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TECHNOLOGYTECHNO-ECONOMIC COMPARISON BETWEEN CONVENTIONAL STEAM
PYROLYSIS AND OXIDATIVE DEHYDROGENATION OF ETHANE FOR THE
PRODUCTION OF ETHYLENESamyukta Pingali^{*1}, Gennaro J. Maffia² & Anne M. Gaffney³^{*1}Department of Chemical Engineering, Manhattan College, NY, USA;²PhD Department of Chemical Engineering, Manhattan College, NY, USA;³PhD, Department of Chemical Engineering, University of South Carolina, SC, USADOI: <https://doi.org/10.29121/ijesrt.v9.i10.2020.8>

ABSTRACT

Facilities based on both Conventional Steam Pyrolysis (CSP) and Oxidative Dehydrogenation (ODH) are methods of producing and separating an alkene, such as ethylene, from an alkane, such as ethane. The CSP system is a time honored and historic process consisting of an endothermic reaction to crack ethane into ethylene followed by a separation system to remove hydrogen and methane. Distillation is then used to purify the ethylene to polymer grade. The ODH method comprises subjecting a feedstock containing ethane to exothermic oxidative dehydrogenation using an M1 catalyst to produce an ethylene stream. The ethylene stream is distilled and/or passed through membrane separators to purify and recover the ethylene. The ODH reaction system comprises at least one tubular reactor, a heat management unit coupled to the ODH reactor, and at least one membrane separation unit comprising a facilitated membrane exchanger. The ODH reactor is configured with tubes packed with the M1 catalyst to convert ethane to ethylene. Additionally, the ethylene produced is reported to be refractory, thus avoiding secondary reactions. The heat management unit is configured to reduce the temperature of the ethylene product stream and recovering the heat of reaction. These processes and the associated economics are discussed. The economic assessment indicates that the ODH route is superior in the three key areas in the cost of production: variable costs, fixed costs and capital recovery.

KEYWORDS: Oxidative Dehydrogenation, Steam Pyrolysis, Facilitated Membranes, Process Economics and Sensitivities.

1. INTRODUCTION

Oxidative dehydrogenation (ODH) catalysts, such as Mixed Metal Oxide catalysts for converting ethane to ethylene began receiving attention in the late 1970s after Journal of Catalysis published an article entitled, "The Oxidative Dehydrogenation of Ethane over Catalyst Containing Mixed Oxide of Molybdenum and Vanadium" followed by a major advance in the 1980s; in part due to substantial research being conducted on remote natural gas [1, 2] and the shale gas available in mid-Atlantic states in the US. The selectivity and conversion to ethylene are the two parameters commonly used to measure the catalyst productivity. The original M1 catalyst was refined at ABB Lummus in the early 2000s and achieved high selectivity at high conversion [3]. The discovery of an abundance of North American shale gas over the past decade has resulted in an enormous growth in US tight oil and shale gas production. A steep decrease in the US dependence on foreign energy resources coupled with new opportunities for US manufacturing is causing growth across the petrochemical industry.

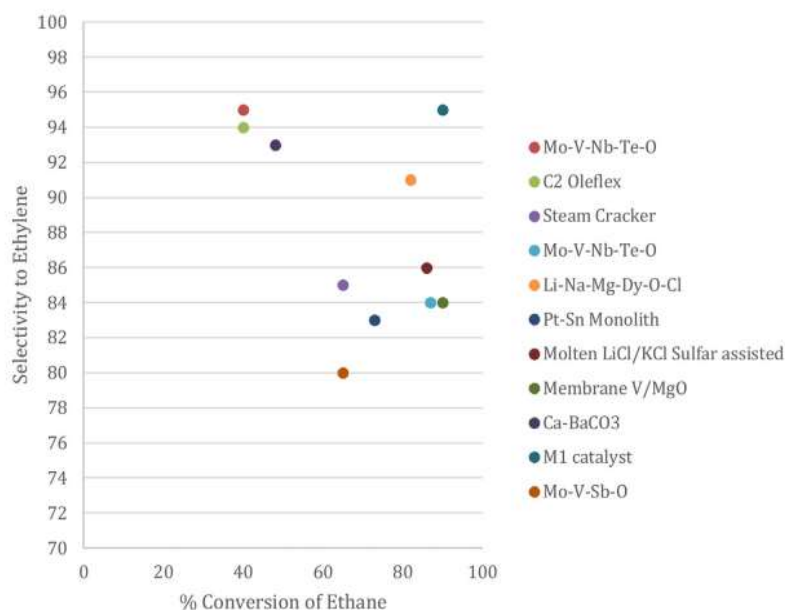


Figure 1. Variety of catalysts for the Oxidative Dehydrogenation of Ethane (C2-ODH) including the M1 catalyst

2. BACKGROUND ON THE SUPPLY/DEMAND OF LIGHT OLEFINS

Ethylene, the lightest olefin, is an organic intermediate used for manufacturing many downstream chemicals such as polyethylene, ethylbenzene, 1,2-dichloro-ethane, ethylene oxide, ethanol, polyvinyl acetate and many more important chemicals. Polyethylene, the most common plastic used worldwide, is the most notable end product of ethylene accounting for nearly 60% of the capacity. In the US, 90% of the manufactured ethylene is produced from natural gas and accounts for 20% of the world's capacity. Worldwide, conventional steam pyrolysis (CSP) is the current means for producing ethylene. CSP is a non-catalytic, high temperature, and low-pressure process that thermally cracks a feedstock of ethane, propane, or liquid fuels fed to the reactors along with diluent water the choice of feedstock depends greatly on geographic location, cost, and availability of hydrocarbons. The process is extremely energy and capital intensive, yielding many byproducts, requiring extensive separations and purification [5]. The US has transitioned mostly to a gas feedstock for crackers due to the abundant supply of low-cost ethane. In the US, ten additional ethane cracker expansion projects are driving the steep increase in ethylene capacity. Global ethylene capacity is 160 MTPA and is projected to reach 230 MTPA by the year 2025 [5]. Aspen-HYSYS is used to simulate and compare the respective CSP and C2-ODH plant design. Preliminary Techno-Economic Analyses (TEA) shows the superiority of C2-ODH over conventional methods for producing ethylene. Required netback (RNB) is an economic approach commonly used for assessing the attractiveness of new vs current technology [6]. RNB is based on calculation of the sum of Variable Costs, Fixed Costs and Capital Recovery.

The nation's goal to increase energy efficiency and reduce the carbon footprint calls upon many industries to relook at the way we produce and consume energy. The oil and gas industry has practiced thermal cracking of petroleum and petroleum fractions for the past 100 years. The thermal cracking of petroleum fractions produces an extensive list of compounds, including ethylene and other alkenes and diolefins that are utilized across the petrochemical industry. Ethylene is conventionally produced from ethane by steam pyrolysis or steam cracking, which systems have hundreds of individual pieces of equipment and more than twenty sections, some containing many unit operations. These sections of the systems are used to recover and purify major products of the ethane to ethylene reaction. Production plants which include the many sections are capital intensive and costly to operate. The conventional thermal process of converting the ethane to ethylene achieves an ethylene selectivity of 80 - 85 % at an ethane conversion of 55 - 65 %. As shown in Figure 1., the kinetic parameters associated with the ODH process are superior in both conversion and selectivity thus reducing the required netback (RNB). The conventional process is endothermic and is conducted at a temperature between 800° C and 900° C, making the process energy intensive and costly. Oxidative dehydrogenation (ODH) has been investigated as an alternative for producing ethylene from ethane. Ethane is reacted with oxygen in the presence of a mixed metal oxide (MMO)

catalyst to produce the ethylene. The ODH of ethane is exothermic and, therefore, the ODH reaction is more energy efficient than the steam cracking process. If the ODH reaction is quenched quickly, byproduct production is minimal. However, the ethylene conversion, ethane selectivity, and ethylene yield are highly dependent on the catalyst used and reaction conditions. As discussed by Gaffney *et. al* [6], the ethylene is separated from combustible, reactive, or non-reactive byproducts by cryogenic separation, distillation, or membrane separation. However, cryogenic separation and distillation are expensive and energy - intensive techniques. Additionally, the membrane separation is not selective and only separates the ethylene from the combustible, reactive, or non-reactive byproducts.

3. GENERATING THE METRICS – METHODOLOGY

Metrics can be generated from components of the Required Netback (RNB), posited in per mass unit of the ethylene product, and can be used to assess advantages of new technology versus conventional processing. The metrics generated are divided into several categories: process economics, energy productivity, process intensification, and environmental impact. These industry metrics are applied to new technologies and are used to assess risk and decide investments.

A method of producing and separating an alkene, such as ethylene, from an alkane, such as ethane, is disclosed in previous US Patents [7, 8], as is a system configured to produce the alkene from the alkane. The system includes an ODH reactor coupled with a heat management unit and a distillation/membrane separation unit. No sole alkene super-fractionator, such as a distillation column, is utilized in the system to recover the alkene. In company literature, Imtex, Inc. [9] reports that the membrane separation unit alone may be utilized to recover the alkene. CSP consists of 23 sections of separate unit operations as illustrated in Fig 2. ODH requires less than half of these sections.

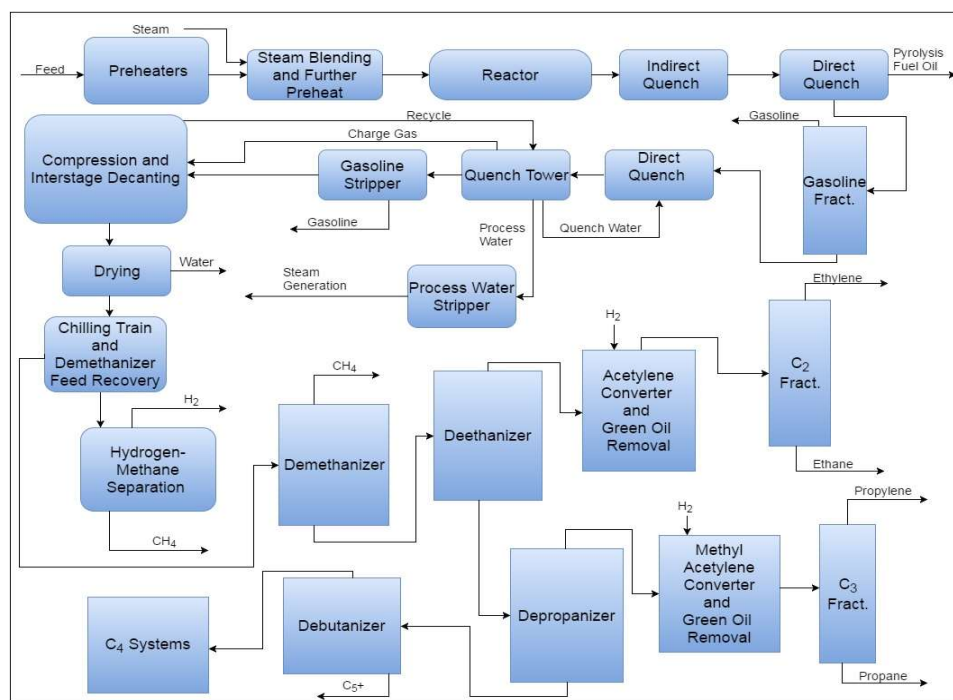


Figure 2. Process Flow Diagram for liquid crackers in conventional steam pyrolysis

4. MATERIALS AND METHODS

When compared to conventional systems and methods of alkene production and alkane separation, the process described in US Patent [8], lowers the carbon footprint by 30% or more, lowers the energy consumption up to 75% and also exhibits reduced capital and operating costs. On increasing the purity of the alkene exiting the ODH

reactor and on improving the separation efficiency, a higher chemical or polymer grade alkene (i.e.- ethylene) with zero energy per pound and zero carbon footprint is produced. Such a case has been labeled E-zero.

The ethane content in the feedstock depends on the origin of the feedstock, such as ethane from natural gas, shale oil or a byproduct recycled within a pyrolysis plant. This in turn will determine the volume of ethane present and is up to 95% by volume of ethane. Impurities are removed by adsorption before the ODH reaction to prevent catalyst poisoning and undesirable byproduct formation. For other alkane to alkene conversions, the feedstocks include compounds having 2 to 8 carbon atoms and a combination of one or more such compounds. The ethane feedstock is introduced into the ODH reactor with an optional diluent such as steam, nitrogen, carbon dioxide or even the ethylene produced. This is done in order to minimize the extent of the exotherm during the reaction. During the design, care must be taken to avoid the flammability region in the reactor. Three reactors in series are expected with oxygen introduction at the beginning and then between each reactor.

The catalyst is a mixed metal oxide (MMO) selected to provide ethane conversion of 90 mole % or higher. It also provides high ethylene selectivity greater than 95 mole %. The catalyst particle size varies between 0.1 cm and 0.5 cm and includes at least one atom each of molybdenum, vanadium, niobium, tellurium, antimony and oxygen (depends on oxidation state of other elements). The MMO catalyst is produced by conventional techniques as described in previous patents [10, 11]. The catalyst is housed within the ODH fluidized, packed or circulating bed reactor where the ethane feedstock and oxygen are introduced and reacted in vapor phase. The ethane feedstock and the oxygen can be introduced into the ODH reactor in one or more separate streams or combined and introduced as a single stream. The feedstock is reacted between a temperature between 150 to 500°C and inlet pressure of between 0.1 bars to 30 bars for a residence time between 0.1 to 15 seconds.

Acetic acid, acetylene, or combinations of the two are produced in trace quantities depending on the reaction conditions and catalyst used. If any acetylene is produced it is hydrogenated and removed from the existing olefins plant using conventional equipment. The rate of the reaction depends on the configuration of the ODH reactor, the partial pressure of ethane, and frictional pressure drop when multiple series reactors are used. The conversion and selectivity of ethylene can be up to 98% with no secondary reactions. It is cooled down by the method of heat integration and management before being introduced to a membrane or other conventional techniques for further purification.

5. RESULTS AND DISCUSSION

5.1 Oxidative Dehydrogenation

Oxidative Dehydrogenation has been explained in the preceding research papers. It is an alternative to conventional steam pyrolysis, involves catalytically dehydrogenating ethane in the presence of oxygen to form ethylene [2, 3, 7]. As previously discussed by Maffia *et. al* [12], the process is called oxidative dehydrogenation (ODH). In this process, the product is largely limited to ethylene with small amounts of carbon monoxide and carbon dioxide as byproducts. The effluent also contains water (produced in the reaction plus whatever enters with the feed), residual ethane, some residual oxygen, and nitrogen if introduced with the oxygen (e.g., as air). The ODH of ethane is thermodynamically favored and can be carried out at lower reaction temperatures without the formation of coke.

5.2 Oxidative Dehydrogenation Catalyst Scale-Up

The commercial M1 catalyst may be scaled up using the approach of concurrent engineering [13]. A synthesis strategy has been proposed for the combining nanoparticles of TeVO₄ with clusters of MoNbTeO_y to form a single-phase catalyst, in which the vanadium-rich Te-O active sites that activate the alkane to form alkene are properly distinguished by MoNbTeO_y zones [14]. This strategy results in a mixed metal oxide catalyst that is useful for both ethane and propane oxidative dehydrogenation. It can be anticipated that such a systematically ordered single-phase catalyst leads to an incomparable selectivity, thus making commercial application within reach. To validate this computational design, it is essential to develop a ReaxFF force field or ANN potential based on the QM derived reaction mechanism so that one can simulate the reaction processes in large simulation models with longer simulation times. By employing data analytics, data mining and machine learning, a set of M1 catalyst predictors may be arrived at leading to commercially viable catalyst scale-up. The M1 catalyst predictors

allow for the evaluation of activity, selectivity, and conversion at commercially relevant operating conditions. This scale-up approach allows for rapid catalyst synthesis modification while accommodating for variation of alkane feedstock composition.

5.3 Cost of Production

Cost of Production (COP) is an economic model used to analyze the start-up of new and conventional technologies. Figure 3. is a flowchart illustrating the dependency of economic variables needed to calculate margins of production.

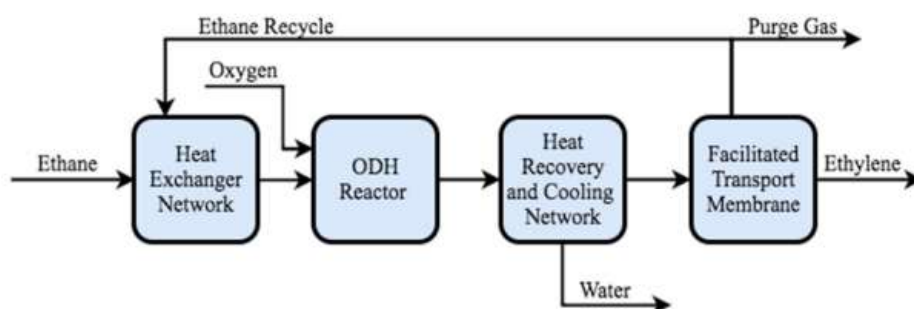


Figure 3. Block Flow of C2-ODH Process

COP has three separate components: variable costs, fixed costs, and capital recovery. The margin for ethylene pricing is defined as the difference between market price and the cash cost (sum of Fixed and Variable Costs). Positive margins are favorable for new technology and result in significant returns on investment. Cash costs fixed and variable costs, and capital recovery, capital expenses for a chosen payback period, are summed to calculate the required realizations. The required realization is used to calculate the selling price needed to achieve for a chosen rate of return (ROR). Approximately 1.5% of the required realization calculated is added back to the required realization, accounting for selling, general, and administrative (SG&A) expenses to get an RNB. RNB is a common metric used to evaluate the potential margins for investing in a new plant or technology; it is the selling price needed to cover capital investments, operating expenses, raw materials, etc. for a chosen payback period. RNB incorporates a “hurdle rate” to the required realization giving the price per kg of product. Spot price, the current selling price of any product, is compared to a calculated RNB to understand economic impacts. If the RNB of a new technology is lower than the market price, then the technology shows economic promise. Further comparison can be done to compare state-of-the-art technologies’ COP to the new technology to see if shutdown economics are reached. Shutdown economics refer to a new technology that has lower RNB than conventional technologies’ cash costs. According to reports, the margin for ethylene production was less than ten cents per pound since March 2018 and dropped to less than five cents in 2019, almost hitting an all-time low of a below zero margin in September of 2019 [15]. In 2020, with the onset of COVID-19, the prices were comparable with the energy and fuel market prices of 10 cents [16].

Fixed costs are those incurred regardless of production rate. Fixed costs include labor, foreman, supervision, maintenance, plant overhead, direct overhead, and insurance. For instance, fixed costs due to labor is calculated by dividing the operating expenditure of labor per year by the production capacity. The plant capacity is needed to reference labor cost as cost per kg of product produced. The product of usage, shifts, and a rate is the capital expenditure of labor per year. The usage refers to number of engineers per shift. The rate refers to the salary of an engineer per annum. Foreman costs are typically to be 1/3 of the labor costs. Supervision costs are assumed to be 7.5% of the labor costs. Variable costs are dependent on the production rates and are usually just raw materials and utilities. By-products are added as negative raw materials. Utilities are charged as the type of energy that is required. Consequently, utilities and raw materials are the main components of variable costs. Capital recovery is defined as the capital cost divided by a capital factor that represents the return on investment. The greater the return on investment, the greater the capital recovery figure. The number of years for a capital investment to “break even” is noted as a payback period before taxes. A relationship between the before tax payback period and

the ROR, noted as the After-Tax Return on Investment (ATROI), can be generated as outlined in Figure 4. with a basis of 15-year plant life.

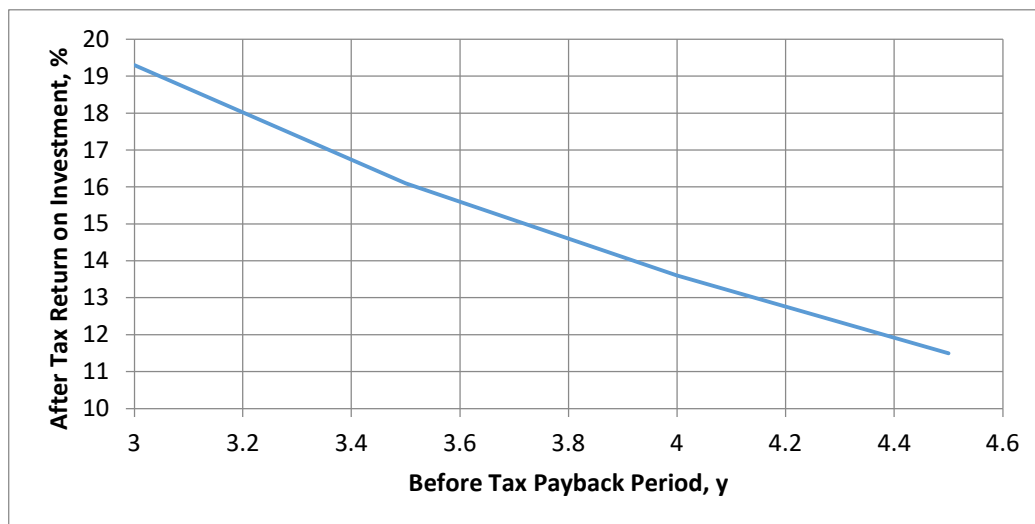


Figure 4. Relationship between before tax payback period and the ATROI

Table 1. Components of the cost of production (COP)

Variable costs = costs depending on the amount of ethylene produced (VC)
Fixed costs = costs incurred irrespective of how much ethylene is produced (FC)
Cash costs = VC + FC
Capital recovery = costs incurred to return the capital investment at a certain rate of return usually identified as the hurdle rate (CR)
Required netback = VC + VC + CR, the total cost to cover the cash cost and a profit corresponding to a certain rate of return (RNB)

Table 2. Cost of production (per pound of ethylene) using CSP

COMPONENTS	CSP Cost (\$/lb)
Capital Recovery	0.152
Fixed Costs	0.075
Variable Costs	
1. Raw Material	0.0896
2. Utilities	0.06

5.4 Process Economics

Economic evaluations for the various technologies are based on the required netback (RNB) as the metric using instantaneous production economics. The basis for this economic analysis is the sum of the various aspects of the cost of production (COP). These are listed in Table 1. Table 2 describes the cost of production per pound of ethylene using conventional steam pyrolysis (CSP). If the COP for a new technology is less than the spot or contract prices, the new technology shows some promise. If the RNB for the new competing technology is less than the cash costs of the conventional then this scenario achieves the shutdown economics level. Comparison of the production economics between the CSP and ODH for the production of ethylene from ethane is presented in Table 3. The overall comparison of CSP and ODH based on the analysis is summarized in Tables 3 and 4. The



performance of ODH is better at all levels, showing lower cash costs and lower netback. However, shutdown economics are not achieved in this case. That is the RNB for ODH is slightly higher than the Cash Costs for the RNB and hence the operator of an ODH plant would need to accept lower margins in order to achieve shutdown economics. As a sensitivity, a more aggressive case was prepared and is presented in Table 5. The following assumptions were made to account for sensitivity: 1. Reduced contingency for ODH, 2. Improved energy, 3. Improved heat integration - pinch technology, 4. Additional improvement via HYSYS simulation. This case results in a summary table which exhibits shutdown economics as presented in Table 6.

Table 3. Production cost comparison between CSP and ODH (\$ per pound of ethylene)

COMPONENTS	CSP Cost (\$/lb)	ODH Cost (\$/lb)
Capital Recovery	0.152	0.094
Fixed Costs	0.075	0.049
Variable Costs		
1. Raw Material	0.0896	0.0797
2. Utilities	0.06	0.0338

Table 4. Summary economics for the cases in Table 3.

COMPONENTS	CSP Cost (\$/lb)	ODH Cost (\$/lb)
RNB	0.3822	0.2603
CASH COSTS	0.2302	0.1663

Table 5. Production cost comparison between CSP and ODH (\$ per pound of ethylene)- aggressive case

COMPONENTS	CSP Cost (\$/lb)	ODH Cost (\$/lb)
Capital Recovery	0.152	0.063
Fixed Costs	0.075	0.040
Variable Costs		
1. Raw Material	0.0896	0.0797
2. Utilities	0.06	0.0226

Table 6. Summary economics for the cases in Table 3.- aggressive case

COMPONENTS	CSP Cost (\$/lb)	ODH Cost (\$/lb)
RNB	0.3822	0.2083
CASH COSTS	0.2302	0.1453

6. CONCLUSIONS AND FUTURE RESEARCH

On shifting from the endothermic ethane cracking technology to an exothermic catalytic selective oxidative dehydrogenation process, shutdown economics have been demonstrated in this economic model. Additionally, with the inclusion of olefin metathesis, further intermediate petrochemicals may be produced, thus shifting away from a conventional pyrolysis route.

Research topics requiring further experimental work are included in Table 7.

Table 7. Future Scope

1.	Life studies and attrition rates of the existing M1 catalyst
2.	Oxygen adsorption, recovery, and recycle
3.	ODH using existing process streams within olefins plants
4.	Scale-up studies at current processing plants
5.	Development of a low temperature/low pressure metathesis catalyst
6.	ODH studies on new molecules such as 2-methyl-2-butene for isoprene production

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