m^3
Steam	0.03$/kg

[a] [24].
[b] [25].
[c] Company contact.

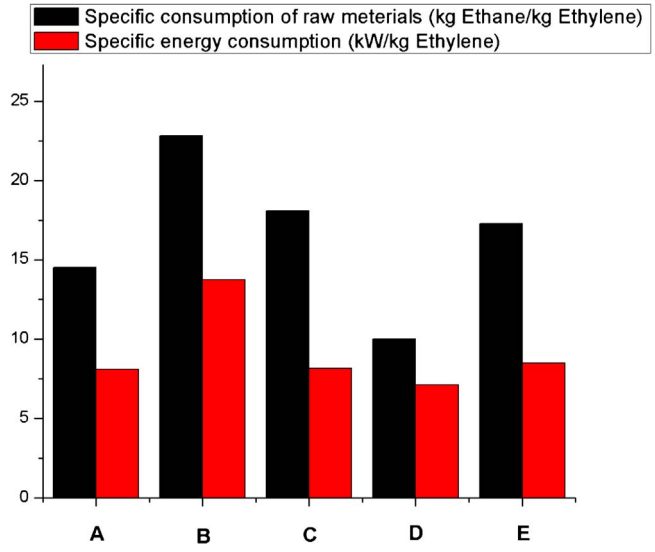

Fig. 2. Process performance metrics of different ODH processes.

2.3. Process economics

The process economics were analyzed using Aspen Process Economic Analyzer 8.4 software. The project life was considered to be 10 years. The cost of raw materials and products are shown in Table 2. All projects were evaluated and compared based on the net present value (NPV) with a desired rate of return of 20%.

2.4. Process safety analysis

The process safety was accessed using "Comprehensive Inherent Safety Index (CISI)" method [26]. This method is very effective and useful at the early stage of the conceptual process design and development to reduce the process hazards. In this method, the process safety score for equipment comes from two sources: equipment safety score (equipment capacity, temperature, pressure) and chemical safety score. The chemical safety score comes from chemical severity score (individual chemical flammability, explosiveness, toxic limit, corrosiveness and flow rate) and chemical reactivity score (chemical mixture reactivity, flammability, explosiveness, toxic gas generation, flow rate). A higher safety score indicates higher risk.

3. Results and discussion

3.1. Process performance

The pinch for heat exchange for all the processes was 10 °C and the separation efficiency for all the gas-liquid separators was 96–97%. Fig. 2 indicates the overall performance of different processes conditions as listed in Table 1. It indicates that process D has the lowest specific raw materials (kg ethane/kg ethylene) and energy consumption (kW/kg ethylene). This could be attributed to the higher selectivity and low reaction temperature for the ODH process.

3.2. Process economics

Fig. S1 shows process equipment capital cost scenario for different process components as labeled in Fig. 1. It shows that the capital cost for the membranes, component 3, is the highest throughout the whole process and the membranes cost for process D is the lowest as compared to the other processes. The second highest capital intensive equipment is the compressor unit, component 2, and process D demonstrates the lowest cost. A cryogenic distillation, component 4, is the 3rd highest capital cost followed by the reactor cost. A cause effect diagram (Fig. S2) indicates that amount of nitrogen, selectivity, and reaction temperature increases the reactor capital cost. It was found that the amount of oxygen and nitrogen increases the membrane capital cost (results not shown). Fig. S3 shows the overall capital cost with process D being the lowest which can be attributed to the cost of the membrane (Fig. S1). Not surprisingly, it was found that the amount of oxygen, steam and nitrogen in the feed increase the overall capital cost. Fig. S4 shows the comparison of revenue and operating costs; the raw materials cost did not demonstrate significant changes amongst the processes investigated. It was found that Process E had the highest operating costs while process D the lowest. The cause-effect analysis (Fig. S5) indicates that the amount of oxygen, steam and nitrogen in the feed increase the

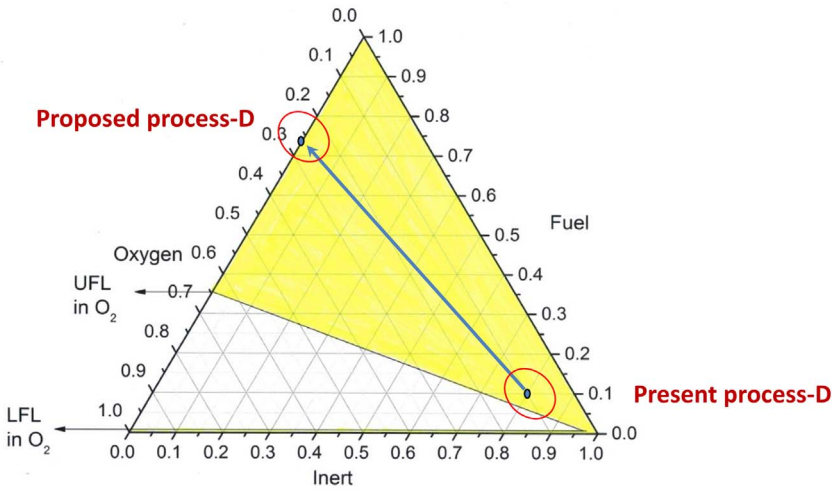

Fig. 3. Flammability diagram for ethane at 360 °C.

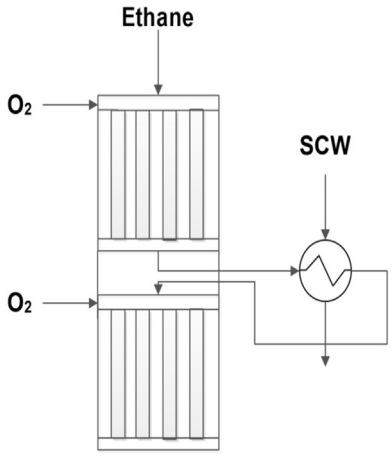

Fig. 4. proposed ODH reactor set-up.

operating cost. Likewise, the profitability analysis (Fig. S6) indicates that process D suffers the least loss.

3.3. Process safety

Fig. S7 shows the process safety analysis results around each process. It indicates that the compressor section is the most vulnerable equipment in terms of safety and the compressor process safety score for process D is the lowest in comparison to other four processes. The amount of nitrogen in the feed increase the safety risk due to the requirement of high capacity compressors and higher cooling loads (results not shown). Cryogenic distillation is the second highest vulnerable equipment in terms of safety, due to the heating and cooling of high volume of ethane and ethylene. The overall safety score is shown in Fig. S8. It indicates that process D has the lowest safety score indicating the safest process out of the five. The cause-effect analysis (Fig. S9) indicates that the amount of nitrogen in the feed increase the process safety score, making it more vulnerable.

3.4. Proposed staged approach

Fig. 3 shows the flammability diagram with a safe zone indicated by yellow for the reaction temperature of 360 °C. The bottom point ("present") in the diagram indicates the patented feed composition where steam and nitrogen have been used (process D). The use nitrogen and steam as a diluent affords a leaner mixture while keeping the composition at the reactor outside the flammability region; the diluent also serves as a heat transfer medium to compensate the exothermicity of the reaction. If these two inerts are to be avoided, then the alternate option is the top point, where oxygen is fed at the stoichiometric ratio to the ethane. Fig. 4 shows the proposed reactor set-up, where in each stage oxygen is fed as the limiting reactant to attain a certain conversion and all oxygen is consumed. In this case, ethane serves as a heat transfer medium of the exothermic reaction [27]. The reactant mixture is cooled using supercritical water (SCW) and fed to the next stage where it is mixed with a fresh limiting amount of oxygen. In a typical arrangement, the estimated conversion around each stage is 10% and the temperature rise is 150 °C. The M1 catalyst has demonstrated resilience when exposed to intense redox conditions. For example, Grasselli et al. found no structural collapse when the M1 phase is reduced in oxygen amounts equivalent to 70 layers from the surface [28]. The authors found that the M1 crystallites could be restored to their original oxidation state by pulsing air.

In the process proposed here, the same reaction temperature, conversion and selectivity of process D is used. Here ethane is preheated and sent to the reactor and pure oxygen (obtained by cryogenic distillation of air) is also preheated before each stage of the reactor (Fig. 5). The process economics were not found to be significantly impacted by the switch from air to oxygen (result not shown). At the end of the reaction, the reactor effluent is cooled, water is separated

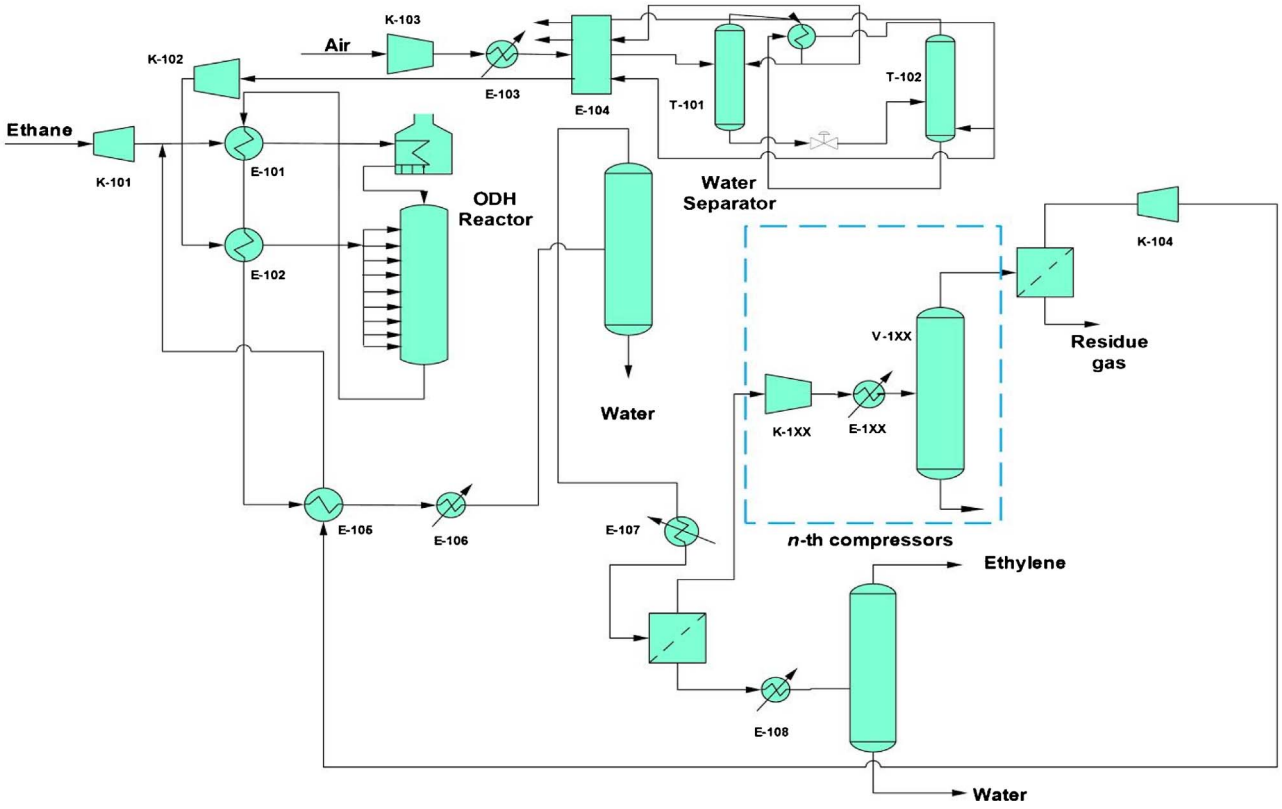

Fig. 5. Proposed ODH process using O_2.

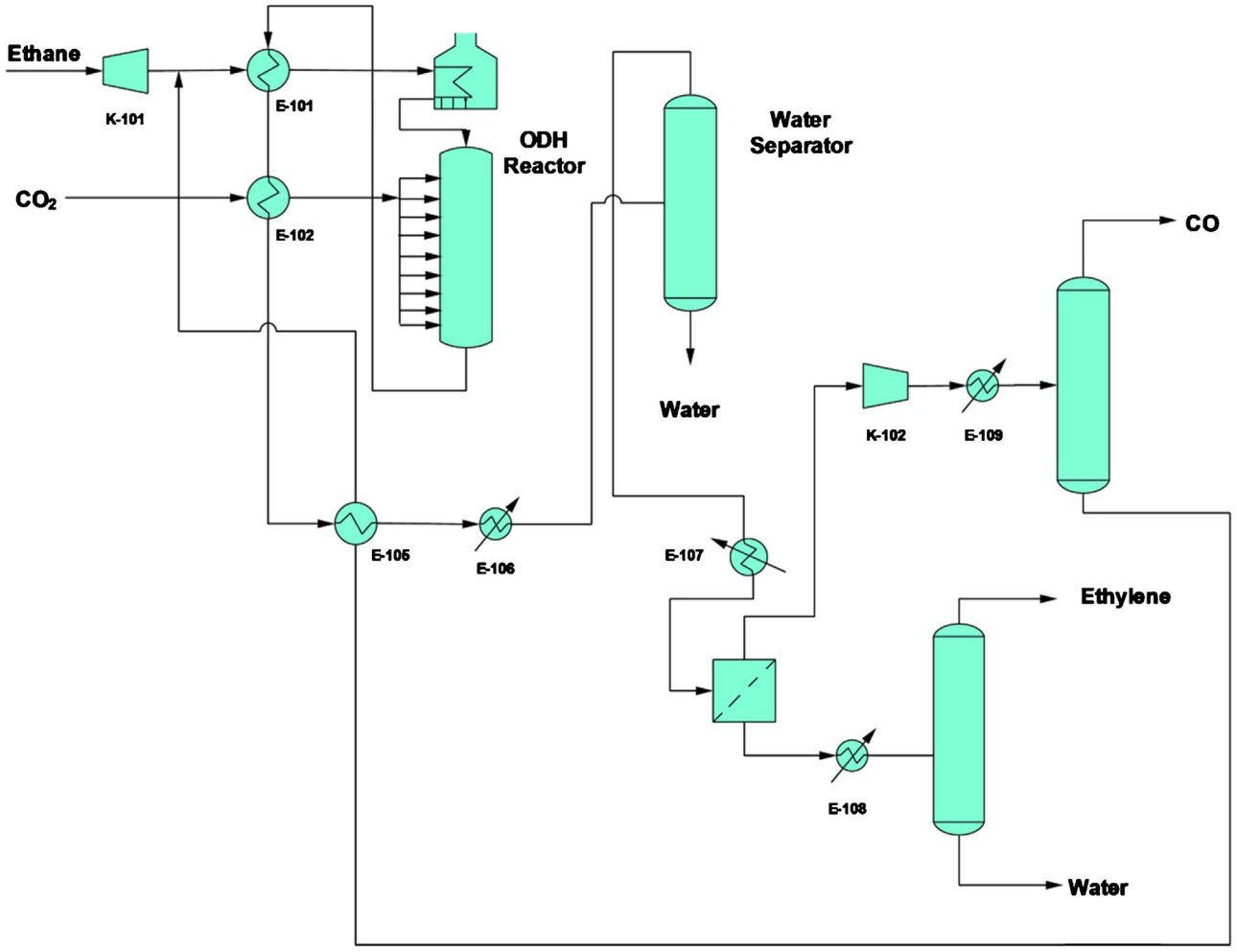

Fig. 6. Proposed ODH process using CO_2.

and ethylene is separated using a proprietary membrane developed by Compact Membrane Systems Inc. The operating condition and the cost data were provided in public disclosure by Compact Membrane Systems Inc. [29]. The advantages of membrane separations over conventional cryogenic distillation are simplicity of operation and installation, milder operating conditions, flexibility of operation with compact modules and a significant reduction in consumption of electricity and fuel, the flexibility to integrate with other separation units that may constitute an effective hybrid processes for improved economy and desired purity levels. Unpublished proprietary experimental data indicated that this proposed membrane system has a very high separation efficiency (99.9%) for ethylene. The by-products indicated in patent data are mainly CO_2 and water [20,21]. Residual water is separated by cooling to obtain polymer grade ethylene. The ethylene free stream is compressed to 60 bar and fed to a CO_2 separation membrane system (MEDAL™) [22]. Following this, ethane is recycled back to the reactor.

In another proposed process, CO_2 can be used as an oxidant instead of O_2. Following this route, CO is produced in addition to water and ethylene. In this process, the same reaction temperature, conversion and selectivity of process D is used. Ethane is preheated and sent to the reactor and carbon dioxide (obtained from refinery as a waste) is also preheated before each stage of the reactor (Fig. 6). At the end of the reaction, the reactor effluent is cooled, water is separated and ethylene is separated using the same membrane [29]. The residual water from the ethylene is separated by cooling to obtain polymer grade ethylene. The ethylene free stream is cooled and ethane is separated out as a liquid and recycled back to the reactor. The mixture of by-product CO and H_2O can be further used in a water gas shift reaction.

Table 3 shows the expected outcome of the proposed processes in terms of process profitability. It shows that by eliminating the use of nitrogen and steam and by incorporating membrane separation for ethylene, the staged process can be made profitable using CO_2 and the energy consumption can be reduced (profitability is indicated even with a price of oxygen at 0.11 $\$/m^3$). The result in Table 3 further indicates that the ODH process is superior if CO_2 is used as a reactant instead of O_2 (this includes a cost of CO_2 at 0.15$/kg). Fig. S10 shows process safety score comparison between process D and the proposed processes D using O_2. It shows that the safety score for the reactor, compressor, membrane are reduced significantly. This overall safety score is reduced to 239.2, if CO_2 is used as a reactant instead of O_2.

Table 3
Expected outcome of the proposed staged process using CO_2.

Parameters	D	DproposedO_2	DproposedCO_2
NPV	- 4.38 (billion)	122 (million)	140 (million)
Specific energy consumption (KW/kg ethylene)	7.11	3.9	3.71
Specific consumption of raw materials (kg ethane/kg ethylene)	10	1.86	3.25

3.5. Proposed modification of the M1 catalyst

Fig. S11 shows the effects of catalyst compositions and other parameters on the ethane conversion based on the same patent data [20,21]. It indicates that, the Nb and Te content in the catalyst increase ethane conversion. Similar results are found for the case of ethane selectivity (Fig. S12). These cause and effect analyses were restricted to the catalyst composition ranges of $V_{0.29\text{-}0.4}$, $Nb_{0.11\text{-}0.17}$, $Sb_{0.01\text{-}0.07}$, $Ca_{0\text{-}0.03}$, $Te_{0\text{-}0.21}$ based on the patent results [20,21]. Nonetheless, within this small range, a typical composition of $MoV_{0.29}Nb_{0.17}Sb_{0.01}Te_{0.21}O_x$ points to promising catalytic activity. In the M1 phase the V^{5+} ions are considered to activate alkanes/paraffin [30]. The presence of Te^{6+}/Te^{4+} role is attributed to stabilize the M1 phase [31]. The presence of Nb is believed to promote rapid desorption of the desired products so as to prevent further oxidation and increase the selectivity [32].

The main aspect of a partial oxidation reaction comprises the first C—H bond activation for oxidative dehydrogenation (ODH), considered as the rate determining step in the overall process [33]. The strength and nature of acid/base sites play an important role in the ODH. Oxides of metals in a high oxidation state such as V^{5+} or Mo^{6+} are characterized by a covalent metal to oxygen bond and behave as an acidic oxide. Strong acidity favors full and over oxidation, whereas weak acidity favors partial oxidation. It was observed that a complex of Nb-Te isolates the active V^{5+} sites to avoid a high lattice O surface mobility, neutralize strong acidity associated with $V^{5+}$and thus avoid over oxidation [33,34]. However, it was found that Te leaves the M1 phase in presence of high concentration of O_2 and high reaction temperature (> 460 °C). Thus, the precise control of oxygen concentration and reactor temperature is a prerequisite to maintaining a high stability of the M1catalyst in the ODH process [32]. These results support the exploration of the proposed staged approach where oxygen can be more readily controlled.

The cause-effect analyses (Figs. S11 and S12) also indicate that the presence of nitrogen has a minor negative impact on the ethane conversion and no impact on the selectivity. Further analysis indicates that the presence of steam in the oxygen feed (ethane to oxygen ratio 0.4–0.5) has no impact on the conversion or selectivity (results not shown). In other works, steam is found to be inert towards conversion and selectivity [35]. For the case of oxygen, similar results were found in a kinetic study [36], indicating the lower dependency of ethane conversion to the inlet partial pressure of oxygen compared with that of ethane. This lower O_2 dependency on conversion also enables high selectivity to ethylene for this mixed oxide type of catalyst. MoVTeNbO$_x$ catalysts show a relatively large capacity of oxygen recombination, i.e. the oxygen is rapidly released from the first surface layers into the gas phase. In fact, this may be the reason why the Langmuir–Hinshelwood mechanism adequately represents observed kinetic phenomenon instead of the Mars–van Krevelen mechanism [36].

The oxygen dependency of an M1 catalyst can be further reduced and catalytic activity can be improved by adding promoters with excellent oxygen storage and oxidation capability. A previous study shows that the addition of nanosized CeO_2 to the M1 phase improves the catalyst activity [37]. Thus, there are opportunities around reducing the oxygen dependency of the M1 catalyst by using different oxides (e.g., Fe_2O_3, La_2O_3) or mixed oxides (e.g., CeO_2-La_2O_3, CeO_2-ZrO_2, CeO_2-La_2O_3-Al_2O_3) [38,39]. These oxide/mixed oxide promoted M1 materials should be explored as catalysts for the proposed ODH process using CO_2 as a reactant since this requires catalysts with highly active oxidation/reduction cycle properties [40]. CO_2 is a mild oxidant in the dehydrogenation of ethane and presents numerous advantages in managing the exothermicity of the reaction, improving the selectivity to ethylene, reducing the formation of coke and maintaining long term catalyst stability [41].

4. Conclusion

The Oxidative Dehydrogenation (ODH) route promises enhanced profitability and a smaller footprint for ethylene production. This research study demonstrates how key process parameters influence profitability and safety. In particular nitrogen and steam can be minimized and from this conclusion a staged-oxygen feed process is proposed. The M1 catalyst with its robust redox stability presents an excellent opportunity to pursue this reactor concept in combination with ‘oxide-engineered’ composite systems. In addition, the use of CO_2 as an oxygen source promises an enhancement. As a more selective and lower temperature alternative to the steam pyrolysis practice currently in place, the ODH process can be more profitable and safer by making greater use of membrane separation technology. Regardless of the savings, it may be unlikely to supplant a well-established large-scale practice in the near-term. Thus the key motivation for pursuing processes such as those proposed here remains in developing small modular systems that can access stranded resources in remote locations.

U.S. Department of Energy Disclaimer

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cattod.2017.05.041.

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