**Oxidative dehydrogenation of ethane under a cyclic redox scheme-
Process simulations and analysis**

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Abstract

Steam cracking of ethane is an energy intensive process (15-25 GJ_{th}/tonne ethylene) involving significant coke formation and CO₂/NO_x emissions. We propose an alternative two-step redox (or chemical looping) oxidative dehydrogenation (CL-ODH) scheme where hydrogen, produced from ethane cracking, is selectively oxidized by lattice oxygen from a redox catalyst, in the first step. Regeneration of the lattice oxygen in a subsequent step heats the redox catalyst, with the sensible heat providing the thermal energy needed for the cracking reaction. The overall process provides minimal parasitic energy loss and significantly reduced CO₂/NO_x formation, while favoring ethylene formation through the removal of hydrogen. In the current study, the CL-ODH process is simulated with ASPEN Plus® using experimental data on a Mn-based redox catalyst. The CL-ODH is compared with steam cracking for an ethylene production capacity of 1 million tonne/year. Results indicate that the CL-ODH process, with 85% single-pass ethane conversion, provides 82% reduction in overall energy demand and 82% reduction in CO₂ emissions. The overall downstream section consumes approximately 23.5% less energy, with 32.1% less compression work. Increase in the ethane conversion further reduces the energy demand downstream. For every tonne of ethylene, the process has 7.35 GJ_{th} excess fuel energy whereas cracking requires an external fuel input of 1.42 GJ_{th}.

Keywords: Ethylene; cracking; ethane oxidative dehydrogenation; chemical looping; process simulations

1 Introduction

Ethylene is an important building block for the petrochemical industry and has the largest production volume among important base petrochemicals [1,2]. At present, ethylene is mainly used to manufacture polyethylene (>50%), followed by vinyl chloride, ethylene oxide and ethyl benzene [3]. The global ethylene production capacity was at 143 million tonnes per annum (MTA) in 2013, a 27% increase compared to the 2005 production capacity. A compound annual growth rate of 6% is further anticipated till 2020 and beyond [4–7].

A significant fraction of ethylene is commercially produced via high-temperature pyrolysis of hydrocarbon feedstocks in the presence of diluting steam, also known as steam cracking [3,8]. Typical feedstocks for steam cracking include those derived from crude oil, such as naphtha, gas oil, etc. and those derived from natural gas, such as ethane and propane. [6,8]. While naphtha accounts for 55% of global ethylene production capacity, ethane is the primary feedstock in regions such as the United States and Middle East. The increasing availability of shale gas in the U.S. is also making ethane cracking more favorable from a process-economic standpoint [3,8,9]. When ethane is used as the feedstock, the desired (overall) reaction (Reaction 1) involves decomposing ethane into ethylene and hydrogen, which is achieved via a complex network of gas phase radical reactions.

In such a process, a mixed stream of ethane feed and steam is preheated to the initial cracking temperature (500°-680°C) and is fed into a high-temperature reactor (750°-875°C) to complete the cracking reaction, with residence times of 0.1-0.5 s. Key operating parameters that affect the performance of the process and the product distributions include the gas residence time, the partial pressures of the feedstock and steam, and the temperature profile in the reactor, [3,9].

Despite being practiced and optimized for more than 50 years, steam cracking has a number of limitations from chemical equilibrium, energy utilization, and environmental viewpoints. Firstly, ethane cracking is limited to a practical single-pass ethane-conversion of 67-70% and an ethylene yield of around 55% [6] due to equilibrium limitation and coke formation. Although steam dilution reduces the rate of coke formation, steam cracking furnaces nevertheless need to be periodically shut down and regenerated with air to avoid coke build-up. The use of diluting steam increases the parasitic energy consumption whereas the need for periodic regeneration leads to an increase in the capital investment (for parallel units) and operating costs [7,9,10]. The total energy demand of ethane cracking ranges between 15 and 25 GJ/tonne ethylene [8,9] which is satisfied by combustion of carbonaceous fuels such as methane. This leads to the production of 1-1.2 ton CO₂/tonne ethylene and considerable amount of NO_x [8]. Therefore, new technologies that overcome these limitations are highly desirable.

The oxidative dehydrogenation (ODH) of ethane, in the presence of a heterogeneous catalyst, is an attractive alternative to steam cracking. ODH has the potential to provide higher olefin yields since the formation of water as opposed to hydrogen (Reaction 2) effectively removes the equilibrium constraints on ethane conversion. Moreover, the required energy is supplied by hydrogen oxidation [11,12].

Despite these advantages, oxygen co-feed ODH has significant limitations. The requirement of pure oxygen or oxygen-enriched air requires an air separation unit (ASU), which adds to the capital and operating costs. The high reactivity of the olefins poses another challenge in developing a suitably selective catalyst. Moreover, the oxygenate byproducts are difficult to separate [9]. The flammability of the gas mixture containing oxygen and fuels in the single step ODH imposes additional safety concerns. Over-oxidation of the alkanes and olefins to CO and CO₂ can cause hot spots in the reactor and reduce product selectivity. [8,13,14]. The current study investigates a two-step, redox based process for ethane chemical looping-oxidative dehydrogenation (CL-ODH) in an O₂-free environment. The first step involves selective oxidation of the hydrogen produced from ethane cracking using the lattice oxygen from a redox catalyst at a high temperature. The sensible heat of such catalyst provides the thermal energy needed for the cracking reaction. This is accompanied by simultaneous reduction of the catalyst.

The reduced catalyst is subsequently regenerated (and reheated) in air to complete the redox loop. In such a CL-ODH process, the absence of gas phase oxygen a) inhibits the non-selective reaction pathways, b) reduces the explosion hazard [14–16], and c) decreases parasitic energy losses by eliminating ASU and providing tighter temperature control [17]. The overall process also provides significant reduction in NO_x and CO_2 emissions. However, despite of the advantages of CL-ODH over both steam cracking and oxygen co-feed experiments, this novel process, has not been analyzed to date.

In a previous work, we have reported a highly effective, alkali doped MnO_x -MgO redox catalyst for the abovementioned CL-ODH scheme [17,18]. High ethane conversion and ethylene selectivity as well as satisfactory redox stability and oxygen carrying capacity are achieved using such a redox catalyst. The current study investigates the performance of the CL-ODH process by conducting comprehensive process simulation and analyses based upon preliminary experimental yield data from an alkali doped MnO_x -MgO. Single-pass ethane conversions of 66%, 85% and 90% are analyzed and the results are compared with a state-of-the-art ethane steam cracking process. Sensitivity analyses are performed on key process parameters such as ethane conversion, product distribution, unit-wise and total energy requirement of the process. Using ASPEN Plus[®], the reactor and process conditions are optimized and the potential advantages of the redox-based ODH process are also validated based on comprehensive process analyses. For a single-pass ethane conversion of 85%, as compared to the steam cracking process, the overall downstream section energy demands of the ODH case are shown to drop by 23.5% with 32.1% less compression work. This leads to 82% drop in the overall energy demand and 82% reduction in CO_2 emissions. The energy demand for ODH decreases with increasing single-pass ethane conversion.

2 Process descriptions

Figure 1a is a simplified process flow diagram of a state-of-the-art ethane steam cracking process. Pre-heated ethane is thermally cracked in the presence of steam, which functions as a diluent for higher conversions and as a coke-retardant. The feed mixture is passed through the tubes of up to twelve cracker furnaces, which are heated by combustion of fuels to provide considerable heat input at high temperatures ($\sim 1,000^\circ\text{C}$). The hot product stream from the furnace, at approximately 850°C , is first rapidly cooled to $300^\circ\text{--}400^\circ\text{C}$ using transfer line heat exchangers to avoid further cracking and preserve the composition. It is further quenched to near ambient temperature using water or oil [3,6]. The stream is then compressed to a pressure of around 40 bar with a multi-stage compressor. Drying and acid gas removal units are located at the intermediate compressor stages. The drying unit consists of an adsorption column of molecular sieves and precedes the acid gas removal units to avoid formation of hydrates [6]. The stream is then caustic washed to remove the acid gases such as CO_2 .

The compression stages are followed by a train of distillation columns which sequentially separate the light components from the heavy fraction, yielding high purity ethylene. The sequence begins with the removal of methane and lighter components, primarily hydrogen, from higher molecular mass components, using a demethanizer. The bottom product is routed to a deethanizer column where acetylene, ethane, and ethylene are separated and C3+ components exit as the bottom product. The overhead mixture is subsequently treated with hydrogen to remove acetylene and then fractionated in the C2-splitter to give ethylene product and ethane-recycle. The bottom product from the deethanizer is depropanized to separate C4+ components. Depropanizer bottoms are sent to a debutanizer for separation of the C4 materials, raw pyrolysis gasoline, C5 materials and aromatics [6]. In the C3-splitter, propylene is recovered as a valuable product and propane is recycled. Traditionally, the front-end demethanizer process sequence was used in cracking process. In alternative configurations, a front-end deethanizer or depropanizer can be used. While the front-end deethanizer option can be advantageous in certain cases [6], it is not investigated in the current study for the purpose of direct comparison with the ODH process.

The ethane ODH process is depicted in Figure 1b. The major difference from steam cracking is the absence of the energy-intensive furnaces, which are replaced by a reactor-regenerator configuration. The hydrocarbon and CO_x yields used in the current work are based upon experimental results of an alkali doped Mn-Mg oxide similar to that reported in previous work [17,18]. As this system involves mixed oxides [18] that are not available in the ASPEN Plus[®] database, the system is simplified to a MgO supported MnO_x. Mn₃O₄ (Mn at 8/3+ average valence state) is used as the simulated oxygen carrier phase, which donates its lattice oxygen during the ODH reaction. Meanwhile, the Mn cation is reduced to a 2+ average valence state (MnO), as shown in Reaction 3. The reaction involves the combustion of hydrogen to water. The reduced redox catalyst, (also known as an oxygen carrier), is subsequently regenerated using air in the regenerator, following a highly exothermic Reaction 4. While slow reduction kinetics [19] and propensity for deep oxidation [20,21] would make undoped Mn₃O₄ unsuitable as a practical oxygen carrier, the thermodynamics of MnO_x/MgO give satisfactory simulation results. Comparing the ASPEN Plus[®] database values for such a surrogate catalyst with our experimental data indicates that the surrogate catalyst exhibits similar heat of reaction and heat capacity values when compared to actual redox catalysts. In the current study, the reducer is operated at 850°C and the regenerator at 950°C, both at near-atmospheric pressure. The re-oxidized redox catalyst particles are recirculated to the reducer to complete the redox loop. It is noted that the redox catalyst not only provides its lattice oxygen but also carries heat required for ODH reactions. Unconverted ethane and propane from the downstream separation block are recirculated to achieve higher overall conversion. Heat loss for the redox process is assumed to be 1% of the total thermal output whereas redox catalyst loss is assumed to be negligible. The hot, oxygen-depleted air from the regenerator is used to generate high pressure steam. The gaseous output from the reducer is treated through a chain of downstream separation units which are nearly identical to the steam cracking. All of the ethane and propane are recycled to the reducer, the

heat requirements of which are met entirely via the heat stored in the re-oxidized solids, owing to their high heat capacity and suitable temperature difference (ΔT) between the reducer and regenerator. The heat needed by the cracking furnaces represents a major energy requirement for steam cracking. In contrast, exothermicity of the regenerator is used to compensate the heat needed for the ODH reactor, thereby lowering the upstream energy demand in ODH. In the following sections, the overall energy requirement for the ODH process is evaluated and compared with that of ethane cracking.

3 Simulation assumptions

ASPEN Plus[®] simulator [22] is used to determine the process performance of ethane CL-ODH and compare it with steam cracking. The processes are simulated for an ethylene production capacity of 1 million tonnes per year. The cracking process (Case I) and the ODH reference case (Case II) with an ethane single-pass conversion of 85% are simulated. ASPEN Plus[®] modules, property methods, and physical property databanks are summarized in Table 1. The carbon yields for the various processes are listed in Table 2. These are based on the experimental results as given in previous work [17,18]. Although small amount of CO_x from coke burning can be observed during redox catalyst regeneration, the yield is negligible, and is thus excluded from the simulation. The yields assumed for propane (recycled) cracking [6] as well as for propane ODH are given in the supplementary document. The drying unit is modeled as a flash column, where almost all of the water is condensed, and the acid gas removal (AGR) unit is placed at the exit of the compressor. A Sep block is used to simulate the AGR with the energy consumption accounted for. The solids used in the simulation include Mn₃O₄ and MnO with MgO added as an inert to mimic the actual catalyst [18]. The key operating assumptions and parameters used in the simulations are listed in Table 3.

4 Process modeling

The feed is considered as a mixture of 95% ethane and 2.5% of propane and methane, by volume, at a preheated temperature of 650°C. Such a gaseous mixture is also known as ethane-mix and is normally used as a feedstock in industrial practice [23]. In the case of a cracking furnace, steam is also fed at 650°C. As mentioned earlier, Mn₃O₄ is used as the oxygen carrier in the ODH case. In the process simulation, the Mn₃O₄ particles are initially fed into the reducer, from the exit of which they are transported to the regenerator. There is a ΔT of 100°C, between the reducer and regenerator, with the regenerator being higher at 950°C. In the regenerator, the reduced oxygen

carrier is fully oxidized in 10% excess air, preheated to 650°C, via Reaction 3, prior to the recirculation to the reducer for another redox loop.

The product gases in both the cases are cooled to a temperature of 30°C, to avoid further cracking. Heat released from the rapid cooling process is assumed to be completely utilized to generate steam and to preheat the ethane and air feeds. The exothermicity of the regenerator can also produce low pressure steam and reduce the upstream energy demand. The cooled gases are flashed to remove the water from the stream. In the present model, this flash column functions as a drying unit and is placed before the compressor, rather than between the initial stages of compression. The dry stream is then compressed to a pressure of 42 atm [6], using a 4-stage isentropic compressor, with the exit stream at 25°C. No H₂S is assumed to be in the product stream, with CO₂ being the primary component of acid gas. Negligible energy consumption is assumed for the caustic wash. For ODH, where there is substantially more CO₂ in the product stream, an amine scrubbing process is assumed with an energy consumption of 0.11 MW-hr/tonne CO₂ [24]. The operating conditions of the downstream columns, for the cracking process, are listed in Table 4 [25]. The compressed stream is cooled to -100°C which leads to the separation of hydrogen and CO prior to methane removal. The refrigeration requires a high duty and removes 97% of the hydrogen and 63% of the CO, reducing the load on the demethanizer. The ethane and propane obtained from the C2 and C3-splitters respectively, are completely recycled to the reducer at 650°C. The reflux ratio for each column is fixed as twice that of the R_{min} . For direct comparison, the C2-splitters in both cases are modeled with the same number of stages and with the same recovery. The concentration of acetylene in the final, polymer-grade ethylene stream needs to be less than 5 ppm. A deacetylenizer is used to hydrogenate the acetylene in the overhead stream of deethanizer. [5][9] Purified hydrogen for acetylene hydrogenation is obtained through pressure swing adsorption (PSA). A 80% hydrogen recovery is assumed, with the purity being 99% and a pressure drop of 1 bar [26]. Operating conditions of the deacetylenizer are based on the study of an industrial cracking unit (Table S3 of the supplementary document) [27].

Since the process consumes different forms of energy such as thermal energy, steam, and electricity, it is helpful to convert them into a same thermal basis for process comparison. An HHV efficiency of 85% is considered for the thermal to steam energy conversion, whereas 40% (HHV) efficiency is considered for thermal to mechanical energy conversion [8]. Using the condenser and reboiler duties of the columns, as calculated by ASPEN Plus[®], the power needed for refrigeration is calculated using the power-temperature graph as given in literature [28]. The refrigerants chosen for each unit are listed in Table 5.

5 Results and discussion

5.1 Reactor product distributions

The feed and exit gas compositions of the two cases are presented in Table 6. For ethane cracking, a steam dilution of 0.3 kg/kg fresh feed, is assumed [6]. In the ODH case, conversion of H_2 to H_2O is fixed at 71%, for thermal sufficiency. The energy demand for the columns is accounted for by condenser refrigeration, based on the simulated duty. For the same final ethylene throughput, there is a 64% drop in the amount of hydrogen at the reactor output for ODH when compared to cracking. As a result, the total molar output is reduced by 15%. Owing to higher CO_x and $C3+$ selectivity, the ODH case requires 11.4% more fresh ethane feed. Meanwhile, ODH leads to a 76% increase in the molar output of $C2+$ components from the reactor. Due to the 63% drop in the amount of unreacted ethane flowing through the system, the total mass of the product stream is higher in the case of steam cracking. As a part of the analysis, the High Value Products (HVPs) are considered which include the $C2+$ olefins, $C5$ compounds and aromatics.

5.2 Energy distribution

ASPEN Plus® simulation of the ethane cracking process indicates an energy consumption of 15.2 GJ/tonne ethylene. This is in agreement with the study of Ren et.al [8] which states 15-25 GJ/tonne ethylene. Depending on the temperatures in the condensers of the columns, the refrigerants are chosen as shown in Table 5 and the corresponding refrigeration power can be calculated [28]. For the cracking process, 61% of the upstream energy is required to suffice the endothermicity of the furnace, as shown in Figure 2. Quenching of the hot gases generates high pressure steam and recovers additional energy. The compression step requires 47% of the downstream energy, while the refrigeration for the demethanizer feed, and the $C2$ splitter demand 29% and 14% respectively. The $C2$ -splitter is the most energy-intensive separation column. Figure 2a shows the section wise energy distribution in cracking process and the ODH reference case (overall and downstream). The energy distribution for steam cracking is presented in Table 7.

5.3 Process comparisons

Unlike steam cracking which requires significant amount of energy for the endothermic cracking reactions and steam generation, the CL-ODH case is operated based on cyclic redox reactions (Reactions 3 and 4) which are net exothermic. The regenerator replenishes the oxygen in the carrier via the highly exothermic Reaction 4. The heat loss in the reactors is assumed to be 1% and is accounted for in the regenerator output. The oxygen-lean hot air leaving the regenerator is used to generate high pressure steam, and is counted as available upstream energy in the ODH case. As a result, the upstream and overall energy requirements for ODH are reduced significantly. The exothermicity of the regenerator and the absence of steam further reduce the upstream energy (thermal) demand and take the upstream section from 218.9 MW_{th} net endothermic for cracking to 115.2 MW_{th} net exothermic for the ODH case, as shown in Table 7.

This accounts for the most significant reduction in energy demand in ODH compared to steam cracking.

The main downstream energy savings in the ODH case are in the compression section, where there is a 32.1% drop, due to a corresponding drop in the total moles of the product gases, on a dry basis. The overall drop in the downstream energy requirement is 23.5%. An overall drop in the total mass flowing downstream reduces the energy for refrigeration prior to the demethanizer. This reflects in the reduced refrigeration duty needed to cool the feed to the demethanizer. The small amounts of CO and CO₂ present in cracking product case do not add significant energy of separation. The amine scrubbing unit is likely to be required for the ODH case, due to the high CO₂ content of 3.2 vol% (dry basis). Overall, 0.11 MW-hr of work/tonne of CO₂ captured is needed for the process [24]. For the simulated plant capacity, this accounts for 1.36 MW (electric)-demand for the ODH case, which assumes a 100% CO₂ removal. There is 3.2 vol% of CO present in the outlet for the ODH case as well, on a dry basis, compared to 300-400 ppm for the cracker output. The PSA unit adds to the energy expense downstream, contributing an energy requirement of 2.2 kW-hr (electric)/kg H₂ separated [26]. Based on the assumptions of the PSA mentioned earlier, this sums up to a requirement of 0.7 and 0.2 MW_{th}(thermal) energy for the cracking and ODH case respectively, owing to lesser amount of hydrogen to be separated in the PSA for the ODH case. Overall, the ODH case provides an 82% drop in the overall energy demand of the plant, compared to cracking, for a 1 million tonne capacity of ethylene per year.

The deacetylenizer in both cases operates at high pressures (~35 bar) and temperatures of 50°-70°C [27]. The reactant gas from the top of a deethanizer is at a very low temperature (-47°C). For ODH, the pre-demethanization refrigeration removes 63% of the CO with the remaining passing on to the demethanizer (DM). Less mass is fed to the DM in the ODH case. The condenser duty of the deethanizer (DE) is reduced due to a considerable drop (~60%) in the amount of ethane flowing into the DE, owing to the high single-pass ethane conversions. The ODH case showed a 5% drop in the condenser duty. As shown in Table 6, the amount of propane+propylene in the ODH case is twice of that in cracking. As a result, the cooling duty of the ODH-C3 splitter is twice that of cracking. Key comparisons between the energy demands are shown in Figures 3 and 4.

5.4 Emission comparisons

The fuel gases produced during the process, which include CO, CH₄ and H₂, can be burned to (partially) satisfy the energy requirements. In Figure 5 it is assumed that all of the fuels are combusted to extract their energy value. Using the $\Delta H_{\text{reaction}}$ as given in Table 8 and the available fuel, as given by ASPEN Plus[®], the total available energy from the fuels is calculated. Figure 5 compares the available energy from the fuels, energy demand from the process, and the net energy production/consumption. For the ODH case, there is 7.35 GJ_{th} excess as compared to the cracking process, which has a 1.42 GJ_{th} deficit for every tonne of ethylene produced.

However, for the same amount of ethylene, the ODH case requires more ethane in the feed than cracking, which translates to an energy-penalty for the system. On the other hand, it also gains an energy-credit in the form of C3+ compounds. If these are taken into account, using the lower heating values (LHV) of ethane and C3+ compounds [29], the ODH case has an overall energy-penalty of 3 GJ_{th} for every tonne of ethylene produced.

In the case of cracking, negligible amount of CO₂ is present in the product gases. Based on the total energy demand and available CO and CH₄, as given in Table 8 and Figure 5, 2176.3 kmol/hr of CH₄ is required to meet the demand of 483.4 MW_{th}. In the case of the ODH, after burning the CO, combustion of 292.7 kmol/hr of CH₄ is required for energy consumption. By assuming an emission factor of 60 kg CO₂/GJ electricity, the cracking process leads to an emission of 1.2 tonne CO₂/tonne ethylene [8] as compared to 0.22 tonne CO₂/tonne ethylene for the ODH case. Therefore CL-ODH provides 82% drop in CO₂ emissions. Unlike cracking which generates significant amount of NO_x from fuel burning [30], ODH case has significantly lower NO_x emissions as well.

6 Sensitivity analysis

6.1 Ethylene yield

The effect of ethane single-pass conversion is also studied. Two additional cases are considered for the redox ODH process; one at 66% single-pass ethane conversion (similar carbon yield as cracking) and one at 90%. The carbon yields of the various products are listed in Table 9. The exit gas composition and the energy distribution and demand-reduction, relative to the reference and cracking case, are analyzed.

As shown in Table 10, with an increase in the ethane conversion, there is a corresponding increase in the amount of heavier hydrocarbons (C3+) produced. The total molar flow-rate on a dry basis decreases at higher conversions, which corresponds to a drop in the compression work. As the heavier hydrocarbon content increases, the mass throughput increases.

The effect of the change in the ethane conversion on the section wise and overall energy (thermal) demand can be seen in Figures 6 and 7. With an increase in the ethylene yield, the overall energy demand of the process drops from 154 to 87 to 54 MW_{th} as the single pass ethane conversion increases from 66% to 85% to 90%. The available energy from the regenerator, quench, and the hot exit-air, increases with an increase in the single-pass ethane conversion, which thereby reduces the overall energy demand. A better way of comparison among the processes is by using the output of the HVPs, as shown in Figures 8 and 9, where each value is expressed per tonne of HVP. From Figure 9, it can be seen that as the ethane single-pass conversion increases from 66% to 90%, the CO₂ emissions decrease from 0.31 to 0.17 tonne CO₂/tonne ethylene. This translates to 0.27 and 0.13 tonne CO₂/tonne HVP respectively. With respect to the cracking case, which

emits 1.2 tonne CO₂/tonne ethylene [8], the increase in ethane conversion from 66% to 90% leads to a reduction in CO₂ emissions from 74% to 87%.

6.2 Effect of pressure drop

Solid circulation in the CL-ODH process leads to a pressure drop, which requires additional compression work [27]. The following analysis calculates the amount of work needed to negate the pressure drop in the ODH reactors. Pressure drops of 0.1, 0.2, 0.3 and 0.4 atm are studied and the corresponding energy requirements are presented in Figure 10. Although the reactor pressure drop related to solids circulation can increase the overall energy demand for ODH, the energy related to solids circulation is anticipated to be small. Even with a conservative assumption of 0.4 atm pressure drop for each reactor, the energy loss adds up to 0.43 GJ/tonne HVP. Under such a scenario, ODH is still 79.2% less energy intensive than cracking.

6.3 Regenerator air requirements

The effect of increasing the amount of air in the regenerator is studied in this section for the ODH reference case. As shown in Figure 11, excess air in the regenerator decreases the exothermicity of the regenerator and demands more heat input to preheat the air to 650°C, but there is more available heat from the hot exit air. Overall, there is a decrease in the net available energy from the regenerator section, with an increase in the amount of air. Excess air would result in unnecessary energy expenditure to heat the input air and then extract heat from it at the outlet. The overall energy demand (MW_{th}) of the process increases with an increase in the amount of air fed. This is shown in Figure 11. The optimum is likely to be $\leq 20\%$ excess air, which can be achievable using the Mn-based redox catalysts.

7 Conclusion

The present study compares a redox ethane ODH process with the traditional steam cracking process. Unlike the endothermic steam cracking process, redox ODH is net exothermic due to selective combustion of H₂ byproduct. The use of Mn based redox catalyst under a cyclic redox scheme eliminates the needs for air separation. The exothermicity of the regenerator and the available energy from the hot regenerator exhaust enable the upstream section of the ODH process to be 115.2 MW_{th} exothermic as compared to 218.9 MW_{th} net endothermic for a cracker. For the same ethylene throughput, ethane ODH with 85% single-pass ethane conversion results in 32% less molar flow. This translates to significant drop in compression work for downstream separations. Overall, the ODH reference case consumes 82% less energy over cracking, i.e. steam cracking has an energy demand of 15.2 GJ/tonne ethylene whereas the ODH process demands 2.7 GJ/tonne ethylene. By burning all the fuel produced in the process (CO, H₂ and CH₄), the ODH case has 7.35 GJ_{th} excess fuel energy as compared to the cracking process, which has a 1.42 GJ_{th} deficit for every tonne of ethylene produced. The redox ODH process also provides 82% reduction in the CO₂ and NO_x emissions over steam cracking. Increase in single-pass ethane conversion for redox ODH can lead to further reduction in energy demand and less

CO₂/NO_x emissions. The energy requirements for solids circulation in redox ODH lead to an energy-penalty of less than 0.6 GJ_{th} per tonne of ethylene produced. To summarize, redox ODH represents a potentially attractive option for ethylene production with significantly reduced pollutant emissions and energy consumptions.

8 Acknowledgement

We acknowledge the funding support from Advanced Research Project Agency-Energy (ARPA-E) of the US Department of Energy (Grant DE-AR0000327), Kenan Institute, and EcoCatalytic Technologies LLC.

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Figures

Figure #	Image size (column fitting)
1	1.5
2	1.5
3	1
4	1
5	1
6	1
7	1
8	1
9	1
10	1
11	1

Figure 1: a) Simplified process flow diagram of ethane cracking process [DM: Demethanizer, DA: Deacetylenizer, DE: Deethanizer, DP: Depropanizer, DB: Debutanizer, C2 split: C2-splitter, C3 split: C3-splitter, PSA: Pressure Swing Adsorption] b) Simplified schematic of the cyclic redox ODH (CL-ODH) process (temperatures for key units and streams are listed for the reference case)

Figure 2: a) Section wise energy distribution and b) overall energy distribution for a steam cracking process

Figure 3: Comparison of the energy distributions

Figure 4: Relative energy demand (section wise and overall)

Figure 5: (Thermal) Energy surplus and emissions

Figure 6: Thermal energy (MW_{th}) comparison for the ethane ODH cases

Figure 7: % Reduction in the energy demand

Figure 8: Thermal energy distribution comparison

Figure 9: Thermal energy demand and emission comparison

Figure 10: Effect of pressure drop

Figure 11: Effect of excess air on the thermal energy demand (MW_{th})

Tables

Table 1: ASPEN Plus® modules, property methods and databanks

Stream class	MIXCISLD
Databank	PURE, AQUEOUS, SOLIDS, INORGANIC
Solid components	Mn ₃ O ₄ , MnO, MgO
Property method	PR-BM and STEAM –TA for steam cycles
Unit operation models	
Regenerator, Reducer and Deacetylenizer	RStoic
Pressure changers	MCompr
Heat exchangers	Heater
Distillation columns	DSTWU
Separators/Flash columns	Sep/Flash2

Table 2: Carbon yield for the two cases

	Case I: Cracker	Case II: ODH reference
Ethane conversion	65%	85%
Carbon yield (%)		
Ethane	35.0%	15.0%
Methane	3.4%	6.0%
Acetylene	0.5%	0.2%
Ethylene	56.1%	65.0%
Propylene	1.2%	2.4%
Propane	0.1%	0.3%
Butadiene	2.1%	2.4%
Butenes	0.2%	2.4%
Butanes	0.2%	0.0%
C ₅ 's	0.6%	0.5%
Benzene	0.5%	2.4%
Toluene	0.1%	0.5%
CO	0.0%	1.5%
CO ₂	0.0%	1.5%

Table 3: Simulation conditions and assumptions

Ambient condition	T = 25°C, P = 1 atm
Reaction assumptions	As per the carbon yield distribution in Table 2
Heat loss in chemical looping reactors	1% of the total thermal output
Chemical looping reactor operating pressure	1 atm
Deacetylenizer operating pressure	42 atm
Compressor specifications	4 stage with intercooler at 25°C Isentropic efficiency of 0.72
Air feed (to the regenerator)	10% excess
Discharge temperatures to the environment	Temperature: 25°C
Thermal energy to steam efficiency	85%
Thermal energy to electric energy efficiency	40%

Table 4: Column details [25]

Unit	Key component recoveries				Reflux ratio	Pressure (bar)		
	Light key	Recovery	Heavy key	Recovery		Condenser	Reboiler	
Demethanizer	Methane	99.90%	Ethylene	0.50%	3	26	27	Partial condenser with all vapor distillate
Deethanizer	Ethylene	99.99%	Propane	0.10%	0.6	10	11	
Depropanizer	Propylene	99.99%	Iso-butylene	1.40%	4.6	10	11	
C2-splitter	Ethylene	99.00%	Ethane	0.06%	2.7	4	11	
C3-splitter	Propylene	99.60%	Propane	0.24%	18	16	18	
Debutanizer	Iso-butane	99.90%	Butadiene	0.10%	8.6	4	5	

Table 5: Choice of refrigerant [28]

Unit	T required deg C	Refrigerant
Demethanizer	-95	Ethylene
Deethanizer	-43	Ethane
C2 splitter	-76.3	Ethane
Fractionation	-110	Ethylene
Depropanizer	25	Propylene
C3 splitter	34	Propylene
Debutanizer	32	Propylene

Table 6: Exit gas and solid streams

Mole flow (kmol/hr)				
	Cracking (Case I)		ODH reference (Case II)	
Feed				
Ethane	4807.0		5353.3	
Methane	126.5		140.9	
Propane	126.5		140.9	
Total	5060.0		5635.0	
Steam	2500		NA	
Final ethylene output (after the downstream purification)	4077			
Output from Cracker or ODH reactor				
Ethane	2580.4		943.1	
Methane	704.2		894.9	
Acetylene	74.5		14.0	
Ethylene	4242.1		4163.9	
Propylene	82.6		140.6	
Propane	19.5		60.9	
Butadiene	80.5		74.8	
Butenes	7.5		75.8	
Butanes	15.6		1.1	
Pentanes	19.9		12.6	
Benzene	14.0		49.8	
Toluene	2.4		9.0	
CO ₂	0.0		279.2	
CO	0.0		279.2	
H ₂	4441.9		1616.6	
H ₂ O	2497.9		3918.4	
Total Flow (kmol/hr)	14782.9		12533.9	
Total Flow (kg/hr)	276549.0		276442.0	
Solid stream flowrates and compositions (Case II)				
	Solids in		Solids out	
Temperature (°C)	950		850	
Pressure (atm)	1		1	
	million kg/hr	wt%	million kg/hr	wt%

Mn ₃ O ₄	1.26	20.82	0.17	2.85
MnO	0	0	1.01	16.96
MgO	4.79	79.18	4.79	80.19

Table 7: Comparison of the energy consumption

Comparison			
		Cracking	ODH reference
Ethane conversion		65.0	85.0
Flow (tonne/hr)	Ethylene	114.2	114.2
	Fresh Feed	152.2	168.8
Upstream (MW _{th})	Reactor (Endothermicity)	235.9	0.0
	Regenerator ¹	n/a	-33.2
	Ethane recycle	50.0	18.6
	Propane recycle	1.2	1.2
	Feed pretreatment	77.9	86.0
	Steam heat	47.6	n/a
	Air preheat	n/a	72.0
	Exit gas cool ¹	n/a	-76.1
	Quench ¹	-193.6	-183.7
Downstream ² (MW _{th})	Compressor	123.2	83.6
	Demethanizer	13.5	15.4
	Deethanizer	5.4	2.7
	Depropanizer	1.2	1.2
	C2-splitter	37.1	34.8
	C3-splitter	1.2	2.4
	Debutanizer	0.0	0.1
	Deacetylenizer	5.5	4.6
	CO ₂ scrubbing	0.0	3.4
	PSA	0.7	0.2
	Fractionation	76.9	53.8
Upstream Subtotal (MW _{th})		218.9	-115.2
Downstream Subtotal (MW _{th})		264.5	202.2
Net (MW _{th})		483.4	87.0
Net (GJ _{th} /tonne ethylene)		15.2	2.7
¹ Steam energy from thermal with 85% conversion ² Converted to thermal assuming 40% conversion			

Table 8: $\Delta H_{\text{reaction}}$ and molar flow rate of the fuel

Heat release (LHV)		
$CO + \frac{1}{2}O_2 \rightarrow CO_2$	282	kJ/mole
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	800	kJ/mole
$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$	239	kJ/mole
Molar flowrate (kmol/hr)		
	Cracking	ODH
CO	0	279.1
CH ₄	703.8	894.0
H ₂	4247.9	1496.0

Table 9: Carbon yield for the different ethane ODH cases considered

%Carbon yield			
Component	Case III	Case II	Case IV
	ODH low	ODH reference	ODH high
Ethane conversion	66%	85%	90%
Ethane	34.10%	15.00%	10.00%
Methane	3.30%	6.00%	7.00%
Acetylene	0.50%	0.19%	0.19%
Ethylene	56.10%	65.00%	65.03%
Propylene	1.20%	2.38%	2.50%
Propane	0.10%	0.25%	0.25%
Butadiene	2.10%	2.38%	2.50%
Butenes	0.20%	2.38%	2.50%
Butanes	0.20%	0.03%	0.03%
C ₅ 's	0.60%	0.50%	0.80%
Benzene	0.50%	2.38%	5.00%
Toluene	0.10%	0.50%	1.00%
CO	0.50%	1.50%	1.60%
CO ₂	0.50%	1.50%	1.60%

Table 10: Exit gas composition of the ethane ODH cases

Mole flow (kmol/hr)			
	Case III	Case II	Case IV

Feed			
Ethane	4774.7	5353.3	5606.9
Methane	125.65	140.9	147.6
Propane	125.65	140.9	147.6
Total	5026	5635.0	5902.0
Final ethylene output (after the downstream purification)	4077		
Output			
Ethane	2457.1	943.1	691.7
Methane	601.2	894.9	902.2
Acetylene	42.3	14.0	14.0
Ethylene	4111.6	4163.9	4172.5
Propylene	92.8	140.6	147.5
Propane	48.2	60.9	63.1
Butadiene	75.7	74.8	78.6
Butenes	7.3	75.8	79.7
Butanes	10.1	1.1	1.1
Pentanes	17.3	12.6	20.1
Benzene	12.0	49.8	104.8
Toluene	2.1	9.0	18.0
CO	150.2	279.2	295.9
CO ₂	150.2	279.2	295.9
H ₂	1411.3	1616.6	1703.3
H ₂ O	3417.1	3918.4	4315.9
Total Flow (kmol/hr)	12606.5	12533.9	12904.3
Total Flow (kmol/hr)(Dry)	9189.4	8635.5	8588.4
Total Flow (kg/hr)	288697.0	276442.0	284259.0
Total Flow (kg/hr) (Dry)	227189.2	205910.8	206572.8